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Universal Energy Systems
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MATERIALS LABORATORY
AIR FORCE WRIGHT AERONAUTICAL LABORATORIES
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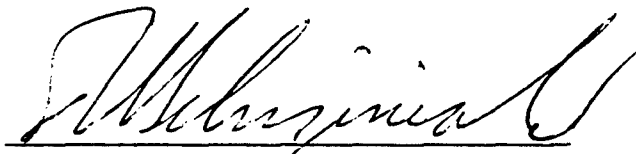
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) This report looks at the nature of toughness, ways to enhance toughness, and discusses the method considered to be most promising for increased toughness of ATX resin systems. The concepts considered were of secondary mechanical relaxation, inclusion of subphases, softening of crosslink density, and finally of increasing loose chain ends. The most promising method proposed was to build in loose chain ends that can dissipate energy in the region of high stress near a growing crack. (over)		

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This report has developed a model of the polymerization process that joins an insight into the post-gelation state and some molecular weight measurements were made to determine the optimum length of loose chains that should be built into the material.

FOREWORD

The major portion of the research reported herein was performed under contract at the Materials Laboratory of the Air Force Wright Aeronautical Laboratories, Wright-Patterson AFB. This work was interrelated with the work of WUD 44, "Failure Mechanisms and Life Predictions of Polymeric Materials," an in-house research effort at the Materials Laboratory.

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This work is Part I of two parts covering the study of toughening mechanisms in high-temperature thermosets.

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Introduction

The Air Force Materials Laboratory and their supported research contractors have prepared and polymerized a number of acetylene terminated monomers (ATX). Some of these materials show intriguing possibilities for structural resins because of their high temperature stability. The number of resins that can be made with this type of monomer is so large that considerable guidance is needed early in the development of structural resins if the full potential of these materials is to be realized.

It has been my challenge to seek methods which could be used to increase the toughness of these resins. Although some ATX resins already show considerable toughness, this mechanical characteristic will probably limit their usefulness unless it can be improved.

This report will first summarize the measurement and nature of toughness. Then it will state some concepts which might be utilized to enhance the toughness and finally, it will discuss the method considered the most promising for increasing toughness. This method involves building in loose chain ends that can dissipate energy in the regions of high stress near a growing crack. A model of the polymerization process is developed and some properties in the post-gelation state are calculated. In order to estimate the length of the loose chains that should be built into the material, some measurements have been made to determine the molecular weight between entanglements for two resins, PPQ-401 and P-1700.

1. Measurement and Nature of Toughness

There are a variety of measurements of toughness; elongation at break or energy stored at break in a tensile specimen; impact resistance of a notched or unnotched specimen; and the measurement of crack growth in specimens of various geometries. The philosophy of physical tests is either to use a test that is modelled closely to service conditions so that the results can be used without extensive analysis or to design tests that measure separately various material constants that can be used to predict performance under service conditions. Tests that neither model service conditions nor measure separate physical parameters are common, but their use should be avoided. In these tests the danger is always present that geometrical or other factors are buried in them that can lead to misinterpretation of results. The typical impact test is an example of this type of test. Here the results are known to depend upon the specimen geometry in ways that are not fully understood. When the geometry is standardized, the results of the impact test should be taken only as indicative of impact strength. To use the impact test to make detailed material comparisons or to predict service behavior would be hazardous.

In recent years, it has become popular to measure crack growth to determine toughness in polymers.¹ Jones et al.² have selected a test of crack growth using a compact tensile specimen that requires only a minimum amount of material. This test was adapted from a similar test used to characterize metals. The measurements are made under mode I conditions, which means that the stresses are perpendi-

cular to the crack plane at the crack tip. This test yields either a critical stress intensity factor K_{IC} or a critical energy per unit of surface G_{IC} . Both measurements require the determination of the crack dimensions which in this form of the test are obtained by comparing the surface markings on the fractured surfaces with the jumps in the measured stress.

For some sample geometries K_I is directly measured from the observed stress and sample shape, while for others G_I is obtained directly. If the material is isotropic and linearly elastic then they are related with the modulus E by $G = \frac{\pi K^2}{E}$. For thick samples, Poisson's ratio also enters.

As an example of the influence of changing the modulus upon toughness, it was found in a study of loading inorganic glass with small particles of a higher modulus that not only were the modulus and K_{IC} increased, but G_{IC} increased also.³ This improvement in G_{IC} by a rigid inclusion may be one of the beneficial effects of the aluminum powder used in some of the epoxy resins designed as adhesives. The original purpose of the aluminum powder was to reduce the thermal expansion coefficient, but the aluminum may also increase the toughness of the adhesive.

It is important to realize that for a given polymer G_{IC} should not be considered as a single number.⁴ A spectrum of values exists which depend upon time, temperature and moisture content just as exists for the other mechanical properties of the polymer. Measurements of G_{IC} which have been made on thermosetting materials are

insufficient to permit predictions of this spectrum or to draw parallels with the results from other tests.

Fracture mechanics has been developed where the determination of this full spectrum may not be necessary. It is assumed that the material in the sample is divided into two parts, the near zone and the far zone. The near zone consists of that material that has or will be highly distorted and disrupted by the crack. The thickness of this layer is indeterminate but is commonly considered to be only a few molecular diameters at most. No attempt is made to analyze the deformations in this material but to characterize its failure by a parameter J_{IC} . This region is considered to be so small that the parameter is thought to be independent of sample size and shape. It may also be relatively insensitive to moisture content and temperature.

The far zone serves as the source of energy to drive the crack growth. If the material is isotropic, linear and elastic, then G and J are identical. On the other hand, if the material is elastic but nonlinear, then one can obtain a quantity J_I from the strain energy U determined by various crack areas by $J = - \frac{\partial U}{\partial a}$.

If the material shows plastic flow, there exists a pseudo energy function which can describe the stretching of a material as distinct from the relaxation of stresses. There is usually little material undergoing relaxation in crack growth measurements, so the pseudo energy function can be used to determine J .

If the material shows a viscoelastic response, it is sometimes possible to model this (often by a power law) so that the viscoelasticity may be taken into account.⁵ Therefore, even if the material

in the far zone is severely damaged, viscoelastic and nonlinear, these characteristics may be modeled and specified so that a J will result that is a measure only of the crack formation proper. This may be only a small percentage of the gross values of G_{IC} measured without taking the various complications into account.

In at least one material, the resulting J had the time, temperature and moisture dependence removed from it by the analysis so that it may be possible to extract a quantity J that is directly related to molecular characteristics.⁶ If this is true in general, then one can design materials for crack resistance with more rationality. The actual crack resistance of a material will include J and also the mechanical characteristics of the material away from the growing crack.

The usual development of resins has required a multiplicity of tests and approaches in order to overcome the confusion resulting from tests dependent upon poorly defined parameters. This duplication and rechecking of tests makes very expensive the development of a new resin that must meet very high performance standards. This is particularly true in the case of the ATX resins because here many different resins are potentially possible. Therefore, it is important to utilize precise tests to guide the development.⁷

Under the most naive of crack models, G_{IC} is the energy of the surface formed from the elastically stored energy. It may be compared to the surface energy determined from contact angle measurements. For some ceramics the comparison is quite good,⁸ but this

is not the case for polymers.¹ Table 1 (page 7) shows the theoretical and experimental surface energies for a group of polymers. Since values of 200 J/m² for G_{IC} are commonly observed in these materials, Table I shows that the correlation of G_{IC} with the surface energy is insufficient to understand G_{IC} . The surface energy includes the energy to disrupt the van der Waal's bonds, but in reality, the growth of a crack will also include the rupture of covalent bonds. Table I also lists Kausch's estimate of the contribution to G_{IC} by bond rupture.¹ This estimate is based upon a generous number of molecular chains that must be broken in order to form a surface. The contribution from this source is also insufficient to explain G_{IC} .

Kausch has also estimated the elastic energy stored in a highly strained chain at the surface. He assumes this elastic energy, unlike the elastic energy in the continuum model is lost to thermal energy. While this latter estimate can be as much as 8 J/m² under the most favorable conditions, it is still insufficient to explain the experimental value of G_{IC} . It may be sufficiently large if it is compared to J_{IC} found according to the method of ref. 5.

Thus, it is clear that most of the energy measured in G_{IC} is energy that is lost in regions which are one or more molecular chain lengths from the growing crack. It may be better to term this quantity the strain energy release rate rather than surface energy. If the material demonstrates plastic flow, large amounts of energy

TABLE 1. MOLECULAR CONTRIBUTIONS TO G_{Ic} .

		SURFACE ENERGY			
		HDPE	PP	PMMA	BADABA
γ_{EXP}	0.031 J/m ²		0.029	0.039	0.039
γ_{THEOR}	0.029		0.052	0.102	--

Measured G_{Ic} is about 200 J/m².

ESTIMATED ENERGY
FROM BROKEN BONDS

2.9

1.3

0.4

--

Estimated Energy Stored Before Breaking in Completely Extended Chains is About 8 J/m²

can be chewed up. Multicrack formation or crazing can contribute significantly to G_{IC} in some materials. In fact, any source of energy dissipation under high strain will contribute to G_{IC} . An ideal material would be one which shows little viscoelasticity at small strains but has an energy loss mechanism that comes into play at high strains. The molecular mechanism to achieve this can be different in different materials.

II. Concepts to Increase Toughness

Secondary Mechanical Relaxation

The impact strength of many homopolymers has been attributed to the secondary mechanical relaxations found below the glassy transition.^{1,9} Since impact strength of a notched sample is essentially crack growth under high rates of loading, the same molecular parameters should appear in G_{IC} with a spectrum shifted in frequency. Some of these mechanical relaxations are unquestionably the result of motion of side groups, freeing of rotations or other rather well-established molecular motions. For other relaxations, tentative descriptions of the molecular motion are offered. Frequently, it is the presence of a relaxation that is correlated with impact toughness, with no quantitative effects computed.

I have seen no quantitative estimate of the expected contribution of this mechanism to the impact strength except an indirect statement of Newman and Strella.¹⁰ They estimated that the increase in impact strength of a rubbery subphase accounts for only about 10

percent of the observed increase in impact strength for a material containing a rubbery subphase. This subphase contributes a loss peak in these materials comparable to those from the mechanical relaxations of secondary molecular motions in other polymers. If this indirect argument is valid, then these relaxations by themselves are insufficient to understand much toughening of materials. On the other hand, it is quite possible that the mechanical relaxations are too small at small strains to explain the increase in impact strength and G_{IC} , but that at high strains, the mechanism becomes important in explaining the increase. This could be true if the relaxation merely indicated the presence of a molecular motion that would become an important energy loss mechanism at high strains. I know of no observations of such nonlinearity with respect to strain for these relaxations.

In any case, the design of molecular structures that utilizes the phenomena of secondary relaxation seems to be beyond present capabilities. One might try a random approach in an effort to build in secondary relaxation. Whether these secondary relaxations would result in improved toughness is an open question. The ATX resins have a small imaginary modulus G'' and yet they show a moderate amount of toughness which seems to imply that it comes from a different mechanism than secondary relaxations. The potential variations possible in the molecular structure, the expense and time required to develop possible resin candidates, and the lack of intermediate goals discourage any attempt to build in secondary relaxation in the absence of a logical approach.

Heterogeneous Mechanisms

The most popular concept to toughen resins uses a rubbery subphase within the resin matrix. This concept has led to the development of impact-resistant polystyrene; polyvinyl chloride and other thermoplastics. It has also been used in some epoxy resin adhesives such as FM-73. The mechanism for the functioning of this subphase has been attributed to the rubber particle either crack-blunting¹¹ or forming a bridge across a crack holding the two sides together.¹² Only slowly do the particles tear so that the crack can open, thereby releasing large amounts of stored energy to heat. The measurements of Scott and Phillips, who found that the addition of a rubbery phase into an epoxy resin can increase G_{IC} from 300 to 3000 J/m²,¹³ are typical of the effectiveness of this mechanism. Unfortunately, this toughening mechanism is not as effective in adhesive layers or in composite matrices as in the neat resin. The value of G_{IC} for an epoxy resin between aluminum plates is reduced to 1500 J/m² in a layer 200 microns thick, and to 1150 J/m² in a layer 100 microns thick.¹⁴ The reduced magnitude of G_{IC} , whether between plates or in a composite, is still considerably larger than the G_{IC} of the neat resin.

The reason for this reduction is not completely clear. It may be only a geometric restriction on the volume where energy absorption takes place. Dr. R. Schapery, in a personal discussion, has pointed out another possible explanation. He describes a calculation of a

rubbery sphere imbedded in a matrix under triaxial tension.¹⁵ The calculation indicates that the spherical surface becomes unstable as the triaxial tensile stress reaches 5/6 times Young's modulus for the rubber. The instability would predict drastic changes in the mechanical characteristics of a material containing rubbery particles at large tensile stresses that would possibly lead to void formation and eventual failure. The presence of rigid walls for adhesive layers or of rigid fibers in fibrous composites promotes triaxial stress. Thus, it may be possible that there are limitations on the effectiveness of such a toughening mechanism in resins used under such circumstances.

The choice of the material for a rubbery phase produces some problems in the ATX resins. For the resin containing a rubbery subphase to show thermal stability comparable to that of the resin itself, a very unusual stability for an elastomer is required. There are candidates for elastomers, such as some fluorocarbons, that show potential usefulness at these high temperatures, but their development is still being explored. Even after the material is selected, it must either be dispersed to a uniform concentration in the uncrosslinked matrix, or it must be adjusted so that it will precipitate at the proper time during polymerization. It is known that for these particles to toughen the resin, they must adhere strongly to the matrix. The fluorocarbons under development, or other elastomers with high temperature stability, may be difficult to design to adhere to the matrix. In any case, the knowledge

required is of a high order. While the use of rubbery particles may be the eventual solution to the toughening problem, it does not appear to be fruitful at present. Currently, sufficient challenge exists in selecting a resin itself, without also looking for an elastomer that would possess the appropriate balance between compatibility and incompatibility to toughen the resin.

Softening of Crosslink Density

The approach to toughen the ATX resins which adjusts the crosslink density and introduces loose chain ends appears to be the most promising at present. Such changes will affect other properties, such as lowering the glassy transition temperature T_g . However, some of the ATX resins show such high values of T_g that considerable tradeoffs can be made without greatly diminishing the attractiveness of the material.

It should be noted that the modulus well below the glassy transition is independent of the crosslink density. A reduction in crosslink density lowers T_g , but if T_g is still above the temperature range of interest, the modulus is independent of crosslinking. Nonetheless, it is proposed that G_{IC} will depend upon crosslink density and the presence of loose chain ends even well below the glassy transition. In part, this proposal is based upon the behavior of epoxy systems in which some formulations utilize such structures to increase toughness. Unfortunately, G_{IC} data are not available for these systems. In part, this proposal is based upon the theory that

the crosslink density is important when high strains lead to failure. At high strains, triaxial forces are believed to permit molecular motions that cannot take place under the normal small strains involved in modulus measurements. Although the proposal is plausible, it has not been checked experimentally. Loose chain ends may not give the desired effect in the ATX resins, but since behavior at high strains is under consideration, the usual measurement at small strains of the modulus and viscoelasticity cannot invalidate this proposed mechanism. Only toughness measurements can test the proposal.

Loose Chain Ends

Several preparative techniques may be used to produce loose chain ends in the crosslinked polymer. One technique is to cure the material incompletely so that some unreacted groups will remain forming loose ends. It is not clear if some of the toughness already present is due to an inability of the material to cure completely because the glassy temperatures are very high. The curing reaction becomes sluggish as the glassy transition temperature becomes comparable to the cure temperature. Higher cure temperatures are of limited effectiveness since thermal degradation takes place at these temperatures. It is possible that some of the differences in elongation at break observed by different experimenters are the result of different cure conditions.

Although an incomplete cure will enhance the toughness, it may be a mistake to design a resin that depends upon unreacted groups for

development of its desired properties. If reactive groups remain in the cured sample it is always possible for reactions to take place that will produce a material more brittle than the designer envisioned. Nevertheless, proprietary epoxy resins based upon MY-720 are being used although it is impossible to cure them completely.

Another technique to produce loose ends is to add a portion of the monomer that has only one acetylene end group. This monofunctional monomer will leave some loose ends which can be calculated from a model to be described later. A monofunctional compound somewhat larger than the monomer can also be added so that the end groups will be longer.

Still another technique would be to add some of the corresponding thermoplastic material. The addition of a monofunctional material, either the same as the monomer or somewhat larger has the advantage that phase separation is not likely since the added compound will be reacted into the network. The disadvantage of this technique is that these compounds must be synthesized. In several instances, the corresponding thermoplastic has already been developed so that it is only a matter of compounding before curing. The corresponding thermoplastic of the ATS resins is P-1700 and for BADABA resins, the thermoplastic is PPQ-401 (Table 2, pages 15+16).

It is thought that these thermoplastic resins are so similar in molecular structure to the corresponding crosslinked resin that they will remain compatible throughout the curing. If they do form a separate subphase, toughness may be increased by this mechanism. The

TABLE 2. TYPICAL CHEMICAL STRUCTURES

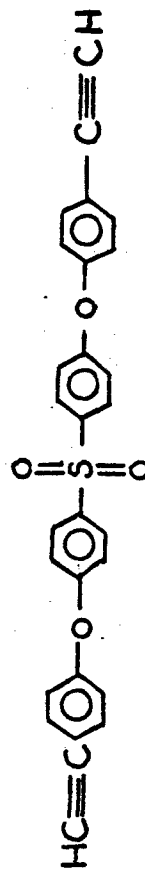
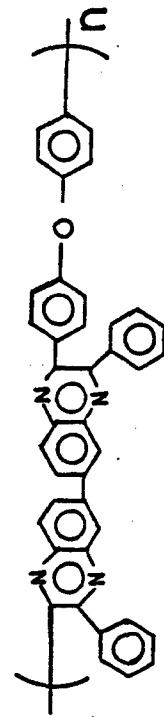
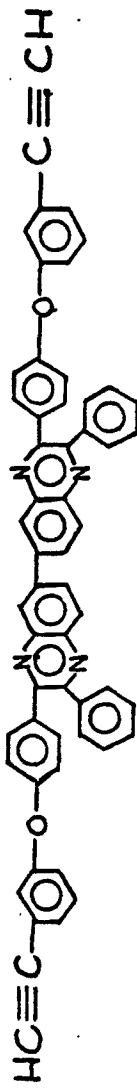
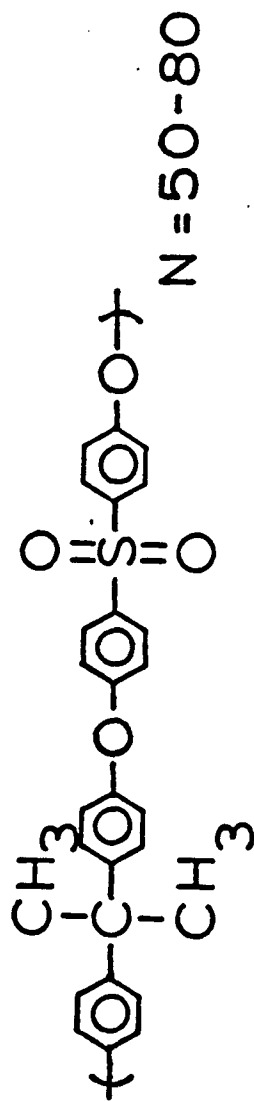
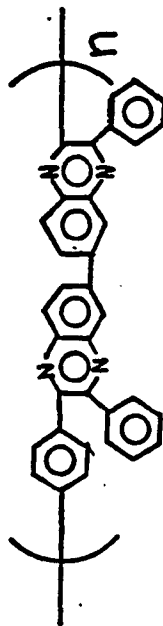


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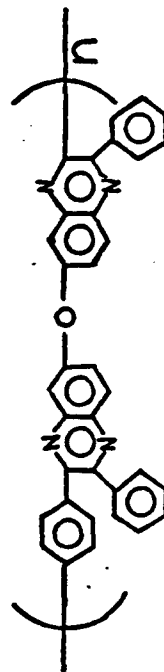


P-1700

N = 50-80



From ref. 22



From ref. 23

development of this enhancement would require a different experimental plan if multiple phases were present than if the toughness depended upon loose chain ends.

Based upon our study of entanglements described later in this paper, a very high molecular weight of a loose end is not needed. The PPQ-401 and P-1700 have such a short molecular weight between entanglements that only polymers with low molecular weights are needed. Thus, the crosslinked network will make up a large fraction of the resin so that only a small number of loose ends would be required to increase the toughness.

The use of mixtures of diacetylene monomers has been proposed in searching for a tougher resin. The mixture of two different monomers is predicted by the author to have properties that are a linear interpolation between those of the two homopolymers. While mixtures may be important in optimizing the properties, no great increase in toughness is anticipated. Thus, trying to increase the toughness of a resin by using a mixture of monomers rather than a single one is not a likely experimental approach.

III. Statistical Model Acetylene Polymerization

The mechanism of acetylene polymerization continues to be actively studied and the reaction products are more closely defined as evidence accumulates.¹⁶ For this study a model was accepted in which it was assumed that clusters of acetylene groups would react together to form possibly, but not necessarily, a polyene. This

reaction is considered to occur rapidly compared to the overall reaction, and the cluster, once reacted, becomes inert and cannot add more acetylene groups. This implies that the character of the crosslinking does not change during the course of the reaction.

Each monomer includes two acetylene groups so that the clusters crosslink together, eventually forming a tightly crosslinked structure. It is assumed that the reactivity of an acetylene group is the same regardless of what happened to the other end of the monomer. No electronic interaction between the acetylene groups for a monomer of the size studied would be expected, but since one step of the reaction is a diffusion to the site of cluster growth, the restriction upon the diffusion of a molecule with one end reacted may possibly affect the reactivity. In this study, it is desired to ignore any such effect. The observation that the monofunctional model compounds produce larger clusters of reacted acetylene groups than our estimate of the cluster size in the resin indicates that this may not be a completely valid assumption.¹⁶

We also assume that no cycles are formed so that any molecular framework is simply connected. This assumption is incorrect as the gel point is approached, but its validity probably does not greatly affect the conclusions of this study. The outcome of relaxing this assumption will be discussed later.

The mathematics used to calculate the approach to the gel point and postgelation have been extensively developed. Flory's combinatorial arguments are correct, but treacherous. The mathematics used below

were developed to study statistics of human and animal populations.¹⁷

Let α be the probability that any acetylene group has reacted, so that the probability that no reaction has taken place is $P_0 = 1 - \alpha$. Let P_n for $n = 1, 2, \dots$ be the probability that n other groups have reacted with the group under consideration. Since these are probabilities, $\sum P_n = 1$. The mean number attached to a given end group is $m = \sum nP_n$. Rather than consider various probabilities of various numbers and how they combine, the probability generating function is introduced $g(z) = \sum P_n z^n$.

The parameter z is artificial and no physical meaning should be attached to it. However, if the substitution $z = e^{-s}$ is made and the summation is replaced by an integration over a continuous probability distribution, then the pgf becomes the Laplace transform of the distribution function. The partition function in statistical mechanics is just a pgf with $z = \exp(-1/kT)$ and the energy is the index n .

The pgf loses no information that is contained in the set of probabilities P_n since the separate probabilities can be regained from the function $g(z)$ by differentiating the appropriate number of times and setting $z = 0$. The normalization condition is the condition $g(1) = 1$ and the mean of the random variable is $g'(1) = m$. Higher moments may be obtained by evaluating higher derivatives at $z = 1$.

While this is convenient, the real advantage of the pgf is obtained in the consideration of a combination of independent events. For example, if $g(z)$ is the pgf of the number of groups attached to an acetylene group, then $g(z)^2$ is the pgf of the combined number of groups

attached to two acetylene groups. It is necessary that the probabilities be independent for this to be true.

If not only the groups attached directly to an acetylene group are considered, but if all of the molecules attached either directly or indirectly are considered, the pgf of this is $\pi(z)$. With the assumption of independence, it is found that

$$\pi(z) = zg[\pi(z)] \quad (1)$$

where the factor z comes from the end monomer and $g(\pi)$ comes from the groups attached at one end, each of which in turn has pgf of π .

When both ends of a given monomer are considered, then the pgf of all groups attached to either end (counting the monomer also) is

$$Q(z) = \pi g(\pi). \quad (2)$$

Therefore, if Equation 1 is inverted to give $\pi(z)$, the resulting function can be inserted into Equation 2 to find the pgf of the number of monomers attached directly or indirectly to a given monomer. The inversion of Equation 1 is

$$\pi(z) = \sum_{n=1}^{\infty} \frac{1}{n!} \frac{d^{n-1}}{dt^{n-1}} g^n(t) \Big|_{t=0} z^n \quad (3)$$

The ability to work out this expression depends upon the choice of g . For example, if a geometric distribution is chosen with

$$g(z) = (1 - \alpha) + \frac{\alpha(1 - r)z}{1 - rz} \quad (4)$$

then Equation 3 becomes

$$\pi(z) = \sum_{n=1}^{\infty} (1 - \alpha)^n r^{n-1} C_n z^n \quad (5)$$

where

$$C_n = \sum_{s=0}^{n-1} \left(\frac{\alpha - r}{r(1-\alpha)} \right)^s \cdot \frac{(2n-s-2)!}{s!(n-s)!(n-s-1)!}$$

While Equation 5 is an explicit expression which may be evaluated, it is usually of sufficient interest to find only the first and second moments of Q . This can be done by taking the first and second derivatives of Equations 1 and 2, and inserting $z = 1$. The number and weight averages of the molecular weights of the polymer may be obtained from these moments, remembering that the monomer is not to be counted in the averages. Thus the quantity $Q(z) - (1 - \alpha)^2 z$ describes the pgf for monomers only within the polymerized portion, rather than Q itself.

The results for a geometric distribution are

$$g(1) = 1 ,$$

$$\pi(1) = 1 ,$$

$$g'(1) = \frac{\alpha}{1-r} ,$$

$$\pi'(1) = \frac{1-r}{1-r-\alpha} ,$$

$$g''(1) = \frac{2\alpha r}{(1-r)^2} ,$$

$$\pi''(1) = \frac{2\alpha(1-\alpha)(1-r)}{(1-r-\alpha)^3} ,$$

$$Q(1) = 2(1 - \alpha/2) \quad , \quad (6)$$

$$Q'(1) = 2(\pi'(1)-1) + 2\alpha(1 - \alpha/2) \quad ,$$

$$Q''(1) = 2\pi''(1) + 2(\pi'(1) - 1)^2 \quad .$$

The gel point is at $\alpha = 1 - r$ where both M_n and M_w go to infinity. As the extent of reaction α goes to zero,

$$M_n \rightarrow \frac{2 - r}{1 - r} \quad (= 3.22 \text{ for } r = 0.55)$$

$$M_w \rightarrow \frac{4 - 3r + r^2}{2 - 3r + r^2} \quad (= 4.07 \text{ for } r = 0.55)$$

Comparisons With Experiment

Pickard et al. have studied the polymerization of some ATX resins at low extents of reaction with the gel permeation chromatograph (GPC).¹⁸ This permits the distribution of molecular weights to be followed as the cure progresses up to the gel point, at least in principle. Unfortunately, the distribution is extremely broad, so that the numbers for the averages depend upon how one estimates the high molecular weight. Thus, Pickard's results contain sizeable experimental errors.

To make comparisons with experiment, the model has one parameter governing the geometric distribution. It was evaluated by comparing the weight and number average at the lowest extents of reaction. This choice yields a gel point that is experimentally consistent with the

measurements. With a more detailed description of the reaction distribution, a better fit could have been obtained at the cost of evaluating more parameters. It was considered advantageous to use a single parameter distribution for simplicity because the effect of additional parameters would influence only the details of the conclusions and not the general trend.

Figures 1 through 9 (Pages 24 through 32, inclusive) show a calculated GPC curve based upon the polymerization parameter $r = 0.55$. The calculation includes the first 20 oligomers and is plotted versus the logarithm of the molecular weight to approximate the dependency commonly found in GPC studies. The peaks are smeared with a gaussian to approximate the finite resolution of the GPC column. The parameter S_2 on the figures is the fraction of the total weight found in the lowest 20 oligomers.

The large peak on the left is the unreacted monomer. As the extent of reaction α increases, the unreacted monomer gradually becomes smaller. The next peak is the dimer which increases a small amount as the reaction proceeds. The higher oligomers gradually merge into a broad peak. The difficulty in determining the molecular weight from the GPC for such a system can be seen. The contribution to the molecular weight can be estimated only to the extent that the broad tail can be measured with precision.

Even after the gel point is reached at $\alpha = 0.45$, the concentration of the lowest 20 oligomers shows no marked change. However, in a GPC column, the gelled material would be retained on the column.

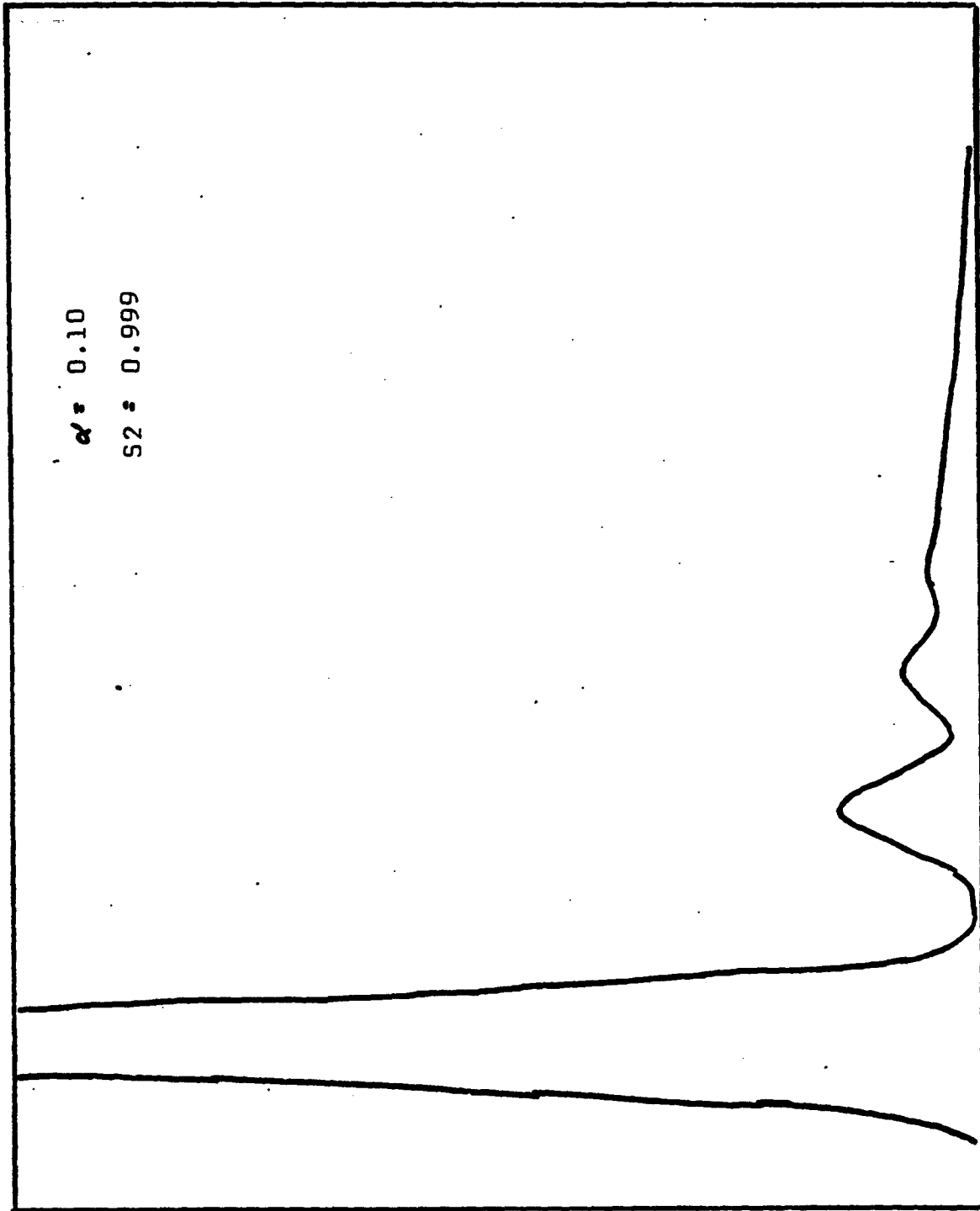


FIGURE 1. GPC CURVE - $\alpha=0.10$; $S_2 =0.999$.

$\alpha = 0.15$

$S_2 = 0.998$

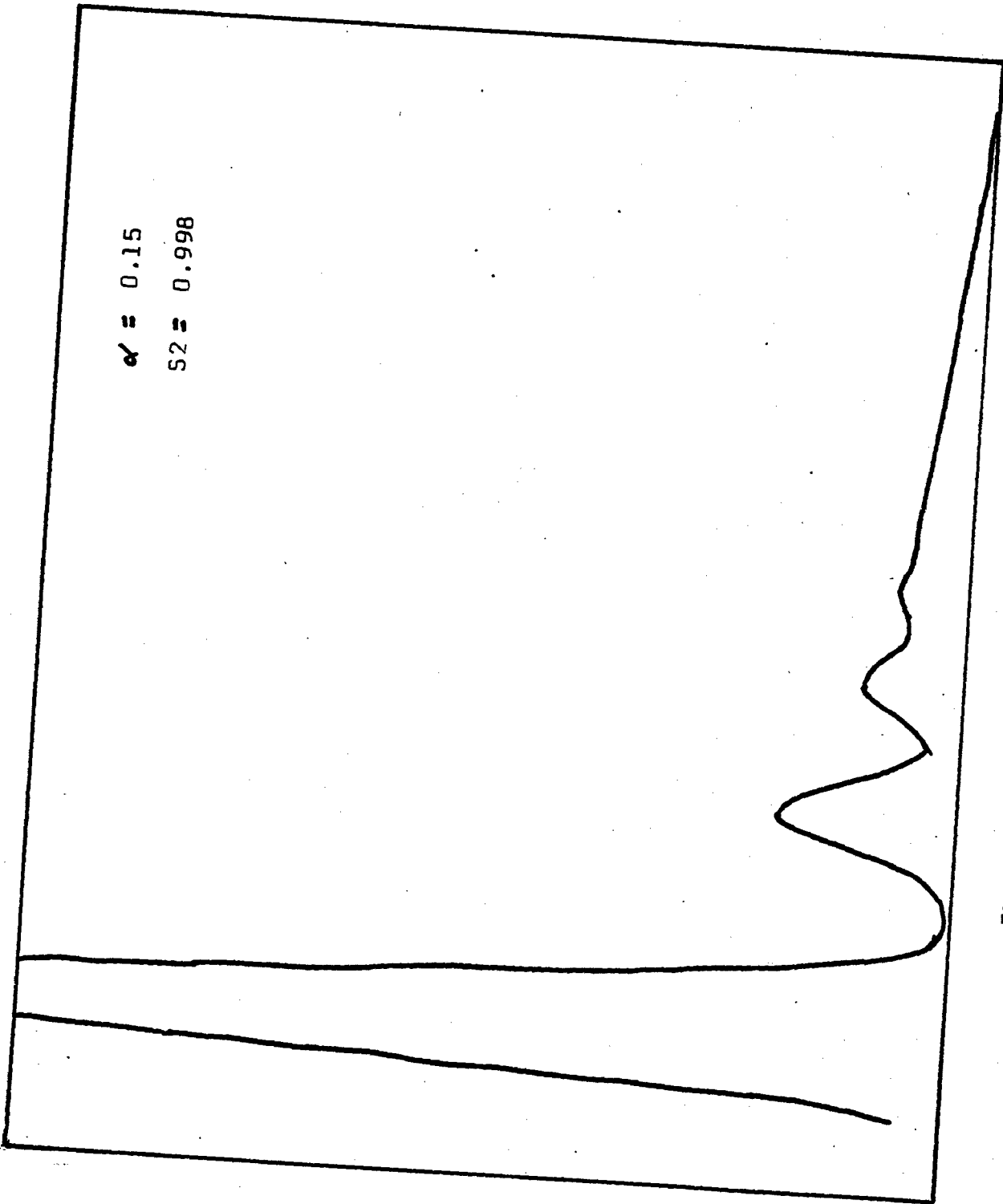


FIGURE 2. GPC CURVE - $\alpha=0.15$; $S_2=0.998$.

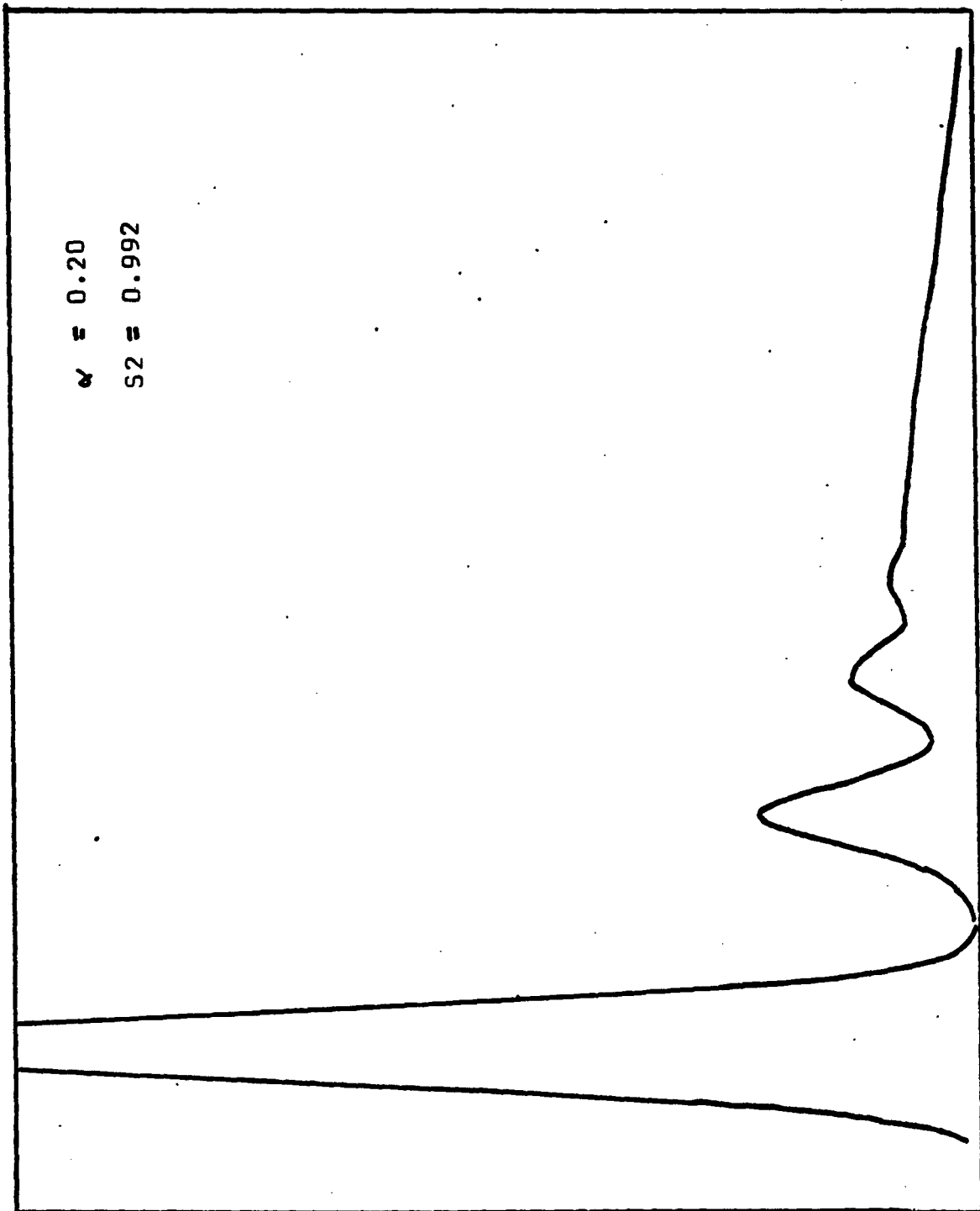


FIGURE 3. GPC CURVE - $\alpha=0.20$; $S_2=0.992$.

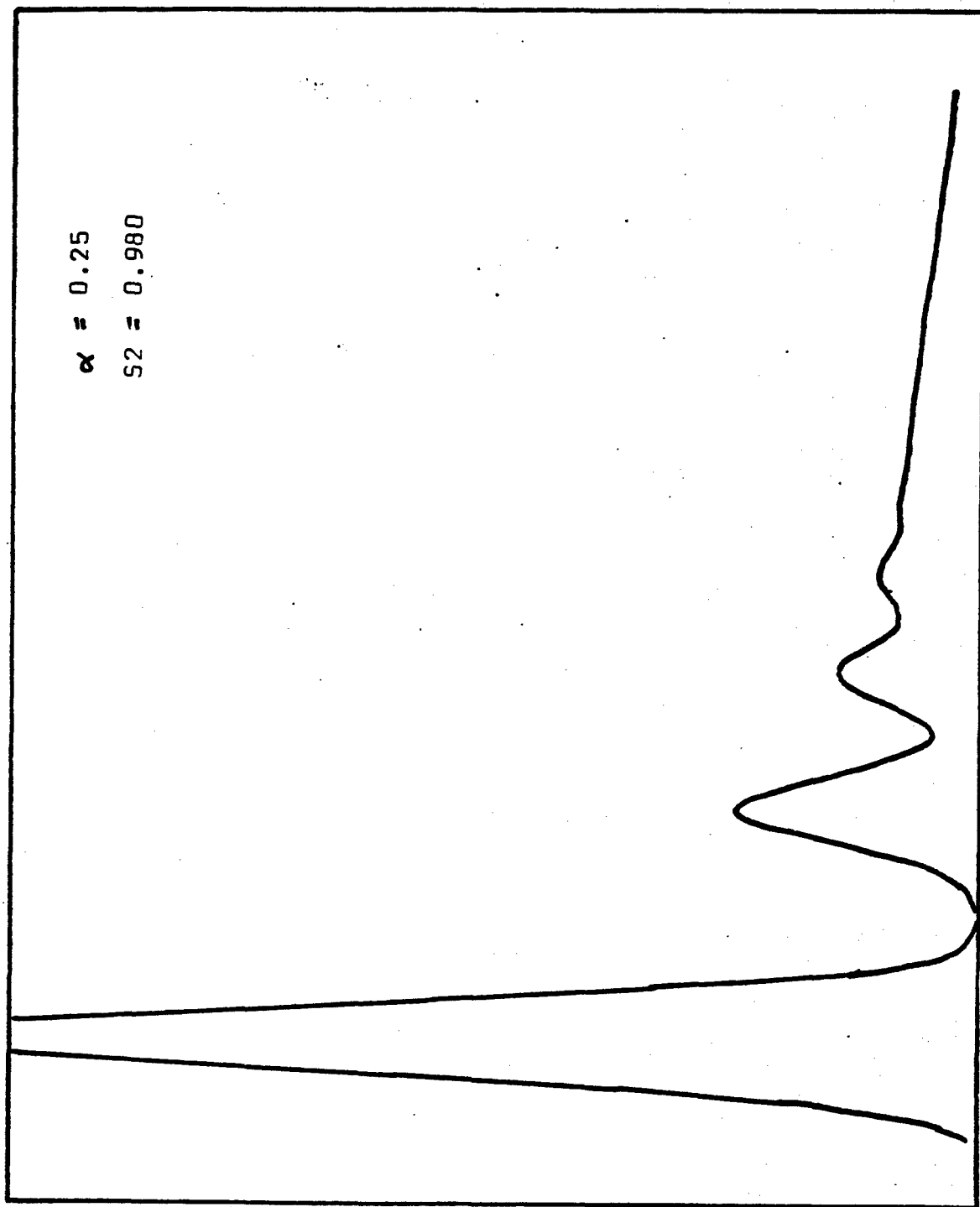


FIGURE 4. GPC CURVE - $\alpha=0.25$; $S_2=0.980$.

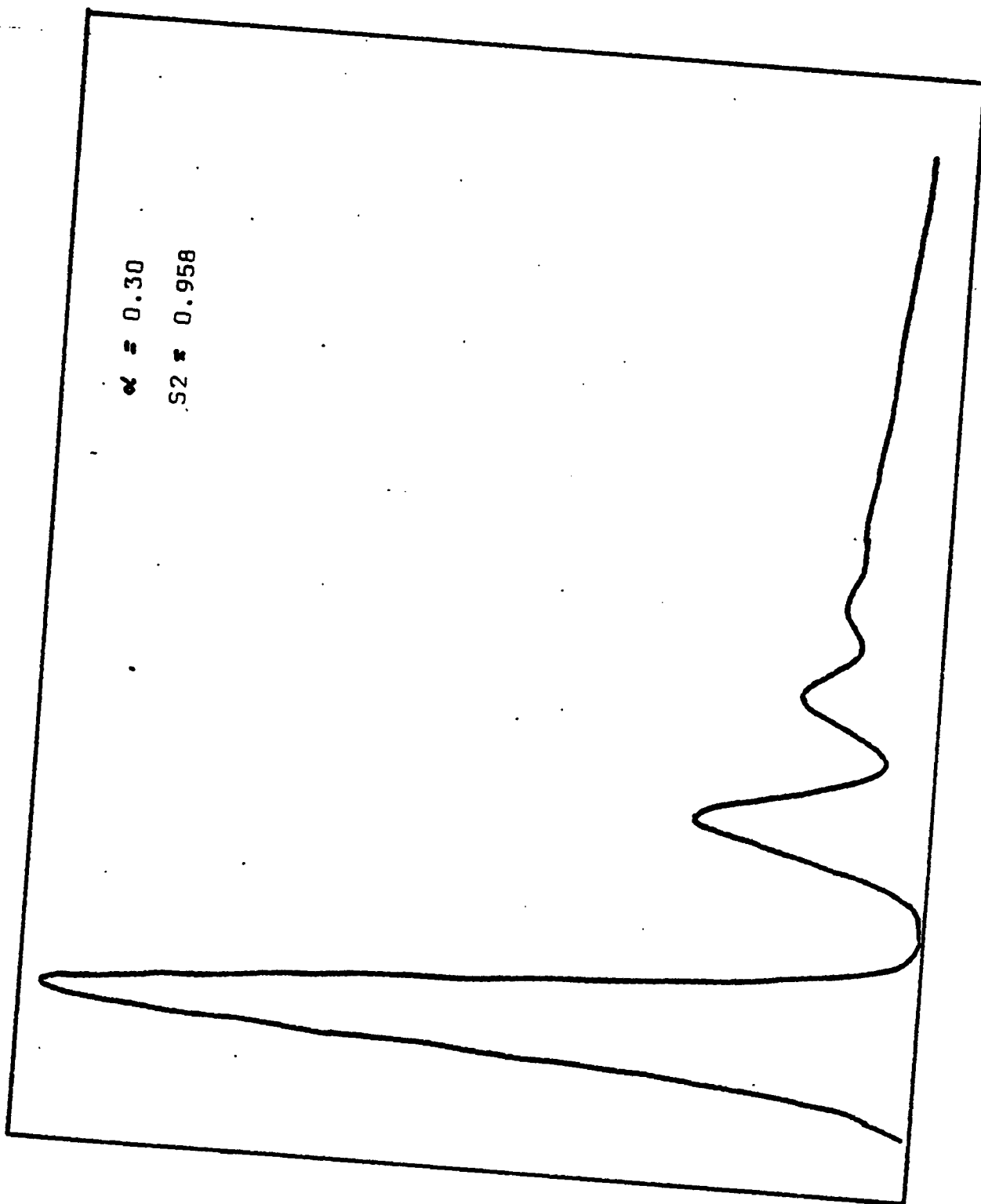


FIGURE 5. GPC CURVE - $\alpha=0.30$; $S_2=0.958$.

$\alpha = 0.35$
 $S_2 = 0.921$

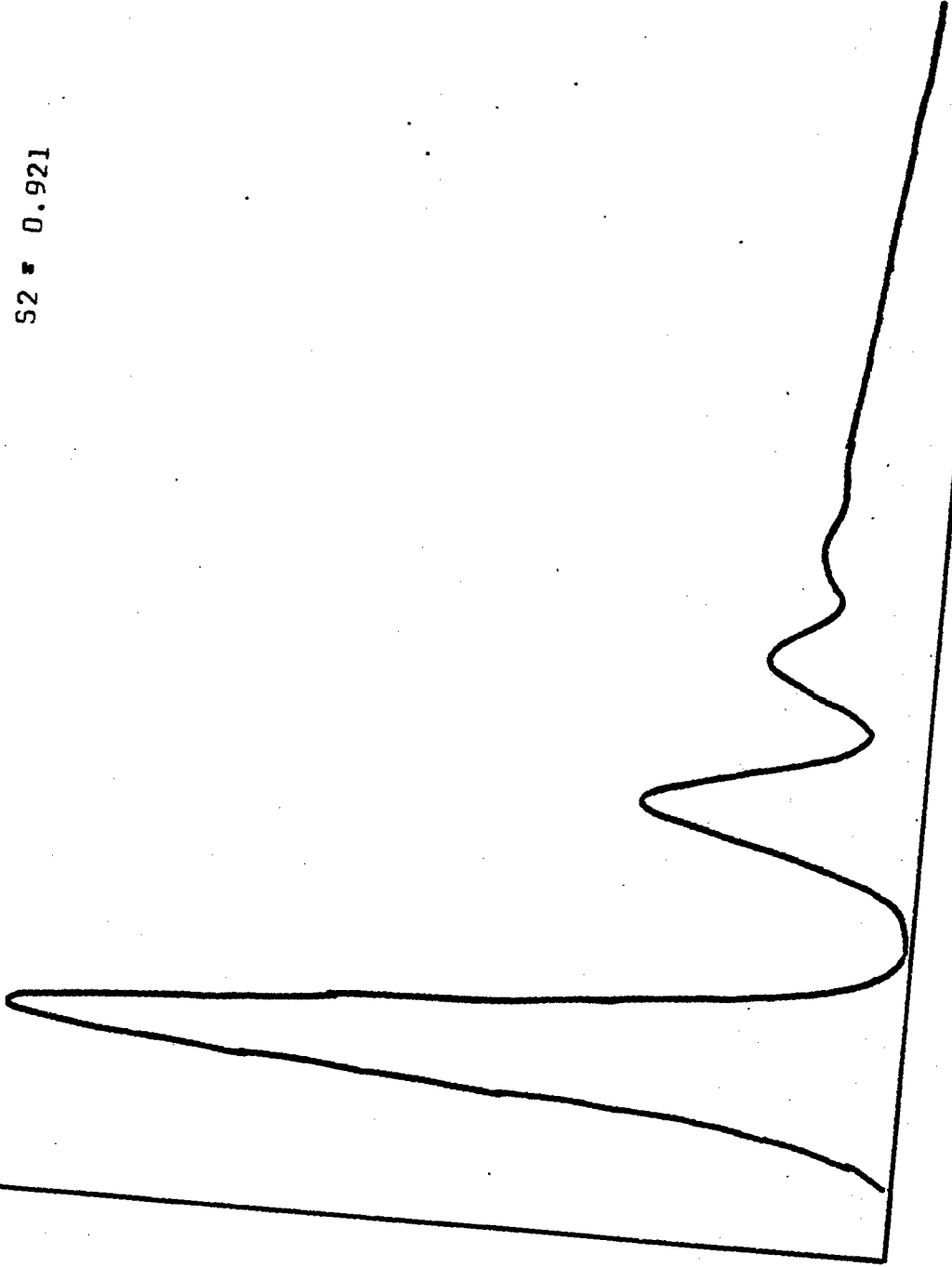


FIGURE 6. GPC CURVE - $\alpha=0.35$; $S_2=0.921$.

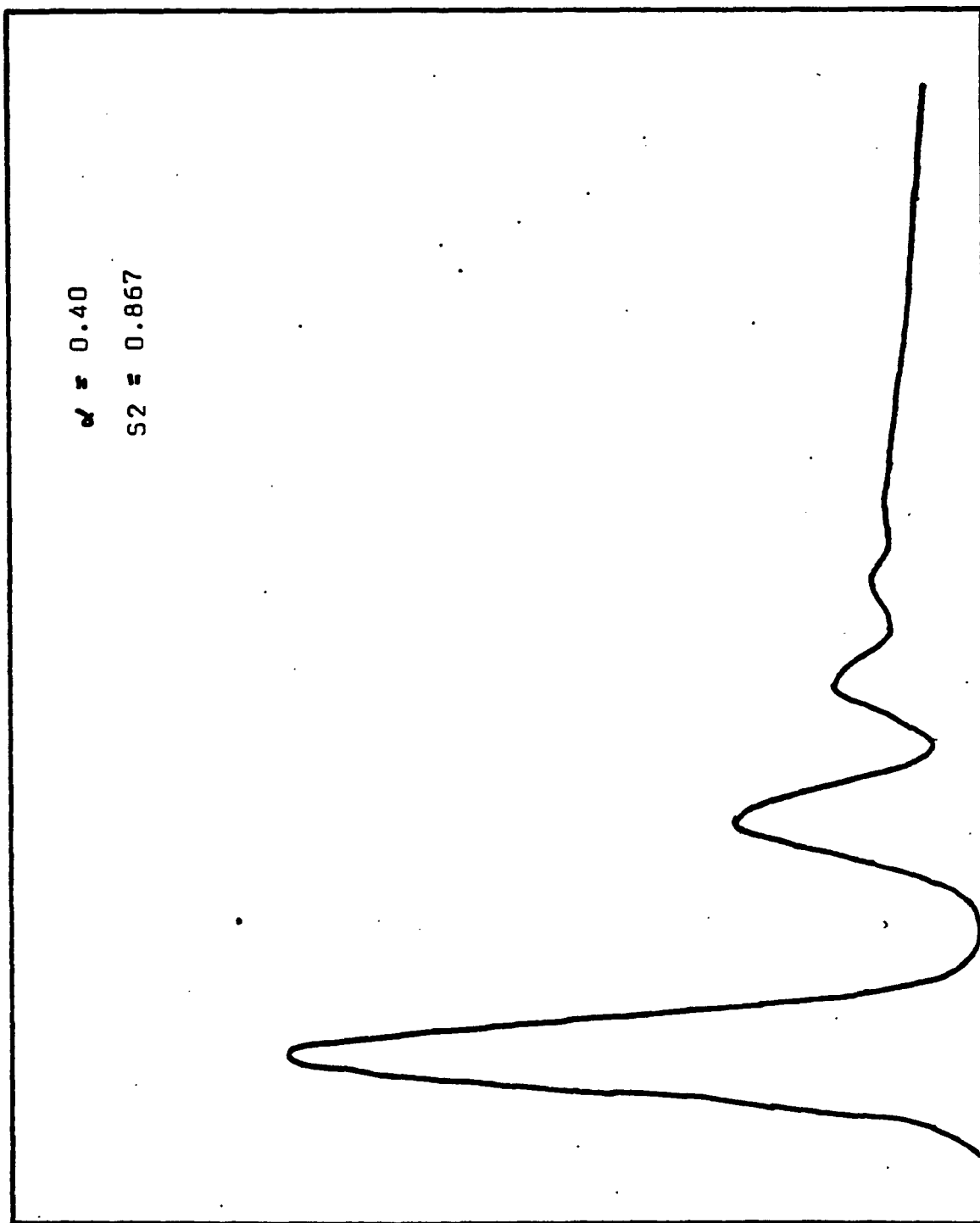


FIGURE 7. GPC CURVE - $\alpha=0.40$; $S_2=0.867$.

$\alpha = 0.45$

$S_2 = 0.794$



FIGURE 8. GPC CURVE - $\alpha=0.45$; $S_2=0.794$.

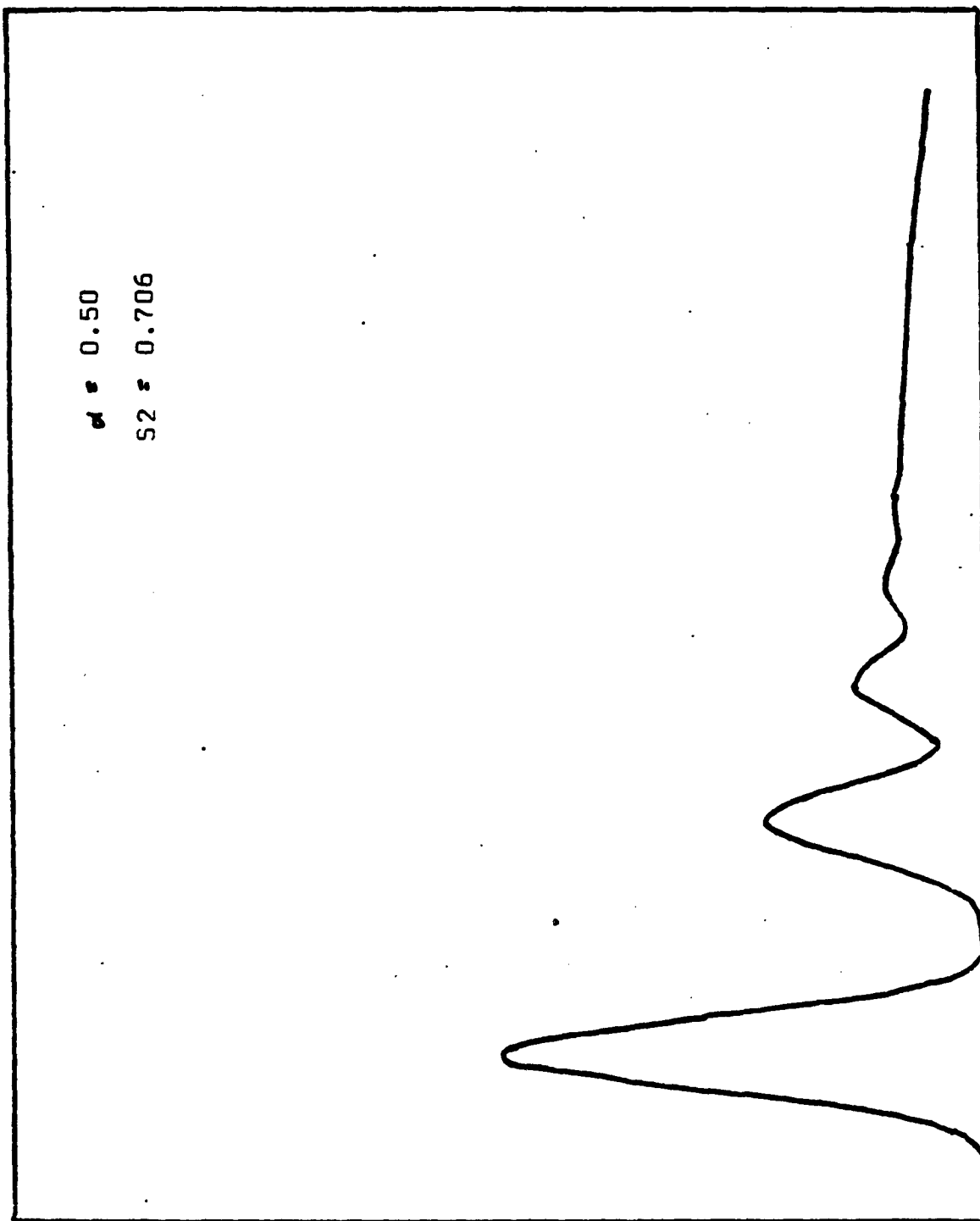
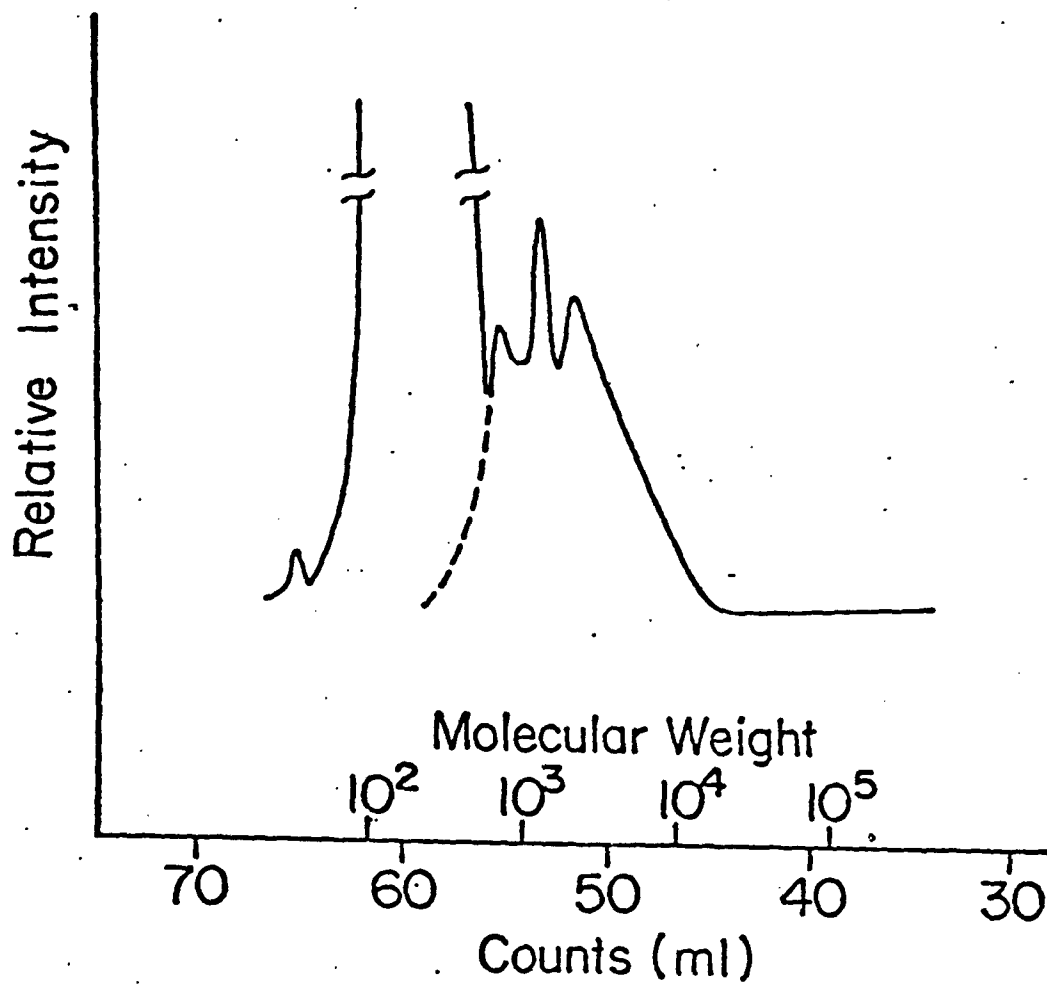


FIGURE 9. GPC CURVE - $\alpha=0.050$; $S_2=0.706$.

There cannot be a single sized cluster produced by the reaction of acetylenes. Figure 10 (page 34) shows a GPC curve of a reaction production carried only to a low degree of polymerization. In addition to the monomer it shows several peaks. Since the reactive product is at a very low conversion, one does not anticipate products formed where the acetylene on both ends of a monomer has reacted.

In order to obtain a distribution with the minimum of adjustable parameters, we assume that $g(z)$ is a geometrical distribution except for $n = 0$. This distribution has a long tail to higher molecular weights already at very low degrees of polymerization. It is the distribution one would expect if the polymerization were limited by some type of termination reaction that is independent of molecular size. It is possibly even close to the distribution one would obtain if the termination is a result of steric effects limiting the size of a cluster, although the assumptions made concerning these interactions will modify the details of the distribution. With the assumption for the form of $g(z)$, the number average, weight average, and ratio of molecular weights are compared with a sequence of runs by Pickard that were stopped at different conversions.¹⁹ These data are shown in Figures 11, 12 and 13 (pages 35, 36 and 37). The scatter in the data is large but it appears that a choice of r between 0.50 and 0.55 would fit the experimental points best.

Choosing a different parameter of polymerization would not influence the Figures 1 through 9 greatly. As long as the reaction produces a broad distribution in each cluster, similar results would be found. However in comparing the curve in Figure 10 (page 34), the



From ref. 18.

FIGURE 10. EXPERIMENTAL GPC CURVE AT LOW CONVERSION.

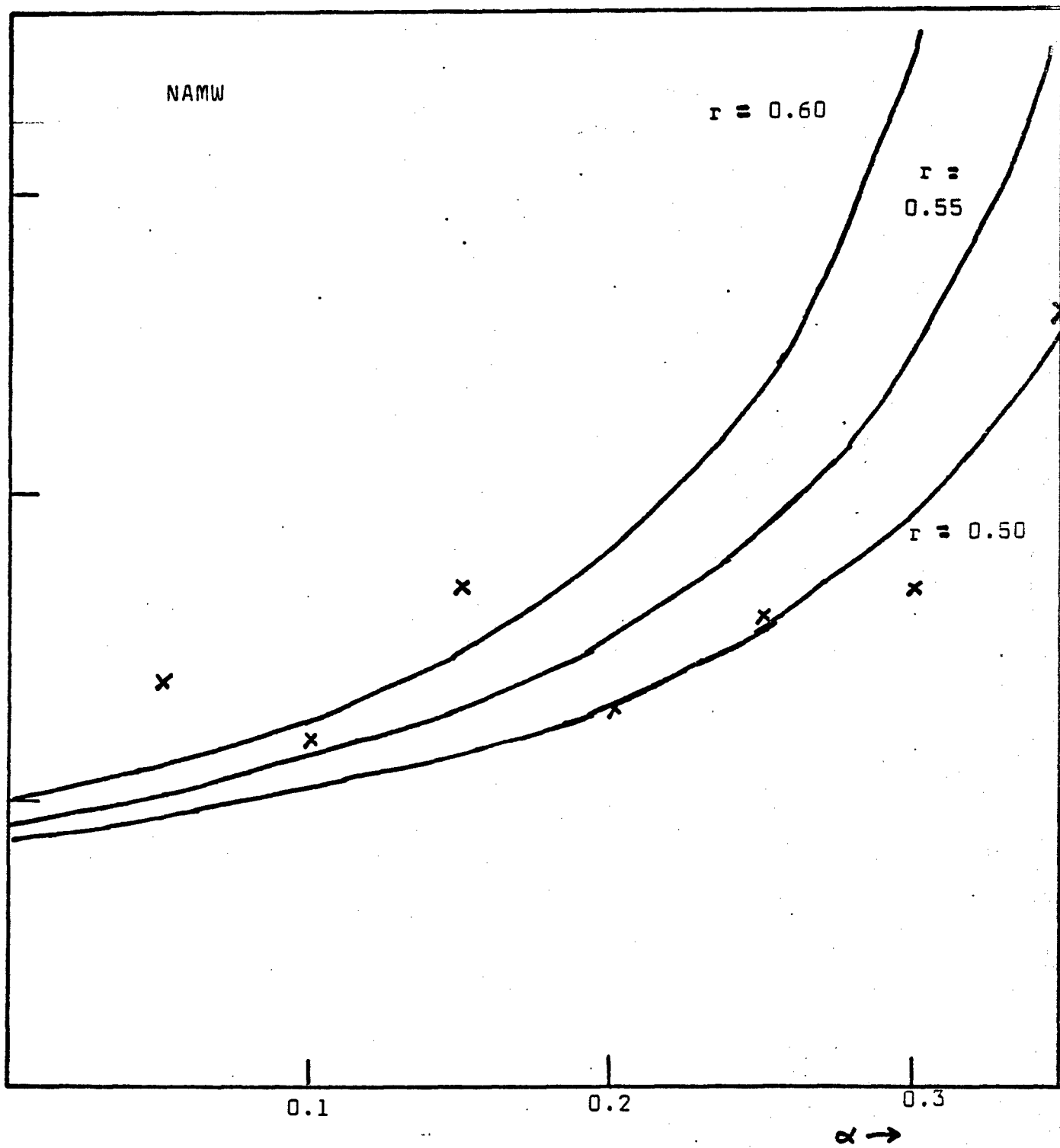
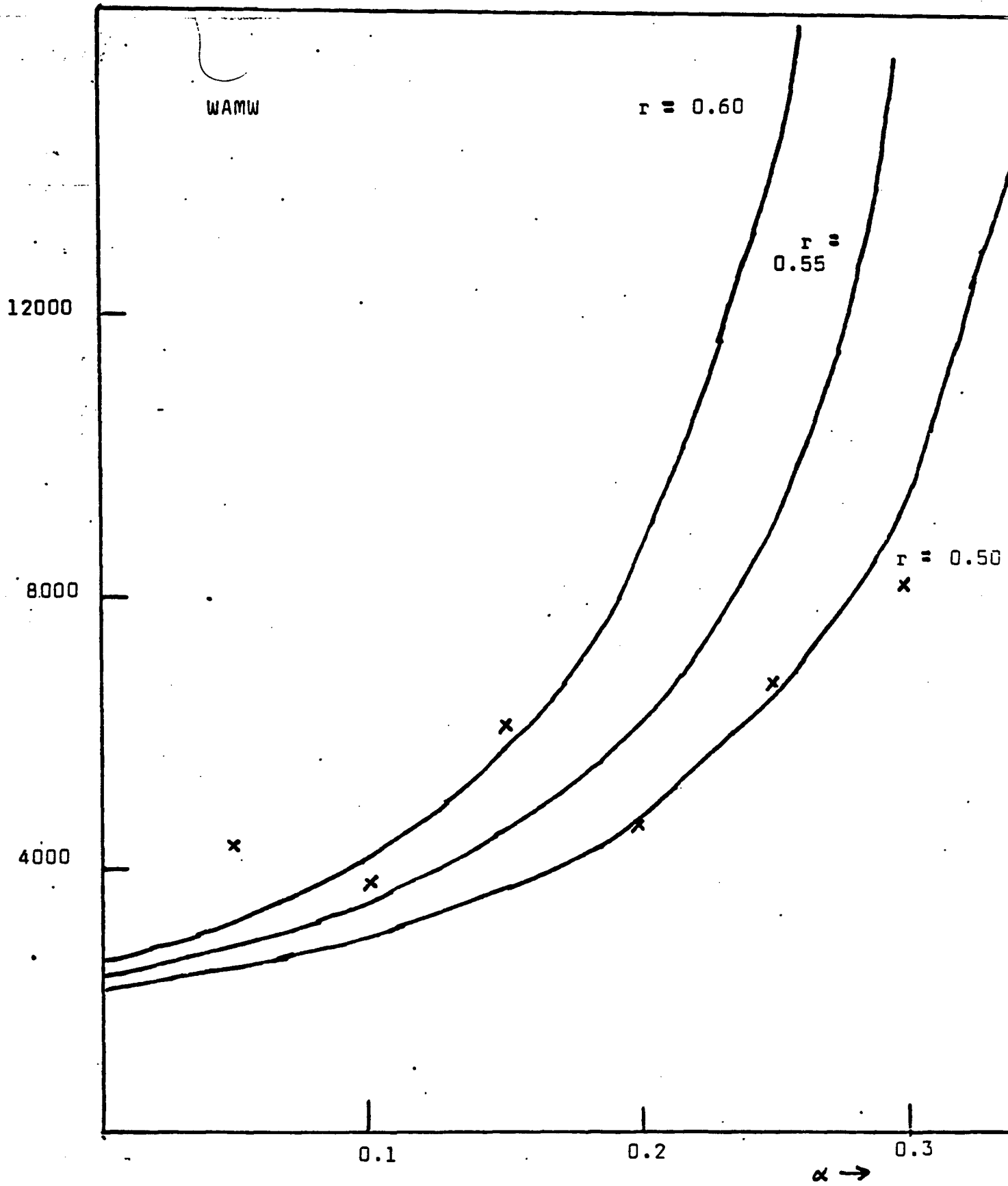


FIGURE 11. COMPARISON FOR NAMW OF THEORY AND EXPERIMENT.



RE 12. COMPARISON FOR WAMW FOR THEORY AND EXPERIMENT.

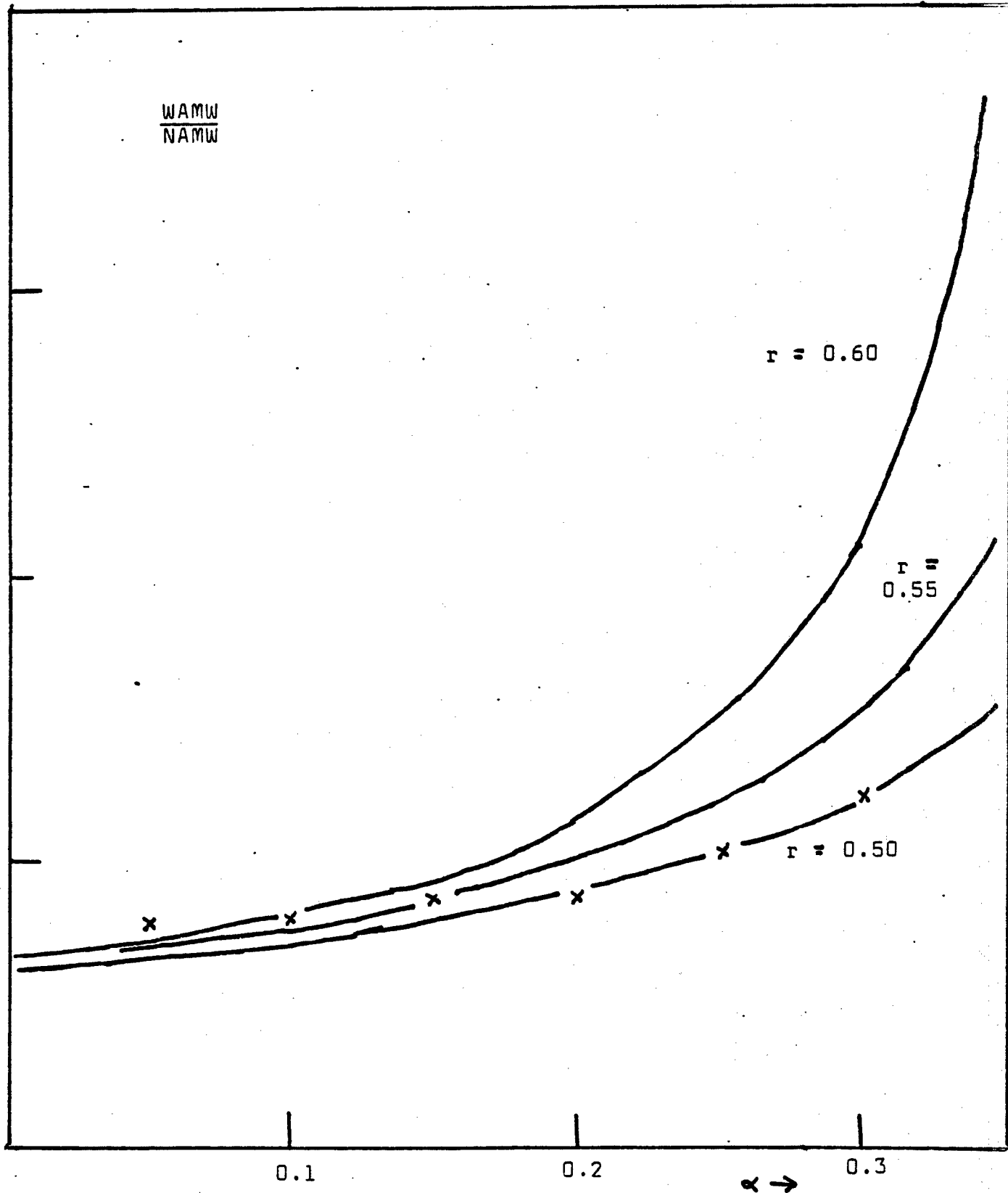


FIGURE 13. COMPARISON OF MOLECULAR WEIGHT RATIO.

enhanced character of the trimer peak indicates that the reaction may favor the trimer more than would be seen for the assumed geometric distribution. This is not surprising because under certain dilute conditions, the trimer product predominates.

The model permits calculations even in the postgelation state. An example is shown in Figure 14 (page 39) where the acetylene groups are almost completely reacted. Most of the molecules will then be linked into the crosslinked structure, but those that are not reacted at both ends can be important to the toughness of the material. The probability that a molecule picked at random would have one end free is indicated by the line $N = 1$. If it has a free end or if it is linked to one molecule which is unreacted at the other end, the probability is given by the line $N = 2$. The probability that an end is not connected to the crosslinked structure but can be attached directly or indirectly to a finite number of monomers is indicated by the line $N = \infty$.

It is seen that even for $\alpha = 0.95$, the probability of loose ends is appreciable. If these loose ends contribute to the toughness, the degree of cure or the amount of monofunctional reagent will be an important factor in the toughness.

The model can make a variety of predictions in the post-gelation state and are inaccessible directly to experiment, but are of great interest in terms of predicting the mechanical properties. The assumptions of independence and simple-connectedness become suspect in the postgelation state but the predictions may serve as a qualitative guide to probabilities.²⁰

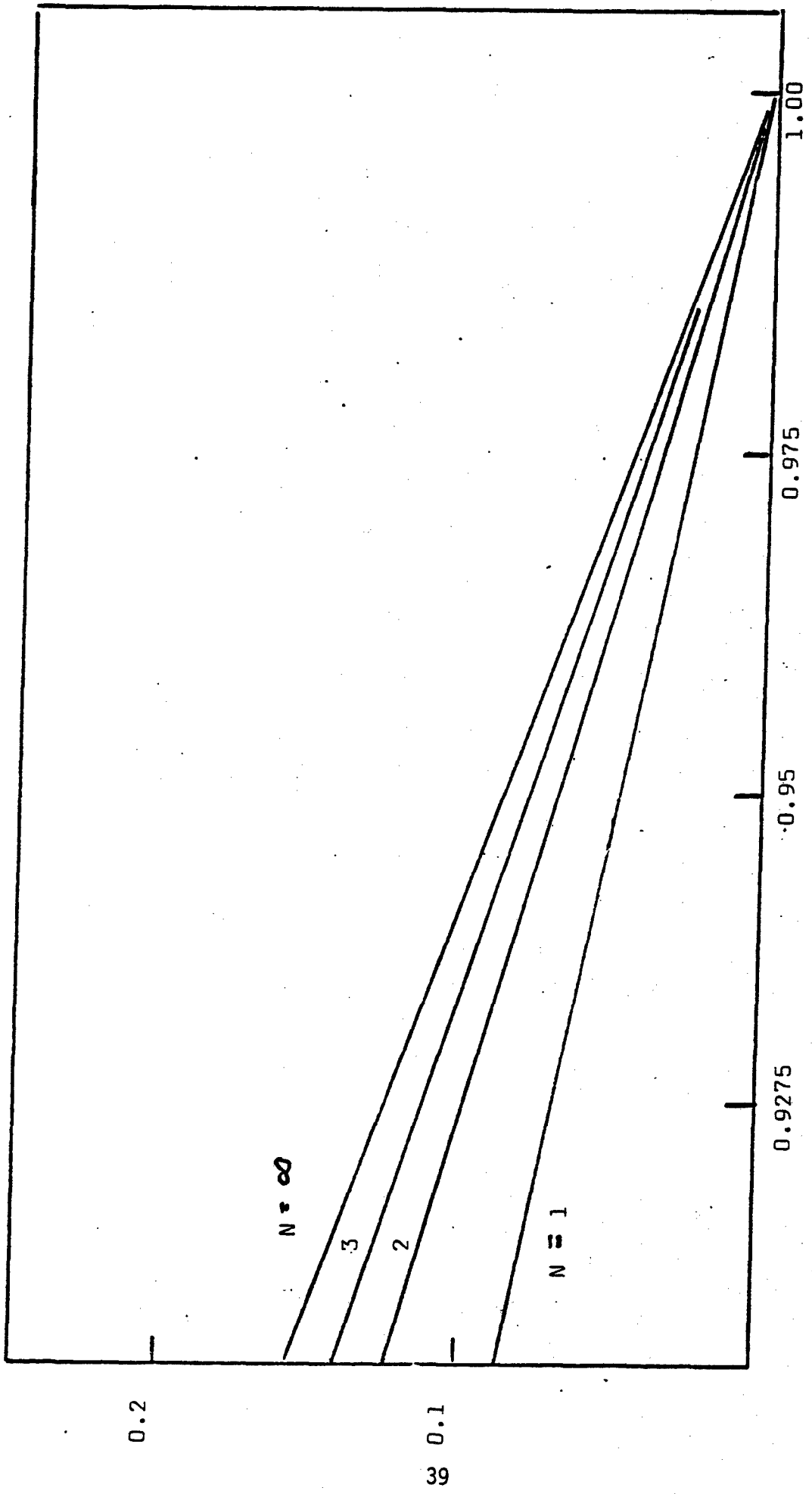


FIGURE 14. PREDICTIONS OF FREE CHAIN ENDS OF N MONOMER UNITS AT HIGH CONVERSIONS.

IV. Estimation of Entanglement Length

Background

The question of the length of these loose ends can be answered from the entanglement length. The classic method for determining the entanglement length of a polymer chain is to observe the viscosity of a series of linear polymers with narrow molecular weights.^{21,22} At low molecular weights, the viscosity is roughly proportional to the molecular weight. At higher molecular weights, it becomes proportional to about the 3.4th power of the molecular weight. This sharp break in the molecular weight dependence of the viscosity determines the critical molecular weight, which has conventionally been expressed as twice the molecular weight between entanglements. This critical value presumably occurs when entanglements convert the separate flow of the individual molecules into a coupled flow. An alternate method is to vary the concentration of polymer in a solution and to observe the concentration at which there is a marked increase in concentration dependence. Although this may introduce some extraneous questions of solvent-polymer interactions, it does not require a series of fractions of known molecular weights. These methods are restricted to unbranched polymers unless complex corrections are made.

The measurements were made in conventional solution viscometers in a temperature bath. Several runs were taken at each concentration to reduce random errors. Systematic errors may occur from the dilution process and from surface adsorption on the viscometer walls. However, even though sizeable errors occur, the magnitudes obtained can be used to design experiments that introduce the short entanglements which relax during high stresses.

The corresponding thermoplastics for BADABA and ATS are PPQ-401 and P-1700, respectively. These thermoplastic materials have the same backbone structure but lack the terminal acetylene groups (see Table II, pages 15 and 16). It is thought that the entanglement lengths for these materials should model that of loose chain ends in the thermosetting material. A determination of the critical molecular weight for these two thermoplastics was carried out.

PPQ-401

Two samples of PPQ-401 were used, one with a known MW of 150,000 (determined by Don Wiff) and another (RR-269-64A) of unknown MW. The first sample was very small, about 0.1 g. The solvent used was 1,1,2,2 tetrachloroethane. The first set of solutions was not sufficiently concentrated to yield a good break in the curve versus concentration. However, judging by a single point above the critical value, the critical concentration was estimated to be near 1.41 g/dl. The polymer was estimated to have a density of 1.2 g/ml so that the volume fraction at the critical conditions was 1.18×10^{-2} . Using Wiff's value for the mode of the distribution of 150,000, this yields $M_c = 1760$. The second sample showed a strong break versus concentration at 2.63 g/dl, or volume fraction of 0.022. The intrinsic viscosities of the two samples were 1.67 and 0.84, respectively.

Hagnauer determined the relationship of the intrinsic viscosity to the molecular weight for a similar polymer. The polymer (Table II, pages 15 and 16) differs in the location of an ether linkage. He found

$[\eta] = 8.6 \times 10^{-4} M^{0.63}$ in m-cresol and after making a theoretical correction for branching, predicted the expression $[\eta] = 2.3 \times 10^{-4} M^{0.76}$ in m-cresol.²³

Russian scientists have studied the polymer with an ether linkage between the two adjacent quinoxaline groups rather than in its location in PPQ-401. They found $[\eta] = 4.0 \times 10^{-4} M^{0.71}$ in m-cresol and $[\eta] = 7.2 \times 10^{-4} M^{0.64}$ in chloroform.²⁴ The four sets of parameters yield estimates for the unknown molecular weight of 56,000, 49,000, 48,000 and 62,000. Taking the last estimate as the most reliable since it is in the most similar solvent, the critical molecular weight of 1360 is obtained. While the exact number is elusive, it seems apparent that the critical molecular weight is very small.

P-1700

Although time did not permit a more precise determination of the entanglement length for P-1700, a preliminary run was made on a single, fractionated sample of MW 56,100. The solvent used was DMAC. The break was observed at $c = 4.055$ g/dl, resulting in a volume fraction of 0.0338 with the assumed density of 1.2. The critical molecular weight is then 1900, which is only slightly larger than that found for PPQ-401.

Comparison With Other Polymers

Most flexible polymers have much larger and longer groups between entanglements. The small size of M_c observed with the polymers in

this study is assumed to be the result of the rigid character of these molecules. Even for rigid chains, however, the reported values are usually larger than those observed in this study. For example, Helminiak and Berry found a value of $M_c = 9120$ for cis-syndiotactic poly (phenylsilsesquioxane), a ladder polymer.²⁵ There have been some aromatic hetrocyclic polymers with M_c between 631 and 668 reported.²⁶ These are polyelectrolytes which in some cases are in a salt-containing solution.

If the entanglement lengths are the same as those observed above, then the length of a dangling chain need not be very long to be effective in producing toughness. This means that a number of dangling chains can be introduced before the glassy transition temperature is lowered seriously. These values should be checked and extended to verify that some effect related to the polymer-solvent interaction is not being studied. Frationated samples of P-1700 are available but the necessary runs have yet to be made.

V. Conclusions

Proposal for Toughening

In order to toughen a resin, it is proposed that seeking a slightly more open crosslinked structure than in the completely reacted diacetylene monomers appears to be the most promising path to follow. It is proposed that some monofunctional reagent be added to the system, rather than stopping at an intermediate state of cure which must then be determined. This addition of a monofunctional

monomer will automatically result in some dangling chain ends. Even though the modulus far below the glassy transition temperature will not be changed, greater toughness is predicted. This must be traded off against the reduction of the glassy transition which will be lowered by an amount proportional to the amount of monofunctional monomer added. The molecular weight between entanglements indicates that the monofunctional monomer should be from one to three times the length of the monomers BADABA or ATS. The amount to be added must be determined by experiment.

References

1. Kausch, H. H., Polymer Fracture, Springer Publishing Co., 1978.
2. Jones, W. B., Jr., Personal communication.
3. Swearingen, J. C., Beauchamp, E.K., Eagan, R. J., "Fracture Toughness of Reinforced Glasses" in Fracture Mechanics of Ceramics, Vol. 4; Editors: Bradt, Hasselman and Lang (1977).
4. Yamini, S. and Young, R. J., "Stability of Crack Propagation in Epoxy Resins," Polymer 18, 1975 (1977).
5. Schapery, R. A., "Nonlinear Fracture Analysis of Viscoelastic Composite Materials Based on a Generalized J Integral Theory," Proc. of the Japan-U.S. Conference on Composite Materials, Tokyo, Jan. 1981.
6. Schapery, R. A., Personal communication.
7. Eddy, S. R., Lucarelli, M. A., Helminiak, T. E., Jones, W. B., and Pickelsimer, L. G., "Evaluating New Polymers as Structural Adhesives," Adhesive Age, p. 18, Feb. 1980.
8. Lawn, B. R., Hockey, B. J. and Weidenhorn, S. M., "Automatically Sharp Cracks in Brittle Solids: An Electron Microscopy Study," J. Materials Sci., 15, 1207 (1980).
9. Hartmann, B. and Lee, G. F., "Impact Resistance and Secondary Transitions," J. Appl. Polymer Sci., 23, 3639 (1979).
10. Newman, S., and Strella, S., "Stress-Strain Behavior of Rubber-Reinforced Glassy Polymers," J. Appl. Polymer Sci., 9, 2297 (1965).
11. Kinloch, A. J., and Williams, J. G., "Crack Blunting Mechanism in Polymers," J. Materials Sci., 15, 987 (1980).
12. Kunz-Douglas, S., Beaumont, P. W. R. and Ashby, M. F., "A Model for the Toughness of Epoxy-Rubber Particulate Composites," J. Materials Sci., 15, 1109 (1980).
13. Scott, J. M., and Phillips, D. C., "Carbon Fibre Composites with Rubber Toughened Matrices," J. Materials Sci., 10, 551 (1975).
14. Bascom, W. D., Cottingham, R. L., Jones, R. L., and Peyser, P., "The Fracture of Epoxy and Elastomer-Modified Epoxy Polymers in Bulk and as Adhesives," J. Appl. Polymer Sci., 19, 2545 (1975).
15. Williams, M. L., and Schapery, R. A., "Spherical Flow Instability in Hydrostatic Tension," Int. J. Fracture Mechanics, 1, 64 (1965).
Gent, A. N. and Lindley, P. B., "Internal Rupture of Bonded Rubber Cylinders in Tension," Proc. Roy. Soc., A249, 195 (1959).

16. Pickard, J. M., Jones, E. G., and Goldfarb, I. J., "The Kinetics and Mechanism of the Bulk Thermal Polymerization of Bis(4-(3-ethynylphenoxy)phenyl)sulfone," *Macromolecules*, 12, 895 (1979).
17. Harris, T. E., *The Theory of Branching Processes*, Springer Publishing Co. (1963).
18. Pickard, J. M., *et al.*, "Thermal Oligomerization of Bis(4-(3-ethynylphenoxy)phenyl) sulfone and 4-(3-ethynylphenoxy)phenyl phenyl sulfone," *Macromolecules*, 13, 1289 (1980).
19. Pickard, J. M., Personal communication.
20. DeGennes, P. G., *Scaling Concepts in Polymer Physics*, Cornell University Press, (1979).
21. Bueche, F., *J. Chem. Phys.*, 25, 599 (1956).
22. Berry, G. C., and Fox, T. G., "The Viscosity of Polymers and Their Concentrated Solutions," *Adv. Polymer Sci.*, 5, 261 (1968).
23. Hagnauer, G. L. and Mulligan, G. D., "Polymerization Kinetics and Characterization of a Poly(phenylquinoxaline)," *Macromolecules*, 6, 477 (1973).
24. Timofeyva, G. I., *et al.*, "The Relative Molecular Weight Distributions for Polyphenylquinoxaline Synthesized in Various Media," *Polymer Sci., USSR*, 21, 67 (1979).
25. Helminiak, T. E., and Berry, G. C., "Properties of the Ladder Polymer Cis-Syndiotactic Poly(phenylsilsesquioxane) in Solution," *J. Polymer Sci., Symposium* 65, 107 (1978).
26. Hanley, T. R., Helminiak, T. E., and Benner, C. L., "Extension of Aromatic Heterocyclic Polymers in Salt Solution," *J. Appl. Polymer Sci.*, 22, 2965 (1978).