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Modeling of Polymer Networks for Application to Solid Propellant Formulating

H. E. Marsh

June 15, 1979

National Aeronautics and
Space Administration

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ABSTRACT

As part of the Solid Propellant Chemistry Program, research was conducted over a period of years aimed at the development of methods for predicting the network structural characteristics formed by the curing of pourable elastomers. This report summarizes the results of this work. It emphasizes the logic which was applied in the development of mathematical models.

For simple systems (those which contain only one kind of branching component), models have been developed and verified which, from a few simple measurements of composition and extent of reaction, predict the conditions necessary for incipient gelation, and for the postgel state, the fraction of gel and sol and the cross-link density. Cross-link density is a factor in modulus. A parameter representing the length of effective chains can be calculated from these models also. This parameter has not been verified; however, it correlates with extensibility. A distribution of pendent chains, according to length, representing the noneffective branching in the network is also predicted by the models.

A universal approach for modeling has been developed and has been verified by comparison with other methods in application to a complex system.

Several applications of network models to practical problems are described briefly.

MODELING OF POLYMER NETWORKS FOR APPLICATION TO SOLID PROPELLANT FORMULATING

I. INTRODUCTION

One of the chief goals of solid propellant development at JPL during the last two and one-half decades was the development of formulations with mechanical properties and durability sufficient to maintain mechanical integrity in the most demanding of case-bonded configurations under a variety of environmental and use conditions. Continual efforts to improve the efficiency of this work through systematization of formulation studies led to an interest in theories of polymer network formation and their potential use in formulating. Research in this area was conducted concurrently with propellant studies during most of that period. For a number of years, network polymer studies were funded as a distinct work unit in the JPL solid propellant program. The work reported here was done for NASA. However, because of its wider implications for government and industry, concepts and results were shared with the solid rocket community through papers presented at meetings of the Joint Army, Navy, NASA, Air Force (JANNAF) Propellant Characterization Working Group [X10,X25] and of the American Institute for Aeronautics and Astronautics (AIAA) [X19,X24,X27].

This report has two objectives. The first objective is to collect in one document all of the important elements of this research. The other objective is to explain, in a way useful to students of this subject, the reasoning and associated mathematical techniques learned in the work.

The basic theoretical concepts regarding the formation of three-dimensional polymer networks were established many years ago by Carothers, [1] Flory, [2] and Stockmayer.[3] These contributions inspired considerable exploration of the correlations between theoretical and experimental gel points in various condensation polymer systems [2,4,5,6,X16,X17] and beyond gelation into the postgel state. [7-15,X28] The work described in this report was based mostly on Flory [2,16-18] and in the later stages on Mocosko and Miller. [14]

The objectives of this research evolved with the work. Eventually, two overall objectives emerged, and all others became subordinate to them. This report will show that the basic elements of the first of these objectives, development of a universal method of modeling, has been achieved. Actually, two methods exist, the one developed in this work, and another contributed by Mocosko and Miller. [14] The second objective, which was to apply techniques developed in this research to practical propellant problems, has not been done in the quantitative way that was planned. On the other hand, qualitative application of principles learned from the research were helpful in the design of formulation studies aimed at the development of specified sets of mechanical properties in propellants. The most notable case, a fully case-bonded end-burning rocket, is discussed in Section IV. Also in that section, several other propellant problems and anticipated approaches to their quantitative solutions are discussed briefly.

The other sections of the report deal with model development, qualitatively and graphically in Section II and quantitatively in Section III. The organization of the latter section reveals a difficult problem which, until recently, prevented the development of a universal approach to modeling. For completeness of documentation, the reference list includes all of the publications relating to this work. [X1-X32] Not all of them are cited in the discussion.

This research could not have been done without the help and encouragement of a number of people. First interest in the approach of P.J. Flory was stimulated by A.J. Havlik. Besides the several coauthors (S.Y. Chung, J. Heller, J.H. Hodgkin, G.C. Hsu, J.J. Hutchison, F.J. Martinelli, D.E. Udlock, C.J. Wallace, and J.F. Wolfe), others who helped extensively with the experimental program are R.F. Fedors and F. Tervet. Critical mathematical corrections were given by P.J. Flory and W.H. Stockmayer. W. Gin deserves special appreciation for continuing encouragement and support. The report benefits considerably from careful reviews by R.F. Landel and J.D. Ingham.

II. QUALITATIVE DESCRIPTION OF NETWORK FORMATION

A. General Features

According to Meares [19], a random coil is the most relaxed state for a polymer chain because this state permits the greatest freedom for thermal, lateral motions of chain elements by rotation about single bonds. If the two ends of a chain are moved farther away from each other by the application of external force, lateral motions are restricted, and these restrictions "set up a tension along the length of the molecule", which is manifested mechanically as modulus.

In a general way, modulus and ultimate strength of cross-linked elastomers depend upon the concentration of chains that are connected to the structure in such a way that they must respond to strain in only one way, uncoiling and recoiling. Such chains are connected at both ends to the main structure or network as backbone elements. They are called effective chains, and their connections with the network are at points called cross-links. The structural function of a cross-link is its interconnection of three or more effective chains. It is important to point out here that, as will be shown later, not all branching points are cross-links.

All other chains in a polymer are to be found in either of two structural conditions. Some are tied only at one end to the network (by means of the non-cross-linking branch points just mentioned), as pendent chains. The others are not attached at all to the main structure. This last group of chains consists of a mixture of unreacted starting ingredients and polymer molecules in wide ranges of sizes and branching complexity. During mechanical deformation of cross-linked elastomers under near-equilibrium conditions (low extension rate and temperatures well above glass-transition and melting temperatures), pendent chains and non-network chains are free to remain coiled and to retain their lateral motions. Thus, they do not contribute to modulus under these conditions. This effect is often enhanced experimentally by plasticization with a compatible, low-viscosity solvent. At higher rates of extension, this freedom is correspondingly reduced; such chains then contribute to the viscoelastic behavior.

The mixture of material not attached to the network is known as the <u>sol</u>. In a corresponding sense, the main structure or network is known as the <u>gel</u>. These terms derive from the fact that the two portions can be separated completely by extraction with a compatible solvent. Obviously, the higher the fraction of material in the gel, the higher will be the concentration of effective chains. Thus, in a general way, strength is dependent on gel fraction.

One very important feature of the gelation of castable elastomers is the point at which it begins in the curing process, a state known as the <u>incipient gelation</u> point. This critical state is, as will be discussed later, dependent upon a combination of composition and extent of reaction.

Besides enabling the separation of sol and gel fractions, solvents have another effect on cross-linked polymers. They produce swelling. In general, those polymers having longer effective chains will imbibe more of a compatible solvent than those with shorter effective chains. Volumetric expansions of over 2000% have been observed. [X18]

In the sense of review, consider the macrostructure of cross-linked polymers from a different viewpoint. Another name for these materials is space polymer, implying that the network, one giant molecule, occupies the entire volume of its container. Theoretically, one could trace a continuous path of chemical linkages from any point on the inside wall of the vessel to any other. A very clear idea of the polymeric network is obtained by imaging a three-dimensional arrangement of chicken wire. This last pictorial conception presupposes the branch points to be trifunctional. There are systems with higher functionalities, and, in castable systems in which a potential for higher than trifunctional branch points exists, the network will contain a distribution of all that are possible.

The chicken wire model is good as far as it goes. To bring it up to the state of the previous discussion, we must add pendent chains to the network (by snipping some wires), and fill the space between network chains with sol. Depending on starting composition and the purity and extent of the link-forming chemical reaction, the fraction of material (and structural volume) sacrificed to sol and pendent chains can range from zero (perfect chicken wire) to almost one-hundred percent. A diagram of an imperfect network, based on trifunctional branch units, is shown in Figure 1. Notice that the word "potential" is used in Figure 1 in reference to two cross-link sites and the interconnectiong effective chain. This label is necessary because we have no way of knowing whether the dashed lines at the extremities of the diagram lead into an infinite network or to pendent chains. If only one of the ten dashed lines were to lead into the network, the two branching sites would not be cross-linking, and the connecting chain would not be effective. Two are needed. However, not just any pair will make these elements structurally effective. In this diagram, twenty-five pairs will, and twenty will not.

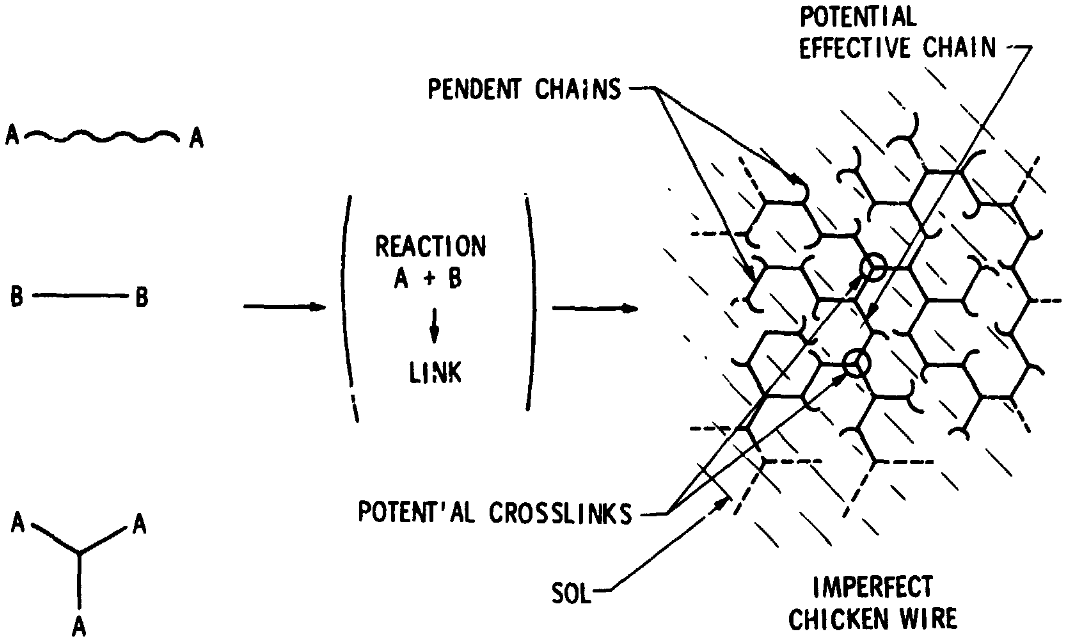


Fig. 1. Representation of the formation of a cross-linked polymer by the condensation of polyfunctional reactants.

The two network imperfections just discussed, sol fraction and pendent chains in the network, are predictable by the models of this report. Several others are known to exist, which are not treated by the models of this report and will not be discussed further. One such imperfection is the presence of small loops in the network, caused by stereochemical factors. Another is microgel, a condition near incipient gelation, caused by high dilution, in which an infinite or space network is replaced by discreet, insoluble particles. One other imperfection is chain entanglement, which acts mechanically somewhat like cross-linking.

B. Examples

Up to this point, no specific polymerizing systems have been mentioned. Identification of the very large list to which network modeling might apply will not be attempted here. Instead, a few of the systems dealt with in this work will be described to illustrate the kinds of problems we are trying to solve.

As far as solid propellant binders go, we have been concerned chiefly with those which depend on urethane formation for generation of polymeric linkages,

$$\text{R-OH} + \text{R'-NCO} \longrightarrow \text{R-O-CO-NH-R'}$$

alcohol isocyanate urethane

On the other hand, in the verification of models, esterification,

$$\text{R-OH} + \text{R'-COOH} \longrightarrow \text{R-O-CO-R'} + H_2O$$

alcohol carboxyl ester

was used as to avoid in the early stages of the work the uncertainties and complications of dealing with not-well-characterized competing side reactions.

Urethane-cured propellant binders are generally composed of three basic components. They are: a prepolymer (usually bifunctional in hydroxyl and having number-average molecular weights ranging from 1000 to around 3000 or more), a trihydroxy cross-linking agent, and a diisocyanate curing agent. A considerable variety of cross-linking and curing agents are used. The best known are, respectively, trimethyol propane and 2,6-tolylene diisocyanate. Some urethane binder recipies include a catalyst. Others do not.

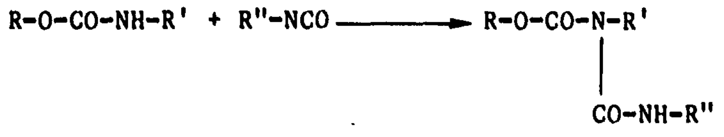
The selection of which of several available prepolymers will be used in propellant formulating is dependent on practical considerations. Some of these considerations are cost, resistance to high temperature, low glass transition temperature, and castability when heavily filled (with oxidizer and powdered metal fuel). The prepolymer characteristics that are treated in network modeling are mixtures of functionality and unequal reactivity.

Some commercial poly(propylene oxide) prepolymers are telechelic, which means the hydroxyl functional groups are located at each end of the chain. A small degree of imperfection exists, which results in a small percentage of the prepolymer molecules being monofunctional. Approximately 85% of the hydroxyls are secondary; the remainder are primary. The specific material used in this work was Union Carbide's PPG 2025, elastomer grade.

Most current attention in propellant formulation is focused on a class of prepolymers called HTPB's (hydroxyl terminated poly(butadiene)). The process for synthesizing one subclass of HTPB's was designed to produce perfect bifunctionality; however, the number-average functionality typical of such products is 1.7 hydroxyls per molecule instead of 2. The most popular HTPB, chiefly on the basis of cost, is a product named R-45M manufactured by Atlantic Richfield Company (ARCO). Its functionality generally runs around 2.3 to 2.4, indicating the presence of trifunctional molecules, and possible higher. The hydroxyl groups on HTPB's are said to be secondary. The Union Carbide Company developed a process [X9,X12,X21,X23] for synthesizing almost perfect bifunctional polydiene prepolymers which would not be costly in large volume production. With butadiene, isoprene, or dienes having still longer side chains, this process can produce any of the four combinations possible from the following options: hydroxyl or carboxyl functionality and unsaturated or saturated hydrocarbon chain structure. Some of the other HTPB's also can be saturated without becoming crystaline.

Numerous other binder systems have been developed and used, some of them thermochemically energetic. The most important of the latter, known as double base (nitrocellulose plus energetic plasticizer), has not, until recent years, depended upon the formation of network structures to produce required mechanical properties. One other large class will be mentioned because they are still used in very large quantity and because theoretical modeling would be applicable to their network structures. We have not, however, studied them in this regard. In this class, the prepolymer chains are poly(butadiene), and the functional groups are carboxyls. These are cured either with epoxides or aziridines to form substituted ester links. Some of the prepolymers used in these systems are called carboxyl-terminated polybutadiene (CTPB). The others have the carboxyl groups randomly distributed along the chain. One such prepolymer is a copolymer of butadiene and acrylic acid (PBAA). The other is a terpolymer containing acrylonitrile as well as butadiene and acrylic acid (PBAN). The randomness in the location of functional groups in the chains of these materials produces also a random distribution of functionality.

The variety of propellant binder prepolymers just discussed illustrates the two problems in modeling cited earlier, mixed functionality and unequal reactivity. Other problems exist for practical systems because of complications in the chemistry of curing. For example, from the earliest days of work with urethane-cured binders, formulators observed that another reaction occurs, besides urethane formation, which results in the consumption of more than calculated isocyanate and in the production of more cross-linking. A crude model was developed, [X25] which correlated with propellant mechanical property data. This model was based on the assumption that allophanate formation was the cause of the deviation from simple theory. Allophanate is formed by the reaction of an isocyanate with a urethane:



$$\mathrm{R{-}O{-}CO{-}NH{-}R'} + \mathrm{R''{-}NCO} \longrightarrow \mathrm{R{-}O{-}CO{-}}\underset{\substack{|\\ \mathrm{CO{-}NH{-}R''}}}{\mathrm{N}}\mathrm{{-}R'}$$

This correlation was good for propellants based on poly(propylene oxide) prepolymers, but was erratic with hydrocarbon prepolymers. The existence of still another side reaction is suspected.

In model verification studies, the esterification system used most frequently contained the following ingredients: trifunctional carboxyl, 1,3,5-pentanetricarboxylic acid; bifunctional carboxyl, sebacic acid; and bifunctional hydroxyl, 1,10-decanediol. p-Toluene sulfonic acid was used as catalyst. Model compounds free from ambiguous reactions are difficult to acquire. The pentane tricarboxylic acid cross-linking agent was chosen because it was the least expensive of the few free of such problems. Its use added a new dimension to modeling, unequal reactivity. The carboxyl on the number-3 carbon is secondary, and therefore, less reactive than all the others in the system, which are primary. This difference showed up in incipient gelation measurements, and a specific theoretical model was developed which correlated with those measurements. [X16] In postgelation studies [X28] with this system, the necessity of dealing with this more complex model was avoided by formulating and curing so that carboxyl consumption was very near complete.

C. Starting Components and Their Fates

In terms of forming networks, and the modeling of this process, four general classes of molecular components were either identified or implied in the preceding discussion of examples.

1) Nonfunctional Components never become part of the network. Their effect on mechanical behavior is in the viscous mode (in contrast to elastic), as also is true of the low molecular weight sol fraction generated in the cure. Some fraction of the molecules in some commercial prepolymers is nonfunctional.

Sometimes, nonfunctional plasticizer is included in formulations to provide certain desired effects, such as increased fluidity or lower T_g. It the presence of nonfunctional components is not accounted for in modeling, the effect on results is a false value for average molecular weight of the prepolymer and for the average length of various network chains. Otherwise, these components are not treated in modeling.

2) Monofunctional Components are frequently found in prepolymers. Their effects on structure are: increase in sol fraction, decrease of cross-link density, and the generation of pendent chain structure, or branching complexity, in the network itself. Practical advantage was taken of the effects of added monofunctional components in the development of a solid propellant with unusually low modulus. [X19] As theory had predicted, very low cross-link density was obtained without the sacrifice in quality control that would have been encountered by the direct method of decreasing cross-linking agent concentration.

3) Bifunctional Components are required for the growth of chains, both in the network and in the sol fraction.

4) Branching Components are those which have functionalities greater than two. No network is possible without their presence. The functionalities of these components can range from three on up. One of the problems in modeling is the treatment of systems having more than one kind of branching component.

The chief question in developing theoretical models of network polymers is this: What are the fates of the branching components? The fates of the mono- and bifunctional components are important also, but primarily in regard to the effects of their fates on those of the branching components.

The components of a typical network-forming system are illustrated in Figure 2. In such a system, polymers would be formed by extensive reaction of A with B to form chemical bonds. This particular system (identified in shorthand as 3,2,1/2,1) will be used throughout the discussion on modeling.

Consider the branching component. What can happen to it as the reaction progresses? As a result of what happens to it, what will its structural function be? In the first place, any one, two, or all three of its A's can react with B's; of course, none may react.

It is clear that, in order to answer the questions of the fate and function of any particular branching component, we must first determine the fates of its individual branches. This question can be asked and answered in stages. First, does the A in question react? Then, if it reacts, how many different kinds of components can it react with; what is the probable distribution of these possibilities? In one of the approaches to modeling used in this work (introduced in 1941 by Flory [2]), the different kinds of components asked about here are the set whose members are all of the possible lengths of chain composed of

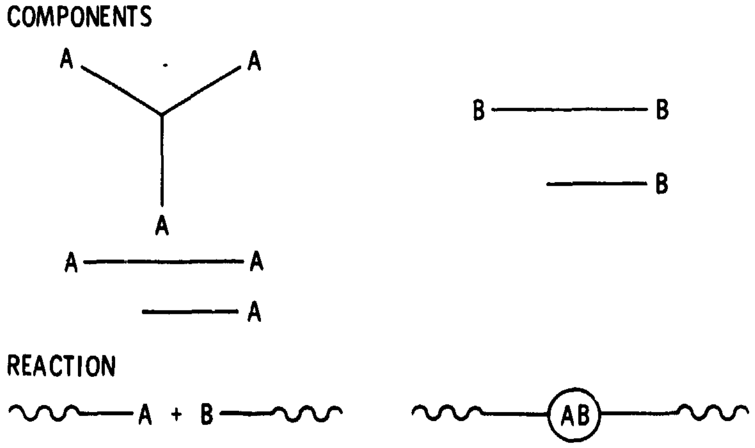


Fig. 2. Components of the 3,2,1/2,1 system.

alternating B-B and A-A components. From this point on, the questions become more specialized, depending upon the approach being followed and on the system itself.

Pursuing the Flory approach, the next question is, what is at the end of the chain? In the case before us, a branch chain can terminate in any of the following end structures: another A-functional branching component, a monofunctional A or B component, or a bifunctional A or B component whose other functional group has not reacted. The last four possible end structures are free-end terminals. The first mentioned terminating possibility, another branching component, allows, but doesn't require, the original branching component to be a true cross-link. Because our knowledge of the system at this point does not include the fates of the two other branches of the particular branching component whose fate we are interested in, and also because we are just as ignorant of the fates of the other two branches of the trifunctional chain end just added, all we can say is this: The particular branching component can have any one of three functions. These are a cross-link, simultaneously a chain extender and a foot of a pendent chain, or a cap of the free end of a chain. Also, we are unable to say in this state of our knowledge whether the particular unit is in the sol or network fraction of the polymer.

Having ascertained the fates of the individual branches of branching components, by making use of Flory's method, we come to a point where it can be visualized that any particular branching component can be in any one of four distinct states. Which state it is in depends upon how many of its branches terminate in other branching components (connected) as compared to how many terminate as free ends (not connected). The four possibilities are illustrated in Figure 3. A key factor, which is essential to the development of postgelation

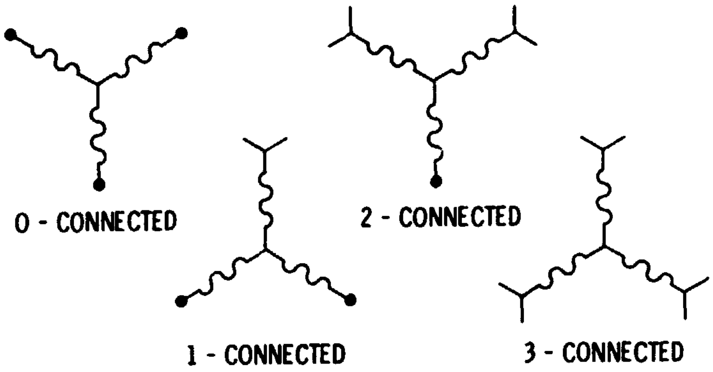


Fig. 3. Four possible fates of a trifunctional branch unit.

models, is apparent. Those branching components whose branches all terminate in free ends (0-connected) cannot possibly be connected to the network; they must then exist as part of the sol. Any of the other states can exist in either the network or the sol. Their possible functions can be seen to be as follows: 1-connected branching components must be free-end terminals; 2-connected units are chain extenders. The 3-connected branching components are the only kind of this set which, at this point in the conceptual process, still have a choice of fates and consequent functions. Again, these branching components are allowed, but not required, to be true cross-links.

At this point, we are on the threshold of a hierarchy of branch units. Labeling the set of i-connected branching components as 1st-order branch units in the hierarchy, consider their distribution throughout the whole polymer. As previously mentioned, all 0-connected branch units must be in the sol fraction. However, as to the distribution of the other three types between sol and network, we are ignorant. Let's put them together as building blocks according to function. Each 1-connected unit is a chain end. Likewise, each 3-connected unit is the locus of three chain ends. Half the sum of these two sets represents the total number of 1-order chains in the polymer. This leaves only one place for the 2-connected branch units to be. That place is in these chains as an extender.

Now, we can visualize the second order of branch units, which were just constructed using 1-order branch units as building blocks. These, too, can be distributed into the four types, i-connected. Where, in the 1-order set, the free-end terminals were monofunctional components and unreacted A or B groups, the corresponding 2-order free-end terminals are 1-order, 1-connected branch units. Likewise, the 2-order branching terminals are 1-order, 3-connected branch units. Again, at the second order, all of the 0-connected branch units are relegated to the sol fraction, and the distribution between sol and gel of the 1-, 2-, and 3-connected, 2-order branch units is still unknown. The 2-order units can be sorted into building blocks and distributed in the same way as before, resulting in a 3-order set of branching units, and so on.

The process just described is illustrated in Figure 4. It can be seen in this illustration that each chain is divided into two half-chains. This artifact is not absolutely necessary, but it helps to keep a proper count of the various elements for use in subsequent calculations of the concentrations and lengths of chains. A presentation of a fully-developed, 3-order, half-chain is given in Figure 5.

As the process of calculating ever higher orders of branch unit distribution proceeds, two parameters are observed to approach asymptotic limits. The concentration of branch units which survive as 3-connected through the hierarchy decreases with increasing order, approaching the cross-link density. The accumulated mass of material represented by the 0-connected branch units plus associated half-chains approaches the mass of the sol fraction. Thus, as the effects of increasing order on the values of such parameters decrease to insignificance, a full accounting of the locations and functions of all components is achieved.

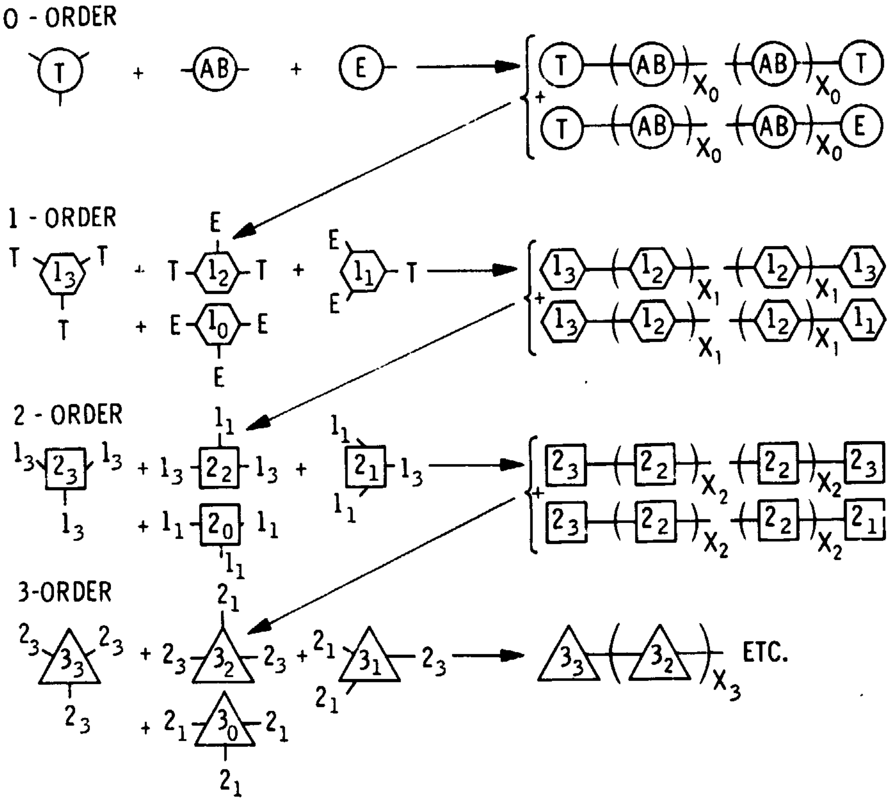


Fig. 4. The building of a hierarchy of branch units and chains.

III. MATHEMATICS OF MODELING

Before the development of the mathematical expressions describing network characteristics is presented, it is necessary to make a general statement regarding the status of modeling. As will be seen in the following pages, the models are on firm ground up to a point. Beyond that point, further study will be necessary. For simple systems, methods for calculating the following characteristics are well established: incipient gelation conditions, sol and gel fractions, and cross-link density (or effective chain concentration). These all have been verified either by experiment, or by cross comparison with other methods, or both. Expressions for calculating, in complex systems, the conditions for incipient gelation and α's for both pre- and postgelation have been verified by

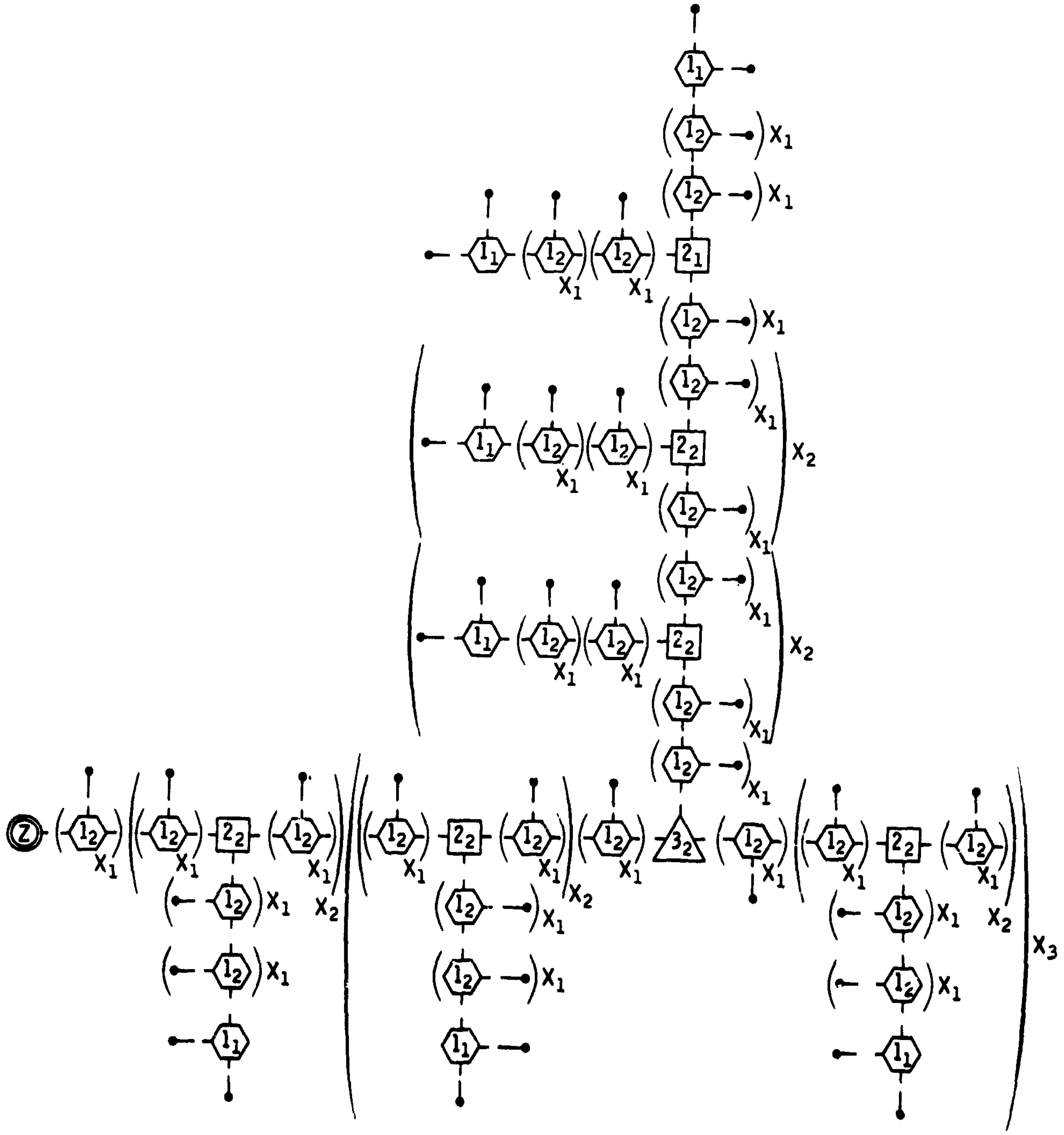


Fig. 5. Example: A 3-order half-chain.

cross comparisons. Sol/gel fractions and cross-link density are straightforward consequences of this.

Methods for calculating the lengths and distributions of network chains were presented in a prior publication, [X28] and are given here. These models have not been verified. However, as described below, a very good correlation was obtained between a parameter, L_x, representing effective chain length and extensibility. Questions raised by technical review of this report have made it necessary to reconsider some aspects of this part of the postgel model. For example, in reference X28, the term L_x, cited above, was called Average Effective Chain Length. Now, it's not clear whether or not this is an average and, if so, what kind. This and other parameters will need further study. Throughout the rest of the report, especially in Section IIB5C, appropriate acknowledgment and comments will be made, and the term, L_x, will be identified as The Parameter Representing Effective Chain Length.

This section of the report describes the derivation of the mathematical models. In Appendix A, the use of these expressions is illustrated by the calculation of postgel characteristics of two compositions. Appendix A serves another purpose. This is to show the interesting effects on network characteristics caused by the presence of monofunctional components.

In the previous section, the scenario for the development of a model was unfolded. This scenario is based on the fundamental question, what is the probability that a given branch of a branching component leads to another branch exclusively? This question and the remainder of the scenario will be treated quantitatively below with the simple 3,2,1/2,1 system, yielding expressions for calculating sol and gel fractions, cross-link density, a parameter representing length of effective chains, and distributions of pendent network chains. This method will be referred to as the α-method. Another approach which will be called P_F-method, from which some of the same network characteristics can be calculated, also will be applied to the same simple system. The scenario of the P_F-method is based on the question, what is the probability that a given branch leads exclusively to a finite chain?

The difference between these two questions is in the paths which lead to the required ultimate ends. For the α-question, a positive result is reached in tracking a chain when the first new branch unit is encountered, regardless of how many bifunctional units are passed by. Any free-end terminal (or finite end) is a negative result. In answering the P_F-question, the tracing continues through any number of branch units, and consequently along every new chain generated at these points. In this case, a positive result is the presence of a finite end on every one of these branches. Continuation of any one of these chains into an infinite structure produces a negative result.

Reference is made to simple systems to identify difficulties experienced with the α-method in efforts to develop models for complex systems. The distinguishing factor is the nature of the branching components. Simple systems contain only one kind of branching component (i.e., 3,2,1/2,1; 4,2,1/2,1;.... f,2,1/2,1). Any of several conditions cause a system to be complex. One is mixed branching components (e.g., 3,2,1/3,2,1 or 4,3,2,1/2,1). Another is unequal reactivity between the functional groups on the branching component of an otherwise simple system. Still another cause of complexity is the existence of side reactions (e.g., urethane systems).

The difficulty, mentioned above, with the use of the α-method on complex systems was in the development of true expressions for determining α. This problem has now been solved. Later in this section treatment of complex systems by both methods will be presented.

A. Assumptions

In his first paper on calculating the structures of three-dimensional polymers, [2] Flory made the assumptions that like groups are equally reactive and that the equality holds despite the changing status of the host structure as the reaction proceeds. Other assumptions generally made are: no side reaction occurs; no intramolecular reaction occurs. When intramolecular reaction occurs in branched or network structures, closed loops are created. As will be seen later, the assumption that no intramolecular reaction exists is essential for the mathematical modeling of the incipient gelation state. Flory [2] and others [5] attributed discrepancies between experiment and theory to the failure of this assumption to hold in practice. The Stanford Research Institute and JPL experimental procedures [X14,X15,X16,X20] appeared to avoid this problem. Nevertheless, the potential for loop formation exists, and its probability must increase to significance as gel fraction increases. Complete reaction of a "perfect composition" (i.e., a stoichiometrically balanced mixture with no monofunctional components) would, for example, be one hundred percent gel, one large molecule with countless closed loops in many sizes. This observation is made also by Macosko and Miller. [14]

The assumption of no side reaction applies to the cases of this section. However, in many practical systems it does not, and as far as we have gone with it, [X25] side reactions can be accounted for.

B. Simple Systems

1. The 3,2,1/2,1 System

The 3,2,1/2,1 system is illustrated symbolically in Figure 2. Its composition is defined by the following parameters:

r = ratio of B-functional groups to A-functional groups.

a_3 = fraction of A-functional groups contributed by the tri-A component.

a_2 = fraction of A-functional groups contributed by the bi-A component.

a_1 = fraction of A-functional groups contributed by the mono-A component.

b_2 = fraction of B-functional groups contributed by the bi-B component.

b_1 = fraction of B-functional groups contributed by the mono-B component.

The extent of reaction is represented by:

p_A = fraction of A-functional groups reacted.

p_B = fraction of B-functional groups reacted.

As a consequence of the conservation of chemical units, the following relationship holds

$$r = p_A/p_B$$

2. Flory's Branching Coefficient

An essential step of the scenario in the previous section is the determination of Flory's branching coefficient, α, for use in calculating the relative concentrations of i-connected branch units. [28] Flory defines α as the probability "that any given one of the functional groups of a branch unit leads, via a sequence of bifunctional units, to another branch, rather than to a terminal group". [2]

In the case at hand, what is the probability, α, that an A of a branch unit reaches another branch unit through a chain of alternating B-B and A-A units?

The intellectual process used repeatedly in probability modeling goes as follows. A question is asked; its possible answers are identified; part, or all, of the probability distribution of those possibilities is calculated. Often, the question has to be broken down into a sequence of subquestions. The question in the preceding paragraph is a good example.

The first subquestion is this: What is the probability that the particular A has reacted with a bifunctional B? This question asked in a more general way is, what are the possible states of A? There are three: not reacted, $(1-p_A)$, reacted with monofunctional B, p_Ab_1, and reacted with bifunctional B, p_Ab_2. Only the last of these three probabilities is of interest in getting the answer, α, to the overall question.

The next subquestion is obvious. What is the probability that the second B of the new B-B component reacts with an A-A? Through an analogous series of subquestions, the answer is found to be p_Ba_2.

This is a good point to call attention to three fundamental principles in dealing with probabilities, even though they may not be new knowledge to most readers. First, when all of the available options, or possibilities, are properly weighted, so that their weights add up to one (such as, in the present case, concentration: $1 = a_1 + a_2 + a_3$, and $1 = b_1 + b_2$), those weights can be treated as probabilities. Second, when an event depends upon the occurrence of some previous event, the probability of its occurrence is the product of the two individual probabilities. Application of this principle gives a probability of the sequential structure, up to this point, of $p_A b_2 p_B a_2$. Third, the sum of the probabilities of all possible events that can occur is one. The last principle is illustrated with aid of the structures in Figure 6. These structures represent all of the possible fates of a particular A-branch. The sum of their probabilities is one:

$$1 - p_A + p_A \left(b_1 + b_2 \left(1 - p_B + p_B (a_1 + a_2 + a_3)\right)\right) = 1 \qquad (1)$$

Returning to the main question, finding α, we see that the process just described can now be recycled any number of times and that, for n cycles, the

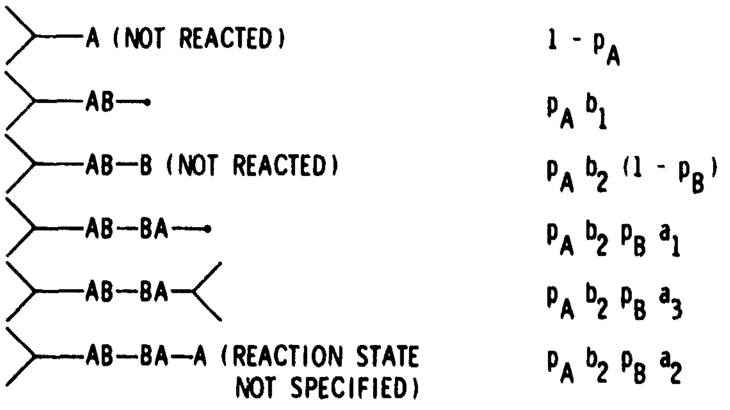


Fig. 6. Example: Quantitative accounting of all possible fates of an A-branch up to, and including, a second addition reaction step.

probability will be $(p_A p_B b_2 a_2)^n$. This, and the rest of the process, are illustrated in Figure 7. Theoretically, there's no limit to the possible number of cycles, or lengths of chain, from zero to infinity. Another principle of probability requires us to sum the probabilities of all of the possible ways, which in this case is every length from zero to an infinite number of --AB-BA-- units. The resulting infinite series is a geometric progression, whose sum is the simple algebraic expression shown in equation 2.

$$\alpha = \sum_{n=0}^{\infty} (p_A p_B b_2 a_2)^n \; p_A p_B b_2 a_3 = \frac{p_A p_B b_2 a_3}{1 - p_A p_B b_2 a_2} \qquad (2)$$

This equation is the expression for calculating Flory's branching coefficient in 3,2,1/2,1 systems (including subsets) for any composition and state of reaction.

3. An Alternate Method for α

In taking another look at equation 2, we notice that it contains two of the probabilities identified in Figure 6. What is the significance of the relative positions of these two terms in equation 2? In the first place, $1-p_A p_B a_2 b_2$ is equal to the sum of probabilities of all of the other five possible terminations.

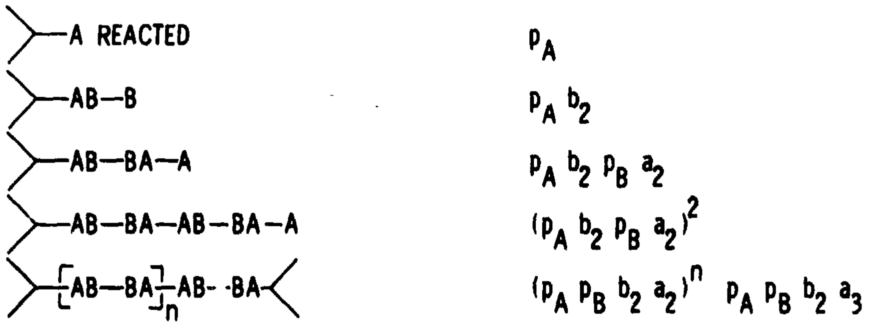


Fig. 7. Development of the expression for calculating the probability of leading from one branch in a 3,2,1/2,1 system, through a chain of —AB—BA— units, to another branch unit.

Furthermore, if we reframe Flory's question to ask about the first five terminations in Figure 6, we find that the results take the same form, each with a different numerator, but all with the same denominator, $1-p_Ap_Ba_2b_2$, and these results add up to one. Obviously, the sixth termination in Figure 6 is different from all of the others. It alone has the potential for continuation (within the framework of the α-question, in which continuation through other branch units is not a consideration); it represents a fate which is forever indefinite.

These observations lead to a new method for calculating the branching coefficient α. This is based on a restatement of its definition. The branching coefficient is that fraction of all possible definite chain terminals that are branching, regardless of chain length, wherein a chain must start with a branch and end at or before another branch. The algebraic result in a 3,2,1/2,1 system is identical with equation 2.

Two methods have just been illustrated for determining Flory's α. These are applicable, without problem, to simple systems such as 3,2,1/2,1, 4,2,1/2,1 and so on. With more complex systems, such as 3,2,1/3,2,1, 4,3,2,1/2,1 and systems with unequal reactivity, problems arise in attempts to use these methods. Methods for solving these problems will be presented later.

4. Incipient Gelation

The particular state of reaction of a given composition at which gel begins to form is known as the incipient gelation point. Flory [2,16,17] reasoned that this point should correspond to a theoretical state at which an infinite molecule just becomes possible. In a system which contains branch units which are trifunctional only, if we begin with a particular branch unit and concern ourselves with only two of its branches, what do we find? We find that the probability of each of these two branches being connected to other branch units is α. In other words, the probability of continuation (in the sense of adding branch units) from this point is 2α. Whatever that value is found to be, except zero, we have additional branch units to ask the same question about. Perhaps it's better to put it in terms of groups of units. Randomly select a representative sample of n branch units and ask about two branches each. We find that they have $2n\alpha$ branch units connected to them. These in turn will have $2n\alpha(2\alpha)$ new branch units connected to them, and so forth. Continuation of the process produces a series of values for the probability of continuation: $n(2\alpha)$, $n(2\alpha)^2$, $n(2\alpha)^3$... $n(2\alpha)^x$... . It is easy to see that there is only one value of α, 1/2, for which the successive values of continuation probability neither decreases nor increases. Thus, this critical value, $\alpha_c = 1/2$, for simple trifunctional systems is the lower limit for the possibility of the formation of an infinite molecule. Flory goes on to show that for all simple systems, which contain branch units of only one functionality, f, $\alpha_c = 1/(f-1)$. It is evident that the assumption that no intramolecular reaction occurs is necessary for this definition of critical α.

The concept of the correspondence between α_c and the gel point was verified experimentally by Flory. [2] We also found excellent experimental correlation [X16,X17] in systems including monofunctional components. In both investigations, the critical point was identified by the rapid approach to infinity of the viscosity of a polymerizing mixture. Additional verification was obtained by sol/gel extractive separation. Subcritical reaction mixtures dissolved completely. When a mixture was supercritical, insoluble, swollen gel was recovered.

Experimental verification of theoretical models cannot always be trusted. Sometime ago, the author thought he had derived a good model for 3,2,1/3,2,1 systems (containing both trifunctional A molecules and trifunctional B molecules).

Some experimental results were obtained which supported the model (See Appendix B, reference X17). Nevertheless, as pointed out by Stockmayer (see Appendix C, reference 20), the model was not compatible with other, established elements of polymer network theory. Fortunately, Stockmayer's advice was received before any publication (beyond the conference preprint) was possible. The general problem of modeling systems with mixed functionality has been, until recently, very troublesome. This subject is treated in Section IIIC.

Another method for verifying models is to compare them with other models, mathematically if possible, or numerically. Such a model exists for the critical state, incipient gelation. Treating the transition from liquid to gel as an analogue of the condensation of a saturated vapor, Stockmayer [3,21,22] devired the following relationship:

$$p_A p_B = \frac{1}{(f_{f,A} - 1) \quad (f_{f,B} - 1)} \qquad (3)$$

where

f_f = functionality-weighted average functionality.

In the 3,2,1/2,1 case,

$$(f_{f,A} - 1) = 2a_3 + a_2$$

$$(f_{f,B} - 1) = b_2$$

Mathematical equivalence exists for all simple cases (i.e., f,2,1/2,1 and all subsets) between equations 2 and 3 when $\alpha = \alpha_c = 1/(f-1)$.

5. The Postgel State

The model, so far as it has been developed here, can predict the conditions for incipient gelation. Aside from model verification, this physical state has little practical value. Such things as modulus and extensibility of compositions cured past the gel point are of much greater interest. So, the objective now is to complete the quantification of the scenario so as to make possible the determination of effective chain concentrations and the parameter representing lengths of effective chains.

In order to get effective chain concentration, we will have to sort chains and count them. One way to count (and classify chains) is to count ends. For example, if we knew the concentration of true cross-link sites (T_x) in a simple trifunctional system (3,2,1/2,1), we would also know that the effective chain concentration would be $\nu_e = 3T_x/2$.

The following development makes the assumption that calculations based exclusively on the fates of branching components give an adequately true picture of the structure. This means that the mass fraction (and its derivative, chain length contribution) of linear oligomers (including monomeric bi- and monofunctional ingredients) is insignificantly small. This fraction, although it can reside only in the sol, is automatically distributed by this assumption between sol and gel. So far, this assumption appears justified on two counts. It is implicit in the work of others [14,18], and no significant effect was observed outside the range of experimental error in our verification studies. [X28]

Previously, we found that branch units could be classified according to four different fates. These are shown symbolically in Figure 3. The branching coefficient, α, discussed above, allows us to calculate the relative concentrations of these fates. The probability that any given arm is connected to another branch unit is α. All arms that are not connected terminate in any one of the several kinds of free ends described earlier. This probability is $1-\alpha$. The result of this calculation is given in equations 4 through 7 for the four states shown in Figure 3.

0-connected: $T_0 = T(1-\alpha)^3$ (4)

1-connected: $T_1 = 3T(1-\alpha)^2\alpha$ (5)

2-connected: $T_2 = 3T(1-\alpha)\alpha^2$ (6)

3-connected: $T_3 = T\alpha^3$ (7)

where

$T = a_3/3$ moles of branch units per equivalent of A.

Another probability principle is illustrated here. The branches of the 1- and 2-connected units are mixed. There are three independent ways to arrange these configurations. Therefore, the probabilities of each of the three ways must be added. This element of the model is verified by the sum.

$$T = T_0 + T_1 + T_2 + T_3 = a_3/3 \tag{8}$$

a) Sol and Gel Distributions

As was observed earlier, 100 percent of the 0-connected branch units must be in the sol fraction. Therefore,

$$T_{S,0} = T_0 = T(1-\alpha)^3 \tag{9}$$

Flory's calculations [16] show that when the sol fraction alone is considered, a different branching coefficient, α', applies to the fates of branches. Specifically for simple trifunctional systems (3,2,1/2,1),

$$\alpha' = 1 - \alpha \qquad \text{for } \alpha > 0.5. \tag{10}$$

Thus,

$$T_{S,0} = T_S(1-\alpha')^3 = T_S\alpha^3 \tag{11}$$

combination of equations 9 and 11 gives and expression for sol fraction.

$$w_S = \frac{T_S}{T} = {\frac{1-\alpha}{\alpha}}^{3} \tag{12}$$

This equation is identical to Flory's. [16] Experimental verification will be taken up later.

Now, with a branching coefficient, α', applicable to the sol fraction, the distribution of sol branch units according to fate can be calculated in the same manner as was just done for all branch units.

$$T_{S,0} = T_S\alpha^3 \tag{13}$$

$$T_{S,1} = 3T_S\alpha^2(1-\alpha) \tag{14}$$

$$T_{S,2} = 3T_S\alpha(1-\alpha)^2 \tag{15}$$

$$T_{S,3} = T_S(1-\alpha)^3 \tag{16}$$

The reader will notice a striking similarity between the two sets of equations, 4-7 and 13-16. In fact, as far as their α-factors are concerned, they are mirror images. This is a consequence of the relationship between α and α' for simple, trifunctional systems (equation 10). Further differences between absolute quantities (T_i vs $T_{S,i}$) depend upon the relationship between T and T_S (equation 12).

Having calculated the quantities (per mole of A) of branch units, distributed according to how many of their branches are connected to other branch units, both in the whole polymer and in the sol, we can then calculate the quantities of them in the gel by difference.

$$T_{G,0} = 0 \tag{17}$$

$$T_{G,1} = T_1 - T_{S,1} \tag{18}$$

$$T_{G,2} = T_2 - T_{S,2} \tag{19}$$

$$T_{G,3} = T_3 - T_{S,3} \tag{20}$$

b) Cross-link Density and Effective Chain Concentration

So far, we've singled out and counted three kinds of branch units in the gel fraction. Their possible functions were described earlier as: free-end caps $T_{G,1}$, chain extenders $T_{G,2}$, and branching sites $T_{G,3}$. Only some of the 3-connected units can be cross-links because either one or two of a 3-connected units' branches can terminate in a 1-connected unit, resulting in a pendent chain. This results in a degradation of function from cross-linking to chain extension or free-end capping. Diagrammatic studies of assemblies of these units shows this effect of 1-connected units to be a one-for-one neutralization of 3-connected units. Thus, the cross-link density is simply the difference between the concentrations of 3- and 1-connected units in the gel.

$$T_x = T_{G,3} - T_{G,1} \tag{21}$$

$$\nu_e = 3T_x/2 \tag{22}$$

As will be seen in Appendix A, equation 21 reduces to a simple function of α and a_3. Both T_x and ν_e have the dimensions moles per mole of A. It is a simple matter to transform them into more common units of moles per unit volume. As pointed out in Section II C, the same values of T_x can be calculated by a laborious, cyclical process using equations 23 through 25, given in the next section. This same statement applies to calculation of the sol fraction; see equation 12.

The model for cross-link density has been verified two ways, experimentally and theoretically. The theoretical verification was shown by agreement with an independent method, [14] which will be treated in a later section.

In order to avoid problems of trying to measure accurately the extent of chemical reaction in cured rubbers, we chose an experimental program which provided mutual verification of the cross-link density and the sol/gel fraction parts of the model. [X28] Polyester formulations were mixed, and their cures were driven as close as possible to completion. Measurements were made of sol fraction and of equilibrium modulus (which is proportional to effective chain concentration [23]). Values ranged from 0.12 to 0.70 sol fraction and from 0.5 to 238 moles/m^3 of effective chains. Branching coefficients, α, were calculated from equations 12 and 22. Figure 8 illustrates the correlation. Extents of reaction calculated from these results ranged from 0.91 to 1.04.

c) Effective Chain Length and Other Characteristics

The remainder of this model is constructed by putting into algebraic form the heirarchal parameters illustrated in Figures 4 and 5. The parameter, x_n (chain extension coefficient), is simply a device for dividing up all of the n-order, 2-connected branch units (chain extenders) in the gel fraction and distributing them equally among all of the n-order half-chains. Each n-order, 3-connected branch unit has three half-chains; each n-order, 1-connected unit has one. The relationship is

$$x_n = \frac{(T_{G,2})_n}{3(T_{G,3})_n + (T_{G,1})_n} \tag{23}$$

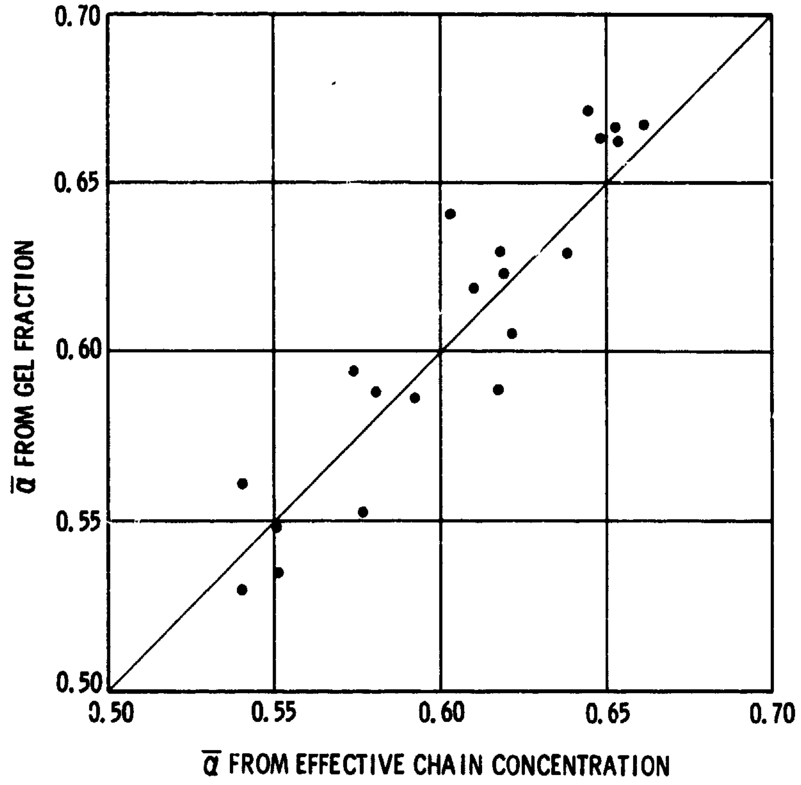


Fig. 8. Experimental verification of the 3,2,1/2,1 model by the correlation of α calculated from two independent measurements.

The values of $(T_{G,1})_1$, $(T_{G,2})_1$, and $(T_{G,3})_1$ were calculated as $T_{G,1}$, $T_{G,2}$, and $T_{G,3}$ from $\alpha_1 = \alpha$ as described earlier (equations 17-20). We need a way to calculate higher order branching coefficients, $\alpha_2, \alpha_3, \ldots \alpha_n \ldots$, so that we can calculate higher order $(T_G)_n$'s in the same manner. This way is provided by the principle used in the second method for calculating α, which was described in section III B3; α_n is the fraction of (n-1)-order chain ends that are branching. This is expressed in equation 24,

$$\alpha_n = \frac{3(T_3)_{n-1}}{3(T_3)_{n-1} + (T_1)_{n-1}} \qquad (24)$$

Notice that, as with α itself, α_n's are calculated for the whole mixture, while x_n's deal with the gel fraction only.

In the process of stepping from one order to the next higher one, all of the 1-connected and 2-connected units become paraphernalia to the 3-connected units. Thus, these branch units, along with the 0-connected units, lose viability as potential cross-links. Therefore, only the surviving 3-connected units are distributed in the next order. This is expressed in equation 25,

$$(T)_n = (T_3)_{n-1} \tag{25}$$

With the chain extension coefficients, x_n, a variety of network (gel fraction) characteristics can be calculated. Distributions of pendent chains according to size are treated in Appendix A and in an earlier paper. [X28] Only effective chain length will be treated here.

As the order, n, ascends, x_n becomes smaller. Numerical calculations have demonstrated that x_n becomes insignificant at conveniently low values of n in most cases. Other consequences are: α approaches one; $(T)_n$ approaches T_x; and $\Sigma (T_0)_n$ approaches T_s. A corollary is the survival of $3(T)_n/2$ chains interconnecting the cross-links, each one supporting pendent chains.

To determine the parameter representing effective chain length, L_x, let us examine Figure 5. The little tick on the right side of the ⓩ represents a 0-order half-chain. Assign it an average length, L_o. (See Appendix A and reference number X28. The dimension of L_o is chain atoms.) The value of L_o is readily calculated by assuming that all of the bifunctional components are distributed equally among the potential chain terminals, one set each to free-end terminating groups and 3 sets each to branching components.

Connected to the starting 0-order half-chain in Figure 5 (cited in the preceeding paragraph) are, on the average, x_1 1-order 2-connected units; adding $2x_1$ more 0-order half-chains. If the process stopped here, there would be a 1-order half-chain. Its length would be $L_o(1 + 2x_1)$. The next addition is x_2 2-order 2-connected units, and this amounts to adding $2x_2$ more 1-order half-chains. The resulting length is $L_1(1 + 2x_2)$, and so on. This process is illustrated in the following expressions.

$$L_1 = L_o(1 + 2x_1)$$

$$L_2 = L_1(1 + 2x_2) = L_o(1 + 2x_1)(1 + 2x_2)$$

$$L_3 = L_2(1 + 2x_3) = L_o(1 + 2x_1)(1 + 2x_2)(1 + 2x_3)$$

$$- -$$

$$L_n = L_o(1 + 2x_1)(1 + 2x_2)(1 + 2x_3)\ \ldots\ (1 + 2x_n) \qquad (26)$$

Equation 26 is a general expression for the length of any n-order half-chain, and equation 27 shows the parameter representing effective chain length to be the sum of two n-order half-chains at an n high enough for x_n to be insignificantly small.

$$L_x = 2L_n \quad \text{for} \quad X_n \longrightarrow 0 \qquad (27)$$

At the beginning of Section III, it was observed that the nature of the relationship between L_x and the distribution of effective chain lengths is yet to be investigated.

See Appendix A for an illustration of the use of the expressions developed in this section.

Experimental verification of the elements of this model which predict sol and gel fractions and cross-link density was rigorous. Sol/gel fractionation was measured directly. Effective chain concentration (cross-link density) was calculated from equilibrium modulus measurements using a relationship [23] derived from the kinetic theory of polymer networks. We are not aware of an appropriate measurement for verifying the model for average length of effective chains. However, it is known that the extensibility of network polymers depends on effective chain length. In gereral, the maximum extension at break is inversely proportional to the half-power of the effective chain concentration, $(\lambda_b)\max = k\nu_e^{-1/2}$ [24]. However, Landel and Fedors [25] observed that the proportionality constant depends on, among other things, "the detailed structure of the network." Certainly, the fraction of chain material in the form of dangling chain ends would be one of these structural factors. Such an effect is clearly shown by means of the α-model in the sample calculations of Appendix A. Although he didn't measure $(\lambda_b)_{max}$, Oberth's results [26] show the dangling chain effect experimentally. We didn't measure $(\lambda_b)_{max}$ either. However, as can be seen in Figure 9, we obtained a very good correlation between extension at break and the parameter representing effective chain length in Instron test of dog-bone

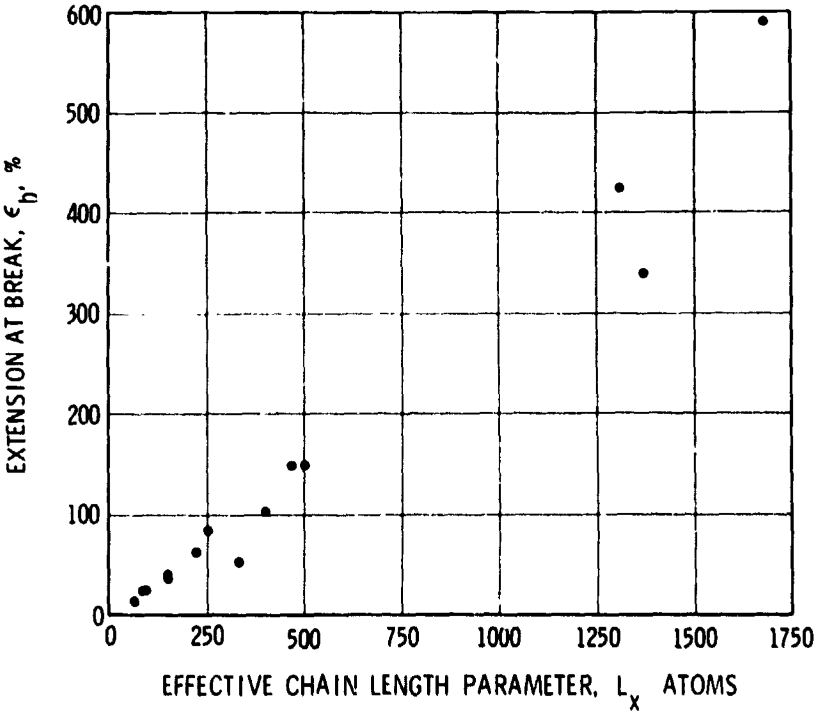


Fig. 9. Correlation of extensibility with theoretical length of effective chains.

specimens pulled at a slow rate at a temperature significantly higher than T_m and T_g. Our experiments were too limited for testing the dangling chain effect cited above.

6. Status of the α-Model for Simple Systems

The mathematical development of a modeling approach to network structure which depends on the calculation of Flory's α is nearly completed. The applicability of this approach to simple systems has been demonstrated. The extension of the approach to complex systems is described in Section IIIC2. Relationships predicting the conditions for incipient gelation and the postgel characteristics, sol fraction and cross-link density are verified. More study is needed to refine the meanings and calculations for the realationships predicting the postgel characteristics, effective chain length, and other chain distributions.

A series of graphs appear in Figures 10 through 12 to illustrate some of the things this model can predict with 3,2,1/2,1 systems. Figure 10 shows the distribution of i-connected branch units as functions of α. Figure 11 shows the distributions between sol and gel of the 1-, 2-, and 3-connected branch units. In Figure 12, the variations of the network characteristics, effective chain concentration and length, are shown. Appendix A shows how some of these characteristics can be calculated from a measurement of sol fraction. The same results would be obtained from direct measurement of reaction extent or another indirect measurement, cross-link density.

7. An Alternate Method for Network Characteristics

Recently, Mocosko and Miller [14] introduced an entirely different approach to network modeling. This method is general. For example, the 3,2,1/3,2,1 system presents no problem. It requires less calculation than the method just

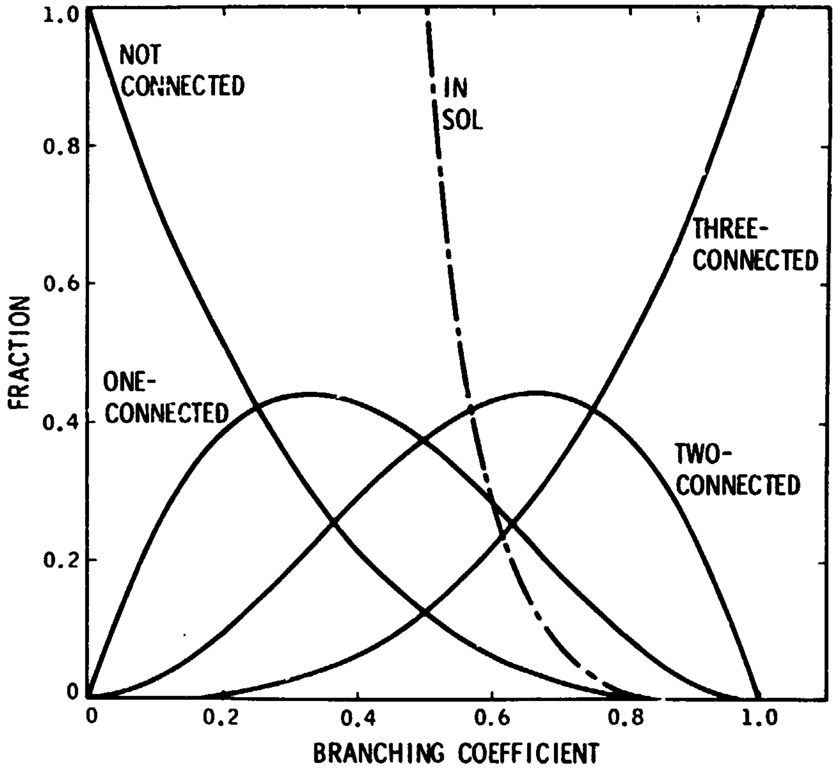


Fig. 10. Generalized distribution of branch units for 3,2,1/2,1 systems.

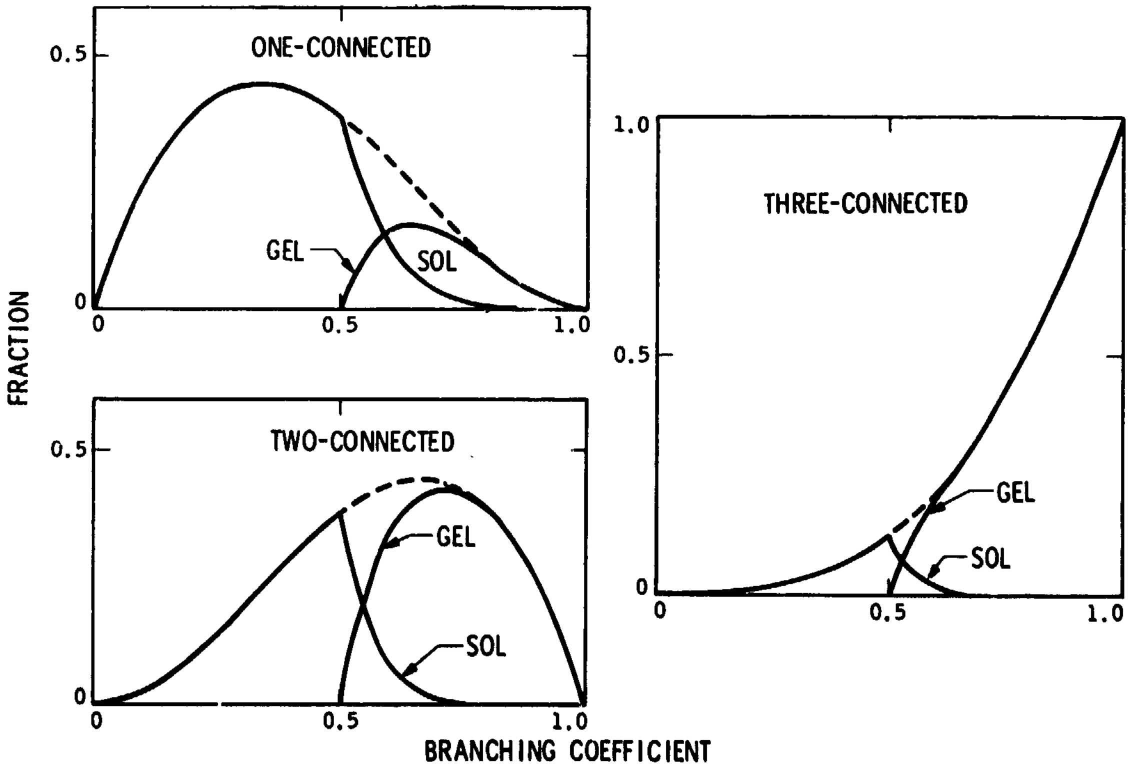


Fig. 11. Generalized distribution of branch units between sol and gel for 3,2,1/2,1 systems.

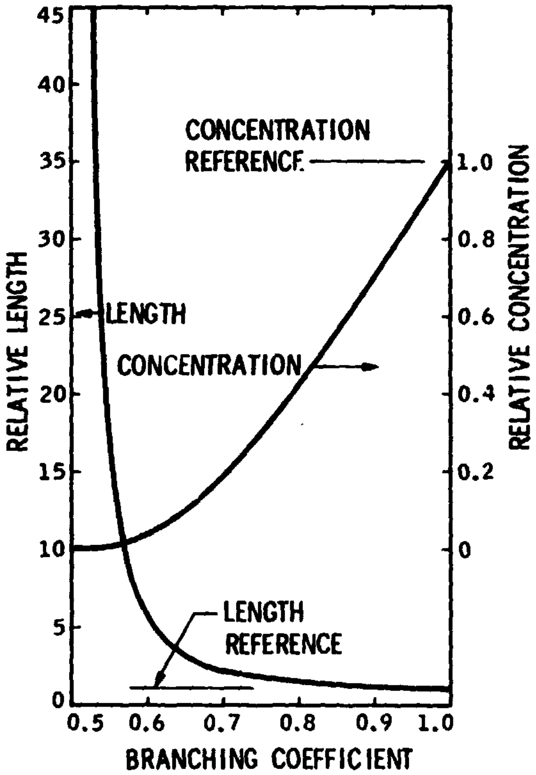


Fig. 12. Generalized effective chain characteristics for 3,2,1/2,1 systems.

reviewed. With simple systems, we have shown the two methods to be in perfect agreement for the calculation of parameters common to them both (e.g., sol fraction and cross-link density). At incipient gelation, it agrees with Stockmayers method. [3] Although Macosko and Miller don't mention it, it appears that their method should also give effective chain length. It is not clear, however, how one would calculate pendent chain distrbutions from their method.

There are two elements to the contribution of Mocosko and Miller. Their fundamental parameter is the answer to a different question than Flory's α. [2] They utilize a more powerful method of dealing with probabilities to answer the question. Later, we will show that α can be obtained this way as well.

a) The Question

Macosko and Miller, in the same manner as Flory, [2] start with a randomly selected branch unit in the composition and ask about one of the branches. However, instead of asking the probability that the particular branch will lead to another branch unit, they ask the probability that it will lead eventually and exclusively to a finite end (a free-end terminal).

b) Getting the Answer

Any attempt to answer this question by the methods employed so far in this paper would lead to considerable complexity. Macosko and Miller solve this problem by using a recursive method. As will be shown in the following discussion, the method is a stepwise process of subquestions which leads to a set of equations from which all dependent variables, except the one originating in the first question, are eliminated by substitution.

An element of this method is the use of conditional probability. $P\big((X)\,|\,(Y)\big)$ is the probability of the event X only in the case where event Y occurs. The symbol used by Macosko and Miller [14] to express the probability that a particular A-branch will lead exclusively to a finite end (or ends) is $P\,(F_A^{out})$. In our work, we shortened it to P_F and called it the "finite chain coefficient." The first expression answers the P_F-question.

$$
\begin{aligned}
P_F &= P\Big((F_A^{out})\;\Big|\;(\text{A reacts})\Big) \times P(\text{A reacts}) \\
&\quad + P\Big((F_A^{out})\;\Big|\;(\text{A doesn't react})\Big) \times P(\text{A doesn't react}) \\
&= P(F_B^{in})\; p_A + (1)(1-p_A) \qquad (28)
\end{aligned}
$$

Clearly, if the A does not react, the conditional probability of a finite end is one. Hence the unity in the second term. If the A does react, the answer depends on what happens at the next station, the B-functional group it joined. The next relationship accounts for the fact that there are two possible kinds of B-functional groups in 3,2,1/2,1 systems.

$$P(F_B^{in}) = b_2 P(F_B^{out}) + b_1(1) \tag{29}$$

If the B unit is monofunctional, again a finite chain is certain. If it is bifunctional, there is only one exit, and it presents next the same kind of question as the original one.

$$P(F_B^{out}) = P(F_A^{in}) p_B + (1)(1-p_B) \tag{30}$$

The next step is analogous to that which generated equation 29. In this case, however, there are also trifunctional options.

$$\begin{aligned} P(F_A^{in}) &= a_3\left(P(F_A^{out})\right)^2 + a_2 P(F_A^{out}) + a_1(1) \\ &= a_3 P_F^2 + a_2 P_F + a_1 \end{aligned} \tag{31}$$

The squared P_F in the first term expresses the fact that only when both of them are finite can a positive answer be obtained. The final solution is obtained in two steps: elimination of undesired variables and solution of the quadratic.

$$P_F = 1 - p_A + p_A\left(b_1 + b_2\left(1-p_B + p_B(a_1 + a_2 P_F + a_3 P_F^2)\right)\right) \tag{32}$$

$$P_F = \frac{1 - p_A p_B b_2 (a_2 + a_3)}{p_A p_B b_2 a_3} \tag{33}$$

The other root is 1. For all simple systems, f,2,1/2,1, where f = 3,4,5..., an algebraic relationship between Flory's branching coefficient, α, and Macosko and Miller's "finite chain coefficient" $P_F = P\ (F_A^{out})$, was derived. It is shown in equation 34.

$$\alpha = \frac{1 - P_F}{1 - P_F^{f-1}} \tag{34}$$

When f = 3, this expression reduces to

$$\alpha = \frac{1}{1 + P_F}$$

c) The Postgel State

In a similar fashion to the earlier model (see equations 4-7), the branch units can be classified according to how many of their branches lead to finite ends. This distribution is shown in the following expressions.

$$\text{3-Finite:} \quad T_{F,3} = TP_F^3 \tag{35}$$

$$\text{2-Finite:} \quad T_{F,2} = 3TP_F^2(1-P_F) \tag{36}$$

$$\text{1-Finite:} \quad T_{F,1} = 3TP_F(1-P_F)^2 \tag{37}$$

$$\text{0-Finite:} \quad T_{F,0} = T(1-P_F)^3 \tag{38}$$

In assigning functions according to these fates, it is important to recognize that if a chain end is not finite (P_F), it must be infinite ($1-P_F$), meaning it is connected to the network. So the first functional distinction to be identified is between sol and gel. The 3-finite branch units are the sol; all the others are the gel. The function of another class of branch units is also easily identified. Since all branches of a 0-finite branch unit are infinite, these units must be the junctures between effective chains, or in other words, they must be cross-links.

With simple f,2,1/2,1 systems, both models, the one based on branching coefficient and the other based on finite chain coefficient, agree mathematically on cross-link density and sol fraction. We are unable to say at this time what further correlation can be made between the two methods. However, it would appear there is at least one more parameter to test -- effective chain length. Consider a 1-finite branch unit. One of its branches is finite, but the other two are infinite. So the function of this type of unit must be a chain extender in an effective chain. From the relative concentration of such branch units, one should be able to calculate effective chain length.

8. Yet Another Method for α

The recursive method introduced by Macosko and Miller [14] is very powerful. It is general, and it is simple to use with less chance of producing faulty relationships. It ought to be an efficient way to calculate the branching coefficient, α. It is:

Let $\alpha = P\left(Br_A^{out}\right)$ = probability that a given A-group leads to another branch unit.

$$\alpha = P\left(\left(Br_A^{out}\right) \middle| (\text{A reacts})\right) * P(\text{A reacts})$$

$$+ P\left(\left(Br_A^{out}\right) \middle| (\text{A doesn't react})\right) * P(\text{A doesn't react})$$

$$= P(Br_A^{in})P_A + (0)(1-p_A) \tag{39}$$

$$P\left(Br_B^{in}\right) = b_2 P\left(Br_B^{out}\right) + b_1(0) \tag{40}$$

$$P\left(Br_B^{out}\right) = P\left(Br_A^{in}\right) p_B + (0)(1-p_B) \tag{41}$$

$$P\left(Br_A^{in}\right) = a_3(1) + a_2 P\left(Br_A^{out}\right) + a_1(0) = a_3 + a_2\alpha \tag{42}$$

Elimination of all dependent variables but α from these expressions yields equation 2. Examination of equations 39-42 in comparison with equations 28-31 shows that the framework of the recursive method stays the same. It is only the answers to the individual subquestions that change.

C. Complex Systems

For a number of years, the 3,2,1/3,2,1 system stood as a barrier to the development of a universal method of modeling. One might ask why the pursuit was continued when the P_F-method of Macosko and Miller became available. Besides the challenge, which didn't dissappear, there were other reasons for attempting to develop a universal method based on Flory's α:

1) It appears that the α-method yields quantitative characterization of the network structure in finer detail than the P_F-method, particularly in regard to pendent chain distribution.

2) The experience of this work indicates that it is helpful in the development of specific models to use one method as a check on the other.

1. The 3,2,1/3,2,1 System by Finite Chain Coefficient

Derivation, by the recursive method, of expressions for determining P_F's of complex systems from composition and extent of reaction is straightforward. In the case of f,2,1/g,2,1 systems, two distinct coefficients exist, representing the finite chain probabilities of the A- and B-functional branches. Where both f and g are 3, the intermediate solution, corresponding to equation 32 in the simple system, is a pair of quartic equations.

$$P_{F,A} = 1 - p_A + p_A\Big(b_1 + b_2\big(1 - p_B + p_B(a_1 + a_2P_{F,A} + a_3P_{F,A}^2)\big) + b_3\big(1 - p_B + p_B(a_1 + a_2P_{F,A} + a_3P_{F,A}^2)\big)^2\Big) \tag{43}$$

$$P_{F,B} = 1 - p_B + p_B\Big(a_1 + a_2\big(1 - p_A + p_A(b_1 + b_2P_{F,B} + b_3P_{F,B}^2)\big) + a_3\big(1 - p_A + p_A(b_1 + b_2P_{F,B} + b_3P_{F,B}^2)\big)^2\Big) \tag{44}$$

This type of mathematical complexity varies as the complexity of the branching components varies.

In this (3,2,1/3,2,1) system, instead of four, there are eight classes in the fate distribution of branch units (corresponding to equations 35-38 for the 3,2,1/2,1 system). These are 3-, 2-, 1-, and 0-finite A-functional branch units and another four B-functional units. As before, the sol consists of all of the 3-finite units, and the concentration of 0-finite units corresponds to the cross-link density.

2. The 3,2,1/3,2,1 System by Branching Coefficient

The chief error in earlier attempts to model complex systems by the α-method (See Appendix B, reference X17) was a failure to recognize the necessity for calculating several distinct branching coefficients. In the early work, an average α was calculated, but it was the wrong average. (See Appendix C, reference 20.) No reason has been found for the misleading agreement between the false model and the experimental data presented in Appendix B.

For the 3,2,1/3,2,1 system, four branching coefficients must be calculated. Expressions for their calculation are easily derived by any of the three methods described earlier. (See sections IIIB2, IIIB3, and IIIB8.) The branching coefficient for a chain beginning with an A-functional branch unit and terminating in another A-functional branch unit is

$$\alpha_{AA} = \frac{p_A p_B b_2 a_3}{1 - p_A p_B a_2 b_2} \tag{45}$$

The coefficient for a chain beginning with an A-functional branch and terminating in a B-functional branch unit is

$$\alpha_{AB} = \frac{p_A b_3}{1 - p_A p_B a_2 b_2} \tag{46}$$

The other two expressions, for chains beginning with B-functional branch, are analogues:

$$\alpha_{BB} = \frac{p_A p_B a_2 b_3}{1 - p_A p_B a_2 b_2} \tag{47}$$

$$\alpha_{BA} = \frac{p_B a_3}{1 - p_A p_B a_2 b_2} \tag{48}$$

The 3,2,1/3,2,1 model represented by these expressions was verified two ways, both theoretical. Experimental verification has not been done, but is desirable. The proofs involved the models of Stockmayer [3] and Flory [2,16,17] in the first case and of Macosko and Miller [14] in the second. In both cases, we failed to find algebraic relationships which would show direct equivalence between the two models because of the quartic equations and other similar complexities. Therefore, numerous numerical examples were generated, and consistent equivalence was demonstrated by calculation.

The following procedure was used to demonstrate that the four branching coefficients are true for the 3,2,1/3,2,1 in the critical state, incipient gelation. A large number of theoretical, critical compositions were generated using equation 3. For each case, the four critical α's were calculated using equations 45-48. These sets of coefficients were tested for their uniqueness in predicting the lower limit for the possibility of formation of an infinite molecule, as described by Flory [2,16,17] and in Section IIIB4 of this report. The following relationships were derived for this test.

Let n_i = the number of A-branches at the i-th station

m_i = the number of B-branches at the i-th station

Then,

$$n_{i+1} = 2(n_i \alpha_{AA} + m_i \alpha_{BA}) \tag{49}$$

$$m_{i+1} = 2(n_i \alpha_{AB} + m_i \alpha_{BB}) \tag{50}$$

Only at incipient gelation, do the following equalities hold

$$\ldots n_{i-1} = n_i = n_{i+1} \ldots$$

For postgel verification of the 3,2,1/3,2,1 α-model, the following relationships between the α- and P_F-models were derived using the recursive method.

$$P_{F,A} = \alpha_{AA}P^2_{F,A} + \alpha_{AB}P^2_{F,B} + 1 - \alpha_{AA} - \alpha_{AB} \tag{51}$$

$$P_{F,B} = \alpha_{BA}P^2_{F,A} + \alpha_{BB}P^2_{F,B} + 1 - \alpha_{BB} - \alpha_{BA} \tag{52}$$

Numerical consistency between equations 51 and 52 was demonstrated for a variety of theoretical compositions in randomly selected postgel states.

The fate distribution of branch units, as illustrated in Figure 3, demonstrates further the claim made in Section IIIC that the α-method yields greater detail than the P_F-method. For simple systems, both methods produced four types of branch units. (See equations 4-7 and 35-38.) The P_F-method produced eight types in the 3,2,1/3,2,1 system, as described in Section IIIC1. Now, we will show that for the same system, the α-method produces twenty different types of branch units.

Let ${}_AT = a_3/3$ = the moles of A-functional branch units per equivalent of A.

${}_BT = b_3/3$ = the moles of B-functional branch units per equivalent of B.

Let the following subscripts, placed behind the symbol T in groups of three, represent the connections of the three branches of each particular unit:

0 = not connected

A = connected to an A-branch unit

B = connected to a B-branch unit

Then, the 0-connected, A-functional branch units have the following concentration:

$$ {}_AT_0 = {}_AT_{000} = {}_AT(1-\alpha_{AA}-\alpha_{AB})^3 \qquad (53) $$

The concentration of 1-connected, A-functional branch units is

$$ {}_AT_1 = {}_AT_{00A} + {}_AT_{00B} \qquad (54) $$

where $\quad {}_AT_{00A} = 3\,{}_AT(1-\alpha_{AA}-\alpha_{AB})^2\alpha_{AA}$

and $\quad {}_AT_{00B} = 3\,{}_AT(1-\alpha_{AA}-\alpha_{AB})^2\alpha_{AB}$

The concentration of 2-connected, A-functional branch units is

$$ {}_AT_2 = {}_AT_{0AA} + {}_AT_{0BB} + {}_AT_{0AB} \qquad (55) $$

where $\quad {}_AT_{0AA} = 3\,{}_AT(1-\alpha_{AA}-\alpha_{AB})\alpha_{AA}^2$

$\quad {}_AT_{0BB} = 3\,{}_AT(1-\alpha_{AA}-\alpha_{AB})\alpha_{AB}^2$

$\quad {}_AT_{0AB} = 6\,{}_AT(1-\alpha_{AA}-\alpha_{AB})\alpha_{AA}\alpha_{AB}$

The 3-connected, A-functional branch unit concentration is

$$ {}_AT_3 = {}_AT_{AAA} + {}_AT_{AAB} + {}_AT_{ABB} + {}_AT_{BBB} \qquad (56) $$

where $${}_{A}T_{AAA} = {}_{A}T\alpha_{AA}^{3}$$

$${}_{A}T_{AAB} = 3\,{}_{A}T\alpha_{AA}^{2}\alpha_{AB}$$

$${}_{A}T_{ABB} = 3\,{}_{A}T\alpha_{AA}\alpha_{AB}^{2}$$

$${}_{A}T_{BBB} = {}_{A}T\alpha_{AB}^{3}$$

An analogous set exists for B-functional branch units.

Continuation of the development of the postgel model of the 3,2,1/3,2,1 system, following the procedure laid out in Section IIIB5, would require further distribution of these branch units between sol and gel fractions. The simple relationship (equation 10) for the branching coefficient specific to the sol fraction applies only to the simple 3,2,1/2,1 system and its subsets. We have been unable to find a corresponding set of alpha-primes for this system so far. This does not mean, however, that no further α-model characterization can be done. Combination, at this point, of the two methods will permit the calculation of the needed distributions. In place of equation 12, the following relationships could be used.

$${}_{A}T_{S} = {}_{A}T(P_{F,A})^{3} \tag{57}$$

$${}_{B}T_{S} = {}_{B}T(P_{F,B})^{3} \tag{58}$$

3. Unequal Reactivity

The problem of modeling systems in which the reactivity of like groups differs required attention early in the work because of a circumstance stated in

Section IIB. That circumstance was the necessity of using 1,3,5-pentane tricarboxylic acid in verification studies. In their gelation studies of a 3,2/2 system containing that compound, Heller, et al., [X15] found good agreement with simple theory in compositions having excess hydroxyl, but they observed a systematic deviation from simple theory when carboxyl was in excess. This apparent asymmetry was possible because these experiments were conducted so as to approach complete reaction as nearly as possible. The excess hydroxyl compositions behaved normally because essentially all carboxyls were consumed, and the effect of the less-reactive secondary carboxyls became insignificant. In Figure 13 the deviation in the excess carboxyl experiments can be seen to be dependent upon stoichiometric ratio.

This particular system was modeled by following the example of Flory [2] in a still simpler case, 3/2. The 3,2/2 model, with the algebra corrected by Flory, is described in Appendix D. (Reference X16.) The curve in Figure 13 is the best fit of the data to the relationship (Equation 13, Appendix D), yielding an

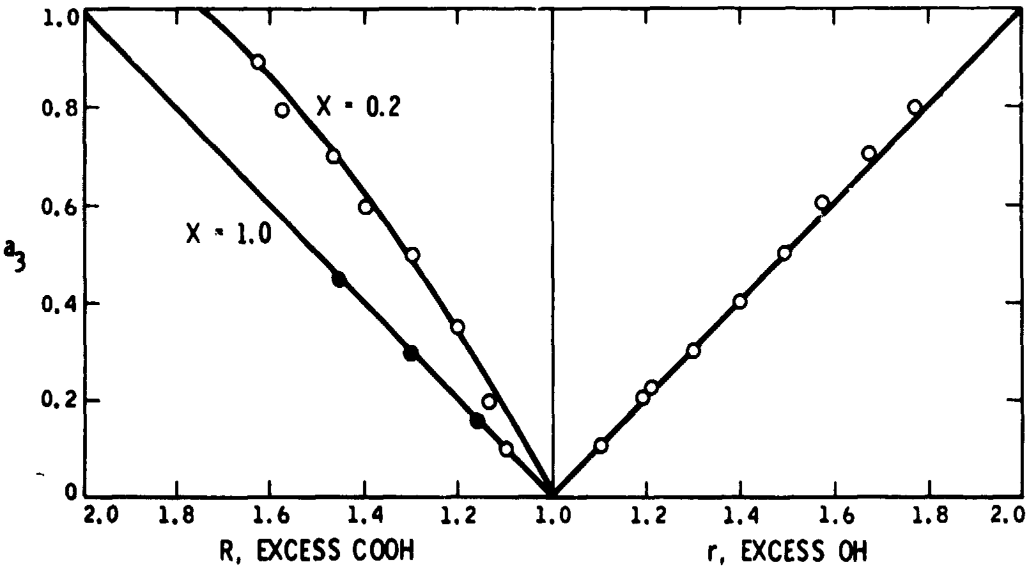


Fig. 13. Incipient gelation, theory and experiment. The symbol X, represents the ratio of reactivity of secondary to primary carboxyls. Open dots are data from a system containing 1,3,5-pentanetricarboxylic acid. The filled dots are data from the same system containing benzene-tricarboxylic acid instead.

approximate value of 0.2 for the ratio of the extents of reaction of secondary to primary carboxyl.

Flory's approach to the problem of unequal reactivity is standard in the sense that α is equal to the probability of a chain ending in a branch divided by the sum of the probabilities of all definite terminals. (See Section IIIB3) The difference is that the probabilities that a given branch unit will be chain extending (continuing) or branching are incorporated into the relationship. The experimental correlation and results of later studies, which will be described below, indicate that the relationships in Appendix D hold for incipient gelation and for at least one other singular condition, complete reaction. On the other hand, there is considerable doubt as to their applicability to postgel conditions in general.

Recently, this system (generalized to 3,2,1/2,1 by the addition of monofunctional components) was treated as a complex system in the manner described in Section IIIC2. Here again, four branching coefficients are determined for the four different situations: primary A to primary A, primary A to secondary a, secondary a to secondary a, and secondary a to primary A. A key step in this derivation is a pair of factors, f_A and f_a, which determine the relative probabilities that the reaction which attaches a branch unit to the end of the chain is with a primary A or a secondary a.

$$f_A = \frac{(a_2 + (2/3)a_3)p_A}{(a_2 + 2/3)a_3)p_A + (1/3)a_3p_a}$$

$$f_a = \frac{(1/3)a_3p_a}{(a_2 + (2/3)a_3)p_A + (1/3)a_3p_a}$$

The expressions for branching units are

$$\alpha_{AA} = \frac{p_A p_B b_2 f_A a_3}{1 - p_A p_B a_2 b_2} \tag{59}$$

$$\alpha_{Aa} = \frac{p_A p_B b_2 f_a a_3}{1 - p_A p_B a_2 b_2} \tag{60}$$

$$\alpha_{aa} = \frac{p_a p_B b_2 f_a a_3}{1 - p_A p_B a_2 b_2} \tag{61}$$

$$\alpha_{aA} = \frac{p_a p_B b_2 f_A a_3}{1 - p_A p_B a_2 b_2} \tag{62}$$

As with the 3,2,1/3,2,1 case, these four expressions were found numerically to give α's unique in providing the conditions for constant probability of continuation of a chain at incipient gelation. Further verification was obtained by the derivation, from the above relationships, of the same expression for critical stoichiometric ratio of 3,2/2 systems as Equation 13, Appendix D.

This α-model has not been studied in regard to its predictions of postgel characteristics. However, agreement with a P_F-model of the same system is to be expected, by analogy with the 3,2,1/3,2,1 model (Section IIIC2). Macosko and Miller also expanded their method to account for unequal reactivity. [27] It has not been applied to the work reported here.

IV. SOLID PROPELLANTS AND OTHER PRACTICAL PROBLEMS

The ultimate aim of research in the relationships between the structures of polymeric materials and their mechanical behavior is the development of the capability for designing *a priori* such products on the basis of measured characteristics of the components and with a minimum of formulation studies.

A semiquantitative theory, functionally stating the dependence of the stress-strain response (including rupture) on a number of binder molecular parameters, plus filler effects, for filled and unfilled elastomers is described by Landel, et al. [24, 28-32]

One characteristic, effective chain concentration, must be measured for each elastomer, [25] thus limiting complete a priori predictive capability. The network modeling techniques described in this report should, with certain limitations, help considerably to satisfy this need. One of these limitations is the inability to develop a satisfactory network model without adequate knowledge of the chemistry of curing. Workable models, however, are sometimes possible with good approximation of the chemistry. The allophanate model, discussed below, is a good example. Another limitation in the practical use of network models is the inability to predict the extent of reaction in commercial or other large scale stepwise polymerizations. On the other hand, determination of the extent of reaction actually achieved, or some other appropriate, readily determined characteristic such as sol fraction, should suffice to give a great deal of information about the final product.

Following are brief descriptions of some propellant problems for which network modeling has been applied or contemplated.

A. Solid Propellants with Very Low Moduli

Modern solid propellant rocket motors owe their high performance, to a large extent, to the fact that the propellants are rubbery enough to withstand the deformations of thermal cycling and pressurization while being bonded to the interior chamber surfaces. This form of construction is known as case-bonding. The rocket performance gain comes from the reduction in the weights of interior insulation and metal wall afforded by case bonding. [X22] In these configurations, the propellant takes over a large fraction of the insulation task. The triaxial strains on the propellant are relieved considerably by a central cavity known as the perforation.

Some early solid propellant motors were end-burners. Instead of burning from the surfaces of perforations to the chamber wall, these propellants burned from the rear face to the other end of a long, cylindrical grain. The important features of these designs were long burning time and low thrust. Performance was low in these end-burners because case-bonding had not been developed; the propellants available then were not rubbery.

Long burning times are still needed for certain applications. However, performance cannot be sacrificed. For this reason, the development of a case-bonded, end-burning rocket was undertaken at JPL. This effort resulted in satisfactory demonstration of a new technology. [X11]

The chief requirement of the propellant for high-performance case-bonded end-burner applications was a considerable reduction in modulus from generally accepted practical levels. This posed a problem because, for other purposes, we had explored compositions with reduced concentrations of cross-linking agent and found them to be too sensitive to processing variations to produce reproducible propellant mechanical properties.

This problem was solved [X19] by studying formulations with intentionally added monofunctional components. The contribution of network modeling to the solution of this problem was the prediction that the reduction of cross-link density by the addition of monofunctional components would lead to formulations less sensitive to processing variations than those obtained by direct reduction in branching component concentration. This prediction was accomplished by error analysis of equation 2.

It should be noted, however, that Landel and Fedors [25] indicate that such binders will have a decreased strain-at-break capacity (at fixed ν_e) compared to a binder without such monofunctional components.

B. The Functionality Distribution of Prepolymers

The diversity in prepolymer functionality distributions was described in Section IIB. One of the proposed uses for the false 3,2,1/3,2,1 model [X17] was the development of an analytical method, using gelation measurements, for the determination of the functionality distribution of elastomer ingredients. [X10] Hudson and Muenker [33] developed a chromatographic fractionation method which gave reasonable separation of zero-, mono-, and bifunctional components of prepolymers. Ashcraft [X9] adapted their method to thin layer chromatography and used it for qualitative screening of prepolymer synthesis products. Strecker and French [4] used gelation in a method of analysis for functionality-weighted-average functionality. Oberth [34] claims that number-average functionality provides a better prediction of mechanical behavior and describes a gelation method for determining it.

The question is, do the distributions of functionalities in prepolymers affect the mechanical behavior of elastomers made from them? According to the verified models described in this report, there is no effect on the gel point. Gelation is sensitive only to the functionality-weighted-average functionality regardless of the distribution. A corollary to this fact is, functionality distribution cannot be determined by gelation measurements.

The postgel state is different. One pronounced effect can be illustrated by a simple calculation. That effect is the limitation in the curing potential produced by monofunctional components. For example, the weighted-average functionality of the following A-functional mixtures is the same.

Mixture	a_1	a_2	a_3
X	0	0.4	0.6
Y	0.1	0.2	0.7

However, the cross-link density (calculated by equations 2 and 21 of this report) of the X mixture, when cured with a bifunctional B component, is over one-third higher than that of the Y mixture at any equivalent stoichiometric ratio, r, and extent of reaction, p_A, including one. Differences in effective chain length are calculated also, but they are smaller. In Appendix A, other differences are shown.

Clearly, the investigation of functionality distribution would be useful to propellant development. Such investigation should include both analysis methodology and mechanical behavior effects. Network modeling should contribute to both areas.

C. Urethane-Cured Systems

The main features of the problem of modeling urethane propellant binders are described in Section IIB. Appendix E, reference X25, describes the model for urethane cures which accounts for the simultaneous extra consumption of isocyanate groups and extra cross-link generation by allophanate formation. Correlation of cross-link density calculated from the model with tensile modulus of polyether-urethane propellants is shown in Figure 14. The model calculations made to produce this graph assumed that the cure reaction was complete (all isocyanate was consumed) because reliable measurement of extent of reaction was not possible.

The good fit of the data in Figure 14 may be fortuitous considering the assumption that was just mentioned. This model has, however, an even greater deficiency; the multi-α approach for complex systems had not been developed at

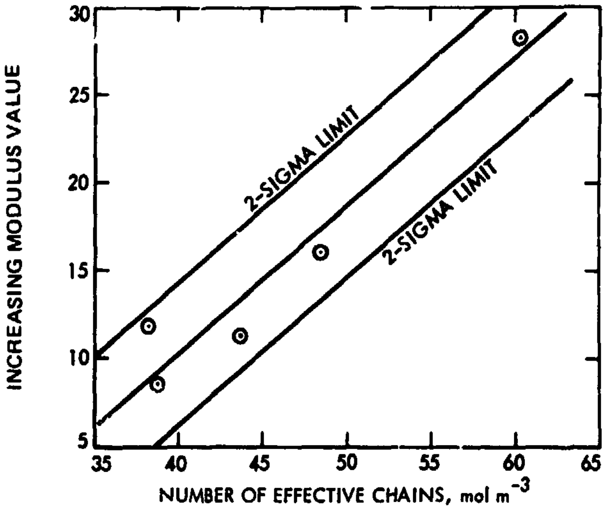


Fig. 14. Solid propellant tensile data correlate with a network model which accounts for allophanate cross-linking. Propellant binder was urethane-cured; prepolymer was hydroxyl-terminated poly (propylene oxide).

that time. How deficient this model is for practical use, cannot be assessed without further investigation. At least one large element of such study would be an attempt to apply tne principles of complex system modeling. (Section III.C.)

In Section II.B, failure of the allophanate model to correlate tensile properties of urethane-cured hydrocarbon systems was mentioned. A few exceptions were encountered, however. These are shown in Figure 15. The fact that these propellants were all made with samples of saturated, telechelic prepolymers from the Union Carbide research program [X23] instead of the unsaturated polydienes used in the other studies is a clue to one way to approach this problem. New modeling efforts for urethane-diene propellants should include the possibility that additional cross-linking is generated by reactions of carbon-carbon double

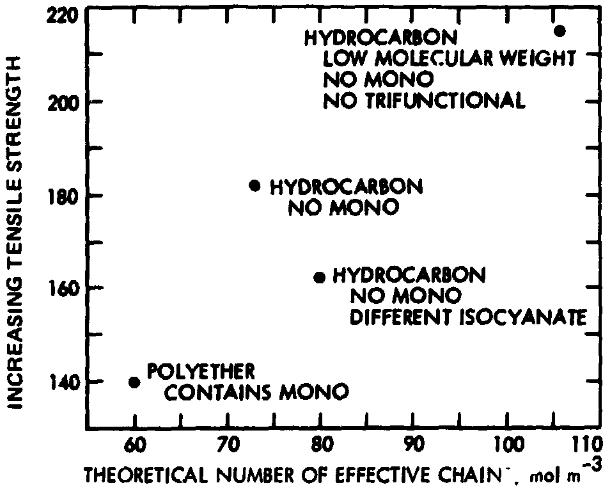


Fig. 15. Solid propellant tensile data. Hydrocarbon prepolymers were hydroxyl-terminated, saturated polyisoprene.

bonds. Other reactions under consideration also are isocyanate trimer formation and the reaction of postallophanate active hydrogens with isocyanate.

D. Sophisticated Comparison of Prepolymers

Results like those shown in Figure 15 are unusual. Each of the hydrocarbon prepolymer samples was so small that only one small propellant batch could be made from it. Not only did they all cure, which is the first concern with new materials, but they cured to properties which related in a reasonable way with those of the well established polyether propellant. The usual experience with new prepolymers is a significant change (from past propellants) in the property-formulation relationships, and such relationships are usually obtained only after considerable exploratory work aimed at bringing the best out of the new material.

Usually, the propellant chemist is in a poor position to analyze the causes of differences between propellants made from different prepolymers. The work described in this report offers new tools that can be applied to this problem.

An ideal program for comparing prepolymers would be one in which propellants would be made on a common basis, such as equal cross-link density, for example. Such an arrangement would allow better identification and intepretation of the effects (both practical and theoretical) of prepolymer characteristics. The sample calculations in Appendix A are a good example of the kind of prepolymer comparison anticipated here.

E. Propellant Aging Studies

An understanding of the mechanisms of changes that take place during the aging of solid propellants can lead to the development of more durable compositions. Network changes are of key interest. Layton [35] and Raisor [36] have taken significant steps in this direction. It is expected that network modeling could contribute considerably to the development of significant results from this type of investigation.

V. CONCLUSIONS

The major objective of this research program, which was to develop methods for modeling the formation of polymeric network structures applicable to the formulation and characterization of composite solid propellants, is almost completely achieved. The chief obstacle to reaching this objective has been eliminated by the development of a generalized approach to modeling based on Flory's [2] branching coefficient (α). and by the introduction by Macosko and Miller [14] of an approach based on a different parameter, the "finite chain coefficient" (P_F). In this report, these approaches are identified as α-method and P_F-method.

Difficulty in model derivation relates to system complexity. Simple systems are those with only one kind of branching component (f,2,1/2,1 in which f = 3,4,5 ..., or n). Mixed functionalities (f,2,1/f,2,1; f,2,1/g,2,1; f,g,2,1/2,1; etc.)

cause systems to be complex. Complexity is caused also by unequal reactivity and by side reactions.

Difficulties are encountered with each method as complexity increases. For example, a way to calculate sol fractions of the several types of branch unit (in complex systems), a necessary step in the α-method, has not been found yet. On the other hand, in the P_F-method, the number and degree of the polynomials for calculating P_F's increase. In future work, it is expected that combining the two methods will provide better efficiency.

In terms of the classification (simple and complex) of systems, the following list of specific achievements is given:

A. Simple Systems

1) The parameters, α and P_F, are related by a simple algebraic expression.

2) The two methods agree with respect to sol fraction and concentration of effective chains.

3) Model predictions of incipient gelation, postgel sol fraction and effective chain concentration in 3,2,1/2,1 systems have been verified experimentally.

4) α-Model predictions of effective chain length correlate with extensibility.

B. Complex Systems

1) A special α-Model for a 3,2/2 system in which one group of the trifunctional ingredient was less reactive than all other like groups was verified experimentally at the incipient gelation state.

2) The generalized α-method yielded a model for the unequally reactive 3,2/2 system which agrees with the earlier one (see B1 above).

3) For the 3,2,1/3,2,1 systems, the generalized α-method yielded a model which agrees with Stockmayer's expression for incipient gelation.

4) The model cited in B3 was found compatible with the P_F-Model for the same system in a pair of expressions relating α's and P_F's for the postgel state.

5) A crude model for urethane-cured polyether solid propellants accounted for the side reaction, allophanate formation, sufficiently well to give good correlations of cross-link density with tensile strength and tensile modulus.

Continued work with network modeling is identified in two categories, theoretical and applications. The chief theoretical investigations are: further study of relationships for describing network chain type and length distributions, first for simple systems and second for complex systems; a broader range of verification experiments; a direct measurement for effective chain length; incorporation of network models into a scheme developed by others [25] for prediction of mechanical properties of solid propellants, and other elastomers, *a priori* from molecular parameters. Several applications for network modeling are described in Section 4.

DEFINITION OF SYMBOLS

Symbol	Definition	Text Page
Numerals		
3,2,1/2,1, etc.	A symbolic representation of A-with-B reacting systems in which the numerals before and after the slash identify the functionalities present of A and B molecules respectively. Three represents trifunctional; 2 is bifunctional; etc.	12, 19
i = 0, 1, 2, or 3 in i-connected	Describes the fate of a branch unit in terms of how many, i, of its branches are connected to other branch units.	14
n = 0, 1, 2, ..., ∞ in n-order	Indicates an order in a hierarchy in which n-order, 3-connected branch units acquire lower-order branch units as elements in their branches.	15
Capitals		
A	Symbol representing a functional group on a molecule that reacts with a B to form a chemical bond between them.	12
A	In the unequal reactivity case, a primary A (more reactive).	50
B	Same as A, above.	12
L_n (for n = 1, 2, 3, ..., n)	The length, in chain atoms, of a half chain that is n-order in the hierarchy.	35

DEFINITION OF SYMBOLS (Continued)

Symbol	Definition	Text Page
L_x	A parameter representing effective chain length, in chain atoms.	35
$P(Br_A{}^{in})$	The probability that one of the other branches of a molecule bearing a particular A-branch will lead to a branch unit.	44
$P(Br_A{}^{out})$	Equivalent to α. The probability that a particular A-branch will react and lead ultimately and exclusively to a branch unit.	43
$P(Br_B{}^{in})$	The same as A, above.	44
$P(Br_B{}^{out})$	The same as A, above.	44
P_F	An abbreviation for $P(F_A{}^{out})$ in 3,2,1/2,1 systems; see below.	40
$P_{F,A}$	An abbreviation for $P(F_A{}^{out})$ in 3,2,1/3,2,1 systems; see below.	45
$P_{F,B}$	An abbreviation for $P(F_A{}^{out})$ in 3,2,1/3,2,1 systems; see below.	45
$P(F_A{}^{in})$	The probability that the other branches of a molecule bearing a particular A-branch lead exclusively to finite ends.	41
$P(F_A{}^{out})$	The probability that a particular A-branch leads exclusively to a finite end or ends.	40
$P(F_B{}^{in})$	The same as A, above.	41
$P(F_B{}^{out})$	The same as A, above.	41

DEFINITION OF SYMBOLS (Continued)

Symbol	Definition	Text Page
T	The concentration of trifunctional molecules, reacted or not, in a 3,2,1/2,1 system, in moles per equivalent of A.	29
T_i (for $i = 0, 1, 2,$ or 3)	The concentration of i-connected branch units, in moles per equivalent of A.	29
T_s	The concentration, in the whole mixture, of branch units distributed to the sol fraction, in moles per equivalent of A.	29
T_g	G loss transition temperature	37
T_m	Melt temperature	37
T_x	The concentration, in the whole mixture, of branch units that are cross-links, cross-links in moles per equivalent of A.	28, 31
$T_{F,i}$ (for $i = 0, 1, 2,$ or 3)	The concentration of those branch units that have i branches leading to finite chains in moles per equivalent of A.	42
$T_{G,i}$ (for $i = 1, 2,$ or 3)	The concentration, in moles per equivalent of A, of those branch units that are in the gel fraction and that have i connections with other branch units.	31
$T_{s,i}$ (for $i = 0, 1, 2,$ or 3)	The concentration, in moles per equivalent of A, of those branch units that are in the sol fraction and that have i connections with other branch units.	29

DEFINITION OF SYMBOLS (Continued)

Symbol	Definition	Text Page
$(T)_n$	The concentration, in moles per equivalent of A, of those branch units that function as branch units at the order n in the hierarchy.	34
$(T_i)_n$	The concentration, in moles per equivalent of A, of those branch units that are i-connected at the order n in the hierarchy.	33
$(T_{G,i})_n$	The concentration, in moles per equivalent of A, of those branch units that are in the gel fraction and are i-connected at the order n in the hierarchy.	32
${}_AT$	The concentration of A-functional branch units in a 3,2,1/3,2,1 system, in moles per equivalent of A.	48
${}_BT$	The same as A, above.	48
${}_AT_i$ (for $i = 0, 1, 2,$ or 3)	The concentration, in moles per equivalent of A, of A-functional branch units that are connected, through any lengths of chains, to i other branch units.	49
${}_AT_S$	Equivalent to T_S for A-functional branch units in 3,2,1/3,2,1 systems.	50
${}_BT_S$	The same as for A, above.	50

DEFINITION OF SYMBOLS (Continued)

Symbol	Definition	Text Page
A^{T}_{XXX} (for X = 0, A or B)	The concentrations, in moles per equivalent of A, of A-functional branch units in 3,2,1/3,2,1 systems according to their ten possible fates in terms of the states of their three branches: 0 signifies not connected; A or B signifies connection to A or B branch units.	49
Lower Case Letters		
a	In the unequal reactivity case, a secondary A (less reactive).	52
a_i (for i = 0, 1, 2, 3, ...)	The fraction of A-functional groups contributed by i-functional A molecules.	21
b_i (for i = 0, 1, 2, 3, 4, ...)	The fraction of B-functional groups contributed by i-functional B molecules.	21
f (for f = 3, 4, ...)	The functionality of branch units in simple systems. It applies only to determining critical gelation conditions.	26
f_A	In the unequal reactivity case, the fraction of reacted A groups that are primary (more reactive).	52
f_a	In the unequal reactivity case, the fraction of reacted A groups that are secondary (less reactive).	52

DEFINITION OF SYMBOLS (Continued)

Symbol	Definition	Text Page
$f_{f,A}$	The functionality-weighted average functionality of all A-functional molecules in a mixture.	27
$f_{f,B}$	The same as for A, above.	27
i	(See Numeral list.)	14
m_i	The number of B-branches at the i-th station in a sequence of stations emanating from a point in a network.	47
n	(See Numerical list.)	15
n_i	Same for A-branches in m_i, above.	47
p_A	The fraction of A-functional groups reacted.	21
p_B	The fraction of B-functional groups reacted.	21
r	The ratio of B-functional groups to A-functional groups in a mixture.	21
w_S	The weight fraction of sol.	30
X_n	Chain extension coefficient. At order n in the hierarchy, the average number of n-order bifunctional branch units per n-order half-chain.	32

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DEFINITION OF SYMBOLS (Continued)

Symbol	Definition	Text Page
Greek Letters		
α	Branching coefficient. The probability "that any given one of the functional groups of a branch unit leads, via a sequence of bifunctional units, to another branch rather than to a terminal group" (Flory [2]).	22, 24
α'	α calculated for the sol fraction alone.	29
α_c	The critical value of α at which gelatin theoretically will begin.	27
α_n	α calculated for functioning branch units at order n in the hierarchy.	33
α_{AA}	The probability that one of the branches of an A-functional branch unit connects to another A-functional branch unit. In 3,2,1/3,2,1 systems.	46
	In unequal reactivity systems.	53
α_{AB}	A to B; same as above.	46
α_{BA}	B to A; same as above.	46, 7
α_{BB}	B to B; same as above.	46
α_{Aa}	A to a; same as above.	53
α_{aA}	a to A; same as above.	53
α_{aa}	a to a; same as above.	53

DEFINITION OF SYMBOLS (Continued)

Symbol	Definition	Text Page
$(\lambda_b)_{max}$	The maximum extension to break in a cross-linked polymer.	36
ν_e	The concentration of effective chains, in moles per unit volume.	28, 31

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APPENDIX A

A SAMPLE CALCULATION OF THE NETWORK CHARACTERISTICS OF TWO SIMPLE COMPOSITIONS

This appendix has two purposes. The use of α-model relationships for calculating network characteristics in a practical type of problem will be illustrated. Some effects of prepolymer functionality distribution variations will be shown.

1. A Problem Example

Suppose one has two prepolymers to compare. These prepolymers have many similarities and one principal difference, functionality distribution. How would the network structures of elastomers made from them compare under a given set of identical conditions?

Actually, this problem was put together by doing part of it in reverse so as to synthesize a particular set of identical conditions. However, this presentation will proceed as though the two systems were being characterized in parallel. The following specific parameters were selected as reasonable to be set identical in studies where the basic characteristics of components and reaction are known in advance: equivalent weight (the moles of functional group per gram of prepolymer), extent of reaction, and effective chain concentration (cross-link density) in the cured elastomers. A few other assumptions will be identified at appropriate places. These were made chiefly to reduce the complexity of this example.

2. The Prepolymers

The following things are assumed to be the same for both prepolymers:

1) Chain backbone is 1,4-polyisoprene

2) The prepolymer represents all of the A-components in the recipe.

3) All A-functional groups are equally reactive.

4) Equivalent weights are the same for all A-functional components (mono-, bi-, and trifunctional)

$$E_A = E_{A,1} = E_{A,2} = E_{A,3} = 1000 \frac{g}{\text{mol A}} \tag{1}$$

The assumed functionality distribution of the two prepolymers are listed in Table 1.

Table 1. Prepolymer Functionality Distributions

Symbol	Definition	Prepolymer I	Prepolymer II
T	Mole fraction of trifunctional component	0.25	0.01262
D	Mole fraction of bifunctional component	0.25	0.9874
M	Mole fraction of monofunctional component	0.50	0

Other differences derive from the above differences. They are: molecular weight (MW), number-average functionality (f_n), and functionality-weighted-average functionality (f_f). The last two are calculated by the following relationship:

$$f_n = \frac{3T + 2D + M}{T + D + M} \tag{2}$$

$$f_f = \frac{9T + 4D + M}{3T + 2D + M} \tag{3}$$

Table 2. Other Prepolymer Differences

	Prepolymer I	Prepolymer II
MW	1750	2013
f_n	1.75	2.013
f_f	2.143	2.019

At first glance, one might assume that prepolymer I would not be suitable for formulating cross-linked 3,2,1/2,1 products because f_n is less than 2. The verified models of this report all agree, however, that it does have sufficient functionality. This assessment is clear in terms of Stockmayer's model (equation 3 in the report), which shows that f_f is the important criterion. As long as the product, $(f_{f,A}-1)(f_{f,B}-1)$, is greater than 1, gelation is possible.

3. The Curing Agent

The curing agent is assumed to be 100% bifunctional in B and to have an equivalent weight ($E_B = E_{B,2}$) of 500. Since there is no monofunctional B-component, System I is 3,2,1/2, and System II is 3,2/2. Both are subsets of 3,2,1/2,1.

4. Overall Polymerizing Composition

It is assumed that the two compositions are made with a stoichiometric ratio equal to unity. The compositional parameters used in modeling (as listed in Section IIIB1 of this report) are calculated as follows:

$$a_3 = \frac{3T}{3T + 2D + M} \tag{4}$$

$$a_2 = \frac{2D}{3T + 2D + M} \tag{5}$$

$$a_1 = \frac{M}{3T + 2D + M} \tag{6}$$

and so forth.

A practical problem identified in Section IVI of the report is illustrated in Table 3. In solid propellant batch processing, critical ingredient concentrations as low as $a_{3,II}$ are very hard to hold in satisfactory relative accuracy.

Table 3. Compositions

	Composition I	Composition II
r	1.0	1.0
a_3	0.4286	0.01882
a_2	0.2857	0.9812
a_1	0.2857	0
b_2	1.0	1.0
b_1	0	0

5. The Reaction

The simple reaction of A with B to form chemical bonds, with no side reactions and no elimination products, is assumed. Since

$$r = 1 \quad , \quad p_A = p_B = p \quad .$$

6. Synthesized Characterization Study

Here, it is assumed that the experiment was conducted in the following manner:

1) The two recipies, I and II described above, were mixed and cured in a reproducible manner.
2) After cure, the sol fractions were extracted and measured.
3) All of the other characteristics were calculated from these results. In turn these are:

w_G	gel fraction
α	branching coefficient
p	extent of reaction
ν_e	effective chain concentration

$L_{n,G}$	half-chain lengths in the gel
L_x	effective chain length
$P_{n/x}$	numbers of n-order pendent chains per effective chain
PL_n	length of n-order pendent chains

In the practical sense, this type of experiment is one in which random variation is evident in all measurements. For example, the mechanical properties of solid propellants vary (over 10%) from batch to batch under conditions of careful recipe and process control. Simple functional group analysis of prepolymers is not a great deal better. Certainly, functional group analysis of cured elastomers would be more difficult. This is the reason we chose to fractionate sol from gel to determine extent of reaction in our model verification studies. (See Figure 8 in the report.)

7. Extent of Reaction from Sol-Gel Fractionation

In the following calculations, values of w_s (sol fraction) were assumed to have been measured. The other parameters were calculated by the following relationships.

$$\alpha = \frac{1}{1 + w_s^{1/3}} \tag{7}$$

This equation is a rearrangement of equation 12 in the report.

$$p = \left(\frac{1}{a_3/\alpha + a_2}\right)^{1/2} \tag{8}$$

Equation 8 is a rearrangement of equation 2 of the report, embodying the assumptions that $p_A = p_B$ and $b_2 = 1$. The results are listed in Table 4.

Table 4. Postgel State

	Composition	
	I	II
w_S	0.3000	0.0002500
w_G	0.7000	0.9997
α	0.5990	0.9407
p	0.9994	0.9994

8. Cross-link Density

Cross-link density and effective chain concentration are usually expressed on a volume basis, often in the units, moles/m^3. The dimensions of these parameters in equations 21 and 22 of this report are moles/equivalent of A. Full details of the calculation of the necessary conversion factor are described in reference X28. Because of assumptions in this problem (no zero-functional components, no elimination product, specific gravity = 1, r = 1, and all E_A's = 1000), the conversion factor reduces simply to $10^6/1500 = 2/3 \times 10^3$ equivalents of A/m^3 for both I and II systems.

The calculation of T_x from equation 21 of the report entails first the solution of most of the equations in the sets numbered 4-7 and 13-20. The result of doing this algebraically is simpler.

$$T_x = \frac{a_3}{3}\left(\frac{2\alpha - 1}{\alpha}\right)^3 \qquad (9)$$

$$\nu_e = (2/3) \times 10^3 \times (3/2)T_x = 10^3 T_x \qquad (10)$$

Equation 9, like most of the relationships in this appendix, is specifically applicable to 3,2,1/2,1 systems.

Table 5. Cross-Link Density Effective Chain Concentration

Symbol	Dimensions	Composition I	Composition II
T_x	moles/equivalent of A	0.005160	0.005160
ν_e	moles/m^3	5.160	5.160

9. Parameters for Chain Calculations

The basic nature of the relationships needed to calculate chain sizes and distributions, as so far developed, are given in Section III of the report. The relationships will be considered here in greater detail as applicable to this problem. Some of this detail includes mathematical short cuts specific to 3,2,1/2,1 systems.

The two sets of parameters needed, in equation 26 of the report, to calculate half-chain lengths are sufficient for all other chain characteristics. The set, $x_1, x_2, x_3, \ldots, x_n$, are the chain extension coefficients illustrated in Figure 5; L_o is the average length of 0-order half-chains in the gel fraction.

L_o is determined by dividing the mass of the gel by the number of 0-order half-chains in the gel and multiplying this quotient by the specific length of the chain material.

$$L_o = \frac{w_G W L_{sp}}{HC_G} \tag{11}$$

where

w_G = gel fraction (see Table 4).

W = grams of polymer per equivalent of A. In the previous section, W was found to be 1500 for both systems.

L_{sp} = the number of chain atoms per gram. Extention of assumption 1 of Section 2 to the cured polymer allows the use of the specific chain length of 1,4-polyisoprene, 4/68 = 1/17.

HC_G is calculated as follows: In the gel fraction, there are (referring to the report, Figure 3 and equations 18-20) $T_{G,1}$, $T_{G,2}$, and $T_{G,3}$ moles per mole of A, respectively, of 1-connected, 2-connected, and 3-connected branch units. Each one has 3 0-order half-chains. For every 2-connected unit, an additional half-chain is contributed by the terminating group. Likewise, two extra half-chains are contributed by the two terminals in each 1-connected unit. Algebraically, the result is

$$HC_G = 3T_{G,3} + 4T_{G,2} + 5T_{G,1} \qquad (12)$$

For the 3,2,1/2,1 case this calculation can be simplified greatly by algebraic substitution.

$$HC_G = \frac{a_3(2\alpha - 1)}{\alpha^3} \qquad (13)$$

Table 6. Gel Half-Chains

		Composition	
Symbol	Dimensions	I	II
HC_G	Moles of half-chain per equivalent of A	0.3948	0.01992
L_0	Chain atoms per 0-order HC	156.4	4427

The calculation of x_n's is indicated in the report by equation 23. The tedium of this calculation is greatly reduced by algebraic substitution of appropriate relationships implied in Section IIIB5e (e.g., $(T_{G,3})_n = (T_3)_n - (T_{S,3})_n$ (20), $(T_3)_n = (T)_n\,\alpha_n^3$ (7), $(T)_n = (T_3)_{n-1}$ (25), etc.) and by the parameter,

$R_n = (1-\alpha_n)/\alpha_n$, specific to 3,2,1/2,1 systems and subsets. The resulting procedure is as follows:

Starting with $R_1 = \frac{1 - \alpha}{\alpha}$, (14)

Cycle (for n = 1,2,3,...)

$$x_n = \frac{1}{R_n + \frac{1}{R_n}}^{*} \quad (15)$$

$$R_{n+1} = x_n^2 \quad (16)$$

until x_n becomes insignificant.

The results for the two systems are as follows:

Table 7. Chain Extension Coefficients

Composition	I		II	
n	R_n	x_n	R_n	x_n
1	6.694×10^{-1}	4.623×10^{-1}	6.300×10^{-2}	6.275×10^{-2}
2	4.481×10^{-1}	3.732×10^{-1}	3.969×10^{-3}	3.969×10^{-3}
3	2.008×10^{-1}	1.930×10^{-1}	1.575×10^{-5}	1.575×10^{-5}
4	4.033×10^{-2}	4.027×10^{-2}	2.481×10^{-10}	2.481×10^{-10}
5	1.627×10^{-3}	1.626×10^{-3}		
6	2.646×10^{-6}	2.646×10^{-6}		
7	7.003×10^{-12}	7.003×10^{-12}		

---

[*] Notice that a more conventional expression for x_n would be:

$$R_n/(R_n^2 + 1) .$$

The form in equation 15 is convenient to use with hand calculators.

10. Chain Lengths

As was pointed out in Section III of the report, the relationships for calculating lengths and relative frequencies of various network chains require more study. However, as these relationships now stand, they present a reasonable picture of network structure in terms of relative trends. Thus, the characteristics calculated from this point on in the present examples should be viewed in the light of this caveat.

Using the values from Tables 6 and 7, the average lengths of half chains in the gel according to order were calculated as follows:

$$L_0 = L_0$$

$$L_1 = L_0(1 + 2x_1)$$

$$L_2 = L_1(1 + 2x_2)$$

- - - - - - - - - - -

$$L_n = L_{n-1}(1 + 2x_n) \qquad (17)$$

Table 8. Average Gel Half-Chain Lengths

	Composition	
Order	I	II
0	156.4	4427
1	301.1	4983
2	525.8	5023
3	728.7	5023
4	787.4	5023
5	790.0	
6	790.0	
7	790.0	

11. The Parameter Representing Effective Chain Length

The parameter L_x was calculated by using the data from Table 8 in equation 27 of the report.

Table 9. Effective Chain Length Parameter

Composition	I	II
L_x	1580	10045

12. Some Pendent Chain Distributions

This section will deal only with a set of pendent chains which will be called primary, because they originate in effective chains. It must be recognized, however, that primary pendent chains are not merely linear chains of varying lengths dangling from effective chains. Figure 5 in the report illustrates a more realistic situation, which is analogous to the old rhyme about fleas with littler fleas.

As a first assumption, it seems reasonable that an effective chain would have the same number of n-order pendent chains as it has n-order 2-connected branch units. Thus, on an effective chain composed of two n-order half-chains, there would be:

$$P_{n/x} = 2x_n \text{ n-order pendent chains}$$

$$P_{(n-1)/x} = 2x_{n-1}(1 + 2x_n) \text{ (n-1)-order pendent chains}$$

$$P_{(n-2)/x} = 2x_{n-2}(1 + 2x_{n-1})(1 + 2x_n) \text{ (n-2)-order pendent chains}$$

$$- -$$

$$P_{1/x} = 2x_1(1 + 2x_2)(1 + 2x_3) \ldots (1 + 2x_{n-1})(1 + 2x_n) \text{ 1-order pendent chains.} \qquad (18)$$

Analysis of Figure 5 of the report shows that a 1-order pendent chain is composed of two 0-order half-chains and that the remaining n-order pendent chains are composed of two (n-1)-order half-chains plus a (n-1)-order pendent chain. Thus,

$$(PL)_1 = 2L_0$$

$$(PL)_2 = 2L_1 + (PL)_1 \qquad (19)$$

etc.

The results of applying equations 18 and 19 to compositions I and II are as follows:

Table 10. Distribution of Pendent Chains on Effective Chains

Composition	I		II	
n	$P_{n/x}$	$(PL)_n$	$P_{n/x}$	$(PL)_n$
1	2.426	312.8	0.1261	8854
2	1.121	914.8	0.007938	18820
3	0.4184	1966	0.0000315	28860
4	0.0808	3423	4.962×10^{-10}	38900
5	0.003252	4998		
6	0.000005292	6578		
7	1.401×10^{-11}	8157		
Total	4.049		0.1341	

12. Conclusions

This sample calculation illustrates on a theoretical basis a very important fact of life in the formulating of addition-polymerizing cross-linked elastomers. Whenever any factor exists (in this case, it was the presence of a monofunctional ingredient), which tends to cause the formation of pendent chains, a less efficient network structure results. Material that is tied up in pendent chains is not available for the production of length in effective chains. Based on the findings of the work described in this report, one would expect composition I to be considerably less extensible then II, even though the equilibrium moduli would be expected to be nearly the same. Such differences have been observed qualitatively in solid propellant work.

APPENDIX B (Reference X17)

The average branching coefficient (α in equation 7) is wrong. See Appendix C for explanation.

POLYMER PREPRINTS 12(1) 3//1

GELATION STUDIES II: Complex Trifunctional Systems

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Introduction

In 1941, Flory[1] introduced a model for gelation based entirely on probabalistic reasoning. A key feature of this model is the gel point or incipient gelation boundary, which is the critical condition, defined by the relative concentrations of mutually reactive polyfunctional compounds in a mixture and the varying extent of reaction of their reactive groups, at which an infinitesimal amount of infinite three-dimensional network forms. Flory and many others found that the theoretical gel point corresponds closely to experimental conditions at which polymerizing mixtures change from being viscous liquids to weak, rubbery solids. Flory's model is of such a nature that it is necessary to derive a specific relationship for each case, depending upon the number of functionalities present in the two complimentary reactive classes, such as 3/2, 3,2/2, 3,2,1/2, 3,2/2,1, etc. It is true, however, as this paper will show, that the simpler cases are easily obtained by reducing a more complex case that includes them (e.g., all the above from 3,2,1/3,2,1).

Reasoning from a general model, Stockmayer[2] developed a simple relationship between the essential parameters for the gel point useful for all cases, n,n-1 n-2,...,1/m,m-1,m-2,...,1.

Since it can be readily shown that Stockmayer's relationship agrees with those based on Flory's model for simple systems, it has been generally assumed that the Stockmayer equation is general, and therefore universal. As a consequence of this apparent universality, and because of its simplicity, Stockmayer's relationship has been adopted by many workers in the calculation of gelation criteria in polycondensation systems.

We have found that there is a degree of complexity beyond which the agreement between the two models no longer holds. That is when the system has trifunctional branching units in both of the two complimentary reactive group subsets. Furthermore, with careful experimentation designed to eliminate ambiguous factors (as described in the preceding paper)[3], we have shown the Flory model to be the more universal of the two.

Besides illustrating the above claims, this paper will also demonstrate a subsidiary point, the effect of monofunctional ingredients.

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OF POOR QUALITY

The General Trifunctional Case

Excluding unequal reactivity, side reactions, and intramolecular reaction, the general case for systems containing trifunctional branching units (3,2,1/3, 2,1) consists of six units, a tri-, di-, and mono-functional unit in each of the two complementary reactive group subsets:

$$A{-}\overset{A}{\overset{|}{-}}{-}A \qquad B{-}\overset{B}{\overset{|}{-}}{-}B$$

$$A{-}{-}{-}A \qquad B{-}{-}{-}B$$

$$-{-}{-}A \qquad -{-}{-}{-}B$$

The parameters used by Flory[1] and in I[3] are also used here, and are added to.

Let $r = 1/R = \Sigma B / \Sigma A$ = the ratio of all B's to all A's.

By material balance,

$P_B = P_A/r$ = the fraction of all B's that have reacted,

and $P_A = P_B/R$ = the fraction of all A's that have reacted.

Let ρ_A = the fraction of A's contributed by the trifunctional unit functional in A.

σ_A = the fraction of A's contributed by the difunctional unit functional in A.

μ_A = the fraction of A's contributed by the monofunctional unit functional in A.

$$\rho_A + \sigma_A + \mu_A = 1$$

The parameters, ρ_B, σ, and μ_B, are defined in the same way for units functional in B.

<u>Stockmayer's Relationship</u>

The useful equation developed by Stockmayer[2] represents the relationship between functionalities, relative concentrations, and exctents of reaction only at the critical or gel point. It is usually represented as,

$$P_A P_B = \frac{1}{(f_A - 1)\ (f_B - 1)} \tag{1}$$

where f_A and f_B are weighted average functionalities,

$$f_A = \frac{\Sigma\, f_i^2 A_i}{\Sigma\, f_i A_i} \quad \text{and}$$

$$f_B = \frac{\Sigma\, f_i^2 B_i}{\Sigma\, f_i B_i}$$

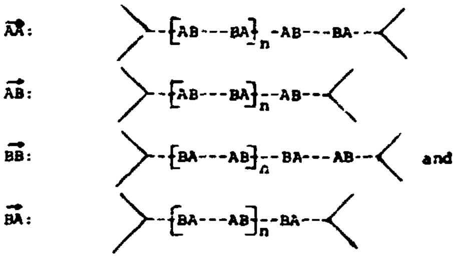
In terms of the parameters defined above for the general 3,2,1/3,2,1 system, equation (1) becomes

$$r_c = (2\rho_A + \sigma_A)\ (2\rho_B + \sigma_B) \tag{2}$$

when the reactive group not in excess has fully reacted, $P_A = 1$ in this case.

Flory's Model Applied to the 3,2,1/3,2,1 System

As defined by Flory[1], the branching coefficient, α, is the probability that "any given one of the functional groups of a branch unit leads, via a sequence of bifunctional units, to another branch rather than to a terminal group." In this general system, there are four different ways this can occur:



The probability product for each of these ways not only begins with a term for the probability that the chosen functional group has reacted (P_A or P_B), as is the case with the simpler systems[1,3] but also with a term for the probability, $\rho_A/(\rho_A + r\rho_B)$, that it is an A that is chosen, or that it is a B, $r\rho_B/(\rho_A + r\rho_B)$. The probability for all $\overrightarrow{AA}$'s is the sum of the probabilities of all possible lengths of chain, $n = 0, 1, 2, \ldots, \infty$:

$$\alpha_{AA} = \sum_{n=0}^{\infty} \frac{\rho_A (P_A P_B \sigma_A \sigma_B)^n P_A P_B \sigma_B \rho_A}{\rho_A + r\rho_B}$$

$$= \frac{P_A P_B \sigma_B \rho_A^2}{(\rho_A + r\rho_B)(1 - P_A P_B \sigma_A \sigma_B)} \qquad (3)$$

Correspondingly, the probabilities of all possible $\overrightarrow{AB}$'s, $\overrightarrow{BB}$'s, and $\overrightarrow{BA}$'s are:

$$\alpha_{AB} = \sum_{n=0}^{\infty} \frac{\rho_A (P_A P_B \sigma_A \sigma_B)^n P_A \rho_B}{\rho_A + r\rho_B}$$

$$= \frac{P_A \rho_A \rho_B}{(\rho_A + r\rho_B)(1 - P_A P_B \sigma_A \sigma_B)} \qquad (4)$$

$$\alpha_{BB} = \frac{r P_A P_B \sigma_A \rho_B^2}{(\rho_A + r\rho_B)(1 - P_A P_B \sigma_A \sigma_B)} \qquad (5)$$

and

$$\alpha_{BA} = \frac{r P_B \rho_A \rho_B}{(\rho_A + r\rho_B)(1 - P_A P_B \sigma_A \sigma_B)} \qquad (6)$$

The probability for the general 3,2,1/3,2,1 system, then, is the sum of the probabilities of the four different ways to meet the conditions of the definition:

$$\alpha = \frac{P_A P_B \sigma_B \rho_A^2 + r P_A P_B \sigma_A \rho_B^2 + P_A \rho_A \rho_B + r P_B \rho_A \rho_B}{(\rho_A + r\rho_B)(1 - P_A P_B \sigma_A \sigma_B)} \qquad (7)$$

It is convenient to use r or R according to whichever is greater than one. Thus, equation (7) represents the condition, $\Sigma B > \Sigma A$, and $P_B < P_A$. P_B can be eliminated by the substitution of P_A/r for it,

$$\alpha = \frac{P_A^2\sigma_B\rho_A^2 + rP_A^2\sigma_A\rho_B^2 + 2rP_A\rho_A\rho_B}{(\rho_A + r\rho_B)(r - P_A^2\sigma_A\sigma_B)} \qquad (8)$$

A relationship symetrical to equation (8) can be derived for a system in which $\Sigma A > \Sigma B$,

$$\alpha = \frac{RP_B^2\sigma_B\rho_A^2 + P_B^2\sigma_A\rho_B^2 + 2RP_B\rho_A\rho_B}{(R\rho_A + \rho_B)(R - P_B^2\sigma_A\sigma_B)} \qquad (9)$$

The experimental part of this investigation is conducted in a manner such that incipient gelation boundaries are found at complete reaction of the group that is not in excess. When B groups are in excess and all A's are consumed ($P_A = 1$), equation (8) becomes,

$$\alpha = \frac{\sigma_B\rho_A^2 + r\sigma_A\rho_B^2 + 2r\rho_A\rho_B}{(\rho_A + r\rho_B)(r - \sigma_A\sigma_B)} \qquad (10)$$

Flory[1] has shown that the theoretical gel point is reached when the degree of branching, α, attains a value of $1/(f-1)$, where f is the functionality of the branch unit. In trifunctional systems, then, $\alpha_c = 1/2$. Thus, the relation derived from equation (10) that represents the incipient gelation boundary when the minor reactive group has fully reacted is,

$$2(\sigma_B\rho_A^2 + r_c\sigma_A\rho_B^2 + 2r_c\rho_A\rho_B) = (\rho_A + r_c\rho_B)(r_c - \sigma_A\sigma_B) \qquad (11)$$

Comparison of Flory and Stockmayer Models

Equation (2) and (11) both purport to represent the incipient gelation boundary for the general 3,2,1/3,2,1 system in which all A groups have reacted. For all simple systems (those which have only one type of branching unit, either A or B functional, but not both), these two relationships are equivalent. As an example, equation (2) and (11) both reduce to $r_c = (2\rho_A + \sigma_A)(\sigma_B)$ for a 3,2/2,1 system.

The equivalence of the two relationships ceases to exist for complex trifunctional systems, those in which branch units functional in both A and B exist. For example, in the case of a 3/3 system in which all A groups have reacted at the gel point, equation (2) specifies that the ratio of all B groups to all A groups, r_c, must be 4; whereas, equation (11) specifies a ratio of 3.

The matrix in Figure 1 illustrates the distribution of all 49 possible combinations according to agreement or lack of agreement between the two theoretical models. For all combinations designated by check marks, equations (2) and (11) are equivalent. For those designated by a question mark, the two equations are not equivalent. All those combinations designated NO cannot in any proportion of components form gels.

Critical Experiment

Calculations of simple trifunctional systems based on Flory's and Stockmayer's models are equivalent and correlate with experiment[3]. The two models are not equivalent in the calculation of complex trifunctional systems. A set of experiments was undertaken to determine which of the two models, if either, is the more general.

The previous paper, I[3], describes an accurate method for determining gel points of polyesterifications of model compounds. This method eliminates perturbation due to intramolecular cyclization by allowing transesterification equilibration to take place. It further avoids the difficulties of determining extents of reaction by allowing the reactive group not in excess to be completely consumed. Complications due to side reactions were neither expected nor encountered with esterification. Correlations between calculated and measured critical stoichiometric ratios ($r_c = \Sigma B/\Sigma A$ at incipient gelation) were all within 2.5%.

This method was applied to a system containing a trifunctional alcohol and a trifunctional carboxylic acid. The alcohol, trimethylol ethane, was found to be free from the various drawbacks[3] encountered with other trifunctional alcohols. 1,3,5-Pentane tricarboxylic acid was used for the other branching unit. The use of this acid placed a restriction on the experiment: Only combinations excess in hydroxyl could be expected to correlate with either theoretical model because of the special treatment, described in I[3], necessary to account for the lower reactivity of the secondary carboxyl. It was found necessary, during the course of the experiments, to conduct the highly cross-linked condensations in a diluting solvent. The mineral oil, Nujol, at a concentration of 50% was found to be satisfactory.

The data from this set of experiments are given in Table I. They clearly show a close correlation with the Flory model and a systematic lack of correlation with the Stockmayer model.

Systems Containing Monofunctional Components

Reduction of either equation (2) or equation (11) to expressions describing the two simple systems, 3,2,1/2 (type I) and 3,2/2,1 (type II), gives rise to two distinct relationships which show widely different effects of monofunctional components or impurities. These effects are illustrated in Figures 2 and 3 Monofunctional influence is represented by a parameter, $F_A = \sigma_A/(\sigma_A + \mu_A)$ or $F_B = \sigma_B/(\sigma_B + \mu_B)$, which is a practical term when dealing with prepolymers composed of a mixture of difunctional and monofunctional components. The term, F, is directly related to number average functionality of such two-component prepolymers, $f_n = 2/(2-F)$.

The relationships illustrated in Figures 2 and 3 have a number of practical implications. However, only one will be mentioned here. The effect of monofunctional components or impurities on gelling capability is very large in Type II systems. Type I systems, are capable of tolerating much more monofunctional. In the latter, the branch unit, having the same reactive group as the monofunctional unit, is able to compensate directly for its presence.

Gel point data showing correlation with theory are given in Table II.

Conclusions

1) Although the two theoretical models for network polymer formation originated by Flory and Stockmayer are identical at the gel point for simple systems (those having trifunctional branch units functional in only one of the two complementary reactive groups: A-functional or B-functional but not both), the two models are not identical for complex systems (those having both A-functional branch units and B-functional branch units).

2) Flory's theory is more general. It correlates accurately with the measured incipient gelation boundary of a complex system (3,2/3,2) in which 1,3,5-pentane-tricarboxylic acid and trimethylol ethane were the branch units. Stockmayer's equation deviated systematically from the same data.

3) The sensitivity of the gelling capability of simple systems to the presence of monofunctional components depends on whether or not that component is functional in the same reactive group as the branch unit. The branch unit compensates for the monofunctional unit when they both have the same reactive groups. Compensation is lacking in the opposite case, and thus monofunctional components interfere with gelation to a larger degree.

REFERENCES

1. P. J. Flory, J. Amer. Chem. Soc., 63, 3083 (1941).

2. W. H. Stockmayer, J. Polym. Sci., 9, 69 (1952).

3. J. H. Hodgkin, F. J. Martinelli, J. Heller, and H. E. Marsh, Jr., the preceding paper in this session.

TABLE 1

COMPARISON OF FLORY AND STOCKMAYER THEORIES

(3,2/3,2) System PTA, TME; r > 1

ρ_A	ρ_B	α	±	% Error Flory	% Error Stockmayer
0.005	0.500	0.502	0.002	0.4	0.5
0.113	0.500	0.503	0.002	0.6	4.3
0.210	0.500	0.495	0.002	1.0	8.4
0.328	0.500	0.506	0.004	1.2	6.4
0.505	0.100	0.501	0.002	0.2	0.3
0.512	0.300	0.503	0.002	0.6	3.2
0.526	0.500	0.511	0.001	2.3	9.9
0.371*	0.400	0.509	0.002	1.8	5.6
0.461*	0.500	0.506	0.002	1.2	9.5
0.651*	0.700	0.505	0.004	1.0	16.2
1.00	1.00	0.500	0.003	0.0	33.0

*Run in solvent: Nujol 50% by weight.

TABLE 2

MONOFUNCTIONAL SYSTEMS

ρ_A	f_A	f_B	α	% Error
0.255	1.90	2.0	0.505	1.0
0.506	1.905	2.0	0.500	0.0
0.752	1.905	2.0	0.503	0.6
0.256	2.0	1.901	0.501	0.2
0.506	2.0	1.905	0.500	0.0
0.753	2.0	1.905	0.505	1.0
0.251	1.801	2.0	0.500	0.2
0.505	1.802	2.0	0.501	0.2
0.256	2.0	1.802	0.505	1.0
0.505	2.0	1.802	0.501	0.2
0.255	1.705	2.0	0.503	0.6
0.507	1.701	2.0	0.506	1.2
0.508	2.0	1.698	0.505	1.0
0.505	1.50	2.0	0.506	1.2

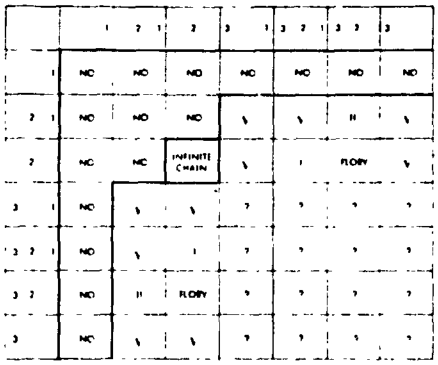


FIGURE 1

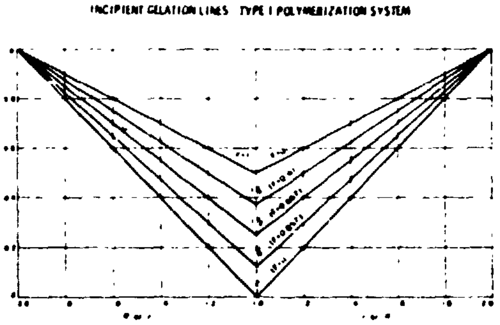


FIGURE 2

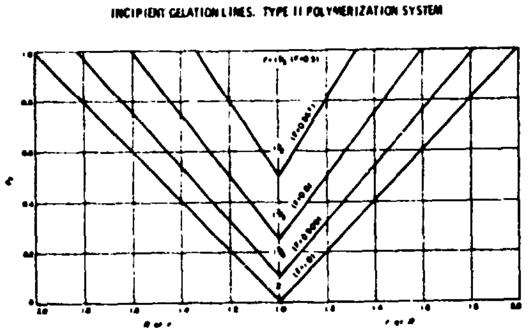


FIGURE 3

APPENDIX C (Reference 22)

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Department of Chemistry · TEL. (603) 646-2501

March 16, 1971

Dr. H. E. March, Jr.
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Pasadena, California 91103

Dear Dr. Marsh:

It was quite a surprise to open the new volume of Polymer Preprints and find your two papers with Hodgkin, Martinelli and Heller on gel points in polyester systems. I haven't been active in this sort of work for a long time, and the discovery was a pure accident.

To come at once to the point, I think that your experimental work is excellent, but that the reasoning in the second paper is unfortunately erroneous. I believe that the "Flory" methodology must inevitably lead to your eq.(2) and not to (11). Without the time to do a complete study of your method, I would like at the moment just to offer the following comments:

(a) You seem to think (p. 602) that transesterification equilibration will eliminate perturbation due to intramolecular cyclization. I can't understand this idea, and would be interested to know your reasoning. In my opinion, such ring structures must have a certain nonzero stability under equilibrium conditions, and there is really no way to eliminate them. If this is so, then a comparison with experimental data, such as your Table 1, p. 603, is not a reliable way to test the correctness of a theory which specifically postulates absence of rings.

(b) Derivations of gel points which agree with eq.(2) were published some years ago by Kahn and by Case. I don't have the references at hand. See also the paper by Fogiel, Macromolecules 2, 581 (1969). These derivations all consider the reproduction of a given kind of unit or structure.

(c) We can perform an exercise with a simple case, corresponding to your 3/3 system, with

$$\sigma_A = \sigma_B = 0 \text{ and } \rho_A = \rho_B = 1.$$

Let us try to combine your approach with that of Flory's original 1941 paper (p. 3085). He considers the number of branches Y_i on the i'th circle. However, here we have two kinds of branch units, so let us call the number of branches of these two kinds on the i'th circle X_i and Y_i according to whether they are of type A or B. Then we could write

$$X_{i+1} = 2P_B Y_i \; ; \quad Y_{i+1} = 2P_A X_i \quad . \qquad (1)$$

The condition for gelation would be

$$(X_{i+1} + Y_{i+1})/(X_i + Y_i) > 1 \quad , \qquad (2)$$

and after substitution of (1) into (2) we have

$$(2P_A + 2P_B Q_i)/(1 + Q_i) > 1 \quad ; \quad Q_i = Y_i/X_i \qquad (3)$$

According to your method, we must now put $Y_i/X_i = r = \Sigma B/\Sigma A$, and with $P_A = 1$ we then recover $r_c = 3$, as you do.

However, the assumption that $Y_i/X_i = r$ is <u>not justified</u>! (The two kinds of functional groups have to react one-for-one, whatever their initial ratio in the pot.) A correct treatment results if we recognize that the ratio Y_i/X_i must become independent of the index <u>i</u> in infinite networks. Therefore we must have

$$Y_{i+1}/X_{i+1} = Y_i/X_i \quad , \qquad (4)$$

but from (1) we also have

$$Y_{i+1}/X_{i+1} = (P_A/P_B)(X_i/Y_i) \qquad (5)$$

Both of these relations are satisfied simultaneously if and only if

$$Y_i/X_i = (P_A/P_B)^{1/2} = r^{1/2} \quad . \qquad (6)$$

If we use this relation in (3), then with $P_A = 1$ we get $r_c = 4$, which indeed is "my" result; but I think it could also correctly be called "Flory's" result.

(d) A general gel-point method should also be able to handle cases involving different polyfunctional reactants of either or both types A and B. I think your scheme would encounter fresh troubles if you tried to extend it to such cases.

I will be at the LA meeting on Monday, Tuesday and most of Wednesday, and am staying at the Biltmore. I would be glad to meet you to discuss these questions further.

Yours sincerely,

Walter H. Stockmayer

Walter H. Stockmayer

WHS:wo
cc: J. H. Hodgkin
P. J. Flory

P.S. There is no denying the <u>practical</u> superiority of your equation, but I think this must be regarded as an empirical stroke of fortune.

APPENDIX D (Rewritten from Reference X16)

Algebra of equations 8, 9, 11, and 13 was corrected by P.J. Flory.

GELATION STUDIES I: SIMPLE TRIFUNCTIONAL SYSTEMS

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SYNOPSIS

A new method for studying the theories of polymer network formation has been devised. Cross-linking reactions are carried out in a recording viscometer, which allows for the accurate determination of incipient gel points and also serves as a high-speed stirrer. The molten, non-stoichiometric mixtures are reacted to completion, thus eliminating the inaccuracies inherent in the determination of reaction extent. Use of an esterification reaction, which is reversible and has negligible side reactions, eliminates a number of the other theoretical and practical problems of previous methods. Flory's network theory has been modified and applied to the reactions of simple model compounds, and the experimental results are in very close agreement with the theory. Unequal reactivity of like groups on the cross-linking reagents has also been considered; the accuracy of this method allows the reactivity ratio of the different groups to be calculated using a modification of the network theory.

Introduction

A complete understanding of the conditions under which three-dimensional polymer networks are formed is of considerable theoretical and practical importance. While the basic theoretical concepts were established many years ago by Carothers,[1] Flory,[2] and Stockmayer,[3] accurate experimental verification of these concepts have not yet been totally successful and a number of explanations attempting to account for the discrepancies have been advanced.[2,4]

One of the most difficult problems in dealing with gelled polymers is the inherent difficulty in accurately determining the incipient gel point and the extent of reaction.[5] A further complication is the occurrence of some intramolecular reaction which has been neglected in the theoretical treatment and which can lead to discrepancies between experiment and theory well beyond those due to experimental error.[2] In an effort to achieve a better understanding of the various parameters influencing polymer network formation we have developed a sensitive and accurate method for detecting the incipient gel point and have applied the method to a chemical reaction that was driven to completion, thus eliminating any uncertainty resulting from inaccuracies in the determination of extent of reaction. We believe that the use of an equilibrium reaction effectively eliminates perturbation due to intramolecular cyclization, since the reactions were carried out either in concentrated solution or heat.

The purpose of this paper is to describe the method and to apply it to the simple case of one trifunctional and two difunctional compounds under the conditions of both equal and unequal reactivity of functional groups. Future papers will examine the effects of monofunctional units, of more than one type of branch unit (e.g., a tricarboxylic acid and a triol in the same reaction mixture), and of branch units with more than three functional groups. One practical goal of this long range program is the development of a method for determining the functionality distributions[6] of prepolymers used in solid propellant binders for rockets. Most prepolymers of this type (usually having either carboxyl or hydroxyl functional groups) are mixtures of zero-, mono-, di-, and often higher-functional molecules.[7,8]

Theory

The theoretical treatments of polymer gelation generally make four basic assumptions. The first three are that no intramolecular reaction occurs, that there are no side reactions, and that like groups have equal reactivity. The fourth assumption is that the equality of reactivity of like groups holds true "regardless of the status of other groups belonging to the same unit,"[3] including the size of the polymeric units to which they are bound.

Fundamental to the treatment of gelation of systems of reactive polyfunctional molecules is the concept, probability of branching, or branching coefficient, α, introduced by Flory.[2] In general terms, the branching coefficient represents the probability that a chain selected at random from a system containing polyfunctional molecules is a part of an infinite network. Mathematically, α is the probability that one end of the randomly selected chain terminates in a branch; which of the two ends is considered is a result of arbitrary choice. The system here is defined not only by its composition but also by its state of reaction. It is assumed that all chains have equal likelihood of selection, independent of length.

Flory has defined the incipient gel point[2] as that condition represented by $\alpha = \alpha_c = 1/(f-1)$, where f is the functionality of the branching unit. Thus, for a system in which the branching unit is trifunctional, $\alpha_c = 1/2$. This is the critical probability above which infinite networks are possible and below which they are not. Flory went on to describe experiments that showed reasonably accurate correspondence with theory. Subcritical systems were very viscous liquids; systems that had reacted beyond α_c were elastomeric gels, only part of which were extractable.

Two different definitions of α are used by Flory in the paper introducing these concepts. For simple systems, in which equal reactivity is assumed (Cases 1 and 2),[2a] α is defined as the probability (I) that "any given one of the functional groups of a branch unit leads, via a sequence of bifunctional units, to another branch, rather than to a terminal group." We will call this α_I. For Case 3,[2a] which takes into account the effect of unequal reactivity, a different probability calculation (II) was found necessary.

The starting point of the randomly selected chain in this case is a functional group at any given position in the chain, and the fate of the end of that chain opposite from the direction of probability calculation is not considered. An additional variant in this second treatment is the definition of branches. Branch units with only two functional groups that have reacted are considered to be chain extenders, not branches. Only those in which all three groups have reacted are identified as branch sites. We will call this branching coefficient α_{II}. The second probability term, α_{II}, applies also to cases of equal reactivity. Although the expressions for α_I and α_{II} are not equivalent for the same system, Flory shows that they agree at the gel point[2a]. We will use both definitions in this paper--α_I for a system having equal reactivity and for another in which unequal reactivity has no influence, and α_{II} where the effect is present.

Applying definition I to a polycondensation system containing two difunctional components (A-A and B-B) with a single trifunctional component  $(\text{A}\overset{\text{A}}{\perp}\text{A})$, Flory[2] derived the probability of formation of the chain,

$$\succ\!\!-\text{A}[\text{B-BA-A}]_n\text{B-BA}-\!\!\prec$$

as

$$\alpha_n = [P_A P_B (1-\rho)]^n P_A P_B \rho \qquad (1)$$

where ρ= ratio of A's contributed by the branch unit to total A's and P_A and P_B are the fraction of A's and B's respectively that have reacted.

Then, summing the terms for all possible lengths of chain, we have

$$\alpha_I = \sum_{n=0}^{\infty} \alpha_n = \frac{P_A P_B \rho}{1-P_A P_B(1-\rho)} \quad . \qquad (2)$$

At incipient gelation, $\alpha_I = 1/2$, and Eq. (2) becomes

$$P_A P_B = 1/(1 + \rho) \qquad (3)$$

which is equivalent to Stockmayer's relation[3] for the same system. Letting $r = 1/R$ = ratio of all B's to all A's = $\Sigma B/\Sigma A$, it follows from material balance that $r = P_A/P_B$, and $R = P_B/P_A$. By substitution, Eq. (3) can be written

$$R_c = P_B^2(1+\rho) \qquad (4)$$

or

$$r_c = P_A^2(1+\rho) \qquad (5)$$

Equation (4) is used to describe mixtures at the gel point containing an excess of A-groups and (5) is used to describe mixtures containing an excess of B-groups. It is convenient to consider two types of systems, designated as Y and Z and defined respectively as one having the groups attached to the trifunctional unit in excess and one where that group is not in excess. At present we are dealing with mixtures containing tri-A's so that a type Y system is one where A-groups are in excess.

If,in order to eliminate the experimental problems of determining reaction extent, the reactions are allowed to proceed to completion, then either P_A or P_B may be set equal to one (note that $P_A = P_B = 1$ only if $R = r = 1$), and equations (4) and (5) reduce respectively to

$$R_c = 1 + \rho \quad \text{for Y systems} \qquad (6)$$

and

$$r_c = 1 + \rho \quad \text{for Z systems} \qquad (7)$$

Equations (6) and (7) describe the relationship between reagents in a simple 3,2/2 system at incipient gelation. A plot of these equations is shown in Fig. 1. There is no mathematical distinction between the gel boundaries of Y and Z systems of this simple case. According to theory, any mixture whose parameters lie inside the "V" will gel, while mixtures with parameters outside the "V" will not gel. The lines themselves represent all points of incipient gelation.

Flory[2a] and others[9] have pointed out the necessity of taking into consideration unequal reactivities of the groups on the trifunctional branching unit, and Flory has analyzed the problem for a stoichiometric mixture of a trifunctional compound such as glycerol (where there are two primary groups and one secondary group) and a complementary bifunctional compound, a dibasic acid in this case (Reference 2a, Case 3). The branch compound used in this study (1,3,5-pentanetricarboxylic acid) also has two primary groups and one secondary group. It was necessary to expand Flory's treatment in order to account for two added factors. These are (1) varying concentration of a primary dibasic acid, and (2) nonstoichiometric compositions. The latter condition is necessary to obtain gel-point compositions at complete reaction.

Definition II of the branching coefficient is applied to a model system that is the same as that treated above, with a single exception--one functional group on the trifunctional compound has a different reactivity then the others:

$$\mathrm{A}\!-\!\!\overset{\displaystyle a}{|}\!\!-\!\mathrm{A} \;+\; \mathrm{A}\text{——}\mathrm{A} \;+\; \mathrm{B}\text{——}\mathrm{B}\ .$$

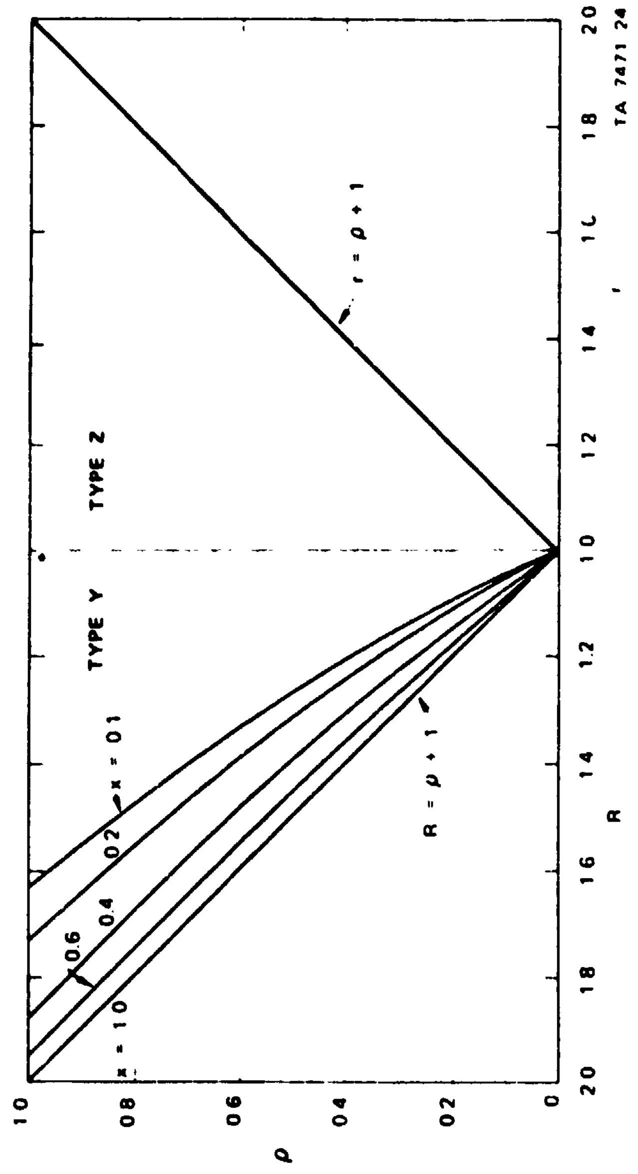


Figure 1 r Versus ρ and R Versus ρ for Various Values of x.

Otherwise all A's are equally reactive. The parameters used in this treatment are the same as before, with the following additions:

ρ = Fraction of A's plus a's contributed by the branch unit.

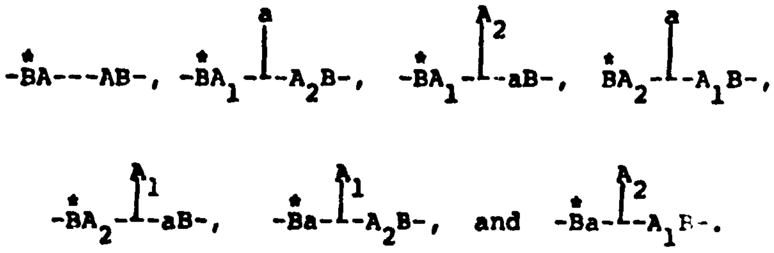
$R = 1/r = \Sigma(A+a)/\Sigma B$ = Ratio of all A's, regardless of reactivity, to all B's

$P = P_B$ = Fraction of B's that have reacted

P' = Fraction of A's that have reacted

P'' = Fraction of a's that have reacted.

In accordance with Definition II, the probability that any given $\overset{*}{B}$ has reacted to a chain-extending unit is the sum of all the possible ways, which are illustrated in the following diagrams:



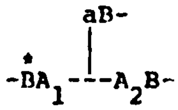
$-\overset{*}{B}A---AB-$, $-\overset{*}{B}A_1-\overset{a}{|}-A_2B-$, $-\overset{*}{B}A_1-\overset{A_2}{|}-aB-$, $\overset{*}{B}A_2-\overset{a}{|}-A_1B-$,

$-\overset{*}{B}A_2-\overset{A_1}{|}-aB-$, $-\overset{*}{B}a-\overset{A_1}{|}-A_2B-$, and $-\overset{*}{B}a-\overset{A_2}{|}-A_1B-$.

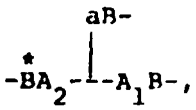
That sum is

$$\theta_2 = PP' + \frac{3\rho\ PP'P''\ (1-2P')}{(3-\rho)\ P' + \rho P''} \qquad (8)$$

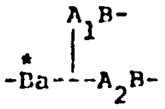
The probability that any given $\overset{*}{B}$ has reacted to a branch is, by the same reasoning,



$-\overset{*}{B}A_1 - \overset{\overset{aB-}{|}}{-} - A_2B-$



$-\overset{*}{B}A_2 - \overset{\overset{aB-}{|}}{-} - A_1B-$, and



$-\overset{*}{B}a - \overset{\overset{A_1B-}{|}}{-} - A_2B-$,

$$\theta_3 = \frac{3\rho\ P(P')^2\ P''}{(3-\rho)\ P' + \rho P''} \tag{9}$$

The probability of branching is then calculated as the sum of all possible lengths of successive chain-extending units proceeding from the randomly selected $\overset{*}{B}$ to a terminal, times the probability that the terminal is a branch,

$$\alpha_{II} = \sum_{n=o}^{\infty} \theta_2^n\ \theta_3$$

$$= \theta_3/(1-\theta_2) \tag{10}$$

At the gel point ($\alpha_{II} = 1/2$), the expression resulting from the substitution of Eqs. (8) and (9) into (10) reduces to

$$3\rho PP'P'' = (1-PP')\ ((3-\rho)\ P' + \rho P'') \tag{11}$$

Equation (11) reduces further to Eq. (3) at the special condition of $P' = P''$, thus confirming the equivalence of the two bases of calculation, Definitions I and II, at incipient gelation.

Material balance calculation of the system at any degree of polymerization gives the following relationship:

$$R = 3P/[(3-\rho)P' + \rho P''] \quad . \tag{12}$$

By defining an effective reactivity ratio $x = P''/P'$, letting $P = 1$ and eliminating P' between Eqs. (11) and (12), the equation for the incipient gelation boundary is found to be

$$R_c = \frac{1}{1 - (1-X)\ \rho/3} + \frac{X\rho}{(1-(1-X)\rho/3)^2} \qquad (13)$$

Equation (13) is plotted in Fig. 1 for various values of x. [Note that Eq. (13) reduces to Eq. (7) for x = 1.] Thus, in cases where the unequal reactivity of the trifunctional reactive groups affects the gel point (type Y systems), the boundary curves lie inside the "V".

Experimental Section

Apparatus--Formation of a gel is preceded by a rapid increase in molecular weight, with its accompanying increase in viscosity, until viscosity becomes essentially infinite. Thus, an apparatus based on the principle of a Cóuette viscometer wherein the force required to rotate one concentric cylinder within another is recorded, provides a means of continuously monitoring the viscosity of the reaction. Figure 2 is a diagram of the apparatus used for gel point determinations.

In this work, a dc motor was used to drive a Teflon cylinder within a cylindrical glass vessel. Teflon cylinders of various sizes could be chosen for different viscosity ranges. The field of the dc motor was held at a constant voltage by a regulated power supply, and a variable voltage was supplied to the motor armature by a second regulated power supply.

Armature current of this dc motor is proportional to the torque. It was monitored continuously and recorded on a strip-chart recorder. Rotational velocity was determined, also continuously, from the calibrated

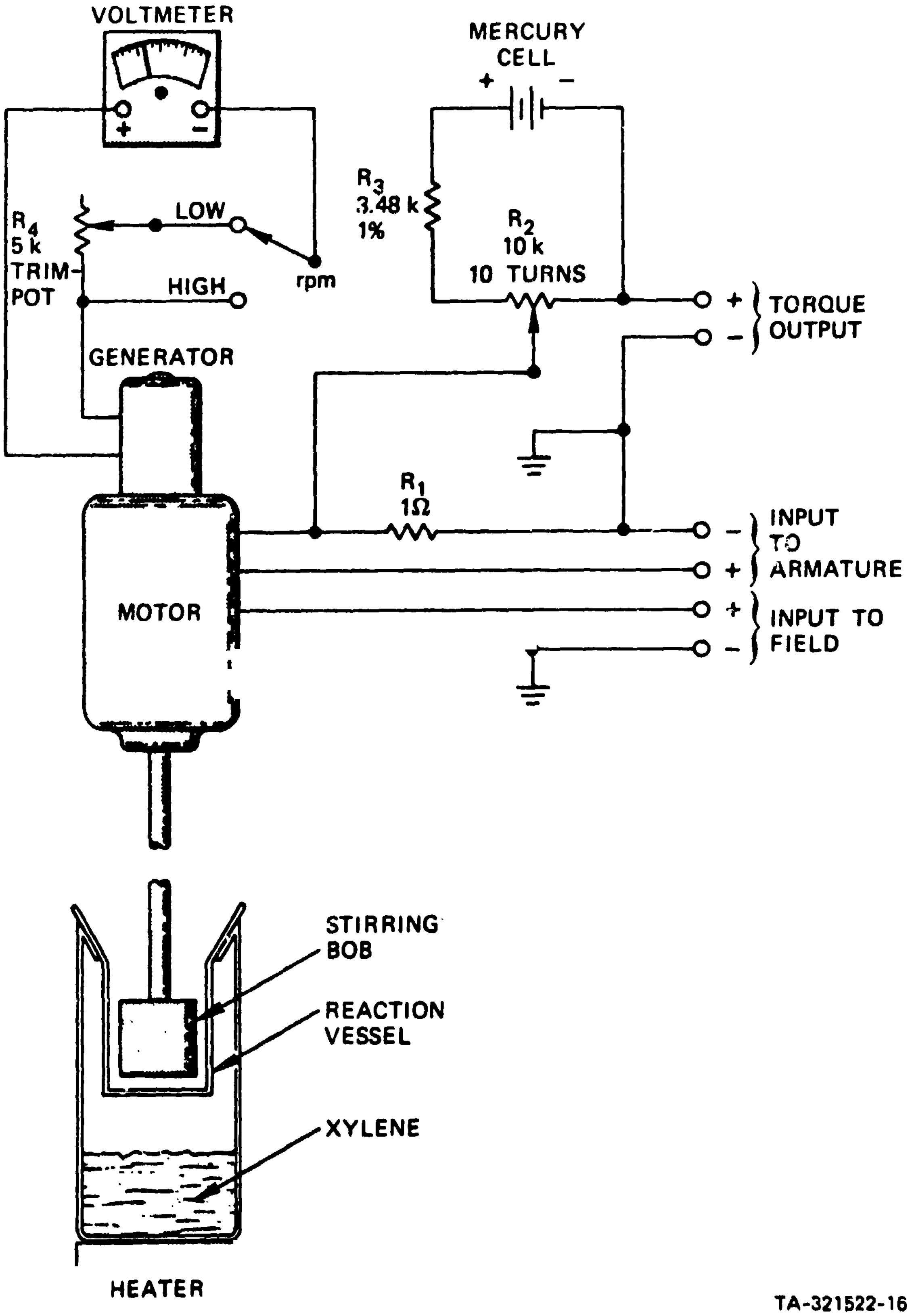


Figure 2 Apparatus for Gel Point Determinations

voltage of a small dc generator on the same shaft. Since dimensional parameters did not change throughout a given run, and since there was no need to determine absolute viscosity, nominal values of the geometrical and electrical factors were lumped into a constant, K, and viscosities versus time were calculated from the two curves as $\eta = K\, i/\omega$, where i is armature current, and ω is rotational velocity.

Materials--Sebacic acid and 1,3,5-pentanetricarboxylic acid (PTA) were obtained from Aldrich Chemical Co. and used as received. Decanediol was obtained from Matheson, Coleman and Bell and was recrystallized twice from chloroform. Acid numbers and hydroxyl numbers were used as criteria for purity, which was approximately 99 percent. The 1,3,5-benzenetriacetic acid (BTA) was prepared by the method of Newman and Lowrie.[10]

Procedure--A mixture of the ingredients at known R or r and ρ values was prepared by weighing each ingredient (± 0.01 percent) directly into the glass reaction cylinder. The cylinder was heated and maintained at ~140°C by means of a xylene vapor bath. After the mixture had at least partially melted, the Teflon cylinder was inserted, and stirring was begun. The viscosity of the mixture decreased as it came to temperature; when a constant value was reached, the stirring rate was set at 500 rpm and a "zero torque" reading was taken. A gentle stream of nitrogen was then directed into the reaction vessel, and the catalyst, p-toluene sulfonic acid (0.25%), was added. Since independent experiments had shown that reaction rate increased with stirring rate, the latter was then increased to between 2000 and 3000 rpm. Shortly after catalyst addition, bubbles formed in the polymer melt and rose rapidly to the surface. The torque output increased with a corresponding decrease in stirring velocity as the reaction proceeded, and if the rpm dropped below ~2000, it was readjusted by increasing the potential on the armature. After a period of time (30 minutes to 2 hours), the viscosity of the mixture no longer increased, signalling the end of the reaction. The rpm were reduced to ~600 where another small increase in the torque readout took place due to equilibrations at that speed. Finally, a constant torque reading was taken at 500 rpm.

The basic experimental approach was to prepare a nongelling mixture and allow the reaction to proceed until a constant viscosity reading was reached, at which point complete reaction was assumed. The mixture was then brought nearer to the theoretical gel point by adding a calculated amount of one of the ingredients and the reaction again allowed to proceed to constant viscosity. This procedure was repeated until the gel point was reached. Gel points were confirmed by extraction.

For a type-Y system, diol was added to the mixture, thereby decreasing R and bringing the mixture closer to gelation. For a type-Z system, triacid was added in order to decrease r. However, addition of triacid also increased ρ so that the gel point was approached more rapidly. The amounts of ingredients necessary to achieve the desired ρ, R, or r values for a predetermined total weight of mixture were determined from a computer program, which listed the amounts of diol and corresponding R values for a type-Z system and the amount of triacid with corresponding ρ and r values for a type-Y system. The proximity to the incipient gel point was estimated by the increase of viscosity with each amount of material added. The reproducibility of this procedure was confirmed by preparing a different nongelling mixture and proceeding to the gel point by adding different quantities of the reactant.

Results and Discussion

As already mentioned, the theoretical treatment is predicated on a number of assumptions that place severe requirements on the chemical reaction and experimental procedure used to verify the theory. We have found that an esterification reaction, when allowed to proceed long enough so that chain extending and branching linkages can equilibrate by means of transesterification reactions, meets all requirements of the theory. Thus, esterification proceeds with no side-reactions, can be driven to 100-percent completion, and is not significantly afflicted with cyclic structures, provided these are allowed to reequilibrate with network structures. A number of reactions other than simple esterification were tried, primarily to eliminate the necessity of removing a reaction product in order to get complete reaction.* None of the alternative reactions, however, was found to be totally free from side reactions.

Early experiments indicated that proper choice of trifunctional cross-linking agents is very important, and a number of compounds were tried and found unsuitable. For example. glycerol, tricarballylic acid, and 1,2,6-hexanetriol underwent decomposition. The melting temperature of the 1,3,5-benzenetricarboxylic acid was too high, and trimethylolpropane sublimed out of the reaction mixture. The compound eventually chosen and used for most of this work was 1,3.5-pentanetricarboxylic acid (PTA). However, 1,3,5-benzenetriacetic acid (BTA) was used in a few type-Y experiments as an equal-reactivity control.

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*Other reactions tried in an earlier study[11] were: acyl halide with epoxide, aziridine, or alcohol; mixed acid anhydride with epoxide or aziridine, and substituted amine with carboxylic acid. In the present investigation, two more reactions were tried: transesterification yielding a volatile ester byproduct and bromo-alkane with a sodium salt of an aryl sulphonamide.

The data obtained from type Y systems containing PTA differed considerably from those obtained from type-Z systems, and from type-Y systems containing BTA. With the last two systems, viscosity increase was usually negligible as the gel line was approached, but when the actual gel point was reached, the viscosity either increased beyond the limits of detection of the instrument, or the gelled mixture agglomerated around the stirrer shaft. Because of this abrupt change, the value of critical r could be located with a 0.2% precision. Results obtained with type Z systems are shown in Table I and plotted in Figure 3. BTA type Y data are also plotted in Fig. 3.

Experiments with type-Y systems containing PTA, on the other hand, did not exhibit an abrupt change in viscosity, and curves similar to those obtained by Flory[2] were obtained. Figure 4 shows one experiment at $\rho = 0.2$.

Due to the absence of an abrupt change in viscosity, R_c values had to be obtained by extrapolating to the point at which viscosity becomes infinite (see Appendix). The results of this treatment are shown in Table II and, together with the previous data, are plotted in Fig. 3.

The values of R_c and their corresponding ρ values were substituted into Eq. (13) and the quantity x was calculated at each ρ. The average x-value is 0.20 (excluding, on a statistical basis, the value $x = 0.57$). Resubstituting the average x-value into Eq. (13), R_c values were calculated for each ρ and shown in Table II. The curve described by these points is plotted in Fig. 3; correlation of the experimental points with this curve is quite good except at the lowest ρ values, where the deviation corresponds to an increase in x.

Table I

CRITICAL r-VALUES FOR TYPE Z EXPERIMENTS

ρ	r_c Calc*	r_c Obs	Percent Deviation
0.108	1.108	1.099	0.82
0.206	1.206	1.190	1.33
0.227	1.227	1.207	1.63
0.301	1.301	1.296	0.38
0.358	1.358	1.332	1.92
0.401	1.401	1.395	0.43
0.504	1.504	1.486	1.20
0.607	1.607	1.570	2.30
0.704	1.704	1.663	2.41
0.802	1.802	1.763	2.17

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* Calculated using Eq. (7)

Table II

CRITICAL R-VALUES FOR TYPE Y EXPERIMENTS

ρ	x	R_c Calc*	R_c Obs†	Percent Deviation
.1	.57	1.056	1.082	2.44
.2	.31	1.114	1.133	1.66
.35	.16	1.209	1.200	0.74
.5	.18	1.312	1.301	0.84
.6	.22	1.386	1.396	0.72
.7	.20	1.465	1.464	0.07
.8	.18	1.550	1.536	0.90
.9	.18	1.640	1.623	1.05

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* Calculated using Eq. (13) with $x = 0.20$.

† See Appendix.

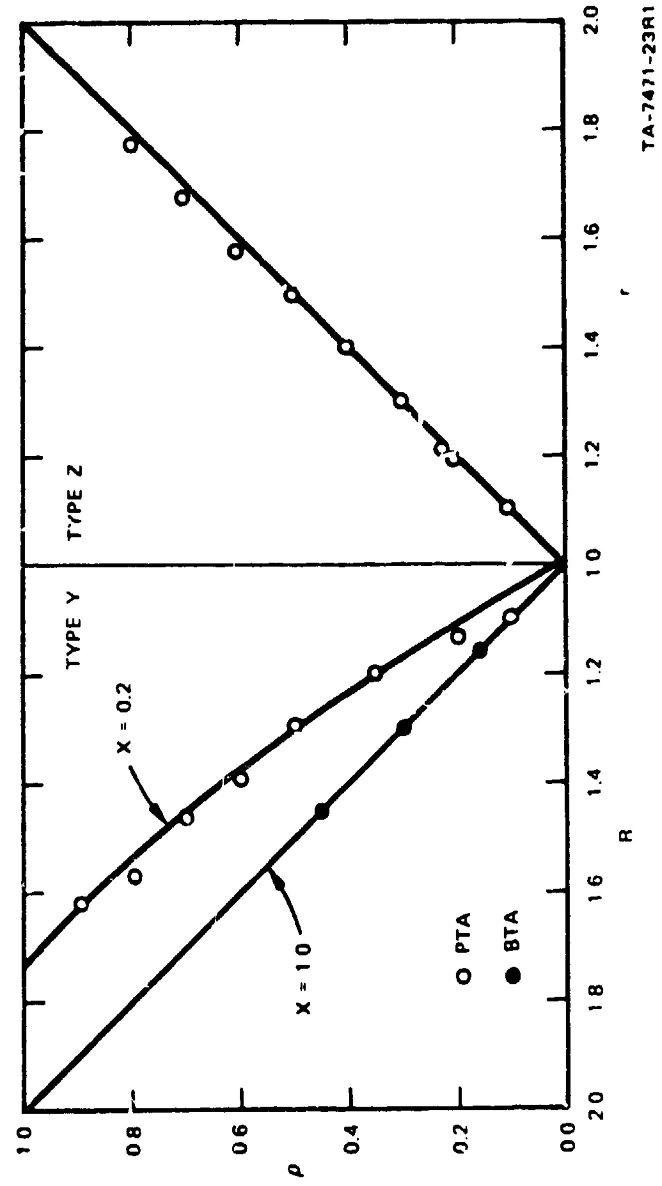

Figure 3 Incipient Gel Points for PTA and BTA

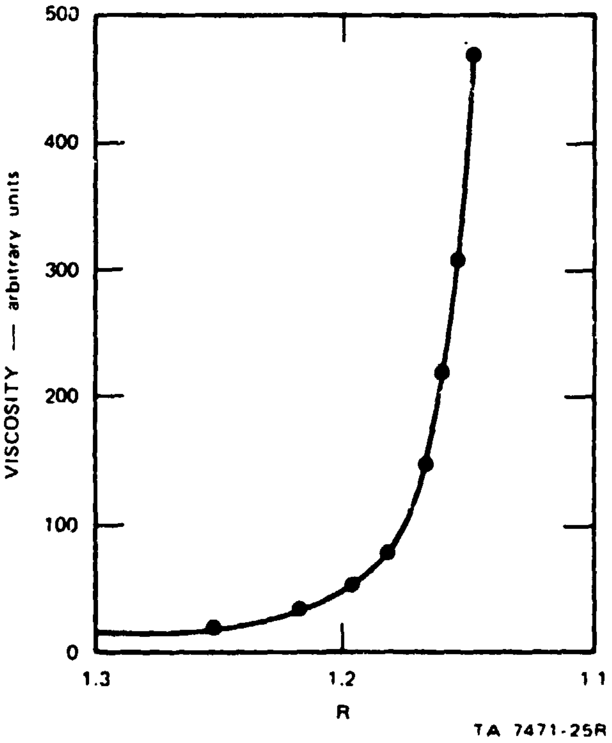

Figure 4 R Versus η For ρ=0.2

The difference in behavior between type-Y and type Z systems can be attributed to the lower reactivity of the secondary carboxyl in 1,3,5-pentanetricarboxylic acid. In the case treated here, a type-Y system contains an excess of carboxylic acid groups so that the mixture is brought to the gel point by addition of diol. Because carboxylic acid groups are in excess, reaction of a primary carboxyl group will occur in preference to a secondary group, and formation of unbranched high-molecular weight chains will be favored. Gelation will occur only after the majority of the primary carboxylic acid groups have reacted, and branching reactions involving the less reactive secondary carboxylic acid groups become significant. Hence, experimentally one notes a gradual increase in viscosity until the gel point is reached.

In the type-Z system treated here, hydroxyl groups are in excess, so that the mixture is brought to the gel point by addition of triacid. Since the reaction is forced to completion after each addition of triacid, the secondary carboxylic acid groups are forced to react, and differences in reactivity are of no consequence. Hence, highly branched structures form first. Since, as measured by the rotating cylinder, these do not significantly alter the viscosity of the reaction mixture, the apparatus will detect an abrupt viscosity change only after the composition is such that gelation can take place.

Experimental verification of the hypothesis that the different behavior of Y and Z systems is due to unequal reactivities of the primary and secondary carboxyl groups on the trifunctional unit was achieved by using 1,3,5-benzenetriacetic acid (BTA) in which all three primary carboxyl groups are equally reactive. Thus, in type-Y experiments with BTA carried out at $\rho = 0.15$, 0.30, and 0.45, not only was there an abrupt increase in viscosity at the gel point characteristic of type-Z systems, but the data fitted Eq. (6), thus confirming equal reactivity of all carboxylic acid groups. The results are shown in Fig. 3 as the solid circles.

An analysis of the uncertainties due to slight impurities in the starting material was carried out. The maximum error in R and r remains relatively constant at 1 to 2 percent over their entire range. However, the maximum error in ρ increased from about 1 percent for $\rho > 0.5$ to greater than 5 percent for $\rho < 0.2$. Thus, the observed deviations in R_c at the lower ρ values could be due to impurities. At higher ρ values, the method provides a reliable technique for determining relative reactivity ratios for trifunctional compounds.

The results of this study support Flory's theory that the value of the parameter α determines whether or not systems of this type will gel. The slight deviations from the theoretical incipient gelation line at the higher ρ values for the type-Z system could be due to difficulty in achieving complete reaction in highly cross-linked systems. Analysis of Eq. (4) shows the fractional error in r to be independent of ρ and equal to $(1-P^2)$. For example, a 2-percent deviation can take place even though the reaction goes to 99-percent completion.

This paper presents the results of research carried out at the Stanford Research Institute under Contract No. NAS7-689, and the results of one phase of research carried out at the Jet Propulsion Laboratory, California Institute of Technology, under Contract No. NAS7-100, both sponsored by the National Aeronautics and Space Administration.

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APPENDIX E (Reference X25)

NETWORK POLYMER FORMATION STUDIES*

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ABSTRACT

The formulating of liquid elastomers, such as solid propellant binders for the attainment of specified mechanical properties is an empirical art. Two new probability sub-models of the formation of polymer network have been generated which show promise of contributing to the advancement of formulating from an art to a science.

The first of these models accounts for the extra crosslinks produced by a significant side reaction present in the formation of polyurethane elastomers. The second model provides a method for determining the effective number of chains on the basis of formulating parameters. Effective chains are those which are connected at both ends in the network and therefore are capable of deforming elastically under load.

Both models have been qualitatively verified in preliminary experiments. Suitable accounting for the side-reaction-produced crosslinks in polyurethane elastomers was demonstrated by a series of test formulations composed of well characterized components. The compositional boundary between gelling and non-gelling formulations was a narrow region which included the theoretically predicted value. Measurements of sol-gel ratios and effective chains correlated with the model for some urethane formulations. In another set of experiments, it was shown that the theoretical effective number of chains correlated very well with the moduli and tensile strength of a variety of solid propellants having polyurethane binders.

INTRODUCTION

The formulation of composite solid propellant binders, either for the attainment of desired mechanical properties or in search of the maximum mechanical capabilities of a new binder system, is largely an empirical art. The same is true for the tailoring of established propellants when the introduction of new lots of ingredients causes undesirable property changes. Probably, there are as many systematic approaches to these problems as there are formulators. Nevertheless, there is usually a considerable amount of costly tedium involved in these activities. The development of a method which can significantly reduce the quantity of such labor by relating the properties to formulating parameters in a fundamental way is still a worthwhile goal.

This paper describes an approach based on network polymer theory which we are developing. It comprises two theoretical models, one of which

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* This paper presents the results of one phase of research carried out at the Jet Propulsion Laboratory, California Institute of Technology, under Contract No. NAS7-100, sponsored by the National Aeronautics and Space Administration.

applies specifically to urethane-cured binder systems. The other model is general. The combined model has been subjected to limited testing, both theoretical and practical. The results of these tests are mixed. Good matching between theoretical and experimental data was frequent enough to indicate that the models are basically sound. However, the kinds of mismatch observed suggest that some refinement may be necessary. All in all, considering the complexity of these polymeric systems and the assumptions that had to be made, the models appear promising.

THEORY

In 1941, Flory (1) introduced a model for gelation applicable to condensation-crosslinked polymers based entirely on probabalistic reasoning. A key feature of this model is the gelpoint or incipient gelation boundary, which is the critical condition, defined by the relative concentrations of mutually reactive polyfunctional compounds in a mixture and the varying extents of reaction of their reactive groups, at which an infinitesimal amount of infinite, three-dimensional network forms. Flory's model is of such a nature that it is necessary to derive a specific relationship for each case. Reasoning from a general model, Stockmayer (2) developed a simple relationship between the essential parameters for the gel point useful for a much wider range of cases. The two models are in agreement at incipient gelation.

Flory and many others found that the theoretical gel point corresponds closely to experimental conditions at which polymerizing mixtures change from being viscous liquids to weak, rubbery solids. In a previous study (3) we obtained excellent correlation with the two of 3,2/2* systems perturbed by presence of monofunctional components, 3,2,1/2 and 3,2/2,1.

In the present study, we chose Flory's approach because of two limitations in Stockmayer's more general relationship. First, the latter applies only to the condition of incipient gelation. Our concern is with conditions beyond this point that are necessary for the formation of rubbery networks. Second, Stockmayer's relation assumes a single reaction, no variations in rate, and unchanging functionality. This study deals with two competing reactions having different rates and with the formation of additional reactive groups as the main reaction progresses.

A Urethane Model. Of the major curing systems used in solid propellant manufacture, the urethane reaction comes closest to fitting simple network theory. Nevertheless, most formulators find a uniform deviation. This deviation shows up as the attainment of highest tensile strength and modulus when formulations are around five to ten percent off from one-to-one stoi-

* A shorthand is used to identify functionality sets as follows. The numerals 1, 2, and 3 represent mono-, di-, and tri-functional species. Numerals in front of the slash refer to A functional groups, and those after the slash refer to B groups, where one A reacts with one B to form a link (such as an alcohol with an isocyanate to form a urethane). For example, the system identified by 3,2/2,1 contains tri-, and di-functional A molecules and di- and mono-functional B molecules. There are 49 possible combinations of the general 3,2,1/3,2,1 system. Proportions of the various species are not specified in this symbolism.

chiometry (4). This range holds for polyether-urethane binders. However, the deviation appears to be higher in the case of HTPB formulations.

In the formulating systems studied here, three competing reactions are likely (5), isocyanate dimerization, biuret formation, and allophanate formation. One only must be selected for the construction of a simple model. Dimerization is rejected because it would produce only one of the two effects inferred from data, stoichiometric shift. The other effect, extra crosslinking, would be produced by either of the other two possible reactions. Of these two, biuret is rejected, because in practice its occurrence is restricted to as low a level as possible by maintaining dry conditions in order to avoid carbon dioxide gas bubbles in the product. Thus, the following model assumes that allophanate formation is the only significant side reaction.

The main reaction in curing of binders composed of polyfunctional alcohols and isocyanates is:

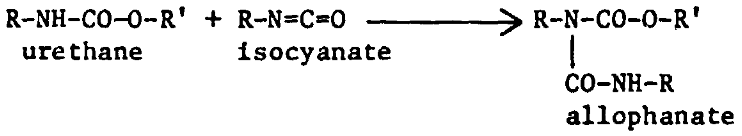
$$\underset{\text{isocyanate}}{\text{R-N=C=O}} + \underset{\text{alcohol}}{\text{R'-OH}} \longrightarrow \underset{\text{urethane}}{\text{R-NH-CO-O-R'}} \qquad (1)$$

Extents of reaction are represented by the probabilities,

P_{OH} = OH reacted/OH total,

P_{NCO} = NCO reacted/NCO total.

Once a urethane is formed, it too is reactive with further isocyanate, but less so:



$$\underset{\text{urethane}}{\text{R-NH-CO-O-R'}} + \underset{\text{isocyanate}}{\text{R-N=C=O}} \longrightarrow \underset{\text{allophanate}}{\begin{array}{l}\text{R-N-CO-O-R'}\\ \quad | \\ \text{CO-NH-R}\end{array}} \qquad (2)$$

It is clear that, when R and R' are parts of continuing chains, each new allophanate becomes a new branch point, a potential crosslink. Since propellant binder cures are slow, we assume that there is sufficient time for the relative extents of urethane and alcohol reactions with isocyanate to be governed by equilibrium, rather than kinetic, factors. Thus, where

P_U = U reacted/U total,

that equilibrium can be simply expressed as

$X = P_U/P_{OH}$.

Defining stoichiometry of the formulation as

R = NCO Total/OH total,

we are able to relate the extents of reaction of the main reactants at any state of cure as

$$P_{NCO} = P_{OH}\,(1 + XP_{OH})/R. \qquad (3)$$

Most practical propellant binder systems use diisocyanates of reasonably good purity. With the exception of ARCO R-45M, most crosslinking agents (usually alcohols) are also reasonably pure. Prepolymers are generally known, or assumed, to be mixtures of difunctional and monofunctional molecules. (The presence of non-functional prepolymer does not count in the model.) For these reasons, a 3,2,1/2 system is chosen for generation of a urethane curing model. This model is shown in Figure 1.

Formulations are specifically defined in terms of the components illustrated in Figure 1 by the following parameters (along with R, defined above):

ρ = fraction of OH contributed by tri-functional components
σ = fraction of OH contributed by di-functional components
μ = fraction of OH contributed by mono-functional components

$$\rho + \sigma + \mu = 1 \tag{4}$$

It must be pointed out that the functionality distributions of prepolymers and other ingredients, such as the prepolymer R-45M, must be known or estimated for the setting of these parameters.

The key to Flory's approach for developing gelation relationships is the parameter, α, known as the degree of branching. It is defined as the probability that an arm of a branching unit (any site capable of extending chains in more than two directions) is connected through a series of di-functional units to another branching unit. This probability ranges from zero to one. It is pointed out here, for reference, that Flory showed a critical point to exist when α = 1/2 in systems having branching units with three functional groups. That critical point is the gel point mentioned earlier. The second model in this paper, for determining sol/gel ratio and number of effective chains (see below), deals with α's greater than 1/2.

The general approach to determining expressions for α applied to the urethane system is illustrated in Figure 2. It will be noticed that only half the possible configurations are counted in this model. This apparent lack of rigor was chosen, because it is a great deal simpler, we have had troubles with the more complex models in the past, and the data obtained so far are in pretty good agreement with the simpler model. The probabilities of connection of an arm of a tri-functional ingredient to another tri-functional ingredient and also to a urethane (as an allophanate branching unit) are expressed as follows:

$$P_{TT} = \frac{P_{OH}\,P_{NCO}\,\rho}{1 + X\,P_{OH}} \left(\frac{P_{OH}\,P_{NCO}\,\sigma}{1 + XP_{OH}}\right)^{n} \text{, and} \tag{5}$$

$$P_{TU} = \frac{P_{OH}P_{NCO}XP_{OH}}{1 + XP_{OH}} \left(\frac{P_{OH}P_{NCO}\sigma}{1 + XP_{OH}}\right)^{n} \tag{6}$$

Fundamental to this derivation is the fact that any isocyanate that has reacted will have reacted with (1) an OH from a tri-functional source which itself, then, is in a reacted status, ρP_{OH}, or (2) an OH from a di-functional source, also in reacted status, σP_{OH}, or (3) a similarly defined mono-functional OH, $\mu\ P_{OH}$, or (4) a urethane group of equivalent status $XP_{OH}{}^{2}$. The sum of all these possibilities is $P_{OH}(1 + XP_{OH})$. The total number of possible ways that the defined connections can be made, which is the probability sought after, is obtained as the summation of all of the possible lengths of chain to do it:

$$\alpha = \sum^{n=\infty} P_{TT} + \sum^{n=\infty} P_{TU}. \tag{7}$$

When these series are summed, the expression becomes

$$\alpha = \frac{P_{OH}P_{NCO}\ (\rho + P_{OH}X)}{1 + P_{OH}X - P_{OH}P_{NCO}\sigma} \tag{8}$$

A necessary condition exists: When X is zero, meaning no allophanate crosslinking occurs, equation 8 reduces to the more familiar relation for the simpler 3,2,1/2 system. Reduction further to the familiar Flory expression for 3,2/2 systems when $\mu = 0$ has been demonstrated before (3).

Elimination of P_{NCO} between equations 8 and 3 gives the following expression in which the two parameters, P_{OH} and X (which are difficult to measure directly and accurately) are given in terms of ρ and R (which are measured when a formulation is weighed out) and α, which is determinable from the second model, below.

$$\alpha = \frac{P_{OH}^{2}\ (\rho + P_{OH}X)}{R - P_{OH}^{2}\sigma} \tag{9}$$

A Model For Sol/Gel Ratio And Number Of Effective Chains. Whenever a system such as that illustrated in Figure 1 is formulated and cured so that α exceeds 1/2, two consequences occur. (1) Some of the mixture becomes *gel* and some remains *sol*. The gel fraction is conceived of as an infinite network and is insoluble. Sol fractions are mixtures of finite molecules of varying molecular weight. They are soluble. (2) Some of the chains in the gel fraction are secured at both ends and thus are elastically effective in supporting an imposed load and in providing a restoring force for equilibrium deformations. These chains are called *effective chains*. Polymer physicists have established the relationships between the number of effective chains and other properties, such as equilibrium modulus. Sol/gel and number of effective chain measurements will be discussed later.

The purpose of the second model is to determine sol/gel ratios and numbers of effective chains from formulating parameters through the probability relationships explained in the previous section. This model is more general. It should apply to any sub-model of the general 3,2,1/3,2,1 system, including those, such as the urethane model, in which unequal reactivity and other accountable factors operate. The generation of this model starts with consideration of further significance of α to the status of all of the branch units in the mixture.

First, how many branch units are there? When $X = 0$, the number of branch units is $\rho/3$. In the case of the urethane model above, the number of branch units per mole of OH is

$$T = \rho/3 + XP_{OH}^{2}. \tag{10}$$

Next, we ask, what kinds of branch unit are there, and what is their distribution? As Figure 3 illustrates, there are four kinds of branch unit. Respectively, they have 0, 1, 2, or 3 connections to other branch units. By definition, the probability that any given arm of any given branch unit is connected to another branch unit is α. The distribution of these four types in the total polymer mixture is then calculated as the following probabilities:

$$T_3 = \alpha^3 T, \tag{11}$$

$$T_2 = 3\alpha^2(1-\alpha)T, \tag{12}$$

$$T_1 = 3\alpha(1-\alpha)^2 T, \text{ and} \tag{13}$$

$$T_o = (1-\alpha)^3 T. \tag{14}$$

A clue to determining sol/gel ratios is given in the fact that it is not possible for any of those branch units which have zero connections with other branch units to be parts of infinite networks. Thus, all T_o must be in the sol fraction. The other element of this critical determination is in the demonstration by Flory (1) that $\alpha'=(1-\alpha)$ applies to molecular size distributions of post-gelation sol fractions in the same way that α applies to pre-gelation mixtures. Combination of these two elements is as follows:

$$T_{s,o} = T_o, \text{ and} \tag{15}$$

$$T_{s,o} = (1-\alpha')^3 T_s = \alpha^3 T_s, \tag{16}$$

where T_s = the number of branch units in the sol fraction per mole of OH total, and $T_{s,o}$ = the corresponding number of zero-connected* branching units in the sol fraction. Solving together equations 14 and 16 gives

$$\frac{T_s}{T} = \frac{(1 - \alpha)^3}{\alpha^3} \tag{17}$$

Equation 17 is identical to Flory's expression for sol fraction (1) if it is assumed that the concentration of branching units in the sol fraction is the same as that in the overall mixture. The gel fraction is determined by difference,

$$\frac{T_G}{T} = 1 - \frac{T_s}{T} . \tag{18}$$

---

*"Connected" here and in the following text is short for "connected to other branch units."

Now, to get at effective chains, we have to determine the distribution of the kinds of branching units in the gel fraction. This is done as follows: First, we determine the distribution in the sol fraction; then, we subtract the number of each kind in the sol fraction from its respective number in the total mixture. Following the reasoning that led up to equation 16, the remainder of the sol distribution is:

$$T_{s,1} = 3(1-\alpha)\alpha^2 T_s, \tag{19}$$

$$T_{s,2} = 3(1-\alpha)^2 \alpha T_s, \text{ and} \tag{20}$$

$$T_{s,3} = (1-\alpha)^3 T_s. \tag{21}$$

The distribution in the gel fraction is

$$T_{G,o} = 0 \tag{22}$$

$$T_{G,1} = T_1 - T_{s,1} \tag{23}$$

$$T_{G,2} = T_2 - T_{s,2}, \text{ and} \tag{24}$$

$$T_{G,3} = T_3 - T_{s,3}. \tag{25}$$

Any connected arm of any branch unit in the gel fraction is half of a chain. How do we decide which are effective and which are not? First, consider those arms of branch units which have two connections, as illustrated in Figure 3. Those arms are definitely parts of continuing chains. However, their parent branch units function as di-functional units. They will be in the middle of longer chains, and therefore are not needed for counting. All arms of all three-connected branch units are potentially effective half chains, and they would be if they all led to other 3-connected branch units. If this were the case, the number of effective chains would be $3T_{G,3}/2$. However, some of them lead to 1-connected branch units, which are terminating. Each of these cancels a half chain. Therefore, the number of effective chains per mole of OH is

$$N = (3T_{G,3} - T_{G,1})/2. \tag{26}$$

The dimensions of N are: moles of effective chain per mole of OH. For comparison with physically measured values, whose dimensions are moles per cubic centimeter, N is converted to ν_e/W in moles per gram. This approximation is justified, because polymer specific gravity is close to one.

Some Consequences Of The Combined Model. A small computer program was generated combining the relationships of the two models. The parameters of a number of the urethane gumstock formulations that were made for this study are displayed in graphical form here to illustrate the effects of some of the variables.

The major effect illustrated by this model is the possibility of infinite networks formed by the crosslinking from the allophanate reaction alone. This is shown in Figures 4 and 5, which respectively are plots of gel fraction and number of effective chains against extent of OH reaction for a formulation composed of 1.05 equivalents of diisocyanate and 1.0 equivalent of a dihydroxy prepolymer, but no crosslinking agent. At $X < 0.03$, alpha does not reach 0.5, and gelation is not predicted. Notice that both gel fraction and effective chains reach their maximum at $X = 0.05$. This is a consequence of the model and the fact that the formulation was set with $k = 1 + X$ for $X = 0.05$. It is important to point out that this formulation cured. Its data will be discussed below.

Figures 6 and 7 illustrate the same effect with a formulation which contains a crosslinking agent and a prepolymer consisting of 3% monofunctional and 97% difunctional molecules.

The effects of monofunctional additive is shown in Figures 8 and 9. Two changes are readily seen to result from the replacement of 0.05 (out of 0.3) equivalents of trifunctional component with the same number of eqivalents of monofunctional. The beginning of gelation ($\alpha = 0.05$) shifts from 0.9 to 0.87. The possible number of effective chains is reduced by almost one half.

EXPERIMENTAL METHODS

The procedures described here apply to a preliminary investigation of the applicability of the combined model to the prediction of gel fraction and number of effective chains in urethane gumstocks. Correlation of model parameters with the mechanical properties of solid propellant formulations was tested also. For these, no procedures will be described.

Polymer Preparation. Polymers were prepared by urethane cures. Nominally bifunctional hydroxyl-terminated prepolymers plus trihydroxyl crosslinking agents and monofunctional hydroxyl compounds were cured with diisocyanates. The prepolymers used were hydroxy-telechelic polyisoprene (HTPI, 1.98 number average functionality, around 2700 molecular weight, prepared by Union Carbide under JPL contract 951210) and polypropylene glycol (PPG, 1.92 number average functionality, around 2025 molecular weight, manufactured by Union Carbide). Trimethylol propane (TMP, Celanese Chemical) was used as crosslinking agent. The curing agent was 2,4-tolylene diisocyanate (TDI, Du Pont). Ferric acetyl acetonate (FeAA) was used as a catalyst.

HTPI or PPG was mixed with TMP and heated to 140°F. Decanol was then added with stirring followed by TDI and FeAA. After degassing in a vacuum oven for 10 minutes, the reaction mixture was cured in the oven at 160°F for various lengths of time, ranging from three hours to 21 days.

Gel Fraction Determination. For the determination of the extent of gelation, as measured by the gel fraction, two methods of sol removal were used. The most effective method consisted of an automatic soxhlet extraction with benzene solvent. Previous studies had confirmed that 43 hours of continuous extraction were adequate for sol removal by this procedure. Repetitive soak extractions with fresh solvent, generally for a total of 10 days, was also employed in early studies.

Effective Chains Determination. Based on the kinetic theory of rubber-like elasticity (6,7) a convenient expression relating the number of effective chains in a network polymer to the stress-strain analysis obtained from stretching that polymer has been presented in the literature (8) as follows:

$$\frac{\nu_e}{W} = \frac{ml_o}{3A_oR'T'} \qquad (27)$$

where m = initial slope of stress-strain curve,

l_o = unswollen, undeformed length,

A_o = unswollen, undeformed cross-sectional area.

The experimental procedures for carrying out the stress-strain analysis are described in the following paragraph.

First, polymer films whose thickness ranged from 1/16 to 1/8 inch were made in teflon coated molds with the aforementioned curing method. Specimens for stress-strain analysis were then stamped from the film with a dog-bone cutter. The specimens were measured to obtain l_o and A_o; small pins were inserted for viewing the degree of elongation by means of a cathetometer and then the specimens were swollen in suitable solvent, generally benzene or hexane, for approximately 48 hours prior to the elongation tests. Weights were added to the balance. Care was taken to see that the specimen was not overstretched during loading. Several minutes were allowed for the specimen to equilibrate with the new load. The jack which held the bottom of specimen was lowered to adjust the pointer of the balance to the middle of the scale. The new length of the specimen was recorded. At least 15 increments of weight and corresponding elongations were taken for each polymer specimen. From these data, a straight line was usually obtained, which yielded the slope of stress-strain analysis--m in equation 27.

RESULTS AND DISCUSSION

Gumstock Studies. The first and easiest datum obtained from the gumstock formulation studies was the answer to the question, did the sample gel or not after a reasonable time of cure? To a very large degree, the samples separated into gelling and non-gelling categories in a systematic way very similar to expectation from the model. The data for the 400 series of formulations, in Figure 11, illustrate this. The theoretical lines in this diagram are based on the assumption that $X = 0.05$. The dashed lines represent the calculated effect of the small amount of monofunctionality in the PPG prepolymer. The outstanding significance of these results is that the dividing line between gelation and no gel lies between 0.94 and 0.98 (with one exception) for the extent of OH reaction, P_{OH}.

The above mentioned observations do not prove the urethane model; however, they support it. The results of one single formulation #203 definitely prove one element of the model, which is that a crosslink-producing reaction takes place in the absence of trifunctional ingredients. This formulation was composed of 1.05 equivalents of TDI and 1.0 equivalent of HTP (a difunctional prepolymer).

The other data from these tests are gel fraction $G = T_G/T$, and measured effective chains, ν_e/W. What is unknown is the extent of reaction, P_{OH}, and the allophanate factor, X. Ideally, the values of these parameters could be derived analytically from a set of data. However, because of the preliminary nature of this investigation, this was not possible. Instead, the data from each formulation were compared with model-computed parameters in a manner similar to that illustrated in Figure 12 (formulation 405). This diagram illustrates that for each specific value of X, there is a unique set of corresponding ν_e/W and G values. Thus, by plotting the measured data, it is possible to identify the range of X values that fit. this specific case, it is inferred that X lies between 0.05 and 0.08. Once a value of X is determined, it is possible, if desired, to calculate the corresponding value of P_{OH}.

Another way to analyze the correlation between the measured results and the model is shown in Figure 13. As Figure 12 illustrates, the model requires that ν_e/W and G must correspond for a given formulation. A corollary is that it is possible to calculate one from the other. All of the data obtained in this investigation are treated in this manner and plotted in Figure 13, with the assumption that $X = 0.05$, effective chains measured versus effective chains calculated through the model from gel fraction measurements. Considering the experimental accuracy exhibited here, reasonable correspondence is evident.

It is evident in Figure 13 that the precision of sol/gel measurements in this work was considerably lower than that of the effective chain measurements. Furthermore, the error usually ranged toward high values of gel fraction, if the assumption, $X = 0.05$, is correct or nearly so. Most of the formulations which gave this problem contained the polyisoprene prepolymer, HTPI, and it was found necessary in this work to formulate these compositions without catalyst because of pot-life problems. The coupling of this fact with the extra heating given sol/gel samples in the Soxhlet extractor leads to the speculations that these formulations may not have reached as high a cure in the usual treatment for effective chain measurement and that a significant amount of extra curing took place during extraction. This was tested by measuring effective chains of three HTPI samples after different lengths of cure. As the data in Table I show, the above speculation is plausible.

TABLE I

CURE TIME EFFECT ON EFFECTIVE CHAINS
IN UNCATALYZED FORMULATIONS

TIME	ν_e/W		
	Sample A	Sample B	Sample C
7 days	9-12	64-70	36-43
15 days	53-54	109-123	127-146
18 days	78-84	110-132	-----
From Gel Frac.	41-52	286	130-200

A special case of deviation from the model is indicated in Figure 13 by the three sets of data marked M. These are the only formulations that were measured which included significant amounts of the monofunctional ingredient, decanol. At this time, we are unable to account for this problem.

Propellant Property Correlations. It is clear that considerable research will be needed before this model, or improved versions of it, will be ready for use in directly formulating solid propellant binders. For one thing, it is expected that the variables X and P_{OH} should be harder to pin down in the more complex systems that propellant formulations are than in gumstocks. Furthermore, the properties of propellants that are of interest are not the same as the fundamental properties discussed in the previous section. Nevertheless, it seemed worthwhile checking the model against data sets from the previous propellant development studies.

The data plotted in Figure 14 are from a study with polyether-urethane formulations in which modulus was varied by varying the relative fractions of tri-functional and monofunctional OH ingredients. The modulus value used here is the stress at 3.7% elongation. This arbitrary measurement is used in such studies because of the ease with which good precision can be obtained. (These measurements are generally made at 2 in/min on 2 in dogbone specimens at room temperature.) The specific correlation represented in Figure 14 was chosen from a very large number of possible fits as the one having the lowest variance. Remarkably, this fit gives 0.05 and 1.0 as values for X and P_{OH}. The latter value is not easy to believe, in view of the results with gumstocks, but $X = 0.05$ is.

The data in Figure 15 illustrate that correlation of tensile strength (at maximum load) appears to be possible even though the main chain-forming binder ingredients are different materials. (Volumetric loading of solids is the same in these formulations.) Also shown in this graph is another instance of allophanate crosslinking in the absence of tri-functional components. Theory predicts a high modulus in this formulation. A high modulus is indicated in the tensile test results.

GLOSSARY

A_o = unswollen, undeformed cross-sectional area.

G = gel fraction of a polymer specimen.

l_o = unswollen, undeformed length of a polymer specimen.

m = initial slope of stress-strain curve.

N = moles of effective chain per mole of OH.

P = reaction extent.

R = ratio of isocyanate groups to hydroxyl groups in the initial formulation.

R' = gas constant.

T = number of branch units per mole of OH.

T' = temperature, ^{o}K.

W = weight of a polymer specimen.

X = allophanate factor; equilibrium reaction extent of allophanate formulation to that of urethane formation.

Greek Letters

α = degree of branching; the probability that an arm of a branching unit is connected through a series of difunctional units to another branching unit.

μ = fraction of OH contributed by mono-functional components.

ν_e = moles of effective chain in a polymer specimen.

ρ = fraction of OH contributed by tri-functional components.

σ = fraction of OH contributed by di-functional components.

Subscripts

G = Gel fraction of a network polymer.

i (i = 0, 1, 2, 3) = distribution of the type i branch unit (i.e., 0, 1, 2, or 3 connections to other branch units) in the total polymer mixture or the respective fraction.

NCO = Isocyanate groups.

OH = Hydroxyl groups.

S = Sol fraction of a network polymer.

T = A tri-functional ingredient.

U = Urethane groups; or a urethane branch unit.

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FIGURES

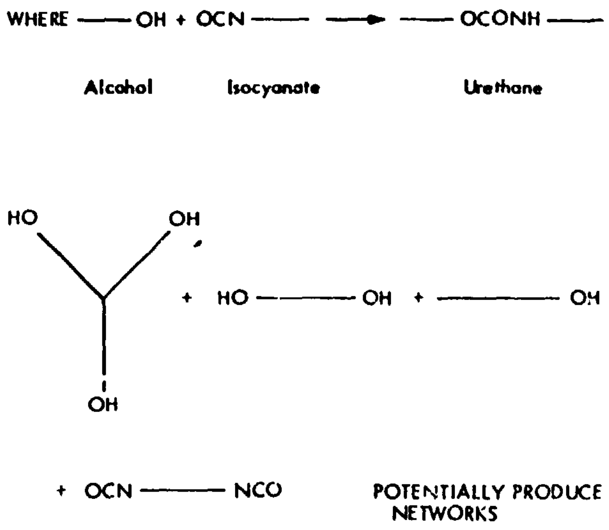
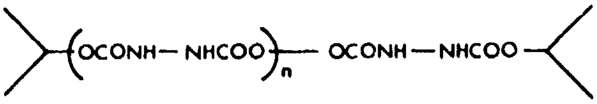
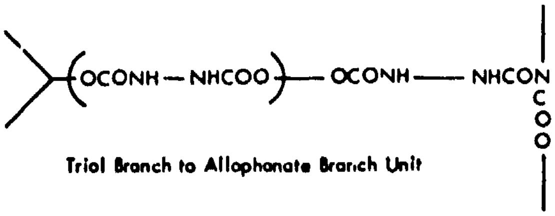


Figure 1. A 3,2,1/2 model typical of urethane binder compositions.



Triol Branch to Triol Branch Unit



Triol Branch to Allophanate Branch Unit

Figure 2. Illustration of the two basic ways of connecting chains formed in the urethane model.

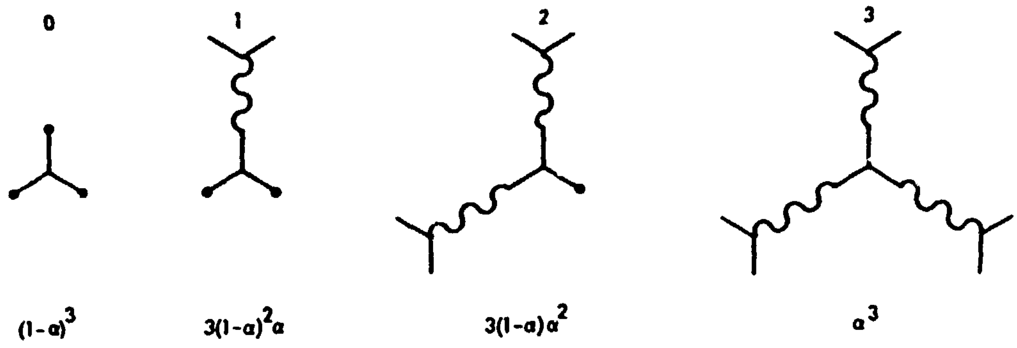


Figure 3. Four possible kinds of branch unit.

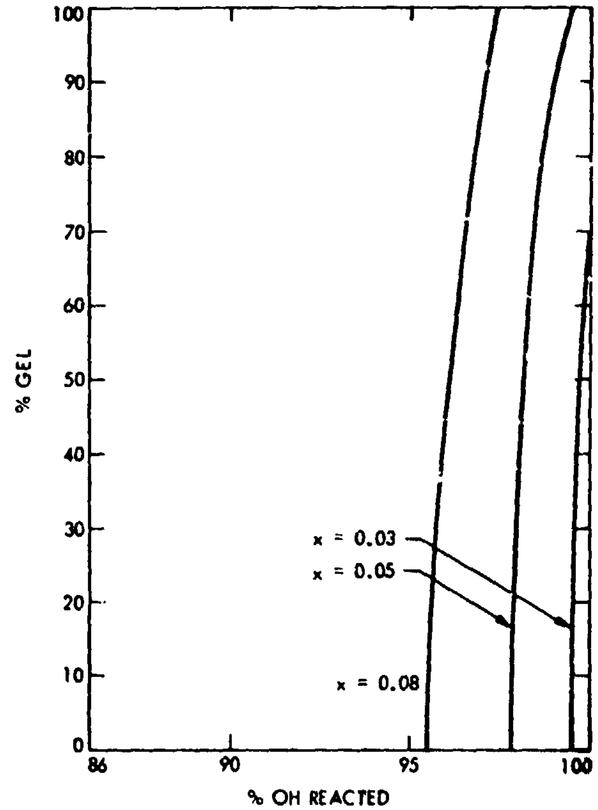


Figure 4. Gel fraction predicted by the combined model for a formulation consisting of 1.05 equivalents of TDI and 1.0 equivalent of HTPI. Effect of X is shown.

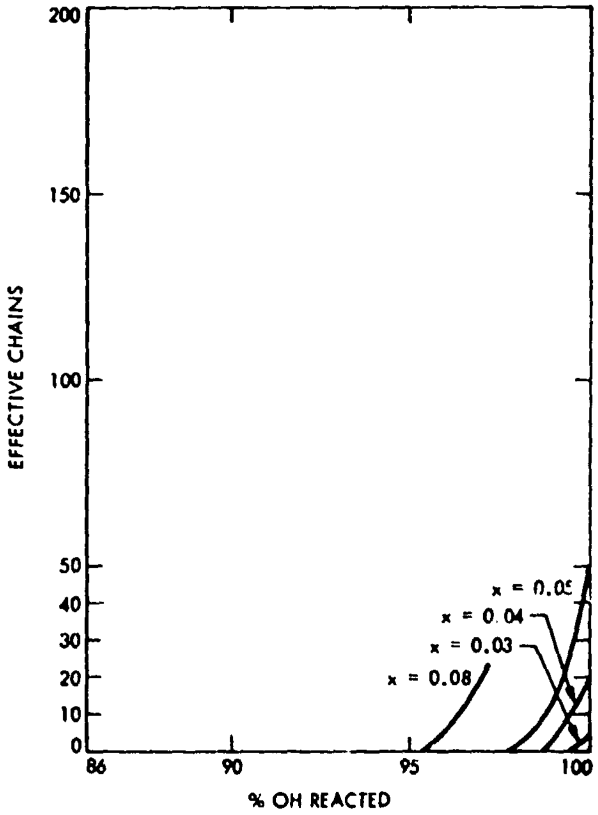


Figure 5. Effective chains predicted by the combined model for the formulation in Figure 4.

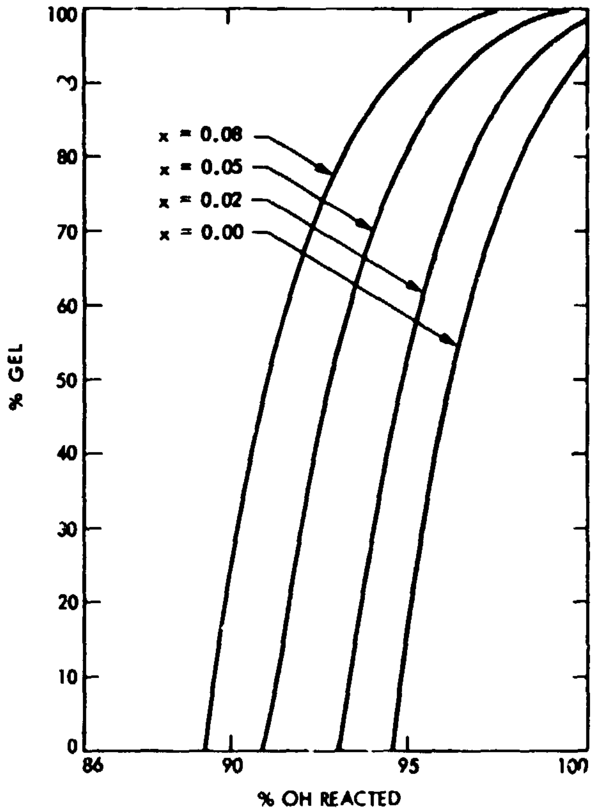


Figure 6. Predicted gel fraction for a formulation consisting of 1.05 equivalents of TDI, 0.8 equivalents of PPG, and 0.2 equivalents of TMP.

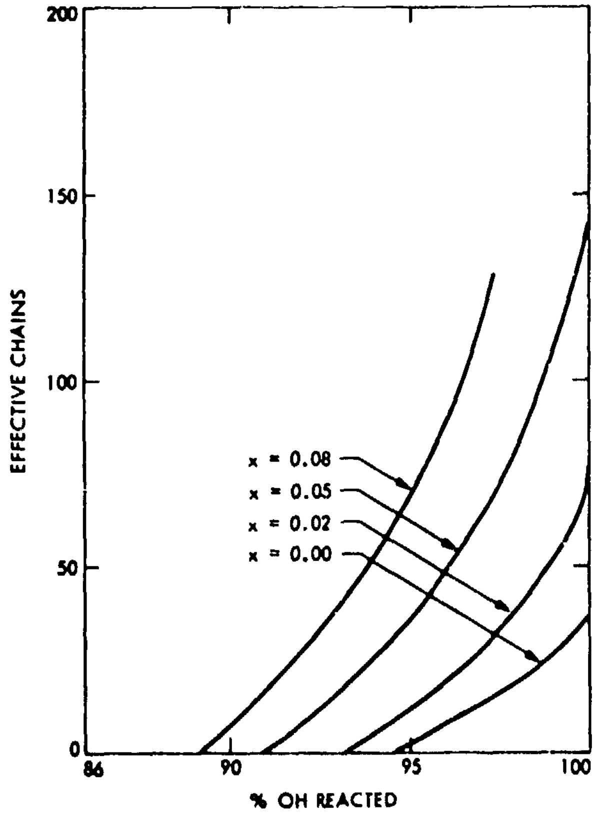


Figure 7. Predicted effective chains for the same formulation as in Figure 6.

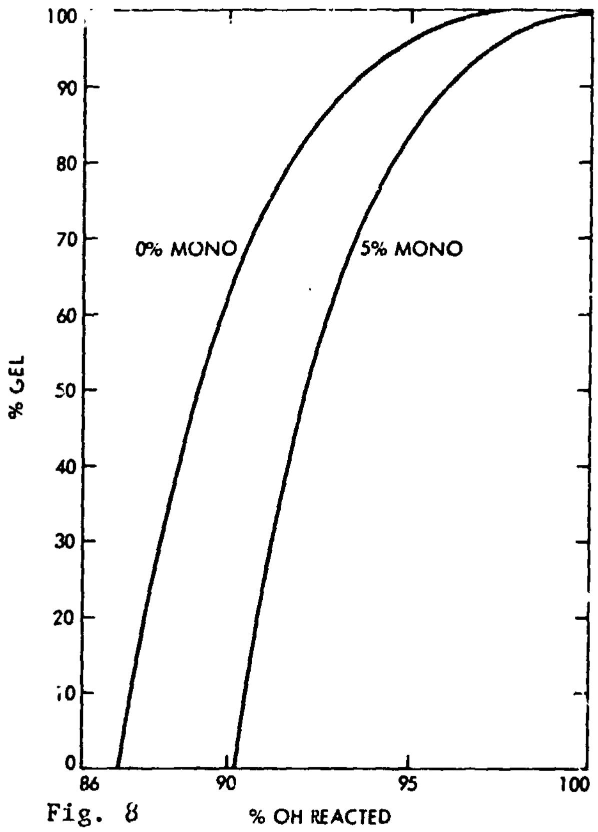


Fig. 8

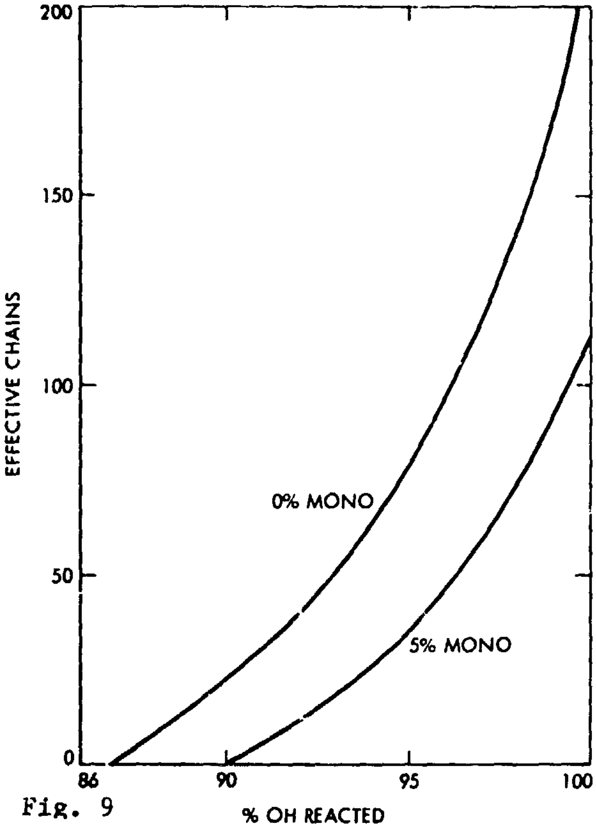


Fig. 9

Figure 8. Effect on gel fraction when 0.05 equivalents of decanol are substituted for 0.05 equivalents of TMP in a formulation originally containing 1.05 TDI, 0.3 TMP and 0.7 HTPI.

Figure 9. Similar effect (as in Figure 8) on effective chains.

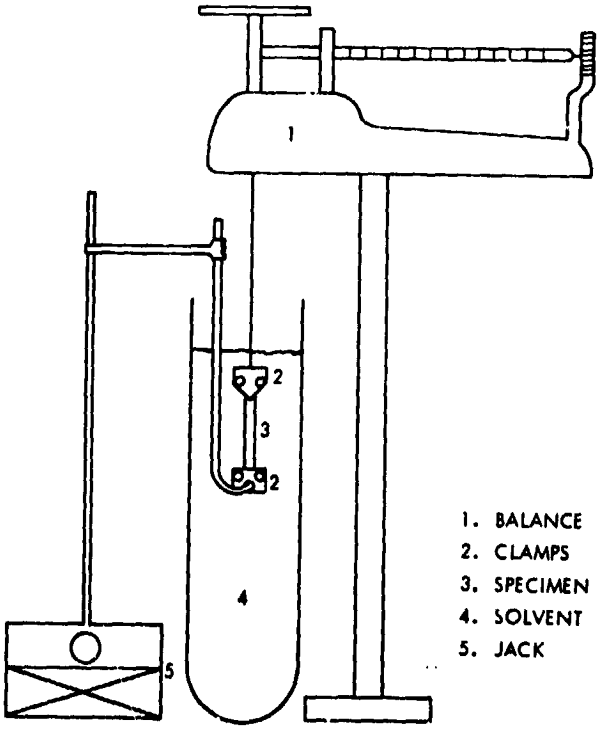


Figure 10. Apparatus for measuring equiliburium modulus & effective chains.

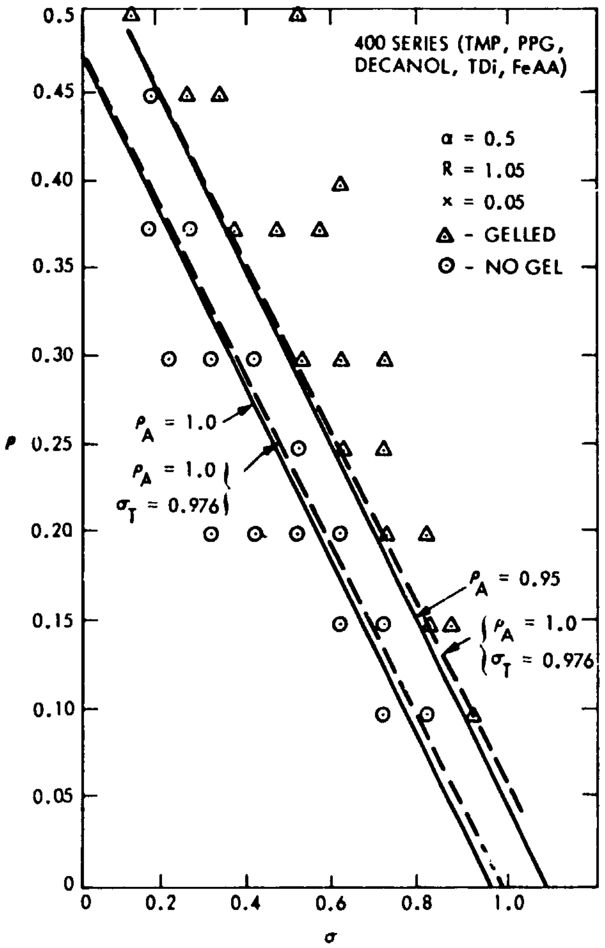


Figure 11. Gel-no gel boundary, theoretical and experimental.

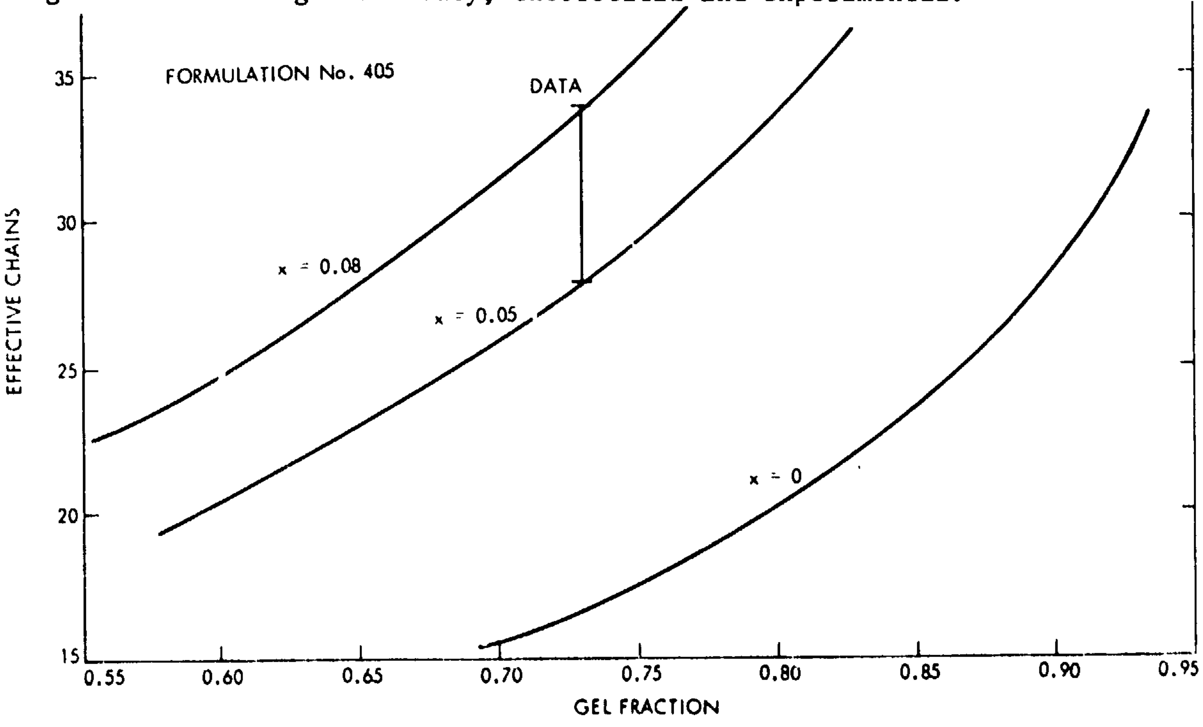


Figure 12. Method to estimate value of X from sol/gel and effective chain.

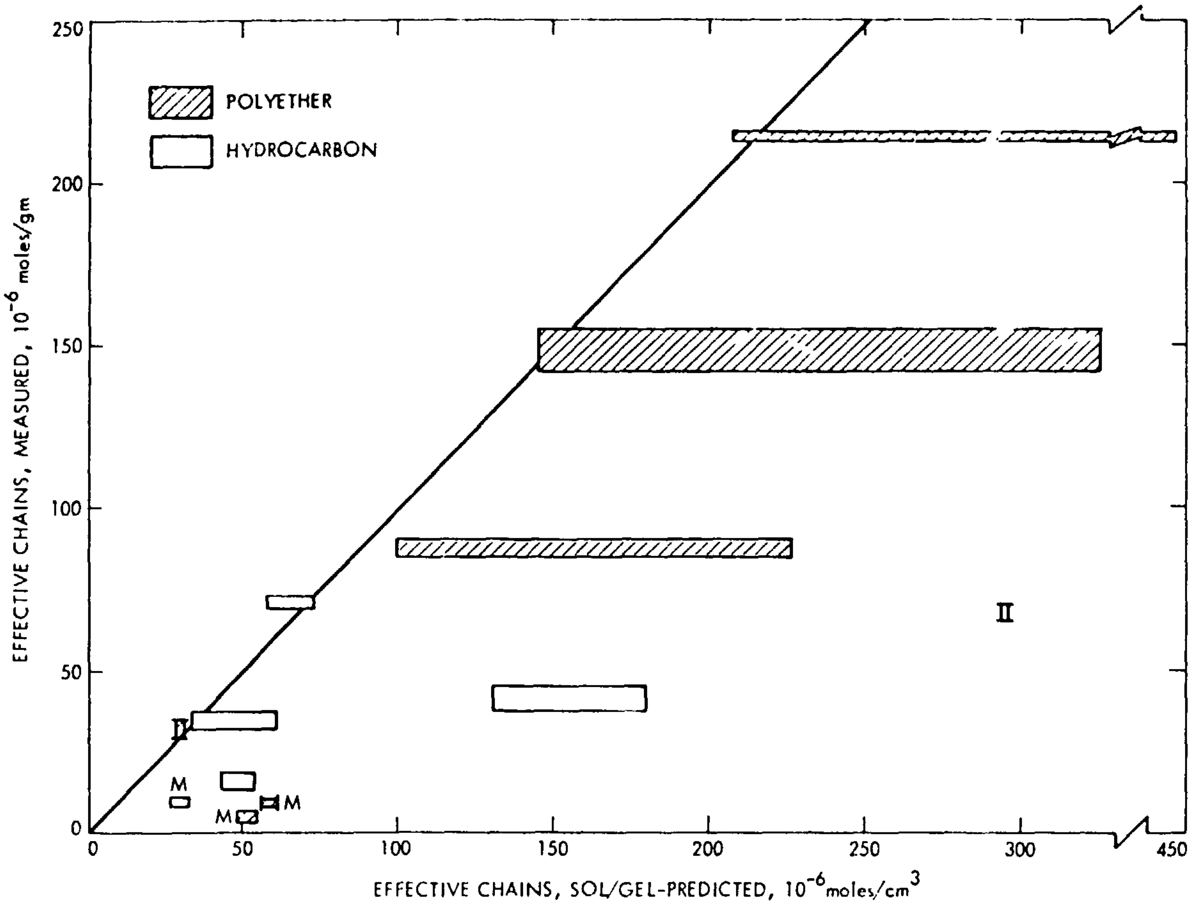
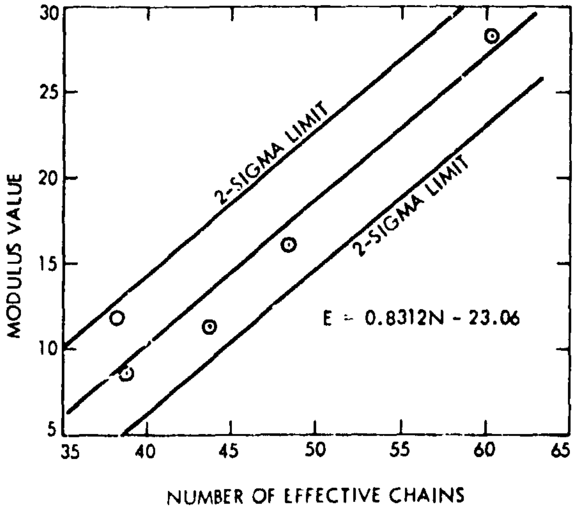


Figure 13. Testing of all experimental data against the combined model, with X assumed to be 0.05.



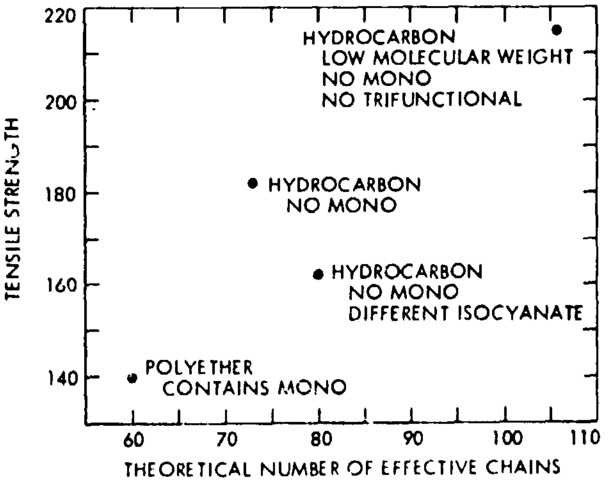


Figure 14. Propellant modulus correlated with number of effective chains.

Figure 15. Propellant tensile strength correlated with effective chains.