

THE UNIVERSITY OF MICHIGAN
INDUSTRY PROGRAM OF THE COLLEGE OF ENGINEERING

VISCOSITY OF DILUTE SOLUTIONS OF LINEAR
AND BRANCHED POLYVINYL ACETATE

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ABSTRACT

The dilute solution viscosity properties of fractions of two linear and one branched sample of polyvinyl acetate in benzene and of two linear and one branched fraction in several solvents were measured at 35°C. Values of total slope, b (from plots of η_{sp}/c vs. c), and intrinsic viscosities were obtained under the requirement that $k' + \beta = 0.500 \pm 0.002$.

Empirical plots of $\log b$ vs. $\log [\eta]$ gave lines which were straight within the limits of accuracy of the data. For the linear fractions in benzene, Huggins' k' was constant and the slope of the $\log b$ vs. $\log [\eta]$ line was 2; for the branched fractions in benzene, k' increased with $[\eta]$ and the slope of the $\log b$ vs. $\log [\eta]$ line was greater than 2. The $\log b$ vs. $\log [\eta]$ plots form the basis for a "one-point" method for determining $[\eta]$.

Consideration of these data along with results reported in the literature indicates that k' is measurably sensitive to branching only for fractions possessing a certain minimum combination of size and complexity. However, in some cases where the variations of k' are inconclusive, use of the slope of the $\log b$ vs. $\log [\eta]$ line may provide a reliable indication of branching. It was found that a comparison between the branched and linear series could also be made at constant values of $[\eta]$ or b .

Two linear fractions in different solvents obeyed a type of Huggins relationship in which k' did not vary with solvent and the slope of the $\log b$ vs. $\log [\eta]$ line was 2. For a higher molecular weight branched fraction, however, k' varied from solvent to solvent and the slope of the log-log plot was about 1.7. These data do not support a reference point concept of "true" intrinsic viscosity based on a simple linear relationship between b and $[\eta]$.

Preliminary results dealing with the effects of the shear rate indicated that the measured viscosity properties of branched fractions may be more seriously affected by changes in shear rate than those of linear fractions.

VISCOSITY OF DILUTE SOLUTIONS OF LINEAR
AND BRANCHED POLYVINYL ACETATE*

I. INTRODUCTION

The viscosity properties of dilute polymer solutions are recognized to be influenced by the molecular weight, structure, shape, and chemical nature of the polymer, and by the nature of the polymer-solvent interaction. Considerable interest exists in the identification of some viscosity reference point in terms of which differences in molecular and structural properties can be measured.

Of course, in a sense $[\eta]$ and k' in the Huggins¹ relationship

$$\eta_{sp}/c = [\eta] + k' [\eta]^2 c \quad (1)$$

represent reference points, where $[\eta]$, the limiting viscosity number or intrinsic viscosity, is independent of concentration effects but varies with molecular weight, polymer structure, solvent, and shear rate. The Huggins constant k' is sensitive to many of these variables also, but in a given solvent, its value appears to be subject mainly to variations in polymer structure.^{2,3}

The relationship of Flory and Fox,⁴

$$[\eta]_{\theta} = K M^{1/2} \quad (2)$$

defines a reference point for $[\eta]$ under the condition that the net thermodynamic polymer-solvent interaction is zero.

* A preliminary account of this work was presented at the Ann Arbor High Polymer Research Conference, July 25, 1955.

Eirich and Riseman⁵ and Streeter and Boyer⁶ have suggested that, with a given fraction in different solvents, the total slope b in the viscosity relationship,

$$\eta_{sp}/c = [\eta] + bc, \quad (3)$$

can vary in a linear manner with $[\eta]$. Cleverdon and Smith⁷ have extended this idea and have proposed the existence of a "true" limiting viscosity number $[\eta]_{\text{T}}$ which varies with the molecular weight but is independent of solvent, and which represents $[\eta]$ under the unique condition of zero hydrodynamic interaction. They suggested further that there may be some relationship between $[\eta]_{\text{T}}$ and $[\eta]_{\theta}$.

The viscosity properties of fractions of two linear samples and one branched sample of polyvinyl acetate in benzene, and of two linear fractions and one branched fraction in several solvents were measured. The intrinsic viscosities and slope constants were calculated under the arbitrary requirement that $k' + \beta = 0.500 \pm 0.002$; the following plots were made: k' vs. $[\eta]$, and $\log b$ vs. $\log [\eta]$. From the results it may be seen that straightforward comparisons of the viscosity properties of linear and branched polyvinyl acetate fractions may be made at constant values of b (hydrodynamic interaction) or at constant values of $[\eta]$ (hydrodynamic volume). However, no apparent basis for a reference-point concept of intrinsic viscosity at zero hydrodynamic interaction was found.

II. EXPERIMENTAL

A. Materials

1. Solvents. The following reagent grade solvents were employed: acetone, carbon tetrachloride (Merck and Company), methyl alcohol, benzene

(Baker and Adamson), chloroform, toluene (J. T. Baker and Company), trichloroethylene, 1,2-dichloroethane, methyl acetate (Eastman Organic Chemicals), and amyl acetate (Mallinckrodt Chemical Works). Technical grade n-hexane was obtained from the Phillips Petroleum Company.

2. Polyvinyl Acetate. Three samples of polyvinyl acetate were used in this study.

The first and second samples were prepared by bulk photopolymerization of vinyl acetate ("Niacet Vinyl Acetate, DPA", Carbide and Carbon Chemicals Company) using α, α' -azodi-isobutyronitrile (Eastman Organic Chemicals) as the initiator. Conditions were selected from those specified by Burnett, George, and Melville⁸ in order to lead to the formation of relatively linear molecules. The monomer was fractionated at a pressure of approximately 300 mm of mercury under an atmosphere of oxygen-free nitrogen using a column, 2 cm in diameter and 60 cm long, that had been packed with glass helices. Middle fractions having a boiling range of 0.1°C were transferred to pyrex tubes containing the initiator. After the contents had been degassed three times and sealed at 10^{-4} mm of mercury, the tubes were mounted on a small turn-table and rotated end-over-end at 1 rpm at a distance of 30 cm from a mercury lamp. The assembly was placed in a cold-room held at -19°C. Further details of the experiments and the results are given in Table I. No reduction in the values of $[\eta]$ or k' for Samples 1 and 2 was observed after hydrolysis and reacetylation by methods similar to those of Wheeler, Ernst, and Crozier.⁹ It was therefore assumed that the two polymers were essentially linear in structure.

It should be noted, however, that Burnett, George, and Melville found from four to six fragments of initiator per molecule of polymer formed under conditions similar to those listed above. While the results of the

hydrolysis and reacetylation experiment mentioned above and the viscosity measurements given below strongly support the assumption that Samples 1 and 2 are linear, the findings of Burnett, George, and Melville must place that assumption on a tentative basis.

The third sample was a commercial product of the high conversion type supplied by the Colton Chemical Division of the Air Reduction Company and identified as Colton Polyvinyl Acetate Beads No. 1000. The polymer was relatively high in molecular weight, $[\eta]$ in benzene at 35°C being 3.0, and it was also relatively branched as indicated by a reduction in the values of $[\eta]$ and k' after hydrolysis and reacetylation. The values of $[\eta]$ and k' were originally 3.0 and 0.39, respectively, and, after hydrolysis and reacetylation, 1.11 and 0.35.

B. Fractionation of Polyvinyl Acetate

Samples 2 and 3 were separated into eleven and ten primary fractions, respectively, by procedures generally similar to those described by Wagner,¹⁰ and by Blease and Tuckett,¹¹ in which n-hexane was used to precipitate the polymer from a 1.5 percent solution in acetone at 35°C . The hexane was added dropwise to the well-stirred solution of the polymer in acetone until the mixture became cloudy. The quantity of hexane to be added in a given case was estimated in advance by the method of Blease and Tuckett¹¹ in order to yield a fraction weighing approximately 1 gram. The precipitate was first dissolved by raising the temperature of the bath a few degrees, and then allowed to re-form by slowly lowering the bath temperature to 35°C . The mixture was allowed to settle for 24 hours, after which the precipitate in gel form was withdrawn, dissolved in benzene, and isolated in a fluffy condition by freeze-drying. The procedure was repeated for the isolation of the remaining

fractions. Viscosity data for the fractions in benzene are summarized in Tables II, III, and IV.

In the fractionation of Sample 1 (which was presumably lower in molecular weight than Samples 2 and 3) a special effort was made to obtain a relatively large quantity of narrow fractions of moderately high molecular weight. From 20 g of Sample 1 in 1500 ml of acetone a first fraction weighing about 10 g and a second fraction weighing about 1 g were combined. From the combination a first fraction weighing about 10 g was isolated and then separated into four fractions, Nos. 1-1, 1-2, 1-3, and 1-4. From the combined mother liquors of these operations three fractions were separated, Nos. 1-5, 1-6, and 1-7.

C. Viscosity Measurements

The viscosity measurements were made with a modified Ubbelohde suspended-level viscometer manufactured by the Canadian Laboratory Supplies, Ltd., Montreal, Quebec, according to a design developed at the Polymer Corporation, Sarnia, Ontario.¹² The capillary was approximately 18.5 cm long and had an inside diameter of 0.0356 cm. All measurements were made at $35.0 \pm 0.02^\circ\text{C}$; the flow times for chloroform and benzene at that temperature were approximately 56 and 99 seconds, respectively. A kinetic energy correction of $20/t$ was subtracted from all flow times. The shear rates at free fall for benzene and chloroform were approximately 1300 and 2200 sec^{-1} , respectively.

A preliminary study of the effect of shear rate on viscosity was made using the viscometer described above. Flow times reproducible to within ± 0.2 percent were obtained in the range 500 to 5,000 sec^{-1} . The viscosity behavior of Fraction 1-2 in benzene or chloroform was unaffected by shear rate, while the viscosity of Fraction 2-4 in benzene was affected

only slightly. However, the effect of shear rate on viscosity was appreciable with the branched Fraction 3-5, and marked with the branched Fraction 3-3. These results seem to indicate that shear effects become significant at lower values of free-fall intrinsic viscosity for the branched Series 3 than for the linear Series 1 and 2. The relationship between branching and the shear dependence of the viscosity properties will be discussed in a later publication.

In a group of aging experiments in air, no significant changes in $[\eta]$ or b for polyvinyl acetate in benzene occurred during 8 hours at 60°C, and, accordingly, solutions of the polymer were judged to be sufficiently stable for viscosity measurements at 35°C in open apparatus.

D. Treatment of Viscosity Data

The quantities of interest are defined for dilute solutions by the relationships given by equations 1, 3, and 4,

$$\ln \eta_r/c = [\eta] - \beta [\eta]^2 c, \quad (4)$$

in which η_r is the relative viscosity, $[\eta]$ is the intrinsic viscosity or limiting viscosity number at free fall, β is the slope constant, and c , the concentration, is in units of g/dl.

Values of $[\eta]$, k' , β , and b were obtained from double plots^{13,14} according to equations 3 and 4 under the condition that $k' + \beta = 0.500 \pm 0.002$. In one case, Table IV, Heller's reciprocal and triple plot method was applied.

The data were plotted according to the empirical relationship

$$\log b = \log S_1 + S_2 \log [\eta] \quad (5)$$

for various fractions of a polymer sample in a given solvent. When S_2 , the slope of the line, has the value of 2, S_1 is equivalent to Huggins' constant k' . When S_2 has a value other than 2, as is the case for branched fractions, then the whole relationship

$$\eta_{sp}/c = [\eta] + S_1 [\eta]^{S_2} c \quad (6)$$

is dimensionally incorrect unless a fractional power of volume is assigned to S_1 .

A similar relationship was used for a given fraction in different solvents,

$$\log b = \log F_1 + F_2 \log [\eta] \quad (7)$$

in which F_1 and F_2 represent the intercept (at $[\eta] = 1$) and the slope, respectively.

III. RESULTS AND DISCUSSION

A. Viscosity Properties of Various Fractions in a Given Solvent

The viscosity data for the fractions of Samples 1, 2, and 3 are summarized in Tables II, III, and IV. It may be seen that k' is essentially constant for the linear fractions of Series 1 and Series 2 but increases with increasing $[\eta]$ for the branched fractions of Series 3.

A graph of k' vs. $[\eta]$ for all of the fractions is shown in Figure 1. The difference of some 0.06 k' units between the values of k' for the linear fractions having the highest values of $[\eta]$ and the values of k' for the branched fractions at corresponding values of $[\eta]$ supports the view that k' is a function of the degree of branching of polyvinyl acetate in benzene. It may be recalled that Cragg and Manson¹⁵ have shown a very similar relationship between k' and $[\eta]$ for fractions of copolymers of styrene and divinylbenzene.

It is interesting that a single straight line seems to best represent all of the points for both the low and the high viscosity fractions of the branched Series 3 (Figure 1). The minimum value observed for k' is shown by a low molecular weight member of the branched series rather than by a linear fraction. Thus, it appears that the variations in the values of k' do not clearly indicate the presence of branching in these fractions of polyvinyl acetate having intrinsic viscosities lower than about 2.8. In other words, the size or complexity of the molecules contained in the fractions having values of $[\eta]$ lower than 2.8 must be insufficient to affect the value of k' .

As shown in Figures 2 and 3, the viscosity data for the fractions of Series 1, 2, and 3 were plotted according to the relationship given in equation 5. For the linear fractions (Figure 2) k' is essentially constant and equal to S_1 (the value of b when $[\eta]$ is unity), and S_2 is equal to 2. Thus the linear fractions conform to the Huggins relationship (equation 1). For the branched fractions (Series 3, Figure 3), however, S_1 is as low, if not lower, than the lowest value of k' and S_2 is greater than 2. The straight line fits the data well and there is no evidence of discontinuity in the curve for the low values of either $[\eta]$ or k' .

In reference to Figures 2 and 3 two points may be noted. First, the least square values of S_1 and S_2 are 0.314 and 2.11, respectively, for all fractions of the three samples plotted on the same graph (not shown). These values form the basis for a "one-point" method of determining $[\eta]$:

$$\eta_{sp}/c = [\eta] + 0.314 [\eta]^{2.11} c. \quad (8)$$

A convenient nomograph can be constructed and the values of $[\eta]$ in benzene can be determined with fair accuracy (1-5 percent) by the measurement of one

value of η_{sp}/c at a concentration sufficiently low that the condition that $k' + \beta = 0.500 \pm 0.002$ would be fulfilled. Of course, if the polyvinyl acetate sample is already known to be linear, then the relationship

$$\eta_{sp}/c = [\eta] + 0.337 [\eta]^2 c \quad (9)$$

would be the more appropriate.

The second point to be noted in regard to Figures 2 and 3 is that the log-log relationships do not afford comparisons at zero hydrodynamic interaction (as measured by b) or zero hydrodynamic volume (as measured by $[\eta]$). Yet they do allow for comparisons to be made, e.g., between the linear and branched polymers, at a finite value of b or $[\eta]$. Thus, when b is unity, equation 10 holds,

$$[\eta] = (1/s_1)^{1/s_2} \quad (10)$$

and the intrinsic viscosity equals 1.72 for the linear and 1.68 for the branched fractions, respectively. Hence, at a given degree of hydrodynamic interaction the linear polyvinyl acetate has the greater hydrodynamic volume (as measured by $[\eta]$). Conversely, at a given value of $[\eta]$ the branched series exhibits greater hydrodynamic interaction than does the linear series. Thus, at least in this case, structural differences may be inferred from measurements of b and $[\eta]$.

It was originally thought that the direct calculation of slope might afford a more accurate indication of branching, crosslinking, or association (for example, through polar end groups) than the calculation of k' , which involves both the error in slope and the square of the error in intrinsic viscosity; with this possibility in mind some of the viscosity data given in the literature were examined. Since these data were obtained by the

use of different procedures, and, moreover, are generally given as smoothed values, it is difficult to make meaningful comparisons. However, it may be noted that data for fractions of high conversion GR-S,¹⁶ high molecular weight dextran,¹⁷ and copolymers of styrene and divinylbenzene (0.01 to 0.02 percent divinylbenzene)¹⁵, all of which show variations in k' indicating non-linearity or, perhaps, some kind of association, appear to yield values for S_2 greater than 2; on the other hand, low molecular weight silicones that have been crosslinked by nuclear irradiation¹⁸ have normal values of k' and a value for S_2 of 2. But, in the following cases in which k' varies little from normal values in spite of the fact that non-linearity or association was probably present, the slope S_2 is, indeed, greater than 2: fractions of polystyrene crosslinked with 0.003 percent divinylbenzene,¹⁵ fractions of low conversion (32-45 percent), fairly high molecular weight GR-S,¹⁶ and fractions of cellulose nitrate.¹⁹ Thus, as long as the size or complexity of the polymer molecules is sufficient to permit accurate calculation of the slope b , it is possible that S_2 may be more sensitive to non-linearity or association than is k' . A more general test of this conclusion would require more original, unsmoothed viscosity data than are normally reported.

As indicated in the Experimental section it is possible that the differences observed between the viscosity properties of the branched and linear fractions may be associated with differences in shear behavior.

B. Viscosity Properties of a Single Fraction in Several Solvents

The linear fractions 1-2 and 1-3 and the branched fraction 3-5 were selected for study in various solvents. The data are recorded in Tables V, VI, and VII, and in Figures 4 and 5.

Surprisingly, the values of k' of Fractions 1-2 and 1-3 in different solvents were found to be essentially constant. Accordingly, the

value of F_2 in equation 7 is approximately 2, and the value of F_1 , 0.35, is close to the average value of k' . Thus, the behavior of Fractions 1-2 and 1-3 in different solvents is an example of a case proposed by Eirich and Riseman⁵ in which the total slope b is proportional to $[\eta]^2$. It is remarkable that the relationship

$$b = 0.35 [\eta]^2$$

holds equally well for the various fractions of Series 1 and 2 in benzene and for Fractions 1-2 and 1-3 in various solvents.

For the higher molecular weight branched Fraction 3-5, however, the values of k' did change markedly in different solvents, as seen in Table VII. Unfortunately, owing to the limited number of data for Fraction 3-5, the values of F_1 and F_2 cannot be given with certainty. The values of F_1 and F_2 for the line, as drawn in Figure 5, are 0.63 and 1.71, respectively.

It is quite clear from Figures 4 and 5 that the proportionality between b and $[\eta]$ does not involve the first power of $[\eta]$. Therefore, the relationship proposed by Eirich and Riseman⁵ and by Cleverdon and Smith⁷

$$b = \gamma + \sigma [\eta] \tag{10}$$

where γ and σ are constants, does not hold for polyvinyl acetate. Examination of some of the literature revealed wide variations in the relationship between b and $[\eta]$; F_2 was found to vary from approximately 0.9²¹ to about 2.0.²² Hence, no simple relationship between b and $[\eta]$ ^{1.0} for fractions of a polymer in several solvents appears to exist.

Again, as suggested for a series of fractions in the same solvent, the effects of rate of shear upon the viscosity properties may contribute to the differences observed between the branched and linear fractions in different solvents.

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TABLE I
POLYMERIZATION DATA FOR
POLYVINYL ACETATE

Sample No.	Mercury lamp, watts	Conc. initiator, moles/l.	Polymerization time, hr.	Percent conversion	$[\eta]$ in benzene, 35°C.
1	100 ^a	73.9×10^{-4}	8.5	13.6	1.50
2	85 ^b	2.33×10^{-4}	37.5	10.7	3.11

^aAH-4, General Electric Company

^bAH-3, Hanovia Chemical and Manufacturing Company

TABLE II
VISCOSITY DATA^a FOR FRACTIONS OF
SERIES 1 IN BENZENE

Fraction No.	Slope, b	$[\eta]$	k'	β	$k' + \beta$
1-1	2.34	2.61 ₅	0.34 ₂	0.15 ₈	0.500
1-2	1.43	2.09 ₀	0.32 ₇	0.17 ₂	0.499
1-3	1.20	1.85 ₅	0.34 ₉	0.15 ₁	0.500
1-4	0.70	1.44 ₀	0.33 ₈	0.16 ₀	0.498
1-5	0.81	1.53 ₆	0.34 ₃	0.15 ₅	0.498
1-6	0.49	1.20 ₈	0.33 ₆	0.16 ₅	0.501
1-7	0.30	0.93 ₀	0.34 ₃	0.15 ₆	0.499

^aIn order to avoid errors, caused by rounding off, in the sum $k' + \beta = 0.500 \pm 0.002$, it was necessary in all calculations to carry the uncertain digit indicated by a subscript in the third decimal place.

TABLE III
VISCOSITY DATA FOR FRACTIONS OF
SERIES 2 IN BENZENE

Fraction No.	Slope, b	$[\eta]$	k'	β	$k' + \beta$
2-1-1	8.60	4.94 ₅	0.35 ₂	0.14 ₈	0.500
2-1-2	6.25	4.23 ₀	0.34 ₉	0.15 ₁	0.500
2-2	6.00	4.15 ₀	0.34 ₈	0.15 ₁	0.499
2-3	5.60	4.11 ₅	0.32 ₈	0.17 ₁	0.499
2-4	5.00	3.90 ₀	0.33 ₀	0.16 ₈	0.498
2-5	4.45	3.69 ₅	0.32 ₆	0.17 ₄	0.500
2-6	4.03	3.37 ₅	0.35 ₃	0.14 ₅	0.498
2-7	3.20	3.07 ₅	0.34 ₁	0.15 ₉	0.500
2-8	2.88	2.84 ₅	0.35 ₅	0.14 ₇	0.502
2-9	2.23	2.57 ₅	0.33 ₆	0.16 ₃	0.499
2-10	1.28	1.93 ₄	0.34 ₂	0.15 ₈	0.500
2-11	0.62	1.39 ₆	0.31 ₈	0.18 ₂	0.500

TABLE IV
VISCOSITY DATA^a FOR FRACTIONS OF
SAMPLE 3 IN BENZENE

Fraction No.	Slope, b	[η]	k'	β	$k' + \beta$
3-1	16.77	6.10 ₅	0.45 ₀	0.05 ₀	0.500
3-2	14.84	5.85 ₅	0.43 ₃	0.06 ₈	0.501
3-3	11.94	5.32 ₀	0.42 ₂	0.07 ₈	0.500
3-4	8.90	4.70 ₀	0.40 ₃	0.09 ₇	0.500
3-5	5.82	3.88 ₆	0.38 ₅	0.11 ₅	0.500
3-6	3.94	3.26 ₂	0.37 ₀	0.13 ₁	0.501
3-7	1.88	2.30 ₀	0.35 ₅	0.14 ₅	0.500
3-8	0.95	1.69 ₀	0.33 ₃	0.16 ₅	0.498
3-9	0.45	1.19 ₃	0.31 ₇	0.18 ₃	0.500
3-10	0.1024	0.58 ₄	0.30 ₅	0.19 ₅	0.500

^aAverage values from Heller's triple and reciprocal plots.

TABLE V
VISCOSITY DATA FOR FRACTION 1-2^a IN NINE
SOLVENTS AND TWO SOLVENT MIXTURES

Solvent	Slope, b	[η]	k'	β	k' + β
Chloroform	3.93	3.34 ₀	0.35 ₂	0.14 ₉	0.501
1, 2-Dichloro- ethane	2.83	2.92 ₀	0.33 ₂	0.16 ₆	0.498
Mixture 1 ^b	2.52	2.81 ₂	0.31 ₉	0.18 ₀	0.499
Trichloroethy- lene	2.10	2.55 ₅	0.32 ₂	0.17 ₆	0.498
Methyl Acetate	1.98	2.43 ₅	0.33 ₅	0.16 ₃	0.498
Acetone	1.53	2.10 ₄	0.34 ₆	0.15 ₆	0.502
Benzene	1.43	2.08 ₈	0.32 ₇	0.17 ₂	0.499
Mixture 2 ^c	1.11	1.85 ₈	0.32 ₀	0.18 ₀	0.500
Amyl Acetate	0.98	1.71 ₆	0.33 ₂	0.16 ₆	0.498
Toluene	0.71	1.46 ₀	0.33 ₃	0.16 ₇	0.500
Methyl Alcohol	0.64	1.38 ₀	0.33 ₆	0.16 ₃	0.499

^a $M_v = 7.7 \times 10^5$, according to the relationship of Howard²⁰ for polyvinyl acetate in acetone: $\log M_v = 5.43 + 1.43 \log [\eta]$.

^bComposition, by volume: 50 parts acetone + 50 parts chloroform.

^cComposition, by volume: 90 parts carbon tetrachloride + 10 parts chloroform.

TABLE VI
VISCOSITY DATA FOR FRACTION 1-3^a
IN FOUR SOLVENTS

Solvent	Slope, b	[η]	k^i	β	$k^i + \beta$
Chloroform	2.69	2.80	0.34 ₄	0.15 ₆	0.500
1, 2-Dichloro- ethane	1.90	2.63	0.34 ₂	0.15 ₇	0.499
Benzene	1.20	1.85 ₅	0.34 ₉	0.15 ₁	0.500
Toluene	0.62	1.32 ₆	0.35 ₃	0.14 ₈	0.501

^a $M_V = 6.6 \times 10^5$, according to Howard's relationship²⁰.

TABLE VII
VISCOSITY DATA FOR FRACTION 3-5^a
IN SIX SOLVENTS

Solvent	Slope, b	$[\eta]$	k'	β	$k' + \beta$
Chloroform	14.18	6.01 ₅	0.39 ₂	0.10 ₈	0.500
Benzene	5.82	3.88 ₆	0.38 ₅	0.11 ₅	0.500
Acetone	5.79	3.65 ₀	0.43 ₅	0.06 ₇	0.502
Methyl Acetate	4.51	3.13 ₀	0.46 ₁	0.04 ₁	0.502
Toluene	3.23	2.58 ₅	0.48 ₃	0.01 ₆	0.499
Methanol	3.07	2.47 ₅	0.49 ₈	0.00 ₀	0.498

^a $M_V = 1.7 \times 10^6$, according to Howard's relationship²⁰.

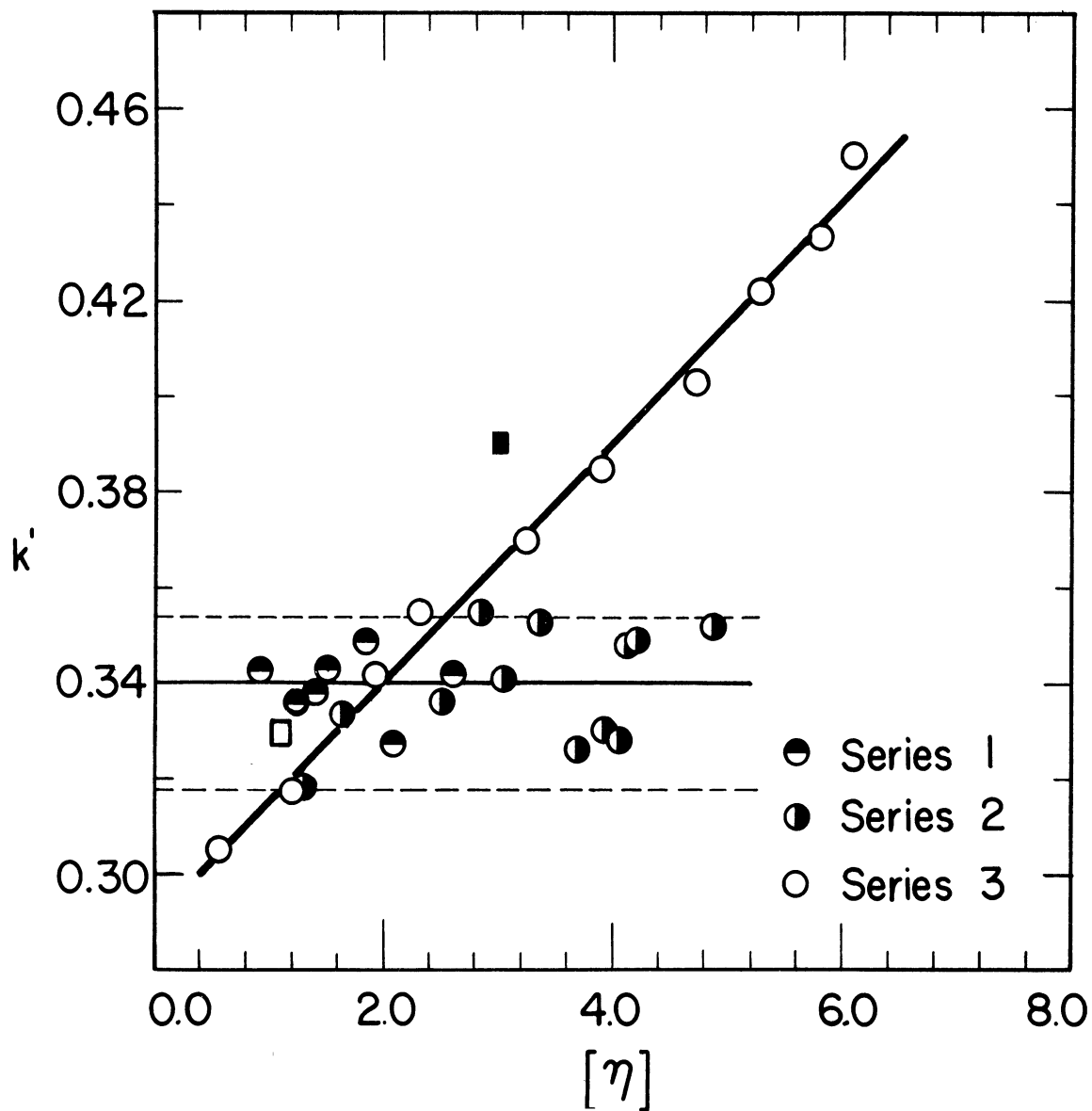


Fig. 1. Relationship between k' and Intrinsic Viscosity for Fractions of Series 1, 2, and 3, in Benzene, at 35°C.

- - Whole polymer, Series 3
- - Whole polymer, Series 3, after hydrolysis and reacetylation

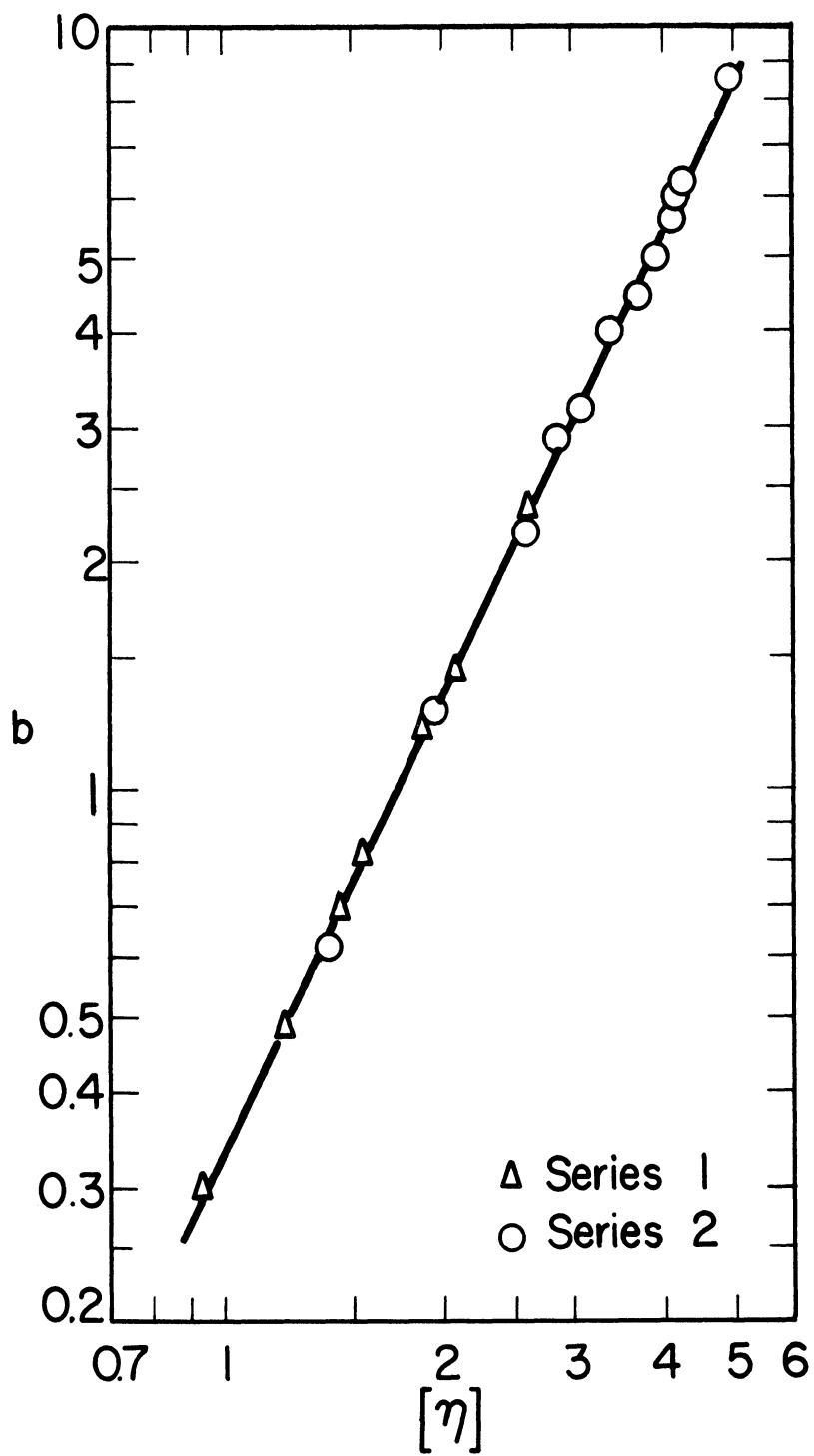


Fig. 2. Viscosity Data for Fractions of Series 1 and 2. in Benzene, at 35°C. ($S_1 = 0.337$; $S_2 = 2$)

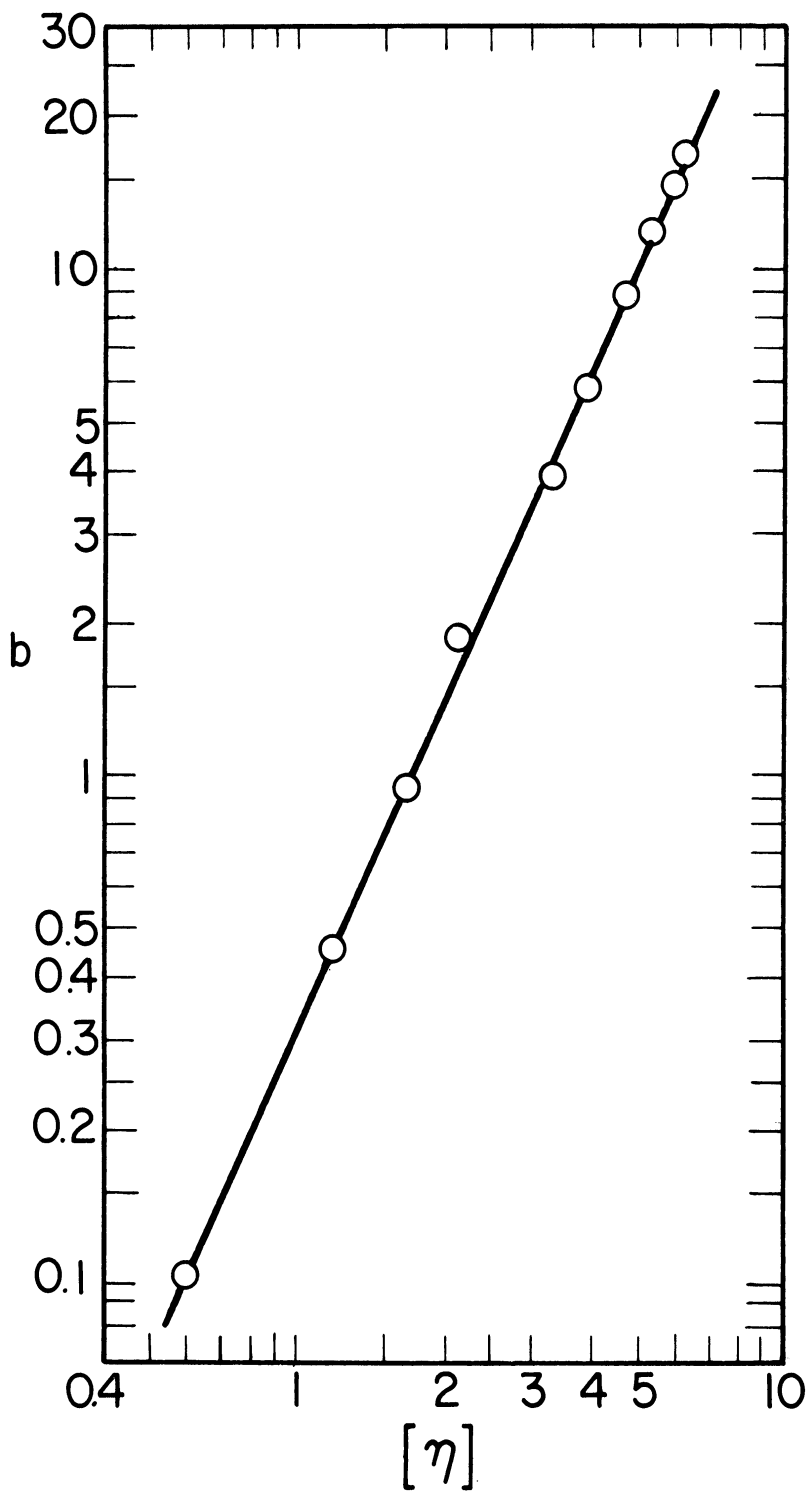


Fig. 3. Viscosity Data for Fractions of Series 3, in Benzene, at 35°C. ($S_1 = 0.31$; $S_2 = 2.16$)

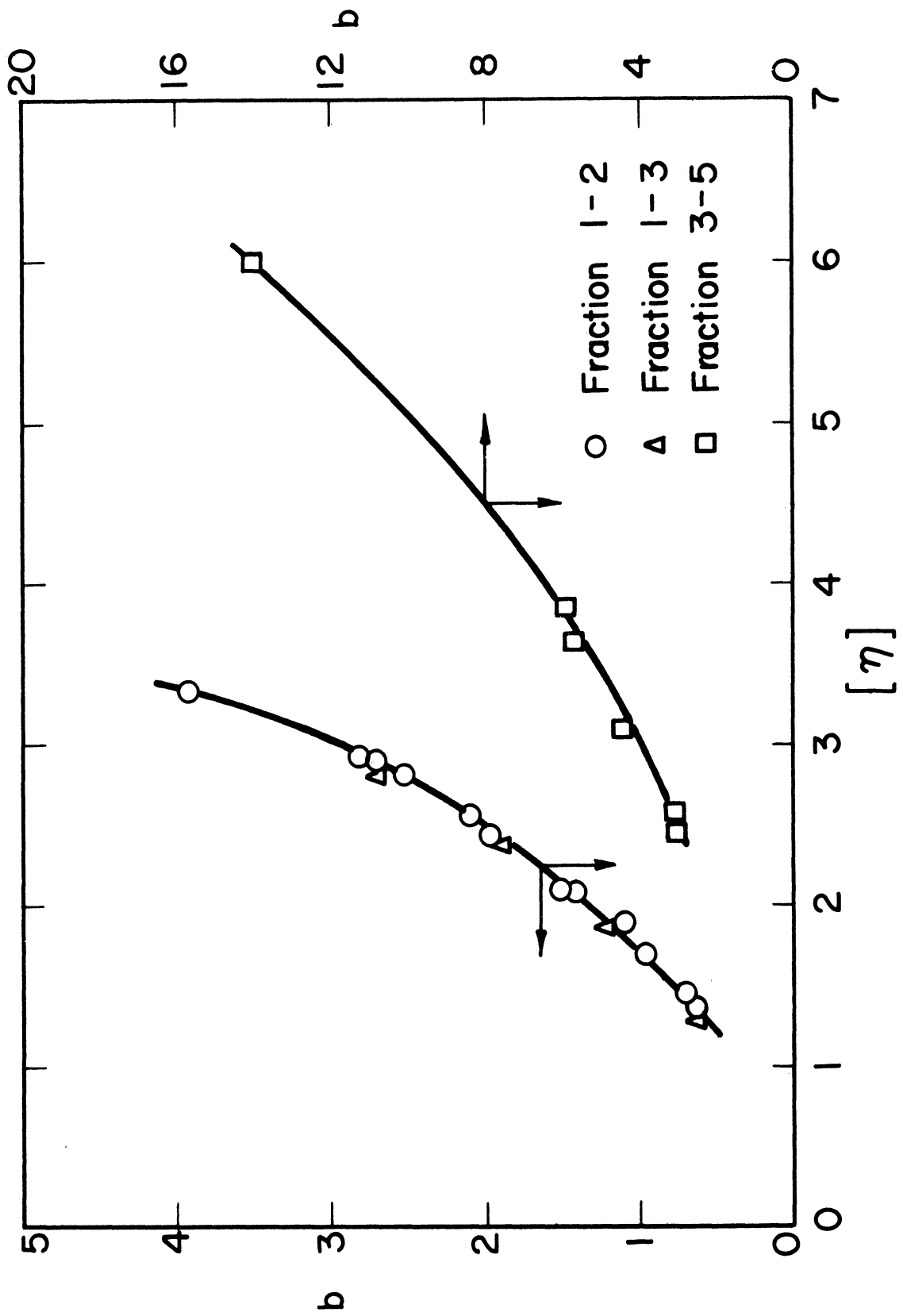


Fig. 4. Viscosity Data for Fractions 1-2 and 3-3 in Different Solvents.

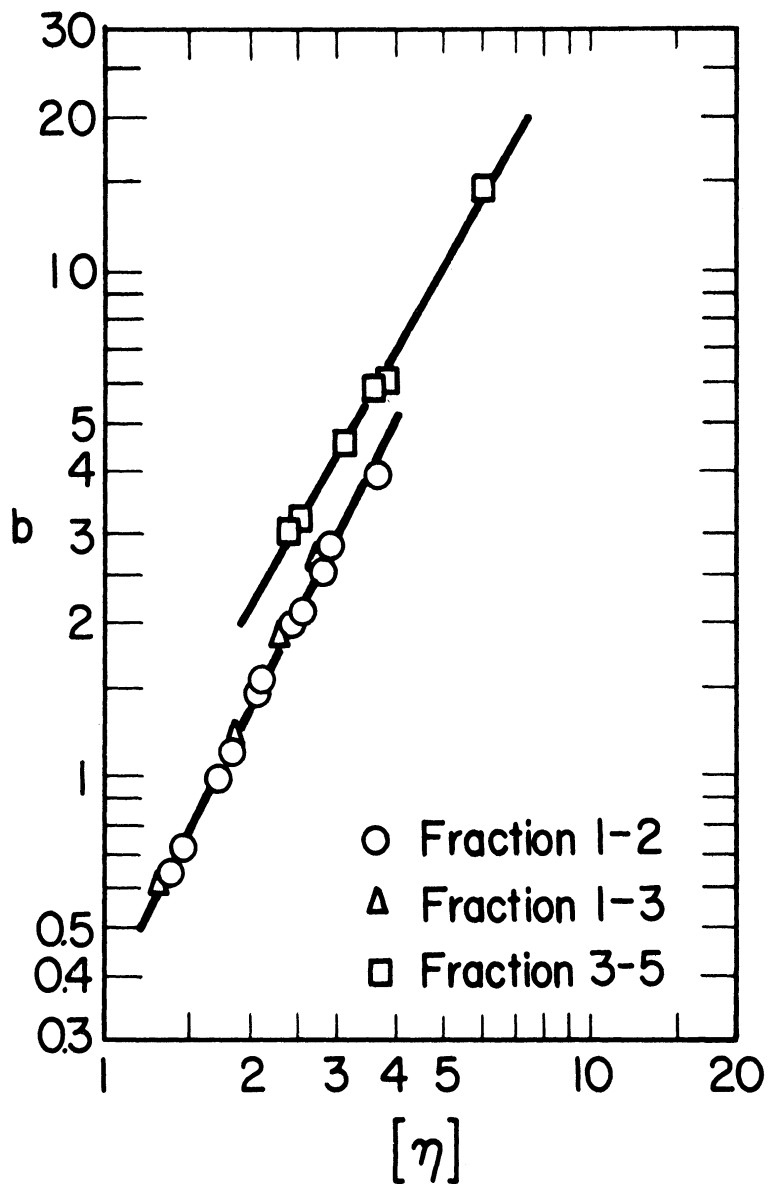


Fig. 5. Relationship between $\log b$ and $\log [\eta]$ for Fractions 1-2, 1-3, and 3-5 in Different Solvents. ($F_2 = 2$ for Fractions 1-2 and 1-3; $F_2 = 1.7$ for Fraction 3-5)