RtD 6429-MS-02

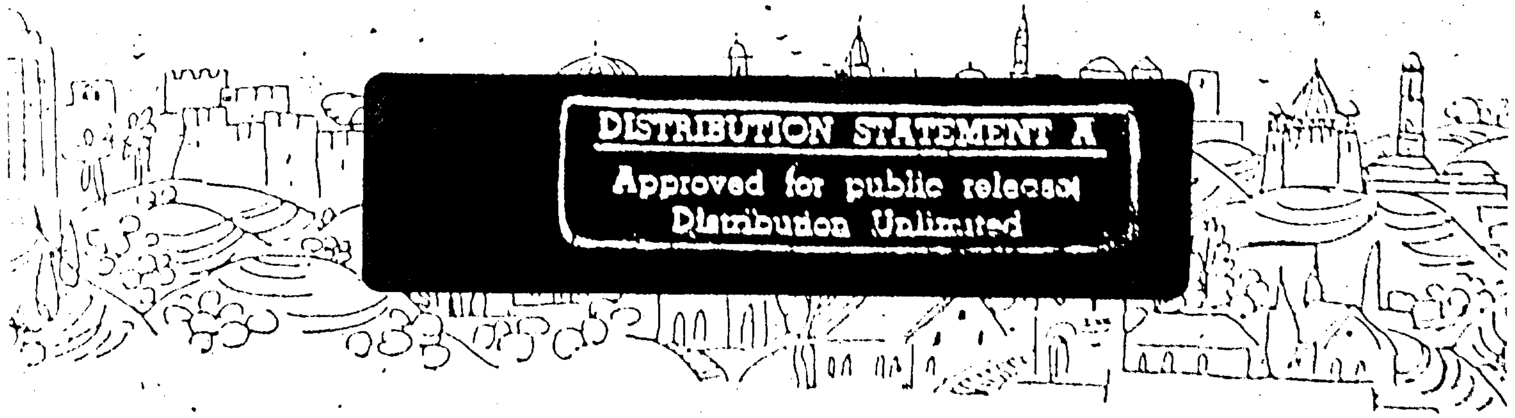
# Networks 90

## 10TH POLYMER NETWORKS GROUP MEETING
## AND
## IUPAC 10TH INTERNATIONAL SYMPOSIUM ON POLYMER NETWORKS

①

20-25 MAY 1990
JERUSALEM ירושלים

## PROGRAMME AND ABSTRACTS



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## 10TH POLYMER NETWORKS GROUP MEETING
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## IUPAC 10TH INTERNATIONAL SYMPOSIUM ON POLYMER NETWORKS

DAJA 45-90-M-0227

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## PROGRAMME AND ABSTRACTS

# CONTENTS

TIMETABLE ........................................................................4
SCIENTIFIC PROGRAMME COMMITTEE ..........................................5
LOCAL ORGANISING COMMITTEE ................................................5
ACKNOWLEDGEMENTS ...........................................................6
GENERAL INFORMATION ........................................................7-8
SCIENTIFIC PROGRAMME ....................................................9-27
  MONDAY, 21 MAY 1990 .......................................................11-16
  TUESDAY, 22 MAY 1990 ...........................................................17
  WEDNESDAY, 23 MAY 1990 ..................................................18-23
  THURSDAY, 24 MAY 1990 ......................................................24-26
  FRIDAY, 25 MAY 1990 ..............................................................27
ABSTRACTS ..........................................................L-1—L-48
P-1—P-54
INDEX ..................................................................I — V
LIST OF PARTICIPANTS ........................................VII — XVIII

# TIMETABLE

**SUNDAY, 20 MAY**

| | |
|---|---|
| 18:00—21:00 | Registration |

**MONDAY, 21 MAY**

| | |
|---|---|
| 08:00 | Registration, continued |
| 09:00—09:30 | OPENING REMARKS |
| 09:30—10:35 | SESSION 1 |
| 10:35—11:10 | Coffee Break |
| 11:10—12:10 | SESSION 1, continued |
| 12:10—14:00 | Lunch Break |
| 14:00—15:25 | SESSION 1, continued |
| 15:30—18:00 | POSTER SESSION 1 |
| 18:30 | COCKTAIL RECEPTION |
| 19:00—20:30 | Dinner Break |
| 20:30—21:30 | SESSION 1, continued |
| 21:30 | Informal continuation of Poster Session 1 |

**TUESDAY, 22 MAY**

| | |
|---|---|
| 08:45—10:10 | SESSION 2 |
| 10:10—10:40 | Coffee Break |
| 10:40—12:30 | SESSION 2, continued |
| 12:50—14:30 | Lunch Break |
| | Afternoon tour of Jerusalem |

**WEDNESDAY, 23 MAY**

| | |
|---|---|
| 09:00—10:50 | SESSION 3 |
| 10:50—11:30 | Coffee Break |
| 11:30—12:35 | SESSION 3, continued |
| 12:35—14:00 | Lunch Break |
| 14:00—15:25 | SESSION 4 |
| 15:30—18:00 | POSTER SESSION 2 |
| 18:00—20:30 | Dinner Break |
| 20:30—21:50 | SESSION 5 |
| 21:50 | Informal continuation of Poster Session 2 |

**THURSDAY, 24 MAY**

| | |
|---|---|
| 09:00—10:50 | SESSION 6 |
| 10:50—11:30 | Coffee Break |
| 11:30—12:30 | SESSION 6, continued |
| 12:30—14:00 | Lunch Break |
| 14:00—15:25 | SESSION 6, continued |
| 15:25—16:00 | Coffee Break |
| 16:00—17:40 | SESSION 7 |
| 19:30 | CONFERENCE DINNER |

**FRIDAY, 25 MAY**

| | |
|---|---|
| 09:00—10:50 | SESSION 8 |
| 10:50—11:15 | Coffee Break |
| 11:15—12:45 | SESSION 8, continued |
| 12:45 | CONCLUDING REMARKS |

## SCIENTIFIC PROGRAMMME COMMITTEE

**F. Boue**, France
**W. Burchard**, FRG
**K. Dusek**, Czechoslovakia
**B. Eichinger**, USA
**M. Gottlieb**, Israel
**J. Klein**, Israel
**O. Kramer**, Denmark
**S. Ross-Murphy**, UK
**A. Silberberg**, Israel
**R. Stadler**, FRG
**R.F.T. Stepto**, UK

## LOCAL ORGANISING COMMITTEE

**M. Gottlieb**, Ben Gurion University
**S. Alexander**, Weizmann
**Y. Cohen**, Technion
**E. Ganani**, RAFAEL
**J. Klein**, Weizmann
**J. Kost**, Ben Gurion University
**G. Lidor**, IAI
**A. Silberberg**, Weizmann
**G. Tanny**, Gelman Membranes

* * *

**Conference Coordinator — E. Soussan, MELIA-TE'UM**

# ACKNOWLEDGEMENTS

**The Organising Committee wishes to express appreciation to the following for their support of the conference.**

Association of Plastic Manufacturers, Israel

Ben Gurion University of the Negev

Bromine Compounds Ltd., Israel

Bank Hapoalim Ltd., Israel

Deutsche Forschungsgemeinschaft, FRG

DSM Research, The Netherlands

European Research Office of the US Army

Exxon Chemical Company, USA

Gelman (Israel) Research and Development Ltd.

RAFAEL, Israel

Israel Academy of Sciences and Humanities

Israel Military Industry

Leiser Boards Ltd., Israel

National Council for Research and Development, Israel

Ministry of Science and Technology, Israel

Ministry of Industry and Trade, Israel

Ministry of Tourism, Israel

Technion, Israel Institute of Technology —
    Polymer Morphology Group

The British Council

The Weizmann Institute of Science

The Weizmann Institute — Polymer Physics Group

# GENERAL INFORMATION

## CONFERENCE VENUE

Mitzpeh Rachel Kibbutz Hotel
Jerusalem
Tel: 02-702555
Fax: 02-733155

## CONFERENCE SECRETARIAT

Melia-Te'um Congress Organisers
POB 8388
Jerusalem 91082
Israel
Tel: 02 667402
Fax: 02 637572
Telex: 25628 TEUMJ IL

## REGISTRATION DESK

The Registration Desk will be open during all Conference sessions.

## BADGES

The personal envelope you received upon registration contains your name badge. Please wear this badge to all Conference sessions and activities.

## MEALS

Participants who have either purchased the conference package or single nights at the conference hotel or at the Zohar hotel have received their meal vouchers in their personal envelope.

Participants who wish to purchase meal vouchers can do this at the Registration Desk.

## FLIGHT RECONFIRMATION

Please note that I.A.T.A. regulations require that outgoing flights be reconfirmed at least 72 hours prior to departure.

We will be happy to reconfirm your flight for you but in order to do so you must complete your flight reconfirmation form and return it to the Registration Desk no later than MONDAY AT 14:00 hrs. After this time we will not be able to assist you.

# SCIENTIFIC PROGRAMME

The scientific programme includes lecture and poster sessions.

## LECTURE SESSIONS

All lecture sessions will be held in the Lecture Hall.

## POSTER PRESENTATIONS

All posters will be on display for the entire meeting. Authors are requested to mount their posters on the panel with the corresponding reference number, by 14:00 hrs on Monday, 21 May and to leave them until 12:30 hrs on Thursday, 24 May.
Assistance will be available in the Poster Hall from 08.00 hrs on Monday.

Authors are requested to be present by their posters at the time indicated in the programme.

Coffee will be served in the Poster Hall during the poster sessions.

## INDEX NUMBERS

Next to the title of each lecture or poster is a number preceded by L or P (abstract). These numbers refer to the page number where each abstract can be found on the corresponding page in the abstract sections of this book.

## INSTRUCTIONS TO SPEAKERS

Speakers are requested to adhere strictly to the time allotted them by the chairperson.

## TECHNICAL EQUIPMENT

A slide projector, overhead projector and blackboard will be available in the lecture hall. Please hand the slides to the projectionist 15 minutes before the start of the session and collect them immediately following presentation. Equipment for slide and transparency previewing is available on request.

# SOCIAL EVENTS

## COCKTAIL RECEPTION

Monday, 21 May 1990 at 18:30 hrs

## TOUR OF JERUSALEM

Tuesday, 22 May 1990. Departure at 14:30 hrs.

## CONFERENCE DINNER AND ENTERTAINMENT

Thursday, 24 May 1990, at 19:30 hrs

# SCIENTIFIC PROGRAMME

## MONDAY, 21 MAY 1990

09:00

### OPENING REMARKS

**J. Yortner**, Israel Academy of Sciences and Humanities

**M. Gottlieb** (Israel)

### SESSION 1

### DYNAMICS, ELASTICITY THEORY, STRUCTURE-PROPERTY

Chairperson: A. Silberberg (Israel)

| | | |
|---|---|---|
| 09:30-10:15 | **DYNAMICS OF SLIP LINK NETWORKS**<br>S.F. Edwards (UK) | L-1 |
| 10:15-10:35 | **STRUCTURAL EFFECTS IN SWOLLEN MODEL NETWORKS**<br>C. Cohen, S.K. Patel (USA) | L-2 |
| 10:35-11:10 | **COFFEE BREAK** | |
| 11:10-11:30 | **ELASTICITY THEORY: MOLECULAR THEORY OF THE MOONEY-RIVLIN EQUATION AND BEYOND**<br>B.E. Eichinger (USA) | L-3 |
| 11:30-11:50 | **ELASTICITY OF POLYMER GELS: EFFECT OF SOLVENT QUALITY ON THE SHEAR MODULUS OF POLY(VINYL ACETATE) NETWORKS**<br>F. Horkay, M. Zrinyi (Hungary)<br>E. Geissler, A.-M. Hecht (France) | L-4 |
| 11:50-12:10 | **INTERPRETING THE PROPERTIES OF MODEL HDI- AND MDI-BASED POLYURETHANE NETWORKS**<br>R.F.T. Stepto (UK), B.E. Eichinger (USA) | L-5 |
| 12:10-14:00 | **LUNCH BREAK** | |

## MONDAY, 21 MAY 1990

### SESSION 1, continued

### DYNAMICS, ELASTICITY THEORY, STRUCTURE-PROPERTY

Chairperson: S. Ross-Murphy (UK)

| | | |
|---|---|---|
| 14:00-14:45 | **RELAXATION OF ENTANGLED POLYMERS IN MELTS**<br>J. des Cloizeaux (France) | L-6 |
| 14:45-15:05 | **THE CONCEPT OF INTRINSIC CHAIN STRESS IN POLYMER NETWORKS**<br>J.J. Weiner, J. Gao (USA) | L-7 |
| 15:05-15:25 | **DYNAMIC MECHANICAL BEHAVIOUR AND THE DC CONDUCTIVITY OF POLY- (N,N-DIETHYLACRYLAMIDE) GELS IN THE COLLAPSE REGION**<br>M. Ilavsky, J. Hrouz, J. Nedbal (Czechoslovakia) | L-8 |

## MONDAY, 21 MAY 1990

15:30-18:00

## POSTER SESSION 1

**RUBBER ELASTICITY: A PHENOMENOLOGICAL APPROACH INCLUDING ORIENTATIONAL INTERACTIONS BETWEEN CHAIN SEGMENTS** P-1
B. Deloche, E.T. Samulski (France, USA)

**CHAIN SEGMENT ORDERING IN STRAINED BIMODAL PDMS NETWORKS: A NUCLEAR MAGNETIC RESONANCE INVESTIGATION** P-2
B. Deloche, R. Oeser (France)

**SMALL ANGLE NEUTRON SCATTERING ON PDMS MODEL NETWORKS** P-3
R. Oeser, J. Herz (France)

**CHARACTERIZATION OF A $A_2$ HOMOPOLYMERIZATION NETWORK POLYMERS OF 2,2 BIS(4-CYANATOPHENYL)PROPANE BY $^{13}$C NMR AND LIGHT SCATTERING** P-4
A.M. Gupta, C.W. Macosko (USA)

**CHARACTERIZATION OF ORIENTED MICROFIBRILLAR NETWORKS BY ELECTRON MICROSCOPY AND X-RAY SCATTERING** P-5
Y. Cohen, E. Garstein (Israel) E.L. Thomas (USA)

**NEUTRON SCATTERING AND SWELLING PROPERTIES OF END-LINKED PDMS NETWORKS** P-6
E. Geissler, A.-M. Hecht, S. Mallam (France)
F. Horkay, M. Zrinyi (Hungary)

**ON THE ELASTIC AND SWELLING BEHAVIOUR OF POLY(VINYL ALCOHOL) AND POLY(VINYL ACETATE) NETWORKS FILLED WITH ANISOMETRICAL COLLOIDAL FERRIC(III)-HYDROXIDE PARTICLES** P-7
M. Zrinyi, H.-G. Kilian, K. Dierksen, F. Horkay, F. Csempesz (Hungary, FRG)

**EFFECT OF NEUTRAL SILICA PARTICLES ON THE STRUCTURE AND SWELLING OF PDMS NETWORKS** P-8
F. Horkay, M. Zrinyi (Hungary)
E. Geissler, A.-M. Hecht (France)

15:30-18:00 **POSTER SESSION 1,** continued

| | |
|---|---|
| **SOME ASPECTS OF RHEOLOGY AND MORPHOLOGY OF EPOXY RESINS SUBJECTED TO COMPLEX STATES OF STRESSES**<br>D. Katz, S. Bron (Israel) | P-9 |
| **CONTINUOUS TIME SIMULATION OF TRANSIENT POLYMER NETWORKS: RHEOLOGICAL PROPERTIES**<br>P. Biller, F. Petruccione (FRG) | P-10 |
| **THE NETWORK STRUCTURE OF POLYETHYLENE GELS**<br>M. Kunz (FRG), L. Aerts (Belgium),<br>M. Moeller (The Netherlands) | P-11 |
| **NON-HORIZONTAL "RUBBER-PLATEAUS" DISPLAYED BY POLYSTYRENE — POLYISOPRENE — POLYSTYRENE TRI-BLOCK COPOLYMER SOLUTIONS IN N-TETRADECANE**<br>P.H.J. Spitteler, P.F. Mijnlieff (The Netherlands) | P-12 |
| **STRUCTURE OF FILLED AND UNFILLED ELASTOMERS: THERMOPOROMETRIC MEASUREMENTS**<br>A. Pouchelon, M. Soria, L. Moll (France) | P-13 |
| **EXTRACTION, EQUILIBRIUM PHOTOELASTIC AND DYNAMIC MECHANICAL BEHAVIOUR OF POLYURETHANE NETWORKS BASED ON POLY(OXYPROPYLENE)DIOLS AND TRIISOCYANATE**<br>M. Ilavsky, J. Hrouz, K. Bouchal, K. Dusek (Czechoslovakia) | P-14 |
| **THE REVERSIBLE NETWORK FORMATION IN POLY(DIMETHYLSILOXANES) WITH SIDE CARBOXYL GROUPS**<br>L.Z. Rogovina, O.A. Tchegolichina, V.G. Vasiliev, V. Yu. Levin, A.A. Gchdanov (USSR) | P-15 |
| **THE ROLE OF MECHANICAL PHENOMENA DURING THE FORMATION OF NETWORK POLYMERS**<br>B.A. Rozenberg (USSR) | P-16 |
| **CREEP MEASUREMENTS ON GELATIN GELS**<br>P.G. Higgs, S.B. Ross-Murphy (UK) | P-17 |
| **CORRELATION OF IMPACT STRENGTH AND ENERGY TO FRACTURE OF NETWORKS EPOXIDE-DICY**<br>M.A. Markevitch, S.I. Nazarenko (USSR) | P-18 |

## MONDAY, 21 MAY 1990

15:30-18:00 **POSTER SESSION 1,** continued

| | |
|---|---|
| **PLASTIC DEFORMATION IN GLASSY EPOXY NETWORKS**<br>E. Oleynik (USSR) | P-19 |
| **CORRELATIONS BETWEEN SYNTHESIS AND MORPHOLOGY IN SIMULTANEOUS INTERPENETRATING POLYMER NETWORKS**<br>M.T. Tabka, J.M. Widmaier, G.C. Meyer (FRANCE) | P-20 |
| **INTERPENETRATING POLYMER BLENDS FORMATION**<br>M. Kozlowski (Israel) | P-21 |
| **NUCLEAR REACTION ANALYSIS: A STUDY ON THE INTERFACE FORMATION IN POLYMER MIXTURES BELOW THE CRITICAL POINT**<br>U. Steiner, K. Chaturvedi, O. Zak, G. Krausch, G. Schatz, J. Klein (Israel, Switzerland, FRG) | P-22 |
| **FORCED RAYLEIGH SCATTERING FOR THE STUDY OF DIFFUSION IN COMPLEX GEL SYSTEMS**<br>W.G. Griffin, M.C.A. Griffin (UK) | P-23 |
| **SOLVENT SORPTION CHARACTERISTICS OF PARTICLES AND FILMS OF CARBOXYLATED STYRENE/BUTADIENE EMULSION COPOLYMERS**<br>N. Oger, D. Charmot (France) | P-24 |
| **SWELLING AND RELEASE STUDIES OF pH AND GLUCOSE SENSITIVE HYDROGELS**<br>M. Goldraich, J. Kost (Israel) | P-25 |
| **EFFECT OF ULTRASOUND ON SKIN STRUCTURE AND PERMEABILITY**<br>M. Machluf, J. Kost (Israel) R. Langer (USA) | P-26 |
| **KINETICS OF INTERFACE FORMATION BETWEEN WEAKLY INCOMPATIBLE POLYMER BLENDS**<br>J.L. Harden (USA) | P-27 |

## MONDAY, 21 MAY 1990

18:30 **COCKTAIL RECEPTION**

19:00-20:30 **DINNER BREAK**

### SESSION 1, continued

### DYNAMICS, ELASTICITY THEORY, STRUCTURE-PROPERTY

Chairperson: R. Stadler (FRG)

| | | |
|---|---|---|
| 20:30-20:50 | **THE MECHANICAL AND OPTICAL PROPERTIES OF MODEL PTHF NETWORKS**<br>R.S. Stein, L. Jong, A. Hanyu, F. Fontaine, W.L. Wu (USA) | L-9 |
| 20:50-21:10 | **THE INFLUENCE OF THE CHAIN-LENGTH DISTRIBUTION ON THE STRESS-STRAIN BEHAVIOUR OF NETWORKS**<br>H.G. Kilian (FRG) | L-10 |
| 21:10-21:30 | **VARIATION OF CHAINS RADIUS OF GYRATION AT DEFORMATION OF NETWORK WITH STERIC RESTRICTIONS**<br>L.S. Priss (USSR) | L-11 |
| 21:30 | Informal continuation of Poster Session 1 | |

## TUESDAY, 22 MAY 1990

### SESSION 2

### INTERPENETRATING NETWORKS

Chairperson: E.T. Samulski (USA)

| | | |
|---|---|---|
| 08:45-09:30 | **INTERPENETRATING DOUBLE DIAMOND NETWORKS IN MULTIPHASED POLYMERS**<br>E.L. Thomas (USA) | L-12 |
| 09:30-09:50 | **TOUGHENING TETRAFUNCTIONAL EPOXY RESIN WITH POLYETHERIMIDE**<br>A.H. Gilbert, C.B. Bucknall (Israel, UK) | L-13 |
| 09:50-10:10 | **PVME-CROSS-PS SEMI-INTERPENETRATING POLYMER NETWORKS: ON THE RELATION BETWEEN NETWORK TOPOLOGY, PHASE BEHAVIOUR AND MECHANICAL PROPERTIES IN THE GLASS TRANSITION AND TERMINAL REGION**<br>R. Stadler, M-I. Felisberti (FRG) | L-14 |
| 10:10-10:40 | **COFFEE BREAK** | |
| 10:40-11:25 | **SMALL ANGLE NEUTRON SCATTERING FROM INTERPENETRATING NETWORKS**<br>R. W. Richards (UK) | L-15 |
| 11:25-11:45 | **COMPOSITION — PROPERTIES — NETWORK MICROSTRUCTURE. RELATIONSHIP OF RUBBER MODIFIED EPOXY FORMULATIONS**<br>H. Dodiuk, S. Kenig (Israel) | L-16 |
| 11:45-12:30 | **DIRECT IMAGING OF IPN SYSTEMS AND SYNTHESIS BY-PRODUCTS IN CONTROLLED ELECTRON BEAM RADIATION-DAMAGED CRYO-TEM SPECIMENS**<br>Y. Talmon (Israel), M.K. Lindemann (USA) | L-17 |
| 12:30-14:30 | **LUNCH BREAK** | |

**WEDNESDAY, 23 MAY 1990**

## SESSION 3

## EXPERIMENTAL TECHNIQUES

Chairperson: R. Stein (USA)

| | | |
|---|---|---|
| 09:00-09:45 | **ENHANCEMENT OF INHOMOGENEITIES IN GELS UPON SWELLING AND STRETCHING**<br>J. Bastide, E. Mendes, Jr., F. Boue, M. Buzier, L. Leibler, J. Prost (France) | L-18 |
| 09:45-10:05 | **DYNAMICS AND STRUCTURE OF GELATIN GELS**<br>C. Wu, W. Schrof, E. Lueddecke, D. Horn (FRG) | L-19 |
| 10:05-10:50 | **MOLECULAR ASPECTS OF POLYMER NETWORK DEFORMATION: SMALL ANGLE NEUTRON SCATTERING AND $^2$H NMR STUDIES**<br>W. Gronski, F. Forster, W. Pyckhout-Hintzen, T. Springer (FRG) | L-20 |
| 10:50-11:30 | **COFFEE BREAK** | |
| 11:30-12:15 | **CHAIN AND OLIGOMER ORIENTATION IN DEFORMED NETWORKS**<br>E.T. Samulski, A.I. Nakatani (USA) | L-21 |
| 12:15-12:35 | **GELATION AND VITRIFICATION OF EPOXY RESINS MONITORED BY ULTRASONICS MEASUREMENTS**<br>J. R. Emery, D. Lairez, D. Durand (France) | L-22 |
| 12:35-14:00 | **LUNCH BREAK** | |

## WEDNESDAY, 23 MAY 1990

### SESSION 4

### DIFFUSION

Chairperson: M.V. Tirrell (USA)

| | | |
|---|---|---|
| 14:00-14:45 | **DIFFUSION THROUGH RUBBERY AND GLASSY POLYMER MEMBRANES**<br>C.A. Smolders, E. Smit, I. Blume, M.H.V. Mulder (The Netherlands) | L-23 |
| 14:45-15:05 | **NETWORK STRUCTURE OF POLY (METHACRYLIC ACID) AND ITS RELATION TO DIFFUSIVE TRANSPORT**<br>A.M. Weiss, K. Adler, A.J. Grodzinsky, M.L. Yarmush (Israel, USA) | L-24 |
| 15:05-15:25 | **DIFFUSION BEHAVIOUR IN SOLUTIONS OF FLEXIBLE POLYMERS: A COMPARISON BETWEEN EXPERIMENTAL RESULTS AND THEORETICAL PREDICTIONS**<br>B. Nystrom, J. Roots (Norway) | L-25 |

## WEDNESDAY, 23 MAY 1990

### POSTER SESSION 2

15:30-18:00 **VOLUME PHASE TRANSITION OF D N A AND REENTRANT PHENOMENON** P-28
E. Takushi (Japan)

**DEMIXING AND POLYMERIZATION IN SYSTEMS OF ANISOTROPIC GLOBULAR PARTICLES** P-29
P.L. San Biagio, F. Bruge, S.L. Fornili,
M.B. Palma Vittorelli (Italy)

**VISCOSITY AND VISCOELASTICITY OF A GEL-FORMING POLYMERIC SOLUTION IN THE COURSE OF ITS SPINODAL DEMIXING PRECEDING GELATION** P-30
A. Emanuele, M.B. Palma-Vittorelli (Italy)

**ON THE PERIODIC PRECIPITATION PATTERN AND MOVING REACTION BAND IN CHEMICALLY CROSSLINKED POLY(VINYL ALCOHOL) GELS AND IN THIN SILICA GEL LAYERS** P-31
M. Zrinyi, L. Galfi, E. Smidroczki, Z. Racz,
F. Horkay (Hungary)

**ON THE THERMOREVERSIBLE GELATION OF TAMARIND GUM IN THE PRESENCE OF SULFATE IONS** P-32
P. Lang, W. Burchard (FRG),
M. Dentini, V. Crescenzi (Italy)

**THERMOREVERSIBLE GELATION OF SYNDIOTACTIC POLY(METHYL METHACRYLATE)** P-33
S. Thijs, H. Berghmans (Belgium)

**SUGAR COATED HYDROGELS FROM POLYALLYLAMINE. PREPARATION AND CHARACTERIZATION OF MICROGELS AND THE SOL-GEL TRANSITION OF THE CROSSLINKING IN WATER** P-34
P. Denkinger, W. Burchard (FRG), A. Rey (Spain)

**ASSOCIATION OF END-FUNCTIONALIZED POLYSTYRENES INDUCED BY A BIFUNCTIONAL DINITROPHENOL COMPOUND** P-35
G. Merkle, P. Lutz, W. Burchard (FRG)

## POSTER SESSION 2, continued

| | | |
|---|---|---|
| 15:30-18:00 | **PROBABILITY MODELS OF NETWORK FORMING POLYMER SYSTEMS WITH INTRAMOLECULAR REACTION**<br>C. Sarmoria, D.R. Miller (USA) | P-36 |
| | **BRANCHING KINETICS OF EPOXY POLYMERIZATION OF 1,4-BUTANEDIOL DIGLYCIDYL ETHER WITH CIS-1,2-CYCLOHEXANEDICARBOXYLIC ANHYDRIDE**<br>C. Wu (FRG), B. Chu, G. Stell (USA) | P-37 |
| | **BOUNDARY CONDITIONS FOR IONOTROPIC GELATION OF POLYURONIDES**<br>E.E. Braudo (USSR) | P-38 |
| | **CROSS-LINKING INDEX, MOLECULAR WEIGHT-DISTRIBUTION AND RUBBER EQUILIBRIUM MODULUS DURING MULTIFUNCTIONAL CROSS-LINKING**<br>K. te Nijenhuis (The Netherlands) | P-39 |
| | **THE PREPARATION AND CHARACTERISATION OF NOVEL POLYETHER GELS**<br>P.R. Knowles, C. Price (UK) | P-40 |
| | **MONITORING OF PROPERTY AND STRUCTURAL CHANGES DURING POLYMERIZATION AND CURE REACTIONS BY ULTRASONIC METHODS**<br>A. Shefer, M. Gottlieb, G. Gorodetsky (Israel) | P-41 |
| | **REAL TIME DIELECTRIC MEASUREMENTS OF NETWORK FORMATION IN A CROSSLINKING EPOXY AMINE SYSTEM**<br>D. Lairez, J.R. Emery, D. Durand (France)<br>D. Hayward, R.A. Pethrick (UK) | P-42 |
| | **FREQUENCY DEPENDENCE OF VISCOELASTIC PROPERTIES OF SOME PHYSICAL GELS NEAR THE GEL POINT**<br>G. Cuvelier, B. Launay (France) | P-43 |
| | **CHEMORHEOLOGY OF HIGH TEMPERATURE THERMOSETS**<br>I.J. Goldfarb (USA) | P-44 |
| | **DIRECT EVIDENCE OF CROSSLINKS BY METATHESIS DEGRADATION**<br>K. Hummel, E. Hubmann (Austria) | P-45 |

## WEDNESDAY, 23 MAY 1990

### POSTER SESSION 2, continued

| | | |
|---|---|---|
| 15:30-18:00 | **NETWORK BUILD-UP BY POLYETHERIFICATION IN POLYEPOXY-POLYAMINE CURING: THEORY AND EXPERIMENT**<br>K. Dusek, J. Somvarsky, L. Matejka, M. Ilavsky, A. Vazquez (Czechoslovakia, Argentina) | P-46 |
| | **A GENERALIZATION OF THE THEORY OF NETWORK BUILD-UP BASED ON THE THEORY OF BRANCHING PROCESSES**<br>J. Somvarsky, K. Dusek (Czechoslovakia) | P-47 |
| | **SYNTHETIC MODELS FOR BIOLOGICAL NETWORKS: ON THE FORMATION OF SUPRAMOLECULAR STRUCTURES BY COOPERATIVE CLUSTER FORMATION**<br>R. Stadler, C. Hilger, J. Hellmann, L.L. de Lucca Freitas (FRG) | P-48 |
| | **FORMATION OF ENDLINKED CIS 1,4 POLY (ISOPRENE) NETWORKS**<br>Y. Yagen, G. Barnes, M. Gottlieb (Israel) | P-49 |
| | **RHEOLOGICAL KINETIC STUDIES OF THE GELATION OF Cr(+3)/POLYACRYLAMIDE SOLUTIONS**<br>M. Molinari, G. Gallino, T.P. Lockhart (Italy) | P-50 |
| | **VISCOELASTIC BEHAVIOUR OF BETA-LACTOGLOBULIN GEL STRUCTURES**<br>M. Stading, A-M. Hermansson (Sweden) | P-51 |
| | **MODELLING FIBRIN(0GEN) COAGULATION VIA A CATION-DRIVEN MECHANISM**<br>G. Marx (Israel) | P-52 |
| | **A KINETIC APPROACH TO CROSSLINKING POLYMERIZATION**<br>H. Galina (Poland) | P-53 |
| | **HIGH FREQUENCY DYNAMIC PROPERTIES OF POLYMER MELTS UNDERGOING CURING AND SOL-GEL TRANSITION**<br>M. Gandelsman, M. Gottlieb, G. Gorodetsky (Israel) | P-54 |
| | **INFLUENCE OF THE CONDITIONS OF TRANSITION OF SOLUTION-NETWORK-SOLID STATE ON THE PROPERTIES OF MICROFILTRATION MEMBRANES**<br>N.P. Leksovskaya, Z. Yu. Chereysky, I.G. Ruban, O.I. Nachinkin (USSR) | P-55 |

## WEDNESDAY, 23 MAY 1990

| | | |
|---|---|---|
| 18:00-20:30 | **DINNER BREAK** | |

## SESSION 5

## DID WE HAVE IT WRONG ALL ALONG?

Chairperson: W. Burchard (FRG)

| | | |
|---|---|---|
| 20:30-20:50 | **1.5 YEARS LATER: S.A.N.S. LOZENGES/BUTTERFLIES PATTERNS IN DEFORMED POLYSTYRENE NETWORKS**<br>F. Boue, J. Bastide, M. Buzir, E. Mendes, F. Zidinski (France) | L-26 |
| 20:50-21:10 | **UNIAXIAL ORDER INDUCED IN A STRAINED PDMS NETWORK**<br>B. Deloche, P. Sotte, J.Herz (France) | L-27 |
| 21:10-21:30 | **COMMENTS ON THE FREE-ENERGY-OF-MIXING TERM IN THE FLORY-REHNER THEORY OF POLYMER NETWORKS GELS**<br>P.F. Mijnlieff (The Netherlands) | L-28 |
| 21:30-21:50 | **ENERGY ELASTIC CONTRIBUTIONS TO THE DEFORMATION BEHAVIOUR OF ELASTOMERS**<br>D. Goeritz, R. Grassler (FRG) | L-29 |
| 21:50 | Informal continuation of Poster Session 2 | |

## THURSDAY, 24 MAY 1990

### SESSION 6

### GELATION, SOL-GEL TRANSITION

Chairperson: S. Alexander (Israel)

| | | |
|---|---|---|
| 09:00-09:45 | **GROWTH PROCESS OF POLYMERS NEAR THE GELATION THRESHOLD**<br>M. Adam (France) | L-30 |
| 09:45-10:05 | **SOL-GEL TRANSITION IN BIOPOLYMERS**<br>M.A.V. Axelos, M. Kolb (France) | L-31 |
| 10:05-10:50 | **RELAXATION PHENOMENA NEAR THE SOL-GEL TRANSITION**<br>J.E. Martin, D. Adolf (USA) | L-32 |
| 10:50-11:30 | **COFFEE BREAK** | |

### SESSION 6, continued

### *GELATION, SOL-GEL TRANSITION*

Chairperson: K. Dusek (Czechoslovakia)

| | | |
|---|---|---|
| 11:30-11:50 | **MOLECULAR DYNAMICS SIMULATIONS OF POLYMER NETWORKS**<br>G.S. Grest, M. Murat (USA), K. Kremer (FRG) | L-33 |
| 11:50-12:10 | **A NEW DESCRIPTION FOR $A_f$ HOMOPOLYMERIZATION: MONTE CARLO SIMULATIONS**<br>A.M. Gupta, R.C. Hendrickson, C.W. Macosko (USA) | L-34 |
| 12:10-12:30 | **ON THE FRACTAL NATURE OF THE STRUCTURE OF PARTICLE GELS**<br>T. van Vliet, L.G.B. Bremer, P. Walstra (The Netherlands) | L-35 |
| 12:30-14:00 | **LUNCH BREAK** | |

## THURSDAY, 24 MAY 1990

## SESSION 6, continued

## GELATION, SOL-GEL TRANSITION

Chairperson: Y. Cohen (Israel)

| | | |
|---|---|---|
| 14:00-14:45 | **EXPERIMENTAL OBSERVATION OF THE SOL-GEL TRANSITION**<br>H.H. Winter (USA) | L-36 |
| 14:45-15:05 | **A DEFINITION OF THE CONCEPTS "GELATION TEMPERATURE" AND "GELATION CURVE" BY MEANS OF RELAXATION TIME SPECTRA**<br>K. Visscher, P.F. Mijnlieff (The Netherlands) | L-37 |
| 15:05-15:25 | **SPINODAL DEMIXING, PERCOLATION, AND GELATION OF BIOSTRUCTURAL POLYMERS**<br>M.U. Palma, P.L. San Biagio, D. Bulone, F. Madonia, L. Di Stefano (Italy) | L-38 |
| 15:25-16:00 | **COFFEE BREAK** | |

## THURSDAY, 24 MAY 1990

## SESSION 7

## CHEMISTRY AND STRUCTURE IN NETWORK FORMATION

Chairperson: R.F.T. Stepto (UK)

| | | |
|---|---|---|
| 16:00-16:20 | **ANHYDRID CURING OF EPOXY RESINS VIA CHAIN REACTION**<br>W. Burchard, V. Trappe (FRG), B. Steinmann (Switzerland) | L-39 |
| 16:20-16:40 | **NETWORK FORMATION IN POLYURETHANES DUE TO ALLOPHANATE, BIURET AND ISOCYANURATE FORMATION**<br>K. Dusek, M. Spirkova, M. Ilavsky (Czechoslovakia) | L-40 |
| 16:40-17:00 | **POPULATIONS OF SPECIES FORMED ON CROSSLINKING PREFORMED POLYMER CHAINS**<br>G.C. Eastmond, J.E. Richardson (UK) | L-41 |
| 17:00-17:20 | **NETWORKS FROM DICYANATE OF BISPHENOL A AND DIPHENOLS**<br>M. Bauer, J. Bauer (DDR) | L-42 |
| 17:20-17:40 | **MONTE CARLO CALCULATION OF A PARTIAL REACTION IN RADICAL CROSSLINKING OF 1,4-POLYBUTADIENE**<br>M.G. Martl, R. Saf, K. Hummel (Austria) | L-43 |

## FRIDAY, 25 MAY 1990

### SESSION 8

### SCALING, ENTANGLEMENTS, AND REPTATION

Chairperson: J. Klein (Israel)

| | | |
|---|---|---|
| 09:00-09:45 | **ELASTICITY, NONAFFINE BEHAVIOUR, AND THE BREAKDOWN OF HYPERSCALING IN TENUOUS NETS**<br>S. Alexander (Israel) | L-44 |
| 09:45-10:05 | **RELAXATION OF ENTANGLED POLYMERS AT THE CLASSICAL GEL POINT**<br>M. Rubinstein (USA), S. Zurek, T.C.B. McLeish, R.C. Ball (UK) | L-45 |
| 10:05-10:50 | **POLYMER/POLYMER INTERDIFFUSION**<br>F. Brochard-Wyart (France) | L-46 |
| 10:50-11:15 | **COFFEE BREAK** | |

### SESSION 8, continued

### SCALING, ENTANGLEMENTS, AND REPTATION

Chairperson: B.E. Eichinger (USA)

| | | |
|---|---|---|
| 11:15-12:00 | **DIFFUSION IN MICROSTRUCTURED POLYMERS**<br>M. Tirrell, M.S. Kent, N. Balsara, T.P. Lodge (USA) | L-47 |
| 12:00-12:45 | **STRONGLY KNOTTED POLYMERS**<br>P.G. de Gennes (France) | L-48 |
| 12:45 | **CONCLUDING REMARKS** | |

# ABSTRACTS

# Dynamics of Slip Link Networks

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## Abstract

As an alternative to using statistical mechanical calculation of the free energy of a network, one may go directly to the dynamics of the molecules and derive the dynamical constitutive equation. This has several advantages:

1) There does not need to be separation of microscopic and macroscopic behaviour i.e. one can avoid the calculation of a free energy and the subsequent assumption that this free energy can be employed in Navier's equations. In polymer problems this separation is not valid.

2) Transport coefficients have a structure for networks, and this cannot be obtained from static statistical mechanics.

3) The permanent constraints of the network invalidate conventional Gibbs formula and need difficult generalizations such as the replica method. A dynamical approach avoids this.

[illegible]

A deviation of the elastic equations of motion will be given will allow a comparison with the tube model theory of viscoelasticity of the melt. Several interesting new results will be shown.

# STRUCTURAL EFFECTS IN SWOLLEN MODEL NETWORKS

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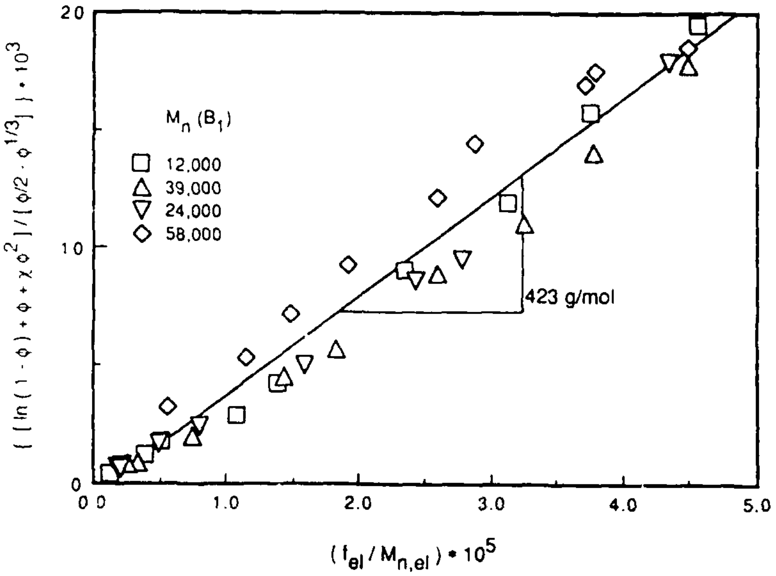
In order to gain a better understanding of the relationship between structure and thermodynamic properties in polymer networks swollen to equilibrium in a good solvent and to examine and evaluate various models and theories, we have synthesized "model" polydimethylsiloxane (PDMS) networks with various amounts of pendant chains. The PDMS networks were prepared by endlinking mixtures of monovinyl ($B_1$) and divinyl ($B_2$) PDMS chains with a tetrafunctional crosslinker and a platinum catalyst. The $B_2$ had a number average molecular weight of $17.9 \times 10^3$ g/mol (or 17.9K) and a polydispersity of 1.24, as measured by gel permeation chromatography. The $B_1$ molecular weights were 11.9K, 23.5K, 39.0K, and 58.0K, and the corresponding polydispersities ranged from 1.17 to 1.34. The mole fraction of $B_1$ was varied from zero to 70%. The networks were prepared at 35°C in the bulk (no solvent) and at stoichiometric ratios that should produce networks with minimum swelling. The sol fraction of all the prepared networks was extracted and its value determined.

The physical measurements that we have performed on these networks, so far, consist of the degree of equilibrium swelling in toluene and of the cooperative diffusion coefficient of the swollen networks obtained from dynamic light scattering experiments. We expressed the data on the degree of equilibrium swelling in terms of the polymer volume fraction at equilibrium, $\phi$, and analyzed it using the Flory-Rehner model (1) and the Macosko-Miller model of nonlinear polymerizations (2). The latter model was used to calculate the density of elastic chains, $v_e$, which can be expressed as $\rho_2 f_{el}/M_{n,el}$ where $\rho_2$ is the density of the polymer, $f_{el}$ is the weight fraction of elastic material in the dry extracted network and $M_{n,el}$ is the number average molecular weight of the elastic chains. Values of $f_{el}$ and $M_{n,el}$ were determined using the Macosko-Miller model, the stoichiometry of the reactants, and the values of the sol fractions. The cooperative diffusion coefficient data was analyzed in terms of scaling laws and the c* theorem (3) which also makes predictions about the dependence of $\phi$ on $M_{n,el}$.

In the figure shown here, we plot the swelling data in the form of the Flory-Rehner model which predicts a direct proportionality between the quantity plotted on the ordinate versus $f_{el}/M_{n,el}$ which we have calculated with the Macosko-Miller model. We see that for all four series of networks synthesized, the proportionality is indeed reasonably well obeyed. However, the slope of the best fit line is 423 g/mole and does not correspond to what one would expect on the basis of the Flory-Rehner model. For the affine deformation hypothesis, this model would predict a slope of $\rho_2 v_1 = 104$ g/mole where $v_1$ is the molar volume of the solvent. For a phantom network, the predicted slope would be even lower. It is likely that the major reason for this discrepancy is the interpenetration (or interspersion) of the chains (4,5). It is straightforward to calculate that for our model networks prepared without $B_1$, the chains are still highly interspersed when swollen to equilibrium. It then follows that the equilibrium swollen networks do not satisfy the c* theorem.

Dynamic light scattering measurements confirm the violation of the c* theorem which predicts a dependence of D on molecular weight between crosslinks of $M^{-3/5}$. We find, however, that D scales as $\phi^{0.73}$ and appears to be independent of network structure. These results indicate that the scaling law $D \sim \phi^{3/4}$ is more general than the way it has been derived which makes use of the c* theorem and is restricted to linear chains between crosslinks (3).



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# ELASTICITY THEORY: MOLECULAR THEORY OF THE MOONEY-RIVLIN EQUATION AND BEYOND

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A fundamental theory of elastomers is difficult because it requires a detailed study of many body interactions. A theory of elasticity must address the following: (1) data in uniaxial extension follow the Mooney-Rivlin equation if the extension ratio is not too large, (2) in biaxial extension the Mooney-Rivlin stress-strain relation is inadequate, (3) the $C_2$ term decreases with swelling, and (4) the Frenkel-Flory-Rehner theory is inaccurate. The Mooney-Rivlin free energy density is

$$A/V = C_1(\lambda_1^2 + \lambda_2^2 + \lambda_3^2) + C_2(1/\lambda_1^2 + 1/\lambda_2^2 + 1/\lambda_3^2) \quad . \qquad [1]$$

If $Z_c$ and $Z_u$ represent the partition functions for crosslinked and uncrosslinked polymers, one may write $Z_c = Z_u(Z_c/Z_u)$ and treat $Z_c/Z_u$ by a perturbation scheme.

Define the $(3 \times 3)$ gyration tensor $S$ by $S = (N+n_1)^{-1}YY'$ where there are $N$ polymer segments, $n_1$ solvent molecules, and $Y$ is a $3 \times (N + n_1)$ matrix of coordinates. Let $dS$ be the volume element associated with $S$. The transpose of a matrix or vector is denoted by the prime symbol. The distribution of $S$ that will give an elastic equation of state is

$$P(S) = Z_c(S)/Z_u(S) = \frac{\int \exp\left\{-\frac{1}{kT}\left[V_c(\bar{b};X,x) + V_c(b;X,x)\right]\right\} dX\,dx/dS}{\int \exp\left\{-\frac{1}{kT}\left[V_u(\bar{b};X,x) + V_u(b;X,x)\right]\right\} dX\,dx/dS} \qquad [2]$$

since the elastic free energy is $A_{e\ell}(S) = -kT\ell nP(S)$. The value of $S$ that minimizes $A_{e\ell}(S)$ is $S^\circ$; it is the solution of $\partial P(S)/\partial S|_{S=S^\circ} = 0$. Thus,

$$\Delta A_{e\ell} = A_{e\ell}(S) - A_{e\ell}(S^\circ) = -kT\ell n[P(S)/P(S^\circ)] \quad . \qquad [3]$$

The bonded potential will be written as

$$\frac{1}{kT}\overline{V}(b;X) = \gamma tr(XKX') \qquad [4]$$

where $\gamma = 3/2 < \ell^2 >_0$, and $< \ell^2 >_0$ is the mean square length of one statistical bond in a chain. The matrix $K$ is a Kirchhoff matrix which describes the connectivity of the network $(K_c)$ or the linear chains $(K_u)$. The nonbonded interactions are handled with the replacement

$$\overline{V}(\bar{b};X) \rightarrow \int a[\rho(\mathbf{r})]d\mathbf{r} \qquad [5]$$

where the integral of the (Helmholtz) free energy density $a[\rho(\mathbf{r})]$ is taken over the volume of the system. The density $\rho(\mathbf{r})$ is an implicit function of the coordinates $X$ through the standard equation

$$\rho(\mathbf{r}) = \sum_{j=1}^{N} \delta(\mathbf{r} - X_j) \qquad [6]$$

where the $X_j$ are the the coordinates of segment $j$. Now expand the free energy as a function (not functional) of the density fluctuations about the mean density $\overline{\rho}$. This gives

$$\overline{V}(\bar{b};X) \approx a(\overline{\rho})V - \frac{1}{2}a''(\overline{\rho})\overline{\rho}^2 V + \frac{1}{2}a''(\overline{\rho})\int[\rho(\mathbf{r})]^2 d\mathbf{r} \quad . \qquad [7]$$

with this eq. [2] becomes

$$P(S) = \frac{\int \exp[-(a''/2kT)\int[\rho_c(\mathbf{r})]^2 d\mathbf{r} - \gamma tr(XK_cX')]dX/dS}{\int \exp[-(a''/2kT)\int[\rho_u(\mathbf{r})]^2 d\mathbf{r} - \gamma tr(XK_uX')]dX/dS} \quad . \qquad [8]$$

The segment density at $\boldsymbol{r}$ from a chain CM at $\boldsymbol{r}'$ is $\rho_S(\boldsymbol{r} - \boldsymbol{r}')$, and the total segment density is

$$\rho(\boldsymbol{r}) = \int \rho_S(\boldsymbol{r} - \boldsymbol{r}')\rho_C(\boldsymbol{r}')d\boldsymbol{r}' \qquad [9]$$

where $\rho_C(\boldsymbol{r}')$ is the density of chain CM in volume element $d\boldsymbol{r}'$. The Fourier version of $\rho_S(\boldsymbol{r})$ is

$$\hat{\rho}_S(\boldsymbol{k}) = \sum_{p=1}^{n} \exp\left[-(\frac{1}{3} - u + u^2) < s^2 >_0 k^2\right] \qquad [10]$$

for a chain of $n$ segments, where $u = p/n$. Crosslinks alter the term $(\frac{1}{3} - u + u^2)$ in eq. [10] by perturbing the Kirchhoff matrix elements via connections between the chain and the rest of the network.

Factor $\exp(-\frac{1}{2}k_\alpha k_\beta S^{\alpha\beta})$ from the series expansion of the Fourier version of eq. [6] to get

$$\sum_j \exp(-k_\alpha x_j^\alpha) = \nu \exp(-\frac{1}{2}k_\alpha k_\beta S^{\alpha\beta})F(\boldsymbol{k}) \quad , \qquad [11a]$$

where $$F(\boldsymbol{k}) = 1 + \frac{i}{3!}k_\alpha k_\beta k_\gamma S^{\alpha\beta\gamma} + \frac{1}{4!}k_\alpha k_\beta k_\gamma k_\delta(S^{\alpha\beta\gamma\delta} - 3S^{\alpha\beta}S^{\gamma\delta}) + \ldots \qquad [11b]$$

to terms of $0(k^4)$. Using these principles allows one to write

$$\begin{aligned}\int [\rho(\boldsymbol{r})]^2 d\boldsymbol{r} = \frac{N^2}{(4\pi)^{3/2}|S|^{1/2}}\Bigg\{ & B_1 - B_2 a\left(\frac{1}{S_1} + \frac{1}{S_2} + \frac{1}{S_3}\right) \\ & + B_3 a^2\left(\frac{1}{S_1^2} + \frac{1}{S_2^2} + \frac{1}{S_3^2}\right) + \frac{B_4 a^2}{|S|}(S_1 + S_2 + S_3) + \ldots\Bigg\}\end{aligned} \qquad [12]$$

where the $B_i$ are constants that derive from the "shape tensors" $S^{\alpha\alpha\beta\beta\ldots\sigma\sigma}/S_\alpha S_\beta \ldots S_\sigma$.

We have arrived at the elastic equation of state

$$A_{el}(S) = D_1(S_1 + S_2 + S_3) + D_2\left[\left(\frac{1}{S_1} + \frac{1}{S_2} + \frac{1}{S_3}\right) - b'\left(\frac{1}{S_1^2} + \frac{1}{S_2^2} + \frac{1}{S_3^2}\right)\right] \qquad [13a]$$

where $$D_1 = 3\nu kT\kappa_1/2 < r^2 >_0 \qquad [13b]$$

and $$D_2 = \frac{cV_2^2/|S|^{1/2}}{\beta\phi_2^2 + \overline{V}_1\phi_1/kT(1 - \phi_1\chi')} \qquad [13c]$$

with use of Helfand and Tagami. Here $b'$ and $c$ are the two free parameters of the theory. The quantity $V_2 = N\overline{V}_2$ is the volume of the elastomer evaluated at the mean density. Use of minimization eliminates $c$.

Eq. [13] gives the reduced stress as

$$\frac{\sigma_1 - \sigma_2}{\lambda^2 - 1/\lambda} = [f] = 2C_1 + 2C_2/\lambda - 2C_3/\lambda^3 \qquad [14a]$$

where $$C_1 = \left(\frac{D_1 S_\alpha^\circ}{V}\right)\left(\frac{5 - 11b}{5 - 7b}\right) \quad , \qquad [14b]$$

$$C_2/C_1 = 2/(5 - 11b) \qquad [14c]$$

and $$C_3/C_1 = 4b/(5 - 11b) \quad . \qquad [14d]$$

The coefficients of the non-gaussian terms are shown to depend upon the presence and quality of a diluent, which modifies the magnitude of the density fluctuations.

# ELASTICITY OF POLYMER GELS: EFFECT OF SOLVENT QUALITY ON THE SHEAR MODULUS OF POLY(VINYL ACETATE) NETWORKS

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In polymer solutions the concept of good and poor solvent is related to the temperature. At the theta temperature the attractive and repulsive forces compensate, and the polymer chain obeys Gaussian statistics. By changing the temperature the interactions between monomers can be altered which results in progressive transition between different regions characterized by different chain statistics. Experimental information is mainly available on the conformation of single chains in solution.

Much fewer studies have been performed on gels. Systematic investigations of both elastic and swelling properties of polymer networks as a function of solvent quality are lacking.

Our objective in the present study was therefore to investigate the temperature dependence of the shear modulus and the equilibrium concentration of swollen networks above and below the theta temperature. It was desirable from our point of view to select a polymer-solvent system for which the gradually alteration of the interactions between monomers was possible by changing the temperature. For this reason we chose poly(vinyl acetate) gels cross-linked by glutaric aldehyde. Isopropyl alcohol, a theta solvent for poly(vinyl acetate) at 52 °C, was selected as the diluent. Shear modulus measurements were performed on the gels in equilibrium with excess amount of diluent, at eight different temperatures between 30 °C and 70 °C. At 70 °C isopropyl alcohol can be considered as a good solvent for poly(vinyl acetate), while below the theta temperature the solvent becomes progressively poorer.

Experimental findings obtained for gel homologues will be discussed and compared with theoretical predictions.

## ACKNOWLEDGMENT

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# INTERPRETING THE PROPERTIES OF MODEL HDI - AND MDI - BASED POLYURETHANE NETWORKS

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Systematic studies of the formation and properties of model polyurethane networks based on polyoxypropylene(POP) triols and tetrols reacting with hexamethylene diisocyanate(HDI) and 4,4-diphenylmethane diiscoyanate (MDI) have provided data (1-3) which enable network structures and properties to be correlated and intepreted directly in terms of reactant amounts, structures, molar masses and functionalities, and the dilution of preparation. The data concerned are gel points and the sol fractions and small-strain moduli of the networks at complete reaction. In the present contribution, comparisons using data from two laboratories are made and the interpretations given by different theoretical analyses compared. Such analyses are important for the general prediction of the structure and properties of network materials from the formulations used to prepare them, and particularly for investigating relationships between the absolute value of modulus and network structure.

Data from Stepto and collaborators(1,3) on stoichiometric amounts of POP triols and tetrols reacting with HDI in bulk and at various dilutions in nitrobenzene have been analysed in the smallest-loop approximation(3,4). Gel points have been correlated with modulus at complete reaction. It has been shown that the networks behave affinely at small strains, with the moduli of the networks less than the values expected for perfect network structures. The moduli of dry networks decrease with increasing dilution of preparation, and the decrease is larger for trifunctional than for tetrafunctional networks. The trends have been shown to be quantitatively consistent with inelastic loop formation causing network imperfections.

A Monte Carlo(MC) analysis of some of the data by Lee and

Eichinger(5) has confirmed the occurrence of smallest loops and their dominance in causing reductions in modulus. Further, the MC analysis gives excellent predictions of the variations of gel point and modulus with dilution. However, the absolute values of moduli appear to be higher than those found experimentally, indicating some undercounting of loops towards the end of the reaction.

Data of Dusek and Ilavsky(2) and those of Stepto and collaborators(1) on stoichiometric reaction mixtures of a POP triol with MDI are also compared. The two sets of data are shown to be consistent with each other and to display a behaviour distinct from that of the HDI-based systems. Moduli again decrease with dilution of preparation, but are markedly higher than those of HDI-based networks from the same POP triol. Smallest-loop analysis shows that inelastic loops decrease the modulus and interactions between chains (incipient segmentation) cause a compensating effect.

Again, there is agreement between the smallest-loop analysis and the MC analysis of Lee and Eichinger(5). In general, MC-predicted moduli follow the experimental moduli. Due to the occurrence of loops and dangling ends, moduli decrease as the dilution of preparation increases and as the reactant ratio moves away from stoichiometry. However, the predicted values are now lower than the experimental values, in clear contrast to the results for HDI-based networks.

The work reported here, which compares theoretical interpretations and their implications, forms part of the collaborative programme of work carried out under the IUPAC Working Party on Polymer Networks.

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# RELAXATION OF ENTANGLED POLYMERS IN MELTS

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The stress relaxation function $G(t)$ defines the relaxation properties of polymer melts and the experimentalist measures

$$G''(\omega) = \omega \int_0^\infty \mathrm{d}t \cos \omega t \, G(t)$$

Here, we consider blends consisting of polymers belonging to the same chemical species but with different masses. Let $\varphi_A$ be the volume fraction for the polymers $A$ of mass $M_A$.

The simple reptation assumption of Doi-Edwards consists in writing

$$G(t) = \sum \varphi_A p_A(t) \qquad [1]$$

where $p_A(t)$ is a function defining the reptation process. Moreover, a simple expression of $p_A(t)$ was derived by P.G. de Gennes, namely

$$p_A(t) = \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left[-(2n+1)^2 t/\tau_A\right] \qquad [2]$$

where $\tau_A$ is a relaxation time proportional to $M_A^3$.

However, experimental studies (in particular by R. Colby on polybutadiene) show that this approach is not completely realistic for two reasons

1) A polymer cannot be considered as moving among fixed obstacles and the fact that two interacting polymers move with respect to each other must be taken into account. Thus, the double reptation idea leads to the formula

$$G(t) = \left[\sum_A \varphi_A p_A(t)\right]^2$$

which contrary to [1] is in rather good agreement with the experiment.

2) The function $p_A(t)$ is not only a function of $(t/\tau_A)$ where $\tau_A$ is a relaxation time. To reproduce the experimental results, *it is necessary* to introduce another parameter, which (for instance) may be the number $H_A$ of stress points per polymers ($H_A \propto M_A$).

Here, we derive expressions of $p_A(t)$ more general than [2], by starting from the idea that the motion of a polymer along a stress point can be simulated by assuming that the stress point diffuses (or slides) along the polymer. Thus, expressions of $p_A(t)$ can be deduced from solutions of diffusion equations of the form

$$\frac{\partial P}{\partial t}(x,t) = \frac{\partial}{\partial x}\left[D(x,t)\frac{\partial}{\partial x}P(x,t) + F(x,t)P(x,t)\right]$$

Two possibilities have been studied and will be presented here

1) The diffusion coefficients depend only on $x$ (for instance: $D(x,t) = A^2(x)$ and $F(x) = A'(x)A(x)$)

2) The diffusion coefficients depend only on $t$ ($D(x,t) = D(t)$ and $F(x,t) = 0$).

Both approaches lead to interesting results. In particular, the second one enables us to derive a fairly realistic expression of $p_A(t)$ from first principles.

Moreover, this theory can explain why the viscosity of monodisperse melts consisting of entangled polymers seems to increase proportionally to $M^{3.14}$.

# THE CONCEPT OF INTRINSIC CHAIN STRESS IN POLYMER NETWORKS

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If we consider the collection of atoms forming a network of a rubber-like solid, we can identify two principal types of atomic interactions: the covalent interactions responsible for the long-chain molecules and the noncovalent interactions between pairs of atoms of the same chain or of different chains. In many treatments of rubber elasticity (1), the covalent and noncovalent interactions are regarded as operating on two completely decoupled systems. The covalently-bonded chains are treated as entropic springs in tension. The two-body noncovalent interactions, describing excluded-volume repulsion and long-range attraction, are regarded as producing only a hydrostatic or isotropic contribution to the system's state of stress, whether it is in its undeformed reference state or in a deformed state.

Recent computer simulations of polymer melts and networks, (2)-(4), contradict this conventional view. At realistic densities we find that there is strong, deformation-dependent, coupling between the covalent bond structure and the noncov[illegible] interactions and that, as a consequence, the latter make a significant nonhydrosta[illegible] anisotropic contribution to the stress.

These results demonstrate the need to consider both covalent and noncovalent interactions on an equal footing. To do this we make use of the generalized virial theorem (5) that rigorously describes the state of stress in any collection of interacting atoms. As a consequence of this theorem the stress in a polymer network can be written in the form (6)

$$\frac{vt_{ij}}{kT} = \sum_{\gamma} x_{ij}(\gamma) \qquad [1]$$

where $t_{ij}$, i, j = 1, 2, 3, is the macroscopic stress tensor referred to a fixed laboratory frame $x_i$, v is the volume of the system, k is Boltzmann's constant, T is temperature, $x_{ij}(\gamma)$ is the contribution to the stress made by chain $\gamma$, and the sum is over all of the chains of the system. We make the simplifying assumption that network junctions are not subject to thermal fluctuations and introduce a local coordinate system $\bar{x}_r(\gamma)$ with $\bar{x}_1(\gamma)$ in the direction of the end-to-end vector of the $\gamma$ chain. By the usual laws of tensor transformation we may then write

$$x_{ij}(\gamma) = \bar{x}_{rs}(\gamma)\, a_{ri}(\gamma)\, a_{sj}(\gamma) \qquad [2]$$

where $a_{ri}(\gamma)$ is the matrix of direction cosines between the $x_i$ and $\bar{x}_r$ coordinate systems, the summation convention on repeated indices is used, $x_{ij}(\gamma)$ is the chain stress referred to the laboratory reference frame $x_i$ and $\bar{x}_{rs}(\gamma)$ is the same tensor referred to the local coordinate system $\bar{x}_r(\gamma)$.

We term the quantity $\bar{x}_{rs}(\gamma)$ the intrinsic chain stress (6) and regard it as the appropriate generalization, for interacting chains, of the concept of the axial chain force used in discussing isolated chains. It appears natural to make the assumption that $\bar{x}_{rs}$ is a cylindrical tensor, i.e. one with $\bar{x}_{11}$ and $\bar{x}_{22} = \bar{x}_{33}$ as its only non-zero components. Then $\bar{x}_{11}$ corresponds to the axial force exerted by the chain while $\bar{x}_{22} = \bar{x}_{33}$ represent the radial stresses exerted by the chain in response to its confining environment.

In order to assess quantitatively the implications of the intrinsic stress concept, we have applied it to a simple four-chain model of a polymer network subject to a uniaxial deformation. The resulting stress-strain relation is a generalization of the classical formulation that exhibits both the Mooney effect in a dry network (6) and the decrease in this effect that is observed in swollen networks (7).

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# DYNAMIC MECHANICAL BEHAVIOR AND THE DC CONDUCTIVITY OF POLY(N,N-DIETHYLACRYLAMIDE) GELS IN THE COLLAPSE REGION

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The dynamic mechanical behavior at frequency $\omega$=1 Hz and the DC conductivity of networks of poly(N,N-diethylacrylamide) and copolymers of diethylacrylamide with sodium methacrylate (MNa) (molar ratio $x_{MNa}$=0-0.05) swollen in deionized water were measured in the temperature range 20-80°C.

With increasing temperature, at $T_c$ polymer chains collapse from random coil to more compact globular conformations. In the region of globular conformations ($T > T_c$) a heterogeneous turbid structure is observed in the networks. The collapse is reflected in increase of the storage modulus $G'$; the magnitude of this increase decreases with ionization. The dependence of the loss modulus $G''$ on temperature allows us to conclude that the magnitude of losses in the collapsed state is affected rather by $x_{MNa}$ (the modulus $G''$ increases with increasing ionization) than by the heterogeneous structure of the networks.

While in the low-temperature range ($T < T_c$, expanded state) the volt-ampere (V-A) behavior all networks have a semiconductive character (conductivity increases with increasing temperature), in the high-temperature range ($T > T_c$) the conductivity of the network without charges rapidly decreases with increasing temperature (metallic character). The presence of charges on the chain raises the conductivity and shifts the temperature of the change in conductivity $T_c$ to higher values. In the collapse region of ionized networks anomalies were observed on V-A characteristics.

# THE MECHANICAL AND OPTICAL PROPERTIES OF MODEL PTHF NETWORKS

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Model networks of poly(tetrahydrofuran) have been prepared by end-linking prepolymer with a crosslinking agent using coupling reactions having well-defined chemistry. The resulting networks were characterized using infrared spectroscopy, NMR, and sol content measurements.

Stress strain curves were obtained, both in the dry and swollen states and were compared with predictions of the Flory-Erman and Erman-Monnerie theories. The experimental modulus was found to exceed that predicted on the basis of stoichiometry.

Bimodal networks containing known ratios of long and short chains were prepared and examined as above. These were labelled with deuterium where either the long or short components carried the label. This permitted the measurement of segmental orientation of either type of chain by observing infrared dichroism arising from C-D or C-H bands. Segmental orientation differences were found to be less than predicted using the affine Kuhn-Grün calculation.

Segregation of chains during the crosslinking reaction was studied using the small-angle neutron scattering facilities of the National Institute of Standards and Technology. These measurements demonstrated initial preferential reaction of the short chain components with each other, leading to networks having short chain clusters.

The deformation of these labelled bimodal networks was studied by small-angle neutron scattering which complemented the infrared dichroism measurement of segmental orientation.

Stress-induced crystallization of the bimodal networks was compared with that of unimodal ones, using birefringence as a techniques. Higher crystallization rates of the bimodal ones were found. It is postulated that this is a consequence of the more highly oriented short chain regions serving as nucleating sites.

# The influence of the chain-length distribution on the stress-strain behaviour of networks

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Within the framework of the van der Waals theory of networks one has the opportunity to discuss the influence of the chain-length distribution on the stress-strain curves of networks. Because van der Waals network is considered as a conformational gas with weak interactions, strain-energy is equiparted. To satisfy this condition, chains of different length must in average be stretched to different degrees so as to reach simultaneously the maximum chain extension. In terms of an "equivalent monomodal network" this condition leads to a unique definition of the maximum strain in the network with a chain-length distribution. By describing stress-strain experiments it is then possible to elicit a new structure parameter which identifies the existence of a chain-length distribution. Attempts of charaterizing the chain-length distribution are presented. Representative examples will be discussed.

In addition, the theoretical conception allows to reflect conditions of mechanical stability for networks with a very broad chain-length distribution. A special role of very long chains is indicated. It might be that these results are also of interest for the understanding of deformation in transient networks.

# VARIATION OF CHAINS RADIUS OF GYRATION AT DEFORMATION OF NETWORK WITH STERIC RESTRICTIONS

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According to Flory theory (1) the properties of real polymer networks are intermediate between the properties of affine and phantom networks. The calculation made on this basis (2) for the variation of the chains radius of gyration $R_g$ at the network deformation contradicts to the experimental data on SANS. These data lie on the border of the theoretically admissible area and even beyond these limits (Fig.2). This makes one doubt the supposition of the affine chain deformation in the real networks and stimulate creation of ideas about the mechanism of the non-affine chain deformation (3). However, the theory of Flory considers the influence of steric restrictions (arising due to the impossibility of chains intersection) only on fluctuation of junctions, whereas in the real networks they act along the whole chain contour. Hence it is natural to attempt at calculating $R_g$ for this case.

The model taken for the calculation is shown in Fig.1. Here the double line, 1, depicts the channel contour, i.e. some mean position of the chain among the neighbours surrounding it. The thick line, 2, presents the instantaneous conformation of the chain. The chain and the channel are connected by the harmonic potential shown as springs in the picture. The latter ones are rigidly connected with the chain and slide freely along the channel. Thus, in this model fluctuations of the intermediate points of the chain are restricted only in the direction normal to the channel contour and they are free along it. The theory of rubber-like elasticity built on this model agrees well with the experimental data for the stress-strain dependences and also allows to describe a broad range of regularities for the coefficient $C_c$ ($C_2$ analogue in Mooney-Rivlin equation (4)) dependence on different factors (5).

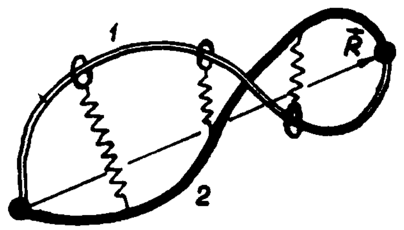

Fig.1

Calculation of $R_g$ is done for one tie between the chain and the channel. For the uniaxial deformation it gives:

$$\langle R^2_{g\parallel}\rangle = \frac{\lambda^2 R_0^2}{36} + \frac{N\ell^2}{144}\left\{3 + \frac{6A}{K} + 3D(1-B) + A^2\left[\frac{D}{\lambda}\left[1+(\lambda^2-2)B\right]\right]\right\} \quad [1]$$

$$\langle R^2_{g\perp}\rangle = \frac{R_0^2}{\lambda} + \frac{N\ell^2}{144}\left\{3 + \frac{6A}{K} - \frac{3D}{\lambda^3}(1-\lambda^3 B) + A^2\left[\frac{D}{2\lambda^4}(\lambda^3-2)+\lambda^6 B\right]\right\} \quad [2]$$

where $\lambda$ is extention ratio, $R_0^2$ is mean square distance between junctions in undeformed state, $B=(\tan^{-1}\sqrt{\lambda^3-1})/\sqrt{\lambda^3-1}$, $D=\lambda^3/(\lambda^3-1)$, $A=KNl^{2}/(KNl^{2}+6)$, K is stiffness of the spring, N is number of segments in the chain, l is their length.

Theoretical dependences calculated with these formulae for the affinely displacing junctions1,3 and the freely fluctuating junctions 2,4 are compared in Fig.2 with the corresponding dependences of the classic theory(2) 5,6 and experimental data of Beltzung et al (6) for polydimethylsiloxane cross-linked in the bulk by an end-linking process. The values of the constants were chosen from the condition $C_2=C_1$ ($C_c=1.6C_1$). The dependences calculated with formula [1] are situated somewhat lower than the ones calculated with the classic theory and the experimental data turn out to be within the theoretically admissible interval, remaining at its lower limit. The results of the calculation by formula [2] practically coincide with the results of the classic calculation.

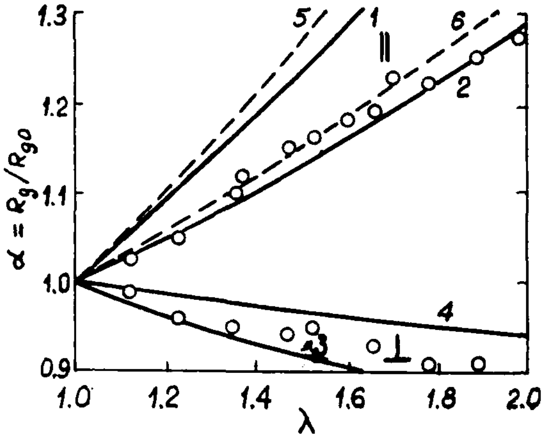

Fig.2

The obtained results demonstrate the following:

-account for the steric restrictions displaces the position of the theoretical dependences, thus improving the agreement with experiment;

-this agreement cannot be considered quite satisfactory because in the presence of steric restrictions the fluctuations of junctions cannot be fully free and experimental points must be situated higher relative to curve 2.

One should think that the reason for this incongruity is connected with the fact that in the considered model it is supposed that the chain fluctuations do not depend on the strain. The refinement of the model in this direction should lead to further lowering of the theoretical dependences.

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# INTERPENETRATING DOUBLE DIAMOND NETWORKS IN MULTIPHASED POLYMERS

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Interpenetrating Polymer Networks (IPNs) are an idealized concept, hardly realized in practice. Interpenetrating *phase* networks, where instead of intertwinned chains, one has intertwinned microphases are readily prepared as equilibrium morphologies (1). Each microphase is three dimensionally continuous so that the composite material is bicontinuous. We have discovered an ordered bicontinuous (the so called "OBDD" structure) interpenetrating microdomain morphology in linear diblock, star diblock and binary and ternary blends of diblock copolymers and homopolymer(s). These systems can be viewed as model mateials offering the opportunity to test structure-property relationships for a new class of microcomposites.

The figure shows the dramatic dependence of mechanical properties for diblock copolymers of different microdomain morphology. The data are for polystyrene/polyiosprene (PS/PI) star diblock copolymers with a PS volume fraction of 27%. At this particular composition, a star diblock with 6 or more arms (6, 8, 12 or 18, the highest arm number investigated thus far) exhibits the OBDD morphology. Due to the three dimensional network of PS channels the material is esentially thermoplastic in nature. For star diblocks with 5 or fewer arms at this composition and arm molecular weight, the equilibrium morphology is that of hexagonally packed cylinders in a matrix of PI which exhibits elastomeric behavior. The enormous mechanical property differences of such subtly chemically different materials arises from the 3D-3D bicontinuous nature of the OBDD microcomposite compared to the 1D-3D cylindrical microcomposite.

We .approach the understanding of the mechanical behavior of these biphasic microcomposites along lines first proposed by Newnham(2). Here, emphasis is placed on geometry and topological connectedness of phases in controlling physical properties. The triply-periodic bicontinuous microdomain morphology of the double diamond structure affords a novel type of microcomposite with potential for enhanced properties over conventional multiphase polymeric materials.

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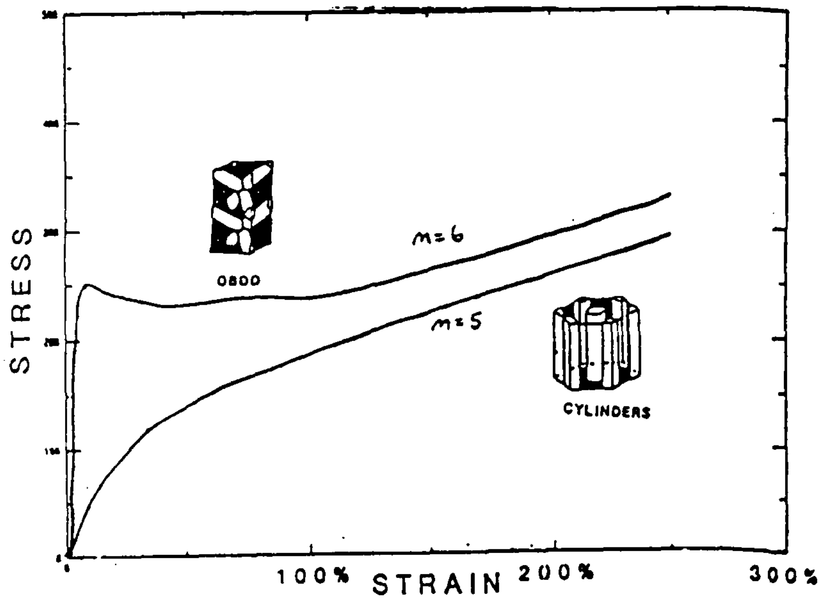

# TOUGHENING TETRAFUNCTIONAL EPOXY RESIN WITH POLYETHERIMIDE

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## Introduction

Epoxy resin-based aereospace composite matrices intended for relatively high service temperatures are by necessity highly crosslinked, and therefore particularly brittle materials. The traditional method of toughening epoxies involves a CTBN rubber modifier demixing as a rubber rich phase during cure(1). Highly crosslinked tetrafunctional epoxy resins, however, are limited in their 'toughenability" by this method(2,3). Such modification significantly reduces the stiffness and glass transition temperature of the resin, as the in-situ phase separation process inevitably leaves some rubber in the continuous epoxy phase(4). Thermoplastic additives have recently been considered a possible alternative(5,6) and the aim of this work is to investigate the way polyetherimide modifies the fracture behaviour of a tetrafunctional epoxy resin.

## Experimental

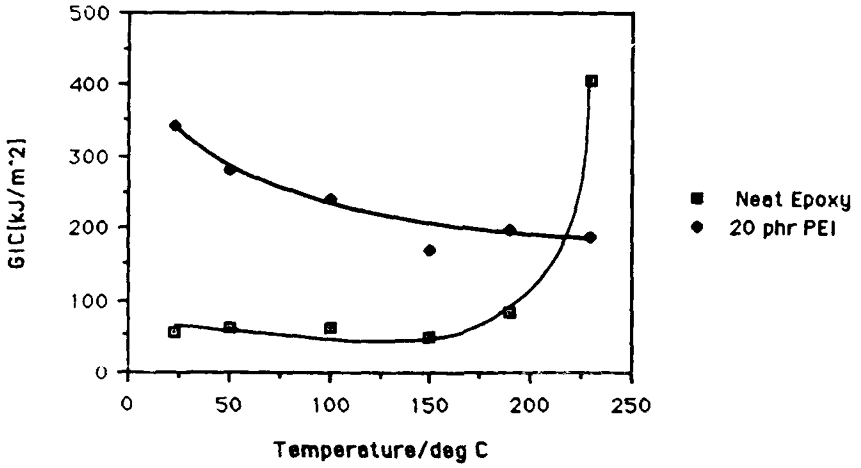
Ciba Geigy ARALDITE MY720 TGDDM-based epoxy resin was cured with 30phr Ciba Geigy HT976 (DDS) hardener. The polyetherimide (PEI) used was General Electric Co. ULTEM 1000. Blends containing between 0 and 30phr PEI were prepared by dissolving the thermoplastic in dichloromethane, combining with the epoxy prepolymer, and then removing the solvent under vacuum. All blends were cured according to a standard cure schedule(7). Dynamic mechanical analysis of cured blends was performed at 10Hz using a Polymer Laboratories DMTA machine. Fracture toughness( $K_{IC}$) and Young's modulus in flexure (E) testing were performed in the three point bend mode at a crosshead speed of 1.3mm/min. in accordance with ASTM E399-78a and ASTM D790-81 respectively. $G_{IC}$ values were calculated according to the equation $G_{IC}=(1-\upsilon^2)K_{IC}^2/E$ , where the Poisson's ratio $\upsilon$ was taken as 0.4, an average obtained from a number of creep tests.

## Results and Discussion

Dynamic mechanical analysis and examination of fracture surfaces by scanning electron microscopy provide clear evidence that at all concentrations a PEI rich phase demixes during cure. Phase inverted domains appear at concentrations of 5phr and above. The glass transition temperature of the thermoplastic rich phase is always lower than in the neat material, most probably due to plasticisation by a low molecular weight species(8).

| Blend | $K_{IC}$ [MPa.m$^{1/2}$] | E [MPa] | $G_{IC}$ [kJ.m$^{-2}$] | Transition Temperature/$^{o}$C α | α' |
|---|---|---|---|---|---|
| Neat PEI | 3.56 | 3.30 | 3.303 | 221 | - |
| Unmodified Epoxy | 0.48 | 3.59 | 0.055 | 265 | - |
| 5phrPEI | 0.73 | 3.52 | 0.131 | 264 | 205 |
| 10phr PEI | 0.82 | 3.62 | 0.160 | 264 | 212 |
| 20phr PEI | 1.17 | 3.47 | 0.340 | 266 | 200 |
| 30phr PEI | 1.53 | 3.80 | 0.530 | 265 | 209 |

The presence of a thermoplastic rich phase produces a significant toughening of the resin, without a major reduction in material stiffness. At 30phr PEI $G_{IC}$ is an order of magnitude greater than in the neat material. At this concentration the thermoplastic rich phase forms the major phase uniformly throughout the material.



A comparison of the fracture energy values measured for the neat epoxy and a blend containing 20phr PEI at elevated temperature is illustrated in the graph above. Both materials exhibit the transitions in the mode of crack propogation expected for cross-linked thermosets, namely stable brittle to unstable brittle to ductile yielding with increasing temperature(9). As observed for other epoxy resins, the neat epoxy of this study is toughest when plastic yielding is the failure mode. Unlike rubber toughened and particulate filled epoxies(10,11), thermoplastic modified tetrafunctional epoxy exhibits a continous decrease in fracture energy with increasing temperature. As the glass transition of the thermoplastic rich phase is approached, the fall in modulus causes the calculated $G_{IC}$ to level off. ($G_{IC}$ is inversely proportional to E as described above). Examination of fracture surfaces by SEM reveals ductile drawing of the thermoplastic phase as a likely source of toughening(12). As the temperature is increased, the yield stress of the thermoplastic rich phase will diminish, consequently reducing its contribution to energy absorbtion as the crack propogates.

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# PVME-CROSS-PS-SEMI INTERPENETRATING POLYMER NETWORKS ON THE RELATION BETWEEN NETWORK TOPOLOGY, PHASE BEHAVIOUR AND MECHANICAL PROPERTIES IN THE GLASS TRANSITION AND TERMINAL REGION

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Most published work on interpenetrating and semi-interpenetrating polymer networks is based on immiscible polymer pairs. Only recently crosslinked multicomponent system based on miscible polymer pairs find increasing interest(1-3). From a practical point of view semi-IPN's are interesting because of the possibility to tailor materials of defined damping characteristics, while the influence of crosslinking of one or both polymeric components on the phase separation behaviour is of more fundamental interest.

The present work summarizes our recent results obtained on PVME-cross-PS-semi-IPN's. For low crosslink densities, miscible semi-IPN's are obtained, while phase separation is observed for higher crosslink densities. Small angle light scattering, DSC and electron microscopy are used to characterize the phase behaviour. The dynamic-mechanical analysis of amorphous polyvinylmethylether-cross polystyrene semi-interpenetrating polymer networks is analyzed as a function of composition, crosslink density and frequency. The miscible semi-IPN's which are obtained at low levels of crosslinking (1 and 2 mol.-% of x-linker) show a rather broad damping maximum at intermediate compositions. Upon increasing the crosslink density, the mechanical damping broadens and finally two damping maxima, related to phase separation between the two components, are observed. Phase separation induced by crosslinking, results in bicontinuous materials is discussed as a possiblility to generate high damping-high modulus materials.

In addition experiments are reported, in which spinodal like phase separation is induced by penetration of water into the homogeneous networks. After phase separation the soluble linear PVME chains are extracted and a glassy microfoam is obtained, whose morphology is determined by the crosslink density and the composition of the original semi-IPN.

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# SMALL ANGLE NEUTRON SCATTERING FROM INTERPENETRATING NETWORKS

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The application of small angle neutron scattering (SANS) to the evaluation of structural features of interpenetrating networks (IPNs) will be illustrated by the results obtained for IPNs based on polydimethyl siloxane as host network. Two quest networks will be discussed. Firstly, deuteropolystyrene, which appears to exist as discrete zones at low volume fractions and for which a structure factor may be extracted on the assumption that the deuteropolystyrene zones are spherical. Parameters characterising the zone size, Porod radius (1), correlation length (2) etc. (3) were extracted from the SANS data and the basis of these methods will be set out (4). The values will be compared with theories (5,6) of zone size in IPNs and the dependence on IPN composition specifically investigated.

The second IPN has polymethacrylic acid (PMAA) as the host network and these materials may display a considerable uptake of water depending on their PMAA content. To generate scattering contrast, these materials were swollen to equilibrium in heavy water and apart from zone sizes, SANS indicated the existence of a diffuse region at the boundary between PMAA zone and PDMS matrix. However, there was no evidence for the existence of a structure factor in this system. Continuity of the PMMA network was proved by the observation that potassium chloride diffuses through these water swollen IPNs and the variation of the diffusion co-efficient with composition will be discussed.

Finally, on the basis that the deuteropolystyrene zones were of colloidal dimensions, and that a structure factor was obtainable, it was attempted to model the mechanical properties of these IPNs as colloidal dispersions (7). For this purpose the structure factor was Fourier inverted to produce an effective pair interaction potential (8) from which the modulus could be calculated. The success, or otherwise, of this attempt to model bulk properties will be discussed together with the factors which influence the magnitude of the values obtained.

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# Composition - Properties - Network Microstructure Relationship of Rubber Modified Epoxy formulations

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A series of room temperature curing epoxy systems that exhibit practical elevated temperature properties have been developed and studied with respect to their final mechanical and thermal properties and the resulting network microstructure.

When the highest possible functionality of both resins and curing agents, which are amenable to room teperature curing, was used, the highest shear properties at elevated temperatures was realized. Upon substituting the trifunctional reactants by a difunctional resin and lower functional curing agent, a reduction in shear properties was observed accompanied by a simultaneous increase in peel strength, especially in the intermediate temperature range. A detailed thermal analysis has indicated that the curing activation energies of the studied systems are lower compared to high temperature curing compositions.

The developing network of the low temperature curing formulations are unique, exhbiting two and three-phase morphologies depending on the specific constituents employed. A conventional two-phase network of matrix and rubber was observed when the basic composition comprising the tetra and trifunctional reactants were used. However, when the trifunctional resin and high functional curing agent were substituted by lower functional ones, or a silane was added to the basic system, a three-phase microstructure developed, In this case the precipitated elastomeric phase was concentrated in defined regions.

This unique microstructure is the result of the specific polymerization kinetics and thermodynamic interactions between the system reactants. The relationship between the composition employed, the resulting properties and the developing network microstructure, of this unique system, was evaluated but requires a more detailed study.

# DIRECT IMAGING OF IPN SYSTEMS AND SYNTHESIS BY-PRODUCTS IN CONTROLLED ELECTRON BEAM RADIATION-DAMAGED CRYO-TEM SPECIMENS

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As in the microstructural analysis of any other system, one would like, ideally, to get direct images of the microphases forming an IPN, or the core-and-shell (CAS) structure that is formed instead. Transmission electron microscopy (TEM) is well suited to give such direct high resolution images, but the usefulness of those is very limited by the poor inherent contrast between different polymers. In a few cases contrast may be enhanced by preferential staining, but this method is not always reliable, and may actually change the microstructure observed. We demonstrate here an alternative method to study IPNs by TEM. Although electron beam radiation damage is usually a deleterious phenomenon, it can be used to enhance contrast, if used in a controlled manner. The method is based on the preferential etching by the electron beam in the TEM of polymer particles embedded in a matrix of crystalline ice, and works well when one component is hydrophilic while the other is hydrophobic.

Organic materials irradiated by an electron beam can be classified into two main groups: "scission-type", where scission is the main radiolytic process, and "crosslinking-type", where crosslinking is predominant (1). The former lose mass rapidly, whereas the latter can withstand high radiation doses with little mass loss. The presence of water in the sample, as in a frozen latex TEM specimen, changes the radiolytic behavior of the irradiated organic substance (2-4). Some materials lose mass very rapidly, but at the same time expand as they become lace-like in appearance. Other materials lose little mass, do not expand, and a cavity forms in the ice around the irradiated particles. We have found that the behavior of a specific polymer does not necessarily follow the above mentioned classification, but is related also to whether the polymer is hydrophilic or hydrophobic, i.e., even a crosslinking-type polymer, if it is hydrophilic, undergoes massive radiation damage if irradiated in the presence of water. Our technique is based on these effects.

Water affects electron beam radiolysis because it is a very good source of free radicals, which are quite mobile in the ice matrix even down to 80 K. The effect of water presence is most pronounced at the organic material/water (ice) interface (5). As a hydrophilic polymer particle contains some adsorbed water throughout its bulk, it will undergo severe damage when irradiated by the electron beam.

If a two-stage latex is made of one hydrophilic component and a hydrophobic one, it is quite easy to determine whether the product is an IPN, or a CAS particle. A CAS particle with a hydrophobic shell will undergo little damage under the electron beam, whereas a reverse geometry will lead to massive damage in the shell with little damage to the core. An IPN particle made of these components will undergo damage throughout its cross-section, although the degree of expansion will be less than that in a pure hydrophilic particle of the same size (6). Smaller particles formed during the second stage of the polymerization will be visualized, of course, and identified according to their radiolytic behavior (7,8).

In this presentation we discuss the principles of electron beam radiation damage in presence of ice. We describe the preparation of frozen latex specimens for cryo-TEM, and the experimental procedure for in-situ contrast enhancement and direct imaging of the specimens. We demonstrate the applicability of the technique with images taken with IPN and CAS systems of various compositions, and discuss the extension of the technique to samples other than latexes,. such as two-component thin films.

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# ENHANCEMENT OF INHOMOGENEITIES IN GELS UPON SWELLING AND STRETCHING

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When swollen at saturation gels usually exhibit a much stronger scattering than semi dilute solutions, at low scattering amplitudes. It will be shown how a percolation process can be used to modelize the growth of such defects in some systems, namely the gels prepared by random crosslinking of semi dilute solutions of very long chains (1). Predictions of this model will be compared to experimental data. According to this model, one expects also a separation of entangled crosslinking inhomogeneities upon stretching of the gel (2). As a consequence, "butterfly" iso-intensity patterns should show up. The experiment has been done: highly swollen gels have been enlongated, and indeed such types of curves have been found. This observation might be connected to the "original" butterfly patterns which were found in rubbers containing free labeled chains (3) (and also in some types of uncrosslinked melts under certain relaxation conditions) (4,5).

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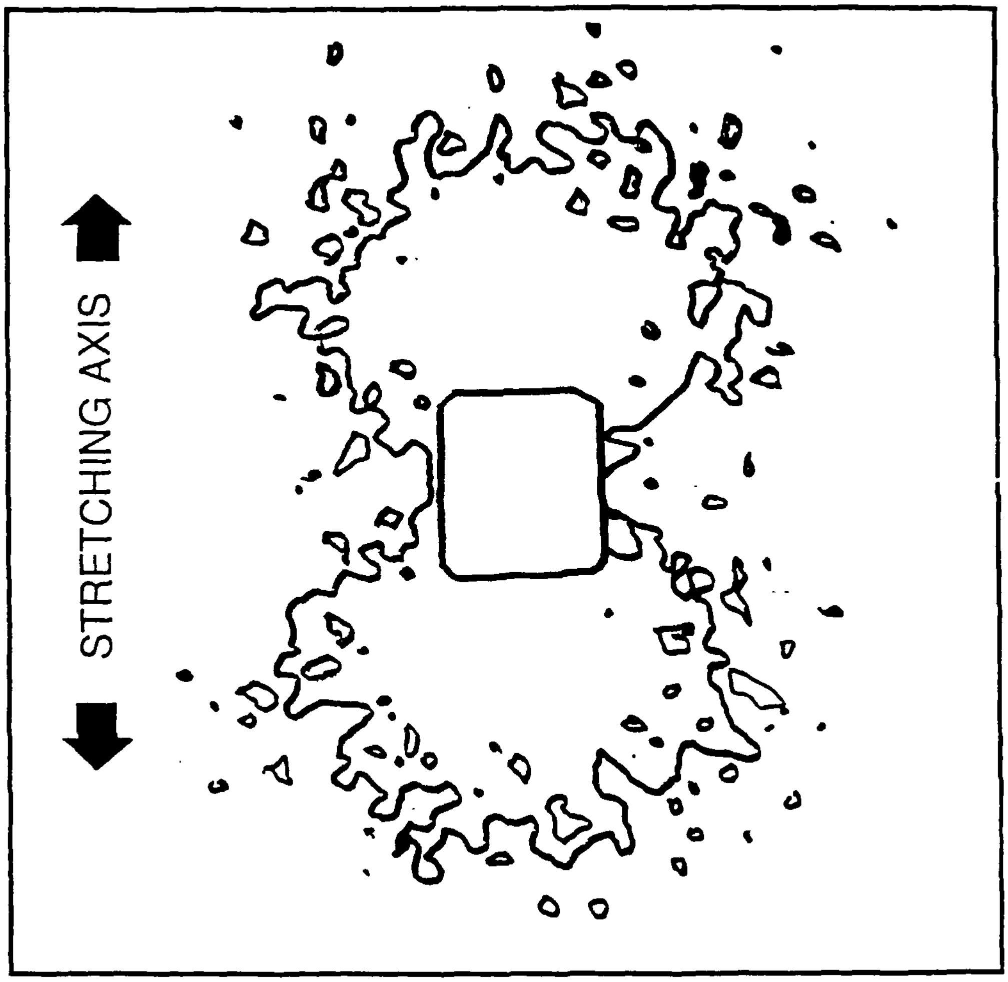

Isointensity pattern obtained for a gel prepared by statistical crosslinking, elongated by a factor λ-1.35 at a swelling degree approximately equal to 12.

# DYNAMICS AND STRUCTURE OF GELATIN GELS

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The structure of gelatin gels is investigated by Holographic Relaxation (HRS) , which is also called Forced Rayleigh Scattering (FRS). As a probe the small fluorescein molecule is doped into the gelatin gel, and the translational diffusion coefficient of this sensor molecule is measured. A very "anomalous" HRS waveform is observed, which is shown in Figure 1. Two different enviornments for the sensor molecule can be derived from this "decay-rise-decay-rise-decay" waveform by using a four exponential function fitting (1). Continuous line in Figure 1 represents such a kind of fitting. One environment is interpreted as a "coarse" network ("gel phase") formed by aggregation of renaturated rod-like collagen, the other as a "fine" network ("sol phase") formed by entanglements of the gelatin coils.

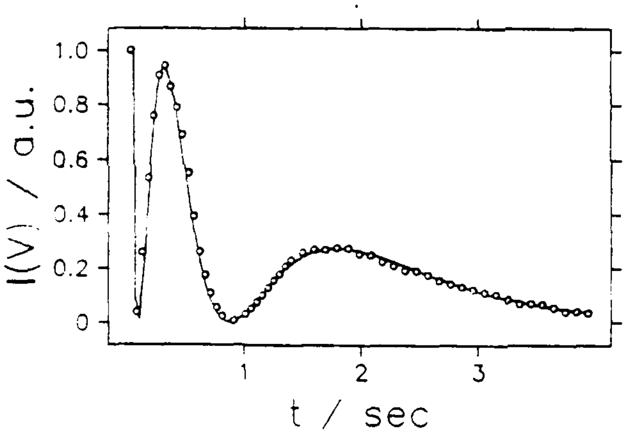

Figure 1. Typical HRS curve measured at 25°C from gelatin solution doped with 0.02% fluorescein as probe molecules below the gelation temperature. The gelatin concentration is 15% (w/w).

By labelling the gelatin molecules covalently with fluorescein-isothiocynate, the translational diffusion of the labelled gelatin molecules in the network and the network itself are probed (2). If the background intensities (both coherent and uncoherent) are very small and can be neglected, which is the case in our experiments, the HRS spectrum can be expressed as

$$I(t) = [s(t) + g(t)] \qquad [1]$$

where $s(t)$ [$= \sum S_i \exp(-\Gamma_i t)$] is the contribution from the "sol-phase" and $g(t)$ [$= G$] is from the "gel-phase", which is constant at a given temperature below the gelation threshold. A typical temperature ramped HRS (TR-HRS) spectrum is shown in Figure 2.

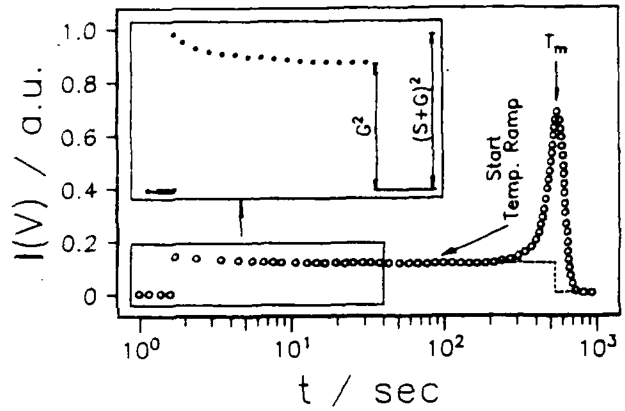

Figure 2. Typical temperature ramped HRS curve measeured at 25°C from gelatin solution (15% w/w) labelled with fluorescein-isothiocynate (0.7 mol/mol). The solution is matured at 25°C for 17 hours before the measurement.

The diffusivities of the labelled gelatin molecules can be evaluated from the initial decay by using a cumulant's method. From Eq. [1], we know that $I(t) \cong (S + G)$ at $t = 0$ where $S = \Sigma S_i$, and $I(t) = G$ at $t >> \Gamma^{-1}$. The insert in Figure 2 shows graphically G and (S + G) . Therefore, we can calculate the gel/sol ratio from the values of G and (S+G). After the relaxation stops, the temperature ramp was started. An ideal intensity profile after the ramp should follow the dot-line in Figure 2, but the experimental curve is different, which has a remarkable increase in intensity as the temperature rises and a sharp drop at the gel melting temperature (Tm). It has been proved experimentally that this unexpected increase in TR-HRS spectrum is from different diffraction efficiencies at different temperature. G/(S+G), Tm and D of different concentration gelatin solution are listed in the following table.

| C (w/w,%) | G/(S+G) (%) | Tm / °C | D / 10 cm sec |
|---|---|---|---|
| 1.00 | 0.0 | 19.1 | 8.85 |
| 3.00 | 55.4 | 27.6 | 8.34 |
| 5.00 | 72.4 | 30.5 | 7.24 |
| 6.67 | 87.7 | 31.8 | 7.47 |
| 11.00 | 90.2 | 32.0 | 7.22 |
| 15.00 | 90.7 | 32.6 | 7.52 |

All samples are matured at 25°C for 17 hrs befor measurement. Errors are 2% for G/(S+G) and Tm; 7.5% for D.

In comparison with TR-FRAP (3), we have to point it out that TR-HRS has (i) a higher signal/noise ratio ; (ii) a well defined baseline for calculation of G/(S+G); and (iii) a more accurate Tm.

Chi Wu gratefully acknowledges the Alexander von Humboldt-Stiftung for awarding him a research followship and the warm hospitality from BASF AG during his stay in Germany. The authors are indebted to Mr. Kren for his help in the experiments.

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# MOLECULAR ASPECTS OF POLYMER NETWORK DEFORMATION SMALL ANGLE NEUTRON SCATTERING AND $^2$H NMR STUDIES

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Recent results are reported on small angle neutron scattering(SANS) and $^2$H NMR stiudies on isotropic and uniaxially deformed polybutadiene networks obtained from a random 4-functional crosslinking reaction (1) of anionically prepared 1,4-polybutadiene chains of uniform molecular weight and of cis-1,4-polybutadiene. The structure of the networks has been varied by variation of the cross-link density, polymer volume fraction during cross-linking and the degree of swelling in butadiene oligomers. The experimental investigations are complemented by Monte Carlo (MC) simulations of the formation of the networks and of network chains in uniaxially strained networks (2).

**Isotropic networks**

By MC simulations of the cross-linking reaction the number of elastically active junctions, intramolecular loops and loop-lsize distribution has been determined as a function of polymer concentration during cross-linking from bulk to semidilute solution (3). The number of active junctions as obtained from evaluation of the SANS data on strained networks by Ullmans theory (4) is in agreement with the MC results (5). Despite a high fraction of intramolecular loops for cross-linking and low polymer concentration during cross-linking ($v_2=0.06$) in semidilute solution the SANS measurements show no deviation of the dimensions of labeled primary chains from the unperturbed value measured in the uncrosslinked melt.

$^2$H NMR transversal relaxation messurements on the melt and isotropic networks with primary chains of different primary molecular weight have shown the presence of two relaxation processes which are associated with slow motions of the interior of chains on a semilocal scale subject to restrictions of cross-links and entanglements and of faster motions of chain segments at chain ends. The assignment of the processes has been confirmed with triblock copolymers having a deuterated middle block or deuterated end blocks. The correlation time of the first process decreases with decreasing cross-link density until a plateau value is reached at an average molecular weight between cross-links of $M_c$ = 20 000. The process associated with chain ends is independent of cross-link density.

**Uniaxially strained networks**

The SANS measurements performed on strained networks cross-linked in bulk and in semidilute solution containing long deuterium labeled primary chains with several crosslinks were evaluated by Ullman's theory (4) for multilinked chains. The deformation of the primary chains in networks cross-linked in bulk can be described by a junction affine mechanism whereas the networks prepared in solution exhibit phantom behaviour.

The two-dimensional scattering profile of free low molecular weight deuterated polybutadiene chains dissolved in the networks exhibits "butterfly patterns" during strain similar to those of free chains in PDMS (6) networks but differing in detail from published measurements. The anisotropy of the radius of gyration of the labeled primary chains in the strained networks has been correlated to the local orientation as measured by the quadrupolar splitting of the $^2$H NMR resonance . The experimental relation between both quantities can be explained by MC calculations for a "dipolar-like"model of orientation under the assumption that the measured global anisotropy of the primary chains is the same as that of subchains having a length approximately equal to the average molecular weight between cross-links.

The $^2$H NMR transversal relaxation of strained networks was studied up to an extension ratio of $\lambda = 4.0$ for networks prepared from stereoregular cis-1,4-polybutadiene in order to avoid complications arising from the isomerism of polybutadiene. A remarkable difference in the dependence on $\lambda$ was found for the two components observed in the isotropic networks. The classical dependence on $\lambda^2-\lambda^{-1}$ of the orientation was observed only for the slower moving interior parts of the primary chains while the faster moving segments at chain ends exhibit a weaker dependence proportional to $\lambda$. The orientation of the free chains has the same magnitude as the orientation of dangling chain ends and has the same $\lambda$-dependence. The dynamics of the chains is also affected by deformation. The correlation times of both components of the primary chains increase with strain. The dynamics of free chains which are characterized by only one relaxation time is similar as that of dangling ends and changes in parallel to free chain ends with increasing strain. $^2$H NMR measurements on endlinked PDMS networks containing free PDMS chains have been recently published by Sotta et al. (7). These studies at relatively small extension ratios indicated that the orientation of network chains and free chains are indistinguishable and both follow a $\lambda^2-\lambda^{-1}$ dependence by virtue of strong orientational correlations. The present observations on statistically cross-linked polybutadiene networks with dangling ends lead to a more differentiated view and show that that the local orientation as measured by NMR is affected by structural and dynamical features of the network.

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# CHAIN AND OLIGOMER ORIENTATION IN DEFORMED NETWORKS.
# A NMR STUDY

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In order to use NMR to study deformed polymer networks it is necessary to have a methodology that is sensitive to very low degrees of orientational order: Small chain extensions are encountered in mechanically deformed samples and there is nearly isotropic motional averaging within fluid networks. Here we consider the quadrupolar interaction tensor, **q**, expressing the coupling between the nuclear quadrupole moment and the (residual) electric field gradient at the deuterium nucleus because the coupling is characterized by a rather large NMR interaction (~ 250 kHz). In a deformed network the average of **q** is non-zero and, coarsely speaking, <**q**> acquires the symmetry of the motionally averaged macromolecular arrangement in the oriented, fluid network. In the case of uniaxial environments <**q**> is conveniently given in terms of S, the principal element of an orientational order tensor, S, and the residual interactions appear as splittings in the high resolution NMR spectra:

$$\Delta\nu \approx qS\, P_2(\cos\Omega) \qquad [1]$$

where q is the principal element of the interaction tensor in its local principal axis system (the C—D bond), and $S = \langle P_2(\cos\theta)\rangle$ gives the average orientation of the C—D bond vector relative to the strain direction ( $\Omega$ is the angle between the strain director and the magnetic field). In eq [1] $\theta$ is the time dependent angle between the strain director and the C—D bond in the chain segment. It is clear from eq [1] that a measurement of the magnitude of the splitting $\Delta\nu$ together with the independently determined q yields in a very straight-forward manner, the *magnitude* of the order parameter characterizing the average orientation of the C—D bond in a labelled chain segment. However, interpreting observed values of S at the microscopic level is very challenging.

In a deformed network above its $T_g$ the segmental motions within the tethered, distended chain are anisotropic and the averaging of the quadrupolar coupling is incomplete. Qualitatively speaking, <**q**> is determined by the residual segmental orientational order in the network. This may be expressed with an order parameter S related to the average orientation of a hypothetical chain segment *k* relative to the chain end-to-end vector ***a***. According to classical (Gaussian) descriptions of polymer chains, S is predicted to be inversely proportional to *N*, the number of segments spanning ***a***, and proportional to the strain on the network. In networks subjected to uniaxial extension, S is proportional to $(\lambda^2 - \lambda^{-1})$, where $\lambda = L/L_0$ is the deformation ratio.

A decade ago deuterium NMR ($^2$H NMR) was used by Deloche and Samulski[1] to monitor the anisotropic rotational diffusion of deuterium labelled swelling agents in uniaxially deformed elstomeric networks. Since then a number of publications have appeared wherein $^2$H NMR has been used to follow the behavior of swelling agents and labelled chains in deformed networks.[2] Additionally, there is recent evidence that this technique might be extended to transient networks — polymer melts — that are deformed by shear stresses.[3]

Herein we attempt to understand the $^2$H NMR linshapes that result when deuterium labelled poly(dimethyl siloxane)-$d_6$ networks are uniaxially strained. Our focus is on the microscopic reorientational processes that the chain segments exercise in the deformed networks. These processes may be placed into a general context by examining how flexible oligomers respond to the uniaxial field characteristic of liquid crystals, e.g., the behavior of oligomers as solutes in nematic solvents. Recent work in our laboratory suggests that excluded volume interactions dominate the flexible solute's response to the nematic mean field.[4] While such interactions are undoubtedly operative in the deformed network, in the case of the labelled PDMS sample, the connectivity of the probe ( i.e., the probe segment is a component of the network itself) and local heterogeneity (dynamical and structural) complicate the analysis of polymer reoreintation. We will describe efforts to quantitatively simulate observed $^2$ NMR spectra of deformed PDMS networks.

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# GELATION AND VITRIFICATION OF EPOXY RESINS MONITORED BY ULTRASONICS MEASUREMENTS.

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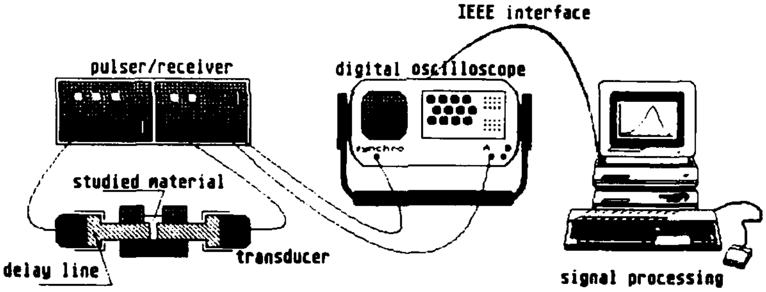
The propagation of an ultrasonic sinusoidal wave in a condensed medium is governed by its elastic modulus M for a longitudinal wave and G for a shear wave. M is a function of the compressibility K and of the shear modulus G according to the relation $M=K+4/3G$. If the medium is viscoelastic these moduli are complex and the real and imaginary parts can be determined by measuring the ultrasonic velocity V and the absorption coefficient $\alpha$. These quantities are frequency dependent and can be interpreted in terms of structural properties.

During the cure of an epoxy resin, these parameters are considerably modified as the reaction progresses and in principle the ultrasonic spectrum can show the evolution of the structuration of the medium in real time. This was the motivation for our development of an original technique of digital signal processing by Fast Fourier Transform which allows us to follow the ultrasonic spectrum (longitudinal or shear waves) (figure 1).

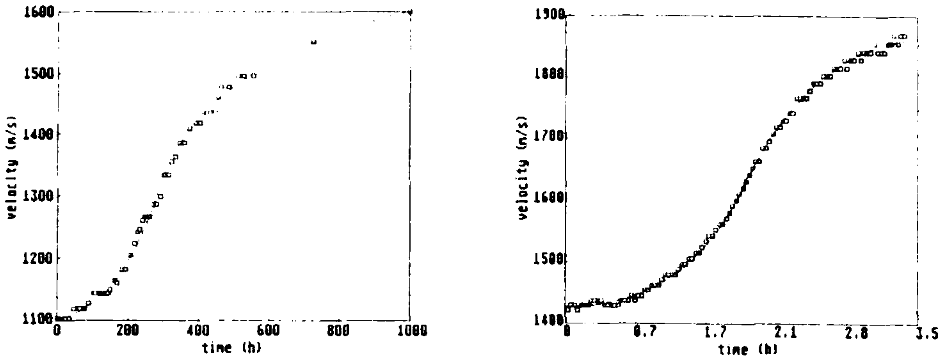
figure n°1: setup



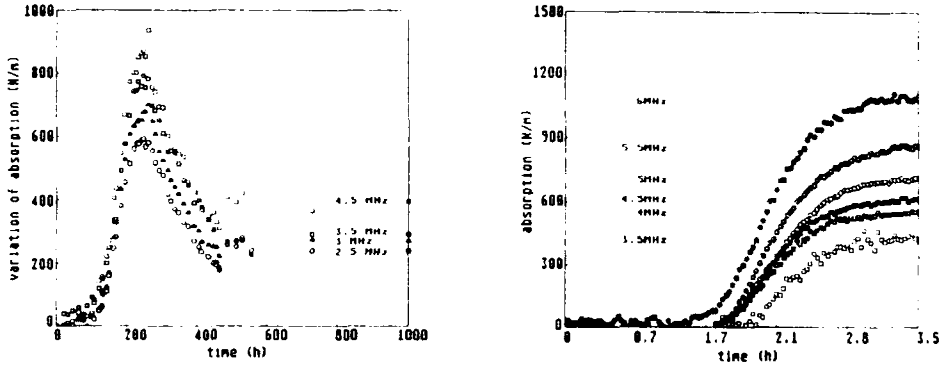
This technique has been applied to the study of epoxy networks for two types of diepoxy-diamino systems: one having a high glass transition temperature (diglycidyl ether of bisphenol A (DGEBA) with diaminodiphenyl sulfone (DDS) as curing agent) and the other with a low glass transition temperature (butanediol diglycidyl ether (BDGE) with hexamethylene diamine or (HMDA)).

For the two systems, the ultrasonic velocity shows a continuous increase until a limit (figures 2 and 3). The DGEBA-DDS system shows a sharp maximum of ultrasonic absorption and for the BDGE-HMDA the absorption increases monotonically (figures 4 and 5).

figures n°2 & 3: variation of the velocity during the cure of:


DGEBA-DDS (120°C)        BDGE-HMDA (50°C)

figures n°4 & 5: variation of absorption during the cure of:


DGEBA-DDS (120°C)        BDGE-HMDA (50°C)

During the cure of the DGEBA-DDS system two transitions are succesively encountered: gelication followed by vitrification which is responsible of the maximum observed in the frequency range permitted by the traducers bandwidth. In the second system the glass transition temperature remains lower than the temperature of cure so that the changes are due only to the increase of the connection of the constitutive units of the resins undergoing to gelation.

* This work was made in collaboration with the "Centre Commun de Recherche Louis Blériot, Aérospatiale, Suresnes, France".

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# DIFFUSION THROUGH RUBBERY AND GLASSY POLYMER MEMBRANES

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## ABSTRACT

Investigations on transport phenomna through polymer membranes offer an interesting possibility for experimental and theoretical exploration of diffusion in polymers. Several experimental methods are available:

1) Equilibrium and transient sorption measurements (gravimetrically, dilatometrically, pressure decay) leading to values for the sorption coefficients, S, and the diffusion coefficients, D.

2) Steady-state and transient permeation measurements giving values for the permeability coefficients, P (= D.S), and the diffusion coefficients, D, respectively.

When modelling sorption and permeation phenomena important problems are found in giving explicit expressions for the pressure- (or sorbent concentration) dependence of P, D and S and in trying to give interpretations on a molecular basis for the transport phenomena observed.

During the past few years we have explored two distinctly different cases of transport through membranes:

a) Sorption and permeation of chlorinated hydrocarbons in typically elastomeric (rubbery) membranes, over a broad range of vapour activities. The evaluated diffusion coefficients clearly show the effect of the penetrant. Both an increase in D-values at low vapour activity is found, due to plasticization effects, as well as decreased D-values at high vapour activity, presumably due to solvent clustering.

b) Diffusion and permeation of gases ($CO_2$ and $CH_4$) in glassy polyimide membranes. The glassy membranes investigated consisted of a series of polyimide polymers with a systematic variation of the molecular structure (only the diamine monomers used were varied). For this well defined series of polymers the permeation and diffusion data could be correlated with molecular parameters occurring in expressions for the actvation energy of diffusion.

# NETWORK STRUCTURE OF POLY(METHACRYLIC ACID) AND ITS RELATION TO DIFFUSIVE TRANSPORT

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**Introduction and Overview**: Real time control of the permeability of crosslinked polyelectrolyte membranes, using either electrical or chemical stimuli, has been described previously(1–6). In particular, large changes in the permeability(1,2,7,8) and mechanical properties(9–12) of poly(methacrylic acid) (PMAA) or other membranes have been induced by altering either the pH or ionic strength of the solution surrounding the membrane, or by application of a transmembrane electric field. These physicochemical phenomena are in large part governed by the chemical and physical structure of the membrane. Thus, further understanding of membrane network structure is required to correlate structural properties such as crosslink density, with the observed transport properties.

This paper focuses on the relationship between diffusive transport and membrane composition (crosslinker content and relaxed polymer volume fraction) in membranes whose permeability can be actively controlled in real time. As before(1), pH induced changes in permeabilities were measured. These yielded permeability as a function of hydration at constant crosslink density. Then, by correlating bath pH to membrane hydration, and because the hydration of the PMAA membrane can be varied by altering bath pH, the transport properties of membranes of different crosslinker content and/or relaxed polymer volume fraction were compared *at constant hydration*.

**Materials and Methods**: PMAA membranes with different crosslinker content and water content were prepared using a formulation adapted from Sefton(13,14). Crosslink density was calculated from stress–strain curves, using the method of Meissner and Janacek(15). Details of the experimental apparatus can be found in Weiss et al(14). Permeability of PMAA membranes to a 10000 MW dextran was measured using a transport apparatus described elsewhere(1,7). Briefly, the apparatus consisted of a plexiglass transport cell in which a membrane was clamped between upstream and downstream baths, two spectrofluorometers which monitored the downstream concentration of each solute, a computer equipped with an A/D card, and a chart recorder. In addition, there were two pH meters and two temperature probes which input to the computer, as well as a cooling bath, heating coils, and computer controlled automatic burettes to allow control of pH and temperature. Details of the transport experiments can be found in Ref. (14,16).

**Results and Discussion**: Figure 1 shows a plot of effective crosslink density $\frac{\nu_e}{V_p}$ versus twice the crosslinker concentration ($c = [\text{TEGDMA}]$). The line with unity slope represents 100% crosslink efficiency between the bifunctional crosslinker and the monomer; the best-fit line through the data has the form:

$$\frac{\nu_e}{V_p} = 0.053 + 0.479(2c)$$

Thus, the slope of the line of Eq. [1] suggests that the crosslinking efficiency was about 48%, consistent with other methacrylates such as pHEMA(17).

The membrane permeability was seen to be very sensitive to changes in the amount of crosslinker added to the membrane formulation at the time of polymerization. Figure 2 shows that the permeability at constant hydration decreased with an increase in the amount of crosslinker added to the membranes during polymerization. Crosslink densities based on Figure 1 are included in Figure 2. Other transport measurements show that at constant hydration, the membrane permeability increases with increasing water content at the time of polymerization, even though the monomer:crosslinker ratio was coustant(14). Subsequent tensile measurements on an additional series of membranes with increased water content at the time of polymerization confirmed that the effective crosslink density $\frac{\nu_e}{V_p}$ of such membranes was consistently lower than $\frac{\nu_e}{V_p}$ for membranes cast at a lower water content (data not shown).

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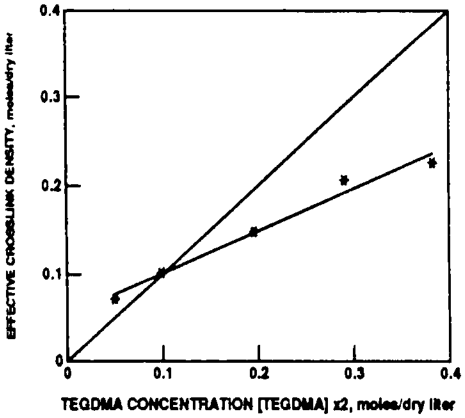

Figure 1.

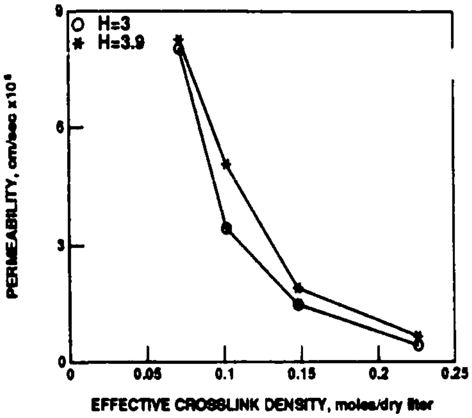

Figure 2.

# DIFFUSION BEHAVIOUR IN SOLUTIONS OF FLEXIBLE POLYMERS: A COMPARISON BETWEEN EXPERIMENTAL RESULTS AND THEORETICAL PREDICTIONS

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In this work, the concentration and molecular-weight dependence of the translational diffusion coefficient D for a large body of experimental data for polystyrene at good and marginal solvent conditions are analyzed in the framework of a recent theoretical model (1). This model is constructed with the aid of renormalization-group methods and a new scheme (2) to incorporate the hydrodynamic effect on polymer solution dynamics in the semidilute regime. The resulting model, expressed on a closed analytical form, takes into account the gradual screening of both hydrodynamic and excluded-volume interactions. The model yields expressions which can be directly compared with experimental results without any adjustable parameter. Furthermore, the model constitutes a basis for construction of universal plots on the form $D/D_0$ versus $k_D \cdot c$, where D is the diffusion coefficient at polymer concentration c, $D_0$ is that at infinite dilution, and $k_D$ expresses the first-order concentration dependence of D

The data representing the reduced diffusion coefficient are observed to be a universal function of the dynamic scaled variable $X \equiv k_D \cdot c$. In the range of X-values corresponding to effective semidilute solution behaviour, the experimental diffusion data are found to be consistent with the theoretical prediction incorporating gradual screening of hydrodynamic interactions. However, in the regime of higher X-values the theoretical model fails to coincide with the experimentally observed behaviour. The conjecture is that this variance between theory and experimental results essentially reflects an inability of the renormalization-group results to describe correctly the osmotic compressibility for solutions of strongly overlapping chains.

In addition to these results, some other aspects on polymer solution dynamics, e.g., distribution of relaxation times and the wave vector dependence of decay rates, at marginal solvent conditions will be discussed.

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# 1.5 YEARS LATER: S.A.N.S LOZENGES/BUTTERFLIES PATTERNS IN DEFORMED POLYSTYRENE NETWORKS.

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Observations were reported at Networks 1988 of unexplained additional scattering observed mainly along the direction parallel to stretching in uniaxially deformed melts and networks containing *mobile labeled species* (butterfly patterns[1,2]). We have continued our study on *polystyrene melt*, containing small chains dispersed in a matrix of long entangled chains, behaving as a rubber for a certain time range ("rubbery plateau"). We show that, meanwhile the *intrachain* correlation function $S_1(q)$ is isotropic and characteristic of undeformed well dispersed Gaussian chain, the *interchain* corr. function $S_2(q)$ is the responsible for the butterfly effect observed in a melt; its amplitude and variation in q is now quantitative. We have also measured the *scattering at very small angle* using several tricks; this gives a *peak of intensity around* $5.10^{-3}Å^{-1}$ observed together with butterfly scattering for large elongations.

For a better understanding we have *trapped deuterated chains* in a polystyrene network. On the precursor chains (of various mol.weight $M_{prec}$) are fixed chemical sites for subsequent crosslinking by chemical bonding of two sites. Their ratio per monomer, R, makes two successive sites separated by an average mol.weight $M_{mesh} \sim 1/R$. Before the crosslinking, done in solution or in dry state, are incorporated deuterated chains ($M_{tr}$ ), with no such sites, thus not chemically attached to the network. One can study by SANS their conformation and their arrangement in the network sample, in the reaction bath (with solvent), or in dried state, isotropic or deformed above $T_g$. In the last case we follow after a fast deformation the relaxation with time towards equilibrium under strain. When the ratio $M_{tr} / M_{mesh}$ is increased, the elastic energy of dilatation of the net is less and less balanced by the entropy of mixing preventing ideal mixing. Experimentally, in reaction bath or in dried state, S(q) shows a transition from ideal scattering of a free chain in solution or melt towards additional fluctuations.revealed at small q by additional scattering increasing with R. The latter, in equilibrium under strain, becomes larger in direction parallel to the stretching and smaller in direction perpendicular; this gives "butterfly" patterns on a bidimensional X,Y neutron detector. Their shape can also be correlated with R or $M_{tr}$ . A *peak of intensity* is observed for large deformation of the network at larger q than for melt and more pronounced [4b].

Using these data, we will discuss whether the effect would occur as well in a perfectly regular network or is related to the heterogeneity of the network (the chains being expelled in "softer" _ less crosslinked _ regions), whether stress induced demixing is occuring or whether the increase of scattering could be due to an effect of desinterpenetration[3,4a] as when diluting a semidilute polymer solution (c>c*(overlapp)). Hard regions can be viewed as in a solvent of soft regions (or viceversa) and would be diluted along the directions corresponding to expansion of the network (eg parallel); on the contrary, in directions of compression (e.g. perpendicular ), enhanced interpenetration would abate the scattering.

For trapped chains in networks under strain at intermediate stages before reaching equilibrium, *lozenge patterns* appear, likelyto be combinations of butterflies with ellipses due to classical rubber deformation. The similarity with lozenges observed formerly in case of long chains multiply linked to the network (or multiply entangled in a long chains melt)[5] will be discussed.

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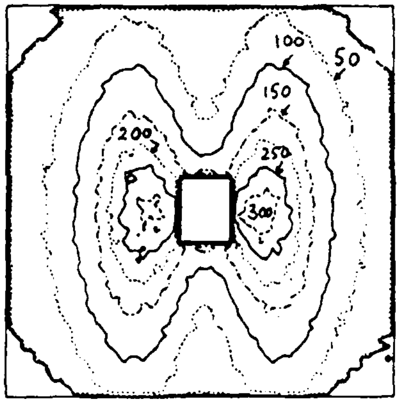
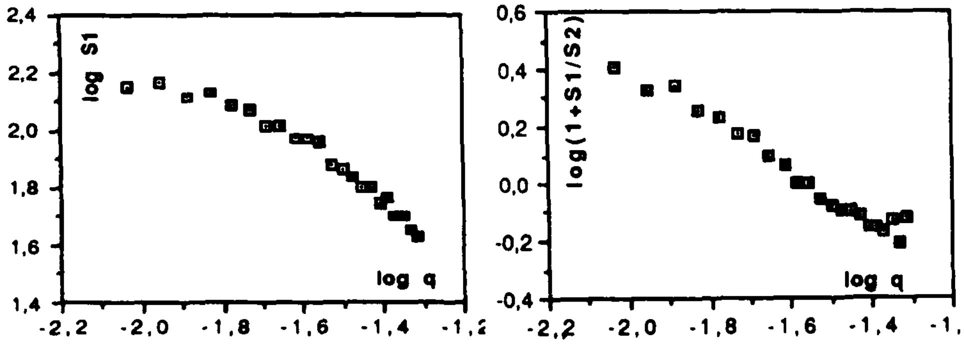


Butterfly and peak for trapped chains in a network stretched by 3 (R=1/44).



Log(($S_1$(q)) and log(1+$S_2$(q)/$S_1$(q)) (preliminary data).

# UNIAXIAL ORDER INDUCED IN A STRAINED PDMS NETWORK

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The orientational order generated in an uniaxially strained network is studied.Experiments were performed on an end-linked polydimethylsiloxane network using the deuterium NMR technique. A detailed analysis of the spectra shows that the inhomogeneities of the network structure contribute to the NMR lineshape and that the segmental motions become uniaxial around the external force direction (1). The observed dynamics uniaxiality appears as a new evidence for cooperative orientational interactions between chain segments in the deformed networks.

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# Comments on the free-energy-of-mixing term in the Flory-Rehner theory of polymer network gels.

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*Key words: Swelling; polymer network gels; mixing term; excluded volume.*

Recently (1), on the basis of accurate measurements on swelling poly(vinylacetate) networks, the correctness of the so-called mixing term in the Flory-Rehner theory was questioned. Doubts expressed agreed with earlier ones (2) from an analysis of available swelling-experiment data.

The quantity studied was the chemical potential ($\mu$), per mole, of the swelling agent (subscript 1) in the gel (superscript I) as a function of the degree of swelling. The expression, the validity of which was investigated, was:

$$\mu_1^I = \mu_{0,1}^I + \mu_{1,el}^I + \mu_{1,mix}^I \qquad [1\text{-a}]$$

when using for $\mu_{1,mix}^I$ the expression

$$\mu_{1,mix}^I = RT\,[\ln(1 - \frac{1}{q}) + \frac{1}{q}] + \Delta_{inter}\,\mu_1^I \quad ; \qquad [1\text{-b}]$$

$\mu_{0,1}$ is the chemical potential of the pure swelling agent at the ambient temperature (T) and pressure (p); $\mu_{1,el}^I$ is the "contribution" of the network to $\mu_1^I$; q is the degree of swelling, which equals $1/\phi$ where $\phi$ is the volume fraction of the network material in the gel, and $\Delta_{inter}\,\mu_1^I$ is the contribution of specific interactions between the swelling agent and the network material. The expression [1-b], used for $\mu_{1,mix}^I$, has been taken from the Flory-Huggins lattice theory of solutions (superscript soln) of <u>free</u> polymer molecules, where it reads:

$$\mu_1^{soln} = \mu_{0,1} - RTm_{pol} + RT[\ln(1-\phi) + \phi] + \Delta_{inter}\,\mu_1^{soln} \qquad [2]$$

in which $m_{pol}$ is the molarity (moles per mole of solvent) of the polymer.

Eq. [1-a], combined with eq. [1-b], has often been used to check theoretical expressions for $\mu_{1,el}^I$ by measurements, in various ways, of $\mu_1^I - \mu_0^I$, and, mostly, on setting $\Delta_{inter}\,\mu_1^I$ equal to $\Delta_{inter}\,\mu_1^{soln}$; for simplicity we will consider athermal systems and, thus, remove the terms $\Delta_{inter}\,\mu_1$ from equations [1-b] and [2].

Expressions for $\mu_{1,el}^I$ were obtained from those for the conformational entropy $S_{cc}^n$ of the network (superscript n) by

$$\mu_{1,el}^I = -T\left(\frac{\partial\ S_{cc}^n}{\partial\ N_1^I}\right)_{p,T} = -\,TV_1\left(\frac{\partial\ S_{cc}^n}{\partial\ V^I}\right)_{p,T} \qquad [3]$$

where $N_1^I$ is the number of moles of the swelling agent in the gel, $V_1$ its molar volume (considered a constant) and $V^I$ the volume of the gel. The quantity $S_{cc}^n$ is obtained from $S_{cc}^n = k \ln W_{id}^n$ , where k is

Boltzmann's constant, and $W^n_{id}$ the number of conformations, consistent with the overall gel dimensions, of the network, without taking into account restrictions due to excluded volume. In this way Flory and other investigators arrived at expressions for $\mu^I_{1,el}$ resembling expressions in the theory of rubber elasticity. Excluded volume effects were assumed to be properly accounted for by the term $\mu_{1,mix}$.

In 1969, the background of eq.[1], and in particular the splitting up of the quantity (see eq.[1-a]) $(\mu^I_1 - \mu^I_{0,1})$ into two separate terms, was investigated (3). A straight-forward analysis led to:

$$\mu^I_1 = \mu^I_{0,1} - TV_1 \frac{\partial S^n_{cc}}{\partial V^I} - TV_1 \frac{\partial(S^n_{ath} - S^n_{cc})}{\partial V^I} = \mu^I_{0,1} - TV_1 \frac{\partial S^n_{cc}}{\partial V^I} + \Delta_{e.v.}\mu^I_1 , \qquad [4]$$

where $S^n_{ath}$ denotes the real conformational entropy of the network, and where the subscript e.v. stands for "excluded volume".

Next, it was noticed that the third term on the right-hand side of eq. [2] is, within the frame of the Flory-Huggins lattice theory, nothing but $\Delta_{e.v.}\, \mu^{soln}_1$, the excluded volume contribution to the solvent chemical potential in a polymer solution. With this statement, and using $\phi = 1/q$ and omitting $\Delta_{inter}\, \mu^I_1$, we may write eq. [1-b] as

$$\mu^I_{1,mix} = \Delta_{e.v.}\, \mu^{soln}_1 = \text{(compare eq. [4])} - TV_1 \frac{\partial(S^{soln}_{ath} - S^{soln}_{ideal})}{\partial V^{soln}}$$

and thus, also using eq. [3], eq. [1-a] as

$$\mu^I_1 = \mu^I_{0,1} - TV_1 \frac{\partial S^n_{cc}}{\partial V^I} - TV_1 \frac{\partial(S^{soln}_{ath} - S^{soln}_{ideal})}{\partial V^{soln}} \qquad [5]$$

Eqs. [4] and [5] are equivalent only when, at equal polymer fractions,

$$\frac{\partial(S^n_{ath} - S^n_{cc})}{\partial V^I} = \frac{\partial \Delta_{e.v.}\, S^n}{\partial V^I} = \frac{\partial(S^{soln}_{ath} - S^{soln}_{ideal})}{\partial V^{soln}} = \frac{\partial \Delta_{e.v.}\, S^{soln}}{\partial V^{soln}} \qquad [6]$$

The validity of this condition was investigated, and is was shown that it was certainly not satisfied at high degrees of swelling of gels with a high degree of crosslinking.

Recently (1), is was stated that the dependence of the term $\mu^I_{1,el}$ on q agreed rather well with statistical theory, and that, therefore, deviations from a behaviour according to eq. [1-a] on using eq. [1-b] had to ascribed to shortcomings of eq. [1-b]. This makes an investigation into the validity of the condition [6] again actual.

Calculations about excluded-volume effects, in polymer solutions as well as in polymer networks, are extremely complicated. Nevertheless, some general trends can, maybe, be indicated. This will be discussed in the presentation.

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# ENERGY ELASTIC CONTRIBUTIONS TO THE DEFORMATION BEHAVIOR OF ELASTOMERS

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The problem concerning the origin of energy elastic contributions with regard to the entropy elastic behavior of networks appeared to have been solved in the nineteen–sixties by two important developments:

Theoretically, Flory (1960) took volume changes and intramolecular energy effects into account (1,2). He developed the following relationship predicting the difference in the temperature coefficients of the restoring force at constant volume and constant pressure:

$$\left(\frac{\partial f}{\partial T}\right)_{V,L} - \left(\frac{\partial f}{\partial T}\right)_{p,L} = \frac{f\beta}{\lambda^3-1}$$

where $\beta$ is the volume expansion coefficient and $\lambda = L/L_0$.

The second important event was an experimental development by Allen and coworkers (3), who constructed equipment with which the temperature coefficient of the force could be measured both at constant volume and constant pressure. Their experiments on crosslinked natural rubber appeared to verify the predictions of Flory exactly. Consequently, since that time, energy elastic contributions have been attributed to intramolecular effects.

Eight years later Allen et al (4) repeated their experiments using much improved equipment. These later experiments, carried out on dried and swollen systems, showed in all cases a major contradiction with Flory's theory. However, this work was given little attention in the literature. In addition, Allen et al (1971) measured the volume as a function of the strain. For this quantity too there was no agreement with Flory's predictions. Christensen and Hoeve had already pointed out this discrepancy previously (5).

Energy elastic contributions to the stress–strain behaviour of networks, which are caused by changes in the intermolecular interaction of chain segments, are consequently not correctly described bei the theory of Flory.

Our own measurements on the strain–dependent changes in internal energy and volume lead to a relationship for the stress–strain behaviour of networks which takes intermolecular contributions into account.

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# GROWTH PROCESS OF POLYMERS NEAR THE GELATION THRESHOLD

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We will review experimental results obtained recently on the determination of the laws governing the growth process of polymer clusters as the gel point is approached. The sol gel transition is a critical phenomenon of connectivity, below the gel point the system is a liquid while above the gel point the system is an elastic medium.

Mainly three kind of chemical reactions were used to synthesize the polymers:

- polycondensation of difunctional and trifunctional monomers
- radical copolymerisation of difunctional monomers (styrene) and tetrafunctional monomer (divinylbenzene)
- crosslinking of linear chain by irradiation (polystyrene $+\gamma$ rays) or end linking of PDMS chains by tetrakis (allyloxy) ethane.

The chemical reaction is quenched near the gelation threshold either by cooling or by poisonning the remaining reactif groups. The chemical reaction can also proceed until total consumption of one of the monomers which concentration is initially smaller than the concentration of the other monomer ($p = [NCO]/[OH] < 1$, in polycondensation of diisocyanate plus trialcool). The degree of advancement of the chemical reaction, $p$, is usually determined by titration of one of the unreacted monomers. Its value at the gelation threshold, $p_c$, is measured by dissolution procedures. Usually the quenched samples are dissolved in a good solvent and the different quantities are obtained from an extrapolation to zero concentration of measurements performed in dilute solutions.

The mean weight average molecular weight, $M_w$, increases as the gel point is approached as:

$$M_w \sim | (p - p_c)/p_c |^{-\gamma} \qquad \text{with} \qquad \gamma = 1.7 \pm 0.05$$

The value of the exponent $\gamma$ is obtained by taking the mean value of the experimental results obtained on five different systems by five different research groups.

The $z$ average radius of gyration $R_z$ is a function of the mean weight average molecular weight $M_w$ : $M_w \sim R_z^{(3-\tau)D}$, where $\tau$ is the exponent which characterizes the mass distribution and $D$ is the fractal dimension of the swollen polymer clusters. $(3-\tau)D$ was measured by six research groups on six different chemical systems and found to be: $(3-\tau)D = 1.71 \pm 0.14$.

The exponent $D$, measured by neutron scattering on fractionated samples, was found to be: $D = 1.98 \pm 0.03$. Similar experiments performed on unfractionated samples lead to: $(3-\tau)D = 1.59 \pm 0.05$ thus $\tau = 2.2 \pm 0.04$.

An indirect result of size exclusion chromatography is the determination of the relative value of the fractal dimensions of branched $D$ and linear $D_{\text{lin}}$ monodisperse polymers. Two research groups on two different systems found:

$$D/D_{\text{lin}} = 1.2 \pm 0.04 \quad \text{(compared to 1.18 expected theoretically)}$$

One of the main results of the last decade is the experimental evidence of the universal mass distribution curve:

$$\phi(M/M^*) = (M/M^*)^{\tau-1} f(M/M^*)$$

where $\phi(M/M^*)$ is the weight fraction of polymer clusters having a relative mass $M/M^*$ and $f(M/M^*)$ is a cut-off function which ensure that there is no mass much larger than $M^*$, the mass of the largest polymer cluster. Three different research groups have determined this universal curve on three different chemical systems. The measured exponent is: $\tau = 2.29 \pm 0.05$.

Having determined the exponent $\tau$ one can deduce the fractal dimension of unswollen polymer clusters: $Dp = d/(\tau - 1) = 2.36 \pm 0.1$, but an exponent $D = 2$ was measured in dilute solution: polymer clusters swell under dilution. Theoretically the variation of the second virial coefficient $MA_2$ and the intrinsic viscosity $[\eta]$ was found to follow:

$$MA_2 \sim [\eta] \sim M_w^x \qquad \text{with} \qquad x = \frac{3}{3-\tau}\left(\frac{1}{D} - \frac{1}{Dp}\right) = 3/8$$

Experimental results lead to the conclusion that $MA_2$ as well as $[\eta]$ are both function of $M_w$ thus polymer clusters swell under dilution. The exponent $x$ was found to be $x = 0.31 \pm 0.07$, if the average is taken on the different experimental results.

The weight fraction of the gel phase, $G$, was measured for $p > p_c$ by two research groups. One group, deducing the exponent $\beta = \gamma(\tau - 2)/(3 - \tau)$ from $\gamma$ and $\tau$ values measured below the gel point, found that $G^{1/\beta}$ is a linear function of $p$. The other group determined the ratio of exponents $\gamma/\beta$ which is equals to 4.5 or 3.6 (the percolation value is 4).

Two exponent values were measured ($\gamma$ and $\tau$) on different chemical systems. They were found to be independent of the chemical system (within experimental error) and very close to exponent values calculated by computer simulations following the percolation model. Therefore, the sol-gel transition is a critical phenomenon of connectivity belonging to the same class of universality as percolation.

References will be given in the oral presentation.

# SOL - GEL TRANSITION IN BIOPOLYMERS

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Rheological measurements have been performed on pectin biopolymers (1) close to the sol-gel transition.Two different experimental setups - steady state and oscillatory shear measurements - show scaling of the viscoelastic properties. The results of both types of measurements are consistent with each other and with scalar percolation theory (2).

Pectin molecules consist of linearly connected α(1-4) D -galacturonic acid units and their methyl esters. When the degree of esterification is reduced below 50% gelation occurs by way of interaction with divalent ions such as calcium. The crosslinks between different pectin polymers are extended zones with a helical structure. These junction zones consist of pairs of galacturonic acid block regions. Calcium ions are bound cooperatively in the electronegative cavities formed by these pairs. The presence of methyl ester groups in the primary backbone limits the extent of the junction zones. This material leads to a type of network which is known as "reversible gel " (3). The making and the breaking of crosslinks can be induced by changing the temperature, polymer or calcium concentration or the amplitude of the deformation.

For a given polymer concentration and temperature, one passes from the viscous sol phase to the elastic gel phase by increasing the ratio $R = 2\,(Ca^{2+}) / (COO^-)$. From rheological measurements close to the gel point on fully cured gels the viscosity $\eta$ has been determined as a function of the shear rate and the complex shear modulus $G^*$ as a function of frequency. The polymer concentration was chosen such that the polymer coils overlap weakly ($c\,[\eta] = 4.5$). The temperature was kept constant at 20 ± 0.1 °C. Viscosity measurements were performed over a range of shear rates between 0.017 and 128 $s^{-1}$. The dynamical measurements were performed using a controlled stress rheometer with a cone and plate device. A low deformation of 0.04 was maintained whatever the frequency range explored between $10^{-3}$ and 10 Hz.

Scaling analysis of our data allows to determine the exponents s, t, Δ, used to describe the viscoelastic singularities (1),(4) :

$$\eta_o \approx \epsilon^{-s} \qquad [1a]$$
$$G_o \approx \epsilon^{t} \qquad [1b]$$
$$G' \approx G'' \approx \omega^{\Delta} \qquad [1c]$$

$\eta_o$ is the newtonian viscosity, $G_o$ the equilibrium elastic modulus, G' (G") the storage (loss) part of $G^*$ and $\epsilon = |(R-Rc)/Rc| << 1$, Rc is the value of R at the gel point. The data was analyzed in terms of a two parameters fit to evaluate both Rc and the corresponding exponent from dynamical measurements alone, avoiding the calculation of Rc by separate static measurements. The same value Rc = 0.086 ± 0.001 is obtained form all measurements. Below the gel point the measurement of the newtonian viscosity yields s = 0.82±0.05 and above the gel point the equilibrium elastic modulus yields $t = 1.93 \pm 0.08$. Similar values were obtained for other polymeric systems in semidilute solution (5),(6).

The exponent $\Delta$ can be evaluated without knowing Rc explicitely by determining the modulus $G_x$ and frequency $\omega_o$ where the storage modulus G' crosses the loss modulus G", for different $\epsilon$ :

$$G_x(\omega_o) = G'(\omega_o) = G''(\omega_o) \approx \omega_o^{\Delta} \qquad [2]$$

The measured value is $\Delta = 0.71 \pm 0.02$. The scaling law $\Delta = t/(s + t)$ resulting from the scaling form for G* is well satisfied by these exponents (4). The numerical values of the exponents are in good agreement with the scalar percolation model (7),(8). In addition to the scaling exponents, we have determined the scaling functions for $\eta(\gamma,\epsilon)$ and $G^*(\omega,\epsilon)$. As an example, we show in Fig. 1 the data collapse of $\eta$:

$$\eta(\gamma,\epsilon) = \eta_o(\epsilon)\, \psi(\gamma/\gamma_o(\epsilon)) \qquad [3]$$

where we assume that $\gamma_o \approx \epsilon^{\nu z}$. The scaling ansatz predicts that $\psi(x) \approx x^{-s/(s+t)}$ for large x.

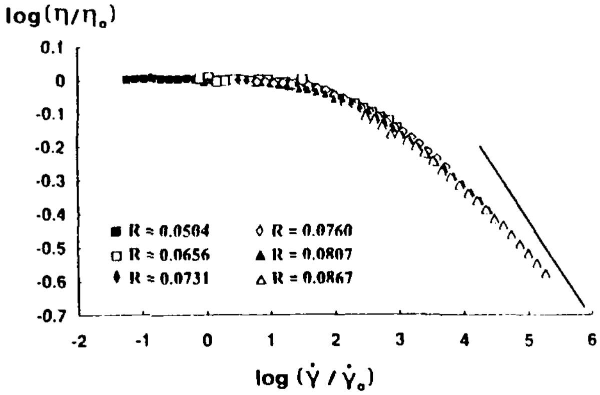

Fig. 1:
Data collapse of the shear rate dependent viscosity, $\eta/\eta_o$ versus $\gamma/\gamma_o$ (log-log). The straight line indicates the expected asymptotic behaviour.

The remarkable feature of the sol-gel transition in pectin biopolymers is the accuracy and the consistency with which the predictions of percolation theory are reproduced. The results presented are corroborated by measurements on gels which are not fully cured. We conclude that among the different models of dynamical gelation processes proposed so far (9), the scalar model accuretly describes one class of sol-gel processes.

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# RELAXATION PHENOMENA NEAR THE SOL-GEL TRANSITION

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Near the sol-gel transition, light scattering studies show that fractal branched polymers are formed whose mean size diverges as a power law at the gel point (1,2). These observations are readily understood in terms of the percolation model (3), and so should not be too surprising. However, the unusual *fractal-time* dynamics that accompanies the critical slowing down of the sol-gel transition is surprising and is unprecedented in other polymeric systems. The connection between fractal time and the sol-gel transition was first made through quasielastic light scattering from the microscopic, thermally-driven density fluctuations that occur at the sol-gel transition (4). In these measurements, it was found that the scattered photons give rise to detection events that break the time axis into a disconnected fractal set. Thus the two-point correlation function of detection events, also known as the intensity autocorrelation function, is a power law whose exponent is the codimension of the fractal set. Of course, in a fractal time set there is no identifiable time scale, so averge times must diverge at the gel point. We have demonstrated the divergence of two average times and have shown how this unusual critical slowing down can be explained.

On macroscopic length scales the critical slowing down is manifested in the viscoelastic behavior of the incipient gel (5,6,7). We have developed a dynamical scaling description of the sol-gel transition that relies on a length-scale-dependent viscosity and the overall geometrical self-similarity of the clusters (7). This dynamical scaling decription gives a frequency dependence that is equivalent to that demonstrated by Cates (8), and additionally predicts the divergence of the zero-shear viscosity, the equilibrium shear modulus, and the recoverable equilibrium creep compliance. This dynamical scaling theory also predicts the superposition of time- or frequency-dependent viscoelastic data taken near the sol-gel transition, when the horizontal and vertical axes are appropriately scaled by a characteristic time and an energy density, respectively (9). In general, the predictions for viscoelastic properties are in good agreement with experimental data (7,9) on epoxy resins when it is assumed that hydrodynamic interactions are strongly screened in the melt - the so-called Rouse limit. However, there are notable exceptions to this agreement, and these exceptions remain an active area of research.

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# MOLECULAR DYNAMICS SIMULATIONS OF POLYMER NETWORKS

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We describe how molecular dynamics simulatons for a relatively simple coarsed grained model can be very useful for investigating the static and dynamic properties of polymer networks and other macromolecular liquids. We show that it is important to use a simplified coarsed grained model instead of a detailed microscopic model if one is interested in studying on today's supercomputers large systems which also relax slowly. As examples of how this technique can be used for highly connected networks, we review our results for three systems, gelation/percolation clusters, site-diluted random tethered polymer membranes and crosslinked polymer melts.

Gelation clusters generated just below the sol-gel transition have been studied recently by Flory theory (1,2) and by neutron scattering (3). It is found that these gelation clusters swell when the excluded volume interaction from the nearby clusters are screened (removed). Their fractal dimension is observed to change from 2.5 to 2. Since percolation clusters at the percolation threshold $p_c$ are in the same universality class, we generated a number of large percolation clusters containing a few thousand monomers and diluted them. In agreement with the neutron scattering data, we find that their fractal dimension to reduced to 2. We also see no deviation from Flory theory.

The possible existence of a crumpling transition in two-dimensional tethered membranes embedded in three-dimensions has been a problem of great interest recently (4-7). In a search for ways to eliminate the local bending energy which has suppressed the expected crumpling transition up to now we studied site diluted membranes. We constructed a triangular tethered membrane and random eliminated sites, so that the fraction of monomers $p < 1$. We found that these random membranes are rough on small length scales but flat asymptotically. To quantify this more precisely, we measured the ratio $\phi = \lambda_3/\lambda_3^o$ where $\lambda_3$ is the largest eigenvalue of the interia matrix at equilibrium and $\lambda_3^o$ is its value when the membrane is perfectly flat. We find that $\phi$ decreases linearly with decreasing $p$. The membranes are shown to have anisotropic scattering functions. Only when $p \rightarrow p_c^+$, do the membranes become isotropic, indicating that at least in this case random site-dilution is not sufficient to produce a crumpling of two-dimensional membranes.

Finally, we discuss some preliminary results for crosslinked polymer melts. We compare our results for the dynamic structure function S(q,t) with recent neutron scattering experiments and discuss how the radius of gyration of the networks change under swelling.

# A NEW DESCRIPTION FOR $A_f$ HOMOPOLYMERIZATION: MONTE CARLO SIMULATIONS

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Currently there are two main theories that predict the structure build-up during polymerization—branching theory(BT)(1) and percolation(2). Both of these simplify the problem by making several limiting assumptions. Branching theory does not allow loops in the pre-gel stage, and percolation overestimates the same. Branching theory further assumes that the local environment of a reactive unit is a faithful representation of the bulk state. This has come to be known as the mean field approximation, a condition insured by very small diffusive times over reaction times. Percolation in most cases is a computer simulation model performed on the basis of simple connectivity rules ignoring the dynamics of chains and monomers. As a result it is expected to be accurate only during situations where units can only react with others in the immediate neighborhood, a condition satisfied in a case were diffusion is virtually absent.

Computer simulations give a unique opportunity to study various growth effects in a controlled fashion. We have developed the following algorithm, which is more sophisticated than both percolation and branching theory models, to gain a better understanding of how diffusion, substitution effects, spatial separations, and cycles affect network formation.

The algorithm is a Monte Carlo simulation that runs and monitors an irreversible reaction in which monomers combine to form a network. The number of initial monomers and their functionality is variable. The reaction is simulated in a cube by assigning three random coordinates to each monomer during initialization and following the listed steps:

Execution
1) Select two unreacted functional units (nodes) randomly.
2) Considering the relationship between the two nodes (substitution effects, spatial separation, cycles) calculate a probability of reaction 'p'.
3) Choose a random number 'r' between 0 and 1. If $r < p$ then the chosen nodes will react - proceed to 4. If $r > p$ then the nodes do not react - go to 1.
4) Bookkeeping: Update connectivity, distribution, conversion, moments etc.
5) Based on the current conversion value, should we quit? (The program will halt at a specified conversion.) no - loop to 1, yes - go on.
6) End

The probability calculation is made on the following basis: assume that two nodes have been randomly selected and now are being considered for reaction. Using the pre-assigned coordinates and periodic boundary conditions, their distance of separation can be calculated. The following functions determine the probability of reaction based on this distance of seperation. In the case we call the 'uniform potential', the two candidate nodes can be any distance apart and still react. This corresponds to the Branching Theory. The case of the 'hard core potential' is more akin to the percolation model. Here the probability of reaction is unity up to a given separation distance and zero everywhere else. In the intermediate case called the 'soft potential' the probability of reaction is some function of the distance between the two sites. We have used an exponentially decaying function. The softshell potential is an easy empirical way of considering diffusion limitations sensitive to the polymerization conditions and the structure build-up process.

Calculations of the probability of cyclization are more interesting. When the two chosen nodes are found to be on the same molecule, a cycle would result if they are reacted. The interunitary distance (the number of monomers) between the two nodes on the molecule can be calculated by exploring the connectivity array. This distance can then be scaled to a spatial separation and one of the space potentials can be used. Ideally, we could use the geometry of the molecule to determine the exact spatial separation of the nodes but this information is difficult to maintain through diffusive motions.

Substitution effects(3) can alter, in a positive or negative way, the probability of reaction for two nodes based on the state of reactivity of the monomers adjacent to the nodes. For example, consider that nodes i and j on monomers m and n, respectively, have been selected. For a first shell substitution effect, only the state of reactivity of nodes on monomers m and n are considered. For a second shell substitution effect, the reactivity of the first adjacent neighbors are also considered. Third shell includes the next level of neighbors, and so on. We have done simulations showing a change in gel point for first and second shell substitution effects.

Since we treat all molecules as point particles for diffusive motions, the distance calculations must be sensitive to the actual volume spanned by the molecule. This is achieved by considering each point mass to be evenly distributed in a sphere whose radius is determined as a scaling function of its mass. Then a random choice of the active functionality is made within the sphere and the interunitary distance calculated on this basis.

The importance of diffusion remains an unanswered question in polymerization. In cases where the BT results accurately predict the experimental observations, diffusion is expected to be sufficiently fast compared to reaction rates. We plan to extend our code for quantitatively studying the importance of diffusion rates. The problem is obviously non trivial. Two parameters, the direction and distance, need to be determined before we can allow a molecule to move. Direction can be determined by calculating the density profile in the reaction cube. Distance can be calculated on the basis of known scaling laws of mass to diffusion coefficients, and relationships between reaction and diffusion rates.

Some results of our work are shown here. In Fig 1, the analytic branching theory results are shown with uniform potential simulations for different populations. It can be seen that as the population size increases the results tend to the branching theory value. In Fig 2, a qualitative difference is shown between the different spatial potentials. For the hard potential where only close neighbors are allowed to react, gelation is delayed. This signifies the importance of diffusion. Both of these examples used $A_3$ homopolymerization without cycles. For $A_3$, branching theory predicts a gel point of .5. We are presently studying the importance of cyclization, diffusion effects and substitution effects. Analysis of Monte Carlo statistics with respect to finite size effects and noise effects shall also be reported. The universal classes within these simulations shall also be explored.

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Simulation results

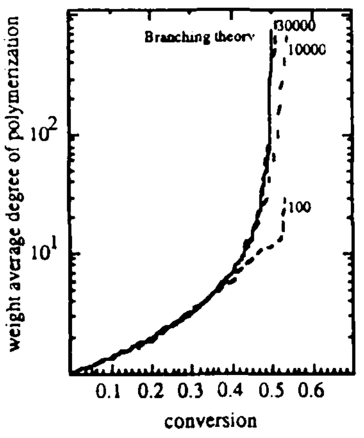

Fig 1

Effect of spatial potential

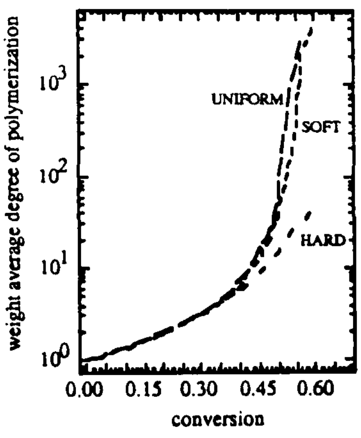

Fig 2

## ON THE FRACTAL NATURE OF THE STRUCTURE OF PARTICLE GELS

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Both experimental and numerical simulation studies on aggregation of particles in the absence of streaming indicate that often aggregates are formed with a fractal nature (e.g. 1,2). Characteristics of aggregates with a fractal-type structure are: firstly, their geometric structure is scale invariant ( self similar) for length scales clearly larger than the diameter of the aggregated primary particles; and secondly, the volume (number) of aggregated primary particles $N_p$ in an aggregate is proportional to its radius $R$ to a power $D$ where $D$, the so-called fractal dimensionality, is smaller than 3. Taking into account that the volume of an aggregate is proportional to $R^3$ this implies that the volume fraction $\Phi_a$ of particles in an aggregate may be expressed by (3):

$$\Phi_a = (R/a)^{D-3} \qquad [1]$$

where a is the radius of the primary particle. The fractal clusters will grow until their volume fraction is equal to that of the total dispersion. Then they jointly occupy the total volume and a gel is formed. This implies that the formed gel consists of a collection of aggregates with a fractal structure with dimensionality $D$, although the gel as a whole has a dimensionality of 3.

Based on this model for the geometrical structure of a gel, the following simple relation between the permeability coefficient $B$ and the volume fraction primary particles $\Phi$ may be deduced (3):

$$B = K\ \Phi^{2/(D-3)} \qquad [2]$$

where $K$ is a constant independent of $\Phi$.

Similar equations may be deduced for the relation beween $\Phi$ and the modulus $G$ of the network, based on the following general equation and the model outlined above.

$$G = \sum N_i\ C_i\ (\mathrm{d}^2A/\mathrm{d}x^2)_i \qquad [3]$$

where $N$ is the number of stress-carrying strands per unit area of cross-section perpendicular to the applied stress, d*A* the change in Gibbs energy when the particles in the strand are moved apart over a distance dx and *C* is a characteristic length, determined by the geometry of the network, relating the macroscopic strain to the distance over which a bond between two particles is extended or compressed. Subscript *i* refers to the bond type considered. Because of the scale invariancy of the clusters, the number of contact points between two of them will be independent of *R* so *N* will be proportional to $R^{-2}$. As long as the measurements are done in the so-called linear region, both the term $d^2A/dx^2$ and, for straight strands between the clusters, C will be independent of *R* and $\Phi$. This results in :

$$G = K' \ \Phi^{2/(3-D)} \qquad [4]$$

where *K'* is a constant independent of $\Phi$. However, the strands connecting two fractal clusters are normally bend. It may be shown that then, for measurements in the linear region, *C* will be proportional to $R^{-1}$, and we obtain in stead of equation [4]:

$$G = K'' \ \Phi^{3/(3-D)} \qquad [5]$$

Based on equation [2], [4] or [5] the fractal dimensionality may be obtained by studying particle gels of various particle concentrations. Examples will be given for gels formed by the aggregation of latex particles or of casein particles (the main protein in milk). In all cases a fractal dimensionality was found of about 2.3, which is higher than follows from numerical simulations of fractal aggregates. This is presumably due to some interpenetration of the fractal clusters before a gel is formed.

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# EXPERIMENTAL OBSERVATION OF THE SOL-GEL TRANSITION

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A network polymer at its gel point is in a critical state between liquid and solid. Linear viscoelasticity reduces to a simple behavior which is described by the **gel equation** for the stress (J. Rheol., **30**, 367 (1986) and **31**, 683 (1987)):

$$\tau(t) = \int_{-\infty}^{t} S\,(t-t')^{-n}\,\dot{\gamma}(t')\,dt'$$

in which the strain history is defined by the rate of deformation tensor $\dot{\gamma}$. Molecular parameters determine the front factor, S, and the relaxation exponent, n. The above power law relaxation behavior seems to be a universal property at the gel point. It has been found with a large variety of chemically or physically crosslinking polymers, i.e. with all crosslinking polymers which we studied above the glass transition temperature. Initially, we assumed that the relaxation exponent has the same value for all gels as it might be expected for a critical state. However, measured values between 0.15 and 0.8 indicate that the relaxation exponent may cover the entire range between 0 and 1. Several recent experiments will be discussed.

The universality of the power law relaxation behavior of polymers at the gel point allows a most accurate determination of the instant of gelation (Polym. Eng. Sci., 27, 1698 (1987)). The gel point is reached when the comlex rheological behavior reduces to power law relaxation in the terminal frequency range (fractal behavior, mechanical selfsimilarity).

The simple technique of Fourier Transform Mechanical Spectroscopy (J. Non-Newt. Fluid Mech., 27, 17 (1988)) not only allows the direct determination of the gel point. It also allows, by extrapolation, to predict the distance from the gel point in a sol. Recent advances of the technique and a set of applications will be given.

Physical gelation seems to follow the same general frame work as chemical gelation. This will be demonstrated with two different polymer systems.

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# A definition of the concepts "gelation temperature" and "gelation curve" by means of relaxation time spectra.

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*Key Words: Thermo-reversible Gelation, Dynamic Structure, Boltzmann Superposition Principle, Gelation Curve.*

*"THE COLLOIDAL CONDITION, THE GEL, IS ONE WHICH IS EASIER TO RECOGNIZE THAN TO DEFINE".*

This well-known phrase contains the essence of the problem of giving an operational definition of the gel state. The problem confines itself to the consistency of a given definition with the properties of the gel state that can be observed experimentally.

In various papers on thermo-reversible gelation, a system is said to have become a gel when a "three dimensional network, extending through the whole system" has formed. For a thermoreversible gel, however, the detailed structure changes continuously. Consequently, one might disagree about how long the network must keep the same structure in order that the system can be called a gel. And when temperature, as it is in systems said to be thermoreversibly gelating, is the parameter bringing about the change from "sol" to "gel", which temperature should be elected as "the gelation temperature"?

One problem is that of agreeing about how long such a network should exist may we call the system a gel. A more basic problem is that the presence of a molecular network with non-permanent crosslinks can only be concluded at by interpreting macroscopic observations with a molecular model.

In our contribution we propose a definition of "gelation temperature" based on an analysis of macroscopic behaviour alone; the existence or non-existence of a molecular network and, thus, the lifetime of such a network, are of no concern.

The macroscopic information we focus our attention on is the temperature dependence of certain properties of the relaxation-time spectrum that, when present, may reflect themselves in the dynamic moduli as a function of frequency, and also in the zero-shear rate viscosity $\eta_0$ of a system.

Our proposal is not connected with any specific model, but it has a general molecular background which we first will discuss.

In any system in which particles (molecules or parts of molecules) exert distance-dependent forces on each other, thermal motion leads, locally, to a continuous increase and decrease of molecular potential energy. This potential energy is directly related to the position of all particles in a small volume element. The instantaneous position of certain particles in the volume element relative to eachother may result in a local shear stress, fluctuating in time, in that volume element. We will call the assembly of the relative positions of and the forces between the particles in concern a substructure. Within one volume element, small but still containing many particles of each kind, there may be a whole variety of substructures, each one of which gives its own contribution to the local shear stress.

Substructures can form and disappear and, temporarily, store potential energy and loose it again; and the collection of all substructures of a certain type, picked from all volume elements of the system, will possess a characteristic decay-time of their contribution to shear stress. In a system in thermodynamic equilibrium, the positive and negative contributions to the macroscopic shear-stress of the system compensate each other, for each type of substructure individually. In a system which has been subjected to a (small) deformation, say a step in shear, the distribution of substructures over their states of deformation is temporarily disturbed, and the shear stress of the system as a whole will differ from zero. The contribution of any particular collection of substructures to this shear stress will fade away according to the characteristic decay-time of that collection. The overall-fading away, after a unit step in shear, is nothing but the relaxation function of the system. If known completely, dynamic moduli as well as $\eta_0$ can be derived from it. The central information it contains is the relaxation time spectrum, a macroscopic property of a system (1), (2).

We will define "thermoreversible gelations" as a phenomenon occurring when the relaxation time spectrum has certain properties with respect to its temperature dependence; we will investigate what these properties imply for dynamic moduli and zero-shear rate viscosity. By that, we will arrive at the definition of a "gelation temperature" (3).

Next, we investigate measured behaviour of solutions (five concentrations) of a polystyrene-polyisoprene-polystyrene tri-block copolymer in n-tetradecane at various temperatures. The "behaviour measured" is: zero-shear rate viscosity, and dynamic moduli over eight decades in frequency; the latter ones are real decades; time-temperature superposition which can be used for permanent gels (4), (5) is not applicable to thermoreversibly gelating systems.

At each concentration, the gelation temperature can be determined quite accurately. Its value, plotted versus concentration, gives the "gelation curve", the line separating the gel region from the non-gel region.

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# SPINODAL DEMIXING, PERCOLATION, AND GELATION OF BIOSTRUCTURAL POLYMERS.

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We study the self-organization of extended, self-supporting biopolymeric networks from solutions. Processes occurring in the instability region of solutions, that is in the region encompassed by the spinodal line in the T,c plane (1), has been shown to play unsuspected roles in processes of this type. In the case of rod-like polypeptides, it has been suggested on the basis of structural evidence that the spontaneous, spatially modulated polymer clustering due to the kinetic mechanism of spinodal demixing (2) generates per se the network of necessary crosslinks (3). This mechanism, however, applies to the special case of rod-like particles only (3). More often, actual polymer attachments and conformational changes are required for the self-organization of networks. In such a more general case, spinodal demixing occurring in the sol phase has been shown to act as the initial triggering step of the cascade of processes involved (4-8). This has suggested regarding spinodal decomposition more broadly as a mechanism capable of bringing selectively closer specific solutes, thus promoting their interaction (6).

As it is well known, the spinodal demixing mechanism is non-nucleate, and it is due to the undamped fluctuations of concentration occurring in the region of thermodynamic instability and growing within a narrow window of wavelengths (2). Final concentrations in the two types of regions correspond to intersections of the T=const. straight line with the coexistence line.

Anomalously large, damped fluctuations of concentrations have also been evidenced to have a triggering role in the self-assembly of bioelastomeric structures. This is observed in the region of thermodynamic stability, when the instability region is approached closely enough to warrant sufficiently large amplitudes and lifetimes of the concentration fluctuations (9,10).

In the present work, a brief summary of the pertinent previous work from our laboratory on various systems will be followed by novel data which concern the representative biostructural polysaccharide Agarose. The data confirm and specify how a microphase spinodal decomposition provides the prerequisite condition for polymer coil-to-double-helix transition and cross-linking (4-8) required for gelation (11). The spinodal line is not amenable to a classical mean-field description. Data also confirm the prediction that at sufficiently low polymer concentrations, a percolative polymer network which characterizes gelation, can still be obtained in the sparse mesoscopic regions where polymers cluster as a result of spinodal decomposition. In these conditions, and if adequate time is allowed, mesoscopic "gel" regions are indeed observed by Photon Correlation Spectroscopy to drift through the far more abundant lower concentration phase, while the macroscopic sample remains a fluid. This brings into a new light the notion of "non-gelling" concentration.

Consideration of the schematical phase diagram combining the spinodal and the gelation lines illustrates under which conditions gelation is rate- limited by the kinetics of the spinodal process, rather than by that of the coil-helix transition and consequent self-organization of the network. The Flory-Onsager phase diagram for the rod-like double helical sections offers a qualitative picture of the kinetic mechanism of the long-known self-organization of helices in bundles (5)(11).

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# ANHYDRID CURING OF EPOXY RESINS VIA CHAIN REACTION

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The common curing of epoxies is a step reaction. On each step an epoxy ring is opened and a hydroxy group is formed. These OH-groups can react further via ether bonds and form thus a branching point. Even after complete curing a number of non-reacted OH-groups are left, and these may cause an undesired uptake of moisture.

The formation of free OH-groups is fully avoided if anhydrids are used as curing reagents. The reaction follows, however, no longer a step mechanism but rather should be a chain reaction that resembles a living polymerization. To prove this conception a linear model was studied with phenylglycidylether/phtalicacid anhydrid (PGE/PSA) as comonomers. 1-Methyl imidazole (1-MI) was used as initiator. The molecular weight was found to increase linearly with $\alpha|M|/|I|$ as is expected for a living chain reaction ( $\alpha$ is the extent of epoxide consumption, and $|M|$ and $|I|$ are the molar concentrations of monomer and initiator). The obtained polymers obey in DMF the scaling laws of flexible linear chains in a marginal solvent.

The study with this linear model is now extended to the crosslinking reaction, where bisphenol-A diglycidylether (BADGE) and PSA were used. The point of gelation has been estimated by the cascade branching theory to occur at $\alpha_c = 0.366$. Furthermore, the radius of gyration $R_g$, the hydrodynamic radius $R_h$ and the angular dependence of the scattered light could be calculated as a function of the extent of reaction $\alpha$. Experiments are in progress to compare the predicted conformational properties with the measured ones. Finally, the critical behavior in the pre-gel and post-gel states is studied.

# NETWORK FORMATION IN POLYURETHANES DUE TO ALLOPHANATE, BIURET AND ISOCYANURATE FORMATION

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In polyurethane systems with isocyanate groups in excess, side reaction can occur which give rise to trifunctional branch points (1). Of these, the formation of allophanate groups from urethane and isocyanate groups, biuret groups from urea and isocyanate groups, and isocyanurate groups by trimerization of isocyanate groups are the most important ones. In diol-diisocyanate systems, these side reactions cause gelation and network formation and in polyol-diisocyanate or diol-polyisocyanate systems an increase of crosslinking density is observed.

Formation of crosslinked structures was described by a theretical approach based on the theory of branching processes, in which the branched and crosslinked structures are built up from structural fragments represented by halves of diisocyanate and diol molecules and urethane, urea, allophanate, biuret and isocyanurate units formed thereof (2). For systems poly(oxypropylene)-4,4'-diisocyanatodiphenylmethane (MDI), a relatively good agreement was reached between the calculated and experimental sol fractions at several reaction temperatures (2).

In this contribution, the theoretical treatment has been extended to the problem of elastically active network chains (EANC). In the usual theoretical procedure, the number of EANC's is derived from the number of elastically active branch points which are represented, in the diol-diisocyanate case, by allophanate, biuret, or isocyanurate units from which three paths extend to infinity. With respect to the equilibrium elastic response, this is a correct treatment only if such branch point is adjoined by long elastomeric (soft) chains of the diol. If two such branch points are connected by a short and relatively stiff sequence of hard units derived from diisocyanate, this sequence is not considered to contribute to the number of EANC's. In the theory, this requirement is fulfilled by proper weightings. A sequence issuing from an active branch point is counted if and only if an effectively unbranched sequence of hard units is terminated by an elastomeric (soft) sequence. The other connections between active branch points are in fact burried inside the clusters of hard units and are not active in rubber elasticity.

The theoretical approach allows us also to calculate the size averages of these clusters in which hard units are connected by covalent bonds. For this purpose, the soft (diol) units are split into two halves and their weight is put equal to zero. The size of the hard clusters increases with increasing excess of isocyanate and depends on the relative rate of formation of the respective branch units. Under certain conditions, these hard clusters can form an infinite network which corresponds to a phase inversion in the system.

The theoretical predictions of the concentration of EANC's are compared with equilibrium elastic moduli of poly(oxypropylene)diol-MDI systems differing in the excess of isocyanate groups and extent of side reactions.

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# POPULATIONS OF SPECIES FORMED ON CROSSLINKING PREFORMED POLYMER CHAINS

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During the crosslinking of an assembly of preformed polymer chains a variety of complex crosslinked soluble species are formed; these species are subsequently incorporated into network structures. For an assembly of preformed chains of equal length (and potential functionality) Flory determined the critical conditions for network formation (1). Stockmayer subsequently extended these calculations to assemblies of primary chains with non-equal lengths or functionalities (2). Flory and Stockmayer also calculated the populations of primary chains (monomers), pairs of chains attached by one crosslink (dimers), species consisting of three primary chains linked by two crosslinks (trimers) and more complex species for the case where the preformed chains are of equal length (2,3). For random crosslinking where functional groups on chains react to form crosslinks at random and no crosslinks are wasted by forming intramolecular crosslinks the weight fractions $W_n$ of soluble species comprising n primary chains and (n-1) crosslinks are given by

$$W_n = n^{n-1}(\gamma e^{-\gamma})^n/n!\gamma, \qquad [1]$$

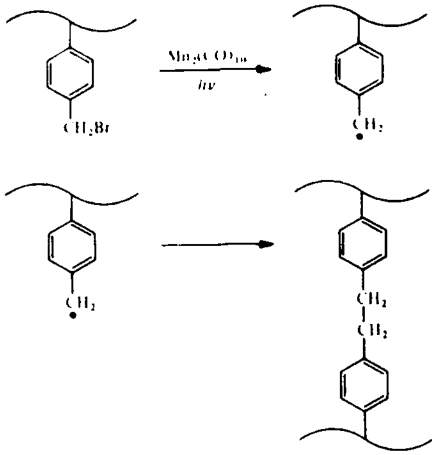
where $\gamma$ is the crosslinking index and is the average number of crosslinked units per chain. In general it is difficult to identify individual species during a crosslinking process experimentally and to test these relations.

While studying the formation of graft copolymers by initiating free-radical polymerization from preformed polymers we identified reaction conditions under which the kinetics of network formation were consistent with predictions from Flory's theory for random crosslinking. That is where the time to incipient gelation ($t_g$) is given by

$$t_g = \frac{c}{\bar{P}_w I}$$

where c and $\bar{P}_w$ are the concentration and degree of polymerization of crosslinkable units and I is the rate of formation of crosslinked units (4). In general these conditions, for "ideal" crosslinking, were low rates of radical formation and relatively high concentrations of preformed polymer (~1% w/v). At high rates of radical formation or low [polymer] deviations from simple kinetic behaviour were observed. These deviations and reaction conditions were consistent with non-random crosslinking and excessive intramolecular crosslinking under "non-deal" conditions.

Using anionically prepared poly(p-methylstyrene), subsequently functionalised by bromination of the methyl groups, we were able to test equation [1] (5). This preformed polymer had a narrow molecular-weight distribution and uniform functionality. Crosslinking was achieved by gradual removal of the bromine in a photoactivated redox reaction with manganese carbonyl. Reaction conditions under which kinetics of network formation were ideal and non-deal were established. The simplified reaction scheme is



In this scheme I is the rate of radical formation.

Samples of preformed polymer were crosslinked to identify the gel point and to different degrees of crosslinking less than the critical crosslinking index required for network formation. Gel permeation chromatography was used to examine the reaction products and it was found possible to determine the weight fractions of monomer, dimer and trimer species. Populations of individual species of greater complexity could not be determined. We previously reported on the populations of monomer and dimer (5).

Results indicate that under conditions of ideal crosslinking the weight fractions of the three species determined conform closely to those calculated from [1] for crosslinking indices up to about half that corresponding to incipient network formation. At higher crosslinking indices weight fractions of uncrosslinked species continued to conform with calculation but those of dimer and trimer species deviated from the calculated values.

At high rates of radical formation we have demonstrated that weight fractions of individual species deviate from those predicted. These reaction conditions conform to an increased probability of intramolecular crosslinking through forming a second radical on a chain during the lifetimes of a previously-formed radical. Reaction conditions and observations are consistent with intramolecular crosslinking and loop formation under these conditions.

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# NETWORKS FROM DICYANATE OF BISPHENOL A AND DIPHENOLS

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The polycyclotrimerization of aromatic cyanic acid esters in bulk in the presence of a few amounts of phenolic hydroxyl groups follows a two-step reaction mechanism. After the formation of an iminocarbonic ester by addition of a cyanato and a hydroxyl group, a triazine and a phenolic hydroxyl group are formed in a second step by further addition of two cyanato groups. In that way, the resulting network consists of trifunctional triazine junction points which are connected via the Bisphenol A unit. It was shown that the experimentally found gel-conversion-dependence can be well described by a cascade model without any substitution effect and intramolecular cyclization.

Basing on this twostep reaction mechanism of cyanato with phenolic hydroxyl groups and an additional side-reaction of the iminocarbonic ester in the presence of hydroxyl groups in the concentration range greater than 5% it is possible to decrease the number of elastically active network chains by admixture of diphenols. If the formed iminocarbonic ester consists of two parts with equal acidity, most of the diphenol-monomers are integrated into the network and produce triazine rings, which act as elements of network chains or as dangling ends. In contrary to this behavior the tendency to integrate the diphenol into the network decreases as the acidity of it increases, so that most of the diphenol-monomers remain in the sol.

The network building process is described by a combined kinetic-cascade-model. An experimental verification is given through measurements of the dependencies of gel-conversion-curves, critical conversions at the gel-point, elastic moduli, glass transition temperatures and thermal stabilities on the additional amount of the diphenols using the monomer combinations dicyanate of Bisphenol A with Bisphenol A and with Tetrabrom-Bisphenol A.

# MONTE CARLO CALCULATION OF A PARTIAL REACTION IN RADICAL CROSSLINKING OF 1,4-POLYBUTADIENE

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Complex structures limit the possibilities for experimental investigations of real networks. Various approaches are employed to determine distributions of crosslink functionalities and chain lengths. Experimental studies on "ideal networks" with many known parameters can help one to understand network formation and properties (1). A different approach to the study of network structures is provided here by means of computer simulation.

In a series of previous investigations we used the Monte Carlo technique to simulate the subsequent modification of 1,4-polybutadiene coupled with partial double bond shift (2-4). The simulation starts with the build up of the structure of a polymer chain. Substitutions sites are selected by random calls. The decisions for substitution and double bond shift are made by comparing reactivities of hydrogen abstraction and probabilities of double bond shift with random numbers. The results were confirmed by experiments and theoretical derived distribution functions for borderline cases (5).

The program has been adapted to study a partial reaction of the radical crosslinking of 1,4-polybutadiene. This type of reaction is of great industrial importance, but little is known about the structure of the vulcanisates. Simulation showed that in principle the structures of vulcanisates cannot be investigated by spectroscopic methods. For low degrees of crosslinking their sensitivity is too low and for higher degrees of crosslinking the instruments cannot resolve the vast number of different structures (6).

Our present investigation is concerned with the frequency distribution of the molecular weight $M_c$ between crosslinks. The formation of crosslinks is assumed to occur in the following steps: Formation of radicals from a low molecular compound, hydrogen abstraction in the polymer chain resulting in polymer radicals and finally mutual substitution of two polymer chains. The reaction is complicated by partial double bond shift. The distribution of $M_c$ depends significantly on the extent of the double bond shift. In accordance with the proposed reaction model periodic maxima and minima of the frequencies of $M_c$ result as a function of the degree of crosslinking and the degree of double bond shift. The results are discussed with respect to structure-property relationships.

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# RELAXATION OF ENTANGLED POLYMERS AT THE CLASSICAL GEL POINT

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The static properties of polymers near the gelation transition are well understood in the framework of scaling theories (1,2). If linear sections between crosslinks are relatively short (e.g., condensation polymerization with a high content of branching agent), the transition is described by the percolation theory (3). If these sections are long and heavily overlapping (as in the vulcanization reaction), the classical Flory-Stockmayer model applies (4-6). The range of validity of the two limits can be determined by the Ginzburg criterion (7), but has not been tested yet.

The dynamic properties of polymer gelation are not as well understood. The self-consistent effective medium theory (for unentangled systems) does not lead to a unique result for gelation (8). Any dynamical behavior ranging from Zimm to Rouse is possible. Experimentally, Rouse dynamics is usually observed (9,10), but there is no satisfactory explanation of this fact.

Near the classical gelation transition the long linear sections between branch points are well entangled. The effect of these entanglements on the viscoelastic behavior of a gelling system can be treated (11) in the framework of the tube model (12). Below we outline the main results of Reference 11.

The classical (Flory-Stockmayer) theory corresponds to percolation on a Cayley tree (3). All branched polymers created in such a process are therefore loopless trees. Let us choose a linear section of a polymer between branch points i and j. Cutting this section divides the branched polymer into two trees with longest chemical paths $m_i$ and $m_j$. The length of the smaller of these two longest chemical paths is called the "seniority" of the ij section (11). Treating the surrounding chains as an entanglement net, we note that the only way for the ij section to relax its orientation is for one of these two trees to fold back on itself without enclosing any obstacles. Thus the relaxation of a single branched polymer is similar to the arm retraction of entangled stars (13). The retraction time increases exponentially with the number of entanglements per arm. Therefore, the smaller of the two longest chemical paths would fold back and relax the ij section much faster than the bigger one. So seniority m of the section directly corresponds to its relaxation time:

$$\tau_m \sim \exp(\alpha m), \qquad [1]$$

$$\alpha = \nu M_x / M_e(0) \qquad [1a]$$

where $\nu$ is a constant of order unity, $M_x$ is the molecular weight between branch points and $M_e$ is the molecular weight between entanglements.

Near the gel point, the entanglement net is not permanent; it is made of branched polymers which relax their constraints with time. Since the relaxation times of sections with different seniorities are distributed exponentially (11), we can assume that, for the relaxation of sections of seniority m, all surrounding sections with seniorities lower than m do not contribute to the entanglement net and effectively act as solvent (14). Thus the molecular weight between effective entanglements is

$$M_e(m) = M_e(0)/C(m) \qquad [2]$$

where C(m) is the concentration of sections with seniorities larger or equal to m. It can be shown (11) that $C(m)=\beta/m^2$, where $\beta$ is a constant and therefore

$$\tau_m \sim \exp\ [\alpha\beta(1-1/m)]. \qquad [3]$$

Note that as seniority m increases to infinity the corresponding relaxation time $\tau_m$ goes to a finite time $T_\infty \sim \exp(\alpha\beta)$. This effect of dynamic dilution (11,14) leads to a very unusual stress relaxation function:

$$G(t) = G_0[\ln(T_\infty/t)/\alpha]^4/\beta^2 \qquad [4]$$

The nonphysically rapid relaxation of large clusters is prevented by a transition to unentangled Rouse motion (8-10) at length scales corresponding to percolation statistics (inside the critical region). The timescale separating entangled and Rouse regimes is close to $T_\infty$.

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# POLYMER /POLYMER INTERDIFFUSION

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Polymer/Polymer interdiffusion has important applications in engineering : adhesion, welding of plastics, polymer "metallurgy". A large number of experiments and conflicting theories have appeared during the recent years. We review the interdiffusion of $P_A P_B$ polymer bends for two situations :

1. *Compatible pairs* Three types of junctions are considered (a) the two polymer are identical (auto-adhesion) the two polymers are chemically identical, but the A chains are much larger than the B chains (c) the two polymers are chemically different, but compatible. The main parameters which controls the kinetics of interdiffusion of two blocks A,B of polymer melts is the mutual diffusion coefficient associated to composition fluctuations. On the other hand, if one monitors the brownian motion of one labeled A (or B) chain,what is seen is the self diffusion coefficient $D_{SA}$ (or $D_{SB}$). We construct a general formula for the mutual diffusion coefficient $D_M$ in term of *three* microscopic friction coefficients. For small chains ($N_{A,B}<N_E$) we find that $D_M$, $D_{SA}$ and $D_{SB}$ are three independant transport coefficients for entangled polymer chains ($N_{A,B}>N_E$) we describe the interdiffusion by the motions of A and B chains inside *moving tubes*. Only for this case where *both* polymers are entangled we find a relation between $D_M$, $D_{SA}$ and $D_{SB}$. For long versus small entangled chains, the interdiffusion is controlled by the *small chains* ; we can interpret this fast diffusion as a swelling of the network of the long chains by the more labile small chains.

For compatible and chemically different species the force of mixing is mainly enthalpic, and $D_{MUT}$ is strongly *enhanced (for small chains,* $D_{MUT} = D_0$, a monomer diffusion coefficient - for long chains with $N_A = N_B = N$, $D_{MUT} = D_0/N$).

2. *Weakly incompatible pairs* Even for uncompatible pairs, there is a non zero interfacial width. For PSH/PSD, the interfacial region is large ( 500Å), and is controlled by reptation. Diffusion equations are not directly applicable, because the A and B chains are reflected at the interface : one must construct a molecular model. We generalise an earlier calculation to assymetrical cases, where the H chains are much larger.

# DIFFUSION IN MICROSTRUCTURED POLYMERS

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Copolymers and mixtures of polymers are avenues toward producing new polymer materials with properties that are some hybrid of homopolymer properties. Hybrid, of course, does not imply that properties of these materials lie somewhere "in between" the properties of the pure constituents. The nature of these multicomponent polymers can be entirely different from any of the components. Due to thermodynamic interactions and other controllable aspects of the structures of the molecules, microstructures can develop from microphase separation among the segments. Block copolymers with thermoplastic elastomeric properties and spinodally decomposed polymer blends are two examples.

This lecture will present data on measurements of diffusion coefficients in polymer fluids that contain mixtures of different polymer segments (copolymers and blends). Diffusion sets the basic time scale for large scale molecular motion. Data on diffusion are therefore useful in understanding the rates of phase separation and equilibration processes, as well as for the molecular interpretation of rheology and processing operations. Many such materials are synthesized and/or processed in solution so that solution diffusion data as well as melt diffusion data are useful. Sample preparation or processing history may move a material away from equilibrium, diffusion influences the trapping of nonequilibrium states.

Data have been obtained on the radii of gyration of copolymers and macromolecules in polymer-polymer-solvent mixtures from which one can track the degree of contraction of coils as the concentration of polymer in solution increases.(1) Measurements of polymer diffusion coefficients in these solutions have been made by dynamic light scattering over the range from dilute solution to over 60% polymer concentration.

Measurements of self-diffusion coefficients in toluene solutions of block copolymers of styrene and isoprene have been made, as a function of concentration, at concentrations below and above that at which these solutions microphase separate in an ordered lamellar phase. In the lamellar phase, the resistance to self-diffusion is composed of a frictional part due to the concentrated polymer solution and a thermodynamic part due to the pattern of composition variation in the lamellar phase.(2)

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# STRONGLY KNOTTED POLYMERS

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A long ring polymer synthesized in good solvent conditions should have very few knots, while the same polymer synthesized in θ conditions should have many. Typical effects for the latter case are a) the size of the coil (as observed in good solvents) should vary like $M^{1/2}$ b) the rings should adsorb less easily than the linear chains c) in a melt form the different rings tend to segregate from each other (partially or totally) and this may have important mechanical consequences.

# RUBBER ELASTICITY : A PHENOMENOLOGICAL APPROACH INCLUDING ORIENTATIONAL INTERACTIONS BETWEEN CHAIN SEGMENTS.

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NMR observations in uniaxially strained networks show that the stress-induced chain orientation involve orientational interactions between chain segments (and diluents). This result leads to add an anisotropic contribution to the Flory interaction parameter. Introduction of such a correction in the network free energy enables us to reproduce stress-strain data in uniaxially deformed samples and yields a solvent-dependent maximun in the dilation modulus of isotropically swollen networks (1).

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# CHAIN SEGMENT ORDERING IN STRAINED BIMODAL PDMS NETWORKS : A NUCLEAR MAGNETIC RESONANCE INVESTIGATION

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The deuterium NMR technique is used for monitoring the segmental ordering of both short chains ($M_n$=3000) and long chains ($M_n$=25000) in bimodal PDMS networks under uniaxial stress. The induced orientational order depends of the weight fraction W of short chains among long chains ($5\% < W < 85\%$). However for a given fraction W and for a given elongation of the network the segmental orientation is similar on both kind of chains. This result is inconsistent with non-interacting chain descriptons.

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## Small Angle Neutron Scattering on PDMS model networks

- use of different tetrafunctional crosslinkers
- Bimodal networks with different isotopic labelling
- comparison with mechanical data, swelling experiments and NMR-experiments

Model networks with a monomodal meshsize distributions with a small percentage of deuterated polymers have been prepared following the Strasbourg recipe[2]. An extension of this study was done using a tetrafunctional cyclosiloxan, whose compatibility with the reaction mixture is better than the formerly used tetraallyloxyethane. Both crosslinkers give sensibly different results as well in neutron scattering as concerning complementary measurements ( mechanical and swelling data, NMR-data[3] ).

Bimodal networks have been prepared from varying ratios of a mixture of molecular weight ( M ) 3000 and 25000.
In one series of experiments parts of the large chains were labelled and the variation of the the radii of gyration as a function of macroscopic deformation was recorded.
In a second series analogous experiments were made with the small chains labelled.
We define a modell independant parameter of microscopic deformation for each system. The variation of this parameter with increasing average meshsize is studied for small labelled chains and for the large labelled chains.
An analysis of the microscopic deformation-behaviour is made in terms of classical theories.

The relationship macroscopic-microscopic deformation are resumed by comparison of the swelling ratios and moduli on one hand with the SANS and NMR data on the other hand

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# CHARACTERIZATION OF A $A_2$ HOMOPOLYMERIZATION NETWORK: POLYMERS OF 2,2 BIS(4-CYANATOPHENYL)PROPANE BY $^{13}C$ NMR AND LIGHT SCATTERING

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In the present work measurements of the number average degree of polymerisation ($^{13}C$ NMR) and the weight average degree of polymerization (light scattering) as a function of conversion ($^{13}C$ NMR, FTIR)for the reaction of bifunctional bis(4-cyanatophenyl)propane monomers are reported.

The structure of the monomer with carbon peak identifications for the NMR spectra are shown in Fig 1a. The principal reaction, which is heat or catalyst initiated, is the trimerization of three cyanate functional units to form the triazine ring(1). The structure of the polymer with an upfield portion of the NMR is shown in Fig 1b. The monomers are prepared by reacting the bisphenols with cyanogen chloride in presence of an HCl acceptor. The monomer is a crystalline solid of approximately 99.5% purity, a melting point of 79° c, and a specific density of 1.259. It was used as obtained. The homopolymerization was conducted in a three necked flask immersed in an oil bath at 200° c. Pure nitrogen was constantly run through the flask to flush the somewhat volatile monomer. The polymer was stirred briskly and consistently with a magnetic bar. Samples were withdrawn from the flask at regular intervals for characterization. The withdrawn samples were quenched in an ice bath to freeze all reaction. Refractive index measurements during polymerization, which were correlated to conversion values from both FTIR and NMR allowed easy monitoring of the reaction extent.

The conversion of the withdrawn samples was measured by both FTIR and NMR. For NMR the samples were dissolved at room temperature, for at least a day, in $CDCl_3$. Then solution $^{13}C$ was performed using inverse gated decoupling on a 200 MHz Bruker and a 500 MHz General Electric spectrometer. The identification of the seven magnetically distinct carbons (see Fig 1 for carbon identification and the spectra for the corresponding peaks) in the monomer is straightforward. Two dimensional spectra shall be investigated to complete basis for peak assignments and product identification. Conversion is determined by the disappearance of the peak at 108.88 ppm (carbon 1, Fig 1) ratioed against the peak at 42.66 ppm (carbon 6, Fig 1). FTIR was also used to follow conversion. Here one of the strong cyanate doublet at 2270 $cm^{-1}$ is ratioed against the invariant $-CH$ stretching at 2875 $cm^{-1}$. Conversion was also measured by correlating the FTIR and NMR results with the change in the polymer refractive index, which is a much simpler and faster tool.

Determination of $(DP)_n$ using $^{13}C$ for the bifunctional cyanate polymerization through the trimerization reaction has been shown by Fang(2). The classical way of counting end groups is extended by accounting for the backbone carbons, as is made possible by this novel application of NMR. Each of the four distinct aromatic carbons (2-5, Fig 1) in the unreacted monomer can exist in one of the four possible magnetic configurations, depending on the state of reactivity of the two functional units on the monomer. This forms the basis of determination of $(DP)_n$. Of the four possibilities to follow, the carbon peak (carbon 4, Fig 1) at 148.88 ppm was monitored, because it is completely decoupled. Work on determining $(DP)_w$ using light scattering is also underway.

Present indications suggest that instead of the 50% conversion suggested by Branching theory at gelation, the polymer does not gel till between 60 and 65%. A number of options are being pursued to explain this behavior. Among the two obvious ones are an alternate chain lengthening chemistry without branching (for example dimerization) and an earlier onset of diffusion controlled regime during polymerization. Substitution effect and cyclization could also contribute to this effect. Our characterization techniques shall help us answer this question. Work shall also be reported and interpreted in terms of the measured critical exponents near gelation. Theoretical discussion shall be in light of some recent work using Monte Carlo simulations.

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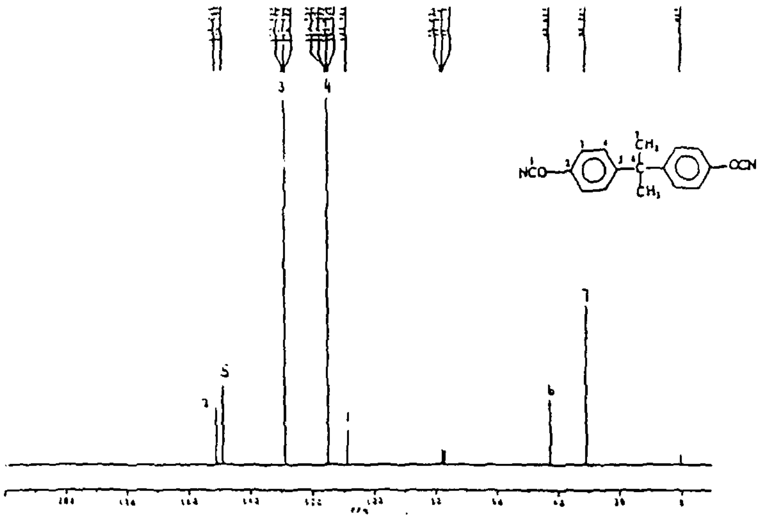

Fig1a: $^{13}C$ NMR spectra for the monomer. The monomer strcture with peak numbers is inset.

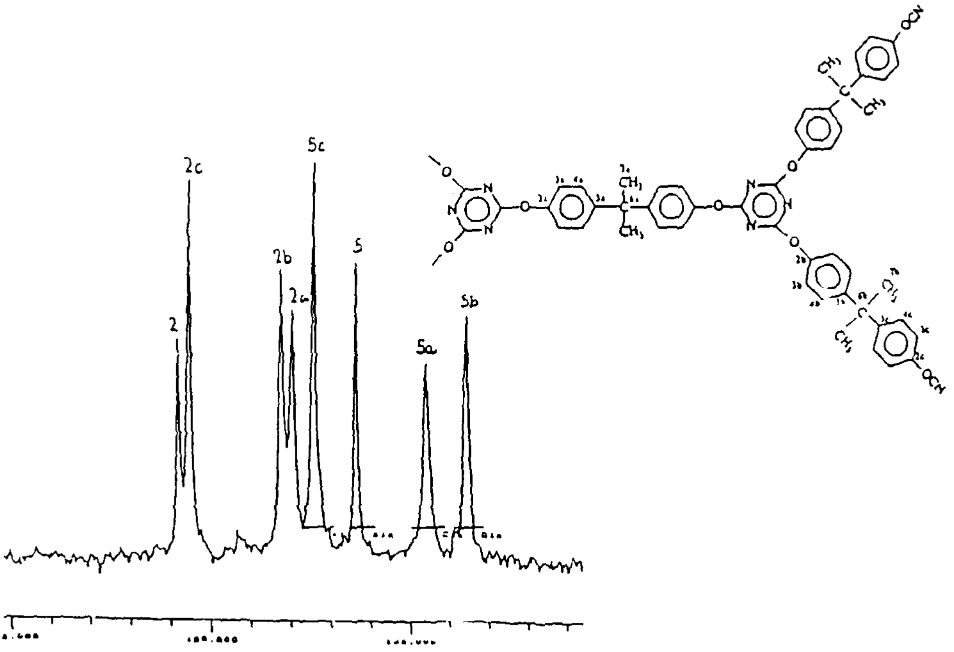

Fig 1b: An upfield portion of the $^{13}C$ NMR for carbon peaks 5 and 2. The polymer structure is inset.

# CHARACTERIZATION OF ORIENTED MICROFIBRILLAR NETWORKS BY ELECTRON MICROSCOPY AND X-RAY SCATTERING

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Networks of oriented microfibrils can be found in nature, as part of structural and connective elements, as well as in synthetic polymer systems. Of special interest are synthetic rigid polymers, from which fibers and films having very high tensile modulus and strength can be obtained. In a typical spinning process, an oriented liquid crystalline solution of the rigid polymer, which is obtained by extrusion through a die and uniaxial extension in an air-gap, is coagulated when immersed in a nonsolvent. We have studied the development of microstructure during coagulation in water of oriented solutions of the rigid polymer poly(p-phenylene benzobisthiazole) - [PBZT] in polyphosphoric acid. In previous studies the oriented microfibrillar network of PBZT was observed by transmission electron microscopy (TEM) of microtomed sections [1]. The width of the microfibrils was typically less than 100 Å and "Y" shaped junctions between oriented microfibrils were observed. By means of small-angle X-ray scattering measurements (SAXS) the average cross-section dimension of the microfibrils was determined, and the volume fraction of microfibrils in the network was estimated as less than 20% [2]. In order to maintain the open network structure the wet-coagulated fiber or film was impregnated with an epoxy resin, which prevented structural change which would have occurred during drying. However, the scattering pattern from the epoxy-impregnated network in the larger angle "Porod" region is dominated by the scattering from small scale density fluctuations within the epoxy matrix.

An alternative procedure for maintaining the open microfibrillar network is critical-point drying. Water within the coagulated network is replaced by acetone and finally liquid $CO_2$ at high pressure. Raising temperature beyond the critical temperature of $CO_2$ followed by a reduction in pressure yields a dried sample which did not experience the surface forces which occur in a common drying process. The scattered intensity in the "Porod" region, measured on an absolute scale, is now much weaker, and contains information related to the microfibrillar morphology only. The solid phase of the rigid polymers is fully crystalline. The origin of scattering in the "Porod" region are the boundaries of the microfibrils, defects within them and density fluctuations due to lattice vibrations. Critical-point dried samples can also be heat treated at elevated temperatures (600°C) which are commonly used in the processing of the high performance materials.

In this presentation we outline the procedure for characterizing the oriented microfibrillar morphology by means of SAXS measurements and report on measurements of critical-point dried microfibrillar networks before and after heat treatment. A model of the internal defect structure within the microfibrils, and its changes upon heat treatment, are presented.

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# NEUTRON SCATTERING AND SWELLING PRPOERTIES OF END-LINKED PDMS NETWORKS

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Small angle neutron scattering measurements are described for a series of polydimethyl siloxane (PDMS) networks swollen in octane and toluene. Cross-links were introduced in the dry state by linking of the hydroxyl terminated chains (M=40,000 Daltons) with excess cross-linking agent, ethyl triacetoxy silane. Using an incident neutron wavelength of 6Å and a sample-detector distance ranging between 2.8 and 20m, the scattering properties of the gel were measured and compared with those of the equivalent polymer solution.(1)

The spectra of the gels are significantly different from those of the solution: in addition to a clearly resolved Lorentzian signal as for solutions, at small angles extra forward scattering is detected. Contrast variation techniques (2) were applied to investigate the nature of this excess signal. It was found that the features that give rise to this scattering have the same chemical composition as the pure polymer.

A model is proposed to account for the contribution to the observed scattering behaviour arising from heterogeneities and constraints due to cross-links. This model describes the spatial distribution of polymer in the gels, and provides an estimate for the relative amplitude $<\Delta c^2>^{1/2}/<c>$ of the static concentration fluctuations. The variation of the correlation length as a function of network swelling is also investigated and compared with that from the soluitons.

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# ON THE ELASTIC AND SWELLING BEHAVIOUR OF POLY(VINYL ALCOHOL) AND POLY(VINYL ACETATE) NETWORKS FILLED WITH ANISOMETRICAL COLLOIDAL FERRIC(III)-HYDROXIDE PARTICLES

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It has been a long time known, that an important improvement in both, elastic and swelling properties of networks can be made by incorporating filler particles into an elastic matrix.

A new method to prepare filler-loaded poly(vinyl alcohol) (PVA) and poly(vinyl acetate) (PVAc) networks has been developed. Preparation and characterization of anisometrical colloidal ferric(III)-hydroxide filler was made separately from the cross-linking reaction.

The random distribution of individual colloidal filler particles was evidenced by transmission electron microscopy.

Not only individual particles, but also aggregates can be introduced into the networks as a result of coagulating the sol before mixing it with the PVA solution. Filler-loaded PVAc networks were obtained from PVA networks by a polymer analogous reaction.

We have studied the effect of strong colloidal interactions on the equilibrium swelling degree and on the modulus.

A filler induced gel collapse was for the first time observed, when the strength of repulsion forces between filler particles is decreased by screening the Coulombic interactions.

Comparing the modulus with the viscosity of equivalent solution, it turned out that the Einstein-parameter ( in the Smallwood-Einstein equation) is not the same as usually expected.

An attempt is made in order to interpret the results in terms of colloid stability and rubber elasticity.

# EFFECT OF NEUTRAL SILICA PARTICLES ON THE STRUCTURE AND SWELLING OF PDMS NETWORKS

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The elastic and osmotic properties of end-linked polydimethyl siloxane networks, perpared in the presence and in the absence of silica filler particles, and swollen in toluene, are investigated. The elastic moduli are obtained from two kinds of measurements (1):
a- uniaxial compression at constant volume, and
b- isotropic deswelling observations.
In the latter esperiments, the gels are brought to equilibrium with polymer solutions of known osmotic pressure. Diffusion of the polymer into the gel is prevented by a semipermeable membrane (2). The values of these two elastic moduli, which derive from deformations of different symmetry, are compared both for the unfilled and for the filled gels. In addition, the swelling pressures of the filled and unfilled systems are obtained from the deswelling measurements. The effect of neutral filler particles on the osmotic properties of the gels is described.

For all the samples studied, the elastic moduli vary with polymer volume fraction $\varphi$ as $\varphi^{1/3}$.(3) Appreciable reinforcement of the elastic modulus is observed in the presence of the filler particles. The filler also significantly affects the concentration dependence of the swelling pressure of the gels. The latter, after correction for the filler volume, can be described by a power law relation that is in satisfactory agreement with scaling theory.(4,5)

Structural information from small angle neutron scattering in the same networks is also compared with the macroscopic results.

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# Some Aspects of Rheology and Morphology of Epoxy Resins Subjected to Complex States of Stresses

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Static (extensional) and dynamic (torsional oscillations) loads were applied simultaneously at various temperatures on epoxy based specimens and their strength was subsequently checked. This combination of stresses was chosen in order to simulate to a certain extent the real service conditions of a structural part. The specimens were prepared from the commercial DGEBA Epon Resin 828 crosslinked with different hardeners in various proportions. The applications of combined stresses and the strength testing were performed while the specimens were in glassy, leathery and rubbery state.

It was found that the strength of the specimens depended markedly on their thermo-mechanical history. An unexpected increase of strength at break measureed at room temperature was recorded for those investigated compositions which were subjected to combined stresses at temperatures lower than their Tg. The same combinations of stresses, when applied at temperatures close or above Tg of the resins, led to a softening of the resin. These effects were qualitatively correlated with changes induced by the combinations of stresses on the glass transition temperature of the resins, as shown by DSC measurements and on the fracture surface morphology revealed by SEM micrographs.

# CONTINUOUS TIME SIMULATION OF TRANSIENT POLYMER NETWORKS: RHEOLOGICAL PROPERTIES

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A continuous time simulation algorithm is applied to transient polymer network models in order to study their rheological predictions. The physically interesting class of configuration-dependent loss and generation rates is examined. This class of models is known to lead to good qualitative predictions for the material functions in standard flow situations. The central quantity of the simulation is the lifetime of a network strand. This lifetime is calculated according to a proper distribution, which depends on the orientation and length of the strand and, thus, on the strength of the flow and on the specific functional form of the loss rate. The equation of motion of the strands are integrated analytically during their lifetime and the material functions are evaluated as ensemble averages. The procedure works much more efficiently than a previous simulation algorithm for transient network models so that it becomes possible to compare the predictions with experimental findings quantitatively.

# THE NETWORK STRUCTURE OF POLYETHYLENE GELS

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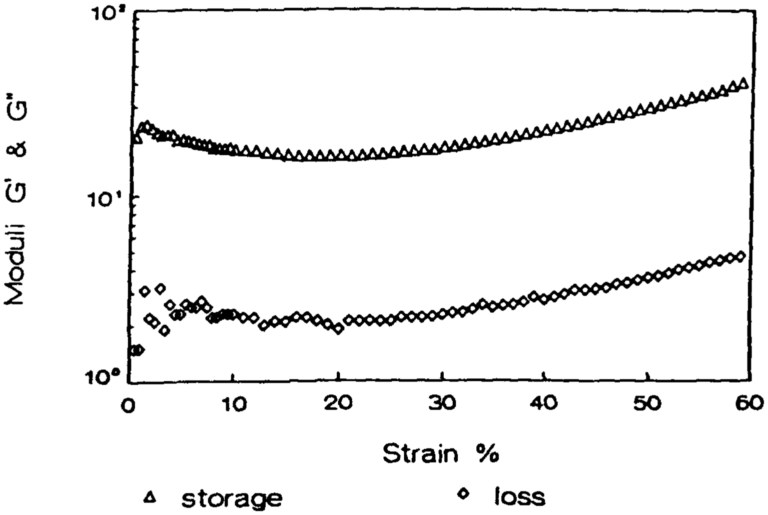
Gels, prepared by cooling dilute solutions of UHMW polyethylene are used as precursors for ultra high strength polyethylene fibres (1). The present paper is directed towards the investigation of the structure and the properties of the wet gels formed initially.
Electron microscopic experiments have been exploited to study the morphology of these gels still containing the solvents. DSC measurements were used to determine the melting behaviour. The mechanic properties were investigated with plate-plate geometry in a stress rheometer.
Polyethylene gels were prepared from solutions of UHMW PE (Hizex 240 M, $M_w \approx 1.5 * 10^6$) in xylene and decaline according to the preparation method reported by Smith and Lemstra (2). The concentrations varied between 0.5 and 6% wt and the crystallization conditions were kept constant. In a second series of experiments, solutions of the same concentration were crystallized with different cooling rates.
To prepare the gels for transmission electron microscopic studies the solvent was replaced by a mixture of methacrylate monomers (Lowicryl HM 20) in several extraction steps (3). Polymerisation initiated by UV irradiation over 36 hours at -40°C resulted in hard blocks suitable for ultramicrotomy. The embedded samples were stained with $RuO_4$ (4). Ultramicrotomed sections were examined in a ZEISS CEM 902 transmission electron microscope with integrated electron energy loss spectrometer.
The gel structure consists of single crystals. A three-dimensional isotropic network is formed by located stapling in bi- and multilamellar aggregates. The lamellae are conected to each other via aligned parts of interlayers formed by noncrystalline material at the surface of the crystals. With increasing concentration of the starting

solution the network density increased while the crystallinity and the melting point did not change. With decreasing cooling rate the crystallinity, crystal thickness and size increased. The lamellar thickness of 6-9 nm was much smaller than reported on low molecular weight samples crystallized at comparable temperatures (5).
For rheological measurements hot solutions were cooled inbetween the two plates of a Rheometrix RMS 705F rheometer (6). The measurements were performed at 20°C and special care was taken to avoid solvent evaporation. G' and G'' of the initially formed gels increase with increasing frequency and polymer concentration. The most dilute sample (0.5% wt) shows a reproducible strain hardening effect (see figure below), whereas the more concentrated gels do not show such an effect up to 60% strain.



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# Non-horizontal "rubber-plateaus" displayed by polystyrene - polyisoprene - polystyrene tri-block copolymer solutions in n-tetradecane

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*Key words: block copolymer solution, physical gelation, rubber plateau, activation enthalpy*

As is commonly known the tri-block copolymer polystyrene - polyisoprene - polystyrene can form macroscopic networks when it is dissolved in a selective solvent like n-tetradecane.

The network consists of clusters (domains) of polystyrene which are interconnected by polyisoprene chains.

We studied these systems by mechanical spectroscopy ($10^{-3}$- 10 Hz) Typical concentrations are in our case 1 to 5 percent by weight. The molecular mass of the polystyrene ends was varied from $9 \cdot 10^3$ to $14 \cdot 10^3$ and that of polyisoprene from $12 \cdot 10^4$ to $30 \cdot 10^4$ Dalton.

The storage modulus $G'$ of these systems, plotted versus frequency, displays a non horizontal rubber plateau and collapses below a certain frequency $\omega^*$. This frequency is associated with a characteristic time $\tau$. The temperature dependence of $\tau$ leads to an activation enthalpy of about $4 \cdot 10^4$ kT. The same activation enthalpy can be found from the temperature dependence of the zero shear viscosity (1).

When a temperature step is imposed upon a diblock copolymer solution, in which only a starlike micelle structure is formed, an exponential decay with time in the viscosity is observed. We ascribe it to the establishment of a new equilibrium of the micellar size distribution. The temperature dependence of the time constants leads to an activation enthalpy which is concentration and temperature independent and is about equal to that found in the triblock copolymer systems. It must be concluded that, in all cases mentioned above, the disappearance of chain ends from a domain is the dominant process in the kinetics.

The average time of residence of a chain end in a domain plays a basic role in the explanation of the frequency dependence of the plateau. It can be shown that a series of relaxation times can be based upon this time of residence.

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# STRUCTURE OF FILLED AND UNFILLED ELASTOMERS :

# THERMOPOROMETRIC MEASUREMENTS

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The knowledge of the structural parameters of elastomeric network, is of great importance for the manufacturer whose job is to propose his products with the best compromise of properties. Unfortnately, the current methods for analyzing the networks indicate only mean values of the measured characteristics and they generally fail in cases of the filled industrial products.

Our emphasis in this area has been on adapting a technique to characterize the structure of the network and especially the distribution of the molecular weigths between crosslinks, the thermoporometry developped by several research teams was chosen.

Significant effort has been placed on the choice or the solvent, the corresponding experimental conditions and the treatment of the data. Only one solvent, the MEC, leads to the desired effect with silicone rubbers, but problems appear for interpretating the results due to the semicristalline nature of the network in the conditions of the experiments. Nevertheless, when expressed in terms of average values, the obtained results are compatible with those of swelling and they well explain the mechanical properties of the elastomers.

# EXTRACTION, EQUILIBRIUM PHOTOELASTIC AND DYNAMIC MECHANICAL BEHAVIOR OF POLYURETHANE NETWORKS BASED ON POLY(OXYPROPYLENE)DIOLS AND TRIISOCYANATE

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The extraction, dynamic mechanical and equilibrium behavior of two series of networks prepared from tris(4-isocyanatophenyl)ester of thiophosphoric acid (TI, number average molecular weight $M_n$=465, average functionality f=2.97) and two poly(oxypropylene)diols (PPD, $M_n$=2000, $f_n$=1.98; $M_n$=400, $f_n$=1.93) was examined. The networks were prepared with different ratios of reactive groups $r_o$ in the region $r_o=[OH]_{PPD}/[NCO]_{TI}=0.5-1.8$; for the sake of comparison another series of samples was also prepared in the range of the excess of NCO groups ($r_o<1$), in which cyclohexanol (CHNOL) was so dosed during the preparation as to make $r=([OH]_{PPD}+[OH]_{CHNOL})/[NCO]_{TI}=1$. The reaction proceeded at 80°C for 24 h using dibutyltindilaurate(~0.01 wt%) in order to obtain the highest possible conversion of minority groups.

It was found that the expected increase in the weight fraction of the sol $w_s$ accompanying the deviation from stoichiometry takes place for both series of networks only in the case of samples with the OH groups in excess ($r_o>1$). In the range $r_o<1$ an increase in the $w_s$ is observed only with networks prepared with CHNOL. The same is valid also for the equilibrium shear modulus $G_e$. While in the region $r_o>1$ the values of $G_e$ decrease for both series of networks in the region $r_o<1$ the expected decrease in $G_e$ is observed only for networks with CHNOL. Networks not containing CHNOL have too low $w_s$ and too high $G_e$ values in the range $r_o<1$, thus suggesting a possible additional crosslinking due to side reactions when the NCO groups are in excess. The dependences of $w_s$ and $G_e$ on $r_o$ are compared with the theoretical ones calculated from the theory of branching processes. The comparison leads to a conclusion that a permanent interchain contribution to the equilibrium modulus is probable. Independence of the stress-optical coefficient on the composition of samples suggests that the networks are homogeneous.

In the region of the excess of OH groups the time and temperature position of dynamic mechanical functions with increasing $r_o$ is displaced towards lower temperatures or shorter times while the fractional free volume increases. The half-width of the retardation spectra increases with increasing deviation from stoichiometry for both series of networks. Analysis shows that the detailed structure of an elastically active network chain (both the length of the EANC backbone and the length of the dangling chains) affects the total width of the retardation spectra.

# THE REVERSIBLE NETWORK FORMATION IN POLY (DIMETHYLSILOXANES) WITH SIDE CARBOXYL GROUPS

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The structurization of the new type ionomers- poly (dimethylsiloxanes) with side COOH- groups, divided by n (n=30+80) siloxane units ($PDMS_{COOH}$) is investigated by the measuring of its rheological and thermochemical properties both in the condensed state and in the solution in the low-molecular siloxane liquid.

The intrinsic and effective viscosity, the flow curves, the activation energy of viscous flow, the elasticity modulus are evaluated as well as the displacement of the glass transition, melting and flow temperatures as a result of temperature processing of $PDMS_{COOH}$.

The results obtained show that the feature of the structurization of $PDMS_{COOH}$ consists of the transition from liquid to rubberlike state (in the case of solutions - to the gel state) by the temperature increase (up to 140°C) and in the liquifaction of the system by the cooling to the room temperature, the liquifaction carrying out for the long time.

These processes are brought about by the reversible transition of intramolecular hydrogen bonding between COOH groups to the intermolecular ones (that is to the physical network formation) at high temperatures, as a consequence of the more pronounced helix formation of macromolecules at these temperatures which is typical to PDMS chains. This effect is the more pronounced the smaller is the distance between COOH groups and the greater in the time of the holding of the sample at the 140°C.

The evaluation of the distance between network crosslinks from the elasticity modulus shows that no more than one fourth of the number of COOH groups participate in the intermolecular interactions.

# THE ROLE OF MECHANICAL PHENOMENA DURING THE FORMATION OF NETWORK POLYMERS

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Network polymers are usually utilized as binders. In this case, their formation proceeds in contact with solid surface of a filler or base. The distinction of the structure and properties of epoxy network polymers formed under such conditions are discussed.

It has been shown that the main factor resulting in the change of the structure and properties of the network polymers formed in contact with solids is the presence of mechanical field due to chemical and thermal shrinkage and internal stresses caused by the relaxation of previously deformed filler or internal stresses attributed to the phase transformation of a filler in the course of network polymer formation.

The kinetics of the internal stresses formation in epoxy network polymers has been studied in different model experiments by photoelasticity and dilatometry methods and X-ray analysis (1-3). The gradient of the internal stresses and glass transition temperature of a matrix near the boundary of inclusion have been investigated. A distinct correlation between these two parameters has been discovered.

It has been found that apart from the decrease of $T_g$ of the network polymer formed in the field of mechanical strength one can observe the increase of sol-fraction, as well as the decrease of equilibrium elastic modulus and the occurrence of the structure stresses, i.e., the residual stresses, which are never annealed (4).

The changes in the structure and properties of the network polymers obtained on the boundary with solid surface are accounted for by mechanodestruction of active elastic chains of the network being formed in a fairly narrow region of conversion near gel point, where the network polymer is very sensitive to mechanical loads(5). The degree of damage depends on the level of the internal stresses and the kinetics of the curing process, which determines the stay period in a "danger" zone for forming polymer.

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# CREEP MEASUREMENTS ON GELATIN GELS

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At the molecular and macromolecular distance scales,(1) the nature of the cross-links or 'junction zones' in gelatin gels is now largely understood, although there are still some aspects which are controversial. The primary junction zones are formed from triple helical collagen-like sequences, separated along the chain contour by residues in the 'disordered' conformation. Whether these triple helices involve three separate intermolecularly wound peptide chains, or an intramolecular hairpin folded chain with a second chain, as suggested by the concentration dependent order of kinetics observed by chiroptical techniques,(2,3) has not been established. Certainly the topological consequences of the latter model are less profound.

Although there is no dispute about the formation of the collagen-like triple helix it was thought that this was followed by substantial aggregation of triple helices leading to extended 'quasi-crystalline' junctions, as envisaged in the 'fringed micelle' model of polymer crystallisation. More recent work,(4,5) has cast doubt on this picture. The junction zones do not have a large cross-sectional radius of gyration, and both the gel modulus, and the absolute optical rotation appear to increase slowly, but without limit, even when plotted on a log time axis. This effect is probably associated with the 'flipping' of <u>cis</u>-proline residues.(3,6) It appears that the junction zones are not much broader than a collagen triple helix with a slow 'shuffling of partners' in the triple helix as the peptide chain achieves a more ordered state.

Small controlled strain oscillatory measurements (7) have shown that the storage modulus $G'(\omega)$ of gelatin gels is almost constant down to frequencies lower than $10^{-2}$ rad $s^{-1}$, and $G''(\omega)$ is lower than, but parallel to G'( ), as expected for a gel network.(8,9) Over typical oscillatory frequencies there is no indication of 'terminal flow', at least reasonably below the gel melting temperature. Gelatin gels are therefore much more solid than typical entangled melts of linear chains, where motion of large regions of chain (eg. reptation) lead to substantial reduction of stress on equivalent timescales. At the same time these oscillatory experiments leave open the question of the exact behaviour at very long times, in other words are gelatin gels viscoelastic solids, or merely very high viscosity fluids (or glasses)?

The present work describes creep measurements on a series of concentrations of gelatin gels well above the critical gel concentration $C_0$, using a high precision constant stress rheometer. The following factors are crucial to any such experimetnal study of gelatin:

1. Measurements of gel modulus and helix fraction show that these continue to increase slowly, long after the initial setting of the gel. It is therefore essential to wait sufficiently long before beginning the experiment that any additional change during the duration of the experiment is negligible.

2. The mechanical properties of gelatin gels change rapidly with temperature. DSC measurements have also shown up differences between gel samples cooled directly to a low temperature, and those cooled in two stages, even after a considerable waiting period at the final temperature.(2) Therefore a very reproducible cooling regime must be employed.

3. Gel moduli vary rapidly with concentration, in particular at high concentrations an approximate $C^2$ dependence is seen; at lower concentrations the dependence is more pronounced.(1) The stress has to be chosen so that

for each concentration a measurable strain is obtained, but the linear viscoelastic region is not exceeded.

Results for the concentration dependence of compliance are close to those expected from dynamic oscillatory measurements of gel modulus, and from theory, with J being proportional to $C^{-1.7}$. The concentration dependence of the creep phase (long time limit) viscosity also follows an approximate power law behaviour, with an exponent close to $C^{1.1}$. This exponent is consistent with relaxation in the sol fraction, and in regions of dangling chain attached to the gel. At concentrations closer to $C_0$ we predict that a higher power law regime will prevail.

In gelatin gels the actual number of cross-links is a very complex function of concentration, temperature (and also, of course, of time), so that whilst the number of residues in the helical conformation is known (from OR and DSC), the length of the helical sequences and thus the number per chain is difficult to estimate. Despite this, Djabourov and co-workers (4,10) were able to show that, for a range of temperatures, the proportion of residues in the helical conformation was constant at the gel point, whilst Durand et al (11,12) found the same generality of behaviour as a function of concentration.

Overall therefore, it appears there must be some cancellation of effects giving rise to the simple power law behaviour observed for a wide range of concentrations. Since any particular chain presumably consists of regions of essentially rod-like helical chain (the persistence length, q, of triple helical collagen is ~ 180 nm) and more flexible polypeptide chain (q ∼ 2 nm), the exact relationship between J and C (in particular the pre-exponential factors) is almost certainly more complex. Recent progress has been made in examining the aggregation of physical models of semi-flexible chains.(13,14)

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# CORRELATION OF IMPACT STRENGTH AND ENERGY TO FRACTURE OF NETWORKS EPOXIDE-DICY.

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**Strain-strength behaviour of epoxy networks obtained in curing reaction of oligomer mixture under action of DICY was studied.**

Initial oligomers were distinguished from each other by molecular weight and epoxy group functionality. Structure and mechanical properties of the networks were modificated by changing MW and functionality of oligomers, and concentration of curing agent.

It was founded that curing of these systems is connected with the reaction epoxyde-amine and epoxyde-hydroxyl. The end of the reaction takes place after disappearing of epoxy groups.

It is following from the analysis of fracture curves of epoxy networks that the samples show initial stage of plastic yielding under loading.

It was shown that values of modulus of elasticity, strength and fracture strain under tension increase under increasing of network linkages.

It was shown that the correlation dependence between Izod impact strength and work of fracture of epoxy networks is:

$$a(\mathrm{kJ/m^2}) = 1.7 + 2.5\ 10^{-3} A(\mathrm{kJ/m^3})$$

The dependence between relaxation time of motions in the networks under loading which are responsible for dissipation energy of shear defects and fracture time of samples is discussed.

The mechanism of deformation in the networks which is connected with forming of shear defects (dislocation type) is considered. The possibility of conformational transitions in polymer is decreased under fast loading therefore the concentration of shear defects increases. This situation leads to increasing of fragility of the networks.

# PLASTIC DEFORMATION IN GLASSY EPOXY NETWORKS

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Epoxy networks are widely used today in many types of materials mainly as a polymeric matrix in advanced composites. In these circumstances an important desirable property of the polymer is its toughness, i.e. the ability of a polymer to absorb mechanical energy without failure.

In the paper the mechanism of mechanical energy absorption by glassy epoxy-amine networks is discussed.

The experimental measurements of plastic deformation kinetics (deformation calorimetry), plastic deformation recovery on heating, molecular motions in deformed polymer are presented. These experimental results have allowed us to formulate the new ad hoc mechanism of plasticity: the nucleation, propagation and termination of specific metastable plastic defects.

Kinetic (activation energies, activation volumes) and thermodynamic properties of these plastic defects are analysed.

The comparison of network deformation behaviour with that of different linear glassy polymers is considered.

The role of plastic defects in cure process during solid sample deformation of epoxy-aromatic amine systems is also considered.

# CORRELATIONS BETWEEN SYNTHESIS AND MORPHOLGY IN SIMULTANEOUS INTERPENETRATING POLYMER NETWORKS

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Interpenetrating polymer networks (IPNs) constitute a new approach to the problem of the mutual incompatibility of polymers, as both components are intimately combined in their network form. Different morphologies may be achieved by varying, for a given pair of polymers, one or more synthesis parameters like the respective amount of each component or the crosslink density of the network. Another route consists in changing the kinetics, i.e. varying the respective location of the two conversion versus time curves. This latter possibility was investigated in our laboratory for polyurethane/poly(methyl methacrylate) in situ IPNs. The kinetics of IPN formation were obtained by Fourier transform infra-red (FTIR) spectroscopy. The miscibility and morphology of these IPNs were investigated through dynamic mechanical measurements and transmission electron microscopy.

In this work, polyaddition and radical copolymerization are initiated together, simply by heating at 60°C immediately after the addition of stannous octoate, the catalyst of the polyaddition reaction. Depending on the amount of catalyst and initiator added, the relative position of the conversion versus time curves, which are not superposable as the reaction mechanisms of the systems are different, is modified. When decreasing the amount of catalyst, the methacrylic network, which usually forms in presence of the elastomeric network, may be obtained prior to complete conversion of the isocyanate groups. Hence, for a given composition, IPNs having different structures are obtained. The loss tangent versus temperature curves show broad transitions and are dependent of the amount of stannous octoate. With 0.1% catalyst, two peaks appear at -56°C and 130°C respectively, indicative of two quite separated phases. When the amount of stannous octoate is increased, no elastomeric transition is observed. The general aspect of the curve indicates that phase separation is less pronounced than for the former IPN. Finally, the material obtained with 1.0% stannous octoate shows a rather flattened curve. These results are confirmed by transmission electron microscopy: a two-phase morphology is observed when IPNs are prepared with low amounts of catalyst whereas no distinct domains are visible in the case of rather high concentration.

# Interpenetrating Polymer Blends Formation

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Most of polymer pairs are immiscible, forming multiphase systems, where one of the components is a continuous matrix within which the other component is dispersed. Under specific conditions stratified or co-continuous structures may exist [1,2]. The special group of thermoplastic polymer systems, called co-continuous/interpenetrating phase materials or interpenetrating polymer blends of non-equilibrium morphology, to some extent, similar to that of interpenetrating polymer networks [3-4]. In contrast to the "true" IPNs, where at least one of the components is polymerised and/or cross-linked in the presence of the other, interpenetrating polymer blends (IPBs) are obtained by mixing of components in a molten state up to the co-continuous morphology formation, subsequently fixated by quenching. For better knowledge of the factors infuencing IPBs preparation the model blend LDPE/PS was investigated. Co-continuous structures were shown to be formed in the phase inversion region.These were dependent on the viscosity ratio of the component and their volume fraction at the particulate conditions of IPB formation according to the modified Jordhamo et al. [5] equation:

$$\left( \frac{\eta_1(\dot{\gamma})}{\eta_2(\dot{\gamma})} \cdot \frac{\phi_2}{\phi_1} \right)_{p,T} \cong 1$$

The influence of the residence time in the high shear zone of the mixing block on the phase morphology has been shown. Reducing the interfacial tension by addition of a suitable compatibilizer, acting as an emulsifier, make co-continuous structure preparation more easy. The non-equilibrium character of the morphology and the scale, being two orders of magnitude higher in comparison to IPNs, still remain present as a nature of the specific class of the heterogeneous polymer materials. Detailed studies of the phase stability and methods of the morphology fixation are welcomed both from the theoretical and the practical point of view.

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# NUCLEAR REACTION ANALYSIS: A STUDY ON THE INTERFACE FORMATION IN POLYMER MIXTURES BELOW THE CRITICAL POINT

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We describe a method to determine directly the composition profile of deuterated polymer chains in thin films. This technique is based on the $^2H(^3He,^4He)^1H$ nuclear reaction. The energy spectrum of $^4He$ particles emerging from the nuclear reaction contains information on the depth in the sample at which they were emitted and a concentration versus depth profile of the deuterated species can be computed. Its inherent resolution (14nm FWHM at the sample surface) is comparable or smaller than the radius of gyration of many high molecular weight polymers.

This nuclear reaction analysis has been applied to measure directly the interfacial composition profile between two weakly incompatible polymer phases. Polystyrene (hPS) and its deuterated analog (dPS) are characterized by weakly repulsive molecular interactions. For the molecular weights used in this study (hPS: $M_w$=2.89M, dPS:$M_w$=1.03M), the hPS/dPS mixture has an accessible upper critical solution temperature $T_c \cong 200°C$. We find that the spatial extent of the interface, the interfacial width $w$, grows with time towards a finite limiting value $w_{eq}$ for temperatures $T<T_c$. The variation of $w_{eq}$ is in quantitative agreement with the predictions of mean-field theories.

In contrast to diffusion controlled interpenetration ($T>T_c$), where the interface grows without limit as $w \sim \sqrt{t}$, we find that the interfacial width increases more slowly than $\sqrt{t}$ for $T<T_c$. Examining the development of the interfacial width before reaching equilibrium value, we find, that its variation with time can be represented by a power law behavior $w \sim t^\alpha$, with an exponent $\alpha = 0.34 \pm 0.06$. This is in accord with recent theoretical studies which predict that $w$ should grow slower than $w \sim \sqrt{t}$, with an effective exponent $\alpha$ which lies between $1/4 \leq \alpha < 1/2$.

# FORCED RAYLEIGH SCATTERING FOR THE STUDY OF DIFFUSION IN COMPLEX GEL SYSTEMS

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Forced Rayleigh scattering (FRS) is a light scattering technique for studying the self-diffusion of molecules over a wide range of values of diffusion coefficient. Probe molecules are labelled with a photochromic dye and mixed into a sample of unlabelled material; a transient diffraction grating is then photobleached in the sample. The intensity of light scattered by the transient grating measures the grating strength whose characteristic decay is determined by the self-diffusion of the dye-labelled probe molecules. An FRS apparatus has been designed and built at Reading for the study of diffusion in random mesh structures such as concentrated biopolymer solutions and gels; some novel features of the apparatus design will be described. The photochromic dyes may be associated physically or covalently to macromolecules such as proteins and carbohydrates. By means of specific labelling the diffusion of one component of a complex mixture may be monitored. Protocols for labelling polymers will be described in the context of possible perturbations of macromolecular structure and how this may be reduced to an acceptable level.

An estimate of the pore size of a gel may be obtained by comparing the self-diffusion coefficients of molecules of different sizes in free solution and in the gel. Results will be presented for gel systems such as gelatin and PVC.

# SOLVENT SORPTION CHARACTERISTICS OF PARTICLES AND FILMS OF CARBOXYLATED STYRENE/BUTADIENE EMULSION COPOLYMERS

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Solvent sorption isotherms of latex polymer particles are measured using a home-built vapor pressure differential manometer. Swelling ratio versus partial pressure are recorded for a serie of acrylated styrene/butadien emulsion copolymers of various crosslinking densities. By applying the classical Flory-Huggins-Rehner treatment to these isotherms, interaction parameter $\chi$ is obtained as well as its dependance upon polymer volume fraction, and also an estimation of Mc, the number average molecular weight between crosslinks.

The uptake rate of solvent into films of coalesced particles is then investigated by weighing film samples in solvent vapor at constant activity. Solvent sorption kinetic curves approach a typical Fickian diffusion scheme. More interesting is the relation between equilibrium swelling ratios and gel content of the copolymer film : it shows a marked maximum, which is not observed when the polymer is in aqueous dispersion.

This unexpected feature can be explained if we assume a highly ordered film structure with segregated microphases rich in carboxylated sites. These "clusters" act as ionic crosslinkages. Thus covalent crosslinking seems to control swelling characteristics of carboxylated SBR films through two antagonistic mechanisms: hence a decrease in covalent crosslink density i) increases the mesh size of the S/B network ii) promotes ionic microphase segregation, due to an increase in chain mobility.

Thus by simple swelling experiments performed both on latex particles and on coalesced polymer particle films, one can discriminate between covalent crosslinking and ionomeric type interactions.

# SWELLING AND RELEASE STUDIES OF pH AND GLUCOSE SENSITIVE HYDROGELS.

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Incorporation of ionic groups into hydrogels cause the swelling properties of the latter to vary with pH. By immobilizing an enzyme on the pH sensitive hydrogel, it becomes capable of responding specifically to glucose (1). (The enzyme, glucose oxidase, causes glucose to be converted to gluconic acid. The gluconic acid, in turn, decreases the pH in the microenvironment of the hydrogel and therefore affects its swelling). This property makes the ionic hydrogels attractive as glucose sensor or glucose responsive drug delivery system.

Hydrogels were prepared by chemical polymerization of solutions containing hydroxyethyl mathacrylate, N,N-dimethylaminoethyl methacrylate, tetraethyleneglycol dimethacrylate, ethylene glycol, water, glucose oxidase, ammonium persulfate, sodium meta bisulfite and releasing substance. The solutions were poured between two glass plates. Disks were punched from the polymerized hydrogel slabs and then placed in the buffer of choice or in a glucose solution. Water uptake and release rate of the incorporated substance were detected throughout the experiment at several constant pH values and glucose concentrations, as well as after step changes in pH and glucose concentration.

As expected the hydrogels displayed faster and higher swelling and release rates at lower pH values or at higher glucose concentrations. The response of the system to step changes in pH from 7.4 to 5.8 was faster than in the opposite direction (5.8 to 7.4). During the swelling process the water permeating into the hydrogel follows a swelling front, on the other hand, the deswelling process first effects the outer layer of the hydrogel. Therefore, the water leaving the hydrogel must cross a zone of lower permeability where deswelling has already taken place. The effect of parameters such as copolymer composition, crosslinking density, buffer ionic strength and releasing substance on swelling kinetics and release rates will also be discussed.

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# EFFECT OF ULTRASOUND ON SKIN STRUCTURE AND PERMEABILITY

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The nature and state of lipids are often important regulators in many biological membrane functions and properties. In particular, the stratum corneum barrier function has been attributed to the interstitial lipids for lipophilic solutes, or to a more polar (intercellular pathway) for polar solutes (1). The composition and physical structure of the lipoidal and hydrophylic routes can affect its barrier properties. We previously reported on the effect of ultrasound on transdermal drug delivery to rats and guinea pigs (2). We also suggested and demonstrated the feasibility of pulsatile drug delivery from implantable devices controlled by ultrasound (3). The objective of this research is to explore the effect of ultrasound on stratum corneum composition and structure, in order to understand and characterize the permeability enhancement phenomenon.

The membranes evaluated were hairless mice and human skin. The permeating molecules were: KCl, salicylic acid, and hydrocortisone. Transport cells composed of two compartments separated by the membrane of interest were used to obtain permeability data. KCl was detected by electrical conductivity measurments, salicylic acid [$^{14}$C] and hydrocortisone [$^{3}$H] radioactivity was determined in a liquid scintillation counter.

To evaluate the effect of ultrasound on membrane structure and permeability, an ultrasonic probe (Sonopuls 434, Enraf Nonius Delft 1 MHz, or Vibra Cell 250, Sonics and

Materials 20 KHz) was immersed into one of the compartments and the solution was exposed to ultrasound. The temperature of the solutions were controlled. The membranes before and after the ultrasound exposure were also evaluated by fourier transform infrared spectroscopy (FTIR) and differential scanning calorimetry (DSC).

It was found that ultrasound enhances drug permeability through skin and synthetic membranes. The extent of enhancement depends on the nature of the permeating molecule and can be externally regulated by the ultrasound frequency, intensity or duration. The magnitude of cavitation affects the degree of permeability enhancement.

Phenomena that might elucidate the mechanism of ultrasound enhancement such as: structural changes of stratum corneum, mixing, cavitation, and temperature will be discussed.

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# KINETICS OF INTERFACE FORMATION BETWEEN WEAKLY INCOMPATIBLE POLYMER BLENDS

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ABSTRACT: A mean field model of interface formation between weakly incompatible polymer blends is used to investigate the time development of interfacial composition. Interface width as a function of time exhibits two power law growth regimes; a $t^{1/2}$ growth law at early times crosses over to a $t^{1/4}$ growth law before relaxing towards the equilibrium interfacial profile. Results are in qualitative agreement with recent experiments on interface formation kinetics of partially incompatible mixtures of deuterated and protonated polystyrenes(1). Predictions for both the scaling growth regimes and the kinetics of the final approach to the equilibrium interfacial profile are discussed in detail and compared critically with experimental results.

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# VOLUME PHASE TRANSITION OF D N A
# AND REENTRANT PHENOMENON

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We present observations of a discontinuous phase transition of Deoxyribonucleic acid (D N A) and Acrylamide gels in the ethanol-water mixtures.(1,2)

D N A in water (20%) is cross-linked by using E G D E (50% of D N A) at PH 10, 55°C for 3 hours after 4 hours stirring. The volume changes at the transitions are 8.2 - 15 times at 79% ethanol.

Reentrant volume phase transitions of Acrylamide gel (Ionized by sodium acrylate) are observed at 21% ($V/V_0$:15) and 71% ($V/V_0$:16) ethanol concentrations at 23°C.

Fig.1 D N A

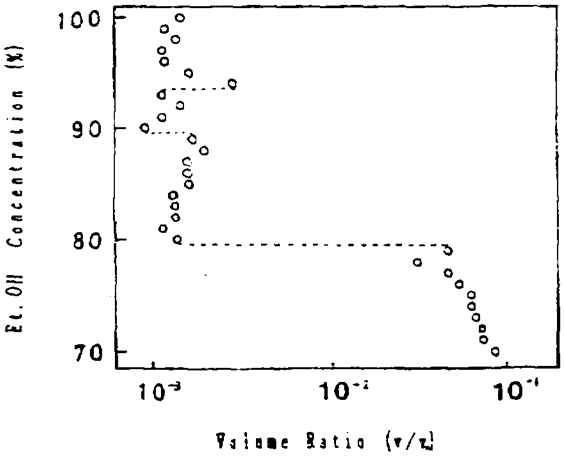
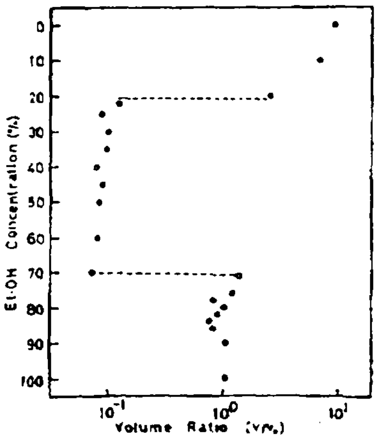


Fig.2 Acrylamide



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# DEMIXING AND POLYMERIZATION IN SYSTEMS OF ANISOTROPIC GLOBULAR PARTICLES

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We report results of recent experiments and of ongoing Molecular Dynamics simulations, relevant to the process of self-assembly of extended supramolecular structures of globular macromolecules.

Elastic and Quasi-Elastic Light Scattering experiments have allowed determining the regions of thermodynamic instability of solutions of adult human hemoglobin HbA and of its slightly different, but pathological, mutant species HbS. The latter, a globular molecule having specific, symmetry-breaking hydrophobic contact regions at its surface (1) is probably the best-studied protein capable of self-assembly (1). Fitting of the spinodal line (i.e. of the line encompassing the region of instability in the T,c plane) has provided the long-wanted (2) Flory-Huggins entalpy and entropy values for these systems. Compounding the spinodal line with the long- known gelation line (1), allows novel views on the process of self-assembly and on the role of spinodal decomposition (3-8). Experiments at deoxy HbS concentration of about 12% w/v, that is just outside the region of macroscopic gelation, support the idea of a "mesoscopic gelation" occurring in the sparse mesoscopic regions where polymers cluster as a consequence of quenching in the instability region and subsequent spinodal demixing. Shapes of the birefringent aggregates so obtained are commented and compared with shapes obtained in statistical simulation as specified below.

Molecular Dynamics simulations of spinodal demixing (9) of a system of particles were performed to the purpose of studying the shapes of clusters resulting from demixing. The study concerned the dependence of shapes upon the existence and effectiveness of specific attachment regions on the otherwise spherical Lennard-Jones (LJ) particles. Attachment points were modelled by a modified Stockmayer potential, obtained by superposing to the LJ potential an electric dipole potential, truncated by an S-shaped tapering function. The latter had the purpose of actuating a smooth and selectable cut-off, thus determining a smoothly localized attachment area on the particle "surface". The simulated bidimensional system contained several thousands particles in a square box with periodic boundary conditions. Simulations were performed on Trasputers-based parallel arrays (10,11). At the start, the system was brought in its region of thermodynamic instability. The evolution of its subsequent demixing and of the resulting shapes of clusters were followed up to 1000 ps. for different values of dipole strength.

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# VISCOSITY AND VISCOELASTICITY OF A GEL-FORMING POLYMERIC SOLUTION IN THE COURSE OF ITS SPINODAL DEMIXING PRECEDING GELATION

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We report on a time-resolved experimental study of low-shear viscosity and viscoelasticity of aqueous solutions of the representative, repetitive and essentially uncharged biostructural polysaccharide, Agarose (1-2). In the conditions chosen for our experiments, these systems undergo spinodal demixing, which precedes in time, and in fact triggers, gelation (3-5). A very large peak of viscous dissipation of energy accompanies the demixing process. The size of this increase is up to two orders of magnitude. In the course of demixing and long before the occurrence of gelation, the response to small-strain, low-frequency oscillatory shear becomes complex. The elastic component overwhelms very rapidly the dissipative one. Its value, however, remains orders of magnitude smaller than that which sets in as a result of later-occurring gelation.

Self-organization of a self-supporting polymer network starting from aqueous sols of Agarose has been observed to occur *in vitro* , upon temperature-quenching through the following sequence of steps: i) spinodal demixing (3-5); ii) coil to double helix transition, entailing crosslinking (1)(6); iii) progress of crosslinking, to reach and go past the percolation threshold for gelation (6) and iv) gel curing, i.e. association of double helices in bundles, to the extent allowed by local constraints (1). These steps have been resolved in their time and temperature dependence by Optical Rotation measurements, Photon Correlation Spectrometry, Elastic Light Scattering, and Turbidity Spectrometry (3-6).

Aqueous agarose solutions, prepared as previously described (3-4), were quenched into the region of thermodynamic instability, and directly put in a low-shear, rotating cup viscometer, operating at constant shear (Contraves LS30). The shear was varied in the range 0.016÷0.2 $sec^{-1}$, sufficiently low to warrant a laminar regime. After a delay time depending upon concentration and quenching temperature, a large viscosity peak followed by a return towards normal values, was observed in coincidence with the appearance of a small angle light scattering monitoring the occurrence of spinodal demixing. This delay time exhibited a critical behavior. No other signal monitoring coil-helix transition or gelation was detected at this time. The shear dependence of the viscosity surge followed an inverse power law $\Delta\eta/\eta$=const.$S^{-p}$ with $p=1.86\pm0.06$ (7-8).

The behavior of the viscosity peak follows very accurately Onuki's predictions concerning shear viscosity during spinodal demixing, based on mode coupling (9-11). As a consequence of the very large correlation length, concentration fluctuations had a long mean-life-time $\tau$. This made it possible to explore in the present experiments the range $S\tau>1$, although working in the low shear, laminar regime. Determination of the shear dependence of the extra dissipation in the course of demixing was allowed for the first time by the combined use of off-critical concentrations and shallow quenches. In this way the kinetic process of demixing was sufficiently slow to allow time-resolved studies, while concentration differences within the decomposing sol were large enough to give rise to well measurable signals.

Using the viscometer in its oscillating mode (±7.5°) the onset of a viscoelastic signal was revealed, simultaneous to the viscosity peak. In the course of spinodal demixing and notwithstanding its steady and remarkable increase, this signal remained at least two orders of magnitude lower than that corresponding to gelation. A viscoelastic behavior occurring during spinodal demixing is expected on a qualitative basis, although detailed theories are not yet available.

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# ON THE PERIODIC PRECIPITATION PATTERN AND MOVING REACTION BAND IN CHEMICALLY CROSSLINKED POLY(VINYL ALCOHOL) GELS AND IN THIN SILICA GEL LAYERS

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The formation of rhytmic pattern of precipitate, when an electrolyte diffuses into a gel containing another electrolyte, is known as the Liesegang phenomenon [1]. A weakly soluble salt is formed as a result of diffusion and chemical reaction that yields precipitates in the form of bands paralell to the front of the diffusing electrolyte.
A study of Liesegang band formation is presented with emphasis on the dependence of the precipitation patterns on the initial concentration of reactant, as well as on the role of precipitate solubility.
Formation of $Mg(OH)_2$ , $Cr(OH)_3$ and $HgJ_2$ precipitates were studied in chemically crosslinked poly(vinyl alcohol) gels and in silica gel sheets with layer thickness of 0.2 mm. These gels effectively prevent convection and sedimentation of the solid phase.
A cross-over from Liesegang pattern formation to moving band (heterogeneous traveling wave [2]) has been observed.
The experimental results will be interpreted in terms of diffusion reaction equations.

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# On the Thermoreversible Gelation of Tamarind Gum in the Presence of Sulfate Ions

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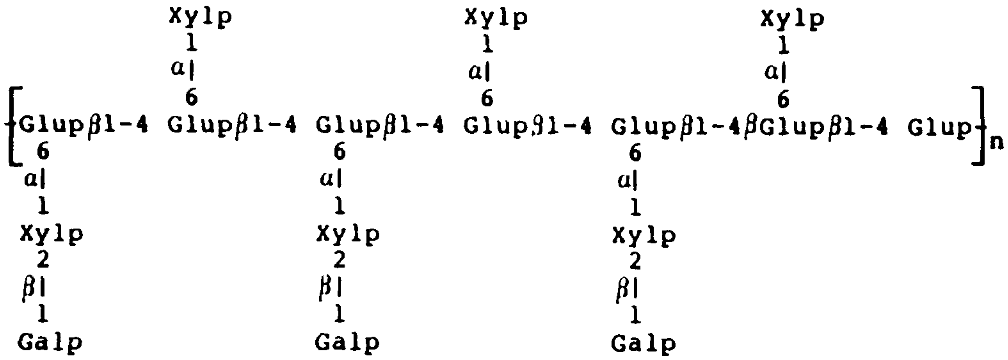
Tamarind Gum is a kernel polysaccharide from the Tamarind tree (tamarindus indica) with the following average structure.



$$\left[\begin{array}{ccccccc} & \mathrm{Xylp} & & \mathrm{Xylp} & & \mathrm{Xylp} & \\ & 1 & & 1 & & 1 & \\ & \alpha| & & \alpha| & & \alpha| & \\ & 6 & & 6 & & 6 & \\ \mathrm{Glup}\beta 1\text{-}4 & \mathrm{Glup}\beta 1\text{-}4 & \mathrm{Glup}\beta 1\text{-}4 & \mathrm{Glup}\beta 1\text{-}4 & \mathrm{Glup}\beta 1\text{-}4 & \beta\mathrm{Glup}\beta 1\text{-}4 & \mathrm{Glup} \\ 6 & & 6 & & 6 & & \\ \alpha| & & \alpha| & & \alpha| & & \\ 1 & & 1 & & 1 & & \\ \mathrm{Xylp} & & \mathrm{Xylp} & & \mathrm{Xylp} & & \\ 2 & & 2 & & 2 & & \\ \beta| & & \beta| & & \beta| & & \\ 1 & & 1 & & 1 & & \\ \mathrm{Galp} & & \mathrm{Galp} & & \mathrm{Galp} & & \end{array}\right]_n$$

The native Gum has a molecular weight of 830 kilodalton and shows an almost ideal coil behaviour in aqueous solution. Similar to other reported polysaccharides, Tamarind Gum forms gels in the presence of high concentrations of mono- or oligosaccharides. It also exihibits thermoreversible gelation in the presence of sufficiently high concentrations of sulfate ions.

Results of light scattering investigations on the native polysaccharide and on the thermorevesible gelation of the gum in presence of $Na_2SO_4$ are presented.

In dilute sulfate solution the gum does not show a deviation from the normal behaviour in pure water. However it exihibts an enormous increase of molecular weight and dimension if a critical concentration ratio is exceeded

A slow motion mode in the time correlation function is detected in dynamic light scattering, which appears typical for a gelling system.

# THERMOREVERSIBLE GELATION OF SYNDIOTACTIC POLY(METHYL METHACRYLATE)

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Syndiotactic poly(methyl methacrylate) (s-PMMA) is an interesting polymer because of its ability to form ordered structures in many solvents. This phenomenon is thermoreversible, organization being introduced on cooling. The final structure of the solution depends strongly on the solvent.

Cooling of moderately concentrated solutions of s-PMMA in toluene or o-xylene results immediately in the formation of a rigid, transparent gel. A two step mechanism different from the well known crystallization gelation was proposed and called conformational gelation. It was supported by the combination of the data obtained with different experimental techniques.

Infrared observations reveal the occurence of a fast intramolecular transition from a random coil to a regular conformation. The exact conformation of the polymer chain is not yet clear. The formation of an extended helical conformation with the main chain bonds in a close to an all trans conformation is suggested.

In a second step, this intramolecular conformational transition is followed by an intermolecular association of the regular sequences. This results in the formation of a three dimensional network. At high enough temperature, this transition is much slower than the change in molecular conformation and its occurence can be detected by rheological observations. These associations represent the physical cross-links responsible for network formation. The nature of these cross-links is still not resolved because the poor X-ray diffraction data.

The formation of ordered structures of s-PMMA in toluene has also been investigated by high resolution proton n.m.r.-spectroscopy and light scattering. Mechanical characteristics of the network were obtained by rheology. The phase behaviour of s-PMMA in toluene, studied by calorimetry, deviates from the well known systems. Apparently, the behaviour of s-PMMA in solution, leads to a special kind of structuration with specific characteristics.

# SUGAR COATED HYDROGELS FROM POLYALLYLAMINE. PREPARATION AND CHARACTERIZATION OF MICROGELS AND THE SOL-GEL-TRANSITION OF THE CROSSLINKING IN WATER

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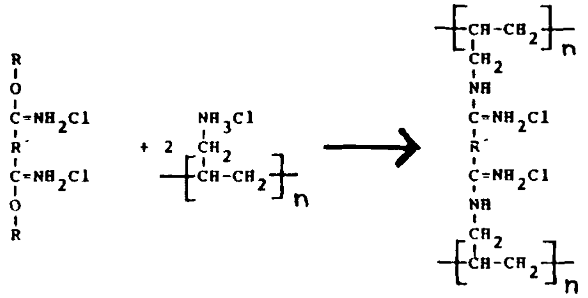
Microgels and hydrogels have been synthesized by crosslinking polyallylamine with a bisimidoester in water at pH 10



The resulting amidine bond is stable under neutral conditions. The network formed at higher pH is not stable, hydrolysis occurs after several hours. This hydrolysis is prevented when the pH is changed again to pH 7. The formation of microgel or hydrogel depends as usual on the amount of crosslinker, which is added to the polymer solution. The products (highly branched, soluble clusters) have been studied by static and dynamic light-scattering in aqueous solution and by viscometry. Intramolecular reactions (ring formation) is favoured in very dilute solutions of the polymer ($c \ll c^*$). The hydrodynamic radii and the intrinsic viscosity are reduced compared to the properties of the molecules obtained at $c^*$. Furthermore the point of gelation is shifted to higher cross-linker content. The gelation process was followed by time dependent rheological measurement (i.e. $G'$ and $G''$).

In a second approach polyallylamine has been modified by graphting maltonolactone to the chain followed by crosslinking with the same reagent as before. Sugar coated microgel could be prepared. Characterization of the product is in progress.

# ASSOCIATION OF END-FUNCTIONALIZED POLYSTYRENES INDUCED BY A BIFUNCTIONAL DINITROPHENOL COMPOUND

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Amino-terminated polystyrenes (PS) were synthesized by anionic polymerisation. The technique enables to introduce the same tertiary amino group either by initiation, with dimethylaminopropyl-lithium (DMAP-Li), or by termination, of living PS-carbanions with dimethylaminopropylchloride (DMAPCL). Monofunctional, bifunctional, and trifunctional (star-molecules) PS-samples have been prepared. These amino-end-capped polymers were found to exhibit no association in solution.

A well defined association is induced, however, by an acid-base mechanism of the amino end groups with the phenol groups of the bifunctional 2.6.dinitrohydroquinone-4-adipinic acid- diester. A doubling in molecular weight was observed with monofunctional PS. The association with two and three functional polymers leads to a chain extension and branching, respectively. The increase in molecular weight and in size has been measured by static and dynamic light scattering.

Dinitrophenol compounds show an absorption in the UV-VIS-region. Thus the degree of association ("extent of reaction") could be measured directly by UV-VIS-spectroscopy. Furthermore, the temperature dependence of the complex formation can be observed by determining the equilibrium constant. Knowing the equilibrium constant, it is possible to calculate the degree of association and the molecular weight of the associated products with the aid of cascade branching theory. A comparison with the experiment leads to the conclusion, that the two dinitrophenol groups are not equal e.g. the association of the second phenol group is hindered by the complex formation of the first group. Substitution effect and intramolecular association (ring formation) apparently play a significant role and have to be taken in consideration for a complete description.

# PROBABILITY MODELS OF NETWORK FORMING POLYMER SYSTEMS WITH INTRAMOLECULAR REACTION

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Sarmoria, Vallés and Miller (1) present models of stepwise polymerizations with intramolecular reaction for both linear and network forming systems. Intramolecular reaction is limited to the formation of the smallest N sizes of closed rings. For linear systems N may be any finite number. For network forming systems with N=1 they give an exact solution to the model, and for N=2 part of the solution is approximate.

This work is now extended to exact solution of network models with N=2. The solution combines kinetic and Markovian analyses. It has been implemented for $A_f$ homopolymerization in a FORTRAN program that identifies the molecular structures that are needed to describe the reaction process, recognizes all possible reactions between these structures and establishes the system of differential equations for the rate of change of concentration of structures with time. Once the differential equations are solved, all molecular parameters in the pregel and postgel regions may be calculated using the theory of branching processes (cascade theory). We have compared the results obtained with this model with those of simpler approximate models, and have sought guidelines to help decide which model is more appropriate in different situations.

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# BRANCHING KINETICS OF EPOXY POLYMERIZATION OF 1,4-BUTANEDIOL DIGLYCIDYL ETHER WITH CIS-1,2-CYCLOHEXANEDICARBOXYLIC ANHYDRIDE

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The copolymerization of epoxy (1,4-butanediol diglycidyl ether (DGEB)) with anhydride (cis-1,2-cyclohexanedicarboxylic anhydride (CH)) in the presence of benzyl dimethyl amine (CA) as a catalyst produces a branched epoxy polymer (1,2). We Show that the branching kinetics of the copolymerization reaction and the molecular weight distribution of the branched polymers can be modelled by Smoluchowski's coagulation equation (3).

In the simplest relevant application of this equation to our problem, the overall rate kernel w(u,v) that describes the branching probability in the equation turns out to be proportional to the sum of active sites on the two polymers with a time dependent coefficient. Using this kernel, the equation can be solved analytically (4). Therefore, using the equation, number of epoxy polymer molecules (Nn) with different branching points (n), molecular weight distribution (MWD) and weight averaged molecular weight (Mw) of the branched copolymers at different reaction stages (i.e., different conversion extent (p)) before the gelation threshold can be calculated theoretically with different initial conditions.

Figure 1, Figure 2 and Figure 3 respectively show the calculated Nn, MWD and Mw (continuous lines in the Figures) where it is assumed that the distribution of epoxy polymer molecules is exponential in the number of branching points or, equivalently, active sites, at some early stage of reaction.

The calculated values are then compared with the experimental results obtained by using small angle X-ray scattering (SAXS) at the State University of New York (SUNY) X21A2 beamline, National Synchrotron Light Source (NSLS), Brookhaven National Laboratory (BNL) and laser light scattering (LLS), and chemical analysis. Experimental data are also presented in Figure 3 by hollow squares. Satisfactory agreement between experimental results and the use of the coagulation equation is attained. To our knowledge, Smoluchowski's coagulation equation is first time applied for modelling the kinetics of epoxy polymerization.

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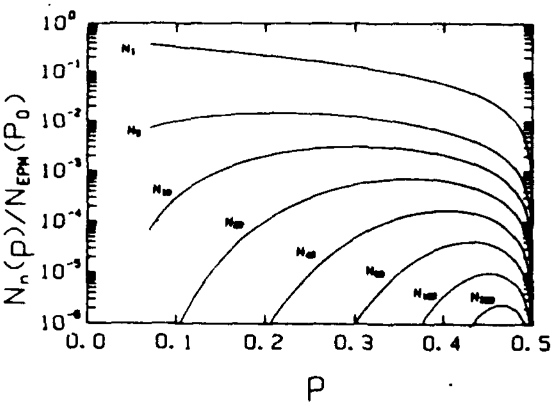

Figure 1. Plot of calculated number of epoxy polymer molecules with n branching points versus different conversion extent (p) for different values of n.

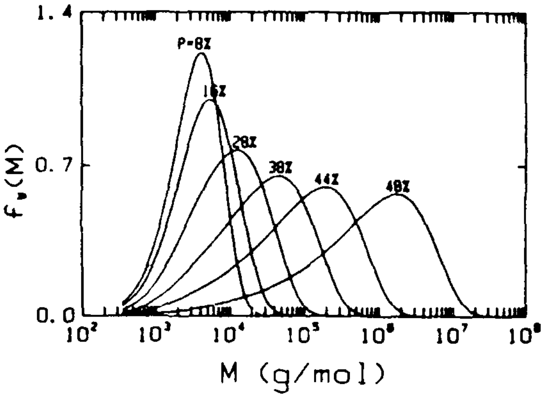

Figure 2. Plot of calculated weight distribution versus M at different conversion extent.

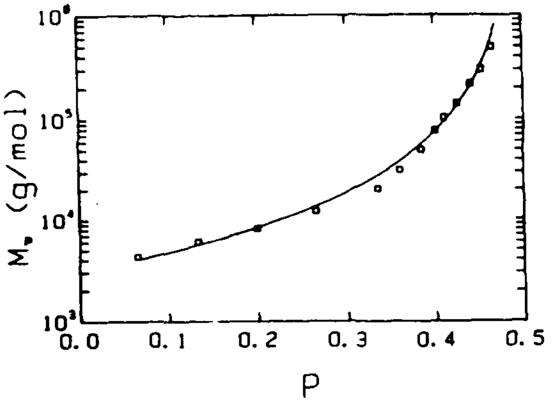

Figure 3. Plot of weight average molecular weight Mw versus different extent of conversion (p).

# BOUNDARY CONDITIONS FOR IONOTROPIC GELATION OF POLYURONIDES

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A method of the constructing of phase diagrams for the liquid solution-gel transition by the crosslinking of polyuronides by metal ions is developed. The method is based upon the registration of the minimal concentration of the crosslinking agent required for a gelation of a droplet of the polymer solution introduced into the solution of the crosslinking agent (the salt of a polycoordinative metal).

At high concentrations of a crosslinking agent the boundary concentration of the polyuronide reaches a constant, minimal value. This concentration, called the critical concentration of gelation (CCG), does not depend, as a rule, on the nature of the crosslinking agent. It is determined by the molecular mass and by the conformations of macromolecules only.

At lower concentrations of a crosslinking agent the boundary concentration of the polyuronide is governed by its affinity to the crosslinking agent . This affinity series for divalent metal ions reverses by the transition from sodium alginate to sodium pectate. The same holds for the affinity of these polyuronides to monovalent cations, i.e. to $Na^+$ and $K^+$ ions, the affinity being characterized by their activity coefficients. The analogy appears to stem from the general features of the combined Coulombic and ion-dipole binding by a polyuronide of divalent cations on the one hand and of the pure Coulombic binding of monovalent cations on the other hand, both kinds of the binding being of electrostatic nature.

The analysis of phase diagrams by the mean-field approximation enables to calculate the stoichiometric coefficient of the crosslinking reaction, i.e., the reaction order with respect to the polymer, and the apparent binding constant. The last is an effective one, being averaged over the cooperative binding isotherm. Such an analysis has shown in particular that trivalent cations, like divalent ones, bind only two polyuronides chains. Alginate gels also under the action of $Ag^+$ ions, the CCG in the last case being substantially higher than that of multivalent ions.

The CCG of alginate increases by the degradation of the polyuronide chain, by the introduction of urea into the solution and by the growth of the ionic strength. The linear dependence of the reciprocal value of the CCG on the square root of the ionic strength obviously reflects the changes of coil dimensions of the polyuronide. The growth of the ionic strength results also in the two-fold diminution of the number of the reactive groups in the alginate macromolecules and in the decrease of their affinity tp $Ca^{2+}$ ions. This provides the production of macroscopically homogeneous gels used in the food industry.

The coincidence of the stoichiometric coefficients for the $Ca^{2\pm}$ alginate system determined by the above-described method and by the constructing of the binding isotherm points to the fact that cyclisation processes are unessential.

# Cross-linking index, molecular weight distribution and rubber equilibrium modulus during multifunctional cross-linking.

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By Flory (1) and Stockmayer (2) the cross-linking index $\gamma$ in a cross-linking system was defined as the mean number of cross-links per primary polymer molecule as a whole. They derived a relationship between $\gamma$ and the sol fraction $w_s$ for tetrafunctional cross-linking. In this paper multifunctional cross-links are taken into account.

## A Theory

### a) monodisperse polymer

The relationships between $\gamma$, the solfraction $w_s$ and the rubber equilibrium shear modulus $G_e$ are given by:

$$\gamma = -\ell n\, w_s/(1 - w_s^{\frac{1}{2}f-1}) \qquad [1]$$

$$G_e M/(cRT) = 2 \cdot [\gamma \cdot (f-2)/f \cdot (1-w_s^{\frac{1}{2}f})/(1-w_s)-1] \cdot (1-w_s) \qquad [2]$$

$$\gamma_c = \gamma(w_s \rightarrow 1) = 2/(f-2) \qquad [3]$$

These relationships reduce to those of Flory (1) and Stockmayer (2) by substitution of f=4.

### b) polydisperse polymer

The equations above can be applied to polydisperse polymers with molar mass distribution w(y), by changing $\gamma$ into $\bar{\gamma}_w = \Sigma\, w(y)\gamma(y)$, i.e. the weight average cross-linking index in the system as a whole, whereas the molecular weight M has to be replaced by $\bar{M}_w$. However, in this case the relationships only hold in the region just after the gel point, so that they are less common than those for monodisperse polymer.

### c) known molar mass distribution

If the molar mass distribution is known the necessary approximations in b) are not needed and exact results can be obtained. For a Flory distribution and a Schulz-Flory distribution we obtain:

$$\text{Flory distribution: } \bar{\gamma}_w = 2 \cdot (w_s^{-1/2}-1)/(1-w_s^{\frac{1}{2}f-1}) \qquad [4]$$

$$G_e\bar{M}_n/(cRT) = 2\cdot[(1-w_s^{\frac{1}{2}f})/(w_s^{1/2}\cdot(1-w_s^{\frac{1}{2}f-1})\cdot(f-2)/f-1]\cdot(1-w_s^{1/2}) \qquad [5]$$

$$\text{Schulz-Flory distribution: } \bar{\gamma}_w = 3 \cdot (w_s^{-1/3}-1)/(1-w_s^{\frac{1}{2}f-1}) \qquad [6]$$

$$G_e\bar{M}_n/(cRT)=[4(1-w_s^{\frac{1}{2}f})/(w_s^{1/3}(1-w_s^{\frac{1}{2}f-1})(1+w_s^{1/3}))(f-2)/f-2](1-w_s^{2/3}) \qquad [7]$$

## B Results

### a) Network formation in aqueous gelatin solutions

From measurements of Djabourov et al. (3,4,5) on gelatin solutions $\bar{\gamma}_w$ was calculated using a Flory distribution of and a functionality of the triple helix cross-links $f = 6$. Results of $\bar{\gamma}_w$ are plotted against $\chi$, i.e. the amount of helix formation (see Fig. 1). From linear extrapolation to the gel point the critical value of $\chi$ appears to be $\chi_c = 0.069$. This value is close that calculated by Djabourov et al. ($\chi_c = 0.065$) and to the value calculated for tetrafunctional cross-links in monodisperse gelatin ($\chi_c = 0.067$) (6).

### b) Network formation in semidilute PVC-solutions

From SAXS measurements by Dorrestijn et al.(7) during gelation of 10% PVC solutions it appeared that the number of crystalline cross-links is constant, at least in the range of $G_e > 750$ N/m², viz. $3.7 \times 10^{22}$ m⁻³, their mutual distance being 30 nm. From this value the functionality of the cross-links was calculated as a function of $G_e$ for various molar mass distributions, with $\bar{M}_w = 240$ kg/mol. Results are shown in Fig. 2. For $G_e < 1000$ N/m² the functionality of the cross-links is rather small. For that reason also results are shown for mutual cross-link distances of 50, 100 and 150 nm and a Flory distribution of molar masses. Results are better then.

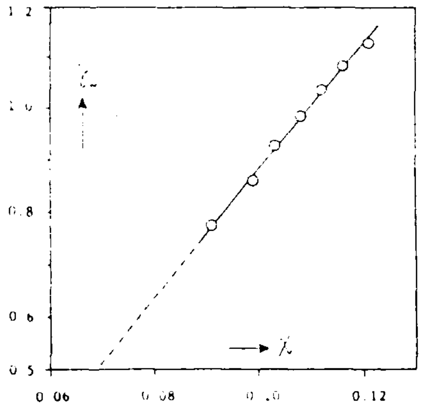

Fig.1 Cross-linking index against helix content in a gelatin gel

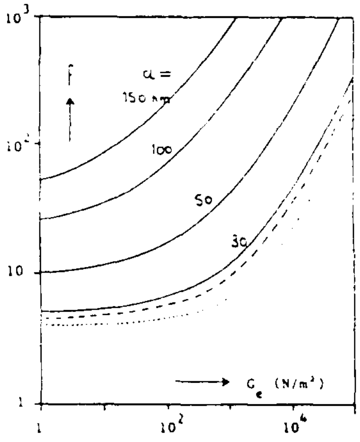

Fig.2 Functionality of cross-links in a PVC gel against rubber modulus
... Eq.(1) --- Eq.(6) —— Eq.(4)

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# THE PREPARATION AND CHARACTERISATION OF NOVEL POLYETHER GELS

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Poly(ethylene oxide) end-capped with n-alkane chains forms a physically crosslinked gel in aqueous media. The crosslinks, which occur through end group association, have structures somewhat similar to micellar cores. By changing the length of the n-alkane chains it is possible to vary the rigidity and thermal stability of the crosslinks. A variety of end capped poly(ethylene oxide) gels have been synthesised and characterised. Degrees of swelling have been compared with results predicted by network theory.

# MONITORING OF PROPERTY AND STRUCTURAL CHANGES DURING POLYMERIZATION AND CURE REACTIONS BY ULTRASONIC METHODS

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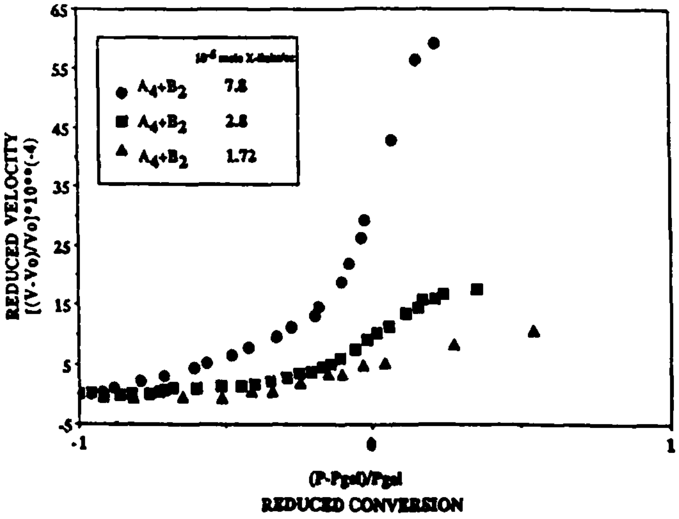
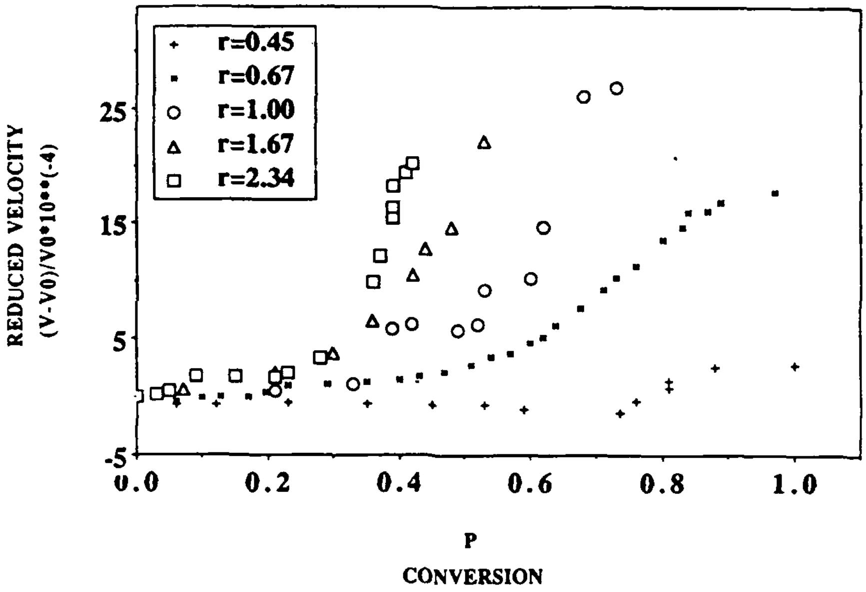
Acoustic methods, mostly in the ultrasonic frequencies, have been proposed as means for on-line monitoring of changes occurring in the course of polymerization and crosslinking reactions. Their main advantage embodied in their highly non-interfering nature is balanced by the uncertainty as to the type of viscoelastic information available at the high frequencies at which these techniques are most efficient. It is not obvious that structural and hence mechanical changes occurring in polymerizing and curing systems are actually manifested at ultrasonic frequencies. In addition, the simplest method of application of ultrasonic waves is in the form of longitudinal waves which combine bulk and shear deformations. Unlike shear, it is not clear to what extent are bulk deformations sensitive to changes of the nature discussed here. For this reason we embarked on a program in an attempt to evaluate the true potential of ultrasonic techniques in the study of reactions involving polymeric species.

In this work we have focused on systems with well controlled chemical reactions and relatively far from the glassy state. Polydimethyl(siloxane) with its very low glass transition temperature was the polymer of choice. A large number of systems involving PDMS molecules carrying either SiH or vinyl functional groups have been studied. These functional groups were either at chain ends or randomly distributed along the chain backbone. The polymers were reacted by means of the hydrosilation reaction to form either long linear molecules or crosslinked systems. The extent of chemical reaction was monitored by IR spectroscopy at the wave number corresponding to the SiH bond stretch. Changes in sound velocity of longitudinal waves at 10 MHz were measured by an acoustic interferometer.

Relative velocity changes for three endlinked systems differing in the crosslink density are shown in Fig. 1. It clearly demonstrates that wave velocity changes are sensitive to the degree of crosslinking. In addition it is quite evident that gelation is manifested by a sharp increase in velocity. All three curves collapse into one master curve when normalized velocity is plotted against the relative distance from the gel point. The actual gel point is positioned at exactly half the total increase in normalized velocity. Figure 2 depicts the effect of stoichiometric ratio between the reactants. The curves corresponding to various stoichiometric ratios are horizontally shifted in accordance to the shift in the gel point. Here again all curves may be collapsed into a master curve by the appropriate normalization. When the crosslinking of the system is achieved by means of reaction between vinyl groups along the chain backbone and bifunctional SiH molecules different behavior is observed (Fig. 3): The gel point in this system is not characterized by the s-shaped curves shown earlier and the velocity increases linearly with conversion. The increase in velocity is proportional to the crosslink density of the system. Similar behavior is observed in the cases of chain extension or replacement of end groups. The results may be rationalized by means of changes in the glass transition temperatures which has also been determined.

The main conclusion from this work is that ultrasonic methods are very sensitive to different types of reactions leading to the modification of polymeric systems. With the appropriate analyses these methods may eventually become useful for on-line characterization of different types of polymeric reactions leading to structural changes in the system.

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REDUCED VELOCITY
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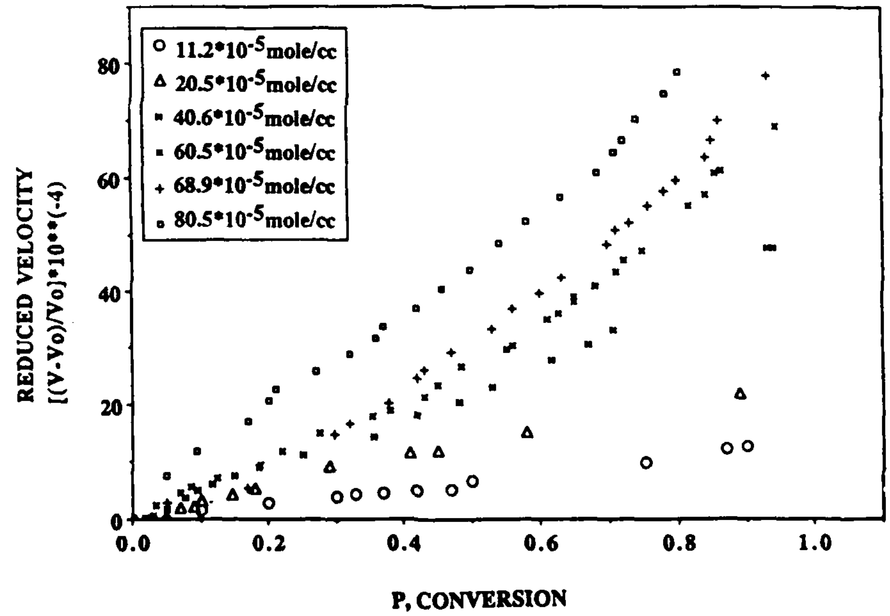
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▫ 80.5*10-5mole/cc
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P, CONVERSION

# REAL TIME DIELECTRIC MEASUREMENTS OF NETWORK FORMATION IN A CROSSLINKING EPOXY AMINE SYSTEM

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Real Time dielectric measurements are reported on the network formation and cure of an epoxy resin system based on the diglycidyl ether of bisphenol A (DGEBA) and diamino diphenyl sulphone (DDS) in equally molar amounts, over a temperature range from 120°C-180°C. The method used for obtaining the dielectric data involved a frequency response analyser controlled by a computer system and allowed collection of data over the frequency range from $10^{-1}$-$10^{5}$Hz in the period of approximatively two minutes. Cells were designed so that it was possible to perform measurements of the dielectric characteristics of the material at the cure temperature (figure.n°1).

Analysis of the dielectric spectrum evolution was carried out in two parts; one concerned with the low frequency long time processes, and the other concerned with the higher frequency short time processes. The initial dielectric response of the media was dominated by a large ionic conduction process, characterised by the $\omega^{-1}$ dependence of the dieclectric loss. As the cure proceeded so this conductivity contribution decreased, consistent with the network formation reducing the mobility of the ionic species. In addition to this characteristic conductivity contribution a large dominant dielectric loss feature was observed. Preliminary modelling of this feature indicates that it may be associated with the generation of a heterogeneous structure within the sample. The initial cure of the material close to the electrodes is believed to be faster than in the bulk. As the material forms a more homogeneous medium between the electrodes, so this relaxation disappears. This low frequency short time analysis will be developed in a following paper. The aim of this communication is mainly to treat of the higher frequency dielectric processes which are characterised by loss features varying in position ($\omega_o$) with time and similar to those of the glass transition process. These parts of the data were fited using a numerical method to the Havriliak-Negami (1) relaxation model which allows to describe the relaxation processes in terms of power laws for low and high frequency behaviour (2): $\varepsilon'' \sim \omega^{m}$ for $\omega \ll \omega_o$ and $\varepsilon'' \sim \omega^{-n}$ for $\omega \gg \omega_o$. We found that during the cure of the resin the high frequency exponent is approximatively constant and equal to 0.4 but that the low frequency exponent decrease from 0.8 to 0.5 (figure.n°2). The physical significance of these results may be in those of the exponents n and m. Some authors (3,4) link high and low frequency behaviour respectively with intermolecular and intramolecular correlations of dipolar motions. It seems natural that the low frequency exponent varies as the cure proceeds and the correlation lenght of intermolecular interaction increases.

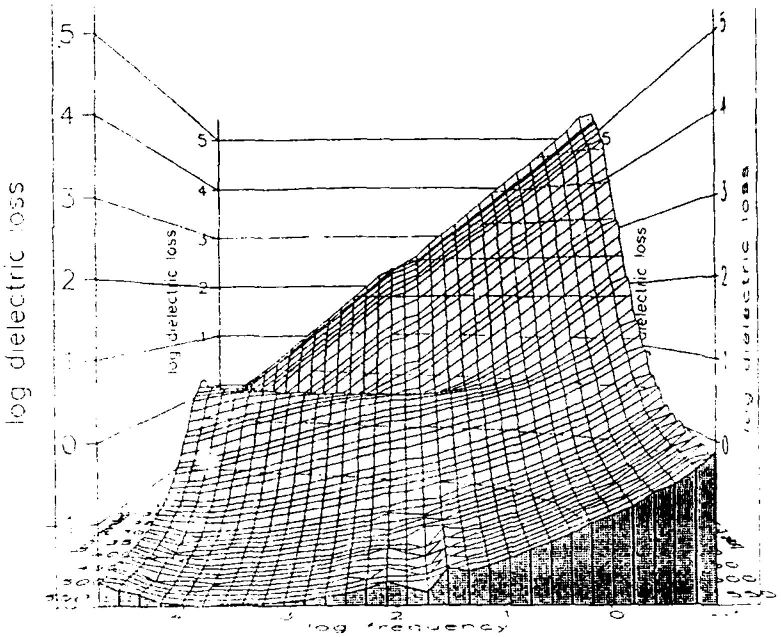
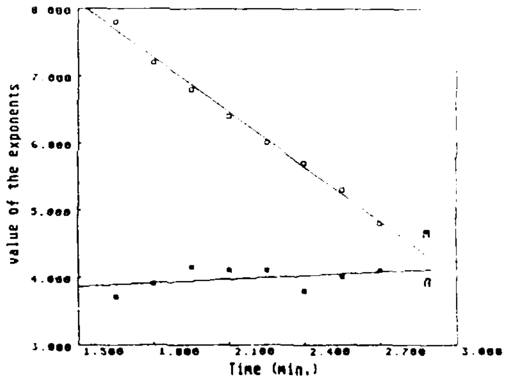


figure n°1:
*Evolution of*
the dielectric loss
spectrum during
the cure at 140°C

figure n°2:
Evolution of the exponents m and n
during the cure at 140°C



This work illustrates the way in which dielectric technique can be used to characterise cure in epoxy resin systems and to investigate the changes in the dynamics of the network. These measurements are complemented by rheological measurement of the systems as a function of time which were performed with a Strathclyde Rheometer.

- This work wade made in collaboration with the "Centre Commun de Recherche Louis Blériot, Aérospatiale, Suresnes, France"

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Similar observations have been made by Winter & Chambon (2) on a chemical gel (PDMS) for which the crosslinking has been stopped at different degrees of reaction, the same power law behaviour corresponding to the gel point. In more recent works (3,4), these authors have shown that the critical behaviour near the gel point is characterized by $G''/G' = tg\varphi = tg(n.\pi/2)$ independently of the frequency, the power-law exponent n being equal to 0.5 only in stœchiometric conditions.

These results can be discussed according to the percolation theory which predict, at the percolation threshold, a power-law relationship between the complex modulus and the frequency with a phase angle $\varphi_c = n.\pi/2$. Durand *et al.* (5) have obtained a good experimental agreement with this theory for a polyurethan system near the gelation threshold with n=0.7 in agreement with theoretical predictions. Martin *et al.* (6) have also obtained a value of n=0.7 for epoxy resins.

Recently, on a physical gel (purified pectins in presence of calcium) Axelos *et al.* (7) also observed a scaling exponent n=0.71.

Even if the experimental values of n did not always correspond to the predicted ones, the power law behaviour $G', G'' \alpha\ \omega^n$ seems to be characteristic of the gel point.

In practice, a good criterion to precisely locate the percolation threshold for many physical gels is to determine the experimental conditions where $G'(\omega) \simeq G''(\omega)$ whatever the frequency and follow a power law.

The viscoelastic properties may correspond to an equilibrium state and can be used to determine critical gelation concentrations or temperatures (8,9,10), or may be associated to a transitory state if the system is still evolving. In the latter case, a "gelling time" can be determined if the kinetics is sufficently slow compared with the experimental time.

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# CHEMORHEOLOGY OF HIGH TEMPERATURE THERMOSETS

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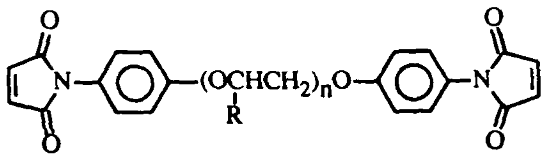
The use temperatures of thermoset resins for high performance structural applications are generally limited by the glass transition temperatures of the cured resins. To produce high temperature resins necessitates very high processing temperatures to preclude premature vitification of the curing resin which slows or even stops the curing reaction. The exact nature of this retardation of the curing reaction rate when vitrification occurs is not completely understood. An understanding of this phenomena may predict conditions under which a thermoset resin could be fully cured at temperatures below its final glass transition temperature and predict the appropriate kinetics to use under these conditions. The solution to this problem could greatly improve the processibility of high temperature resins and provide routes to field repair technologies for high performance reinforced composites.

One approach to the understanding of the effect of the network structure on the cure and resultant properties is to prepare a series of polymers of known, varied structures and determine the effect on the cure kinetics, vitrification and resultant mechanical properties. Bismaleimides are high performance addition-polymerized network-forming monomers that are increasingly being used as matrix resins for graphite reinforced composites(1). This paper descibes a study of the cure and resultant properties of a series of bismaleimides with varying length of backbone and pendant groups.

Bismaleimides of the structure shown below



where n=1-4 and R=H, $C_2H_4$, $C_4H_9$ and $C_6H_{13}$, were prepared from the corresponding bismaleamic acids by an acetic anhydride-catalyzed ring closure(2). Glass transition temperatures and cure kinetics were determined by differential scanning calorimetery (3) and the effects of vitrification during cure was determined by Torsion Impregnated Cloth Analysis(4). The effects of the change of network topology on these properties will be described.

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# DIRECT EVIDENCE OF CROSSLINKS BY METATHESIS DEGRADATION

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The structure of crosslinks in polymers is difficult to investigate even by modern analytical methods. Structure presumptions are mostly based on the analogous behaviour of low molecular model compounds. But for the example of subsequent crosslinking of 1,4-polybutadiene, coupled with partial double bond shift, computer simulation showed that, for the same reaction, the structures in the polymer may be different from those in low molecular model compounds (1). In most cases, spectroscopic investigation is not sensitive enough for the investigation of crosslink structures in polymers, both if the crosslinks are present in low concentrations and if a great number of similar structures are present at higher crosslinking degrees (2). Degradation methods adjusted to the type of the polymer may be superior in some cases because the various units can be isolated and characterized in the form of individual degradation products.

In our investigations into the degradation of polymers with C=C double bonds by metathesis degradation with symmetrical olefins in the presence of the catalyst $WCl_6/(CH_3)_4$, we found some examples of crosslink degradation products. Direct evidence of crosslinks was given for 1,4-polybutadiene crosslinked by dicumyl peroxide in solution (3). The crosslinks in a butadiene-divinylbenzene-ethylvinbylbenzene copolymer were identified (4). Branching points were found in an alternating butadiene-propene copolymer (5). The structure of crosslinks in a modification product of an alternating butadiene-propene copolymer, received by bromination and subsequent reaction with 1,6-bis(bromomagnesium)hexane, was elucidated (6). The present paper describes further examples of metathesis investigations of crosslinked polymers, for example the degradation products of butadiene-dimethyldivinylsilane copolymers and of subsequently crosslinked cyclopentadienyl-substituted polybutadiene. Metathesis degradation provides information about the crosslink itself and the environment of the crosslink. For example, whether the crosslink neighbours 1,4- or 1,2-linked butadiene units can be distinguished.

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# NETWORK BUILD-UP BY POLYETHERIFICATION IN POLYEPOXY-POLYAMINE CURING: THEORY AND EXPERIMENT

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In curing of polyepoxides with polyamines, a hydroxyl group is formed which in turn can react with an epoxy group under formation of an ether group and a new OH group. By repetition of this reaction, polyether chains are formed. This reaction is very important in applications of epoxy resins where usually an excess of epoxy groups over amine hydrogens is used (cf. e.g. (1)). Polyetherification belongs to the class of initiated polyreactions where the OH group is the initiating species. The theoretical treatment of network formation based on assemblage of structures from small structural fragments (monomer units) is incorrect because it ignores stochastic correlations originating in the effect of the history of initiation on the final distributions (2). A correct theoretical treatment has been based on the kinetic theory (2) and applied to postetherification (3, 4). The assemblage method can yield a reasonable approximation if the framents size is sufficiently increased (5).

However, all theoretical models assume so far a simple polyether chain growth initiated by the OH group ( a kind of living polymerization). The real mechanism is more complex (6): there exist alternative branches for the polyether chain growth; in one of the branches the initiator can be split off and participate in the initiation again; another initiating species ($I_2$) can be formed directly from the epoxy component (cf. Scheme I for a monoepoxide initiated by a product with one OH group).

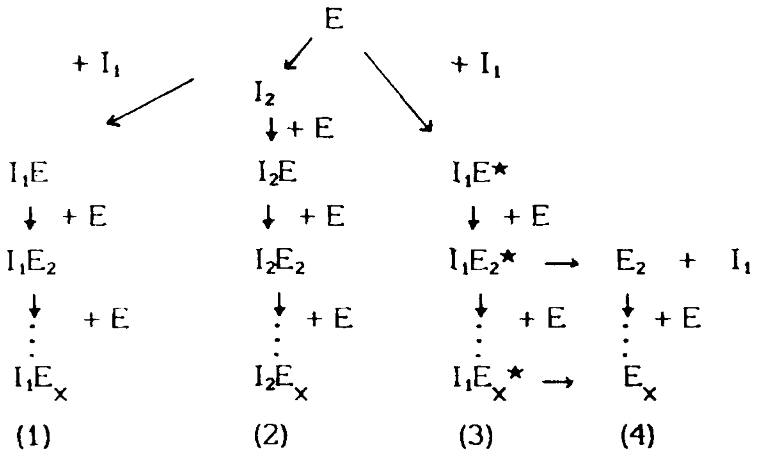
The set of reactions in Scheme I was solved using the kinetic theory of network formation. The strategy was as follows: The connections between epoxy groups in diepoxide (and the formed initiating species) were cut and the points of cut labelled. A system composed of monofunctional fragments was obtained. Kinetic theory was applied to generate the distribution of chemical clusters (superspecies) varying in the number of epoxide units. In the last step, these clusters were recombined by restoring the connections via joining the labelled points of cut. For the last step, the theory of branching processes was used. Parameters such as gel point conversions, sol fractions and concentration of elastically active network chains were derived. In the kinetic generation step, the degree-of-polymerization distributions of branches 1-4 were described by the corresponding generating functions (gf) $g_i(z)$

and the time dependence of the distributions was given by differential equations of the generating functions $dg_i(z)/dt = F(g_i(z),z))$ where t is time and z is the variable of the gf. Because no analytical solution was available, a method of moments was used in which the differential equations for the gf were transformed into differential equations for the moments which were solved numerically.

Examples demonstrate the effect of reinitiation and relative growth rates of the branches. The experimental results show that the polyether chain length is much smaller than would correspond to simple initiated polyreaction (branch 1) which is in agreement with the reinitiation and secondary initiation mechanisms.

Also, the data on sol fraction and concentration of elastically active network chain in systems diglycidyl ether of Bisphenol A (DGEBA)-poly(oxypropylene)diamine and triamine are compared with the theory.

Scheme 1



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# A GENERALIZATION OF THE THEORY OF NETWORK BUILD-UP BASED ON THE THEORY OF BRANCHING PROCESSES

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The theory of branching processes (TBP) (cascade theory) applied to network buid-up generates branched and crosslinked structures from units and employs a recursive method (cascade substitution) and probability generating functions (pgf) for description of distributions and their transforms (1). The TBP was used for treatment of a number of simple and more complicated branching reactions. However, for complicated (e.g. multicomponent) reactions, a generalisation of the approach appears useful (2). This generalisation makes posible to treat rigorously also higher-shell substitution effects within the framework of the higher-order Markovian statistics. Here we will limit ourselves with the first-shell substitution effect. Also, the problem of cyclisation will not be discused.

The structures are assembled from building (e.g. monomer) units via their oriented bonds. In general an oriented bond $XklY$ has a meaning of sequence $X \rightarrow k \rightarrow l \rightarrow Y$ looking out of the unit $X$ via its reacted group $k$ to the reacted group $l$ of unit $Y$. The variable of the pgf, $\underline{z}$, is associated with the bond and bears the respective subscript, $z_{XklY}$. Furthermore, it is useful to distinguish between pgf variables that are associated with the *multiplicative (branching) process* and variables that characterise *a property* of the unit $\underline{Z}$ (underlined quantities mean vectors). The $Z$'s may have one subscript, $Z_X$, if they characterise the whole unit $X$, or two subscripts if they characterise a certain part of the unit.

The state of a unit is characterised by the type of the unit and by types and numbers of oriented bonds issuing from the unit. Thus the pgf for the number fraction distribution of units, $F_{0n}(\underline{Z}, \underline{z})$, can be written as

$$F_{0n}(\underline{Z}, \underline{z}) = \sum_X n_X F_{0Xn}(\underline{Z}, \underline{z}) = \sum_{\underline{a}, \underline{b}} p(\underline{a}, \underline{b}) \prod Z_X^{a_X} \prod z_{XklY}^{b_{XklY}} \tag{1}$$

where $n_X$ is the number fraction, $p(\underline{a}, \underline{b})$ is the probability of finding a unit composed of $\underline{a}$ "objects" and issuing $\underline{b}$ bonds. The components of $\underline{a}$ may have a meaning of the number of constituent units, molecular weights, etc.

The pgf for units already connected to another unit (in the first and higher generations) are obtained by differentiation

$$F_{YlkX}(\underline{Z}, \underline{z}) = \frac{\partial F_{0n}(\underline{Z}, \underline{z})}{\partial z_{XklY}} \Bigg/ B_{XklY} \tag{2}$$

where $B_{XklY}$ is the number of bonds $XklY$.

$F_{YlkX}$ describes the distribution of bonds issuing from a unit $X$ if this unit is already connected to (rooted) — via a bond $kl$ — a unit $Y$. The cascade substitution

$$u_{YlkX} = F_{YlkX}(\underline{Z}, \underline{u}) \tag{3}$$

offers the derivation of gf for the degree-of-polymerisation or molecular-weight distributions, extinction probabilities, etc.

Two interesting conclusions important for the application of the TBP can be mentioned:

(1) *Transformation of distributions*. A pseudo-weight fraction distribution $w(\underline{l}) = (\underline{1} \cdot \underline{l})n(\underline{l}) / \sum(\underline{1} \cdot \underline{l}')n(\underline{l}')$, where $n(\underline{l})$ is the number fraction of molecules composed of $l_1, l_2, \ldots$ units of type $1, 2, \ldots$, is the basic information obtained by cascade substitution. It leads to weight-fraction distribution and, routinely, by differentiation, to distributions corresponding to higher moments. The number distribution, $N(\underline{Z})$, (important for derivation of a number of structural parameters) can be obtained from $W(\underline{Z})$ by integration, which may be not easy, or by combinatorial arguments. These are based on the fact that an $L$-mer has $L - 1$ bonds; if one selects units, he will find the molecule $L$ times, if one selects bonds, he will find it $L - 1$ times. The probability that a bond belongs to an $L$-mer is obtained by convolution of distributions of the two subtrees issuing from randomnly selected bond in either direction. These arguments lead eventually to the formula for $N(\underline{Z})$:

$$N(\underline{Z}) = \frac{F_{0n}(\underline{Z}, \underline{u}(\underline{Z})) - \frac{1}{2}\sum B_{XklY}\, u_{XklY}(\underline{Z})\, u_{YlkX}(\underline{Z})}{1 - \frac{1}{2}\sum B_{XklY}} \tag{4}$$

(2) *Multistage processes*. Multistage network formation processes are important in technology. They can be generaly treated in such a way that the products of one stage represent initial components in the next stage while track is beeing kept of the unreacted functional groups (3) (variable $\underline{Z}$). This procedure involves transformation of $W(\underline{Z})$ into $N(\underline{Z})$. An analysis shows that the results are identical if the structures are built-up in one step (from the identical ensemble of units and bonds), if and only if bonds of the same type formed in different stages are distinguished.

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# SYNTHETIC MODELS FOR BIOLOGICAL NETWORKS: ON THE FORMATION OF SUPRAMOLECULAR STRUCTURES BY COOPERATIVE CLUSTER FORMATION

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In previous work we have studied in detail the formation and viscoelastic properties of thermoreversible polymer networks with temporary junctions based on binary hydrogen bond complexes(1-5). As a model system we chose the interaction between highly polar urazole groups which were added to unpolar polybutadiene chains via polymer analogous reaction of 4-phenyl-1,2,4-triazoline-3,5-dione in an ene-reaction. IR-spectroscopic studies showed that the complex formation between two functional groups can be treated as a simple thermodynamic equilibrium. In the case of polar groups attached to the polymer chain the mole fraction of complexed units at a given temperature and concentration is lower than in the low molar mass model compound. This behaviour can be explained by topological constraints: the functional groups attached to the polymer chain have a reduced probability to form a complex.

In order to understand the underlying principles in the association behaviour of polymer systems with strong noncovalent chain-chain interactions we started the investigation of systems, where the association behaviour is no more characterized by an anticooperative complex formation, but where a supramolecular structure is formed as a consequence of a cooperative association behaviour, in analogy to biopolymer structures(6-9).

Again multiple hydrogen bond interactions are used as dominant noncovalent interaction for supramolecular structure formation. Crystal structure analysis of low molecular weight hydrogen bonding systems provides a framework for the relationships between chemical structure and resulting hydrogen bond complex structures. In addition, hydrogen bonded structures can be studied in detail by a variety of spectroscopic techniques, among the most important is IR-spectroscopy. Thus detailed information about the local complex formation can be obtained.

For a system characterized by a cooperative association behaviour the following requirements must be fulfilled:

i) the structural unit must be able to form stable complexes

ii) the complexes are additionally stabilized by the formation of a threedimensional supramolecular structure.

Typical for structures formed by a cooperative complex formation is a 'melting' of the structure in a first order transtion upon heating, as for the helix-coil transition.

In present work our first successfull attempts to cooperative structure formation are reported. Multifunctional polar groups, statistically attached to a polymer chain form linear association chains or branched structures, which, under certain circumstances form ordered clusters characterized by a melting endotherm. Phase separation between the association polymer and the covalent backbone gives rise to a stable thermoplastic elastomer system.

The cooperative structure formation in simple synthetic systems provides unique opportunities to model more complex biological gelling systems.

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# FORMATION OF ENDLINKED CIS 1,4 POLY(ISOPRENE) NETWORKS

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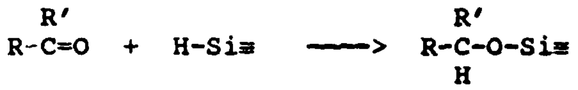
Unlike the usual vulcanization processes, at which random networks are obtained by crosslinking at random sites along the polymer backbone, endlinking reactions allow the formation of networks with controlled and well defined structure. These are useful in studying the relationship between properties of elastic networks and their structure. Several such networks based mainly on PDMS, PIB, PBD, and PS have been described in the literature. Here we describe methods for the formation of endlinked PIP (cis 1,4 Polyisoprene) networks of controlled structure.

By means of the selective cleavage technique described by Solache and Cantow (1), the PIP molecule is converted into reactive a,w-dicarbonyl or a,w-diol telechelics, which may be further reacted with the appropriate crosslinkers.

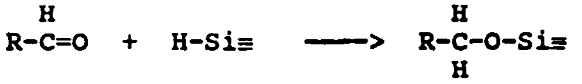
The molecular weight of the a,w reactive PIP telechelic is controlled by the duration of the cleavage reaction (Fig. 1). The reaction is quenched at the desired point by the addition of water to the reaction mixture. The relative simplicity by which different chain lengths may be obtained allows for a great variety in the molecular parameters of the final networks. The kinetics of the reactions are easily monitored by means of FTIR spectroscopy in which the rate of formation of ketones and aldehydes is followed in the first stage. Their disappearance and the formation of the hydroxyl group is followed in the second stage.

Endlinking has been achieved in this work by means of the reaction with the silane group of a multifunctional crosslinker according the following hydrosilation reaction schemes:



$$R-\overset{R'}{C}=O \; + \; H-Si\equiv \; \longrightarrow \; R-\underset{H}{\overset{R'}{C}}-O-Si\equiv$$

[1]



$$R\text{-}\overset{H}{C}\text{=}O \;+\; H\text{-}Si\equiv \;\longrightarrow\; R\text{-}\underset{H}{\overset{H}{C}}\text{-}O\text{-}Si\equiv \qquad [2]$$

$$R\text{-}OH \;+\; H\text{-}Si\equiv \;\longrightarrow\; R\text{-}O\text{-}Si \;+\; H_2 \qquad [3]$$

These hydrosilation reactions are catalized by various metallic catalysts, such as Pt, Zn, Ni, Rh and others.

The reactions leading to the formation of the network are easily monitored by several techniques: The disappearance of the carbonyl, hydroxyl, and hydrosilane groups are characterized by distinct well defined absorption bands in FTIR which is easily quantified by the appropriate calibration. The formation of the C-O-Si bond is identified by means of $C^{13}$ nmr.

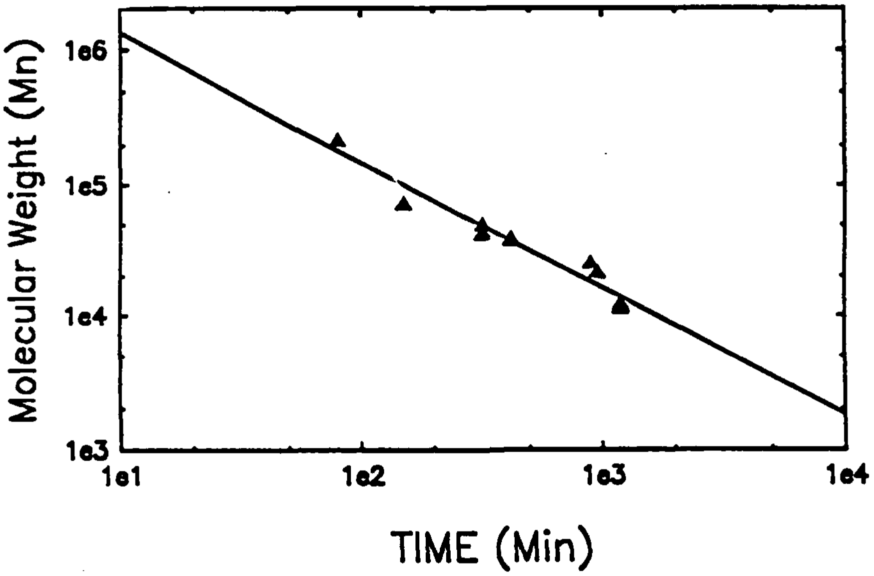


Fig.1 Mn of the PIP telechelics (as determined by FTIR end-group analysis) vs. time allowed for cleavage reaction.

(1) J. Solache-Orozco and H.J. Cantow, Polym. Bull. 1984, 12, 203-208.

# RHEOLOGICAL KINETIC STUDIES OF THE GELATION OF Cr(+3)/POLYACRYLAMIDE SOLUTIONS

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Gels formed from dilute aqueous solutions of synthetic and biopolymers crosslinked with Cr(+3) are of increasing importance for enhanced oil production. Their more reliable field application will depend strongly on an gaining improved understanding of the kinetics and mechanism of the gelation reaction. On the basis of previous chemical [1] and rheological kinetic studies [2] it has been suggested that the rate determining step for the gelation of Cr(+3)/polyacrylamide solutions is the dimerization of Cr(+3). We have re-examinded the kinetics of gelation of Cr(+3)/polyacrylamide solutions by means of dynamic rheological measurements and have employed what we believe to be a novel approach for the treatment of rheological gelation data. In this approach some implicit assumptions of previous gelation kinetic studies on Cr(+3)/polymer solutions have been eliminated, and new conclusions about the gelation reaction have been reached.

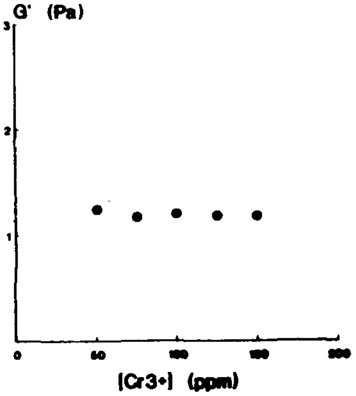
Kinetic Treatment. The derivation of a kinetic expression for the gelation of aqueous Cr(+3)/polyacrylamide solutions relies on the following hypothesis: Independent of the initial [Cr(+3)], at the point of gelation (defined as the time in which G' = G" [3]), a constant number of crosslinks have formed and hence, a constant quantity of Cr(+3) will have reacted. In addition, it is assumed that there is a single rate determining step first order in Cr$^{+3}$ and [P] (the polymer reactive group concentration). From these considerations a kinetic expression has been derived which describes the gelation time as a function of an absolute rate constant k, the initial [Cr(+3)] ([Cr]$^{o}$) and [P] ([P]$^{o}$), and the concentration of Cr(+3) crosslinks [Cr$_{XL}$] at the time of gelation:

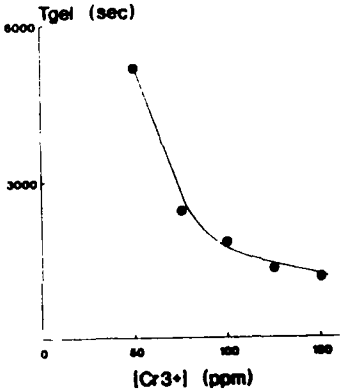
$$T_{gel} = -1/k([P]^{o} - [Cr]^{o}) \times \ln \left[ \frac{[P]^{o}}{[Cr]^{o}} \; \frac{[Cr]^{o}-[Cr_{XL}]}{[P]^{o}-[Cr_{XL}]} \right]$$

Although electrostatic effects can complicate the kinetic behavior, it is observed in practice that they can be reduced or eliminated for carefully selected compositions.

Experimental Results. Kinetic studies have been carried out on aqueous solutions of polyacrylamides hydrolyzed 2.2, 4.2, and 8.5% in the presence of 30-250 ppm Cr(+3) in buffered solutions. Two observations provide evidence in support of the hypothesis that the number of crosslinks at the gelation time is independent of the initial [Cr(+3)]: (1) The values of G' at the crossover with G" are very nearly constant over a wide range of initial [Cr(+3)] **(Fig.1)**. (2) The amount of Cr(+3) reacted at the point where G'=G" should be equal to the minimum number of Cr(+3) crosslinks necessary to form a gel; preliminary results indicate that [Cr(+3)]XL, derived from the kinetic treatment, are in agreement with values determined from rheological measurements on equilibrated gels **[4]**.

The good fit of the derived kinetic expression to the experimental gelation data **(Fig.2)**, provides strong evidence that the gelation reaction is first order in Cr(+3), rather than second order as suggested previously **[1,2]**. Some success in accounting for the effects of solution pH on gelation has also been achieved with more complex kinetic models that take into account the acid-base chemistry of Cr(+3) and the polymer reactive groups.





CAPTIONS

Fig.1 (left above)-Plot showing G'(=G") at time of gelation for various [Cr(+3)] for a solution (pH4.8) of 4.2% hydrolyzed polyacrylamide. Fig.2 (right)- Fit of the kinetic expression derived to the data for gelation time as a function of [Cr(+3)] (same solutions as Fig.1).

ACKNOWLEDGEMENTS

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# VISCOELASTIC BEHAVIOUR OF β-LACTOGLOBULIN GEL STRUCTURES

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The viscoelastic properties of aggregate gels and fine-stranded gels have been investigated by dynamic rheological measurements (1). The gels were made from β-lactoglobulin dissolved in destilled water and were studied in the pH range 2.5-9.0. Gels formed at pH 4-6 were opaque, aggregate gels while gels formed at pH below or above this range were transparent, fine stranded gels.

The onset of gelation of 12% β-lactoglobulin gels at intermediate pH, when measured at the G'-G" crossover at 1 Hz or at the development of a measurable G', takes place at temperatures far below the temperature of denaturation, see fig.1. This is not the case at higher or lower pH where the onset of gelation is above the temperature of denaturation. The heating rate during gel formation was varied between 0.008 and 1°C/min. The gelation temperature of the fine-stranded gels was found to increase with an increasing heating rate.

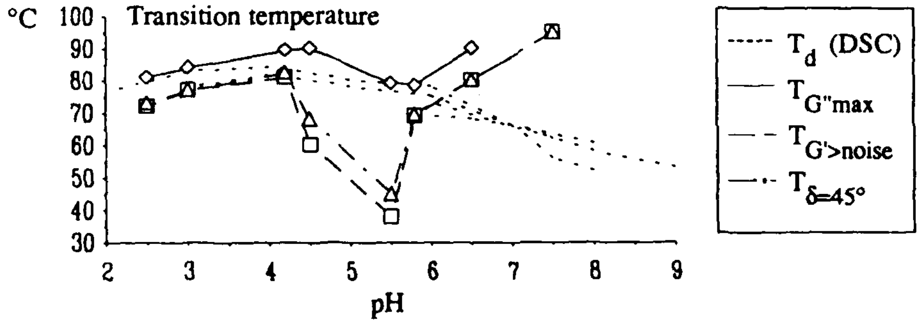

*Fig. 1. The gelation temperature of 12% β-lactoglobulin measured with three different methods, at a maximum in G" (G"$_{max}$), when G' exceeds the noise level ($T_{G'>noise}$) and at the G'-G" crossover ($T_{\delta=45°}$). The dotted line shows denaturation temperatures ($T_d$) taken from the litterature (2-6).*

The aggregate gels were more strain sensitive during gelation and more frequency dependent than the fine-stranded gels. They also had a higher storage modulus than the fine-stranded gels at a constant β-lactoglobulin concentration of 12% (w/w). The critical concentration for gel formation was lower for the aggregate gels than for the fine-stranded gels, and as low as 1% in the pH range 4.5-5.5. This indicates a very open structure.

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# Modelling Fibrin(ogen) Coagulation via a Cation-Driven Mechanism

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The sensitivity of thrombin- and reptilase-induced fibrinogen coagulation to specific divalent cations has been explored in a number of recent studies (1-3). Essentially, it was observed that at physiologic levels of Ca(II) (2 mM) and Zn(II) (~20 uM) accelerate the induction of gelation. Moreover, these cations each independently and additively modify a range of physical properties of the gels, including gel turbidity, ultrastructure and viscoelasticity. Mechanistic insight into the cation-sensitive gelation process was had by the observation that soluble fibrin oligomers (protofibrils) can be induced to undergo phase change by Ca(II) and Zn(II). The SEM and TEM electron microscopic ultrastructure of the resultant protofibrin gels are indistiguishable from normally formed fibrin, though they exhibit significantly reduced viscoelasticity. Based on these findings, graphic Schema for fibrin gelation are presented which tie the proteolytic release of fibrinopeptides (FPA and FPB) to two lateral packing directions, each of which is independently modulated by Ca(II) and Zn(II). The graphic notation developed here appears to be applicable to the formation of other bio-macromolecular ensembles which result in gels.

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# A KINETIC APPROACH TO CROSSLINKING POLYMERIZATION

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The classical theories of polymer network formation provide the means for predicting various parameters of polymerizing systems, such as, e.g., the size distribution of molecular species. The sufficient input parameters are usually the reaction paths and conversion degree. Various theories of this kind differ mainly in the statistical language applied.

In the late 70's, Kuchanov (1) demonstrated that for kinetically controled (irreversible) polymerization processes, the classical statistical theories were intrinsically inadequate except for the random polymerization with constant and equal reactivities of reacting sites. In a paper with Povolotskaya (2) he proposed a kinetic equation that could be used for evaluating at least moments of molecular size distribution in a model (tree-like) kinetically controlled polymerization of a tri-functional monomer.

In this work, similar equations are used (which are in fact generalized versions of the Smoluchowski coagulation equation) to demonstrate explicitly the differences in predictions made by one of the statistical theories (cascade theory) and the kinetic method. Average degrees of polymerization are calculated up to the gel point for model homo- and copolymerization systems where species react with the first shell substitution effect that modifies reactivity of the reacting sites.

It is shown that in irreversible homopolymerization, the kinetic theory predicts the gel point to occur always at lower conversion than does statistics. In alternating (tree-like) copolymerization of two- and tri-functional monomers, however, the kinetic method does allow the gel point to shift towards higher conversion than predict statistical theories. In experimental verification of the statistical theories such a shift was always attributed to intramolecular cyclization and never to substitution effect.

The applicability of the statistical and kinetic methods to equilibrium and kinetically controlled processes, respectively, are discussed in terms of the probability theory.

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# HIGH FREQUENCY DYNAMIC PROPERTIES OF POLYMER MELTS UNDERGOING CURING AND SOL-GEL TRANSITION

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A great interest in the dynamic properties of cured polymer systems is generated, on one hand, by their close connections with the more general problem of the dynamics of critical phenomena, and, on the other hand, by a number of possible applications. In the present work a system of linear chains in melt or in concentrated solution is considered in the process of curing reaction. It is suggested, that a curing agent i.e. a low-molecular polyfunctional substance $A_f$ with f active groups per molecule is inserted into the polymer system, and the A-groups react with active terminal B-groups on the polymer chains. In the intermediate stages of the $A_f+B_2$ reaction various random structures are present in the reaction vessel. Structures bellow the transition point can be described by means of the Flory-Stockmayer theory. Although the structural relationships can be evaluated quantitatively in many detail and quite accurately, the determination of the dynamic properties of the cured system still remains an open problem.

We have developed a simple theoretical model for the computation of the dynamic moduli of such a system over the range of high frequencies of the dynamic loading comparable with the characteristic frequency of dynamic glass transition of the starting linear polymer subjected to curing. It is suggested that within this range the slow processes of relaxation of branched clusters as a whole do not contribute to the dynamic module of the system, and the approach of 'affinity' for the movements of branching points is valid on all stages of the curing reaction. In the framework of this approach the dynamic modulus of the system is the sum of the contributions from the linear parts of chains of three different types: the parts of chains between adjacent branching points ('strands'), the linear chains with both free ends ('free chains') and the chains with one end connected to a branching point and the second end free ('dangling chains'):

$$G(\omega) = \sum_{k=1}^{\infty} \left( F(k)\, \delta G_F(kN,\omega) + D(k)\, \delta G_D(kN,\omega) + S(k)\, \delta G_S(kN,\omega) \right)$$

Here N is the degree of polymerization of starting chains suggested to be monodisperse, $\delta G_{F,D,S,}(kN,\omega)$ are the contributions to dynamic moduli from the processes of relaxation of 'free chains', 'dangling chains' and 'strands' correspondingly with degree of polymerization equals kN; S(k), F(k) and D(k) are the concentrations of 'strands', 'free chains' and 'dangling chains' consisting from k starting linear chains. A similar relation can be obtained in the case of continuous molecular mass distribution of the starting polymer.

In terms of equal activities of all the groups taking part in the curing reaction the distribution of the linear elements of the structure is simply expressed through the current value of conversion. The contribution from each linear element to the dynamic modulus was evaluated in terms of either the Doi-Edwards theory or the simple Rouse theory (depending on the length of the linear element in comparison with the threshold of the formation of entanglements). As a result, the theoretical dependencies of the storage and loss components of the shear dynamic modulus of the cured system from the conversion and frequency were computed at various starting ratios of the numbers of active groups of polymer and curing agent, various functionality of the curing agent and various molecular mass distributions of starting linear chains. It was shown, that in the case when the starting linear polymer is not entangled these dependencies are sensible to the change of the gel structure due to the curing reaction (Fig. 1) and, hence, principally, they may be used for the quantitative characterization of the structure of the non-complete gel.

At last, some possible generalization of the assumption of 'affinity' over the range of lower frequencies and its application to the dynamics of the system in the vicinity of the sol-gel transition is discussed.

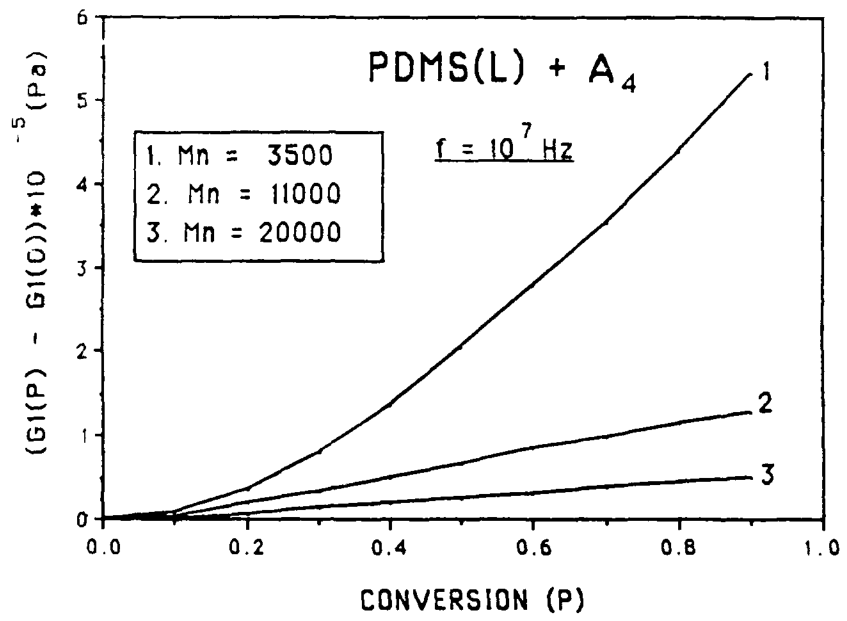

Fig. 1 Typical theoretical plots of the change of the storage shear modulus of cured polymer with conversion: G1(0), G1(P) are the storage module of the starting linear polymer and the cured polymer at the conversion P correspondingly. (The parameters chosen for the computation correspond to linear (L) starting PDMS with exponential MM distribution of Flory; T = 30°C, the frequency of loading: f=10MHz.)

# INDEX

Adam, M., 24
L-30
Adler, K., 19
L-24
Adolf, D., 24
L-32
Aerts, L., 14
P-11
Alexander, S., 24,27
L-44
Axelos, M.A.V., 24
L-31
Balsara, N., 27
L-47
Barnes, G., 22
P-49
Bastide, J., 18,23
L-18,L-26
Bauer, J., 26
L-42
Bauer, M., 26
L-42
Berghmans, H., 20
P-33
Biller, P., 14
P-10
Blume, I., 19
L-23
Bouchal, K., 14
P-14
Boue, F., 18,23
L-18,L-26
Braudo, E.E., 21
P-38
Bremer, L.G.B., 24
L-35
Brochard-Wyart, F., 27
L-46
Bron, S., 14
P-9
Bruge, F., 20
P-29
Bucknall, C.B., 17
L-13
Bulone, D., 25
L-38
Burchard, W., 20,23,26
L-39
P-32,P-34,P-35
Buzier, M., 18
L-18
Buzir, M., 23
L-26
Charmot, D., 15
P-24
Chaturvedi, K., 15
P-22
Chereysky, Z.Y., 22
Chu, B., 21
P-37
Cloizeaux, J. des, 12
L-6
Cohen, C., 11
L-2
Cohen, Y., 13,25
P-5
Crescenzi, V., 20
P-32
Csempesz, F., 13
P-7
Cuvelier, G., 21
P-43
Deloche, B., 13,23
L-27
P-1, P-2
Denkinger, P., 20
P-34
Dentini, M., 20
P-32
Di Stefano, L., 25
L-38
Dierksen, K., 13
P-7
Dodiuk, H., 17
L-16
Durand, D., 18,21
L-22
P-42
Dusek, K., 14,22,24,26
L-40
P-14,P-46,P-47

Eastmond, G.C., 26
L-41
Edwards, S.F., 11
L-1
Eichinger, B.E., 11,27
L-3, L-5
Emanuele, A., 20
P-30
Emery, J., 18,21
L-22
P-42
Felisberti, M.I., 17
L-14
Fontaine, F., 16
L-9
Fornili, S.L., 20
P-29
Forster, F., 18
L-20
Freitas, L., 22
P-48
Galfi, L., 20
P-31
Galina, H., 22
P-53
Gallino, G., 22
P-50
Gandelsman, M., 22
P-54
Gao, J., 12
L-7
Garstein, E., 13
P-5
Gchdanov, A.A., 14
P-15
Geissler, E., 11,13
L-4
P-6,P-8
Gennes, P.G. de, 27
L-48
Gilbert, A., 17
L-13
Goeritz, D., 23
L-29
Goldfarb, I., 21
P-44
Goldraich, M., 15
P-25
Gorodetsky, G., 21,22
P-41,P-54
Gottlieb, M., 11,21,22
P-41,P-49,P-54
Grassler, R., 23
L-29
Grest, G.S., 24
L-33
Griffin, M., 15
P-23
Griffin, W.G., 15
P-23
Grodzinsky, A.J., 19
L-24
Gronski, W., 18
L-20
Gupta, A., 13,24
L-34
P-4
Hanyu, A., 16
L-9
Harden, J.L., 15
P-27
Hayward, D., 21
P-42
Hecht, A.-M., 11,13
L-4
P-6,P-8
Hellmann, J., 22
P-48
Hendrickson, R.C., 24
L-34
Hermansson, A-M., 22
P-51
Herz, J., 13,23
L-27
P-3
Higgs, P.G., 14
P-17
Hilger, C., 22
P-48
Horkay, F., 11,13,20
L-4
P-6,P-7,P-8,P-31
Horn, D., 18
L-19
Hrouz, J., 12,14
L-8
P-14

Hubmann, E., 21
    P-45
Hummel, K., 21,26
    L-43
    P-45
Ilavsky, M., 12,14,22,26
    L-8,L-40
    P-14,P-47
Jong, L., 16
    L-9
Katz, D, 14
    P-9
Kenig, S., 17
    L-16
Kent, M.S., 27
    L-47
Kilian, H.G., 13,16
    L-10
    P-7
Klein, J., 15,27
    P-22
Knowles, P.R., 21
    P-40
Kolb, M., 24
    L-31
Kost, J., 15
    P-25,P-26
Kozlowski, M., 15
    P-21
Krausch, G., 15
    P-22
Kremer, K., 24
    L-33
Kunz, M., 14
    P-11
Lairez, D., 18,21
    L-22
    P-42
Lang, P., 20
    P-32
Langer, R., 15
    P-26
Launay, B., 21
    P-43
Leibler, L., 18
    L-18
Leksovskaya, N.P., 22
Levin, V.Y., 14
    P-15
Lindemann, M.K., 17
    L-17
Lockhart, T.P., 22
    P-50
Lodge, T.P., 27
    L-47
Lueddecke, E., 18
    L-19
Lutz, P., 20
    P-35
Machluf, M., 15
    P-26
Macosko, C.W., 13,24
    L-34
    P-4
Madonia, F., 25
    L-38
Mallam, S., 13
    P-6
Markevitch, A.A., 14
    P-18
Martin, J.E., 24
    L-32
Martl, M.G., 26
    L-43
Marx, G., 22
    P-52
Matejka, L., 22
    P-46
McLeish, T.C.B., 27
    L-45
Mendes, E., 18,23
    L-18, L-26
Merkle, G., 20
    P-35
Meyer, G., 15
    P-20
Mijnlieff, P.F., 14,23,25
    L-28,L-37
    P-12
Miller, D., 21
    P-36
Moeller, M., 14
    P-11
Molinari, M., 22
    P-50

- Moll, L., 14
  - P-13
- Mulder, M.H.V., 19
  - L-23
- Murat, M., 24
  - L-33
- Nachinkin, O.I., 22
- Nakatani, A.I., 18
  - L-21
- Nazarenko, S.I., 14
  - P-18
- Nedbal, J., 12
  - L-8
- Nijenhuis, K.te, 21
  - P-39
- Nystrom, B., 19
  - L-25
- Oeser, R., 13
  - P-2,P-3
- Oger, N., 15
  - P-24
- Oleynik, E., 15
  - P-19
- Palma, M.U., 25
  - L-38
- Palma-Vittorelli, M.B., 20
  - P-29,P-30
- Patel, S.K., 11
  - L-2
- Pethrick, R.A., 21
  - P-42
- Petruccione, F., 14
  - P-10
- Pouchelon, A., 14
  - P-13
- Price, C., 21
  - P-40
- Priss, L.S., 16
  - L-11
- Prost, J., 18
  - L-18
- Pyckhout-Hintzen, W., 18
  - L-20
- Racz, Z., 20
  - P-31
- Rey, A., 20
  - P-34
- Richards, R.W., 17
  - L-15
- Richardson, J.E., 26
  - L-41
- Rogovina, L.L., 14
  - P-15
- Roots, J., 19
  - L-25
- Ross-Murphy, S.B., 12,14
  - L-6
  - P-17
- Rozenberg, B.A., 15
  - P-16
- Ruban, I.G., 22
- Rubinstein, M., 27
  - L-45
- Saf, R., 26
  - L-43
- Samulski, E.T., 13,17,18
  - L-21
  - P-1
- San Biagio, P.L., 20,25
  - L-38
  - P-29
- Sarmoria, C., 21
  - P-36
- Schatz, G., 15
  - P-22
- Schrof, W., 18
  - L-19
- Shefer, A., 21
  - P-41
- Silberberg, A., 11
- Smidroczki, E., 20
  - P-31
- Smit, E., 19
  - L-23
- Smolders, C.A., 19
  - L-23
- Somvarsky, J., 22
  - P-46,P-47
- Soria, M., 14
  - P-13
- Sotte, P., 23
  - L-27
- Spirkova, M., 26
  - L-40
- Spitteler, P.H.J., 14
  - P-12
- Springer, T., 18
  - L-20

Stading, M., 22
P-51
Stadler, R., 16,17,22
L-14
P-48
Stein, R.S., 16,18
L-9
Steiner, U., 15
P-22
Steinmann, B., 26
L-39
Stell, G., 21
P-37
Stepto, R.F.T., 11,26
L-5
Tabka, M.T., 15
P-20
Takushi, E., 20
P-28
Talmon, Y., 17
L-17
Tchegolichina, O.A., 14
P-15
Thijs, S., 20
P-33
Thomas, E.L., 13,17
L-12
P-5
Tirrell, M.V., 19,27
L-47
Trappe, V., 26
L-39
Van Vliet, T., 24
L-35
Vasiliev, V.G., 14
P-15
Vazquez, A., 22
P-46
Visscher, K., 25
L-37
Walastra, P., 24
L-35
Weiner, J.H., 12
L-7
Weiss, A., 19
L-24
Widmaier, J.M., 15
P-20
Winter, H.H., 25
L-36
Wu, C., 18,21
L-19
P-37
Wu, W.L., 16
L-9
Yagen, Y., 22
P-49
Yarmush, M.L., 19
L-24
Yortner, J., 11
Zak, O., 15
P-22
Zidinski, F., 23
L-26
Zrinyi, M., 11,13,20
L-4
P-6,P-7,P-8,P-31
Zurek, S., 27
L-45

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