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CHARACTERIZATION, RHEOLOGY AND SHEAR INDUCED REACTIONS OF POLY(VINYL ACETATE)

A Dissertation Presented

By

SURENDRAKUMAR HUKAMCHAND AGARWAL

Submitted to the Graduate School of the
University of Massachusetts in partial fulfillment
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Department of Polymer Science and Engineering

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Dedicated

To My Family

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Finally, I would like to thank my friends and colleagues in the Polymer Science and Engineering Department for all the stimulating discussions.

ABSTRACT

Characterization, Rheology and Shear Induced Reactions of Poly(Vinyl Acetate)

(September, 1980)

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Poly(vinyl acetate) (PVAc) has been characterized in terms of its molecular weight, molecular weight distribution and long chain branching. This was done by gel permeation chromatography on-line with low-angle laser light scattering photometry. The effect of shear on long chain branching of PVAc was also investigated. On shearing, 80% of the decrease in molecular weight was found to occur due to scission of long chain branches through the acetate group.

The rheological properties of PVAc were measured in benzyl alcohol and diethyl phthalate over a broad range of shear rates and concentrations. Steady shear viscosity, first normal stress difference and dynamic viscoelastic data were obtained by a Rheometric RMS 7200 Mechanical

Spectrometer. The high shear data (up to 10^6 sec^{-1}) were obtained from a high shear concentric cylinder viscometer. The viscosity-shear data could be superimposed on the Graessley master curve (derived for $\bar{M}w/\bar{M}n = 1.65$ for PVAc) at lower shear rates for all concentrations but not at higher shear rates. The steady-flow and dynamic oscillatory behavior were intercorrelated by a constant shift factor.

To test for mechanochemistry, solutions of PVAc in toluene were sheared in a Virtis-60 homogenizer. The extent of degradation was measured by gel permeation chromatography. The effects of shearing time, stirring speed and concentration were investigated. It was observed that molecular weight decreased and molecular weight distribution narrowed on intense shearing. The chain scission was found to occur randomly. The extent of degradation was more at lower concentration but concentration was not a sensitive variable. This is likely because turbulent flow was generated during stirring and was believed to be the most probable cause for bond rupture.

Attempts were also made to synthesize block and graft copolymers of vinyl acetate with styrene and methyl methacrylate using vinyl acetate macroradical, generated by shear, as an initiator. This project was of limited success.

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CHAPTER I

CHARACTERIZATION, RHEOLOGY AND SHEAR INDUCED REACTIONS OF POLY(VINYL ACETATE)

Introduction

A brief and general introduction is provided for the thesis studies on characterization, rheology and shear-induced reactions of poly(vinyl acetate) (PVAc). Each chapter carries a specific introduction directed to the particular thesis project.

Chapter II describes the molecular characterization of PVAc most widely used. The branching distribution in the original PVAc has been investigated using gel permeation chromatography on-line with low-angle laser light scattering. The effects of chemical and mechanical scission on branching distribution have been investigated. It has been shown that 80% of decrease in molecular weight on shearing is due to the rupture of long branches through the acetate group.

Chapter III presents a study of the temporary, reversible viscosity loss (shear thinning) for rheological measurements on PVAc in benzyl alcohol and diethyl phthalate solutions. It is shown that solvent effects are important even in concentrated solutions. The applicability of the Graessley viscosity-shear rate master curve for branched PVAc is examined over a wide range of shear rate and concentration. The steady-flow and dynamic oscillatory behavior of PVAc solutions are shown to be intercorrelated by a constant shift factor.

In Chapter IV the permanent viscosity loss which occurs when polymer is subjected to high shear, as during processing, is investigated. Presented are the effects of shear on polymer molecular weight, molecular weight distribution and the location of bond rupture during high-speed stirring.

The possibility of producing block and graft copolymers using macroradicals generated by shear as the initiator has been explored in Chapter V. The mechanical synthesis is aimed at the production of block and graft copolymers using polymer-monomer as well as polymer-polymer systems. This project was of limited success.

PVAc has been available commercially in the United States since about 1930.(1) Commercial PVAc is manufactured by an emulsion process. It possesses excellent adhesion to many surfaces. It may be used as a latex or emulsion in application areas such as adhesives, paints, and textile and paper treatments. As an adhesive, PVAc finds application in can labeling, packaging, spackling materials and white glues. It may be used as a vinyl surface coating, paper and fabric coating, in laminating and as a textile finishing treatment.(1-5) PVAc is non-toxic and indeed has been used in chewing gum.(2) It also serves as a major raw material for poly(vinyl alcohol) and poly(vinyl acetal).

PVAc has been chosen for this research because it provides a potential alternative route for producing styrene-vinyl acetate block and graft copolymers that cannot be produced by classical radial copolymerization, as discussed in Chapter V. Its basic rheology also had not been explored.

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CHAPTER II

MOLECULAR CHARACTERIZATION AND EFFECT OF SHEAR ON THE DISTRIBUTION OF LONG BRANCHING IN POLY(VINYL ACETATE)

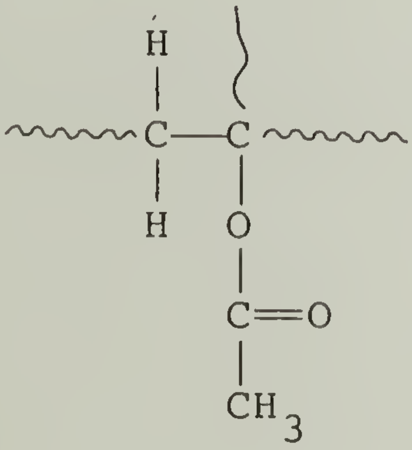
Summary

Poly(vinyl acetate) (PVAc) of $\bar{M}w$ 750,000, $\bar{M}w/\bar{M}n$ 3.85 and $\bar{B}n$ (long branches per molecule) 2.2 was subjected to chain scission by mechanical (high-speed stirring) as well as chemical (saponification and reacetylation) methods to investigate the effect of shear on the branching distribution. The extent of long branching was measured by gel permeation chromatography on-line with low-angle laser light scattering photometry. It was concluded that (i) the branches through the acetate group are long and are ruptured preferentially on shearing, (ii) the branches through the α- and β-carbons are not broken on shearing, (iii) the extent of long branching through the acetate group is about 67% of total branching, (iv) on shearing, 80% of the decrease in molecular weight is due to rupture of the long branches through the acetate group. The remaining 20% of the decrease in molecular weight results from the main chain scission; and (v) the poly(vinyl alcohol) derived from branched PVAc contains a smaller but

nevertheless significant amount of branching.

Introduction

During the polymerization of vinyl acetate extensive branching occurs by chain transfer to polymer and terminal double bond reactions.(1-8) Branching frequency increases rapidly with conversion and causes a concomitant broadening of the molecular weight distribution.(4,9-14) The branch points have been previously shown to exist in three chemically distinct structures, through the α-carbon (structure I), the β-carbon (structure II), and through the acetate group (structure III).(15)



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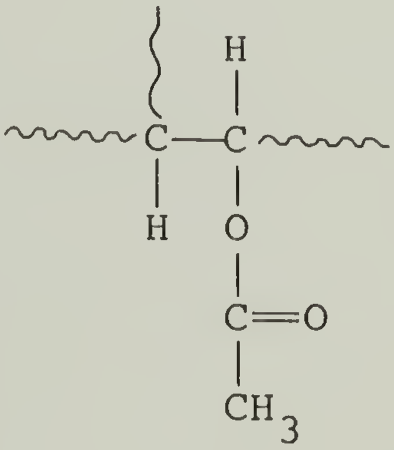

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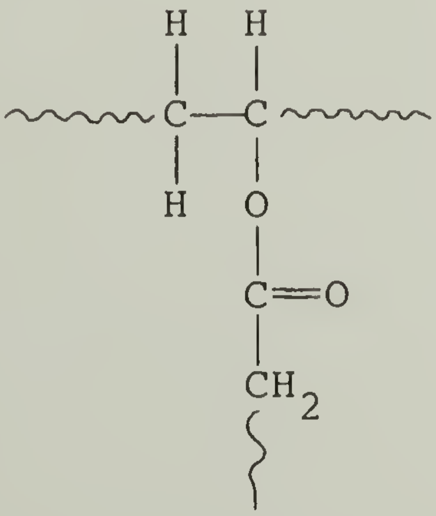
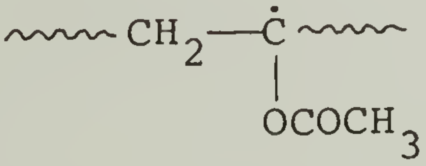


III

Branches may be "short" or "long." Since long branches mainly affect the hydrodynamic properties of the polymer, and are thereby measurable by intrinsic viscosity measurements, we will be concerned exclusively with the measurement of long branches. The amount of branching through the acetate group was estimated to be about 70% of the total by Graessley and his coworkers.(15) However, this percentage will obviously depend on the conditions of polymerization.

On shearing of branched poly(vinyl acetate) (PVAc) to rupture, it is not certain which main chains or branch units will be ruptured. The strength of a -C—O- bond is higher than that of a -C—C- bond.(16,17) As a result, -C—C- bonds would be expected to be ruptured preferentially. It has been shown, using electron spin resonance, that



$$\sim\sim\sim CH_2-\underset{\displaystyle OCOCH_3}{\underset{|}{\dot{C}}}\sim\sim\sim$$

is the principal radical observed on shearing.(18,19) However, Goto and Fujiwara(20) have determined using chemical methods that stirring a solution of PVAc in cyclohexanone did not result in chain scission at the -C—C- linkage, but rather at the pendant ester linkage.

The purpose of our study is to investigate which bonds are ruptured on shearing; that is, whether scission occurs at the main chains or at the branch points shown in structures I, II and III or at a combination of them. To accomplish this, we have carried out chain scission by mechanical as well as by chemical methods. Branching through the acetate group (structure III) can be detected from changes in molecular weights when a sample is saponified to poly(vinyl alcohol) (PVA) and acetylated back to PVAc. The PVAc so obtained has a lower molecular weight than the original PVAc prior to saponification because branches through the acetate group are broken on saponification and are not re-formed on acetylation.(21) The branches through the α-carbon (structure I) and the β-carbon (structure II) are not affected by saponification since they are non-hydrolyzable. Hence, PVA obtained by saponification of branched PVAc remains partially branched.(15) To investigate which branches, if any, are ruptured on shear and to what extent, four samples were prepared as described in Table 2.1.

Previously, branching in PVAc has been determined kinetically(1,3,6,7,15), by gel permeation chromatography (GPC) combined with viscometry(22-24), GPC combined with ultracentrifugation(24) and GPC on-line with low-angle laser light scattering (LALLS) photometry.(25,26) We used GPC on-line with LALLS to analyze branching in PVAc before and after chain scission.

TABLE 2.1

DESCRIPTION OF POLY(VINYL ACETATE) SAMPLES

Sample #	Sample Description
1	Original branched PVAc
2	From sample #1 by saponification and re-acetylation for removal only of branches through acetate group
3	After high-speed stirring of a toluene solution of sample #1 (0.03 g/ml)
4	From sample #3 by saponification and reacetylation

Experimental

Materials. The PVAc used was obtained from Polyscience, Pa. It had a $\bar{M}w$ 750,000, $\bar{M}w/\bar{M}n$ 3.85 and $\bar{B}n$ (long branches per molecule) 2.2.

Saponification. A 5% methanolic potassium hydroxide solution was added with stirring to ten times its volume of a 2% methanol solution of PVAc at room temperature. The agitation was continued overnight to insure complete alcoholysis.(21) The PVA obtained was then filtered and repeatedly washed with methyl acetate.

Reacetylation. The drained, but not dry, PVA was then dispersed in an acetylating solution in approximate proportions of 40 ml of solution for each gram of PVA. The acetylating solution consisted of one volume of pyridine, five volumes of acetic acid and fifteen volumes of acetic anhydride. The dispersion was agitated slowly at room temperature for 24 hrs. longer than the time required for the PVA to dissolve.(1) The reconstituted PVAc was recovered by precipitation with a large excess of water at room temperature. The PVAc was washed extensively with water, purified by reprecipitation into water from an acetone solution and dried overnight under vacuum at 40°C. The purified PVAc was then dissolved in benzene and freeze-dried to remove the last traces of the acetylating solution.(7,15)

High-speed stirring. High-speed stirring was achieved by use of a Virtis-60 homogenizer (see Figure 4.1). The homogenizer was fitted with a teflon cylinder mounted to a stainless steel shaft. A 250 ml round glass flask with five flutes was used as a degradation vessel. The degradation vessel was set in a cooling cup and temperature was maintained at 10 ± 0.5°C by packing the cooling cup with crushed ice. The toluene solution of PVAc (0.03 g/ml) was agitated at 50,000 rpm for 5 hrs. to achieve extreme agitation and shear. A turbulent flow was generated during shearing and was believed to be the most probable cause for bond rupture.(27)

Refractive index increment measurements. The refractive index increments ($\Delta N/\Delta C$) of all samples were measured in tetrahydrofuran (THF), Fisher certified-grade, at 25°C using a Chromatix KMX-16 differential refractometer. This unit incorporates a He-Ne laser source which operates at the same wavelength as the LALLS (6333 Å). The concentration range was varied from 2 to 5 g/l. The variation in $\Delta N/\Delta C$ values obtained for the four samples was less than 2%. The average value of $\Delta N/\Delta C$ used here was 0.054 ml/g.

Gel permeation chromatography on-line with low-angle laser light scattering photometry. The GPC used was a Water Associates Model 201 equipped with four μ-styragel columns of nominal pore size 10^3, 10^4, 10^5 and 10^6 Å. The LALLS used was a Chromatix KMX-6, Chromatix Inc., Cal. The inlet of the LALLS was fitted with a 0.5 μ fluoropore filter (Millipore Corporation, Mass.). This filter provided a good signal relatively free from dust particles, without removal of the high molecular weight fraction of the sample.

The flow rate used was 1 cc/min. at 25°C. Injection volumes were 0.5 cc and concentrations were 1 to 2.5 x 10^{-4} g/ml. The output from both the Refractive Index and the LALLS detectors was displayed on a dual pen recorder. The scattered intensity, as measured by the LALLS, is a product of the concentration and the molecular weight, whereas the differential refractometer is sensitive only to the concentration. As a result the LALLS is extremely sensitive to the high end of the MWD and correspondingly less sensitive to the low end. This results in an offset between the output of the two detectors which increases with the MWD and makes calculation of the molecular weights of the sample at both ends of the chromatogram imprecise for broad MWD samples. This may, of course, be electronically compensated as described by Hamielec and Ouano.(25)

Calculation of intrinsic viscosity, $[\eta]_i$. From a GPC/LALLS system a measure of $\bar{M}wi$ is obtained; that is, the weight average molecular weight at any point across the polymer distribution. Through the use of universal calibration, which relates hydrodynamic volume, $[\eta]M$, to the elution volume, the corresponding value for the intrinsic viscosity, $[\eta]_i$, is obtained by dividing the hydrodynamic volume by the corresponding molecular weight. In this way, a series of values for $[\eta]_i$ and $\bar{M}w_i$ are generated.

A problem which needs to be considered here is which average of the molecular weight is correct for use in universal calibration. If it were $\bar{M}n$ as recently proposed$^{(25)}$, dividing $[\eta]\bar{M}n$ by $\bar{M}w$ would result in an incorrect value for the intrinsic viscosity. We chose to avoid this problem by using the $1/(\alpha+1)$ average of the hydrodynamic volume, ϕ, where $\phi = [\eta]M$ and α is the Mark-Houwink exponent. That is, it can simply be shown that:

$$\bar{M}w = \frac{\Sigma\ Ci(\phi/K)^{1/(\alpha+1)}}{\Sigma\ Ci} \qquad (1)$$

where Ci is the concentration and K is Mark-Houwink constant. Consequently dividing the $1/(\alpha+1)$ average of ϕ by $\bar{M}w$ will result in a correct average for the intrinsic viscosity.$^{(28)}$

Since α in Eq. 1 is an unknown, some means of evaluating α must be available before it is possible to calculate the correct average of ϕ. In addition, some correction for axial dispersion should be applied. To resolve both of these we chose to use the method of Benoit et al.(29) The use of this method has previously been described in detail.(28) It is sufficient to note that, although α may vary with the molecular weight for a branched polymer, the method is insensitive to the exact value of the α and consequently an average may be used. The average value of α used here was 0.644.(27)

A series of values of $[\eta]_i$, the intrinsic viscosity of branched polymer, and $\bar{M}w_i$ were generated across the distribution of the polymer using a computer program.(30) The value of intrinsic viscosity, $[\eta]_{\ell_i}$, for the corresponding linear polymer, at any molecular weight, $\bar{M}w_i$, was obtained using the following Mark-Houwink relationship for linear PVAc:(22)

$$[\eta]_{\ell_i} = 1.877 \times 10^{-4}\ \bar{M}w_i^{\,0.686} \qquad (2)$$

The viscosity ratio, g, at any molecular weight $\bar{M}w_i$, was then obtained by dividing the intrinsic viscosity of the branched polymer by that for the corresponding linear polymer.

Results and Discussion

It is well accepted that polymers in solution with long branches are more compact than are their corresponding linear analogs. As a result, the intrinsic viscosity of polymers with long chain branching is smaller than that for linear polymers of the same molecular weight. Figure

2.1 compares intrinsic viscosities as a function of molecular weights for the four PVAc samples under study. At any molecular weight, the intrinsic viscosity of the original polymer (sample #1) is much smaller than that of the linear PVAc with the difference in intrinsic viscosity increasing with molecular weight. This indicates that sample #1 is highly branched, and the extent of branching increases with molecular weight. On shearing the intrinsic viscosity of the polymer at a given molecular weight is increased but resultant molecular weight is decreased (sample #3). This means that on shearing the polymer has become less branched, indicating that branches are preferentially ruptured leading to an increase in intrinsic viscosity at the resultant lower molecular weight. On saponification and reacetylation of the sheared sample (sample #3), a further increase in the intrinsic viscosity at the resultant lower molecular weight is observed. This is consistent with saponification of additional branches joined through the acetate group (sample #4). The intrinsic viscosity at a given molecular weight of the saponified and reacetylated polymer (sample #2) is much higher than that of the original branched polymer but the average molecular weight is much lower. This is because on saponification the branches through the acetate group (structure III) are broken and not reformed on acetylation. However, any branches through the α- and β-carbons (structures I and II) would not be affected by

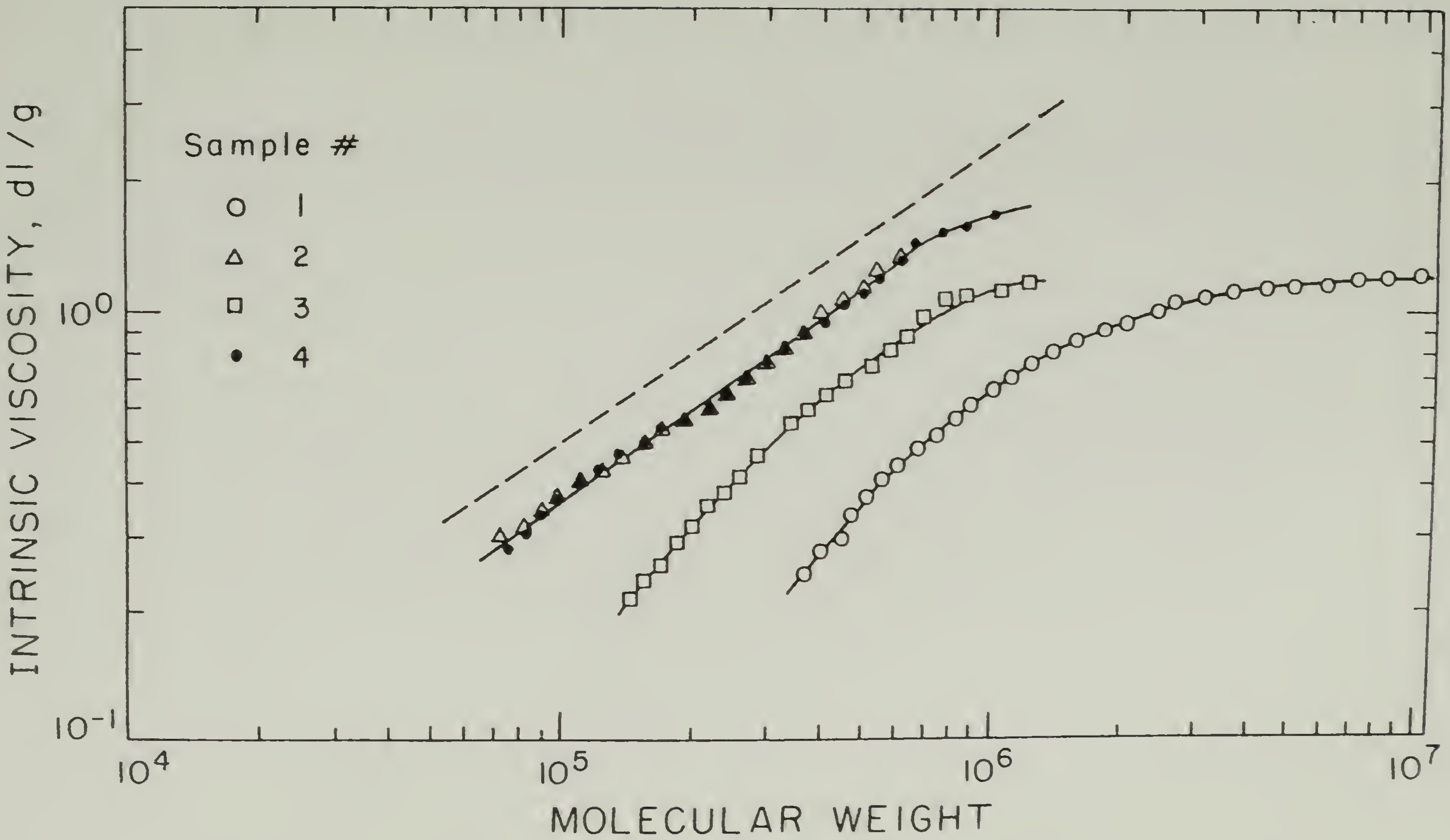


Figure 2.1. Intrinsic viscosity as a function of molecular weight for four samples of poly(vinyl acetate) of different branching in THF at 25°C. The dotted line is for linear polymer.(22)

saponification since these branches are non-hydrolyzable. Hence the saponified and reacetylated sample contains a smaller but significant amount of branches. This implies that any PVA derived from a branched PVAc will not be linear. It is interesting to note that the data for sample #2 and 4 coincide (see Figure 2.1). This qualitatively indicates that, on shearing, non-hydrolyzable branches (structure I and II) are not broken and the branches through the acetate group (structure III) are preferentially ruptured. Those left are then removed on saponification and reacetylation.

The viscosity ratio, g, as a function of molecular weight for the four samples is shown in Figure 2.2. The value of g depends on the type and location of the branches as well as on the number of branch points per molecule.(31) The value of g is 1.0 for a linear polymer and decreases with increase in branching. We observe that the value of g for sample #1 is low and decreases with increase in molecular weight, indicating that the extent of branching increases with molecular weight. The value of g increases towards 1.0 on saponification and reacetylation (sample #2). This is because the branches through the acetate group are removed on saponification and reacetylation. The average value of g for sample #2 is 0.74, compared to 0.20 for sample #1. This implies that about 67% of the branching in PVAc occurs through the acetate group. This is in agreement

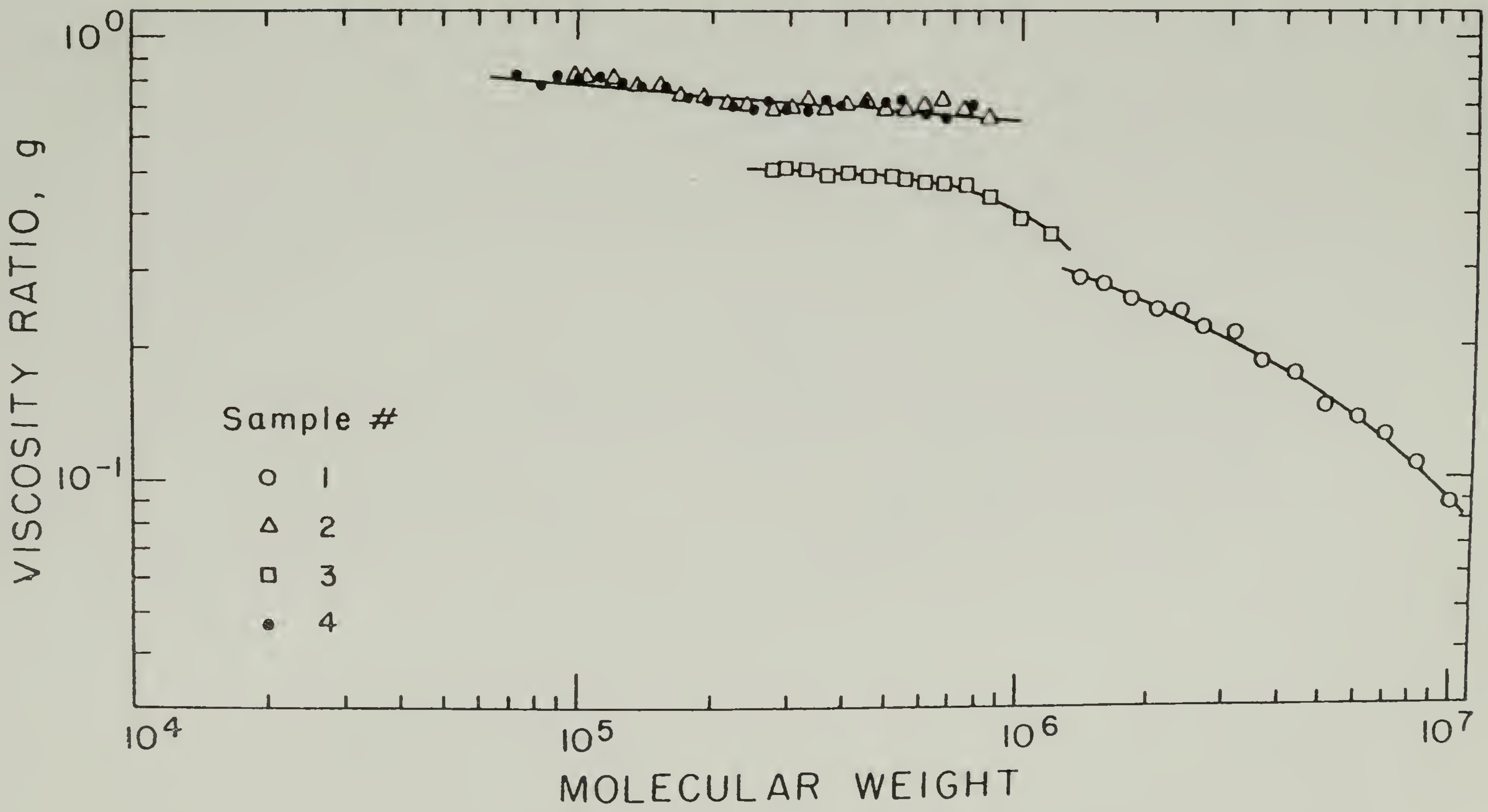


Figure 2.2. Viscosity ratio, g, as a function of molecular weight for four samples of poly(vinyl acetate) of different branching in THF at 25°C.

with the results of Graessley et al.,(15) who determined that about 70% of the branches in PVAc were through the acetate group (structure III). The effect of shearing (sample #3) on the value of g is also shown in Figure 2.2. Comparison of the data for sample #1 and 3 indicates that in addition to the decrease in molecular weight, the value of g increases, indicating the removal of some long branches as a result of shearing. In addition, Figure 2.2 shows the results of shearing followed by saponification and reacetylation (sample #4). It is apparent that saponification and reacetylation of the sheared sample #3 results in removal of the remaining branches through the acetate group, as indicated by the coincidence of the data for sample #2 and 4.

The number average molecular weights, $\bar{M}n$, for the four samples are compared in Table 2.2. Each scission, whether by shear or by saponification and reacetylation, increases the number of molecules by one without altering the number of repeating units. Thus, by counting molecules before and after scission, we obtain:(15)

$$\text{chain scission/molecule} = \frac{(\bar{M}n)_b - (\bar{M}n)_a}{(\bar{M}n)_a} \qquad (3)$$

where subscripts b and a signify before and after saponification - reacetylation or shear. The number of chain

TABLE 2.2

COMPARISON OF POLY(VINYL ACETATE) SAMPLES

Sample #	$\bar{M}n$ from GPC	chain scission/ molecule
1	194,800	-
2	78,875	1.47
3	144,000	0.35
4	76,625	1.54

scissions per molecule thus calculated is shown in Table 2.2.

We may also calculate the amount of scission that occurs on shearing at linkages other than the pendant ester linkages. This is obtained from the difference in the number of scissions per molecule between the sheared and saponified and reacetylated sample (#4) and the sample which was only saponified and reacetylated (#2). This difference is 0.07. This indicates that shear results in only 0.07 scissions per molecule through linkages other than the pendant ester linkages. The remaining 0.28 scissions per molecule (see Table 2.2) on shear must then occur through the acetate group. This implies that 80% of the decrease in molecular weight, on shearing, occurs due to rupture of long branches through the acetate group (structure III). The coincidence of the data for sample #2 and 4 (see Figures 2.1 and 2.2) indicates that branches through the α- and β-carbons (structures I and II) are not ruptured on shearing. Hence the remaining 20% of the decrease in molecular weight must occur due to main chain scission.

Since the strength of the -C—O- bond is higher than that of -C—C- bond, it would be expected that on shearing -C—C- bonds would be ruptured preferentially. However, our results as well as those of Goto and Fujiwara(20) indicate that the rupture occurs preferentially through the -C—O- bond of the ester group. This implies that the branches through the acetate group must be long, since long chains would be expected to rupture on shearing,(17,32) particularly as they can participate in entanglements.

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CHAPTER III

CONCENTRATION DEPENDENCE OF RHEOLOGY FOR POLY(VINYL ACETATE) SOLUTIONS

Summary

The rheology of a poly(vinyl acetate) (PVAc) of $\bar{M}w$ 1.75 x 10^6 and $\bar{M}w/\bar{M}n$ 6.0 in diethyl phthalate and benzyl alcohol solutions has been investigated. The polymer concentration was 0.01-0.20 g/ml. The low shear rate viscosities, first normal stress differences, dynamic viscosities and moduli were measured by a Mechanical Spectrometer and the high shear values were obtained by a high shear concentric cylinder viscometer. Consistent with the stress trend, it was observed that at lower concentration and higher temperature, non-Newtonian effects occurred at higher shear rate and that the variation in viscosity with shear rate was greater at higher concentration.

Solvent effects were found important even in concentrated solutions and increase in viscosity with concentration was more in diethyl phthalate than in a better solvent benzyl alcohol. The critical concentration at which "entanglement" occurs was found to be about 0.05 g/ml in both solvents. The viscosity data could be superimposed on the Graessley viscosity-shear rate master curve

derived for $\bar{M}w/\bar{M}n = 1.65$ at lower shear rates for all concentrations but not at higher shear rates. At low shear rates and frequencies, steady shear viscosity and dynamic viscosity coincided so that the low shear rate viscosity, so called the zero-shear viscosity, could be easily determined. The validity of various relationships which correlate steady-flow and dynamic oscillatory behavior was examined. It was found that steady-flow and dynamic oscillatory behavior were intercorrelated by a constant shift factor.

Introduction

Rheological measurements have been made on poly (vinyl acetate) (PVAc) by several investigators. Kishimoto(1) studied the diffusion coefficient of methanol in PVAc and the steady flow viscosity of PVAc-diethyl phthalate system. Shear creep measurements have been made on PVAc fractions and blends of fractions by Ninomiya and coworkers.(2,3) They found that over wide ranges of molecular weight and molecular weight distribution, the steady state compliance was proportional to $\bar{M}_{z+1}\bar{M}_z/\bar{M}_w$ as predicted by the Rouse theory. Ninomiya and coworkers(4,5) also studied the stress relaxation of PVAc fractions and their blends.

Thermodynamic and dynamic mechanical properties of PVAc were measured in several different solvents by Ferry et al.(6-9) They found that viscosity of PVAc depended greatly on the choice of solvent for comparison at equal weight concentration, but only slightly so if relative viscosities were compared at equal volume concentration. The viscosity dependence on temperature and concentration was found similar to that exhibited by solutions of other linear amorphous polymers. Their study was, however, confined to low stresses where the flow is essentially Newtonian. A complete characterization of the viscous behavior of polymer solutions, of course, must include study of deviation from Newtonian behavior at higher shearing stresses.

Viscosity and normal stress difference as a function of shear rate were examined for PVAc in concentrated solutions (0.17 - 0.35 g/ml in diethyl phthalate) by Graessley et al.(10-12) The study on linear PVAc showed that its behavior was similar to that of other linear polymers.(10) The study on branched PVAc showed that at moderate concentrations (0.17 - 0.225 g/ml) the viscosities were depressed by branching, in fair accord with the Bueche theory and the shape of the viscosity-shear rate master curve was the same for all branched samples, regardless of molecular weight distribution and independent of branching density, temperature and concentration.(11) However at higher concentrations (0.35 g/ml) the data showed viscosity enhancement by branching,(12) a characteristic which has been observed by Berry and coworkers(13) in undiluted branched PVAc. The purpose of this paper is to examine the applicability of such information over a broad range of shear rates and concentrations for a commercial PVAc and to intercorrelate the steady-flow and dynamic oscillatory behavior.

Experimental

Materials. The PVAc used throughout was obtained from Polyscience, Pa. It had a $\bar{M}w$ 1.75×10^6 and $\bar{M}w/\bar{M}n$ 6.0 as measured by gel permeation chromatography on-line with low-angle laser light scattering. It was highly branched. To avoid solvent loss due to evaporation during solution preparation and rheological measurements, high-boiling solvents were used. Solvents were Eastman Organic Chemicals diethyl phthalate (b.p. = 295°C) and Matheson Coleman & Bell benzyl alcohol (chlorine free, b.p. = 205°C). They were used without further purification.

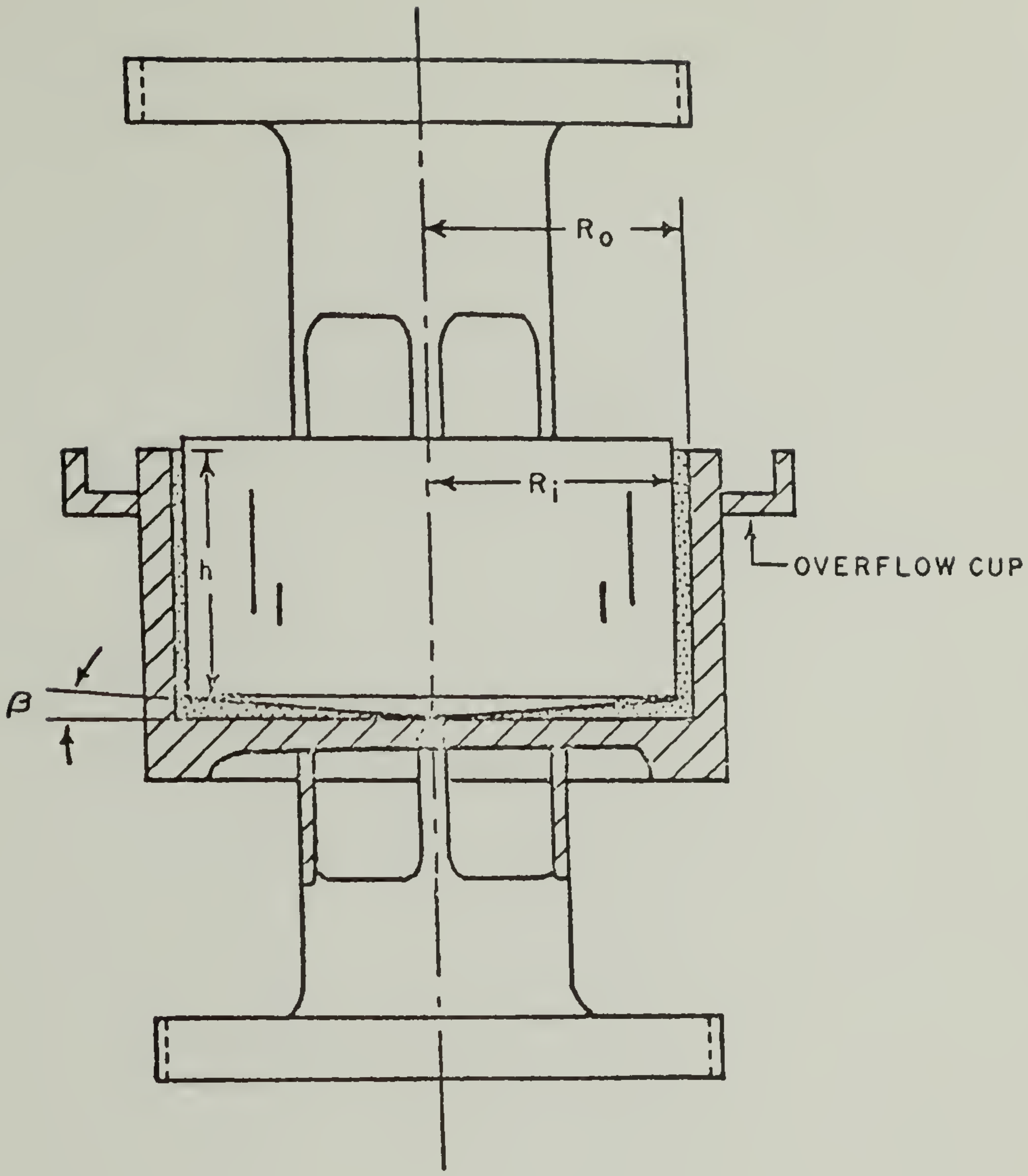
Solutions were prepared at room temperature (25°C) by dissolving a known amount of PVAc in glass bottles to give the desired concentrations of 0.01, 0.05, 0.10, 0.15 and 0.20 g/ml. To enhance the dissolution, solvent and polymer were added in the bottle so as to form alternate layers of solvent and polymer. The bottles were turned over twice a day without agitation to avoid any possible mechanical degradation due to use of high molecular weight

PVAc. It took five to forty days for the mixtures to become homogeneous solutions. Concentrations were checked again by taking a known weight of each sample in a tared aluminum pan and drying it under vacuum to a constant weight and were found to be the same.

Methods. Low shear steady viscosity, first normal stress difference and dynamic data were obtained by a Rheometrics RMS-7200 Mechanical Spectrometer. A cone of 0.04 radian angle and a platen of 100 mm diameter were used for all measurements. Dynamic measurements were made over a frequency range of 1.59 mHz - 15.9 Hz (10^{-2} - 10^{+2} rad/sec). All data reported herein represented the averages of many measurements. A computer program was used to calculate dynamic viscosity and dynamic moduli.(14) Steady shear measurements were limited at high shear rates by a flow instability which, beyond a rather well-defined shear rate, caused the sample to exude from the platen-cone gap.(10,15-16) For accurate measurements of total normal force, one must consider an inertial contribution which is neglected in the simple theory but may be significant at high deformation rates or when large diameter measuring platens are used. A computer program was used to calculate steady shear viscosity and corrected first normal stress difference.(14)

All measurements were made at 25 ± 0.5°C. For higher concentrated solutions (0.15 and 0.20 g/ml), steady shear measurements were also made at 75 ± 0.5°C. High temperature was obtained by using a forced convection environmental chamber which presented the problem of solvent evaporation. To reduce solvent evaporation during measurements we used coni-cylinder geometry instead of cone-platen geometry (see Fig. 3.1). It was possible to make measurements at 75°C for PVAc in diethyl phthalate (b.p. = 295°C) but reliable measurements could not be made in lower boiling benzyl alcohol (b.p. = 205°C) even with coni-cylinder geometry. Shear heating as measured by thermocouple imbedded in the platen was negligible.

The high shear data were obtained from a concentric cylinder viscometer.(17,18) In this viscometer, a narrow thickness of test fluid was held by surface tension between cylinders. The inner cylinder was rotated at known speeds and the resultant torques were measured on the outer cylinder. The extension of the inner rotating cylinder above and below the ends of the outer cylinder eliminated end effects. The narrow gap virtually guaranteed a homogeneous shear field and laminar flow in the test fluid. The temperature in both cylinders was controlled through the use of a common thermostating heat transfer fluid. The inner cylinder was 2.54 cm in diameter and 6.35 cm in length. The calibrated thickness of the test fluid was 3.318×10^{-4} cm.(19)



R_o = 26.07 mm

R_i = 25.00 mm

h = 15.30 mm

β = 0.040 rad

gap = 0.050 mm

Uses: Steady, transient and oscillatory shear flow

Equations: $\dot{\gamma} = 25\omega$

$T_{12} = 10M$ (M in gm-cm; T_{12} in dyne/cm^2)

$T_{11} - T_{22} = 100 F_z$ (F_z in gm; $T_{11} - T_{22}$ in dyne/cm^2)

Figure 3.1. Coni-cylinder geometry.

For polymer concentrations up to 0.10 g/ml, the samples were introduced in the gap through the use of screw driven syringes.(20) The higher concentrated solutions (0.15 and 0.20 g/ml) could not be introduced in the gap through the use of screw driven syringes due to high viscosity and hence the gap was filled by coating both the inner and outer cylinders with polymer solution and then the inner cylinder was placed very carefully in the hollow outer cylinder. The measurements for 0.15 and 0.20 g/ml samples were made at 75 ± 0.5°C so that torques generated were not too large to damage the instrument. The viscosities of solvents and dilute samples were measured by Ubbelhode viscometer #150 and Ostwald viscometer #100, both of which gave the same results.

Results and Discussion

One of the most important properties of polymeric fluid is the non-Newtonian viscosity, that is, the fact that viscosity of the fluid changes with shear rate. This is known as shear thinning or pseudoplastic behavior. At low shear rates, the shear stress is proportional to shear rate $\dot{\gamma}$ and the viscosity approaches a Newtonian value η_0, the low shear limit. At higher shear, a departure from Newtonian behavior occurs and viscosity decreases with increasing shear rate. The range of shear rates over which the transition from η_0 to the so-called power-law region occurs is more narrow for narrow molecular weight distributions (MWD). As MWD is broadened, the transition region is also broadened and shifted to lower shear rates.(21,22)

Fig. 3.2 shows the effects of concentration and temperature on the apparent steady-flow viscosity (η_a) vs. shear rate ($\dot{\gamma}$) curve for PVAc in diethyl phthalate. Since the MWD of our polymer is broad, the transition region is broad. Moreover, as concentration is decreased or temperature is increased, the transition region is further broadened and shifted to higher shear rates, i.e., critical shear rate, $\dot{\gamma}_0$, the shear rate at which η_a departs from η_0, is increased. Thus we observe that at low concentration and high temperature, non-Newtonian effects occur at high shear rates consistent with the stress trend. At high concentrations, the variation in apparent viscosity with shear rates is large. For example, at 0.10 g/ml concentration, there is a 100-fold decrease in viscosity when the shear rate is increased from 10 to 10^5 $\sec^{-1}$ while at 0.01 g/ml concentration, the corresponding decrease is only about 4-fold. The infinite shear rate viscosity (η_∞) is not reached for any sample. Similar results for PVAc in benzyl alcohol are shown in Fig. 3.3.

Zero-shear viscosity (η_0). The zero-shear viscosity of a polymer solution is a complex function of several variables such as molecular weight, polymer concentration, tempera-

Figure 3.2. Effects of concentration and temperature on apparent steady-flow viscosity vs. shear rate for PVAc in diethyl phthalate. Open symbols are by mechanical spectrometer and filled symbols are by high shear viscometer.

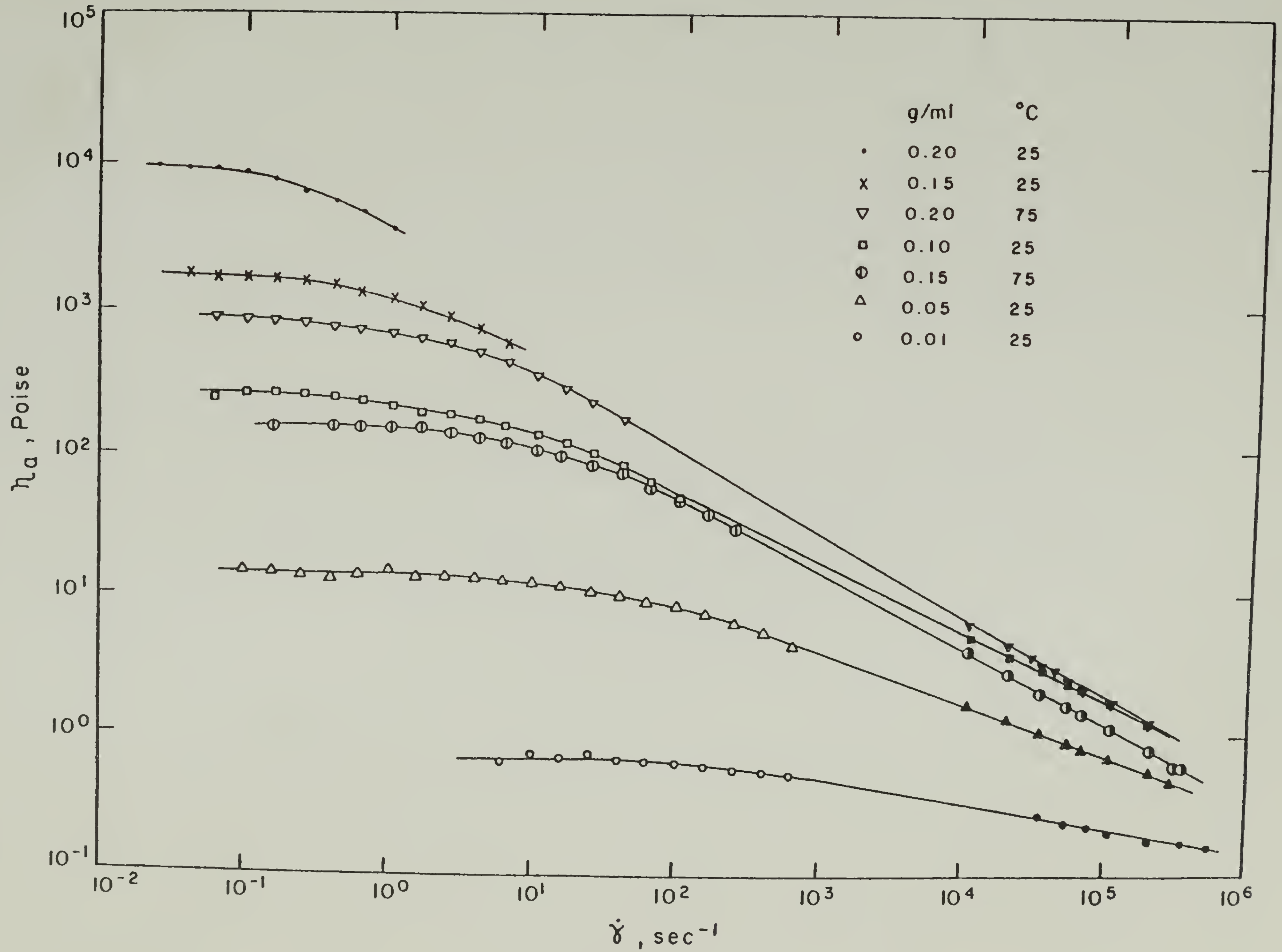

g/ml
°C
• 0.20 25
x 0.15 25
▽ 0.20 75
□ 0.10 25
Φ 0.15 75
△ 0.05 25
○ 0.01 25
10⁵
10⁴
10³
10²
10¹
10⁰
10⁻¹
ηa, Poise
10⁻²
10⁻¹
10⁰
10¹
10²
10³
10⁴
10⁵
10⁶
γ̇, sec⁻¹

Figure 3.2

Figure 3.3. Same as Fig. 3.2., for PVAc in benzyl alcohol.

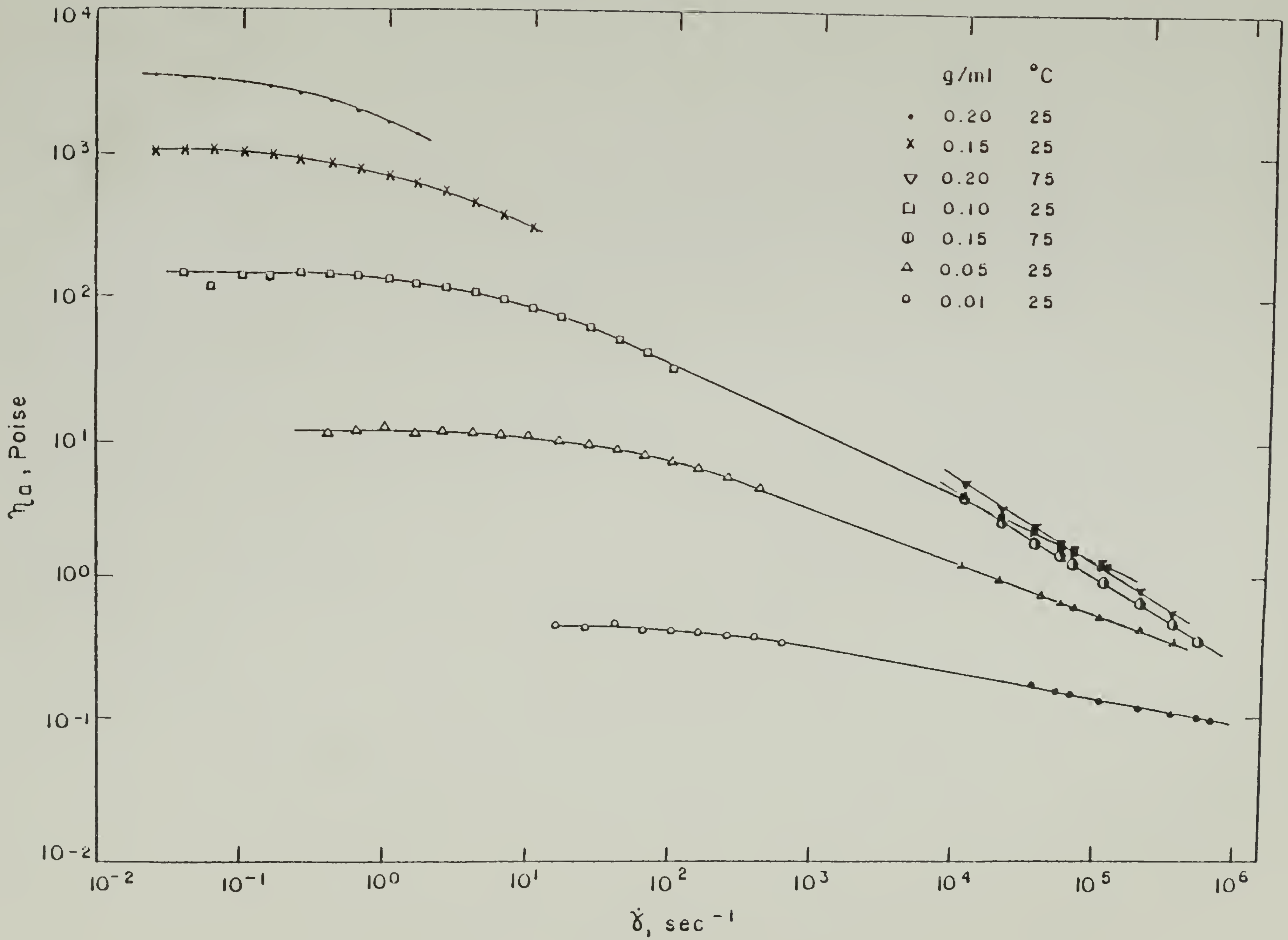

g/ml °C
• 0.20 25
x 0.15 25
▽ 0.20 75
□ 0.10 25
⊕ 0.15 75
△ 0.05 25
○ 0.01 25
η_a, Poise
10^4
10^3
10^2
10^1
10^0
10^{-1}
10^{-2}
10^{-2}
10^{-1}
10^0
10^1
10^2
10^3
10^4
10^5
10^6
$\dot{\gamma}$, sec^{-1}

Figure 3.3

ture, solvent, molecular structure, etc. The concentration dependence of η_0 of PVAc in diethyl phthalate and benzyl alcohol solutions at 25°C is shown in Fig. 3.4. A two decade change in concentration extends over nearly five decades of η_0. The η_0 vs. C curve shows a smooth curvature rather than a sharp break. The critical concentration, C_c, at which entanglement occurs is about 0.05 g/ml in both solvents. This corresponds to a value of $C_c\bar{M}w$ of 87,500. The value of M_c, the critical molecular weight for onset of entanglement coupling as determined from the molecular weight dependence of viscosity, has been reported as 24,500.(23)

The plots of η_0 vs. C above 0.05 g/ml are highly linear as indicated by the least squares regression correlation coefficients of over 0.98 and the slopes are 4.69 and 4.20 in diethyl phthalate and benzyl alcohol respectively. This indicates that solvent effects are important even in concentrated solutions and that viscosity increases more rapidly with concentration in diethyl phthalate than in benzyl alcohol. Usually it is observed that $\eta_0 \sim C^5$ but Ferry et al.(9) have found that the slopes of η_0 vs. C curves for PVAc depend upon temperature, molecular weight and solvent (see Table 3.1). For a given molecular weight of the polymer at a constant temperature, the slope depends upon the goodness of the solvent. For example, both 1,2,3-trichloro propane and methyl ethyl

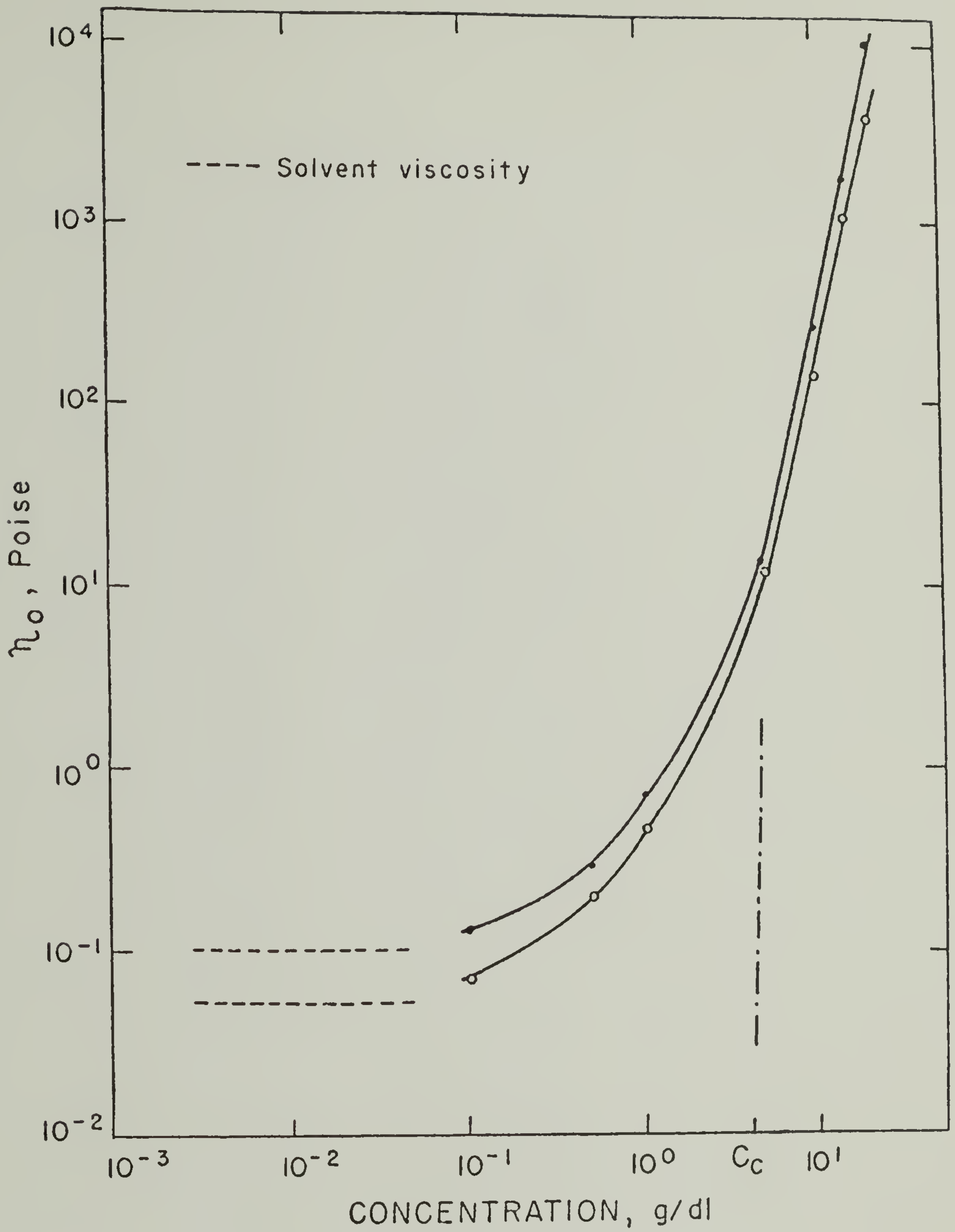


Figure 3.4. Low-shear-rate viscosity vs. concentration for PVAc at 25°C. Filled symbols are diethyl phthalate solutions and open symbols are benzyl alcohol solutions.

TABLE 3.1

COMPARISON OF SLOPES OF LOG η_0 VS. LOG C FOR POLY(VINYL ACETATE) SOLUTIONS

$\bar{M}n$	Solvent	Temp. °C	$\delta \log \eta_0/\delta C^{1/2}$ (b) $(g/ml)^{-1/2}$	Slope of log η_0 vs. log C
62,000 (a)	1,2,3-trichloropropane	8	6.9	3.18
		25	6.3	2.90
		50	5.7	2.63
140,000 (a)	1,2,3-trichloropropane	15	9.0	4.15
		25	8.7	4.01
		35	8.5	3.92
	methyl isobutyl ketone	15	11.3	5.21
		25	10.3	4.74
		35	9.7	4.47
	methyl ethyl ketone	25	9.1	4.19
280,000 (a)	1,2,3-trichloropropane	8	9.4	4.33
		25	9.0	4.15
		50	8.3	3.82
840,000 (a)	1,2,3-trichloropropane	8	11.3	5.21
		25	10.6	4.88
		50	10.0	4.61
290,000 (c)	diethyl phthalate	25	-	4.69
	benzyl alcohol	25	-	4.20

(a) From Ref. 9. (b) Data given in this form by Ferry et al.(9)
(c) From this study.

ketone are good solvents for PVAc but the former is the better of the two. It can be seen from the data of Ferry et al. in Table 3.1 that the slopes for PVAc of $\bar{M}n$ 140,000 at 25°C in 1,2,3-trichloro propane and methyl ethyl ketone are 4.01 and 4.19 respectively indicating that viscosity increases with concentration faster in methyl ethyl ketone than in better solvent 1,2,3-trichloro propane.

In our case, both diethyl phthalate and benzyl alcohol are good solvents for PVAc but benzyl alcohol is better than diethyl phthalate as evident from the values of intrinsic viscosity of 3.50 and 2.25 dl/g in benzyl alcohol and diethyl phthalate respectively. Fig. 3.5 shows the plot of zero-shear relative viscosity (η_γ) versus concentration. Though the values of η_γ in diethyl phthalate and benzyl alcohol are rather close, it is seen that in the beginning η_γ in diethyl phthalate is less than η_γ in better solvent benzyl alcohol. With increasing concentration, η_γ in diethyl phthalate increases faster than that in benzyl alcohol as seen before and eventually becomes more than it. Other authors have also observed that in poor solvent η_γ increases faster than in gold solvent and eventually exceeds it.(9,24,25) The cross-over concentration for PVAc in diethyl phthalate and benzyl alcohol is about 0.15 g/ml which is the same as that for polystyrene in toluene (good solvent) and decaline (poor solvent).(25)

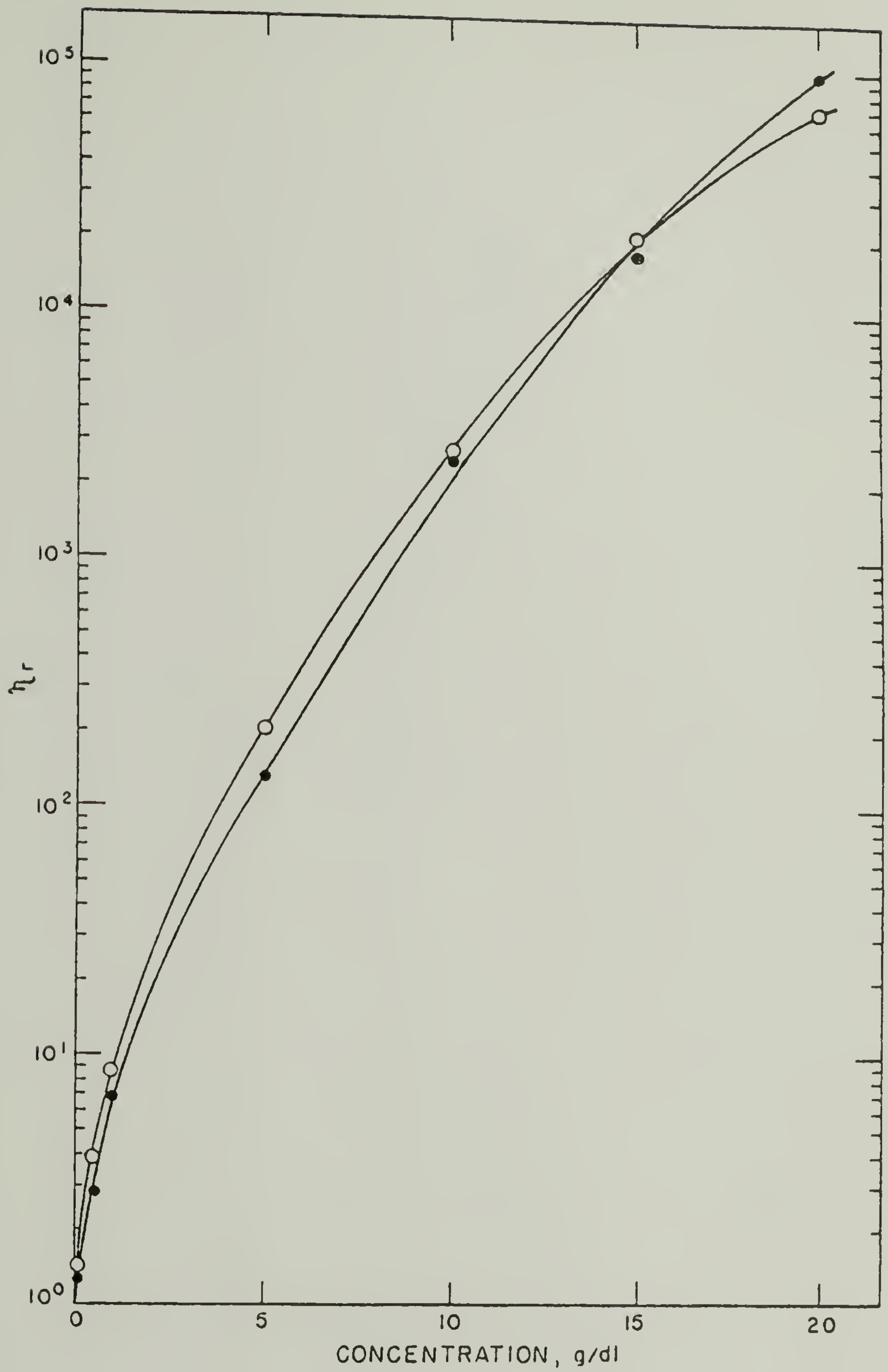


Figure 3.5. Zero-shear relative viscosity vs. concentration for PVAc at 25°C. Filled symbols are diethyl phthalate solutions and open symbols are benzyl alcohol solutions.

Superposition of viscosity-shear rate data. Graessley and Prentice(11) have shown that viscosity-shear rate data for branched PVAc of different MWDs could be superimposed on a single log-normal master curve (derived for $\bar{M}w/\bar{M}n = 1.65$). This was attributed to the fact that MWD and branching had somewhat compensatory effects on the form of the master curve and hence unlike the behavior of linear systems, the form of viscosity-shear rate master curve for branched samples did not change appreciably as MWD broadened. However the superposition of viscosity data on the master curve was done for concentrated PVAc solutions ($C > 0.17$ g/ml) and for shear rates < 100 sec^{-1}. In this paper we have tested the superposition of viscosity data at higher shear rates (up to 10^6 sec^{-1}) and lower concentrations.

The experimental data were plotted on a log-log paper as reduced viscosity, (η_a/η_0), vs. shear rate for each concentration and temperature. The experimental curves were then shifted horizontally to achieve the best fit with the theoretical master curve. Fig. 3.6 shows the superposition of viscosity-shear rate data in diethyl phthalate on Graessley master curve. It is seen that at lower shear rates, the data superimpose very well on the master curve but at higher shear rates, the data deviate from the master curve. The lower is the concentration of the solution, the more is the deviation of the data from the master curve. This deviation is due to the fact that

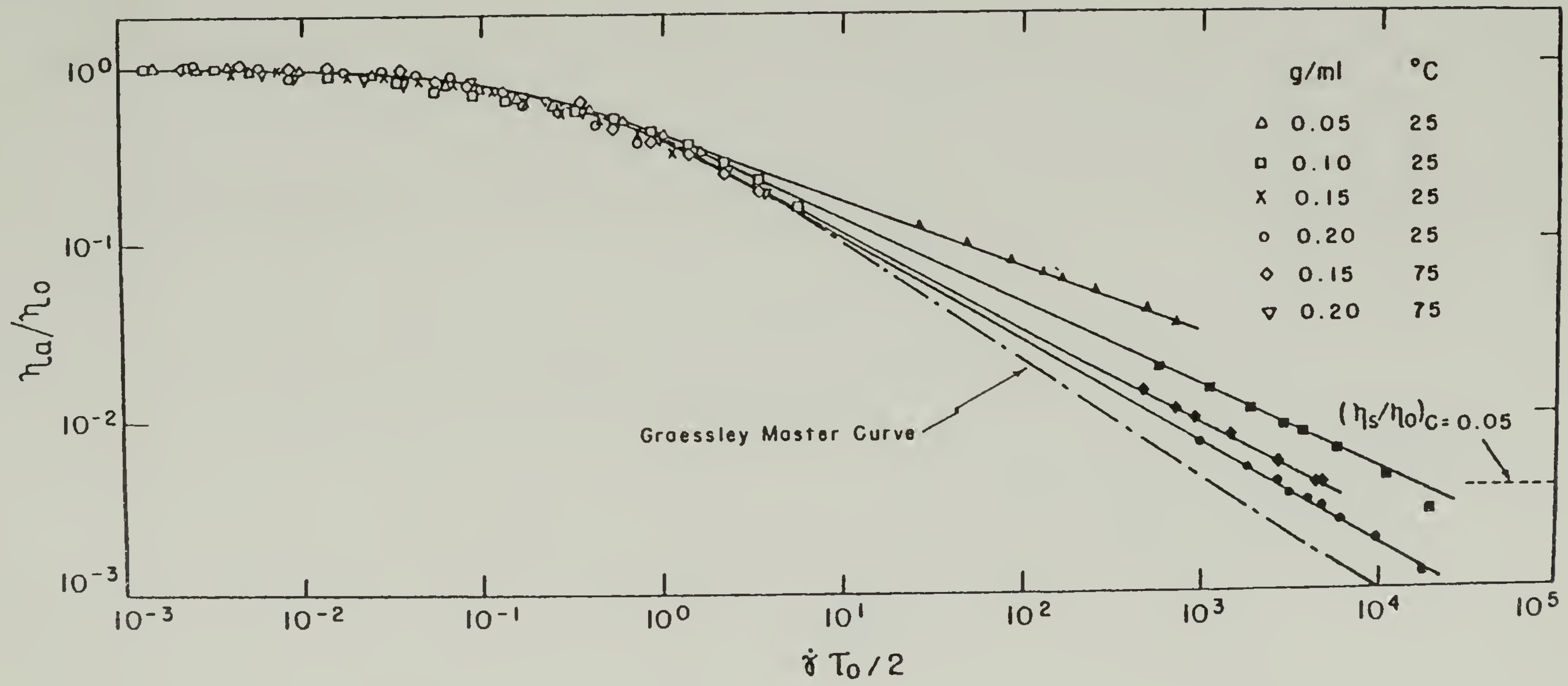


Figure 3.6. Superposition of viscosity shear-rate data for PVAc in diethyl phthalate on Graessley master curve.(11) Open symbols are by mechanical spectrometer and filled symbols are by high shear viscometer.

the value of reduced viscosity η_a/η_0 for each concentration cannot be less than η_s/η_0, where η_s is solvent viscosity. As the concentration decreases, η_0 decreases rapidly (see Fig. 3.4) and hence the ratio η_s/η_0 increases. Therefore the deviation of data from the master curve increases as concentration is decreased. η_s is negligible compared to η_a at all concentrations and shear rates shown, i.e., $\eta_a/\eta_0 \approx (\eta_a-\eta_s)/(\eta_0-\eta_s)$. The value of η_s/η_0 for 0.05 g/ml solution is shown by dotted line in Fig. 3.6. The similar behavior is observed for PVAc in benzyl alcohol (Fig. 3.7). Hence it is concluded that Graessley master curve can be used to superimpose the viscosity-shear rate data at lower shear rates for all solutions above the critical concentration but data cannot be superimposed at higher shear rates.

Extensive branching occurs in PVAc during polymerization by polymer transfer and terminal double bond reactions. Branching frequency increases rapidly with conversion and causes a concomitant broadening of the MWD.(11,12,26-28) The wide distribution of molecular weights in our high molecular weight PVAc is accompanied by branching and the superposition of the viscosity data at lower shear rates on the Graessley master curve (derived for $\bar{M}w/\bar{M}n = 1.65$) may be due to compensatory effects of MWD and branching on the form of the master curve.

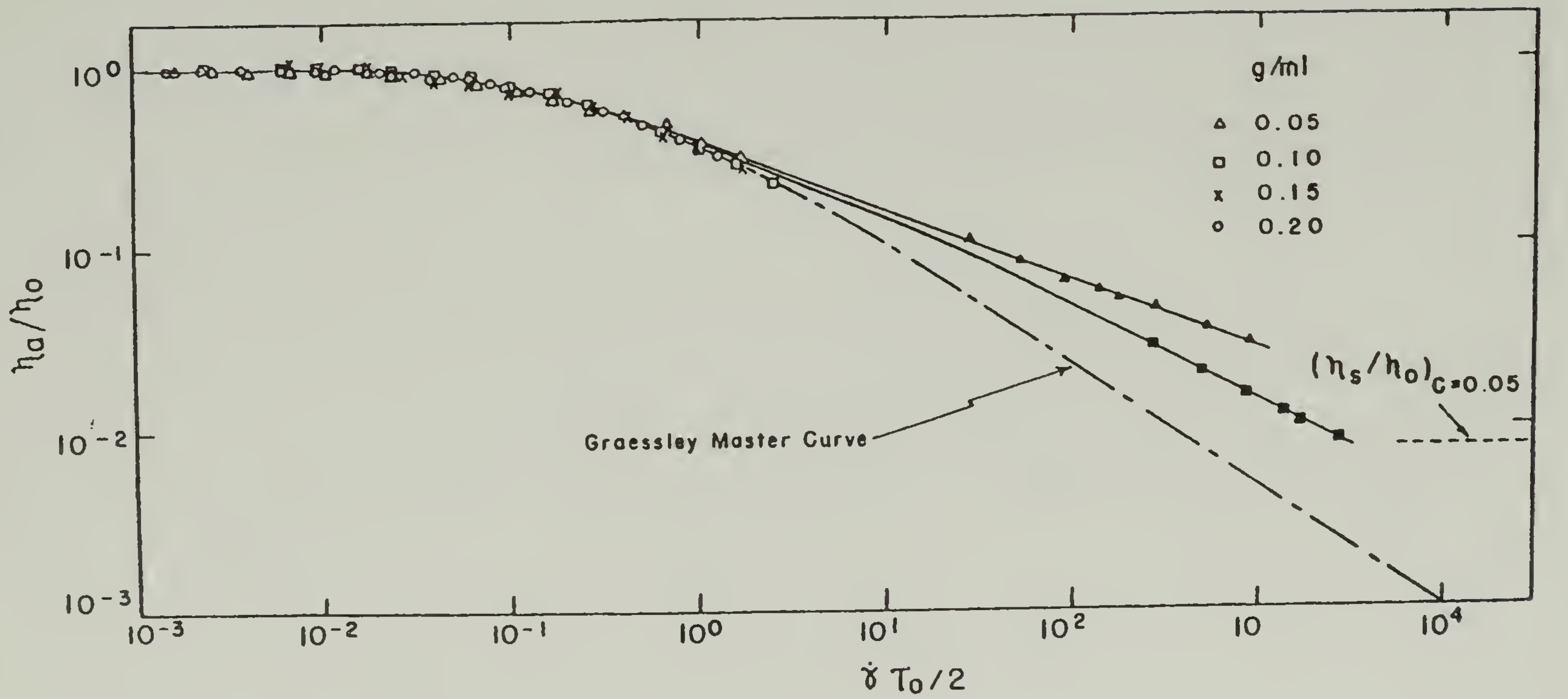


Figure 3.7. Same as Fig. 3.6, for PVAc in benzyl alcohol at 25°C.

Relaxation times. Real polymer solutions and melts cannot be characterized by a single relaxation time, nonetheless for simplicity we use a single time for interpretation. For concentrated solutions, the Rouse(29) relaxation time (τ_R) is given by

$$\tau_R = \frac{6\bar{M}w\eta_0}{\pi^2 CRT} \tag{1}$$

where C is polymer concentration, R is the gas constant and T is absolute temperature. The experimental relaxation time τ_0 obtained by shifting the experimental viscosity-shear rate data to achieve the best fit with the theoretical master curve is of the same order of magnitude as the Rouse relaxation time τ_R (see Table 3.2). The similar behavior has been observed by others.(11,12,29,30)

Relationship of steady shear to dynamic properties. The relation between steady flow and dynamic behavior is an important problem which has been studied theoretically and experimentally by many investigators. Usually it is observed that apparent steady-flow viscosity and dynamic viscosity (η') coincide with each other at low shear rates and frequencies but at high frequencies η' decreases more rapidly than η_a.(31) Based on their work on polystyrene melts and solutions of polyisobutylene in decalin, Cox and Merz(32) suggested that η_a vs. $\dot{\gamma}$ curves matched

TABLE 3.2

CALCULATED SINGLE RELAXATION TIMES FOR POLY(VINYL ACETATE) SOLUTIONS AT 25°C

Concentration g/ml	Diethyl Phthalate		Benzyl Alcohol	
	τ_0, sec.	τ_R, sec.	τ_0, sec.	τ_R, sec.
0.20	1.40	2.147	0.78	0.794
0.15	0.37	0.504	0.30	0.310
0.10	0.11	0.116	0.05	0.062
0.05	0.005	0.0116	0.0052	0.01
0.20 (a)	0.160	0.165	--	--
0.15 (a)	0.027	0.037	--	--

(a) at 75°C

complex viscosity ($|\eta^*|$) vs. ω curves, i.e.,

$$|\eta^*| = \sqrt{(\eta')^2 + (\eta'')^2} = \eta_a\Big|_{\dot{\gamma}=\omega} \tag{2}$$

This empirical relationship was confirmed by Wales et al.(33) and Onogi et al.(34-37) for polyethylene, polystyrene, poly(methyl methacrylate) and poly(vinyl acetate) melts, by Adamse et al.(38) for polypropylene melts and by Porter et al.(22,39) for poly(1-olefin) and polyethylene melts. Shroff and Shida(40) and Mendelson et al.(41) also found that the empirical relationship of Cox-Merz was valid for high-density polyethylenes and for low-density polyethylenes that have low values of weight-average number of branches per molecule, but not for low-density polyethylenes having large value of weight-average number of branches per molecule. Williams and Bird(42) have suggested that $\eta_a(\dot{\gamma})$ should be the same as $|\eta^*(\omega K)|$, where K is a constant varying from 0.91 to 1.12. The dilute solution theory for rigid dumbbells predicted the identity of η_a and $|\eta^*|$ for small values of arguments.(43) Data of Harris(44) on solutions of narrow MWD polystyrene in Aroclor showed that $|\eta^*|$ followed η_a more closely than η' did but the Cox-Merz relationship did not apply.

Continuum theory of Spriggs(45) predicted the following relationships:

$$\eta_a(\dot{\gamma}) = \eta'(K\omega) \tag{3}$$

$$\psi_{12}(\dot{\gamma}) = \frac{2\eta''(K\omega)}{K\omega} = \frac{2G'(K\omega)}{(K\omega)^2} \tag{4}$$

where K is a shift factor. Osaki et al.(46) found that Eqs. 3 and 4 were in good agreement with the experimental data for polybutadiene in xylene (no shift factor was required) but were not valid for poly(methyl methacrylate) in diethyl phthalate. Many other authors have also found that $\eta_a(\dot{\gamma})$ was the same as $\eta'(K\omega)$ where K = 0.667 - 0.714(47,48) or K = 0.435 - 0.455.(49,50) Williams and Bird(42) derived K = 0.806 theoretically on the basis of the three-constant Oldroyd model. However Onogi et al.(34) and Yamamoto(51) found that correlation between steady flow and dynamic behavior could not be obtained by a constant shift and that the constant K increased with increasing $\dot{\gamma}$ or ω.

Huseby and Blyler(52) gave the following correlations based on the theory of Pao:(53-55)

$$\eta_a = \{\eta'[1 + 2\cot^2\delta]\}_{\omega=\dot{\gamma}} \tag{5}$$

where

$$\cot\delta = \frac{G'}{G''} \tag{6}$$

and

$$T_{11} - T_{22} = 2G'[1 + 2\cot^2\delta]_{\omega=\dot{\gamma}} \tag{7}$$

where $T_{11} - T_{22}$ is the first normal stress difference. In terms of coefficient of first normal stress difference,

$$\psi_{12} = \frac{T_{11} - T_{22}}{\dot{\gamma}^2} = \frac{2G'}{\omega^2} [1 + 2 \cot^2 \delta]_{\omega=\dot{\gamma}} \qquad (8)$$

In the limiting case as ω → 0, cot δ → 0 and the Eqs. 5 and 7 reduce to expressions derived by Coleman and Markovitz(56) for second order fluids:

$$\lim_{\dot{\gamma}\to 0} \eta_a = \lim_{\omega\to 0} \eta' = \eta_0 \qquad (9)$$

and

$$\lim_{\dot{\gamma}\to 0} (T_{11} - T_{22}) = \lim_{\omega\to 0} 2G' \qquad (10)$$

Thus the second order fluid theory predicts that the lower limiting values for apparent steady shear viscosity and dynamic viscosity should be identical and the first normal stress difference is given by 2G' at low shear rates.

Philippoff(57) observed that in the lower ranges of frequencies (taken as equivalent to low shear rates) the steady flow viscosity and dynamic viscosity were same and at higher frequencies correlation between the two viscosities could be obtained by using an equation similar to Eq. 5, but only for monodisperse polymers. Osaki et al.(46,58,59) and Philippoff(60) found that at low frequencies the data for a number of polymer solutions were in good agreement with Eqs. 9 and 10. Huseby and Blyler(52) have shown that the data of Osaki et al.(46,59) at high shear rates could be represented better by Eq. 5. However they found that the flow viscosity of linear polyethylene melts calculated via the Pao correlation was much more Newtonian than that observed experimentally. There seems to be little question that Eq. 9 is valid but the validity of Eq. 10 is less certain, simply because few comparisons have been made.(61)

None of the above equations explicitly incorporate MWD. One cannot predict a priori which, if any, of the equations will be valid for a given polymer system, though Cox-Merz relationship is generally obeyed for polymer melts. We have tested the validity of Eqs. 2, 3, 5 and 9 for PVAc in diethyl phthalate and benzyl alcohol solutions at different concentrations in Figs. 3.8-3.11. The dashed lines (——·——) and (-----) represent flow curves calculated from the dynamic data using Eq. 2 and 5 respectively. The solid lines represent flow curves calculated from the dynamic data using Eq. 3.

It is seen that in all cases at low rates of shear and at low frequencies, apparent steady shear viscosity and dynamic viscosity coincide with each other. This indicates the validity of Eq. 9 and enables the determination of η_0. The Cox-Merz relationship (Eq. 2) is not obeyed and $|\eta^*|$ is always less than η_a though $|\eta^*|$ follows η_a more closely

Figure 3.8. Test of Eqs. 2, 3, 5 and 9 for PVAc at 25°C. (o) and (Δ) compare apparent steady-flow viscosity with dynamic viscosity. Open symbols are diethyl phthalate solutions (Fig. a) and filled symbols are benzyl alcohol solutions (Fig. b). C = 0.20 g/ml.

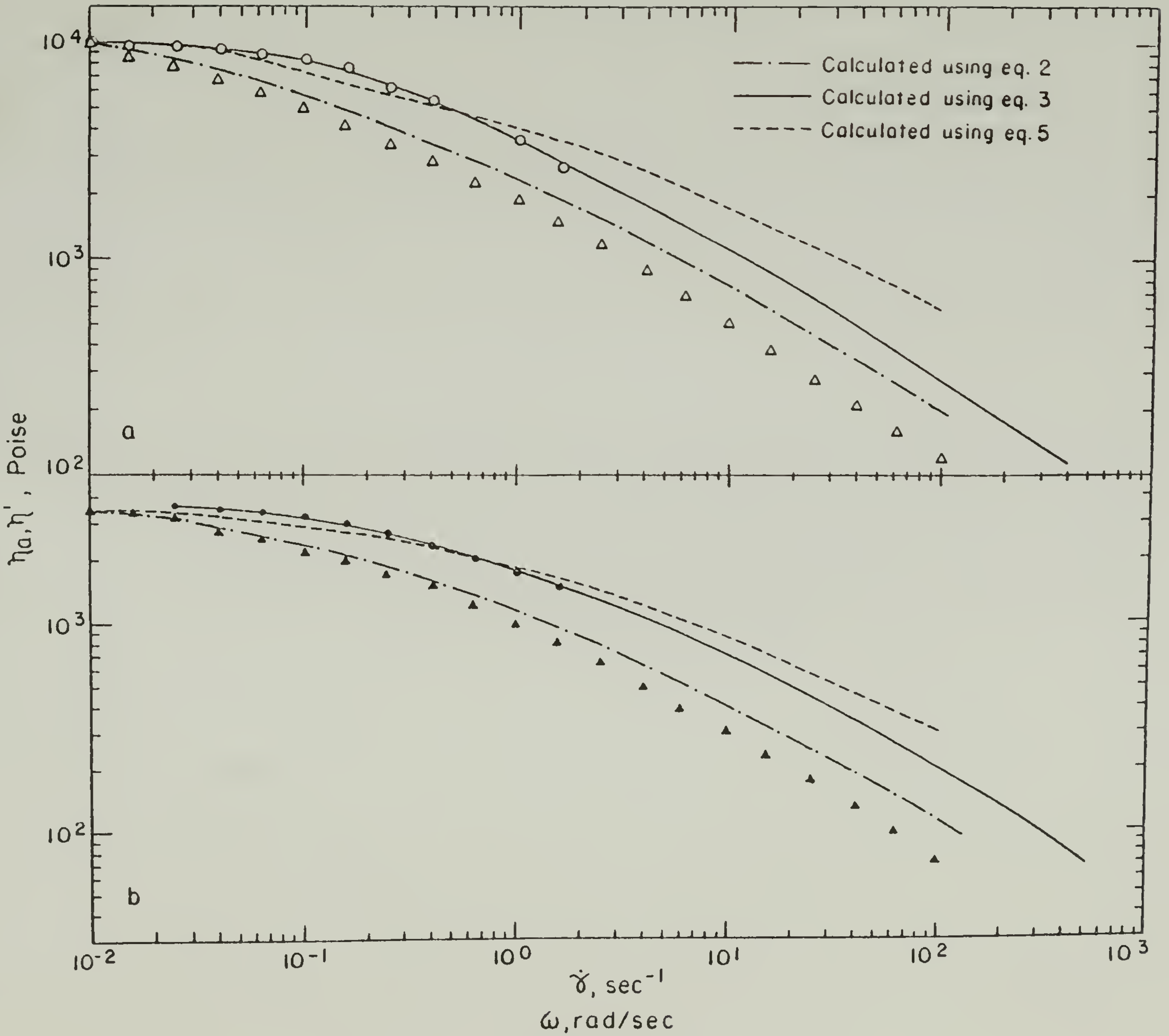

Calculated using eq. 2
Calculated using eq. 3
Calculated using eq. 5
a
b
10^4
10^3
10^2
η_a, η', Poise
10^{-2}
10^{-1}
10^0
10^1
10^2
10^3
$\dot{\gamma}$, sec^{-1}
ω, rad/sec

Figure 3.8

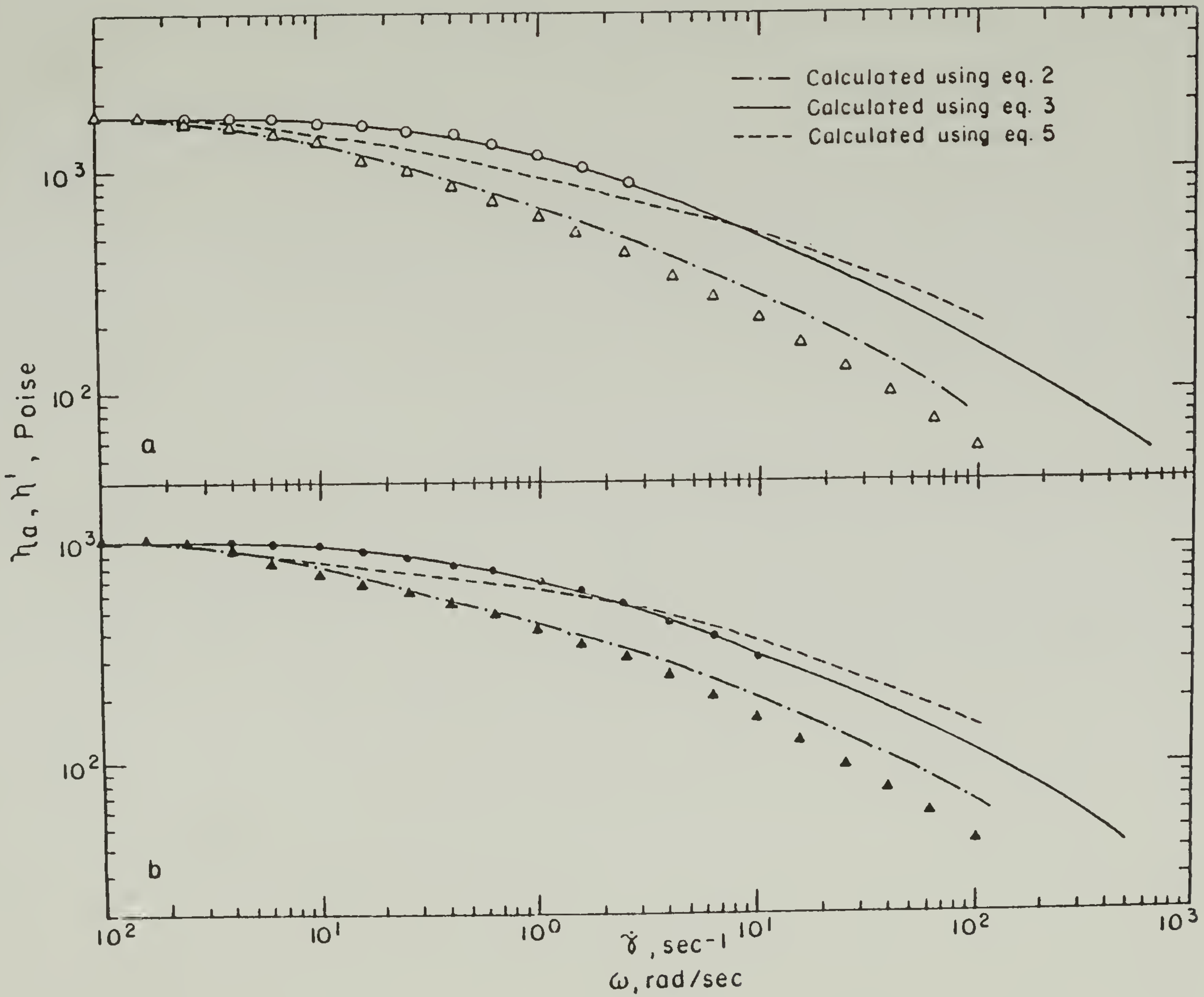


Figure 3.9. Same as Fig. 3.8, for C = 0.15 g/ml.

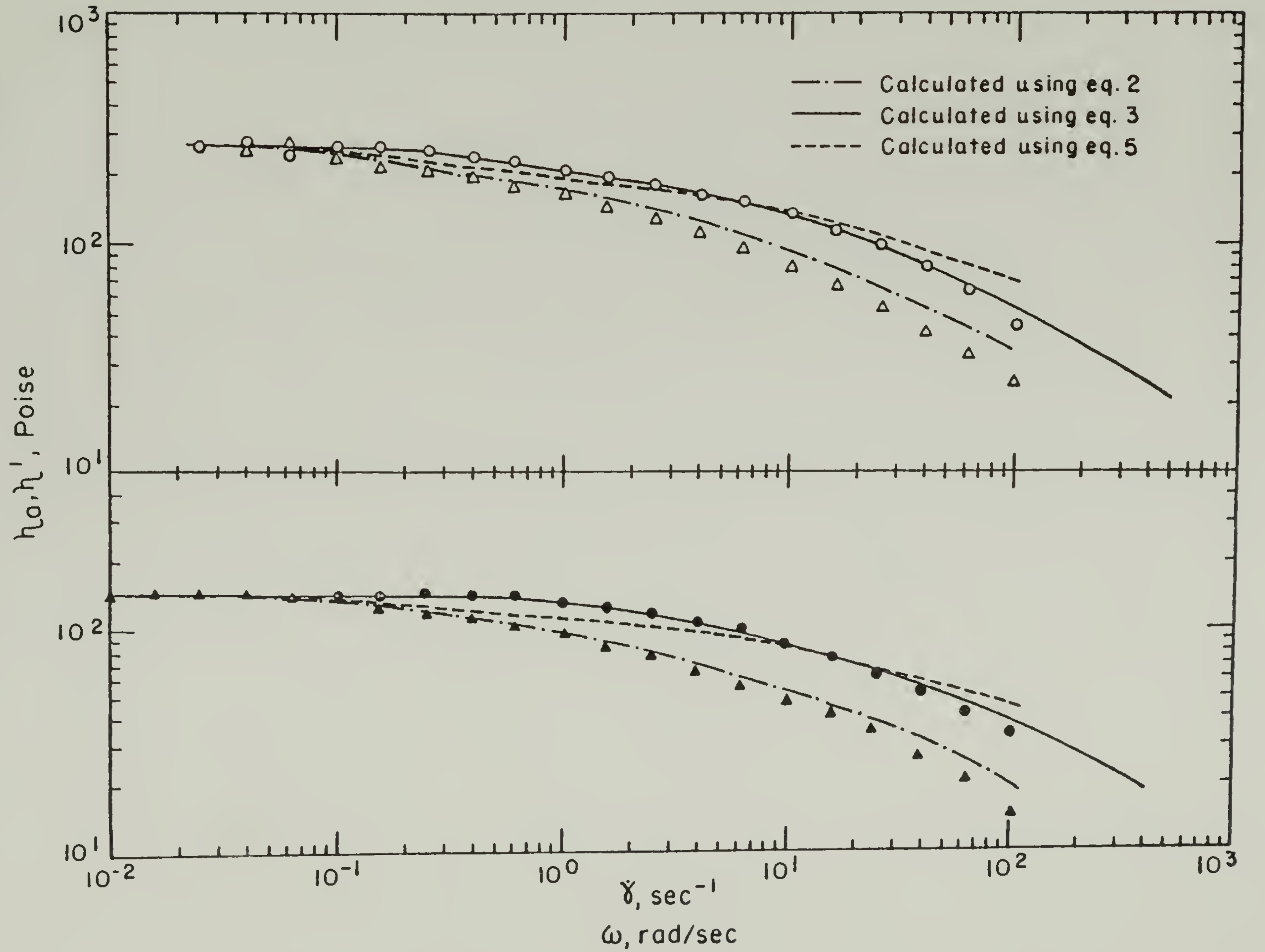


Figure 3.10. Same as Fig. 3.8, for C = 0.10 g/ml.

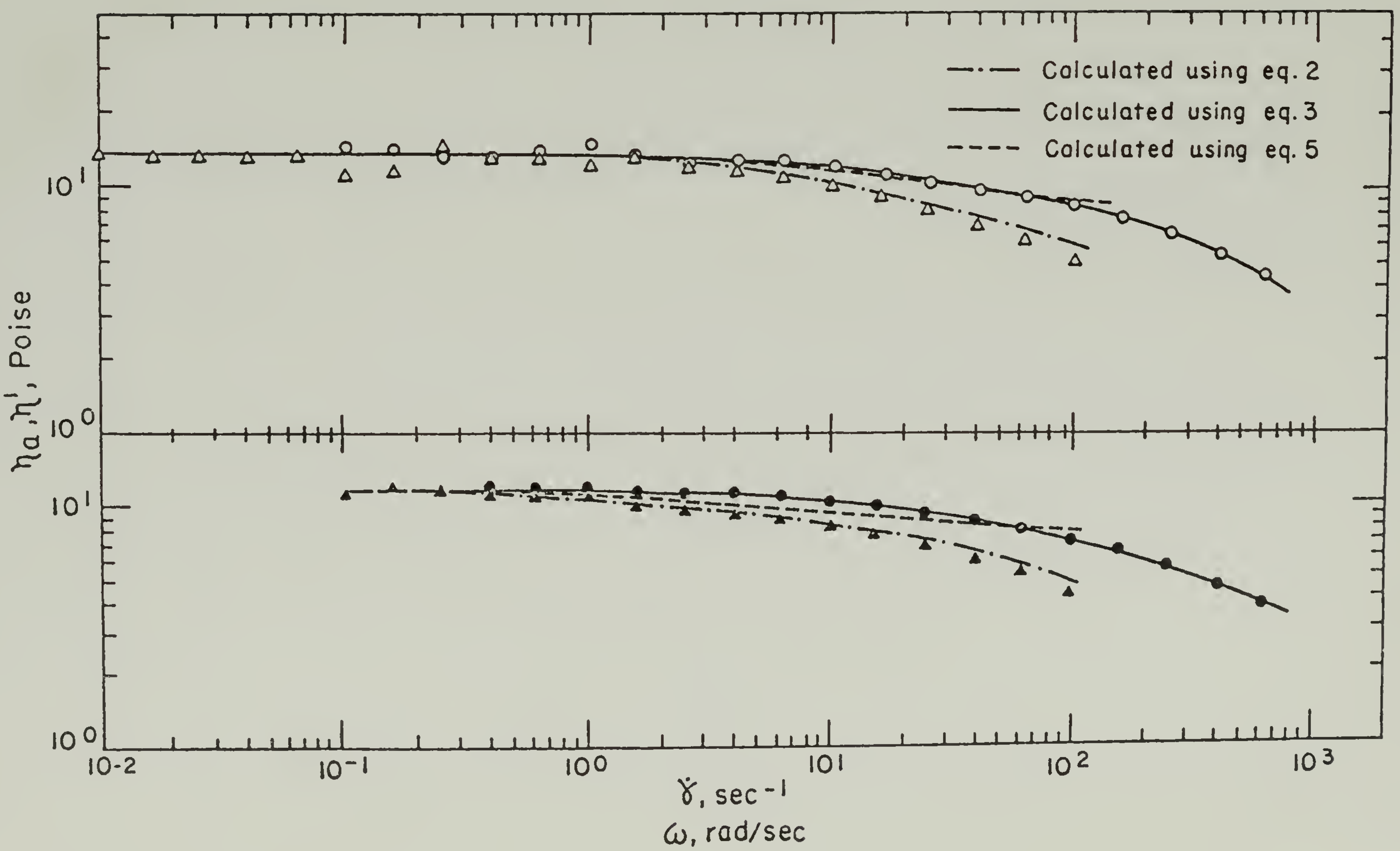


Figure 3.11. Same as Fig. 3.8, for C = 0.05 g/ml.

than does η' as observed by Harris.$^{(44)}$ The steady shear viscosity predicted by Eq. 5 is at first less than η_a observed experimentally but then becomes more than η_a at high shear rates. The cross-over shear rate increases as concentration is decreased.

We observe that η_a lies on the curve predicted by Spriggs correlation (Eq. 3) at all shear rates. This means that η_a and η' have the same shape but are shifted with respect to each other, along the $\dot{\gamma}$ - ω axis, by a factor K. Hence the correlation between steady flow and dynamic behavior can be obtained by a constant shift. This is of great importance as the rate of shear cannot be measured up to high values owing to shear heating, where as dynamic measurements, especially using the method of reduced variables, are feasible and then can be used to extrapolate to inaccessible range of the steady shear experiments.

In Figs. 3.12 and 3.13 the coefficients of first normal stress difference are compared with those obtained from the dynamic data using Eqs. 4 and 8. It is seen that the experimental data follow very closely the curve calculated via Spriggs correlation (Eq. 4) and that the coefficient of first normal stress difference predicted by Eq. 8 is much less than that observed experimentally for all concentrations. However the shift factors used for viscosity function and the coefficient of first normal stress difference were not always equal and lay between

Figure 3.12. Test of Eqs. 4 and 8 for PVAc in diethyl phthalate at different concentrations and 25°C. (●) represents experimental data for coefficient of first normal stress difference, ψ_{12}. (———) and (----) represent ψ_{12} calculated from dynamic data using Eqs. 4 and 8, respectively.

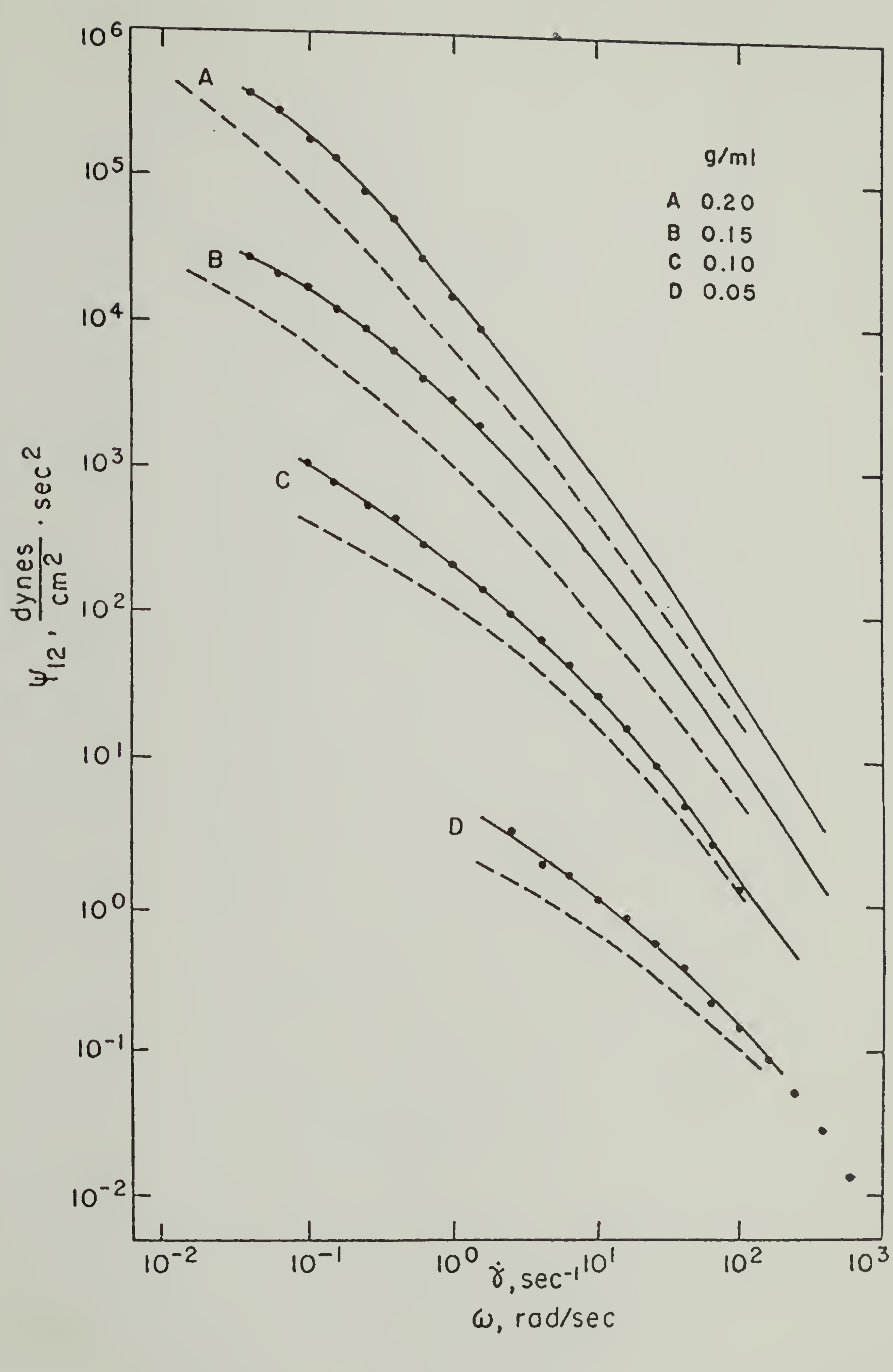

10^6
10^5
10^4
10^3
10^2
10^1
10^0
10^{-1}
10^{-2}
$\Psi_{12}, \frac{dynes}{cm^2} \cdot sec^2$
A
B
C
D
g/ml
A 0.20
B 0.15
C 0.10
D 0.05
10^{-2}
10^{-1}
10^0
10^1
10^2
10^3
$\dot{\gamma}$, sec^{-1}
ω, rad/sec

Figure 3.12

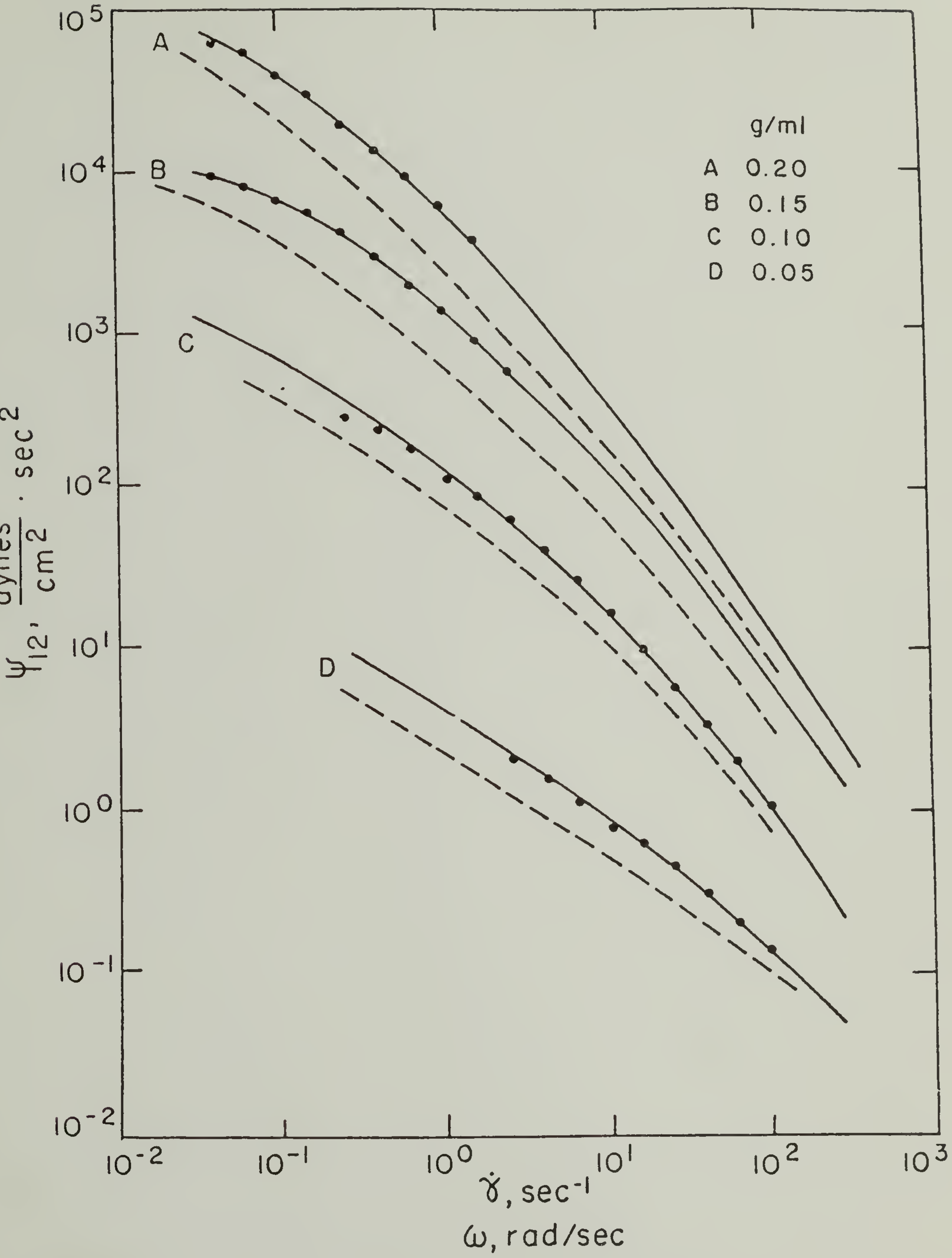


Figure 3.13. Same as Fig. 3.12, for PVAc in benzyl alcohol.

0.2 - 0.4. The correlation between steady-flow and dynamic oscillatory behavior is very important for predicting normal stress differences because at high shear rates flow instability is developed causing the sample to exude from the plate-cone gap and making the measurements of normal stress differences extremely difficult.

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CHAPTER IV

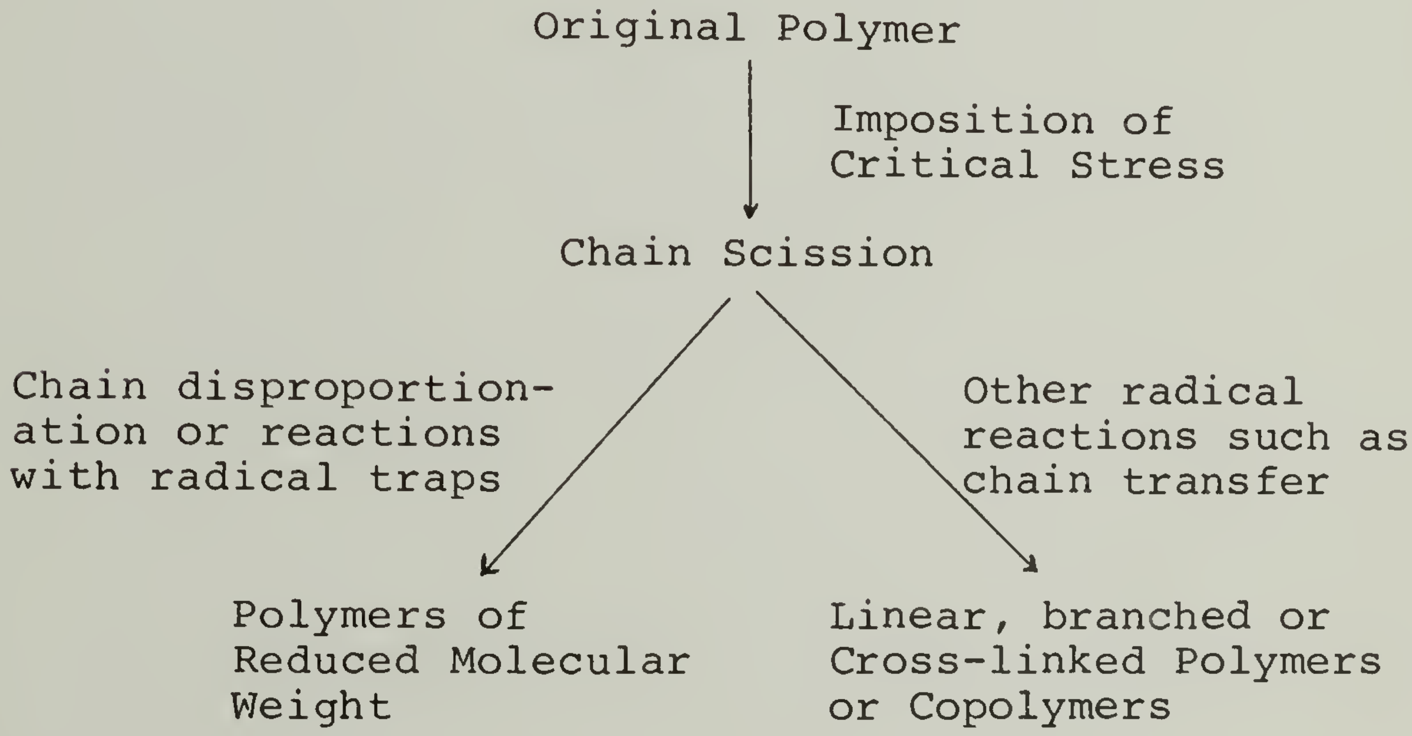
SHEAR DEGRADATION OF POLY(VINYL ACETATE) IN TOLUENE SOLUTIONS BY HIGH-SPEED STIRRING

Summary

A poly(vinyl acetate) (PVAc) of $\bar{M}w$ 750,000 and $\bar{M}w/\bar{M}n$ 5.10 in toluene solution was sheared in a Virtis-60 Homogenizer. The polymer concentration was 3.0-12.0 gm/100 ml and test temperature was 10 ± 0.5°C. The extent of degradation was measured by gel permeation chromatography (GPC). It was concluded that on shearing (i) the molecular weight decreases rapidly at the beginning of shearing, and thereafter decreases ever more slowly towards a limiting value, (ii) the molecular weight distribution is narrowed, (iii) no degradation occurs up to 5000 rpm and thereafter increases with stirring speed, (iv) degradation is more at lower concentrations but concentration is not a sensitive variable, and (v) the chain scisson occurs randomly. The Mark-Houwink relationship for PVAc in THF at 25°C was derived as $[\eta] = 2.47 \times 10^{-4} \times \bar{M}v^{0.644}$.

Introduction

When polymer solutions are sheared, agitated or extruded, shearing force is created between polymer and solvent, and where present, between polymer chains through entanglements. This force acts on the polymer to cause chain deformation and extension. The degree of deformation depends on the force applied. If the force is sufficient, polymer chains may be broken, leading to formation of macroradicals. Macroradicals may then either recombine or more likely otherwise react to form short or modified polymer molecules.(1) The pattern of reaction may be described as follows:(2)



Goto and Fujiwara, using a Homomixer, investigated the rupture of poly(vinyl acetate) (PVAc) in cyclohexanone dilute solutions.(3) They concluded that chain scission does not occur at the C-C linkage, but occurs at ester linkage of the pendant group, if long branches are present and a decrease in solution concentration or solvent power or an increase in Homomixer rotational speed causes an increase in degradation. In other studies, $-CH_2-\underset{H}{\dot{C}}-O-CO-CH_3$ was detected as the principal radical by electron spin resonance spectra.(4-7) The degradation kinetics of PVAc on cold milling have been investigated by Baramboim.(8,9) It was found that decrease in molecular weight follows the equation

$$M_t = a\ e^{-Kt} + M_{lim}$$

where M_t is the molecular weight at any time t, M_{lim} is the limiting molecular weight after which no more degradation occurs under the test conditions, K is the degradation rate constant and $a = M_{in} - M_{lim}$ with M_{in} being the initial polymer molecular weight. The observation of M_{lim} on degradation of PVAc has also been demonstrated by many other investigators.(3,10-12) The degradation of PVAc has also been studied during capillary flow.(13) Ceresa has reported the molecular weight changes on degradation of PVAc plasticized with benzene.(11)

In a series of studies, PVAc solutions were irradiated by ultrasonic waves.(12,14-19) Degradation decreases on increasing polymer concentration(17) and on using a poor solvent.(15) Kosino and Miyagawa concluded that PVAc degradation in an acetone solution on ultrasonic irradiation occurred mainly by cavitation.(18) Ovenall et al. followed the consumption of the radical acceptor 1,1'-diphenyl-2-picrylhydrazyl on ultrasonic irradiation of PVAc in benzene solutions.(12) Nakano et al. prepared a block copolymer of PVAc and methacrylic acid by sonic irradiation at 200 KHz.(19) Ceresa synthesized styrene-vinyl acetate block copolymer by cold mastication of PVAc swollen with styrene.(20) In one study, Goto and Fujiwara agitated PVAc plus vinyl acetate in a Homomixer at 30,000 rpm in a nitrogen atmosphere at 65°C.(21) They found that the macroradicals generated by mechanical scission of PVAc initiated the polymerization of vinyl acetate monomer. In addition to the formation of block and graft copolymers, there are other positive opportunities for the use of polymer mechanochemistry. These include induction of favorable changes in molecular weight, molecular weight distribution, branching and cross-linking.

Degradation of PVAc by mechanical methods has been widely described, but the extent of reaction has been generally measured by either viscosity changes or by free radical production. Neither of these approaches reveal changes in molecular weight distribution or location of chain scission. In this study, solutions of PVAc were agitated in a Virtis-60 homogenizer to study the effect of shearing time, stirring speed and solution concentration on shear degradation of PVAc in toluene. To obtain the more meaningful and complete results, gel permeation chromatography was used to determine the molecular weight distributions of the starting and shear-reacted samples. The measures of number-average molecular weight, $\bar{M}n$, were particularly important. This is because the difference between $1/\bar{M}n$ for before and after reaction is proportional to the minimum number of bonds ruptured. The relative changes in weight-average molecular weight, $\bar{M}w$, and the number-average molecular weight, $\bar{M}n$, have been used to evaluate the location of bond rupture and distributional changes.

Experimental

Materials. The PVAc used throughout was obtained from Polyscience. It had a $\bar{M}w$ of 750,000 as measured at the University of Massachusetts by GPC. The heterogeneity index, $\bar{M}w/\bar{M}n$, was 5.10. Toluene (spectrophotometric grade) was supplied by Allied Chemical Company whereas tetrahydrofuran (THF) and acetone were obtained from Fisher Scientific Company.

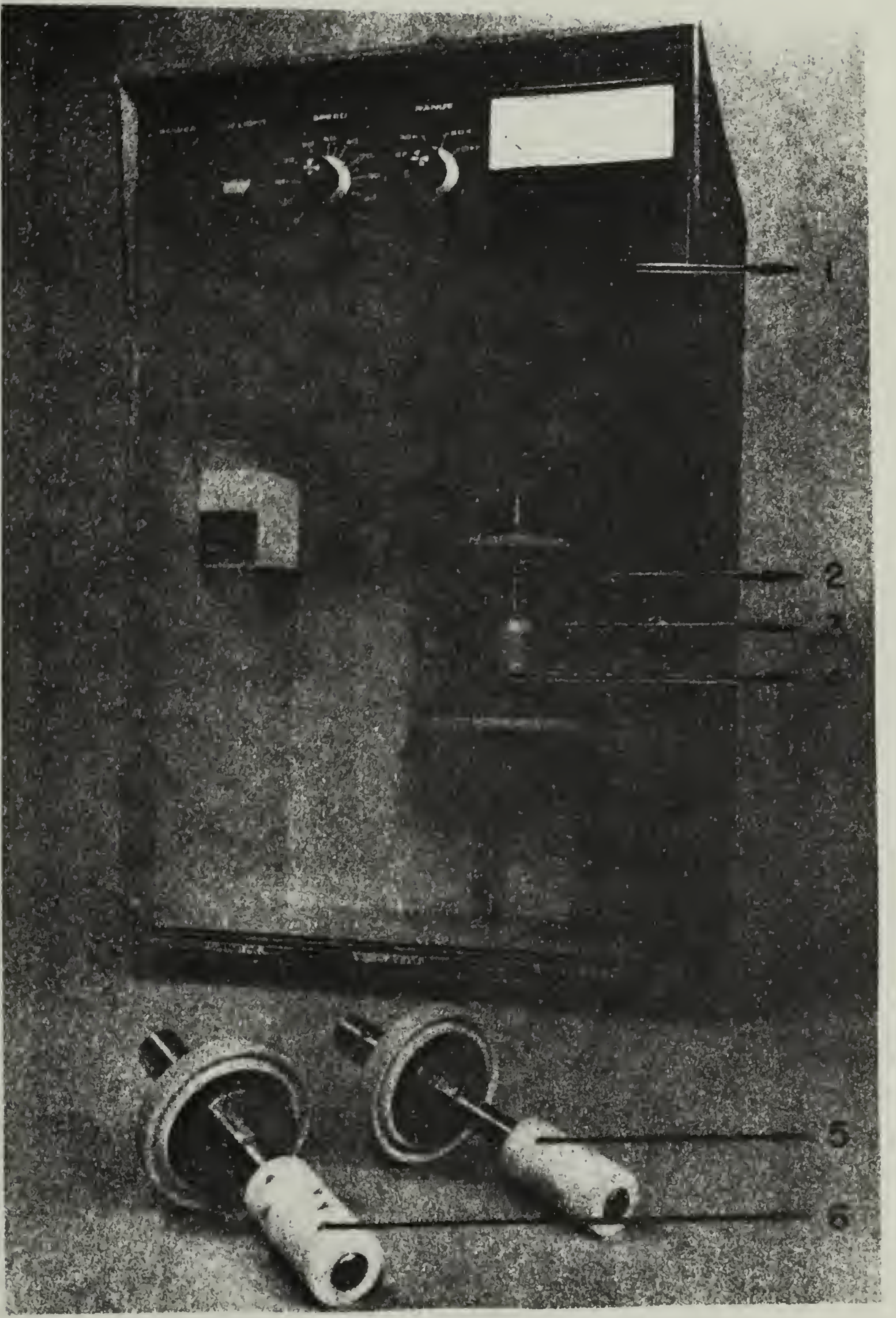
High-speed stirring. Known amounts of PVAc were placed in volumetric flasks. The required volume of toluene was then added and allowed to dissolve at room temperature (25°C) for one or more days depending on the solution concentration. High-speed stirring was achieved by use of the Virtis-60 homogenizer (variable speed $\leq$ 60,000 rpm) (Fig.

4.1). This homogenizer was fitted with a teflon cylinder (dia. 1.9 cm) connected to a stainless steel shaft. A 250 ml round glass flask with five flutes was used as a degradation vessel for all runs. The degradation vessel was set in a cooling cup and temperature was maintained at 10 ± 0.5°C by packing the cooling cup with crushed ice.

Eddies were observed on shearing PVAc solutions in toluene. The transparent solutions became milky after agitation due to formation of micro bubbles. This suggests that turbulent flow was generated and was the most probable cause for bond rupture. All reactions were carried out in the presence of air. Approximately 80 ml of solution was used for each run for speeds up to 30,000 rpm and about 60 ml of solution was used for higher speeds. This limit avoided the splashing of the solution during agitation. All solutions were filtered before agitation. Samples were withdrawn at various intervals for GPC analysis.

<u>Gel permeation chromatography</u>. A Waters Associates GPC Model 200 equipped with an automatic injection system was used. The conditions were as follows: solvent: THF; temperature: 25°C; columns: 10^7, 3×10^5, 3×10^4, and 3×10^3 Å normal pore size; sample concentration: 0.5 mg/ml; flow rate: 1 ml/min. Polystyrene (PS) standards in

Figure 4.1. High-speed stirring apparatus: (1) Virtis-60 homogenizer, (2) cooling cup, (3) 250 ml round glass flask with five flutes, (4) Teflon cylinder, (5) Teflon cylinder mounted on a stainless steel shaft and (6) five blades and six discs mounted on a stainless steel shaft.


SPEED
RANGE
1
2
3
4
5
6

the molecular weight range 10^4 - 2×10^6 with narrow distributions ($\bar{M}w/\bar{M}n < 1.2$) were obtained from the Pressure Chemical Company, Pittsburgh, Pa. Intrinsic viscosities $[\eta]$ of these standards were measured with an Ubbelhode Viscometer in THF at 25°C. The Mark-Houwink constants K and a were calculated from a linear plot of $\log[\eta]$ vs. log M and were found to be 1.90×10^{-4} and 0.68 respectively. These values are consistent with those obtained by Cane and Capaccioli who reported K as 1.8×10^{-4} - 2.8×10^{-4} and a as 0.66 - 0.69 for PS ($\bar{M}n$ = 24,000 - 806,000 and $\bar{M}w/\bar{M}n$ = 1.2 - 6.4) in THF at 25°C.(22) The GPC universal calibration curve for PS was obtained using these samples.(23)

To find the Mark-Houwink constants for PVAc in THF at 25°C, three samples of PVAc obtained from Polyscience were used. Their $[\eta]$ were measured in acetone and the viscosity-average molecular weights ($\bar{M}v$) were found to be 149,000, 346,000 and 720,000 using the following Mark-Houwink relationship:(24) $[\eta] = 1.76 \times 10^{-4} \times \bar{M}^{0.68}$. Two fractions of PVAc were obtained as GPC elution cuts from the highest and lowest molecular weights. The lower end GPC cut of PVAc of $\bar{M}v$ 149,000 and the higher end GPC cut of PVAc of $\bar{M}v$ 720,000 were collected in a beaker during GPC fractionation and were dried at room temperature under vacuum for two days. The $[\eta]$ of these two fractionated samples were measured in acetone using the technique of subsequent dilutions and $\bar{M}v$ were found as 90,000 and 1,448,000 respectively using the above Mark-Houwink relationship. The acetone solutions were dried under vacuum for two days to recover the fractionated samples. The $[\eta]$ of the three unfractionated and two fractionated samples of PVAc were then measured in THF at 25°C.

Figure 4.2 shows a log-log plot of $[\eta]$ vs. $\bar{M}v$ for PVAc in THF at 25°C. All five points lie on the straight line obtained by the least squares method. The Mark-Houwink constants K and a for PVAc in THF at 25°C were calculated as 2.47×10^{-4} and 0.644 respectively. These values are in good agreement with those obtained by prior investigators. Nichols found the Mark-Houwink exponent a for PVAc in THF at 25°C as 0.64.(25) Goedhart and Opschoor derived the following Mark-Houwink relationship for PVAc in THF at 25°C: $[\eta] = 3.5 \times 10^{-4} \times \bar{M}w^{0.63}$, using a viscometric detector.(26)

The universal PS calibration curve was then transformed to PVAc calibration curve using the following equation:

$$M_{PVAc} = \left[\frac{[\eta]_{PS}\ M_{PS}}{2.47 \times 10^{-4}}\right]^{\frac{1}{1.644}}$$

A computer program was used to calculate $\bar{M}w$, $\bar{M}n$ and $\bar{M}w/\bar{M}n$

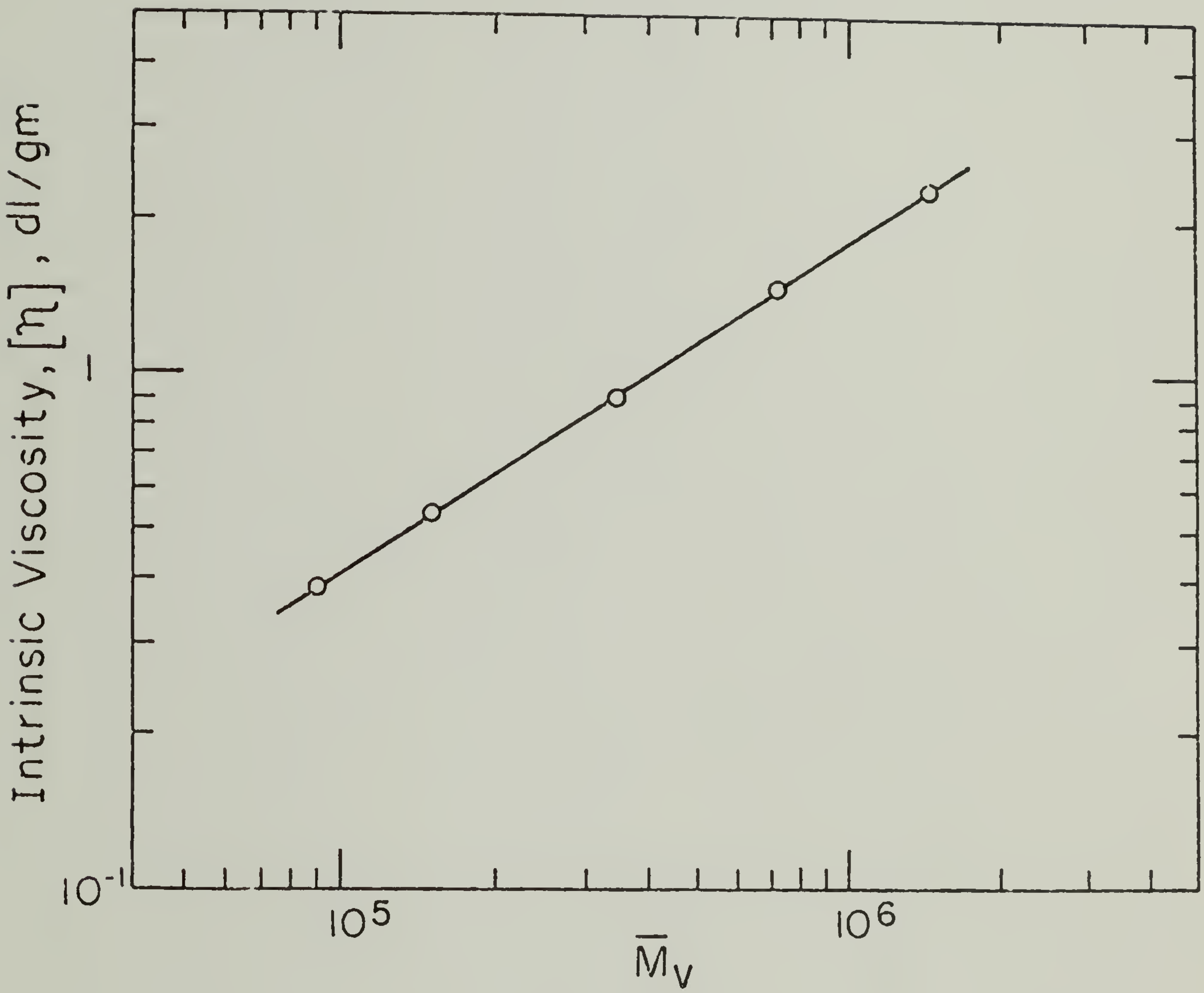


Figure 4.2. Intrinsic viscosity, [η], vs. $\bar{M}v$ for PVAc in THF at 25°C.

from GPC chromatograms. In Table 4.1 molecular weights of three unfractionated and two fractionated samples of PVAc obtained by viscometric measurements and by GPC are compared. PVAc of $\bar{M}w$ 750,000 and $\bar{M}w/\bar{M}n$ 5.1 was used throughout for degradation studies. Band spreading corrections for GPC were not employed.

Results and Discussion

Effect of shearing time. A common feature of mechanochemical processes is an exponential decrease in molecular weight with time. The toluene solution of PVAc (3.0 gm/dl) was sheared at a constant speed of 30,000 rpm. The molecular weight decreases rapidly at the beginning of shear, and thereafter decreases ever more slowly towards a limit. It can be seen from Figure 4.3 that a limiting molecular weight is nearly reached in 5 hours. The change in molecular weight is superimposed by an alteration of molecular weight distribution (MWD). The changes in MWD are important because they influence polymer performance. The PVAc used in this study had a broad initial MWD ($\bar{M}w°/\bar{M}n° = 5.10$). The MWD is narrowed on shearing. The heterogeneity index decreases rapidly at first followed by an ever more gradual decrease (Figure 4.3). The $\bar{M}n$ obtained by GPC is used to calculate chain scission which equals $(\bar{M}n° - \bar{M}n)/\bar{M}n$. Figure 4.4 shows how the total number of chain scissions per molecule increases with shearing time.

TABLE 4.1

COMPARISON OF MOLECULAR WEIGHTS OF POLY(VINYL ACETATE) USED FOR CALIBRATION BY VISCOMETRIC AND GPC MEASUREMENTS

Sample Number	Source	$\bar{M}v\mathrm{x}10^{-3}$ from [η] measurements in acetone $[\eta]=1.76\mathrm{x}10^{-4}\mathrm{x}M_v^{-0.68}$	$\bar{M}v\mathrm{x}10^{-3}$ from [η] measurements in THF $[\eta]=2.47\mathrm{x}10^{-4}\mathrm{x}M_v^{-0.644}$	$\bar{M}w\mathrm{x}10^{-3}$ from GPC	$\bar{M}w/\bar{M}n$ from GPC
1	Polyscience	149	149	154	4.81
2	Polyscience	346	340	350	4.20
3	Polyscience	720	722	750	5.10
4	High End GPC Cut, Sample 1	1448	1450	1500	2.74
5	Low End GPC Cut, Sample 2	90	91	88	2.84

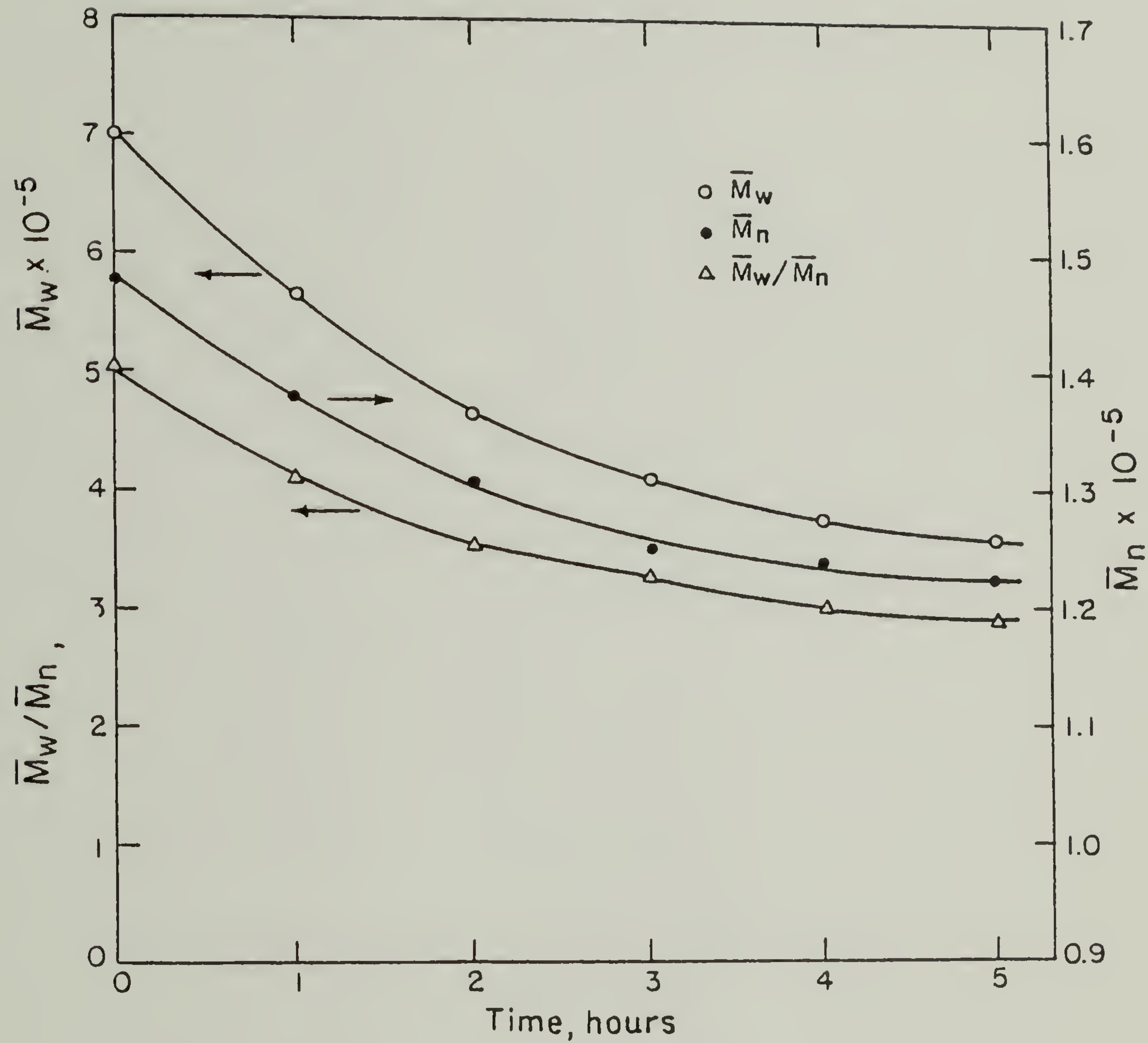


Figure 4.3. Shear degradation of PVAc in toluene (3.0 gm/dl), stirring at 30,000 rpm.

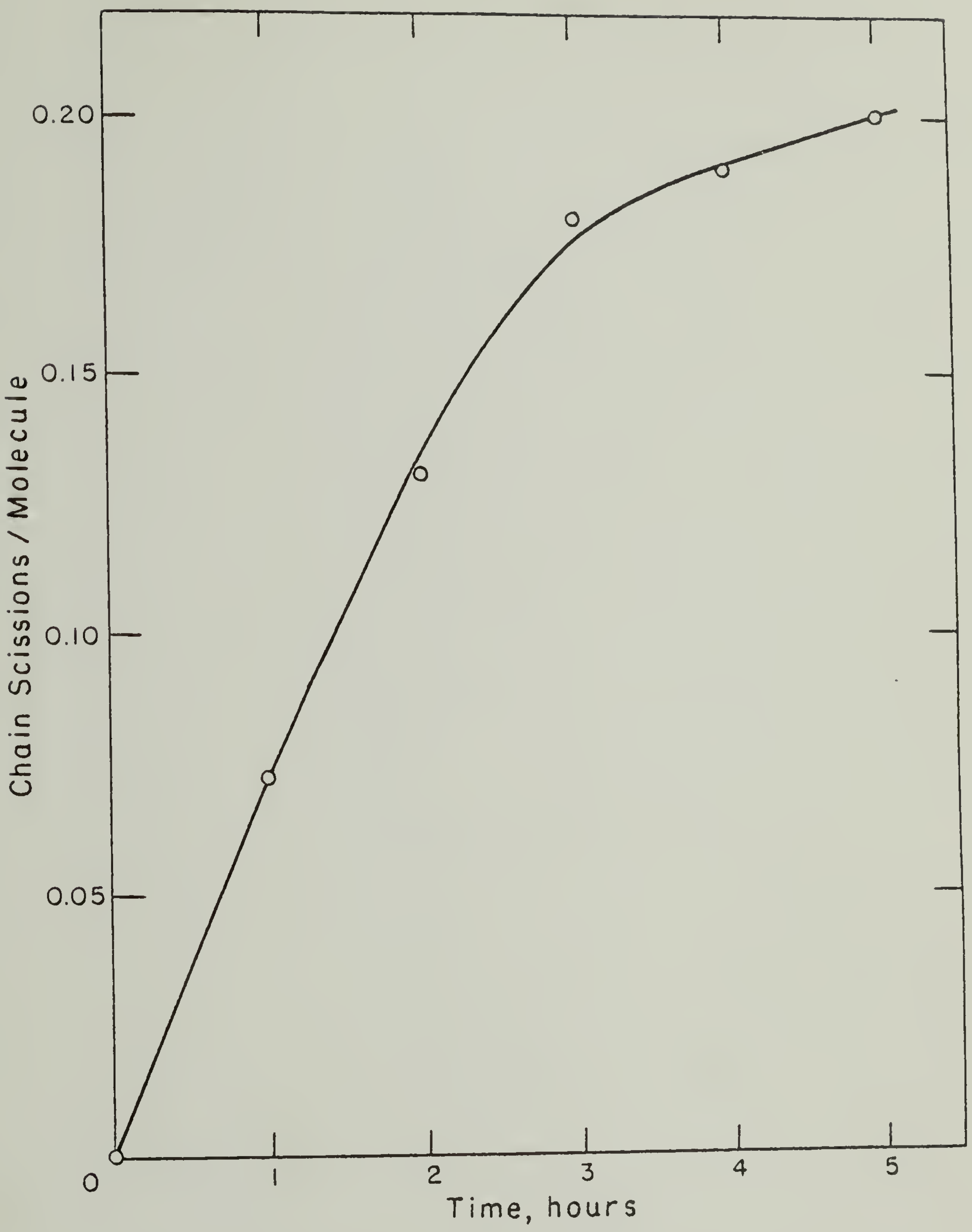


Figure 4.4. Chain scissions per molecule as a function of time for PVAc in toluene (3.0 gm/dl), stirring at 30,000 rpm.

The PVAc chain may break at a C-C bond in the main chain(4-7) or at a C-O bond in the ester linkage if long branches are present.(3) The macroradicals formed may terminate by disproportionation or chain transfer reactions. Recombination is unlikely because oxygen present acts as a radical acceptor. Oxygen reacts readily with macroradicals to form peroxyradicals which deactivate by hydrogen abstraction.(27-29) The abstracted hydrogen atom may be on the acetate group, or it may be on the main chain vinyl links.

Various criteria have been used to assess the location of bond rupture. The relative changes in $\bar{M}w$ and $\bar{M}n$ provide a somewhat preferred criterion for random scission because it utilizes the maximum information available and essentially includes the other criteria commonly used. The relative changes in $\bar{M}w$ and $\bar{M}n$ are fairly sensitive to variations in $\bar{M}w/\bar{M}n$ but less so to details of MWD.(30) The curve in Figure 4.5 represents the theoretical behavior of random chain scission with an initial $\bar{M}w°/\bar{M}n°$ of 5. The relative changes in $\bar{M}w$ and $\bar{M}n$ for shear degradation of PVAc ($\bar{M}w°/\bar{M}n° = 5.1$) in toluene solution at 30,000 rpm are shown by open circles (o) which lie on the theoretical curve indicating that chain rupture occurs randomly under the experimental condition of turbulent flow.

<u>Effect of stirring speed</u>. Variations in stirring speed are

Figure 4.5. The relative changes in $\bar{M}w$, $\bar{M}w/\bar{M}w°$, vs. the relative changes in $\bar{M}n$, $\bar{M}n/\bar{M}n°$, for shear degradation of PVAc in toluene (3.0 gm/dl) compared with the theory for random scission with $\bar{M}w°/\bar{M}n° = 5$ (———).(30) (o) stirring speed = 30,000 rpm, shearing time = 0-5 hrs. (●) stirring speed = 0-50,000 rpm, shearing time = 5 hrs. at each speed.

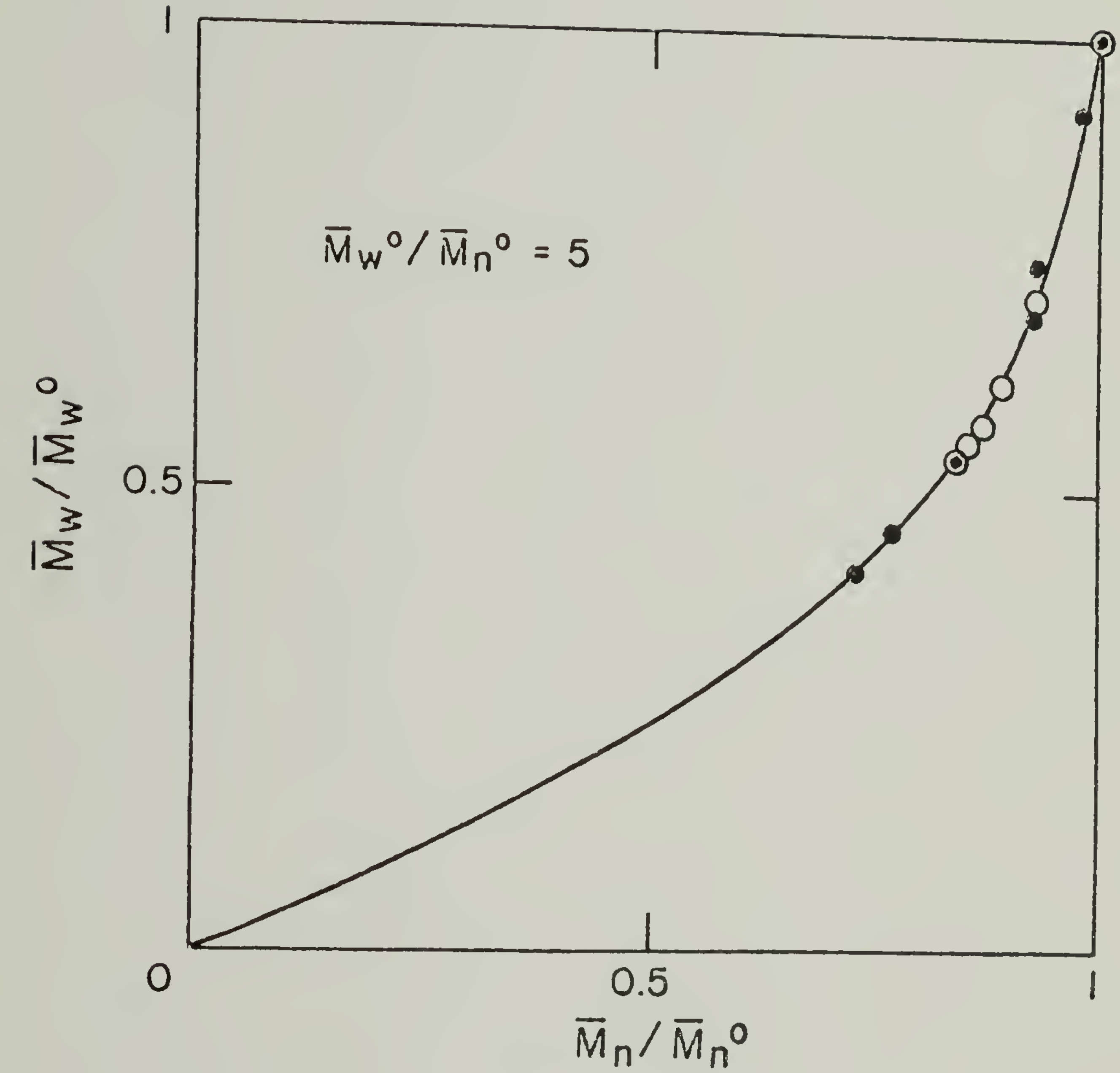

$\overline{M}_w^o/\overline{M}_n^o = 5$
$\overline{M}_w/\overline{M}_w^o$
$\overline{M}_n/\overline{M}_n^o$
0
0.5
1
0.5
1

Figure 4.5

a direct demonstration of dependence of degradation on applied shear. The toluene solution of PVAc (3.0 gm/dl) was agitated at different speeds from 0 to 50,000 rpm. At each speed a fresh original solution was used and each solution was sheared for the same time (5 hrs). There is no change in molecular weights and MWD, i.e., no reaction up to 5,000 rpm. Above 5,000 rpm the molecular weight decreases rapidly with increasing speed, consistent with a minimum critical force required to cause chain scission.$^{(31-34)}$ MWD correspondingly decreases rapidly after 5,000 rpm with increasing speed followed by an ever more gradual decrease (Figure 4.6). Figure 4.7 presents this information in terms of chain scission per molecule. The relative changes in $\bar{M}w$ and $\bar{M}n$ at different rotational speeds are compared with the theoretical behavior for random scission for an initial $\bar{M}w°/\bar{M}n°$ of 5 (Figure 4.5). The experimental data (closed circles) fit the theoretical curve indicating that chain rupture occurs randomly.

<u>Effect of concentration</u>. Toluene solutions of PVAc in the concentration range 3.0 - 12.0 gm/dl were sheared in the homogenizer at 30,000 rpm for the same time (5 hrs). An assembly of five blades and six discs was used for agitation instead of the Teflon cylinder (Figure 4.1). This shear geometry produced more degradation. Generally the higher concentration, i.e., the more viscous, solution is

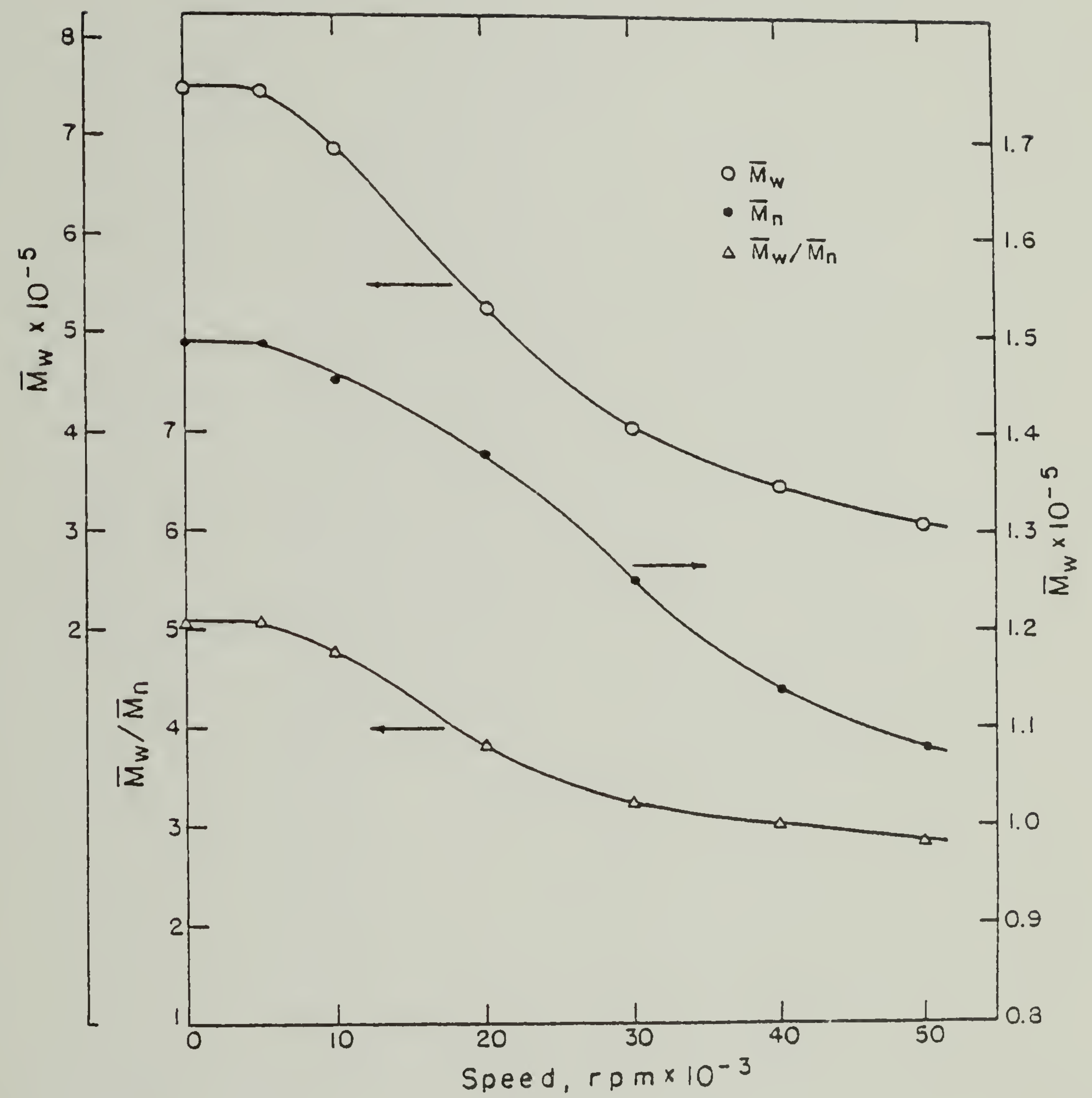


Figure 4.6. Shear degradation of PVAc in toluene (3.0 gm/dl) for 5 hrs. at each speed indicated.

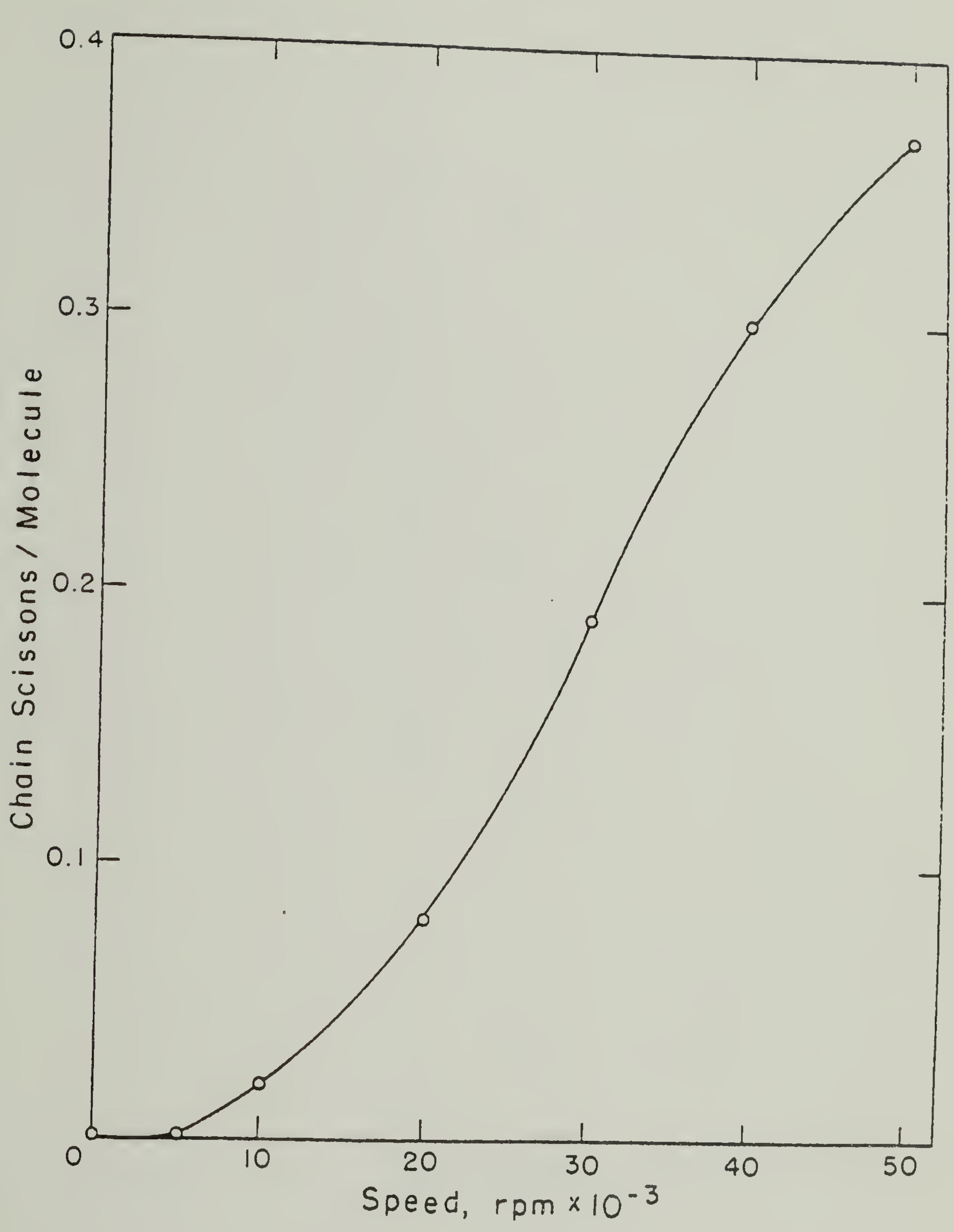


Figure 4.7. Chain scissions per molecule as a function of stirring speed for PVAc in toluene (3.0 gm/dl).

expected to exhibit more degradation because of higher stress.(35-37) But it can be seen from Figures 4.8-4.10 that concentration does not have substantial effect on degradation of PVAc in toluene solution in the range 3.0 - 12.0 gm/dl and that degradation is actually more at the lower concentration. This is consistent with turbulent flow being the most probable cause for bond rupture rather than lamellar shear. Likewise, concentration does not have much effect on MWD with the narrowest distribution being reached at the lowest concentration (Figure 4.11).

The results obtained in this study agree qualitatively with those of Goto and Fujiwara.(3) They studied shear degradation of PVAc in cyclohexanone in the concentration range 1.2 - 4.0 gm/dl. But in their study, the extent of degradation was measured only by $[\eta]$ and did not involve the determination of $\bar{M}n$ or MWD. Hence their results could not provide information on changes in MWD and location of bond rupture as has been done in this study.

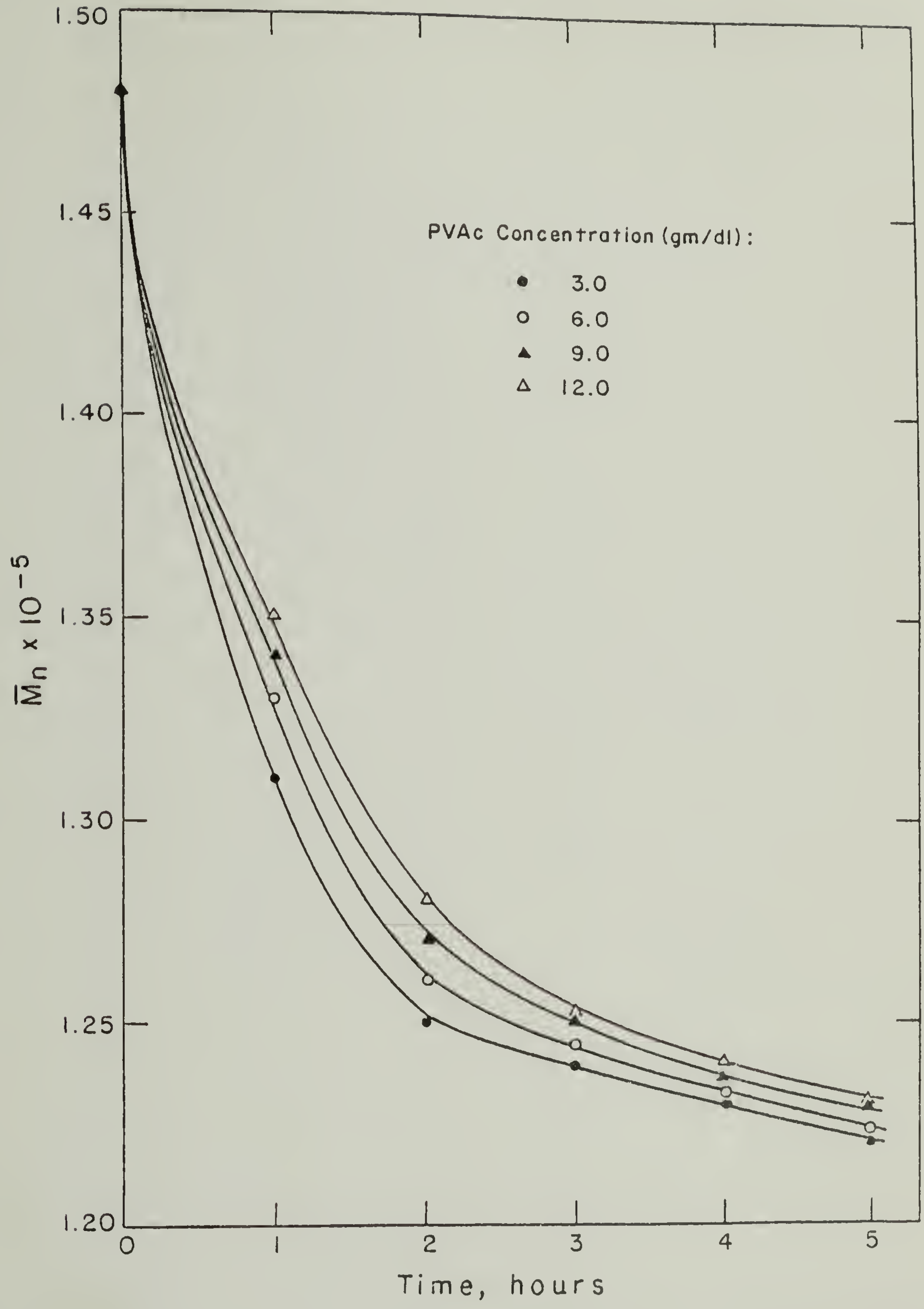


Figure 4.8. Number-average molecular weight, $\bar{M}n$, vs. time for shear degradation of PVAc in toluene, stirring at 30,000 rpm.

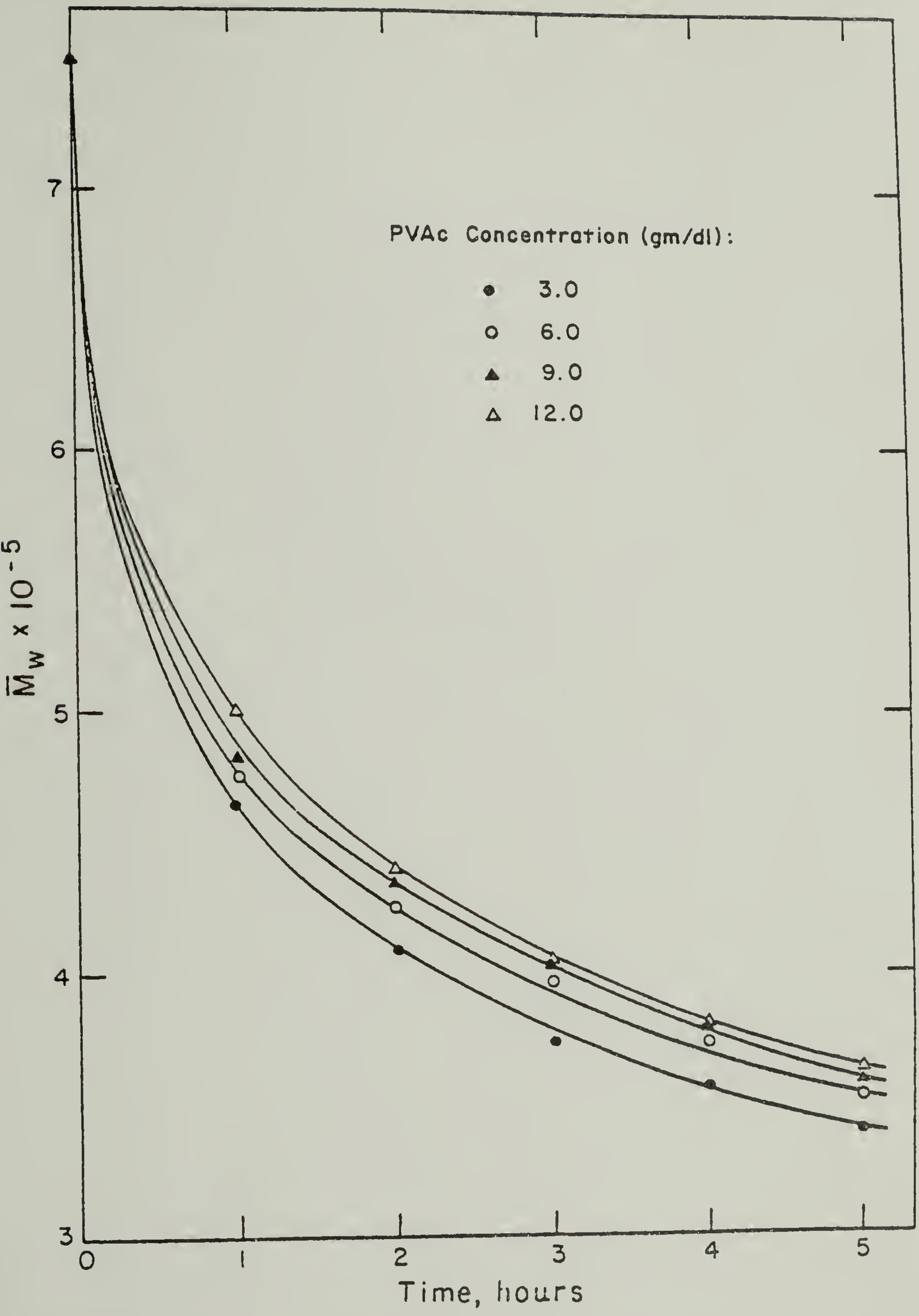


Figure 4.9. Weight-average molecular weight, $\bar{M}w$, vs. time for shear degradation of PVAc in toluene, stirring at 30,000 rpm.

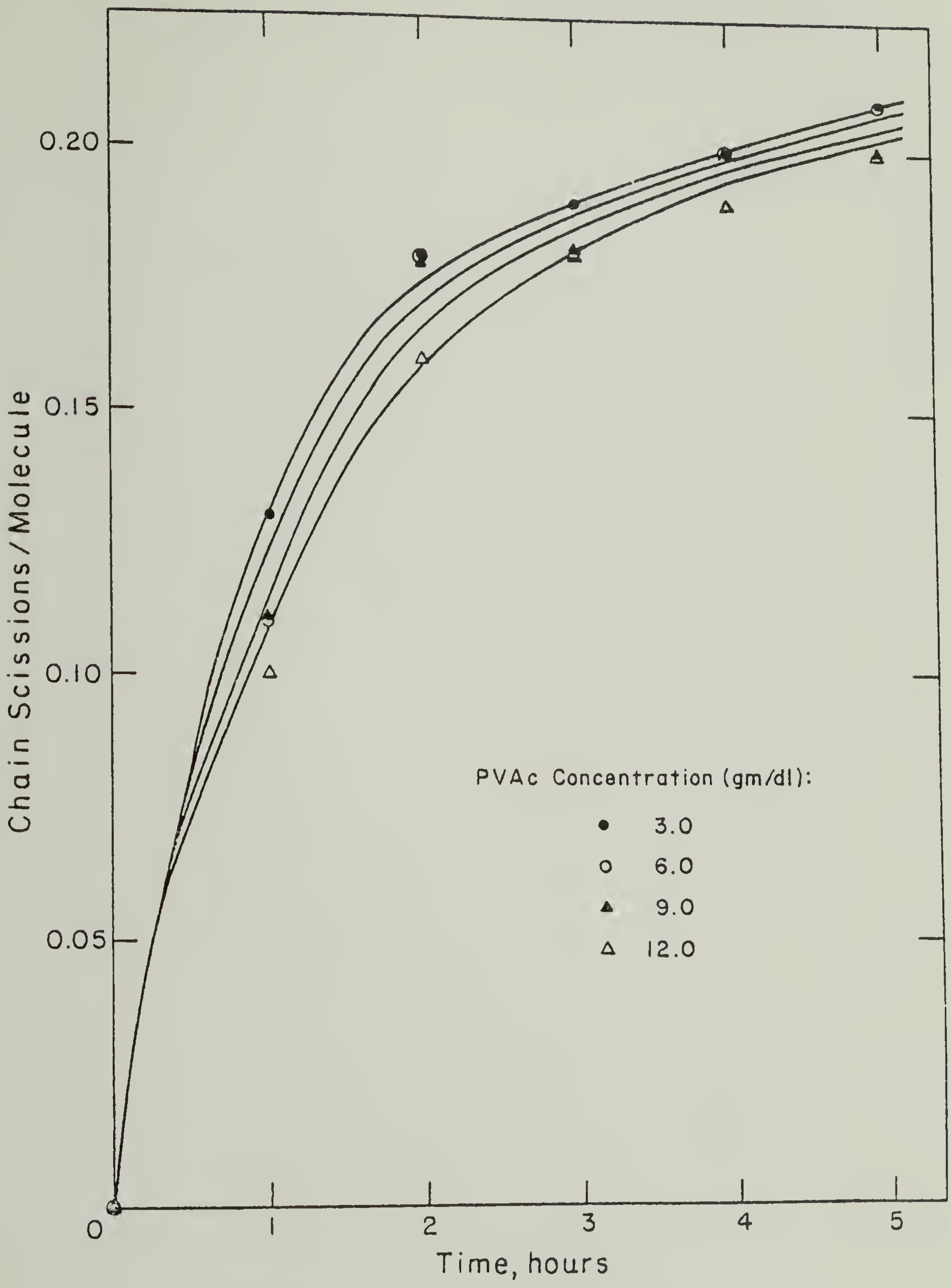


Figure 4.10. Chain scissions per molecule as a function of time for PVAc in toluene, stirring at 30,000 rpm.

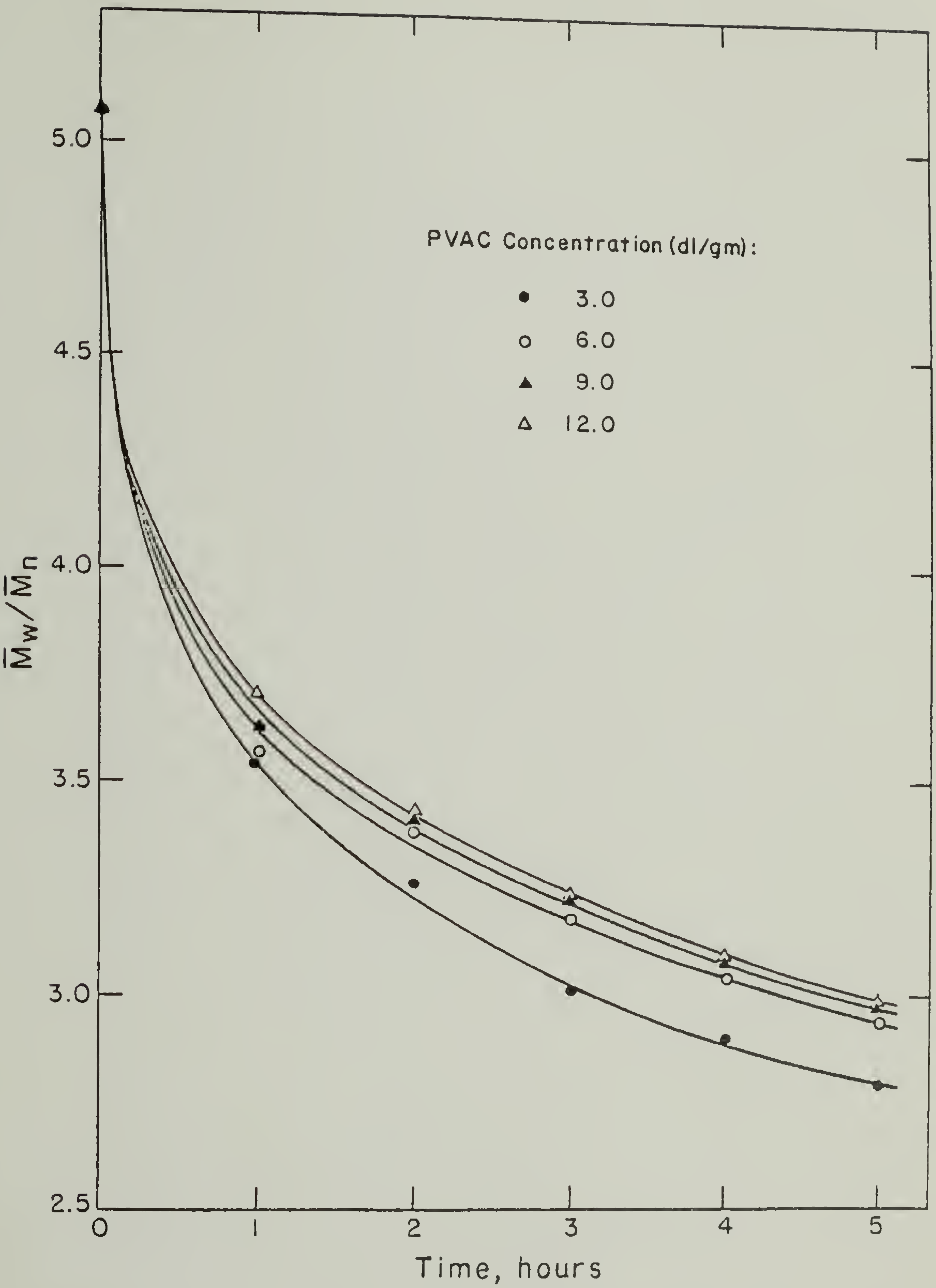


Figure 4.11. Heterogeneity index, $\bar{M}w/\bar{M}n$, vs. time for shear degradation of PVAc in toluene, stirring at 30,000 rpm.

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CHAPTER V

ATTEMPTS AT MECHANICAL SYNTHESIS OF BLOCK AND GRAFT COPOLYMERS OF VINYL ACETATE WITH STYRENE AND METHYL METHACRYLATE

Summary

Solutions of poly(vinyl acetate) (PVAc) in styrene and in methyl methacrylate and solutions of PVAc and polystyrene in benzene were sheared in a nitrogen atmosphere. Mechanical activation was achieved by high-speed stirring in a Virtis-60 Homogenizer. The sheared samples were characterized by precipitation technique, infrared spectroscopy and gel permeation chromatography. It was observed that on shearing no block or graft copolymer was formed even after careful removal of oxygen and moisture from the reaction system. Only a decrease in molecular weight was achieved. It was probably due to the facts that (i) the conversion of mechanical energy to free radical production was low and hence the rate of radical production was slow, (ii) traces of oxygen act as a radical acceptor. Oxygen readily reacts with the macroradicals to form peroxyradicals, which deactivate by hydrogen abstraction and (iii) the few macroradicals generated by shear

might terminate by disproportionation or by reactions with moisture, solvent, and so on. It was also observed that the complete separation of block and graft copolymers from their homopolymers was very crucial and incomplete separation led to erroneous results.

Introduction

The mechanical synthesis of block and graft copolymers is a method of sizeable versatility. It can be performed directly during polymer processing and in standard equipments, such as internal mixers, extruders and injection molding machines. The reaction can be carried out in solid, molten, rubbery or solution state. The structure of copolymers depends on reaction conditions. By altering reaction conditions, it is possible to regulate, within wide limits, the rate of polymer breakdown and thus influence the composition of resulting products.(1) The mechanical synthesis of block and graft copolymers can be carried out either by subjecting a polymer to mechanical activation in the presence of a polymerizable monomer(1-8) or by subjecting a mixture of two or more polymers to mechanical activation.(1,9,10)

Polymer-monomer system. If the mechanochemical reaction is conducted in the presence of a polymerizable monomer, the macroradicals generated by shear can initiate the polymerization of the monomer present:

$$P\dot{m} + sR \longrightarrow Pm - R\dot{s}$$

The block copolymers may also undergo degradation:

$$Pm - Rs \longrightarrow Pm - R^{\cdot}_{s-x} + R^{\cdot}_{x}$$

$$Pm - Rs \longrightarrow P^{\cdot}_{m-x} + P^{\cdot}_{x} - Rs$$

As a consequence, multisegment block copolymers may be formed. Generally, chain transfer to monomer by polymer radicals also occurs to an appreciable extent, and the final product is, therefore, made up of homopolymers, multisegment block copolymers and branched and grafted structures.(1)

Polymer-polymer system. The mechanochemical activation of a mixture of the polymers involves the following steps:(1)

1. Mechanical scission:

$$Pm - Pn \longrightarrow P\dot{m} + P\dot{n}$$

$$Rs - Rt \longrightarrow R\dot{s} + R\dot{t}$$

2. Recombination:

$$P\dot{m} + P\dot{n} \longrightarrow Pm - Pn$$

$$R\dot{s} + R\dot{t} \longrightarrow Rs - Rt$$

3. Cross combination:

$$P\dot{m} + R\dot{s} \longrightarrow Pm - Rs$$

$$\mathrm{P\dot{m}} + \mathrm{R\dot{t}} \longrightarrow \mathrm{Pm} - \mathrm{Rt}$$

$$\mathrm{P\dot{n}} + \mathrm{R\dot{s}} \longrightarrow \mathrm{Pn} - \mathrm{Rs}$$

$$\mathrm{P\dot{n}} + \mathrm{R\dot{t}} \longrightarrow \mathrm{Pn} - \mathrm{Rt}$$

4. Scission of chains by mechanically activated macroradicals:

$$\mathrm{P\dot{m}} + \mathrm{Rs} - \mathrm{Rt} \longrightarrow \mathrm{Pm} - \mathrm{Rs} + \mathrm{R\dot{t}}$$

5. Chain transfer from mechanically activated macroradicals to macromolecules:

$$\mathrm{P\dot{m}} + \mathrm{R} - \mathrm{R} - \mathrm{R} \longrightarrow \mathrm{Pm} + \mathrm{R} - \dot{\mathrm{R}} - \mathrm{R}$$

6. Termination by disproportionation:

$$\mathrm{Pm} - \mathrm{R\dot{s}} + \mathrm{Pn} - \mathrm{R\dot{t}} \longrightarrow \mathrm{Pm} - \mathrm{Rs} + \mathrm{Pn} - \mathrm{Rt}$$

7. Termination by reaction with solvent, radical acceptors, oxygen, and so on.

The composition of block copolymers depends on the relative rates of reactions 2 and 3, which are determined by the relative radical reactivity.

Copolymerization of styrene and vinyl acetate. Copolymers of styrene and vinyl acetate cannot be produced by classical radical copolymerization because styrene radical is highly stabilized by resonance but vinyl acetate radical is not stabilized by resonance.(11,12) As a consequence, vinyl acetate radical is about 100-1,000 times more reactive than styrene radical towards a given monomer, while styrene monomer is about 50-100 times more reactive than vinyl acetate monomer towards a given radical.(13) It is, therefore, observed that reaction of a growing vinyl acetate radical with styrene monomer is highly exothermic (22.5 KCals/mole) and occurs rapidly, whereas the reaction of the growing styrene radical with vinyl acetate monomer is energetically not favored and hardly occurs.(14) This is clearly shown in Table 5.1 by the absolute values of propagation rate constants for the addition reaction of a radical to a monomer at 60°C.(15)

Seymour and Stahl(16) synthesized block copolymers from occluded vinyl acetate macroradicals. First stable vinyl acetate macroradicals were prepared by heating 1 g of vinyl acetate in 19 g of solvent at 50°C in the presence of 0.06 g of tert-butyl peroxypivalate for 96 hrs. Block copolymers were then prepared by adding 1 g of vinyl monomer to the vinyl acetate macroradicals and heating the system at 50°C for 96 hrs. While it was not possible to obtain good yields of block copolymers by heating styrene with vinyl acetate macroradicals, presumably because of chain transfer, good yields of block copolymers were obtained when methyl acrylate, MMA, acrylic acid, vinyl pyrolidone and acrylonitrile were used as blocking monomers. Ceresa(2) synthesized vinyl acetate block copolymers by cold mastication of PVAc swollen with styrene.

It can be seen from Table 5.1 that if vinyl acetate

TABLE 5.1

PROPAGATION RATE CONSTANTS FOR HOMOADDITION AND CROSSADDITION REACTIONS(15)

Monomer	Polymer Radical, K_p, liters $mole^{-1}sec^{-1}$		
	Methyl methacrylate	Styrene	Vinyl acetate
Methyl methacrylate	734	352	247,000
Styrene	1740	176	370,000
Vinyl acetate	37	3.2	3,700

macroradicals are generated in the presence of styrene or MMA, copolymerization should occur readily. This chapter describes the attempts at the mechanical synthesis of block and graft copolymers of vinyl acetate with styrene and MMA. Mechanical activation was achieved by high-speed stirring in a Virtis-60 Homogenizer. Solutions of PS-PVAc in benzene were also sheared in an attempt to form block and graft copolymers. The sheared samples were separated by precipitation technique and characterized by infrared (IR) spectroscopy and gel permeation chromatography (GPC).

Experimental

Materials. PVAc and polystyrene were obtained from Polyscience and Pressure Chemical Company respectively. Hexane was obtained from Eastman Organic Chemicals, whereas benzene, methylene chloride and methanol were supplied by Fisher Scientific Company. Methyl methacrylate (99%) and styrene (99%) were obtained from Aldrich Chemical Company. Nitrogen (N_2) (oxygen free grade) was supplied by Union Carbide Corp.

PVAc was purified by dissolving in benzene to give about 0.02 g/ml concentrated solution which was slowly precipitated in hexane. The precipitates were dried at 40°C and 25 mm of Hg in nitrogen atmosphere for four days.

The monomer (styrene or MMA) was washed with 10%

aqueous sodium hydroxide solution to remove inhibitors and then with distilled water. After washing, it was stirred with anhydrous magnesium sulfate for 24 hrs. To remove the traces of moisture, it was then stirred with calcium anhydride for 24 hrs. Finally, the monomer was distilled under vacuum at 35°C and used immediately. Before starting the distillation, the system was purged with nitrogen. After the distillation was over, nitrogen was again passed through the system, the flask containing the monomer was removed quickly and closed with a septum. Nitrogen was bubbled through purified and distilled monomer for a couple of hours.

Nitrogen (oxygen free) used throughout was dried by passing it through a mixture of dry ice and acetone. To prepare a solution of desired concentration, a known amount of polymer was taken in a dry and clean flask. The flask was closed with a septum and purged with nitrogen. The aliquot volume of the solvent was added with the help of a syringe under nitrogen atmosphere and allowed to dissolve.

Methods. High-speed stirring was achieved by use of a Virtis-60 Homogenizer (variable speed $\leq$ 60,000 rpm) (see Fig. 4.1). This homogenizer was fitted with a teflon cylinder or a combination of blades and discs connected to a stainless steel shaft. Different shapes of flasks were used as reaction vessels. This allowed us to vary the intensity of the shear field at a given rotational speed. The shear field was inhomogeneous and not well-defined. Temperature control was achieved by using a cooling cup or by passing thermostated water through a jacketed reaction vessel.

The homogenizer was placed in a dry box. The flask containing the solution was also put inside the dry box. The dry box was purged with nitrogen and at the same time nitrogen was bubbled through the solution. Then the solution was transferred from the flask to the reaction vessel and sheared at a known stirring speed. During agitation nitrogen was passed through the reaction vessel as well as through the dry box. It was observed that if the inlet to pass nitrogen was at the bottom of the reaction vessel, nitrogen flow helped the solution to splash out of the vessel. Hence the reaction vessels with inlet at the top were used so that a positive pressure of nitrogen was maintained above the solution, which helped to reduce the splashing of the solution during agitation. Samples were characterized by precipitation technique, IR spectroscopy (Perkin-Elmer IR Spectrometer-283), and GPC (Water Associates Model 200).

Results and Discussion

Polymer-monomer system. PVAc was sheared in presence of styrene and MMA monomer in the hope that macroradicals generated by mechanical activation of PVAc might initiate the polymerization of the monomer present to form block and graft copolymers.

Poly(vinyl acetate)-styrene. PVAc ($\bar{M}w$ = 750,000; $\bar{M}w/\bar{M}n$ = 5.10) in styrene (0.20 g/ml) was sheared for 1 hr at 30,000 rpm and 20 ± 0.5°C in nitrogen atmosphere. The sheared solution was separated into fractions by the precipitation technique given in Fig. 5.1. Fraction I was not obtained and IR of fraction II was the same as that of pure PVAc, indicating that no homo- or copolymerization of styrene occurred. The GPC chromatograpm showed that MW was decreased and MWD was narrowed. Hence macroradicals were formed but were stabilized presumably because of chain transfer. This result is similar to that obtained by Seymour and Stahl,(16) who also were not able to obtain good yields of block copolymers by heating styrene with occluded vinyl acetate macroradicals, but were able to obtain good yields of block copolymers when methyl methacrylate, acrylonitrile, vinyl pyrolidone, methyl acrylate and acrylic acid were used as blocking monomers. When PVAc in styrene was sheared in air, no homo- or copolymerization of styrene occurred and the GPC chromatograms showed that MW was decreased and MWD was narrowed on shearing (see Fig. 5.2). This is in accord with that observed by

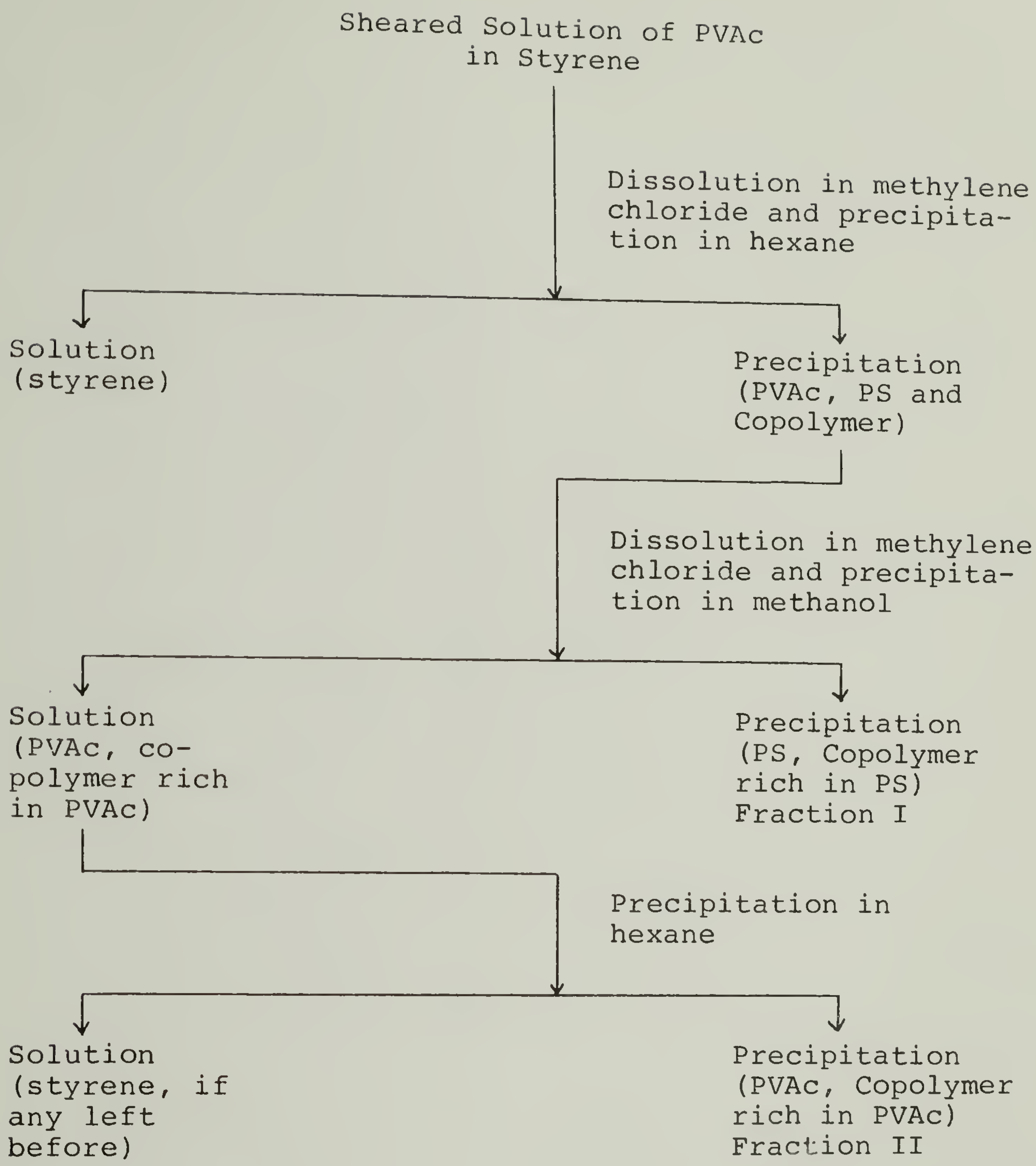

Figure 5.1. Precipitation technique for isolation of styrene-vinyl acetate copolymer for polymer-monomer system.

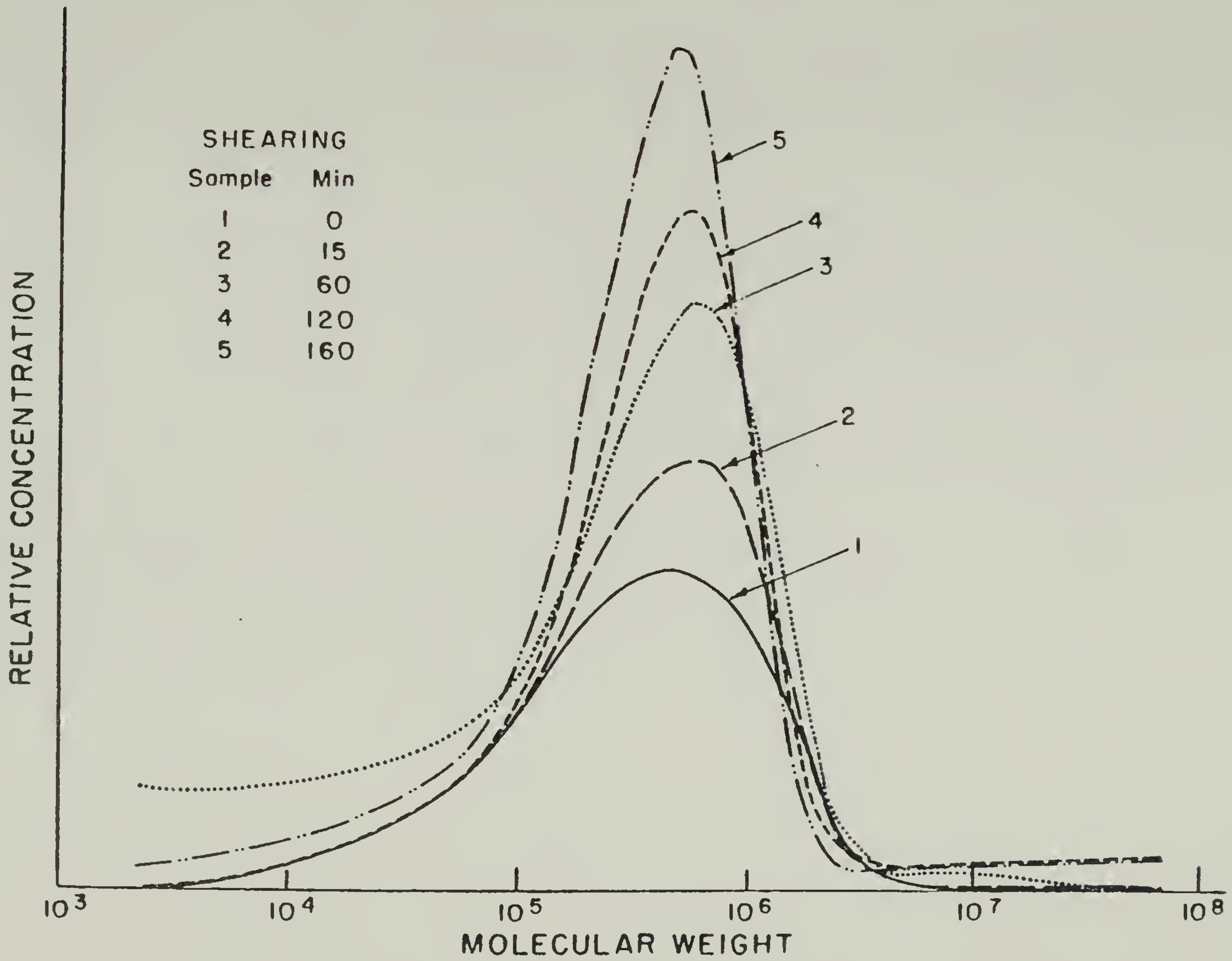

Figure 5.2. Shear degradation of PVAc in styrene (0.20 g/ml) at 10°C in air.

others.(17-22)

Poly(vinyl acetate)-methyl methacrylate. PVAc ($\bar{M}w$ = 1.75×10^6; $\bar{M}w/\bar{M}n$ = 6.0) in MMA (0.03 g/ml) was sheared at 40,000 rpm and 20 ± 0.5°C for 3 hrs. with Teflon cylinder in nitrogen atmosphere. The sheared solution was separated by the precipitation technique given in Fig. 5.1. Fraction I was not obtained and the IR spectrum of fraction II was identical to that of pure PVAc. The GPC chromatogram of the sheared polymer (fraction II) showed that MW was decreased and MWD was narrowed. Hence, when shearing of PVAc in MMA was conducted in nitrogen atmosphere, no homo- or copolymerization occurred and only a classical decrease in MW was obtained, indicating that macroradicals generated by mechanical activation died probably by abstraction or other chain transfer reactions.

It was felt that an increase in temperature might cause macroradicals to initiate the polymerization of monomer because at higher temperature, the reactivity of polymer radicals and monomer is increased though the lifetime of radicals is decreased. Hence PVAc in MMA was agitated at a temperature of 50 ± 0.5°C, other reaction conditions were the same as before. It was observed that the solution became viscous on shearing. The stirring was stopped after 1 1/2 hrs. because the solution remained in the reaction vessel after 1 1/2 hrs. was not enough for agitation. The sheared solution was separated into fractions by the precipitation technique given in Fig. 5.1. As before, fraction I was not obtained and IR spectrum of fraction II was the same as that of pure PVAc. The GPC chromatogram of the sheared polymer (fraction II) indicated that MW was decreased and MWD was narrowed on agitation.

It implied that during agitation the solution became more concentrated and viscous due to solvent loss and not because of homo- or copolymerization of MMA. There could be several reasons for the failure of the attempts to synthesize block and graft copolymers of VAc-MMA by mechanical synthesis. For example, the chain scission per molecule over a period of 3 hrs. was only 0.2. This indicated that the rate of radical production was slow. Hence, the macroradicals generated by shear were probably not enough to initiate block and graft copolymerization and the few macroradicals formed might have been stabilized by abstraction or chain transfer reactions. Though dry and oxygen free nitrogen was used, the traces of moisture and oxygen present would be enough to kill the few macroradicals formed. Moreover, oxygen is also dissolved in the solution. Oxygen acts as a radical acceptor. Oxygen reacts readily with macroradicals to form peroxyradicals, which deactivate by hydrogen abstraction.(23-25) The following attempts were made to improve the reaction conditions.

Freezing and thawing. To remove oxygen dissolved in the solution, freezing and thawing "cycling process" was used. However, it should be remembered that degradation of polymers in solution can occur by freezing.(26-30) The degradation force in the cycling process is believed to be the stresses at the crystallizing point of the solvent. This assumes that the rate of macromolecule migration is slower than the rate of crystallization. A review of mechanochemistry by freezing and thawing has been compiled in a new text.(31)

40 ml of PVAc in MMA (0.03 g/ml) was taken in a 100 ml round bottom flask. The flask was closed with a 3-way stopcock. Nitrogen was bubbled through the solution for 1 hr. The flask was then closed and immersed into a four liter dewar containing liquid nitrogen. When the solution was found to freeze completely, vacuum (2.5×10^{-2} mm of Hg) was applied for 20 mins. After this time the flask was closed and removed from the dewar and placed in methanol maintained at 50°C until the sample thawed completely. After thawing was complete, the flask was again immersed into dewar containing liquid nitrogen and the cycles of freezing and thawing were repeated. Samples were withdrawn at various intervals for GPC analysis. It was observed that there was no change in MW on freezing up to

30 cycles. This result is similar to that obtained by Porter et al.,(30) who also observed that there was no degradation on freezing of solutions of polystyrene in p-xylene for molecular weights below two million. The MW of PVAc used in this study was 1.75 million.

After 30 cycles of freezing and thawing, the solution was agitated at 30,000 rpm and 15°C for 4 hrs. in nitrogen atmosphere. To increase the intensity of shear, a narrow gap reaction vessel and a modified blade discs geometry was used. On selective precipitation of sheared solution, no homo- or copolymer of MMA was obtained. The IR spectrum of the sheared polymer was the same as that of pure PVAc. The GPC chromatogram showed that MW was decreased and MWD was narrowed ($\bar{M}w = 830{,}000$; $\bar{M}w/\bar{M}n = 3.46$). The chain scission per molecule was found to be 0.21. Thus even after removing the dissolved oxygen from the solution and increasing the intensity of shear field, no homo- or copolymerization of MMA occurred.

One distinguishing feature of mechanochemistry is that it has a negative temperature coefficient, i.e., the efficiency of degradation increases with decreasing temperature.(1) Hence PVAc in MMA (0.03 g/ml), after removal of dissolved oxygen by freezing and thawing, was agitated at 30,000 rpm for 4 hrs. in nitrogen atmosphere at 5°C. The chain scission per molecule was calculated to be 0.32 as compared to 0.21 observed at 15°C. This indicates that more degradation occurs at lower temperature, i.e., the temperature coefficient of mechanochemistry is negative. However, still no homo- or copolymerization of MMA was observed.

Polymer-polymer system. Solutions of PVAc-PS in benzene (0.12 g/ml) were agitated at 30,000 rpm in nitrogen atmosphere. The sheared solution was separated by the precipitation technique given in Fig. 5.3. Fraction I was made into a film by compression molding at a temperature of 260°C and pressure of 25,000 psi. The IR spectra of films of fraction I, pure PS and pure PVAc are compared in Fig. 5.4. The IR spectrum of fraction I showed the characteristic absorption bands of styrene due to aromatic ring at 3030, 1600, 1495, 760 and 700 cm^{-1}(32) as well as the presence of the absorption bands at 1740 and 1250 cm^{-1}, characteristic of ester group.(33) This suggested that the fraction I may be a copolymer of vinyl acetate-styrene. However, if the separation was not complete, traces of PVAc left in fraction I would give absorption bands in IR spectrum. To make sure that PVAc was removed completely, the fraction I was extracted with methanol for 24 hrs. in a Soxhlet extractor. The IR spectrum of the fraction I after extraction still showed the presence of absorption bands at 1740 and 1250 cm^{-1} (see Fig. 5.5) but the intensity

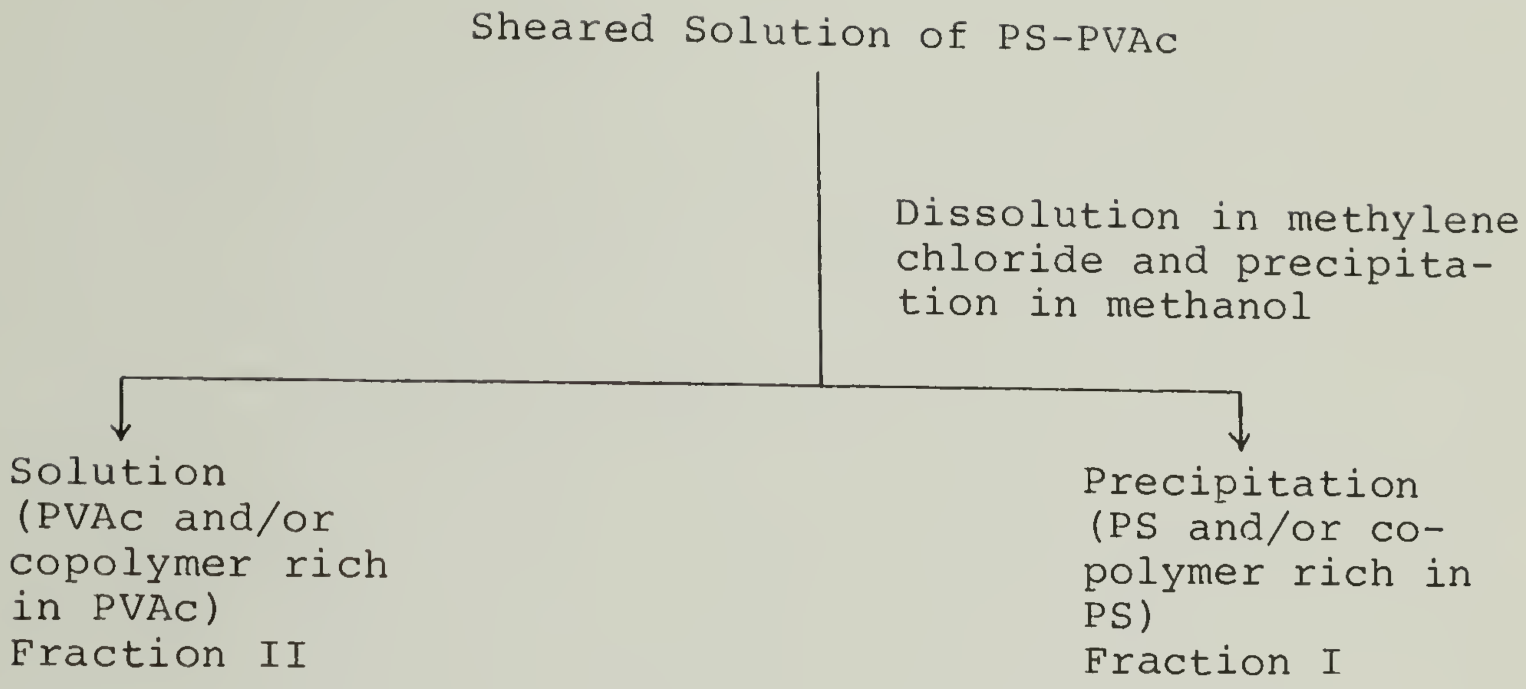

Figure 5.3. Precipitation technique for isolation of styrene-vinyl acetate copolymer for polymer-polymer system.

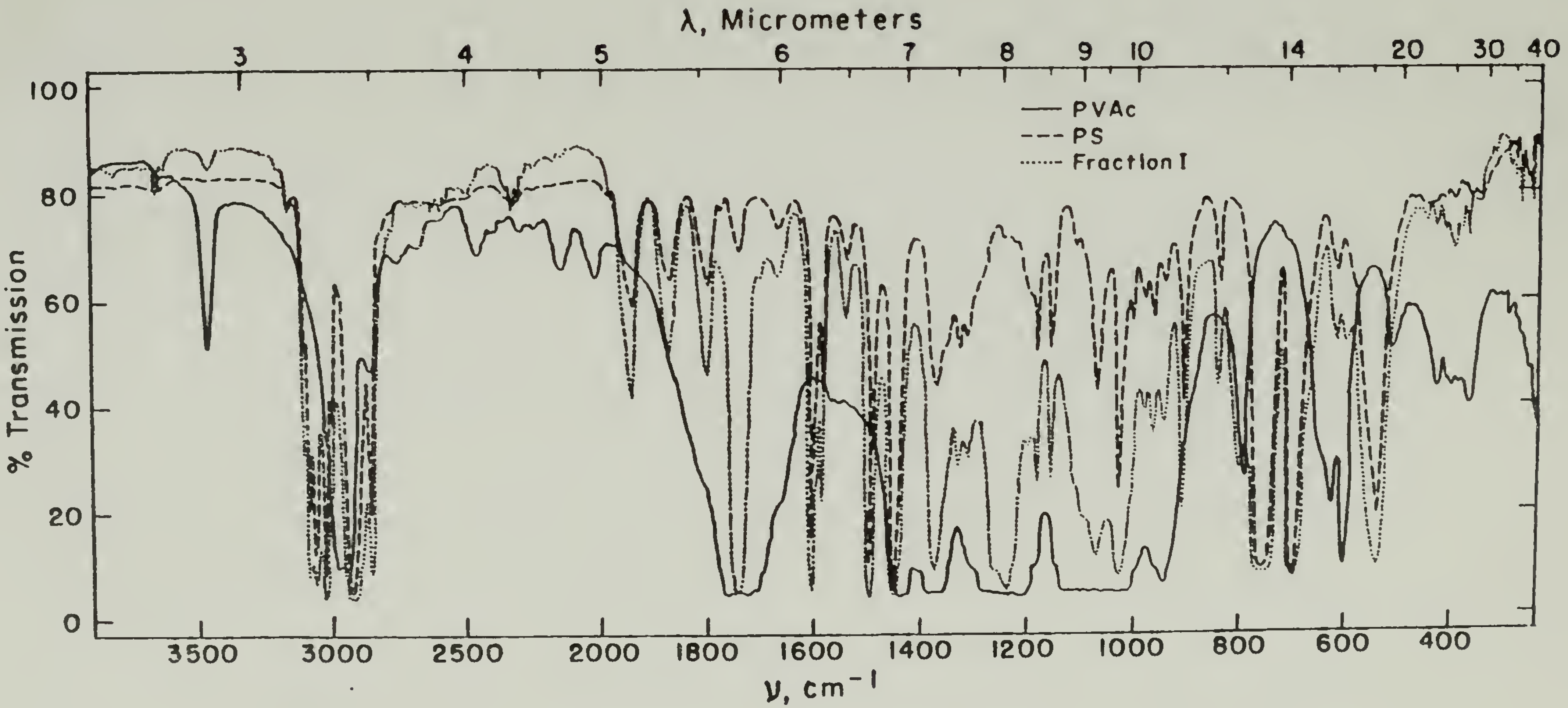

Figure 5.4. Comparison of IR spectra of PVAc, PS and fraction I.

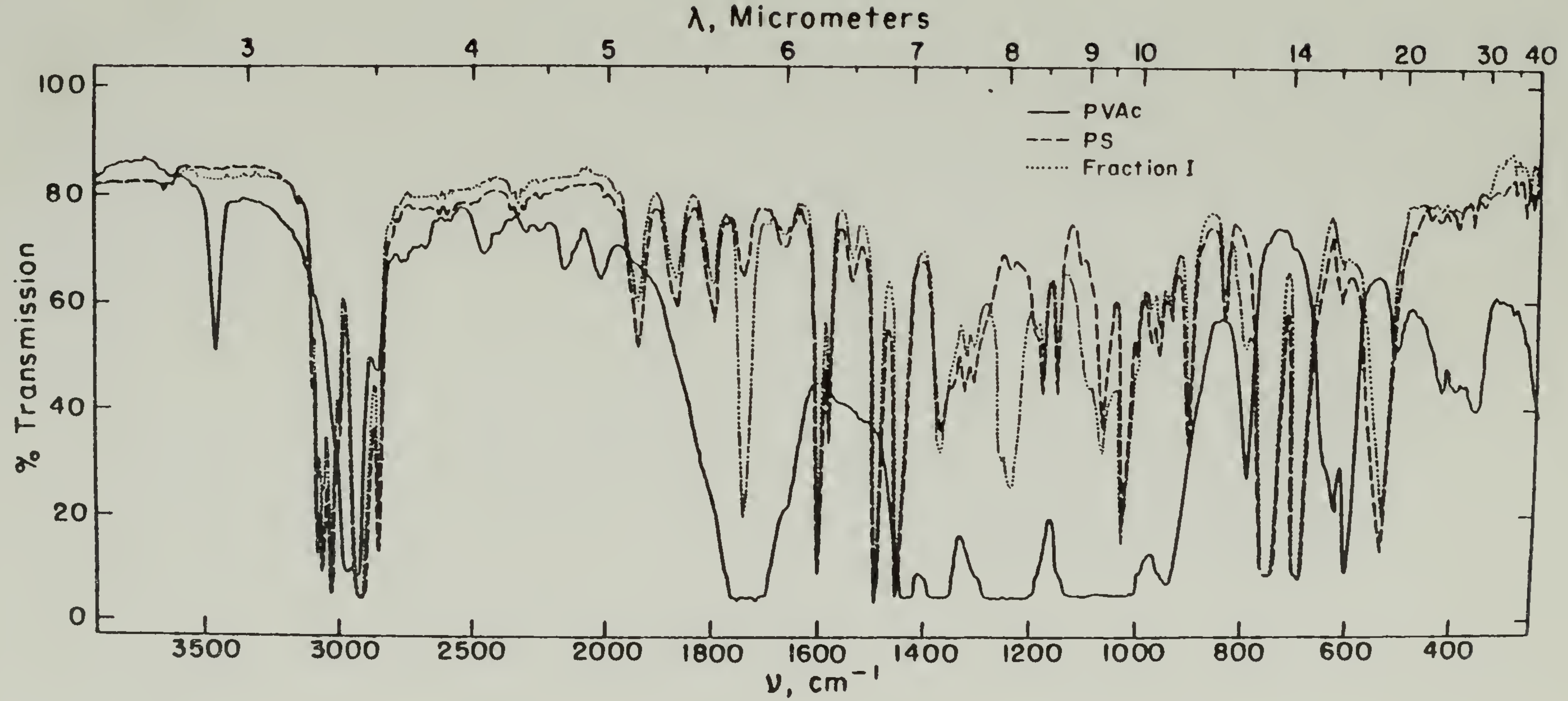

Figure 5.5. Comparison of IR spectra of PVAc, PS and fraction I after extraction with methanol.

of bands was somewhat decreased. This suggested that absorption bands at 1740 and 1250 cm^{-1} might be due to incomplete removal of PVAc from fraction I. A film was obtained from fraction II by solvent evaporation. The IR spectrum of fraction II was identical to that of pure PVAc, indicating that fraction II was pure PVAc (see Fig. 5.6).

To verify whether the absorption bands observed at 1740 and 1250 cm^{-1} were due to copolymerization or due to incomplete separation, a blank experiment was conducted, in which the original unsheared solution of PS-PVAc in benzene was separated by the precipitation technique given in Fig. 5.3. The ppt's (fraction I) were extracted with methanol for 8 hrs. and dried at 25°C and 25 mm of Hg for two days. The IR spectrum of fraction I was compared with that of pure PS and PVAc in Fig. 5.7. The IR spectrum of fraction I showed the absorption bands at 3030, 1600, 1495, 760 and 700 cm^{-1}, characteristic of PS and absorption bands at 1740 and 1250 cm^{-1}, characteristic of PVAc. Though the intensity of peaks at 1740 and 1250 cm^{-1} was small, it clearly indicated that the separation was definitely incomplete and even after extraction with methanol, PVAc was not completely removed. To remove PVAc completely, fraction I was redissolved in methylene chloride to give a solution containing at the most 5% polymer. This time, instead of adding polymer solution to the precipitating agent,

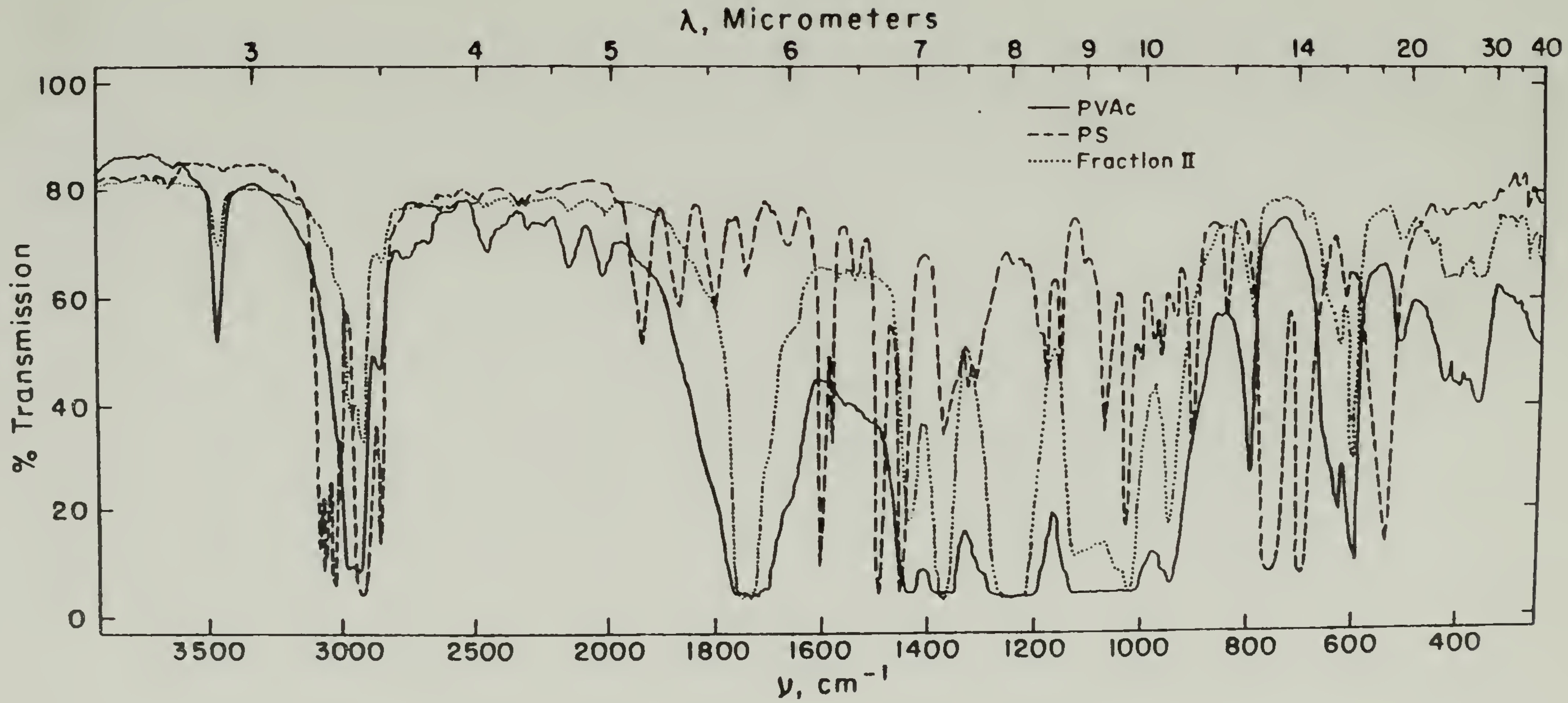

Figure 5.6. Comparison of IR spectra of PVAc, PS and fraction II.

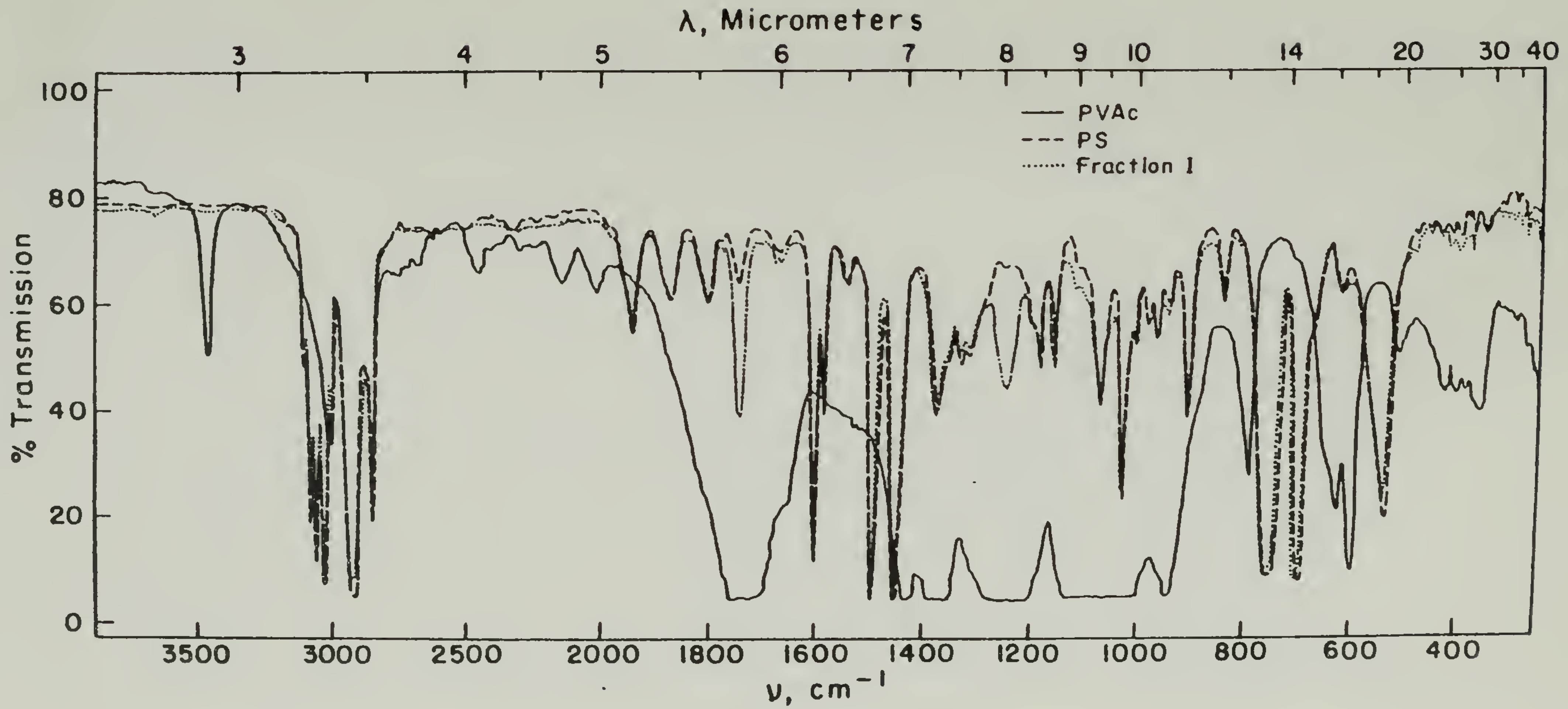

Figure 5.7. Comparison of IR spectra of PVAc, PS and fraction I after extraction with methanol for blank experiment.

15-to-20-fold amount of methanol was added dropwise to the methylene solution under vigorous stirring. The precipitates were filtered, washed and dried. The IR spectrum of these precipitates (fraction I') was the same as that of pure PS and showed no peaks at 1740 and 1250 cm^{-1}, indicating that the separation was complete (see Fig. 5.8). Hence the precipitation technique given in Fig. 5.1 was modified to that given in Fig. 5.9.

A PS-PVAc solution in benzene (0.05 g/ml) was agitated at 30,000 rpm for 25 mins. under nitrogen atmosphere. The sheared solution was separated by the modified precipitation technique and characterized by IR spectroscopy. The IR spectrum of fraction I' was identical to that of pure PS and that of fraction II was identical to pure PVAc. This indicated that the separation by the modified precipitation technique given in Fig. 5.9 was complete and no block or graft copolymer was formed on shearing PS-PVAc solution in benzene under nitrogen atmosphere.

Generally for isolation of polymers, the reaction mixture or the polymer solution is added dropwise to the large amount of precipitating agent under vigorous stirring. However we observed that a complete separation was obtained by adding the precipitating agent to the polymer solution. By this method the polymer which could not be removed even by extraction was also easily precipitated.

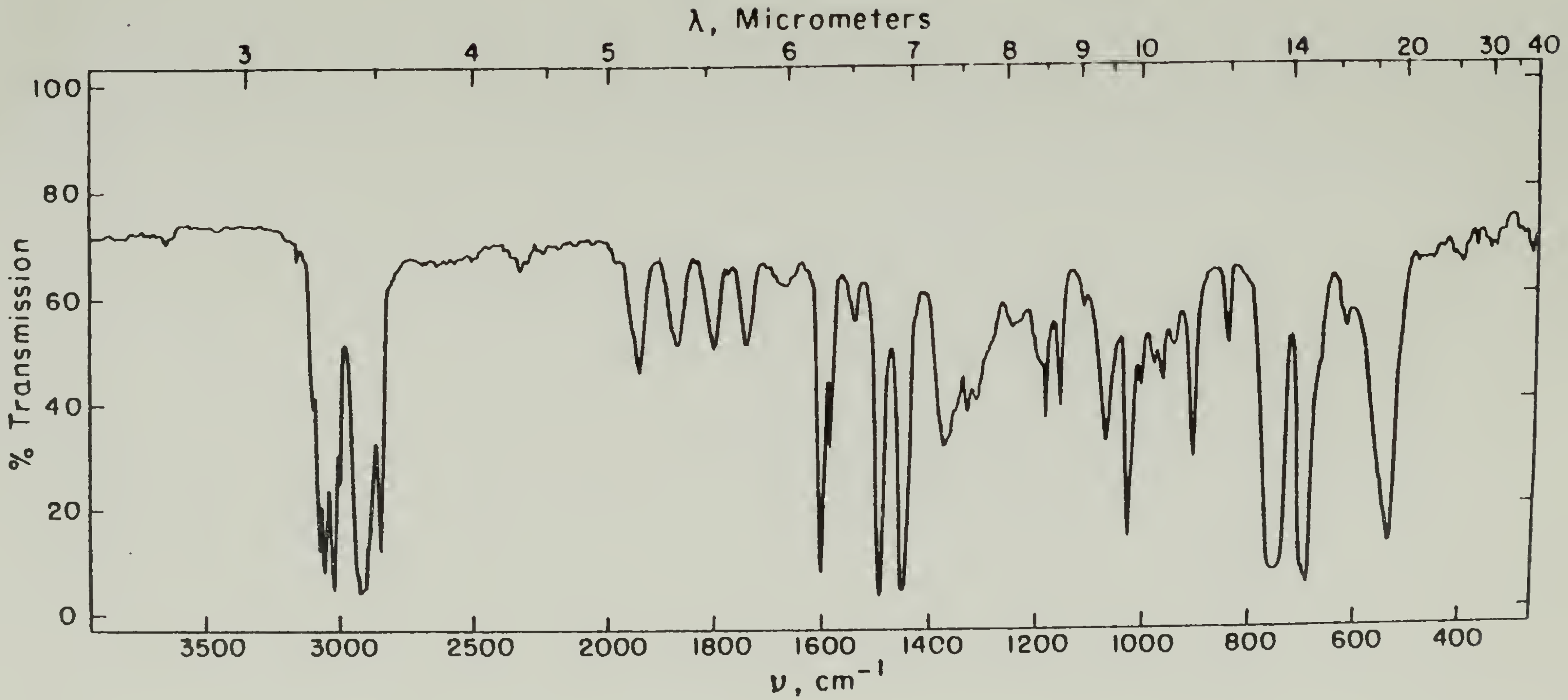

Figure 5.8. IR spectrum of fraction I'.

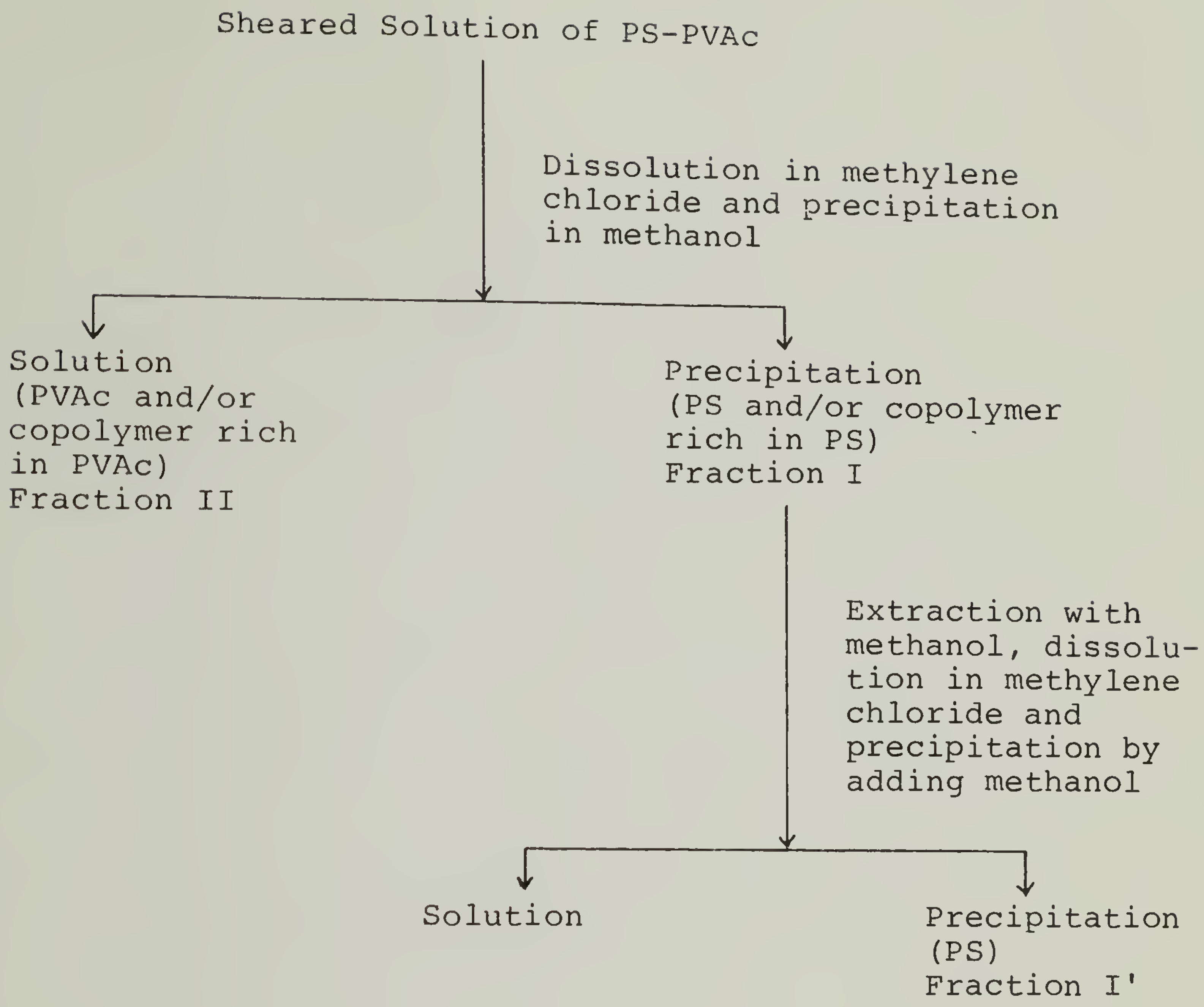

Figure 5.9. Modified precipitation technique for isolation of styrene-vinyl acetate copolymer for polymer-polymer system.

Conclusions

Casale and Porter$^{(1)}$ have reported that mechanically induced reaction in a dilute solution, by high-speed stirring, is not readily achieved since interpolymer interactions, for example by collisions and through entanglements, are rare. We also observed that block and graft copolymers of vinyl acetate could not be produced by mechanical activation of PVAc solutions in styrene, MMA and PS. There could be various causes for the failure of the attempts to synthesize block and graft copolymers. The conversion of mechanical energy to free radical production was low and the rate of radical production was slow. Therefore the macroradicals generated by shear were probably not enough to initiate block or graft copolymerization and the few macroradicals formed might have been stabilized by abstraction or chain transfer reactions. Though we used dry and oxygen free nitrogen, the traces of moisture and oxygen left would be enough to inhibit the reaction.

We have merely described our observations in the thought that they will show that mechanically induced reactions in solution, by high-speed stirring, are not readily achieved. Since the conversion of mechanical energy to free radical production in solution is low, one should use higher shear field to produce a large number of macroradicals. However, if one attempts to generate higher stresses by increasing the solution concentration or by reducing the gap, the solvent loss due to shear heating becomes a problem. Mechanical synthesis, therefore, should be conducted at lower temperature so that the efficiency of chain scission is higher as well as the solvent loss is minimized. It is also necessary to use a very inert atmosphere as traces of oxygen and moisture inhibit the reaction. The complete separation of copolymers from the corresponding homopolymers is very crucial because if the separation is not complete, erroneous results can be obtained. Thus this chapter presents the problems which one encounters during mechanical synthesis of block and graft copolymers.

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