



1.0



2.8



2.5

5.0



3.15



2.2

6.3



3.5



2.0

12.5



4.0



1.8



1.1

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4.5



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1.4



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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER ARU 20678.15-CH	2. GOVT ACCESSION NO. N/A	3. RECIPIENT'S CATALOG NUMBER N/A
4. TITLE (and Subtitle) NETWORK POLYMERS FORMED UNDER NONIDEAL CONDITIONS		5. TYPE OF REPORT & PERIOD COVERED FINAL 10 Oct 83 - 30 Sep 86
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) PROFESSOR C.W. MACOSKO		8. CONTRACT OR GRANT NUMBER(s) DAAG29-83-K-0149
9. PERFORMING ORGANIZATION NAME AND ADDRESS University of Minnesota Department of Chemical Engineering and Materials Science		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS U. S. Army Research Office Post Office Box 12211 Research Triangle Park, NC 27709		12. REPORT DATE December 9, 1986
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) Office of Research Administration Univeristy of Minnesota		13. NUMBER OF PAGES
		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report) NA		
18. SUPPLEMENTARY NOTES The view, opinions, and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Epoxies, Acrylates, Glass Transition Temperature, Cyclization, Network parameters, viscosity, gelation, modulus.		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Under this grant we have studied the formation of polymer networks under nonideal conditions. The work accomplished falls into three categories: (1) probability models for determining molecular weight relations and network parameters, (2) study of epoxy systems, and (3) study of vinyl-divinyl systems. The general theoretical work on probability models has comprised the following: (a) the crosslinking of chains with arbitrary length and site distribution, b) A ₂ and B ₂ step polymerization with cycles, and (c)		

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anic, network-forming systems. Several nonidealities in epoxy systems have been and are being analyzed. Substitution effects and secondary reactions in epoxy-amine systems, (DGEBA-DDS, and TGDDM-DDS) have been characterized and incorporated into a branching theory, and good agreement with experimental results obtained. Another problem in these systems is the effect of vitrification, so the variation of Tg with conversion has been studied for DGEBA-DDM and epoxy-novolac systems. In vinyl/divinyl systems, the formation of loops and the reduction in pendant double bond reactivity have been studied. A kinetic model was developed to predict the conversion of pendant double bonds to crosslinks and cycles, that information being employed in a branching theory. Good viscosity correlations were obtained. Further theoretical studies of cyclization were initiated as groundwork for systems for which cyclization may play an even larger role (e.g. in the formation of microgels).

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**NETWORK POLYMERS FORMED UNDER NONIDEAL
CONDITIONS**

FINAL REPORT

Christopher W. Macosko

December 1986

U.S. ARMY RESEARCH OFFICE

CONTRACT OR GRANT NUMBER: DAAG29-83-K-0149

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STATEMENT OF PROBLEM STUDIED (OVERVIEW)

Network polymers constitute about 25% of all polymer products, the proportion in high performance applications - high strength composites, protective coatings, electronic encapsulants, medical implants - being even higher. But because they are insoluble and their molecular structure is more complex than linear polymers, molecular characterization of network polymers is much more difficult. The understanding of relations between network polymer structure and properties is correspondingly less certain.

The first step in understanding network polymers lay in the analysis of network formed under ideal conditions: stepwise systems with equal reactivity, no substitution effect, no secondary reactions, no loop formation, and no vitrification or phase separation. In our work, model silicone and urethane systems were chosen as most nearly attaining these ideals. The corresponding theoretical analysis (branching theory) was based on the recursive nature of the network polymers, which permits relatively simple derivation of average structural parameters such as crosslink density, sol fraction, dangling chains, gel point, and molecular weight before gelation. Our success with ideal networks, both experimentally and theoretically, inspired us to attack the more complex problems of networks formed under nonideal conditions.

One important class of networks are those formed from epoxides reacting with diamines, which are used extensively in aerospace applications and in electronics. These systems may exhibit several nonidealities, such as substitution effects (among the amino-hydrogens) and secondary reactions (etherification). Another complication is diffusion control of the reactions as the glass transition temperature exceeds the cure temperature. These problems translate into difficulties in determining the structure of the network. In the case of substitution effects and secondary reactions, correct determination of the structure entails characterization of the reactions combined with branching theory appropriately modified to include those nonidealities. In the case of vitrification, an understanding of how the glass transition temperature changes with conversion is needed before the appropriate branching theory can be employed. Once the structure of the network is defined, structure-property relations can be used or correlations developed.

Another important class of networks are those formed by free radical polymerization, a great fraction of those being used in molding applications, composites, radiation cured coatings, and so forth. These systems present a host of nonidealities: the number of reactions (initiation, propagation, termination (both coupling and disproportionation), and transfer), nonideal copolymerization, vitrification, phase separation, Trommsdorff effect, and formation of cycles. If one looks first at cyclization, the characterization of the reactions are again the important first step, and it is complicated by these intramolecular reactions which are difficult to analyze directly. Once this characterization is performed, the recursive analysis can be employed to determine the structure, which again can be related to property via relationships or correlations.

The above is certainly not an exhaustive list of common nonidealities. Others worthy of study include the crosslinking of chains of arbitrary length and site distribution (in vulcanization, for example), ring formation in stepwise systems, and networks formed by living (anionic) copolymerizations.

SUMMARY OF RESULTS

Probability Models

Professor Doug Miller

The following work was accomplished or is in progress:

Two manuscripts coauthored by D.R. Miller and C.W. Macosko have been tentatively accepted for publication by Journal of Polymer Science, Physics Edition subject to minor revisions. They are entitled "Molecular Weight Relations for Crosslinking of Chains with Length and Site Distribution" and "Network Parameters for Crosslinking of Chains with Length and Site Distribution."

A model has been developed for $A_3 + B_2$ copolymerization with cyclization which treats small cycles exactly (using kinetic analysis assuming Gaussian end-to-end distances) and larger cycles approximately (using Gordon's spanning-tree approximation). Enrique Vallés is currently doing some numerical calculations with it to evaluate it.

A model for anionic polymerization to the gel point has been constructed and a program written. No cyclization is permitted. This model is being used by Lutz and co-workers at Strasbourg to study an α MS + DIB system.

The theory has been worked out for a model of anionic polymerization (living polymers crosslinking) which allows cyclization. It is based on spanning-tree concepts. Execution is planned under the new proposal.

EPOXY NETWORKS

Structure-Property Relations for Model Epoxy Networks

Sue Ann Bidstrup, Ph.D.

Rheological and molecular changes during epoxy-amine cure were monitored. An understanding of the relationship between bond formation, structure and mechanical properties has been sought. For this study, two common epoxy-amine systems have been chosen: diglycidyl ether of bisphenol A (DGEBA) and tetraglycidyl diamino diphenyl methane (TGDDM) both cured with diamino diphenyl sulfone (DDS).

Branching theory utilizing the recursive nature of the branching process and elementary laws of probability has been developed to predict average structural parameters. The possibility of a substitution effect among the amino-hydrogens and the existence of an etherification reaction was included in the derivation. This model was applied to the DGEBA-DDS and TGDDM-DDS system to obtain predictions for a variety of molecular parameters (including weight average molecular weight (M_w), weight average molecular weight of the longest linear chain (M_{LLC}), gel point and sol fraction) as a function of the extent of reaction, the stoichiometric ratio and the ratio of rate constants between the various cure reactions.

The predictions of the recursive models were tested by stopping the reaction after a designated time interval during the cure and subsequently analyzing for certain structural parameters and the conversion of functional groups. Epoxide conversion was monitored by differential scanning calorimetry, Fourier transform infra-red spectroscopy and titration. Weight average molecular weight was measured during the cure by static light scattering. The weight fraction of soluble material at a particular conversion, gel point and critical stoichiometric ratio were determined by extraction experiments. Excellent agreement was obtained between the structural analysis and predictions of the recursive theory for the DGEBA-DDS systems with excess amine or at stoichiometric theory for the DGEBA-DDS systems with excess amine or at stoichiometric concentrations. The predictions of the recursive theory were lower than the data obtained for the

TGDDM-DDS system. This may be a result of cyclization occurring in the system or the limited ability of the statistical model to account for stochastic correlations.

The viscosity of the reacting system was measured as a function of conversion of epoxide groups. Weight average molecular weight (M_w) and molecular weight of the longest linear chain (M_{LLC}) predicted from the branching theory were considered as possible correlating parameters for the viscosity of the system. The friction factor ζ was also calculated during the cure. Good correlation was obtained between viscosity and ζM_w for the DGEBA-DDS system at balanced stoichiometry.

Glass Transition Temperature in Epoxy Networks

Arturo Hale

A literature survey has shown that the prediction of T_g as a function of conversion in thermosetting systems is still an open problem. The case of epoxy resins is especially important, since in several of these systems the glass transition temperature may reach and even pass the cure temperature, and the reaction becomes diffusion controlled. Thus, a full description of the kinetics of the polymerization reaction requires knowledge of how T_g changes with conversion.

Due to the lack of published data describing the variation of T_g with degree of conversion, we have collected this kind of data for a DGEBA-DDM system. We have also studied the behavior of novolac-epoxies cured with novolacs. This system finds application in the encapsulation of integrated circuits. The basic chemistry has been studied by DSC and NMR using model compounds. It has been found that no significant amount of competing reactions takes place if the concentration of catalyst is low enough. The dependence of T_g on conversion was studied for epoxy-novolacs with different functionalities. T_g shows a very steep increase at high conversions, which could be due to a reaction taking place between secondary hydroxyls and epoxide groups.

ACRYLATE NETWORKS

Formation-Structure and Structure-Property Relationships During Vinyl-Divinyl Copolymerization

Donald T. Landin

The network forming copolymerization of vinyl and divinyl monomers has been investigated. An understanding of the relationship between bond formation, polymer structure, and polymer properties has been sought. The main focus of this understanding is on the pre-gel portion of the reaction. The viscosity of the reaction mixture is the polymer property of primary interest at this time.

The particular chemical system studied consisted of methyl methacrylate with small amounts (0-5% v/v) of ethylene glycol dimethacrylate. The radical addition polymerization was initiated with azobisisobutyronitrile. A transfer agent was used to control the primary chain length.

Bond formation was studied experimentally by measuring monomer conversion and pendant vinyl conversion as a function of reaction time. Monomer conversion was found to go by first order kinetics at low conversions. ^1H NMR analysis showed that in this system the different monomeric units go into the polymer equally. Pendant vinyl conversion was measured by ^1H NMR. When plotted vs. monomer conversion, it gives a nearly linear plot with a positive slope and a positive y-intercept. The y-intercept is attributed to cycles formed during the formation of a primary chain. The slope of the plot is due to crosslinking and cycles formed after a crosslink has formed. This concept of cyclization is incorporated into a kinetic model for the polymerization. Rate constants are obtained from experimental data. Pendant vinyls has a lower reactivity than monomeric vinyls. The kinetic model can be used to predict the conversion of pendant vinyls to primary cycles, secondary cycles, and crosslinking.

A branching theory utilizing the recursive nature of the branching process has been developed to predict polymer structure. The monomer and pendant vinyl conversions provide the input information for the theory. Expressions for weight average molecular weight (M_w), weight average molecular weight of the longest linear chain ($M_{1,w}$), weight fraction of solubles, and crosslink density are derived.

The viscosity of the reaction mixture is measured as a function of time and then related to conversion. $M_{1,w}$ correlates the viscosity well as the viscosities of different systems fall onto one curve.

Chainwise Crosslinking with Cyclization

Neil Dotson

Theoretical study of departures from treelike structure in free-radical, crosslinking systems has been initiated, concentrating first on cyclization (intramolecular reaction of pendant vinyl groups). The groundwork for two theoretical approaches, a probabilistic model and a simulation model, has been performed.

The probabilistic model is based on competing reactions (ring, chain) and employs equilibrium chain statistics. The work thus far has been limited to single cycle growth on an isolated primary chain, as this should be indicative of the extent of pendant conversion extrapolated to zero monomer conversion at low crosslinker levels, which has been measured by several researchers, including Landin. Comparisons between theory and experiment show that the model fairly consistently overpredicts. Possible causes for this are excluded volume effects and end-to-backbone effects. This model is also incapable of predicting any crosslinker concentration dependence, another weakness which must be resolved.

A simple Monte Carlo simulation model, similar to that of Herrmann, Stauffer, and Landau (*J. Phys. A.*, **16**, 1221 (1983)), has also been used to study the zero-conversion limit. The advantage of this method is its explicit embeddedness in space, so that structures more complicated than a single cycle can be built up naturally. This model has been extended to include implicit small molecule motion, but still lacks macromolecular motion. Future work will address this problem, as well as the question of the lattice constraint and of higher conversion situations.



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PUBLICATIONS

New (attached as appendices)

"Calculation of Average Network Parameters Using Combined Kinetic and Markovian Analysis" (D.R. Miller and C.W. Macosko), submitted for publication in "Biological and Synthetic Networks", Elsevier, to appear 1987.

"Cyclization and Reduced Reactivity of Pendant Vinyls During the Copolymerization of Methyl Methacrylate and Ethylene Glycol Dimethacrylate" (D.T. Landin, C.W. Macosko) submitted to *Macromolecules*, 1986.

"Structural and Rheological Changes During Epoxy Crosslinking" (S.A. Bidstrup and C.W. Macosko), to appear in proceedings from symposium on Crosslinked Epoxies, Prague July 14-17, 1986.

Previously Reported

"Molecular Weight Relations for Crosslinking of Chains with Length and Site Distribution" (C.W. Macosko and D.R. Miller), *Journal of Polymer Science, Physics Edition*, accepted for publication 1986.

"Network Parameters for Crosslinking of Chains with Length and Site Distribution." (C.W. Macosko and D.R. Miller), *Journal of Polymer Science, Physics Edition*, accepted for publication 1986.

"Structure-Rheology Relations for Model Epoxy Networks" (Sue Ann Bidstrup and C.W. Macosko) presented at SAMPE meeting, April 7-10, 1986.

"Rheological Changes during Crosslinking" (C.W. Macosko), *British Polymer Journal*, **17**, 239-245 (1985).

"Heat Transfer and Property Development in Liquid Silicone Rubber Molding" (C.W. Macosko and L.J. Lee) *Rubber Chem. Tech.*, **58**, 436-448 (1985).

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"Ring-chain Competition Kinetic Models for Linear and Nonlinear Step-reaction Copolymerizations" (C. Sarmoria, E.M. Vallés and D.R. Miller) *Makromol. Symp.*, **2**, 69-87 (1986).

"Rheological Changes During the Copolymerization of Vinyl and Divinyl Monomers" (D.T. Landin and C.W. Macosko) in "Characterization of Highly Crosslinked Polymers," eds. S.S. Labana and R.A. Dickie, ACS Symposium Series, **243**, 33-46 (1984) Washington, D.C.

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"Structural and Rheological Changes During Epoxy Crosslinking" (S.A. Bidstrup and C.W. Macosko) *Soc. Plast. Eng. Tech. Papers*, **30**, 278-281 (1984).

"Molecular Weight Change During Vinyl-Divinyl Copolymerization" (D.T. Landin and C.W. Macosko) presented at European Networks Group Meeting, Manchester, England, September, 1984.

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DEGREES AWARDED

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Donald T. Landin, Ph.D. 1985; currently polymer scientist, 3M Company, St. Paul, Minnesota.

APPENDIXES

"Calculation of Average Network Parameters Using Combined Kinetic and Markovian Analysis" (D.R. Miller and C.W. Macosko), submitted for publication in "Biological and Synthetic Networks", Elsevier, to appear 1987.

"Cyclization and Reduced Reactivity of Pendant Vinyls During the Copolymerization of Methyl Methacrylate and Ethylene Glycol Dimethacrylate" (D.T. Landin, C.W. Macosko) submitted to *Macromolecules*, 1986.

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Calculation of Average Network Parameters Using Combined Kinetic and Markovian Analysis

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Theoretical models are useful for calculating various average parameters during network formation such as weight average molecular weight before gelation, the gel point, and weight fraction solubles, and concentration of pendant chains and elastically effective junctions after gelation. These models and their methods of solution may take various forms; the most common are kinetic models and Markovian models. The kinetic approach applies to a larger class of systems; however, it may become intractable, especially for branching polymerizations, because a large number of differential equations must be solved. The Markovian approach (sometimes referred to as the statistical or cascade approach) is attractive because it permits more direct calculation of average properties by exploiting the recursive structure of the material. An optimal approach would combine the two methods. This paper surveys some systems which can be efficiently analyzed with a combined methodology.

The kinetic approach and the Markovian approach can be contrasted by considering the gel point of an ideal, A_f stepwise homopolymerization. Before gelation, the kinetic approach models the concentration of each size of molecule. If P_i represents a polymer consisting of i A_f monomers then:



at a rate proportional, ideally, to $[(f_i - i + 1)(f_j - j + 1)]$ for $i, j \geq 1$. Differential equations are solved to find the concentration of different molecular sizes as a function of time or conversion. Analytical solution of these equations is quite difficult for even the simplest systems (Dusek, 1985a; Ziff, 1980; Ziff and Stell, 1980) and appears to be impossible for complex systems, and thus the equations must be solved numerically. From the concentration of different species the weight average molecular weight is computed.

Gelation occurs when the weight average molecular weight diverges.

The Markovian approach is based on the fact that the A_f monomers combine randomly in an ideal homopolymerization, i.e. all intermolecular AA bonds are equally likely to form. This results in a branching structure which has a recursive structure with lack-of-memory which can be exploited by various analysis methods (Flory, 1953; Gordon, 1962; Macosko and Miller, 1976; Burchard, 1983). For illustration we use the "in-out" recursion: let EW_A^{out} equal the expected weight seen looking out from a randomly chosen A-site (directions 1 in Figure 1). At conversion α :

$$EW_A^{out} = \alpha EW_A^{in} + (1 - \alpha) 0 \quad (2)$$

where EW_A^{in} is the expected weight looking into a random A-site (directions 2 in Figure 1).

$$EW_A^{in} = M_A + (f-1) EW_A^{out} \quad (3)$$

Finally the weight average molecular weight is:

$$M_W = M_A + f EW_A^{out} \quad (4)$$

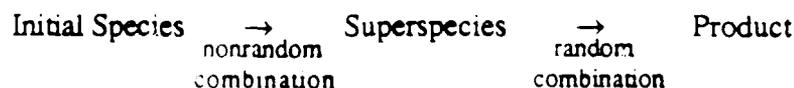
Solving the above three equations gives:

$$M_W = M_A + \alpha M_A / [1 - \alpha (f - 1)] \quad (5)$$

and gelation occurs at $\alpha_c = 1 / (f - 1)$, which is identical to the answer computed using kinetic analysis.

The Markovian analysis assumes that the species combine in a totally random way. There are many systems for which this is not true. In these cases we recommend combining the two methods. This idea is not new; several authors have used it implicitly and Dusek (1986) has explicitly presented it as a formal approach to analyzing different systems.

In a combined analysis the aspects of the reaction which are not totally random are treated kinetically to obtain "superspecies" which are combined randomly and thus can be treated using a Markovian analysis:



The two steps in this model may either correspond to two distinct sequential steps or they

may be occurring simultaneously, in which case the construct is merely a convenient way to think about the process. This paper discusses several different systems whose average properties can be computed efficiently using a combined kinetic-Markovian approach.

Copolymerization with Substitution Effect

Consider an A_3 plus B_2 copolymerization for which there is a first shell substitution effect on the A_3 monomers. This system has been analyzed by numerous authors, including Miller and Macosko (1980). By explicitly recognizing the combined kinetic-Markovian approach some clarity is revealed; it is a good example for illustrating the concepts.

We define seven superspecies: four types of A-monomer and three types of B-monomer. Let:

A_3^i = A-monomer with i reacted sites, $i = 0, 1, 2, 3$

B_2^i = B-monomer with i reacted sites, $i = 0, 1, 2$

k_i = rate constant for reaction of A_3^i functionality with a B functionality, $i = 0, 1, 2$.

From a kinetic analysis we can find the concentration of each of the seven superspecies by solving the following system of kinetic equations:

$$\frac{d}{dt} A_3^0(t) = -3k_0 A_3^0(t) (2B_2^0(t) + B_2^1(t)) \quad (6)$$

$$\frac{d}{dt} A_3^1(t) = (3k_0 A_3^0(t) - 2k_1 A_3^1(t))(2B_2^0(t) + B_2^1(t)) \quad (7)$$

$$\frac{d}{dt} A_3^2(t) = (2k_1 A_3^1(t) - k_2 A_3^2(t))(2B_2^0(t) + B_2^1(t)) \quad (8)$$

$$\frac{d}{dt} A_3^3(t) = k_2 A_3^2(t) (2B_2^0(t) + B_2^1(t)) \quad (9)$$

$$\frac{d}{dt} B_2^0(t) = -2B_2^0(t) (3k_0 A_3^0(t) + 2k_1 A_3^1(t) + k_2 A_3^2(t)) \quad (10)$$

$$\frac{d}{dt} B_2^1(t) = (2B_2^0(t) - B_2^1(t)) (3k_0 A_3^0(t) + 2k_1 A_3^1(t) + k_2 A_3^2(t)) \quad (11)$$

$$\frac{d}{dt} B_2^2(t) = B_2^1(t) (3k_0 A_3^0(t) + 2k_1 A_3^1(t) + k_2 A_3^2(t)) \quad (12)$$

The seven superspecies are shown in Figure 2. The combination is random: any pair of reacted A-site and reacted B-site is equally likely to combine. Thus instead of thinking of the system as two species, A_3 and B_2 , combining together in a rather complicated, not

completely random way (substitution effect), we think of seven superspecies which combine in a completely random way. Furthermore the seven superspecies go to complete reaction. The resulting structure is a branching process with seven types of components: it can be analyzed using any of several methods (the pgf approach of Gordon (1962), the recursive approach of Macosko and Miller (1976), the analysis of generation sizes as mentioned by Burchard (1983), or even the Flory-Stockmayer combinatorial approach (Flory, 1953)). The point is that by the construct of superspecies it is possible to identify a Markovian branching process which can then be analyzed using existing techniques.

Homopolymerization with Substitution Effect

Consider an A_f homopolymerization with first-shell substitution effect. At first glance this might be considered as a special case of the above copolymerization example, but in general it is more complicated. For this case it is necessary to define more complicated superspecies of A-monomers, if our goal is a Markovian branching structure.

For a general first shell substitution effect homopolymerization we have a matrix of kinetic rates:

$$\underset{\sim}{\mathbf{K}} = \begin{bmatrix} k_{00} & k_{01} & k_{02} & \cdots & k_{0, f-1} \\ k_{10} & k_{11} & k_{12} & \cdots & k_{1, f-1} \\ \cdot & & & & \\ \cdot & & & & \\ \cdot & & & & \\ k_{f-1, 0} & k_{f-1, 1} & k_{f-1, 2} & \cdots & k_{f-1, f-1} \end{bmatrix} \quad (13)$$

where

$k_{i, j}$ = rate at which a monomer with i reacted sites forms a bond with a monomer with j reacted sites

and

$$k_{i, j} = k_{j, i}$$

We define the superspecies by labelling each reacted site of a monomer with a pair of integers (m, n) , where m signifies that it is the m^{th} site to react on the monomer and n signifies that the site with which it reacts is the n^{th} site to react on the monomer to which it belongs, $1 \leq m, n \leq f$.

The superspecies for an A_2 homopolymerization with first shell substitution effect are shown in figure 3; there are seven of them. The situation is similar for general f except the number of superspecies increases rapidly: for $f = 3$ there are 40 superspecies.

These superspecies combine randomly into a Markovian branching structure: an (m, n) site combines with an (n, m) site. By having such complicated superspecies we have created a system without longer range dependencies which exist in other models of homopolymerization with general first-shell effect.

Crosslinking of Pre-made Chains

Consider a system which forms by crosslinking of premade chains which have arbitrary distributions of mass and functionality. In this case the chains play the role of superspecies so the two stages are distinct: manufacture of the functional polymer (typically kinetically controlled) and then random crosslinking using radiation or a small monomer (typically Markovian). This case is treated by Miller and Macosko (1986a, 1986b).

Copolymerization with Cycles

Consider an $A_3 + B_2$ copolymerization in which intramolecular bonds are allowed to form. Sarmoria et al. (1986a) have analyzed a special case of this system in which the only allowable intramolecular bonds are those which close a cycle consisting of a single B_2 monomer forming two bonds with a single A_3 monomer. They define 13 superspecies which correspond to the possible configurations within one shell of A-monomers and four superspecies corresponding to B-monomers. The concentration of the various superspecies are kinetically modelled assuming a Gaussian end-to-end distance and competing ring-chain reactions. The superspecies are then combined randomly into a Markovian branching structure.

Sarmoria et al. (1986b) have extended the above model to include larger cycles. Cycles involving a single B_2 are modelled as before, but larger cycles are modelled using the spanning tree approximation of Gordon and Scantlebury (1966). In this case, as the polymerization is proceeding, intermolecular bonds are labelled with α 's, intramolecular bonds are labelled with σ 's, and the unreacted sites with ω 's. The intramolecular bonds on cycles with more than one B_2 are then broken (each site retaining its σ -label). This results in a tree structure made up of 22 different superspecies. As before the superspecies reflect all possible configurations within the first shell surrounding an A-monomer. The 22

superspecies are shown in Figure 4. Numerous variations on these models are possible.

Step Reactions which Produce a Secondary Site

Consider an $A_f + B_g$ copolymerization such as an f -functional epoxy and a g -functional cresol; such a system is used for transistor encapsulation. In these systems bond formation between two sites creates a new site. One of the initial reactants can react with this site, often in a chainwise manner. The block of connected sites generated from one initial reaction is one of the superspecies, although in this context it might be more appropriate to call them "super-bonds." Figure 5 shows the situation.

Bokare and Gandhi (1980) and Dusek (1985b) have analyzed the reaction of epoxy and diamine with polyetherification using a combined kinetic-Markovian approach. Riccardi and Williams (1986 a,b) have also studied these systems. Other such systems include isocyanate and hydroxyl with allophanate formation.

Anionic Copolymerization of Vinyl with Divinyl Monomers

Worsfold (1970) and Lutz et al. (1982) describe anionic copolymerizations. Lutz et al. consider α -methylstyrene (α -MS) plus 1,3-diisopropenylbenzene (1,3-DIB). This system is depicted on Figure 6; the chemical structure is shown only in unreacted species. The superspecies are the living polymer chains, when a 1,3-DIB monomer is part of a chain its other group may be unreacted (labelled with ω in Figure 6) or reacted in which case the monomer acts as a crosslink (and the other group is labelled with an α). The relevant properties of the superspecies are computed from a kinetic analysis; these properties are very similar to those needed in the analysis of the crosslinking of ready-made chains studied by Macosko and Miller (1986a,1986b). The superspecies are then randomly combined together into a Markovian structure and the product analyzed by branching theory. Dusek and Somvasky (1985) have also studied similar systems using a combined kinetic-Markovian analysis.

Acknowledgements

This work was supported by a grant from the U. S. Army Research Office. The authors thank Neil Dotson for helpful discussions and preparation of the manuscript.

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FIGURE CAPTIONS

Figure 1. Schematic of a typical branched molecule after degree of polymerization α .

Figure 2. Initial species, superspecies and product for $A_3 + B_2$ copolymerization with first shell substitution effect on A_3 .

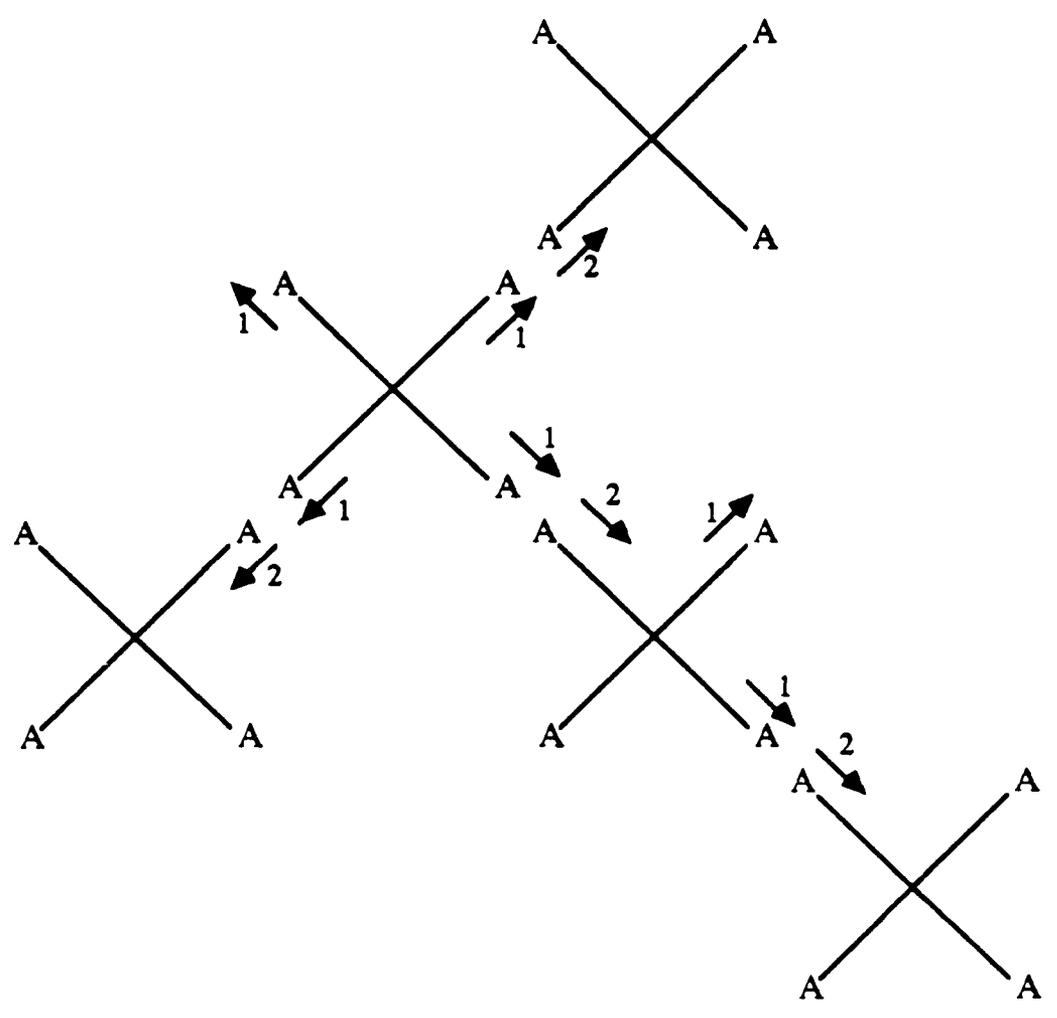
Figure 3. Species, superspecies and product for A_2 homopolymerization with first shell substitution effect.

Figure 4. Superspecies for $A_3 + B_2$ copolymerization with cycles.

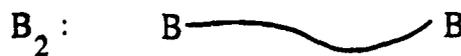
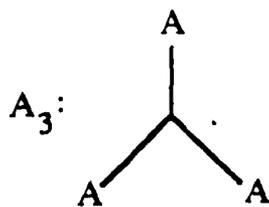
Figure 5. $A_f + B_g$ copolymerization with secondary B-site produced.

Figure 6. α -MS + 1,3-DIB copolymerization.

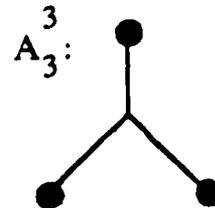
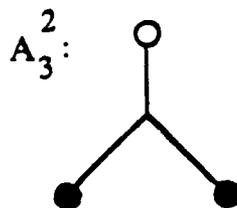
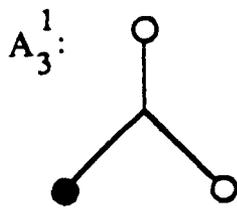
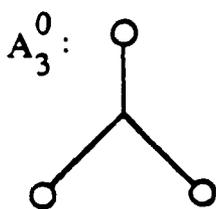
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INITIAL SPECIES



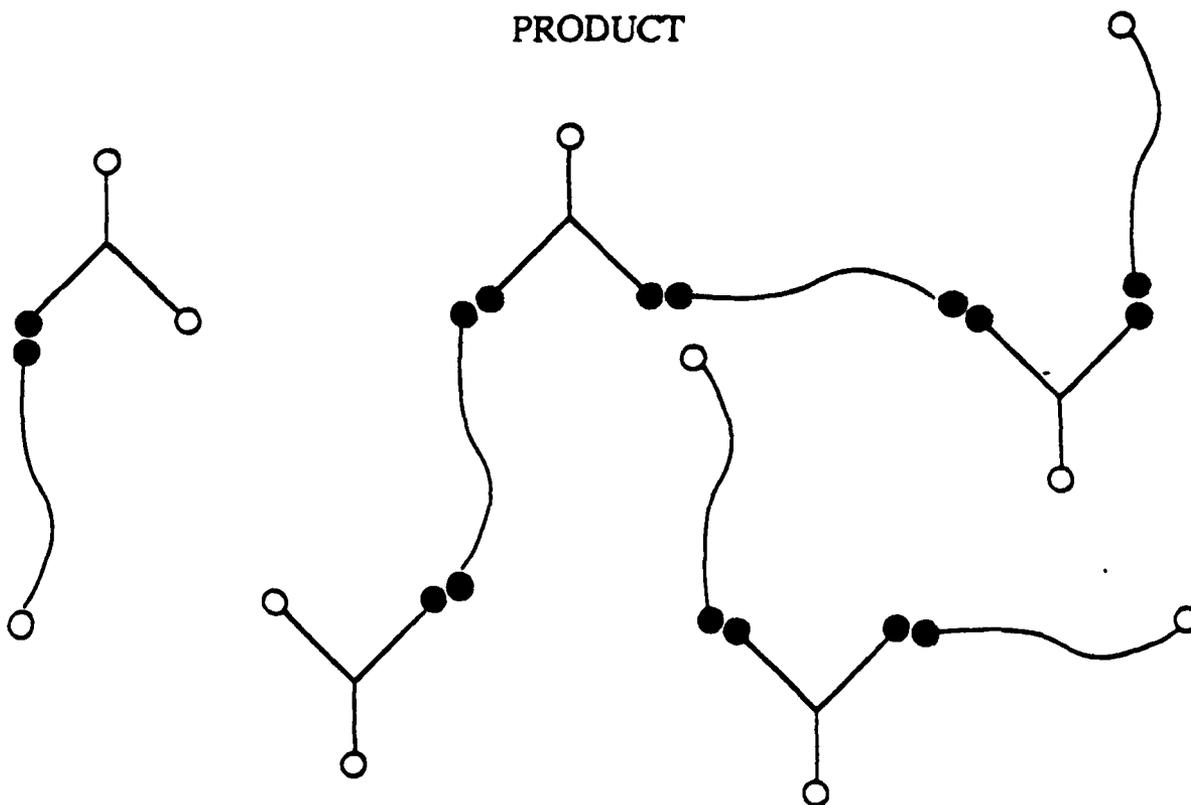
SUPERSPECIES



○ : Unreacted

● : Reacted

PRODUCT



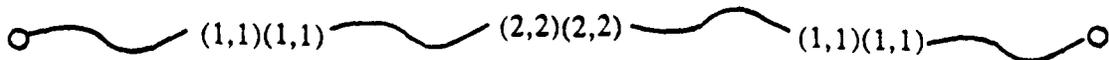
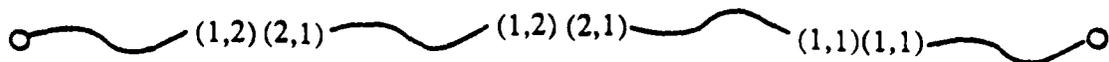
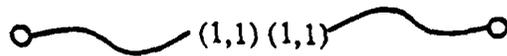
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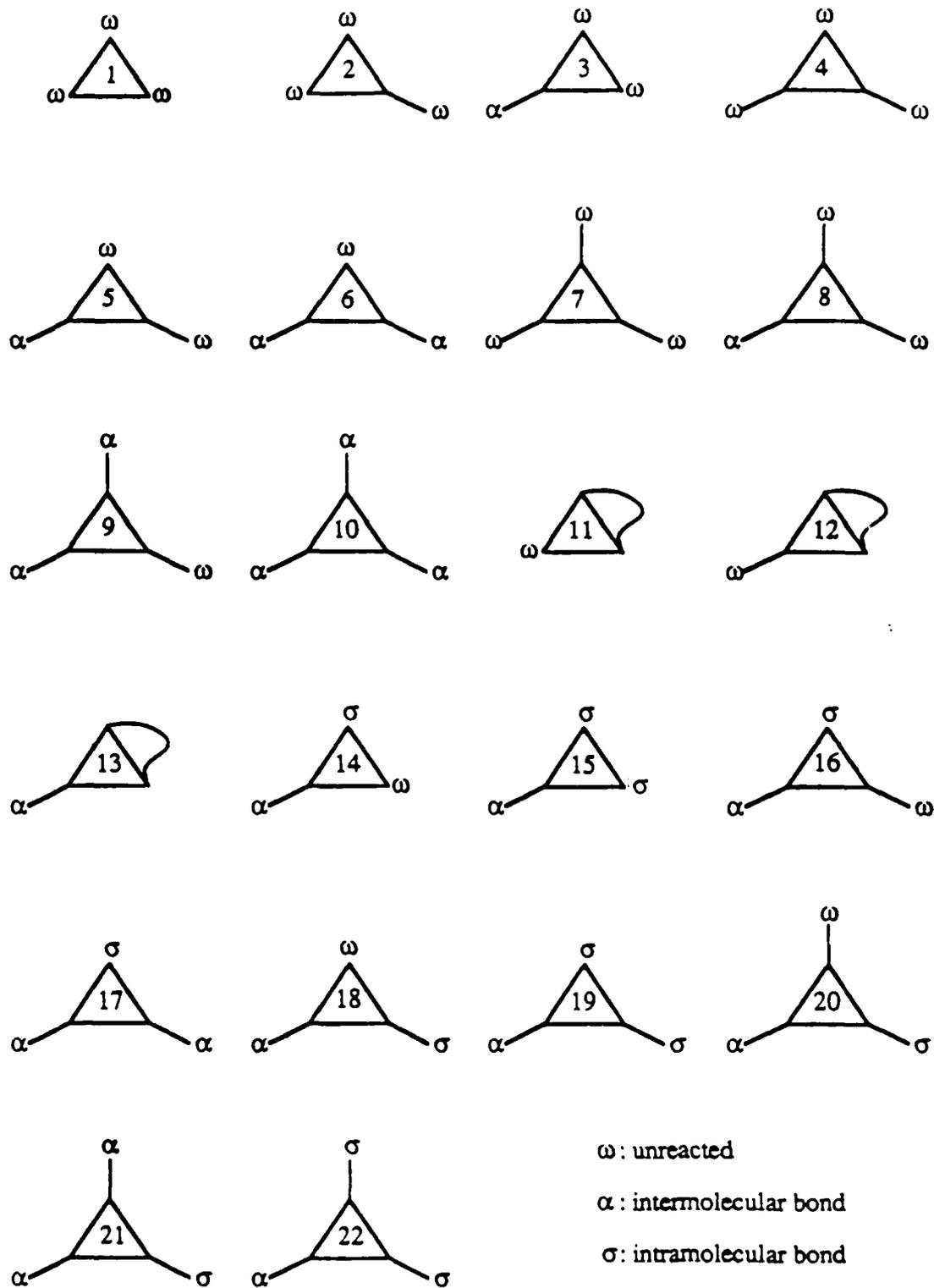


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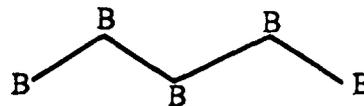
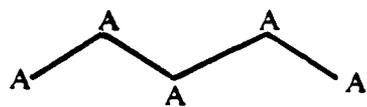


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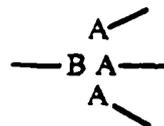
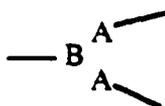




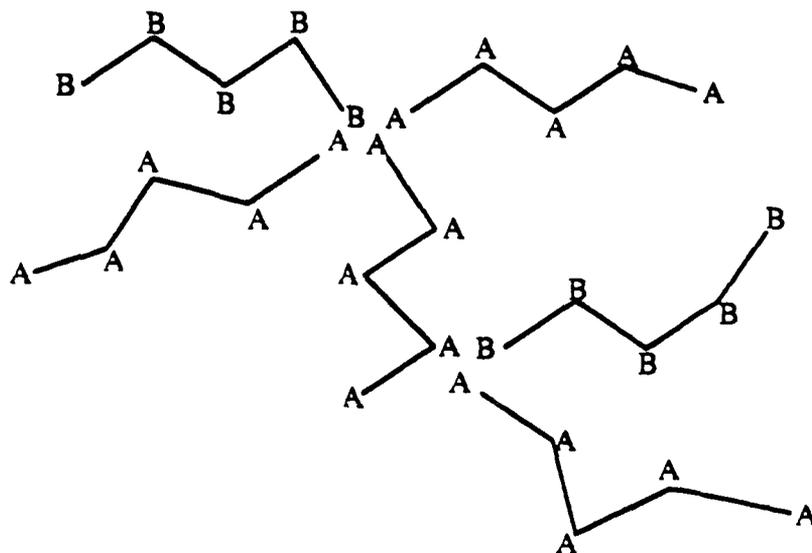
SPECIES



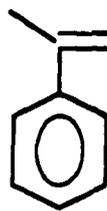
SUPER-BONDS



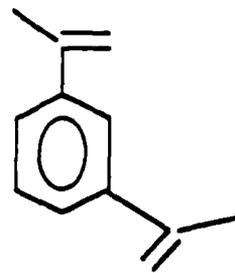
PRODUCT



UNREACTED SPECIES

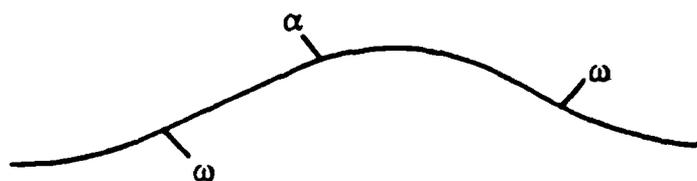


α -MS

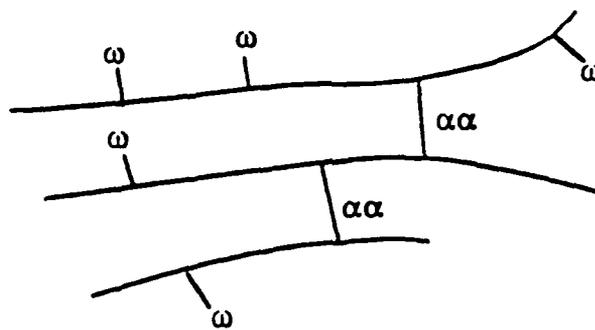


1,3-DIB

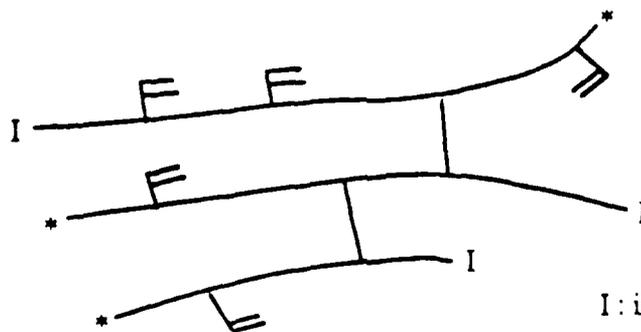
SUPERSPECIES



PRODUCT WITH LABELS



PRODUCT



I : initiated end

* : live end

Cyclization and Reduced Reactivity of Pendant Vinyls During
the Copolymerization of Methyl Methacrylate and Ethylene
Glycol Dimethacrylate

D. T. Landin and C. W. Macosko

Abstract

Methyl methacrylate was copolymerized with small amounts of ethylene glycol dimethacrylate. Monomer and pendant vinyl conversion as a function of time were measured up to the gel point. Pendant vinyl conversion was determined by ^1H NMR. Plots of pendant conversion vs. monomer conversion exhibit a positive y-intercept indicating the tendency to cycle during the formation of a primary chain. For bulk systems, this amounted to approximately 3-4% of pendant vinyls and the proportion in cycles increased with dilution. The slope of the pendant vs. monomer conversion plot is attributed to the formation of crosslinks and subsequent cycles. A kinetic model is

INTRODUCTION

Understanding the behavior of pendant vinyls is key to the study of network formation by addition polymerization involving multifunctional vinyl monomers. During such a polymerization, pendant vinyls are created when the first vinyl unit of a multifunctional vinyl monomer reacts and the group is added to a polymer chain. The pendant vinyl can then react or remain pendant. The reactivity of the pendant vinyl may be the same as that of the monomeric vinyl or it may be increased or reduced. If it reacts with a growing chain to which it is not already chemically attached, it forms a crosslink. Cyclization occurs if the pendant vinyl is already attached to the chain with which it reacts.

This behavior of pendant vinyls affects the prediction of network properties such as crosslink density, sol fraction, and critical conversion for gelation. The first theories which connected structural properties and extent of reaction were those of Flory¹⁻² and Stockmayer³⁻⁴. These theories assumed equal reactivity of monomeric and pendant vinyls and all reacted pendant vinyls were crosslinks (no cyclization). Walling⁵ showed that for the methyl methacrylate - ethylene glycol dimethacrylate and vinyl acetate - divinyl adipate systems there was a large discrepancy between the gel point calculated from the Flory-Stockmayer theory and that found experimentally. He attributed the discrepancy to diffusion control of the reaction. In a series of papers, Gordon and Roe⁶ disputed

developed which includes constants for cyclization and pendant reactivity. Values for these constants for the chemical systems studied are evaluated. The average pendant vinyl reactivity is found to be approximately half that of monomeric vinyl reactivity.

this explanation and instead attributed the discrepancy to the formation of cycles. There is extensive experimental evidence of the inadequacy of the Flory-Stockmayer theory for several systems⁷⁻¹⁵. Two explanations for the discrepancy between observed and theoretical gel points are the formation of cycles¹⁶ and a reduced reactivity of the pendant functional group.^{14,17}

In this work, conversion of monomeric and pendant vinyls and the gelpoint are determined experimentally for the vinyl-divinyl system of methyl methacrylate with small amounts of ethylene glycol dimethacrylate. A simple model is proposed which includes the possibility for both cyclization and reduced reactivity. This provides a framework within which to organize and study the data.

EXPERIMENTAL

Methyl methacrylate (MMA) and ethylene glycol dimethacrylate (EGDMA) were obtained from Aldrich. MMA was washed with a 10% aqueous potassium hydroxide solution and EGDMA was used as received. The monomers were mixed to give the chemical systems shown in Table 1. Azobisisobutyronitrile (AIBN) from Kodak was added to the solutions in the amount 0.3% by weight. To some solutions, 1% by volume dodecanethiol was added as a transfer agent. The reaction mixture was poured into several 6 inch glass test tubes each capped with a rubber septum. The tubes were placed in a 60°C water bath for varying amounts of time.

Tubes were removed from the bath and polymer was precipitated in methanol to which a small amount of diphenyl picryl hydrazyl (DPPH) had been added.

The conversion of monomer was determined by drying and weighing the precipitated polymer. Conversion vs. time data for the polymerization under these conditions are shown in Figure 1. Neither the addition of EGDMA or the addition of transfer agent changed the conversion vs. time results.¹⁶

Gel points were determined by observing the time at which the reaction mixture would no longer flow. The gel point conversion was then obtained from the conversion vs. time plot. These results are listed in Table 2.

Proton nuclear magnetic resonance, ¹H NMR, was used to determine the conversion of pendant vinyls. The precipitated polymer was dissolved in chloroform and then reprecipitated in methanol. The polymer was dried and then dissolved in deuterated chloroform with 1% v/v tetramethylsilane (TMS). This solution was used for NMR analysis. NMR spectra were obtained with a Nicolet NT-300 WB (Nicolet Analytical Instruments). A one-pulse sequence was used with a 45° pulse, 2 second delay time, and 2.05 second acquisition time. Approximately 100 acquisitions were obtained per spectrum. Quadrature detection was used and the spectral window was 4000 Hz. The spectra were machine integrated.

An NMR spectrum for sample 2N is shown in Figure 2. A blowup of the region from 4.0 to 6.5 ppm is shown in Figure

3. The 3 peaks from 0.7 to 1.25 ppm are from methyl groups adjacent to reacted vinyl groups. The peaks from 4.0 to 4.5 ppm are from the $-OCH_2-$ protons on EGDMA. The two peaks at 5.65 and 6.2 ppm are from unreacted vinyl groups. The peak at 3.55-3.7 ppm is due to $-OCH_3$ protons from MMA.

The areas under the $-OCH_2-$ and $-OCH_3$ peaks are used to determine copolymer composition through the equation

$$\frac{[EGDMA]}{[MMA]} = \frac{\sum A(-OCH_2-)/4}{A(-OCH_3)/3} \quad (1)$$

where $A(-OCH_2-)$ and $A(-OCH_3)$ are the areas under the peaks. Using Equation 1, the polymer ratio is found to be identical to the monomer ratio (Table 1) indicating monomeric vinyl reactivities are equal as found by previous workers¹⁵.

Pendant conversion is given by the equation

$$p_p = \frac{\sum A(-C=CH_2)/2}{\sum A(-OCH_2-)/4} \quad (2)$$

where p_p denotes pendant conversion.

In some cases, it was very difficult to eliminate all monomer from polymer. When this happened, the spectrum appeared as in Figure 4. It was difficult to separate the monomer and polymer $-OCH_2-$ peaks so an alternative analysis was used. This analysis used the equation

$$p_p = \frac{\alpha - \beta(\gamma + 1)}{\alpha + \beta} \quad (3)$$

$$\begin{aligned} \text{where } \alpha &= \sum A(-CH_3)/3 \\ \beta &= \sum A(-C=CH_2)/2 \\ \gamma &= [MMA]/[EGDMA] \end{aligned}$$

Intrinsic viscosity was used to determine the molecular weight of MMA with no EGDMA polymerized under the same conditions as those with EGDMA. Measurements were made at

30°C with a 0.46 mm diameter Ubbelohde viscometer. Ethyl acetate (EtOAc) was used as solvent. Using the equation

$$[\eta] = KM^a$$

where K and a for MMA in EtOAc at 30°C are¹⁹

$$K = 6.75 \times 10^{-3}$$

$$a = 0.72$$

The molecular weights were

$$M = 2.47 \times 10^5$$

for MMA without any transfer agent and

$$M = 5.21 \times 10^4$$

for MMA with transfer agent.

RESULTS AND DISCUSSION

Plots of pendant vinyl conversion vs. monomer conversion are shown in Figures 5-7. Figure 5 shows the effect of increasing amounts of EGDMA. Lines have been drawn through the data points using a least squares fit to better show the trend of the data. All systems show a positive y-intercept. This indicates that in the limit of zero conversion, pendant vinyls have reacted or in other words as the first polymer chains are forming, pendant vinyls are reacting. Since crosslinking is a second order reaction and in the limit of zero conversion polymer chains are infinitely dilute, this loss of pendant vinyls must be

due to cyclization. Cyclization during the formation of a primary chain will be called primary cyclization.

From Figure 5, it can be seen that within this range of crosslinker concentration, increasing the EGDMA does not change the proportion used up in primary cycles. The effect of a different primary chain length is shown in Figure 6. Samples with and without transfer agent have the same proportion of pendant vinyls in primary cycles, however the slopes are much different. Figure 7 shows the effect of dilution. A greater proportion of pendant vinyls are used in primary cycles as the dilution is increased.

The y-intercept and slope from each pendant conversion curve and the gel point conversion for each chemical system investigated are listed in Table 2.

In developing a model to describe this behavior, the slope of the pendant conversion curve is attributed to the formation of crosslinks and to secondary cycles. Secondary cycles are those formed with a pendant vinyl attached to a polymer chain which has just been connected to the propagating radical chain by a crosslink. The process of crosslinking and secondary cyclization is illustrated in Figure 8. The contributions of crosslinking and secondary cyclization to the slope can be separated at the gel point since the conversion of pendant vinyls to crosslinks necessary for gelation is known theoretically.

KINETIC MODEL

A detailed development of the kinetic model is found in the Appendix. Three constants of concern are:

r_3 - reactivity ratio of pendant vinyl to monomeric vinyl

k_{pp} - constant for primary cyclization

k_{ps} - constant for secondary cyclization.

The primary cyclization constant is obtained from the y-intercept of the pendant conversion vs. monomeric conversion plot. The slope of this plot is not enough information to determine r_3 and k_{ps} alone. A further piece of information is needed. This is obtained by using network theory. The pendant conversion to crosslinks necessary for gelation is obtained theoretically from the equation²⁰

$$p = \frac{1 - q}{2a_4q} \tag{4}$$

where p is the conversion of pendant vinyls to crosslinks necessary for gelation, q is the probability that a monomeric unit incorporated in a polymer chain is not a chain end and a_4 is the proportion of vinyl functional groups which are on divinyl monomer units.

To obtain a unique pair (k_{ps}, r_3) of values which gives both the correct slope and the correct crosslink conversion at gelation, k_{ps} vs. r_3 giving the correct slope and k_{ps} vs. r_3 giving the crosslink conversion are plotted.

The k_{ps} vs. r_3 plot for pairs giving the correct slope of the pendant conversion plot is determined by using the kinetic model developed in the Appendix. A value for r_3 is chosen and the slopes obtained using three different values for k_{ps} with the r_3 value are used to find the k_{ps} value giving the correct slope by linear regression. This is repeated for several different r_3 values.

The k_{ps} vs. r_3 plot for pairs giving the correct conversion to crosslinks at gelation is also determined using the kinetic model. Once again, a value for r_3 is chosen. The conversion to crosslinks at the experimentally determined monomer conversion of gelation is calculated with this r_3 value and three different k_{ps} values. The k_{ps} value giving the crosslink conversion predicted by Equation 4 is determined by linear regression. This is repeated for several r_3 values.

The intercept of the two curves gives the values for r_3 and k_{ps} . Figure 9 shows this plot for sample 2T. With and without transfer agent, the reactivities are similar but the amounts of secondary cyclization are very different. Table 2 shows r_3 and k_{ps} as determined for several of the systems investigated. When the amount of crosslinker is held constant and the chain length varied, the pendant reactivity is fairly constant while the number of secondary cycles per crosslink increases with increasing chain length. This may be so because a longer chain has a greater concentration of pendant vinyls surrounding a radical end. In the case of

systems 2N and 2T, the system with transfer agent has a k_{ps} equal to 2.7 and the system without transfer agent a value of 19.7. This is reasonable because the primary chain length in the system without transfer agent is nearly six times larger than in the system with transfer agent. Both the pendant reactivity and the number of secondary cycles change as the primary chain length is held constant and the amount of crosslinker is varied. Pendant reactivity decreases as the amount of crosslinker is increased. This is probably due to an increase in steric screening effects caused by increasing the number of branches in the vicinity of a pendant vinyl as well as decreasing the mobility of the macromolecule. The number of secondary cycles increases as the amount of crosslinker is increased. This is once again due to the greater concentration of pendant vinyls surrounding a radical end.

Once the constants have been determined, the model can be used to predict total conversion of pendant vinyls and conversion to crosslinks, primary cycles, and secondary cycles. These predicted conversions are shown as a function of monomer conversion in Figure 10 for system 2T. These conversions can now be used in a branching theory to predict molecular parameters.^{16, 21}

CONCLUSIONS

Vinyl-divinyl network formation has been investigated by determining the conversion of pendant vinyls as a function of monomeric vinyl conversion, using this

information to shape the concept of cyclization and crosslinking, and formalizing these concepts by incorporating them in a kinetic model for the rate of polymerization. Plots of pendant conversion vs. monomer conversion exhibited a positive y-intercept indicating the loss of pendant vinyls during the formation of a primary chain. This loss was attributed to the formation of primary cycles. Primary cyclization increased with increasing dilution. The slope of the plot indicated the formation of secondary cycles with the formation of crosslinks. The kinetic model along with experimental conversion curve data provided a means to estimate the number of secondary cycles and the reactivity of the pendant vinyl. The amount of secondary cyclization increased with increasing length of the primary chain. The pendant vinyl reactivity was found to be approximately half that of monomeric vinyls.

This approach to understanding network formation is that of developing a model which is consistent with the available experimental data, and as is true with models, it is only an approximation. Primary cyclization has been assumed to occur at a constant rate. This is probably not so since as the reaction progresses, the concentration of pendant vinyls not connected by a primary chain to a particular radical end increases and provides competition. Pendant reactivity in this model is not that of an isolated vinyl in a very dilute system. Instead it must include contributions from many different sources in one term. It

is not surprising then that it is less than the reactivity of monomeric vinyls.

Acknowledgement

This research was supported by a grant from the Army Research Office, Polymer Chemistry Program.

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APPENDIX

With the concept of primary and secondary cyclization in mind, a kinetic scheme for the vinyl-divinyl copolymerization can be written. In this scheme,

A = vinyl on monovinyl monomer

B = vinyl on divinyl monomer

P = pendant vinyl

a = vinyl in polymer from monovinyl monomer

b = first vinyl from divinyl monomer incorporated in polymer

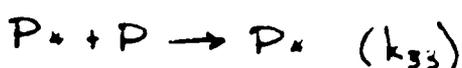
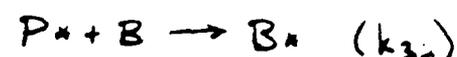
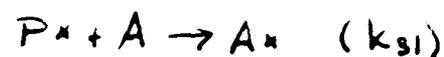
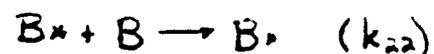
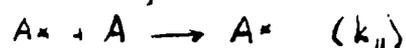
p = pendant vinyl incorporated in polymer

pp = pendant vinyl in primary cycle

px = pendant vinyl in crosslink

ps = pendant vinyl in secondary cycle

The propagation steps are written as



The equations for the time rate of appearance and disappearance of species A and B are

$$-\frac{d[A]}{dt} = k_{11}[A^*][A] + k_{21}[B^*][A] + k_{31}[P^*][A] \quad (5)$$

$$-\frac{d[B]}{dt} = 2(k_{12}[A^*][B] + k_{22}[B^*][B] + k_{32}[P^*][B]) \quad (6)$$

Pendant vinyls are both produced and consumed so an equation for the time rate of change has terms for both.

Contributions to the term for disappearance come from reaction to crosslinks, primary cycles, and secondary cycles. The equation for P becomes

$$\begin{aligned} -\frac{d[P]}{dt} &= (1 + k_{ps})(k_{13}[A^*][P] + k_{23}[B^*][P] + k_{33}[P^*][P]) \\ &\quad - \frac{k_{pp}}{2} \frac{d[B]}{dt} - (k_{12}[A^*][B] + k_{22}[B^*][B] + k_{32}[P^*][B]) \end{aligned} \quad (7)$$

where k_{pp} is the fraction of pendant vinyls in primary cycles and k_{ps} is the average number of secondary cycles formed per crosslink. Differential equations are also written for the appearance of species in the polymer. These are

$$\frac{d[a]}{dt} = -\frac{d[A]}{dt} \quad (8)$$

$$\frac{d[b]}{dt} = -\frac{1}{2} \frac{d[B]}{dt} \quad (9)$$

$$\frac{d[pp]}{dt} = -\frac{k_{pp}}{2} \frac{d[B]}{dt} \quad (10)$$

$$\frac{d[p^*]}{dt} = k_{31}[P^*][A] + k_{32}[P^*][B] + k_{33}[P^*][P] \quad (11)$$

$$\frac{d[ps]}{dt} = k_{ps} \frac{d[p^*]}{dt} \quad (12)$$

Combining Equations 5 and 6 gives

$$\frac{d[A]}{d[B]} = \frac{[A](k_{11}[A^*] + k_2[B^*] + k_{31}[P^*])}{2[B](k_{12}[A^*] + k_{22}[B^*] + k_{32}[P^*])} \quad (13)$$

Assuming quasi-steady state and using the accompanying equations

$$\begin{aligned} k_{12}[A^*][B] &= k_{21}[B^*][A] \\ k_{23}[B^*][P] &= k_{32}[P^*][B] \\ k_{31}[P^*][A] &= k_{13}[A^*][P] \end{aligned} \quad (14)$$

Equation 11 becomes

$$\frac{d[A]}{d[B]} = \frac{[A](k_{11}/k_{12}[A] + B + k_{13}/k_{12}[P])}{2B([A] + k_{22}/k_{21}[B] + k_{23}/k_{21}[P])} \quad (15)$$

If r_{ij} is defined as

$$r_{ij} = k_{ii}/k_{ij}$$

Equation 15 becomes

$$\frac{d[A]}{d[B]} = \frac{r_{11}[A]([A] + [B]/r_{12} + [P]/r_{13})}{2r_{21}[B]([A]/r_{21} + [B] + [P]/r_{23})} \quad (16)$$

Equations 6 and 7 combine to give

$$\frac{d[P]}{d[B]} = \frac{(1+k_{ps})r_{32}[P]([A]/r_{31} + [B]/r_{32} + [P])}{2r_{23}[B]([A]/r_{21} + [B] + [P]/r_{23})} - \frac{1-k_{pp}}{2} \quad (17)$$

Expressions for the relative changes in the polymer content are also obtained. Dividing Equation 8 by Equation 9 gives the expression

$$\frac{d[A]}{d[B]} = 2 \frac{d[A]}{d[B]} \quad (18)$$

Equation 10 divided by Equation 9 results in

$$\frac{d[PP]}{d[B]} = +k_{PP} \quad (19)$$

Equation 11 divided by Equation 9 and Equation 12 divided by Equation 9 give

$$\frac{d[P_x]}{d[B]} = \frac{r_{32} [P] ([A]/r_{31} + [B]/r_{32} + [P])}{r_{23} [B] ([A]/r_{21} + [B] + [P]/r_{23})} \quad (20)$$

and

$$\frac{d[PS]}{d[B]} = k_{PS} \frac{d[P_x]}{d[B]} \quad (21)$$

Equations 20 and 21 combine to give

$$\frac{d[P_x]}{d[B]} = \left(2 \frac{d[P]}{d[B]} + 1 - k_{PP} \right) / (1 + k_{PS}) \quad (22)$$

A mass balance gives (dropping brackets for concentration in the remaining equations).

$$da + db + d(p_x) + d(p_s) + d(pp) = -(dA + dB + dP) = M^0 dx \quad (23)$$

where M^0 is a constant given by the equation

$$M^0 = A^0 + B^0 + P^0 \quad (24)$$

A^0 , B^0 and P^0 representing initial quantities and dx is some increment of conversion. The integral composition of the copolymer is calculated stepwise. Let

$$U_j = (dA/dB)_j$$

$$V_j = (dP/dB)_j$$

$$U_0 = dA^0/dB^0$$

$$V_0 = dP^0/dB^0$$

and $P^0 = 0$

then

$$(da)_j = M^0 U_j dx / (U_j + V_j + 1) \quad (25)$$

$$(db)_j = M^0 dx / \{2(U_j + V_j + 1)\} \quad (26)$$

$$(dpp)_j = M^0 k_{pp} dx / \{2(U_j + V_j + 1)\} \quad (27)$$

$$(dpx)_j = \frac{M^0(2V_j + 1 - k_{pp})dx / (1 + k_{ps})}{2(U_j + V_j + 1)} \quad (28)$$

$$(dps)_j = k_{ps} (dpx)_j \quad (29)$$

$$(dA)_j = -M^0 U_j dx / (U_j + V_j + 1) \quad (30)$$

$$(dB)_j = -M^0 dx / (U_j + V_j + 1) \quad (31)$$

and $(dP)_j = -M^0 V_j dx / (U_j + V_j + 1) \quad (32)$

where $x = (j + 1)dx$. The integral compositions at the conversion x are

$$a = \sum_{j=0}^n (da)_j \quad (33)$$

$$b = \sum_{j=0}^n (db)_j \quad (34)$$

$$pp = \sum_{j=0}^n (dpp)_j \quad (35)$$

$$px = \sum_{j=0}^n (dpx)_j \quad (36)$$

$$ps = \sum_{j=0}^n (dps)_j \quad (37)$$

$$A = A^0 + \sum_{j=0}^n (dA)_j \quad (38)$$

$$B = B^0 + \sum_{j=0}^n (dB)_j \quad (39)$$

$$P = P^0 + \sum_{j=0}^n (dP)_j \quad (40)$$

where

$$n = \frac{\lambda}{dx} - 1$$

20

To use this kinetic model, values for the rate and cyclization constants must first be obtained. NMR data shows the monomeric vinyls in the MMA-EGDMA system have an equal reactivity. Therefore, r_{12} and r_{21} will be set equal to 1 in this analysis. The reactivity of the pendant vinyl may be different due to influences from the polymer chain and steric hindrance and has not been determined prior to analysis with this model. The constant k_{pp} is equal to the y-intercept of the pendant vinyl conversion vs. monomer conversion curve for each system. The slope of each of these curves is a result of crosslinking and secondary cyclization in combination with the reactivity of the pendant vinyl. If it is assumed that

$$r_{13} = r_{23} = \sqrt{r_{31}} = \sqrt{r_{32}} = r_3,$$

Then there are two unknowns remaining, r_3 and k_{ps} .

Table 1. Chemical systems investigated.

<u>System</u>	<u>Mol % EGDMA</u>	<u>% Dodecanetriol</u>	<u>Vol % in Top</u>
0N	0.60	0	100
0T	0.60	1	100
1N	0.57	0	100
2N	1.14	0	100
2N-50	1.14	0	50
2N-25	1.14	0	25
2T	1.14	1	100
3N	1.70	0	100

Table 2. Slope and y-intercept of pendant conversion plot, gel point conversion, pendant vinyl reactivity and secondary cyclization constant for chemical systems studied.

<u>System</u>	<u>y-intercept</u>	<u>slope</u>	<u>gel point</u>	<u>r_3</u>	<u>k_{ps}</u>
1N	0.0276	3.573	0.097	1.86	9.74
1T	0.0465	0.252	0.409	1.80	0.10
2N	0.0345	4.852	0.061	2.22	19.70
2N-50	0.0724	3.064	-	-	-
2N-25	0.1695	0.692	-	-	-
2T	0.0389	0.783	0.295	2.26	2.70
3N	0.0313	5.550	0.033	2.38	29.23

FIGURES

Figure 1. Monomer conversion vs. time of four systems investigated.

Figure 2. ^1H NMR spectrum of sample from chemical system 2N.

Figure 3. Enlargement of 4.0 to 6.5 ppm region of 2N ^1H NMR.

Figure 4. 4.0 to 6.5 ppm region of 2N ^1H NMR spectrum with residual monomer.

Figure 5. Pendant conversion vs. monomer conversion for systems 1N (\blacklozenge), 2N (\blacklozenge), and 3N (\blacksquare).

Figure 6. ' Pendant conversion vs. monomer conversion for systems 2N (\blacklozenge) and 2T (\blacklozenge).

Figure 7. Pendant conversion vs. monomer conversion for systems 2N (\blacklozenge), 2N-50 (\blacklozenge) and 2N-25 (\blacksquare).

Figure 8. Process of crosslink and secondary cycle formation.

Figure 9. Plot determination of k_{ps} and r_2 for system 2T.

Figure 10. Conversion of pendant vinyls (p_p) to crosslinks (p_{ps}), primary cycles (p_{pp}), and secondary cycles (p_{ps}) as predicted by kinetic model for system 2T.

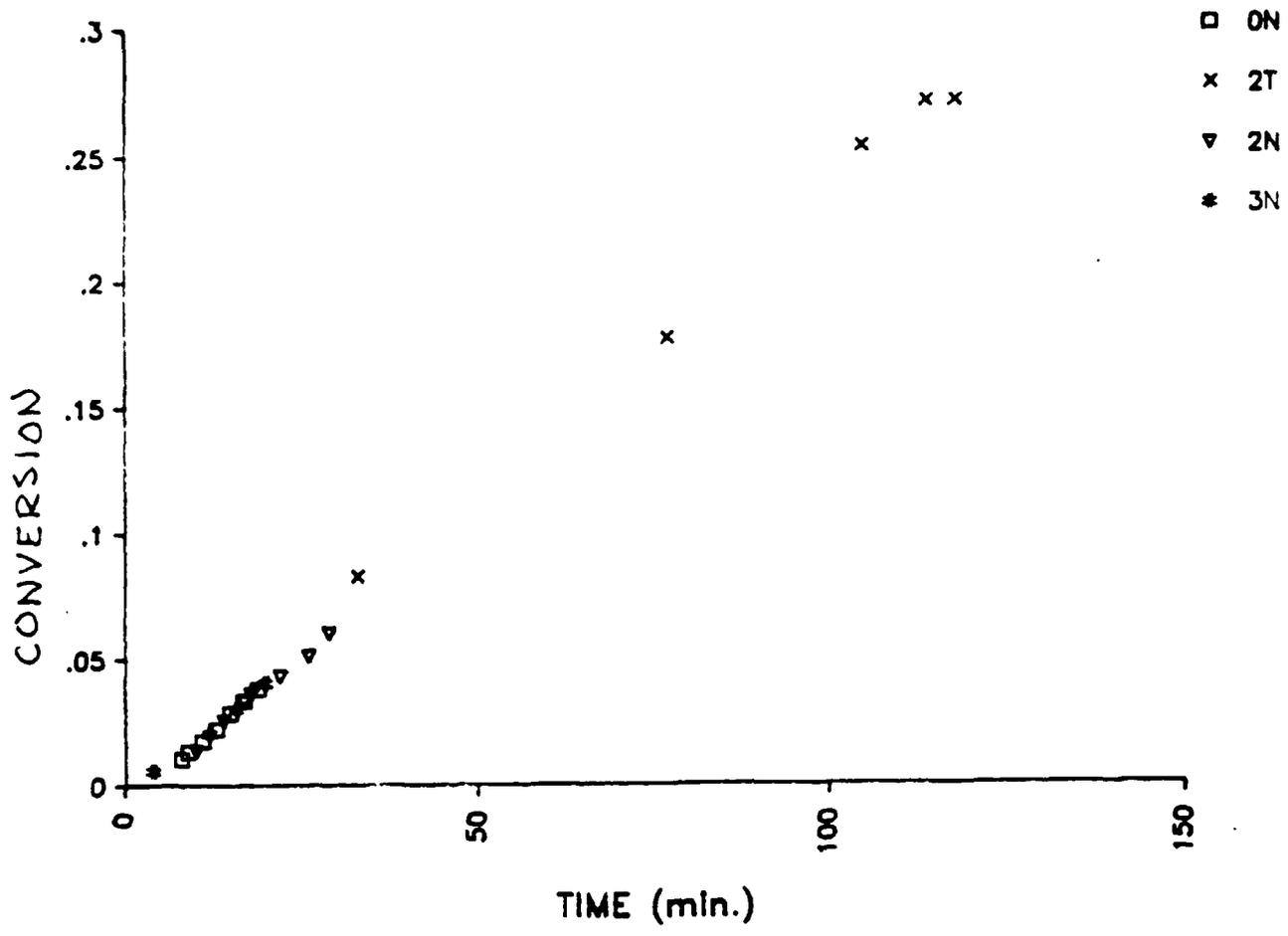
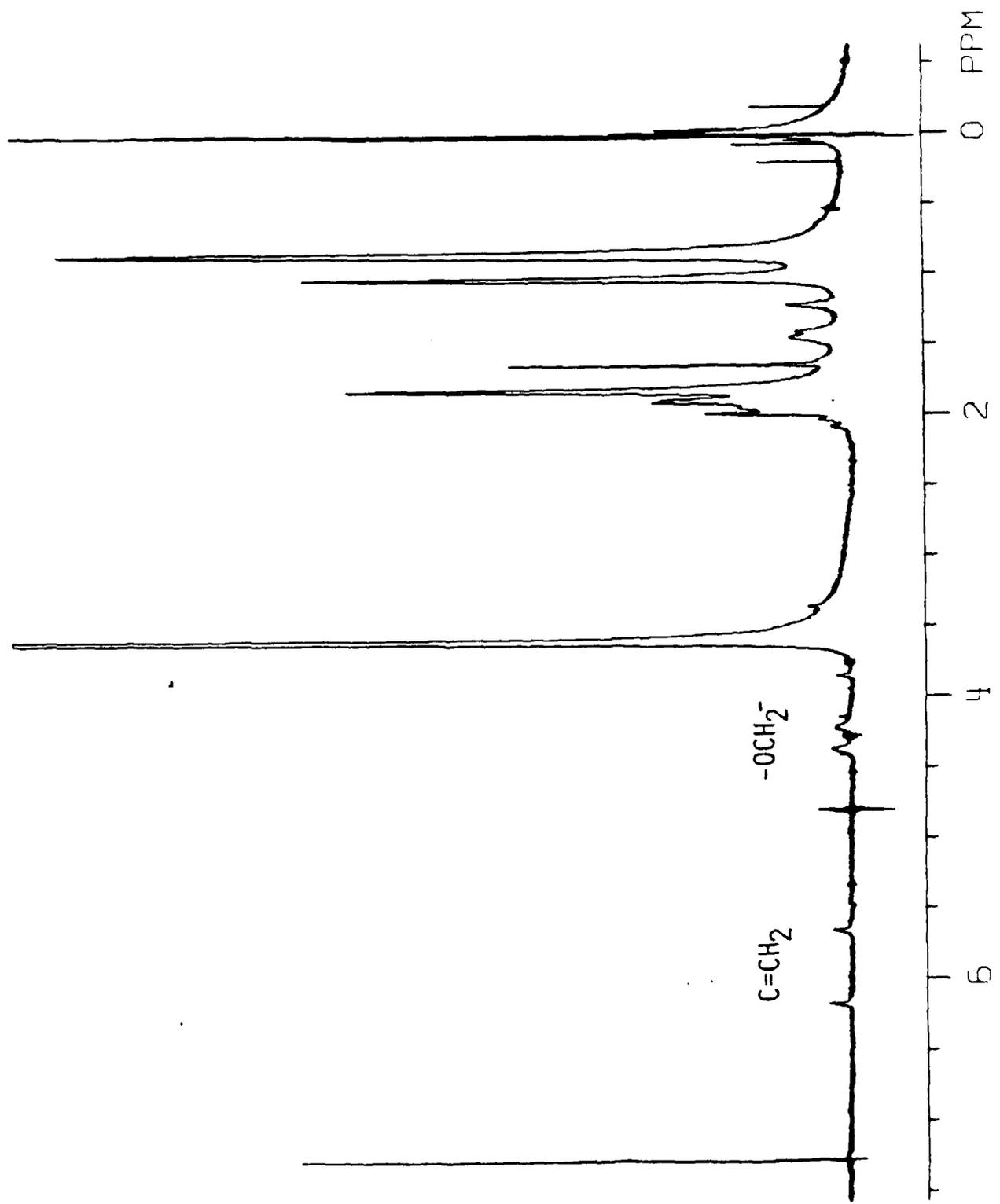
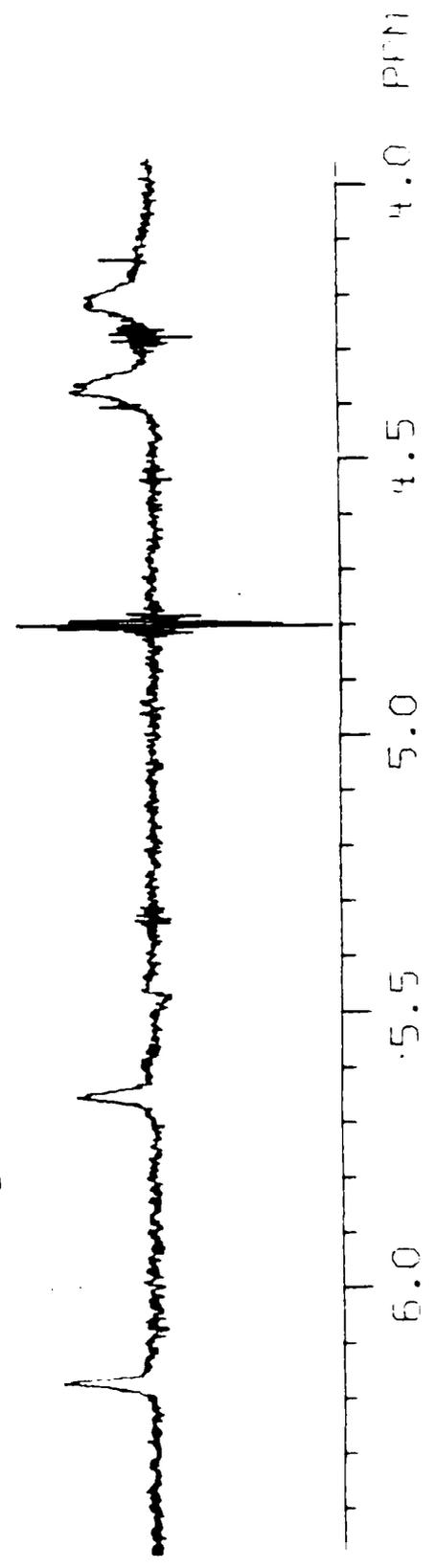


Figure 1.



C=CH₂

-OCH₂-



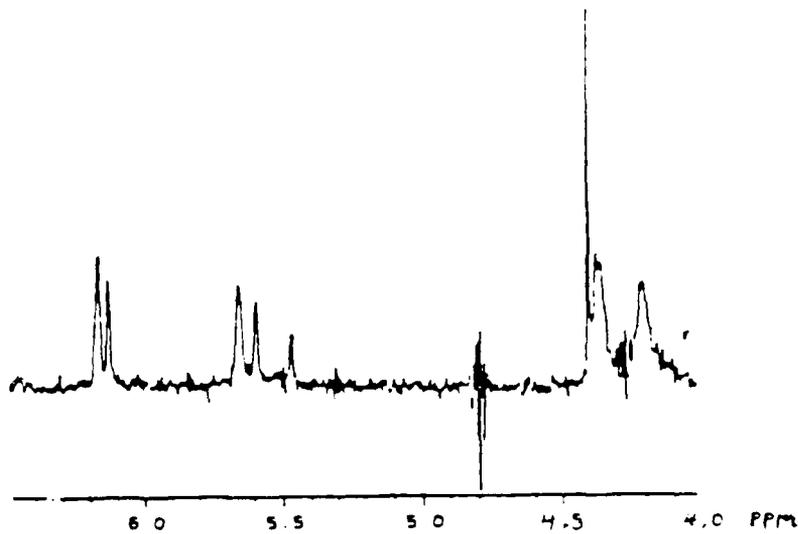


Figure 4.

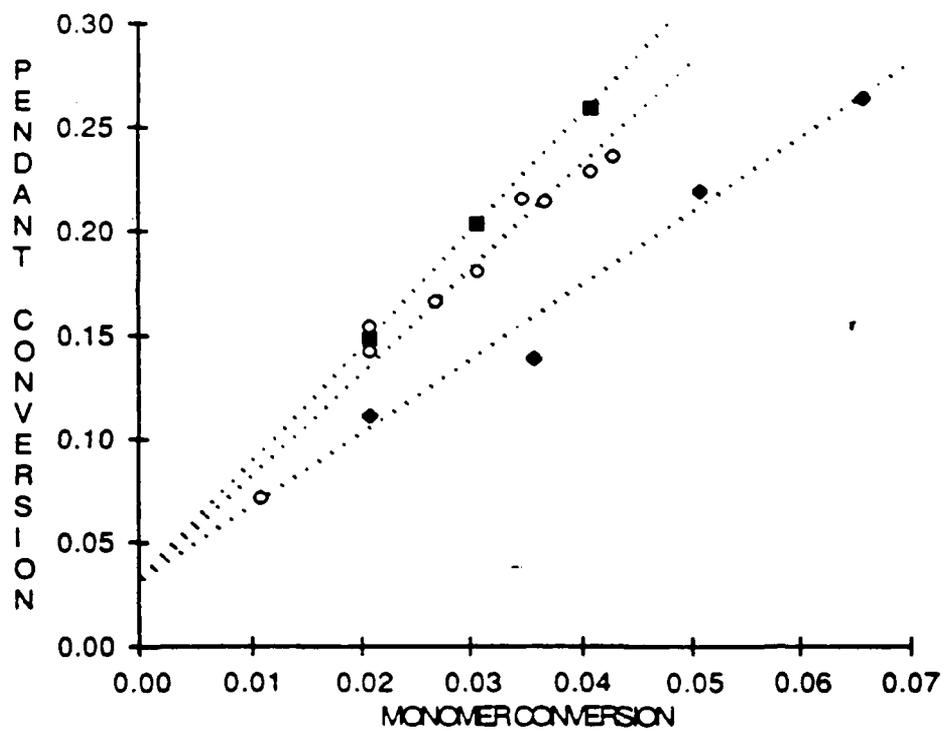


Figure 5

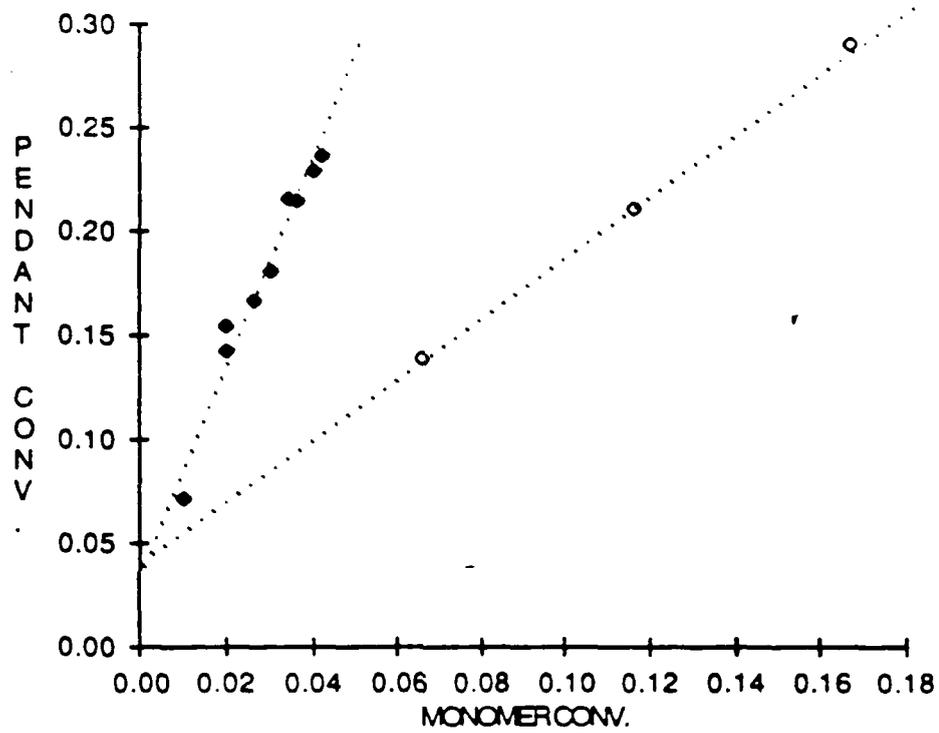


Figure 6

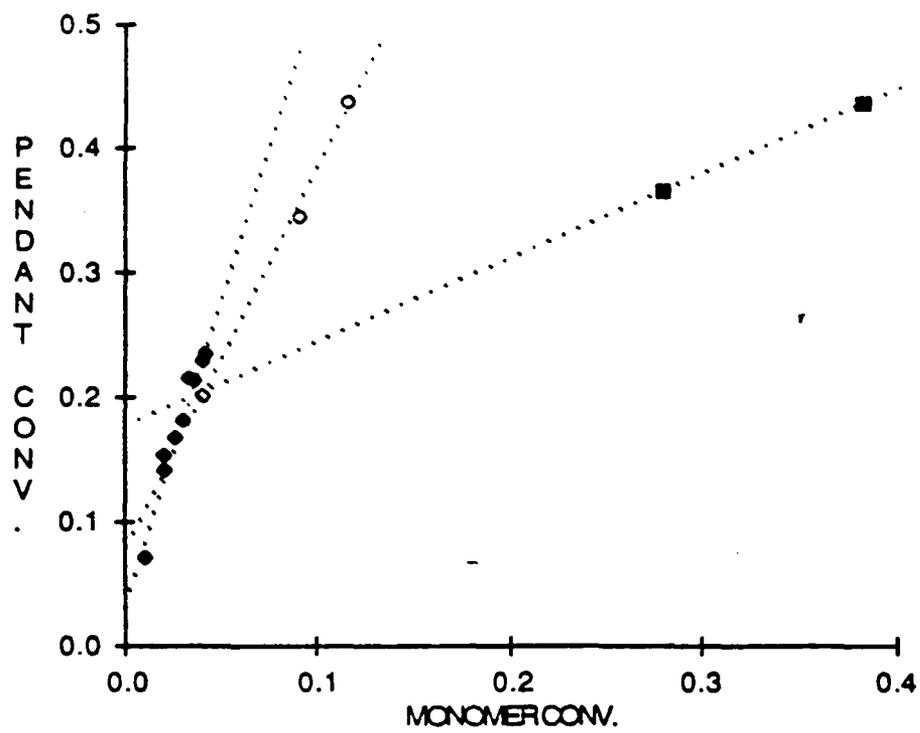
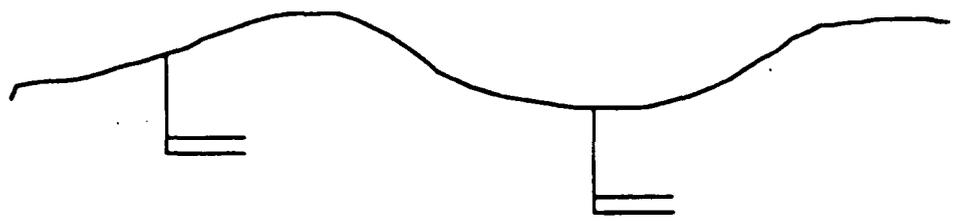
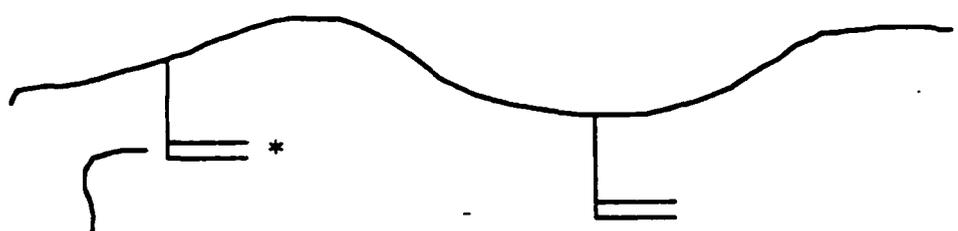


Figure 7



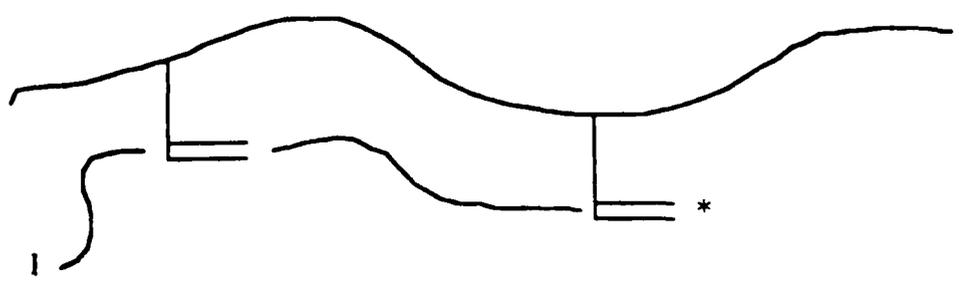
I *

PENDANT VINYL



I

CROSSLINK



I

SECONDARY CYCLE

Figure 8.

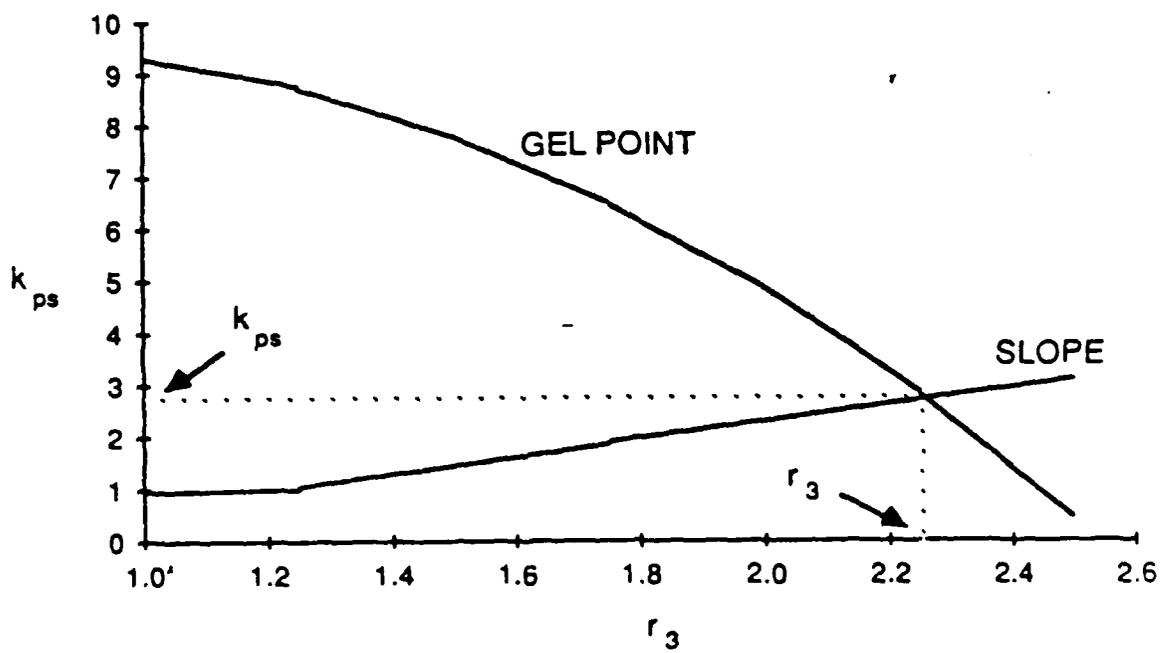


Figure 9.

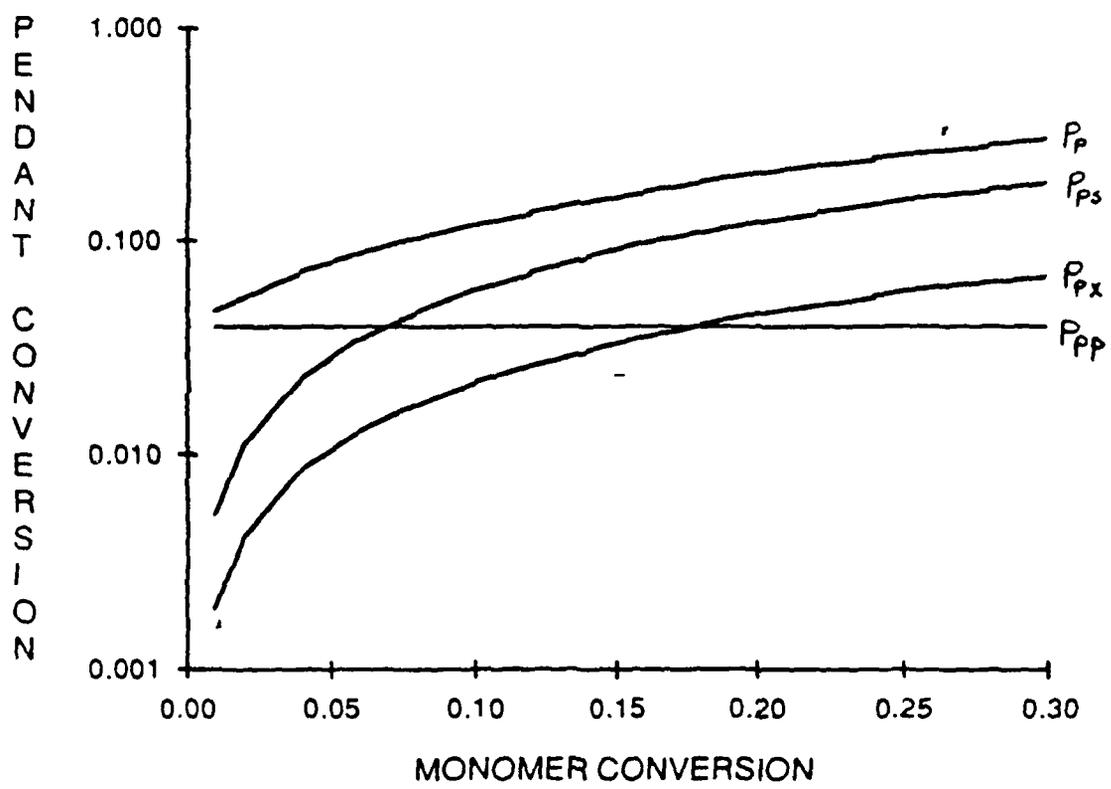


Figure 10

STRUCTURAL AND RHEOLOGICAL CHANGES DURING EPOXY CROSSLINKING

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Introduction

With the increasing use of epoxies, particularly in the aircraft and automotive industries, the establishment of direct correlations between network structure and rheological properties is important. Information concerning structure-rheology relations would assist in the selection of optimum parameters for reactive processing operations. In addition, knowledge of these relationships can provide a general understanding of the polymerization and network formation processes.

The overall strategy for determining and applying structure-property relations for epoxy networks is outlined in Figure 1. In order to develop structure-property relations, it is essential to know the way the network links together. This requires characterization of both the reactants and the linking reaction. Reaction kinetics are utilized in branching theory in order to predict average structural parameters before and after the gel point. Once the structure of the network is ascertained, it will be correlated with rheological properties. Knowledge of these structure-property relations can then be used to form a basis for reactive process models.

This paper discusses the use of branching theory to determine the structural changes which occur during the cure of an epoxy resin with a primary amine. Experimental results are presented to test the ability of these theoretical models to accurately predict certain network properties at various stages of curing. Then these structural changes are correlated with the viscosity rise during the cure.

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Chemical System and Kinetics

In order to derive structure-property relations for any polymer system, specific information is needed concerning the composition of the monomeric units and the chemical reactions which link the units together. However, commercial epoxy resin formulations are generally quite complex. An accurate assessment of the initial composition of the commercial formulation and its cure kinetics is virtually impossible. Therefore, to begin to understand structure-property relations for commercial resins, it is necessary to first investigate and understand network formation in simpler model systems.

The model system chosen for this study consists of diglycidyl ether of bisphenol A (DGEBA) cured with diaminodiphenyl sulfone (DDS). The chemical structure of the epoxy and amine monomer are illustrated in Figure 2. Commercial grade DGEBA was obtained under the trade name DER 332 (Dow) and was purified by recrystallization. The epoxide equivalent weight determined by chemical titration was 173 g/eq. The curing agent DDS is available at 99% purity from the Aldrich Chemical Company.

In order to use branching theory to predict network structure, one needs specific information concerning the cure mechanism. It is necessary to know which reactions occur during the cure, and the ratio of rate constants for these various reactions. Shechter et al.⁽¹⁾ have suggested the sequence of reaction shown in Figure 3 for an epoxy cured with a primary amine.

One factor which must be considered when investigating the formation of epoxide-amine network polymers is the difference between the reactivity of functional groups associated with monomers which have been reacted at one or more sites and those attached to completely unreacted monomers. Once one of the amino or epoxide groups has combined with a bulky group, steric hindrances and mobility restrictions may lower the rate at which the second functional group reacts. This difference in reactivity can have a strong effect on the structural development during curing.

Several workers⁽²⁻⁶⁾ have found that the reactivities of the epoxide groups in DGEBA are independent. In addition, the reactivity of amino groups in diamines also appears to be independent.⁽⁷⁾ However, substitution among the amine hydrogens due to steric effect is to be expected; that is the reactivities of the hydrogens in the primary (rate constant k_1) and the secondary (rate constant k_2) amino groups may be different. The existing results concerning the actual magnitude of the substitution effect in aromatic amines is somewhat controversial.

The reported values for DDS show that the ratio of rate constants (k_1/k_2) range from .2-.6.⁽⁷⁻⁹⁾

The third reaction (etherification) is thought to occur by tertiary amine or base catalyzed mechanisms. Formation of polyether oligomer has not been observed in the DGEBA-DDS systems when the amine is present in excess or at stoichiometric concentrations.^(1,10) However, when epoxide is present in excess, the hydroxyl groups may become serious contenders with the amines for the consumption of epoxy groups.^(10,11)

All three of the reactions which occur in epoxy-amine systems can be accelerated by the presence of alcohol, water or other hydrogen donors.⁽¹⁾ Since a hydroxyl group is a product of the epoxide-amine addition, the course of reaction will be autocatalytic.

Using this information concerning the cure mechanism, a kinetic model for the formation of various types of units during the polymerization. The assumptions made in the kinetic scheme are listed below:

- 1) The reactivities of the epoxide groups are independent
- 2) The reactivities of the amino groups are independent
- 3) The reactivities of the amino hydrogens are dependent
- 4) No etherification occurs
- 5) The presence of hydroxyl groups catalyzes the amine - epoxy reaction
- 6) The ratio of rate constants does not depend on conversion

Suppose the reaction begins with A_4 moles of amine monomer and E_2 moles of DGEBA. Then the stoichiometric ratio is defined as

$$r = 2 E_2 / 4 A_4 \quad (1)$$

If at time t a fraction p_A of the amino-hydrogens has reacted and a fraction p_E of epoxide groups has reacted, then

$$p_A = r p_E \quad (2)$$

Furthermore, assume at time t that there are $A_{4,0}$ moles of A_4 units with 0 reacted sites, $A_{4,1}$ moles of amine units with 1 reacted site, . . . , $A_{4,4}$ moles with 4 reacted sites. Thus, the proportion of amine units which have i reacted sites will be defined as follows:

$$p_{A,i} = \frac{A_{4,i}}{A_4} \quad (3)$$

Then the overall extent of reaction of the amino-hydrogen groups can be written:

$$p_A = \sum_{i=0}^4 (i/4) p_{A,i} \quad (4)$$

Using the above assumptions and notation, the cure of DGEBA with DDS can be described by a system of differential equations (Figure 4). If it is assumed that the ratio of uncatalyzed primary to secondary amine reaction is the same as the ratio of the catalyzed,⁽³⁾ the system of equations have an analytical solution:

$$p_{A,1} = 2x(p_{A,0}^y - p_{A,0}) \quad (5)$$

$$p_{A,2}^* = x^2(-2 p_{A,0}^y + p_{A,0} + p_{A,0}^{\alpha/2}) \quad (6)$$

$$p_{A,2}' = -2x p_{A,0}^y + \alpha x p_{A,0} + 2 p_{A,0}^{1/2} \quad (7)$$

$$p_{A,2} = p_{A,2}^* + p_{A,2}' \quad (8)$$

$$p_{A,3} = x^2\{(\alpha+2) p_{A,0}^y - \alpha p_{A,0} - (2-\alpha)p_{A,0}^{1/2} - 2 p_{A,0}^{\alpha/2} + (2-\alpha) p_{A,0}^{\alpha/4}\} \quad (9)$$

$$p_{A,4} = 1 - p_{A,0} - p_{A,1} - p_{A,2} - p_{A,3} \quad (10)$$

where

$$\alpha = k_2/k_1 = k_5/k_4$$

$$x = 1/(1-\alpha/2)$$

$$y = (1+\alpha/2)/2$$

Through the system of equations (5) - (10), the structural configuration of all the monomer units during the cure is known as a function of the fraction of amine monomeric units which are completely unreacted ($p_{A,0}$), the initial stoichiometric ratio of epoxide groups to amino-hydrogen groups (r), and the ratio of rate constants (α). The reaction vector [$p_{A,1}$, ..., $p_{A,4}$, p_E] is used in the probability model described in the next section for the prediction of structural parameters during polymerization.

Branching Theory

As an epoxy cures with an amine, complex branched molecules are formed. The development of these three dimensional structures determines processing properties, including viscosity, gel point, crosslinking and modulus. Following the structural build-up of the network during polymerization is difficult. Before gelation, branched systems are characterized by a wide molecular weight distribution. Experimental determination of this distribution is difficult. After the gel point part of the reacting system is incorporated into an insoluble gel with an infinite weight average molecular weight. Very few methods exist which can characterize the gel structure. Clearly theoretical relations capable of predicting network structure given the starting materials and the extent of reaction would be valuable.

Several statistical methods have been developed to calculate relations between the extent of reaction and molecular parameters. Flory⁽¹²⁾ and Stockmayer⁽¹³⁾ established the basic theoretical concepts of a tree-like model to describe the branching of a polymer during curing. However, this technique proved only useful for very simplistic, ideal reaction mechanisms. More recently, two other approaches have been developed to extend the basic concepts set forth by Flory and Stockmayer. The first approach by Gordon and co-workers^(14,15) uses the theory of stochastic branching processes and requires deriving probability generating functions. Macosko and Miller^(16,17) have developed an alternative approach for predicting network structure which is based on the recursive nature of the branching process and elementary laws.

Using the recursive approach and the assumptions listed in proceeding section concerning the reaction mechanism, an expression has been derived⁽¹⁷⁾ for the weight average molecular weight as a function of the reaction vector $[p_{A,1}, \dots, p_{A,4}, p_E]$, and the stoichiometric ratio of epoxy to amino-hydrogen groups (r). Figure 5 shows the predicted change of the weight average molecular weight with increasing conversion of epoxy groups for three different stoichiometric ratios. The reaction vector is dependent on the ratio of rate constants of the secondary amine to primary amine reaction, and in Figure 5 α is assumed to be .2.

The gel point is defined as the conversion at which the weight average molecular weight diverges and an infinite network begins to form. As is illustrated in Figure 5, the molecular weight builds very slowly until near the gel point. The conversion at gelation is highly dependent on the initial ratio of epoxy groups to amino-hydrogen groups. An expression can be derived for the gel conversion of epoxy groups (Figure 6), by setting the molecular weight equal to infinity and solving for the conversion as a function of the stoichiometric

ratio.⁽¹⁷⁾ There is a point at which the ratio of epoxide to amino-hydrogen groups is so small that the system will not gel. This is known as the critical stoichiometric ratio. Under the condition that $\alpha = .2$, the critical stoichiometric ratio is predicted to be .42.

The recursive approach can also be used to predict post-gel properties. Using the preceding assumptions concerning the epoxy-amine cure reaction, an expression has been derived for predicting the weight fraction of soluble material.⁽¹⁷⁾ Figure 7 shows the predicted change of sol fraction as a function of epoxide group conversion, assuming $\alpha = .2$.

Another parameter which can be derived from the recursive theory is the weight average molecular weight of the longest chain which passes through a randomly chosen point on the molecule. This structural parameter reflects the hydrodynamic size of a branched polymer and thus has been found useful in correlating the viscosity rise during polymerization.⁽¹⁸⁾ Miller et al.⁽¹⁹⁾ have derived the longest linear chain for a chemical system which has equal reactivity of functional groups of the same type, and where the monomeric molecular weight of the crosslinker is negligible compared to the weight of the other monomer. This derivation has been extended to include the substitution effect and the monomer weight of the amine crosslinker.⁽²⁰⁾ Figure 8 compares the rise of the weight average molecular weight with the molecular weight of the longest linear chain at balanced stoichiometry.

Figures 5 - 8 assume that the ratio of rate constants for the secondary amine to primary amine reaction is .2. However, as discussed in the previous section, the magnitude of the substitution effect in the DDS system is controversial. The literature reports values ranging from .2 - .6. In systems with complicated cure chemistry, it is frequently difficult to ascertain specific values for the rate constant ratios of the various reactions which occur during polymerization. Hence, it is important to consider the sensitivity of the predictions for structural parameters to variations in rate constant ratios. Figure 9 examines the change in gel conversion with the magnitude of the substitution effect. At balanced stoichiometry, when $\alpha = .2$ the predicted gel conversion is .61, while the gel conversion is .59 when $\alpha = .6$.

Experimental

The goal of this study is to develop relationships between rheological properties and the build up of network structure during polymerization. Therefore, it is first necessary to test the ability of the branching expressions to predict molecular parameters. Then these expressions can be combined with rheological and kinetic data to form structure-property models.

As described in previous section, the recursive method is capable of predicting conversion at gelation as a function of the stoichiometric ratio of epoxide to amino-hydrogen groups. This relationship can also be empirically determined. Samples of given stoichiometric ratios were cured in narrow test tubes immersed in a 177°C oil bath. At various reaction times, the samples were removed from the oil bath and rapidly plunged into an ice bath to stop the reaction. The samples were then removed from the test tubes and extracted with tetrahydrofuran. The gel time was designated as the cure time at which the sample just can not dissolve in the solvent. The conversion of epoxide groups at this time is determined by differential scanning calorimetry (DSC).⁽²⁰⁾ These results are plotted along with the predictions of the recursive theory (assuming $\alpha=.2$) in Figure 10. Good agreement is seen between the experimental points and the recursive theory.

The critical stoichiometric ratio predicted by the branching theory can be verified by curing samples with different stoichiometric ratios and performing extraction experiments to determine gel content. Several DGEBA-DDS samples were prepared with the stoichiometric ratio of epoxide to amino-hydrogen groups ranging from .2 to .6. The samples were placed under nitrogen in a 177°C oven for approximately 24 hours, and then were post-cured at 230°C for 8 hours. The samples were then crushed, placed in cellulose thimbles, and extracted for a week in tetrahydrofuran. The critical stoichiometric ratio is the largest ratio of epoxide to amino-hydrogen groups where the polymer is still completely soluble. The critical stoichiometric ratio for DGEBA-DDS was determined to be .40. Comparison between this value and the predicted value from the recursive theory is shown in Figure 10.

The sol fractions of samples cured beyond the gel point were also measured for the DGEBA system. Samples were cured at various time in a 177°C oil bath. The reaction was stopped by quenching in an ice bath. Pre-weighed samples were crushed, placed in extraction thimbles, and extracted in tetrahydrofuran for several weeks, with the solvent exchanged periodically. Then the samples were dried under vacuum until no further weight loss could be detected. The final sample weight was obtained and the weight fraction of solubles was calculated. The conversion of epoxide groups at a given cure time was determined by DSC. Figure 11 shows excellent agreement between theoretical and experimental values obtained for DGEBA-DDS at balanced stoichiometry.

Correlations between structure and rheological properties can be established by simultaneously measuring viscosity and conversion during cure. The steady shear viscosity rise for the DGEBA-DDS system has been monitored using the parallel plate geometry on the Rheometrics System Four Rheometer. The cure was conducted at 177°C under a nitrogen environment. At specific times during the cure, the reaction was stopped in the rheometer by

quenching in liquid nitrogen. Sample was then removed from the rheometer and analyzed for conversion by DSC. Thus, the viscosity rise can be obtained as a function of conversion (Figure 12). Using the recursive theory, the molecular weight of the longest linear chain can be determined at any conversion. Thus in Figure 13 the viscosity is plotted as a function of molecular weight of the longest linear chain. As seen, the viscosity data for different stoichiometric ratios collapses onto a single curve.

It has been shown that the viscosity for many undilute polymers with chain lengths less than 300 - 500 main chain atoms is dependent on the friction factor ζ and molecular weight $M^{(21)}$:

$$\eta \propto \zeta M \quad (11)$$

The friction factor is governed by local intrachain and interchain forces between neighboring segments in the polymer melt. Its magnitude is dependent on the particular polymer system. A general expression has been derived for the friction factor as a function of material properties of the polymer system⁽²¹⁾:

$$\zeta = \zeta_0 \exp\{B/(f_g + \alpha_1 (T - T_g))\} \quad (12)$$

where α_1 is the liquid expansion factor, f_g is the fractional void or free volume at the glass temperature T_g , B is related to the fractional void volume required to be in the vicinity of a segment for that segment to make a jump, and ζ_0^{-1} is an inherent jump factor.

In order to correlate the viscosity rise with molecular weight, it is necessary to calculate the friction factor at any point in the polymerization. Through the examination of several polymer systems, Berry and Fox⁽²¹⁾ found that the inherent jump factor and the ratio B/f_g are generally constant for any system. However, T_g and to a lesser extent α_1 , depend on molecular weight until somewhat longer chain lengths (i.e. greater than ca. 500) are attained; then they too become essentially molecular weight invariant. The ratio $10^{-3}B/\alpha_1$ is in the interval 1.5 to 3.0 with B increasing with the size of any side groups. In order to calculate the friction factor for the DGEBA-DDS system it will be assumed that the ratio $10^{-3}B/\alpha_1$ is a constant, equal to 2.25. The glass transition temperature is more sensitive than this ratio to changes in molecular weight during polymerization. According to the approach of Adabbo and Williams⁽²²⁾ using the DiBenedetto⁽²³⁾ equation, the glass transition temperature increases with increasing extent of conversion as follows:

$$\frac{T_g - T_{g0}}{T_g} = \frac{(E_x/E_m - F_x/F_m)X_g}{1 - (1 - F_x/F_m)X_g} \quad (13)$$

where E_x/E_m is the ratio of lattice energies for crosslinked and uncrosslinked polymer, F_x/F_m is the corresponding ratio of segmental mobilities, X_g is the conversion at the glass transition temperature and T_{g0} is the glass transition temperature at no reaction. The ratios E_x/E_m and F_x/F_m have been determined by fitting equation 13 to conversion versus glass transition temperature data. For the DGEBA-DDS system at balanced stoichiometry, the following constants have been obtained for the DiBenedetto equation⁽²⁴⁾:

$$E_x/E_m = 1.21$$

$$F_x/F_m = 0.74$$

$$T_{g0} = 11^\circ\text{C}$$

Using the typical material constants obtained by Berry and Fox (1968) and the DiBenedetto relationship for glass transition temperature, the friction factor ζ can be estimated for balanced stoichiometry as a function of conversion of epoxide groups. In Figure 14, viscosity is plotted against the product of the estimated friction factor and the molecular weight of the longest linear chain for the DGEBA-DDS system at balanced stoichiometry. Linear regression of the data gives a slope of 1.08 with a regression coefficient of 0.98. Thus, the viscosity rise for the DGEBA-DDS system at balanced stoichiometry fulfills the relation of being dependent on a friction factor and molecular weight to the first power. A possible explanation for the curvature shown in the data points in Figure 14 may be a result of the assumption that B/α_1 is a constant during polymerization.

Acknowledgement

Support of this work by the Army Research Office is greatly appreciated.

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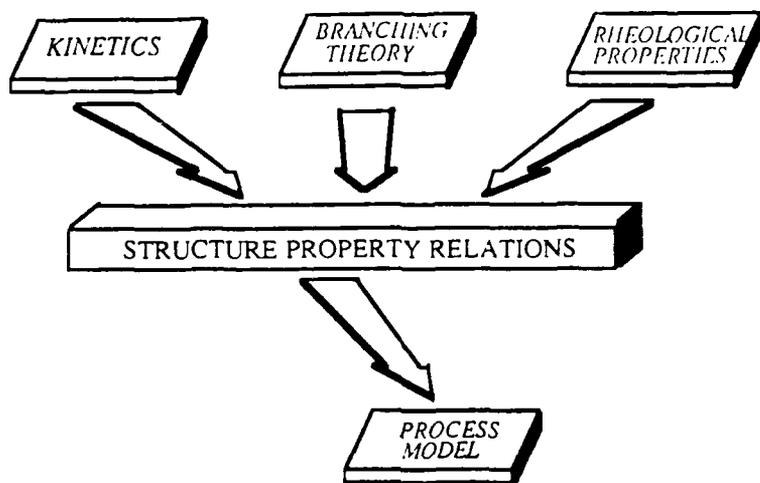
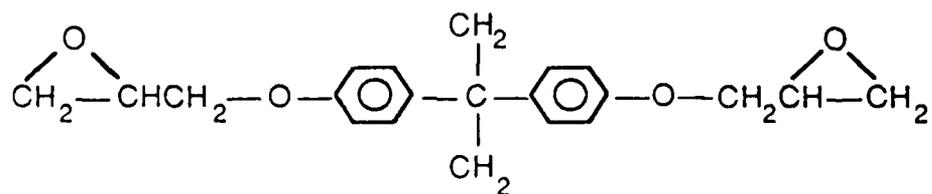
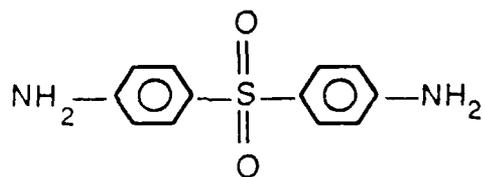


Figure 1. Strategy for determining structure-property relations for epoxy networks.



Diglycidyl Ether of Bisphenol A
(DGEBA)



Diamino-Diphenyl Sulfone
(DDS)

Figure 2. Chemical structure of the DGEBA epoxy monomer and the DDS amine curing agent.

CURE MECHANISM

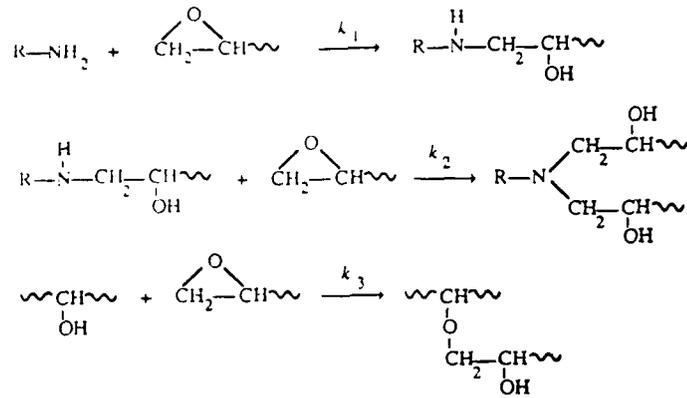
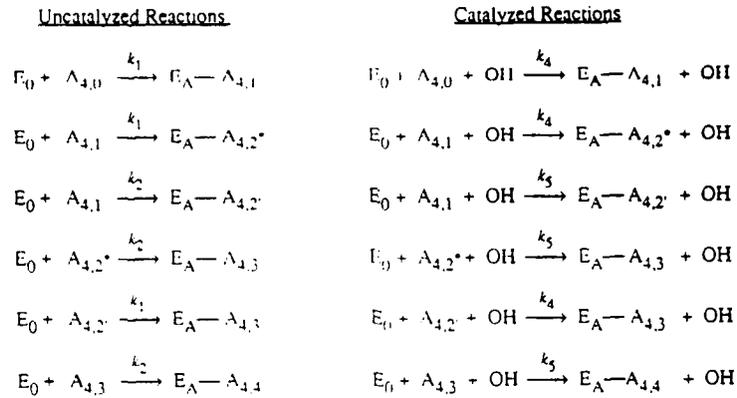


Figure 3. Reaction mechanism for an epoxy cured with a primary amine



$$\begin{aligned}
 \frac{-d[A_{4,0}]}{dt} &= 4[E_0] [A_{4,0}] [k_1 + k_4 [\text{OH}]] \\
 \frac{-d[A_{4,1}]}{dt} &= [E_0] [A_{4,1}] [2k_1 + k_2 + 2k_4 [\text{OH}] + k_5 [\text{OH}]] \\
 &\quad - 4[E_0] [A_{4,0}] [k_1 + k_4 [\text{OH}]] \\
 \frac{-d[A_{4,2}^*]}{dt} &= 2[E_0] ([A_{4,2}^*] [k_2 + k_5 [\text{OH}]] - [A_{4,1}] [k_1 + k_4 [\text{OH}]]) \\
 \frac{-d[A_{4,2}]}{dt} &= [E_0] (2[A_{4,2}] [k_1 + k_4 [\text{OH}]] - [A_{4,1}] [k_2 + k_5 [\text{OH}]]) \\
 \frac{-d[A_{4,3}]}{dt} &= [E_0] ([A_{4,3}] [k_2 + k_5 [\text{OH}]] - 2[A_{4,2}] [k_1 + k_4 [\text{OH}]] \\
 &\quad - 2[A_{4,2}^*] [k_2 + k_5 [\text{OH}]]) \\
 \frac{-d[A_{4,4}]}{dt} &= [E_0] [A_{4,3}] [k_2 + k_5 [\text{OH}]]
 \end{aligned}$$

Figure 4. Kinetic scheme for the DGEBA-DDS system.

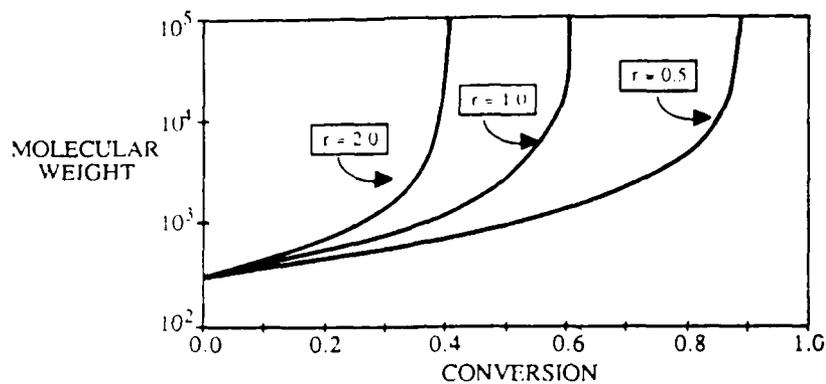


Figure 5. Recursive model predictions for molecular weight as a function of conversion at three different stoichiometric ratios. For the model predictions, the ratio of the secondary amine to primary amine (α) is assumed to be .2.

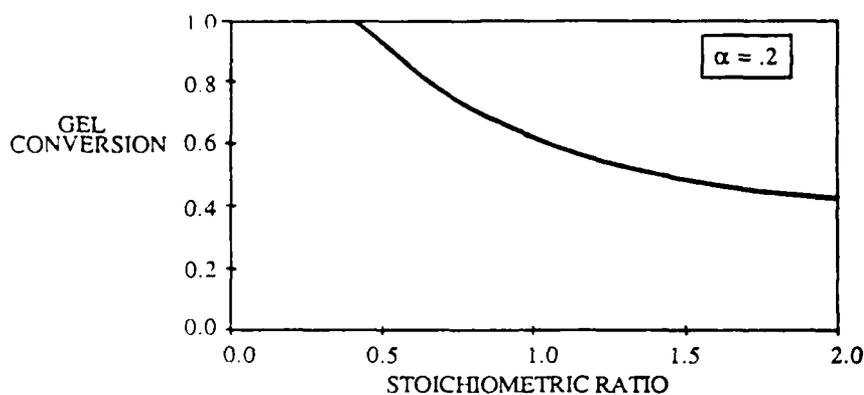


Figure 6. Recursive model prediction for the gel conversion of epoxide groups as a function of the initial stoichiometric ratio of epoxide groups to amino-hydrogens. For the model predictions, the ratio of the primary to secondary amine reaction (α) is assumed to be .2.

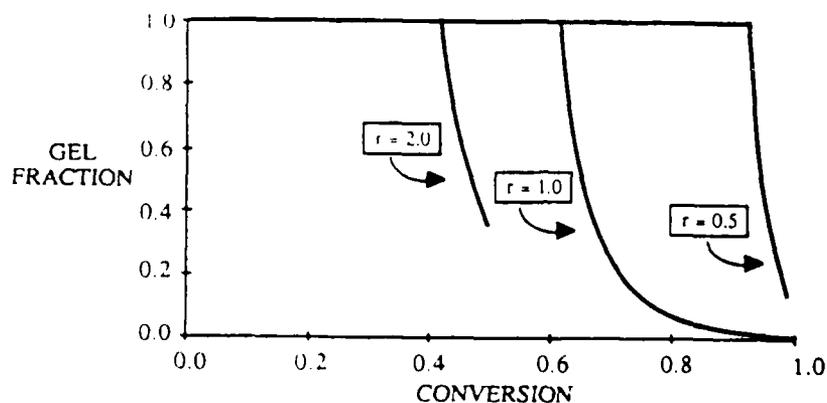


Figure 7. Recursive model predictions for the weight fraction of soluble material versus the conversion of epoxide groups at three stoichiometric ratios.

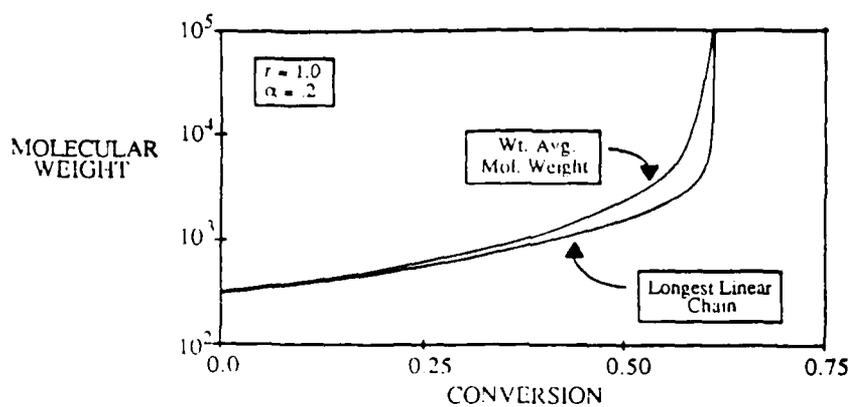


Figure 8. Comparison of the weight average molecular weight and the molecular weight of the longest linear chain at gelation.

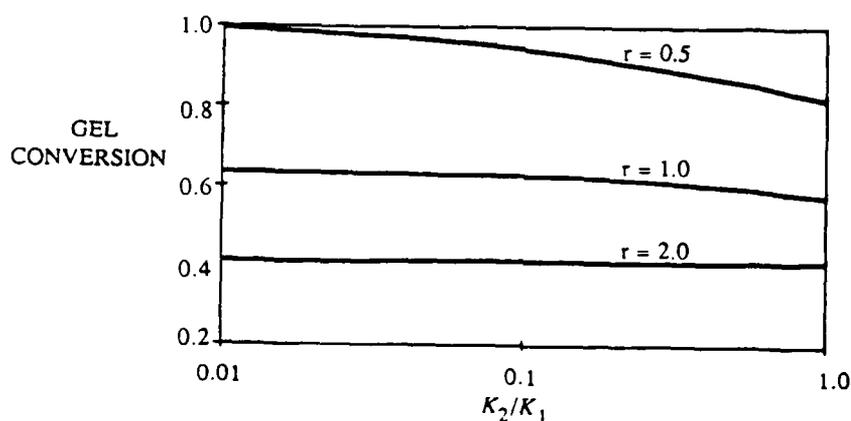


Figure 9. Conversion of epoxide groups at gelation versus the rate constant ratio of the secondary amine to the primary amine reaction for three different stoichiometries.

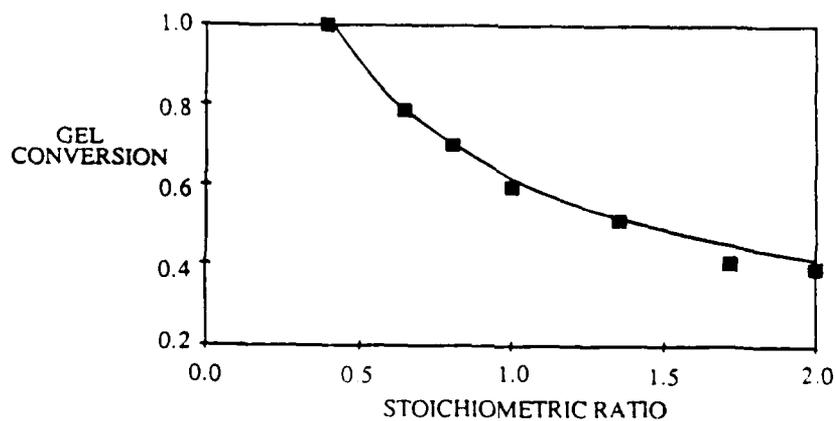


Figure 10. Gel conversion of epoxide groups versus stoichiometric ratio. Predictions of the recursive theory are indicated by the solid line. Experimental gel conversion values (■) were obtained by DSC.

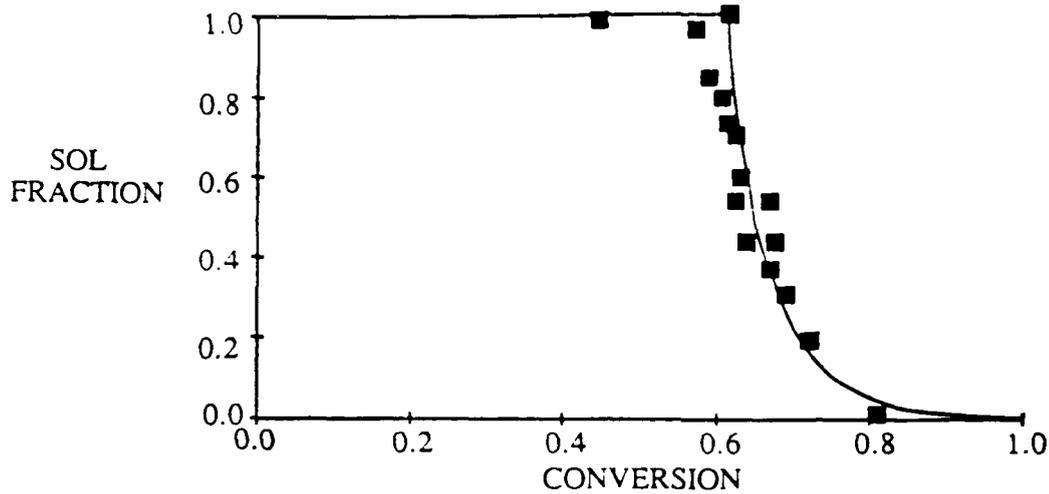


Figure 11. Weight fraction of solubles versus conversion of epoxide groups with balanced stoichiometry. Predictions of the recursive theory are indicated by the solid line and experimental values by the symbol (■).

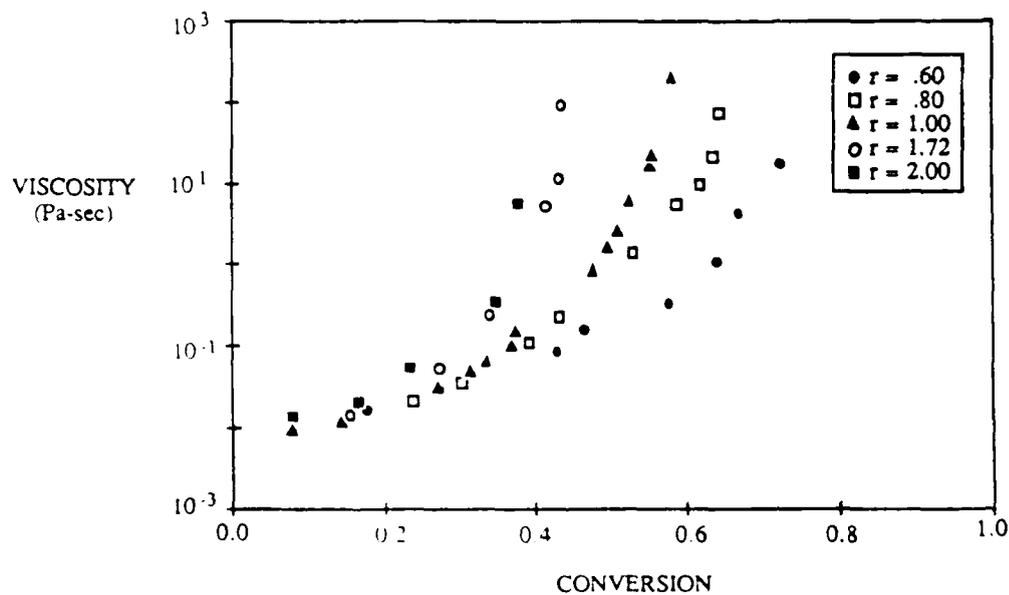


Figure 12. Viscosity rise versus conversion of epoxide groups at stoichiometric ratios ranging from .6 to 2.0.

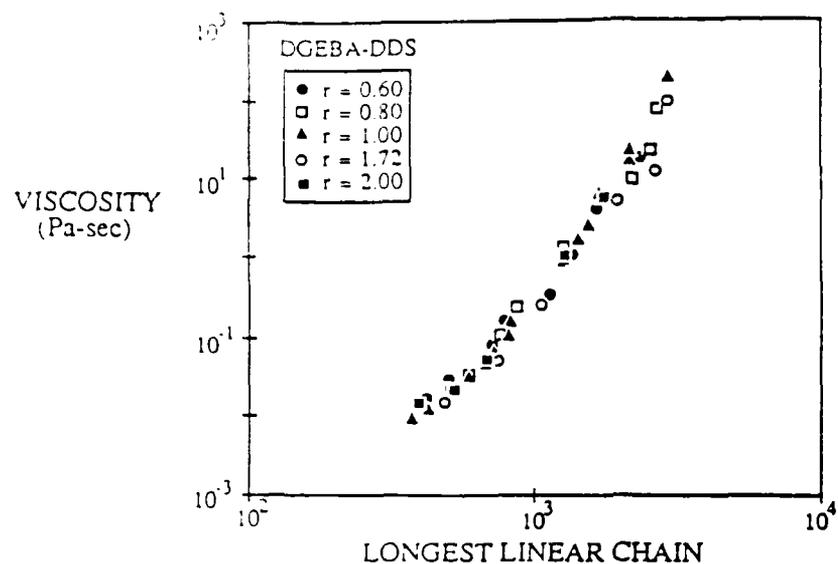


Figure 13. Viscosity rise versus molecular weight of the average longest linear chain at stoichiometric ratios ranging from .6 to 2.0. The molecular weight of the longest linear chain is calculated using the recursive theory assuming $\alpha = .2$.

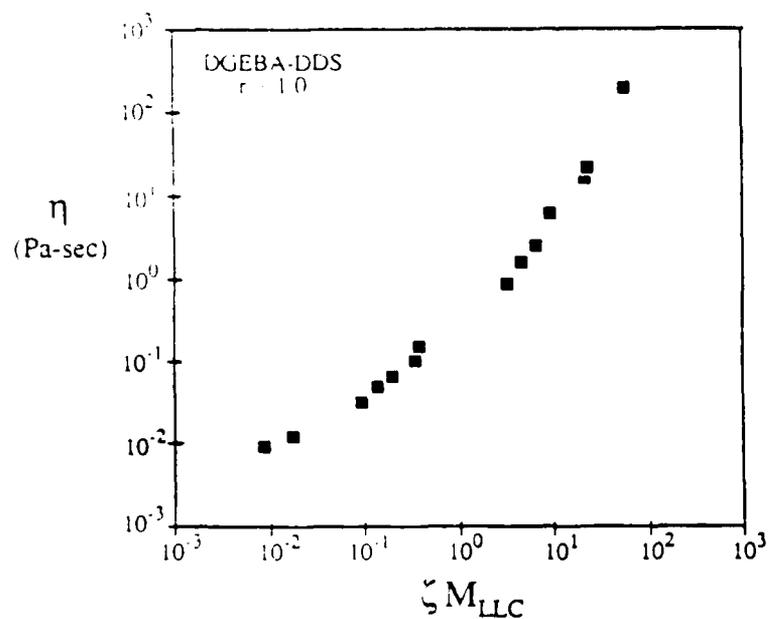


Figure 14. Viscosity rise versus the product of the friction factor and the molecular weight of the average longest linear chain for the DGEBA-DDS system at balanced stoichiometry.

END

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