THE UNIVERSITY OF MICHIGAN

INDUSTRY PROGRAM OF THE COLLEGE OF ENGINEERING

THE EFFECT OF BRANCHING ON THE DILUTE SOLUTION AND BULK PROPERTIES OF POLYVINYL ACETATE

Victor C. Long

A dissertation submitted in partial fulfillment
of the requirements for the degree of
Doctor of Philosophy in the
University of Michigan
1958

October, 1958

IP-330

Doctoral Committee:

Doctor Lindsey M. Hobbs, Co-Chairman
Professor Joseph J. Martin, Co-Chairman
Assistant Professor Samuel Krimm
Professor Maurice J. Sinnott
Assistant Professor Robert C. Taylor

ACKNOWLEDGMENTS

I am exceedingly indebted to Doctor L. M. Hobbs[1] of the Air Reduction Company for his guidance through all phases of this study. I am also grateful to Professor J. J. Martin for his contributions as co-chairman and to the other members of my committee, Assistant Professor S. Krimm, Professor M. J. Sinnott, and Assistant Professor R. C. Taylor, for their helpful advice.

I would like to thank Professor L. H. Cragg of McMaster University, Doctor J. A. Manson of the Air Reduction Company, and Professor R. J. Simha of New York University for their useful suggestions.

Appreciation is also extended to Messrs. G. C. Berry, M. M. Gurvitch, and C. H. Lu, students of the University of Michigan, for their assistance with portions of the experimental work.

---

[1] Formerly Associate Professor of Materials Engineering and Director of Michigan Memorial Phoenix Project on Elastomers, The University of Michigan.

TABLE OF CONTENTS

TABLE OF CONTENTS (CONT'D)

TABLE OF CONTENTS (CONT'D)

APPENDICES

LIST OF TABLES

LIST OF FIGURES

I. INTRODUCTION

A. General Objectives of the Study

The major goal of this study was to contribute to the better understanding of the influence of branching on the properties of high polymers. The solution properties of various molecular weight fractions of both linear and branched polyvinyl acetate were investigated by light-scattering and viscosity techniques. These solution measurements were made both to characterize the fractions and to gain a better theoretical insight into the relation between branching and the various solution and molecular properties. Melt viscosity, an exceedingly important bulk property of all thermoplastic polymers, was measured for selected fractions in order to study the effect of branching on a property of the undiluted polymer.

B. Definition and Occurrence of Branching in High Polymers

Perhaps the simplest way to define branching would be to begin with the definition of a linear polymer. Linear polymer molecules are composed of monomer or structural units connected to one another in a linear sequence or chain-like manner. Thus, each structural unit in a linear molecule is connected to only two other units and is said to be bifunctional. The exceptions, of course, are the two end or terminal units which are monofunctional. Branched structures, then, may be defined as any deviation from linearity, excluding ring structures. Thus, a branched molecule must contain at least one branch point which is the junction of three or more polymer chains. Branch points are usually tri- or tetrafunctional.

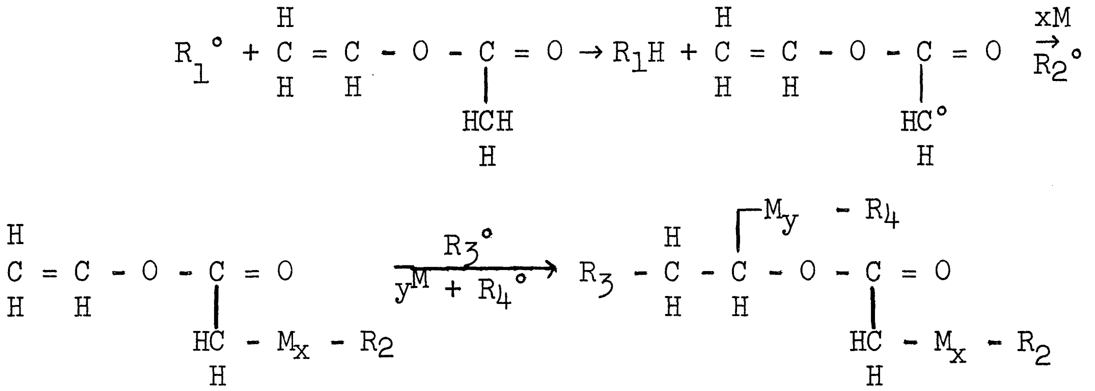
With further consideration, branched polymers can be grouped into two major categories. The materials of the first category are essentially infinite networks of polymer chains, while those of the second consist of finite molecules. In the former class, the polymer chains, which might have represented discrete molecules at one time, have been bound together through proliferated branching or by cross-links. Phenol- or urea-aldehyde resins, drying oils, and glycerol-polyesters are representative materials. Also, vulcanized rubbers and vinyl polymers cross-linked by divinyl compounds belong in this group. And, under some conditions(1), certain vinyl monomers can polymerize into such network structures. It is apparent that some of the infinite network polymers represent very important commercial products. However, the properties of these materials which enhance their value, namely insolubility and infusibility, also forestall investigations on the classical molecular basis. The omission of this type of branching from this investigation by no means implies its lack of importance or need of study.

The second category represents polymers in which the branching is limited. Although the molecular weight may be quite large in some cases, say several millions, the molecules are finite and can be investigated by various physico-chemical techniques. The solution properties of molecules of this type have recently attracted much theoretical and experimental interest. Also, there has been considerable speculation and study concerning the influence of this type of branching on various bulk properties of the polymers.

Before proceeding further, it should be noted that the limited type of branching can also be categorized. This is accomplished by designating the occurrence of branching as either ordered or random. The ordered type of limited branching could be obtained by attaching various fatty acids or alcohols to polymeric poly-alcohols or poly-acids.(2) This type of reaction creates molecules with relatively short, uniform branches attached in a regular manner to relatively long "backbone" chains. It is generally referred to as "feather branching" for obvious reasons.

In the random type(3) of limited branching, the spacing and length of the branches are not uniform on a molecular basis and must be treated statistically. Also, the distribution of branches among the molecules may vary. This leads to a mixture of molecules of varying degrees of branching and results in a marked broadening of the molecular weight distribution. Such non-linear molecules of condensation polymers can be prepared by adding certain trifunctional reactants to the polymerizing system. Limited branched structures of vinyl polymers can be formed by copolymerization with small amounts of divinyl compounds. Numerous experimenters have suggested and tried chemical methods of attaching branches to a backbone chain and have met with varying degrees of success.(4) The natural occurrence of branching in vinyl polymers, however, is of utmost importance in regard to this study and will be discussed in some detail.

Certain polymers, such as polyvinyl acetate(5-10), polyvinyl chloride(11-13), polymethyl acrylate(1,14,15), and polyethylene(16-21) have been shown to contain branching when prepared by free radical processes under various conditions. There are at least two possible side reactions by which this branching may occur.(3) The first branching mechanism involves a chain transfer process with the monomer. A growing free radical encounters a monomer molecule and abstracts an atom or group from it. This transfers the free radical site to the monomer molecule without destroying the unsaturation. Monomer may then add to the reactive site and form a polymer molecule bearing an unsaturated terminal group. This unsaturated terminal group may then be incorporated in the normal growth of another polymer molecule, thus forming a branch. The process is described by the following sequence of reactions,

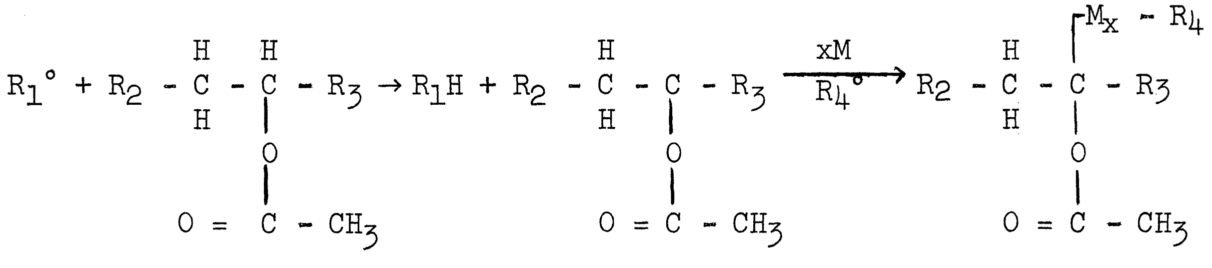


$$R_1^\circ + \underset{H}{\overset{H}{C}} = \underset{H}{C} - O - \underset{\underset{H}{HCH}}{C} = O \rightarrow R_1H + \underset{H}{\overset{H}{C}} = \underset{H}{C} - O - \underset{\underset{H}{HC^\circ}}{C} = O \xrightarrow[R_2^\circ]{xM}$$

$$\underset{H}{\overset{H}{C}} = \underset{H}{C} - O - \underset{\underset{H}{HC - M_x - R_2}}{C} = O \xrightarrow[yM + R_4^\circ]{R_3^\circ} R_3 - \underset{H}{\overset{H}{C}} - \underset{H}{\overset{M_y - R_4}{C}} - O - \underset{\underset{H}{HC - M_x - R_2}}{C} = O$$

where R° represents a polymer free radical, R a polymer chain segment, and M monomer. It can be seen that the monomer molecule involved in transfer becomes a trifunctional branch point.

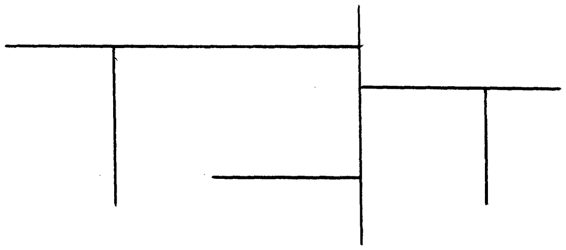
The second branching mechanism involves a chain transfer process with the polymer. In this case, the free radical removes an atom or group from a polymer molecule, and the free radical site is transferred to the polymer molecule. A branch may then grow from this site by the normal addition of monomer. The reaction proceeds as follows,



$$R_1^\circ + R_2 - \underset{H}{\overset{H}{C}} - \underset{\underset{O = C - CH_3}{O}}{\overset{H}{C}} - R_3 \rightarrow R_1H + R_2 - \underset{H}{\overset{H}{C}} - \underset{\underset{O = C - CH_3}{O}}{C} - R_3 \xrightarrow[R_4^\circ]{xM} R_2 - \underset{H}{\overset{H}{C}} - \underset{\underset{O = C - CH_3}{O}}{\overset{M_x - R_4}{C}} - R_3$$

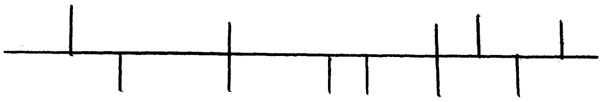
where the symbols are as before. Since a radical is unable to differentiate between the various portions of a molecule, it will attack a branch as well as the original backbone. Therefore, after a given molecule has been involved in several branching reactions, its structure becomes rather complex.

An important point should be noted concerning the two free radical branching mechanisms. Since the length to which a free radical propagated chain may grow is governed by the conditions of the polymerization system, all chains should grow to about the same average length whether propagated from an initiator fragment or from an active site on a monomer or polymer molecule. This implies that all of the major chain units making up a branched molecule of this type are of a given average length. Such branching has often been termed long chain random branching and may be represented pictorially as follows,



where each straight line represents a major chain unit.

Polyethylene appears to be susceptible to intramolecular chain transfer with polymer(21-22), in addition to the intermolecular type described above. Presumably, the chain end bearing the growing free radical doubles back on itself and forms a transient 5- or 6-membered ring. A hydrogen atom is transferred to the radical from the fourth or fifth carbon from the chain end, and, in turn, this carbon becomes the free radical site. The polymer chain may then propagate from the new site by normal addition of monomer, leaving behind a three or four carbon branch. After several such branching reactions, the structure of the molecule may be pictured as follows,



This type of branching has been referred to as short chain random branching. While intramolecular chain transfer should be possible in other polymer systems, its presence was not observed in the polyvinyl acetate samples under study (see II-G-1).

To summarize, branching has been categorized according to molecular size, namely infinite network and limited. The limited type was further divided into ordered and random. "Feather branching" was an example of ordered branching. Random branching was represented by both the long and short chain types.

C. Relations Between Branching and Polymer Properties

1. Solution Properties

The major difference between linear and branched polymer molecules in solution involves their degrees of extension.(23-27) Consider first a single linear polymer molecule in solution. In most polymers, the chain is not extended along a rigid straight line but is arranged in a randomly coiled spatial configuration. That is, the various elements of the chain are statistically distributed throughout a spherical volume about a center of gravity. The volume of solution pervaded by the chain segments may be several hundred times the actual molecular volume, and it is this pervaded volume that is affected by branching. The very nature of branching forces the chain segments of a branched molecule to be more crowded. Therefore, for a given molecular weight, the branched molecule pervades a considerably smaller volume than does a linear molecule. This difference can be detected by measurements of the radius of gyration (see II-F-1-c) or intrinsic viscosity which is related to the hydrodynamic volume (see II-D-1).

Branching usually tends to decrease the solubility of a polymer.(28-30) This can result in anomalies when a polymer sample is fractionated, since fractionation can take place with respect to both molecular weight and degree of branching.

In general, other solution properties are related to the decrease in size or solubility caused by branching.(26) The solution viscosity decreases as the pervaded volume becomes smaller. The compactness of the molecules also decreases the dissymmetry of light scattered by the solution of polymer at a given molecular weight. The second virial coefficient tends to decrease with the decrease in solubility or polymer-solvent compatibility.

Caution must be exercised in assigning a direct relationship between a given property and branching. False conclusions may arise when the property is compared on the basis of intrinsic viscosity if the property is dependent on molecular weight. The property may be assigned a direct sensitivity to branching, although the fundamental difference is actually the difference in molecular weights at a given value of intrinsic viscosity. Further discussion of solution properties will be taken up later under detection of branching (I-D).

2. Bulk Properties

Branching might be considered as functioning in a dual role* in its influence on most of the bulk properties of polymers. Not only does a branch point introduce an irregularity into the polymer chain, but also the branch itself may act as an internal plasticizer. The irregularities in the polymer system resulting from branching tend to reduce the ability of the chains to align and to approach one another closely enough to take full advantage of the intermolecular van der Waals forces. This, of course, discourages the formation of crystallites. Therefore, branching should be expected to show its most pronounced effects on the properties of crystalline polymers, although amorphous polymers are affected in a similar manner to a lesser degree. In general, density, melting or softening point, strength, and stiffness decrease as the degree of branching increases. Likewise, hardness and surface luster decrease, while elongation, impact strength, and permeability usually increase.

The properties of polyethylene have recently been the subject of considerable study.** The presence of short chain branching was found to reduce crystallinity markedly and to influence most of the properties mentioned above. Long chain branching, however, showed little effect on crystallinity, persumably because it introduced fewer branch points per weight of branch, and that the branches were long enough to participate

---

* 2;31, Chap. 3;32, p.33.

** 32, Sec. 38; 33; 34.

in the crystal structure. Studies of "feather branching" have also yielded interesting information regarding the length of the branches and crystallinity. Esters of polyvinyl alcohol and cellulose with various fatty acids were prepared and studied.(2) The melting or softening temperatures decreased, passed through a minimum, and then rose again as the branch length increased. Apparently the crystal structure was first destroyed by the side chains, but as the branches became longer they were able to form a crystal pattern of their own. The occurrence of a minimum softening temperature seems to indicate that there is an optimum branch length, in the order of six to ten carbons, which exerts a maximum degree of plasticization. Similar behavior has been observed with several polyalkyl acrylates and polyalkyl methacrylates(2), although the basic backbone polymers were inherently amorphous.

Branching influences the flow of molten polymers. In polyethylene, short chain branching has been shown to decrease the melt viscosity for a given molecular weight.(34) No effect was found for long chain branching, but it was pointed out that there might have been an insufficient number of branches. Branched polyesters(35) prepared from adipic acid and a polyhydric alcohol also exhibited a decrease in melt viscosity. Polymers formed from ϵ-caprolactam and an octabasic carboxylic acid behaved similarly.(36) The branching in these polymers was in the form of eight chains radiating from an octafunctional central unit. Polymers of this type, but with mono-, bi-, and tetrafunctional central units, showed no effect of branching on melt viscosity. Liquid silicones(37), partially cross-linked by irradiation, displayed the typical depression of viscosity.

Branching can also produce an indirect influence on the physical properties of polymers through its effect on the molecular weight distribution. In most polymer systems, with only minor exceptions(36), branching results in a marked broadening of the molecular weight distribution.(3) Quite often, the presence of very high or very low molecular weight constituents in a sample causes undesirable properties.(38) In many cases branching has received the direct blame for such inferior properties when heterogeneity was actually responsible. The use of the proper type of molecular weight average is quite important, therefore, when comparing the properties of linear and branched samples in order to prevent confusion.

D. Detection of Branching

1. Qualitative Indications of Branching

(a) The Huggins Constant k'

The Huggins constant k' has been shown to be a useful means of detecting the presence of branching. It is derived from the slope of the reduced viscosity-concentration relationship (II-D-1). Apparently, k' is related to the polymer-solvent and polymer-polymer interactions and should be independent of molecular weight. Considerable experimental evidence has been accumulated showing that, for a given polymer in several solvents, k' increases as the solvent power decreases.(39-44) It has also been shown that k' generally is independent of molecular weight, but there have been some reports of a small increase in k' with molecular weight.(41-44)

On theoretical grounds, Simha(39) has predicted that k' should be increased by the introduction of branching into a polymer. This prediction has been born out quite well by many investigations.(45) The usual behavior observed in the cases of fractionated materials is for k' to increase for the higher molecular weight branched fractions (the ones presumably containing the higher degrees of branching). A lower value of k' is obtained for the linear fractions and the lower molecular weight fractions of the branched polymer. To cite several examples, behavior of this type has been observed with branched polyvinyl acetate(40,46,47), polyvinyl chloride(48,49), polyvinyl n-butyl ether(50), and polyethylene.(51,52) Soluble styrene-divinyl benzene copolymers(53) and irradiated polyethylene terephthalate(54) showed similar increases in k'. Also, branched polylactams(36) and dextran(55) behaved in the usual manner. There are still more examples in the literature, with only a few exceptions, so that one must conclude that k' is a useful means of detecting the presence of branching, especially if linear samples are available to provide a basis for comparison. Unfortunately, however, k' does not afford a quantitative measure of branching, and there is no guarantee that small amounts of branching will be detected.(40,45)

It has been suggested by Conrad, Tripp, and Mares(56), and recently supported by others(57-60), that non-Newtonian behavior of polymer solutions can cause high values of k'. A peculiar dependence of shear rate on concentration can cause the slope of the reduced viscosity-concentration relation to increase, resulting in a high value of k'. A difference in the non-Newtonian behavior of solutions of linear and branched polymers could very well be the basic reason for the high values of k' which have been reported. This will be discussed in more detail later (II-E-1-b). This idea does not preclude the usefulness of k' as an agent to detect the presence of branching.

(b) Non-Newtonian Behavior of Polymer Solutions

Recently, differences in the non-Newtonian solution properties of linear and branched polymers have been observed. Dilute solutions of branched graft copolymers of styrene and methyl methacrylate(57) and branched poylvinyl acetate(40) exhibited more non-Newtonian behavior than did the corresponding linear materials when compared on the basis of intrinsic viscosity. A semi-quantitative measure of the shear dependence of viscosity has been developed in this study (II-E-3-a). The degree of shear dependence can be used as a qualitative indication of branching if the comparison is based on intrinsic viscosity.

(c) The Second Virial Coefficient

The effect of branching on such thermodynamic solution properties as the second virial coefficient has received only limited investigation. The second virial coefficient A_2 is defined by the following expansion,

$$\pi/RTc = 1/M_n + A_2c + \dots \qquad (1)$$

for osmotic pressure* and also one for turbidity (see II-F-1-b). In Equation (1), π is the osmotic pressure, R the gas constant, T the temperature, c the polymer concentration, and M_n the number-average molecular weight. The second virial coefficient accounts for the dependence of π/c on concentration which results from the non-ideality of the solution. Actually, A_2 is a measure of the polymer-solvent interactions.

---

* 61, Chap. 4.

Theory predicts that the second virial coefficient should decrease for a given polymer-solvent system as both the molecular weight and degree of branching increase.(26,62-65) Several cases of the molecular weight dependence of A_2 have been observed.(66-68) Lower values of A_2 for branched fractions have also been reported(24,52,55,69), although there has been some difficulty in separating out the molecular weight effect. Quantitative attempts to express A_2 in terms of molecular weight and degree of branching have met with only limited success and have been hampered by the lack of sufficient data of good precision.(26,62-65)

At the present, only a qualitative indication of branching can be obtained from measurements of the second virial coefficient if sufficient data are available to distinguish the influence of molecular weight.

(d) The Particle Scattering Factor

Benoit(70,71) has shown that the shape of the reciprocal particle scattering function is influenced by both the degree of branching and the polydispersity of a polymer sample (II-F-3-b). Serious difficulties arise, however, in the application of this measurement to the estimation of the degree of branching.(26) First of all, the particle scattering factor is not overly sensitive to branching, and before any information can be obtained, the molecular weight distribution of the sample must be known. Also light-scattering measurements are subject to considerable errors. This method is probably of only qualitative usefulness even under the most ideal conditions.

(e) Chemical Means

Any chemical difference introduced into the polymer by branching might serve as the basis for a scheme to detect branching.

An obvious method for measuring the number of branches per molecule is to determine the total number of chain ends in relation to the molecular weight. Usually the concentration of end groups is exceedingly small, unless the degree of branching is high, making analysis quite tedious and inaccurate. However, this method has been successful for polyethylene (see I-D-2-a).

In some cases, the branches may be of a different chemical composition than the backbone chain. This, of course, is true in the case of "feather branching". It can also occur in specially prepared graft copolymers. These materials are synthesized in two steps, using the principle of chain transfer to polymer to form the branches. The first step involves the preparation of a linear backbone polymer. This material is then dissolved in monomer of a different chemical nature, and polymerization is carried out under conditions which favor chain transfer to the linear backbone polymer. The branches which grow from the transfer sites will have the chemical composition of the second monomer. Although some difficulty is encountered in separating the branched copolymer from the unbranched materials, the differences in chemical composition or molecular weight generally make separation possible. The difference in chemical nature of the branches and backbone allows the weight per cent of each to be estimated by various schemes. The branching may be further characterized by knowledge of the molecular weight of the original backbone material and by the estimation of the average chain length of the branches from the conditions of polymerization.

Such graft copolymers of polyvinyl acetate have been prepared by several investigators. For example, polyethylene(72) and acrylonitrile(73) branches were grafted onto polyvinyl acetate. Also various combinations of polyvinyl acetate, polymethyl methacrylate, and polystyrene have been prepared.(1)

An interesting variation of the graft copolymer technique just described involves the preparation of a graft homopolymer using monomer in the grafting step that has been tagged with carbon -14. The amount of branching can be estimated by measuring the carbon -14 content of the resulting branched polymer. This has been done using polyvinyl acetate with fair success.(10)

Actually, the grafting method represents one of the techniques now being used to synthesize "tailor-made" polymer molecules. An excellent and interesting survey of this field has been prepared by Melville.(4)

The branches in certain polymers are attached to the main chain through groups which are subject to chemical attack. These branches can, therefore, be removed, and the degree of branching estimated by measuring the molecular weight before and after removal.

In the case of polyvinyl acetate, the branching can occur at two sites, namely at the tertiary hydrogens on the polymer chain and on the acetate groups. Unfortunately, only the branches on the acetate groups are removed by hydrolysis. It has been shown, however, that an appreciable amount of the branching does occur on the acetate groups and is hydrolyzable.(6,7,40,72,80) The method is by no means quantitative but, since the change in molecular weight is large for the loss of only a few branches, it is sensitive to small amounts of branching.

(f) Other Methods

Meares(74) has related measurements of the second order transition point to branching. The second order transition occurs when the chain segments gain sufficient energy to begin rotation, and the polymer changes from a glassy solid to a rubbery material. The temperature at which the transition takes place, referred to as the glass temperature, decreases as the number of chain ends increase for a given polymer and, therefore, is a function of both molcular weight and degree of branching.

The curvature of the logarithmic plot of intrinsic viscosity versus weight-average molecular weight is apparently sensitive to branching(23), although other factors can influence the curvature.(76) Also, the slope of the logarithmic plot of intrinsic viscosity against the total slope of the reduced viscosity-concentration relationship is affected by the presence of branching.(40) Branching is believed to cause curvature of the reduced viscosity - concentration relationship(76), but it has not been confirmed by others.(48,77,78) None of these methods yields precise information.

Any physical property that is sensitive to branching might be used for control purposes. The basis of comparison should be carefully chosen, however, in order to eliminate the influence of other parameters.

2. Quantitative Indications of Branching

(a) End-group Analysis

As was mentioned earlier, the analysis for end-groups is a useful means of determining the number of branches per molecule providing the concentration of end-groups is large enough to be measured accurately. The degree of validity of the results, of course, will depend upon the accuracy with which both the concentration of end-groups and the molecular weight can be determined. Unfortunately, these measurements do not yield information regarding the length of the branches.

The analysis for initiator fragments, either chemically or by tagging with radioactive isotopes, has been used to measure the chain ends in linear vinyl polymers.* This method has not met with much success in the case of branched vinyl polymers, however, mainly because some of the chain ends are not terminated by initiator fragments due to the occurrence of the transfer reactions producing the branching.

Good results have been obtained for the degree of branching in polyethylene by infrared measurements of the methyl end-groups to methylene groups ratio.(16,19,20,22) The success of this method is largely due to the short chain branching. According to the proposed short chain branching mechanism, (I-B), all of the short branches should be terminated by methyl groups. Also, since these branches are short, the degree of branching may be quite high without a large increase in the molecular weight. This method was also applied to branched polyvinyl chloride after the chlorine had been removed by hydrogenation.(13)

---

* 79, p. 109, 267.

Periodate oxidations have been used to determine the ratio of 1, 6 glucosidic to non-1, 6 glucosidic linkages in various dextrans.(27,81,82) This technique actually determines the number of branch points instead of the chain ends, since the non-1, 6 linkages are generally assumed to be points of branching.(81)

(b) Size-molecular Weight Relationship

As indicated earlier, the major difference in the solution behavior of linear and branched polymer molecules involves their degree of extension. For a given chemical composition and molecular weight, the linear molecule pervades a larger solution volume. Several methods of relating this difference in extension to the degree of branching have been proposed and will be developed in the following discussion.

There are two convenient measures of the degree of extension of polymer molecules in solution. The first is the mean square radius of gyration, S^2, measured by light-scattering. This quantity represents the mean square distance of the various chain elements from the center of gravity of the molecule. The second measure is the intrinsic viscosity, which is actually not a viscosity but has units of volume per unit mass and is related to the effective hydrodynamic volume of the molecule.

Zimm and Stockmayer(23) have expressed the difference in extension in terms of a dimensionless parameter,

$$g = S^2/S_o^2 \tag{2}$$

where S^2 and S_o^2 are the mean square radii of gyration of branched and linear molecules, respectively, of the same molecular weight and chemical nature. Values of g as a function of the number of branches per molecule were obtained by calculating the expected decrease in size for various theoretical models containing either tri- or tetrafunctional, random branching. The values of g decreased from unity as the number of branches was increased.

The determination of the number of branches per molecule by observing the g ratio requires a means by which the value of S^2 can be compared with S_o^2 at the same molecular weight. This may be done by first establishing a relationship between S_o^2 and molecular weight for a series of linear samples. Then the measured values of S^2 and molecular weight for a branched sample may be compared with the corresponding values for a linear sample using this relationship.

One of the assumptions used in calculating g as a function of the degree of branching was that the molecules were in random flight configuration.* That is, the molecules were unperturbed by the presence of solvent, and their over-all dimensions were determined solely by bond lengths and angles. Such a situation is encountered in an ideal solution and is indicated by a value of zero for the second virial coefficient. For values of g to be strictly valid, the mean square radii of gyration should be measured in an ideal solution, but such conditions are often difficult to realize. Fortunately, it has been shown that the error resulting from measurements in an non-ideal solution is rather small.(24,26)

The evaluation of the ratio g from the radii of gyration is usually seriously hampered by differences in the molecular weight

---

* 79, Chap. 10.

distribution of the linear and branched samples, even after fractionation. The radius of gyration measured by light-scattering is a z-average quantity, whereas the molecular weight is based on a weight-average. Some of the averages commonly encountered are defined as follows*,

$$\begin{array}{ll}
M_n = \sum_i N_iM_i / \sum_i N_i & S_n^2 = \sum_i N_iM_iS_i^2 / \sum_i N_iM_i \\
M_v = (\sum_i N_iM_i^{a+1} / \sum_i N_iM_i)^{1/a} & \qquad\qquad\qquad (3) \\
M_w = \sum_i N_iM_i^2 / \sum_i N_iM_i & S_w^2 = \sum_i N_iM_i^2S_i^2 / \sum_i N_iM_i^2 \\
M_z = \sum_i N_iM_i^3 / \sum_i N_iM_i^2 & S_z^2 = \sum_i N_iM_i^3S_i^2 / \sum_i N_iM_i^3
\end{array}$$

where M is molecular weight, N_i is the number of molecules of M_i molecular weight, and a is a constant depending mainly on the polymer-solvent system. The subscripts n, v, w, and z denote number-, viscosity-, weight-, and z-averages, respectively. It can be seen that the various averages converge to a single value as the samples become more homogeneous with respect to molecular weight. It is obvious that values of g calculated from z-average radii of gyration of linear and branched samples of the same weight-average molecular weight will underestimate the degree of branching if the branched sample is more polydisperse. This occurs because the greater polydispersity of the branched sample causes a greater increase of S_z^2 above S_w^2 resulting in a larger value of g than would be obtained if g were calculated from weight average values of size.

---

* 61, p. 2, 112.

One solution to the heterogeneity problem, of course, would be to obtain the radii of gyration and molecular weights both based on the same type of average. Since S^2 is generally only measurable as a z-average quantity, M_z could be measured from sedimentation equilibrium using an ultracentrifuge.* Also, S_w^2 or S_n^2 could be calculated from S_z^2 if an approximate molecular weight distribution can be derived.(5, 67) These values could then be compared on the basis of M_w from light-scattering or M_n from osmotic pressure measurements. Unfortunately, these alternatives are neither convenient nor particularly accurate.

The use of intrinsic viscosity as a measure of size appears to be the most promising way to resolve the polydispersity complication, because the intrinsic viscosity is close to a weight average quantity in many cases.(25) This can be seen by considering the Equation (3) and the following empirical relationship between intrinsic viscosity and viscosity-average molecular weight,

$$[\eta] = KM_v^a \qquad (4)$$

where K and a are constants.** When a is unity, M_v equals M_w and the intrinsic viscosity is a weight-average number. For polyvinyl acetate fractions with an a of about 0.7 [see Equation (33)], M_v/M_w equals 0.97.(5)

The near weight average behavior of the intrinsic viscosity suggests its combination with M_w from light-scattering as a valid means of comparing size providing a correlation with the degree of branching can be developed. Flory and Fox(83,84) have suggested the following relationship

---

* 79, p. 303-308.

** 79, p. 313.

for linear polymers,

$$[\eta] = \Phi' S_o^3/M \qquad (5)$$

where Φ' is a universal proportionality constant. Assuming that Equation (5) holds for branched polymers, it follows that,

$$[\eta] \text{ (branched) } / [\eta] \text{ (linear) } = S^3/S_o^3 = g^{3/2} \qquad (6)$$

when the molecular weights are equal. Thurmond and Zimm(24) have applied Equation (6) to branched styrene-divinylbenzene copolymers with at least qualitative success. The indicated degree of branching was less than that expected, however, and it appeared that Equation (6) over-estimated the effect of branching on the viscosity. Similar behavior has been noted with branched polyvinyl acetate(5), polystyrene(45), and some condensation polymers.(35,36)

Stockmayer and Fixman(26) have developed another method for relating differences in intrinsic viscosities to g and thus the degree of branching. Because of the greater segment density of a branched molecule in solution, they proposed that the hydrodynamic radius might be less sensitive to branching that the radius of gyration. This means that Equation (5) is not strictly valid for branched molecules. To avoid this difficulty, Stockmayer and Fixman calculated the ratio of the hydrodynamic radii of branched to linear molecules of the same molecular weight,

$$h = f^{1/2} [2-f+2^{1/2}(f-1)]^{-1} \qquad (7)$$

where f is the number of branches per molecule. Also the corresponding ratio for mean square radii is

$$g = (3f-2)/f^2 \tag{8}$$

The model used in the calculations was a cruciform molecule, that is one with tetrafunctional branch points. But it was assumed that the relation between h and g obtained from Equations (7) and (8) by the elimination of f would hold for other branched molecules. The relationship between the ratio of intrinsic viscosities and h is given by,

$$[\eta] \text{ (branched)}/ [\eta] \text{ (linear)} = h^3 \tag{9}$$

Therefore, by combining Equation (9) with the relation between h and g, a value of g is obtained from intrinsic viscosity measurements. The degree of branching can then be obtained from g in the usual manner.(23)

Using the above method, Stockmayer and Fixman recalculated the degree of branching for the styrene-divinyl benzene copolymer(24) and the branched polyvinyl acetate(5) mentioned earlier. They obtained degrees of branching which were in good agreement with the expected values. Also, the Stockmayer and Fixman method has been used in the case of branched polystyrene(45), dextran(55), and polyethylene(85) with fair success. At the present time, it appears that this method is the best means of determining the degree of branching.

(c) Knowledge of Polymerization Kinetics

The expected degree of branching can be calculated from kinetic data for systems where the various rate constants of chain transfer and propagation are accurately known.(1,5,86) This method has been shown to be in fair agreement with the viscosity method described above.(26) Although the average degree of branching for the total sample may be predicted quite accurately, the method is not well suited to fractions of the sample, because the degree of branching can vary from fraction to fraction.

(d) Other Methods

In the case of polyethylene, the extent of crystallinity or the density has been calibrated by infrared measurements to yield an accurate measure of the degree of short chain branching.(33) Normally, such properties do not provide quantitative information.

E. The Importance of Studying Branching

A vast number of polymeric materials are now commercially available, each with specific properties suiting it for certain applications. This array of materials, or better, properties, was made possible by the variation of such parameters as chemical nature, molecular weight, plasticizer and filler content, fabrication procedure, and the like. Considering the possible influence of branching on the several properties as mentioned earlier, it is obvious that the degree of branching is also an important parameter to consider. Often, however, the presence of branching has been made the scapegoat to explain certain undesirable properties when the true nature of the difficulty was not fully understood. While branching does have an objectionable effect on some properties in certain cases, a more complete understanding of the subject might lead to many useful applications.

A requirement for a complete branching-property study is a means of detecting and estimating the extent of the branching. Solution properties appear to yield the most revealing information about molecular structure. Therefore, a study of solution properties is important for practical reasons as well as for their theoretical interest.

II. EXPERIMENTAL

A. Experimental Objectives

As stated earlier, the major goal of this investigation was to contribute to the better understanding of the relation between branching and polymer properties. In keeping with this goal, the random type of long chain branching was chosen for study. This type of branching is the form most commonly encountered in soluble commercial polymers, especially certain vinyl polymers. Yet its influence on properties is probably understood least well.

Polyvinyl acetate was selected as the polymer to be used because of its several virtues. It readily undergoes the transfer reactions leading to the desired type of branching, and a significant portion of this branching is removable by hydrolysis, which provides an additional means of characterization. Also, the polymer is amorphous even when linear.* Therefore, variations of the degree of crystallinity with branching will not obscure the other property changes. Finally, polyvinyl acetate is a convenient polymer with which to work and it behaves quite normally in solution. That is, it is not a poly-electrolyte, highly polar, or soluble only under extreme conditions.

In order to evaluate the influence of branching on properties, it was necessary to prepare linear reference polymer on which to base comparisons. Also, an extensive fractionation scheme was required to obtain fractions of reasonably narrow molecular weight distribution, so that the effects of polydispersity would be minimized. Therefore, careful

---

* 87, p. 9.

consideration was given to the preparation of the linear polyvinyl acetate to reduce the branching reactions to a negligible level and, at the same time, to yield polymer which would overlap the branched material with regard to molecular weight on fractionation.

The branched polyvinyl acetate selected for study was a high-conversion product which appeared from the results of an earlier investigation(40) to contain the desired type of branching. Ideally, it might be desirable to use "tailor made"(4, 45) branched polymer for a branching study, especially to expedite the characterization measurements. However, such polymer does not necessarily represent the random type of branching. Also, since fractions of considerable size were required to provide sufficient material for the several measurements, attempts to prepare quantities of "tailor made" branched polymer were judged to be infeasible.

The solution properties of the various linear and branched fractions were investigated both as a means of characterization and because of their theoretical interest.

Solution viscosity measurements were made to obtain the intrinsic viscosity, a measure of size, and the Huggins constant k', apparently related to branching. Also, the non-Newtonian solution behavior of selected linear and branched fractions was investigated because of its possible value as an independent means of detecting branching and its effect on the values of intrinsic viscosity and k'. The importance of viscosity measurements should be stressed. Not only do they yield valuable information, but the equipment required is reasonably simple to operate and certainly relatively inexpensive.

Light-scattering measurements were carried out on selected linear and branched samples primarily to obtain the weight-average molecular weights. This provided a correlation between intrinsic viscosity and molecular weight for the linear material and a means of estimating the degree of branching of the branched sample by the Stockmayer and Fixman method.(26) Other interesting information was also obtained, namely the radius of gyration, the second virial coefficient, and an estimation of the polydispersity of the linear fractions by means of the particle scattering factor. Light-scattering measurements are extremely important because they yield an absolute value for molecular weight as well as the other information mentioned above. However, the equipment investment is quite high, and extreme care must be exercised in making the measurements in order to obtain valid results.

Melt viscosity was chosen as a measurement on the undiluted polymer because of its importance in the fabrication of all thermoplastic materials. With only a few exceptions, the fabrication of such materials involve steps requiring the flow of the molten polymer. The effect of branching on the flow properties is therefore of considerable interest.

B. Materials

1. Solvents

Reagent-grade benzene or methyl ethyl ketone was used as solvent for the various solution measurements. Technical-grade acetone and n-hexane were used in the fractionation of the polyvinyl acetate samples.

2. Polyvinyl Acetate

Five samples of polyvinyl acetate were used in this study. Samples 1, 2, and 5 were linear in nature and were prepared by similar techniques. Samples 3 and 4 were branched, high-conversion type polymers. Samples 1, 2, and 3 have been described in detail in an earlier publication.(40)

(a) Linear Polyvinyl Acetate

The linear samples were prepared under conditions outlined by Burnett, George, and Melville(88) which lead to the formation of relatively linear molecules. Sample 5, of primary importance in this study, was prepared on a larger scale in order to obtain the desired amount of material, and the procedure used follows. Vinyl acetate (Niacet vinyl acetate, DPA, Carbide and Carbon Chemicals Company) was photopolymerized in bulk using azo-bis-isobutyronitrile as the initiator. The monomer was fractionated at a pressure of about 300 mm of mercury under a blanket of dry oxygen-free nitrogen using a column 2 cm in diameter and 60 cm long that was packed with glass helices. The oxygen was removed from commercial nitrogen by passing it through a heated column packed with reduced copper supported on diatomaceous earth.(89) The nitrogen was dried by passing it through a bed of silica gel and then through concentrated sulfuric acid. Middle fractions of monomer having a boiling range of 0.1°C were transferred to Pyrex tubes containing the initiator. The contents of the tubes, approximately one liter in each, were then degassed three times by alternate freezing in liquid nitrogen and thawing of the evacuated material. The tubes were sealed at 10^{-4} mm of mercury while the contests were frozen and then placed in a cold room, -19°C, at a distance of 30 cm from a 100 watt mercury lamp. As soon as the monomer had thawed and reached temperature equilibrium, the lamp was turned on. The tubes were rotated intermittently during the course of polymerization.

The polymer was isolated and freed from the monomer by first diluting the polymerization mixture with acetone and then adding this mixture slowly to an excess of n-hexane. The precipitated polymer was washed with fresh n-hexane and a small portion set aside for determination of intrinsic viscosity. The remaining polymer was dissolved in acetone and reprecipitated again in n-hexane. However, this time the amount of precipitant was adjusted so as to result in incomplete precipitation and thus the removal of a portion of the low molecular weight material. (The low molecular weight tail is undesirable in the fractionation step.) The precipitated polymer was again washed with n-hexane, redissolved in acetone, and stored at -19°C before fractionation.

In order to obtain sufficient material for sample 5, it was necessary to make three batches which were mixed before fractionation. The average molecular weights of these batches were staggered slightly so that the mixture would have a broader distribution of molecular weights about the average. This improved the weight distribution of the fractions somewhat.

The polymerization data are given in Table I for samples 1, 2, and the three components of sample 5. The polymerizations were carried out under conditions which favor the formation of linear molecules, namely low temperature and low conversion.* The linearity of the material was further confirmed by hydrolysis measurements. The samples showed no

---

* 88;79, Chap. 4.

decrease in intrinsic viscosity after hydrolysis and reacetylation which certainly suggested the absence of branching. However, some doubt has been cast on the linearity of the polymer by the findings of Burnett, George, and Melville(88) who claim to have found from four to six fragments of initiator per molecule of polymer formed under conditions similar to those used in this study. Such findings do not necessarily imply branching because the high concentration of initiator fragments could also result from other processes. One explanation offered by these investigators was the formation of methacrylonitrile from disproportionation of the initiator and the subsequent incorporation of this compound into the growing polymer chain. What ever the cause, the hydrolysis data provide a strong argument against branching. Therefore, on the basis of the conditions of polymerization and the hydrolysis study, samples 1, 2, and 5 were judged to be linear and thus suitable reference material on which to base comparisons of the highly branched samples 3 and 4.

(b) Branched Polyvinyl Acetate

The branched polyvinyl acetate was prepared by Mr. Wellman of the Colton Chemical Company according to a suspension polymerization technique similar to that described by Schildknecht.* The high conversion polymer was of high molecular weight and high degree of branching, but was entirely soluble in benzene.

---

* 14, p. 333.

C. Fractionation of Polyvinyl Acetate

1. Fractionation Principles*

The fractionation of a polymer sample according to molecular weight may be accomplished if advantage is taken of the decrease in solubility with increase in molecular weight that is exhibited by a system of polymer homologs. When the environment of a polymer sample in solution is gradually made less desirable, say by lowering the temperature or by adding a precipitant, a second phase eventually is formed. This second phase is actually a more desirable medium for the polymer and thus is more concentrated. For example, if the original polymer concentration is one per cent, the second or "precipitated" phase may contain about ten per cent polymer. The high molecular weight material tends to concentrate in the second phase, because its compatibility with the first phase has been decreased the most. The lower molecular weight species, however, do not find the first phase as undesirable and, therefore, show less discrimination between the two phases. That is to say that the lower molecular weight material has nearly equal concentrations in the two environments. Therefore, if the first phase is sufficiently dilute, and, if the first phase is considerably larger than the "precipitated" one, most of the lower molecular weight polymer will remain in the first phase.

It sould be noted that the solubility of a polymer molecule is also influenced by branching. At a given molecular weight, the solubility generally decreases as the degree of branching increases. This combined

---

* 79, p. 339.

dependence of solubility on molecular weight and branching results in a somewhat broader molecular weight distribution for branched fractions.

2. Fractionation Practice

The fractionation of samples 1, 2, and 3 has been discussed in detail in an earlier publication.(40) A similar procedure was used to fractionate samples 4 and 5, only on a larger scale.

The fractionation technique was based on the partial precipitation method(90, 91) using the solvent - non-solvent system of acetone and n-hexane at 35.0 ± 0.02°C. The precipitant, n-hexane, was added slowly to a vigorously agitated solution of polymer in acetone until the mixture became sufficiently turbid. The turbidity was judged visually by observing an electric lamp through the mixture. The temperature of the system was then raised several degrees until all of the precipitated polymer had dissolved. This was done to eliminate from the fraction any material falsely precipitated by a locally high n-hexane concentration. Next, the fraction was reprecipitated by slowly lowering the temperature to its initial value. After equilibrium had been reached, the agitation was ceased, and the mixture was allowed to settle over night. The gelatinous fraction was then separated, dissolved in benzene, and isolated by freeze-drying.

The freeze-drying technique consisted of freezing the benzene solution of the polymer onto the inside wall of a glass tube, and removing the benzene by sublimation under vacuum. The solution was prevented from thawing by placing a Dewar flask filled with acetone at -10°C around the tube. When most of the benzene had been removed, the Dewar flask was removed, and the polymer was allowed to remain under vacuum at room temperature for an additional 24 hours. The resulting polymer was in a light, fluffy form.

Samples 4 and 5 were fractionated into six and seven primary fractions, respectively, and each primary fraction was again divided into several secondary fractions. The initial concentrations of these materials at the precipitation point were 0.9 and 1 g/dl, respectively. The yields of the various fractions are listed in Tables II, III, and IV.

The code used to designate the fractions consists of a series of numbers. The first number indicates the sample, the second the primary fraction in order of its isolation. The third and fourth members have similar significance for the secondary and tertiary fractions.

D. Intrinsic Viscosity

1. Viscosity Theory*

It was recognized many years ago that the viscosity of dilute polymer solutions could serve as a useful means of characterization.(92, 93) Since the randomly coiled polymer molecules pervade a large region of the solution, a small amount of polymeric solute can cause a marked increase in viscosity. For a given polymer, this increase is related to several variables. Of course, the increase is dependent upon the amount of solute present. The molecular weight of the solute is an important factor since a single molecule has a larger effect on the viscosity than two smaller molecules of an equivalent total weight because it extends over a larger region of solution and causes more resistance to flow. Also, the "goodness"

---

* 79, p. 308, Chap. 14.

of the solvent influences the degree of extension of the polymer chain and thus the increase of viscosity. Both temperature and chemical nature are related to the solvent power.

However, for a given polymer-solvent system and temperature, only the concentration and size or molecular weight of the solute need be considered. The relative increase in viscosity due to the presence of polymeric solute is commonly expressed as the relative viscosity, η_r, which equals the ratio of the solution to solvent viscosities. The incremental increase in viscosity due to the solute is measured by the specific viscosity, $\eta_{sp} = \eta_r - 1$. The reduced specific viscosity, η_{sp}/c, where c is the solute concentration, represents the specific capacity of the polymer to increase the viscosity. It should be noted that the reduced specific viscosity has units of specific volume and might be considered to be the volume pervaded by a given weight of polymer in solution during flow. Actually, the reduced specific viscosity is proportional to the effective hydrodynamic volume, V_e, of the molecule per unit weight, expressed by,

$$\eta_{sp}/c \sim V_e/M \qquad (10)$$

The effective hydrodynamic volume is defined as the volume of a sphere, impenetrable to solvent, that would enhance the viscosity equally as the polymer molecule. The reduced specific viscosity should, therefore, represent a useful characteristic of the polymer molecule in solution.

However, the reduced specific viscosity generally tends to increase as the concentration increases, especially for large degrees of chain extension and high molecular weights. This is apparently due to the enhancement of the viscosity by intermolecular interactions. In order to eliminate this concentration effect, it is convenient to express the reduced specific viscosity in terms of a power expansion of concentration and to extrapolate to zero concentration. The limiting value of the reduced specific viscosity at infinite dilution is referred to as the intrinsic viscosity(94) and is denoted by the symbol $[\eta]$. Since the solutions are usually quite dilute, the first two terms of the power expansion will generally be sufficient to express the relation as a straight line, and therefore one obtains,

$$\eta_{sp}/c = [\eta] + bc \qquad (11)$$

where the total slope b is related to the hydrodynamic interactions.

Huggins(95) proposed the following equation,

$$\eta_{sp}/c = [\eta] + k'[\eta]^2c \qquad (12)$$

where k' is approximately constant for a series of polymer homologs in a given solvent. Varations of k' were discussed earlier (I-D-1-a). A similar expression,

$$\ln(\eta_r)/c = [\eta] + k''[\eta]^2c \qquad (13)$$

where k'' is a constant, represents the concentration dependence of viscosity equally well. Equations (12) and (13) have the intrinsic viscosity as a common intercept, and it can be shown that the sum of k' and -k'' is equal to 0.5.(95)

2. Viscosity Measurements

(a) Viscometer

The viscosity measurements were made with a modified Ubbelohode suspended-level viscometer manufactured by Canadian Laboratory Supplies, Ltd., Montreal, Quebec, according to a design developed at the Polymer Corporation, Sarnia, Ontario.(96) The capillary was 18.5 cm long and had an inside diameter of 0.0356 cm. The suspended-level type viscometer was especially useful since dilutions could be made within the viscometer.

(b) Preparation of Solutions

The solutions were prepared by placing the polymer and the solvent, benzene, in a glass stoppered flask and allowing the mixture to stand over night at 35°C. Both the solvent and solutions were passed through medium grade sintered-glass filters before use. The solution concentrations were determined by evaporation of 10 ml aliquotes to constant weight in tared weighing bottles and were expressed in grams per deciliter. The error in the concentration determination was about one per cent.

Solutions of polyvinyl acetate in benzene were judged to be sufficiently stable for viscosity measurements at 35°C in open apparatus. No significant changes were found in the viscosity functions after aging solutions of polyvinyl acetate in benzene for 8 hours at 60°C in the presence of air.(40)

(c) Flow Time Measurements

Flow times were measured at 35.0 ± 0.02°C to within 0.1 seconds for four or five concentrations, adjusted so as to give relative flow times based on the solvent in the range of 1.15 to 1.7. The flow time for benzene was about 100 seconds.

(d) Kinetic Energy Correction

Viscosity may be expressed by the modified Poiseuille Equation,$^{(97)}$

$$\eta = Adt - Bd/t \qquad (14)$$

where A and B are viscometer constants, d is the liquid density, and t is the flow time. The negative term in Equation (14) is the kinetic energy correction and is required because the liquid leaves the capillary with a small but finite velocity. This results in the incomplete dissipation by viscous friction of the potential energy possessed by the liquid.

The constants A and B were determined by calibrating the viscometer with several pure liquids of accurately known density and viscosity.$^{(98)}$ A plot of η/dt versus $1/t^2$ gave a reasonably straight line with an intercept and slope of A and B, respectively. As will be shown in the next section, only the ratio of B/A was of importance and was found to be approximately 20 which represents a rather small kinetic energy correction.

3. Treatment of Viscosity Data

Equation 14 may be rearranged to give,

$$\eta/Ad = t - B/At \qquad (15)$$

In this study, only the relative viscosity was of interest and is given by,

$$\eta_r = \eta_s/\eta_o = \frac{\eta_s/Ad_s}{\eta_o/Ad_o} = \frac{t_s - B/At_s}{t_o - B/At_o} \qquad (15)$$

where the subscripts s and o stand for solution and solvent respectively, and the assumption is made that the densities of solution and solvent are equal, which is very nearly true for dilute solutions. Thus, the relative viscositites were calculated from the flow times after a correction of 20/t was subtracted.

The viscosity data for each fraction were plotted according to Equations (12) and (13) on a single sheet of paper. This yielded a double plot with the value of the intrinsic viscosity as the common intercept at zero concentration. The arbitary condition that $k' - k'' = 0.500 \pm 0.002$ was imposed because any larger deviations of this sum resulted in appreciable errors in k' and k''. A typical double plot is shown in Figure 1.

The precision of the measurements was about one or two per cent for intrinsic viscosity and about three or four per cent for Huggins k'. The values of intrinsic viscosity, total slope b, Huggins k', and k'' are tabulated in Tables III and IV for the fraction of Series 4 and 5.

E. Dependence of Viscosity on Shear Rate

1. Theory of Non-Newtonian Behavior

(a) Shear Rate and Viscosity

The flow of many dilute polymer solutions is know to exhibit non-Newtonian viscosity behavior. That is, the apparent viscosity varies with the rate at which it is measured. The explanation of such behavior in terms of the nature of polymer solutions becomes rather complex but, while theories are still imcomplete, various explanations have been proposed.

Before proceeding further it is best to consider the significance of viscosity. Actually, viscosity is a measure of the resistance offered when one part of a liquid is moved past another. A shearing force is necessary to overcome this viscous friction and to maintain a velocity gradient throughout the liquid. Viscosity is defined as the ratio of the shearing stress, S, to the rate of the shear, D, where the shearing stress is the shearing force per unit area parallel to the direction of flow, and the rate of shear is the velocity gradient per unit distance perpendicular to the direction of flow. For Newtonian fluids this ratio, and thus the viscosity, remains constant regardless of the flow rate as long as laminar flow is maintained. However, for non-Newtonian fluids, the ratio does not remain constant, and the apparent viscosity generally tends to decrease as the rate of shear increases.

The non-Newtonian behavior of polymer solutions must be attributed to the presence of the polymer because the common solvents employed are Newtonian. Attempts to explain such a phenomenon must therefore be pointed at the behavior of the polymer molecules under the influence of a velocity gradient.

One explanation of the dependence of viscosity on shear rate is based on entanglements and associations between the polymer molecules. This effect is apparently important at low rates of shear where the presence of a small velocity gradient is sufficient to break-down the "structure" of the solution, thus reducing the viscosity.(99, 100) An increase in concentration should enhance the intermolecular interactions, and therefore the degree of non-Newtonian behavior should be a function of concentration. This appears to be true, in general, with polymers such as cellulose nitrate(101) showing a strong concentration dependence and others such as a polyisobutylene(102) exhibiting a lesser dependence.

Deformation and orientation of the polymer molecules is also an important factor to consider. Since the randomly coiled polymer molecules extend over a relatively large domain, they are subjected to considerable shearing forces due to the velocity gradient. Such forces tend to distort and elongate the molecular coils and cause them to orient with the streamlines so as to offer the least resistance to flow. This, of course, results in a lowering of the effective hydrodynamic volume and thus the viscosity.

The susceptibility of a polymer coil to deformation appears to be related to its size and degree of extension. A larger size apparently involves a larger deforming force, and a greater degree of chain extension implies a lower segment density which results in less resistance to deformation. For example, in a given polymer-solvent system, the shear dependence increases as the intrinsic viscosity or molecular weight increases.(100, 102, 104) This demonstrates the effect of size. Also, for samples of different molecular weights dissovled in various solvents so that the intrinsic viscosities or sizes were the same, the sample having the lowest molecular weight, and therefore lowest segment density, showed the most shear dependence.(102) A further example, which is no doubt related to both the size and segment density effects, is the increase in shear dependence with solvent power for a given sample dissolved in various solvents.(103, 104)

Bueche(105) has developed a quanitative method of treating the non-Newtonian behavior. Essentially, the treatment involves a coiled molecular model which is distorted by the velocity gradient. The distortion represents a stretching and compression of the coil at 90° to one another. The velocity gradient also causes the molecule to rotate, so that a given chain segment undergoes an alternate stretching and compression. Assuming that the molecular coil is somewhat stiff and resists these alternating deformations, the viscous energy loss becomes a function of this process. The amount of viscous loss, however, is a function of the frequence of the deformations. At low frequencies, representing low shear rates, the viscous loss is high resulting in high value for viscosity. At high frequencies, or high shear rates, the viscous loss approaches zero and therefore the viscosity decreases.

The treatment takes the final form of,

$$\eta_s - \eta_o = (\eta_s - N_o)_{D=o} [1 - (\tau_o D)^{1/2}] \qquad (17)$$

with

$$\tau_o = 1.98(r/b)(\eta_s - \eta_o)(MM_o)^{1/2} \quad NkTc$$

where M_o is the molecular weight associated with each chain link, N is Avogadro's number, T is temperature, and k is the Boltzmann constant. The ratio (r/b) is a constant for most polymer chains and has a most probable value of 1.88. The other symbols are the same as before (II-D-3). Equation (17) has been shown to fit certain experimental data quite well.

As indicated earlier (I-D-1-b), possible differences in the non-Newtonian behavior of solutions of linear and branched molecules have been detected. The study of such solutions is therefore of interest as a possible means of detecting branching.

(b) Shear Rate and Viscosity Functions

Although it will be discussed later (III-A-4), the influence of the non-Newtonian behavior on the viscosity functions should be mentioned here.

The effect os a shear dependent solution viscosity on the relative viscosity or the reduced specific viscosity is obvious. Since the solution viscosity decreases with increasing shear rate and the solvent viscosity remains constant, the relative viscosity and the reduced specific viscosity must decrease with shear rate. The intrinsic viscosity also behaves similarly because extrapolation to zero concentration does not eliminate the shear effect.

Huggins k' is also influenced by non-Newtonian viscosity behavior (I-D-1-a). It is commonly derived from flow time data measured for several concentrations at a constant shear stress (II-D-3). Since the shear stress is constant and the solution viscosity increases with concentration, the rate of shear must decrease with concentration. The viscosities measured at the higher concentrations are subjected to a lower rate of shear and are therefore decreased less than the viscosities measured at lower concentration and higher shear rates. This causes the slope of the reduced specific viscosity versus concentration plot to be increased, giving high values for the total slope b and Huggins k'.

Because of the effect of non-Newtonian viscosity behavior on the viscosity functions, it is desirable to have information regarding the viscosity behavior as a function of both shear rate and concentration.

2. Shear Dependence Measurements

(a) Apparatus

Viscosities were measured at various flow rates (corresponding to a range of shear rates of about 500 to 5,000 $\sec^{-1}$) using the viscometer and technique described earlier (II-D-2). The flow rate was controlled by the addition of an external source of air pressure to the liquid in the capillary.

The manostat used to control the air pressure was similar to the one used by Sharman, Sones, and Cragg(100) with the addition of a constant-head water supply. The manometer of the manostat was read with the use of a cathethometer. The air pressure during a given run could be held constant to ± 0.2 mm of water which corresponded to about ± 0.2 per cent variation in flow times.

(b) Preparation of Solutions

The benzene solutions of selected linear and branched fractions were prepared for measurement as described earlier (II-D-2-b).

(c) Flow Time Measurements

The flow time measurements on a given solution were made at various pressure levels or shearing stresses. These shearing stresses were then repeated for several other concentrations, as well as for the solvent benzene. This repetition of shearing stresses for solution and solvent enable the relative viscosity to be calculated for each concentration and shearing stress.

(d) Kinetic Energy Correction

Special consideration must be given to the kinetic energy corrections which are applied to the flow times measured at shearing stresses other than that of free fall (no additional external air pressure). It can be shown that, for a given concentration, the kinetic energy correction at free fall (B/At_{FF}) remains constant at all of the other shearing stresses, regardless of the flow times. Consider the more complete form of Equation (14),

$$\eta = \frac{\pi r^4 hgdt}{8LV} - \frac{mdV}{8\pi Lt} \qquad (18)$$

where V is the volume of liquid flowing in time t, g is the acceleration of gravity, m is a constant, h is the effective pressure head driving the liquid through the capillary, and L and r are the length and radius of the capillary respectively. For a given viscometer and solution concentration, Equation (18) shows that the correction B/At is a function of 1/ht only. When h is increased, t decreases in such a manner that 1/ht remains constant (Figure not shown). Therefore, the correction term for kinetic energy remains constant, and thus $20/t_{FF}$ was subtracted from all flow times for a given shear run. This constant feature of the correction term is very important because, while $20/t_{FF}$ is relatively small, $20/t$ would become significantly large at the small values of t encountered at high shearing stresses.

(e) Validity of Method

In order to cover the desired range of shear rates, shearing stresses both above and below that of free fall were required. It was necessary to apply air pressure to the top of the capillary to obtain the high shearing stresses and to the bottom for the low shearing stresses. The justification of using the viscometer in such a manner may be seen from Figure 2 which shows η_{sp}/c versus the rate of shear. No discontinuity occurs on passing through the free fall region, that is from the positive to negative application of air pressure.

Further support for the validity of the method is gained by the agreement of the data with Equation (17), which has been shown to fit data taken by independent investigators working with various polymers and solvents at various temperatures. Figure 3 shows the experimental data points for fractions 2-1-1, 4-1-1-2, and 4-3-2 and the plot of Equation (17), solid lines.

3. Treatment of Shear Data

(a) Measure of Shear Dependence

The relative and reduced specific viscosities were calculated from the corrected flow times in the usual manner. The maximum rate of shear at the capillary wall(57) was calculated from the equation,

$$D = S/\eta_s = rghd/2L\eta_o\eta_r \qquad (19)$$

where the symbols have their usual meanings.

Since the solutions studied exhibited different degrees of non-Newtonian behavior, it was desirable to seek a means of expressing this shear dependence in a quantitative manner. Figure 2 shows the typical non-Newtonian behavior displayed by some of the polymer solutions, that is a decrease in apparent viscosity as the rate of shear increases. Of course, the degree of shear dependence was reflected qualitatively by the shape of such a plot. A horizontal, straight line indicated a Newtonian fluid, and a sharply curving line showed strong shear dependence. In order to obtain a more quantitative measure of shear dependence, further treatment was necessary. It was found that a plot* of c/η_{sp} versus $D^{1/2}$ produced straight lines (see Figure 4). The slopes, J, of these lines were a measure of the shear dependence. Of course J varied slightly with concentration for a given fraction, but, as shown in Figure 5, this variation was essentially linear. In order to eliminate the effect of concentration variation and to place all values of J on a common basis, the extrapolated values of J at zero concentration, $J_{c=o}$, were used in making comparisons of the shear dependence of the various fractions.

The shear dependence data are tabulated in Table V. It should be noted that the method used for treating the data was developed from

---

* This relationship was suggested by Professor L. H. Cragg of McMasters University.

data in the shear rate range of about 500 to 5,000 sec^{-1} and that measurements in a different range might conceivably yield different values.

(b) Other Methods

Several other methods have been suggested in the literature for extrapolating shear data.(102, 106) While these methods represent the data with fairly straight lines, the slopes vary over a smaller range making the slopes a less sensitive measure of shear dependence.

F. Light-Scattering

1. Theory of Light-Scattering*

(a) General

When a light beam impinges on a small, spherical, isotropic molecule, which does not absorb light, the electric field of the light beam induces oscillations of the electrons and nucleus. The molecule then acts as a secondary source of radiation and emits light of the same frequency as the primary source (neglecting Raman scattering) in all directions.

The simplest case of light-scattering by a collection of molecules is, of course, that of a very dilute gas. In this case the molecules act as separate scattering sources, and the net scattering is merely the sum of the individual contributions.

At the opposite extreme is the case of the interaction of light with a crystalline solid. Since the atoms or molecules are arranged in fixed regular positions, there is not net scattering of light due to complete destructive interference. (This is excluding the Bragg effect with X-rays.) This may be demonstrated by considering the material to be com-

---

* 45; 79, Chap. 7; 87, Chap. 7.

posed of mutually cancelling volume elements. The elements must be sufficiently small so that the light scattered from the component molecules may be considered to be in phase. For a given element and point of observation, a corresponding element can always be chosen so that the scattered light will be 180 degrees out of phase. Since there are an equal number of molecules in each volume element, the cancellation of the scattered light will be complete. Although there will be different combinations of pairs for each point of observation, the scattered light is always cancelled.

When considering a pair of volume elements in a liquid, however, the situation is somewhat altered. Although the scattered light may be 180 degrees out of phase, the number of molecules in each element need not be equal at any given instant because of Brownian motion. This fluctuation in density results in incomplete cancellation and thus a net scattering of light.

In the case of liquid mixtures, another type of fluctuation occurs, that is one of local concentration changes. This also results in light-scattering providing the molecules have different polarizabilities or abilities to scatter light.

(b) Polymer Solutions--Small Molecules

Polymer solutions may be treated as binary mixtures, and both the density and concentration fluctuations contribute to the light-scattering. However, since the segments of the polymer molecules must remain linked together, the fluctuations in concentration become much more pronounced than if the components were of low molecular weight and could mingle more freely. In fact, the concentration fluctuations are responsible for the major portion of the light scattering by polymer solutions.

For a given weight of polymer, the concentration fluctuations increase as the number of polymer chains decrease, which corresponds to an increase in molecular weight. It is this behavior that forms the basis for the determination of molecular weight.

By the proper consideration of the system, the following equations relating the solute molecular weight to experimentally measurable quantities have been developed$^{(107)}$:

$$\frac{32\pi^3 n_o^2 \, (dn/dc)^2 c}{3N\lambda_o^4 \, \tau} = Hc/\tau = 1/M + 2A_2c + \ldots \qquad (20)$$

$$\frac{2\pi^2 n_o^2 \, (dn/dc)^2 c}{N\lambda_o^4 \; R_{\theta=90}} = Kc/R_{\theta=90} = 1/M + 2A_2c + \ldots \qquad (21)$$

where $I = I_o e^{-\tau x}$, and $R_\theta = i_\theta \, r^2/I_o$

and

τ - turbidity

I_o - intensity of the incident beam

I - intensity of the transmitted beam

x - distance traversed in medium

θ - scattering angle--zero for transmitted beam

R_θ - reduced intensity at angle θ

i_θ - intensity of the light scattered at angle θ

r - distance from the detector to scattering site

n_o - refractive index of solvent

n - refractive index of solution

c - solute concentration

M - solute molecular weight

λ_o - wave length of the light in vacuum

N - Avogadro's number

A_2 - the second virial coefficient

Equations (20) and (21) are valid under the following conditions. The polymer molecules must be isotropic and sufficiently small, compared to the wave length of the light, to be considered as point sources. The values of reduced intensity and turbidity represent only the scattering contribution of the solute, and therefore the solvent scattering (usually quite small) must be subtracted from the measured solution values. If the incident light is not vertically polarized but umpolarized, the values of the reduced intensity and turbidity must be multiplied by $(1 + \cos^2\theta)$ in order to normalize the scattered light. Under these conditions the light scattered will be symmetrical about the scattering source.

Note the similarity between these equations and Equation (1) for osmotic pressure.

The molecular weight obtained from Equations (20) and (21) will, of course, be an average one, unless the polymer sample is monodisperse. The type of average will be different from the number-average [Equation (3)] obtained by the measurement of a colligative property which merely counts the number of molecules. Since the intensity of light scattered by a molecule is proportional to the square of its molecular weight, the larger molecules are given more importance in an average, and the molecular weight is a weight-average quantity [Equation (3)]. This may be shown by considering

Equation (20) for an ideal solution. One obtains:

$$\tau = H\sum_i c_i M_i = HcM_w$$

and therefore:

$$M_w = \sum_i c_i M_i / c = \sum_i n_i M_i^2 / \sum_i n_i M_i$$

where $c = \sum_i c_i$, n_i is the number of molecules having molecular weight M_i, and $c_i = n_i M_i / N$.

(c) Polymer Solutions--Large Molecules

When the size of the molecular coil approaches the wave length of light, say greater than one-twentieth of the wave length, the molecule may no longer be considered as a point source. Light scattered from the various portions of a molecule will interfere destructively, and this interference will be a function of the scattering angle. The interference at zero scattering angle will, of course, be zero because all of the possible light paths from the primary source to the molecule and on to the detector are equal. Therefore, all of the scattered light will be in phase. However, as the scattering angle increases, the path lengths will deviate more and more from being equal, causing the light scattered from the various portions of the molecule to be more and more out of phase. This results in an unsymmetrical scattering of light about a scattering angle of 90 degrees, with the greatest reduction in intensity at the high angles.

The dissymmetry of the scattered light is not only a function of angle but also depends upon the size of the molecular coil. Therefore, it becomes an important means of determining molecular size. It does, however, complicate the determination of molecular weight somewhat.

To account for this dissymmetry effect, Zimm(108) has shown that the following equation,

$$Kc/R_{\Theta} = 1/MP_{\Theta} - 2A_2c \qquad (22)$$

where P_{Θ} is the particle scattering factor, represents the scattering behavior adequately. In the case of Gaussian chains, the particle scattering factor has been shown by Debye(107) to be given by

$$P_{\Theta} = (e^{-u} + u - 1)\ 2/u^2 \qquad (23)$$

with

$$u = (4\pi \sin \Theta/2)^2\ S^2/\lambda^2$$

where S is the radius of gyration and λ is the wave length of light in the solution.

It is of importance to note that, for a given system, Equations (22) and (23) express the scattered light as a function of scattering angle, solute concentration, molecular weight, and coil size. The proper treatment of light-scattering data measured as a function of angle and concentration will yield values of molecular weight and coil size. This will be developed further under the treatment of light-scattering data (see II-F-3).

2. Light-Scattering Measurements

(a) Light-Scattering Apparatus

Equipment. The light-scattering measurements were made with a Brice-Phoenix light-scattering photometer, model number 1410.* The instru-

---

* 32, p. 120-124; 109; 110.

ment's light source was a mercury arc lamp operated by a constant current regulating unit. The light passed through a monochromatizing filter to isolate the 4360 Å wave lenth, and its intensity could be varied by combinations of neutral filters. The scattering cell was of the cylindrical type with flat entrance and exit windows. The scattered light was detected by a multiplier phototube which transmitted its signal to a galvanometer. The phototube was mounted to rotate about the axis of the scattering cell which enabled measurements at various scattering angles. For details of the design, operation, and maintenance of the photometer see reference 110.

Calibration. The basic calibration of the photometer was made by Dr. J. A. Manson(45) using a solution of Ludox (silica sols), the turbidity of which was determined by means of a Beckman spectrophotometer.(104, 111) From this calibration, the turbidity may be expressed as follows:

$$\tau = 0.131(\pm 0.001)\ T_{90}\ C_n\ \text{cm}^{-1} \qquad (24)$$

where T_{90} is the scattering ratio, defined as the ratio of light scattered at 90 degrees to that transmitted at zero degrees, and C_n corrects for the difference in refractive index between the solvents used for calibration and measurements. The calibration was checked by turbidity measurements on toluene solutions of the "Cornell standard polymer" obtained from the Cornell University. The turbidity obtained agreed within one per cent of the "best" value,(45, 112) which is excellent.

Since scattering measurements were to be made at angles other than 90 degrees, it was necessary to check the scattering cell for symmetry to insure the validity of the calibration at these angles. This was done by using a fluorescein water solution with a scattering power of about one hundred times that of water. If the cell were symmetrical, the solution would fluoresce light symmetrically in all directions. The ratio of the light intensity observed at a given angle to that at 90 degrees varied from unity by no more than one per cent at most angles, and therefore the cell was judged to be sufficiently symmetrical for angular measurements.

The photometer was equipped with four neutral filters which could be inserted into the primary beam to reduce its intensity, so that the galvanometer deflections would be nearly full-scale at all scattering angles. The transmittances of the filters were checked by observing the galvanometer deflections at a given angle with and without the various filters. The transmittance of a filter was calculated as the ratio of the galvanometer deflections with and without the filter.

(b) Preparation of Solutions

The polymer samples were dissolved in methyl ethyl ketone and allowed to stand overnight at 35°C in glass stoppered flasks. The concentration was determined as before (II-D-2-b) from the solution in the scattered cell after the final scattering measurements had been made. Concentrations were expressed in g/cm^3 in this case.

Since dust and other extraneous material are highly scattering, considerable care was exercised to eliminate such material from the measured solutions and solvent. All solutions and solvents (for measurements of background scattering) were first filtered through sintered-glass and then centrifuged (about 25,000 g) in a Servall angle centrifuge, type SS-1A, for four hours. Solvent and solutions were transferred from the centrifuge to the scattering cell by means of hypodermic syringes. To further minimize the dust problem, the measurements were carried out in a "dust free" room, the air being constantly circulated through filters.

(c) Scattering Measurements

For each fraction studied, scattering measurements were made on the solvent and four concentrations of solution at 27°C for several angles. The angles were 0, 28, 30, 45, 60, 75, 90, 105, 120, and 135 degrees, where zero angle represents the exit beams from the scattering cell. The scattering was recorded as the galvanometer deflection, G_Θ, for each angle.

The procedure for a typical run follows: Freshly centrifuged solvent was transferred into the scattering cell which had been rinsed several time with clean solvent. The dissymmetry ratio, that is the ratio of scattering at 45 to 135 degrees, was determined. Theoretically, this ratio would equal unity if the solvent were optically clean. A polar solvent such as methyl ethyl ketone is difficult to clarify completely, and the dissymmetry ratio was generally between 1.1 and 1.2. If the dissymmetry ratio was not usually high, the system was judged to be sufficiently clean, and the scattering was determined at the other angles.

After the solvent scattering had been determined, the measurements were repeated for four concentrations of solution. These concentrations were varied by adding successive amounts of a centrifuged stock solution to the solvent in the scattering cell. The cell was weighed before and after each addition, and the concentration of the final solution was determined. This provided sufficient information from which to calculate the other concentrations.

(d) Treatment of Galvanometer Readings

Filter adjustment. The galvanometer readings were divided by the transmittances of the appropriate neutral filters to account for the reduction of the intensity of the incident light by the filters. Thus, the scattering ratio was calculated as follows:

$$T_\Theta = G_\Theta f_o \,/\, G_o f_\Theta$$

where f is the filter transmittance.

Reflection correction. A portion of the transmitted beam is reflected at the exit face of the scattering cell. This light is then scattered as it passes back through the solution. Since the reflected light is traveling in the reverse direction, its scattering pattern will be the reverse of the primary scattering pattern. Therefore, because of the dissymmetry of the scattered light, the primary scattering will be increased more by the secondary scattering at the higher values of Θ. A method of correction for the secondary scattering has been described by Sheffer and Hyde.(113)

The reflection correction was applied to the scattering data by reducing T_Θ by five per cent of the corresponding T_Θ at the supplementary angle. For example, 0.05 T_{120} was subtracted from T_{60} and 0.05 T_{60} was subtracted from T_{120}. The correcton to T_{28} and T_{30} were estimated by plotting the corrections at other angles versus sin Θ and extrapolating.

Solvent scattering. In order to eliminate the scattering contribution of the solvent and also traces of dust (assuming the scattering from dust is about constant for solvent and solutions), T_Θ for solvent was subtracted from T_Θ for solution after the relection correction had been made. The resulting value was denoted as T_Θ'.

Change in scattering volume with angle. Since the scattering volume viewed by the receiver varies with the viewing angle,(114) it was necessary to normalize T_Θ' by multiplying by sin Θ.

Unpolarized light. T_Θ' was multiplied by $1/(1 + \cos^2\Theta)$ to compensate for the use of unpolarized light.(115, 116) The final corrected scattering ratio was then given by:

$$T_\Theta'Q = T_\Theta'\sin\Theta/(1 + \cos^2\Theta)$$

3. Treatment of Light-Scattering Data

(a) Zimm's Method

At zero concentration Equation (22) reduces to

$$(Kc/R_\Theta)_{c=o} = 1/MP \qquad (25)$$

and, at zero angle, to

$$(Kc/R_\Theta)_{\Theta=o} = 1/M + 2A_2c \qquad (26)$$

since $(P_{\Theta=o}) = 1$ [see Equation (23)]. Also, for low values of u, Equation (23) can be expanded(108) to yield:

$$1/P_\Theta = 1 + u/3 + \ . \ . \ . \qquad (27)$$

Therefore Equation (25) becomes

$$(Kc/R_\Theta)_{c=o} = \frac{1}{M_w}(1 + u/3 + \ . \ . \ . \ ) \qquad (28)$$

for low values of u. It may be seen then that the molecular weight, radius of gyration, and second virial coefficient can be obtained from the intercepts and slopes of Equations (26) and (28).

Zimm(108) has suggested a method of extrapolating the light-scattering data to zero angle and zero concentration. First, Kc/R_Θ is plotted versus $\sin^2\Theta/2 + kc$, where k is an arbitrary constant chosen to give the plot a convenient shape. Lines are then drawn through points of constant angle and extrapolated to values of zero concentration to give points representing Equation (25). A line is drawn through these points and extrapolated to zero angle. Alternately, lines are drawn through points of constant concentration and extrapolated to values of zero angle resulting in points on Equation (26). A line is then drawn through these points and extrapolated to zero concentration.

The final plot takes the form of a grid (see Figure 6). At the lower values of Θ, Equation (25) becomes Equation (28). Therefore, the mutual intercept of Equations (26) and (28) at zero angle and zero concentration gives the value of $1/M_w$. The second virial coefficient is determined by the limiting slope of Equation (26). The mean square radius gyration is calculated from the initial slope (or limiting tangent--see next section) of Equation (28) as follows:

$$S_z^{\,2} = 3\lambda^2 \text{ (initial slope)}/16\pi^2 \,(Kc/R_\Theta)_{\substack{c=0\\ \Theta=0}} \qquad (29)$$

Note that $S_z^{\,2}$ is a z-average quanity.(108)

The light scattering data were treated by the Zimm method. However, to simplify calculations, $c/QT_\Theta{}'$ was plotted versus $\sin^2\Theta/2 + 1000c$. The intercept and slopes were then multiplied by the factor,

$$V = H/0.131C_n = 1.31 \times 10^{-5}$$

to account for the calibration and physical constants of the system [see Equation (20) and (24)]. The various constants used for the polyvinyl acetate - methyl ethyl ketone system follow:

λ_o = 4360 Å

λ = 3150 Å

(dn/dc) = 0.080(67)

n_o = 1.383

C_n = 1.08(45)

Values of Mw, S_z^2, and A_2 are tabulated in Table VI.

(b) Polydispersity

Benoit(70) has shown, that for large values of u, Equation (25) becomes,

$$(Kc/R_\theta)_{c=o} = \frac{1}{M_n}(1/2 + u/2 + \ldots) \qquad (30)$$

Equation (30) represents the limiting asymptote to the experimental curve, Equation (25). The number average values of molecular weight and mean square radius of gyration can be obtained from the asymptote as follows:

$$M_n = 1/2 \text{ (intercept of the asymptote)} \qquad (31)$$

$$S_n^2 = \frac{\lambda^2 \text{ (slope of asymptote)}}{16\pi^2 \text{ (intercept of asymptote)}} \qquad (32)$$

Information concerning the polydispersity of the sample will be obtained if the limiting tangent and limiting asymptote can be located. Zimm(108) has suggested a method of correcting the observed data so that they will fall on the limiting tangent or asymptote. The method involves the assumption of a single peaked, molecular weight distribution which is characterized by a parameter Z. Z is related to the various average molecular weights as follows:

$$Z/M_n = (Z + 1)/M_w = (Z + 2)/M_z$$

Further support for the light-scattering data is afforded by Shultz's work with polyvinyl acetate in methyl ethyl ketone.(67) Values of S_z^2 and A_2 as a function M_w are in excellent agreement (comparisons not shown).

G. Hydrolysis Measurements

1. Hydrolysis Theory

As mentioned earlier (I-D-1-e), certain polyvinyl acetates undergo a marked decrease in molecular weight on hydrolysis and reacetylation.(6, 7, 40, 72, 80) This is generally attributed to the presence of removable long chain branches on the acetate groups, resulting from intermolecular chain transfer with monomer or polymer (I-B).

Of course, such a reduction in molecular weight could also occur if hydrolyzable linkage were formed in the main polymer chain by intramolecular chain transfer at the acetate groups(short chain branching). This reaction can be discounted, however, by considering the results of Wheeler, Ernst, and Crozier.(6) They found that the degree of degradation of polyvinyl acetate by hydrolysis increased as the degree of conversion increased, and that low conversion polymer showed no degradation. Since intramolecular chain transfer is usually considered to be a function of temperature and independent of polymer concentration,(21) the low conversion polymer should show signs of degradation if such a reaction is occurring with hydrogens of the acetate group.

The dependence of degradation on the degree of conversion gives strong support to the presence of long chain branching formed by intermolecular chain transfer with polymer, which is dependent on polymer concentration, as well as temperature.* This does not eliminate the possibility of intermolecular chain transfer with monomer. It is true that transfer with monomer is favored by the high monomer concentration at low conversion, but the step which actually forms the branch (see I-B) is favored by the low monomer concentration at high conversion. That is, the double bond of the monomer which has undergone transfer has a greater probability of being incorporated in the growth of a polymer chain at low monomer concentrations.

The hydrogens on the acetate groups are not the only possible sites of transfer. The tertiary hydrogens on the polymer chain are also very likely sites, which means that some of the branches will be non-hydrolyzable. Various attempts have been made to determine the relative amounts of hydrolyzable to non-hydrolyzable branching but have met with only qualitative success.

Wheeler, Lavin, and Crozier,(7) working with high conversion polyvinyl acetates, and Roland and Richards,(72) working with graft copolymers of polyethylene on polyvinyl acetate have shown that both types of branching are present in significant amounts. Howard,(5) studying polyvinyl acetate and various transfer agents, concluded that transfer with monomer occurred mainly on the acetate group, whereas transfer with polymer was largely at the site of the tertiary hydrogen. More recently, vinyl trimethylacetate has been polymerized in the presence of polyvinyl acetate.(80) Investigation of the graft copolymer indicated that the acetate group was the principle site of branching, but that the tertiary hydrogen also made a small contribution. Therefore, at the present, the

---

* 79, p. 256.

relative occurrence of hydrolyzable and non-hydrolyzable branching is somewhat uncertain.

In the present study, hydrolysis measurements were made on selected samples to support the assumption of linearity in the case of the linear materials, and to estimate the degree of branching in the branched fractions.

2. Hydrolysis Data

The procedure used for hydrolysis and reacetylation was similar to that described by Wheeler, Ernst, and Crozier.(6)

The polymer samples were hydrolyzed by first adding a five per cent solution of methanolic potassium hydroxide to a solution of polymer in methanol (0.75 g/dl) in the volume ratio of one to ten. The mixture was held at 35°C until the precipitation of the polyvinyl alcohol was complete (several hours). The polyvinyl alcohol was then isolated by filtration, washed thoroughly with methanol, and allowed to dry at room temperature.

The polyvinyl alcohol was reacetylated by treatment with a mixture of pyridine, acetic acid, and acetic anhydride in the proportions of 1:5:15. About 40 ml were used for each gram of polymer. The mixture was held at 100°C by a steam bath until dissolution was complete (about one or two days). The mixture was then poured slowly into an excess of distilled water to precipitate the polyvinyl acetate. The polyvinyl acetate was washed with water, dissolved in benzene, and isolated by the freeze-drying technique (II-C-2).

The intrinsic viscosities of the reacetylated samples were measured in the usual manner (II-D-2). Table VIII lists the intrinsic viscosities of the samples before and after treatment. Values of $(M_v)_H$ were calculated from the intrinsic viscosities of the treated branched fractions by Equation (33). These values are tabulated in Table VIII along with M_w before hydrolysis.

Light-scattering measurements were also made in the usual manner (II-F-2) on two of the treated branched fractions in order to obtain $(M_w)_H$ (see Table VIII). Further measurements were not made because the molecular weights were approaching the lower limit of accuracy of the method.

3. Treatment of Hydrolysis Data

(a) Hydrolysis Results (Table VIII)

The unfractionated linear material, sample 5, and two linear fractions, 5-3-2 and 5-6-2, showed essentially no change in intrinsic viscosity on hydrolysis and reacetylation. This strongly supports the assumption that the fractions of Series 5 are linear.

The marked decrease in intrinsic viscosity or molecular weight displayed by the unfractionated branched material, sample 4, and seven fractions of Series 4 indicates the presence of branching.

It is interesting to note that the molecular weight range of the treated fractions is much narrower than the range before treatment. This suggests that the branched molecules are built up from units which, to a rough approximation, have about the same average molecular weight. This is to be expected from the long chain branching mechanism (see I-B).

Since the values of $(M_v)_H$ were calculated from Equation (33), they represent the molecular weights which the treated fractions would have if they were linear. The values of $(M_w)_H$ for fractions 4-1-1-1 and 4-4-2 are slightly larger than the corresponding values of $(M_V)_H$. This difference is undoubtedly due to the presence of some non-hydrolyzable branching, but it is considerably smaller than the difference between M_W and $(M_W)_H$.

(b) Number of Branches per Molecule

The number of branches per molecule for the fractions of Series 4 was calculated from the hydrolysis data by the following equation:

$$n_H = \frac{M_W - (M_V)_H}{(M_V)_H} \qquad (34)$$

It was assumed that the branching was completely removed by the hydrolysis treatment and that $(M_V)_H$ represented the average molecular weight of both the "backbone" and branches. (The values of n_H are essentially weight-average because of the similarity between the weight- and viscosity-averages.)

Of course these assumptions are only approximately correct. Presumably n_H should tend to underestimate the degree of branching but nevertheless it should serve as a useful estimate. Values of n_H are tabulated in Table VIII.

H. Melt Viscosity

1. Theory of Melt Flow

The viscous flow of a molten polymer is generally considered to be accomplished by the successive jumps of chain segments. These segments may be of the order of fifty carbon atoms in length.* According to

---

* 32, p. 151.

this theory,* the melt viscosity is given by,

$$\eta = F/j \tag{35}$$

where j is the jump frequency and F is a statistical factor. The frequency at which the chain segments jump from one equlibrium position to another is dependent upon the temperature and the free volume. The statistical factor expresses the requirement that the jumps of the various segments must be coordinated and is apparently dependent upon total chain length.

In order to study the dependence of the statistical factor on chain length, Fox and Loshaek(120) re-examined isothermal (constant j) viscosity data for a wide variety of polymers. Above a certain critical chain length, depending upon the polymer, a common dependence of viscosity on the 3.4 power of weight-average chain length was found. Below the critical length, the dependence was approximately of the first power.

This behavior may be explained** in terms of the theory proposed by Bueche.(121) Below the critical chain length there is on an average less than one intermolecular chain entanglement per molecule. Under these conditions, the resistance to flow is mainly due to the ordinary friction of one segment flowing past another and should be proportional to about the first power of chain length. The critical chain length apparently represents the condition at which the chains have become sufficiently long to become envolved in an average of one entanglement per molecule. Under this condition and at high chain lengths, the material is a network

---

* 119, Chap. 12.

** 32, p. 151; 120.

of polymer chains. Although there is a certain amount of slippage, the flow is controlled by the viscous drag of a train of entangled chains. Bueche has estimated the viscosity to be proportional to the 3.5 power of chain length which is in excellent agreement with the experimental value of 3.4.

As mentioned earlier (I-C-2), there is experimental evidence showing that branched polymers generally have a lower melt viscosity than linear material of the same molecular weight. This has been explained both in terms of an increase in jump frequency due to an increase in free volume(34) and by a reduction of the coordination factor.(35, 122) These points will be elaborated in the discussion of the melt viscosity results (III-C-2).

2. Melt Viscosity Measurements

(a) Preparation of Samples

The samples were prepared by first aging one per cent benzene solutions of the polymer at 35°C for 24 hours. The solutions were then filtered through a medium grade sintered-glass filter, and the polymer isolated by the freeze-drying technique (II-C-2). The samples were allowed to remain under vacuum, 10^{-4} mm of mercury, at room temperature for at least 48 hours longer than the normal freeze-drying time to insure complete removal of the benzene.

The polymer fractions were then molded into one gram pellets, 0.57 inches in diameter, using a plunger-type mold. The mold was preheated to 155°C, and the sample was inserted and allowed to stand for 15 min under no pressure. The mold assembly was then placed between the heated plates of a press, and pressure was applied and released step by step until a final pressure of 30,000 psi was attained. This alternate application and release of pressure was necessary to release air bubbles trapped in the sample. The sample was held under pressure at 155°C for an additional 15 min and then cooled to room temperature by passing cooling water through the plates of the press. The sample was stored in a dry atmosphere at room temperature after being removed from the mold.

(b) Description and Operation of Plastometer

The viscosity of the molten polymer was measured at 155°C using a Williams Parallel Plate Plastometer(124) according to the specifications of ASTM test D 926-47T.

The sample pellet was placed between the parallel plates of the plastometer, which was housed in an oven maintained at 155 ± 0.5°C. Aluminum foil was used as a parting agent to protect the plates. The lower plate of the plastometer was stationary, but the upper plate was free to move in a vertical direction and was driven by a constant load of 5.0 kg. Therefore, the molten polymer was squeezed between the plates and flowed between them in a radial direction on a circular front. The plate separation was recorded as a function of time.

(c) Heat Stability of the Melt

A check of melt stability and reproducibility was made for several fractions, both linear and branched. For a given fraction, the melt viscosity was run twice on the same piece of material, and the intrinsic viscosity was measured before and after the two runs. Since there was no appreciable decrease in either melt of intrinsic viscosity (see Table IX) the samples were judged to be melt stable. The reproducibility of the melt viscosity measurement was about three or four per cent, depending on the viscosity. The range of the plastometer was from about 10^6 to 10^9 poise with the largest errors near these limits.

(d) Effect of Heterogeneity

The melt viscosities of two mixtures, one linear and one branched, were measured to test the influence of heterogeneity. A mixture was prepared by combining two fractions of different molecular weights in such proportions that the weight-average molecular weights were about midway between. M_w was calculated for a mixture according to Equation (3). The ratio M_w/M_n was about 1.4 for both mixtures.

When melt viscosity was plotted versus weight-average molecular weight (see Figure 15), the points representing the mixtures fell on lines connecting the component fractions. Thus, it was judged that possible differences in the homogeneity of the various fractions (especially between the linear and branched fractions) would not effect the comparison of melt viscosities as long as the comparison was made on a weight-average basis.

3. Treatment of Melt Viscosity Data

(a) Calculation of Melt Viscosity Data

The melt viscosity in poises was calculated by the equation,(124)

$$\eta = 8.21 \times 10^6 \ W/m \ V^2$$

where W is the load on the sample in kg and V is the sample volume in cm^3. In this equation, m is the slope in cm^{-4} sec^{-1} of the straight portion of the line obtained when the reciprocal of the plate separation to the fourth power is plotted versus time. The melt viscosities are tabulated in Table IX.

(b) Viscosity Increment

The relative differences in the melt viscosities of the linear and branched fractions were expressed by,

$$Y = (\eta_B - \eta_L)/\eta_L \tag{36}$$

where the subscripts B and L stand for branched and linear respectively and the viscosities are at a constant value of M_w. Values of Y are given in Table X.

III. CORRELATION OF RESULTS AND DISCUSSION

A. Effect of Branching on Solution Properties

1. Size and Molecular Weight

(a) Intrinsic Viscosity and Molecular Weight

As mentioned earlier (I-C-1), branching results in a marked reduction of the volume pervaded by the polymer molecule at a given molecular weight. This is shown by the logarithmic plot of the intrinsic viscosity versus the weight-average molecular weight, Figure 7, for the linear and branched fractions.

The linear fractions, series 5, fall on a single straight line which is represented by Equation (33)(II-F-3-c). It is important to note that all of the branched fractions, series 4, lay below this line in the direction of smaller size. This indicates that all of these fractions are branched. It was originally anticipated that the lower molecular weight fractions of sample 4 might be essentially linear due to the anomalous solubility behavior caused by branching (II-C-1).

(b) Radius of Gyration and Molecular Weight

The effect of branching on size is also shown by the plot of the z-average mean square radius of gyration versus the weight-average molecular weight, Figure 8. It should be noted, however, that the branched fractions do not display as marked a deviation from the linear line as in the case of intrinsic viscosity, Figure 7. This is especially noticeable in the lower molecular weight region. Such behavior could be explained in terms of polydispersity since two different average values are involved in the comparison. If the branched fractions were more polydisperse, which is generally to be expected, their values of S_z^2 would be higher than if they had the same molecular weight distribution as the linear fractions.

The decrease in size resulting from branching should also be indicated by the ratio M/S^2. Since S^2 decreases with branching, the ratio should increase as the degree of branching increases. This ratio is independent of the molecular weight for a linear polymer in an ideal solvent.(67) Therefore, an estimate of the degree of branching should be available from a single light-scattering run once the value of the ratio had been determined for the linear material. Unfortunately, the use of this method is complicated by polydispersity and the variation of M/S^2 with molecular weight for linear polymer if a non-ideal solvent is used.

As an illustration of the complications, consider the polydispersity study of the linear fractions of series 5 by light-scattering (II-F-3-b). Approximate values of Z were obtained which indicated that the fractionation of the linear polymer was reasonably efficient. The knowledge of Z enabled the calculations of S_w^2 and consequently M_w/S_w^2. The use of weight-average values for both molecular weight and size should eliminate any variations of the ratio due to differences in polydispersity among the linear fractions. However, Table VII shows that M_w/S_w^2 decreases as M_w increases instead of remaining constant. This decrease results from the relative expansion of the molecular coil as a function of molecular weight. The expansion is apparently caused by the variation of the excluded volume effect with molecular weight due to the use of a good solvent.(67) Similar behavior for polyvinyl acetate in methyl ethyl ketone has been observed by Shultz.(67)

The variation of M_w/S_w^2 with M_w for the linear fractions is of sufficient magnitude when compared to the differences between M_w/S_z^2 for the linear and branched fractions (Table VI) to completely nullify the quantitative nature of the measure of branching from a single light-scattering run.

An indication of the effect of polydispersity on the ratio can be obtained by comparing M_w/S_z^2 with M_w/S_w^2 for the linear fractions. The differences are not too great in this case because the fractions have fairly narrow molecular weight distributions. Greater differences should be expected for the branched fractions which presumably are somewhat more polydisperse. If this is the case, then the difference between M_w/S_z^2 for the linear and branched fractions would be decreased.

Burnett, George, and Melville(88) have reported variations of M_w/S_z^2 for polyvinyl acetate ranging from 4.0 for linear polymer to about 15.6 for branched material. The value of 4.0 is in agreement with the values for the linear series of fractions. Actually, 15.6 would correspond to about seventy branches per molecule which is a rather high degree of branching.

2. Second Virial Coefficient

Figure 9 clearly shows the expected dependence of the second virial coefficient, A_2, on both molecular weight and branching (I-D-1-c). The values of A_2 decrease with increasing M_w for both the linear and branched series of fractions. Also, the molecular weight ranges of the two series overlap sufficiently to show that A_2 is lower for a branched fraction at a given M_w.

3. Concentration Dependence of Viscosity

The relationship between the reduced specific viscosity and concentration, Equations (11) and (12), appears to be sensitive to branching (I-D-1-a and f). When the total slopes, b, for the branched and linear fractions of Series 4 and 5 (Tables III and IV) are compared on an intrinsic viscosity basis, the values of b are slightly larger for the branched fractions, but the difference is not marked (figure not shown).

The Huggins constant k' indicates the presence of branching a bit more clearly. Figure 10 shows k' plotted versus intrinsic viscosity for the branched and linear fraction of Series 4 and 5. There appears to be separate relationships for the two series, with k' increasing gradually as the intrinsic viscosity increases. Above an intrinsic viscosity of about two and one-half, the branched fractions generally have values of k' which are larger than those for the corresponding linear fractions. Below this intrinsic viscosity and differences in k' between the branched and linear fractions are within the experimental error.

The behavior of k' as a function of intrinsic viscosity for Series 4 and 5 is an agreement with that reported in an earlier publication(40) for Series 1, 2, and 3. Similar behavior has been reported by others (I-D-1-a).

4. Non-Newtonian Viscosity Behavior

(a) Shear Dependence of Intrinsic Viscosity

The intrinsic viscosities of the shear dependent fractions may be expected to increase as the shear rate of the viscosity measurement decreases (II-E-1-b). An estimate of the intrinsic viscosity at zero shear rate can be obtained from the following equation,

$$1/[\eta]_{D=0} = 1/[\eta] - 1300^{1/2} J_{c=0} \qquad (37)$$

where 1300 corresponds to the approximate shear rate at which the free fall intrinsic viscosities were measured. Equation (37) represents the equation of the c/η_{sp} versus $D^{1/2}$ line at zero concentration.

The difference between the intrinsic viscosities at free fall and zero shear rate was more than five or six per cent only in the case of the branched fractions with intrinsic viscosities above about four. This difference was considerably less for most of the fractions studied, and therefore the free fall intrinsic viscosities were used for the various correlations.

(b) Shear Dependence of the Various Fractions

The variation of the shear dependence, $J_{c=o}$, of the selected linear and branched fractions is of considerable interest. Figure 11 shows a plot of $J_{c=o}$ versus intrinsic viscosity. For a given value of intrinsic viscosity, the branched fractions appear to have a greater shear dependence than the linear fractions. Also, there is a difference between the two branched series of fractions, which presumably indicates that Series 3 is more highly branched. The shear dependence decreases with decreasing intrinsic viscosity until the solutions become essentially Newtonian at an intrinsic viscosity of about two.

$J_{c=o}$ is plotted versus M_w in Figure 12. Although there may be some second order differences, there appears to be a direct relationship between $J_{c=o}$ and M_w for all of the fractions regardless of structure. This indicates that the solutions of branched polymer should become non-Newtonian at a somewhat lower value of intrinsic viscosity.

(c) Shear Dependence and Huggins k'

It may be noted from Table V that the fractions having high degrees of shear dependence also have the high values of k'. This suggests a direct relationship between $J_{c=o}$ and k' which indeed is shown by Figure 13. Such a relationship strongly supports the idea that non-Newtonian viscosity behavior can cause k' to be abnormally high when measured under conditions of free fall (I-D-1-a).

Since k' is related to $J_{c=o}$, and $J_{c=o}$ is dependent upon M_w, an indirect relationship between k' and M_w should be expected. Figure 14 shows the relationship between k' and M_w. In general, k' increases with increasing M_w. Although all of the data seem to fall on a single line regardless of structure, there appears to be a consistant tendency for the branched fractions to have slightly higher values of k' at a given M_w. This difference is essentially within the experimental error of the k' measurement, however, and is certainly overshadowed by the variation of k' with M_w (or shear dependence).

The relationship between k' and shear dependence and consequently M_w is undoubtedly the major reason for reports of k' being a function of molecular weight (I-D-1-a). Also, since branching results in a considerable increase in molecular weight (this increase in molecular weight is often not fully appreciated if the samples are characterized solely by viscosity measurements) the high values of k' reported for branched samples must be due, at least in part, to the greater shear dependence of these samples.

(d) Usefulness of $J_{c=o}$ and k'

The ability of $J_{c=o}$ or k' to serve as a means of detecting the presence of branching appears to be largely a result of direct or indirect dependence on molecular weight. That is, they serve as an indirect measure of molecular weight. Therefore, when comparisons are made on an intrinsic viscosity basis, advantage is taken of the fundamental difference between linear and branched molecules, namely the difference in molecular weight at a given size.

The possibility of obtaining an indication of the molecular weight of branched polymer, as well as a measure of size, from viscosity measurements is quite important. Viscosity measurements are relatively simple to make, and the equipment investment is considerably less than that required for light-scattering. Of course, values of $J_{c=o}$ or k' are not sufficiently precise nor is the theory advanced enough to yield the quantitative measure of molecular weight that is obtainable from light-scattering. However, they are sufficiently sensitive to molecular weight to serve as qualitative indications of branching, provided the molecular weight is above some minimum value.

It should be noted that $J_{c=o}$ appears to be more sensitive to variations of molecular weight than is k', making it a more sensitive indication of branching. Unfortunately, $J_{c=o}$ is more tedious to determine.

(e) Relationship Between Shear Dependence and Branching

The results of the shear dependence study indicate that the solutions of the branched fractions are considerably more non-Newtonian than those of the linear fractions at a given intrinsic viscosity. Also, for a given molecular weight, the shear dependence appears to be approximately equal regardless of structure. It should be possible to account for these results, at least in part, in terms of the general shear behavior of linear polymers discussed earlier (II-E-1-a). That is, the shear dependence is a function of the coil size and inversely proportional to the segment density. Also, the shear dependence increases with increasing concentration, apparently due to increased chain entanglements.

If the above principles are applied to the case of linear and branched fractions which have a common value of intrinsic viscosity, the branched fraction might be expected to be less shear dependent. This is because the branched fraction has a larger molecular weight for the given volume and thus a greater segment density which should make the molecular coil more difficult to deform. However, the opposite shear behavior was observed. One possible explanation, suggested by Jones(57), maybe entanglements resulting from an increase in the number of chain ends introduced by branching. The variation of J as a function of concentration (Figure 5) does support this idea of entanglements, although the changes in J are not as marked as might be expected.

When linear and branched fractions are compared at a given molecular weight, the branched fraction would be expected to have a lower value of $J_{c=o}$ both because of its lower intrinsic viscosity and greater segment density. Something appears to be compensating for these factors and in such a manner as to make $J_{c=o}$ approximately equal for the two fractions. Again, the greater number of chain ends present in the branched material may be the compensating factor.

Without regard to specific mechanisms for the explanation of non-Newtonian behavior, it is important to emphasize the relationship between $J_{c=o}$ and M_w shown in Figure 12. While there may be some secondary variations due to structural differences, the molecular weight appears to be the predominate factor controlling the shear dependence. This strong influence of M_w on $J_{c=o}$ is undoubtedly the reason that a branched fraction has a higher value of $J_{c=o}$ when compared to a linear fraction of equal intrinsic viscosity.

It is interesting to note that polymer solution with a wide variety of viscosities and degrees of non-Newtonian behavior may be prepared by the proper combination of solute concentration, molecular weight, and degree of branching.

B. Degrees of Branching

The number of branches per molecule, n, was determined by four methods. Three of these methods involved the calculation of the branching ratio g (see I-D-2-b). The other utilized the hydrolysis information (II-G-3-b).

The radius of gyration-molecular weight data were treated according to Equation (2) to obtain values of g, and the corresponding degrees of branching were designed as n_s2.

The intrinsic viscosity-molecular weight data were treated by two methods to determine values of g. In the first case, g was calculated by Equation (6), and the resulting degree of branching was termed $n_{[\eta]}2/3$. The second method employed the Stockmayer and Fixman treatment according to Equation (7), (8), and (9) with the degree of branching denoted by n_h3.

The number of branches per molecule determined by the hydrolysis measurements, n_H, was calculated from Equation (34).

The four values of n are compared in Table XI for the more important fractions of Series 4. The values of n_h3 are considerably higher than the three other values of n, which are in fairly close agreement. At first, it might seem justifiable to disregard n_h3 and to assume that the other three methods give the better estimate of the extent of branching. However, there are arguments which support n_h3 as being the most realistic measure of branching.

The values of $n_{[\eta]}2/3$ should be expected to a lower than those of the n_h3 due to the reasoning behind the Stockmayer and Fixman treatment of the intrinsic viscosity-molecular weight data (see I-D-2-b).

Low results for n_S2 are obtained if the branched fractions have a greater polydispersity than the linear fractions (see I-D-2-b), even though the calculations of n_S2 is based on fairly sound principles. For example, if the molecular weight distribution of branched fraction 4-4-1 is assumed to be characterized by a Z of three and the linear fractions by a Z of ten, the value of n_S2 corrected for polydispersity becomes about 8.7 instead of 5.2 as reported. Such a difference in polydispersity between the linear and branched fractions is within reason and certainly causes a large error in n_S2. Of course, 8.7 is still not as high as the n_h3 of 13.7 reported for fraction 4-4-1. This may be due in part to an overestimation of the degree of branching by the Stockmayer and Fixman method or possibly to the experimental uncertainties involved in determining S_z2.

As stated earlier (II-G-3-b), n_H should be expected to underestimate the number of branches per molecule because of the non-hydrolyzable branching. The extent of this underestimation is difficult to access, although it is probably more serious than might be expected from the initial evaluation of the hydrolysis data.

For example, measurements on the hydrolysis product of fraction 4-4-2 yielded values of intrinsic viscosity and $(M_w)_H$ which indicate as many as three branches per molecule when the data is treated by the Stockmayer and Fixman method. As a conservative estimate, assume that the residual degree of branching after the hydrolysis treatment is one branch per molecule. This would mean that the initial branched molecules were composed of mono-branched units connected by hydrolyzable linkages. The value of 3.9 for n_H requires that approximately five of these units were connected to form the original branched molecules of fraction 4-4-2. If this is true, the actual degree of branching for fraction 4-4-2 should be about nine branches per molecule. This, of course, is close to the values of 9.7 reported for n_h3.

While quanitative support for n_h3 cannot actually be obtained from the hydrolysis data, the hydrolysis results do indicate that the n_h3 is a more reasonable indication of the branching than either n_s2 or $n_{[\eta]}2/3$.

The values of n_h3 were judged to be the best available measure of the degree of branching because of the above reasons plus the apparent success of the Stockmayer and Fixman method for predicting the degrees of branching of polyvinyl acetate samples and other polymers as discussed earlier (I-D-2-b). Consequently, n_h3 was used in all correlations requiring the degree of branching.

C. Melt Viscosity

1. Effect of Molecular Weight

Figure 15 shows the melt viscosities plotted versus weight-average molecular weight. The data for the linear fraction of Series 5 are represented by a single line which has a slope of 3.7. This slope is in good agreement with the average value of 3.4 reported for a variety of polymers and with the value of 3.5 predicted by Bueche (II-H-1). Since all of the linear fractions fall on this line, it appears that they are all above the critical chain length, below which the viscosity becomes dependent upon the first power of molecular weight.

2. Effect of Branching

It may be seen from Figure 15 that the branched fractions have higher melt viscosities than do the linear fractions of equal molecular weights. Also, the increase in melt viscosity appears to decrease as M_w decreases, until the lowest molecular weight fractions, 5-7-4 and 4-5-3, show essentially no difference.

In order to examine the relationship between the increase in melt viscosity and branching, values of Y [Equation (36)] were plotted against the number of branches per molecule, n_h3, and the approximate molecular weight of the branches as given by:

$$(M_w)_B = M_w/(1+n_h3)$$

Y expresses the relative increase in viscosity at a given molecular weight. This relative increase, which apparently results from branching, is based on the viscosity of the linear fraction.

Figure 16 shows that there is no correlation between Y and n_h3, but that there is some relation between Y and $(M_w)_B$. This suggests that the length of the branch may be of more importance than the actual number of branches in the effect of branching on melt viscosity.

As indicated earlier (I-C-2), several cases have been observed in which the presence of branching resulted in a decrease instead of an increase in melt viscosity at a given molecular weight. Various explanations have been proposed to account for such behavior in terms of the jump theory of melt flow, Equation (35).

Peticolas and Watkins(34) concluded that the reduction in melt viscosity of branched polyethylene was due to short chain branching. The presence of the short chain branches apparently resulted in a more loosely packed structure and consequently the free volumes was increased. Since the segmental jump frequency, j, is related to the free volume, an increase in the free volume would increase j, and a decrease in the melt viscosity would result.

However, Marshall(123) has shown that the free volume required to account for the reduction in viscosity is not found experimentally. Actually, there appears to be little difference between the densities of linear and branched polyethylenes after they have become molten. Also, the decrease in melt viscosity with increasing temperature was found to be insufficient, in terms of an increase in free volume, to account for the marked reduction of viscosity observed by Peticolas and Watkins.

Even though the difference in free volume is apparently absent, it would seem logical to expect the short chain branches to cause a reduction in the melt viscosity in the same sense as a plasticizer would. That is, to show behavior similar to that displayed by the pendant groups of polymethacrylates reported by Bueche(125) in which they served only to dilute the polymer and act as independent plasticizer molecules.

Moore(122) has taken the opposite stand in concluding that the decrease in melt viscosity for branched polyethylenes is due to a reduction of the statistical factor, F, resulting from the presence of long chain branching. Similar views have been expressed by Weil(35) and by Fox and Loskaek(120).

The reduction in the statistical factor by branching was explained in terms of the compactness of the branched molecule. Owing to this compactness, there is apparently less chance for interchain entanglements to occur, which means that there would be less coordination between the molecules in flow. That is, the "train" of molecules dragged along by a flowing molecule would be smaller, resulting in a decrease in the resistance to flow or a decrease in viscosity. A further decrease in F was predicted because a pull on one of the branches should affect the other segments of the molecule more strongly than the same pull on the end of a linear molecule. This would mean a greater coordination between the flow of the segments of a branched molecule.

The results mentioned above, plus similar findings by Charlesby(37) working with cross-linked silicone oils, seems to provide convincing evidence that branching may indeed decrease the melt viscosity. The results of the present study, of course, are in direct opposition to these findings. However, closer consideration of the branching involved may justify both conclusions.

Consider first the branching present in the fraction of Series 4 for which the melt viscosities were measured. The branchin is presumably of the random long chain type. The molecular weights of the branches appear to vary from 80,000 to 150,000 (Table X). These molecular weights represent chain lengths of 1,740 to 3,260 chain atoms, which should be well above the critical chain length for polyvinyl acetate. For example, Fox and Loshaek(120) have reported values of critical chain length varying from about 300 to 1000 chain atoms, depending upon the polymer. The value of 1000 corresponds to a molecular weight of 43,000 for polyvinyl acetate. A more realistic estimate of the critical chain length for polyvinyl acetate may be about 600 or a molecular weight of 26,000. In either case, the chain length of the branches is above the critical value.

On the other hand, the branched polymers which showed a depression of viscosity had branched lengths which appear to be below or near the critical value.

The branched polylactams (36,120), having eight branches radiating from an octafunctional central unit, had a critical chain length of 550 (324 for the linear polymer). The highest branch length studied was only 250. Similar polymer, but with a tetrafunctional central unit, did not show the typical decrease in melt viscosity reportedly because of insufficient branching. It is interesting to note, however, that both the critical chain length and the maximum branch length studied were about 390.

The critical chain length for the cross-linked silicones(37) was not available. However, the molecular weight of the initial material, before the limited cross-linking, was between 11,000 and 28,000 corresponding to a chain length of 300 to 750 chain atoms. If the length of the branches are assumed to be one half the length of the initial material, it seems reasonable to assume that the branch length was below the critical value.

The case of branched polyethylene is complicated by the presence of both short and long chain branching. The molecular weight of a long chain branch may be expected to be approximately 200,000 corresponding to a branch length of 1,250 chain atoms.(34) This is probably near the critical value because nonpolar polymers generally have higher critical chain lengths.(120) Consequently the long chain branching in polyethylene might be expected to affect the melt viscosity behavior in a manner similar to that noted for polyvinyl acetate. Although the influence of the two types of branching on melt viscosity are still somewhat uncertain, a decrease in melt viscosity resulting from the presence of short chain branching may overshadow any increase due to long chain branching.

The key difference between the branching present in the polyvinyl acetate of this study and that in the other polymers appears to be in the length of the branch. The importance of the branch length is also suggested by the relationship between Y and $(M_w)_B$ shown in Figure 16. Therefore, it is proposed that the observed increase in melt viscosity due to branching should be explained in terms of branch length.

Referring again to the jump theory of melt flow, Equation (35), an increase in the melt viscosity must result from a decrease in the segmental jump frequency or an increase in the statistical factor. Since no difference was noted between the densities of the linear and branched fractions, the segmental jump frequency was presumably independent of the branching. Therefore, the statistical factor must have been increased by the presence of branching.

As discussed earlier, branching has been predicted to decrease the statistical factor because of a lower number of entanglements and because of a greater coordination between the movements of the segments of a branched molecule. In the present study, however, the increase in the statistical factor required to explain the observed increase in viscosity may have been the result of the branch lengths being greater than the critical chain length. Apparently the branches were long enough to become involved in a significant number of interchain entanglements. Now due to the greater coordination between the various portions of a branched molecule, a stress applied to one portion of the molecule should be relayed in a more simultaneous manner to all of the entangled portions of the molecule. If the individual branches were sufficiently entangled, it would seem that this more coordinated action should result in a greater and more complicated resistance to flow than would be found in a more gradual "peeling off" of the entanglements of a linear molecular chain. That is, a pull on one branch should be met by a more coordinated resistance by the other entangled branches which should enhance the resistance to flow.

IV. SUMMARY AND CONCLUSIONS

Polyvinyl acetate fractions were prepared and characterized by viscosity, light-scattering, and hydrolysis measurements. The linear fractions were judged to be sufficiently linear to serve as reference material with which the branched fractions could be compared. The branched fractions were shown to contain the long chain type of branching.

The viscosity and light-scattering measurements yielded results which were consistent with the expected influence of branching on solution properties. For a given molecular weight, the intrinsic viscosity, radius of gyration, and the second virial coefficient were generally lower for branched fractions than for linear ones. Also, for values of intrinsic viscosity above about two and one half, the branched fractions had higher values of Huggins k'.

The study of solution viscosities at various shear rates indicated that the solutions of branched fractions were more non-Newtonian than might be expected. In general, for a given intrinsic viscosity, the branched fractions were more shear dependent than the linear ones. Also, at a given molecular weight, the shear dependence was approximately equal, regardless of structure. It was concluded that the relationship between shear dependence and molecular weight must be the controlling factor responsible for the greater shear dependence of the branched fractions when compared to linear fractions of corresponding intrinsic viscosities.

A direct relationship was found between shear dependence and Huggins k'. This could explain the reports of k' increasing with molecular weight, since the shear dependence increases with molecular weight. Also, this behavior must be responsible, at least in part, for the high values of k' observed for branched fractions when the comparison is based on intrinsic viscosity.

It was concluded that the measurement of shear dependence or k' provides a qualitative means of detecting branching under certain conditions. These methods appear to be based on the fundamental difference between linear and branched molecules, namely a difference in molecular weight for a given size.

After a comparison of various methods for estimating the extent of branching, the Stockmayer and Fixman treatment of the intrinsic viscosity-molecular weight data was chosen as providing the most realistic measure of the number of branches per molecule. It was shown that the usefulness of the radius of gyration for detecting branching was seriously hampered by both differences in polydispersity and the excluded volume effect. Also, the presence of non-hydrolyzable branches caused the hydrolysis data to underestimate the degree of branching.

The relationship between melt viscosity and molecular weight for the linear fractions was in good agreement with the behavior reported for several other polymers.

For a given molecular weight, the presence of branching resulted in an increase in melt viscosity. This is contrary to the influence of branching observed for several other branched polymers. A relationship between the relative increase in melt viscosity and the branch length was noted. Also, the branched polyvinyl acetate fractions had branch lengths which were above a certain critical chain length, while the other branched polymers generally had branch lengths which were below or near the critical chain length. It was concluded that the opposite effects of branching on melt viscosity might depend on whether the branch length was above or below the critical value. When the branch length is sufficiently above the critical value, the branches apparently become adequately entangled to overcome any depressing effect of branching on melt viscosity and an actual enhancement of the viscosity results.

REFERENCES

1. Fox, T. G., and Gratch, S., Ann. N. Y. Acad. Sci., 57, 367 (1953).

2. Mark, H., ibid., 57, 445 (1953).

3. Flory, P. J., ibid., 57, 327 (1953).

4. Melville, H. W., The Plastics Institute Transactions and Journal, 23, 146 (1955).

5. Howard, R. O., Ph. D. Thesis, Massachusetts Institute of Technology, Cambridge, Massachusetts, 1952.

6. Wheeler, O. L., Ernst, S. L., and Crozier, R. N., J. Polymer Sci., 8, 409 (1952).

7. Wheeler, O. L., Lavin, E., and Crozier, R. N., ibid., 9, 157 (1952).

8. Wheeler, O. L., Ann. N. Y. Acad. Sci., 57, 360 (1953).

9. Bosworth, P., Masson, C. R., Melville, H. W., and Peaker, F. W., J. Polymer Sci., 9, 565 (1952).

10. Bevington, J. C., Guzman, G. M., and Melville, H. W., Nature, 170, 1026 (1952); Proc. Roy. Soc. (London), A221, 437 (1954).

11. Bengough, W. I., and Norrish, R. G. W., Nature, 163, 325 (1949); Proc. Roy. Soc. (London), A200, 301 (1950).

12. Hayes, R. A., J. Polymer Sci., 11, 531 (1953).

13. Cotman, J. D., Ann. N. Y. Acad. Sci., 57, 417 (1953).

14. Schildknecht, C. E., "Vinyl and Related Polymers," Wiley, New York, 1952, p. 244-246.

15. Matheson, M. S., Auer, E. E., Bevilacqua, E. B., and Hart, E. J., J. Am. Chem. Soc., 73, 5395 (1951).

16. Fox, J. J., and Martin, A. E., Proc. Roy. Soc. (London), A175, 208 (1940).

17. Thompson, H. W., and Torkington, P., ibid., A184, 3 (1945).

18. Bryant, W. M. D., J. Polymer Sci., 2, 547 (1947).

19. Cross, L. H., Richards, R. B., and Willis, H. A., Disc. Faraday Soc., 9, 235 (1950).

REFERENCES (CONT'D)

20. Rugg, F. M., Smith, J. J., and Wartman, L. H., Ann. N. Y. Acad. Sci., 57, 398 (1953).

21. Roedel, M. J., J. Am. Chem. Soc., 75, 6110 (1953).

22. Bryant, W. M. D., and Voter, R. C., ibid., 75, 6113 (1953).

23. Zimm, B. H. and Stockmayer, W. H., J. Chem. Phys. 17, 1301 (1949).

24. Thurmond, C. D., and Zimm, B. H., J. Polymer Sci., 8, 477 (1952).

25. Zimm, B. H., Ann. N. Y. Acad. Sci., 57, 332 (1953).

26. Stockmayer, W. H., and Fixman, M., ibid., 57, 334 (1953).

27. Wales, M., Marshall, P. A., Rothman, S., and Weissberg, S. G., ibid., 57, 353 (1953).

28. Baker, W. O., Fuller, C. S., and Heiss, J. H., J. Am. Chem. Soc., 63, 2142 (1941).

29. Alfrey, T., Bartovics, A., and Mark, H., ibid., 65, 2319 (1943).

30. Flory, P. J., ibid., 69, 2893 (1947).

31. Schmidt, A. X., and Marlies, C. A., "Principles of High-Polymer Theory and Practice," McGraw-Hill Book Company, Inc., New York, 1948.

32. Billmeyer, F. W., "Textbook of Polymer Chemistry," Interscience Publishers, Inc., New York, 1957.

33. Sperati, C. A., Franta, W. A., and Starkweather, H. W., Jr., J. Am. Chem. Soc., 75, 6127 (1953).

34. Peticolas, L., and Watkins, J. M., ibid., 79, 5083 (1957).

35. Weil, L. L., Ph. D. Thesis, Columbia University, New York, 1945.

36. Schaefgen, J. R., and Flory, P. J., J. Am. Chem. Soc., 70, 2709 (1948).

37. Charlesby, A., J. Polymer Sci., 17, 379 (1955).

38. Merz, E. H., Nielsen, L. E., Buchdahl, R., Ind. and Engr. Chem., 43, 1396 (1951).

39. Simha, R., J. Research National Bur. Standards, 42, 409 (1949); J. Colloid Sci., 5, 386 (1950).

REFERENCES (CONT'D)

40. Hobbs, L. M., Kothari, S. C., Long, V. C., and Sutaria, G. C., J. Polymer Sci., 22, 123 (1956).

41. Manson, J. A., and Cragg, L. H., Can. J. Chem., 30, 482 (1952).

42. Cragg, L. H., and Brown, A. T., ibid., 30, 1033 (1952).

43. Cragg, L. H., and Fern, R., ibid., 31, 710 (1953); J. Polymer Sci., 10, 185 (1953).

44. Cragg, L. H., and Bigelow, C. C., J. Polymer Sci., 16, 177 (1955).

45. Manson, J. A., Ph. D. Thesis, McMaster University, Hamilton, Ontario, 1956.

46. Morrison, J. A., Homes, J. M., and McIntosh, R., Can. J. Research, B24, 179 (1946).

47. Nagai, E., and Sagane, N., Chem. High Polymers (Japan), 11, 218 (1954)

48. Mencik, Z., and Lacikova, J., Makromol. Chem., 14, 118 (1954).

49. Cernia, E., and Ciampa, G., ibid., 16, 177 (1955).

50. Naidus, H., and Mark, H., India Rubber World, 113, 229 (1945).

51. Harris, I., J. Polymer Sci., 8, 353 (1952).

52. Billmeyer, F. W., J. Am. Chem. Soc., 75, 6118 (1953).

53. Manson, J. A., M. Sc. Thesis, McMaster University, Hamilton, Ontario, 1951.

54. Todd, A., Nature, 174, 613 (1954).

55. Senti, F. R., et al., J. Polymer Sci., 17, 527 (1955).

56. Conrad, C., Tripp, V., and Mares, T., J. Phys. and Colloid Chem., 55, 1474 (1951).

57. Jones, M. H., Can. J. Chem., 34, 1027 (1956).

58. Golub, M. A., J. Phys. Chem., 61, 374 (1957).

59. Golub, M. A., Rubber Chem. and Tech., 30, 823 (1957).

REFERENCES (CONT'D)

60. Kapur, S. L., and Gundiah, S., J. Polymer Sci., 26, 89 (1957).

61. Stacey, K. A., "Light-Scattering in Physical Chemistry," Academic Press, Inc., New York, 1956.

62. Zimm, B. H., J. Chem Phys., 14, 164 (1946).

63. Flory, P. J., and Krigbaum, W. R., ibid., 18, 1086 (1950).

64. Kreussling, F., and Ullman, R., J. Polymer Sci., 12, 123 (1954).

65. Kuratic, M., Tamura, M., and Watari, T., J. Chem. Phys., 23, 991 (1955).

66. Oth, J., and Desreux, V., Bull. Soc. Chim. Belg., 63, 285 (1954).

67. Shultz, A. R., J. Am. Chem. Soc., 76, 3422 (1954).

68. Schulz, G. V., and Marzolph, H., Z. fur Elektrochem., 58, 213 (1954).

69. Doty, P., Brownstein, M., and Schlener, W., J. Phys. and Colloid Chem., 53, 213 (1949).

70. Benoit, H., J. Polymer Sci., 11, 509 (1953).

71. Benoit, H., Comp. rend., 240, 533 (1955).

72. Roland, J. R., and Richards, L. M., J. Polymer Sci., 9, 61 (1952).

73. Coover, H. W., and Dickey, J. B., U. S. Patent 2,649,434 (1953).

74. Meares, P., Trans. Faraday Soc., 53, 31 (1957).

75. Newman, S., Loeb, L., and Conrad, C. M., J. Polymer Sci., 10, 463 (1953).

76. Batzer, H., Makromol Chem., 12, 145 (1954).

77. Kapadia, F. H., ibid., 13, 194 (1954).

78. Patat, F., and Elias, H. G., ibid., 14, 40 (1954).

79. Flory, P. J., "Principles of Polymer Chemistry," Cornell University Press, Ithaca, New York, 1953.

REFERENCES (CONT'D)

80. Saburo Imoto, Junji Ukida, and Tsugio Kominami, Kobunshi Kagaku, 14, 101 (1957), through C. A., 52, 1669h (1958).

81. Arond, L. H., Frank. H. P., J. Phys. Chem., 58, 953 (1954).

82. Frank, H. P., and Mark, H., Monatshefte fur Chemie, 85, 21 (1954).

83. Flory, P. J., J. Chem. Phys., 17, 303 (1949).

84. Flory, P. J., and Fox, T. G., J. Am. Chem. Soc., 73, 1904 (1951).

85. Muus, L. T., and Billmeyer, F. W., Jr., ibid., 79, 5079 (1957).

86. Beasley, J. K., ibid., 75, 6123 (1953).

87. Frith, E. M., and Tuckett, R. F., "Linear Polymers," Longmans, Green, and Co., New York, 1951.

88. Burnett, G. M., George, M. H., and Melville, H. W., J. Polymer Sci., 16, 31 (1955).

89. Meyer, F. R., and Ronge, G., Angewandte Chemie, 52, 637 (1939).

90. Wagner, R. H., J. Polymer Sci., 2, 21 (1947).

91. Blease, R. A., and Tuckett, R. F., Trans. Faraday Soc., 37, 571 (1941).

92. Staudinger, H., and Heuer, W., Ber., 63, 222 (1930).

93. Staudinger, H., and Nodzu, R., ibid, 63, 721 (1930).

94. Kraemer, E. O., Ind. Eng. Chem., 30, 1200 (1938).

95. Huggins, M. L., J. Am. Chem. Soc., 64, 227 (1942).

96. Craig., A. W., and Henderson, D., J. Polymer Sci., 19, 215 (1956).

97. Barr, G., "A Monograph of Viscosity," Oxford University Press, London, 1931.

98. Timmermans, J., "Physico-Chemical Constants of Pure Organic Compounds," Elsivier Publishing Company, Inc., New York, 1950.

REFERENCES (CONT'D)

99. Eisenberg, H., and Frei, E., J. Polymer Sci., 14, 417 (1954).

100. Sharman, L. J., Sones, R. H., and Cragg, L. H., J. Appl. Phys., 24, 703 (1953).

101. DeWind, G., and Hermans, J., Recueil des Travaux Chimiques des Pay-Bas, 70, 615 (1951).

102. Fox, T., Jr., Fox, J., and Flory, P., J. Am. Chem. Soc., 73, 1901 (1951).

103. Cragg, L. H., Sones, R. H., and Dumitru, T. E., J. Polymer Sci., 13, 167 (1954).

104. Krigbaum, W. R., and Flory, P. J., ibid., 11, 37 (1953).

105. Bueche, F., J. Chem. Phys., 22, 1570 (1954).

106. Patat, F., and Hartman, J., Makromol. Chem., 18-19, 422 (1956).

107. Debye, P., J. Appl. Phys., 15, 338 (1944); J. Phys. and Colloid Chem., 51, 18 (1947).

108. Zimm, B. H., J. Phys. and Colloid Chem., 52, 260 (1948); J. Chem. Phys., 16, 1093, 1099 (1948).

109. Brice, B. A., Halwer, M., and Speiser, R., J. Opt. Soc. Am., 40, 768 (1950).

110. "Light-Scattering Photometer Operation Manual OM-1000," Phoenix Precision Instrument Co., Philadelphia.

111. Mead, D. J., and Fuoss, R. M., J. Am. Chem. Soc., 64, 277 (1942).

112. Notley, N. T., and Debye, P., J. Polymer Sci., 17, 99 (1955).

113. Sheffer, H., and Hyde, J. C., Can. J. Chem., 30, 817 (1952).

114. Hermans, J. J., and Levinson, S., J. Opt. Soc. Am., 41, 460 (1951).

115. Doty, P. M., and Edsall, J. T., Advances in Protein Chemistry, 6, 35 (1951).

116. Zimm, B. H., Stein, R. S., and Doty, P., Polymer Bull., 1, 90 (1954).

REFERENCES (CONT'D)

117. Flory, P. J., Chem. Revs., 39, 137 (1946).

118. Benoit, H., Holtzer, A. M., and Doty, P., J. Phys.Chem., 58, 635 (1954).

119. Fox, T. G., Gratch, S., and Loshaek, S., "Rheology-Theory and Applications," F. R. Eirich, Editor, Academic Press, Inc., New York, 1956.

120. Fox, T. G., and Loshaek, S., J. Appl. Phys., 26, 1080 (1955).

121. Bueche, F., J. Chem. Phys., 20, 1959 (1952); ibid., 25, 599 (1956).

122. Moore, L. D., Jr., paper presented at the 132nd Meeting of the American Chemical Society, New York, N. Y., 1957.

123. Marshall, D. I., paper presented at the 130th Meeting of the American Chemical Society, Atlantic City, N. J., 1956.

124. Dienes, G. J., and Klemm, H. F., J. Appl. Phys., 17, 458 (1946).

125. Bueche, F., J. Appl. Phys., 26, 738 (1955).

APPENDIX A

TABLES

TABLE I

POLYMERIZATION DATA FOR SAMPLES 1 AND 2 AND THE THREE COMPONENTS OF SAMPLE 5

Sample Number	$[\eta]$ (dl/g)	Per Cent Conversion	Yield (g)	Initiator Concentration (moles/l x 10^4)
1	1.50	13.6	-	73.9
2	3.11	10.7	-	2.33
3a	2.91	4.0	38.3	2.38
3b	3.26	6.9	74.3	2.15
3c	3.33	9.5	97.3	2.08

TABLE II

TAIL FRACTIONS OF SAMPLE 5

Fraction	Yield (g)
5-1-3	2.3
5-2-4	4.8
5-3-4	3.3
5-4-4	6.3
5-5-4	6.3
5-6-4	7.9
5-7-5	9.2

TABLE III

VISCOSITY DATA FOR THE FRACTIONS OF SERIES 4 IN BENZENE

Fraction	$[\eta]$ (dl/g)	Slope, b	k'	$-k''$	$k'-k''$	Yield (g)
4	3.08_0	3.53	0.37_2	0.12_9	0.501	160
4-1-1-1	7.15_0	21.78	0.42_6	0.074	0.500	2.5
4-2-1	5.84_5	13.20	0.38_5	0.11_6	0.501	3.0
4-2-2	5.68_0	11.71	0.36_3	0.13_7	0.500	6.0
4-1-1-2	4.82_0	8.99	0.38_7	0.11_5	0.502	2.5
4-3-1	4.77_0	8.67	0.38_1	0.12_1	0.502	4.3
4-3-2	3.79_0	5.10	0.35_5	0.14_6	0.501	5.0
4-2-3	3.50_0	4.73	0.38_6	0.11_6	0.502	6.0
4-4-1	2.97_0	3.25	0.36_9	0.13_0	0.499	22.5
4-4-2	2.26_0	1.76	0.34_5	0.15_3	0.498	9.0
4-3-3	2.23_5	1.85	0.37_0	0.13_2	0.502	3.0
4-5-1	1.96_2	1.35	0.35_1	0.14_8	0.499	3.5
4-5-2	1.48_5	0.800	0.36_3	0.13_8	0.501	9.0
4-4-3	1.38_5	0.673	0.35_1	0.14_9	0.500	4.8
4-5-3	1.10_4	0.419	0.34_4	0.15_6	0.500	10.0
4-5-4	0.71_6	0.180	0.35_1	0.15_0	0.501	5.2
4-6	0.44_5	0.055	0.27_8	0.22_0	0.498	9.3

TABLE IV

VISCOSITY DATA FOR THE FRACTIONS OF SERIES 5 IN BENZENE

Fraction	$[\eta]$ (dl/g)	Slope, b	k'	-k"	k' -k"	Yield (g)
5	3.41_0	4.02	0.34_6	0.15_3	0.499	202
5-2-2	5.70_5	11.39	0.35_0	0.15_0	0.500	3.7
5-2-1	5.60_3	10.86	0.34_6	0.15_4	0.500	6.6
5-1-1	5.55_0	10.50	0.34_1	0.15_9	0.500	4.5
5-1-2	5.54_0	10.93	0.35_6	0.14_6	0.502	1.9
5-3-1	5.25_0	9.56	0.34_7	0.15_3	0.500	4.2
5-3-2	4.97_0	8.69	0.35_2	0.14_8	0.500	5.8
5-4-1	4.57_0	7.20	0.34_5	0.15_4	0.499	9.0
5-2-3	4.37_2	6.63	0.34_7	0.15_3	0.500	11.2
5-4-2	4.29_0	6.46	0.35_1	0.14_7	0.498	10.2
5-3-3	4.06_0	5.69	0.34_5	0.15_4	0.499	11.6
5-5-1	3.95_0	5.38	0.34_5	0.15_4	0.499	6.6
5-4-3	3.76_0	4.98	0.35_2	0.14_9	0.501	4.5
5-5-2	3.71_0	4.80	0.34_9	0.15_1	0.500	10.8
5-5-3	3.32_0	3.82	0.34_7	0.15_2	0.499	7.7
5-6-1	2.91_5	2.88	0.33_9	0.16_0	0.499	10.2
5-6-2	2.81_3	2.77	0.35_0	0.14_9	0.499	9.4
5-6-3	2.50_0	2.13	0.34_0	0.16_0	0.500	7.4
5-7-1	1.96_1	1.30	0.33_9	0.16_0	0.499	5.4
5-7-2	1.77_0	1.01	0.32_2	0.17_6	0.498	6.3
5-7-3	1.55_7	0.810	0.33_4	0.16_5	0.499	4.0
5-7-4	1.37_2	0.629	0.33_4	0.16_5	0.499	3.5

TABLE V

SHEAR DEPENDENCE DATA

Fraction	[η] (dl/g)	Slope, b	k'	$M_w \times 10^{-6}$	$J \times 10^4$	Concentration (g/dl)
4-1-1-1	7.15	21.78	0.42_6	-	9.80	0
					10.1	0.0248
					10.0	0.0372
					10.4	0.0740
3-3	5.32	11.94	0.42_2	-	8.35	0
					8.70	0.0320
					9.00	0.0640
					9.22	0.0853
					9.47	0.1024
					9.72	0.1280
4-1-1-2	4.82	8.99	0.38_7	12.6	5.64	0
					6.16	0.0561
					6.70	0.1121
3-4	4.47	7.96	0.39_8	10.8	7.10	0
					7.90	0.0362
					7.76	0.0482
					8.12	0.0724
					8.28	0.0965
					8.84	0.1158
					9.18	0.1447
3-5	3.89	5.82	0.38_5	-	6.20	0
					6.75	0.0624
					6.92	0.0936
					7.40	0.1871
4-3-2	3.79	5.10	0.35_5	3.76	4.55	0
					5.10	0.0510
					5.30	0.0765
					6.10	0.1530
4-4-2	2.26	1.76	0.34_5	1.64	0.9	0
					0.96	0.2451
2-1-1	4.95	8.60	0.35_2	2.85	3.13	0
					3.22	0.0583
					3.30	0.1165
2-4	3.90	5.00	0.33_0	2.00	2.80	0
					2.80	0.0602
					2.93	0.0904
					2.97	0.1807
1-2	2.09	1.43	0.32_7	0.795	0.3	0
					0.4	0.1963
					0.5	0.2945

TABLE VI

LIGHT-SCATTERING DATA FOR FRACTIONS OF SERIES 4 AND 5 IN METHYL ETHYL KETONE

Fraction	$[\eta]$ (dl/g)	$M_w \times 10^{-6}$	$S_z^2 \times 10^4$ $(\mathring{A})^2$	$A_2 \times 10^4$ $(cm^3 g^{-2} mole)$	M_w/S_z^2
5-2-1	5.60	3.58	93.4	2.74	3.84
5-3-2	4.97	2.66	68.4	2.30	3.89
5-4-2	4.29	2.28	61.5	2.64	3.71
5-5-2	3.71	1.84	44.0	2.62	4.18
5-6-2	2.81	1.14	27.2	3.42	4.19
5-6-3	2.50	0.991	21.5	3.38	4.61
5-7-2	1.77	0.654	14.6	3.26	4.48
5-7-4	1.37	0.438	10.9	3.39	4.02
4-1-1-2	4.82	12.6	229	0.66	5.50
4-2-3	3.50	6.43	120	1.37	5.36
4-3-2	3.79	3.76	68.8	1.13	5.46
4-4-1	2.97	2.86	50.8	1.33	5.63
4-4-2	2.26	1.64	34.5	1.78	4.76
4-5-1	1.96	1.43	29.9	1.85	4.78
4-4-3	1.39	0.731	14.5	2.39	5.04
4-5-2	1.49	0.730	16.6	2.99	4.40
4-5-3	1.10	0.432	9.1	2.72	4.75

TABLE VII

POLYDISPERSITY DATA FOR FRACTIONS OF SERIES 5

Fraction	$M_w \times 10^{-6}$	$M_n \times 10^{-6}$	$S_z^2 \times 10^{-4}$ (Å)^2	$S_n^2 \times 10^{-4}$ (Å)^2	Z	$S_w^2 \times 10^{-4}$ (Å)^2	M_w/S_w^2
5-2-1	3.58	3.33	93.4	81.2	13	87.2	4.10
5-3-2	2.66	2.43	68.4	57.1	10	62.6	4.25
5-4-2	2.28	2.05	61.5	50.8	9	55.9	4.08
5-5-2	1.84	1.62	44.0	35.4	7	39.1	4.70
5-6-2	1.14	1.07	27.2	23.7	14	25.5	4.47
5-6-3	0.991	0.964	21.5	20.2	32	20.9	4.75
5-7-2	0.654	0.585	14.6	12.2	9	13.3	4.91
5-7-4	0.438	0.380	10.9	8.4	6	9.5	4.61

TABLE VIII

HYDROLYSIS DATA

Fraction	$[\eta]$	$[\eta]_H$	$M_w \times 10^{-6}$	$(M_v)_H \times 10^{-6}$	n_H
4	3.08	1.15	-	0.328	-
4-1-1-1	7.15	1.34	-	0.412[a]	-
4-2-1	5.85	1.39	-	0.435	-
4-4-2	2.26	1.17	1.64	0.336[b]	3.87
4-5-1	1.96	1.03	1.43	0.278	4.14
4-4-3	1.39	0.89	0.731	0.224	2.26
4-5-2	1.49	0.95	0.730	0.247	1.96
4-5-3	1.10	0.85	0.432	0.210	1.06
5	3.41	3.38	-	-	-
5-3-2	4.97	5.03	-	-	-
5-6-2	2.81	2.82	-	-	-

[a] $(M_w)_H \times 10^{-6} = 0.674$.

[b] $(M_w)_H \times 10^{-6} = 0.408$.

TABLE IX

MELT VISCOSITY DATA FOR FRACTIONS OF SERIES 4 AND 5

Fraction	$M_w \times 10^{-6}$	η (Poise)
5-3-2[b]	2.87[a]	1.55×10^9
5-3-2	2.87	1.57×10^9
5-3-3	2.13	4.41×10^8
5-5-3	1.57	1.30×10^8
5-6-2	1.23	5.42×10^7
5-6-3	1.04	3.13×10^7
5-6-3	1.04	3.15×10^7
5-7-2	0.622	4.42×10^6
5-7-4	0.426	1.29×10^6
5-7-4	0.426	1.38×10^6
Mixture 5-3-2 + 5-6-3	2.07	3.33×10^8
4-4-2[c]	1.64	8.92×10^8
4-4-2	1.64	1.03×10^9
4-5-1	1.43	3.10×10^8
4-5-1	1.43	3.13×10^8
4-5-2	0.730	3.83×10^7
4-5-2	0.730	3.53×10^7
4-4-3	0.731	1.52×10^7
4-5-3	0.432	1.27×10^6
4-5-3	0.432	1.17×10^6
Mixture 4-4-2 + 4-4-3	1.25	1.97×10^8

[a] Molecular weights for the fractions of series 5 were calculated from Equation (33).

[b] Intrinsic viscosity before, 4.97_0, and after, 4.91_2, two melt viscosity runs.

[c] Intrinsic viscosity before, 2.26_0, and after, 2.26_3, two melt viscosity runs.

TABLE X

EFFECT OF BRANCHING ON MELT VISCOSITY

Fraction	Y	n_h3	$(M_w)_B \times 10^{-5}$
4-4-2	4.65	9.7	1.53
4-5-1	2.00	11.6	1.13
4-4-3	0.854	7.8	0.83
4-5-2	3.49	5.8	1.07
4-5-3	0.061	4.2	0.83

TABLE XI

NUMBER OF BRANCHES PER MOLECULE FOR FRACTIONS OF SERIES 4

Fraction	$M_w \times 10^{-6}$	n_S2	$n_{[\eta]}2/3$	n_h3	n_H
4-1-1-2	12.6	~ 5.0	~ 15.5	~48	-
4-2-3	6.43	~ 4.4	~ 11.7	~37	-
4-3-2	3.76	4.6	3.8	11.5	-
4-4-1	2.86	5.2	4.4	13.7	-
4-4-2	1.64	2.2	3.3	9.7	3.9
4-5-1	1.43	2.2	3.9	11.6	4.1
4-4-3	0.731	2.2	2.9	7.8	2.3
4-5-2	0.730	~ 0.5	2.2	5.8	2.0
4-5-3	0.432	~ 0.8	1.6	4.2	1.1

APPENDIX B

FIGURES

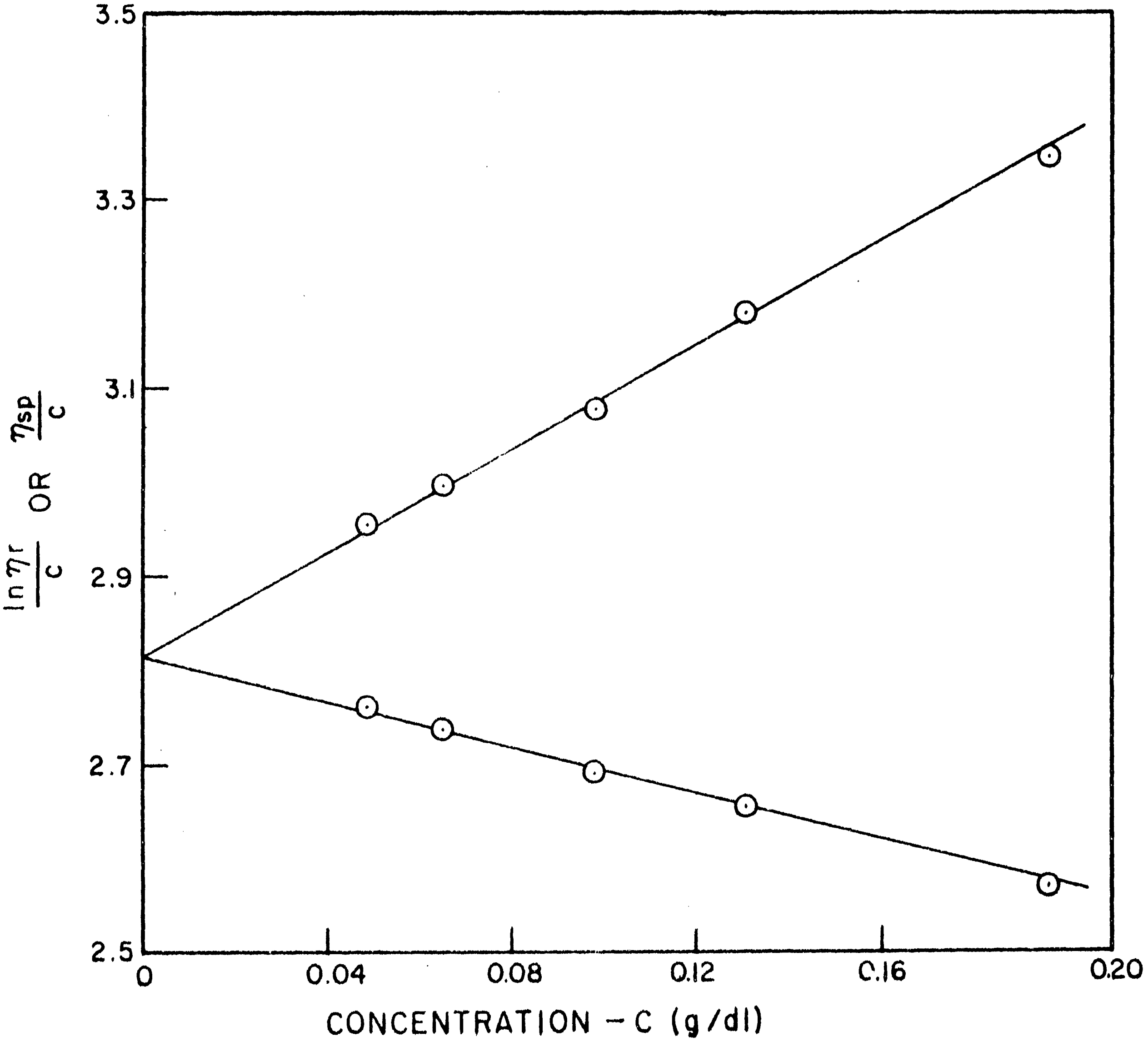


Figure 1. Viscosity Double Plot for Fraction 5-6-2.

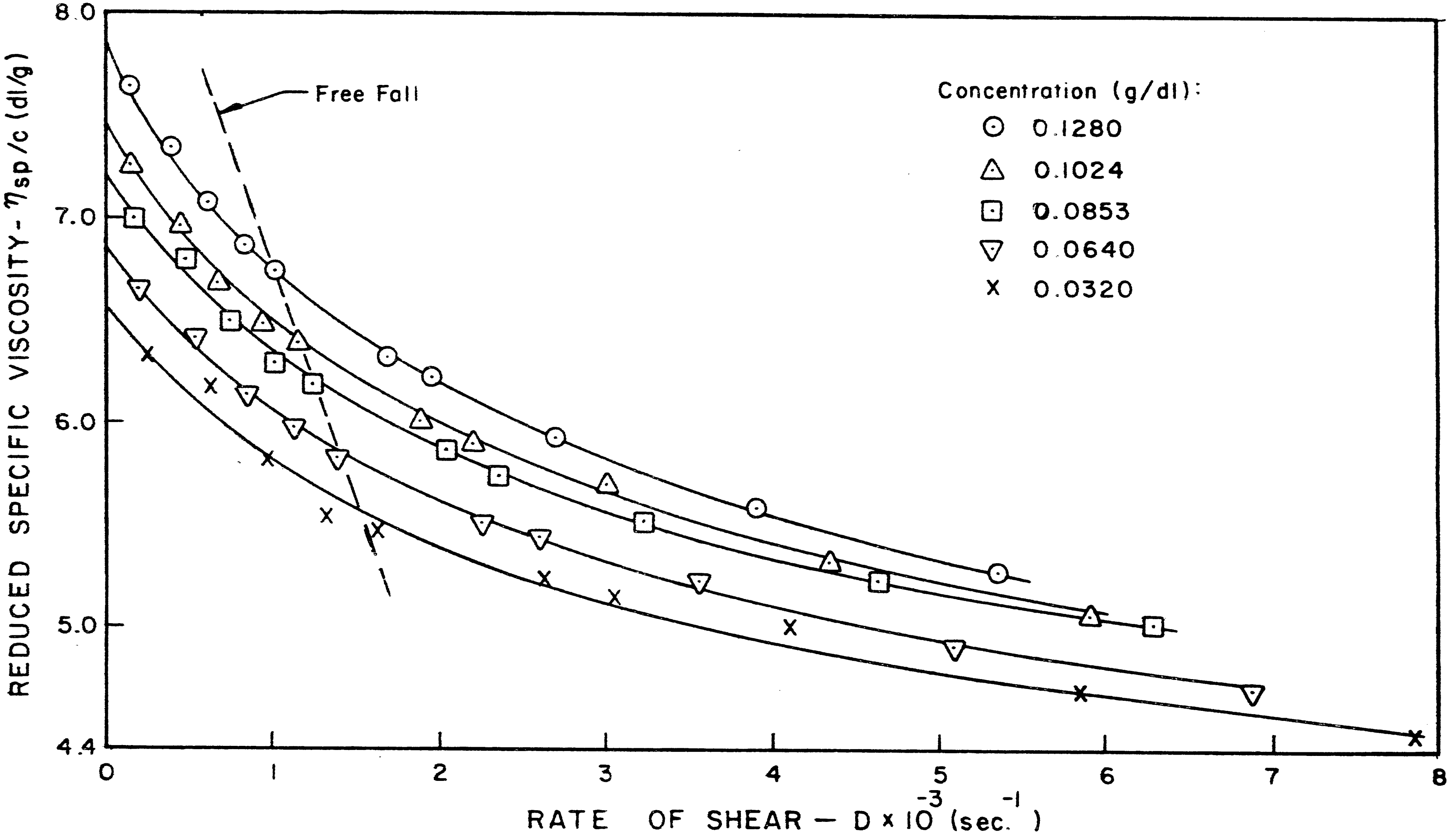


Figure 2. Reduced Specific Viscosity versus Rate of Shear for Fraction 3-3.

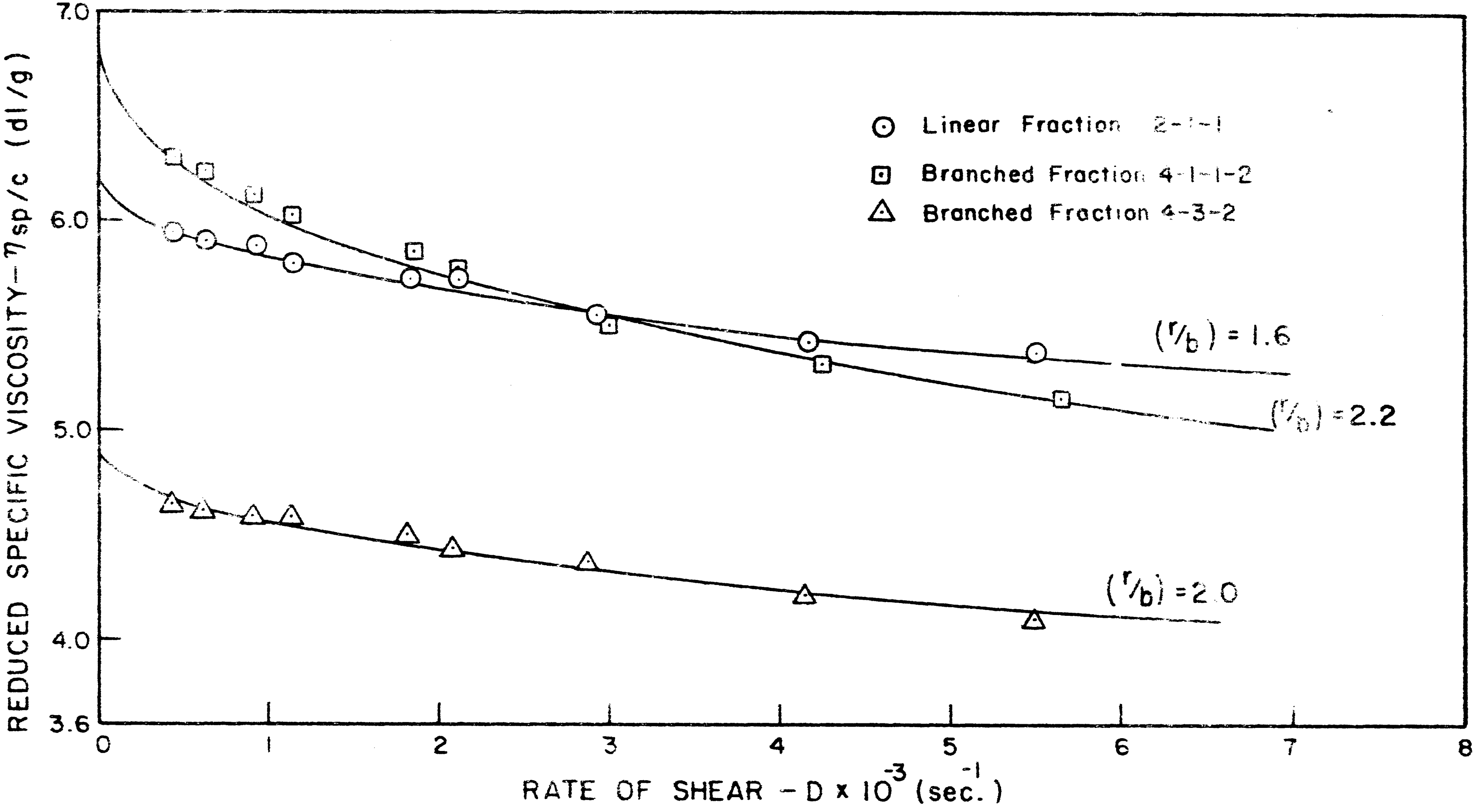


Figure 3. Bueche Equation for Three Fractions.

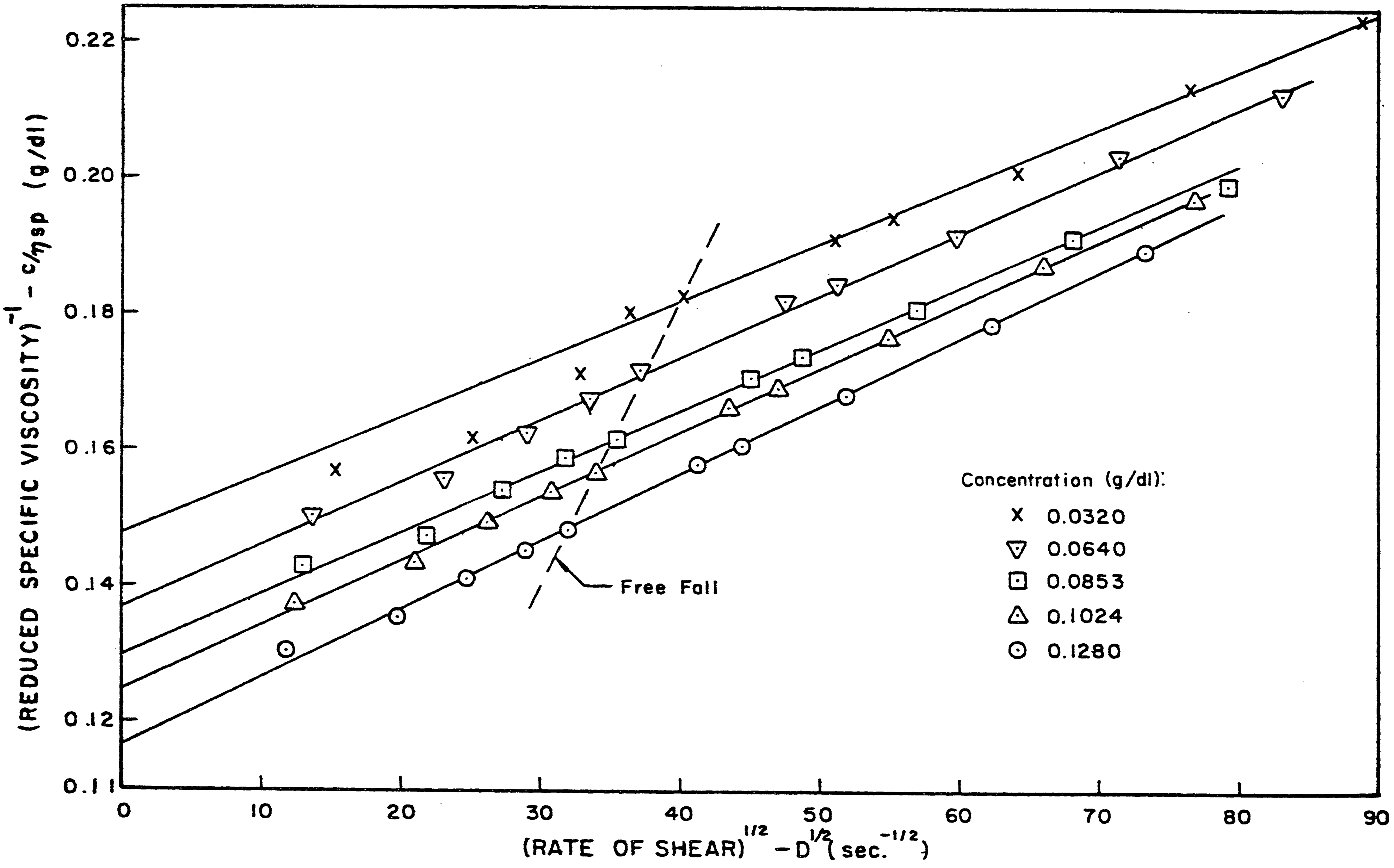


Figure 4. Reciprocal Reduced Specific Viscosity versus Square Root of Shear Rate for Fraction 3-3.

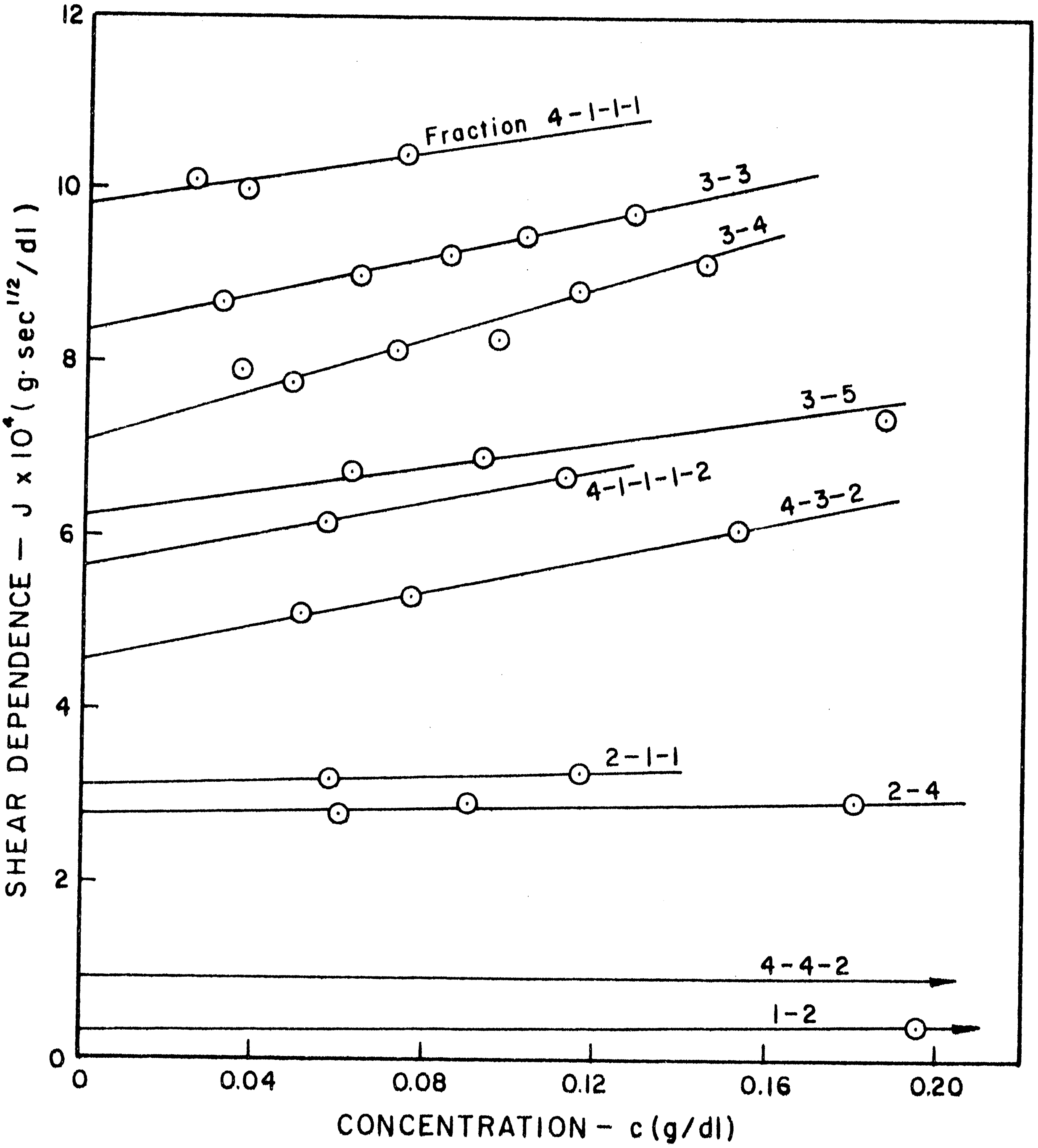


Figure 5. Shear Dependence versus Concentration.

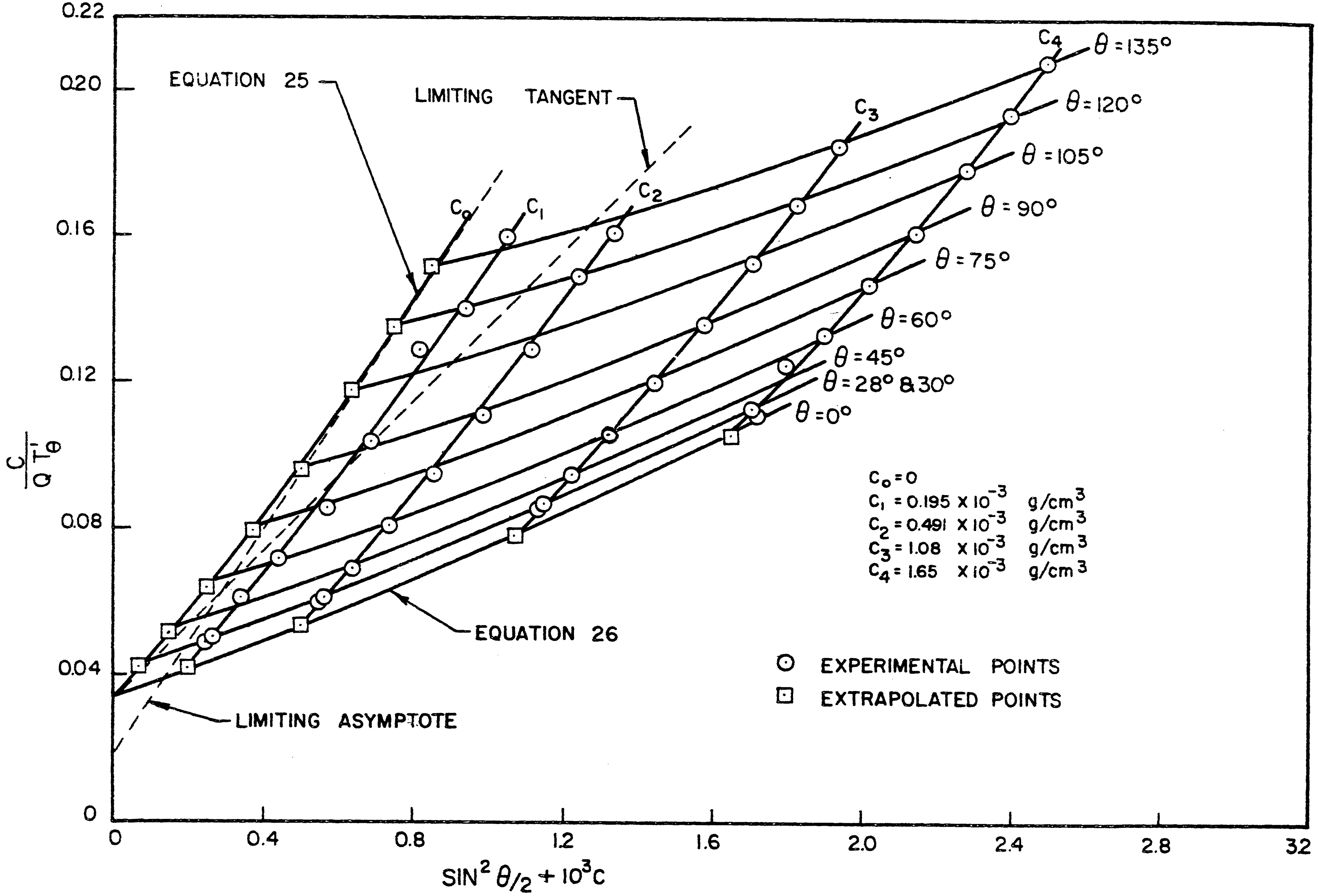


Figure 6. Zimm Plot for Fraction 5-4-2.

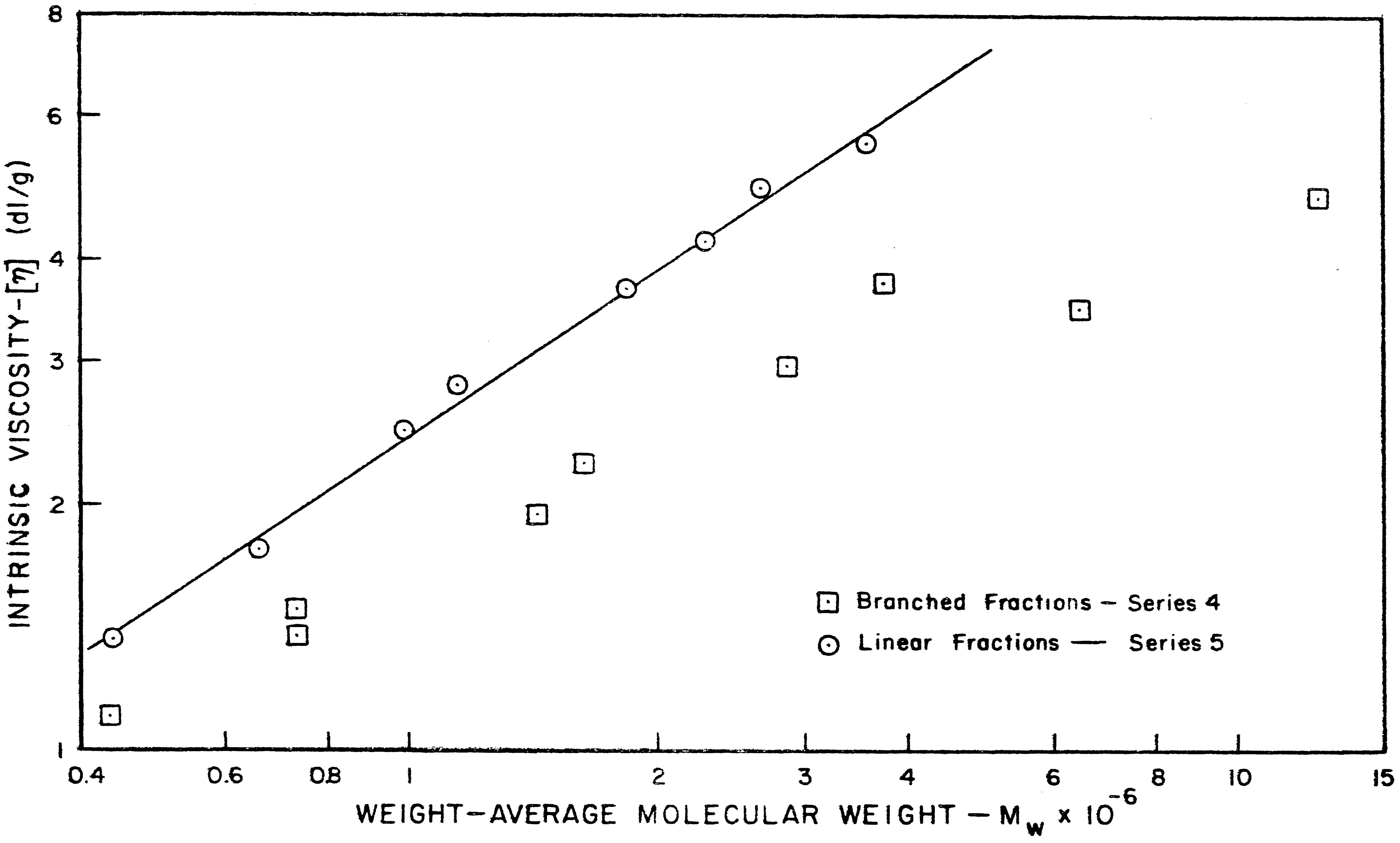


Figure 7. Intrinsic Viscosity versus Weight-Average Molecular Weight.

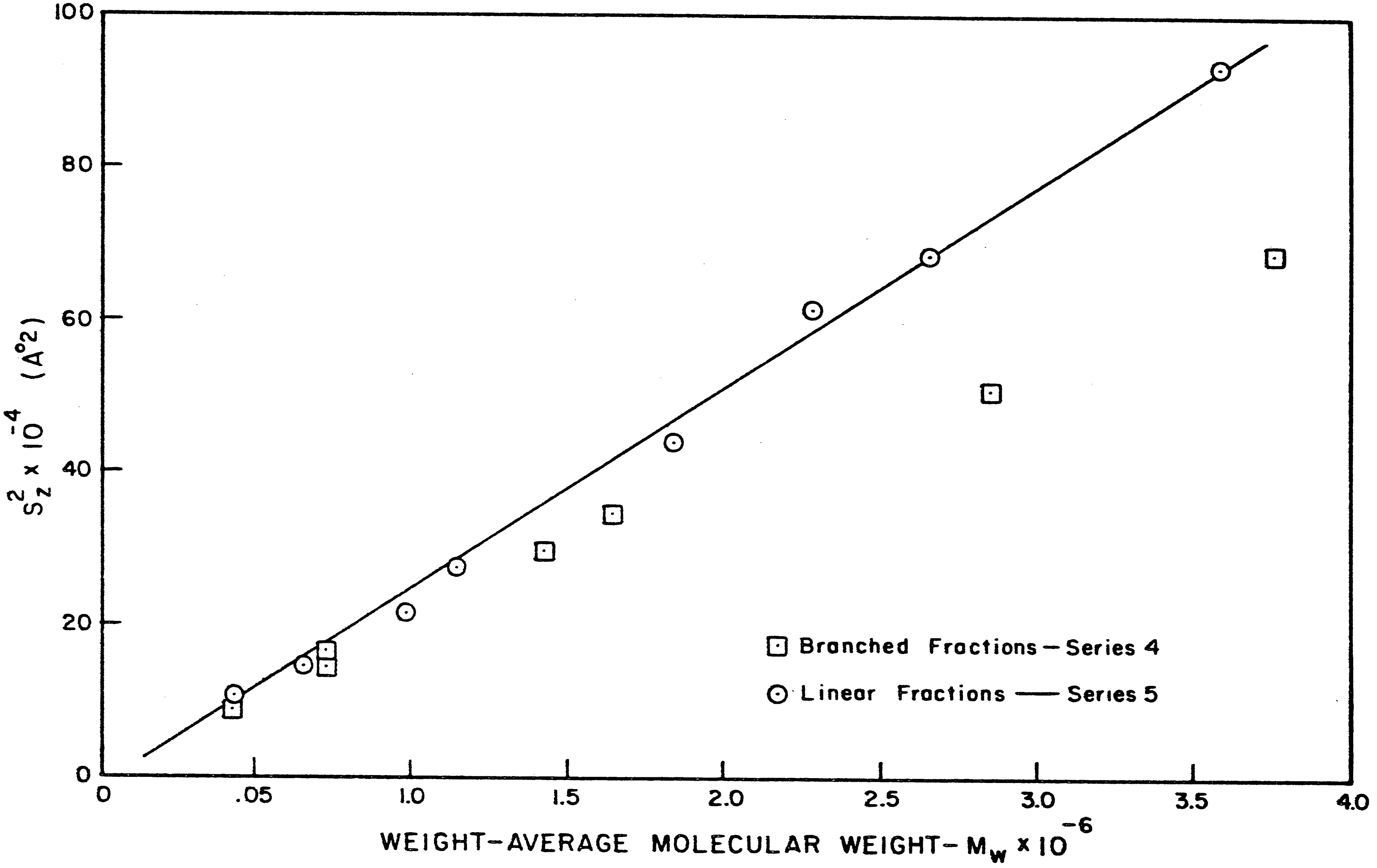


Figure 8. Z-Average Root Mean Square Radius of Gyration versus Weight-Average Molecular Weight.

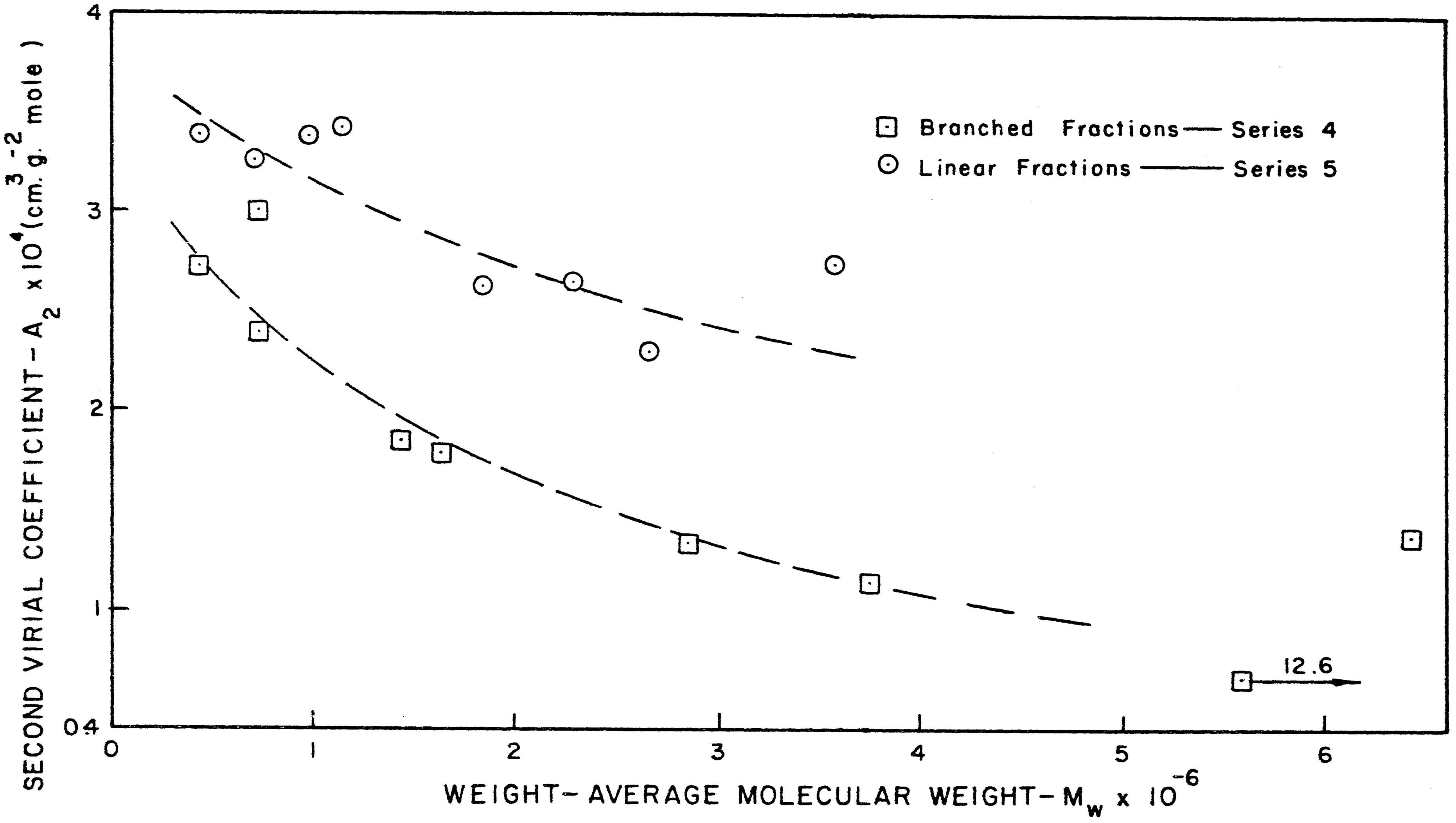


Figure 9. Second Virial Coefficient versus Weight-Average Molecular Weight.

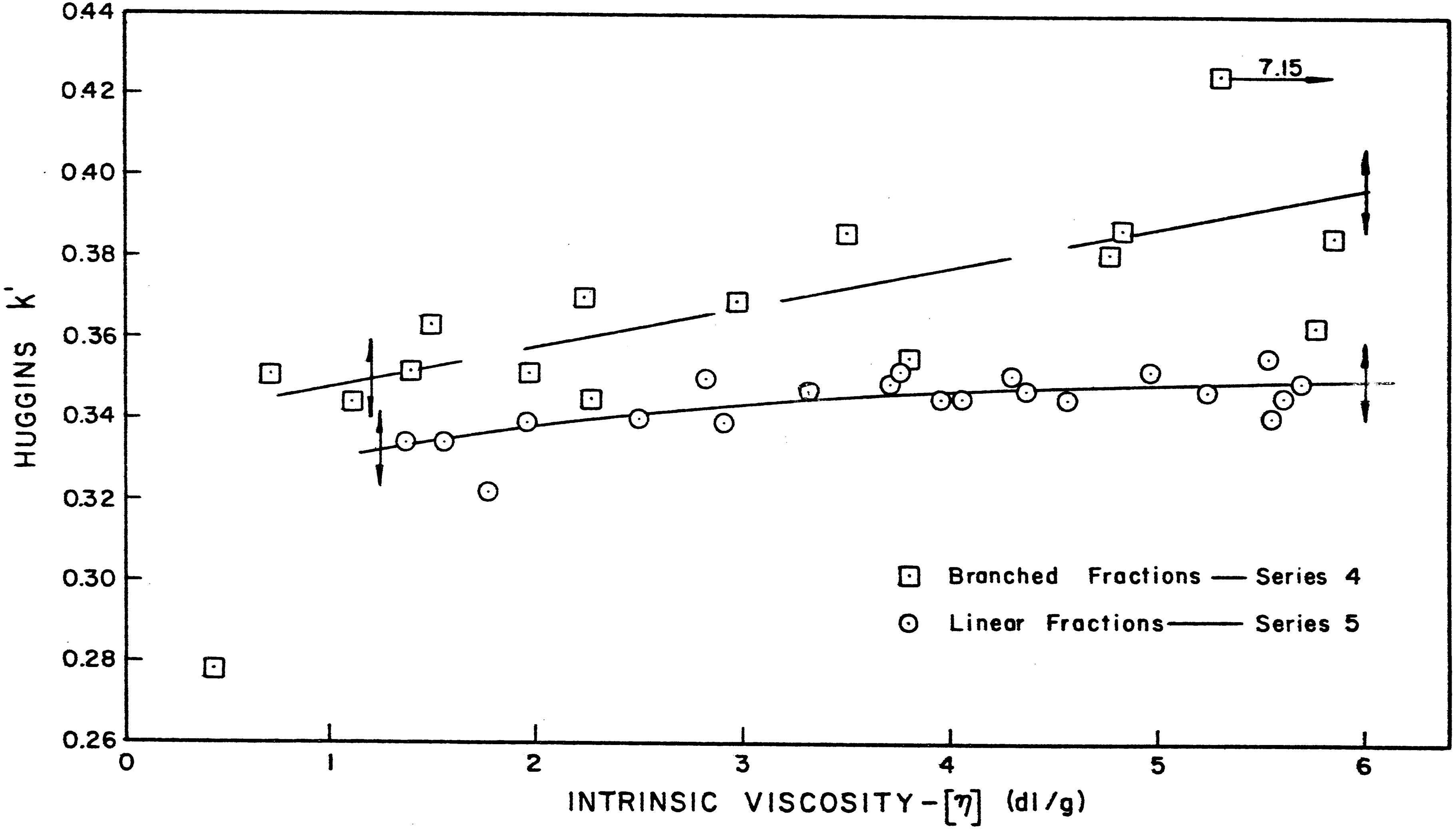


Figure 10. Huggins k' versus Intrinsic Viscosity.

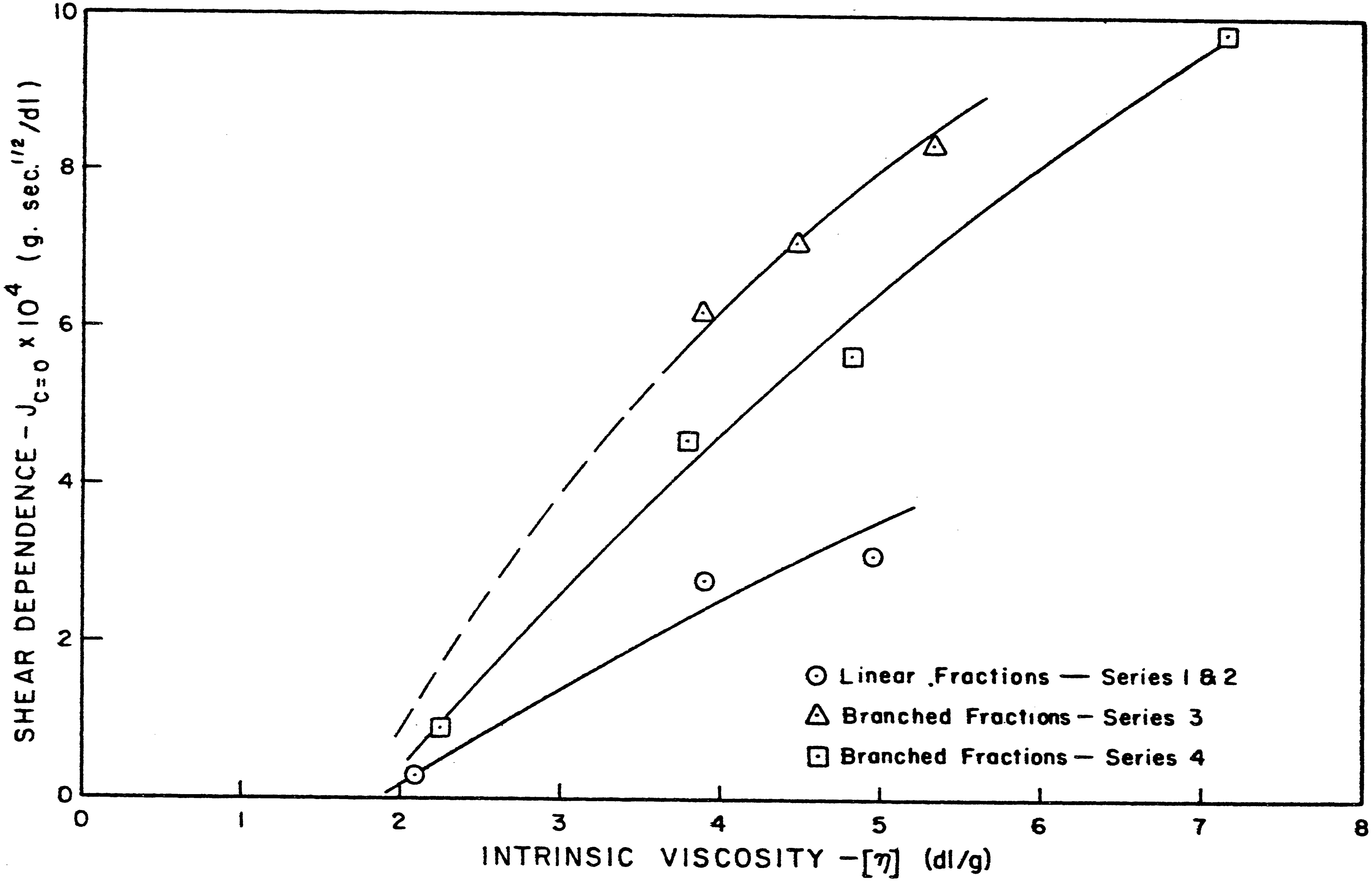


Figure 11. Shear Dependence versus Intrinsic Viscosity.

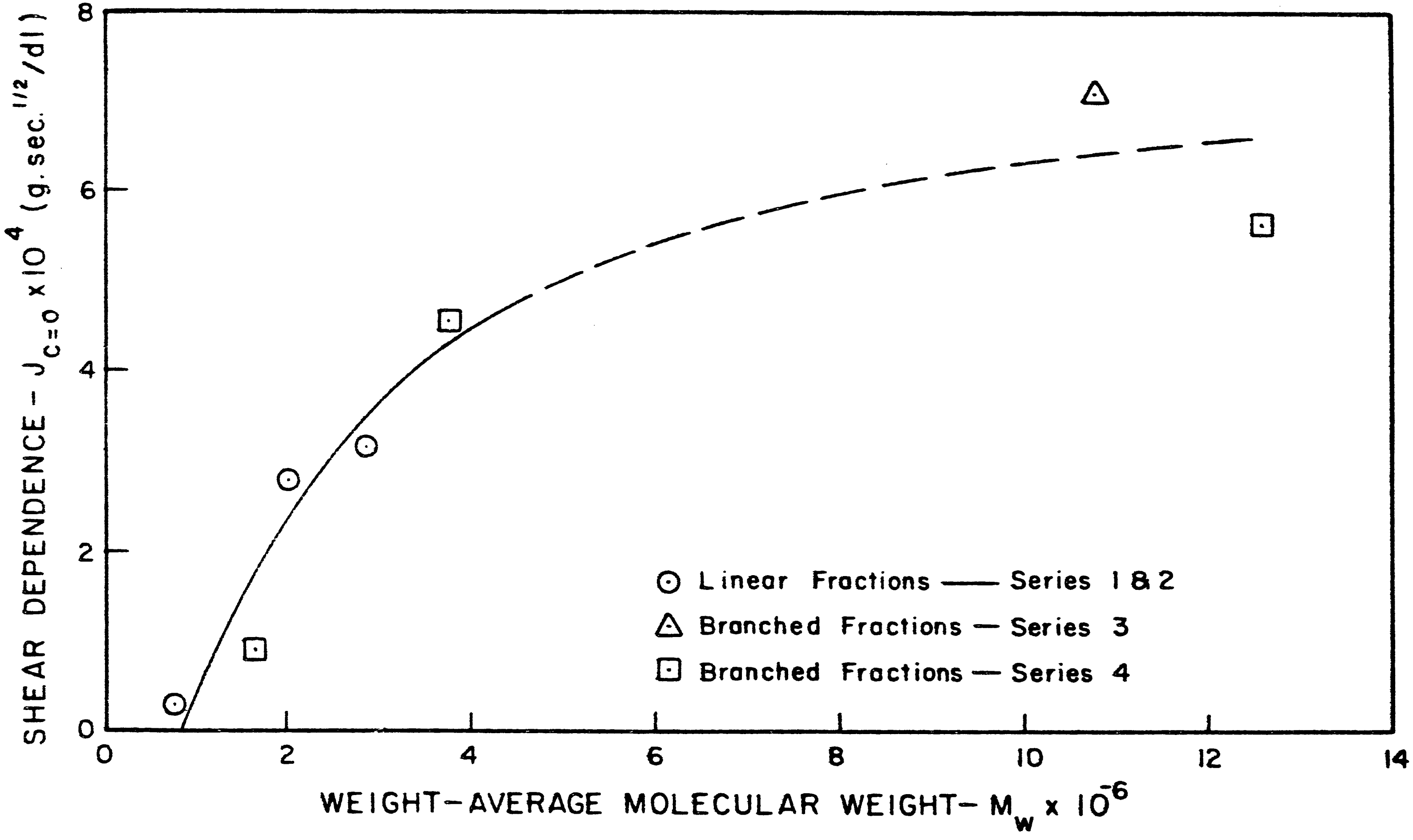


Figure 12. Shear Dependence versus Weight-Average Molecular Weight.

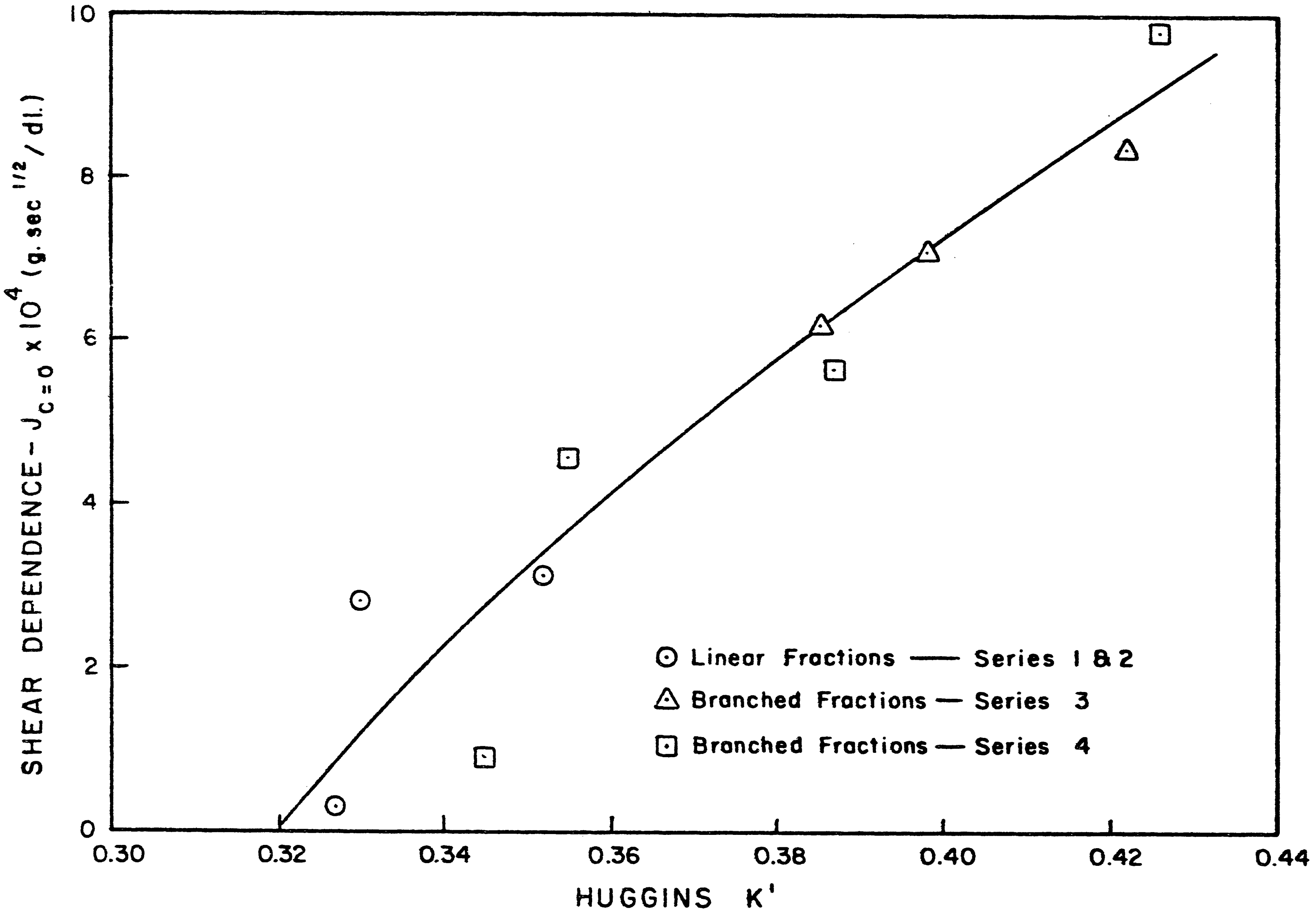


Figure 13. Shear Dependence versus Huggins k'.

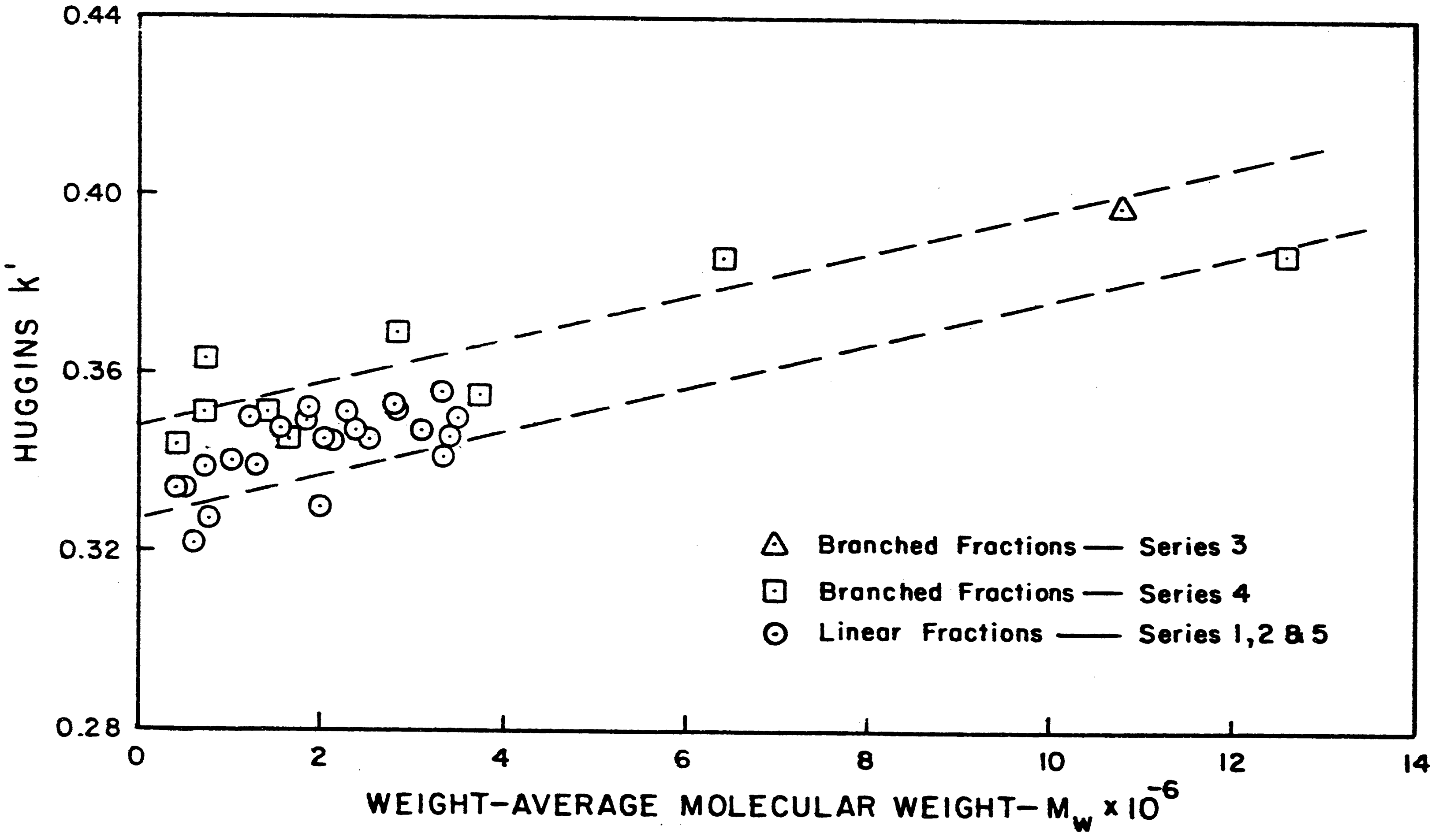


Figure 14. Huggins k' versus Weight-Average Molecular Weight.

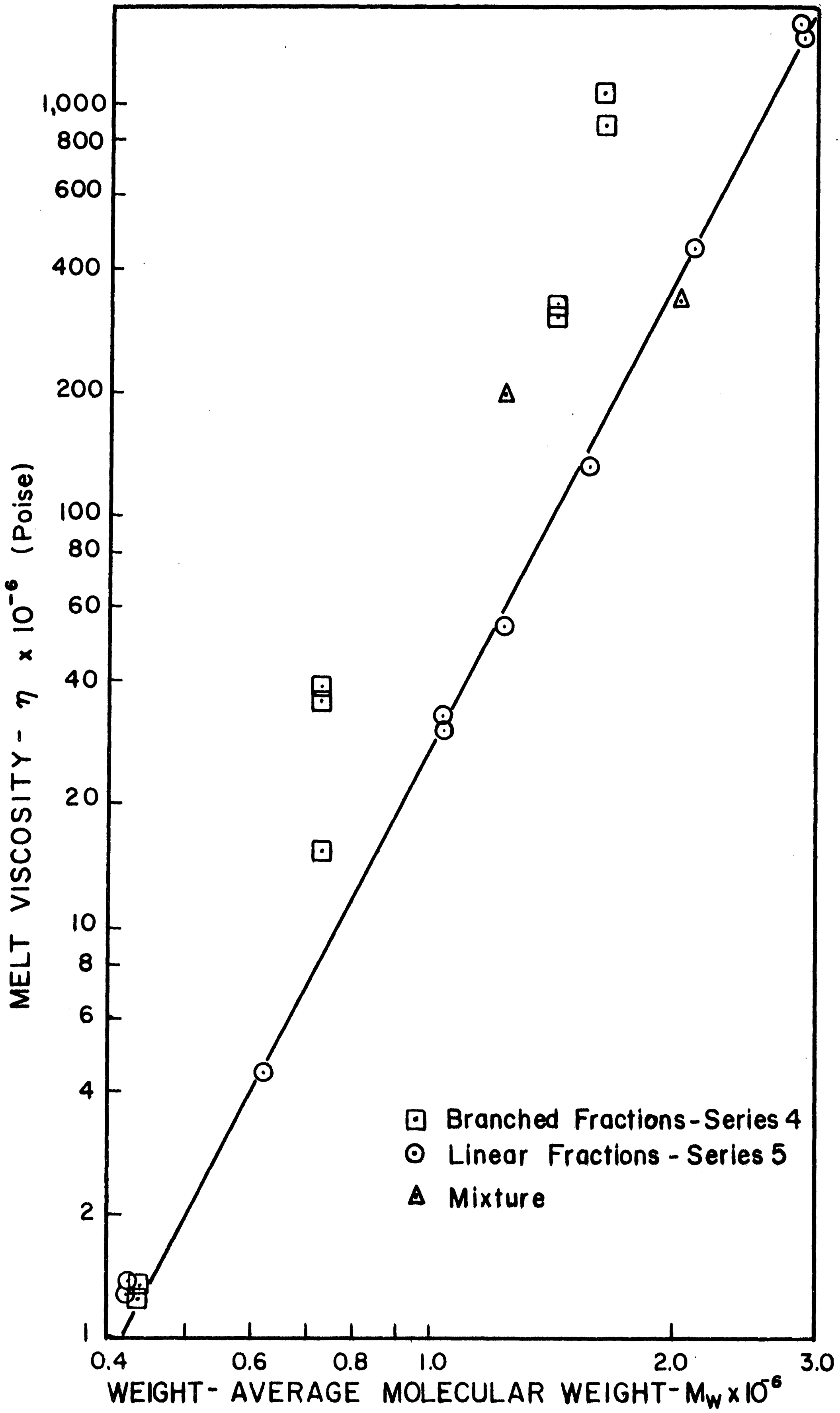


Figure 15. Melt Viscosity versus Weight-Average Molecular Weight.

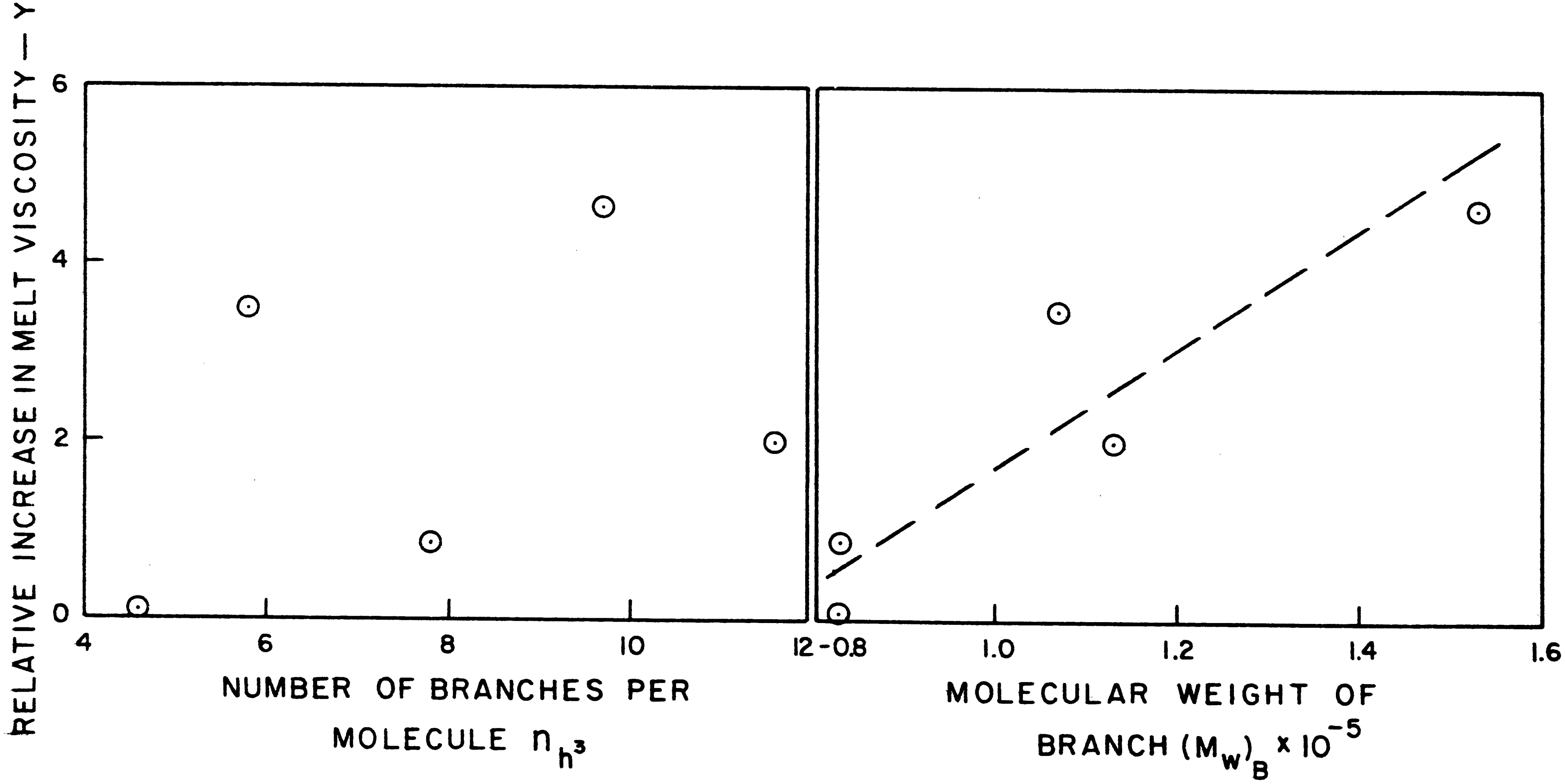


Figure 16. Relative Increase in Melt Viscosity versus Number of Branches Per Molecule and Molecular Weight of Branch.

APPENDIX C

LIST OF NOMENCLATURE AND UNITS

LIST OF NOMENCLATURE AND UNITS

a	Exponent in the empirical relationship between intrinsic viscosity and molecular weight.
A	Viscometer constant.
A_2	Second virial coefficient (cm^3g^{-2} mole).
b	Total slope of the relationship between reduced specific viscosity and concentration (dl^2/g^2).
B	Viscometer constant.
C	Concentration, viscosity (g/dl. or g/100 cm^3), light-scattering (g/cm^3).
C_n	Corrects for the difference in refractive index between solvents used for calibration and the light-scattering measurements.
d, d_s, d_o	Density, density of solution, and density of pure solvent (g/cm^3).
D	Rate of shear (sec^{-1}).
f	Number of branches per molecule.
f	Filter transmittance.
F	Melt viscosity statistical factor.
g	Ratio of the mean-square radius of gyration of a branched polymer molecule to that of a linear one of the same molecular weight.
g	Acceleration of gravity (cm/sec^2).
G_θ	Galvanometer scale reading at angle θ.
h	Ratio of the effective hydrodynamic radius of a branched polymer molecule to that of a linear one of the same molecular weight.
h	Effective head driving liquid through capillary (cm).
H	Parameter relating the turbidity-concentration ratio to the molecular weight.

LIST OF NOMENCLATURE AND UNITS (CONT'D)

i_θ	Intensity of the light scattered at angle θ.
I, I_0	Intensities of the transmitted and incident beams.
j	Melt viscosity jump frequency.
J	Slope of the relationship between the reciprocal of the reduced specific viscosity and the square root of the shear rate ($g.dl^{-1}\ sec^{1/2}$).
k	Boltzman constant ($erg.deg.^{-1}$).
k'	Huggins constant (dimensionless).
k"	Analogous to k' in Equation (12) [see Equation (13)].
K	Constant in the empirical relationship between intrinsic viscosity and molecular weight.
K	Parameter relating the Rayleigh scattering ratio to molecular weight.
L	Length of capillary (cm).
m	Viscometer constant.
m	Melt viscosity determination, slope of the relationship between the reciprocal of the plate separation to the fourth powder and time ($cm^{-4}\ sec^{-1}$).
M, M_i	Molecular weight and molecular weight of species i.
M_n, M_v, M_w, M_z	Number-, viscosity-, weight-, and z-average molecular weights, respectively.
M_o	Molecular weight associated with each chain link.
$(M_v)_H, (M_w)_H$	Viscosity- and weight- average molecular weights of the hydrolyzed sample.
$(M_w)_B$	Weight-average molecular weight of a branch.
n, n_o	Refractive indexes of solution and of pure solvent.

LIST OF NOMENCLATURE AND UNITS (CONT'D)

n_H, n_S^{2}, $n_{[\eta]}^{2/3}$, n_h^{3}	Number of branches per molecule calculated from hydrolysis data, radii of gyration, intrinsic viscosity, and intrinsic viscosity by the Stockmayer and Fixman treatment, respectively.
(dn/dc)	Change of refractive index with concentration.
N	Avogadro's number.
N_i	Number of molecules of species i.
P_θ	Particle scattering factor expressing the reduction in scattered intensity at the angle θ owing to intraparticle interference.
Q	Correction factor to normalize scattered light for changes in scattering volume and use of unpolarized light.
r	Capillary radius (cm).
r	Distance from the detector to the scattering site.
(r/b)	See Equation (17).
R	Gas constant.
R_θ	Reduced intensity of the scattered light at angle θ.
S	Shearing stress (dyne/cm^2).
S, S_o	Radii of gyration of branched and linear polymer molecules (Å).
S_n, S_w, S_z	Number-, weight-, and z-average radii of gyration, respectively (Å).
t, t_s, t_o, t_{FF}	Flow time, flow time of solution, flow time of pure solvent, and flow time at the shearing stress of free fall, respectively (sec).
T	Temperature
T_θ	Scattering ratio at angle θ.
T_θ'	Scattering ratio at angle θ corrected for reflection and solvent scattering.
u	See Equation (23).

LIST OF NOMENCLATURE AND UNITS (CONT'D)

V	Volume (cm^3).
V	Factor accounting for the calibration and physical constants of the light-scattering system.
V_e	Effective hydrodynamic volume.
W	Load on the upper plate of the melt viscometer (kg).
x	Distance light traverses in scattering medium (cm).
Y	Melt viscosity increment, $(\eta_B-\eta_L)/\eta_L$ at a given molecular weight (dimensionless).
Z	Distribution function parameter.
η, η_s, η_0	Viscosity, viscosity of solution, and viscosity of pure solvent (poise).
η_L, η_B	Melt viscosities of linear and branched samples (poise).
η_r	Relative viscosity, η_s/η_o.
η_{sp}	Specific viscosity, η_r -1.
$[\eta]$	Intrinsic viscosity (dl/g or 100 cm^3/g).
θ	Angle between transmitted and scattered beam.
λ, λ_o	Wave length of light in the medium and in vacuum (Å).
π	Osmotic pressure.
τ	Turbidity (cm^{-1}).
τ_o	See Equation (17).
φ'	Parameter relating the intrinsic viscosity to radius of gyration.
5-3-4-1	Fraction identification-Total sample 5, third primary fraction precipitated, fourth secondary fraction precipitated, and first tertiary fraction precipitated.