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MODEL NETWORK POLYMERS

FINAL REPORT

C. W. Macosko

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Department of Chemical Engineering and Materials Science
University of Minnesota
Minneapolis, MN   55455

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crosslinked polymers, polydimethylsiloxane, hydrosilation, viscosity of branched
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theory, ring formation during polymerization

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)
Under this grant we applied and extended a recursive theory which describes
structural features of crosslinking polymers. We developed experimental tech-
niques for synthesizing and characterizing model networks of polydimethylsilo-
xane. We successfully applied the recursive theory to predict basic structural
parameters like: molecular weight, gel point and sol fraction at various stages
during network formation. A recursive relation for the weight average molecu-
lar weight of the longest linear chain through the molecule was developed and
found to correlate viscosity rise during network polymerization. Sol fraction ·

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results were used with the theory to predict crosslink density, junction functionality and trapped entanglement fraction. These parameters were used to test classical and more recent theories of rubber elasticity against stress strain response of the silicone networks. The contribution of chain-chain interactions, often called entanglements, was found to be significant. Twenty publications are listed in the report.

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Under this grant we applied and extended a recursive theory which describes structural features of crosslinking polymers. We developed experimental techniques for synthesizing and characterizing model networks of polydimethylsiloxane. We successfully applied the recursive theory to predict basic structural parameters like: molecular weight, gel point and sol fraction at various stages during network formation. A recursive relation for the weight average molecular weight of the longest linear chain through the molecule was developed and found to correlate viscosity rise during network polymerization. Sol fraction results were used with the theory to predict crosslink density, junction functionality and trapped entanglement fraction. These parameters were used to test the classical and more recent theories of rubber elasticity against stress strain response of the silicone networks. The contribution of chain-chain interactions, often called entanglements, was found to be significant. Twenty publications have been completed under the contract and are listed below.

Key Results

1. Recursive Theory. This program started with the development of simple recursive relations to describe average properties of non-linear polymers (Macosko and Miller, Macromolecules, 9, 199; 206 (1976)). Under this grant these relations were extended considerably, particularly toward systems of practical interest such as those where reactivity of different functional groups is not equal (4, see attached publication list), where reactivity is changed by substitution effects (9), where the starting reactants are oligomeric (5, 21) and where wasted loops can form (8,9). We also derived expressions for several new parameters such as the number of branches per molecule, the weight average of the longest chain through a branched molecule, weight fraction of pendant chains on the gel, average molecular

weight of network chains and molecular weight of the soluble fraction (5).
These relations are particularly helpful in understanding the rheology of
network forming systems as discussed below. We also extended the recursive
theory to predicting average molecular weight of the sequences formed
during linear copolymerization (55). Much of the research under this
grant was devoted to applying the recursive theory to model networks.

2. <u>Hydrosilation Coupling</u>. We developed a method for making well defined ran-
domly branched polymers and networks by coupling vinyl terminated polydi-
methylsiloxane chains with small, multifunctional hydrosilanes using a Pt
catalyst (1,2). We have characterized the reaction and verified its
efficiency (6,7,11,12,15). The reaction is now being used by a number of
other laboratories to produce networks with well defined structure.

3. <u>Methods for Verifying Network Structure</u>. We showed how important it is to
carefully characterize starting reactants, reaction path and final network
polymer in order to define network structure. We developed GPC and LC
methods for characterizing reactants (11,15,18) and infrared methods for
following reaction path (1,6). To verify network structure we used light
scattering molecular weight measurements, conversion at the gel point and
sol extraction (6,7,11,12,15,18).

4. <u>Viscosity and Gelation of Randomly Branched Polymers</u>. We developed several
methods for following the viscosity rise in polymerizing systems (6,8).
This permitted us to identify the gel point accurately and with both
urethane (8) and silicone systems (6) we got good agreement with predictions
from the recursive theory and the extent of reaction. Weight average
molecular weight on samples stopped before the gel point gave good

agreement with predicted values (6,15). We were able to correlate the entire viscosity rise curve to $M_{L,W}$, the weight average molecular weight of a longest linear chain through the branched molecule (6,15). Elasticity measurements (equilibrium compliance) also correlate with $M_{L,W}$. Recently we have extended the theory to randomly branched polymers formed by chainwise copolymerization of vinyl and divinyl monomers. Experimental viscosity results also correlate to $M_{L,W}$ (20). The influence of cyclization (or wasted loops) on molecular weight and the gel point has also been studied (18).

5. <u>Rubber Elasticity</u>. Perhaps the area of our research under this grant which has received the most attention recently is that involved with using model networks to test the classical theory of rubber elasticity and recent new theories. We have developed methods for measuring the dynamic shear moduli on cureing and on polymerized samples (3,17). These methods as well as ordinary tensile tests were used to evaluate the small strain shear modulus on silicone networks with different degrees of crosslinking, molecular weight of the starting chains, and different functionality (2,7, 11,12,13). These results and those of a number of other workers were compared in an extensive review (14). We found all the silicone model network modulus data in good agreement when compared on the basis of the same density of network chains and same functionality. The results show that chain-chain interactions add considerably to the small strain modulus. Their contribution can be treated quantitatively by the trapped entanglement concept of Langley (14). It also appears that chain interactions suppress the mobility of the crosslinking junctions as indicated in Flory's theory (16).

To further te⸱t these rubber elasticity theories we have done some large
strain experiments and have found that Edwards' reptation theory shows
too much strain sensitivity (12) while Graessley's shows too little (19).
Flory's gives closer to the proper shape strain dependence but the absolute
value of the small strain modulus is generally too low (12,19). Clearly
more theoretical work is needed but Flory's model should be quite useful
for design work with elastomers when rescaled by a constant.

6. <u>Viscoelasticity of Rubber Networks</u>. We have found that the loss modulus
for silicone networks correlates with the weight fraction of pendent
material, i.e. polymer chains which do not act as network linkages (7).
Valles has verified this for a wide range of networks in a recent study
(Proceedings of IUPAC Macromolecular Symposium, 1982, p. 565). With John
Ferry's group we have tested the influence of adding long, unattached
chains to silicone networks and found a much larger relaxation time than
expected by reptation theory (13). This indicates that chains in a
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Scientific Personnel

Christopher W. Macosko, Professor, Department of Chemical Engineering and Materials Science, University of Minnesota

Douglas R. Miller, Associate Professor, Department of Operations Research, George Washington University

Edward B. Richter, M.S. November, 1976 (currently project engineer at Procter and Gamble, Cincinatti, Ohio)

Enrique M. Valles, Ph.D. December, 1977 (currently Associate Professor of Chemical Engineering, University del Sur, Bahia Blanca, Argentina)

David J. Yarusso, B.S. June, 1978 (currently Ph.D. candidate, Department of Chemical Engineering, University of Wisconsin)

Barbara J. Ek, B.S. August, 1978 (currently Ph.D. candidate, Department of Chemical Engineering, University of Wisconsin)

David F. Weikart, M.S. November, 1978 (currently engineer at Exxon Chemical, Linden, New Jersey)

Thomas C. Lepsch, B.S. August, 1979 (currently University of Minnesota Medical School)

Moshi Gottlieb, Postdoctoral Fellow and Visiting Professor, 1/78-8/79, 8/81 (currently Associate Professor of Chemical Engineering, Ben Gurion University, Beersheva, Israel)

James Stoos, B.S. June, 1980 (currently Ph.D. candidate, Polymer Science and Engineering, University of Massachusetts)

William J. Hickey, M.S. October, 1980 (currently engineer at Amoco Research, Napierville, Illinois)

Jose M. Castro, Ph.D. July, 1980 (currently Associate Professor of Chemical Engineering, Universidad del Sur, Bahia Blanca, Argentina)

Richard J. Rolando, M.S. July, 1982 (currently engineer at 3M, St. Paul, Minnesota)

Grant S. Benjamin, M.S. candidate, University of Minnesota

Donald T. Landin, Ph.D. candidate, University of Minnesota

Sue Ann Bidstrup, Ph.D. candidate, University of Minnesota

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