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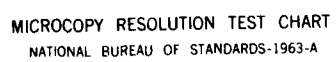
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PROCEEDINGS OF THE AMERICAN SOCIETY FOR COMPOSITES

AFOSR-TR. 87-1884

AD-A189 861



BIOTECHNOLOGY AIDED SYNTHESIS OF AEROSPACE COMPOSITE RESINS

*Co-Sponsored by U.S. Air Force
Office of Scientific Research
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August 25-26, 1987
Stouffer Dayton Plaza Hotel
Dayton, Ohio

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This report stems from a two-day workshop on Biotechnology Aided Synthesis of Aerospace Composite Resins held August 25th and 26th, 1987 at the Stouffer Dayton Plaza Hotel. This workshop was sponsored by the American Society for Composites with support from the Air Force Office of Scientific Research (AFOSR) and the Air Force Wright Aeronautical Laboratories/Materials Laboratory. This workshop was attended by personnel from government and industry representing both aerospace materials and biotechnology communities.					
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BIOTECHNOLOGY AIDED SYNTHESIS OF AEROSPACE
COMPOSITE RESINS

AFOSR-TR. 87-1884

Final Conference Report

Grant No. AFOSR-87-0245

November 1987

American Society For Composites

Dayton, Ohio 45432

This report stems from a two-day workshop on 'Biotechnology Aided Synthesis of Aerospace Composite Resins' held August 25th and 26th, 1987 at the Stouffer Dayton Plaza Hotel. This workshop was sponsored by the American Society for Composites with support from the Air Force Office of Scientific Research (AFOSR) and the Air Force Wright Aeronautical Laboratories/Materials Laboratory. This workshop was attended by personnel from government and industry representing both aerospace materials and biotechnology communities. A program and list of attendees are attached in Appendices A and B, respectively.

Introduction

A previous AFOSR/ML supported workshop on the potential applications of biotechnology to aerospace materials revealed five major areas of interest. The areas identified include 1. biomining, 2. bioelectronics, 3. biodegradation, 4. examination of natural systems for structure/property relationships and novel design concepts, and 5. biosynthesis of chemical intermediates for aerospace resins systems. Following this initial study a workshop was designed to focus on the area of biosynthesis of chemical intermediates for aerospace resins systems.

The goal of the workshop was to explore in depth the use of biotechnology as a novel approach in the preparation of aerospace resin materials, for the purpose of reducing cost in the production of current materials, or to produce new materials of superior properties which are presently unattainable by conventional synthetic routes. The main problems faced in the exploration of this area have been a distinct language barrier and a lack of fundamental understanding between technologies. Therefore, the objectives of this workshop were first to provide an educational background for both aerospace materials and biotechnology communities, and second to promote interaction between the two different communities to stimulate ideas for future work.

The workshop was divided into two sessions. The first session consisted of a series of lectures from both the aerospace materials and biotechnology communities to provide the educational background necessary for communication. The second session comprised of round table discussions on various topics concerning the use of biotechnology in the development of aerospace resin materials. The topics discussed included cost factors involved in the R&D of biotechnology, suggestions for improving communications between the two technologies, the role of the Air Force in promoting interaction and growth in biotechnology and the scientific issues involved in combining biotechnology and synthetic chemistry.

Educational Background

The educational background was provided by six lecturers, three from the aerospace resins community and three from the biotechnology community. The lecturers from the aerospace community included Mr. Donald Schmidt, consultant for carbon-matrix composites; Dr. Fred Arnold, AFWAL/MLBP; and Dr. Ronald Bauer, Shell Development and Research Center. Their presentations covered Carbon-Matrix Composites, Current And Future Molecular Structures Of Aerospace Organic Matrix Resins, and Industrial Perspectives On Current And Future Needs In Aerospace Matrix Resin Chemistry, respectively.

The lecturers from the biotechnology community included Dr. Masato Tanabe, S.R.I. International; Dr. Ronald Huss, Bio-Technical Resources Inc.; and Dr. Denis Ballard, I.C.I.. Their presentations covered Applications of Biotechnology to Synthetic Chemistry for Aerospace Matrix Resins Development, The Application of Hydrocarbon Bioconversion Technology to Aerospace Materials Production, and The Marriage of Biochemical and Chemical Concepts as Demonstrated by Preparation of Polyphenylene, respectively.

The following is a summary of the presentation given at the workshop.

Carbon-Matrix Composites

Carbon-matrix composites are advanced composites used in aerospace technology for high temperature structural applications. The carbon-matrix composites consist of a carbonaceous binder, reinforcing fiber, and sometimes a filler. The carbonaceous binder or matrix resins are derived from thermosetting resins and thermoplastic pitches.

Carbon-matrix composites are made by three principle methods. The first and most common procedure involves the impregnation of a fibrous preform with a carbonizable precursor followed by pyrolyzation in the absence of oxidizing agents. Densification is achieved by additional matrix impregnation and heat treatment cycles. The second method involves the infiltration of a porous article with a high carbon-containing liquid which is then treated to carbonization or graphitization temperatures. The third method involves chemical vapor deposition of carbon on a porous article.

The most important characteristics for the matrix resin of the carbon matrix composite includes a high char yield and easy processability. Some of the factors which effect the processability of the resin material include the release of volatiles, the thermalexpansion coefficient, the viscosity, and the exotherm characteristics.

The char yield of the resin material is the ratio of the weight of the carbon in the original resin to the initial weight of the resin. The ideal molecular structure for high charring resins includes a high degree of aromaticity and high molecular weight. The aromatic rings should be separated by no more than one carbon atom to prevent scission and volatilization of fragmented parts. Nitrogen if present should be located in the ring structure and not in the chain structure.

The present materials used as organic precursors for carbon matrix resins are thermoset resins and thermoplastic pitches. The thermoset resins most widely used include phenolics, polyfurfurals and epoxy novolacs. The best char yield was displayed with polyphenylene, however, synthetic processing of polyphenylene was not efficient. Thermoplastic pitches are used to densify porous carbonaceous articles by impregnation of a porous structure, followed by carbonization. This process is repeated until the desired composite density is achieved. Thermoplastic pitches are made up of four components including asphaltenes, polar aromatics, saturates and naphthene aromatics.

Current And Future Chemistry Of Aerospace Organic Matrix Resins

Research in both industrial and government laboratories has provided a variety of new and unique thermally stable polymers. During the last decade the primary effort has been in the development of new cure chemistry to provide matrix resins with improved moisture resistance, thermal and thermooxidative stability and toughness. New material concepts has also played an important role in structurally tailoring macromolecules for advanced future aerospace systems.

The current and future work in the Air Force on organic matrix resins for fiber reinforced structural composite applications is focused upon two materials technology areas, thermosets and ordered polymers. Within the thermoset technology area, the two major chemical technology areas addressed are acetylene systems and benzocyclobutene systems. Within the ordered polymer technology area, the specific chemical technology addressed is rigid-rod polymer systems such as the benzazole heterocyclics.

The acetylene terminated resin systems consist of molecules with terminal acetylene groups as the chemically reactive moiety for a thermosetting cure reaction. The backbone of the resin molecules can be tailored with various chemical structures and variable chain length. For T_g values in the 200-350°C range such as might be needed for Mach 3^{1/2} airframe uses or for turbine engine applications, aromatic heterocyclic structures such as quinoxalines, imides, thiazoles, and triazines are used in the acetylene terminated resin backbones.

The benzocyclobutene chemistry represents a new versatile technology for high temperature, addition curing resin systems with a hydrophobic cure site and use temperatures in the 500-600 °F range. It also represents a method of vastly improving the thermooxidative stability and toughness of currently commercial BMI resin systems. A number of chemical synthesis routes are available to prepare functionalized benzocyclobutene end-capping agents, however, all of these synthesis routes are expensive. A biologically aided route to these end-capping agents, such as the action of a dehydrogenase on a substituted ortho-xylene, could have a significant impact upon the cost.

The ordered polymer systems developed by the Air Force include linear, rigid rod polymers based upon the polybenzobisimidazole, polybenzobisoxazole and polybenzobisthiazole systems. A potential application area for the ordered, rigid-rod polymers which is currently being studied by the Air Force is molecular composites. Molecular composites essentially refers to composites in which reinforcement of the matrix material is at the molecular level instead of with macroscopic fibers such as graphite. The concept of molecular composites is to mix together coil-like polymers, which serve as the matrix, with rigid-rod polymers, which provide fiber-type reinforcement. Initial mixing followed by film formation affords a planar molecular composite with random molecular orientation in two dimensions. Further orienting of the film will give a uniaxial oriented molecular composite.

Industrial Perspective On Current And Future Needs In Aerospace Matrix Resin Chemistry.

In 1986 the world wide market for advanced composites and high performance adhesives was approximately 20 million pounds. This includes approximately 10 million pounds of resin comprising 90% epoxy resins and 10% bismaleimides, polyimides and thermoplastics systems. The predicted market of advanced composites in the year 2000 is 100 million pounds, which reflects a resin usage of approximately 40 million pounds. The resin systems used will most likely include epoxy, bismaleimides, polyimides and thermoplastics.

Epoxy resins are the most widely used matrix systems in performance composites. The epoxy resin systems are reactive intermediates composed of a mixture of oligomeric materials containing one or more epoxy groups per molecule. The epoxy resins are cured or cross-linked into a three dimensional network by a chemical reaction. The two groups of curing agents used in aerospace technology are aromatic diamines and anhydrides.

Bismaleimides matrix resins display improved thermomechanical properties compared to epoxy resins and are the leading candidate for high temperature (300-500F) advanced composites. The current consumption of bismaleimides is approximately 1.5-2.0 million pounds per year at a cost of \$25-\$50 dollars per pound. The bismaleimides are prepared by reaction of diamine with anhydride. The properties of the bismaleimide can be tailored by varying the structure and molecular weight of the diamine.

Polyimide resins, prepared by the reaction of dianhydride and aromatic diamines, are another system being investigated for high temperature advance composites. The problems of this system have been hydrolytic instability and volatile evolution during cure which are a result of the polyamic acid precursor. The solution to this problem has been the development of PMR polyimides where the precursor cures by addition polymerization.

Polyimides along with polyarylene ethers and polyesters are examples of new high performance thermoplastic resin systems. Thermoplastics are amorphous or crystalline materials which display increased toughness and reduced processing cost. Most of these materials are based on condensation type polymers with difunctional reactive intermediates such as bisphenols, aromatic diamines, aromatic dianhydrides, and other difunctional reactive intermediates. Some examples of commercial high performance thermoplastics include Ultem (GE), PEEK (ICI), and Xydar (Dart Industries). The current market for high performance thermoplastics is approximately 15-17 million pounds per year at a price from \$2-\$90 dollars per pound.

Applications of Biotechnology to Synthetic Chemistry

Biotechnology involves the use of living cells and their active principles to produce a product such as pharmaceuticals, foodstuffs, and commodity chemicals. The products are pure compounds, mixtures, and cell fractions or biomass and are derived from de novo formation, transformation, or degradation of substrates by the living cells.

The most explored area of biotechnology is the use of single cells or microorganisms to mediate biochemical reactions. Such chemical reactions mediated by microorganisms include Oxidations- Hydroxylation, epoxidation, dehydrogenation of C-C bonds; oxidation of alcohols and aldehydes; oxidation of amines; oxidative degradation of alkyl, carboxyalkyl, or ketoalkyl chains; oxidative removal of substituents; oxidative deamination; oxidation of hetero-functions; oxidative ring fission; and amine N-oxides.

Reductions- Reduction of organic acids, aldehydes, ketones and hydrogenation of C-C bonds; reduction of heterofunctions, dehydroxylation; reduction elimination of substituents

Hydrolysis- Hydrolysis of esters, amines, amides, lactones, ethers, lactams, etc.

Condensation- Dehydration; O- and N-acylation; glycosidation; esterification; lactonization; amination

Isomerization- Migration of double bonds or oxygen functions; racemization; rearrangements

Formation of C-C bonds or Hetero-atom bonds

The characteristics for these enzyme-catalyzed reactions include reaction specificity, regio specificity, stereospecificity and mild reaction conditions.

The Application of Hydrocarbon Bioconversion Technology to Aerospace Materials Production

The biological production of alpha, omega-alkanedioic acid is one example of a hydrocarbon bioconversion. The bacterium Rhodococcus and mutants developed in a strain improvement program convert n-alkanes of 10-14 carbons, typically dodecane, to the corresponding alpha, omega-alkanedioic acid, typically dodecanedioic acid, with high yields and conversions. Conversion is defined as the percentage amount in moles of the n-alkane consumed during fermentation by the bacterium without consideration of the product of the bioconversion. Yield is defined as % amount in moles of the n-alkane converted which ends up as alpha, omega alkanedioic acid. The yields were 30-40% with the final product concentrations in the range of 30 to 45 g/liter.

The biochemical pathway for omega-oxidation of hydrocarbons by bacteria consists of a series of single step oxidations. The process begins at one terminus of the n-alkane with oxidation to a primary alcohol then to an aldehyde and finally to a carboxylic acid. The same series of oxidations then proceed at the other terminus. This multiple step bioconversion requires oxygen and

NAD⁺. Because of the multiple step process of the bioconversion the whole cell approach is the most technically feasible.

Typical fermentation process development programs involves four phases:

1. a strain improvement program
2. shake flask and enzymology studies
3. pilot fermentation studies
4. bioreactor designs

The strain improvement is accomplished by mutation/selection methods.

Another example of hydrocarbon bioconversion is a fermentation program developed to convert heptane to heptanoic acid. In this study the bacterium used was Pseudomonas aeruginosa.

Acetylene terminated resins are one of several candidates being considered for potential aerospace applications. The acetylene-terminated resins have good mechanical properties, high thermal stability, good mechanical properties, high thermal stability and good retention properties after moisture exposure. The limiting factor for commercial applications is cost of the precursor meta-hydroxy phenylacetylene. There are two possible biological approaches for production of this precursor. One is the enzymatic approach where a commercially available enzyme would be screened for its ability to selectively hydroxylate phenylacetylene in the meta position under various conditions. The second approach is the use of a microorganism to convert phenylacetylene to meta-hydroxy phenylacetylene.

The Synthesis Of Polyphenylene From A Cis-Dihydrocatechol Biologically Produced Monomer

One example of combining biotechnology and synthetic chemistry is the production of polyphenylene by ICI. In this example benzene is oxidized by oxygen utilizing the dioxygenase enzyme contained in the microorganism Pseudomonas Putida. Genetic manipulation produced a variant which gave exclusively the initial oxidation product of benzene the cis-dihydrocatechol in practical quantities. Derivatives of the latter, in particular the methyl carbonate can be obtained pure and are very stable. They polymerise in the absence of solvent with radical initiators to give a polymer. The latter is soluble in solvents such as acetone and methylene chloride and readily forms coherent coatings and films. On heating, methanol and CO₂ are expelled and polyphenylene is formed as a coating or film. The aromatization can occur under homogeneous conditions in the basic solvent N-methyl pyrrolidone. Surprisingly, these partially aromatized molecules are soluble even at conversion to 30% phenyl groups. The latter studies can be used to measure the glass transition of polyphenylene which was found to be 283 degrees C.

Neutron scattering studies have shown that the precursor polymer is a random coil. Viscosity measurements show that there is a coil-rod transition on aromatization in N-methyl pyrrolidone. Crystallographic data on polyphenylene crystallized above its glass-transition and thermal and electrical properties are described.

Discussion Topics

The discussion topics included; 1. The cost factors involved in R&D of biotechnology, 2. Suggestions for improving communication between technologies, 3. The Air Forces Role in promoting biotechnology, and 4. Scientific Issues involved in using biotechnology to aid in synthesis of composite resins.

The cost factors involved in the R&D of biotechnology are extensive and are higher than many other new technologies. The fact that biotechnology is still a very young science adds to the development costs. The actual cost of a project will be dependent on several factors including the use of whole cell vs selected enzymes, the toxicity of the substance and the product, and the concentration yield of the product.

There was some disagreement within the biotechnology community with respect to the inherent cost of carrying out a commercial biological conversion such as hydroxylation of an aromatic ring. There was general agreement that R&D costs associated with developing a biological conversion of interest to the Air Force would be shared by a company when the company had a internal interest in the conversion from a generic perspective; however, companies will not publicize what their R&D interest areas are. It is thus up to the Air Force to publicize its need and let the interested companies respond.

The suggestions for improving communication between the two technologies of biotechnology and materials science included organizing more workshops, establishing a point of contact for both communities, encouraging the biotechnology community to solicit ideas from the material science communities, and encouraging organization of enzymatic rxn's maybe in the form of a book or catalog. The recommendation for the Air Forces role in improving communication and promoting research was to increase financial support and continue generating white papers or planning documents to stimulate ideas.

The scientific issues discussed determined that biotech was still too underdeveloped to determine feasibility of producing specialty aerospace resins chemicals. The most probable use of biotechnology would be in the production of key intermediates.

**LIST OF ATTENDEES OF BIOTECHNOLOGY AIDED
SYNTHESIS OF AEROSPACE COMPOSITE RESINS
AUGUST 25 - 26, 1987**

George Lee (617)651-9651
DOW Chemical USA
New England Lab/PO Box 400
Wayland, MA 01778

Kevin Carter(201)271-4122
Cellegene Corporation
7 Powder Horn Dr.
Warren, NJ 07060

Luke Fithian(201)271-4108
Cellegene Corporation
7 Powder Horn Dr.
Warren, NJ 07060

Norman W. Thomas(201)271-4124
Cellegene Corporation
7 Powder Horn Dr.
Warren, NJ 07060

John Verbicky(518)387-6177
G E C R D/Bldg K-1
Rm 5 A 62/PO Box 8
Schenectady, NY 12301

Harley Lake(518)387-6378
G E Bldg/KW Rm D 279
Corp Research & Develop
Schenectadey, NY 12345

J.J. Duffy(716)773-8476
Occidental Chemical Corp
2801 Long Rd.
Grand Island, NY 14072

Rich Green(716)722-0133
BIO Products, Div of Kodac
1669 LK Ave/Blvd 82/Rm440C
Rochester, NY 14650

Steven Elliot(302)999-3412
DuPont Company
Chestnut Run/Bldg 705
Wilmington, DE 19898

Warren W. Schultz
OUSDRE
Pentagon, 3D129
Washington, DC 20301

Jim Kvach
DIA/5A
Bolling AFB
Washington,DC 20332-6448

Anthony Matuszko(202)767-4
AFOSR/NC (963
Bolling AFB
Washington,DC20332-6448

Deb K. Chatterjee(301)670-8342
GIBCO/BRL Life Tech Inc
8717 Government Circle
Gaitersburg, MD 20877

James Goff(202)394-2289
Naval Surface Weapons Center
10901 New Hampshire Ave
Silver Springs,MD 20903-5000

Robert Newburg(202)696-4986
Office of Naval Res/Bio Div
800 N Quincy Street
Arlington, VA 22217

Phillip Greenbaun(804)296-5171/X433
US Army Foreign Sci&Tech Ctr
220 7th St NE AIAFRD
Chartollesville, VA 22901

Elias Greenbaum(615)574-6835
Martin Marietta Ener Sys Inc
P.O. Box X
Oak Ridge, TN 37831

Carol Dingman(901)396-2121
Richards Medical Center
1450 Brooks Road
Memphis, TN 38116

Mehmet Gencer(216)447-5385
BF Goodrich Development
9921 Brecksville Road
Brecksville, OH 44141

Bernard Chasman(513)277-7600
3362 Glen Helen Rd
Dayton, OH 45406

Donald Schmidt(513)426-4154
1092 Lipton Lane
Dayton, OH 45430

Fred E. Arnold
AFWAL/MLBP
Wright Patterson AFB
Dayton, OH 45433-6533

Charles Browning
AFWAL/MLBC
Wright Patterson AFB
Dayton, OH 45433-6533

Charles Burt
AFWAL/MLBC
Wright Patterson AFB
Dayton, OH 45433-6533

Tobey Cordell(513)255-9069
AFWAL/MLBC
Wright Patterson AFB
Dayton, OH 45433-6533

Fred Hedberg
AFWAL/MLBC
Wright Patterson AFB
Dayton, OH 45433-6533

James Whitney
AFWAL/MLBC
Wright Patterson AFB
Dayton, OH 45433-6533

Loon-Seng Tan(513)255-9115
U.D. Research Institute
300 College Park Ave
Dayton, OH 45469

Kestutis J. Tautvydas(612)733-8984
Bldg 270-25-06
3M Center
St Paul, MN 55144-1000

Ronald Huss
Bio Tech Resources
10355 7th Street
Manitowac, WI 55220

Robert Detroy(312)391-3519
Allied Signal Corp
50 E Algonquin Rd/Box 5016
Des Plaines, ILL 60017-5016

John Geibel
Phillips Petroleum Co
258 Research Forum
Bartlesville, OK 74004

Ronald Bauer(713)493-7008
Shell Dev Res Ctr
W.Hollow RC/PO Box 1380
Houston, TX 77001

Michael Binion(512)536-3681
18023 Shadey Knoll
San Antonio, TX 78258

John Obringer(303)472-4175
AA Dept of Biology
Colorado Springs, CO 80840

Tom Steelman
Northrop Aircraft
Northrop Ave
Hawthorne, CA 90250

Burt Ensley(805)499-5725
AMGEN
1900 Oak Terrace Ln
Thousand Oaks, CA 91320

Tom Hardy(805)499-5725
AMGEN
1900 Oak Terrace Ln
Thousand Oaks, CA 91320

Masato Tanabe
Stanford Research Inst
333 Ravenwood Ave
Menlo Park, CA 94025

Hugh McDonald(415)588-3475
Genecor Inc
180 Kinball Way
S San Francisco, CA 94080

Yesh P. Sachdeva(415)687-4201
Dexter-Hysol
2850 Willow Pass Rd
Pittsburg, CA 94565

Denis Ballard
PO Box 11 The Heath
Runcorn, Cheshire
WA 74QE ENGLAND

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Final Agenda

BIOTECHNOLOGY AIDED SYNTHESIS OF AEROSPACE COMPOSITE RESINS AUGUST 25 & 26, 1987

Tuesday, August 25th

<u>TIME</u>	<u>SPEAKER</u>	<u>TOPICS</u>
8:00	Ms. Rebecca Schiavone	Welcome
8:10	Dr. James Whitney AFWAL/MLBM	The American Society for Composites role in Biotechnology
8:20	Dr. Anthony Matuszko AFOSR	Biotechnology at the Air Force Office of Scientific Research
8:30	Dr. Fred Hedberg AFWAL/MLBC	The Air Force Program on Biotechnology For Aerospace Materials
8:40	Dr. Charles Browning AFWAL/MLBC	Future Markets for Aerospace Composites
8:50	Mr. Donald Schmidt Consultant	Carbon Matrix Composite Prospective Roles for Biotechnology f
9:50	BREAK	
10:00	Dr. Fred Arnold AFWAL/MLBP	Current and Future Molecular Structures of Aerospace Organic Matrix Resins
11:00	Dr. Ronald Bauer Shell D. R. Ctr.	Industrial Perspective on Current and Future Needs in Aerospace Matrix Resin Chemistry
12:00	LUNCH	
1:15	Dr. Harris Burte AFWAL/MS	Biotechnology and Air Force Materials
1:30	Dr. Masata Tanabe S.R.I.	Applications of Biotechnology to Synthetic Chemistry for Aerospace Matrix Resins Development
2:30	Dr. Ronald Huss Bio-Technical Resources	The Application of Hydrocarbon Bioconversion Technology to Aerospace Materials Production
3:30	BREAK	
3:45	Dr. Denis Ballard I.C.I.	The Marriage of Pyrochemical and Chemical Concepts as Demonstrated by Preparation of Polyphenylene

Continued on next page

4:45 General Discussion and Questions
5:00 AdJourn
6:30 Cocktail reception (C.O.D.Bar)
7:30 **DINNER**

Wednesday August 26th

8:00 Welcome
8:15 Small Group Discussions
10:15 **BREAK**
10:30 Large Group Discussions
12:00 **LUNCH**
1:00 Summary Discussion and Future Directions
3:00 Adjourn

Carbon Matrix Composites Prospective Roles for Biotechnology

L. Scott Theibert
and
Don L. Schmidt

ABSTRACT

Carbon matrix composites (CMC) are composed of a carbonaceous binder, a reinforcing fiber, and sometimes a filler. They are manufactured by the controlled pyrolysis of organic constituents to yield composites with extraordinary properties.

The role of carbon matrices in CMC will be discussed, including their functions, methods of formation, and properties. Matrix precursors based on thermosetting resins and thermoplastic pitches, and their influence on the newly generated carbon structures will also be described.

Some highly speculative roles for biotechnology will also be discussed to stimulate original thinking in this new interdisciplinary materials field.

I. IMPORTANCE: Advanced composites represent one of the most important achievements in materials technology during the past three decades. Organic, metallic and ceramic matrices in combination with high performance fibrous reinforcements have been developed and successfully used in numerous applications.

Carbon matrix composites (CMC) are the most important form of ceramic composites. These unique materials are composed of a carbonaceous binder, a reinforcing agent, and sometimes a filler material. Virtually any thermally stable fiber or filler can be used in combination with the carbon matrix.

II. CARBON MATRIX COMPOSITES

HISTORY: Carbon matrix composites originated in the United States. In 1959, simultaneous research being conducted by the Chance Vought Corporation, the Union Carbide Corporation and the U.S. Air Force Materials

D. L. Schmidt, Consultant, Beavercreek OH 45430
L. S. Theibert, Tech Area Manager, Air Force Wright Aeronautical
Laboratories, AFWAL/MLBM, Wright-Patterson AFB OH 45433-6533

Laboratory lead to composite in various forms (1-3).

Since first generation laboratory curiosities, carbon matrix composites have been improved dramatically. Mechanical properties have more than doubled due to the great advances in carbon fiber strength, elastic modulus and uniformity. Novel reinforcements have also been developed, ranging from unidirectional (1-D) to eleven (11-D) directional. Most applications, however, involve fabric (2-D) and multidirectional (3-D) reinforcements. Matrix densities have been increased from about 87 to 119 lb/ft³ (1.4 to 1.9 g/cc), but the higher values are achievable only with expensive equipment, high pressure processing or many impregnation/carbonization cycles. Novel fabrication and processing methods have also been developed to obtain a wide range of configurations including plates, blocks, cylinders, hollow tubes, frusta, and various machined parts. Manufactured parts remain relatively expensive, but the costs are decreasing as larger volume applications are being developed.

METHODS OF MANUFACTURE: The three principal methods of manufacturing CMC are shown in Figure 1. In general, the product application and desired properties will dictate which process method is used. The most common procedure is to impregnate a fibrous preform (fabric, 3-D, etc) with a carbonizable precursor, and then pyrolyze the composite in the absence of oxidizing species. The resultant porous carbonaceous solid is then densified by additional matrix impregnation and heat treatment cycles. In the second method, a porous article (fibrous preform or voidy solid) is infiltrated with a high carbon-containing liquid, and then heat treated to carbonization or graphitization temperatures. A third method involves the densification of a porous article with chemically vapor deposited (CVD) carbon. Occasionally, two of the methods are used to densify a composite (4-9).

COMPOSITE ATTRIBUTES. The attractive structural properties of CMC materials are illustrated in Figure 2. Strength and stiffness values are an order of magnitude higher than those of polycrystalline graphites. Of equal significance is the wide range of properties which are available by varying the type, percentage and orientation of the fiber, matrix and filler. Additional property changes are achievable by altering the processing conditions (10-12).

CMC materials can accommodate extremely high temperatures and heating rates without appreciable loss of surface material. With increased heating, the material surface temperature rises until the sublimation point is reached and thereafter stabilizes. The composites can be made very strong and stiff by the use of available carbon fibers. A highly anisotropic material is typically obtained, which is caused primarily by the fiber orientation. Short fiber and n-D reinforced composites tend to be more isotropic. At high temperatures (inert atmosphere) the mechanical properties of the composite are largely retained up to about 3,600°F (1,985°C). Above 1,500°F (816°C), the specific strength and specific stiffness of these composites are unequalled by all other known high temperature structural materials. Initial stressing of the composites produces a linear stress-strain relationship until matrix cracking is initiated. Higher stress

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states result in elongation or deformation in a unique pseudo-plastic response until ultimate composite fracture is reached in a nonbrittle mode. Thermal shock resistance is outstanding because of the high temperature, high thermal conductivity and low density. The composites are light in weight, with densities ranging from about 15 to 137 lbs/ft³ (0.02 to 2.20 g/cc). High dimensional stability during heating is exhibited because of the low coefficient of thermal expansion. Wear resistance is also high due to the low coefficient of friction. The composites are chemically 100% carbon, with high corrosion resistance (particularly in acids). The composites are electrically semi-conductive, but large variations in electrical properties can be achieved.

COMPOSITE LIMITATIONS. CMC materials are specialty engineering materials. They have not yet achieved widespread application acceptance because of their relative unfamiliarity to designers, relatively high costs, anisotropic characteristics, long manufacturing times, and low resistance to high temperature oxidation.

Carbon matrix composites in the U.S. presently cost about \$100/lb (\$220/kg) to many thousands of dollars per pound. Multiple matrix impregnation and carbonization cycles are typically employed, which contribute to high composite value. Manufacturing times tend to be long, ranging from weeks to many months depending upon the number of matrix impregnation and thermal processing cycles. Mechanical properties transverse to fibers tend to be low. For example, 2-D composite transverse strengths are generally on the order of 200 to 1,200 psi (1.38 to 8.27 MPa). Similar to brittle materials, the composites fracture strain is on the order of only 0.3 to 1.3%. Most composites are permeable due to microcracking, fiber matrix separation, and in some cases, open pores in the matrix. Of high importance is the composite susceptibility to high temperature oxidation. Oxidative effects become significant at about 660°F (349°C) for carbonaceous composites and 850°F (455°C) for high heat-treated composites. Oxidation has been minimized by modified, glass forming matrix and protective coatings.

APPLICATIONS. Carbon matrix composites have been developed for various aeronautical, biomedical, defense, industrial and space applications as shown in Table 1 (4-6, 12-28). The most important applications are as follows: aircraft brake discs, hypersonic spacecraft nosedcaps, and leading edges, missile nosetips, and heatshields, solid rocket motor nozzle throats and exit cones, liquid fueled engine thrust chambers, and ducting gas turbine engine flaps and seals, turbine wheels, furnace insulation, high temperature bearings, nuclear components, hot pressing molds and dies, prosthetics, planetary entry probe shields, very high temperature mirrors, canisters for space thermoelectric generators, and mechanical fasteners.

III. CARBON MATRICES

INTERNATIONAL RESEARCH. Carbon matrix research has been conducted primarily in the United States, France, and Federal Republic of Germany. Early research in the U.S. involved thermosetting resins like phenolics and two directionally reinforced composites (16). As the need grew for higher strength and higher density composites, chemical vapor deposition (CVD) processes were developed for both two and three directional composites (29-32). Finally, graphitizable matrices derived from thermoplastic pitches became of interest as applications outlets grew rapidly for three directionally reinforced composites (4-6, 19, 33).

Outside the U.S., the most notable matrix research has been conducted by Prof. E. Fitzer at the University of Karlsruhe, FRG (34). In-depth studies were conducted on both crosslinked resins and tar pitches. Elsewhere in the world, matrix research has been lagging. Some of the contributing nations, however, have included: France (35), England (36), Poland (37), Japan (38), Union of Soviet Socialist Republic (39), People's Republic of China (40), and Yugoslavia (41).

IMPORTANCE. The importance of the carbon matrix was recognized as early as 1966 by France et al. when they stated that the "major problem area preventing the realization of the full potential of the carbon or graphite filament is the binder phase". (42) It is now increasingly clear that the next generation of CMC materials will depend heavily on new and improved matrices, oxidation protection, and the ability to process them in a highly controlled and understood manner.

FUNCTION. The functions of a matrix in composites are several fold. They rigidize other constituents (like fibers) for structural and handling purposes. They also preserve the original orientation of the constituents in the composite. The matrix transmits stresses into reinforcing fibers in order to achieve maximum composite strength and stiffness. The matrix reduces the permeability and protects other constituents from degrading environmental conditions. The matrix alters all of the composite properties, and occasionally, the composite properties are dominated by the properties of the matrix (43, 44).

METHODS OF FORMATION. Carbon matrices have been formed by solid-phase, liquid-phase, and gas-phase pyrolysis of organic compounds. Depending upon the precursor conditions, a large number of matrix types can be obtained as shown in Figure 3. Note that each matrix structure possesses its own unique appearance and properties.

Solid Phase Pyrolysis. Thermosetting liquid resins are polymerized into a hard brittle stage by the application of heat or catalyst. Upon further heating, the organic solid is transformed into a non-graphitizable carbonaceous solid without the intermediate liquid state (45). In a thermosetting resin, the carbon atoms are highly crosslinked before the pyrolysis process, and as a result, the mobility and orientation of the

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molecules are suppressed during heat treatment. Mesophase spherules do not form, and reorientation of the crystals is difficult. Consequently, the size of the crystallites are extremely small and the inclusion of large amounts of unoriented structures (three-dimensional bonding) is also observed.

Liquid Phase Pyrolysis. Carbons capable of forming crystalline three dimensional orders upon high temperature treatments are known as graphitizable carbons. These carbons are typically derived from thermoplastic precursors like tar pitches or polymers with low crosslink density. (46)

Gas-Phase Pyrolysis. Pyrolytic carbonaceous and graphitic matrices are formed by gas-phase carbonization of organics. Natural gas, methane or similar hydrocarbon gas are typically used in conjunction with a carrier gas like hydrogen or argon. Pyrolysis takes place at relatively high temperatures and the residual carbon atoms are deposited onto a heated substrate. Pyrolytic deposits have widely different crystalline orientations depending upon deposition condition and heat treatment temperatures (47-50).

CLASSIFICATION. Carbon matrices derived from organic materials are broadly classified as non-graphitizable or graphitizable (51) depending upon the rate of increase in the diameter and on the degree of stacking of layer planes with increase in temperature above 3,632°F (2,000°C).

Non-Graphitic Carbons. Non-graphitic carbons are all varieties of substances consisting mainly of the element carbon with two-dimensional long range order of the carbon atoms in planar hexagonal networks. They are without any measurable crystallographic order in the third direction, apart from more or less parallel stacking. Non-graphitizable carbons are generally formed from precursors that contain large amounts of oxygen, have low hydrogen content, or are highly crosslinked.

Graphitic Carbons. Graphitizable carbon is a non-graphitic carbon which upon heat treatment converts into graphitic carbon having more or less perfect three-dimensional crystalline order. Graphitizable carbons are derived by the pyrolysis of organic materials that pass through a fluid state prior to carbonization. High mobility of the carbon atoms and platelets during pyrolysis is essential to forming a three dimensional ordering characteristic of graphitic materials. Graphitic carbons are distinguishable from disordered carbons by a lower interlayer spacing (d_{002}) and a higher value for (L_a), stack height (L_c) and number of layer planes (N).

Cokes and Chars. The heating of a carbon containing matrix in an inert atmosphere results in the formation of a carbonaceous residue, commonly known as a "coke" or a "char". A coke is a graphitic carbon. Cokes are sometimes referred to as "soft carbons" or "graphitizable carbons". A char is a non-graphitic carbon. Chars are also known as "hard carbons". They can be converted to soft graphite by catalytic graphitization. Soft cokes,

of course, convert to graphite at temperatures in excess of 3,632°F (2,000°C). Matrix properties that increase with heat-induced crystalline ordering include density, permeability, thermal conductivity, oxidation resistance, electrical conductivity and magnetic susceptibility. Properties that decrease as carbon is transformed to crystalline graphite are mechanical strengths, elastic modulus, thermal expansion, hardness, and magnetoresistance.

IV. ORGANIC PRECURSORS

SELECTION CRITERIA. The ideal characteristics of a carbon matrix precursor are listed in Table 2. The matrix precursor should have a very high carbon content. During pyrolysis, a maximum percentage of the matrix carbon should be retained in the residue. The precursor should be fluid at ambient temperatures or slightly elevated temperatures. The viscosity should be low to facilitate penetration (at low pressures) into small pores of a substrate or closely packed fiber bundles. The precursory matrix should wet the substrate surfaces and remain in close proximity during processing. The material should be chemically pure, reproducible, well characterized and inexpensive. During pyrolysis to the carbon state, the matrix should release minimal volatiles and undergo little expansion and contraction. The matrix should soften and flow just prior to carbonization to aid in pore (void) penetration. The pyrolysis should take place in an orderly manner, without significant exotherms, and occur relatively fast. Only moderate temperatures should be necessary, and minimal energy expended in the process. Most of the carbon in the precursor should remain in the residue. The carbon matrix should be strong, contain uniform pore distribution, and be of predetermined density. Finally, the carbon matrix should also be in close association with other composite constituents, but not necessarily bonded to them.

While many selection criteria should be considered in choosing a precursory organic material, processability and char yield are the most important. Processability means appropriate matrix viscosity and orderly conversion to carbon without elaborate process equipment or unusual conditions. Char yield means a maximum carbon yield, but with a predetermined microstructure and properties.

MOLECULAR ARCHITECTURE. The molecular architecture of the ideal charring resin has been studied by some researchers. In general, they noted that the resin should have a high degree of aromaticity and high molecular weight. There should be no more than one carbon atom between aromatic rings. Additional carbon atoms provide more sites for scission and volatilization of the fragmented parts. Nitrogen (if present) should be in the ring structure and not in the chain structure. Other elements such as sulfur do not affect thermal stability. They induce lower char yields and lower conversion efficiencies (52-55).

THERMOSETTING RESINS. Thermosetting resins are one class of organic precursory materials used for the generation of carbon matrices. Many

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types of resins have been developed, but only a few of them have been used extensively for carbon matrix formation. Phenolics, polyisofurals and epoxy novolacs have been the most widely used, based on acceptable char yields, low viscosity in the liquid state, low cost, orderly cure at moderate temperatures, high purity, and multiple sources.

The formation of polymeric carbon from various synthetic resins has been investigated by numerous researchers (36, 52-61). Carbon yield was found to be dictated by the ability of the polymer to cyclize, undergo ring fusion or chain coalescence at the onset of carbonization. Table 3 presents the polymer carbon contents, char yields and the conversion efficiencies for a wide variety of crosslinked resins. The carbon content of the polymer is the elemental carbon present in the virgin monomeric unit. The char yield is the ratio of the weight of the carbon in the original resin to the initial weight of the resin. The commonly used structural epoxy resin had a char yield of only 6%, although the original polymer had a carbon content of 47%. As the aromatic content of the polymers increased, the char yield increased. Epoxidized phenolic, for example, had a 50% char yield. Phenolic resins yielded even larger percentages of carbon, i.e., 60-70%. The best char yield and conversion efficiency was obtained with the highly polycyclic resin polyphenylene. It had a char yield of 85% and a carbon conversion efficiency of 92%. In other words, very little polymer carbon was volatilized during pyrolysis.

Heat treatment of cured resins at elevated temperatures causes weight loss and shrinkage. The weight loss of various resins as a function of increasing temperature is illustrated in Figure 4. As weight is lost from the resin, it also undergoes shrinkage. The amount of linear shrinkage is shown in Figure 5. It increases with weight loss and varies for each of the resin types. If shrinkage of the matrix is restricted during pyrolysis, local stress levels will increase until they are relieved by matrix cracking.

Some of the important characteristics of carbon matrices derived from thermosetting resins are: (a) Char yields generally range from about 45 to 85 weight percent, but 45-55 % by weight are typical values, (b) Char densities are quite low and on the order of 24 lb/ft^3 (1.5 g/cc), (c) Linear shrinkages up to 10-25% occur during pyrolysis, which may induce high stresses and matrix cracking, (d) the char microstructure is glassy and can not be converted to graphitic carbon by heat treatment temperatures even up to $5,432^\circ\text{F}$ ($3,000^\circ\text{C}$), and (e) graphitic or partially graphitic microstructure may be possible by internally generated or externally applied stresses during heat treatment.

THERMOPLASTIC PITCHES. Pitcher are generally used to densify porous carbonaceous articles. The process generally involves impregnation of the porous structure, containment of the pitch during carbonization, and repeated cycles to reach the desired composite density or porosity levels. Since pitch is a solid at room temperature, it must be transformed to a low viscosity fluid prior to impregnation. This operation is typically

performed by (a) raising the temperature of the pitch until it reaches the desired viscosity-temperature level, (b) dissolving pitch particles in a suitable solvent, or (c) dissolving pitch in a compatible resinous fluid. Both coal tar and petroleum pitches have been successfully used as a coke source (5, 6, 62-65). Initial development efforts were concentrated on coal tar pitches because of their availability, low costs, low sulphur content and high carbon yields at high carbonization pressures. Subsequent developmental work also involved petroleum pitches, which provided better viscosity control, lower ash content, and lower quinoline insoluble content.

Pitches consist of many hundred of different species, which depend upon crude composition and refinery process conditions. Pitches are composed of four fractions: asphaltenes, polar aromatics, saturates, and naphthene aromatics. The asphaltene fraction of the pitch produces a liquid crystalline mesophase, which in turn, forms the desired coke matrix structure. In the temperature range of 400° to 500°C, polymerization reactions build large, disklike, polynuclear aromatic molecules. Upon reaching molecular weights in the neighborhood of 1400, they condense in parallel arrays and precipitate from the molten pitch as a liquid crystal (the carbonaceous mesophase). This mesophase forms initially as small spherules of simple structure, coalesces to a viscous bulk mesophase, hardens, and then pyrolyzes to a coke (66-67).

Extensive research on tar pitches as coke precursors has lead to the following conclusions: (a) Pyrolysis takes place in the liquid molten phase because of the lack of a crosslinked structure. (b) The coke yield is approximately 50% at ambient pressure, similar to many crosslinked resins. Pressure carbonization at 10,000 to 15,000 psi increased the char yield to nearly 90%. (c) The coke microstructure was graphitic. Needlelike structure was obtained at low pressure carbonization and a more coarse, iso-tropic structure was noted at higher pyrolysis pressures. (d) High pressure carbonization produced high density cokes, i.e., near 2.0 g/cc. (e) Coke structure is porous to varying degrees. (f) Properties of the coke structure were anisotropic due to the crystalline structure.

PYROLYTIC CARBONS. Pyrocarbons are crystalline forms of carbon that have been deposited from the vapor state. The material is chemically pure carbon, dense, impervious to fluids, brittle, strong, and generally anisotropic in many properties. When observed under plane polarized light, the pyrocarbons can be distinguished as having essentially isotropic, smooth or rough laminar and granular structures.

FROSPECTIVE ROLES FOR BIOTECHNOLOGY

As the field of composites continues to expand at a rapid rate, one must be continually alert of other technologies that offer potential for creating new materials and processes. In this respect, biotechnology offers some real, but limited possibilities. Creative thinking and dedicated

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resources, however, are of paramount importance in expanding the biotechnology horizons to include the field of aerospace materials.

BIOSYNTHESIS OF RESINOUS INTERMEDIATES. Polyphenylenes are generally regarded as the ideal precursory carbon matrix due to their chemical structure and very high carbon contents (68-71). First generation polymers were infusible and insoluble and thus difficult to process. Branched vinyl-terminated and acetylene-substituted polyphenylenes were later developed, which were sufficiently fluid to impregnate fibrous structures, yield 80 to 95% carbon upon high heat treatment, and form graphitizable to nongraphitizable carbons at low (100 psi) pressure (72-73). Several examples of these novel arylacetylenes are copolymers derived from either (a) mixture of diethynylbenzene and ethynylpyrene (74) or (b) a mixture of 1-ethynylpyrene with m-diethynylbenzene. The biotechnology community has demonstrated the ability to produce many specialty chemicals at a cost substantially lower than by using conventional synthetic chemistry. A recent example of how biotechnology might impact the aerospace composite area is provided by the ICI-developed synthesis of polyphenylene. The key step in this synthesis was the microbial induced conversion of benzene, a very low cost commodity chemical, to 3,4-dihydroxycyclohexa-3,5-diene which is subsequently converted by conventional chemical means to a polyphenylene precursor. The potential cost of this precursor at the 1,000,000 pound per year level has been estimated as less than \$10 per pound. It is anticipated that there is more chemistry of this type possible through growth of a dialogue between the biotechnology and materials communities.

BIOCONCENTRATION OF HIGHLY AROMATIC COMPOUNDS. Coal tar and petroleum pitches are low cost sources for carbon matrices. Because they are derived from natural products, they are composed of hundreds of different compounds ranging from low molecular weight paraffinic material to highly aromatic species (75). Only the highly aromatic species are of interest, since they form the desired precursor "mesophase" and the graphitizable carbon structure. Attempts to fractionate pitches using solvent and thermal methods have only been partially successful to date.

Microorganisms may possibly assist the fractionization of complex pitch mixtures by (a) rendering the low molecular weight compounds insoluble in the remaining aromatic species, (b) altering specific hydrocarbon species to make their removal by other separation methods both easier and faster, or (c) concentrating the desired aromatic compounds by some yet to be discovered means.

Some consideration should also be given to materials synthesis by plants. Certain plants may already be concentrating desired aromatic molecules, which could be subsequently extracted in very pure form and very controlled molecular weight distributions. If not, genetic engineering may possibly be employed to induce the plants to produce desirable carbon precursors.

BIOLEACHING OF PITCH PRECURSORS. Petroleum pitch contains a significant amount of sulfur, which must be removed to prevent "puffing" or floating of

the resultant carbon structure. Present chemical extraction methods reduce the sulfur content to less than one percent prior to use, but even that amount is undesirable. Sulfur left in the carbonaceous matrix disrupts the microstructure (induces defects) and is removed only by heat treatments in excess of 2,000°C. Metals and metallic oxides are also undesirable impurities in pitches. Matrix processing temperatures up to about 2,750°C cause vaporization, micro-bubble formation and residual voids. Their impact on structural properties is enormous.

The problem of impurities in pitches becomes particularly acute when the mesophase pitch is used in the manufacture of high performance fibers. By reducing impurity levels significantly, there is great probability that the tensile strength levels can be elevated from the present 300,000 psi to over 1,000,000 psi and the current Young's modulus values could also be increased from present values of 125,000,000 to about 135,000,000 psi.

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TABLE I
APPLICATIONS OF CERAMIC MATRIX COMPOSITES

KEY PROPERTIES	APPLICATIONS
o ABLATION RESISTANCE	o MISSILE NOSETIPS & HEATSHIELDS o SPACECRAFT ENTRY NOSECAPS o PLANETARY ENTRY SHIELDS o MOTOR NOZZLES
o STRENGTH AT HIGH TEMPERATURES	o SPACECRAFT LEADING EDGES o GAS TURBINE ENGINE VANES
o FRICTION COEFFICIENT	o BRAKE DISCS AND LININGS o BEARINGS
o IMPACT RESISTANCE	o SPACECRAFT ENTRY CANISTERS
o THERMAL CONDUCTIVITY	o INSULATION o HEAT PIPES o HEAT EXCHANGERS
o DIMENSIONAL STABILITY	o HOT PRESSING DIES AND MOLDS o SPACECRAFT STRUCTURES o HIGH TEMPERATURE MIRRORS o ENERGY RESISTANT BARRIERS
o BIOCOMPATIBILITY	o PROSTHESES AND IMPLANTS
o CHEMICAL INERTNESS	o FOUNDRY MOLDS & CRUCIBLES o FUSION LINTERS
o LOAD BEARING	o BOLTS, NUTS, SCREWS, AND FASTENERS o AUTOMOTIVE PISTONS AND RODS
o ELECTRICAL CONDUCTIVITY	o HEATING ELEMENTS o ELECTRODES o ELECTRICAL CONNECTORS
o FATIGUE RESISTANCE	o SPRINGS
o RADIATION RESISTANCE	o NUCLEAR COMPONENTS o DUCTING

TABLE 2

IDEAL CHARACTERISTICS OF PRECURSOR ORGANIC MATRICES

- | | |
|---------------------|---|
| o HIGH CARBON YIELD | o WET OTHER CONSTITUENTS |
| o CHEMICALLY PURE | o NO CHEMICAL BONDING
TO OTHER CONSTITUENTS |
| o LONG POT LIFE | o CONTROLLABLE EXOTHERMS |
| o LOW COST | o MODERATE CURE
CONDITIONS |
| o LOW TOXICITY | o FLUID JUST PRIOR TO
CARBONIZATION |
| o SEVERAL SOURCES | o MINIMAL VOLATILE PRO-
DUCTS DURING CURING
AND CARBONIZATION |
| o REPRODUCIBLE | o LOW SHRINKAGE DURING
CURING AND CARBONIZATION |

f

TABLE 2

FEATURES OF HIGH CHAF YIELDING RESINS

- o HIGH CARBON-TO-HYDROGEN RATIO
- o HIGH DEGREE OF AROMATICITY
- o HIGH MOLECULAR WEIGHT
- o ONE CARBON ATOM MAXIMUM BETWEEN AROMATIC RINGS
- o NITROGEN (IF PRESENT) IN THE RING STRUCTURE
- o LOW NON-CARBON ELEMENT CONTENT
- o MINIMAL LABILE PENDANT GROUPS

f

TABLE 6
CHAR YIELDS OF VARIOUS CURED RESINS (44)

POLYMER	POLYMER, CARBON CONTENT, %	CARBON YIELD, %	PYROLYSIS EFFICIENCY, %
PHENOL BASE			
p-Phenylphenol Phenol- Formaldehyde	81	70	84
1,5 Naphthalenediol Formaldehyde	79	63	80
Phenol Furfuraldehyde	76	62	82
Phenol Formaldehyde	81	60	74
RESORCINOL BASE			
Resorcinol Furfuraldehyde	64	60	94
EPOXY BASE			
Polyallylglycidyl Ether	47	6	13
Epoxidized Phenol Formaldehyde	80	50	63
OXYGEN CONTAINING			
Furfuryl Alcohol-Formaldehyde	63	56	89
Furfuryl Alcohol	75	54	72
Furfuryl Ester	75	63	84
Polyphenylene Oxide	80	40	46
SULFUR CONTAINING			
Polysulfone	71	48	66
POLYCYCLIC AROMATIC			
p-Polyphenylene	95	85	92
POLYHETERO-AROMATIC			
Polybenzimidazole	78	74	95
Polyimide	71	60	86

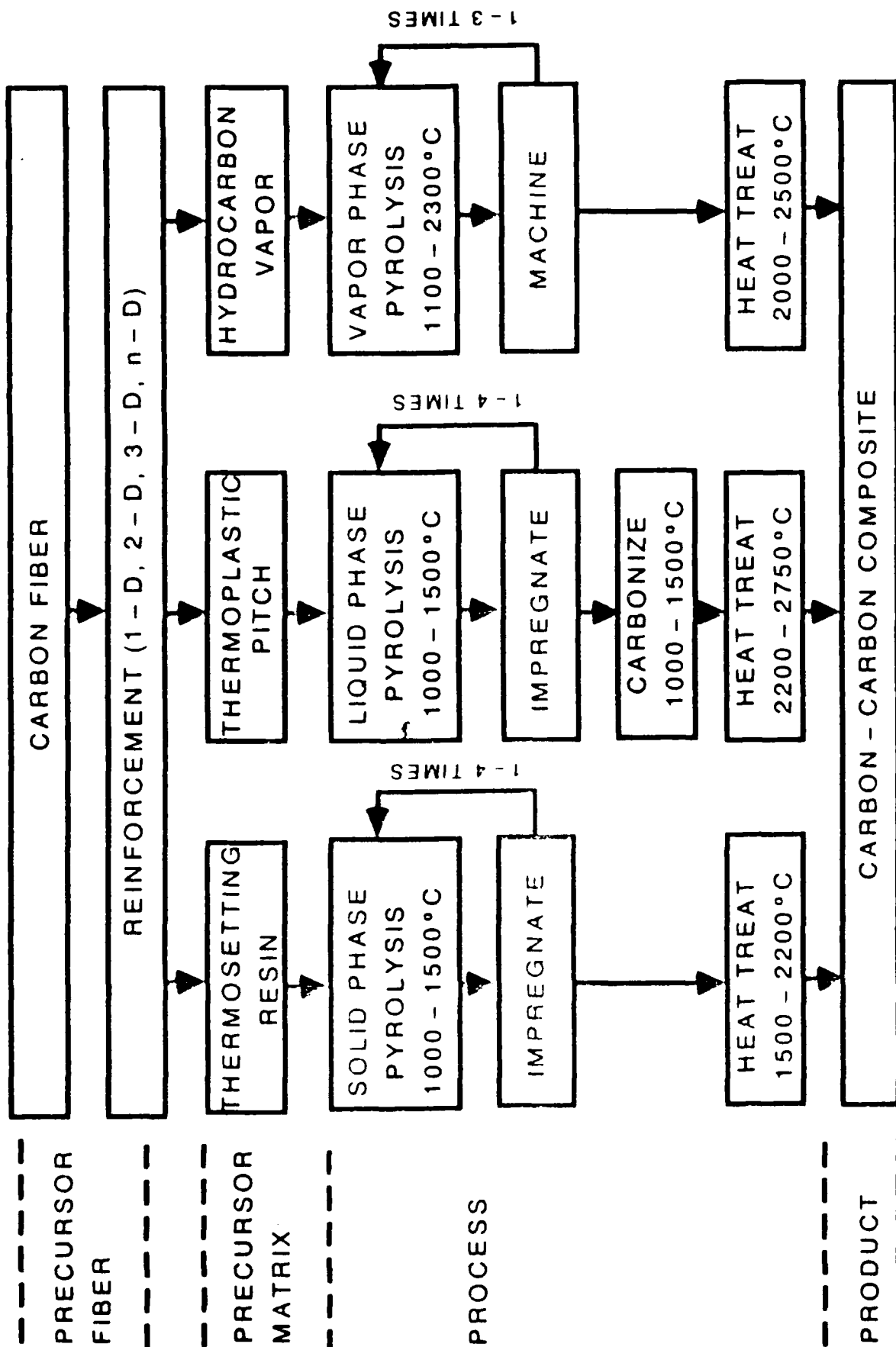
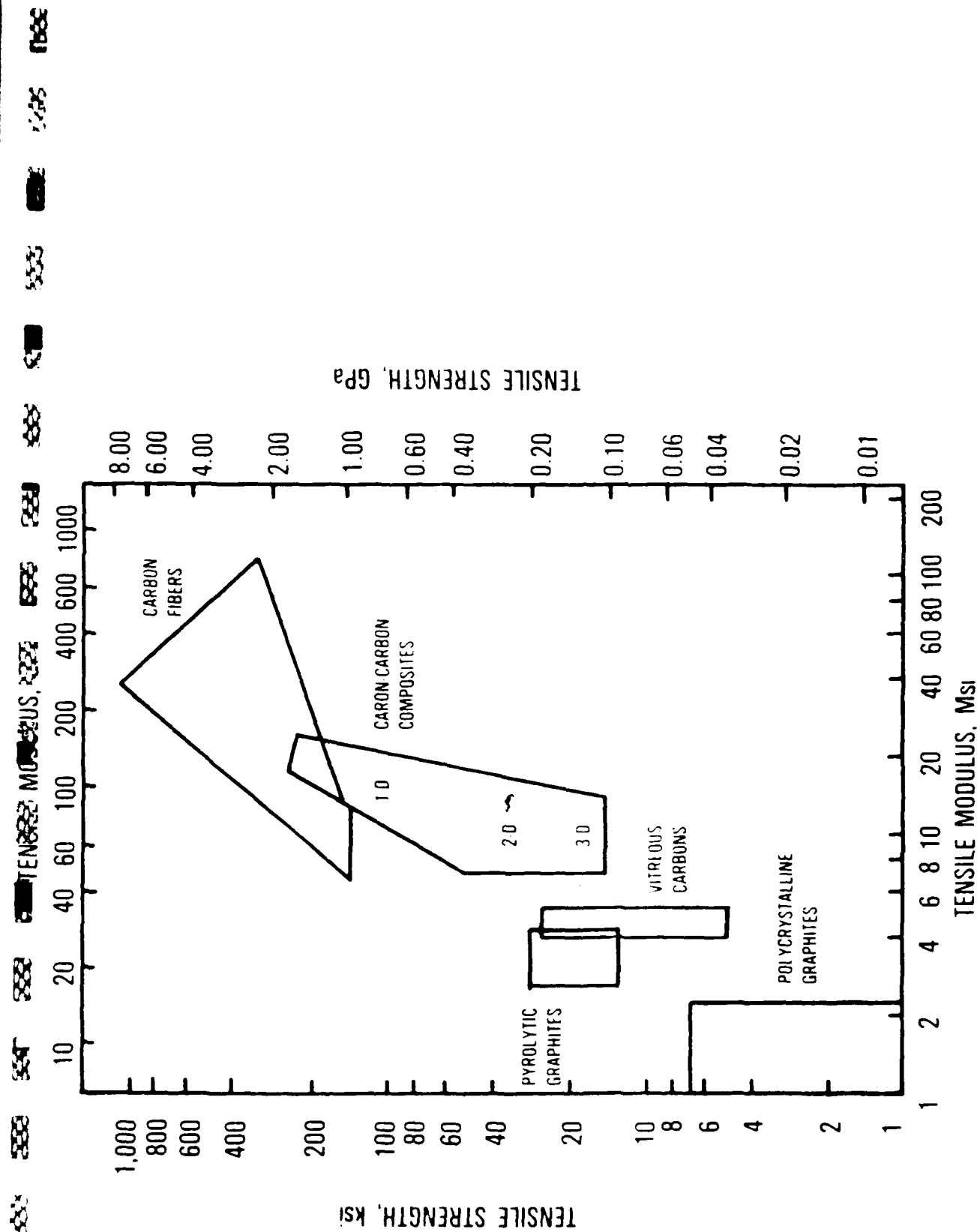


FIG. 1. METHODS OF MANUFACTURE.



1000 900 800 700 600 500 400 300 200 100 0



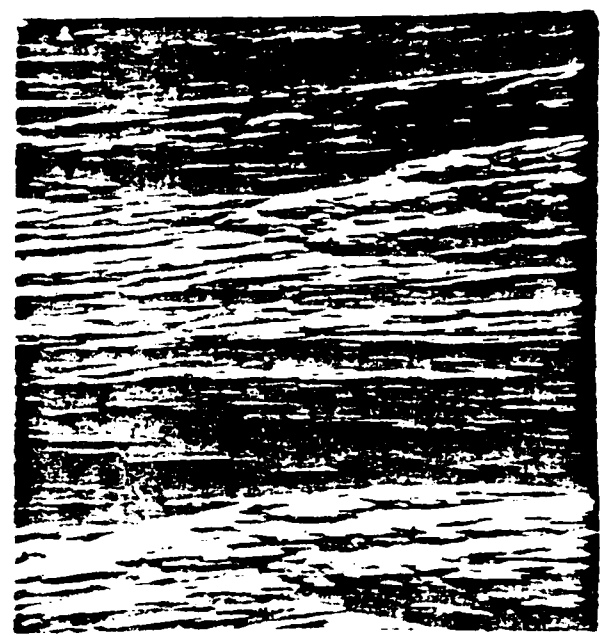
POROUS, NON-GRAPHITIC CARBON



IMPERMEABLE, NON-GRAPHITIC CARBON



GRAPHITIC CARBON



PYROLYTIC CARBON

FIG. 3. MICROSTRUCTURE OF CARBON MATRICES.

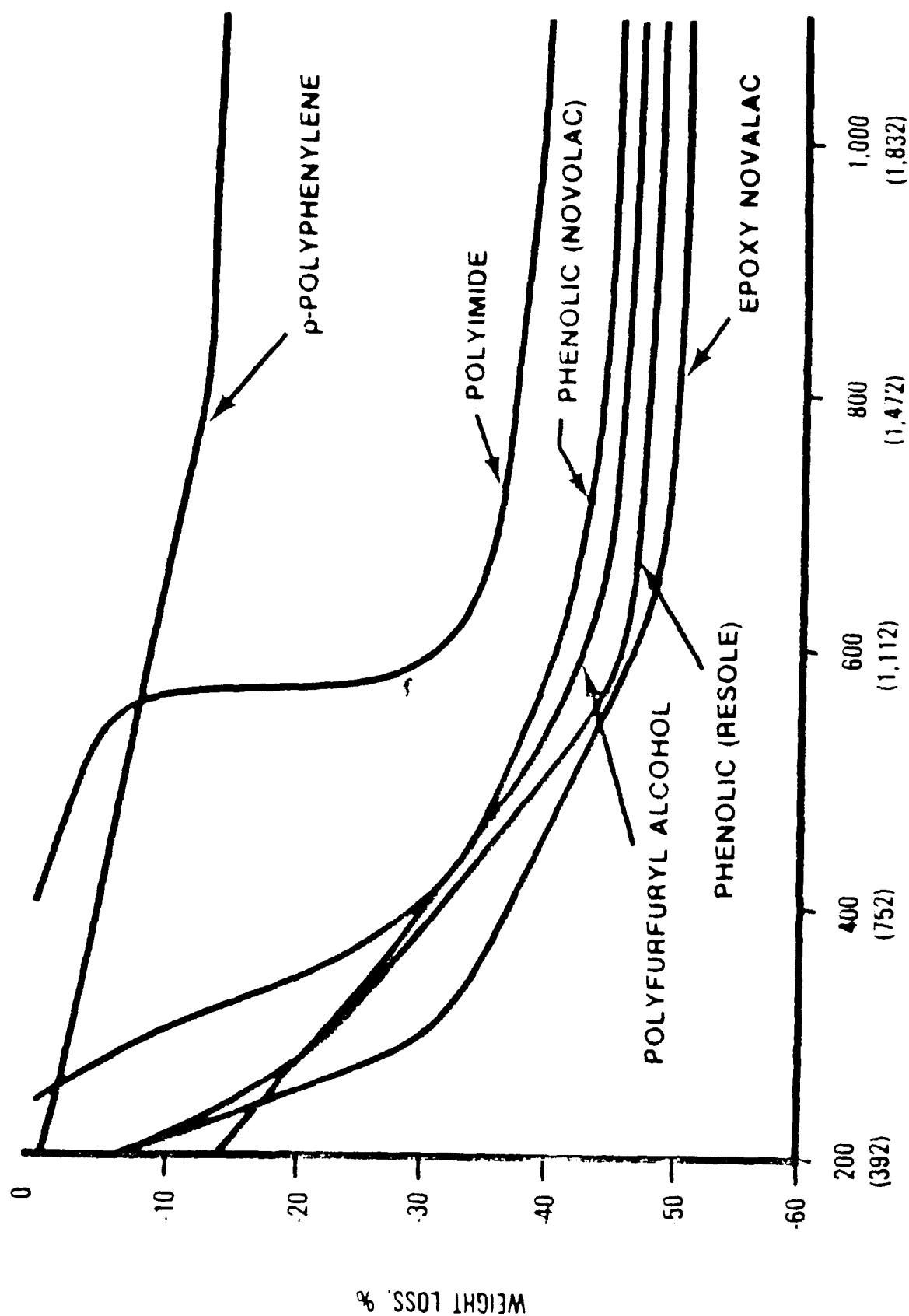


FIG. 4. WEIGHT LOSS OF CURED RESINS DURING PYROLYSIS.

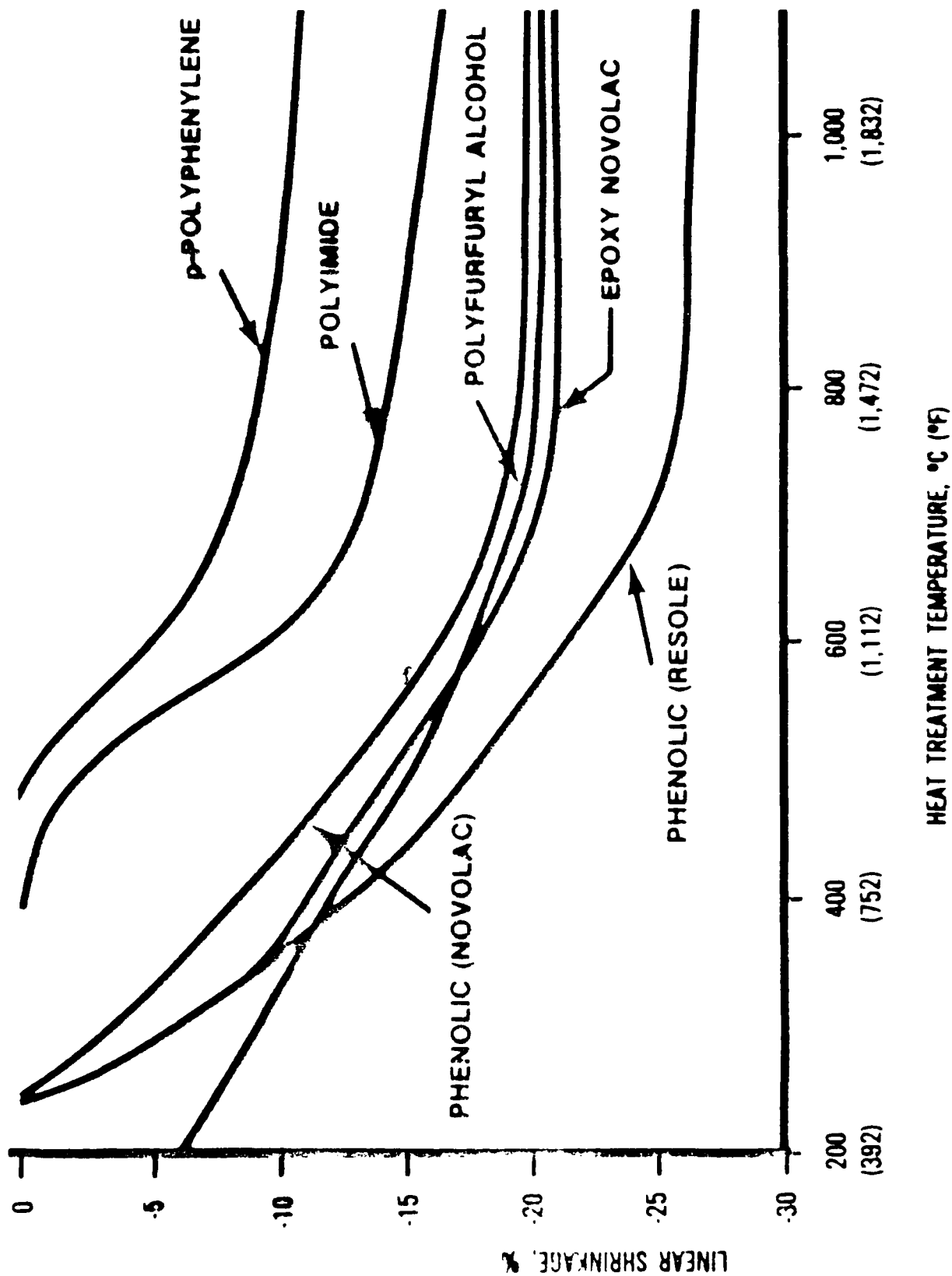


FIG. 5. LINEAR SHRINKAGE OF CURED RESINS DURING PYROLYSIS.

CURRENT AND FUTURE MOLECULAR STRUCTURES
OF AEROSPACE ORGANIC MATRIX RESINS

Fred E. Arnold

AFWAL/MLBP Wright-Patterson AFB
Dayton, OH 45433-6533

Research in both industrial and government laboratories has provided a variety of new and unique thermally stable polymers. During the last decade the primary effort has been in the development of new cure chemistry to provide matrix resins with improved moisture resistance, thermal and thermooxidative stability and toughness. New material concepts has also played an important role in structurally tailoring macromolecules for advanced future aerospace systems.

The lecture will encompass both thermoset and high molecular weight polymer systems which are of considerable interest to the Air Force. Synthetic aspects to thermoset endcapping agents will be discussed as well as monomers required in the ordered polymer technologies. Paramount to the success of a new polymer technology is low cost organic intermediates which are required for a successful transition to the commercial market place. It is anticipated that biotechnology could play an important role in the low cost manufacturing of these new materials.

Industrial Perspective on Current and Future Needs in Aerospace Matrix Resin Chemistry

Ronald S. Bauer

Shell Development Company
Westhollow Research Center
Houston, Texas 77251-1380

INTRODUCTION

The world wide market for advanced composites and high performance adhesives in 1986 was about 20 million pounds. This amounted to approximately 10 million pounds of resin sales in 1986. Currently, epoxy resins constitute over 90% of the matrix resin material used in advanced composites. The total usage of advanced composites is expected to grow to around 100 million pounds by the year 2000 with the total resin usage around 40 million pounds in 2000. Epoxy resins are expected to still make up about 80% of the total matrix resin systems market in 2000. The largest share of the remaining market will be divided between bismaleimides and polyimide systems (12 to 15%), and what are classified as other polymers. Other polymers would include thermoplastics and thermoset resins other than epoxies, bismaleimides, and polyimide systems.

This presentation will review the chemistry of the state-of-the-art and emerging aircraft/aerospace matrix resin systems. Areas will be identified where biotechnology assisted chemical synthesis can be applied to commercial high performance composite matrix resins.

EPOXY RESINS

INTRODUCTION

Probably the earliest and still the most widely used matrix resins in high performance composites are the bisphenol A based epoxy resin systems. Full scale commercial production of epoxy resins began in 1950. Initial significant industrial applications of epoxy resins were in surface coatings, and also potting and encapsulation of electrical components. However, by 1952 epoxy resins were being used in electrical laminates and a filament wound pressure tank for the F-84 jet fighter.

In Figure 1 is given the domestic demand by product type for 1986. Liquids, brominated resins, certain speciality resins and epoxy novolacs all find application in advanced composites. Although liquid epoxy resins accounted for about 62% of the some 318 million pound U. S. epoxy market in 1986, their use in aerospace composites is limited by their ultimate thermomechanical properties. Most high performance epoxy resin based aerospace composites are formulated from specialty resins such as tetraglycidyl methylene dianiline and tetraglycidyl tetraphenol ethane.

Figure 2 gives the structure and properties of some typical liquid bisphenol A epoxy resins. In commercial products the value of n ranges from about 0 to 25, with typical liquid epoxy resins having n values 0 to 1. The structures of a number of the more widely used specialty epoxy resins are given in Figure 3. At the top of the figure are shown the tetra-brominated resins; these are used for fire retardant electrical laminates—usually at levels of about 20% weight bromine. For certain applications it is desirable to modify the relatively hard and brittle bisphenol A systems to improve toughness or their ability to withstand thermal shock. This is frequently accomplished by introducing flexibilizing epoxy resins which are based on long molecules such as dimer fatty acid and polyethylene glycols. For more demanding uses at higher temperatures,

such as aerospace and certain electrical applications, multifunctional epoxy resin systems are used. The epoxy resin based on the tetraglycidyl amine of methylene dianiline is currently the epoxy resin most often used in advanced composites. Tetraglycidyl methylene dianiline cured with diaminodiphenyl sulfone was the first system to meet the performance requirements of the aerospace industry and is still used extensively today.

MANUFACTURE

Liquid epoxy resins are manufactured from bisphenol A and epichlorohydrin as shown schematically in Figure 4. Typically the bisphenol A is reacted with epichlorohydrin to give a bis-chlorohydrin, which is dehydrohalogenated with caustic to give the desired epoxy resin. In practice, both condensation of the bisphenol A with epichlorohydrin and the dehydrohalogenation are carried out simultaneously. A consequence of reacting in this manner is that substantial resin is formed before all the phenolic hydroxyl is consumed, leading to attack by the phenol on the resin epoxide instead of the epichlorohydrin. This results in the formation of some molecules with values of $n=1$ or greater. Glycidylamines such as tetraglycidyl methylene dianiline (TGMDA) are also manufactured by a process similar to the one which is shown in Figure 4. However, the glycidation of amine is carried out by a two step procedure because: 1) the high reactivity of the basic nitrogen compared with that of the phenolic results in free amine reacting with the epoxide as it is formed, resulting in higher molecular weight or even gelled product; 2) having all the epichlorohydrin in contact with the amine could be a potentially explosive situation. Consequently, the manufacture of glycidylamines is carried out in two steps as shown in Figure 5. Even so the advancement process occurs during the epichlorohydrin addition, and is proposed due to reaction of the chlorohydrin with free amine as shown in Figure 6.

As can be seen, even such well established technology as the manufacture of epoxy resins could still be further improved. For example, the preparation of pure monomeric species by the direct epoxidation of the corresponding allylether or allyamine would possibly avoid the problem of advancement during manufacture. Such a route would require essentially complete conversion of the allyl group to an epoxide, but would result in high functionality resin having no residual chlorohydrin or other chlorine containing groups.

CURING AND CURING AGENTS

Epoxy resins are reactive intermediates composed, as we have seen, of a mixture of oligomeric materials containing one or more epoxy groups per molecule. To convert epoxy resins into useful products they must be *cured* or crosslinked by chemical reaction into a three-dimensional network. Crosslinking agents or curing agents, as they are also called, function by reacting with or causing the reaction of the epoxide. The two principal classes of curing agents used in aerospace epoxy resin composites are aromatic diamines and anhydrides. Figures 7 and 8 give the structures and properties of several of the more commonly used aromatic diamine and anhydride curing agents.

Probably the most widely recognized property of cured epoxy resin systems is their excellent adhesion to a very broad range of substrates and reinforcements. A contributing factor to this end is the low shrinkage exhibited by epoxy resin systems during cure, which results in lower stress levels in the composite than is found in other polymer systems with higher shrinkage. Another factor contributing to the excellent strength of articles produced from epoxy resins is that no by-products are formed during cure. Thus, there are no volatiles liberated that can lead to voids, nor are there non-volatiles generated that can act as plasticizers.

As we will see, anhydrides and aromatic amines also are used extensively in high performance resins other than epoxy resins. The ability to place amine groups in a specific position in an aromatic molecule could be of great value as would a similar capability for preparing anhydrides.

BISMALEIMIDES

INTRODUCTION

Bismaleimides are receiving considerable attention as matrix resins for both electrical laminates and high performance aircraft/aerospace structures. Bismaleimides are now the apparent leading candidate for the intermediate and high temperature advanced composite market. That is, they have improved thermomechanical properties over many epoxy resins and phenolics, but retain the good processing characteristics of epoxy resin systems. They have less temperature capability, however, than resins which are more difficult to process such as the PMRs (*in situ* polymerization of monomeric reactants) and LARC-TPIs (*linear aromatic condensation thermoplastic polyimides*). The principal advantages of the BMI's over epoxy resins are: 1) improved environmental resistance at high temperatures 300° to 500°F, 2) improved hot/wet resistance, 3) improved dielectric properties, and 4) resistance to burning and low smoke generation. Also like epoxy resins, bismaleimides release no volatiles on curing, but they result in brittle materials that have a tendency to microcrack.

In Figure 9 are given the structures of some typical maleimides and bismaleimides. Pure bismaleimides, generally, are high melting solids and cannot be directly melt processed into prepreg having tack and drape. Most commercial bismaleimides are systems based on eutectic mixtures or systems where the maleimide double bond has been prereacted with groups such as amines, hydrazides or cyanates to provide prepolymers with lower melting transitions and improved solubility. These bismaleimides may then be formulated with reactive non-volatile resins and liquids which serve as diluents, tougheners and curing catalysts, and serve to make the resins more melt processable. The compositions of some commercial bismaleimides are given in Figures 10, and 11.

Currently, world wide consumption of bismaleimides is between about 1.5 and 2.0 million pounds per year at prices of about \$25 to \$50 dollars per pound. About half of the total is sold as neat or formulated neat resin and the other half as blends with epoxy resin, dicyanates, or other resins.

MANUFACTURE

The usual method of preparation of bismaleimides is from the reaction of maleic anhydride and a diamine. As shown in Figure 12, a bismaleimic acid is initially formed as an intermediate which can undergo cyclodehydration at temperatures of 40-50°C in acetone solvent containing acetic anhydride as a water scavenger. Although not as effective, bismaleimides can also be obtained by a one step thermal cyclodehydration process in acetic acid. It should be obvious that a larger number of bismaleimides are possible by simply varying the structure and molecular weight of the diamine.

CURING AND CURING AGENTS

The double bond of the maleimide is very reactive and can undergo thermal, free radical, and anionic initiated homopolymerization as well as free radical initiated copolymerization with vinyl monomers. The maleimide double bond will also react with the allyl groups in materials such as diallyl bisphenol A and triallyl cyanurate.

The double bonds of bismaleimides can also react with nucleophilic reagents. In particular, primary and secondary amines have been used to chain extend bismaleimides. This reaction known as the Michael addition, is used to prepare the commercially available materials shown in Figures 10 and 11. The variety of bismaleimides and diamines has afforded a large number of commercial bismaleimide systems. These chain extended materials generally have improved processing characteristics and performance over the unmodified bismaleimides.

PMR POLYIMIDES

INTRODUCTION

Polyimides obtained by the reaction of dianhydrides and aromatic diamines as shown in Figure 13 provide thermally stable polymers with a good balance of physical properties. However, the polyamic acid precursor has two shortcomings, hydrolytic instability and the evolution of cure volatiles. Development of polymer precursors capable of curing by addition polymerization known as PMR (for *in situ* polymerization of monomer reactants) polyimides have solved some of these problems. PMR type polyimide composites are finding application in aircraft/aerospace structural components, particularly aeropropulsion structural components where good thermal stability is required. Parts ranging from small compression bearings to large autoclave molded aircraft engine cowls and ducts are being fabricated from materials of this type.

CURING

The first such material, P13N (with P for polyimide, 13 for number average molecular weight of ca. 1300 g/mole and N for nadic end cap), is shown in Figure 14. The PMR concept is shown in Figure 15, and consists of impregnating the reinforcing fibers with a monomer solution mixture dissolved in a low boiling alcohol. The monomers are essentially unreactive at room temperature, but undergo sequential *in situ* condensation and ring opening addition crosslinking reactions at elevated temperatures to form a polyimide matrix.

THERMOPLASTICS

Thermoplastics have over the past few years received considerable attention as matrix resins for aircraft/aerospace composites. Many new high performance thermoplastic materials have been developed offering a balance of chemical, physical, and mechanical properties that make them very attractive for composite applications. Also they offer the potential advantage in composites of low cost manufacturing of fabricated parts. There are already a number of high performance thermoplastics such as polyimides, polyarylene ethers, and polyesters that are commercially available. The structures of three new high performance thermoplastics are given in Figure 16.

The three examples of commercial high performance thermoplastics, Ultem (General Electric), PEEK (ICI), and Xydar (Dart Industries), given in Figure 16 are but a few of the high performance thermoplastics available. Total volume in terms of pounds for all high performance thermoplastics is currently around 15 to 17 million pounds per year with selling prices ranging from \$2.00 to \$90.00 per pound.

There have been over the years many different thermoplastics examined that have not reached commercial success and there a great many more that are currently being evaluated by one research group or another. A great majority of these materials are condensation type polymers based on difunctional reactive intermediates such as bisphenols, aromatic diamines, aromatic dianhydrides, and other types of difunctional reactive intermediates.

CONCLUSIONS

The foregoing is a brief overview of the principal commercial materials being used for high performance aircraft/aerospace matrix resin. A common thread that runs through all of this is, that many of the same type building blocks are employed over and over again in these high performance thermoset and thermoplastic. Some of these building blocks such as hydroquinone, bisphenol A, m-phenylene diamine, methylene dianiline, nadic methyl anhydride, and maleic anhydride are commodity chemicals or are relatively inexpensive. However, for many more of these intermediates they are obtained from difficult multistep synthetic procedures with low overall yields. Perhaps, biotechnology can provide more efficient, less costly routes to some of these classes of materials and with greater purity than currently achievable.

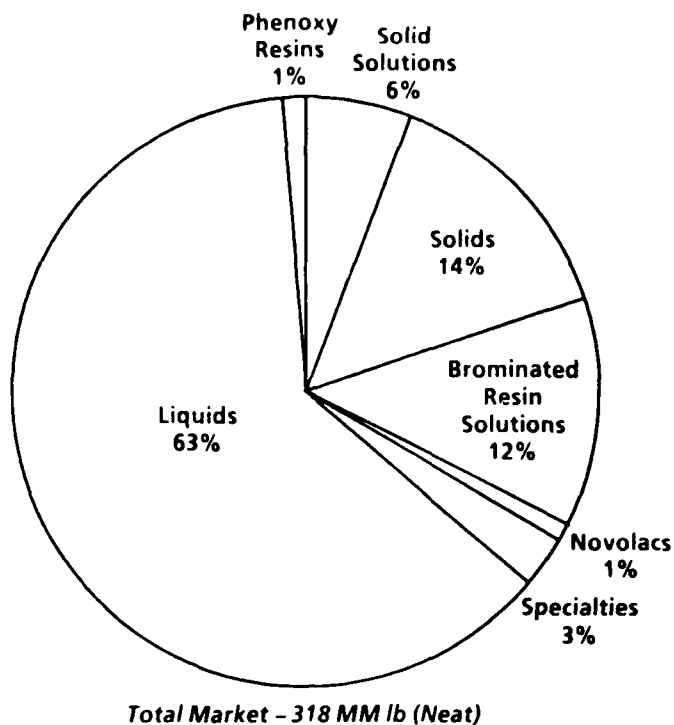
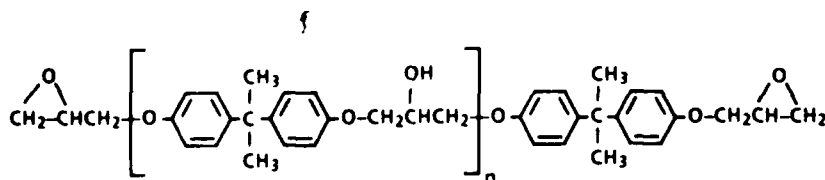


Figure 1. Epoxy Resin Domestic Demand By Product - 1986

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Typical Properties of Selected Liquid Epoxy Resins

Approximate Average Molecular Weight, Mn	Typical EEW Range	Typical Viscosity Range, Poise, 25°C
340	172-178a)	40-60
350	178-186b)	65-95
370	185-192c)	110-150

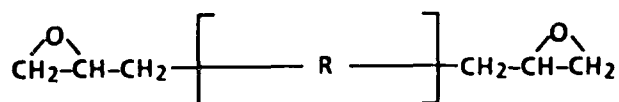
Examples of Commercial Resins

- a) EPON[®] Resin 825, EPI-REZ[®] 508, D.E.R. 332
- b) EPON Resin 826, EPI-REZ 509, ARALDITE 6015, D.E.R. 330
- c) EPON Resin 828, EPI-REZ 510, ARALDITE 6010, D.E.R. 331

EPON is a trademark of Shell Chemical Company.
 EPI-REZ is a trademark of Interez, Inc.
 ARALDITE is a trademark of Ciba-Geigy Corporation.
 D.E.R. is a trademark of Dow Chemical Company.

Figure 2. Structure and Typical Properties of Liquid Bisphenol A Based Epoxy Resins

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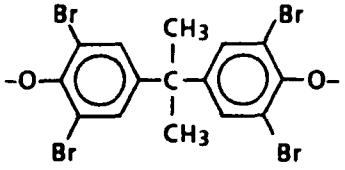
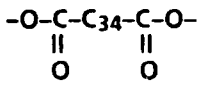
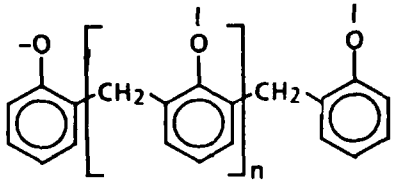
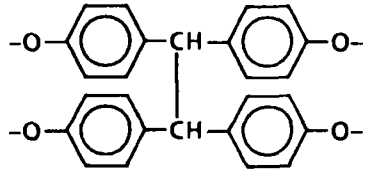
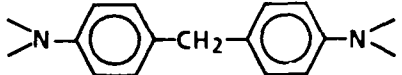
Type		Function
Tetrabromo-BPA		Fire Retardant
Dimer Acid		Flexibility
Polyglycols	$-\text{O}-\left[\text{CH}_2-\text{CH}_2\right]_n-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-$	Flexibility
Novolac		High Performance Resins
Tetraphenol Ethane		
Methylene Dianiline		

Figure 3. Specialty Epoxy Resins

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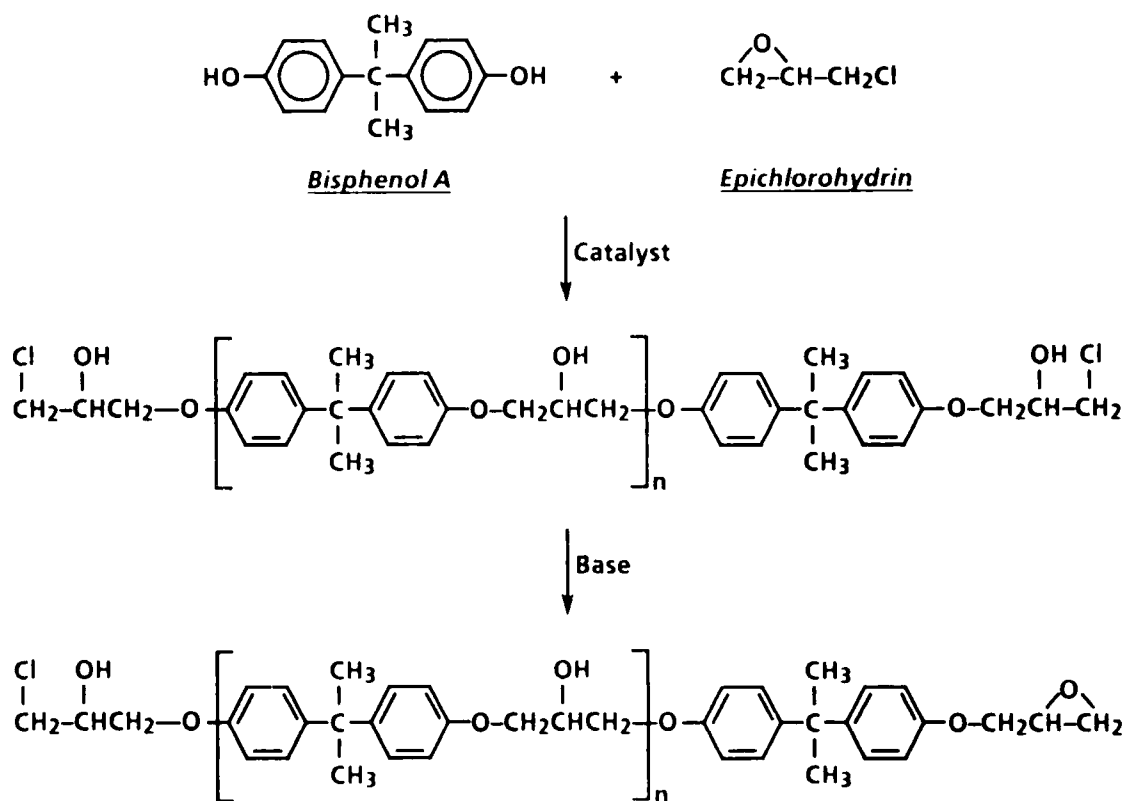


Figure 4. Manufacturing Scheme for Liquid Epoxy Resins (Conventional Resin)

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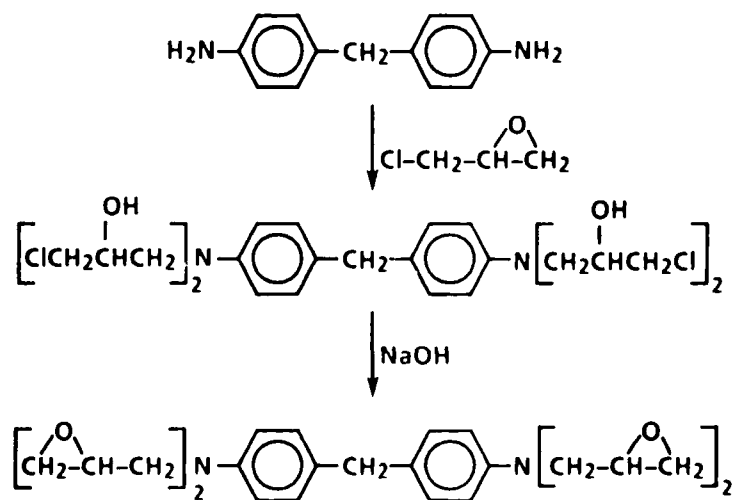


Figure 5. Idealized Manufacturing Scheme for TGMDA

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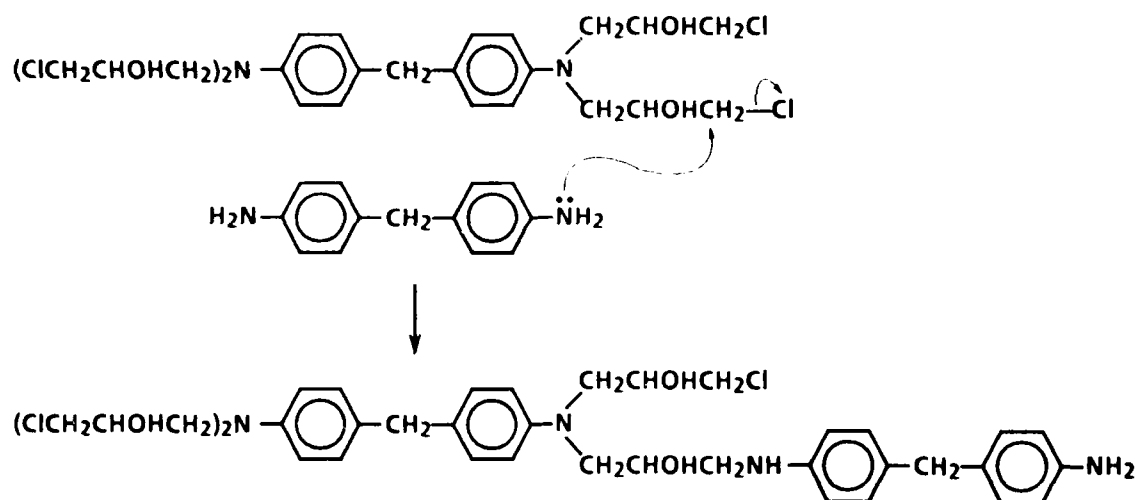
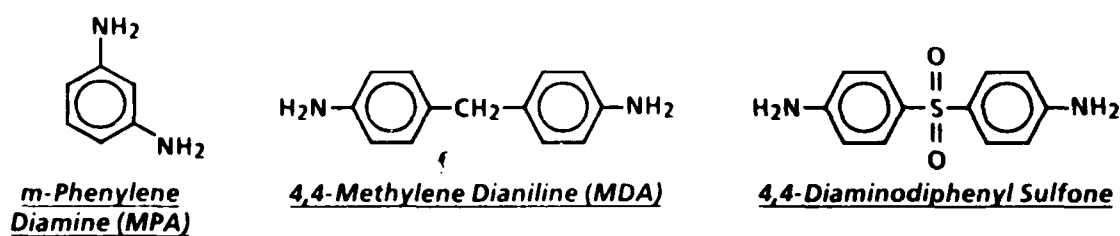


Figure 6. Proposed Scheme for Advancement of TGMDA During Manufacture

M. R. Thoseby, B. Dobinson, and C. H. Bull, *Brit. Polym. Jour.* **18**, 286-291 (1986).

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Amine	Physical State	Equivalent Weight	Usage, phr	Maximum DT ^{a)}
m-Phenylene Diamine	Solid MP, 62-63°C	27	14	150
4,4'-Methylene Dianiline	Solid MP, 92°C	50	27	155
4,4'-Diaminodiphenyl Sulfone	Solid MP, 176°C	62	18	176
Proprietary Amine No. 1	Liquid Viscosity at 25°C 5-20 Poises	48	25	162
Proprietary Amine No. 2	Liquid Viscosity at 25°C 15-40 Poises	38	20	149

a) Deflection temperature obtained with a resin having an EEW = 190 and using the level of curing agent in the usage column.

Figure 7. Structure and Characteristics of Selected Aromatic Diamine Curing Agents

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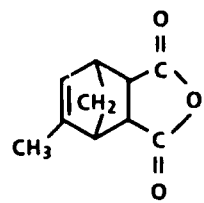
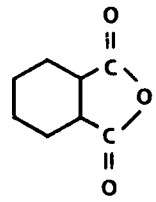
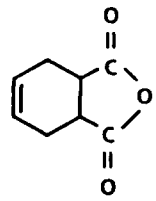
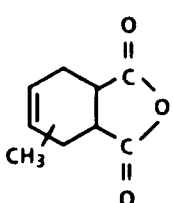
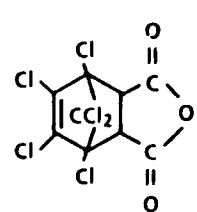
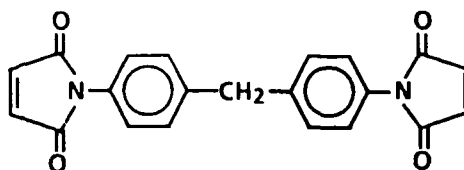
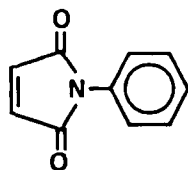
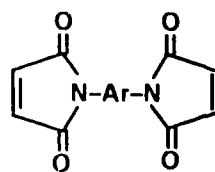
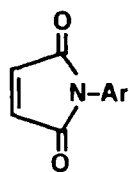
<u>Structure/Name</u>	<u>Physical State</u>	<u>Recommended Optimum Concentration Range (phr)</u>
 Nadic Methyl Anhydride (NMA)	Liquid	80-90
 Hexahydrophthalic Anhydride (HHPA)	Solid (m.p. 35°C)	75-85
 Tetrahydrophthalic Anhydride (THPA)	Solid (m.p. 101-102°C)	75-85
 Methyltetrahydrophthalic Anhydride (MTHPA)	Liquid	75-80
 Chlorendic Anhydride (CA)	Solid (m.p. ~230°C)	100-117

Figure 8. Selected Acid Anhydride Curing Agents

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N-Phenylmaleimide

N,N'-Bismaleimido-4,4'-Diphenylmethane

Figure 9. Maleimides and Bismaleimides

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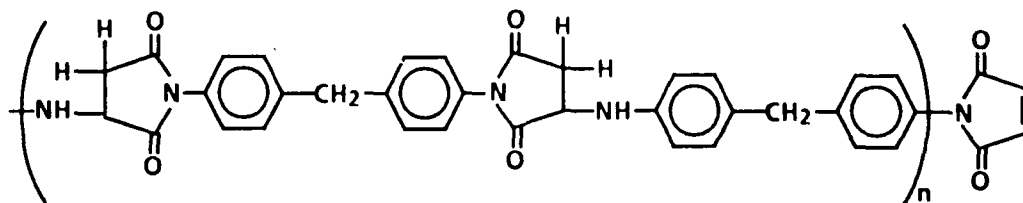
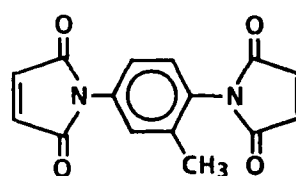
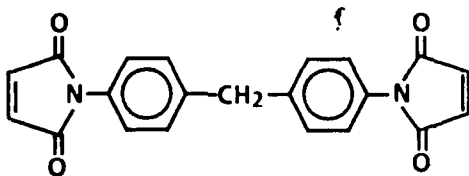


Figure 10. Composition of Keramid 601^{a)}

a) Trademark of Rhône-Poulenc

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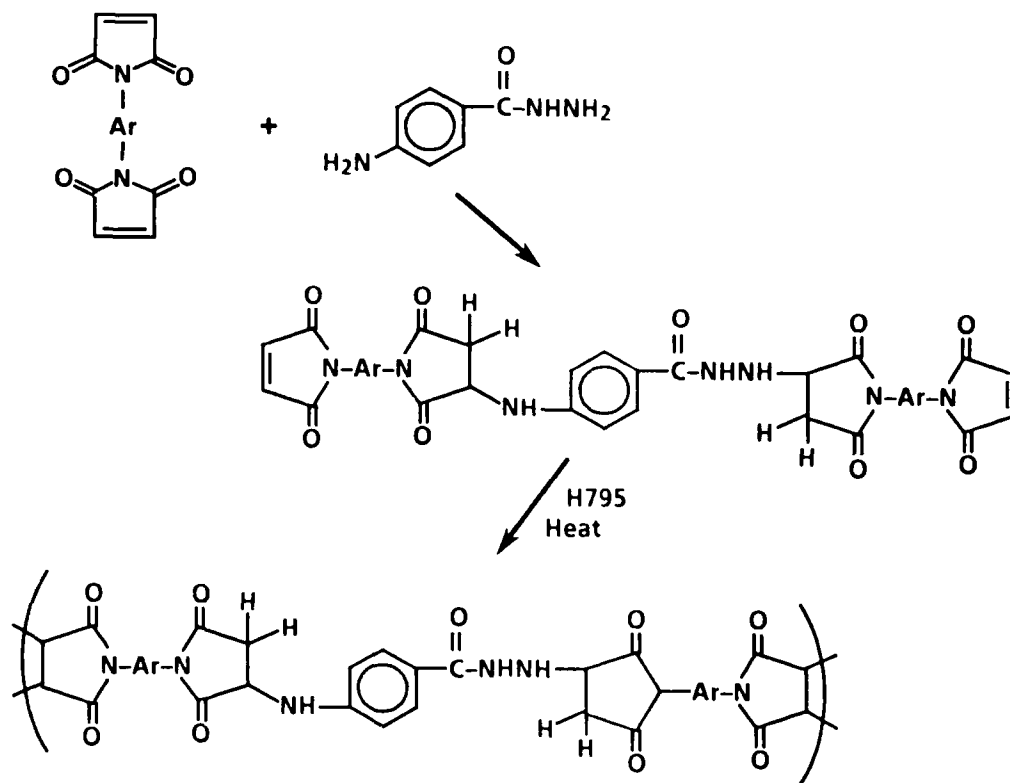


Figure 11. Bismaleimide (H795)
(Technochemie GmbH - West Germany)

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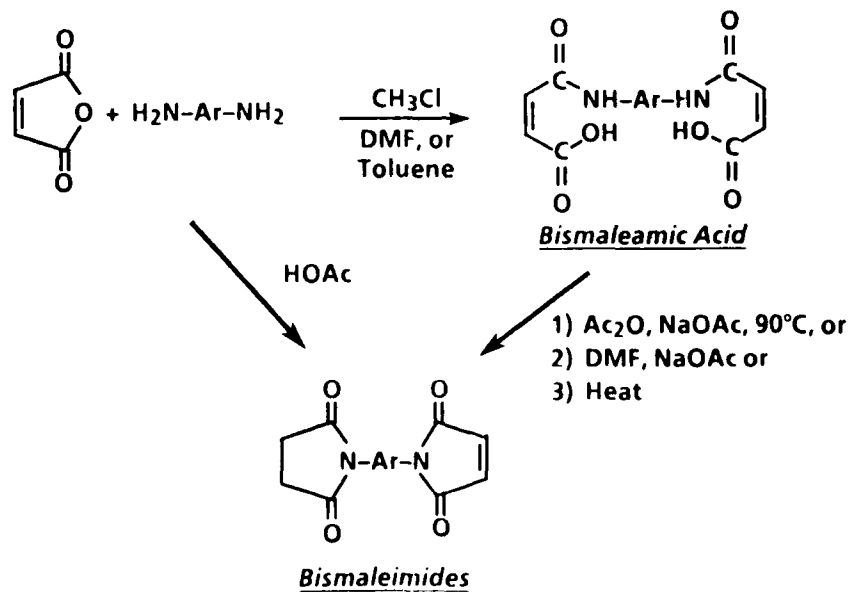


Figure 12. Synthesis of Bismaleimides

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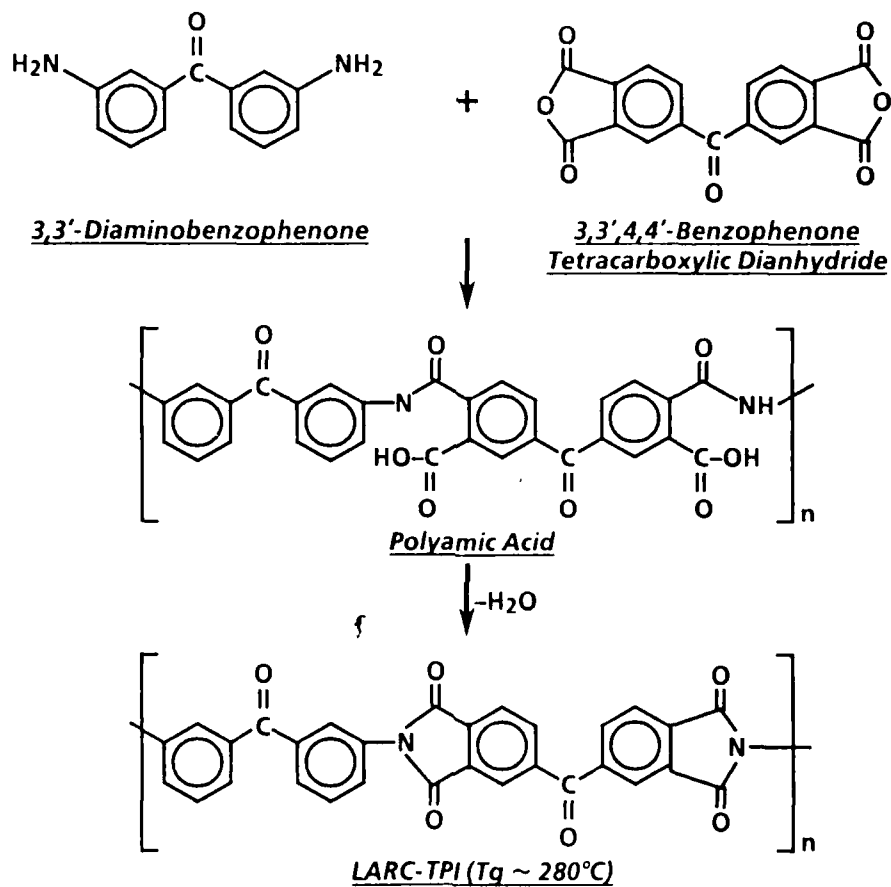
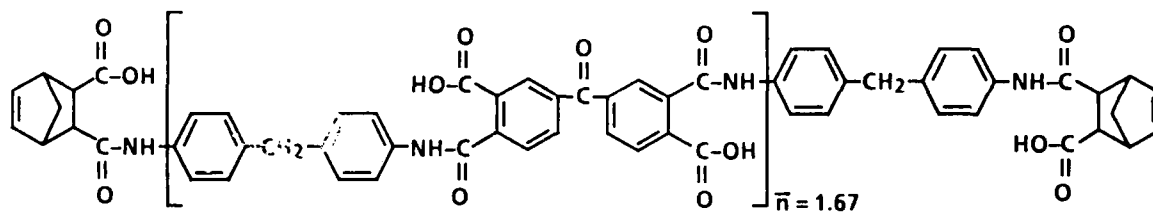


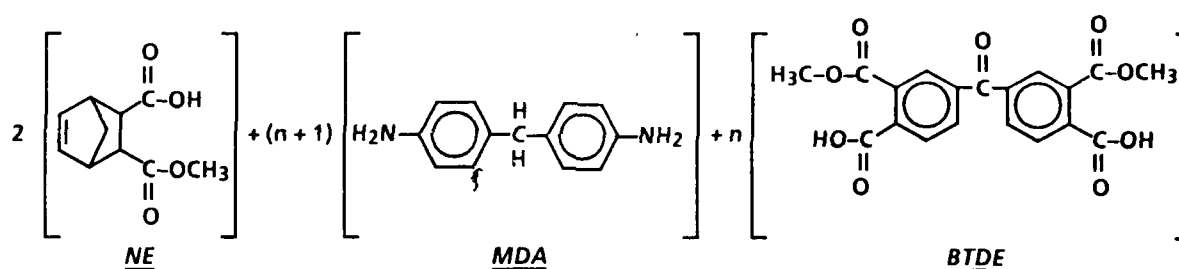
Figure 13. Synthesis Scheme for LARC-TPI

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Ciba-Geigy P13N
Amic Acid Solution in NMP

S. L. Kaplan, D. Helfand and S. S. Hirsh, SPI Tech Conf. Feb. 1972



Monomer Approach (PMR)

T. T. Serafini, P. Delvigs and G. R. Lightsey, J. Appl. Poly Sci. 16, (4), 1972
U.S. Patent 3,765,149, July 1973

Figure 14. Reverse Diels-Alder Addition Polyimides

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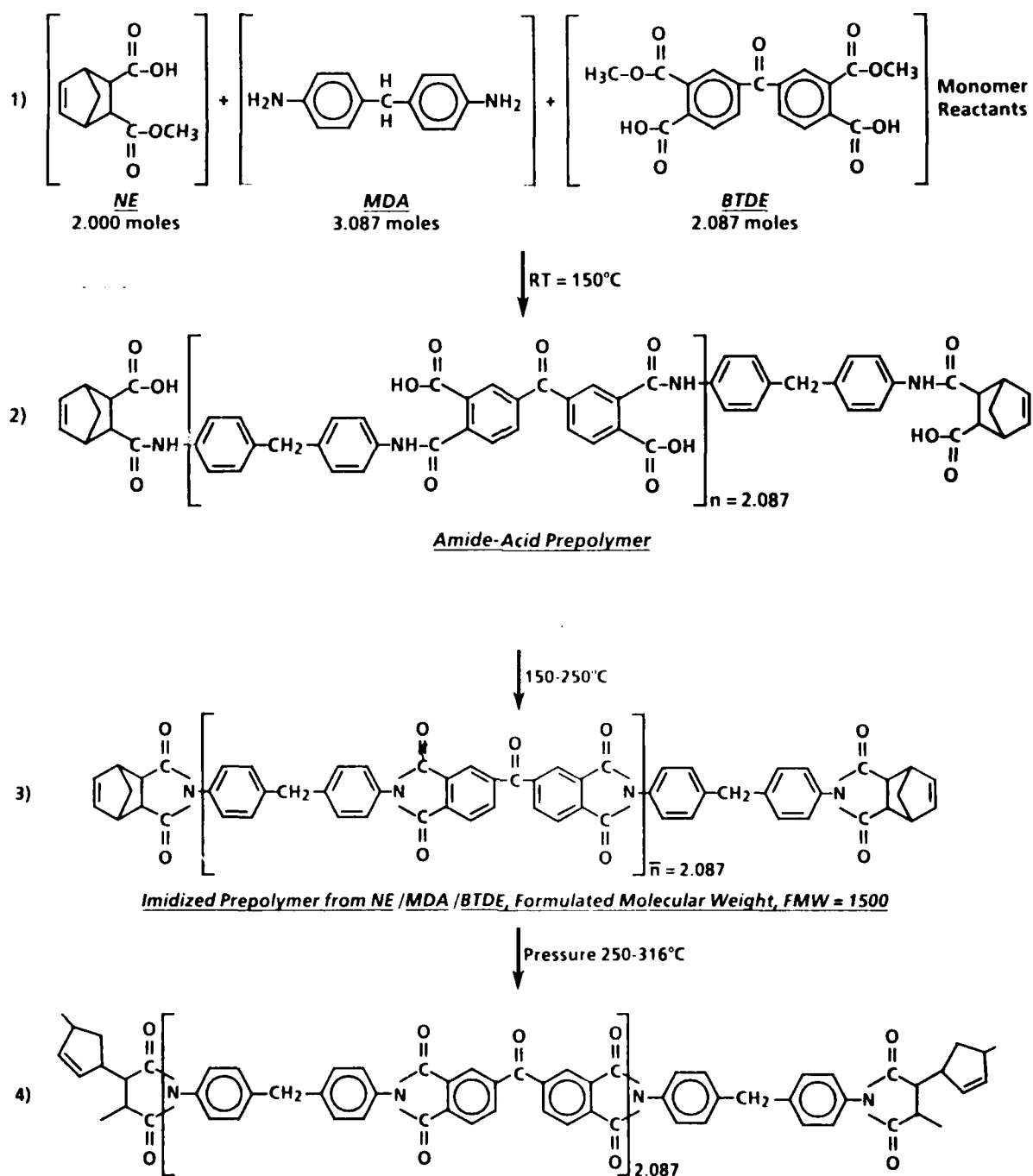
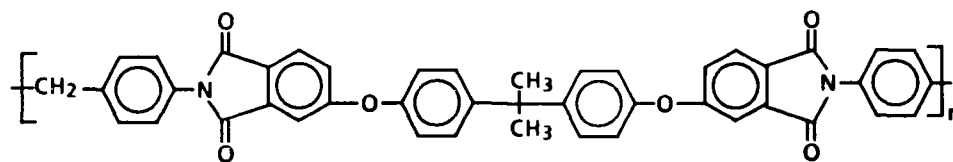
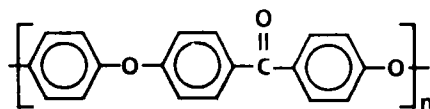


Figure 15. Reaction Scheme for PMR-15 Reverse Diels-Alder Maleimide

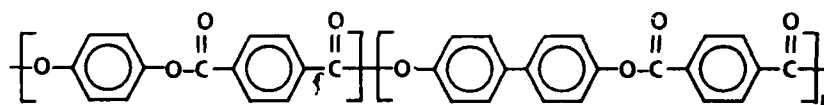
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Ultem



Polyetheretherketone (PEEK)



Xydar (Random Copolymer)

Figure 16. Selected Commercial High Performance Thermoplastics

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Applications of Biotechnology to Synthetic Chemistry for Aerospace Matrix Resins Development

Masato Tanabe

Biotechnology, among the oldest of man's technologies, uses microorganisms as well as higher cells and their active principles, with the aim of achieving desirable conversions of various substrates. Recently, biotechnology has captured scientific, commercial, and public attention because of the wide scope of materials--such as pharmaceuticals, foodstuffs, and commodity chemicals--that can be obtained through its use.

Advances in the constituent sciences of biotechnology (molecular biology, microbiology, genetics, biochemistry, physiology and bio-organic chemistry) have contributed to better understanding of, and greater ability to regulate and manipulate, living systems to produce biomaterials. These desirable products of biotechnology are produced as pure compounds, mixtures, cell fractions, or biomass. They can be either homogenous or heterogenous chemical structures that result from de novo formation or by transformation or degradation of substrates by the living cells. These bioproducts are produced by either a single biochemical reaction or by multistep processes, and they account for essentially the chemical nature of biotechnology.

The most understood, studied and applied area of biotechnology is the use of single cell or microorganisms to mediate biochemical reactions. This technology has been applied to man's needs since antiquity. The ability of microorganisms to produce these desired metabolites is primarily due to the catalytic activity of their enzymes. Microorganisms employ both constitutive and inducible enzymes. These metabolites are produced to benefit the organisms viability and reproduction. Each reaction is catalyzed by a particular enzyme in a highly complex and well-coordinated metabolic pathway. In addition to their usual natural substrates, many of these enzymes accept

Masato Tanabe, Director, Bio-Organic Chemistry Laboratory, SRI
International, 333 Ravenswood Avenue, Menlo Park, CA 94025

other structurally related compounds and thus catalyze unnatural reactions when foreign substrates are added to the fermentation medium. These reaction products can usually be isolated from the medium. Such chemical reactions mediated by microorganisms or their enzyme preparations are called biotransformations. They should be viewed as selective enzymatic modifications of a well-defined pure compound into a defined final product.

Microorganisms are capable of catalyzing many diverse types of chemical reactions. This synthetic diversity is exemplified by the general reaction types shown in Table 1, which lists reactions mediated by microorganisms.

Table 1

REACTION TYPES MEDIATED BY MICROORGANISMS

Oxidations	Hydroxylation, epoxidation, dehydrogenation of C-C bonds; oxidation of alcohols and aldehydes; oxidation of amines; oxidative degradation of alkyl, carboxyalkyl, or ketoalkyl chains; oxidative removal of substituents; oxidative deamination; oxidation of hetero-functions; oxidative ring fission; amine N-oxides
Reductions	Reduction of organic acids, aldehydes, ketones and hydrogenation of C=C bonds; reduction of heterofunctions, dehydroxylation; reductive elimination of substituents
Hydrolysis	Hydrolysis of esters, amines, amides, lactones, ethers, lactams, etc.
Condensation	Dehydration; <u>O</u> - and <u>N</u> -acylation; glycosidation; esterification; lactonization; amination
Isomerization	Migration of double bonds or oxygen functions; racemization; rearrangements

Formation of C-C bonds or hetero-atom bonds

BIOTRANSFORMATION

Biotransformations have many useful characteristics for applications in synthetic chemistry. These characteristics, which are typical for enzyme-catalyzed reactions, include reaction specificity, regio specificity, stereospecificity, and mild reaction conditions, described below.

Reaction specificity. The catalytic activity is usually restricted to a single reaction type. This means that side reactions are not expected as long as one enzyme is involved in a biotransformation.

Regiospecificity. The substrate molecule is usually attacked at the same site even if several groups of equivalent or similar reactivity are present.

Stereospecificity. The reactive center of an enzyme provides an asymmetrical environment and distinguishes between the enantiomers of a racemic substrate. Therefore, only one--or at least preferentially one--of the enantiomers is attacked. On the other hand, if an enzyme reaction produces a new asymmetric center, usually only one of the possible enantiomers is formed and the product is therefore optically active.

Mild reaction conditions. Activation energy of chemical reactions is distinctly lowered by the interaction of substrate and enzyme, and thus biotransformations take place under mild conditions (temperature below 40°C, pH near neutrality, normal pressure). Therefore, even labile molecules can be converted using low energy consumption without undesired decomposition or isomerization.

Because of the above properties, biotransformations provide a method for carrying out synthetic reaction steps that are frequently difficult to accomplish by chemical methods.

With these characteristics and properties, clearly the application of microorganisms and biotransformations to the solution of synthetic problems of organic chemistry will grow in importance. Many biotransformations offer unique synthetic transformations. In planning synthetic strategy, enzymes and biotransformations should be regarded as one more type of catalyst and integrated into the available techniques of classical organic synthesis.

Biotransformations are also well suited for solving problems in organic synthesis because the large-scale production of microbial cells is possible, unrestricted by location or seasonal factors. The production time to produce microbial cells is relatively short and the cost of producing them is comparatively low because the fermentation nutrients are commodity items (cornsteep liquor, glucose, yeast extract, etc.).

Continuing advances in biosynthetic theory focused on:

- Primary, secondary metabolism and biochemical differentiation.
- Biosynthesis, metabolism and regulation.

- Polyacetate derived metabolites.
- The shikimate pathway and its stereochemistry.
- Mealonate derived natural products.
- Stereochemistry and enzymology of biological reactions.
- Developing methodology for elucidating metabolic pathways.

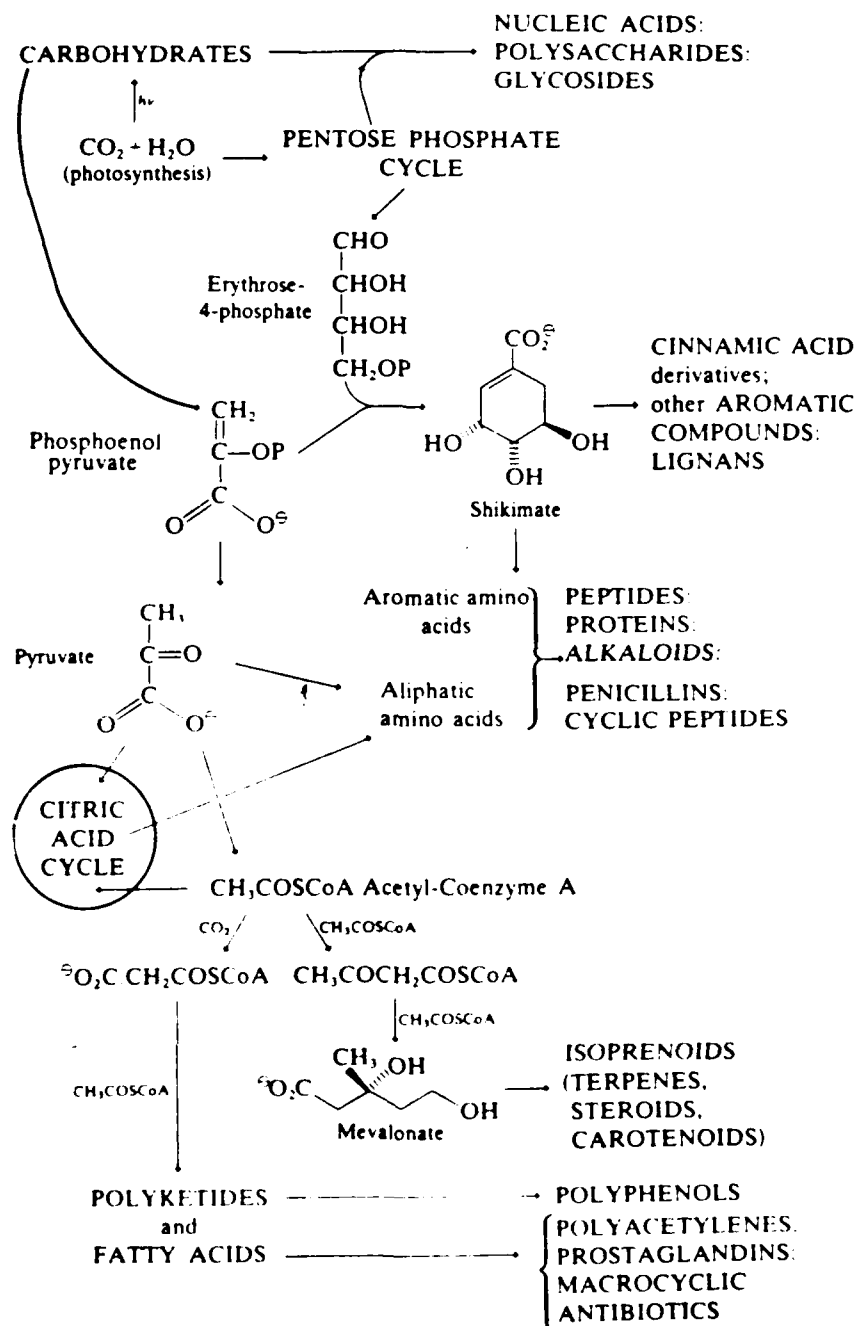
Will facilitate and enhance the use of enzyme systems in organic synthesis.

This presentation will focus on the potential use of the enzymes from primary or secondary metabolism (Chart 1) that are either constitutive or induced enzyme systems available from mammalian, microbial or plant sources.

In discussing "Biotechnology in Synthetic Chemistry and its Applications to Resin Chemistry", several areas will be examined including:

- Material Cost Reduction Through Biosynthesis
 - Bioproducts as chemical intermediates
 - Bioreactions on non-biological molecules
- Materials Not Otherwise Obtainable
 - Bioproducts for direct use
- Learning the Mechanism of a Biophenomenon (Biosynthesis) and Mimic the Process in Non-Biological System
 - Enzyme mimics and models
 - Biomimetic synthesis
- What is Feasible Today - Tomorrow

CHART 1
ENZYMES FROM PRIMARY AND SECONDARY METABOLISM



The Application of Hydrocarbon Bioconversion Technology to Aerospace Materials Production

Ronald J. Huss, Ph.D.
and
Paul E. Swanson, Ph.D.

Bio-Technical Resources, Inc.
1035 South Seventh Street
Manitowoc, Wisconsin 54220

Introduction to Bio-Technical Resources, Inc.

Bio-Technical Resources, Inc. (BTR) is a 25 year old, privately held biotechnology company with its origin in the malting and brewing industries. The primary business has evolved into product and process development for the fermentation, pharmaceutical, chemical, and food industries. The staff consists of approximately twenty scientists and engineers in the fields of microbiology, biochemistry, and chemistry working to develop industrial fermentation systems and biotechnical processes.

BTR is capable of conducting a research program from the conception of an idea for a product or process through scale-up into 250-liter bioreactors. Preceding the initiation of any research program, a detailed technical and economic feasibility analysis is performed. This analysis identifies technical objectives, estimates time required to achieve the objectives, and estimates the economics of existing and alternative technologies.

A typical research program may include all or some of the following components: 1) the conception of an idea for a product or process, (2) estimation of the economic and technical feasibility of the idea, 3) identification of technical and economic objectives, 4) establishment of a work plan, 5) development of analytical methods, 6) initial screening of microorganisms or enzymes for a specific product or process, 7) strain improvement to increase yields and rates, 8) fermentation or other bioprocess development, and 9) scale-up of the process into 1-, 14-, or 250-liter bioreactors.

Research Interests

BTR currently has research interests in widely diverse areas:

1. Development of fermentation processes for specialty chemicals from carbohydrates.
2. Pioneering the application of heterotrophically-grown green microalgae as industrial microorganisms to produce specialty chemicals.
3. Hydrocarbon bioconversions.
4. Application of biological processes to the mining, metallurgical, and catalyst industries.
5. Development of a fermented malt (beer) flavor.

This talk will highlight BTR's past experience, current research programs, and future expectations in the area of hydrocarbon bioconversions.

Hydrocarbon Bioconversion Experience

BTR has been involved in a number of hydrocarbon bioconversion research programs. Some of these can be discussed in detail because the information has been published in the form of patents. Others can only be discussed in general terms due to the proprietary nature of the research.

United States Patent Number 3,773,021 is a "Process for the Biological Production of Alpha, Omega-Alkanedioic Acid." This patent describes the medium composition, the culturing conditions of the bacterium used, the use of a mixture of branched saturated aliphatic hydrocarbons as an inducer, the use of emulsifiers, and the environmental conditions of an aerobic fermentation process. The bacterium developed to perform the bioconversion was originally assigned to the genus Corynebacterium, but has since been renamed Rhodococcus.

Mutants developed in a strain improvement program by a series of mutation and selection steps are on file with the American Type Culture Collection (ATCC). These strains convert n-alkanes of 10 to 14 carbons, typically dodecane, to the corresponding alpha, omega-alkanedioic acid, typically dodecanedioic acid, with high yields and conversions. Conversion is defined as the percentage amount in moles of the n-alkane consumed during fermentation by the bacterium without consideration of the product of the bioconversion. Yield is defined as the percentage amount in moles of the n-alkane converted which ends up as alpha, omega-alkanedioic acid. Yields were in the range of 30% to 40%. Final product concentrations were in the range of 30 to 45 g/liter.

The biochemical pathway for the omega-oxidation of hydrocarbons by bacteria consists of a series of single-step oxidations. The process begins at one terminus of the n-alkane with oxidation to a primary alcohol, then to an aldehyde, and finally to a carboxylic acid. Then the same series of oxidations proceed at the other terminus. This multiple step bioconversion requires oxygen and NAD^+ . Because of the multi-step nature of this bioconversion, the whole cell approach is the most technically feasible.

A typical fermentation process development program like the one described above consists of four phases: 1) a strain improvement program, 2) shake flask and enzymology studies, 3) pilot fermentation studies, and 4) bioreactor design. Strain improvement is accomplished by developing and using mutation/selection methods and other techniques to improve product yield and formation rate. Shake flask and enzymology studies are directed toward understanding and optimizing the mechanism of product formation and release. The pilot fermentation program is conducted to optimize product formation in higher-density cultures, and to determine optimum process conditions.

Another example of BTR's experience in hydrocarbon bioconversion was a fermentation development program to convert heptane to heptanoic acid. This conversion was performed by the bacterium, Pseudomonas aeruginosa. This program presented some unique challenges because of the requirement for adequate oxygen transfer without excessive evaporation of the substrate, heptane.

BTR was also involved in a fermentation development program for the bioconversion of a steroid. A microorganism was used to specifically hydroxylate a steroid.

BTR also has experience in the area of enzymatic bioconversions. B-Glucosidase normally catalyzes the hydrolysis of aromatic B-glucosides and cellobiose. Under appropriate conditions in the presence of alcohols it will catalyze the synthesis of alkyl glucosides. This research demonstrates the variety of technological approaches that can be applied to enzymatic conversions. Enzymatic conversion in nonaqueous systems can be utilized to reverse hydrolytic reactions, alter substrate specificity, and improve enzyme stability. Enzymes can be immobilized to enhance performance and stability. Enzyme stability can also be improved by covalent modification. Biphasic reaction systems, such as aqueous/aqueous, aqueous/nonaqueous, and reverse micelles in a nonaqueous system, can be used to take advantage of the partition coefficients of substrates, products, and enzymes.

Current Hydrocarbon Bioconversion Research

BTR is presently evaluating the technical feasibility of "A Biological Approach to the Synthesis of Meta-Hydroxy Phenylacetylene from Phenylacetylene." This research is sponsored by the Air Force through the Defense Small Business Innovation Research Program.

Acetylene-terminated resins are one of several candidate polymeric resins being considered for potential aerospace applications. The acetylene-terminated resins possess properties required for the proposed applications such as good mechanical properties, high thermal stability and good properties retention after exposure to moisture. A limiting factor for the commercial application of these resins is a cost-effective method for the synthesis of an essential constituent, meta-hydroxy phenylacetylene. Chemical approaches to the synthesis of this monomer have not resulted in an inexpensive product of acceptable quality.

The BTR research program proposes a biological approach to the problem. Two possible biological routes exist. One is an enzymatic approach. Commercially available enzymes such as horseradish peroxidase and lactoperoxidase will be screened for the ability to selectively hydroxylate phenylacetylene in the meta position under a variety of conditions. There is precedence in the literature for the selective enzymatic hydroxylation of aromatic compounds. The other biological approach is a microbial conversion. A variety of microorganisms will be screened for the ability to convert phenylacetylene to meta-hydroxy phenylacetylene. There are numerous examples in the literature of microbial hydroxylations of substituted aromatic compounds, especially by the Pseudomonads. The objective of this research program is to evaluate the two bioconversion systems, microbial and enzymatic, to determine which warrants further development.

Biotechnology-Assisted Chemical Synthesis

The following section summarizes BTR's interests in the area of biotechnology-assisted chemical synthesis.

The technology developed by the current research program to evaluate biological routes for the meta-hydroxylation of phenylacetylene will be applied to other substrates. In general, advantage will be taken of the low substrate specificity of some enzymes to apply technology developed for the specific bioconversion of a specific compound to the specific bioconversion of a general class of compounds. In this case, technology developed for the meta-hydroxylation of phenylacetylene will be evaluated with respect to the specific hydroxylation of other aromatic compounds.

Through its experience with heterotrophically-grown green microalgae, BTR has learned the value of evaluating unique gene pools for products or processes of interest. This same philosophy can be applied to hydrocarbon bioconversions. Enzyme or whole cell systems may already exist for some of the products and processes of interest in the area of hydrocarbon bioconversions. Through screening programs and basic biochemical research, these products and processes may be identified.

Bioconversion systems should be used to supplement and not compete with existing efficient organic synthetic methods. Biological methods should be used when they afford the opportunity for lowering costs of starting materials, are able to shorten a synthetic route, or are capable of reducing multiple step reactions to a single, more economical step.

Enzymes with unique catalytic properties may find application in difficult synthetic reactions. If enantiomeric specificity is required, an enzymatic system may provide a more direct approach than an organic synthetic method. Bioconversion systems may also find application in situations in which mild reaction conditions are required to protect reactive groups or labile compounds. Typically, biological systems operate optimally at moderate temperature, pH and pressure. Reactions at unactivated sites, such as steroid hydroxylations, may be better performed biologically. Nonaqueous enzymology may be used to alter substrate specificity or catalyze "reverse" enzymatic reactions, such as transesterifications.

A continuous dialog between the biotechnology and aerospace materials communities will identify areas in which biotechnology might provide chemical intermediates or catalytic processes which could impact aerospace composites.

THE SYNTHESIS OF POLYPHENYLENE FROM A CIS-DIHYDROCATECHOL
BIOLOGICALLY PRODUCED MONOMER

D G H Ballard, A Courtis, I M Shirley, *S C Taylor

ABSTRACT: Benzene is oxidised by oxygen utilising the dioxygenase enzyme contained in the microorganism Pseudomonas Putida. Genetic manipulation produced a variant which gave exclusively the initial oxidation product of benzene the cis-dihydrocatechol (2) in practical quantities. Derivatives of the latter, in particular the methyl carbonate can be obtained pure and are very stable. They polymerise in the absence of solvent with radical initiators to give a polymer (4). The latter is soluble in solvents such as acetone and methylene chloride and readily forms coherent coatings and films. On heating methanol and CO₂ are expelled and polyphenylene is formed as a coating or film. The aromatisation process is catalysed by bases and can occur well below the glass transition temperature of the precursor polymer of 192°C. The aromatisation can occur under homogeneous conditions in the basic solvent N-methyl pyrrolidone. Surprisingly, these partially aromatised molecules are soluble even at conversion to 30% phenyl groups. The latter studies can be used to measure the glass transition of polyphenylene which was found to be 283°C.

Neutron Scattering studies have shown that the precursor polymer is a random coil. Viscosity measurements show that there is a coil-rod transition on aromatisation in N-methyl pyrrolidone. Crystallographic data on polyphenylene crystallised above its glass-transition and the thermal and electrical properties are described.

INTRODUCTION

The majority of linear polymers containing the aromatic nucleus are synthesised using polycondensation techniques. Examples include poly(ethylene terephthalate) (PET) poly(terephthalamide) (Kevlar) poly(phenylene ether sulphone) (PES) poly(phenylene ether ether ketone) (PEEK) etc.

NB

ICI PLC, New Science Group, The Heath, Warrington, Cheshire, England

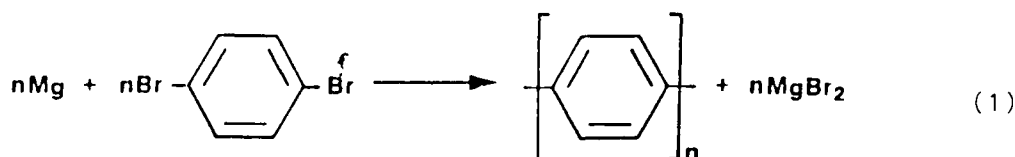
*ICI Biological Products Business, P.O. Box 1, Billingham, Cleveland

An advantage to this synthetic route is that molecular fragments joining the aromatic nuclei can be chosen so as to give melt processability. The disadvantage to this method of synthesis is that the molecular fragments joining the phenyl groups are more susceptible to thermal, oxidative and photochemical attack. These facts have been extensively debated over the last twenty years and form part of the knowledge built up on the relationship between molecular structure and stability in polyaromatic materials. The expectation is that polyphenylene would be the most thermally stable structure of all the linear polyaromatics and consequently various attempts have been made to synthesise this material.

One route to polyphenylene is the direct polymerisation of benzene using a technique developed by P Kovacic and others, ^{1,2,3}. The process is known as an oxidative-cathodic polymerisation and requires large quantities of cupric chloride.

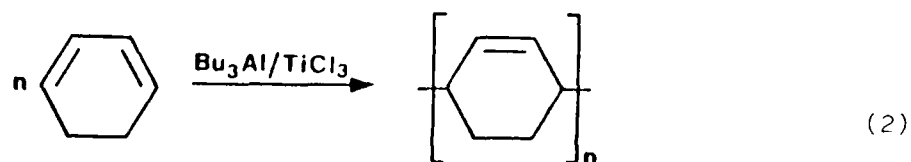
The precise structure of the polymer produced is not known but contains a mixture of 1:2 and 1:4 units plus chemical defects³. The products are more correctly defined as oligomers rather than polymers since the chain lengths are between 10 and 15 phenylene residues. Moreover, it is difficult to remove completely all the CuCl₂ from what is rather an intractable solid. Notwithstanding these criticisms this is a successful route to polyphenylene and powders are produced which can be fabricated by sintering techniques into various shapes².

A second synthesis of polyphenylene is that due to Yamamoto⁴ in which p-dibromobenzene polymerises in the presence of magnesium



using a nickel catalyst. This is one of the few examples of Grignard chemistry being used directly to form a macromolecule. Molecular weight measurements indicate that the growth does not go beyond 10 to 12 phenylene residues. This is because the polymer separates as a crystalline solid and further polymerisation to higher molecular weight is not possible.

An early attempt to use polymers of cyclohexadiene as a route to polyphenylene was by Marvel and coworkers^{5,6,7,8} and involved the direct polymerisation of cyclohexa-1,3-diene using a Ziegler catalyst. This produced poly(cyclohexene) containing 1:4 and 1:2 units.

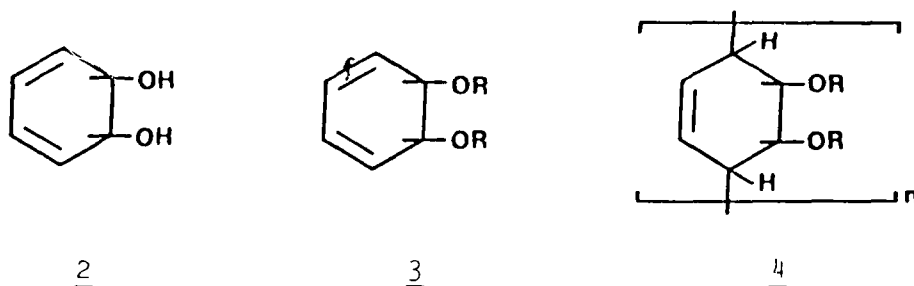


Aromatisation of polymers with structure 1 was attempted by reacting it with bromine followed by pyrolysis to eliminate HBr.

The purity of the products formed by this method is highly suspect as there are a number of bromo-substituted intermediates that might be formed and aromatisation would be incomplete. Furthermore, the fact that reactants and potential products are both insoluble in solvents makes control of the chemistry difficult.

An additional complication is having HBr as the leaving group. Readdition of the latter to unsaturated intermediates formed in the reaction is possible. It is doubtful therefore that this route ever produced "clean" polyphenylene. It is more likely that the structure consisted of small numbers of the fully aromatised molecules admixed with partially aromatised segments.

This paper describes the synthesis of 5,6-cis-dihydroxycyclohexa-1,3-diene (DHCD) 2, the study of the polymerisation of its derivatives 3 and the conversion of the polymers formed 4 into polyphenylene



The advantage of this particular diene is that the polymer formed is soluble in a variety of solvents because of the presence of the solubilising group OR, where R can be CH_3CO , $\text{CH}_3\text{O.CO}$ etc. Moreover, on aromatisation the leaving group ROH is an organic acid which normally cannot add to an unsaturated hydrocarbon in the manner of HBr. Finally this possibility can be completely eliminated by using the methylcarbonic acid which at aromatisation temperatures decomposes into methanol and carbon dioxide.

Although it is possible to produce compounds of the type 2 by conventional organic chemistry, it is more economic to use microbial oxidation of aromatic hydrocarbons. The additional advantage to this route is that the 5,6-cis-dihydroxycyclohexa-1,3-diene formed is the only isomer. Moreover, derivatives of the latter are polymerisable whereas 5,6-trans-dihydroxycyclohexa-1,3-diene obtained by conventional synthetic organic chemistry polymerises with difficulty.

EXPERIMENTAL SECTION

Fermentation

DHCD was produced by the batch fermentation of *Pseudomonas putida* in an LKB 1601 fermenter with working volume of 3-4l. The cells were grown in a mineral salts medium with ethanol as carbon source. Temperature was maintained at 30°C and pH kept constant at 7.5 by automatic addition of NaOH or HCl. Benzene was supplied by passing the in-flowing air (1.2 l min^{-1}) through a round bottom flask containing benzene and the oxygen tension in the fermenter was maintained at 5% saturation by regulation of the relative amounts of air and oxygen added to the culture. The production of DHCD was monitored by the intensity of the UV absorbance at 260 nm. When accumulation reached the maximum level the culture was centrifuged to remove cell debris and the product extracted into methylene chloride using a continuous counter current extraction method. The methylene chloride solution was then concentrated under reduced pressure to a glycol concentration of 0.25 to 0.30 g ml⁻¹ and three times the volume of n-pentane slowly added to the warm solution. The DHCD crystallised out and was recovered by filtration. After washing with pentane the pure product was dried and stored at -40°C.

Derivatisation

The derivatisation of DHCD is exemplified by the synthesis of the diacetate, DHCD-DA. The diol (1.3 mol) was dissolved in pyridine (4.2 mol) in a round bottom flask and cooled to -10°C. Acetic anhydride (4.0 mol) was then added dropwise under nitrogen while maintaining the temperature below 0°C. After addition the reaction was left stirring at 0°C for one hour and then allowed to warm to room temperature. The product was concentrated by removing pyridine on a rotary evaporator at 40°C and the concentrate added to diethyl ether (800 mls) in a separating funnel. This solution was then washed three times with 300 ml aliquots of 10% aqueous sodium bicarbonate and three times with similar quantities of water. After drying over sodium sulphate the ether was removed by rotary evaporation to yield the DHCD-DA as a slightly yellow liquid. This was purified by fractional vacuum distillation at 70°C (0.1 mm Hg) to give product of 99.5% purity in 80% yield.

Bulk Polymerisation

Pure DHCD-DA (15g, 76.5 mmol) and azobisisobutyronitrile (53 mg, 0.32 mmol) AZBI initiator were placed in a 250 ml round bottom flask and degassed by pumping followed by flushing with nitrogen three times. The reaction mixture was then heated to 70°C and allowed to polymerise for 72 hours. The resulting solidified reaction mass was dissolved in chloroform (100 mls) with stirring and the polymer (12 g, 80% yield) recovered by precipitation into hexane (1 litre). The molecular weight of the polymer was determined by gel permeation chromatography (GPC) in chloroform solution using a refractive index detector and confirmed

by low angle laser light scattering, LALLS, using a Chromatix KMX6 instrument.

Polymerisation Kinetics

Most of the kinetic data was obtained for bulk polymerisations up to 10% conversion performed in dilatometer tubes. The monomer and initiator were simply mixed, degassed and poured into the dilatometer under nitrogen atmosphere. The variations of rate with initiator concentration and temperature were obtained in this way. Monomer dependence was determined by dilatometry of benzene solutions of the monomer using exactly the same experimental procedure.

Dispersion Polymerisation

Monomer (1.0g DHCD-PA), initiator (7 mg AIBN) and dispersomer (50 mg X190-242, a comb polymer with poly(methylmethacrylate) backbone and poly(12-hydroxystearic acid)/glycidyl methacrylate side chains in the ratio 2:1 supplied by ICI Paints Division, Slough, UK) were placed in a 50 ml round bottom flask and degassed three times. Heptane (7 mls) was then added and the mixture stirred under nitrogen at 80°C in a water bath. Polymerisation was continued for 48 hours and the polymer recovered by filtration.

Aromatisation

The aromatisation of the polymers of DHCD derivatives in the solid state was studied by thermogravimetric analysis (TGA) under nitrogen or in vacuo using a Perkin-Elmer TGS-2 instrument. Samples of the polymer were loaded into the machine and weight loss monitored as a function of temperature at a fixed heating rate, typically 10°C/min, or isothermally as a function of time at a given temperature, typically 300°C.

Aromatisation in solution was performed by heating the polymer (5% w/v) in N-methylpyrrolidone at 150-200°C. Aliquots were removed at appropriate intervals and quenched by precipitation into methanol. These samples were then characterized by GPC as described above, intrinsic viscosity at 30°C in chloroform, infra-red and TGA. The latter two techniques provide means of determining the degree of aromatisation of the polymer. In infra-red this is by comparison of the carbonyl absorption in the precursor monomer at 1750 cm^{-1} with the aromatic absorption of the resulting phenylene rings at 810 cm^{-1} . The only complication with this infra-red method occurs with the dimethylcarbonate derivative, DHCD-DMC, which shows an additional absorption of 1810 cm^{-1} appearing during the early stages of aromatisation and eventually disappearing again as aromatisation is completed. The peak at 1810 cm^{-1} is typical of a carbonyl absorption in a strained ring structure and the phenomenon has been interpreted as the formation of cyclic carbonate groups (see table 2) produced by the elimination of dimethylcarbonate. On further heating these groups aromatise with loss of water and carbon dioxide. TGA provides the weight loss to complete aromatisation and, by comparison with the

theoretically calculated result, an estimate of the degree of aromatisation occurring during the solution process can be made.

Crystallinity

The X-ray diffraction profile of crystalline polyphenylene shows three characteristic maxima at d spacings of 4.5, 3.9 and 3.2Å equivalent to 2θ values of 19.4, 22.4 and 27.6°. In addition there is normally a characteristic broad diffraction halo peaking at around $2\theta = 19^\circ$ from the amorphous polyphenylene in the sample. The degree of crystallinity can be determined by using a computer program to perform a least squares fit of four Lorentzian profiles at these 2θ values on the observed diffraction pattern. The ratio of the sum of the areas of the three crystalline peaks to the total area of the diffraction pattern including the amorphous halo then gives the desired result.

Glass Transition Temperature

Samples of the precursor polymer were converted to intermediate levels of aromatisation by heating at 300°C under nitrogen for varying periods. The extent of aromatisation was calculated by the infra-red and TGA to complete aromatisation methods described above. The glass transition temperature of each sample was then determined by differential scanning calorimetry (DSC) at 10°C/min using a Perkin Elmer System 7 instrument.

Neutron Scattering

Measurements were made in the solid state on proto/deutero plaques prepared by solution casting. The relevant components were solution blended in 1,2-dichloroethane at 2% w/v concentration and the solution was reprecipitated into ten times its volume of methanol. The polymer blend was reclaimed and dried in vacuo for 24 hours at 60°C. This blend was then redissolved in 1,2-dichloroethane at concentration of 30% w/w and an appropriate amount placed into a moulding frame and the solvent removed by controlled evaporation at 25°C. This procedure produced clear void free plaques 32 mm x 17 mm x 0.5 mm thick which were used in the experiments.

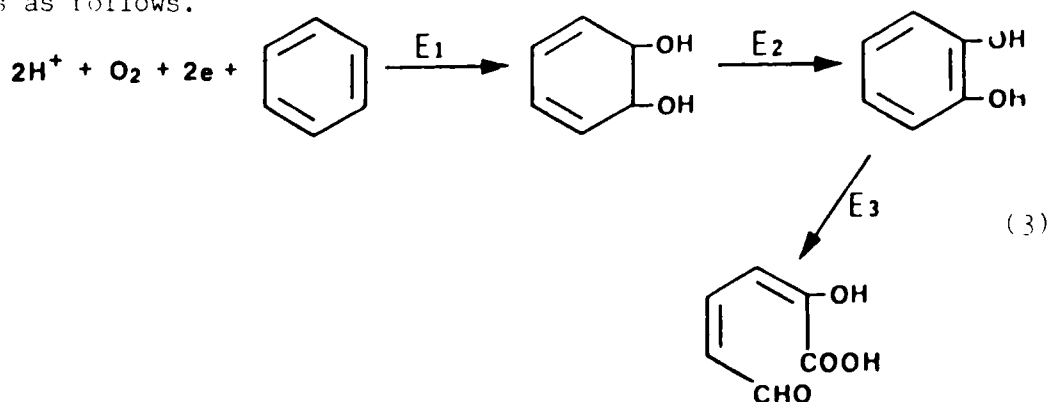
All samples were prepared using the same matrix polymer (H_{12}) in which $M_w = 353K$ and $M_w/M_n = 2.6$. The deuterated (D_{12}) equivalent tag molecules were prepared by molecular fractionation of a 1% solution in acetone at 30°C using methanol as non-solvent of polymer in which $M_w = 812K$ and $M_w/M_n = 2.2^4$.

Neutron Scattering experiments were made on samples containing 10% by weight of the D_{12} tag molecule, but one sample was studied at 5% tag loading from which the concentration dependence of molecular weight was estimated. Details of the samples are provided in Table 5. Details of the SANS measurements are given by Ballard and Schelten¹⁸ and other references given in this review paper.

RESULTS AND DISCUSSION

Microbial Oxidation of Benzene

Although micro-organisms able to oxidize benzene were known in the literature^{10,11} because of their sensitivity and poor rates of oxidation, they lacked the robustness necessary for large scale manufacture of 2. From a manufacturing site contaminated with hydrocarbons over many decades we were able to isolate a new organism, *Pseudomonas putida* 11767. This organism exhibited a high rate of benzene oxidation and was substantially more tolerant of high benzene concentrations. The course of the oxidation within the bacterial cell is as follows.



The dioxygenase E_1 , with the assistance of the co-catalyst nicotinamide adenine dinucleotide in its protonated form (NADH), reacts with oxygen to form 2. The complete oxygen molecule is used in this process and the protons are supplied by the co-catalyst. Subsequently 2 is aromatised by E_2 and NAD^+ is converted back to NADH. A third enzyme, the dioxygenase E_3 converts catechol to a muconic acid. By genetic manipulation we produced a variant of 11767 which lacked enzyme E_2 needed to oxidise 2.

Since DHCD is water soluble it diffuses out of the cell into the surrounding aqueous media and accumulates therein. The organisms presently available will tolerate up to 9.5% liquid benzene in water and the product accumulates to the extent of 40 to 50 g/l without inhibiting the oxidation. Yield on benzene is nearly 100% and DHCD is the only oxidation product. Using this genetically modified organism a process has been developed for the kilogram scale production of DHCD. The organism is used as a catalyst in a well mixed aerated aqueous solution to which benzene and ethanol are added^{12,13}.

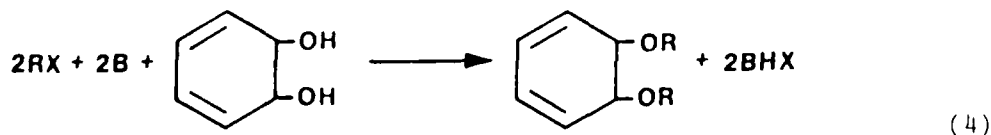
Ethanol is oxidized to carbon dioxide by other enzymes in the organism, thereby supplying the energy required by enzyme E_1 to drive the oxidation of benzene. At the end of the process DHCD is isolated by extraction with methylene chloride.

This process is now operated in 1000 litre reactors to produce DHCD and substituted cis-dihydrocatechols some of which are used as chemical intermediates for fine chemical manufacture.

Derivatives of DHCD

DHCD dehydrates at temperatures in excess of 60°C to give phenol and water. This aromatisation process is catalysed by strong acids.

In basic solutions or neutral media DHCD is quite stable and can be stored indefinitely below 0°C. Derivatisation of the latter can be carried out at and above pH 7.4 without the formation of phenol and the predominant reactions are base catalysed as shown in equation 4, where RX can be an acid chloride, anhydride or iodide and B an organic tertiary base.



The alkylation or acylation is accomplished in pure pyridine or dimethylsulphoxide. If phosgene is the acid chloride a cyclic carbonate is the product. In table 1 is summarised the properties of these derivatives.

Polymerisation of DHCD Derivatives using Radical Initiators

Initial experiments on the polymerisation of DHCD and its derivatives were unsuccessful because of contamination by small amounts of impurities, including traces of phenol. Moreover it was found that the initiating radicals facilitated the formation of phenol, which inhibits polymerisation, when pure DHCD was used. On the other hand, most of the acyl derivatives could be polymerised using radical initiators either as the pure compound or dispersed in an organic solvent in which it is not soluble.

Studies of the Homopolymerisation of DHCD

Initial rates of polymerisation of DHCD derivatives were measured using dilatometry and at high conversions by weighing the polymer produced. In figure 1 is shown a typical conversion time curve obtained gravimetrically using benzoyl peroxide as initiator. Most effective polymerisations were obtained in the absence of solvent and with these conditions polymerisation would proceed almost to completion without difficulty. In figure 2 is shown the variation in molecular weight, as represented by the number average degree of polymerisation ($\bar{M}_n$). If the latter is compared with the dispersity given in figure 3 it is evident that the bulk polymerisation of these monomers is not dissimilar from the polymerisation of acrylic esters.

The relationship between monomer and catalyst concentration and polymerisation rate was obtained from initial rate studies and is

illustrated in figures 4 and 5. Equation 5 summarises the results of these experiments, where $[M]_0$ and $[I]_0$ are the initial monomer and initiator concentrations respectively.

$$R_p = \frac{-d[M]}{dt} = k[M]_0^{\frac{3}{2}}[I]_0^{\frac{1}{2}} \quad [5]$$

The values of the molecular weights of the polymers obtained at these low conversions gave a clearer relationship between the reciprocal of DP_n and the square root of the initiator concentration. This is shown in figure 6 and is a general feature of the polymerisation of vinyl monomers such as styrene and methylmethacrylate.

The molecular weight of the polymer is sensitive to the concentration of monomer and the presence of an aromatic solvent reduces it markedly. High molecular weights can only be obtained in the absence of solvent. Also, the reaction temperature is a parameter to which the molecular weight is even more sensitive and there is a reduction by a factor of 5 to 10 in molecular weight if the polymerisation is carried out at 90°C compared to 60°C.

Measurements of molecular weight in the course of rate measurements also revealed that there was a linear relationship between rate of polymerisation and the reciprocal of the number average degree of polymerisation. From this information we derive values of $k_p/k_t^{\frac{1}{2}}$ for the acetate and methylcarbonate derivatives. A comparison between these values with those obtained for styrene and methylmethacrylate¹⁴ is shown in table 2.

The plot of $1/DP_n$ vs R_p and $1/DP_n$ vs $[cat]^{\frac{1}{2}}$ have positive intercepts. This suggests there is a significant transfer of activity from the propagating chain to monomer. This view is supported by equation 5 which shows an unusually high order with respect to monomer concentration.

The effect of temperature on polymerisation rate is summarised in figure 7. The energy of activation derived from the slope is 16.9 Kcals/mole.

It was also found that the polymerisation had a marked pressure coefficient and that the rate at 400 atmospheres was 5 to 7 times greater than experiments conducted at atmospheric pressures. Also as shown in table 3 molecular weight was not significantly higher.

The deuterated analogues of PHPD are readily obtained by replacing benzene in the mineral oil oxidation with deuterobenzene (C_6D_6). The sequence of reactions which follow are identical, except there is a marked kinetic effect. A comparison was made between the deuterated and protonated acetate monomer in polymerisation. For this purpose we determine the initial rate of polymerisation in the pure monomer

containing one per cent of an initiator and the molecular weight of the polymer produced. The results obtained are given in table 4.

The most important effect of deuteration was to produce a marked increase in molecular weight of the polymer produced. This is well known in radical polymerization of vinyl monomers and is due to the retardation of the bimolecular termination reaction and possibly to differences in the rate of allylic proton or deuterium abstraction from monomer leading to degradative chain transfer.

Polymerisation in organic diluents, in which the polymer is insoluble, has been achieved using dispersing agents. The latter consists of a polymethyl-methacrylate backbone with side chain derived from 12-hydroxystearic acid. Powders of the polymers derived from DHCD acetate, benzoate, and methyl carbonate have been obtained. The polymer consists of spherical particles with a reasonable narrow distribution of particle sizes which can be controlled in the range 20-400 μ m. Although all the derivatives of DHCD can be polymerised using dispersion techniques the benzoate and methyl carbonate do so at particularly high rates and give polymers with molecular weights of up to one million. A preliminary look at the kinetics of the polymerisation has been carried out which shows that at low conversion:

$$R_p = k_p[M][I]^{1/2} \quad (5)$$

where $[I]$ is the concentration of the radical generator azo-bis-isobutyro-nitrile. Similarly, dispersity is less than two at low conversions, with a normal growth mechanism for the macromolecule.

Confirmation and Structure of Poly(DHCD-PMMA) in the Solid State

The availability of the fully deuterated species make conformational studies in solution and in the solid state possible. The use of small angle neutron scattering (SANS) to measure M_w , and the radius of gyration (R_g) by taking advantage of the differing scattering lengths of the proton and deuterium is well established⁹. These experiments were carried out in collaboration with Dr Manfred Stamm and will be reported in detail in a later publication.

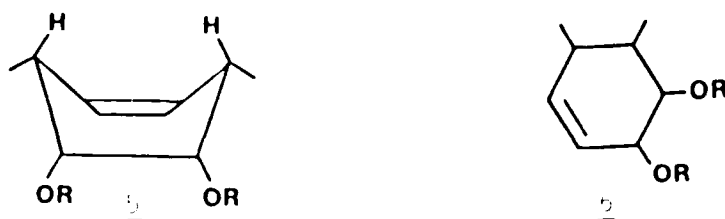
Void free plaques (4 x 12 x 0.5mm) were obtained of mixtures of Poly(DHCD-PMMA) copolymers 3 and 4 of the fully deuterated monomer. All samples were prepared using the same deuterio polymer (DLC) in which $M_w = 252,000$ and $M_w/M_n = 2.1$. The copolymers (DLC) were prepared by fractionation of a polymer in which initially $M_w = 812,000$ and $M_w/M_n = 2.24$. Fractionation was effected using mixtures of acetone and methanol at 20°C. The data obtained are given in table 5. Molecular weights of the fractions were measured by laser light scattering (LALLS) in solution and in the solid state using neutron scattering

(SANS). It was necessary to correct the SALS values of R_w for the fact that they were not independent of polymer concentration. The latter are closer to the SALS values. The corrected SANS values were used to derive the curve shown in Figure 3. From the latter we obtained the relationship:

$$R_w = 1.4 \times 10^{-3} \bar{M}_w^{1/2} \quad (7)$$

This equation is typical of a polymer chain in which there is a gaussian distribution of chain segments around the centre of mass.

In the macromolecule infra-red and ^1H NMR analysis show that the DHCD-BMC residues are predominantly the result of 1:4 addition reaction in the polymerisation. These residues constitute 85% of the polymer and probably have a "boat" shape configuration as shown in 5. The remaining residues are the result of a 1:2 addition reaction

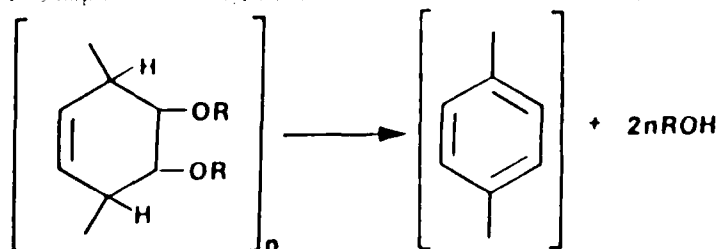


during the polymerisation, as shown in 6. The admixture of these two structural entities is obtained in a molecule which the SANS data shows has a random coil configuration.

Thermal Conversion to Polyphenylene

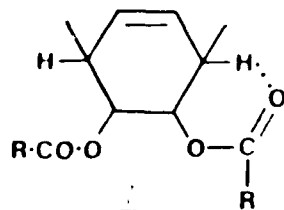
The polymers of DHCD derivatives can be aromatized by heating as fibres or films in the solid state and in solution. The process can be followed using thermogravimetric analysis, infra-red spectroscopy or ^1H NMR. Typical results are shown in Figures 9 and 10.

The principal reactions leading to polyphenylene are shown in Equation 8. The process is accompanied by elimination of two molecules of the acid for each phenylene group formed. Two RSH produced in the examples given in Figure 9 are acetic acid, formic acid and pyruvic acid from the acetate, formate and pyruvate derivative respectively. For practical reasons the preferred derivative is the dimethylcarbonate. The eliminated acid in this case is methylenecarboxylic acid, which decomposes to give methanol and carbon dioxide.



In Tables 6 and 7 is summarized the results obtained from initial rate of decomposition for the thermal degradation. The latter process probably proceeds via a cyclic intermediate 7 and 8.

successful reaction the ortho xylene group is a good leaving group. The kinetic data for the polymerized polymer shows that the presence of the phenon in the ring slows the aromatization process markedly, consistent with an intermediate of type I being formed.



The methylcarbonic acid and methylthiocarbonic acid derivatives of DHCD differ from the simple carboxylic acids in that the aromatisation can be catalysed by strong tertiary nitrogen bases and metal salts. Figure 11 is typical of the effect and shows that potassium bromide catalyses the aromatisation and thereby reduces the temperature at which the process occurs. Additional information is given in table 8, which shows that n-octylamine is far more effective in this role than metal salts. The role of the base in catalysing the aromatisation of the methylcarbonate derivatives is at present not understood.

N-methyl pyrrolidone is a good solvent for poly(DHCD-DMC) and also catalyses the aromatisation. Surprisingly the partially aromatised polymer is soluble in this solvent up to 35 mole percent aromatised. At degrees of aromatisation less than this the polymer can be isolated and dissolved in solvents such as methylene chloride, chloroform etc. In figure 12 is shown a typical decomposition curve. This shows that the aromatisation process is autocatalytic in this solvent. In other words the partially aromatised polymer then forms cyclohexene residues were readily into phenylene groups. This suggests that the presence of phenylene residues adjacent to the cyclohexene residues facilitates aromatisation. In table 9 is given the approximate composition of a partially aromatised polymer in which 30 mole percent of phenylene groups are present. The cyclic carbonate residues (see Experimental Section) are fully aromatised at the much higher temperature of 360°C.

Aromatisation in solution results in a change in molecular weight to be observed. A typical example is shown in table 10. It might be expected that with the increasing weight loss due to aromatisation there would be a corresponding increase in molecular weight so that when the process is complete it would be a third of its initial value. In fact we observe no change at all up to 10 percent aromatisation followed by a reduction of molecular weight at 15 percent aromatisation.

It is evident from table 10 that aromatisation does not produce chain scission at the top of the molecular weight scale. The weight would be reduced significantly. The agreement between the molecular weight of the polymer before and after aromatisation is a good indication that the polymer is a linear polyphenylene. It is suggested by the molecular weight of the polymer before and after aromatisation that the polymer is a linear polyphenylene. The molecular weight of the polymer before and after aromatisation is a good indication that the polymer is a linear polyphenylene. The molecular weight of the polymer before and after aromatisation is a good indication that the polymer is a linear polyphenylene.

length is very long. The data in table 10 in which the molecular weights are obtained by comparison with standard polystyrene molecular weights cannot be correct because as the number of phenylene residues in the polymer increases there is a progressive increase in hydrodynamic volume. This can be demonstrated by comparing the intrinsic viscosities of polymers with different degrees of aromatisation as shown in figure 13.

It is known that the viscosity of a solution of a macromolecule is predominantly dependent on the size of the molecule, expressed as the root-mean square radius of gyration $(\bar{S}^2)^{1/2}$ and not on the nature of the polymer¹⁵. This definition leads to the expression:

$$[\eta] = \Phi \cdot \left(\frac{\bar{S}^2}{M} \right)^{3/2} \cdot M^{1/2} \cdot \alpha^3 \quad (9)$$

where Φ is a constant, M is the molecular weight and α is a parameter expressing deformation of the molecular dimension owing to the polymer-solvent interaction. It is evident from (9) that at a constant molecular weight, $[\eta]$ is markedly dependent on the volume of the molecule V_e , given by:

$$V_e = 4\pi \cdot (\bar{S}^2)^{3/2} / 3 \quad (10)$$

The aromatisation process is accompanied by a transition from a random coil to a configuration which consists of a random arrangement of rigid rods separated by flexible sections of unaromatised molecules. As the aromatised fraction increases the flexible units decline and the average length of the rod-like polyphenylene sections increases. This is shown clearly in figure 14, where the intrinsic viscosity remains constant for the first 20% of conversion to phenylene units, but after this a marked increase in intrinsic viscosity occurs. Since this parameter is a measure of hydrodynamic volume, it must be concluded that this increase results, at least in part, from an increase in the radius of gyration of the molecule as a consequence of chain segments becoming straight as the phenylene units are formed. It is also possible that association of individual chains, through their aromatised segments, i.e. interactions to form larger agglomerates, contributes to the observed increase in viscosity.

Solid State Properties of Polyphenylenes

Polyphenylene in the form of the polymer as far described is available as a thin film, as a variety of granules, fibres, glass, metals, semiconducting plastic films with various properties in excess of 10000 ohm-cm. and the polymer can be drawn to form ultra-thin concentrations of about 50 percent and, semiconducting films, fibres are produced. Polyphenylene is a very soft material and it is not possible to draw the fibres. Any collection of the polyphenylene molecules can only be drawn during the polymerisation process and this is a very much more difficult as the extent of aromatisation increases 90%.

Polyphenylene is a very hard material and it is not possible to draw the fibres. Any collection of the polyphenylene molecules can only be drawn during the polymerisation process and this is a very much more difficult as the extent of aromatisation increases 90%.

is 60 percent crystalline. By controlled aromatization above 185°C, crystallinities of 75-80 percent can be obtained.

The absence of colour suggests that the structure is not coplanar. In table 11 is given the principle X-ray reflections obtained on a polymer powder whose crystallinity was approximately 60 percent. These have been compared with those reported in the literature for para-linked oligophenyls. The most complete study is due to Rietveld, Maslen and Clews¹⁶ of p-terphenyl in which X-ray diffraction was supplemented by neutron diffraction to identify the positions of the hydrogen atoms.

Aromatization of the precursor molecule below its glass-transition temperature (185°C) produces preferentially amorphous polyphenylene powder or coating. Subsequently annealing this powder and following the development of crystallinity at different temperatures produces the results shown in Figure 14a. At temperatures below 240°C there is no recognisable increase in crystallinity. At this temperature there is a step-change in the level of crystallinity. Annealing at temperatures above the latter produces a very high level of crystallinity. If the precursor molecule is aromatised above its glass transition temperature then the crystallinity of the polymers obtainable on subsequent annealing are shown in figure 14b. It would appear that the crystallites formed during the aromatization process impede the reorganisation of the macromolecules so that the maximum possible crystallinity is not achievable.

These crystallites are absent from the polymer produced by aromatization below 185°C. It is evident that the onset of crystallinity in figure 14a is associated with the increase in chain mobility and determines therefore the glass-transition temperature as 285°C for amorphous polyphenylene.

In figure 15 is shown the variation in the glass-transition temperature of the precursor molecule with the extent of aromatization. It shows an increase in T_g from the flexible precursor molecule with increase in rigidity of the molecule as more phenyl groups are formed. The curve finally approaches the T_g of pure amorphous polyphenylene asymptotically. The shape of the curve suggests that the phenyl groups are being formed initially (up to 30%) in blocks and are not uniformly distributed along the chain. In the latter case the T_g would increase more rapidly with the degree of aromatization.

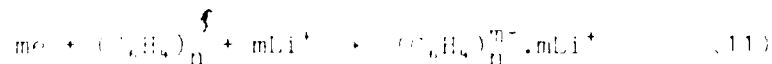
The thermal stability of polyphenylene is related in a very evident related to the thermal treatment of the aromatization process. It is advantageous to carry out the latter in an inert atmosphere completing the process by heating at 500°C and finally at 600°C to remove the unreacted chlorine. In figure 16 it is shown that

such coatings can be used at temperature close to 400°C and in the absence of oxygen even at temperatures of 500°C although there is a significant weight loss initially, probably due to loss of higher oligomers. The films remain coherent, are not carbonised and still retain their good electrical insulation characteristics. Total thermal breakdown only occurs at a significant rate at 600 to 800°C. At these temperatures, in an inert atmosphere, oligophenyls are produced of general composition $H-(C_6H_4)_n-H$ where $n=3$ to 11. No benzene or diphenyl is produced. The reason for the absence of the latter is not clear.

The oxidative stability in air is superior to most other aromatic polymers and coatings can withstand temperatures of 350°C for short periods without significant breakdown. The behaviour at 380°C in air is compared in figure 16 with that in pure nitrogen.

Polyphenylene coatings previously described have electrical conductivities of 10^{-14} to 10^{-15} ohm $^{-1}$ cm $^{-1}$ and in this condition are very good electrical insulators. They have the added advantage of being free of inorganic contaminants.

In table 12 is given examples of the effect of n and p type dopants on the electrical conductivity. The polyphenylene films are pale yellow in colour but on treatment with sodium naphthalide they become black and their conductivity markedly increases to give a semi-conductor. This behaviour is repeated with the strong electron acceptors such as ferric chloride and arsenic pentachloride. The coatings can be used also as an organic cathode in an electrochemical cell in which lithium trifluoromethyl sulphate is the electrolyte.



In their electrical behaviour the high molecular weight polyphenylene films prepared so far apparently differ little from the oligomeric polyphenylenes previously reported in the literature².

EXAFS has proved to be a unique tool in providing structural information to help understand the mechanism of conductivity and stability of doped polyphenylene. For FeCl₃ doping under anhydrous conditions, it has been shown that Fe is bound in a tetrahedrally co-ordinated Fe(III)Cl₄ with an Fe-Cl distance of 2.19Å. This is quite different from FeCl₃ (solid) which is octahedral with an Fe-Cl distance of 2.34Å.

A subsequent paper will describe these results in more detail and give information of the effect of copolymerisation on the electrical conductivity.

CONCLUSIONS

The method described for producing polyphenylene is being used in the study of:

- (1) polymeric electrodes which combine ionic and electron conduction
- (2) alignment layers for liquid crystal display systems
- (3) production of carbon structures
- (4) protective coating for thermally stable polymers in chemically aggressive environments
- (5) catalysts are being developed which will enable a predominantly linear polymer to be prepared

ACKNOWLEDGEMENTS

The work described was carried out in ICI's Corporate Laboratory whose enlightened management made it possible for polymer chemists to use microbiological techniques, an unusual combination of skills. The authors listed in the title were the original team responsible but many others participated in examining the value of this approach to polymer synthesis. These included Paul Holmes, Phillip Cheshire, Anthony Pickering, Alan Nevin, David Twose, W Moran and D Platt.

CAPTIONS TO FIGURES

Figure 1.

Conversion time curves for the polymerisation of various cis glycol derivatives using benzoyl peroxide as initiator, DHCD-DA; DHCD-DB; DHCD-DHC; Temperature 90°C $[M]_0/[I]_0 = 156$

Figure 2.

The degree of polymerisation as a function of conversion. Conditions of polymerisation as for figure 1, DHCD-DB; DHCD-DA.

Figure 3.

The dispersity as a function of conversion. Conditions of polymerisation as for figure 1, DHCD-DB; DHCD-DA.

Figure 4.

Time to 50% conversion of polymerisation of DHCD-DA as a function of monomer concentration, 0.001 M using benzoyl peroxide, $[I]_0 = 5.68$ mM/litre, in benzene at 90°C.

Time to 50% conversion of polymerisation of DHCD-DA as a function of catalyst concentration, 0.001 M using benzoyl peroxide, $[M]_0 = 6.37$ M/litre.

Figure 6.

Relationship between number average degree of polymerisation (DP) and catalyst concentration for the polymerisation of DHCD-DA at 90°C in the absence of solvent, $[M]_0 = 5.5$ mols/l.

Figure 7.

Arrhenius plot of polymerisation rate against temperature for DHCD-DA.

Figure 8.

Plot of R_w against M_w using data in table 5.

Figure 9.

Thermal conversion to polyphenylene at 300°C, poly(DHCD-DA); poly(DHCD-DP);, poly(DHCD-DB);, poly(D⁶-ring DHCD-DA);, poly(D¹² DHCD-DA).

Figure 10.

Thermal conversion to polyphenylene at different temperatures. Poly(DHCD-DMC);, poly(DHCD-DA).

Figure 11.

Catalysed thermal conversion of poly(DHCD-DMC) at 220°C. Catalyst KBr, concentration 2 percent w/w.

Figure 12.

Aromatisation of poly(DHCD-DMC) in N-methylpyrrolidone as solvent. The process was followed using thermogravimetric analysis. Temperature 170°C, polymer concentration 5 percent w/w.

Figure 13.

Aromatisation of poly(DHCD-DMC) in N-methylpyrrolidone as solvent. Samples removed and intrinsic viscosities determined by dilution. A sharp increase in intrinsic viscosity occurs at 20 percent conversion.

Figure 14.

The effect of annealing temperature on the crystallinity of polyphenylenes obtained under differing aromatisation conditions

- (a) amorphous polyphenylene obtained at 150°C
- (b) semi-crystalline polyphenylene obtained at 240°C. Annealing time 17 hours.

Figure 15.

Glass transition temperatures for polymers with different degrees of aromatisation. The figure for 100 percent aromatisation was obtained from figure 14a. Measurements carried out using a differential scanning calorimeter.

Figure 16.

Thermal gravimetric analysis of a polyphenylene coating at 380°C. Sample previously heated to 320° in Nitrogen for 24 hours.

- (a) in nitrogen, initial 1.48 percent loss due to residual higher oligomers
- (b) in air

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Table 1

Properties of Derivatives of DHCD

Derivative	Bpt	Mpt
Diacetate (DHCD-DA)	70 (0.1 mmHg)	40
Dipivalate (DHCD-DP)	110 (0.1 mmHg)	30
Dibenzoate (DHCD-DB)	-	93
Di(p-NO ₂ Benzoate)	-	166
Di(p-Br. Benzoate)	-	159
Dimethoxycarbonyl (DHCD-DMC)	105 (0.1 mmHg)	36
Diethoxycarbonyl (DHCD-DEC)	110	Liquid
Dimethylether (DHCD-DME)	70 (10 mmHg)	Liquid

Table 2

Comparison of ratios at 90°C of kinetic parameters for propagation (k_p) and termination (k_t) for the polymerisation of vinyl monomers¹⁴.

Monomer	$k_p/k_t^{1/2}$
Styrene	0.05
Methylmethacrylate	0.10
DHCD-DMC	0.04
DHCD-DA	0.02

Table 3

Polymerisation of DHCD-DMC at 50°C and 3000 atmospheres in benzene as solvent.

$[M]_0$ Mol/l	$[C]_0$ Mol/l	Conversion per cent	Mw	Mn
2.44	0.0077	75.6	523,770	149,065
2.44	0.031	90.3	422,430	134,580
2.44	0.015	76.3	431,360	157,130
4.11	0.015	70.0	563,050	171,720

Table 4

Effect of deuteration on the initial rate of polymerisation of the DHCD-DA at 40°C.

Monomer	$10^5 R_p$ $\text{l mol}^{-1} \text{Sec}^{-1}$	Mw
$C_6H_6 (O.CO.CH_3)_2$ (H12)	5.75	66,600
$C_6D_6 (O.CO.CH_3)_2$	5.85	55,390
$C_6H_6 (O.CO.CD_3)_2$	6.82	71,530
$C_6D_6 (O.CO.CD_3)_2$ (D12)	7.32	171,810

Table 5

Neutron scattering study of Poly (DHCD-DM) in the Solid State.

SAMPLE CODE	D12 LOADING	10^{-6} Mw LALLS	$\bar{M}_w$ (GPC)	10^{-6} Mw (SANS)	10^{-6} M_w (Saws Corr.)	R_w Å
BLEND 1	10	2.10	1.5	1.53	1.94	364
2	10	1.5	1.4	1.0	1.2	320
3	10	0.860	1.7	0.530	0.627	230
4	10	0.460	1.4	0.368	0.467	174
5	10	0.250	1.9	0.188	0.238	119
1A 10F	10	1.6	1.8	1.46	1.86	326
2A 5F	5	0.440	1.6	0.424	-	171
2A 10F	10	0.440	1.6	0.382	0.485	172

f

Table 6

Kinetic Data for the Aromatisation of Various Derivatives of Poly(DHCD) Obtained From Thermal Gravimetric Analysis Results at 300°C

Derivative	First Order Rate Constant (min^{-1})	Half-Life (min)
poly(DHCD-DA)	0.046	15
poly(D-6 Ring DHCD-DA)	0.021	33
poly(D-12 DHCD-DA)	0.012	58
Poly(DHCD-DP)	0.037	19
Poly(DHCD-DB)	0.034	20

Table 7

Kinetic Data for the Aromatisation of Poly(DHCD-DM) from Thermal Gravimetric Analysis

Temperature °C	First Order Rate Constant (min^{-1})	Half-Life (min)
300	0.12	6
280	0.066	11
260	0.022	32

Table 3

Catalysed Thermal Conversion of
Poly (DHCP-DMC) to Polyphenylene

Catalyst	Mole % w/w	Temp °C	First Order Rate Const. (min ⁻¹)	Approx. Half Life (min)
NaI	2	260	0.733	1
		250	0.386	2
		240	0.115	6
		230	0.052	13
		220	-	-
KI	2	260	2.251	0.3
		250	1.547	0.5
		240	0.554	1
		230	0.262	3
		220	0.080	9
CsI	2	260	2.558	0.2
		250	1.585	0.4
		240	0.684	1
		230	0.478	2
		220	0.173	4
KBr	0.5	220	0.074	9
	2.0	220	0.145	5
(CH ₃ (CH ₂) ₇) ₃ N	0.5	240	-	1
	0.5	220	-	2

Table 2

Composition of partially Aromatized Poly(DHCD-DMC)

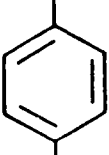
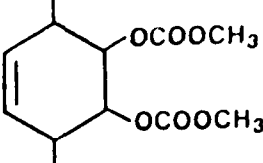
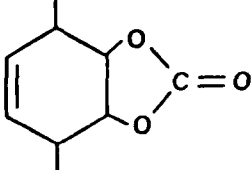
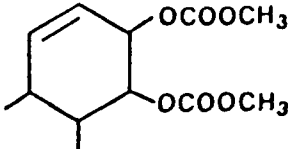
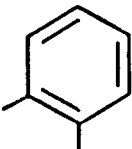
Type of Residue	Amount mole percent	Analysis
	30	IR, 810 cm^{-1}
	50	IR, 1750 cm^{-1}
	5	IR, 1810 cm^{-1}
	9	^1H NMR
	6	^1H NMR

Table 10

Solution Aromatisation of Poly(DHCD-DMC) at 148°C in NMP

Initial concentration 15 percent w/v

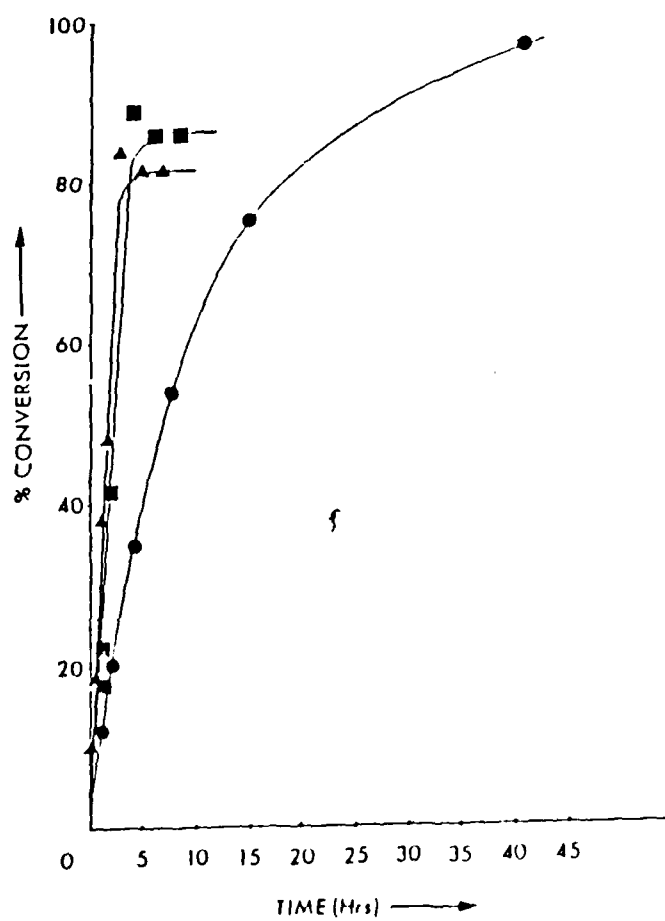
Time (Min)	Aromatisation percent	GPC Results	
		$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
0	0	139,700	2.34
40	6	140,800	2.27
166	15	139,000	3.11
176	16	169,000	4.02
188	18	193,800	4.06
210	20	243,700	6.46
217	22	320,900	7.63
229	26	331,200	12.10

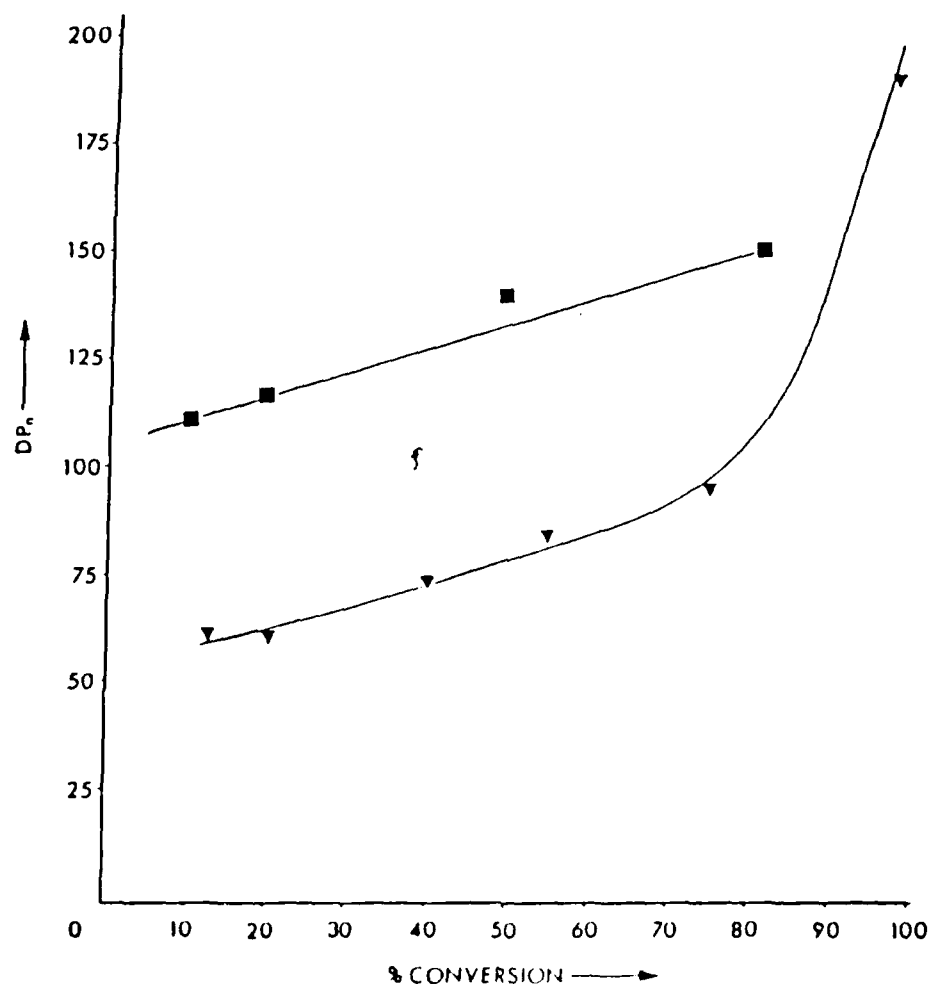
Table 11

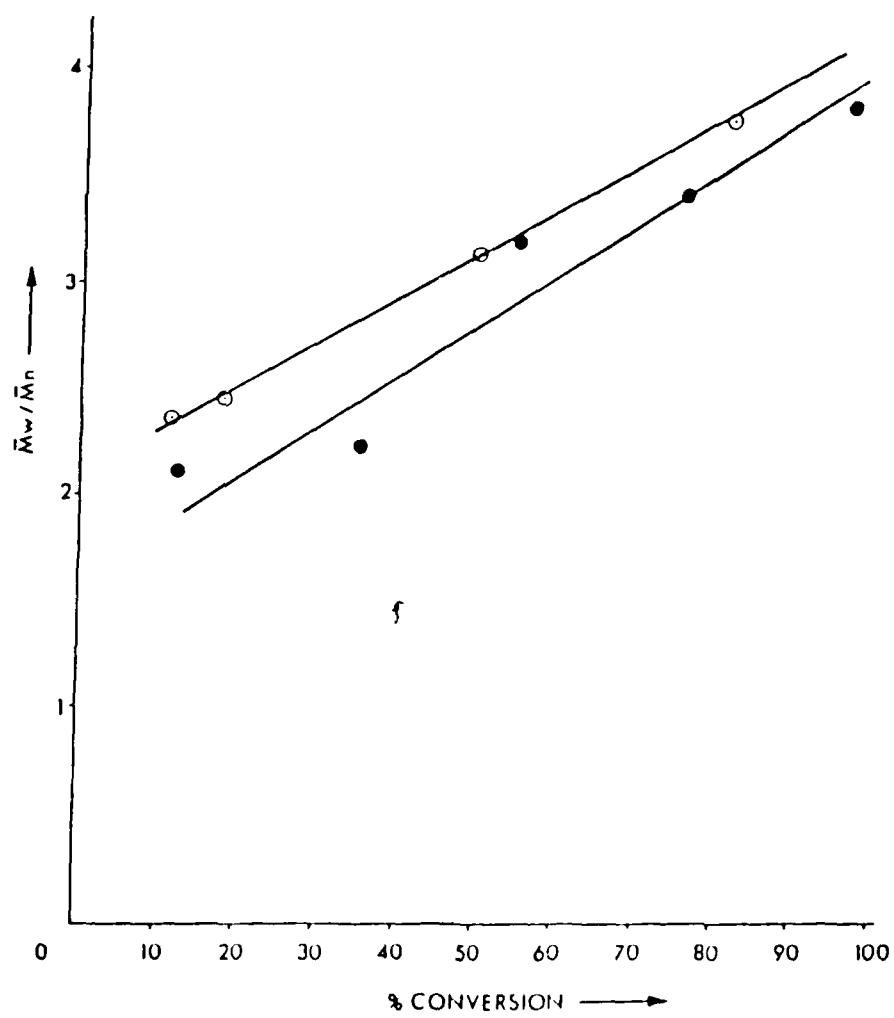
Polyphenylene This paper	p-Terphenyl (13)	
Principle Reflections	Principle Reflections	Structural Feature
4.5	4.40	Distance between phenyl groups in some molecule in the direction of the principle molecular axis
3.9	3.89	Distance between similar centres of phenyl groups in adjacent molecules all lying in the same plane
3.2	3.90	Distance between planes of molecules

Table 10
Electrical Conductivity of polyphenylene

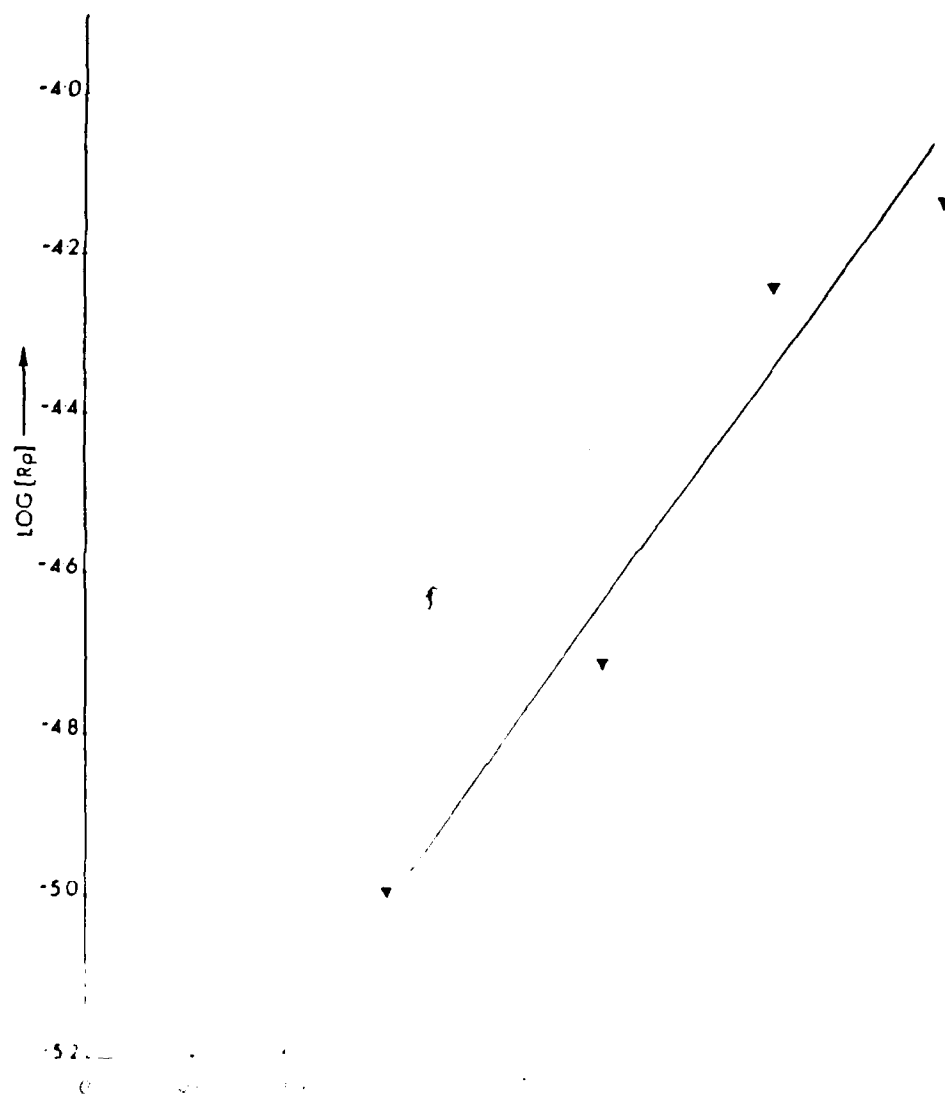
Dopant	Conductivity ohm ⁻¹ cm ⁻¹	Empirical Formula
Sodium Naphthalide	n type 0.6 x 10 ⁻²	-
(C ₆ H ₄) Ferric Chloride (FeCl ₄) 0.12	p type 1.5 x 10 ⁻²	
AsF ₅	p type 1 x 10 ²	(C ₆ H ₄)(AsFs) _{0.42}







20)



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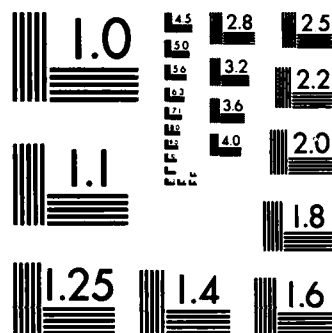
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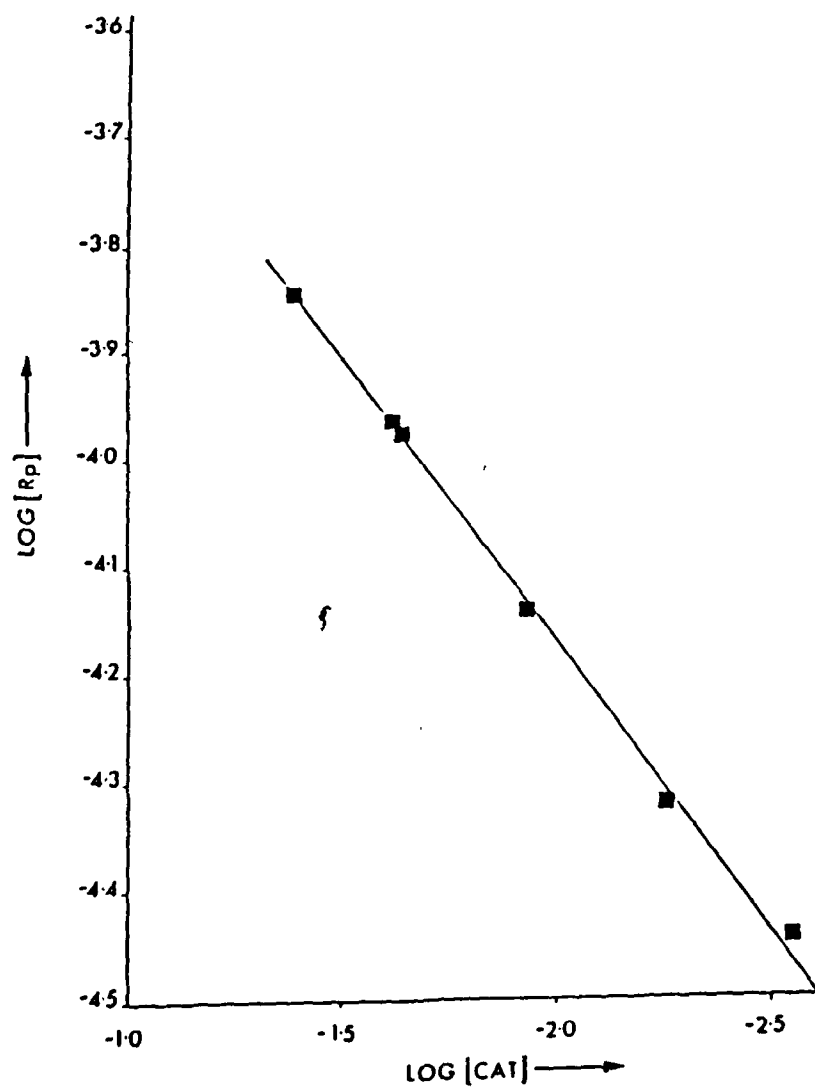
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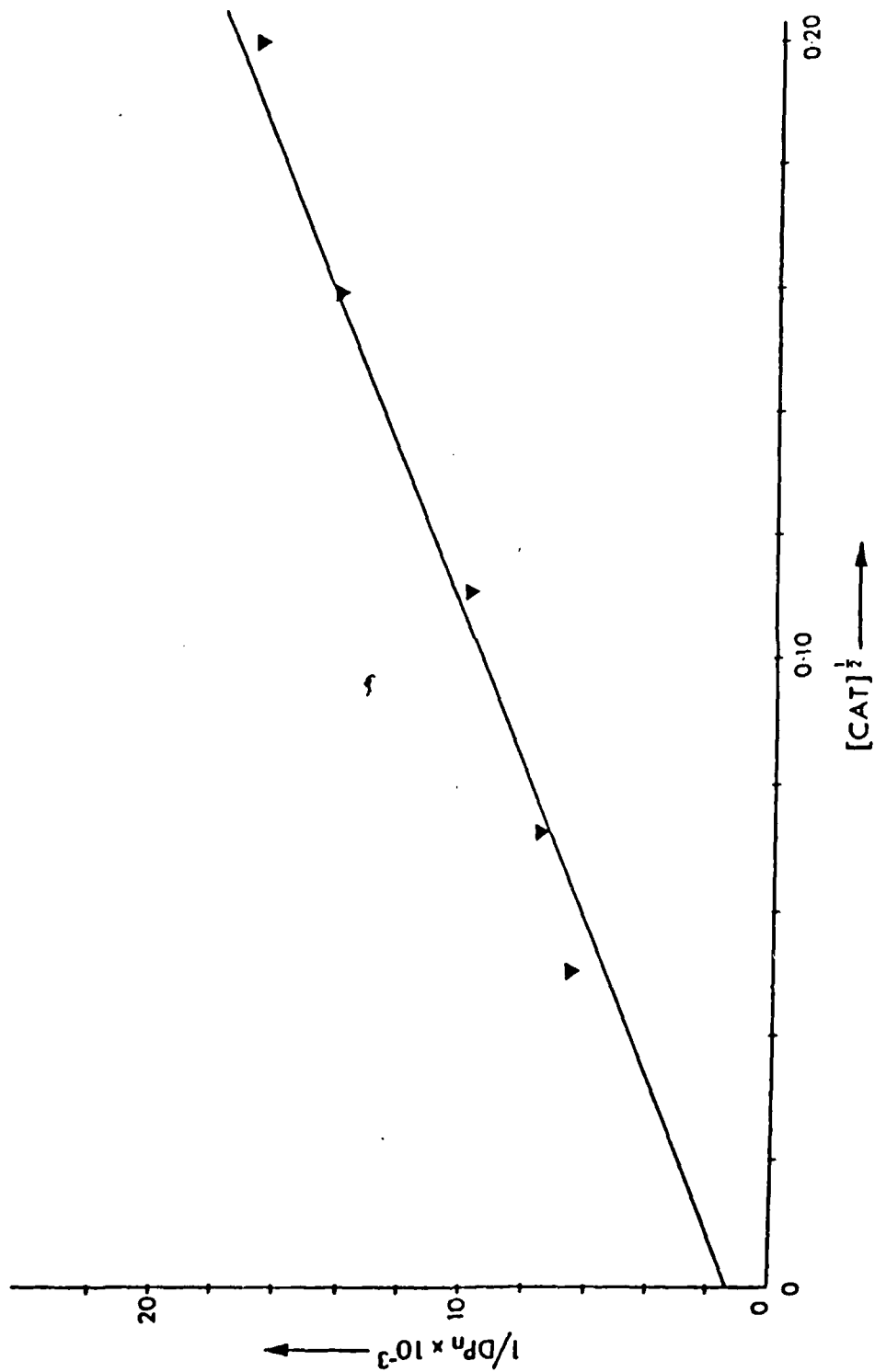
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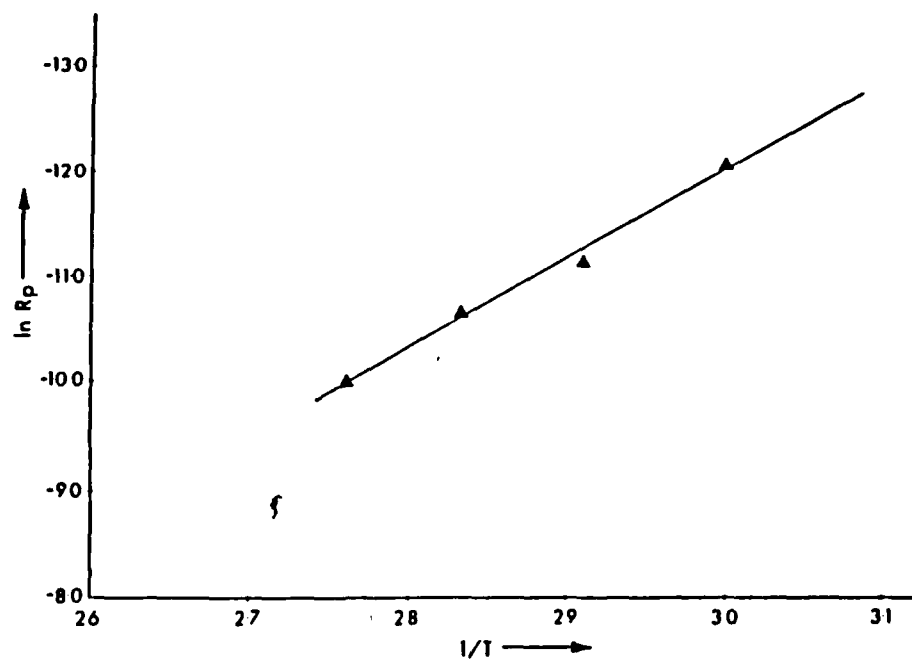


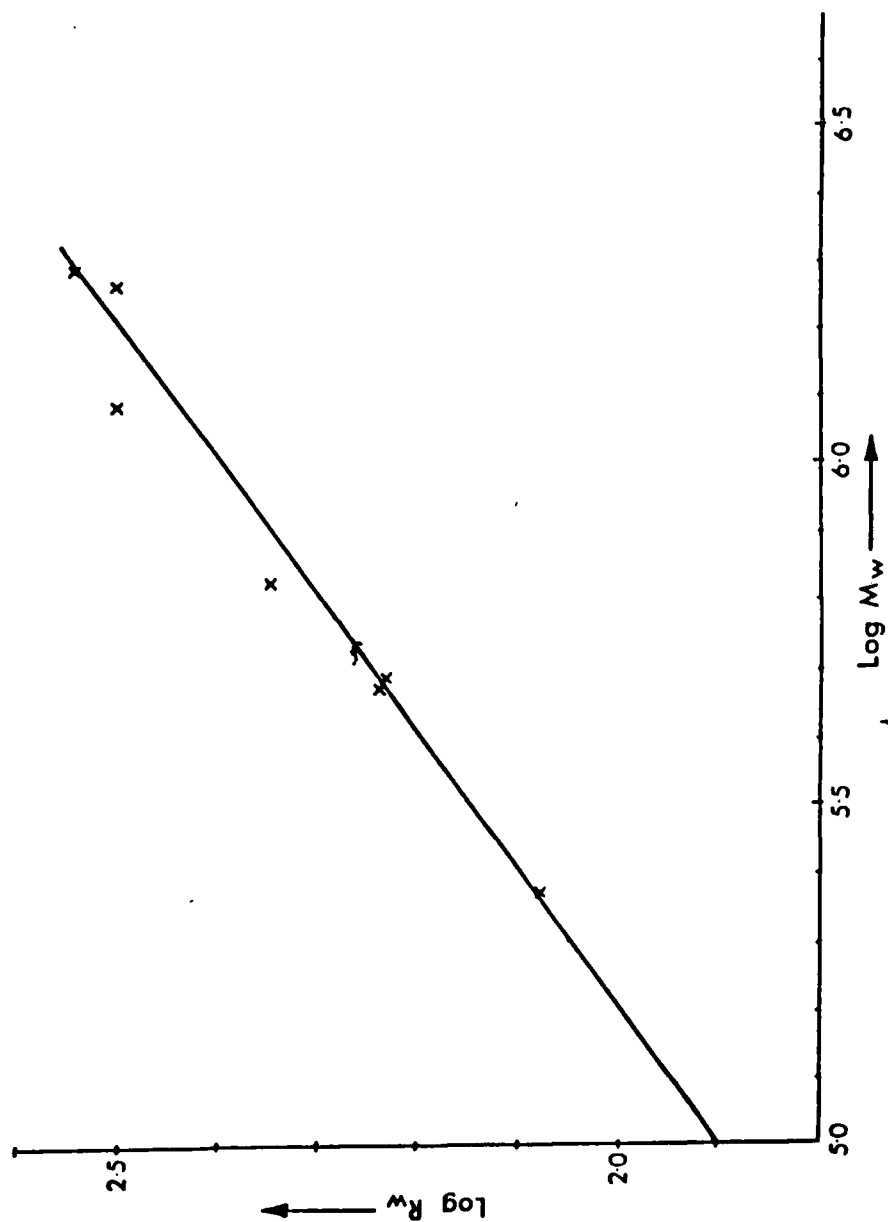


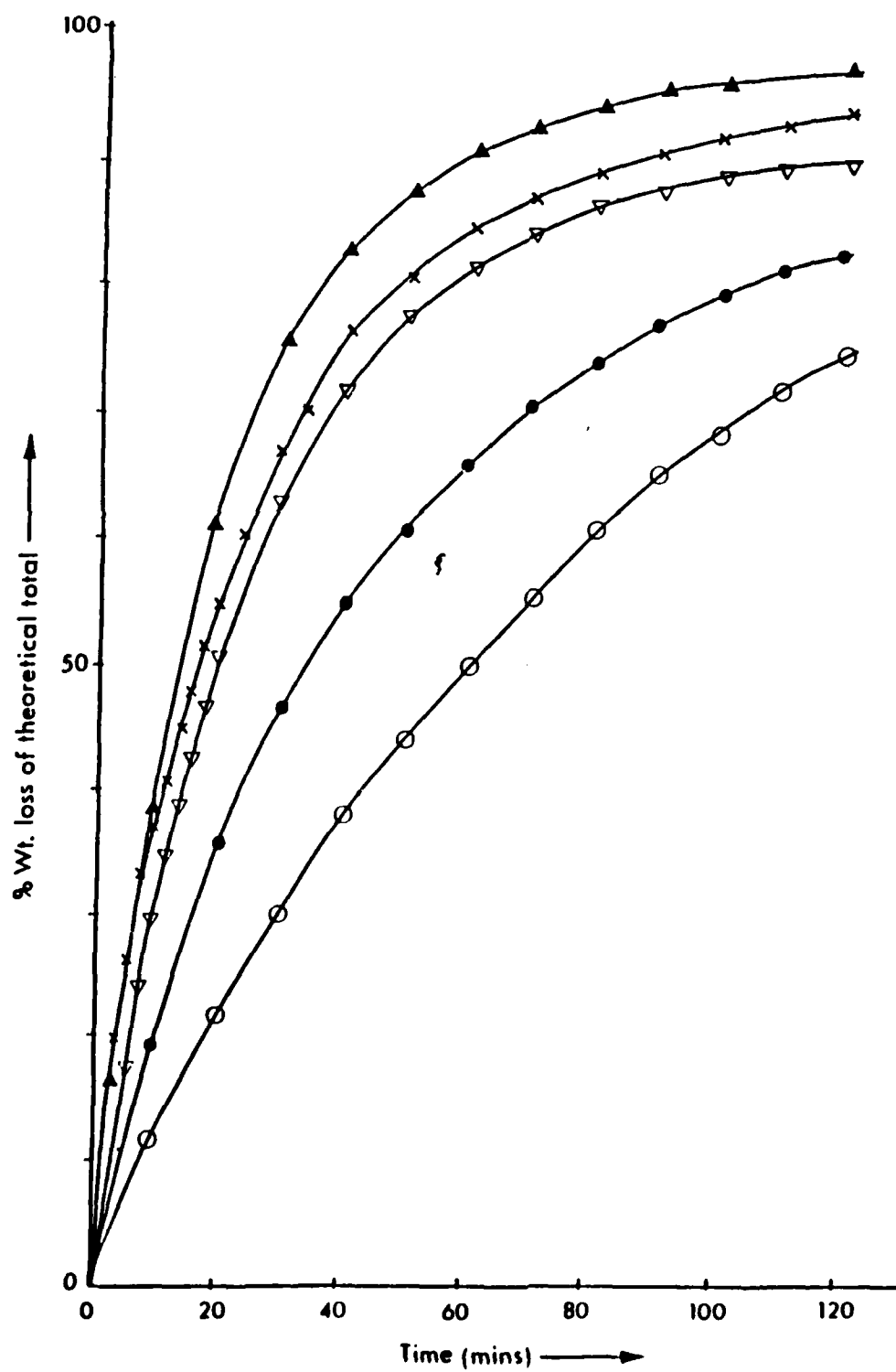
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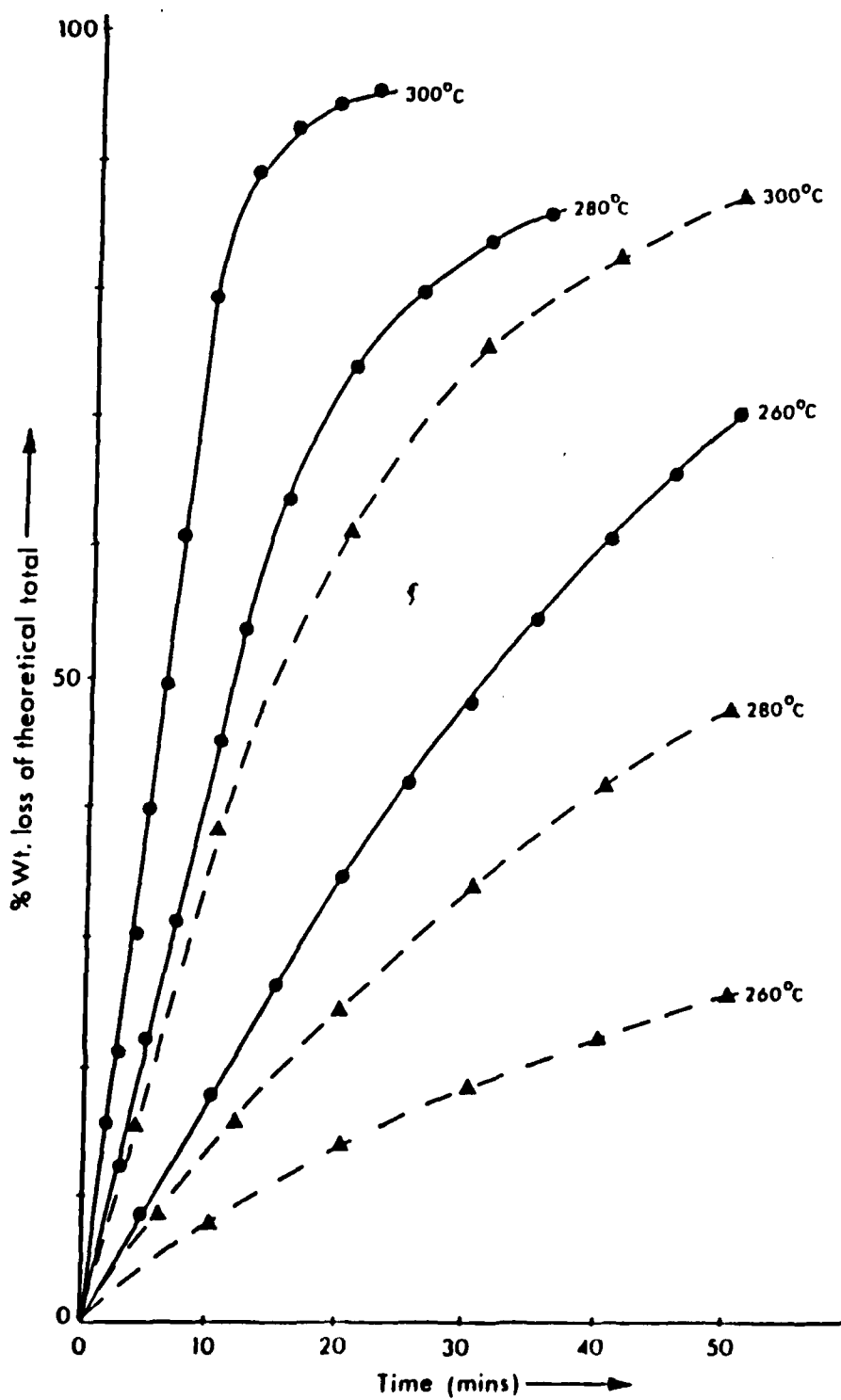


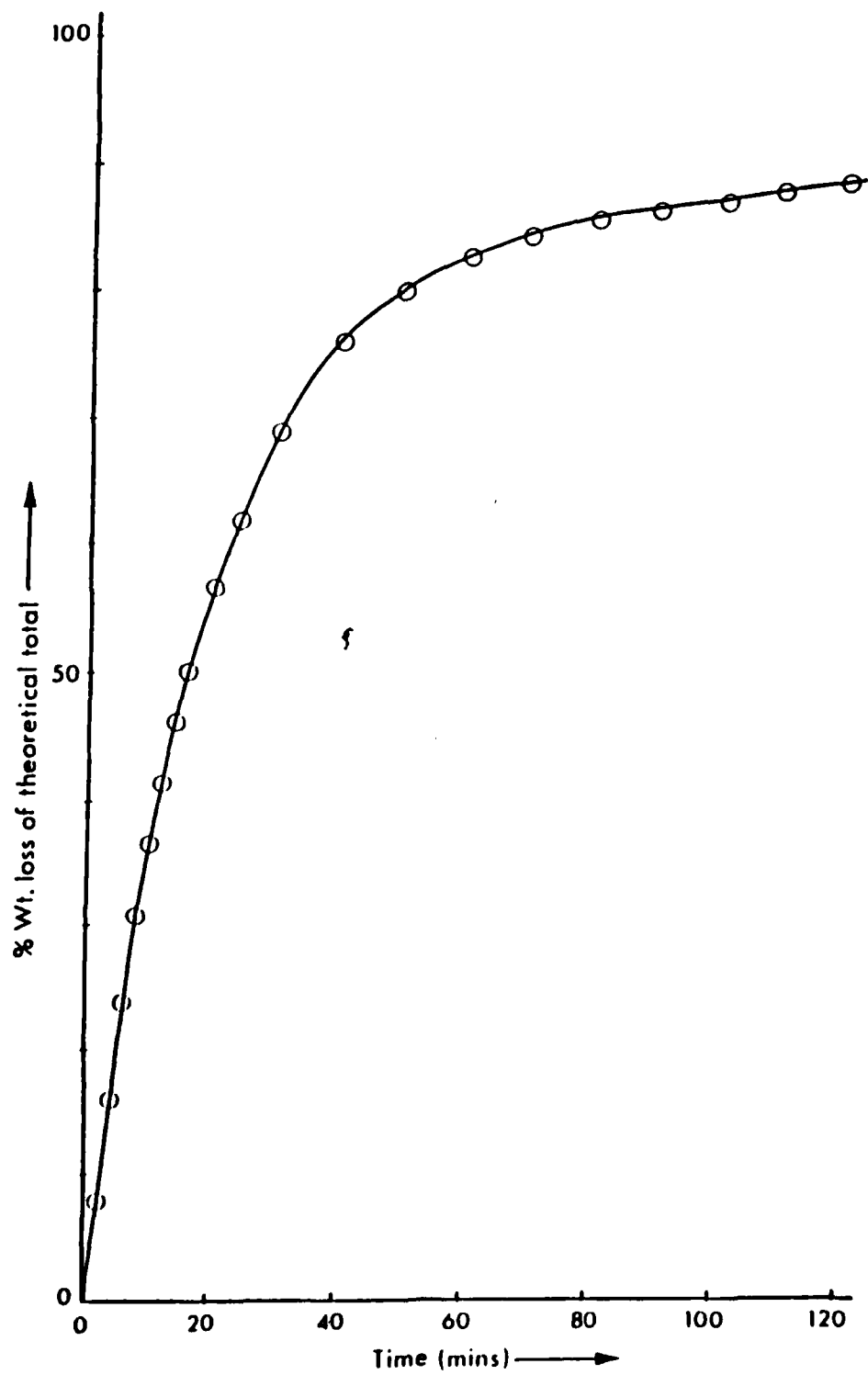


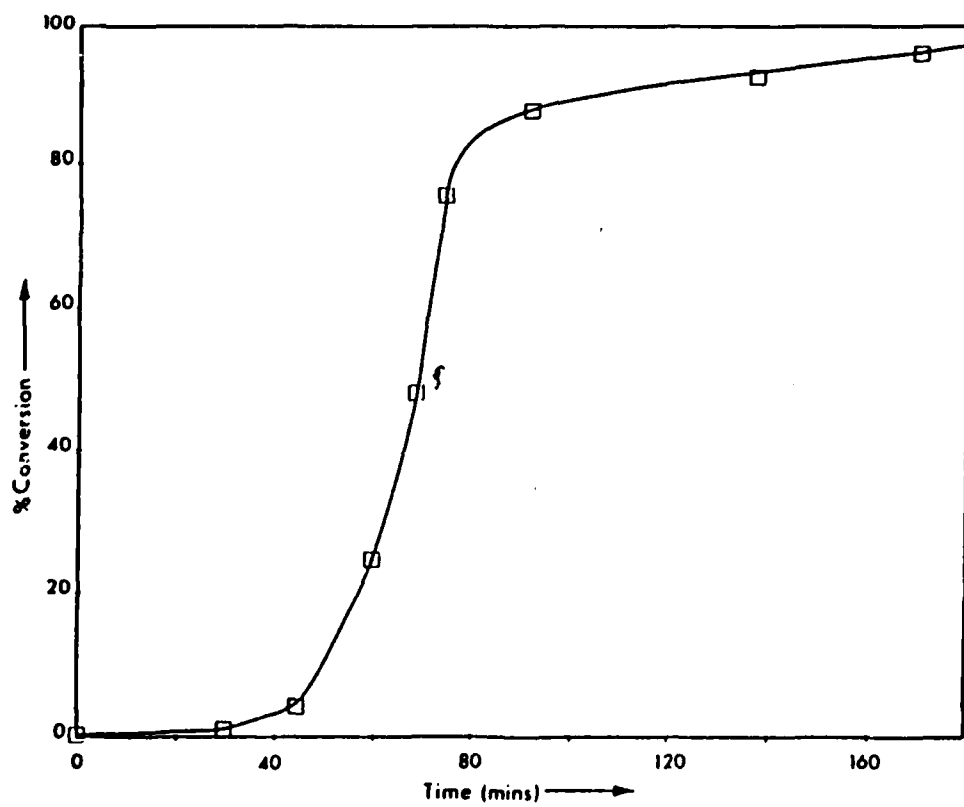


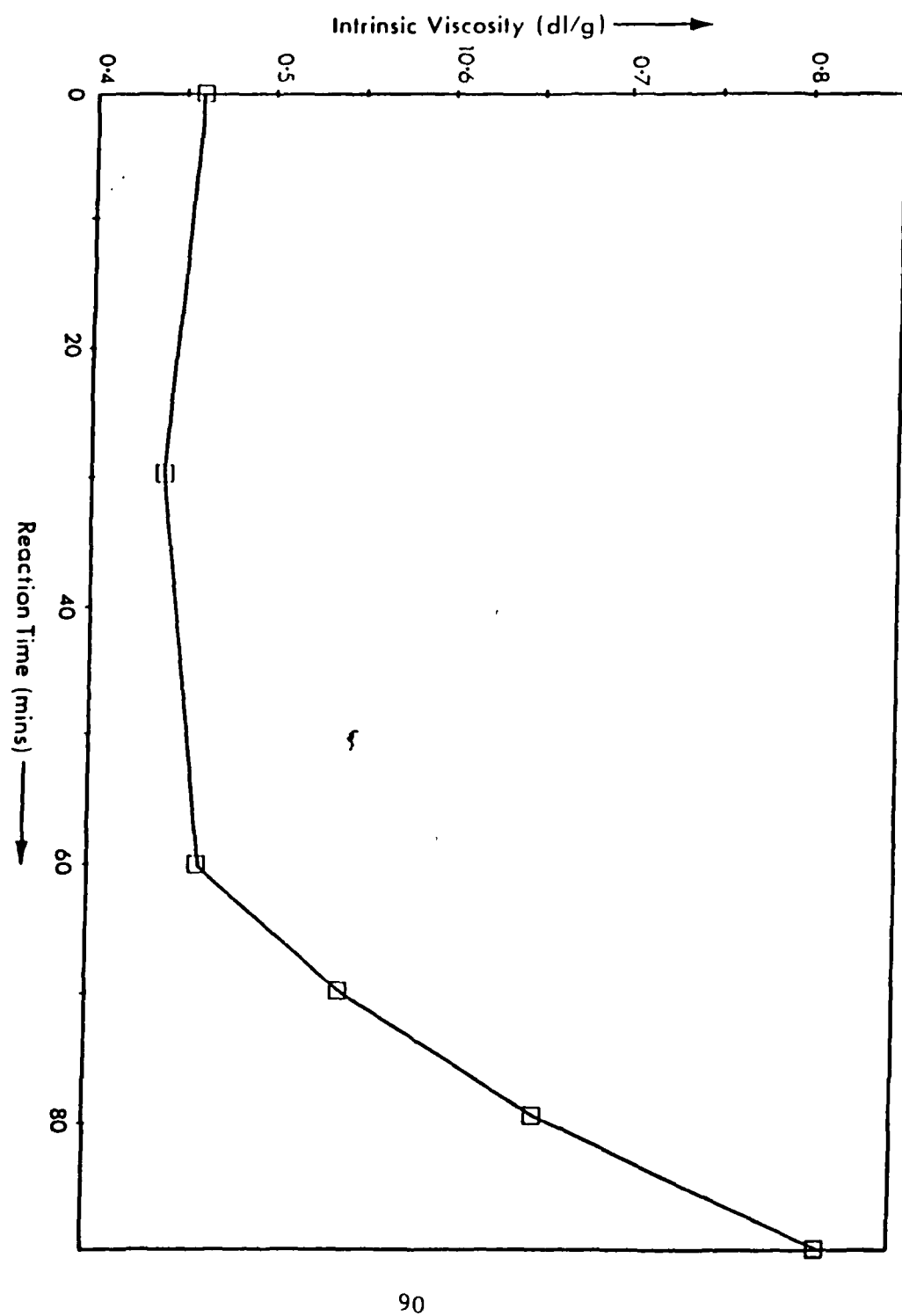


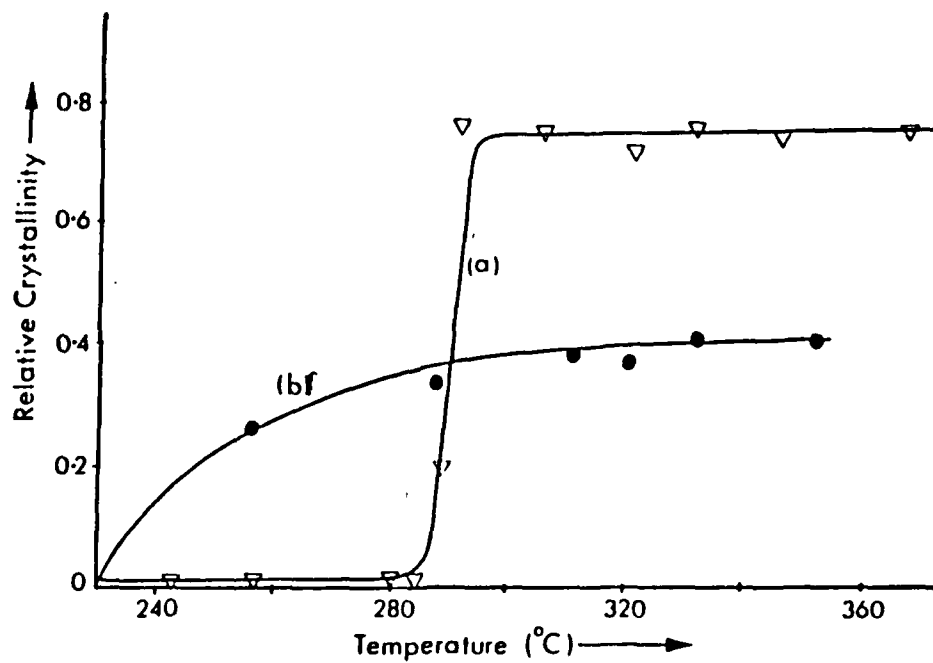


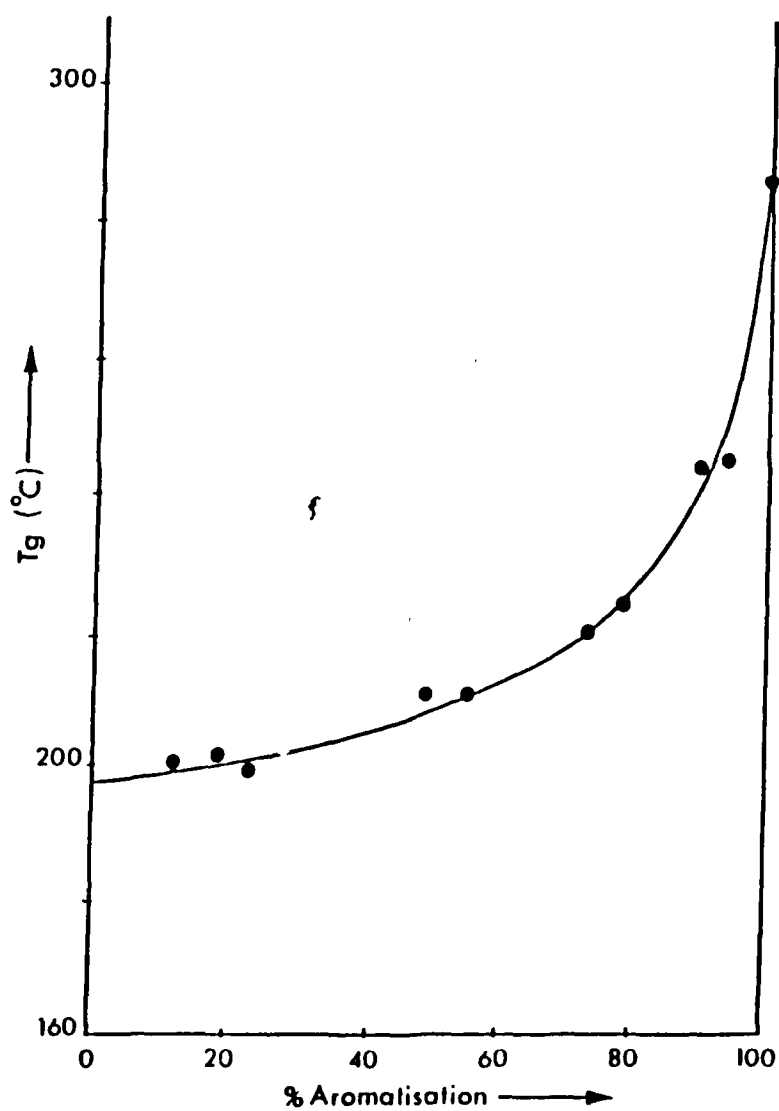












SOCIETY ACTIVITIES

CALENDAR YEAR 1987

CONFERENCES

- JULY 20 - 25 ICCM VI, Imperial College, London, England
(ASC Co-sponsor)
- SEPTEMBER 22-24 University of Delaware, Dr. Roy McCullough
(302-451-1261) and Dale Wilson (302-451-1261)
Co-chairmen. Center for Composite Materials,
University of Delaware Co-sponsor.

SHORT COURSES

- AUGUST 18 - 20 Short Course on Composite Materials
Stouffer Dayton Plaza Hotel, Dayton, Ohio.

WORKSHOP

- AUGUST 25 - 26 Biotechnology Aided Synthesis of Aerospace
Composite Resins. Stouffer Dayton Plaza Hotel,
Dayton, Ohio.

CONFERENCES SCHEDULED FOR 1988, 1989 AND 1991

1988

- MAY AIAA/SDM Conference, May 1988. ASC Co-sponsor.
- JUNE 27 - 29 FOURTH JAPAN-UNITED STATES Conference on
Composite Materials, ASC Co-sponsor, Loews L'Enfant,
Plaza Hotel, Washington, Jack R. Vinson - Chairman.
- SEPTEMBER ASC 3rd Annual Conference on Composites, Seattle,
Washington, Dr. James Seferis (206-543-9371) Chairman.
University of Washington - Co-sponsor.

1989

Virginia Polytechnic Institute and State University,
Blacksburg, Virginia, Dr. K.L. Reifsnider
(703-961-5316) Chairman. VPI - Co-sponsor

1991

ICCM-VIII, Sheraton Waikiki Hotel, Honolulu, Hawaii.
Dr. Som R. Soni (513-878-2774) Chairman.

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