A LIGHT-SCATTERING AND VISCOSITY STUDY OF SOME BRANCHED POLYMERS

A LIGHT-SCATTERING AND VISCOSITY STUDY OF SOME BRANCHED POLYMERS PREPARED BY GRAFT POLYMERIZATION

by

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SCOPE AND CONTENTS:

This study deals with the effects of branching in some high polymers on viscosity behaviour and on the relationship between intrinsic viscosity and molecular weight.

First, the preparation of branched polymers by means of graft polymerization is described. Evidence for the occurrence of grafting, which would result in the growth of polystyrene branches on a main, or backbone, chain composed of polystyrene or a copolymer of styrene and 4-vinylcyclohexene-1, is reviewed.

Next, the design, construction, and calibration of a flexible light scattering photometer is described. The performance of this instrument is shown to be adequate for the determination of the molecular weight and size, as well as the second virial coefficient, of a high polymer in solution.

Finally, properties of the graft polymers in solution are compared with the corresponding properties of linear polystyrene. The relationships found between intrinsic viscosity and molecular weight, as well as the values obtained for the second virial coefficient, confirm the existence of branching in the graft polymers. On the other hand, it is shown that the viscosity slope constant, Huggins' k', the magnitude of which is often used as an indication of branching, is not affected significantly by the branching present in the graft polymers.

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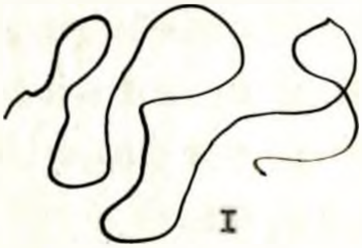
GENERAL INTRODUCTION

Many properties of a branched polymer are different from those of a linear one. Since a branched molecule is less extended in space than a linear molecule of the same molecular weight and chemical nature, properties dependent on molecular extension are affected by the presence of branching. Thus the contribution of structure I to the viscosity of a solution is greater than the contribution of structure II; the branched polymer,for a given concentration and molecular weight, perturbs the flow of a solution less than the linear one (1). Moreover, physical properties that depend on the fitting together of polymer molecules, as, for example, crystallinity, are affected by the irregularities in structure introduced by branches (2, 3). Other properties, such as melting point, tensile strength, solubility, or elasticity, depend, in part, on the amount of branching present in a polymer.


I


II

Because of these effects, the study of branching is important to the understanding of the relationship between molecular structure and physical properties. Since even a polymer assumed to be linear may, in fact, contain variable amounts of branched material, the determination of branching has often been uncertain.

The method most commonly used for the determination of branching is based on a combination of viscosity and light-scattering measurements (see Historical Introduction). With this method, the intrinsic viscosity of a polymer is compared with the intrinsic viscosity of a linear polymer having the same chemical composition and molecular weight (the latter being determined by light-scattering measurements). If branching is present, the intrinsic viscosity is, of course, lower than for the linear polymer; the magnitude of the deviation is taken as a measure of the extent of branching. However, this method is tedious, and requires expensive and elaborate equipment.

Another method, based on viscosity measurements alone, has been suggested. Because viscosity measurements can be made rapidly and accurately with simple equipment, this method, if applicable generally, would be very useful. The only calculation required is that of Huggins' k', the slope constant relating the reduced viscosity of a polymer solution to the concentration. A great deal of empirical evidence has been found, indicating a correlation between the presence of branching and unusually high values of k'.

Since no suitable comparison of the two methods had been made, it was decided to undertake a study of the relationship between Huggins' k' and the degree of branching as determined from measurements of the intrinsic viscosity and molecular weight of branched and unbranched polymers.

The problem was then divided into three parts:

I. The preparation of branched polystyrene, or a copolymer of styrene and 4-vinylcyclohexene-1, having a known number of branches per molecule.

II. The design and construction of a light-scattering photometer suitable for the determination of molecular weight and size, and second virial coefficient, for a high polymer in solution.

III. A comparison of Huggins' k' and the viscosity-molecular weight relationship, obtained for the branched polymers, with those found for linear polystyrene.

HISTORICAL INTRODUCTION

In this section, theoretical and experimental developments pertinent to the study of branching by means of intrinsic viscosity and molecular-weight measurements will be reviewed. The preparation of branched polymers will be discussed; finally, the principles of light-scattering will be briefly considered.

Since the behaviour of dilute solutions is more amenable to theoretical interpretation than the behaviour of solids, this introduction will be concerned chiefly with dilute solutions.

A. Branching in High Polymers

1. Definitions of Branching*

Some high polymers are composed chiefly of molecules in which units of monomer A are joined together in a linear chain, as shown:

-A-A-A-A-A-A-

On the other hand, some polymers, for example, dextran, may contain molecules having a branched structure. If, for example, some trivalent, or "trifunctional", monomer units, A',

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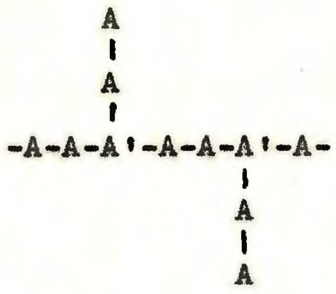
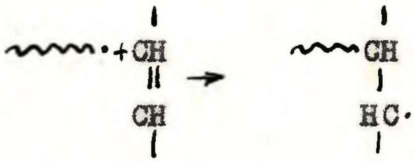
*Definitions given here are consistent with those suggested by Flory (4, p. 390).

are present in the molecule, a non-linear, or branched structure would result:



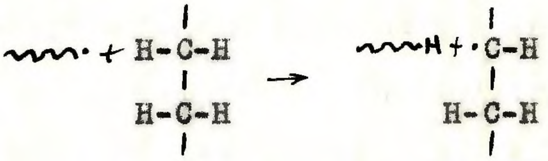
Monomer units acting as branch points may, of course, be tetrafunctional, and so on. Most addition polymers, particularly if prepared at high temperatures to a high percent conversion, appear to be composed of a mixture of branched and linear molecules.

With a polymer molecule containing a residual double bond, a variation of branching, crosslinking, may take place (4, p. 32). A residual double bond may accept a growing free radical, as shown; the active centre formed in this way is then free to react with a monomer molecule, and thus initiate



the growth of another chain. By this process, two otherwise separate molecules become joined, or crosslinked together. Crosslinking may also result from the mutual combination of two branch radicals. The occurrence of crosslinking may result in the formation of very complicated structures; if, for example, crosslinking takes place in three dimensions, an insoluble gel composed of infinitely large molecules results.

Branching may occur by several mechanisms. Thus, if a growing free-radical chain encounters another polymer chain, it may abstract a hydrogen atom from one of the methylene units. The second chain is left with an active centre that can initiate the growth of a branch chain. In other words, the activity of one molecule has been transferred to another. Since these chain transfer processes take place at random, presumably a growth of branches on branches takes place, also at random. A simpler type of branching results from the incorporation of trifunctional monomer units into the chain; in this case the growth of branches occurs at the sites of the trifunctional units.



Chain transfer to monomer may also result in the formation of branches (4, p. 257).

2. Estimation of the Degree of Branching

Theories developed by Flory (4, p. 347), Stockmayer (5, 6), and Walling (7) have been found useful for the estimation of the statistical distribution of branches in a polymer (8). Since these theories and related calculations (9, 10) are applicable mainly to random branching, and especially to cases of crosslinking leading to gelation, they will not be discussed in detail. In principle, the degree of branching may be estimated from kinetic data. If, for example, the frequency ratio of chain transfer to propagation is known, the number of branches per molecule expected may be predicted (11, 12, 13, 14, 15). Since this method requires information about the mechanism and method of polymerization, its use is limited to polymerization systems that have been studied previously. Moreover, this method is not applicable to fractions or mixtures.

The most direct method for the estimation of the extent of branching requires the determination of the molecular weight, and of the number of end-groups per molecule. For example, the ratio methyl end-groups/methylene groups in polyethylene is used as a measure of the degree of branching*; this ratio may be conveniently determined by means of infrared measurements (16, 17, 18, 19). A similar analysis of end-groups may be used with polyvinyl chloride; after carrying out a hydrogenation that

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*The degree, or extent, of branching will be considered as a measure of the number of branches per molecule.

resulted in the removal of chlorine atoms, Cotman (20) estimated the degree of branching by determination of the same ratio. The determination of end-groups is also used in the study of polysaccharides; see, for example, Beckman (21), Manners (22), and Wales and others (23). However, if the number of end-groups is small in comparison with the number of monomer units present in a molecule, this method may be inaccurate. Also, this method gives no indication of whether the branches are long or short.

The most general methods for the study of branching have been based on the effects of branching on such properties as molecular dimensions, intrinsic viscosity, and thermodynamic or hydrodynamic parameters, for example, Huggins' k', and the second virial coefficient (24).

Since this thesis is concerned particularly with these general methods, a survey of theoretical and experimental results pertinent to the effects of branching on properties such as those mentioned in the previous paragraph will follow in later sections.

3. Occurrence of Branching in High Polymers

The adventitious occurrence of branching and cross-linking in a high polymer prepared by addition polymerization is well known. It is true that polymers of methyl methacrylate (12, 25) or styrene (12, 26, 27, 28, 29), are essentially linear in structure, at least when prepared at moderate temperatures.

Nevertheless, some polymers, such as polymethyl acrylate (12, 30, 31), polyvinyl acetate (13, 15, 32, 33), polyvinyl chloride (20, 34, 35), or polyethylene (2, 17, 18, 36, 37, 38), appear to be susceptible to chain transfer reactions resulting in branching.* Crosslinking may also result from irradiation of a polymer (40, 41, 42) or from the vulcanization or curing of a rubber (4, p. 454). Condensation polymers may also be branched; three-dimensional, highly branched structures are formed by the condensation of a bifunctional reactant with a polyfunctional one (4, p. 364). Certainly crosslinking and gelation are characteristic of diene or divinyl polymers (4, 43, 44, 45).

Branching is not restricted to synthetic high polymers. For example, although the glucose units in the amylose component in starch are joined by α-1,4 links, some of the glucose units in the amylopectin component are joined to others by an α-1,6 link as well (21). Other polysaccharides such as dextran (22,) or glycogen are branched. Because of the current importance of dextran as a plasma extender, several studies of its structure have recently been made (23, 46, 47).

4. Preparation of Branched Polymers

(a) Use of Crosslinking Agents

A more complete review of the type of copolymer men-

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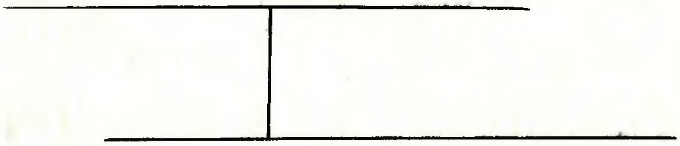
*Even linear condensation polymers may, under rigorous conditions, become branched; Staudinger and others (38,39) found evidence for branching in polymers of 10-hydroxyundecanoic acid.

tioned here may be found in reference 48.

Control of the degree of crosslinking in a product formed by a polymerization resulting in crosslinking is difficult; better control is possible if small amounts of a divinyl compound are copolymerized with the monomer studied. Each divinyl molecule may introduce a crosslink between two otherwise linear molecules; the average number of crosslinks may be easily varied by changing the proportion of divinyl compound used.



Divinylbenzene has often been copolymerized with styrene. Staudinger and co-workers (49, 50, 51, 52), among the first to study copolymers of this type, examined the swelling and viscosity behaviour in considerable detail. Norrish and Brookman (52) carried out similar studies. Swelling properties of styrene-divinylbenzene copolymers have been studied by Breitenbach and his group (53, 54), and by Boyer and Spencer (55).

The viscosity behaviour of styrene-divinylbenzene copolymers prepared in bulk was studied by Walker and Winkler (56), who found deviations from the behaviour of linear polystyrene (see Section 5-C). Manson and Cragg (27, 57) and Johnson and Wolfangel (58) also copolymerized small amounts of divinylbenzene with styrene in order to obtain materials for a viscosity study. Similar polymers were used in a light-scattering study by Outer, Carr, and Zimm (28), Thurmond and Zimm (8), and in an osmotic study by Doty, Brownstein, and Schlener (59).

Other divinyl compounds have been used for similar purposes; the choice of the divinyl compound most suitable for a given purpose has been discussed in detail (48, p. 162). Valyi, Janssen, and Mark used divinyldiphenyl and diisopropenyldiphenyl, which they found to be more stable than divinylbenzene (60). Blaikie and Crozier (61) prepared crosslinked polyvinyl acetate by the use of divinyl adipate or divinyl ethers. Divinyl adipate was also used as a crosslinking agent for vinyl acetate by Walling (7); in the same study, ethylidene dimethacrylate was used as a crosslinking agent for methyl methacrylate. Copolymers of ethylidene dimethacrylate and methyl methacrylate prepared by Smets and Schmets (62) were found to possess residual double bonds, to which could be added styrene, ethyl methacrylate, or methyl methacrylate. Polymers consisting of vinyl acetate branches on a polystyrene backbone were prepared by Saegusa and Oda (63) by the addition of vinyl acetate to polystyrene samples that contained residual double bonds. A rather similar reaction involving crosslinking rather than branching has been studied by Weisgerber and Dyer (64) who found that crosslinking had occurred (apparently by mutual combination of two linoleic branches) in products obtained by the copolymerization of erythryl linoleate with styrene.

(b) Chain Transfer Methods

It is sometimes possible to control the proportion of branched linear polymers by varying polymerization conditions; thus, low temperatures, low conversions, and modifiers to reduce the molecular weight are generally used when a linear polymer is desired (4, p. 259; 43, 65, 66).

However, most methods for the preparation of branched polymers have involved attempts to add or "graft" branches onto polymers that have been prepared previously. With these procedures, based on the transfer of a growing polymer radical to a grown polymer chain, the branching is necessarily random; in other words, the growth of branches on branches already formed is possible. Most of the interest in polymers such as these has been in the unusual properties possessed by many of the products, rather than in the branching itself.

The polymerization of a vinyl monomer in the presence of a vinyl polymer -- of the same, or of a different nature -- is a common example of grafting. In 1933, Houtz and Adkins, using benzoyl peroxide as initiator, polymerized styrene in the presence of polystyrene; they concluded that the original polystyrene molecules had been activated in some way so that styrene molecules could be added (67). Similar experiments were made by Okamura and others (68).

When Merz (69) prepared polycyclohexyl methacrylate in two stages -- one stage, thermal, and the other, catalyzed with benzoyl peroxide --, he found two peaks in the molecular weight distribution curve. In this case, addition of branches to the polymer prepared in the first stage may have occurred during the second stage. Some years after the experiments of Houtz and Adkins, Flory (70) suggested the chain transfer mechanism that has been mentioned above. Mayo, having found evidence that growing polymer chains engage in transfer reactions with solvent molecules, supported Flory's proposal (71).

Tests of the chain transfer proposals were made by Carlin and Shakespeare (72) and Carlin and Hufford (73). In order to avoid the difficulty of distinguishing between branched and linear chains derived from the same monomer, they used a monomer, p-chlorostyrene, that differed chemically from the polymer, polymethyl acrylate. After hydrolysis of the methyl acetate groups, a portion of the resulting product was found to be insoluble in water -- a solvent for polymethyl acrylate -- as well as in benzene -- a solvent for poly-p-chlorostyrene; analysis of this product showed that both p-chlorostyrene and acrylic acid units were present. On the other hand, similar treatment applied to a mixture of polymethylacrylate and poly-p-chlorostyrene resulted in a clean separation of the individual polymers.

After the principle of chain transfer had been accepted, Alfrey and Bandel (74) attempted to increase the extent of transfer in a polymerization by growing radicals of polymer A onto a "backbone" polymer B containing atoms that could be readily abstracted by a free radical. Since polystyrene radicals had been found to transfer more readily to chlorinated than to ordinary hydrocarbons, Alfrey and Bandel used a backbone polymer containing chlorine. In order to facilitate the separation of the three polymers formed -- linear polymer A, linear polymer B, and the graft polymer -- components having solubilities as different as possible were chosen. In this way, they added polyvinyl acetate branches to a copolymer of styrene and vinylidene chloride, and polystyrene branches to a copolymer of maleic anhydride and allyl trichloroacetate. It is thus possible to prepare graft polymers having oil-soluble hydrocarbon branches on a polar backbone -- and *vice versa* -- that have interesting surface-active properties.

Many other types of graft polymers have been prepared by means of chain transfer mechanisms (75, 76). Smets and Claisen (77), using benzoyl peroxide as catalyst, successfully prepared a series of graft polymers -- styrene, vinyl acetate, or vinyl chloride branches on a polymethyl methacrylate backbone, and methyl methacrylate branches on a polystyrene backbone. More recently, Van Paaschen and Smets have prepared polymers having vinylpyridine branches on a polyacrylic acid backbone chain (78). Bevington, Guzman, and Melville (26) prepared branched polystyrene and polyvinylacetate by the polymerization of styrene or vinyl acetate, which had been labelled with carbon-14, in the presence of the corresponding polymer, which had a high molecular weight. Conditions were so arranged that molecules formed during the polymerization were predominately short; the backbone component and the linear by-products of low molecular weight were separated by fractional precipitation. Since the backbone component gained in activity during the polymerization, it was concluded that branching had taken place. Bengough and Norrish prepared graft polymers by the polymerization of vinyl chloride in the presence of polyvinyl chloride (35).

In a study of the polymerization of ethylene in the presence of polyvinyl acetate and diethyl peroxide, Roland and Richards succeeded in preparing products having side chains composed of polyethylene (79). After methanolysis of the polymers and separation of the resultant fragments, it was found that branches had apparently become attached to the backbone at two sites -- at the acetoxy group, and on the main chain.

The occurrence of branching by means of chain transfer to the benzene nucleus of a vinyl acetate group was suggested by Ham as an explanation for the physical properties of copolymers of some vinyl esters with vinyl acetate (80). Recently Smets and Hertoghe (81) made use of the reactivity of the benzene ring in polyvinyl benzoate in experiments with the grafting of vinyl branches onto polyvinyl benzoate.

Some other examples of graft copolymers prepared by chain transfer methods are the following: acrylonitrile branches on polyvinyl alcohol (82), polyvinyl acetate (83), or on polyacrylamide (84); vinyl acetate, styrene, or methyl methacrylate branches on polyvinyl acetate, polystyrene, or polymethyl methacrylate, respectively (12).

An analysis of the kinetics by branching by chain transfer mechanisms was carried out by Fox and Gratch (12), and, more recently, by Voeks (14). Voeks related the frequency of branching to the rate constants for chain propagation and transfer and to reactant concentrations; Fox and Gratch studied, in particular, the conditions necessary for gelation.

The tendencies of several monomers and polymers to take part in graft polymerization by transfer was examined by Hayes (34). His results showed that the activity of a monomer toward graft polymerization decreases in the series vinyl chloride > vinyl acetate > styrene, and that the susceptibility of a polymer to graft polymerization decreases in the series polyvinyl chloride > polyacrylonitrile > polyvinyl acetate > polystyrene.

As well as being useful for the preparation of branched materials, the reactions reported above confirm the validity of the chain transfer mechanism.

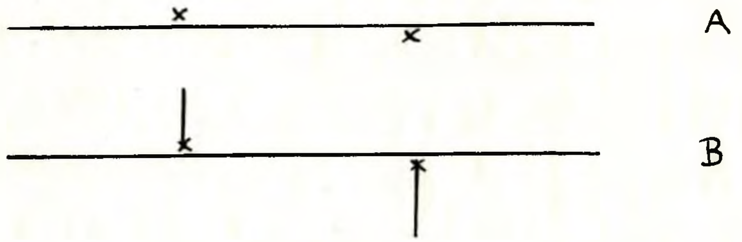
An example of branching by a process similar to chain transfer may be found in the work of Baker (84), who studied reactions with benzoyl peroxide of linear polyesters prepared from ω-hydroxyundecanoic acid.

The modification of naturally occurring polymers by the grafting of branches has received considerable attention. Although the mechanism has not been clearly established as a simple chain transfer process, polymeric branches may be grafted on natural rubber. By this means a product having very desirable resistance to abrasion and exposure may be obtained. As early as 1938, experiments with the modification of rubber were reported by Bacon and others (86, 87). They found that maleic anhydride could be bonded to natural rubber; several patents were issued, for example, to Farmer (88), for the processes used. Later, Compagnon and Le Bras (89,90) polymerized several vinyl monomers, such as acrylonitrile, in the presence of natural rubber; they concluded that at least some of the polymerized monomer was bound to be rubber. More recently, Koolhaas and others (91) succeeded in polymerizing some vinyl monomers, for example, acrylonitrile, methyl methacrylate, and styrene, in the presence of rubber. However, no systematic study of the products obtained from similar reactions was attempted until the initiation of a research program established by the British Rubber Producers' Association for the study of the modification of rubber. Then Bloomfield and others (92) and Merrett (93) reported conclusive proof of the grafting of branches composed of vinyl acetate, methyl acrylate, styrene, and methyl methacrylate, onto rubber molecules; Scanlan (94) and Allen, Merrett, and Scanlan (95) studied the transfer reactions concerned in more detail. Synthetic rubbers have been used in similar grafting experiments by Whitby (96).

Graft polymers may also be prepared by the cold milling of natural rubber in the presence of neoprene (97). Apparently the shearing forces applied during milling are sufficient to rupture molecules of rubber; the resulting free radicals can then, by taking part in transfer reactions, add as branches to other molecules.

(c) Reaction at Specific Sites

A general method for the preparation of branched polymers is based on the growth of branches from reactive groups introduced along the backbone chain (75). Preparation of the branched polymers is accomplished in two stages. First, a backbone polymer, (A), is prepared with reactive groups spaced, at some desired interval, along the chain.



Then, with a monomer that will react with active groups of the backbone, a second polymerization, (B), is carried out. By varying the proportion of active groups in the backbone, the number of branches produced may be varied; by varying the relative proportions of backbone and monomer, the average lengths of the branches added may be varied. Since initiation occurs only at the backbone chain, the formation of linear polymer from the monomer present should not occur. Of course, if either the monomer or polymer tend to take part in chain transfer reactions, the situation will be more complicated.

This method has been applied to both condensation and addition polymerization.

In 1948, Schaefgen and Flory (98) demonstrated a convenient synthesis for branched condensation polymers having a controlled structure. By reaction of a polyfunctional compound, for example, a tetra basic or octabasic non-polymeric acid with ϵ -caprolactam, they succeeded in preparing polymers having four or eight branches composed of poly-ϵ-caprolactam. As well as describing the use of non-polymeric acids, Schaefgen and Flory reported the suitability of polyacrylic acids as backbone polymers. Branched polyesters were prepared by Youngson and Melville (99) by the treatment of a polyhydric alcohol, for example, pentaerythritol, with polymeric polyethylene adipate. Other branched polyesters were prepared by Weil (100) from adipic acid and a polyhydric alcohol. Another condensation polymerization resulting in the formation of branched polymers has been reported recently by Sela and Katchalski (101), who condensed N-carboxylic-α-amino acids with polylysine. Cellulose esters and ethers have also been used as the backbone for a graft polymer. For example, Micheel and Ewers (102,103), using cellulose ethers and carbohydrates as backbone materials, prepared graft polymers having branches composed of proteins. By condensation reactions, Coleman (104) succeeded in preparing polyethylene terephthalate containing ethylene oxide branches; similar branches were grafted onto polyamides by Haas and others (105). Mark (75) and Immergut and Mark (106) have also discussed experiments at the Polytechnic Institute of Brooklyn, dealing with condensations using carboxyl, amino, or hydroxyl groups, spaced along a polymer chain, as starting points.

Enzymatic syntheses have also been used. Having successfully prepared a branched tri-saccharide by this means, Bailey and others (107) suggested that enzymatic synthesis might be adaptable to the preparation of poly-saccharides having higher molecular weights. The conversion of amylose to amylopectin is well known (108); amylopectin is, however, apparently randomly branched.

It is also possible to prepare branches composed of units joined together by means of addition polymerization. In this case, it is necessary that the backbone chain contain functional groups capable of initiating addition polymerization. One way of achieving that type of initiation was developed at the Polytechnic Institute of Brooklyn; Mesrobian and Mark (109) suggested the introduction of hydroperoxide groups, which could later initiate polymerization of a monomer, into a polymer chain. This introduction of hydroperoxide groups was accomplished by Metz and Mesrobian (110) by the oxidation of copolymers of styrene and isopropylstyrene.* The oxidized polymer was then used as initiator in a redox polymerization (equations A-1 and A-2) of styrene or methyl methacrylate -- ferrous ion being used as the reducing agent.

$$\mathrm{ROOH} + \mathrm{Fe}^{++} \rightarrow \mathrm{RO}^{\cdot} + \mathrm{OH}^{-} + \mathrm{Fe}^{+++} \qquad \text{(A-1)}$$

$$\mathrm{RO}^{\cdot} + \mathrm{M}\ (\text{monomer}) \rightarrow \mathrm{ROM}^{\cdot}\ \text{and so on} \qquad \text{(A-2)}$$

Metz and Mesrobian also prepared some branched polymers by heating the polymeric hydroperoxide in a solution containing styrene or methyl methacrylate. A thermal polymerization results, of course, in the formation of linear polymer as a by-product. The fact that, in the case of the emulsion polymers, methyl methacrylate chain units were chemically linked to the backbone polymer was proved by means of precipitation studies,

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*It should be noted that Metz and Mesrobian, whose paper was published after results of grafting experiments made here had been reported (111), were unable to achieve satisfactory oxidation of polystyrene itself.

which indicated the presence of only one major component.

Independently, Hahn and Fischer (112) studied the use of polyfunctional peroxides or hydroperoxides as initiators for thermal polymerization. Hahn and Fischer succeeded in using the following materials as initiators for the polymerization of methyl methacrylate: a perester of polyacrylic acid, polyacrylylbenzoyl peroxide, and a copolymer of methyl methacrylate and isopropenyl hydroperoxide. A peresterified polymer (polymethacrylic acid) was also used as an initiator for the polymerization of styrene and vinyl acetate by Saegusa, Nozaki and Oda (113).

After results described in Part I of this thesis had been reported (111), experiments using oxidized polyisopropylstyrene and polystyrene as initiator for the polymerization of methyl methacrylate and styrene were described by Hahn and Lechtenböhmer (114). In each case, comparison of the relationship found between the intrinsic viscosity and molecular weight (see Section 5-(a), below) with the relationship established for linear polymers led to the conclusion that branching had occurred.

The introduction of peroxide groups into a polymer chain -- in this case, cellulose -- has also been described by Jahn (115); the oxidized cellulose was used to initiate the polymerization of acrylonitrile, acrylic esters, or styrene.

A different approach to the introduction of reactive groups was taken by Melville and his group. Jones, Melville, and Robertson (116) used partially brominated polystyrene as the initiator in the photopolymerization of styrene. Irradiation of the backbone polymer by means of ultraviolet light resulted in the growth of polystyrene branches from the sites of the bromine atoms. Although, as in the case of thermal initiations using polymeric hydroperoxides, linear polystyrene was formed as a by-product, the molecular weight of the by-product was sufficiently different from the molecular weight of the backbone polymer for the successful separation of the two components by fractional precipitation. This method has also been used by Jones (117) for the preparation of branched polystyrene and polyvinyl acetate.

If nuclear radiation is used instead of ultraviolet light, it is not necessary to introduce bromine atoms into the chain; this radiation can induce active centres in an ordinary polymer by abstraction of a hydrogen atom. Thus Behr and others (118) prepared several types of graft polymers having interesting properties by the polymerization of vinyl monomers in the presence of polymers such as polystyrene or polyethylene under the influence of gamma radiation.

5. Effects of Branching on Properties

(a) Effects on Molecular Dimensions and Intrinsic Viscosity

As mentioned earlier, the chief physical difference between a branched and a linear molecule of the same chemical nature is the smaller extension of the former, for a given molecular weight (119). This extension may be expressed -- at least in the case of a linear polymer obeying random-flight statistics (4, Chapter X) -- as R^2, the mean square distance between the ends of the molecule. Since, however, the term "end-to-end distance" loses its meaning when applied to a branched molecule, which has several ends, the use of a dimension having more general applicability is preferable. A dimension suitable for this purpose is the mean square radius of gyration, S^2, -- hereafter called the mean square radius -- which represents the mean square distance of chain elements from the molecular centre of gravity; S^2 is, of course, a suitable measure of dimension for linear as well as branched molecules.* Hence, if the extension of a linear molecule against which a branched one is compared is also expressed as S^2, comparison becomes more meaningful.

Assuming that the configuration of the molecules obeyed random-flight statistics, Zimm and Stockmayer (1) calculated values of S^2 for various kinds of more or less randomly branched molecules. They expressed their results in terms of a dimensionless parameter, g, which is a function of both the number and the distribution of branches in a molecule. The parameter, g, was defined as follows:

$$g = \frac{S^2}{S_o^2}, \qquad \text{(A-3)}$$

where S^2 is the mean square radius** of gyration of a branched

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*For a linear polymer, S^2 is related to R^2 by the expression $R^2 = 6S^2$ (4, p. 422)

**Although this dimension should be obtained in an ideal solution, that is, in a solution obeying van't Hoff's rule, Thurmond and Zimm (8) and Stockmayer and Fixman (24) have found that the error introduced by the determination of dimensions in non-ideal solutions seems small.

molecule of the same molecular weight and chemical constitution as a linear molecule whose mean square radius of gyration is S_o^2. Results of the calculations showed that g decreased slowly from unity with an increase in the number of branches. Calculations of g for various models have also been given by Wales (46), Tsvetkov (120), Billmeyer (121), and Kataoka (122).

Values of S^2 or R^2 may be obtained from measurements of the angular dependence of scattered light, as long as the value of S is greater than about 200 A°. (See section on light-scattering).

Experimental evidence for a decrease in mean square radius owing to branching may be found in results obtained by Bosworth, Masson and Melville (32). After measuring the molecular weight, M, and apparent mean square radius, R^2 (calculated as though the polymer were linear -- see part III of this thesis) for fractions of polyvinyl acetate believed to be partially branched, they found values of M/R^2 ranging from 2.6 to 0.5. In comparison, the value of M/R^2 for polyvinyl acetate made at a low temperature to a low conversion, that is, prepared under conditions favouring the formation of predominantly linear polymer, was found by Burnett, George and Melville (66) to be 0.4. A decrease in M/R^2 was also noted by Bevington, Guzman and Melville for branched polystyrene and polyvinyl acetate prepared by graft polymerization (26), and by Guzman (123) for branched polyvinyl acetate.

Unfortunately, the change of S^2 for a given molecular weight is not as sensitive to branching as might be supposed;

the change may be obscured by polydispersity with respect to molecular weight, even after fractionation (1, 8, 119). This difficulty arises from the fact that the value obtained from S^2 from light scattering measurements is an average in which large molecules are given the greatest weight (24, 124). Specifically, the mean square radius is actually a "z-average" quantity defined by the following expression:

$$S_z^2 = \frac{\sum n_i M_i^2 S_i^2}{\sum n_i M_i^2}$$

where n_i represent~~s~~ the number of molecules having molecular weight M_i (1, 24, 119). Strictly speaking, this z-average dimension should be compared only with a z-average molecular weight (see below); in this way, the same weighting process would operate in the determination of the size average as in the determination of the molecular weight average. However, a z-average molecular weight is available only from studies of sedimentation using an ultracentrifuge; the molecular weight averages most readily available are the number-average molecular weight, M_n -- derived from measurements of colligative properties --, and the weight-average molecule weight, M_w-derived from light scattering measurements. These three averages may be defined as follows:

$$M_n = \frac{\sum n_i M_i}{\sum n_i} \; ; \quad M_w = \frac{\sum n_i M_i^2}{\sum n_i M_i} \; ; \quad M_z = \frac{\sum n_i M_i^3}{\sum n_i M_i^2} \qquad \text{(A-4)}$$

where the symbols are the same as before. Although M_w is much closer to M_z than is M_n, Thurmond and Zimm (8) found that comparison of values of S^2 for slightly crosslinked polystyrene with values of S^2 for linear polystyrene of the same molecular weight gave no clear indication of the expected decrease in S^2. Most accurate estimates of the degree of branching from measurements of S^2 can, therefore, be obtained only if the distribution of molecular weights within a sample is known fairly accurately (24). In such a case, S_w may be calculated from S_z, or else M_z may be calculated from M_w; see, for example, Howard (13) and Shultz (66).

However, the intrinsic viscosity, $[\eta]$, a function (see Part I, Section 6) proportional to the size of a molecule (see below), is close to a weight-average quantity (119); a comparison of intrinsic viscosities and weight-average molecular weights should, therefore, be less sensitive to the distribution of molecular weights than a comparison of mean square radius and weight-average molecular weight.* According to currently accepted theories (4, Chapter XIV), the contribution of a polymer molecule to the viscosity of a solution may be considered as being proportional to the "effective hydrodynamic volume", V_e, of the molecule; the effective hydrodynamic volume represents the volume of a sphere that would enhance the viscosity of the solution to the same extent as the molecule itself. The relationship between intrinsic viscosity and the effective hydrodynamic volume may be expressed as follows:

$$[\eta] \propto V_e / M$$

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*See footnote on page 29.

The viscosity thus has the dimensions of a specific volume. Since the effective hydrodynamic volume may be characterized by a radius proportional to a linear dimension of the polymer coil in solution (125, 126, 127), the following relationship is assumed to hold for a linear polymer:*

$$[\eta] \propto \frac{R^3}{M}, \text{ or } \propto \frac{(R^2)^{3/2}}{M}, \text{ or } \propto \frac{(S^2)^{3/2}}{M} \qquad \text{(A-5)}$$

A proportionality constant Φ has been introduced by Fox and Flory (127), so that expression (A-5) becomes

$$[\eta] = \Phi\frac{(R^2)^{3/2}}{M} = \Phi\, 6^{3/2}\frac{(S^2)^{3/2}}{M} = \Phi'\frac{(S^2)^{3/2}}{M} \qquad \text{(A-6)}$$

The constant Φ' allows for the use of S^2 rather than R^2 (R^2 being equal to S^2 x 6).

Theoretically independent of solvent** or temperature, Φ has a value of approximately 2.1 x 10^{21} for many polymer-solvent systems (4, p. 616). A complication arises, however, from the fact that the molecular weight and dimension used in Flory's original derivation were number-average quantities; hence, the use of other averages would be theoretically permissible only with ideally homogeneous fractions. Fortunately, the

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* It is assumed firstly that the chain length is large, and, secondly, that the distribution of the ends of the coil may be represented by a Gaussian function.

** A very slight dependence on solvent has been noticed in some cases (8, 25, 128), as well as a slight dependence on polymer (129).

eity of a sample with respect to molecular weight,* it is understandable that light-scattering, which yields a weight-average molecular weight, has become a very important technique for the study of branching. In fact, the combination of light-scattering and intrinsic viscosity measurements is considered by Stockmayer and Fixman (24) to be the best method available for the study of branching. The use of number-average molecular weights (38, 39), on the other hand, has been criticized (20, 24, 98, 130) because of the possibility of apparent shifts in molecular weight owing to a change in the molecular weight distribution, which would affect M_n differently from M_w.

Considerable evidence has been obtained for the predicted decrease in intrinsic viscosity; this decrease results in a deviation from the empirical law** (equation A-8) which represents, for many

$$[\eta] = KM^a \qquad \text{(A-8)}$$

(K and a being constants)

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* For an illustration of the effects on the relationship between intrinsic viscosity and molecular weight caused by heterogeneity with respect to molecular weight, compare the results obtained by Frank and Breitenbach (131), who used number-average molecular weights, with those obtained by Levy and Frank (132), and Meyerhoff (133). It is clear that the degree of homogeneity required in a fraction is much less if M_w is used instead of M_n; hence the need for an elaborate fractionation procedure is diminished.

** The more refined relationship developed by Fox and Flory is discussed thoroughly in Flory's book (4, Chapter XIV).

polymers, the relationship between intrinsic viscosity and molecular weight (4, p. 312; 134, 135, 136). If branching is present in a series of fractions, the exponent <u>a</u> is decreased. Although the magnitude of <u>a</u> may, in principle, be used as a measure of branching (1), the precise determination of <u>a</u> requires measurements having greater precision than can be attained experimentally (24).

Deviations from the empirical relation for linear polystyrene were found by Thurmond and Zimm (8) for fractions of styrene-divinylbenzene copolymers. The intrinsic viscosities were consistently lower, for a given molecular weight, than the values for the linear polymer; the deviation increased steadily with increasing molecular weight. Johnson and Wolfangel (58) also noted deviations for similar copolymers.

High molecular weight fractions of polybutadiene, which are more likely to be branched than lower molecular weight ones, were shown by Johnson and Wolfangel (58) and by Pollock and others (137) to have lower ratios of intrinsic viscosity to molecular weight than had low molecular weight ones.

Dextran exhibits a similar behaviour. Recently Senti and others (47) have demonstrated that the intrinsic viscosities of high molecular weight fractions deviate from the linear relation (equation A-8) found for low molecular weight dextran. Thus they confirm earlier results reported by Arond and Frank (138) and by Wales, Marshall, and Weissberg (46).

Although their data were rather scattered, Rathmann and Bovey (139) found a tendency of poly-1, 1-dihydroperfluorobutyl acrylate to have a lower intrinsic viscosity when prepared to a high rather than to a low conversion, that is, when prepared under conditions favourable to branching.

Howard (13), working with polyvinyl acetate, found that the ratio of the intrinsic viscosity of a sample prepared to high conversion to the intrinsic viscosity of a sample prepared to low conversion ranged from 0.61 to 0.94. The top fraction of a series of fractions studied by Chinai and others also had a lower intrinsic viscosity than expected (140). On the other hand, Wheeler, Lavin and Crozier (15) and Saini and others (141) found linear relationships for polyvinyl acetate corresponding to equation (A-8); although Wheeler, Lavin and Crozier used number-average molecular weights, Saini and his group used weight-average ones.

Results with polyethylene are also rather contradictory. Intrinsic viscosities lower than expected for linear polymers were found by Billmeyer (121). Harris (142), on the other hand, found that one equation fitted the data for all samples studied, regardless of the estimated degree of branching; again, molecular weights, determined by means of osmotic pressure measurements, were number-average ones.

The behaviour of polymers branched in a non-random manner is as predicted above. Although Schaefgen and Flory (98) found that the presence of four branches per molecule of the polylactams studied had no measurable effect on the intrinsic viscosity, they found that the presence of eight branches per molecule did lower the intrinsic viscosity for a given molecular weight from the value for a similar linear polymer. A noticeable effect of branching on intrinsic viscosity was found by Youngson and Melville for branched polyesters (143, 144).

So far there are few results available dealing with graft polymers. Hahn and Fischer (112) and Hahn and Lechtenhöhmer (114), working with branched copolymers of polyisopropylstyrene and methyl methacrylate, have found deviations from the curve relating intrinsic viscosity and number-average molecular weight.

A modification of the general procedure described above was used by Wales, Marshall, and Weissberg (46) for the study of branching in dextran. They showed that, if g is determined in an ideal solvent, the use of linear fractions for comparison is unnecessary. Thus no assumptions about the choice of a polymer as a linear standard are required. They used the following equations, derived by combining equation A-7 and the Flory modification of equation A-8 (4, p. 612):

$$[\eta] = K g^{3/2} M^{1/2} \alpha^{3} \qquad \text{(A-9)}$$

$$[\eta]^{2/3} = K^{2/3} g M^{1/3} \alpha^{2} \qquad \text{(A-10)}$$

where K is a constant, and α is a factor to allow for the expansion of a polymer coil owing to the presence of a non-ideal solvent. Working at a temperature at which the solvent became ideal (that is, at which $\alpha = 1$), Wales, Marshall, and Weissberg compared values of g calculated from equations A-9 and A-10 with values computed for different models. Their data were found to noticeable effect of branching on intrinsic viscosity was found by Youngson and Melville for branched polyesters (143, 144).

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where K is a constant, and α is a factor to allow for the expansion of a polymer coil owing to the presence of a non-ideal solvent. Working at a temperature at which the solvent became ideal (that is, at which $\alpha = 1$), Wales, Marshall, and Weissberg compared values of g calculated from equations A-9 and A-10 with values computed for different models. Their data were found to be consistent with a non-random structure for dextran. A rather similar modification was also used by Pollock, Elyash, and De Witt (137), who estimated the degree of branching in polybutadiene.

The conclusions of Wales, Marshall and Weissberg about the structure of dextran were questioned by Senti and others (47), who found that a model based on random branching was not inconsistent with the experimental values of g. Senti and his group also concluded from their data that different relations for linear and branched polymers may exist between the root-mean-square radius from light scattering measurements and the effective hydrodynamic radius concerned in viscosity.

A few attempts have been made to compare the degree of branching estimated by means of viscosity and molecular weight measurements with the degree of branching estimated by independent methods. Progress has been hindered by the fact that accurate independent evidence about branching is seldom available.

Using calculated values of g and values computed by Zimm and Stockmayer (1) for g as a function of the number of crosslinks per molecule, Thurmond and Zimm (8) found the average number of tetrafunctional branch units (each of which represents approximately a crosslink) in a sample of crosslinked polystyrene to be 0.68. From theories of gelation (4, Chapter IX), Thurmond and Zimm had expected a value close to unity for the system, which was close to gelation. This discrepancy might have been caused by defects either in the theories of gelation or in the calculation of the number of branches. Since the theories of gelation had been found fairly satisfactory for some vinyl polymerizations, Thurmond and Zimm concluded that the quantitative estimation of the degree of branching was unsatisfactory. They also cast doubt on the assumed proportionality between Φ and S^3/M (equation A-6); failure of the assumption of proportionality could account for an absolute error in the number of branch points calculated.

An underestimation of the degree of branching expected was found by Pollock, Elyash, and De Witt (137) for polybutadiene. The number of cross linked molecules calculated from values of g was found to be about half the number deduced from gelation experiments by Morton and Salatiello (9) for comparable materials.

Results obtained by Howard (13) with fractions of polyvinyl acetate also showed that the number of branches predicted from calculations of g was lower than the number predicted from the ratio of chain transfer to chain propagation constants. Again, the proportionality between Φ and S^3/M was questioned.

An effect of branching on the viscosity of branched polyesters smaller than expected was found by Schaefgen and Flory (98).

More satisfactory estimates of the degree of branching in some of the cases mentioned above were obtained by Stockmayer and Fixman (24), who refined the procedure for obtaining g. Stockmayer and Fixman showed that, at least for a cruciform molecule, the effective hydrodynamic radius (that is, the radius of the sphere having the effective hydrodynamic volume which defines the intrinsic viscosity - see above) might be not quite as sensitive to branching as is the root-mean-square radius of gyration S. Because of the greater segment density in a branched molecule compared to a linear one having the same mean-square-radius, the proportionality between the effective hydrodynamic radius and mean-square-radius of a branched molecule may be slightly different than the proportionality for a linear one. Stockmayer and Fixman proposed that the ratio of intrinsic viscosities be expressed by a parameter h^3, instead of g:

$$h^3 = \frac{[\eta]\,branched}{[\eta]\,linear} = \frac{Ve\,(branched)}{Ve\,(linear)} \qquad \text{(A-11)}$$

The parameter h represents the ratio of the effective hydrodynamic radius of a cruciform molecule to that of a linear molecule of the same molecular weight; the use of h avoids any assumptions about the relationship between the effective hydrodynamic radius and the root-mean-square radius S. Then Stockmayer and Fixman obtained equations for h and g as functions of the degree of branching; $g^{3/2}$ was, indeed, found to be more sensitive to branching than was h^3. Accordingly, a graph of g as a function of h^3 was plotted.

Assuming that the relation found between h and g would hold for other types of branched molecules, Stockmayer and Fixman recalculated the degree of branching from the results of Thurmond and Zimm (8) and Howard (13). Results found by the new procedure using equation A-11 for both cases were much better; agreement to within 2 percent (8) and 20 percent (13) of the expected values was found. Senti and others (47) also used the Stockmayer-Fixman modification for the study of branching in dextran (see above); they found that the g values thus obtained agreed better with the value for than did values of g calculated by Wales, Marshall, and Weissberg (46). Recently the Stockmayer-Fixman procedure has also been used by Muus and Billmeyer (144) in a study of polyethylene.

Thus, it may be seen that the qualitative detection of branching by a combination of viscosity and light-scattering measurements is well established. On the other hand, while satisfactory results have been obtained in a few cases (24), quantitative determination of the degree of branching is still hindered by three major difficulties. Firstly, independent, unequivocal measurements of the degree of branching are difficult to obtain. Secondly, the proportionality between intrinsic viscosity and molecular weight may be, at least for branched molecules, somewhat different from the assumed one (equation A-6); as yet this matter has not been settled. Finally, no complete study has yet been made of the distribution of both branches and molecular weights in a series of fractions; there have, however, been suggestions that the solubility of branched molecules may be anomalous (119, 130, 145).

(b) Effect on the Second Virial Coefficient

There has been little study of the effect of branching on such thermodynamic parameters as A_2*, the second virial coefficient, defined by the following expression:

$$\frac{\pi}{RTc} = A_1 + A_2 c + A_3 c^2 \ldots \qquad \text{(A-12)}$$

In this equation, π, R, T, and c have their usual significance, A_1 is the first virial coefficient ($A_1 = 1/M$), and A_2 is the second virial coefficient. Another parameter, μ, has been derived (146) from A_2 and is defined by

$$A_2 = \frac{(0.5 - \mu)}{v_1 d_2^2}$$

where v_1 is the volume fraction of solvent, and d_2, the density of the solute.

A second virial coefficient is necessary because of the dependence of π /c on concentration that results when van't Hoff's law is not obeyed; for an ideal solution, π/c becomes independent of concentration and A_2 becomes equal to zero. Hence A_2 is a measure of the solvent-solute interaction, the magnitude of which is directly proportional to the extent of the deviation from van't Hoff's law. When A_2 is large, the polymer molecules tend to avoid one another and polymer-solvent contacts are preferred; when A_2 is negative, the molecules

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*This coefficient is sometimes called B, and sometimes B/RT; in order to avoid confusion, the term "A_2" will be used throughout this thesis.

attract one another and polymer-polymer contacts are preferred. Alternatively, A_2 may be considered as a measure of the volume -- the so-called "excluded volume" -- about the centre of a molecule that cannot, on the average, be occupied by the centre of another volume (4, p. 519; compare the term b, in the (V-b) term of the van der Waal's equation for gases, that corrects for the volume of the gas molecules).

Consideration of theories* relating A_2 to molecular size and structure leads to the expectation that A_2 should be lower for a branched molecule than for a linear molecule of the same molecular weight. As shown by Stockmayer and Fixman (24), equations developed by Zimm (147) relating A_2 to parameters such as the molecular weight can be extended to various types of branched molecules. Although the equations are limited in scope, they predict a decrease in A_2 for a branched molecule. This decrease arises from the compactness,for a given molecular weight, of a branched molecule compared to a linear one; the volume effect is consequently less for the branched molecule. Theories developed by Kurata (150) lead to a similar prediction.

Quantitative data are, unfortunately, scarce, and lacking in precision. Also, unless linear material of the same molecular weight as the branched is available for a comparison, the predicted decrease in A_2 may be obscured by the normal de-

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*Theoretical calculations of the second virial coefficient have, however, had only limited success (24, 147, 148, 149).

crease with increasing molecular weight (151).

The most clear-cut evidence indicating the decrease in A_2 (or increase in μ) caused by branching may be found in the results reported by Thurmond and Zimm (8). They found that values of A_2 -- say, about 0.6 -- for fractions of cross linked polystyrene in butanone tended to be lower than values -- say, about 1.2 -- for linear polystyrene. Also, Doty, Brownstein, and Schlener (59) found values of μ for cross linked polystyrene that were higher than expected.

Other data are less conclusive. Although, for example, Senti and others found that the value of A_2 for dextran fractions decreased from 14.8×10^{-4} to 0.7×10^{-4} while the molecular weight increased from 1.8×10^4 to 9.5×10^6 (see also references 46 and 138), it is impossible to separate the effect of branching from the decrease due to an increase in molecular weight. The magnitude of this decrease is greater than found experimentally for polystyrene (28) and may therefore reflect the presence of branching; nevertheless, the fact remains that a high molecular-weight sample in which branching is expected will have a low value of A_2, regardless of branching.

Some results for μ are contradictory. Muthana and Mark (152) and Billmeyer (121) found a correlation between μ and the degree of branching in polyethylene; on the other hand, Harris (142) reported that no relation between μ and the degree of branching was evident. Another example of constant

μ is given by the results obtained by Smets and Schmets (62) for branched polymethyl methacrylate; however, Huggins' k' (see next section) varied considerably from sample to sample.

Thus the determination of A_2 is useful chiefly for the confirmation of other, more direct, evidence for branching.

(c) Effect on Huggins' k'

The viscosity behaviour, at low concentrations, of many high polymers may be represented by an equation proposed by Huggins (153):

$$\eta_{sp}/c = [\eta] + k'[\eta]^2 c \quad \ldots \qquad \text{(A-13)}$$

where η_{sp}/c, the reduced viscosity, is equal to $(\eta_r - 1)/c$ (where $\eta_r = \eta$ solution/ η solvent), c is the concentration, in g./dl., and k' is a constant for a polymer-solvent system. If values of η_{sp}/c are plotted against concentration, the intercept at zero concentration is equal to the intrinsic viscosity $[\eta]$*.

The form of the equation indicates that the reduced viscosity, η_{sp}/c, of a polymer in solution is higher at finite concentrations than at zero concentration; the increase is proportional to the concentration, and to the square of the limiting effective hydrodynamic volume ($[\eta]$). This concentration effect is analogous to the effect of interactions between pairs

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*In order to avoid the incongruity of calling a function such as $[\eta]$, having the dimensions of specific volume a "viscosity", it has been suggested (154) that $[\eta]$ be called the "limiting viscosity number" and be given the dimensions of ml./g. However, the more conventional term "intrinsic viscosity" is used throughout this thesis.

of independent, dense spheres. Since polymer molecules do not behave as dense spheres, Huggins introducted the correction term k'. However, the constant is not simply a hydrodynamic correction term; it is also a function of the solvent, and, to some extent, the molecular weight of the polymer (111).*

Although Huggins' k' has no clear physical significance (160), it has proved to be a useful parameter for the characterization of polymer-solvent systems. There is ample evidence, for example, that the value of k' for a given polymer is higher in poor solvents than in good ones. These results agree with the prediction by Simha (161) that k' should be higher in poor solvents, where interactions between polymer molecules -- or between segments of the same molecule -- contribute to the concentration dependence of the reduced viscosity more than the interactions between solvent and polymer molecules do.

Simha also predicted that the value of k' should be increased by the presence of branching. The results of many studies have, indeed, fulfilled Simha's prediction that k' should be higher for a branched than for a linear molecule, the k' of which lies usually in the range 0.3 - 0.4. In fact, measurements of k' have been used as indications of the presence of branching (see below).

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*For more details see papers by Cragg and others (155, 156, 157); also, see Bigelow (158) and Manson (159) for more comprehensive surveys of the literature dealing with various aspects of k'.

A large number of observations of high values of k' for polymers prepared under conditions likely to favour the occurrence of crosslinking or branching have been made.*

Considerable work carried out with diene polymers believed to be partially branched led Henderson and Legge (163) to conclude that k' increases with the degree of branching or crosslinking in a polymer. This conclusion was supported by results of a series of experiments conducted in this laboratory by Switzer (164), Brown (155), and Fern (156). When polymers, for example, GR-S, containing branched material were carefully fractionated, the values of k' obtained for the fractions decreased regularly with the intrinsic viscosity. Finally, the values of k' for the lower fractions reached a constant value characteristic of linear species of the same polymer. Also, k' values were higher than usual for polymers prepared at high temperatures, the use of which would tend to increase crosslinking and branching. A similar decrease in k' was found by Mochel, Nichols, and Mighton (165) for fractions of Neoprene GN; values of k' ranged from 0.92 for the top fraction to 0.37 -- a value characteristic of many linear polymers -- for the lowest fraction. Although Pollock, Elyash,

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*Caution must be used, of course, before a high value of k' is attributed solely to branching. As pointed out by Cleverdon, and Smith (162), values of k' may vary greatly from sample to sample owing to differences in such variables as the content of polar impurities. Also (compare the case of μ), k' seems to be slightly dependent on molecular weight (27).

and De Witt (137) obtained values of k' for fractions of polybutadiene, the irregularity of the values obscured any trend that might have existed.

Vinyl polymers susceptible to chain transfer often show large differences in the values of k' for high and low molecular-weight fractions. For example, Menčik and Lanikova (166) found a k' value of 0.33 for a sample of polyvinyl chloride believed to be fairly linear in structure, but a value of 0.51 for the soluble portion of a sample that contained some gel. In another study of polyvinyl chloride, Danusso, Moraglio and Gazzera (167) found values of k' ranging from 0.38 for the lowest fraction to 0.63 for the highest one. For the same polymer, Cernia and Ciampa (168) found the following values of k': branched, 0.41; linear, 0.36.

Naidus and Mark (169), studying fractions of polyvinyl n-butyl ether, found an average value of k', 0.50, for the lower five fractions; in contrast, the average value of k' for the upper five fractions, in which branching might be expected, was 0.80.

The ageing of polyvinyl acetate provides another example of the effect of crosslinking on k'. Morrison, Holmes, and McIntosh (170) noted that, with polyvinyl acetate containing small amounts of ferric ion, which is known to effect crosslinking in polyvinyl acetate, the k' of a solution changed from 0.34 to 0.39 after ageing for three days. They concluded that the effect was due to a change in structure such as could be brought about by branching. An increase in the value of k' due to ageing at 200°C. was also found for polyvinyl acetate by Nagai and Sagane (171).

A comparison of the viscosity behaviour of samples of polyvinyl acetate that had been prepared at low temperature with samples that had been prepared at a high temperature, which would favour branching, was recently completed by Hobbs and his group (172); results showed that the samples presumed to be branched had higher values of k' than the samples presumed to be linear. With polyvinyl acetate prepared to high conversion, however, Howard (13) found no marked change in the value of k' for a high molecular weight sample ($M = 1.8 \times 10^6$) from the value found for a lower molecular weight one ($M = 6.3 \times 10^3$). Similar results were found by Varadaiah (173). No significant changes in k' with molecular weight were found by Hachihama and Sumitomo (174) for polyethyl acrylate; polyethyl methacrylate was found to behave in a similar fashion (129).

A large increase in k' (0.58 to 1.02) for high molecular weights was noticed by Harris (142) for polyethylene, which is known to be highly branched. Values of k' for polyethylene were also determined by Billmeyer (121); unfortunately, the data were badly scattered.

The irradiation of polyethylene terephthalate in a nuclear reactor was found by Todd (42) to yield products having values of k' higher than usual for the ordinary terephthalate.

Charlesby (175), on the other hand, studying polysiloxanes branched by irradiation, found no difference in k' from the value found for linear polysiloxanes; he concluded that k' was not sensitive to a degree of branching corresponding to two branches per molecule.

The study of the viscosity behaviour of starch isomers provides a convincing demonstration of the influence of branching on k'. Speiser and Whittenberger (176) found that the k' for amylopectin, the branched isomer, was 1.49 -- much greater than the value of 0.58 found for amylose, the linear portion. Similar results have been obtained by Wolff, Gundrum and Rist (177). Since a clear separation of the branched from the linear isomer is readily achieved with starch -- though not with other polymers discussed here -- this evidence is especially important. Another branched polysaccharide is dextran; high values of k' have been found for high molecular weight fractions of dextran (47).

Although not many data have been published for polymers that have been branched or crosslinked deliberately, the data available tend to support the conclusion that k' is increased by branching.

With the branched polylactams (1,2,4, or 8 branches per molecule) synthesized by Schaefgen and Flory (98), a slight trend towards an increase in k' may be detected, in spite of considerable scatter in the data. The value of k' ranged from 0.31, for a linear polyester, to 0.40, for the most highly branched materials. The data obtained by Youngson and Melville (99, 143) for branched polyesters also showed, in spite of scatter, a trend towards an increase in k' with the number of branches.

Although Valyi, Janssen, and Mark (60) found no deviations in the value of k' for fractions of polystyrene cross-linked with divinylbenzene from normal values (0.4), Walker and Winkler (56) found unusually large values of k' (for example, 0.80 vs. 0.38 for linear polystyrene) for fractions of soluble copolymers of styrene and divinylbenzene. Other studies of fractions of styrene-divinylbenzene copolymers showed that k' increased progressively from 0.40 to 1.14 as the intrinsic viscosity increased, whereas k' for polystyrene prepared under normal conditions was 0.40 (159). Especially large increases of k' -- which changed from 0.41 to 2 -- were found by Smets and Schmets (152) for polymethyl methacrylate that had been crosslinked with ethylidene dimethacrylate; oddly enough, the maximum value of k' was found for a middle fraction (low molecular weight, and low intrinsic viscosity), rather than for a top fraction.

Measurements of k' for graft polymers have been reported in few cases. When Merz (69) prepared polycyclohexyl methacrylate by means of a two-stage polymerization -- one stage thermal and the other, which would probably involve grafting, catalyzed by benzoyl peroxide -- he found two peaks in the molecular-weight distribution curve corresponding to k' values of 0.35 and 0.68. Results for another graft-type product were obtained by Jones (117), who found that the value of k' for polystyrene containing branches composed of methyl methacrylate varied from 0.4 to 0.8 -- with the high values corresponding to samples with relatively high degrees of branching.*

High values of k' were characteristic of the graft polymers prepared by means of milling rubber in the presence of vinyl monomers (96).

Hence, there have been good indications that the value of Huggins' k' is increased considerably by branching. It should be noted, however, that most of the studies discussed above deal with cases of random branching, that is, with cases in which branches may themselves be branched.

(d) Effect on Other Properties

The effects of branching on the reciprocal particle-scattering function P_θ^{-1} (see next section), on the osmotic pressure curve, and on the curve relating reduced viscosity to concentration will be considered briefly.

Although the curvature of the reciprocal particle-scattering function P_θ^{-1} plotted as a function of angle is sensitive to branching, Stockmayer and Fixman (24) have shown that the effect of branching is so small that masking by variations caused by polydispersity with respect to molecular weight becomes probable. Moreover, the precision with which

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*These results were reported at the same time as results of Part II of this thesis (111).

scattering measurements can be obtained decreases rapidly at small angles because of scattering from residual dust.

Benoit (178) has also shown that the shape of the reciprocal particle-scattering function is related to both the degree of branching and the polydispersity; useful information can be obtained only if only one of the two effects is present, unless precise knowledge of the degree of polydispersity is available.

Kunst and Magat (179) have derived expressions relating the slope of the osmotic pressure curve to the degree of branching; however, detectable effects would be found only for high degrees of branching.

Although Batzer (180) has suggested that the presence of branching in some polyesters causes curvature in the line relating reduced viscosity to concentration (see equation A-13), Patat and Elias (181) found no evidence for such an effect in the case of polyvinyl acetate. Similarly, no effect was found by Kapadia (182) for sol and gel rubber, or by Menčík and Laníkova (166) for polyvinyl chloride.

B. Light-Scattering

Measurements of light-scattering have provided much useful information about the properties and behaviour of high polymers. The molecular weight may be calculated from the intensity of scattering (at right angles to the incident beam), the molecular extension in solution from the angular dependence of the scattering, and the osmotic second virial coefficient from the dependence of the scattering on concentration.

The basic relationships between the scattering of light and molecular properties are briefly reviewed in the following pages; current methods for the treatment of light-scattering data are also outlined. More detail about principles, methods, and applications may be found in references given.

1. Principles of Light-Scattering

(4, Chapter VII; 183; 184, p. 35; 185; 186,
Chapter 7; 187, 188)

A homogeneous, non-absorbing medium readily permits the passage of a beam of light without alteration of its intensity. The presence of non-absorbing particles having a refractive index different from that of the medium results, however, in a disturbance of the incident light beam. If the particles are small and randomly distributed, this disturbance takes the form of scattering of the light. In other words, the oscillating electric field of the light beam induces oscillations in the electrons and nuclei of the particles, which then, acting as secondary sources of radiation, emit light in all directions. If the very small contribution from Raman scattering in neglected, the scattered light has the same frequency as the incident beam and may be characterized by its intensity at a stated angle relative to the incident beam, the angular distribution of intensity, and its state of polarization.

(a) Scattering by a Dilute Gas

The quantitative treatment of scattering by a dilute gas was given by Lord Rayleigh (189). He derived the following expression relating the intensity of scattered light to the characteristics of the particles concerned and of the incident light (in this case, unpolarized and directed horizontally):

$$\frac{i_\theta r^2}{I_o} = \frac{8\pi^4 \nu \alpha^2}{\lambda_o^4} (1+\cos^2\theta) \qquad \text{(B-1)}$$

where i_θ = the intensity of the light scattered at angle θ,
r = the distance from the molecules to the detector,
I_o = the intensity of the incident beam,
ν = the number of scattering particles per c.c., and
λ_o = the wavelength, in vacuum, of the light.

Since the scattered light has two components -- one propagated uniformly in all directions with a vertical plane of vibration, and the other, the intensity of which depends on $\cos^2\theta$, having a horizontal plane of vibration -- the factor $(1+\cos^2\theta)$ is used to normalize the observed scattering so that the scattering will be symmetrical about the scattering source. For the sake of convenience, the term $(1+\cos^2\theta)$ will henceforth not be considered explicitly; it will be assumed that all scattering intensities have been normalized by means of this term. The ratio $i_\theta r^2/I_o$, or R_θ, is often called the "reduced intensity"; for $\theta = 90^\circ$, the ratio is called the "Rayleigh ratio".

The polarizability α may be replaced by a term which is a function of the difference between the dielectric constant of the gas, ϵ, and the dielectric constant of the medium, ϵ_o (which equals unity for a vacuum). In turn, the dielectric constant may be replaced by the square of the refractive index n (measured, of course, at the same wavelength). Thus, for a dilute gas having n close to unity

$$\alpha = \frac{\epsilon - \epsilon_o}{4\pi\nu} = \frac{n^2 - 1}{4\pi\nu} \cong \frac{2(n-1)}{4\pi\nu} = \frac{(n-1)}{2\pi\nu} \qquad \text{(B-2)}$$

Combination of equations B-1 and B-2 gives

$$\frac{i_\theta r^2}{I_o} = \frac{2\pi^2(n-1)^2}{\lambda_o^4} \cdot \frac{1}{\nu} \qquad \text{(B-3)}$$

Since the scattering depends on ν (ν being equal to cN/M), the number of particles per unit volume, either Avogadro's number, N, or the molecular weight, M, may be determined from scattering observations.

It is sometimes convenient to measure the attenuation of the incident beam due to scattering, rather than the intensity of the beam itself. The attenuation may be represented by the turbidity τ, which is equivalent to the extinction coefficient in the equation $I = I_o e^{-\tau l}$ (I being the intensity of the transmitted beam, and l the length of the medium traversed). Integration of i_θ over the surface of a sphere with radius r yields the relation

$$\tau = \frac{8\pi}{3} \cdot \frac{i_0 r^2}{I_0} = \frac{16\pi}{3} \cdot \frac{i_{90} r^2}{I_0} = \frac{8\pi}{3} R_0 = \frac{16\pi}{3} R_{90} \qquad \text{(B-4)}$$

(b) <u>Scattering by an Ideal Polymer Solution: Small Molecules</u>

Although measurements of Rayleigh scattering had been used by Staudinger and Haenel-Immendörfer (190) and Putzeys and Brosteaux (191) for the study of glycogen, and by Gehman and Field (192) for the study of rubber, the application of light scattering to the determination of the molecular weights and sizes of high polymers did not become general until Debye (193, 194) showed how the Rayleigh equation could be extended to polymer solutions.

For the case of dilute (ideal) solutions of small (small, that is, in comparison to λ) isotropic molecules, Debye derived an expression analogous to Equation B-3. Using the refractive index increment, $\frac{n - n_o}{c}$ (n and n_o being the refractive indices for solution and solvent, respectively), Debye replaced the dielectric constant in Equation B-2 in the following way:

$$\begin{aligned} \frac{\epsilon - \epsilon_0}{c} = \frac{n^2 - n_0^2}{c} \cong \frac{dn^2}{dc} \cong 2 n_0 \frac{(n - n_0)}{c} \\ \cong 2 n_0 \frac{dn}{dc} \end{aligned} \qquad \text{(B-5)}$$

Combination of equations (B-1), (B-2) and (B-5) with the relation $\nu = cN/M$ leads to the expression

$$R_{90} = \frac{2\pi^2 n_0^2 (dn/dc)^2 c M}{N\lambda_0^4} = KcM,$$

$$\text{or} \quad K\frac{c}{R_{90}} = \frac{1}{M}, \qquad \text{(B-6)}$$

and the combination of equations (B-6) and (B-4) leads to the expression

$$\tau = \frac{32\pi^3 n_0^2 (dn/dc)^2 c M}{3N\lambda_0^4} = HcM, \qquad \text{(B-7)}$$

$$\text{or} \quad H\frac{c}{\tau} = \frac{1}{M}.$$

The constants H and K are thus characteristic of a given polymer-solvent system; their determination requires only the measurement of the refractive indices and the refractive index increment. It is assumed that the measured Rayleigh ratio or turbidity for the solvent has been subtracted from the corresponding value for the solutions so that the values used in equations (B-6) and (B-7) represent the contribution of the solute to the scattering.

Equations (B-6) and (B-7) are analogous to the van't Hoff equation($\frac{\pi}{RTc}$ = 1/M, where π, R, and T represent the osmotic pressure, molar gas constant R, and the absolute temperature, respectively).

The value of M obtained for a high polymer, which is always to some extent inhomogeneous with respect to molecular weight, is a weight-average quantity (4, p. 291). Since the polarizability α is proportional to the size of the molecule, the intensity of the scattering by a molecule is proportional to the square of the size, or to the square of the molecular weight

$(KcM = K \nu M^2/N)$. Assuming that H is independent of M, the total turbidity of a solution containing polymer molecules having different molecular weights becomes

$$\tau = H \sum c_i M_i$$

where c_i is the concentration of molecules having molecular weight M_i. Alternatively

$$\tau = H c M_w .$$

In this equation, c is equal to $\sum c_i$, and M_w is the weight-average molecular weight defined by

$$M_w = \frac{\sum c_i M_i}{\sum c_i} = \frac{\sum n_i M_i^2}{\sum n_i M_i} .$$

In this relationship, n_i is the number of molecules having molecular weight M_i, and $c_i = n_i M_i/N$.

(c) Scattering by Non-Ideal Polymer Solutions: Small Molecules

For non-ideal solutions at finite concentrations, the limiting expressions (B-6) and (B-7) are no longer valid; in such a case, the particles are no longer far enough apart to be considered as independent, randomly distributed scattering units. Because of the mutual interference of light waves scattered by the particles, the intensity of scattered light observed is, in general, lower than the corresponding intensity for random scattering units.

The problem of the calculation of the decrease in intensity owing to interference was studied by Einstein (195) and Smoluchowski (196). They considered the scattering of light as the result of fluctuations of refractive index within arbitrarily chosen volume elements. These fluctuations arise from two sources -- variations in density and variations in concentration; the result of these variations is a fluctuation in the dielectric constant, and hence, scattering. Fluctuations in density correspond to scattering by the solvent, and may, to a good approximation (197), be neglected if the solvent scattering is subtracted from the total scattering of a solution.

Einstein related the fluctuations in concentration to the concentration dependence of the free energy of dilution of the solvent. Using the osmotic pressure π as a measure of the free energy of dilution, Einstein obtained the following equation for the turbidity due to concentration fluctuations:

$$\tau = \frac{8\pi^3}{3\lambda_0^4} \cdot \frac{RTc}{N\left(\frac{\partial\pi}{\partial c}\right)} \cdot \left(\frac{\partial\epsilon}{\partial c}\right)^2 \qquad \text{(B-8)}$$

For ideal solutions, $\partial\pi/\partial c =$ RT/M; hence the scattering is proportional to the molecular weight of the solute -- a result obtained before in equations (B-6) and (B-7). Combination of equations (B-5) and (B-8) with the substitution of RT/M for $\partial\pi/\partial c$ then leads to equations (B-6) and (B-7) -- the limiting relations at zero concentration.

For non-ideal solutions of moderate concentration*, the

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*Terms corresponding to a higher power of the concentration may be necessary at higher concentrations.

equation

$$\frac{\pi}{RT_c} = A_1 + A_2 c \ldots = \frac{1}{M} + A_2 c \ldots \qquad \text{(B-9)}$$

expresses the concentration dependence of the osmotic pressure. By combination of equations (B-5), (B-8), and (B-9), Debye (193) obtained the following expression:

$$H\frac{c}{\tau} = \frac{1}{M} + 2A_2 c \ldots \qquad \text{(B-10)}$$

The equivalent expression for the reduced intensity is, of course,

$$K\frac{c}{R_{90}} = \frac{1}{M} + 2A_2 c \ldots \qquad \text{(B-11)}$$

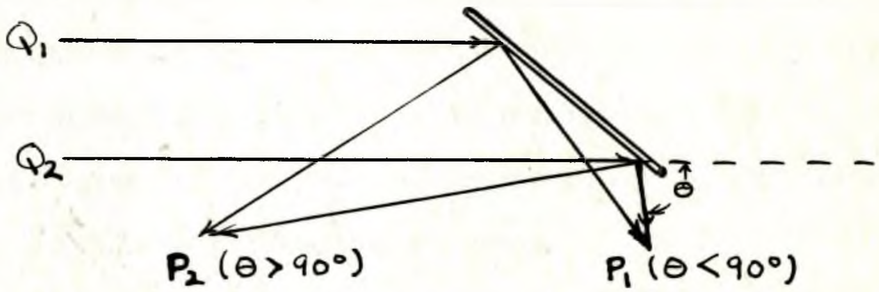
The close relationship between osmotic pressure and light scattering is apparent.

The molecular weight may be calculated from the intercept obtained from a plot of $H \frac{c}{\tau}$ against c; A_2 may be calculated from the slope of the same curve.

If the molecules are anisotropic (that is, if their polarizability is not the same in all directions) a correction is necessary. Although the light scattered at 90° by an isotropic molecule from an unpolarized incident beam is completely polarized in the vertical direction, the light scattered by an anisotropic molecule contains a horizontally polarized, as well as the vertically polarized, component (198). The contribution of the horizontal component is eliminated by the multiplication of R_{90} by the correction factor $(6 - 7\rho_u)/(6 + 6\rho_u)$ and of τ by the correction factor $(6 - 7\rho_u)/(6 + 3\rho_u)$, where ρ_u is the ratio of the horizontal component of the scattered light ($\theta = 90°$) to the vertical component (198, 199, 200).

(d) Scattering by Polymer Solutions. Large Molecules

In the derivations outlined above, it has been assumed that the polymer molecules concerned have been small in comparison with the wavelength of the light. If, however, a linear dimension of a polymer molecule is greater than about one-twentieth of the wavelength of the light, it is no longer possible to consider the molecule as a point source of scattered radiation. Destructive interference between rays scattered by different parts of the molecule occurs, as illustrated in the accompanying diagram. Although the total path length Q_1P_1 is not very different from the path length Q_2P_1, the overall path lengths Q_1P_2 and Q_2P_2 are quite different from each other. The net result is that the total scattering in the backward direction ($\theta > 90°$) is reduced by interferences of the sort taking place between rays Q_1P_2 and Q_2P_2. The angular scattering pattern is, therefore, no longer symmetrical -- as it was for small-particle scattering, after normalization by the $(1 + \cos^2\theta)$ term. The solution is



said to exhibit "dissymmetry." Dissymmetry is conventionally measured by the ratio $z = i_{45}/i_{135}$, though any ratio of the type $i_{(90 - a)}/i_{(90 + a)}$ would serve as well.

Although the existence of dissymmetry makes necessary the use of a correction to R_{90} in order to allow for the decrease of R_{90} caused by intraparticle interference, the dissymmetry has a very useful implication. Since the amount of interference is related to the distribution of segments in the molecule, the dissymmetry is a function of both the size and shape of the molecule in solution. As long as the molecules are large enough (length about 100-200 A°), the dimensions of the molecule may be determined from dissymmetry measurements.

Unfortunately, rigorous calculation of the scattering by large particles is complicated by the fact that the electrical field of the incident beam is distorted by a factor proportional to the ratio of the refractive index of the particle to the refractive index of the medium. In fact, exact calculations have been carried out only for isotropic spheres; see, for example, Mie (201), Heller and Pangonis (202), and La Mer and Barnes (203). However, by assuming that the field of the incident beam is undistorted as long as the refractive index ratio n/n_o is small, Debye (193) was able to obtain expressions for the scattering by several models.

To account for the decrease in the observed intensity of scattered light owing to intraparticle interference, a factor P_θ, the "particle scattering factor", may be introduced (185, 204). The particle scattering factor is defined as follows:

$$P_\Theta = \frac{i_\Theta}{i_\Theta^\circ} = \frac{R_\Theta}{R_\Theta^\circ}$$

where i_θ° and R_θ° are the intensity and Rayleigh ratios, respectively, which would be observed at angle θ in the absence of interference.* Thus, multiplication of the observed values of R_θ or τ by $1/P_\theta$ restores the validity of equations (B-6) and (B-7), provided the concentration is low.

There remains the determination of P_θ and its relation to the particle shape, size, and dissymmetry ratio. Assuming that the electric field of the incident beam is not appreciably distorted by the refractive index difference existing between particle and medium, Debye summed the intensity of scattering observed over all pairs of scattering elements (193). The results for various models are (185, 193, 205, 206, 207)**:

Spheres: $P_\Theta = \left[\frac{3}{x^2}(\sin x - x\cos x)\right]$; $x = \frac{sD}{2}$

Rods: $P_\Theta = \frac{1}{x}\int_0^{2x} \frac{\sin \omega}{\omega}\, d\omega - \left(\frac{\sin x}{x}\right)^2$; $x = \frac{sL}{2}$ (B-12)

Random coil (monodisperse) : $P_\Theta = \frac{2}{x^2}\left[e^{-x} - (1-x)\right]$; $x = \frac{s^2 R^2}{6}$

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*The terms i_θ° and R_θ° correspond exactly to the terms i_θ and R_θ used earlier; the superscript is used here only to distinguish between the <u>observed</u> and the <u>theoretical</u> intensities.

**Expressions for spheres were obtained earlier by Lord Rayleigh and Gans (208,209); in fact, the relationship $R_\theta = KcMP_\theta (1 + \cos^2\theta)$ is called the Rayleigh-Gans scattering law. For calculations of P_θ for various models, see references 210 to 214.

where s is equal to $(4\pi \sin\frac{\theta}{2})/\lambda$, λ is the wavelength of the light in solution, D is the sphere diameter, L the rod length, and R the root-mean-square end-to-end coil distance. Calculations of these relationships were normalized so that the value of P_θ approaches unity as x approaches zero, that is, as D, L, or R decreases, as λ increases to infinity, or as θ approaches zero.

Values of $1/P_{90}$ as a function of the limiting dissymmetry ratio $[z]$ ($[z] = \lim\,(z)_{c \to 0}$) have been computed by Cashin (205) and Doty and Steiner (185), and plotted by the latter authors; curves have also been plotted giving $1/P_{90}$ as a function of D/λ , L/λ , and R/λ (185).

Now the particle scattering factor may be introduced into the expression for a random coil (equation B-12) to give

$$H\frac{c}{\tau} = K\frac{c}{R_{90}} = \frac{1}{MP_{90}} + 2A_2c\ldots \tag{B-13}$$

or, the following general equation holds:

$$K\frac{c}{R_\theta} = \frac{1}{MP_\theta} + 2A_2c\ \ldots. \tag{B-14}$$

Although, strictly speaking, A_2 is valid as a correction term only when P_{90} equals unity, while P_θ is valid only when A_2 equals zero, Zimm (207) has shown that equation (B-13) is valid to a good approximation.

With P_{90} found for the model assumed (usually a random coil), the molecular weight M may be determined from the intercept of a plot of Kc/R_{90} against concentration, and A_2, as before, from the slope of the curve.

The dimension may then be calculated. Since the curves representing the particle scattering factor as a function of dimension are single parameter ones, the linear dimension of a given model may be calculated from a ratio of observed scattering intensities at two angles. The ratio required is conveniently given by the limiting dissymmetry ratio $[z]$. As mentioned above, tables and graphs (185) have been prepared giving D/λ , L/λ , or R/λ as a function of $[z]$. Thus, if values of the dissymmetry ratio z are determined for each concentration used for a molecular weight determination, the value of the appropriate linear dimension may be readily found from the limiting value $[z]$, of the dissymmetry ratio. If only particle dimensions are desired, the extrapolation procedure described by Cleverdon, Laker, and Smith (215) may be used; this procedure requires no knowledge of the concentration. As mentioned earlier, the dimension found is a z-average quantity.

As with small particles, a correction for depolarization may be required. The correction factor appropriate for large particles may be derived from the factors given above by substitution of $2\rho_v$ for ρ_u, where ρ_u equals the ratio H_v/V_v -- H_v and V_v being the horizontal and vertical components of light scattered from an incident, vertically polarized light beam (197, 198).

2. Measurement of the Intensity of Scattered Light

(a) Methods

(i) Dissymmetry method:- In the previous section, it was shown that values of molecular weight, size, and the second virial coefficient may be derived from the measurements of the intensity of light scattered at three angles, and at several concentrations. The dissymmetry method is convenient and rapid; interpretation of the data is fairly straightforward.

One disadvantage is the need for the assumption of a model; sometimes, however, the validity of the model assumed may be tested. If the molecular weight is known from independent measurements, the dimension calculated for a given model from the dissymmetry may be compared with the dimension calculated for the same model from the molecular weight.

(ii) Extrapolation method:- As mentioned above, the effects of intraparticle interference must vanish when x (see equation B-12) is equal to zero. Zimm (207) suggested that this condition could be achieved by extrapolation of scattering data to zero angle (for if $\theta = 0$, then $x = 0$ and $P_\theta = 1$). While the dissymmetry method requires the assumption of a model, use of the extrapolation procedure for the determination of molecular weight requires no assumption about particle shape.

With this method, scattering intensities are measured at several concentrations, and, for each concentration, at several angles. It is clearly desirable to have some angles as close to zero as possible. Two extrapolations are required -- one to zero angle, and one to zero concentration. This double extrapolation may be carried out in two ways.

With one way, the intercepts obtained by extrapolation of the scattering data to zero concentration may be plotted as a function of θ (usually $\sin^2 \frac{\theta}{2}$) and then extrapolated to zero angle (124).

Alternatively, the double extrapolation may, as suggested by Zimm, be made in the same graph. First, values of Kc/R_{90} are plotted against $\sin^2 \frac{\theta}{2} + kc$, where k is an arbitrary constant that serves to spread the data conveniently; then smoothed lines, that eventually form a grid, are drawn through the points at constant angle and constant concentration. Finally, each line is extrapolated to zero concentration or zero angle; the points thus obtained are then joined into two lines that should meet at the same intercept, $\left(K\frac{c}{R_\theta}\right)_{\substack{c=0\\ \theta=0}}$ on the y-axis.

The relationship between $K\frac{c}{R_\theta}$, the molecular weight, and the particle scattering factor P_θ, from which the dimension may be determined is easily found. Expansion of P_θ^{-1} in terms of the parameter (equation B-12) for a random coil gives (207);

$$P_\theta^{-1} = 1 + \frac{x}{3} + \cdots\cdots \qquad \text{(B-15)}$$

From the combination of equations (B-14) and (B-15), the following equation is obtained (after allowance for the fact that the data have been reduced to zero concentration):

$$\left(K\frac{c}{R_\theta}\right)_{c=0} = \frac{1}{M_w}\left[1 + \frac{x}{3} + \cdots\right] \qquad \text{(B-16)}$$

Similar equations may be derived for other particle shapes.

Hence, the intercept at zero angle will be equal to 1/M, if the incident light is vertically polarized, or 1/2M, if the light is unpolarized.* The dimension R may then be calculated from the ratio of the slope of the zero concentration line to the intercept. The second virial coefficient may be calculated from the slope of the zero-angle curve.

Although the value of molecular weight obtained by this procedure is independent of the particle shape, the determination of the particle dimension does require the assumption of a model. As a result, a difficulty may arise when a particle shape is unknown in advance. In such cases, however, a comparison of a curve of P_θ, determined from equation (B-16) as a function of $\sin^2\frac{\theta}{2}$ with the curve expected for various models may be helpful; see, for example, Steiner (206).

Under some circumstances, additional information may be obtained from a plot of $K\frac{c}{R_\theta}$ against $\sin^2\frac{\theta}{2}$. Benoit (178) has shown that if x is large, equation (B-16) becomes

$$\left(K\frac{c}{R_\theta}\right)_{c=0} = \frac{1}{M_n}\left[\frac{1}{2} + \frac{x}{2} + \cdots\right] \qquad \text{(B-17)}$$

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*The factor of two enters here because the polarization term ($1 + \cos^2\theta$), which is equal to unity when $\theta = 90°$, becomes equal to two when θ becomes zero.

The intercept of the curve at zero concentration yields, in this case, $1/2\ M_n$, and the slope, R_n. Benoit also found that the shape of the curve is a function of both the degree of branching and the degree of polydispersity; unfortunately, these variables affect the shape in opposite directions.

Later Holtzer, Benoit, and Doty (216) tested these conclusions in a study of polydispersity in cellulose trinitrate. Although the value of molecular weight found did in fact agree with the number-average molecular weight determined by measurements of osmotic pressure, the expansion used in equation (B-17) was found to hold only for chain lengths greater than about 2000 A°. Recently, Billmeyer and de Than used a similar procedure to determine M_n for some samples of polymethyl methacrylate (217).

Unfortunately, calculations based on the slope of the curve represented by equation (B-16) require very accurate measurements at angles close to zero. Since few instruments permit measurements at angles below about 30 or 35 degrees, and since accurate measurements at low angles such as these are difficult, owing to high forward scattering from impurities, precise calculations of the slope are quite difficult.

(iii) Transmission Method:- Direct measurements of the turbidity from transmission measurements is theoretically possible; in practice, the turbidity of most polymer solutions is too low for precise measurement in this way. Although with larger particles the turbidity may be high enough for measurement with a spectrophotometer, the problem of intraparticle interference requires attention. With the dissymmetry method, the interference may, according to Doty and Steiner (185), be corrected for by an analogous correction derived from measurements of turbidity at two wavelengths. Tables and graphs similar to the ones used for dissymmetry methods have been constructed; the correction term and the particle dimension may thus be determined from the wavelength dependence of the turbidity.

The extrapolation method may also be adapted to the use of transmission measurements. Since the intraparticle interference disappears when P_θ equals unity, it must disappear when χ becomes equal to zero (see equation B-11). In the extrapolation method, this reduction in interference is achieved by making the angle, θ, equal to zero (that is, by extrapolating all data to zero angle); a similar reduction may be achieved by making the wavelength, λ, infinite (that is, by extrapolating all data to infinite wavelength). The most serious restriction arises from the limited range of wavelengths available at which no absorption occurs; a minor difficulty is that measurements of the refractive index increment are required at all wavelengths. Nevertheless, this method has been used successfully several times (185, 218, 219).

Values of molecular weight obtained by means of the three methods appear to agree fairly well with one another; see Doty and Steiner (185).

In summary, the use of light scattering as a technique for the study of polymers has several advantages:

1. The property measured -- either τ or i_θ -- varies directly with the molecular weight. Hence light-scattering, in contrast, say, with osmotic pressure, is more, rather than less, sensitive to high molecular weights.

2. In general, the molecular weights obtained are weight-average ones, which are particularly useful for comparison with intrinsic viscosities. The molecular weights found agree well with values found by other methods (220).

3. Molecular dimensions may be obtained readily, as long as the size is greater than about 200 A°.

4. Thermodynamic information such as the second osmotic virial coefficient may be obtained readily.

5. Light-scattering measurements should, in principle, yield absolute, not relative, values of molecular weight (see next section for qualification of this advantage).

The validity of the light-scattering procedures for the determination of molecular weight is supported by the fact that values obtained from light-scattering measurements for the molecular weights of both polymeric and non-polymeric substances, and for Avogadro's number, agree well with values obtained by other methods; see, for example, Maron and Lou (221), Brice, Halwer, and Speiser (222), and Frank and Mark (220).

(b) Instruments

Many different instruments for the measurement of scattered light intensities have been constructed with variations in such characteristics as the range of scattering angles available, or the method of measuring intensities. A survey of typical examples of the most common types of instrument follows; the usual methods for the conversion of experimental data to absolute values of scattering will also be outlined.

The first measurements of light-scattering were made using visual or photographic methods for determining light intensities (193, 199, 223, 224). Visual turbidimeters have often been used effectively (190, 225-229); photographic methods are still used occasionally (230).

Most modern light scattering photometers, however, use photomultiplier tubes to measure the intensity of scattered light; the sensitivity of modern photomultiplier tubes is sufficient to permit work with very low intensities of scattering.

With some instruments, the current produced by the action of the scattered light on the cathode of the photomultiplier tube is measured directly; because of the high amplification inherent in a photomultiplier, a signal of reasonable magnitude may be obtained even with low-scattering material such as a pure liquid. This procedure, requiring only a sensitive galvanometer, or recorder, is simple and convenient; it has been used frequently (222, 231-239). Often, however, the current received from the photomultiplier is amplified further before measurement (194, 240, 241, 242).

In order to minimize the effects of variations in the intensity of the light source, the ratio of the intensity of the scattered light to the intensity of the incident beam may be taken as a measure of the reduced intensity.

One method for the measurement of the ratio desired involves the reflection of a portion of the incident beam towards a second phototube, which then serves as a monitor (194, 236, 240, 243-246). Another method for achieving the same result was used by Brice, Halwer, and Speiser (222), who designed their instrument so that the photomultiplier, protected by a filter, could be swung into the position corresponding to $\theta = 0$; the ratio of the intensity of scattering at angle θ to the intensity of the transmitted beam was taken as a measure of the reduced intensity. The use of the transmitted rather than the incident beam has the advantage that absorption of light is compensated for. The instrument developed by Brice, Halwer and Speiser (222) has been produced commercially,* and has found wide acceptance by many laboratories (129, 138, 141, 247-255). Other instruments based on the same principle have been used (231, 237). Another commercial instrument,** developed from a design by Oster (256), is also available (257-259).

Another method for the measurement of the ratio i_θ/I_o was used by Zimm (207). In the Zimm apparatus, the currents from the photomultiplier and the monitor are first applied to a null bridge, and then balanced by means of a precision potentiometer, the reading of which is proportional to the ratio desired. The null principle has also been used in other instruments (32, 66, 242, 260, 261, 262). Transmission measurements have usually been made in the Beckman precision spectrophotometer, or its equivalent (185, 218, 219).

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* Phoenix Precision Instrument Company, Philadelphia, Pa.

** American Instrument Company, Silver Spring, Maryland.

(c) Calibration

The light-scattering method for the determination of molecular weight is theoretically an absolute one. However, the determination of absolute values of reduced intensity depends on precise knowledge of factors such as the scattering volume illuminated and the volume "seen" by the photomultiplier; a rigorous analysis of the geometric optics is thus required. For example, Carr and Zimm (197) and Brice, Halwer, and Speiser (222), after considering the optics of their instruments in considerable detail, have obtained absolute measurements of reduced intensity. More recently, Kushner (249), using a modified Brice-Phoenix photometer, has demonstrated the absolute determination of the Rayleigh ratio; also, the instrument developed by Oster (256) has been modified by Kremen (260) in order to permit absolute measurements. Corrections required for the conversion of scattering data to absolute values of reduced intensity have been discussed by Carr and Zimm (197), Brice, Halwer, and Speiser (222), and Hermans and Levinson (263); see Part II of this thesis for other references.

If the corrections required are well-defined, absolute measurements may be made by comparing the intensity of the scattered light with the intensity of a portion of the incident beam. The ratio may be measured directly (194, 264) -- provided the intensity of the incident beam has been weakened by a known factor -- or indirectly, by comparison of the scattering for a solution with the scattering from a secondary standard of known reflectance or transmittance, and intensity distribution (197, 222, 265).

Another, more difficult, method of obtaining absolute values of scattering involves the use of an integrating sphere (197) arranged to collect all the light scattered by a solution. Direct measurements of transmission are also possible; very high accuracy is required.

The most common method for the conversion of experimental data to absolute values of reduced intensity is, the indirect method mentioned above -- namely, the comparison of the scattering for a solution with the scattering from a secondary standard, which has, itself, been calibrated in absolute terms.

Various materials have been used as secondary standards. Blocks of a substance, such as magnesium carbonate or magnesium oxide, the reflectance of which is known, may be used (197, 265); blocks of a solid polymer, for example, polystyrene, have sometimes been calibrated for use as working standards (207,228, 266). Pure liquids such as benzene, toluene, or carbon disulfide, have found wide acceptance as secondary standards* (66, 200, 228, 232, 241).

Two other liquid standards have been found by many laboratories to be convenient. One liquid is a solution of polystyrene; the other is an aqueous dispersion of colloidal silica.

The solution of polystyrene is prepared, at a specified concentration, from a sample of polystyrene distributed by Professor Debye and Dr. A. M. Bueche of Cornell University. Good

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*Although there has been some disagreement concerning the absolute values of Rayleigh's ratio for pure liquids (230, 264, 267, 268, 269), the values obtained by Carr and Zimm (197) and Brice, Halwer, and Speiser (222) are now generally accepted (265).

agreement between the values for the turbidity of this solution determined at different laboratories has been obtained (see Part II of this thesis). Use of this solution as a calibration standard eliminates much uncertainty due to differences between, say, samples of a pure liquid prepared in different laboratories.

Use of the suspension of colloidal silica -- a commercial product, "Ludox" -- was first suggested by Oster (270). The scattering of a solution is compared to the scattering of a diluted portion of the dispersion, the turbidity of which has been previously determined by means of a precision spectrophotometer. This method of calibration has been discussed in some detail by Maron and Lou (221), Kraut and Dandliker (271), and Mommaerts (272). At present, calibration using Ludox dispersions is, perhaps, the method in most common use; see, for example, references 234, 237, 238, 255, or 270 to 274.

I. PREPARATION OF BRANCHED POLYMERS
BY GRAFT POLYMERIZATION

Introduction

In choosing a polymer suitable for the study of branching by viscosity and light-scattering techniques, the following characteristics were considered to be important:

1. The polymer should have a known number of simple, linear side chains.

2. The molecular weight should be high enough (greater than, say, 5×10^5) that accurate measurements of size and intrinsic viscosity could be made.

Unfortunately, most methods available at the time for the preparation of branched polymers were unsuitable for the preparation of samples fulfilling the requirements just listed.

The use of methods based on chain transfer or on the copolymerization of a monomer with a crosslinking agent results in a mixture of linear and branched polymers that is often difficult to resolve into its linear and branched components. Moreover, these methods do not yield polymers with simple branches; both chain transfer and crosslinking result in the growth of branches on branches. This type of complex branching may eventually progress to the point of gelation; in fact, when a crosslinking agent is present, it is difficult to avoid gelation.

Although the condensation of a monomer with a molecule having a known number of reactive functional groups had been used successfully by Schaefgen and Flory (98) to produce polymers having a known number of branches per molecule, the number of branches thus obtained was restricted by the limited number of suitable functional groups -- four or eight, in the case just mentioned -- that could be present in the backbone molecule. Another difficulty with this type of synthesis was that the molecular weights obtained were low (less than 38,000).

When these disadvantages were considered, the technique developed at the Polytechnic Institute of Brooklyn* for the grafting of side chains onto a vinyl-type backbone seemed very attractive. As well as making possible the control of the degree of branching (by variation of the hydroperoxide content of the oxidized backbone polymer; see Historical Introduction), this new method offered the convenience of a product free from linear material.

Several graft polymerizations were therefore made using, as backbone polymers, polystyrene and copolymers of styrene and 4-vinyl-cyclohexene-1 -- these last being expected to oxidize more readily than styrene alone. After the backbone polymers had been oxidized to various degrees, the products were used as initiators in the redox polymerization, in emulsion, of styrene, and, in a few cases, of methyl methacrylate.

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*This technique was described in a lecture at McMaster University by Dr. Herman Mark; the author is grateful to Dr. Mark for helpful comments.

In this section, the preparation of the graft polymers is described. Also, evidence that grafting did occur is presented and discussed. This evidence was obtained from measurements of monomer disappearance, of the decrease in hydroperoxide content of the backbone polymer during reaction, and of the infrared absorption by the polymer before and after the grafting procedure. Finally, measurements of intrinsic viscosity are given.

Further, more direct evidence for grafting, based on intrinsic viscosity and light-scattering measurements, may be found in Part III.

Experimental*

1. Materials

Monomers were provided by the Polymer Corporation, Limited, Sarnia. Before use they were freed from inhibitor by washing with dilute aqueous potassium hydroxide; after rinsing with distilled water they were dried with Drierite. Cumene hydroperoxide (60%) was also provided by the Polymer Corporation. Phenyl-β-naphthylamine and benzoyl peroxide were both Practical grade reagents supplied by the Eastman Kodak Company.

Polystyrene samples used for oxidation were prepared by a method described earlier (159); amounts of dodecyl mercaptan used were, however, variable. Copolymers of styrene and 4-vinylcyclohexene-1 were prepared using a similar recipe; alkylated polymers were made by the method outlined by Metz and Mesrobian (110).

Tetralin, of Certified Chemical grade, was obtained from the British Drug Houses. Other solvents were of technical grade, and were used without further purification.

Inorganic reagents were of the Analar grade supplied by the British Drug Houses, or of equivalent quality. Nitrogen was purified by passing first through freshly-prepared Fieser's solution (275, p. 395) and then through a saturated solution of lead acetate.

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*The author wishes to acknowledge assistance given at various times by the following: Mrs. D. Coleman, Mr. J. Hunt, Mr. D. Wiles, and Mr. L. Murrell. He is also grateful to the Polymer Corporation, Limited, for the donation of materials, and to Dr. H. L. Williams of that company for helpful advice.

2. Oxidations

Solutions of low molecular weight polymers, with a concentration of about 5 g. of polymer per 100 ml. of solution, were oxidized in a 250-ml. gas-scrubbing bottle. The bottle was clamped in an oil bath that was operated at a temperature within the range from 70 to 80°C. -- usually at 75°C. -- with regulation of temperature to within ± 0.2°C. Oxygen was then bubbled through at a rate sufficient to bring about rapid and thorough bubbling without excessive foaming; no attempt was made to regulate the flow of oxygen precisely.

The oxidation of polymers having high molecular weights and hence high viscosities required the use of more dilute solutions, with concentrations ranging down to about 2 g. of polymer per 100 ml. of solution. Where the solution was very viscous, mechanical stirring was necessary; in such cases, a round-bottomed flask equipped with a fritted-glass bubbling tube and a mechanical stirrer was used as the oxidation vessel. In general, these oxidations were less successful than ones using low molecular weight polymers.

After bubbling had been continued for a time estimated to be necessary for the degree of oxidation desired, the product was precipitated immediately by pouring the solution slowly into 600-700 ml. of ethanol or methanol. The polymer was reprecipitated from solution in butanone several times to yield a clean, fibrous product, which was then dried under vacuum at 45°C. to constant weight. The resulting polymer was completely free of the odour of tetralin. It was found that the efficiency of precipitation could be increased, particularly with gummy samples, by adding large amounts of dry ice either to the precipitant or to the solution to be precipitated.

Several oxidations in a soap-water emulsion (276) were tried; however, because of the instability of the emulsions, and because of the low hydroperoxide contents obtained, oxidations in emulsion were not investigated further.

3. Analysis for Hydroperoxide Content*

Determination of the peroxide or hydroperoxide content of a high polymer is difficult. Under conditions normally used for the iodometric determination of hydroperoxide content (277, p. 52), only low molecular weight polymers readily form a uniform and stable suspension; polymers having higher molecular weights tend to agglomerate and thus make the analysis unreliable. Another difficulty is that a given method of analysis may be quite specific and may therefore give quantitative results for only certain hydroperoxides (278); it is therefore impossible to select with certainty a standard of known hydroperoxide content against which the high polymer in question may be legitimately compared. Thus it is probably best to consider analyses for hydroperoxide values as relative measures only.

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*In this thesis, hydroperoxide content is reported as a "hydroperoxide number", that is, the number of hydroperoxide groups per thousand monomeric styrene units.

Several methods of analysis were tried; none was completely satisfactory. Preliminary trials of the dead-stop end-point titration developed by Abrahamson and Linschitz (279) gave irreproducible results. Potentiometric detection of the end-point obtained with the Abrahamson-Linschitz procedure gave better results, some of which are presented in Table I. Data given in Table II show that the observed volumes of 0.002 N sodium thiosulfate required for several unknown solutions agreed well with the calculated values. Although results obtained with this method were reasonably precise, with reproducibility usually better than ± 15%, the method was inconvenient and sensitive to small variations in conditions such as stirring rate.

Most consistent results were found with the spectrophotometric method described by Laitinen and Nelson (280); a Beckman spectrophotometer, model DU, was used. Even though iodometric methods, such as the Abrahamson-Linschitz titration, may give values closer to absolute ones than do methods using ferrous ion (278), such as the Laitinen-Nelson procedure, the convenience and ease with which conditions could be standardized made the spectrophotometric determination preferable. Provided that all solutions had been freshly prepared under an atmosphere of nitrogen, and that a recent calibration graph had been obtained, results, some of which are given in Tables III and IV, for various samples of the same polymer were reproducible to about ± 10 percent in most instances, or, at worst, to within about ± 20 percent.

As shown in Table IV, a definite value for the hydroperoxide number of an unoxidized polymer was found. These values must be characteristic of the samples, for the variation from 0.2 to 0.4 is much greater than the error of measurement (± 10-20 percent).

As mentioned above, the calibration of an analysis for hydroperoxide content is difficult owing to the lack of a suitable standard with a known hydroperoxide content. Since the low molecular weight substance whose structure most closely resembles the structure of a hydroperoxide of polystyrene is cumene hydroperoxide, the purity of a sample of cumene hydroperoxide was determined spectrophotometrically. The average value found, a mean of the results of 13 determinations, was 108 (± 11%), compared to an average value of 62 (± 1%) obtained by means of a conventional iodometric titration (277, p. 52). Although the cumene hydroperoxide is not necessarily a valid standard for the analysis of the hydroperoxide content of a polymer, it is probably the best one available. If cumene hydroperoxide is a suitable standard, the relative values of hydroperoxide number found for the polymers used in this study may be much higher than absolute values.

4. Graft Polymerizations

Graft polymers were prepared in emulsion at 35(± 0.2)° C.; a typical recipe follows (see also Tables VI and VII):

Oxidized polymer (in this case, Hp. no. of 10)	2.0 g.
Styrene, or other monomer	15.0 g.
Soap flakes	5.0 g.
Water	90.0 g.
Potassium pyrophosphate	2.2 g.
Ferrous ammonium sulfate (hexahydrate)	0.2 g.

First, the oxidized polymer was allowed to stand with enough styrene to effect solution. Meanwhile, the amounts of soap and water required were calculated from the proportions indicated above, that is, 5.0 g. of soap and 90.0 g. of water for each 15.0 g. of styrene. The amounts of potassium pyrophosphate and ferrous ammonium sulfate were also calculated from the proportions given above; thus, 2.0 g. of a polymer having a hydroperoxide number of 20 would require double the amounts of pyrophosphate and ferrous salt specified for the example given above. After the water required had been divided into two equal portions, one portion was used for the preparation of the soap solution, and the other for the ferrous-pyrophosphate solution. Both solutions were prepared by heating to 60°C.

As soon as the polymer had dissolved, the two hot solutions were swept out with purified nitrogen, combined, and placed along with the polymer solution in a 250-ml. bottle fitted with a self-sealing gasket under its perforated metal cap. After the bottles and contents had been thoroughly swept out with purified nitrogen, the bottles were capped, and then filled by means of injection through the gasket with a hypodermic needle, with nitrogen to a pressure of between 10 and 15 p.s.i. After vigorous shaking in order to insure emulsification, the sealed polymerization bottles were placed in a rack held in a constant-temperature bath. The rack was arranged so that it rotated the polymerization bottles end-over-end at 33 r.p.m.

If information was desired about the percent conversion of monomer at any given time, aliquot samples were withdrawn through the gasket by means of a syringe, and precipitated in methanol (containing 0.1 percent hydroquinone as a polymerization inhibitor). The percent conversion was then calculated from the dry weight of the polymer precipitated. When the polymerization was judged to have reached the extent desired, the bottles were removed from the bath, and the contents precipitated in methanol-hydroquinone solution. After being aged, preferably overnight, in order that hardening of the polymer granules might take place, the precipitate was washed with hot water, rinsed three times with methanol, and dried to constant weight, at 45°C., under reduced pressure.

Several graft polymerizations in bulk or solution were attempted; the relative amounts of polymer, monomer, and solvent, are given in Table VIII.

5. Infrared Spectra*

Infrared spectra were obtained with a Perkin-Elmer recording spectrophotometer, model 21. Solutions in chloroform of two graft polymers, GC-211 and GC-220, and two blanks, GC-320

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*The author is indebted to Mr. George Perry, Department of Chemistry, and to the Polymer Corporation, Limited, for the infrared measurements.

and GC-321, prepared under similar conditions except for the replacement of oxidized polymer by ordinary polystyrene were examined in calcium fluoride cells throughout the range 1200 to 3800 cm^{-1}. Spectra for films of the samples GC-210, GC-220, GC-250, and GC-320 were obtained independently by the Polymer Corporation, Limited, Sarnia.

6. Intrinsic Viscosity Measurements

Solutions were prepared by allowing the necessary weight of polymer to stand with solvent in a 50-ml. volumetric flask until equilibrium was reached. To loosen swollen particles, the flasks were swirled gently from time to time. Filtration of solutions through a coarse sintered-glass filter was usually necessary in order to remove insoluble matter. The soluble portions were then diluted with solvent and made up to volume at 25.0 (± 0.02)°C. Because only comparative measurements were required, technical grade solvents were used instead of more highly purified ones.

If a significant amount of insoluble material had been noticed, concentrations were determined by evaporation to constant weight, at 60°C., of aliquot samples of solution. Such determinations have been shown to yield concentration values with an accuracy and precision of about ± 1 percent (159). Concentrations were then calculated as g. polymer per 100 ml. of solution.

Values of intrinsic viscosity, or $[\eta]$, were, unless otherwise specified, calculated as before (159) by means of the equation derived by Mead and Fuoss (281):

$$\frac{\ln \eta_r}{c} = [\eta] - \beta [\eta]^2 c \quad \ldots$$

where $[\eta]$ is the intrinsic viscosity, dl./g.,

η_r is the relative viscosity, that is, the ratio η solution/ ηsolvent,

β is a constant, and

c is the concentration, g./dl.

Since Ubbelohde viscometers shown to have kinetic-energy corrections lower than 2% were used (282), η_r is equivalent to t_s/t_o, where t_o and t_s represent the flow times for solvent and solution, respectively. The flow times were measured in duplicate or, if necessary, in triplicate, or until agreement to ± 1 percent was obtained. As may be seen from the data in Appendix A, which consists of a report of results obtained in a viscosity study of a polymer sample distributed to various laboratories by the Commission on Macromolecules of the International Union of Chemistry, the average precision of a viscosity measurement is within ± 1 to 2 percent.

Values of k', the slope constant of the Huggins equation (see equation A-13) were computed from the relation $k' + \beta = 0.50$ (159).

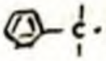
Results and Discussion

1. Oxidations

Some typical results showing the effect of time of oxidation on the hydroperoxide content of low molecular weight polymers (intrinsic viscosities in butanone ranging from 0.47 to 0.82) are presented in Fig. 1. The lengths of the vertical lines represent the approximate maximum error, about ± 20 percent, in the determination of hydroperoxide number. Although the points are rather scattered, perhaps partly because of variations in the rate of flow of the oxygen used, the data show that the maximum hydroperoxide content was usually reached after oxidation for from eight to twelve hours. After oxidation for times longer than about twelve hours, samples usually had fairly low hydroperoxide contents, and, for oxidation periods greater than about fifteen hours, often acquired a yellowish colour suggestive of decomposition.

In order to find out if degradation occurred during oxidation, the intrinsic viscosities of several polymers were determined before and after oxidation (see Table V). No change in intrinsic viscosity was noticed for the low molecular weight polymer or for one of the high molecular weight samples; on the other hand, a slight decrease was noticed for the other high molecular weight sample. Since this work was completed, Metz and Mesrobian (110) and Hahn and Lechtenböhmer (114) have reported decreases in the viscosities of polymers due to oxidation.

The part played by the solvent in the promotion of oxidation is evident in Fig. 1. While high hydroperoxide contents were obtained for solutions of a polymer in tetralin, hydroperoxide numbers for samples oxidized in m-xylene were much lower and very close to values found for unoxidized polymers. Since tetralin is readily oxidized to its hydroperoxide at temperatures used in this study (277, p. 12), catalysis by the solvent, or by its hydroperoxide, seems to be essential for the attainment of a high degree of oxidation. This conclusion is supported by the observations of Metz and Mesrobian (110), who found the oxidation of alkylated polystyrenes to be less efficient in chlorobenzene than in cumene, which can be oxidized more readily*.

The fact that the highest hydroperoxide number found, 9, for oxidized polystyrene corresponded to a hydroperoxide concentration of only about one mole percent indicates that polystyrene is not readily oxidized by molecular oxygen. This finding is in qualitative agreement with the experience of Metz and Mesrobian, who, however, obtained no hydroperoxide concentrations greater than 0.1 mole percent. It is possible that formation of the radical  , a necessary intermediate in oxidation, may be inhibited by steric interference between the bulky phenyl groups of the polystyrene chain. Although Hahn and Lechtenböhmer reported failure to achieve the oxidation of

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*Results of several experiments indicated that cumene was a satisfactory solvent in this case also.

polystyrene to a hydroperoxide in most solvents under drastic conditions, they were able to obtain hydroperoxide numbers of 15 and 22 using dioxane, which tends to contain peroxides (283), as solvent.

Several attempts to obtain hydroperoxide numbers even greater than 16 were made; the following methods were used:

(i) Addition of catalysts to the solution being oxidized.

(ii) Oxidation of a copolymer of styrene with a monomer more susceptible to oxidation than is styrene.

(iii) Oxidation of polystyrene modified chemically in order to increase the susceptibility to oxidation.

Results of these attempts are discussed below. However, none of the methods resulted in any significant increase in the maximum hydroperoxide number observed.

The addition of small amounts (0.02 - 0.08 g.) of catalysts, for example, benzoyl peroxide or cumene hydroperoxide, apparently resulted in an acceleration of both the formation and decomposition of hydroperoxide groups to about the same extent. Thus the use of benzoyl peroxide in the oxidation recipe reduced the time required for attainment of maximum hydroperoxide content to about four hours, but failed to result in a hydroperoxide number higher than 14. Hahn and Lechtenböhmer also found no benefit from the use of benzoyl peroxide; on the other hand, Metz and Mesrobian used that catalyst in their oxidations. Although small amounts of an alkali carbonate are sometimes added to solutions before oxidation in order to neutralize acidic by-products (276), the highest hydroperoxide number observed for three polymers oxidized in the presence of calcium carbonate was 6.2.

Most of the polymers oxidized were copolymers of styrene and 4-vinylcyclohexene-1 (see Table VI for some typical compositions). It had been expected that the 4-vinylcyclohexene-1 groups would readily form hydroperoxides under the conditions used (277, p. 4-7), and that this oxidation would proceed more readily than the oxidation of polystyrene for the following reason. Since the site of oxidation, which should be the carbon atom adjacent to the double bond, would not be incorporated in the polymer chain proper, it should be free from any steric effects that could hinder the resonance between the double bond and the odd electron (see diagram),

and hence hinder the formation of the radical which is an intermediate in the oxidation. However, no satisfying correlation between the 4-vinylcyclohexene content and the hydroperoxide content, for a given time of oxidation, was found.

Since Metz and Mesrobian (110) had reported that oxidation of polystyrene that had been partially isopropylated by means of a Friedel-Crafts reaction gave products with hydroperoxide numbers from 6 to 35, two samples of a low molecular weight polymer were isopropylated in a similar way, and the products oxidized using the procedure given. Again, however, results were disappointing; the highest hydroperoxide number found was 10.5. Since by this time enough polymeric hydroperoxides for a series of graft polymerizations had been obtained, no attempt to increase the yield of hydroperoxide by oxidizing copolymers of styrene and isopropylstyrene (see reference 114) was made.

2. Evidence for Grafting

(a) Conversion Studies

Proof that the presence of a polymeric hydroperoxide in a typical emulsion of styrene resulted in the rapid polymerization of the styrene was obtained from studies of the percent conversion of styrene to polymer as a function of time. Conversion data for a typical graft polymerization, GC-140, are given in Fig. 2; for comparison, data are included for a blank, GC-141, prepared at the same time and under the same conditions by the omission of oxidized polymer from the polymerization recipe. With this example, as with the three other polymerizations studied in this way, more than half the styrene present had been converted to polymer by the time an hour had elapsed after the addition of the oxidized polymer to the emulsion. On the other hand, with the blank very little (less than

3 percent) of the styrene present in the blank had been polymerized by that time.

As indicated by Fig. 2, the initial slope of the conversion curve was invariably regular; considerable scatter occurred, however, for times greater than three hours, by which time the emulsion had usually broken. Since the value of the percent conversion for the <u>total</u> polymer (corresponding to the last point on the curve for GC-140) always fitted in well with the values obtained for aliquot samples taken during the early stages of reaction, this scatter may be attributed to the failure to obtain representative samples from the emulsions during the later stages of reaction.

Further evidence for the initiation of polymerization by oxidized polymers is provided by Tables VI and VII, which give polymerization and conversion data for several series of graft polymers. Similar information is also given for blanks prepared, except for GC-141, by replacing oxidized polymer in the polymerization recipe with ordinary polymer. Except for the samples GC-161 to GC-200, inclusive, much more styrene was polymerized in the presence of oxidized polymer than in the presence of ordinary polymer.

The low values of percent conversion for the samples GC-161 to GC-200 seems to be associated with a low hydroperoxide number for the backbone polymers. -- 1.8 for GC-161, GC-162, and GC-163; 1.9 for GC-180; 3.0 for GC-190; and 2.0 for GC-200. Nevertheless, as will be shown in Table IX, hydroperoxide groups were definitely consumed during the preparation of GC-180, GC-190, and GC-200; no analyses were completed for samples GC-161, GC-162, or GC-163. Except for this general observation, no close relationship between the hydroperoxide content of the backbone polymer and the percent conversion is evident; also, no correlation can be found between the vinylcyclohexene content of the backbone polymer and the percent conversion.

Although the grafting experiments using styrene as the monomer were successful, experiments with methyl methacrylate were disappointing; even after a polymerization time of 16 hours, the percent conversion of monomer was higher than 5 percent in only one of four trials. With that one sample, a turbidimetric titration by the method of Melville and Stead (284) indicated that the polymerized methyl methacrylate was not linked to the backbone polymer.

Several graft polymerizations were made in solution; polymerization and conversion data are presented in Table VIII.

(b) Disappearance of Hydroperoxide Groups

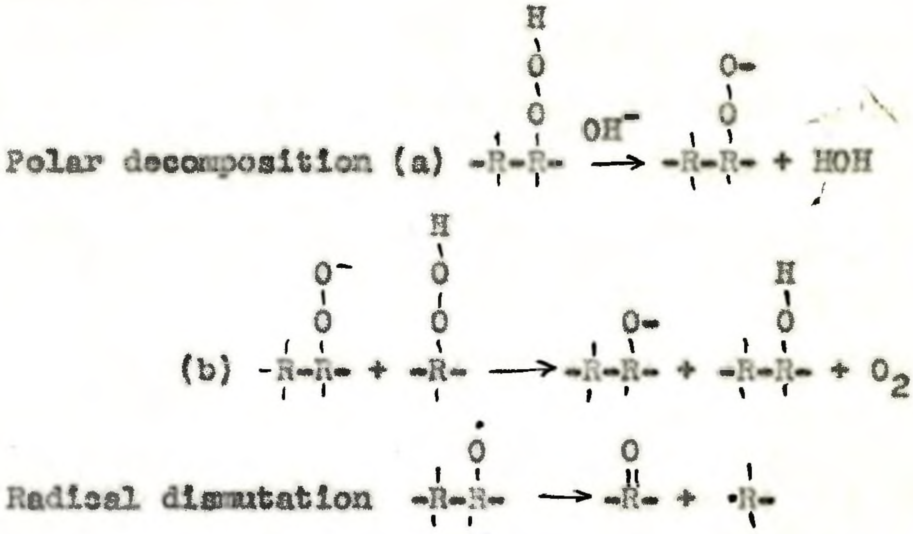
From the studies of conversion discussed above, it is clear that the conversion of monomer to polymer is associated with the presence of an oxidized backbone polymer in the emulsion. Consideration of the data given in Table IX concerning the disappearance of hydroperoxide groups shows that hydroperoxide groups are definitely associated with that conversion. In Table IX the hydroperoxide number observed for a graft polymer is compared with the hydroperoxide number calculated by assuming that the graft polymer is a simple mixture of backbone polymer and polystyrene formed by some side-reaction (even though the data from Fig. 2 and Tables VI and VII makes any such side-reaction very improbable). For convenience, it is assumed that the hydroperoxide number of the polymerized styrene is 0.50, a reasonable value, slightly lower than the average of 0.55 found for the blanks GC-320, GC-321, GC-322, and GC-323. The disparity between the observed and calculated values of hydroperoxide number would in most cases still remain if even lower values were assumed for the hydroperoxide number of the polymerized styrene. The following equation was then used for the calculation:

$$\frac{\text{wt.}_{\underline{bb}} \times \text{hydroperoxide no.}_{\underline{bb}} + \text{wt.}_{\underline{ps}} \times 0.50}{\text{wt. graft}}$$

where the subscripts bb and ps refer to backbone polymer and polymerized styrene, respectively. As shown by the comparison, hydroperoxide groups certainly disappeared in some manner during the graft polymerization.

(c) Absence of Side Reactions

So far in this discussion it has been assumed that in the presence of an excess of monomer a hydroperoxide group disappears by the series of reactions outlined in equations A-1 and A-2. In other words, it has been assumed that the radical $-\underset{|}{\overset{|}{R}}-\underset{|}{\overset{O\cdot}{\overset{|}{R}}}-$ activates a molecule of monomer instead of decomposing by a polar or radical reaction such as is illustrated in the following equations:



Polar decomposition (a) $-\underset{|}{\overset{|}{R}}-\underset{|}{\overset{H}{\overset{|}{\overset{O}{\overset{|}{\overset{O}{\overset{|}{R}}}}}}}- \xrightarrow{OH^{-}} -\underset{|}{\overset{|}{R}}-\underset{|}{\overset{O^{-}}{\overset{|}{\overset{O}{\overset{|}{R}}}}}- + HOH$

(b) $-\underset{|}{\overset{|}{R}}-\underset{|}{\overset{O^{-}}{\overset{|}{\overset{O}{\overset{|}{R}}}}}- + -\underset{|}{\overset{H}{\overset{|}{\overset{O}{\overset{|}{\overset{O}{\overset{|}{R}}}}}}}- \longrightarrow -\underset{|}{\overset{|}{R}}-\underset{|}{\overset{O^{-}}{\overset{|}{R}}}- + -\underset{|}{\overset{|}{R}}-\underset{|}{\overset{H}{\overset{|}{\overset{O}{\overset{|}{\overset{O}{\overset{|}{R}}}}}}}- + O_2$

Radical dismutation $-\underset{|}{\overset{|}{R}}-\underset{|}{\overset{O\cdot}{\overset{|}{R}}}- \longrightarrow -\overset{O}{\overset{\|}{R}}- + \cdot\underset{|}{\overset{|}{R}}-$

The occurrence of such side reactions would result in consumption of hydroperoxide groups and in the formation of radicals that could initiate the formation of linear polymer -- results that would vitiate the conclusion that grafting had taken place. However, no evidence was found for the occurrence of the side reactions illustrated above.

The absence of a polar decomposition induced by the alkaline nature of the emulsion was demonstrated in the following way. Solutions of two polymeric hydroperoxides in benzene were first emulsified using the usual recipe, except for the omission of the ferrous salt, and then rotated in the constant temperature bath for lengths of time ordinarily sufficient to result in the conversion of most monomer to polymer. Since the hydroperoxide numbers, reported in Table X, were found to have been unchanged, within experimental error, by exposure to emulsions, it was concluded that the polymeric hydroperoxides used in this study were stable at the pH existing in the emulsions.

In order to see if a radical-induced decomposition had taken place, infrared spectra for graft polymers GC-211 and GC-220 and for blanks GC-320 and GC-321 were examined for the presence of absorption peaks corresponding to the absorption frequency of the carbonyl group. Although the carbonyl group is readily detected at low concentrations by infrared measurements, no absorption peaks in the range 1720-1730 cm.$^{-1}$ -- a range characteristic of the carbonyl group (285, Chapter 9) -- were found. In fact the spectra for both graft polymers and blanks were quite similar. This finding was confirmed by results obtained with films of the graft polymers GC-210 and GC-220 and blanks GC-250 and GC-320.

Thus the assumption that in the presence of a large excess of monomer the hydroperoxide radicals react with monomer instead of decomposing appears to be valid. It may be concluded, therefore, that the styrene molecules polymerized in the presence of polymeric hydroperoxides were actually linked to the backbone chain at the hydroperoxide sites, that, in other words, grafting had taken place to yield branched polymers. More direct proof of branching, derived from relationships between intrinsic viscosity and molecular weight, may be found in Part III of this thesis.

3. Intrinsic Viscosities

Although very small degrees of crosslinking were found previously to be associated with abnormally high values of Huggins' k' (27) for the unfractionated polymers, values of k' for the graft polymers were no greater than the values characteristic of linear polymers (0.39 to 0.41 in butanone). Values of k' for fractions of the polymers discussed in this section are presented in Table XLIV, and discussed in Part III.

Summary and Conclusions

First the oxidation, by means of molecular oxygen, of polystyrene, of copolymers of styrene and 4-vinylcyclohexene-1, and of partially alkylated polystyrene was successfully accomplished. The polymeric hydroperoxides thus formed, which contained a maximum of 18 hydroperoxide groups per thousand monomeric units, were shown to be capable of initiating the polymerization of styrene in a redox emulsion system.

Since no evidence for a polar or radical-induced decomposition of the polymeric hydroperoxides was found, it was concluded that the chief mechanism for the disappearance of a hydroperoxide group in a polymerization reaction involved the addition of $-\overset{|}{\underset{|}{R}}-O\cdot$ radical to a styrene molecule rather than a dismutation. This mechanism would result in the growth of branches composed of styrene units from each hydroperoxide group that reacted

Although the experimental results thus support the conclusion that branching occurred, values of Huggins' k' for the unfractionated graft polymers were no higher than for linear polystyrene.

II. DESIGN AND CONSTRUCTION OF A LIGHT-SCATTERING PHOTOMETER

Introduction

At the time this study of branching was begun, no commercial light-scattering photometer had gained acceptance as an instrument suitable for critical research. It was decided, therefore, to design and construct a light-scattering photometer suitable for the determination of the absolute molecular weight, size, and second virial coefficient of a high polymer

After the decision to design a photometer had been made, the following requirements were decided upon:

1. The instrument should be capable of measuring the intensity of scattered light within a range of angles from 30 to 135 degrees. Thus, measurements obtained would be suitable for extrapolation to zero angle, as well as to zero concentration.

2. The sensitivity should be high enough to permit measurements of the intensity of light scattered by a pure solvent, the turbidity of which is of the order of 10^{-4} cm.$^{-1}$.

3. The precision of measurement should be as close as

possible to ± 1 percent.

4. In order to minimize the effects of true absorption of light by a solution, or of variations in the intensity of the light source, the instrument should measure the ratio of the intensity of scattering at any angle θ to the intensity of the transmitted beam.

5. The optical and electronic systems should be flexible, so that adjustment or modification might be readily made.

6. The instrument should be simple to operate, and physically rugged.

From consideration of the designs available, it was concluded that the photometers described by Zimm (207), by Brice, Halwer, and Speiser (222) and by Rinfret (260) best fulfilled the requirements given above. Therefore, the design of the instrument described here was based, to a large extent, on the instruments mentioned.

The design and calibration of the light-scattering photometer are described below. Also, corrections required for the conversion of experimental measurements to absolute values of the reduced intensity are discussed; finally, the determination of the molecular weight, size, and second virial coefficient of a high polymer in solution is described.

Experimental

1. Light-Scattering Photometer

(a) Principle of Operation

A beam of monochromatic light is passed into a cell containing the polymer solution being studied. Part of the light scattered by the solution at an angle θ is received by a photomultiplier tube; part of the light transmitted is received by a phototube. Since the light source, a mercury-arc lamp, is operated from line current having a frequency of 60 c.p.s., the light beam is naturally modulated at a frequency of 120 c.p.s. The currents developed at the two phototubes contain, therefore, a.c. components having a frequency of 120 c.p.s.

The a.c. components from the anode of the photomultiplier and from the cathode of the other phototube are applied to a potentiometer bridge; the signal resulting from a difference in the two currents is amplified by a high-gain amplifier (tuned to 120 c.p.s.) and observed by means of a sensitive detector. If the precision potentiometer is adjusted until a null reading is obtained for the difference signal, the setting of the potentiometer gives the ratio of the two currents applied to the bridge. This ratio is proportional to the relative intensities of light received by the two phototubes, and hence to the reduced intensity of light scattered, i_θ/I_o.

Since the ratio measured is equivalent to the ratio of the intensity of light scattered at an angle θ to the intensity of light <u>transmitted</u>, variations due to the intensity of the incident beam or to absorption by the solution are automatically compensated for.

(b) General Construction

The general construction of the light-scattering photometer, which is similar in many respects to the one designed by Brice, Halwer, and Speiser (222), is shown in Figure 3.

All components are enclosed in a case formed from sheet-metal; as shown in Figure 3, the case is divided into compartments. Doors are provided for the lamp and battery compartments; removable covers, the edges of which are lined with black velvet, give access to the scattering chamber and to the compartment containing the collimating system for the incident beam. In order to reduce reflections owing to stray light, the case and compartments are coated with flat black paint; whenever possible, other components are also painted black. Another precaution against stray light is the use of a false floor for the scattering chamber; with the false floor, no light can enter the scattering chamber by way of the slot in the case through which the large graduated disc projects (see below). Failure to observe a scattering reading even when a light was shone upon the case demonstrated the adequacy of the precautions against stray light.

The light source, a Westinghouse AH-4 mercury-vapour lamp, is firmly mounted on a base, which is, in turn, bolted to the floor of the case. In order to permit slight adjustments in the position of the base, the holes drilled for the bolts are slightly larger than the bolts themselves. The provision of a means of cooling the lamp was found to be unnecessary; as long as the wall next to the optical bench is lined with asbestos, excessive heating of the optical bench does not occur.

All optical components required for the collimation of the incident beam are mounted, by means of movable holders, on a section of channel-iron that serves as an optical bench. The holders are clamped rigidly to the optical bench in the position desired by means of set-screws.

At one end of the optical bench the cell table is located. After adjustments for height and for alignment with respect to the incident beam have been made (see below), the cell platform is rigidly fastened in position by means of a set-screw.

Both the cylindrical and semi-octagonal cells used are cemented to square (1 1/4-in. x 1 1/4-in.) bases cut from a sheet of Lucite. Exact centering of a cell on its base is helped by a series of diagonal lines scribed to intersect at the centre of the base. Since a square depression has been cut in the cell table to match the cell base, mounting of the cell in the incident beam is reproducible. After the set-screw holding the cell table in position has been loosened slightly, the cell table (and cell) is rotated until the incident beam meets the surface of the cell at right angles.*

An arm, designed to carry the housing for the photomultiplier tube, is attached to a collar fitted to the shaft holding the cell table. A large disc is also attached to the collar, which is free to rotate about the vertical axis of the cell table. Thus rotation of the disc, the edge of which projects slightly from the photometer case, results in rotation of the arm around the cell table. The disc can be rotated through 360 degrees; by means of a pointer P attached to the case and a scale marked in the rim of the disc, the angle made by the arm with respect to the incident beam may be read. After alignment of the cell table has been completed (see above), the position of the disc relative to the arm is adjusted until the arm is directly in line with the incident beam; the zero mark on the angular scale is then opposite the pointer.

In order to carry the slit-holders, a small optical bench is bolted to the photomultiplier arm. The holders used have been designed so that either slits or lenses can be accomodated. The size and position of these slits defines the size of the light beam received by the photomultiplier.

Two other small optical benches, O_1 and O_2, are fastened to the top of the scattering chamber as shown, these benches are used to carry holders for the slits required to limit the inci-

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*If the scattering chamber is filled temporarily with smoke, observation of the Tyndall beam produced by the incident light reveals any irregularities in the path of the incident beam.

dent and transmitted beams.

In the path of the incident beam, a small light-tight case containing a type 929 phototube, and associated electronic components, is mounted on the wall of the last compartment in the photometer. This compartment is also used to house the batteries required for the photomultiplier. If alignment of the incident beam is necessary, the phototube housing may be removed so that visual observation of the incident beam may be made through a tube, T_2, which projects through the outer wall of the compartment.

The amplifier and detector are enclosed in a separate case, and placed beside the photometer. In order to minimize pickup of hum by the amplifier, the power supply and frequency generator are located approximately four feet away. The rack-type power supply for the phototube is mounted in the bench under the photometer.

(c) Optical System

By means of a convex lens, L_1, an image of the filament of the light source is focused on an aperture, D_1 (2 x 2 mm.). The beam is made monochromatic at F by a combination of Corning filters No. 3389 and No. 5113 (λ = 436 mμ). After having passed through a baffle, T_1, which serves to prevent stray light from reaching the next lens, the light beam is collimated by a condensing lens, L_2. The collimated beam -- now almost parallel -- passes successively through a Compur-Rapid shutter, D_1', an aperture, D_2, and a final defining aperture, D_3, (4 x 8 mm.)

before entering the scattering cell. Provision of a long cable release for the shutter permits control from outside of admittance of the incident beam to the cell.

For this study, a semi-octagonal cell was used. Proof of the symmetry of the cell was obtained by measurement of the fluorescence emitted at 45, 90 and 135 degrees by an aqueous solution (concentration: 3.8 mg./l.) of the sodium salt of fluorescein. After correction for the volume viewed (see Section 2-d) the three values* -- each an average of three readings -- were 0.539 (±0.002), 0.539 (±0.002), and 0.539 (±0.004). Another test, with a higher setting of sensitivity for the photometer, gave results of 1.120 (±0.009), 1.11 (±0.02), and 1.116 (±0.002) for the angles 45, 90, and 135 degrees respectively.

Transmitted light passes through a blackened tube, T_3, and an aperture, D_6 (4 x 4 mm.), into the compartment containing the type 929 phototube.

The solid angle of the scattered light received by the photomultiplier is defined by the two apertures, D_4 and D_5; typical dimensions for these apertures are 3 x 6 mm. and 4 x 4 mm., respectively. A Compur-Rapid shutter, fitted with a cable release leading to the exterior of the case, is used to intercept the scattered beam whenever desired.

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*The terms in parentheses represent the maximum observed deviation of a reading from the average; for example, at 135 degrees all three readings were between 0.543 and 0.535.

The blackened tubes T_3 and T_4 exclude troublesome reflections arising at the edges of the apertures D_1 and D_4 from the photomultiplier.

With a variety of apertures available, the optical arrangements are quite flexible. Since changes in the position or size of slits may be made readily, the photometer can be adapted quickly to suit different optical requirements. For example, if the sensitivity of the photometer seems too low for a given purpose, the sensitivity may be increased simply by the replacement of the apertures with larger ones. In order to reduce undesirable reflections (200, 235), the back and edges of the cell were coated with flat black paint.

(d) Electronic System

(i) Phototubes:- The photomultiplier circuit is shown in Fig. 5. Although 931A-type tubes have been used frequently in light-scattering photometers, the use of 1P21-type tubes instead is often preferred (232, 234, 238, 241, 245). In this work, seven 931A tubes were tried; none was as quiet or as sensitive as the 1P21 tube that was finally selected.

Dry cells were found to be a convenient source of the high voltage required for the photomultiplier. Various combinations of 300-volt and 90-volt batteries were used; usually a voltage of 1000 volts was found to give a good compromise between sensitivity and noise. When a voltage higher than 1000 volts was used, troublesome fluctuations in the signal were observed; with a voltage lower than 1000 volts, the detector was sluggish and the sensitivity low (see also reference 222).

A 929-type phototube, with an associated circuit described in Fig. 4, was found to be quite reliable for monitoring the incident beam. The 300 volts required is supplied by a Lambda regulated power supply, Model 28.

Since the two photocells are arranged to have opposite polarities, the two photocurrents are 180 degrees out of phase.

(ii) <u>The amplifier and detector</u>:- As shown in Figs. 4 and 5, the signals from the two phototubes are led to a potentiometer bridge. Since the two signals are 180 degrees out of phase, a signal representing the difference between the amplitudes of the two signals results. This difference signal is first amplified by a high-gain, narrow-band amplifier, and then detected by a synchronous detector.

The first amplifier used was built at the University of Montreal from a design used by Dr. Marcel Rinfret* (260); unfortunately, after some use the amplifier developed a troublesome instability, which could be eliminated only by reducing the gain to an undesirably low level. For that reason, the amplifier, detector, and 120-cycle amplifier were rebuilt, with modifications intended to improve stability, by Mr. Arthur Dean of McMaster University; schematic diagrams of the new apparatus are given in Figs. 5 and 6.

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*The author is grateful to Dr. Rinfret for making this amplifier available to us, and for the opportunity of spending several days with his research group.

For the first stage of amplification, a type 5693 tube was found to have a lower inherent noise level than the 6SJ7 tube originally used. Microphonic noise was eliminated by mounting the tube socket on rubber.

Because of the high level of background noise, a twin-T feedback network, designed to pass only 120-cycle components to the second stage was found to be necessary (see also reference 207). After amplification by the first stage and removal of harmonics and other noise by the twin-T network, the signal is amplified successively by a 6SN7 and a 6C5 tube, and then applied to the grids of the 6SL7 detector. In order to synchronize the detector with the signal applied, the plate current of the detector is supplied by a 120-cycle generator (see Fig. 6). Close matching of the frequencies at the plates and grids of the detector is made possible by the incorporation of a phase-shifting circuit -- controlled by P2 -- in the 120-cycle generator. The final signal resulting is observed by means of a sensitive galvanometer. In order to reduce the possibility of noise pickup, a great deal of care was taken with the circuit layout and shielding.

A conventional power supply using a 6X5 rectifier provides filament and plate currents.

If suitable adjustments of the gain and sensitivity have been made (see below), a scattering measurement requires only the adjustment of the Helipot (40 k) in the bridge circuit until the 120-cycle component of the voltage across it is at a minimum -- as observed by the galvanometer. The reading of the Helipot then gives the ratio of the currents from the phototubes.

Provided that the photometer had been allowed to warm up for about 30 minutes, stable readings were generally obtained.

(e) Operation

For maximum sensitivity, the current supplied by the 120-cycle generator to the plates of the detector should be exactly in phase with the signal reaching the grid of the detector. Variations in the phase and shape of the output of the generator may be readily accomplished by manipulation of the gain control P_1 and the phasing control P_2 (Fig. 6). In order that the output of the generator may be compared directly with the signal applied to the grid of the detector, the 120-cycle generator and the grid of the detector are provided with terminals which can be connected to the horizontal and vertical plates of a cathode ray oscilloscope. If, with light incident on the 929 phototube, the gain controls of the oscilloscope have been adjusted so that the two signals have the same amplitude, a straight line inclined at an angle of 45 degrees should theoretically be obtained for a perfect phase match. Since neither signal is a perfect sine wave, a perfect straight line is never obtained; however, the controls P_1 and P_2 are adjusted until the best figure -- in practice, a flattish ellipse -- is observed. A simpler procedure requires only the adjustment of P_1 and P_2 for maximum deflection of the galvanometer; the precision of matching obtained in this way is comparable to the precision possible with use of the oscilloscope. The matching of phases requires checking periodically -- say, once a week.

The null point must then be found. First, with the main shutter, D_1', closed,* the galvanometer sensitivity control C_2 is set so that a suitable balance between oscillation and response time is achieved; the position of the control is maintained throughout an experiment. Next, with the gain control C_1 set at approximately two-thirds of its maximum, the null point of the instrument is adjusted by means of control C_3 until the galvanometer needle oscillates uniformly about zero.

After the null point has been found, the shutters S_1 and S_2 are opened; the Helipot knob is then turned until a null is reached again. The reading on the potentiometer scale then indicates the following ratio (or the inverse, whichever is less than unity): 1P21 signal/929 signal. If a null cannot be obtained, the switch S_1 must be reversed to give the inverse ratio, and the null procedure repeated. With cases in which the determination of the null position is difficult, it is helpful to close the main shutter occasionally in order to note the direction of deflection when the shutter is re-opened. If five trials show no consistent direction for the initial deflection, it may be assumed that the null has been reached. In any case, the null point must be checked after each reading.

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*If switch S_2 is turned so that the resistance R is placed in the circuit, the main shutter need not be closed; best results are obtained, however, if the shutter is used instead of S_2.

(f) Calibration

The photometer was calibrated with dilute dispersions, or "solutions", of Ludox,[*] a commercial preparation of colloidal silica; turbidities of the solutions were determined independently, using a precision spectrophotometer. By means of the calibration factor thus found, values of the scattering ratio found experimentally were converted to values of turbidity.

First, a stock solution of Ludox was prepared by sixfold dilution of the commercial product (30 percent silica, by weight) with distilled water. After filtration through an ultra-fine sintered-glass filter, the solution was stored in a tightly stoppered, clean bottle. The stability of the Ludox was improved by the addition of a small amount of gum arabic and mercuric chloride before filtration.

A calibration was begun with the determination of the scattering for clean water.[**] Then some of the stock solution of Ludox was filtered through the ultra-fine sintered-glass filter directly into the scattering cell. After the solution had been mixed by carefully swirling the covered cell, the scattering ratio of the Ludox was determined. Part of the contents was then transferred to a 5-cm. spectrophotometer

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[*] The author wishes to acknowledge the donation of Ludox by the Dupont Company of Canada.

[**] Clarification of the water used is described in a later section.

cell, more clean water and Ludox solution were filtered into the scattering cell, and the scattering of the new solution was determined as before. This procedure was repeated until the scattering of several solutions of Ludox had been obtained.

Turbidities of the solutions were determined, in 5-cm. matched cells, by means of a Beckman spectrophotometer, model DU. Measurements of transmittance were made until the precision of the average of four consecutive readings was ± 0.1 percent transmittance.

A graph giving the scattering ratio as a function of turbidity was then drawn (see Figs. 7 and 8). Once the linearity of the calibration curve had been established, a calibration constant was determined after each change in the sensitivity of the photometer by measurement for two solutions of Ludox of the ratio: scattering ratio/turbidity; the average of the two determinations was then taken as the calibration constant.

In order to compensate for small day-to-day changes in sensitivity, a sealed glass cell containing a solution of Ludox was used as a working standard. Each day the scattering ratio was determined for the solution; if the reading on a given day differed from the reading obtained on the day of calibration, all measurements of scattering were multiplied by the ratio of the reading obtained on the day of calibration to the reading obtained on the given day.

In order to check the calibration of the photometer, the turbidity of a solution of the polystyrene sample distributed by Professor Debye[*] of Cornell University was determined. As outlined in the instructions supplied with the sample, the scattering ratio for a 0.5 percent solution of the sample in toluene was measured (see Results and Discussion).

2. Determination of the Molecular Weight of a High Polymer

(a) Materials

The benzene and toluene used were prepared by distillation of the technical products; they were stored over sodium until use. Measurement of corrected boiling points and refractive indices gave the following results:

Benzene: b.p. 80.5°C.; $n_D^{25} = 1.497$; $n_{436}^{22} = 1.520$

Toluene: b.p. 110°C.; $n_D^{25} = 1.493$; $n_{436}^{22} = 1.517$

The sucrose required for the calibration of the interference refractometer was the Analar grade supplied by British Drug Houses, Limited.

The preparation of the polystyrene fraction used has been described elsewhere (159).

(b) Refractive Index Increment

Values of the refractive index increment, dn/dc, or Δn/c, were obtained by means of a Hilger Rayleigh-type inter-

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[*] The author is grateful to Professor Debye for making this sample available.

ference refractometer. The procedure outlined by Bauer and Fajans (286) was used.

With polymer solutions, evaporation of solvent and subsequent distortion of the interference fringes was troublesome. This problem was solved, without recourse to an expensive cell cover, by covering the interferometer cell with a small sheet of aluminum foil bent into a slightly concave shape. When the sliding thermometer holder was pressed downward on the foil -- which had been placed with the convex side upwards -- a tight seal all around the edges of the cell was made.

Calibration of the interference refractometer was checked by determination of the refractive index increment for dilute aqueous solutions of sucrose at 20°C. Altogether eighteen determinations were made; measurements were made at eleven concentrations, ranging up to 5.7 g/dl. The average result found for $\Delta n/c$, 0.1433 (standard deviation: 0.0010), may be compared with an average value of 0.1436 found by Brice and Halwer (287) and calculated from data given by Browne and Zerban (288).

Values obtained for the refractive index increment by averaging the values found for at least three concentrations are given below, for a solution of polystyrene in benzene at 22°C.:

$$\lambda = 546\ \text{m}\mu; \quad dn/dc = 0.108\ (\pm\ 0.001)$$

$$\lambda = 436\ \text{m}\mu; \quad dn/dc = 0.111\ (\pm\ 0.001)$$

Use of the value 0.111 in the calculation of the optical constant H gives, for a solution of polystyrene in benzene:

$$H = \frac{16.75 \times 2 \quad ^{2} \times N_o^{2} \times (dn/dc)^{2}}{\lambda_o^{4} \times N}$$

or, for a wavelength of 436 mμ and a temperature of 22°C.:

$$H = 4.28 \times 10^{-6} \ \frac{\text{mole-cm.}^{2}}{\text{g.}^{2}}$$

(c) Procedure

(i) Clarification of solvents and solutions:- If consistent values of scattering are to be obtained, the solvent or solution must be optically clean; that is, free from extraneous particles that can scatter light. The presence of dust is particularly objectionable; because of their large size, dust particles scatter a great deal of light in an asymmetric pattern. Although the scattering of the solvent is subtracted from the scattering of the solution, the presence of dust results in fluctuations that make the accurate determination of scattering impossible. Unfortunately, it is impossible to remove all extraneous matter (216); however, the reduction of the dissymmetry of a solvent (except water) to a low value -- say, 1.05 or less (221) -- is generally taken as evidence that the solvent is relatively free from optical impurities.

Satisfactory clarification of benzene and toluene was accomplished by centrifugation in a Servall high-speed, angle centrifuge, model SS-1a, for one hour at maximum speed (corresponding to about $25x10^{3}$g. As long as the dissymmetry ratio of the centrifuged solvent was 1.03 or less, the solvent was judged to be suitable for the rinsing of equipment and for scattering measurements. Although filtration of benzene or toluene through an ultra-fine sintered-glass filter also yielded solvent having a low dissymmetry ratio, the centrifugation procedure was found to be somewhat more convenient.

The clarification of water was more difficult. Centrifugation, at top speed for two hours, of water that had been distilled three times and filtered through an ultra-fine sintered-glass filter yielded a product having a dissymmetry ratio of 1.7 or higher. Best results were obtained by filtration of water first through an ultra-fine sintered-glass filter and then through a Millipore filter disc (255, 289); the dissymmetry ratio of water cleaned in this way ranged from 1.1 to 1.3.

Before use, all equipment, such as syringes, cells, or bottles, which would come into contact with a solvent in solution used in a scattering measurement, was rinsed at least six times with solvent (cleaned by procedures described above) and allowed to dry.

The stock solution of polystyrene used in this study was also clarified by centrifugation; clarification of the Ludox solutions has already been described.

(ii) <u>Measurements of scattering</u>:- After centrifugation of the stock solution of polystyrene, the middle portion of the solution in the centrifuge was removed by means of a clean syringe equipped with a 6-inch needle and transferred to a clean bottle. Care was taken during the removal to avoid any more disturbance of the solution than was necessary. Since some evaporation of solvent took place during the centrifugation, the concentration was determined by weight.

The scattering cell was rinsed six times with clean solvent, and then filled with enough clear solvent to permit clear passage of the incident beam. As long as inspection of the solvent at a low angle in a strong light beam revealed few motes, the scattering of the solvent was determined at 45, 90, and 135 degrees. If more than a few motes were present, or if the dissymmetry ratio was greater than 1.05, a fresh portion of solvent was examined; if the solvent still appeared dirty, the clarification procedure was repeated.

Solutions of polystyrene were prepared for scattering by concentration of a dilute solution, rather than by dilution of a stock solution, in the following way. After the scattering of the solvent had been measured, a small portion of concentrated stock solution (say, 2 ml.) was carefully added by means of a clean syringe to the solvent. Mixing of the solution was brought about by first drawing a portion of the liquid into the barrel of the syringe and then forcing the liquid back into the solution; this procedure was repeated several times. The concentration of the solution was calculated from knowledge of the weight concentration of the stock solution and of the weights of the cell before and after addition of the stock solution.

After measurements of the scattering ratio (that is, the ratio of scattered to transmitted intensity) at 45, 90, and 135 degrees had been made, the procedure was repeated in order to obtain solutions with successively higher concentrations.

Values of the scattering ratios obtained for the solutions were converted to values of relative turbidity or reduced intensity by means of the calibration constant. Thus,

$$\tau \; \alpha \; S_{90} \text{ (solution) x } \frac{\text{(Ludox solution)}}{S_{90} \text{ (Ludox solution)}}$$

where S_{90} is the scattering ratio light scattered/light transmitted, as given by the reading (or its inverse) of the Helipot. Corrections necessary for the calculation of <u>absolute</u> turbidities from the experimental data are discussed in the following section.

(d) Corrections to Observed Data

(i) <u>Contribution of solvent:-</u> As mentioned before, the total turbidity of a solution may be expressed, to a close approximation (197), as the sum of two terms -- one due to the solvent and one due to the solute. It is, therefore, legitimate to subtract the turbidity of the solvent from the turbidity of the solution in order to obtain the turbidity due to the solvent. This procedure also allows for small irregularities in the cell used.

All the measurements of scattering ratios and turbidities mentioned in this thesis have been corrected for the scattering of the solvent[*]; this correction never amounted to more than half the total turbidity, even for the most dilute solution.

(ii) Absorption of light:- Since the ratio of scattered to transmitted light is measured, and, since the scattered beam traverses the same distance through the solution as does the transmitted beam, almost complete compensation for absorption is inherent in the design of the photometer (290).

(iii) Change in scattering volume with angle:- The volume of solution viewed by the receiving system of the photomultiplier is approximately proportional to the sine of the angle made by the receiver with the incident beam (263). Thus, if scattering ratios require normalization in order to be comparable to ratios for scattering at 90 degrees -- as is the case with a Zimm plot -- the ratios must be multiplied by 1/sin θ.

Since, in this study, the scattering at angles of 45 and 135 degrees is used only for determination of the dissymmetry ratio ($^{i}45/^{i}135$), the application of this correction is unnecessary in this case.

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[*] Since the sensitivity of the photometer was never varied throughout an experiment, one determination of the solvent scattering for each experiment was enough.

(iv) Change in state of polarization with angle:- If the light incident upon the cell is unpolarized, the intensity of scattering must be multiplied by a factor $1/(1 + \cos^2\theta)$ (see Historical Introduction, and references 184 and 198) in order to compensate for the presence in the scattered beam of a horizontally polarized component, the intensity of which is proportional to $\cos^2\theta$.

As with the correction for the volume viewed, however, this correction, being symmetrical about 90 degrees, is unnecessary for the determination of the dissymmetry ratio.

(v) Refractive index corrections:- If the scattering ratios for two liquids are to be compared, two corrections are applicable (197, 222, 241, 265).

First, because of refraction, at the cell-air interface, of light leaving the centre of the scattering volume (Fig. 9), the photomultiplier receives light flux from the solid angle θ_1, not from θ_2. In other words, as the refractive index of the scattering medium increases, the solid angle defining the flux received decreases.

Since the ratio giving the flux collected is $\left[\frac{\theta_1}{\theta_2}\right]^2$, the observed scattering ratio must be multiplied by $\left[\frac{\theta_2}{\theta_1}\right]^2$. It has been shown (32, 200, 261, 263) that, as long as the receiving system does not "see" past the edges of the incident beam, this term may, for any shape of cell, be replaced by the square of the refractive index of the solution, n^2. It follows that, if a liquid with refractive index n_a has been used for calibration, scattering ratios for another liquid having refractive index n_b must be multiplied by the term n_b^2/n_a^2. Thus, if aqueous Ludox is used as a calibrating solution, scattering ratios for toluene must be multiplied by n^2 (toluene)/n^2 (water).

If, however, the receiving system does see past the edges of the incident beam, the correction becomes (200, 263):

$$\frac{n_b \, (A + Bn_b)}{n_a \, (A + Bn_a)}$$

where A and B represent the distance from the cell wall to the centre of the beam and the distance from the cell wall to the photomultiplier, respectively. As finally used, the receiving system of the photometer concerned here did "see" past the edges of the beam. With values for A and B of 0.88 and 7.0 inches, respectively, the refractive index corrections C_n required for comparison of polymer solutions to Ludox solutions ($n = 1.334$) become the following, for a temperature of 22°C.:

Benzene: $C_n = 1.29$
Toluene: $C_n = 1.28$
Butanone: $C_n = 1.07$

Hence a scattering ratio S_{90} was converted to a turbidity by means of the following equation (compare section c-ii):

$$\tau \text{ (solution)} = S_{90} \text{ (solution)} \times \frac{\tau \text{(Ludox solution)}}{S_{90} \text{ (Ludox solution)}} \times C_n$$

The second correction is required to allow for the variation of the scattering volume seen by the photomultiplier (197, 265).

Since, however, the ratio of this correction for benzene to the correction for water is close to unity -- 1.02 for a typical arrangement of apertures -- this volume correction has been neglected.

(vi) Depolarization correction:- If the molecules are anisotropic, some depolarization of the scattered light may occur (198, 200). The factors commonly used for correcting observed scattering ratios are:

(1) $\dfrac{6 - 7\rho_u}{6 + 3\rho_u}$ applicable to measurements at $\theta = 0°$

(2) $\dfrac{6 - 7\rho_u}{6 + 6\rho_u}$ applicable to measurements at $\theta = 90°$

where $\rho_u = \dfrac{H_u}{V_u}$ -- H_u and V_u being, respectively, the intensities of the horizontal and vertical components of the light scattered from an unpolarized beam. Values of H_u and V_u are determined by measurements of intensities of scattering at 90 degrees with a Polaroid sheet interposed between the photomultiplier and the scattering cell. With the axis of the Polaroid vertical, V_u is found, while, with the axis horizontal, H_u is measured*. With the type of instrument used

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*It has been pointed out that for large anisotropic molecules the depolarization factor should be modified by substitution of $2\rho_v$ (see Historical Introduction) for ρ_u (184). This substitution would have little effect on the correction factor.

in this work, the correction would become (200):

$$\frac{6 + 3\rho_u}{6 + 6\rho_u}$$

Generally, however, this correction is small for solutions of polystyrene studied at a wavelength of 436 mμ; for example, Brice, Halwer and Speiser (286) and Oth, Oth and Desreux (200) found correction factors for polystyrene ranging from 0.99 to 1.00 for solutions in butanone and toluene, respectively. Since, moreover, no measurable depolarization could be detected for a solution of polystyrene in butanone studied by means of the photometer (equipped with Polaroid sheets) described here, no correction for depolarization was applied.

(vii) Reflection correction:- As the incident beam leaves the flat exit face of the scattering cell, a fraction of the light is reflected towards the centre of the cell. This reflected beam acts as a secondary incident beam; the angular pattern of the light scattered from the reflected beam is, of course, the reverse of the first-order pattern (see Fig. 9-b). Although this effect has been usually ignored, Sheffer and Hyde (291) have shown that the correction may be significant (see also references 200 and 234).

Calculations of this correction were made by the method described by Sheffer and Hyde. For a cell made of glass with a refractive index of 1.55, approximately 4.7 percent of the incident light beam would be reflected at the exit face, provided that the refractive index of the solution is not very different from 1.55. Then the following corrections to scattering ratios S_θ must be made (for a solution in benzene):

1. Reduce S_{90} by 4.7 percent
2. Reduce S_{135} by 4.7 percent of S_{45} to give S'_{135}
3. Reduce S_{45} by 4.7 percent of S'_{135} to give S'_{45}

For relative values of molecular weight and size, this correction is unnecessary. However, the correction has been made for some of the scattering data in this thesis; corrected values are given in parentheses following the uncorrected values.

(viii) <u>Summary of calculations</u>:- Values of S_{90}, the reading obtained from the Helipot scale, were, after correction for the solvent scattering, converted to values of turbidity by the following relationship:

$$\tau = S_{90}\ (\text{solution}) \times \frac{\tau\ (\text{Ludox solution})}{S_{90}(\text{Ludox solution})} \times C_n$$

where C_n = 1.29 for benzene or 1.27 for toluene solutions.

Calculations of $H\frac{c}{\tau}$ and of z (that is, S_{45}/S_{135}) were made. For a solution of polystyrene in benzene, H equalled 4.28×10^{-6} mole-cm.^{2}/g.^{2}, while the value of τ/S_{90} (Ludox solution)* was 5.17×10^{-3} cm.$^{-1}$ per scale division (or 5.42×10^{-3} cm.$^{-1}$ per division, if corrected for reflection).

$$\therefore \quad H\frac{c}{\tau} = \frac{4.28 \times 10^{-6} \times c}{5.17 \times 10^{-3} \times 1.29 \times S_{90}} = 6.46 \times 10^{-4}\frac{c}{S_{90}}$$

or $6.12 \times 10^{-4}\frac{c}{S_{90}}$, if corrected for reflection.

From a graph of $H\frac{c}{\tau}$ as a function of concentration, the intercept and slope were determined. The intercept gave $1/MP_{90}$,** and the slope $2\ A_2$ (see equation B-13). The limiting dissymmetry ratio $[z]$ was found by extrapolation of values of z to zero concentration.

Assuming the model of a monodisperse linear random coil, the value of $1/P_{90}$ corresponding to the value found for $[z]$ was determined from tables given by Cashin (205). After the value of R/λ (where $\lambda = \lambda_0/n_0$) had been found from other tables given in the same reference, R, the root mean square end-to-end distance was calculated.

Corrections for the backward reflection of the incident beam were made as described above.

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*See Results and Discussion for the determination of this value.

**Since the concentration unit used was g./g. of solution instead of g./ml., the value found for $1/MP_{90}$ must be multiplied by the density, 0.878 g./ml.

Results and Discussion

1. Performance

As long as the null point was checked after each reading, measurements of the scattering ratio for a polymer solution generally agreed with each other to within ± 1 percent, or better; the precision of measurement for a pure solvent was from ± 1 to ± 2 percent. Some typical sets of values of the scattering ratio obtained for different solutions of Ludox follow:

0.408, 0.406, 0.406; average: 0.408(±0.001)
0.347, 0.350, 0.350; average: 0.349(±0.002)
0.926, 0.923, 0.923, 0.928; average: 0.925(±0.003)
0.155, 0.153, 0.154, 0.152; average: 0.153(±0.002).

This precision may be compared favourably with the precision obtained with other instruments -- see, for example, Zimm (207), Bosworth, Masson, and Melville (32), and Mariner and Stamm (244).

The maximum precision attainable is apparently limited chiefly by fluctuation in the currents produced in the phototubes. Since the amplitude of these fluctuations varies directly with the square root of the intensity (207), the noise level in the amplified signals is always high with respect to the magnitude of the signal. Although the size of the fluctuations can be decreased by increasing the response time of the galvanometer, measurements are subject to considerable error if the galvanometer is sluggish. Hence it was necessary to achieve, by trial and error, a compromise between quickness of response and sensitivity to the fluctuations.

Since the 120-cycle component is only a small fraction of the total signal from a phototube, the gain of the amplifier must be set at a high level. Nevertheless, with the modified amplifier, it was possible to obtain values of the scattering ratio for a pure solvent with a precision of ± 1 percent, without overloading the amplifier. Drift of values overnight was less than ±1 percent, provided that the batteries were disconnected from the photomultiplier when the instrument was not in use.

2. Calibration

Results of some typical calibration experiments are presented in Table XI and in Figs. 7 and 8. Since the sensitivity of the photometer was different in each case, results found for the calibration constants are, of course, different from each other.

In Fig. 8 (which represents the data given in Set 1, Table XI) values of the scattering ratio, S_{90}, found for a solution of Ludox* are plotted against values of the turbidity determined by means of a Beckman spectrophotometer. It may be

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*The average value of the dissymmetry ratio for the Ludox solution was 1.03; this value may be compared with the following: 1.02 (238, 272), and 1.06 (234).

seen that the curve is essentially linear over its whole range; calculation of the slope by the method of averages (292, p. 126) gives a value of 2.40 x 10^{-2}cm.$^{-1}$ per division. The broken line represents the calibration curve obtained if a correction is made for reflection of the incident beam.

It has been pointed out by Maron and Lou (237) that the slope of a curve giving the scattering ratio of a Ludox solution as a function of turbidity usually increases as the turbidity increases. Fig. 7 shows, however, that no curvature is evident, even at turbidities higher than those encountered in practice. It is legitimate here, therefore, to derive a calibration constant (τ/S_{90}) from measurements made at one concentration of Ludox.

Thus the data presented as Set 2, Table XI, may be used in the calculation of a calibration constant that is applicable to a wide range of turbidities. From these data an average value of 5.17(±0.05) x 10^{-3}cm.$^{-1}$ per division is found for the calibration constant used in the determination of molecular weight reported here.

The validity of the calibration constant determined from Fig. 7 was checked by determination of the scattering ratio for the 0.5 percent solution (in toluene) of the polymer sample, the "Cornell standard polymer," obtained from Cornell University. The following value was obtained for the turbidity at 22°C.:

$$\tau = 2.40 \times 10^{-2} \times S_{90} \times C_n$$

$$= 2.40 \times 10^{-2} \times 0.115\ (\pm 0.001) \times 1.28$$

$$= 3.54\ (\pm 0.02) \times 10^{-3}\text{cm.}^{-1}$$

Agreement between this value and the "best" average value of $3.52 \times 10^{-3}\text{cm.}^{-1}$ reported by Notley and Debye (293) is excellent. Some individual values are listed below:

(1)	Ahlbeck (294):	3.51
(2)	Brice, Halwer, and Speiser (222):	3.50
(3)	Carpenter and Krigbaum (265):	3.60
(4)	Carr and Zimm (197):	3.48
(5)	Doty and Steiner (185):	3.53
(6)	Kronman and Stern (252):	3.5
(7)	Kushner (249):	3.30*
(8)	Maron and Lou (221):	3.50
(9)	Oth, Oth, and Desreux (200):	3.52

It was concluded that the calibration procedure used was satisfactory.

3. Errors

An approximate estimate of the errors involved in the determination of a molecular weight follows:

(a) Reading error, ±1 percent.

(b) Calibration error. Readings of percent transmittance were taken with a precision corresponding to ±0.05 percent transmittance; this error could result in an error of ±2 percent in the turbidity cal-

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*The low value obtained by Kushner may be attributed to the fact that Kushner applied a correction of -4.5 percent to his data in order to allow for reflection of the incident beam.

culated. Since Edelhoch and others (273) found their calibration by Ludox to be different by several percent from a geometrical calibration, it might be safest to assume a calibration error of ±5 percent. Also (see Table XI), neglect of the reflection correction may make calibration readings about 6 percent high.

(c) Error in refractive index increment. Since the refractive index increment term is squared in the calculation of H, the error of ±1 percent in dn/dc causes a possible error of ±2 percent in the constant H.

(d) Errors due to neglect of depolarization and volume correction could amount to, at most, +2 percent.

Hence the error involved in the determination of a relative scattering could amount to, say, ±6 percent (combination of errors (a) and (b)); the error in the determination of absolute scattering could be as great as ±10 to 15 percent. These estimates may be compared with data summarized by Frank and Mark (220) for a cooperative study of the molecular weight of a polymer sample; deviations from the mean ranged from 7.5 percent (butanone solution) to 10.2 percent (benzene solution).

4. Molecular Weight of a High Polymer

Values of the scattering ratios S_{45}, S_{90}, and S_{135} for a polystyrene fraction, F5A2, are given in Table XII; values of Hc/τ and z are also given. In Fig. 10, the scattering function Hc/τ and the dissymmetry are extrapolated to zero concentration. The following values were obtained for the intercepts:

$$\frac{1}{MP_{90}} = 1.5_o, (1.4_9)^{*}; \; [z] = (z)_{c=o} = 2.6_5, (2.8_o)$$

From tables given by Cashin (205), values of $1/P_{90}$ and R/λ may be found as a function of $[z]$. Thus

$$\frac{1}{P_{90}} = 2.47 \; (2.63) \text{ and } \frac{R}{\lambda} = \frac{n_oR}{\lambda_o} = 0.525(0.550)$$

and $M = 1.4_4 \times 10^{-6}$ $(1.5_4 \times 10^{6})^{**}$, and $R = 1.52 \times 10^3$ A°. $(1.59 \times 10^3$ A°.)

Finally, from the slope of the scattering curve, A_2, the second virial coefficient, was calculated to be 3.1×10^{-4}.

These values may be compared with the following values found for the same sample by means of a Brice-Phoenix light-scattering photometer (see Part III):

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*As before, values in parentheses have been corrected for reflection.

**The apparent value for M has been multiplied by the density, 0.878, in order to allow for the fact that concentration should be expressed as g./ml.

$M = 1.33 \times 10^6$; $R = 1.50 \times 10^3$ A.°; $A_2 = 3.0 \times 10^{-4}$

Thus, the values of molecular weight agree within 8 percent and the values for size, within 1 percent.* Since these results were obtained with different stock solutions, solvents, and photometers, the agreement is quite satisfactory. For example, as mentioned above, the deviations for the mean value of the molecular weight for a polystyrene sample that had been distributed to several laboratories was ± 10 percent (220).

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*The close agreement with respect to size is probably fortuitous; uncertainties in extrapolation could easily result in a variation in R of approximately ±5 percent (see Fig. 10).

Summary and Conclusions

A versatile light-scattering photometer, suitable for the measurement of intensities of scattering over an angular range from 35 to 135 degrees, was designed and constructed. The precision of measurement obtainable was ±1 percent for a polymer solution, and ±2 percent for a pure solvent, or better.

Calibration of the photometer by means of solutions of Ludox established a linear relationship between the photometer scale reading and turbidity. In order to check the validity of the calibration, the turbidity of a solution of the "Cornell standard polymer" was determined; the value found after correction for solvent scattering was 3.50×10^{-3} cm.$^{-1}$, in excellent agreement with the accepted value of 3.52×10^{-3} cm.$^{-1}$, an average of results obtained in several other laboratories.

Finally, the molecular weight and size, and the second virial coefficient of a fraction of polystyrene were determined. The results agreed well (to within 8 percent) with results obtained using another calibrated light-scattering photometer.

It was concluded, therefore, that the performance of the photometer constructed was adequate for the study of high polymer solutions.

III. A VISCOSITY AND LIGHT-SCATTERING STUDY OF SOME GRAFT POLYMERS

Introduction

As mentioned in the Historical Introduction, the best method available for the detection of branching in high polymers involves a comparison of the intrinsic viscosity of a polymer suspected of being branched with the intrinsic viscosity of a linear polymer having the same chemical structure and molecular weight. If branching is present, the intrinsic viscosity of the polymer being studied is lower than the intrinsic viscosity of the linear reference polymer; the magnitude of the deviation (expressed as the ratio g -- see equation A-7) is a measure of the average number of branches per molecule. Since errors caused by heterogeneity with respect to molecular weight may be minimized by the comparison of an intrinsic viscosity with a weight-average molecular weight, the use of light-scattering measurements, which yield a weight-average molecular weight, is preferred to other methods for the determination of molecular weight.

Corroboration of the existence of branching may also be obtained from other properties derived from light-scattering measurements; the second virial coefficient, A_2, and the mean square radius, S^2, should be lower for a branched than for a linear polymer of the same molecular weight. Evidence that the value of Huggins' k' (see equation A-13, p. 40) is, in many cases, higher for a branched than for a linear polymer has also been presented.

In Part I of this thesis, indirect evidence of branching in the graft polymers prepared was presented; on the other hand, values of k' found for unfractionated graft polymers were no higher than for linear polystyrene. In order to obtain more direct evidence of both the presence and degree of branching, viscosity and light-scattering measurements were made, both on a series of fractions of linear polystyrene and on a series of fractions of the graft polymers.

In this part of the thesis, results of the viscosity and light-scattering measurements are presented and discussed. Since considerable difficulty was experienced with obtaining reproducible Zimm plots, the results are restricted to measurements of scattering at 45, 90, and 135 degrees.

Experimental

1. Materials

Solvents used for fractionations and precipitations were technical grade. Reagent grade solvents (Eastman Kodak Company), however, were used for light-scattering measurements; only fresh bottles -- each having the same lot number -- were used.

The following values of refractive index were found for the solvents used:

Benzene: $n_{436}^{25} = 1.519$

Toluene: $n_{436}^{25} = 1.516$

Butanone: $n_{436}^{25} = 1.385$

As before, the Ludox solution required for calibration was donated by the Dupont Company.

Polystyrene fraction F21 was obtained from the Monsanto Chemical Company;* fraction T8 was prepared at the university by R.H. Sones (295).

Fraction RP-3-2 was prepared by a single-stage fractionation similar to that used for the graft polymers (see next section). The three-stage fractionation procedure used for the preparation of the linear fractions, F3A2, F5A2, and F7B3, has already been described (159); a similar procedure

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*The author is grateful to the Monsanto Chemical Company for making this fraction available.

was used by Mr. B. Waugh for the preparation of fraction Q_2B_2. The method used for the preparation of the graft samples, including GC-621, has been described in Part I of this thesis.

2. Fractionation

A primary fractionation of the graft polymers was achieved by fractional precipitation from solution, at 45°C., by the progressive addition of a non-solvent.

First, a solution of polymer (concentration about 0.5 percent) in butanone or a butanone-benzene mixture was placed in a separatory funnel that had its stem cut short. The funnel was equipped with a stopper fitted with an inlet tube and a glycerine-sealed paddle stirrer. Then enough non-solvent was carefully added to bring the solution just to the point of precipitation; the addition of a mixture of solvent and non-solvent instead of pure non-solvent sometimes gave more precise control of the precipitation point. Stirring was continued for 30 minutes to ensure the attainment of equilibrium, and the swollen precipitate was allowed to settle.

If the amount of precipitate was judged to be suitable (that is, equivalent to not more than one-fourth of the original weight of polymer), the precipitate was removed through the stopcock of the separatory funnel; if, however, the amount was larger than desired, the precipitate was dissolved by the addition of more solvent, and the precipitation repeated. With some experience, suitable, and more or less equal, amounts of precipitate were readily obtained during fractionations of linear polystyrene. On the other hand, separation of a graft polymer into fractions of approximately equal size was much more difficult; in spite of a great deal of care with the addition of non-solvent, either all or none of the graft polymer tended to be precipitated. In fact, this behaviour resembled the precipitation behaviour of a fairly homogeneous polymer.

After removal, the precipitate, which contained some supernatant liquid from the fractionation vessel, was allowed to stand in a flask held in the fractionation bath. When a complete separation of the precipitate from the supernatant liquid had been obtained, the supernatant liquid was decanted; the precipitate was then rinsed quickly with a small portion of solvent, dissolved in a larger portion of solvent, and finally precipitated by pouring the resulting solution into an excess of methanol or ethanol. The fibrous product resulting from this procedure was recovered by filtration, washed with methanol or ethanol, and dried under reduced pressure at 45°C. to constant weight.

3. Measurements of Intrinsic Viscosity

Values of intrinsic viscosity and Huggins' k' were determined at 25.0 (±0.02)°C. by methods described in Part I of this thesis. Two typical curves representing the dependence of the inherent viscosity, ln η_r/c, on concentration are presented in Fig. 11.

4. Measurements of Light-Scattering

(a) Refractive Index Increment

A value of 0.111, determined in Part II, was taken for the refractive index increment of solutions of polystyrene in benzene.

For a solution of polystyrene in butanone, the value of $\Delta n/c$ at a temperature of 22°C. and a wavelength of 546 mμ was found to be 0.219 (±0.003). The value at 436 mμ was then calculated, using the ratio of the average values at 546 and 436 mμ obtained from data in the report published by Frank and Mark (220). The value thus obtained was equal to

$$0.219 \times \frac{0.231}{0.218}, \text{ or } 0.232\ (\pm 0.003)$$

Although light-scattering measurements were actually made at 27°C., no correction was made for the small variation of the refractive index increment with temperature.*

With these values of $\Delta n/c$, the following values of the constant H may be calculated:

Benzene: $H = 4.32 \times 10^{-6}$ mole-cm.^{2}/g.^{2}
Butanone: $H = 1.57 \times 10$ mole-cm.^{2}/g.^{2}

(b) Calibration of the Photometer

Because of the time required for the rebuilding of the detector and amplifier for the light-scattering photometer

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*A correction would amount to about +1 percent (28); hence the constant H used will be in error by only about 2 percent.

described in Part III, it was impossible to make all the measurements required for the viscosity-molecular weight study without undue delay. Fortunately, permission was granted by Dr. L.M. Hobbs,* of the Department of Chemical and Metallurgical Engineering, University of Michigan, to use one of the Brice-Phoenix light-scattering photometers at the University of Michigan. All measurements reported in this section were made, therefore, with a Brice-Phoenix photometer.

The instrument was calibrated with solutions of Ludox; except for the use of 10-cm. cells in the determination of turbidities, the procedure used was the same as the procedure described in Part II of this thesis. From the data given in Table XIII, and presented graphically in Fig. 12, a value of 0.131 (±0.001)cm.$^{-1}$ per scale division was calculated for τ/S_{90}, where S_{90} represents the ratio of the photomultiplier current generated with the photomultiplier at 90 degrees to the current generated with the photomultiplier at zero degrees. As with the photometer described in Part II, the calibration curve is linear over the range of turbidities occurring in this study. The average dissymmetry ratio [z] for the Ludox solutions was 1.06.

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*The author is very grateful to Dr. Hobbs, and to the Michigan Memorial-Phoenix Project, for permission to use the photometer and for kind cooperation; he also wishes to acknowledge the cooperation given by Mr. R.A. Ahlbeck, who was working with the light-scattering equipment at that time.

In order to check the calibration, the turbidity (corrected for solvent) of a solution of the Cornell standard polymer in toluene (concentration = 0.5 g. polymer per 100 ml. toluene) was determined. The following result was obtained:

$$\begin{aligned}\tau &= 0.131\ (\pm 0.001) \times S_{90} \times C_n \\ &= 0.131\ (\pm 0.001) \times 1.33 \times 0.0204\ (\pm 0.0002) \\ &= 3.56\ (\pm 0.03) \times 10^{-3} \text{cm.}^{-1}\end{aligned}$$

As with the calibration reported in Part II, this result agreed well with values found with other instruments; see, for example, the values listed in Part II.

(c) Procedures

The clarification and measurement procedures were the same as those described in Part II, Section 2.

(d) Corrections to Observed Data

In general, the same corrections were applied to these data as were applied to the data obtained in Part II. Since, however, this study requires only a comparison of the graft with linear polymers, the correction for reflection is not usually given. The following values of the refractive index correction were found for the instrument and solvents used:

Benzene: $C_n = 1.33$
Toluene: $C_n = 1.33$
Butanone: $C_n = 1.08$

(e) Calculations

Combination of values for H and C_n gives the following relationships:

$$\text{Benzene: } H\frac{c}{\tau} = \frac{H \times c}{0.131 \times 1.33\ S_{90}} = 2.47 \times 10^{-5} \times \frac{c}{S_{90}}$$

or $2.34 \times 10^{-5} \times \frac{c}{S_{90}}$ (corrected for reflection)

$$\text{Butanone: } H\frac{c}{\tau} = \frac{H \times c}{0.131 \times 1.08 \times S_{90}} = 1.11 \times 10^{-4} \times \frac{c}{S_{90}}$$

or $1.04 \times 10^{-4} \frac{c}{S_{90}}$ (corrected for reflection).

As before, values of $H\frac{c}{\tau}$ for the linear fractions were extrapolated to zero concentration, $1/MP_{90}$ was determined from the intercept, and A_2 from the slope of the curve. From the limiting dissymmetry, $[z]$, $1/P_{90}$ and R/λ were determined for a random coil with the aid of the tables given by Cashin (205).

Typical curves giving $H\frac{c}{\tau}$ and z as functions of concentration are presented in Fig. 13. As shown by data given in Table XXV for Q_2B_2 and RP-3-2, the reproducibility of results obtained from light-scattering measurements for linear polystyrene in benzene is very good. Since the molecular weights found for fractions Q_2B_2 and F5A2 in butanone agree to within 5 percent of the molecular weights for the same fractions in benzene, the refractive index corrections must be adequate. Duplicate determinations* for graft polymer fractions GC-210-3

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*In each case, the same stock solution was used.

and GC-211-2 in benzene are also in good agreement (see Table XLII). However, values of molecular weight obtained for butanone solutions do not agree with values obtained for benzene solutions; no reason for this failure is evident.

Originally it had been planned to determine the molecular weight and mean square radius of the graft polymers by means of the double extrapolation procedure suggested by Zimm (207). Unfortunately, the precision of measurement obtained at low angles of scattering (30 to 90 degrees) was not high enough to permit accurate extrapolation to zero angle. Hence, it was necessary to assume a random coil model* and proceed as for a linear polymer.

Although the accuracy of the molecular weight found should not, in principle, be affected by this procedure, the exact meaning of the number found for R^2, which represents, for a branched polymer, the mean square end-to-end distance of a linear molecule which would have the same dissymmetry ratio as the branched molecule, is, of course, not clear. However, since for a given molecular weight the dissymmetry of a branched coil must be lower than the dissymmetry of a linear one, the number found for R^2 must be lower than for a linear polymer. Thus a deviation in R^2 from the value expected for a linear polymer will result if branching is present. In fact, the dissymmetry method has been used several

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*In any case, the random coil model is assumed for the calculation of S^2 from the Zimm plot (see Historical Introduction). See also Thurmond and Zimm (8), Wales, Marshall, and Weissberg (46), and Senti (47) -- all of whom used a random coil model for branched polymers.

times in this way to test for branching (32, 47, 65, 139).

In spite of the ambiguity associated with an end-to-end length, the mean square radius of gyration of a branched molecule, S^2, may be obtained in the following way, provided the molecular weight is known. Combination of equation A-3 with the relation $S^2 x 6 = R^2$ gives

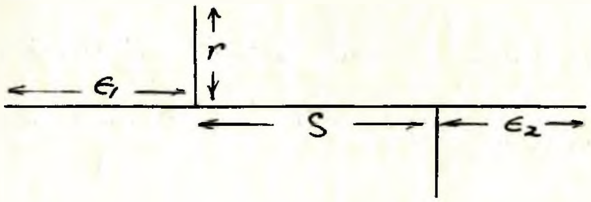
$$\frac{S^2}{S_o^2} = g = \frac{S^2}{R_o^2} \times 6$$

$$\text{or, } S^2 = \frac{R_o^2}{6} \times g$$

where R_o^2 is the mean square end-to-end distance of a linear molecule having the same molecular weight and chemical structure as the branched molecule with the mean square radius of gyration S^2. If, then, g is found from measurements of intrinsic viscosity, preferably in a fairly poor solvent, in this case, butanone, and R_o^2 is obtained from a plot of R_o^2 as a function of molecular weight, the value of S^2 may be readily calculated.

Values of Φ were calculated from values of intrinsic viscosity, mean square end-to-end distance, and molecular weight; values of Φ' were calculated in a similar manner, except for the substitution of mean square radius of gyration for mean square end-to-end distance (see equation A-6).

With molecular weights of the backbone and graft polymers known, values of g were calculated for a model by means of a summation procedure given in a paper by Wales, Marshall and Weissberg (46), and compared with experimental values obtained from intrinsic viscosities. The model chosen consists, as shown, of a linear backbone chain with branches of uniform



length, uniformly spaced along the backbone chain. For the sake of simplicity, it was assumed that $\epsilon_1 = \epsilon_2 = S$; the summation required for the calculation of g for various frequencies of branching was reduced to a convenient form by Dr. P. Beesack of McMaster University (see Appendix D). In the calculations, the first two terms of the summation, being small with respect to the other terms, were neglected.

Results and Discussion

Light-scattering data for the graft polymers studied are presented in Tables XXVI and XLI, inclusive, and summarized in Table XLII, while data for the fractions of linear polystyrene used for comparison are presented in Tables XIV and XXIV, inclusive, and summarized in Table XXV. Viscosity data for the graft and linear polymers are given in Tables XLIV and XXV, respectively.

1. Molecular Dimensions

Evidence of branching in the graft polymers is provided by the data presented in Fig. 14, in which the mean square end-to-end distance R^2 of a polymer molecule* (in benzene) is plotted against molecular weight. Although the relationship between R^2 and M is approximately linear** for the fractions of linear polystyrene, all values of R^2 found for the graft polymers lie below the line for the linear polystyrene. In other words, the apparent mean square end-to-end distance for a graft polymer is less, for a given molecular weight, than the mean square end-to-end distance for linear

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*A small number beside a point on the graph indicates the order in which the fraction appeared during fractionation; thus the number 2, when placed beside a point representing the GC-210 series, indicates the second fraction obtained in the fractionation of GC-210 -- namely, fraction GC-210-2.

**An approximately linear relationship may be expected; see, for example, Carr and Zimm (28), Schulz, Cantow, and Meyerhoff (243), Notley and Debye (293), or Kunst (296).

polystyrene. This behaviour clearly indicates the presence of branching in the graft polymers.

Two other observations may also be made.

First, the effect on R^2 of heterogeneity with respect to molecular weight is probably small. In order to demonstrate the probable magnitude of the effect, the value of R^2 for a linear fraction, RP-3-2, prepared by a single-stage (primary) fractionation procedure similar to the procedure used for the fractionation of the graft polymers, is plotted on the graph. As might be expected -- for a z-average quantity is greater than a weight-average one (see Historical Introduction) -- the value of R^2 lies slightly above the line for the other linear fractions, which, each being a product of a three-stage (tertiary) fractionation, are probably more homogeneous with respect to molecular weight than is fraction RP-3-2; the deviation, however, is very small.

Second, the deviation of a given point from the curve for linear fractions tends to be less for the fractions that were precipitated first during fractionation than for the fractions that were precipitated later.

2. Intrinsic Viscosities

Further evidence for the presence of branching in the graft polymers may be found in Fig. 15, in which log $[\eta]$ is plotted against log M for both linear and graft polymers.

With the fractions of linear polystyrene the following relationships were found between intrinsic viscosity and molecular weight:

$$\text{(solvent: butanone)} \quad [\eta] = 1.3 \times 10^{-4} M^{0.66}$$

$$\text{(solvent: benzene)} \quad [\eta] = 1.9 \times 10^{-4} M^{0.69}$$

The relationship found for intrinsic viscosities in butanone is almost identical with the one found by Doty, Affens, and Zimm (225) -- namely, $1.6 \times 10^{-4} M^{0.66}$ ($2.0 \times 10^6 < M < 1.2 \times 10^7$); the relationship for benzene is similar to one found by Gregg and Mayo (297) -- namely, $[\eta] = 1.7 \times 10^{-4} M^{0.72}$ ($7.0 \times 10^5 < M < 6.0 \times 10^5$).*

The relationship between the intrinsic viscosity of a graft polymer and its molecular weight is, on the other hand, quite different. With the exception of fraction GC-211-1, the intrinsic viscosity of each sample of graft polymer is lower than the intrinsic viscosity of a linear fraction having the same molecular weight. This behaviour is, of course, to be expected if the graft polymers are branched.

These deviations cannot be caused by heterogeneity with respect to molecular weight. As mentioned above, the effect of heterogeneity with respect to molecular weight on the position of the point corresponding to the linear primary fraction RP-3-2 is small, and, in fact, within experimental error.

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*Although Gregg and Mayo determined their molecular weights by means of osmotic pressure, not light-scattering, measurements, their relationship is closer to the one found here than to other relationships found for weight-average molecular weights (298, 299).

Moreover, even if an appreciable effect of heterogeneity existed, for the graft polymers, the value of R^2 -- a z-average quantity -- at a given molecular weight would be <u>higher</u> for a primary fraction of a graft polymer than for a tertiary, and hence more homogeneous, fraction of a linear polymer.

Another difference between the linear and graft polymers is in their fractionation behaviour. When molecular dimensions are plotted against molecular weight (Fig. 14), the size, for a given molecular weight of a fraction of a graft polymer tends to vary inversely with the order in which the fraction had separated during fractionation. This tendency is also evident in Fig. 15; the intrinsic viscosity of the first fractions tends to agree more closely with the intrinsic viscosity expected for a linear fraction of the same molecular weight than the intrinsic viscosity of later fractions. Since the extent of the deviation, measured by the ratio g, is a measure of the degree of branching, this fact must mean that the highly branched materials are more soluble than less highly branched ones. Although such an anomalous solubility has been predicted (300), this effect has seldom been reported; see, however, Baker, Fuller, and Heiss (130) and Alfrey, Bartovics, and Mark (145). In this case, at least, the fractionation behaviour seems to be determined by the size, and hence the degree of branching, of the molecules, as well as by the molecular weights;* with most fractions studied, the effect of the degree of branching on fractionation behaviour seems to be dominant.

Another observation may be made about the viscosity behaviour of the graft fractions (Fig. 16). The relationship between the intrinsic viscosities in benzene and butanone is slightly different for the graft fractions than for the linear ones; the intrinsic viscosity of a graft fraction (in butanone) is relatively higher than is the intrinsic viscosity of a linear fraction. It may be significant that several points corresponding to fractions of some styrene-divinylbenzene copolymers lie very close to the points obtained for the graft fractions.

The relationship between intrinsic viscosity and dimensions is discussed in the following section.

3. The Flory Constant Φ or Φ'

Values of Φ, calculated for the linear fractions of polystyrene, are given in Table XXV. The average value for solutions in benzene is 2.4 x 10^{21}, which agrees with the value (1.9-2.3)x 10^{21} suggested by Flory (4, p. 616); the average of the two values calculated for solutions in butanone is 2.1 x 10^{21}.

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*In fact, little fractionation of the graft polymers with respect to molecular weight seems to have occurred. Molecular weights of the graft fractions are surprisingly similar; this fact may be associated with the difficulty found with fractionation (see Experimental part).

In contrast, individual apparent values of Φ found for the graft polymers (Table XLII) range from 2.3 x 10^{21} to 6.2 x 10^{21}. This behaviour is consistent with branching, for, with a branched polymer, the value found for R from dissymmetry measurements must be lower than the value for a linear polymer of the same molecular weight, and hence the apparent value of Φ ($\Phi = [\eta] \times M/R^3$) should be higher.

If the grafts are branched, however, substitution of S^3 for R^3 in equation A-6 should yield the constant Φ'. If Flory's assumption (4, p. 611) that Φ' is a constant for both linear and branched molecules holds, Φ' should equal 14.7 x Φ, or 3.1 x 10^{22}.

Values (for solutions in benzene) calculated for S^3 (by the method outlined in the Experimental section) and for Φ' are given for the graft polymers in Table XLIII. Results given in the first column of Φ' values were calculated using values of g determined by means of equation A-7; results given in the second column are based on values of g calculated by the Stockmayer-Fixman method (24). The average value of Φ' found was 3.4 x 10^{22} -- in excellent agreement with the value expected. If it is assumed that the values of g found by means of the Stockmayer-Fixman procedure are more reliable than values found directly from a ratio of intrinsic viscosities, then Φ' may be somewhat different for the graft polymers than for linear ones -- 4.5 x 10^{22} (or 3.5 x 10^{22}, if data for GC-140-3, GC-210-2, GC-211-3, and GC-621 are omitted), compared to

3.1×10^{22}.* In any case, the use of S^3 rather than R^3 for the graft polymers results in a proportionality between intrinsic viscosity and molecular size that is similar to the proportionality between the intrinsic viscosity and the molecular size of a linear polymer. This similarity is illustrated in Fig. 17, in which values of S^3/M, for both linear and graft polymers in benzene, are plotted against M. Results obtained for solutions in butanone are badly scattered, and have, therefore, been omitted from Fig. 17.

Again, these results are consistent with the presence of branching in the graft polymers.

Since the fractions of graft polymers were obtained from a single fractionation, they may be more heterogeneous with respect to molecular weight than are the linear fractions, most of which are tertiary ones. Use of a correction term (124) would result in a still higher apparent value of Φ' for the branched polymer.

4. The Second Virial Coefficient, A_2

Further confirmation of the existence of branching in the graft polymers may be found in a comparison of the second virial coefficient, A_2, for linear and graft polymers. As

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*The possibility of a difference has been suggested before (8, 119); a difference has been shown to exist for dextran (47).

shown in Table XXV, values of $A_2 \times 10^4$ for the linear fractions of polystyrene are between 2.6 and 5.4 for solutions in benzene. The values are, as expected, lower for solutions in butanone -- a poorer solvent than benzene; for fraction Q2B2, the value of $A_2 \times 10^4$ drops from an average of 3.8 in benzene to 2.2 in butanone, while for fraction F5A2, the value drops from 3.0 in benzene to 1.6 in butanone. These values are in good agreement with values given in the literature, such as 3.7 (238) for linear polystyrene ($M = 9 \times 10^5$) in benzene, or a range from 0.9 to 1.9 (M from 1.8×10^6 to 6.2×10^5) for solutions in butanone (8).

On the other hand, values of $A_2 \times 10^4$ given in Table XLII for the graft polymers range from -0.3 to 1.6 in benzene. Even though the reproducibility of A_2 is only fair (see Tables XXV and XLII), none of the values for the graft polymers overlapped the range of values found for the linear polymers.[*] As mentioned in the Historical Introduction, the lowering of A_2 by branching has been predicted on theoretical grounds (24); experimental evidence for the lowering has also been obtained (8, 59). Thus, the magnitude of the second virial coefficient in benzene for the graft polymers is consistent with branching.

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[*] It is true that the value of A_2 decreases with increasing molecular weight, and that most of the graft polymers have higher molecular weights than the linear polymers studied; nevertheless, in the range of molecular weights from 1.4×10^6 to 3.2×10^6 -- which include both linear and graft polymers -- values of A_2 are invariably lower for the graft than for the linear polymers.

It is interesting, however, that values of A_2 for solutions of the graft polymers in butanone, ($A_2 \times 10^4$ from 0.9 to 1.1), though lower than for the linear polymers, are higher with respect to the values in benzene than is the case with linear polymers. In other words, with the graft polymers, values of A_2 for solutions in butanone overlap with values for benzene solutions; in fact, in one case, fraction GC-211-2, the value of A_2 in butanone is greater than the value in benzene. Although there are not enough data to permit generalization, the possibility of an unusual effect of solvent on A_2 might be considered. If this effect is real, the graft polymers must be relatively more soluble in butanone than are the linear polymers; this conclusion agrees with the relationship found between the intrinsic viscosities in benzene and butanone (Section 2).

5. The Branching Ratio, g

As shown in Table XLV, values of g found from measurement of intrinsic viscosity range from 0.65 to, approximately, unity; values of g calculated by the Stockmayer-Fixman method (24) range from 0.58 to unity. These experimental values may be compared with values calculated using the model described earlier, and the average number of branches per molecule estimated.

If, for example, fraction GC-211-3 (average molecular weight of the backbone chain equal to 1.36×10^5) is considered, the following values of g may be calculated for two, four, and eight branches per molecule:

2 branches/molecule: g = 0.97
4 branches/molecule: g = 0.62
6 branches/molecule: g = 0.40
8 branches/molecule: g = 0.35

Since the experimental value of g, calculated by the Stockmayer-Fixman method, is 0.46, a model having about five or six branches spaced equally along the backbone chain would correspond to the experimental data, which has not been corrected for reflection of the incident beam.

Application of the reflection correction to the scattering data for the linear fractions and for GC-211-3 leads to a lower value of g, and hence to a higher value for the number of branches per molecule. If this correction is considered, g (SF) becomes equal to 0.43 -- corresponding to a model having six branches spaced equally along a backbone molecule.

The hydroperoxide analyses (see Part I) indicated that graft polymers of the GC-211 series (prepared using the same backbone as used for GC-210) could have 12 branches per molecule. Although the number of branches estimated from the value of g apparently does not agree as well as might be desired with the number estimated from the hydroperoxide content, the following points should be considered:

1. The fractionation behaviour observed for graft polymers suggests that the most highly branched polymers may have remained in solution after the first fractions were pre-

cipitated.

2. The spectrophotometric analysis of cumene hydroperoxide gave a value for hydroperoxide content approximately double the expected value. If this analysis has any bearing on the analysis of the polymers studied here, the results for polymers may be appreciably higher than the true values (see Part I).

3. It is assumed that the analysis for the hydroperoxide content of the graft polymers detects all hydroperoxide groups present. It is conceivable that some unreacted hydroperoxide groups, situated near the centre of a very large, bushy molecule, might be protected by the large swollen branches from attack by the ferrous reagent.

4. It is assumed that each hydroperoxide group in the backbone molecule initiated the growth of a long branch. If some of the branches are only a few monomer units long, they will not contribute to an appreciable decrease in the value of g; at the same time, the existence of each branch of this type will have resulted in the disappearance of a hydroperoxide group.

5. It is assumed that the average molecular weight of the backbone molecule <u>in a given fraction of graft polymer</u> is the same as the average molecular weight of the backbone polymer <u>before</u> the grafting procedure. If the molecular weight of the backbone in the fraction is actually four times the molecular weight of the original backbone material, the value of g, for a model having two branches per molecule, decreases

from 0.96 to 0.75. Since the backbone polymers were unfractionated, the occurrence of such an effect is quite possible.

6. It is assumed that the theories developed by Zimm and Stockmayer (1) and modified by Stockmayer and Fixman (24) yield quantitative values for the degree of branching. Although, in some cases, the degree of branching found from measurements of g agree well with the degree of branching expected from kinetic data (24), no comprehensive comparison with the degree of branching determined directly and unequivocally has yet been made. It may be significant that the presence of eight branches per molecule (M = 1350) was found by Schaefgen and Flory (98) to reduce the value of g to 0.7; this value of g is lower than would be predicted by means of the model used here.

In view of the uncertainties inherent in the assumptions just discussed, the agreement between the number of branches estimated in the two ways may be considered as satisfactory.

6. Huggins k'

So far, all available experimental data presented indicate the presence of branching in the graft polymers. From measurements of intrinsic viscosity and molecular weight, it has been estimated that the most highly branched graft polymers may contain approximately six branches per molecule.

Although it might, therefore, be expected that the value of Huggins k' for the graft polymers would be higher than for linear polystyrene, the data presented in Table XLIV show that values of k' in benzene or butanone are, in fact, no greater for the graft polymers than for linear polystyrene. The following average values were obtained:

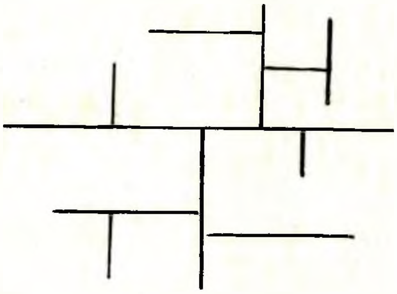
Average k' (benzene) for a graft polymer = 0.34

Average k' (butanone) for a graft polymer = 0.36

No trends with respect to molecular weight may be noticed. These averages may be compared with averages of 0.35 (benzene) and 0.39 (butanone) found previously for linear polystyrene (27). If data for fractions GC-210-1, GC-211-4, and GC-230-1 (in benzene), and data for fraction GC-140-3 (in butanone) -- all of which diverge considerably from the average -- are omitted, agreement between the two sets of values becomes even better.

It is concluded, therefore, that the value of Huggins' k' is not affected by the presence of an average of six linear, or simple, branches per molecule. This result is rather surprising, for it has been shown previously (159) that the incorporation of as little divinylbenzene as 0.01 percent in polystyrene resulted in a detectable increase in k' in butanone (from 0.39 to 0.44 -- see also Historical Introduction). On the other hand, Senti and others (47) found no deviations in the value of k' for fractions of dextran unless the value of g was less than about 0.4; also, Charlesby (175) found that values of k' for polysiloxane samples with two branch points per molecule were no greater than values for linear polysiloxanes.*

Further consideration of the values of k' given in the literature shows that increases in k' with branching have been noticed only with materials that have, or could have, branches that are themselves branched.



The only data available for materials that definitely contain only simple branches is given by Schaefgen and Flory (98); the following average values of k' may be calculated for their branched condensation polymers:

linear; k' = 0.36 (average of 3 determinations)
4 branches/molecule; k' = 0.36 (average of 2 determinations)
8 branches/molecule; k' = 0.38 (average of 4 determinations)

Since the average value of k' for the most highly branched material would become 0.35 if one of the four determinations is omitted, it is questionable that the slight increase in k' with branching is significant. Although Youngson and Melville found some evidence for an increase in k' with the degree of

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*It should be noted that the results obtained by Senti and Charlesby were published after work discussed in this thesis had been essentially completed.

branching in branched polyesters, Schaefgen and Flory have pointed out that the branched polyesters used tend to form gel. Except for data given in this thesis, no information appears to be available for graft polymers containing simple linear trifunctional branches distributed at random along a backbone chain.

In the absence of further evidence, it seems likely that the value of Huggins' k' is affected more by bushy than by simple branching. In other words, a complex, bushy structure with either branches on branches or crosslinks may be required in order that the value of k' be affected by branching. This conclusion is not unreasonable, for the segment density of a polymer molecule consisting of a backbone chain carrying a few long branches should be much less than the segment density of a bushy molecule of the same molecular weight with branches that are themselves branched. In other words, the segments of a bushy molecule should have greater opportunities for contact or interaction with one another than would segments of a less dense molecule. Since Huggins' k' is increased by factors such as association or the use of a thermodynamically unfavourable solvent that tend to promote contacts between polymer segments (see reference 159), the value of k' for a molecule containing a few long branches may, understandably, not be measurably different from the value for a linear molecule.

Summary and Conclusions

A viscosity and light-scattering study of several primary fractions and one unfractionated sample of graft polymers, prepared by polymerizing styrene in the presence of partially oxidized copolymers of styrene and 4-vinylcyclohexene-1, was made; a parallel study was made with fractions of linear polystyrene. The intrinsic viscosities in benzene and butanone, the molecular weight, the molecular size and second virial coefficient in benzene (and, in a few cases, in butanone) were determined.

Confirmation of the conclusion reached in Part I of this thesis that the graft polymers are branched was provided by the following observations:

1. For a given molecular weight, the dissymmetry, and hence the value obtained for the apparent mean square end-to-end distance of the polymer molecule, was lower for a graft than for a linear polymer.

2. For a given molecular weight, the intrinsic viscosity of a graft polymer was, in general, lower than for a fraction of linear polystyrene.

3. Although with graft polymers the values found for the Flory constant Φ calculated using values obtained for R^3 were irregular and much higher than expected for a linear

polymer, the use of S^3, the cube of the root-mean-square radius of gyration, led to an average value for Φ of 3.4×10^{22}--in good agreement with the average value of 3.1×10^{22} found for linear polystyrene.

4. Values of A_2, the second virial coefficient, were much lower for solutions of the graft polymers in benzene than for solutions of the linear ones.

Approximate calculations of the branching ratio g were made for a molecular model consisting of linear branches of equal length, equally spaced along a backbone chain. Comparison of calculated with experimental values of g led to the conclusion that an average of up to six branches per molecule were present in the graft polymers.

In spite of all the evidence for branching, values of Huggins' k' for solutions in benzene and butanone were no greater than values found for linear fractions. It is concluded, therefore, that Huggins' k' is not affected by the presence of six simple branches in a polymer molecule.

Since available evidence for an effect of branching on k' has been obtained for polymers that are crosslinked or branched in a bushy manner, it was also concluded that Huggins' k' may be more sensitive to the bushy type of branching, or to crosslinking, than to simple branching.

Several other observations were also made.

1. Fractionation of the graft polymers tended to be governed by a large extent by size, rather than by molecular

weight. Thus, in most cases, the most highly branched fractions were precipitated later than less highly branched ones.

2. An indication was obtained that, although the intrinsic viscosity of the graft polymers is proportional to S^3/M, the proportionality constant, Φ', may be higher for a graft polymer than for a linear one.

3. Although the data were rather scattered, a graft polymer, for a given intrinsic viscosity in benzene tended to have a slightly higher intrinsic viscosity in butanone than did a linear polymer. Some support for this conclusion may be found in the fact that values of A_2 found for solutions of graft polymers in butanone were higher than expected.

GENERAL SUMMARY AND CONCLUSIONS

Graft polymers were prepared by the redox polymerization of styrene in the presence of oxidized polystyrene or copolymers of styrene and 4-vinylcyclohexene-1; the maximum number of hydroperoxide groups per thousand monomeric units of the oxidized polymers was 18. Evidence that the grafting of polystyrene had occurred was obtained from measurements of monomer disappearance, of the decrease in hydroperoxide content of the backbone polymer during reaction, and of the infra-red absorption by the polymer before and after the grafting procedure.

Measurements of intrinsic viscosity and light-scattering confirmed the presence of branching in the graft polymers. For a given molecular weight, values found for the intrinsic viscosity, molecular size, and second virial coefficient were, in general, lower for fractions of the graft polymers than for fractions of linear polystyrene. It was also observed that the solubility behavior of the graft fractions was anomalous; the fractions showing the greatest tendency to have properties characteristic of branching were the most, rather than the least, soluble.

Comparison of experimental values of the branching ratio g with values calculated for a model having about six linear branches equally spaced along a backbone chain was made; the branching ratios found were consistent with a model having up to approximately 6 branches per molecule.

It had been expected that the values of Huggins' k', high values of which have often been associated with the presence of random branching (that is, branching permitting the growth of branches on branches),or crosslinking, would be higher for the graft polymers than for linear ones. However, in spite of the fact that the presence of branching in the graft polymers was demonstrated, the values of k' for solutions in benzene or butanone were no higher for fractions of graft polymers than for fractions of linear polystyrene (k' in the range 0.3 to 0.4). It was, therefore, concluded that, although k' is apparently increased by the presence of cross linking on a bushy type of branching, it is not measurably affected by the presence of a few linear branches in a polymer molecule.

In order to permit the determination of absolute molecular weight, size, and second virial coefficient, a versatile light-scattering photometer capable of yielding angular scattering measuremants within the range from 35 to 135 degrees was designed and constructed. The precision of measurement was about ± 1 percent for a polymer solution, and about ± 2 percent for a pure solvent. After calibration by means of a solution of colloidal silica, the value found for the turbidity of the "Cornell standard polymer" agreed with results obtained in several other laboratories. Finally, the molecular weight, size, and second virial coefficient found for a fraction of polystyrene agreed well with results obtained for the same fractions by means of another calibrated light-scattering photometer. It was concluded that the performance of the photometer was adequate for the study of high polymer solutions.

SUGGESTIONS FOR FUTURE WORK

1. A detailed study of the angular dependence of scattering for some graft fractions would be very desirable. Values obtained for the molecular weight and dimensions could be compared with those estimated from dissymmetry measurements.

2. It is suggested that values of Huggins' k' be obtained for other types of graft polymers, such as those prepared by the methods given by Metz and Mesrobian, or Hahn and Lechtenböhmer.

3. Since it is possible that the effect of solvent on a branched polymer may be quite different from the effect on a linear one, a comparison of the effects of solvents on branched and linear polymers would be very interesting. Such a study would require the determination in a range of solvents--including good, poor, and ideal ones--of the molecular size and the second virial coefficient. If molecular weights were then determined from both osmotic and light-scattering measurements, and if viscosity measurements were extrapolated to zero rate of shear, values of the Flory constant Φ' for linear and branched polymers could be accurately compared. The results could then be correlated

with the values found for the second virial coefficient; the anomaly noted in this thesis concerning the abnormally large value of A_2 for a branched polymer could thus be examined in more detail.

4. In the viscosity measurements reported here, the effect of rate of shear on viscosity has been neglected. Since little is known about the effects of shear on a branched, as compared with a linear, molecule, a comparison of the effect of shear on various types of branched polymers with the effect on linear ones should be valuable.

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APPENDIX A

Tables

TABLE I

POTENTIOMETRIC DETERMINATION[a] OF HYDROPEROXIDE CONTENT FOR SOME POLYMERIC HYDROPEROXIDES

Sample	Vol. 0.002 N thiosulfate solution required, ml.	Av. vol., ml.
Cumene hydroperoxide[b]	4.9, 4.5, 5.0, 5.0	4.8 (±0.3)
HP-1300	3.0, 3.2	3.1 (±0.1)
HP-1401	4.3, 4.5[c]	4.4 (±0.1)
HP-1402	4.5, 4.5	4.5 (±0.0)
HP-1404	3.0, 4.0	3.5 (±0.5)
HP-1405	1.8, 1.5	1.6_5 ($\pm 0.1_5$)
HP-1406	0.5, 0.8	0.6_5 ($\pm 0.1_5$)
HP-B4	2.9, 2.8, 2.9	2.9 (±0.1)

[a] The use of technical butanone and dried undistilled isopropanol was found to be satisfactory; no detectable blank correction was required.

[b] Concentration; 0.124 g./100 ml. butanone.

[c] Solvent: benzene.

TABLE II

POTENTIOMETRIC DETERMINATION OF HYDROPEROXIDE CONTENT FOR SEVERAL UNKNOWNS[a]

Sample	Vol. thiosulfate solution, ml.	
	Observed	Calculated
A	5.0	4.4
B	4.2	4.3
B	4.6	4.3
C	5.8	5.8
D	3.6	3.6

[a] Unknowns A, B, and C were solutions of cumene hydroperoxide in benzene; D was a mixture of solutions of HP-1402 and HP-1403 in benzene.

TABLE III

SPECTROPHOTOMETRIC DETERMINATION OF HYDROPEROXIDE CONTENT FOR SOME POLYMERIC HYDROPEROXIDES

Sample	Hp. no.[a]	Av. Hp. no.	% Precision[b]
HP-6003	13 , 11	12 (±1)	± 8
HP-8005	4.4, 3.6	4.0 (±0.4)	± 10
HP- 110.07B	4.4, 4.8	4.6 (±0.2)	± 4
HP- 110.07C	14 , 13	$13._5$ (±0.5)	± 4
HP- 110.07R	5.8, 5.7	5.7_5 (±0.05)	± 0.9
HP- 110.12	10 , 8.6	9.3 (±1.3)	± 14
HP- 110.13	15 , 14	14.5 (±0.5)	± 3
HP- 120.01	4.8, 4.5	4.6_5 (±0.1_5)	± 3
HP- 150.00	3.2, 2.9	3.0_5 (±0.1_5)	± 5
HP- 150.01	4.7, 3.8	4.2_5 (±0.4_5)	± 11

[a] Each of a pair of values was obtained using a separate solution; also, each is derived from a set of optical-density readings having an internal precision of ± 1%.

[b] Average precision: ± 6%.

TABLE IV

HYDROPEROXIDE CONTENT OF SOME UNOXIDIZED POLYMER SAMPLES

Sample	Trial[a]	Hp. no.[b]	Av. Hp. no.	% Precision
C-60	1	0.39, 0.39		
	2	0.42, 0.42		
	3	0.44, 0.44	0.42 (±0.03)	± 7
C-60A	1	0.21, 0.19		
	2	0.18, 0.18	0.19 (±0.02)	± 10
C-40	1	0.16		
	2	0.19		
	3	0.25		
	4	0.22	0.21 (±0.04)	± 20

[a] Each trial for a given sample was carried out on a different day from the others.

[b] Each value within a trial represents the determination of Hp. no. for a separate aliquot of one stock solution.

TABLE V

EFFECT OF OXIDATION ON INTRINSIC VISCOSITY[a]

Sample	$[\eta]$ in benzene, dl./g.	
	Before	After
C-70	0.77	0.77
HP(GC-240)	6.19	6.25
HP(GC-241)	5.13	4.88

[a] Intrinsic viscosities were calculated, with a precision of ± 3%, from a measurement of flow time at one concentration, using equation A-13, assuming a value for k' of 0.38.

TABLE VII

VISCOSITY AND CONVERSION DATA FOR BLANK POLYMERS

Sample	Weight, g.		Polymerization time, hr.	Percent Conversion	$[\eta]$ in benzene, dl./g.	
	Polymer	Styrene			Backbone	Product
GC-141[a]	-	22.7	13.5	2.5	-	3.40
GC-250	1.0	18.2	6.0	2.8	1.58	2.38
GC-320	1.0	9.1	5.0	5.6	0.92	1.03
GC-321	1.0	9.1	5.0	2.2	0.92	1.03
GC-322	1.0	9.1	5.0	2.2	0.92	1.02
GC-323	1.0	9.1	5.0	3.3	0.92	1.02

[a] This sample was prepared using the same recipe as for GC-140, except that oxidized polymer was omitted.

TABLE VIII

POLYMERIZATION AND CONVERSION DATA FOR GRAFT POLYMERS PREPARED IN SOLUTION

Sample No.	Wt. backbone, g.	Wt. styrene, g.	Vol. benzene, ml.	Time, hr.	Temp., °C.	Hp. no. backbone	% conversion
GC-510	1.0	8.0	200	19.5	85	6.1	0.0
				43.5	85		10
				95.0	85		13
GC-520	1.0	8.0	100	48.0	83	1.5	11
GC-600	1.00	80	-	2.5	60	5.2	0.0
				7.3	60		2.1
				18.5	60		2.8
GC-601 (blank)	-	80	-	23.0	60	-	0.2

TABLE VIII

POLYMERIZATION AND CONVERSION DATA FOR GRAFT POLYMERS PREPARED IN SOLUTION

Sample No.	Wt. backbone, g.	Wt. styrene, g.	Vol. benzene, ml.	Time, hr.	Temp., °C.	Hp. no. backbone	% conversion
GC-510	1.0	8.0	200	19.5	85	6.1	0.0
				43.5	85		10
				95.0	85		13
GC-520	1.0	8.0	100	48.0	83	1.5	11
GC-600	1.00	80	-	2.5	60	5.2	0.0
				7.3	60		2.1
				18.5	60		2.8
GC-601 (blank)	-	80	-	23.0	60	-	0.2

TABLE IX

DECREASE IN HYDROPEROXIDE CONTENT DURING GRAFTING

Sample no.	Hp. no. of backbone	Hp. no. of graft polymer	
		Calculated[a]	Observed
GC-100	9.5	2.5	(2.0)[a]
GC-110	18.4	3.7	0.60
GC-140	7.7	1.4	0.33
GC-180	1.9	0.97	0.86
GC-190	3.0	1.5	1.1
GC-200	2.0	1.2	0.77
GC-210	9.0	2.4	0.57
GC-211	9.0	1.1	0.97
GC-220	16.0	3.4	0.64
GC-230	7.0	1.7	0.27
GC-240	14.0	2.6	0.42
GC-241	14.0	4.4	(3.6)[a]
GC-621	6.6	-[b]	-[b]

[a] Appears to be anomalous.

[b] Not determined.

TABLE X

EFFECT OF EMULSION CONDITIONS ON THE STABILITY OF A POLYMERIC HYDROPEROXIDE

(All samples dissolved in 20 ml. benzene)

Sample no.	Wt., g.	Time, hr.	Hydroperoxide number Before	 After
HP-110-05	0.60	1.5	4.6	4.9
HP-110-10	0.80	1.0	5.6	5.2

TABLE XI

CALIBRATION DATA[a] FOR MANSON PHOTOMETER

Set	$\tau \times 10^2$ cm.$^{-1}$	S_{90}
1	1.49	0.617 (0.584)
1	1.40	0.573 (0.543)
1	1.33	0.527 (0.499)
1	0.754	0.345 (0.327)
1	0.506	0.228 (0.216)
2	0.865	1.69 (1.61)
2	1.08	2.08 (1.98)

[a] Data given in parentheses have been corrected for reflection.

TABLE XII

SCATTERING DATA[a] FOR POLYSTYRENE FRACTION F5A2
(Solvent: Benzene, T = 22°C.)

Conc. x 10^3 g. polymer/g. solution	S_{45}	S_{90}	S_{135}	$H\frac{c}{\tau}$	[z]
0.858	0.968 (0.950)	0.289 (0.275)	0.433 (0.388)	1.92 (1.91)	2.24 (2.44)
2.92	1.63 (1.59)	0.550 (0.524)	0.990 (0.913)	3.43 (3.42)	1.65 (1.74)
4.37	1.79 (1.78)	0.659 (0.628)	1.27 (1.19)	4.28 (4.37)	1.40 (1.45)
5.08	1.88 (1.82)	0.731 (0.695)	1.37 (1.28)	4.50 (4.48)	1.37 (1.42)

[a] Each value reported for S_θ is the mean of at least two measurements; the precision in each case is ± 1 percent.

TABLE XIII

CALIBRATION DATA[a] FOR BRICE-PHOENIX PHOTOMETER

$\tau \times 10^2$ cm.$^{-1}$	S_{90}
3.57	0.274 (0.260)
4.83	0.368 (0.348)
6.58	0.503 (0.476)
9.75	0.742 (0.703)

[a] Data given in parentheses have been corrected for reflection.

TABLE XIV

LIGHT-SCATTERING DATA FOR LINEAR POLYSTYRENE

Fraction F 21

(Solvent: Benzene)

$c \times 10^3$ g. polymer/g. solution	$S_{45} \times 10^2$	$S_{90} \times 10^2$	$S_{135} \times 10^2$	$H \frac{c}{\tau} \times 10^6$	$[z]$
1.36	1.48	0.634	1.16	4.03	1.28
2.25	2.16	0.969	1.74	4.38	1.24
3.12	2.65	1.20	2.20	4.92	1.20
4.05	3.01	1.41	2.54	5.43	1.18

Intercept = 3.25×10^{-6}

$[z]$ = 1.32

Slope = 8.6×10^{-4}

$1/P_{90} = 1.23$

$n_oR/\lambda = 0.22_2$

$M = 3.34 \times 10^5$

$R = 6.37 \times 10^2$ A°

$A_2 = 4.3 \times 10^{-4}$

TABLE XV

LIGHT-SCATTERING DATA FOR LINEAR POLYSTYRENE

Fraction F $7B3$

(Solvent: Benzene)

$c \times 10^3$ g. polymer/g. solution	$S_{45} \times 10^2$	$S_{90} \times 10^2$	$S_{135} \times 10^2$	$H \frac{c}{\tau} \times 10^6$	$[z]$
1.06	2.23	0.785	1.36	3.33	1.67
1.89	3.21	1.16	2.06	4.01	1.56
2.59	3.90	1.44	2.58	4.43	1.51
3.29	4.42	1.68	3.03	4.84	1.46

Intercept = 2.70×10^{-6}
$[z]$ = 1.78
Slope = 7.0×10^{-4}

$1/P_{90} = 1.60$
$\eta_o R/\lambda = 0.348$

$M = 5.24 \times 10^5$
$R = 9.95 \times 10^2$ A°
$A_2 = 3.5 \times 10^{-4}$

TABLE XVI

LIGHT-SCATTERING DATA FOR LINEAR POLYSTYRENE

Fraction F5A2

(Solvent: Benzene)

$c \times 10^3$ g. polymer/g. solution	$S_{45} \times 10^2$	$S_{90} \times 10^2$	$S_{135} \times 10^2$	$H \frac{c}{\tau} \times 10^6$	$[z]$
0.297	1.55	0.414	0.637	1.77	2.44
0.941	3.51	1.08	1.70	2.16	2.07
1.33	4.26	1.38	2.25	2.39	1.89
1.84	4.83	1.66	2.80	2.75	1.73

Intercept = 7.60×10^{-6}

$[z]$ = 2.60

Slope = 6.0×10^{-4}

$1/P_{90} = 2.42$

$\eta_0 R/\lambda = 0.519$

$M = 1.33 \times 10^6$

$R = 1.50 \times 10^3$ A°

$A_2 = 3.0 \times 10^{-4}$

TABLE XVII

LIGHT-SCATTERING DATA FOR LINEAR POLYSTYRENE

Fraction F3A2

(Solvent: Benzene)

$c \times 10^3$ g. polymer/g. solution	$S_{45} \times 10^2$	$S_{90} \times 10^2$	$S_{135} \times 10^2$	$H \frac{c}{\tau} \times 10^6$	$[z]$
0.264	1.75	0.436	0.65	1.50	2.69
0.538	2.62	0.700	1.07	1.90	2.45
0.993	3.72	1.11	1.71	2.20	2.18
1.31	4.28	1.33	2.12	2.43	2.02

Intercept = 1.36×10^{-6}

$[z]$ = 2.90

Slope = 4.3×10^{-4}

$1/P_{90} = 2.73$

$n_0 R/\lambda = 0.568$

$M = 1.76 \times 10^6$

$R = 1.65 \times 10^3$ A°

$A_2 = 2.6 \times 10^{-4}$

TABLE XVIII

LIGHT-SCATTERING DATA FOR LINEAR POLYSTYRENE

Fraction Q_2B_2 - Trial 1
(Solvent: Benzene)

$c \times 10^4$ g. polymer/g. solution	$S_{45} \times 10^2$	$S_{90} \times 10^2$	$S_{135} \times 10^2$	$H\frac{c}{\tau} \times 10^6$	$[z]$
0.854	0.720	0.149	0.220	1.42	3.27
1.73	1.31	0.283	0.415	1.51	3.15
3.24	2.26	0.502	0.753	1.59	3.00
4.59	2.84	0.671	1.01	1.69	2.81

Intercept = 1.38×10^{-6}

$[z]$ = 3.37

Slope = 8.5×10^{-4}

$1/P_{90}$ = 3.47

n_oR/λ = 0.660

M = 2.20×10^6

R = 1.91×10^3 A°

A_2 = 4.2×10^{-4}

TABLE XIX

LIGHT SCATTERING DATA FOR LINEAR POLYSTYRENE

Fraction Q_2B_2 - Trial 2

(Solvent: Benzene)

$c \times 10^3$ g. polymer/g. solution	$S_{45} \times 10^2$	$S_{90} \times 10^2$	$S_{135} \times 10^2$	$H \frac{c}{\tau} \times 10^6$	$[z]$
0.269	1.92	0.460	0.65	1.45	2.96
0.519	2.96	0.760	1.12	1.69	2.64
1.07	4.47	1.30	2.02	2.03	2.21
1.68	5.26	1.73	2.79	2.40	1.89

Intercept = 1.31×10^{-6}

$[z]$ = 3.35

Slope = 6.4×10^{-4}

$1/P_{90}$ = 3.42

$n_0 R/\lambda$ = 0.656

M = 2.29×10^6

R = 1.90×10^3 A°

A_2 = 3.2×10^{-4}

TABLE XX

LIGHT SCATTERING DATA FOR LINEAR POLYSTYRENE
Fraction T 8
(Solvent: Benzene)

$c \times 10^4$ g. polymer/g. solution	$S_{45} \times 10^2$	$S_{90} \times 10^2$	$S_{135} \times 10^2$	$H \frac{c}{\tau} \times 10^6$	$[z]$
1.64	1.36	0.280	0.41_0	1.44	3.32
3.75	2.48	0.560	0.83_0	1.65	2.99
6.06	3.46	0.816	1.24	1.83	2.79
9.19	4.12	1.05	1.67	2.16	2.46

Intercept = 1.28×10^{-6}

$[z]$ = 3.63

Slope = 8.8×10^{-4}

$1/P_{90}$ = 4.00

$n_0 R/\lambda$ = 0.731

M = 2.76×10^6

R = 2.11×10^3 A°

A_2 = 4.4×10^{-4}

TABLE XXI

LIGHT-SCATTERING DATA FOR LINEAR POLYSTYRENE

Fraction RP-3-2 - Trial 1

(Solvent: Benzene)

$c \times 10^4$ g. polymer/g. solution	$S_{45} \times 10^2$	$S_{90} \times 10^2$	$S_{135} \times 10^2$	$H \frac{c}{\tau} \times 10^6$	$[z]$
0.725	0.445	0.105	0.156	1.70	2.85
1.49	0.827	0.208	0.297	1.77	2.78
2.22	1.17	0.289	0.434	1.90	2.70
3.57	1.75	0.447	0.672	1.97	2.61

Intercept = 1.61×10^{-6}

$[z]$ = 2.91

Slope = 1.08×10^{-3}

$1/P_{90} = 2.75$

$\eta_o R/\lambda = 0.565$

$M = 1.50 \times 10^6$

$R = 1.63 \times 10^3$ A°

$A_2 = 5.4 \times 10^{-4}$

TABLE XXII

LIGHT-SCATTERING DATA FOR LINEAR POLYSTYRENE
Fraction RP-3-2 - Trial 2
(Solvent: Benzene)

$c \times 10^4$ g. polymer/g. solution	$S_{45} \times 10^2$	$S_{90} \times 10^2$	$S_{135} \times 10^2$	$H \frac{c}{\tau} \times 10^6$	[z]
2.22	1.22	0.299	0.435	1.83	2.71
3.27	1.67	0.422	0.643	1.92	2.60
4.36	2.14	0.555	0.843	1.94	2.26
5.37	2.50	0.649	1.01	2.04	2.46

Intercept $= 1.66 \times 10^{-6}$
[z] = 2.88
Slope $= 7.4 \times 10^{-4}$

$1/P_{90} = 2.71$
$n_o R/\lambda = 0.562$

$M = 1.43 \times 10^6$
$R = 1.62 \times 10^3$ A°
$A_2 = 3.7 \times 10^{-4}$

TABLE XXIII

LIGHT-SCATTERING DATA FOR LINEAR POLYSTYRENE

Fraction F5A2

(Solvent: Butanone)

$c \times 10^3$ g. polymer/g. solution	$S_{45} \times 10^2$	$S_{90} \times 10^2$	$S_{135} \times 10^2$	$H \frac{c}{\tau} \times 10^6$	$[z]$
1.12	3.48	1.00	1.65	1.28	2.11
1.99	5.87	1.70	2.80	1.30	2.10
3.16	8.62	2.60	4.23	1.34	2.04
4.56	11.97	3.66	6.16	1.38	1.93

Intercept $= 1.24 \times 10^{-6}$

$[z] = 2.18$

Slope $= 3.2 \times 10^{-4}$

$1/P_{90} = 1.96$

$n_0 R/\lambda = 0.428$

$M = 1.39 \times 10^6$

$R = 1.24 \times 10^3$ A°

$A_2 = 1.6 \times 10^{-4}$

TABLE XXIV

LIGHT-SCATTERING DATA FOR LINEAR POLYSTYRENE

Fraction Q_2B_2

(Solvent: Butanone)

$c \times 10^3$ g. polymer/g. solution	$S_{45} \times 10^2$	$S_{90} \times 10^2$	$S_{135} \times 10^2$	$H\frac{c}{\tau} \times 10^6$	$[z]$
1.18	4.96	1.35	2.08	0.969	2.39
2,09	8.32	2.29	3.51	1.01	2.37
3.55	12.9	3.58	5.56	1.10	2.32
5.04	17.3	4.95	7.64	1.12	2.26

Intercept = 0.910×10^{-6}

$[z]$ = 2.44

Slope = 4.40×10^{-4}

$1/P_{90} = 2.22$

$n_oR/\lambda = 0.485$

$M = 2.14 \times 10^6$

$R = 1.41 \times 10^3$ A°

$A_2 = 2.2 \times 10^{-4}$

TABLE XXV

SUMMARY OF LIGHT-SCATTERING DATA[a] FOR FRACTIONS OF LINEAR POLYSTYRENE

Solvent	Fraction	$[\eta]$ benzene, dl./g.	$[\eta]$ butanone, dl./g.	$R \times 10^{-3}$, A°	$M \times 10^{6}$	$R^3/M \times 10^{21}$	$\Phi \times 10^{-21}$	$A_2 \times 10^{4}$
Benzene	F21	(1.48)	0.73	0.637	0.334	0.772	2.50	4.3
"	F7B3	2.10	1.03	0.995	0.524	1.88	1.45	3.5
"	F5A2	4.05	1.82	1.50	1.33	2.48	2.12	3.0
"	F3A2	4.37	(2.05)	1.65	1.76	2.55	2.22	2.6
"	Q_2B_2	5.82	2.60	1.91	2.20	3.17	2.38	4.2
"	Q_2B_2	5.82	2.60	1.90	2.29	3.00	2.52	3.2
"	T8	(6.75)	3.00	2.11	2.76	3.43	2.55	4.4
"	RP-3-2[b]	(6.10)	2.70	1.63	1.50	2.89	2.73	5.4
"	RP-3-2	(6.10)	2.70	1.62	1.43	2.96	2.67	3.7
Butanone	Q_2B_2	5.82	2.60	1.41	2.14	1.31	2.58	2.2
"	F_5A_2	4.05	1.82	1.24	1.39	1.37	1.72	1.6

Average Φ (benzene) = 2.4×10^{21}
Average Φ (butanone) = 2.2×10^{21}
Average Φ expected (4, p. 616) = 2.1×10^{21}

[a] Data given in parentheses have been calculated from data obtained with a different solvent by means of the equation given in reference 27.

[b] A primary fraction.

TABLE XXVI

LIGHT-SCATTERING DATA FOR GRAFT POLYMER

Fraction GC-140-1

(Solvent: Benzene)

$c \times 10^4$ g. polymer/g. solution	$S_{45} \times 10^2$	$S_{90} \times 10^2$	$S_{135} \times 10^2$	$H \frac{c}{\tau} \times 10^6$	$[z]$
0.966	1.24	0.243	0.356	0.99	3.49
2.11	2.44	0.511	0.746	1.02	3.27
3.11	3.52	0.775	1.15	1.00	3.06
4.04	4.44	0.967	1.45	1.04	3.06
5.18	5.60	1.25	1.89	1.02	2.96

Intercept $= 0.990 \times 10^{-6}$

$[z] = 3.72$

Slope $= 3.20 \times 10^{-4}$

$1/P_{90} = 4.20$

$n_0 R/\lambda = 0.743$

$M = 3.72 \times 10^6$

$R = 2.14 \times 10^3$

$A_2 = 1.60 \times 10^{-4}$

TABLE XXVII

LIGHT-SCATTERING DATA FOR GRAFT POLYMER

Fraction GC-140-1

(Solvent: Benzene)

$c \times 10^4$ g. polymer/g. solution	$S_{45} \times 10^2$	$S_{90} \times 10^2$	$S_{135} \times 10^2$	$H \frac{c}{\tau} \times 10^6$	$[z]$
1.74	2.15	0.466	0.695	0.928	3.10
3.74	3.54	0.783	1.19	1.18	2.98
5.51	4.87	1.10	1.64	1.24	2.97
7.64	6.33	1.49	2.21	1.27	2.87

Intercept $= 1.08 \times 10^{-6}$ $1/P_{90} = 3.18$ $M = 2.58 \times 10^6$

$[z] = 3.20$ $\eta_o R/\lambda = 0.622$ $R = 1.80 \times 10^3$

Slope $= 2.56 \times 10^{-4}$ $A_2 = 1.28 \times 10^{-4}$

TABLE XXVIII

LIGHT SCATTERING DATA FOR GRAFT POLYMER

Fraction GC-140-3

(Solvent: Benzene)

$c \times 10^4$ g.polymer/g. solution	$S_{45} \times 10^2$	$S_{90} \times 10^2$	$S_{135} \times 10^2$	$H \frac{c}{\tau} \times 10^7$	[z]
1.20	1.87	0.473	0.707	6.30	2.64
2.35	3.40	0.870	1.33	6.69	2.56
3.51	4.94	1.28	1.95	6.76	2.53
4.66	6.22	1.64	2.52	7.03	2.47

Intercept = 6.06×10^{-7}

[z] = 2.74

Slope = 2.10×10^{-4}

$1/P_{90} = 2.57$

$n_0 R/\lambda = 0.550$

$M = 3.72 \times 10^6$

$R = 1.59 \times 10^3$

$A_2 = 1.05 \times 10^{-4}$

TABLE XXIX

LIGHT-SCATTERING DATA FOR GRAFT POLYMER

Fraction GC-210-1
(Solvent: Benzene)

$c \times 10^4$ g. polymer/g. solution	$S_{45} \times 10^2$	$S_{90} \times 10^2$	$S_{135} \times 10^2$	$H \frac{c}{\tau} \times 10^{-7}$	$[z]$
1.34	1.68	0.317	0.472	1.05	3.56
2.45	2.89	0.558	0.838	1.80	3.45
3.66	4.16	0.833	1.23	1.10	3.40
4.67	5.20	1.06	1.59	1.10	3.27

Intercept $= 1.04 \times 10^{-6}$
$[z] = 3.78$
Slope $= 1.58 \times 10^{-4}$

$1/P_{90} = 4.36$
$n_o R/\lambda = 0.760$

$M = 3.68 \times 10^6$
$R = 2.19 \times 10^3$
$A_2 = 0.79 \times 10^{-4}$

TABLE XXX

LIGHT-SCATTERING DATA FOR GRAFT POLYMER

Fraction GC-210-2

(Solvent: Benzene)

$c \times 10^4$ g. polymer/g. solution	$S_{45} \times 10^2$	$S_{90} \times 10^2$	$S_{135} \times 10^2$	$H \frac{c}{\tau} \times 10^7$	$[z]$
0.886	1.29	0.314	0.468	6.96	2.76
1.29	1.94	0.463	0.698	6.90	2.78
2.31	3.09	0.764	1.18	7.45	2.62
3.67	4.64	1.20	1.84	7.45	2.52

Intercept $= 6.63 \times 10^{-7}$

$[z] = 2.90$

Slope $= 2.76 \times 10^{-4}$

$1/P_{90} = 2.75$

$n_0 R/\lambda = 0.565$

$M = 3.64 \times 10^6$

$R = 1.63 \times 10^3$

$A_2 = 1.38 \times 10^{-4}$

TABLE XXXI

LIGHT-SCATTERING DATA FOR GRAFT POLYMER
Fraction GC-210-3 - Trial 1
(Solvent: Benzene)

$c \times 10^4$ g. polymer/g. solution	$S_{45} \times 10^2$	$S_{90} \times 10^2$	$S_{135} \times 10^2$	$H \frac{c}{\tau} \times 10^6$	z
1.48	0.890	0.276	0.451	1.32	1.98
2.98	1.67	0.531	0.872	1.39	1.91
4.22	2.34	0.734	1.23	1.42	1.91
5.43	2.91	0.939	1.56	1.43	1.87

Intercept = 1.29×10^{-6}
$[z]$ = 2.00
Slope = 3.10×10^{-4}

$1/P_{90} = 1.79$
$\eta_0 R/\lambda = 0.395$

$M = 1.22 \times 10^6$
$R = 1.14 \times 10^3$ A°
$A_2 = 1.55 \times 10^{-4}$

TABLE XXXII

LIGHT-SCATTERING DATA FOR GRAFT POLYMER
Fraction GC-210-3 - Trial 2
(Solvent: Benzene)

$c \times 10^4$ g. polymer/g. solution	$S_{45} \times 10^2$	$S_{90} \times 10^2$	$S_{135} \times 10^2$	$H\frac{c}{\tau} \times 10^6$	z
1.44	0.903	0.271	0.436	1.32	2.07
2.86	1.66	0.514	0.841	1.37	1.98
4.01	2.28	0.699	1.18	1.42	1.93
5.18	2.86	0.896	1.52	1.43	1.88

Intercept = 1.29×10^{-6}

$[z]$ = 2.08

Slope = 3.10×10^{-4}

$1/P_{90}$ = 1.86

$n_0 R/\lambda$ = 0.412

M = 1.26×10^6

R = 1.19×10^3 A°

A_2 = 1.55×10^{-4}

TABLE XXXIII

LIGHT-SCATTERING DATA FOR GRAFT POLYMER
Fraction GC-211-1[a]
(Solvent: Benzene)

$c \times 10^4$ g. polymer/g. solution	$S_{45} \times 10^2$	$S_{90} \times 10^2$	$S_{135} \times 10^2$	$H \frac{c}{\tau} \times 10^6$	z
1.13	1.60	0.290	0.429	0.965	3.73
2.46	3.42	0.572	0.953	1.06	3.59
3.69	4.90	0.916	1.39	1.00	3.52
5.19	6.58	1.28	1.92	1.00	3.33
6.50	7.96	1.59	2.37	1.01	3.36

Intercept = 1.00×10^{-6}

[z] = 3.88

Slope = 0

$1/P_{90} = 4.64$

$n_0 R/\lambda = 0.780$

$M = 4.07 \times 10^6$

$R = 2.24 \times 10^3$

$A_2 = 0$

---

[a] Polymer sample GC-211 was prepared under conditions similar to those used for GC-210 (see Table VI).

TABLE XXXIV

LIGHT-SCATTERING DATA FOR GRAFT POLYMER

Fraction GC-211-2 - Trial 1

(Solvent: Benzene)

$c \times 10^4$ g. polymer/g. solution	$S_{45} \times 10^2$	$S_{90} \times 10^2$	$S_{135} \times 10^2$	$H \frac{c}{\tau} \times 10^7$	z
1.40	2.06	0.419	0.610	8.25	3.37
2.44	3.58	0.743	1.09	8.10	3.28
3.40	4.95	1.06	1.57	7.96	3.15
5.18	7.20	1.60	2.36	8.00	3.04

Intercept = 8.30×10^{-7}

$[z]$ = 3.50

Slope = 0.60×10^{-4}

$1/P_{90}$ = 3.72

n_oR/λ = 0.690

M = 3.94×10^6

R = 1.97×10^3 A°

A_2 = 0.30×10^{-4}

TABLE XXXV

LIGHT-SCATTERING DATA FOR GRAFT POLYMER

Fraction GC-211-2 - Trial 2

(Solvent: Benzene)

$c \times 10^4$ g. polymer/g. solution	$S_{45} \times 10^2$	$S_{90} \times 10^2$	$S_{135} \times 10^2$	$H \frac{c}{\tau} \times 10^7$	z
1.13	1.63	0.314	0.471	8.89	3.46
2.42	3.20	0.643	0.951	9.30	3.36
4.09	5.19	1.09	1.66	9.26	3.13
5.40	6.68	1.48	2.13	9.01	3.13
6.78	8.10	1.80	2.76	9.30	2.94

Intercept = 9.12×10^{-7}

$[z]$ = 3.60

Slope = 0.20×10^{-4}

$1/P_{90}$ = 3.93

$n_o R/\lambda$ = 0.712

M = 3.79×10^6

R = 2.06×10^3 A°

A_2 = 0.10×10^{-4}

TABLE XXXVI

LIGHT-SCATTERING DATA FOR GRAFT POLYMER

Fraction GC-211-3

(Solvent: Benzene)

$c \times 10^4$ g. polymer/g. solution	$S_{45} \times 10^2$	$S_{90} \times 10^2$	$S_{135} \times 10^2$	$H \frac{c}{\tau} \times 10^7$	z
0.870	1.48	0.350	0.517	6.14	2.87
1.745	2.60	0.644	0.980	6.68	2.65
3.18	4.22	1.11	1.70	7.09	2.48
3.86	4.90	1.32	2.05	7.23	2.39

Intercept = 6.00×10^{-7}

$[z]$ = 3.10

Slope = 3.35×10^{-4}

$1/P_{90} = 3.00$

$n_o R/\lambda = 0.632$

$M = 4.39 \times 10^6$

$R = 1.82 \times 10^3$ A°

$A_2 = 1.65 \times 10^{-4}$

TABLE XXXVII

LIGHT-SCATTERING DATA FOR GRAFT POLYMER

Fraction GC-230-1

(Solvent: Benzene)

$c \times 10^4$ g. polymer/g. solution	$S_{45} \times 10^2$	$S_{90} \times 10^2$	$S_{135} \times 10^2$	$H\frac{c}{\tau} \times 10^7$	z
2.18	3.78	0.779	1.16	6.93	3.26
3.15	5.19	1.08	1.62	7.19	3.21
4.01	6.38	1.36	2.06	7.29	3.10
4.97	7.66	1.68	2.53	7.30	3.03

Intercept = 6.70×10^{-7}

$[z]$ = 3.44

Slope = 1.50×10^{-4}

$1/P_{90}$ = 3.60

n_oR/λ = 0.675

M = 4.71×10^6

R = 1.95×10^3A°

A_2 = 0.75×10^{-4}

TABLE XXXVIII

LIGHT-SCATTERING DATA FOR GRAFT POLYMER
GC-621[a]
(Solvent: Benzene)

$c \times 10^4$ g. polymer/g. solution	$S_{45} \times 10^2$	$S_{90} \times 10^2$	$S_{135} \times 10^2$	$H \frac{c}{\tau} \times 10^7$	z
0.855	1.48	0.272	0.388	7.78	3.81
1.59	2.75	0.508	0.721	7.73	3.79
2.76	4.45	0.825	1.19	8.28	3.74
4.15	6.37	1.19	1.69	8.57	3.76

Intercept = 7.45×10^{-7}

$[z]$ = 3.83

Slope = 2.90×10^{-4}

$1/P_{90}$ = 4.50

$n_o R/\lambda$ = 0.770

$M = 5.29 \times 10^{-6}$

$R = 2.21 \times 10^{3}$ A°

$A_2 = 1.45 \times 10^{-4}$

[a] Unfractionated; prepared by graft polymerization in solution.

TABLE XXXIX

LIGHT-SCATTERING DATA FOR GRAFT POLYMER
Fraction GC-140-3
(Solvent: Butanone)

$c \times 10^4$ g. polymer/g. solution	$S_{45} \times 10^2$	$S_{90} \times 10^2$	$S_{135} \times 10^2$	$H\frac{c}{\tau} \times 10^7$	z
1.09	11.1	2.57	3.88	4.70	2.87
2.15	20.0	4.78	1.26	4.97	2.76
3.06	27.8	6.69	10.1	5.07	2.75

Intercept = 4.50×10^7

$[z]$ = 2.92

Slope = 1.87×10^{-4}

$1/P_{90} = 2.75$

n_0R/λ = 0.568

$M = 5.38 \times 10^6$

$R = 1.64 \times 10^3$ A°

$A_2 = 0.93 \times 10^{-4}$

TABLE XL

LIGHT-SCATTERING DATA FOR GRAFT POLYMER
Fraction GC-210-3
(Solvent: Butanone)

$c \times 10^4$ g. polymer/g. solution	$S_{45} \times 10^2$	$S_{90} \times 10^2$	$S_{135} \times 10^2$	$H \frac{c}{\tau} \times 10^7$	z
1.05	0.770	0.286	0.389	4.94	1.98
1.97	1.33	0.414	0.685	5.28	1.94
2.82	1.84	0.580	0.968	5.38	1.92

Intercept = 4.80×10^{-7}

$[z]$ = 2.03

Slope = 2.13×10^{-4}

$1/P_{90}$ = 1.82

$n_0 R/\lambda$ = 0.402

$M = 3.33 \times 10^6$

$R = 1.16 \times 10^3$

$A_2 = 1.06 \times 10^{-4}$

TABLE XLI

LIGHT SCATTERING DATA FOR GRAFT POLYMER

Fraction GC-211-2

(Solvent: Butanone)

$c \times 10^4$ g. polymer/g. solution	$S_{45} \times 10^2$	$S_{90} \times 10^2$	$S_{135} \times 10^2$	$H\frac{c}{\tau} \times 10^7$	z
0.880	0.919	0.212	0.321	4.60	2.57
1.75	1.70	0.398	0.666	4.86	2.55
2.59	2.40	0.582	0.939	4.92	2.56
3.68	3.28	0.808	1.23	5.04	2.66

Intercept = 4.40×10^{-7}

$[z]$ = 2.53

Slope = 1.90×10^{-4}

$1/P_{90}$ = 2.32

n_0R/λ = 0.503

$M = 4.62 \times 10^6$

$R = 1.45 \times 10^3$

$A_2 = 0.95 \times 10^{-4}$

TABLE XLII

SUMMARY OF LIGHT-SCATTERING DATA FOR GRAFT POLYMERS

Sample[a]	Solvent	$[\eta]$, dl./g.	$R \times 10^{-3}$, A°	$M \times 10^{6}$	$\Phi \times 10^{-21}$	$A_2 \times 10^{4}$
GC-140-1	Benzene	6.38	2.14	3.72	3.14	1.60
GC-140-2	"	6.02	1.80	2.58	3.47	1.28
GC-140-3	"	4.67[b]	1.59	3.72	5.62	1.05
GC-210-1	"	7.22	2.19	3.68	3.29	0.79
GC-210-2	"	4.62	1.63	3.64	5.07	1.38
GC-210-3	"	2.39	1.14	1.22	2.56	1.55
GC-210-3	"	2.39	1.19	1.26	2.34	1.55
GC-211-1	"	7.95	2.24	4.07	3.75	0
GC-211-2	"	6.30	1.97	3.94	4.22	0.30
GC-211-2	"	6.30	2.06	3.79	3.55	0.10
GC-211-3	"	4.28	1.82	4.39	4.06	1.65
GC-230-1	"	7.50	1.95	4.71	6.18	0.75
GC-621	"	6.59	2.21	5.29	4.19	1.45
GC-140-3	Butanone	1.96	1.64	5.38	3.10	0.93
GC-210-3	"	1.24	1.16	3.33	3.43	1.06
GC-211-2	"	2.84	1.45	4.62	5.61	0.95

[a] The final digit in the fraction number refers to the order of appearance of the fraction during fractionation; for example, GC-140-1 represents the first fraction obtained from the whole polymer GC-140.

[b] Average of two values - 4.55 and 4.78.

TABLE XLIII

FLORY CONSTANT Φ' FOR GRAFT POLYMERS

Sample	$g^{3/2}$	S_B^3[a] x 10^{16}, cm.^{3}	Φ' x 10^{-21}	Φ'(SF)[a] x 10^{-21}
GC-140-1	0.853	9.68	31.7	38.8
GC-140-2	0.893	5.60	36.0	42.6
GC-140-3	0.544	6.13	36.7	54.5
GC-210-1	0.921	11.6	33.9	38.3
GC-210-2	0.594	6.42	34.2	53.1
GC-210-3	0.704	1.04	27.3	38.5
GC-211-1	1.02	13.2	32.4	32.9
GC-211-2	0.774	9.62	33.4	45.1
GC-211-3	0.528	7.73	31.7	53.3
GC-230-1	0.844	13.7	33.6	41.6
GC-621	0.552	10.5	42.8	61.4

Average $\Phi' = 33.9 \times 10^{21}$ or 3.4×10^{22}.

Average Φ' (SF) = 45.4×10^{21} or 4.5×10^{22}.

Average expected (assuming $\Phi = 2.10 \times 10^{21}$) = 30.9×10^{21}

or 3.1×10^{22}

---

[a] Values of g required for the calculation of Φ'(SF) were determined by the Stockmayer-Fixman method (24).

TABLE XLIV

VISCOSITY DATA FOR GRAFT POLYMERS

Sample	Solvent: benzene		Solvent: butanone		$g^{3/2}$
	[η], dl./g.	k'	[η], dl.g.	k'	(butanone)
GC-140-1	6.38	0.36	3.07	0.40	0.853
GC-140-2	6.02	0.31	2.50	0.36	0.893
GC-140-3	4.55 4.78	0.34 0.35	1.96	0.24	0.909
GC-210-1	7.22	0.28	3.25	0.38	0.812
GC-210-2	4.62	0.32	2.11 2.07	0.36 0.33	0.594 0.594
GC-210-3	2.39	0.34	1.24	0.31	0.704
GC-211-1	7.95	0.38	3.97	0.36	1.02
GC-211-2	6.30	0.38	2.84	0.36	0.774
GC-211-3	4.28	0.36	2.11	0.33	0.528
GC-211-4	2.86	0.26	1.32	0.42	-
GC-230-1	7.50	0.26	3.53	0.30	0.844
GC-230-2	4.72	0.37	2.21	0.33	-
GC-230-3	4.09	0.35	2.06	0.39	-
GC-230-4	3.51	0.35	1.59	0.39	-
GC-621	6.59	0.39	2.40	0.43	0.552

Average k' (benzene) = 0.34; *cf*. an average of 0.35 for linear fractions (159).

Average k' (butanone) = 0.36; *cf*. an average of 0.39 for linear fractions (159).

TABLE XLV

BRANCHING RATIOS FOR GRAFT POLYMERS
(Solvent: Butanone)

Sample	$[\eta]$,dl./g.		$g^{3/2}$	g	g(SF)[b]
	Graft	Linear[a]			
GC-140-1	3.07	3.60	0.853	0.900	0.78
GC-140-2	2.50	2.80	0.893	0.927	0.83
GC-140-3	1.96	3.60	0.544	0.666	0.47
GC-210-1	3.25	3.53	0.921	0.947	0.88
GC-210-2	2.09[c]	3.52	0.594	0.706	0.52
GC-210-3	1.24	1.76	0.704	0.791	0.62
GC-211-1	3.97	3.90	(1.02)[d]	(1.01)[d]	(1.00)
GC-211-2	2.84	3.67	0.774	0.843	0.69
GC-211-3	2.11	4.00	0.528	0.654	0.46
GC-230-1	3.53	4.18	0.844	0.893	0.78
GC-621	2.50	4.53	0.552	0.672	0.48

[a] Each value given in this column is the intrinsic viscosity of linear polystyrene having the same molecular weight as the graft polymer concerned.

[b] Calculated by method of Stockmayer and Fixman (24).

[c] Average of two values - 2.11 and 2.07.

[d] Anomalous; g cannot, of course, be greater than unity.

APPENDIX B

Graphs and Figures

Fig. 1. Dependence of Hydroperoxide Content on Time of Oxidation

□ percent 4-vinylcyclohexene-1: 0.0; solvent: tetralin
○ percent 4-vinylcyclohexene-1: 0.2; solvent: tetralin
◐ percent 4-vinylcyclohexene-1: 2.0; solvent: tetralin
◒ percent 4-vinylcyclohexene-1: 4.2; solvent: tetralin
◕ percent 4-vinylcyclohexene-1: 8.7; solvent: tetralin
◓ percent 4-vinylcyclohexene-1: 20.0; solvent: tetralin
● percent 4-vinylcyclohexene-1: 0.2; solvent: m-xylene

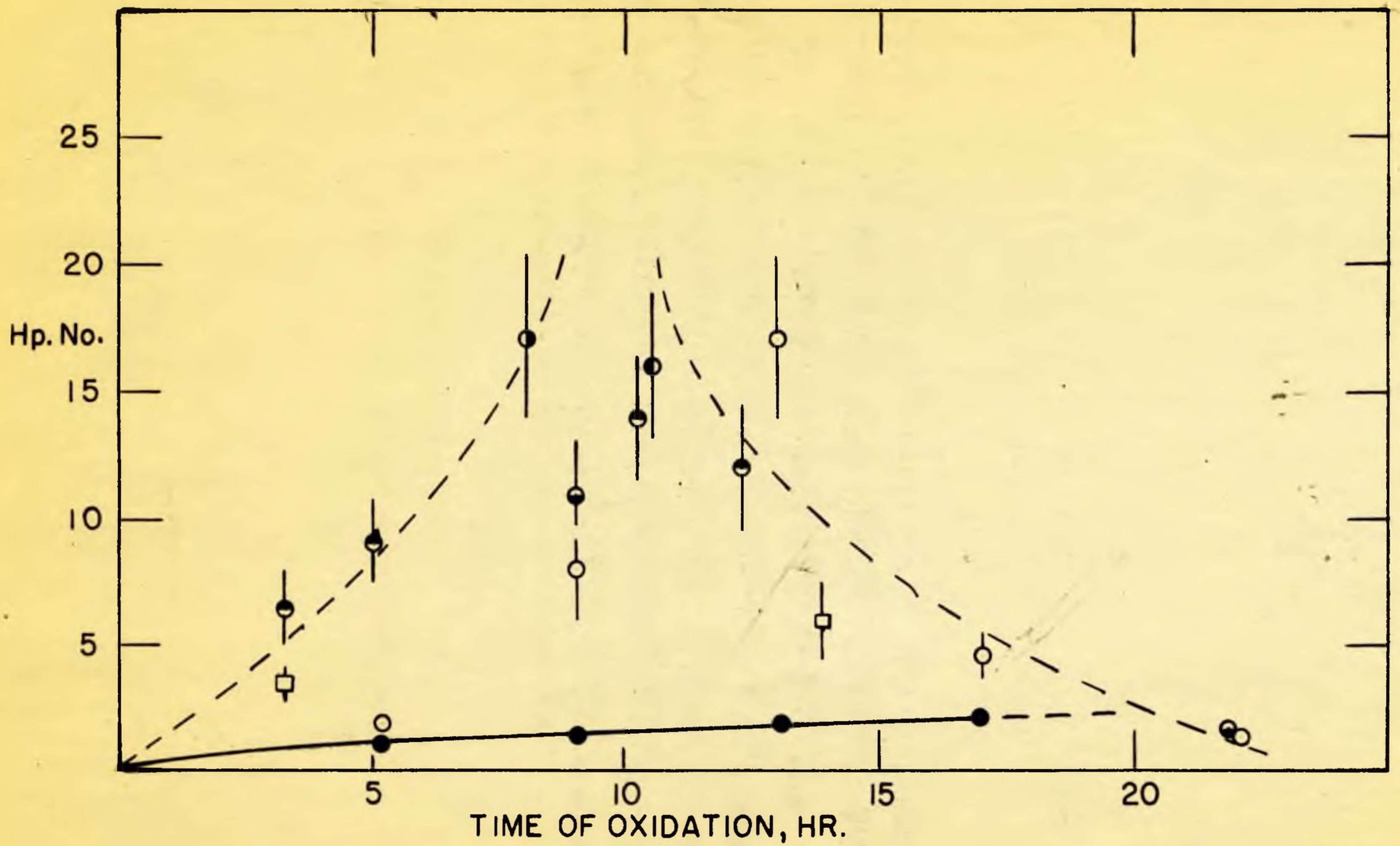

25
20
Hp. No.
15
10
5
5
10
15
20
TIME OF OXIDATION, HR.

Fig. 2. Dependence of Percent Conversion
on Time for a Graft
and a Blank Polymerization

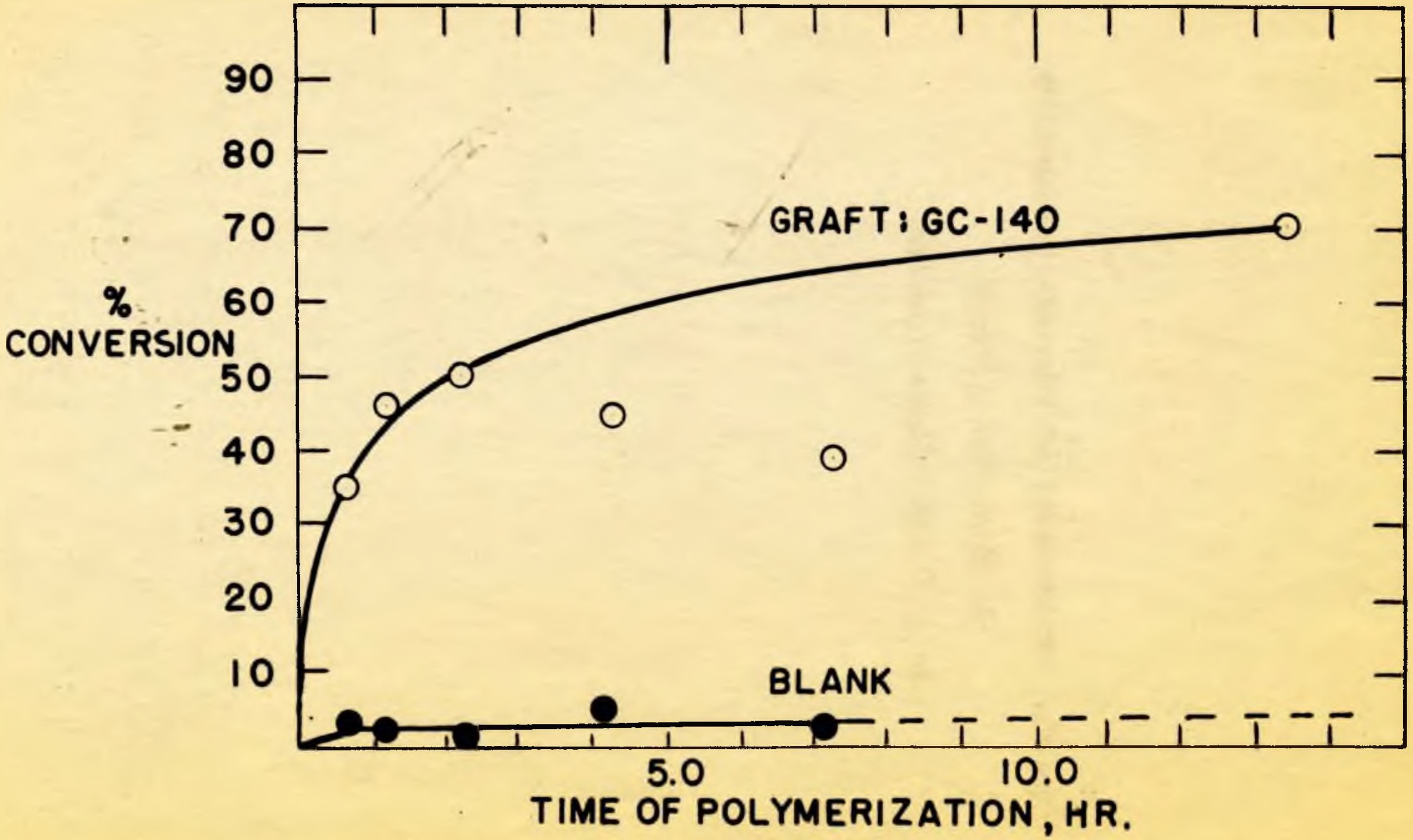

90
80
70
60
50
40
30
20
10
%
CONVERSION
GRAFT: GC-140
BLANK
5.0
10.0
TIME OF POLYMERIZATION, HR.

Fig. 3. General Plan of
Light-Scattering Photometer

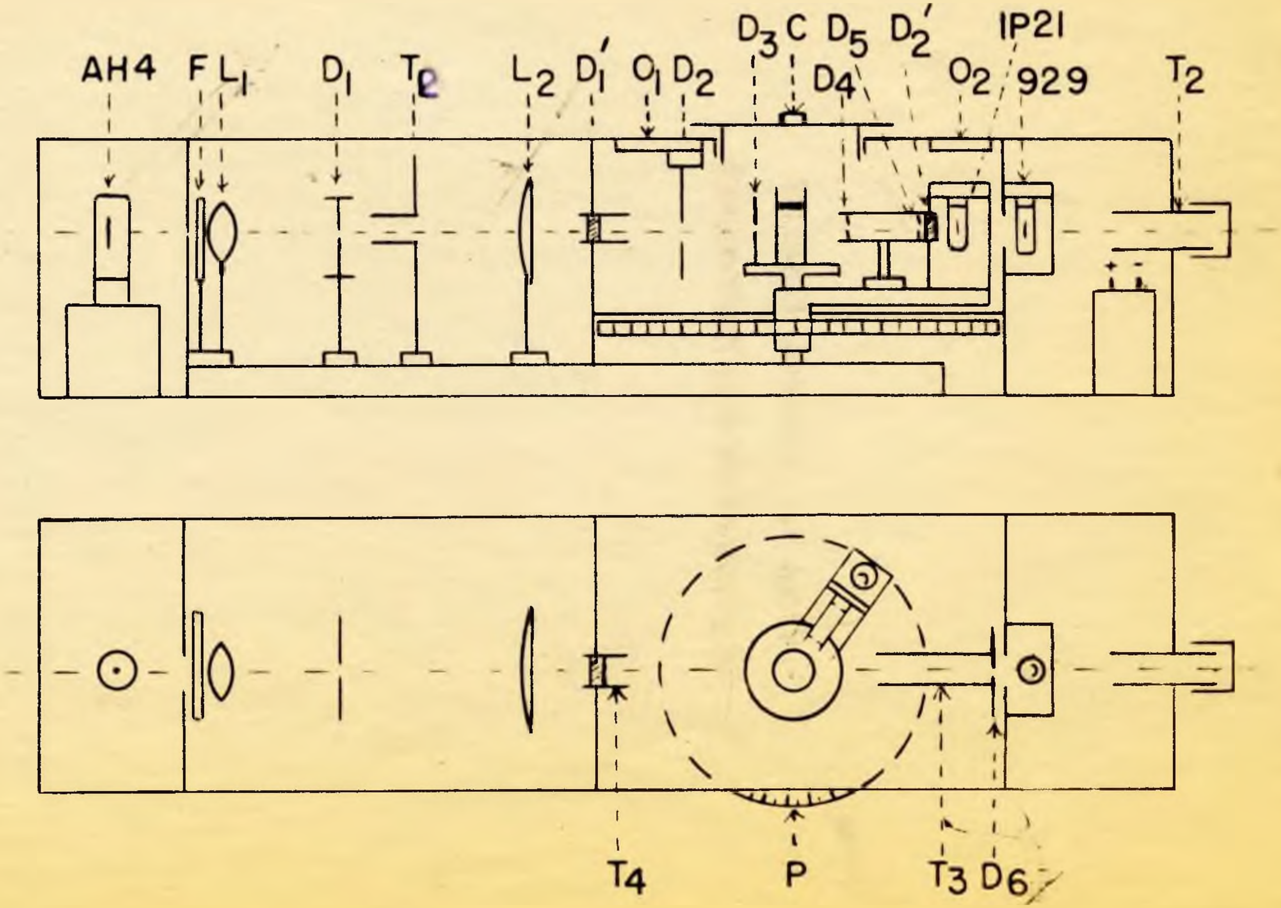

AH4
F
L1
D1
T2
L2
D1′
O1
D2
D3
C
D5
D4
D2′
IP21
O2
929
T2
+
-
T4
P
T3
D6

Fig. 4. General Plan of Electronic System for the Light-Scattering Photometer

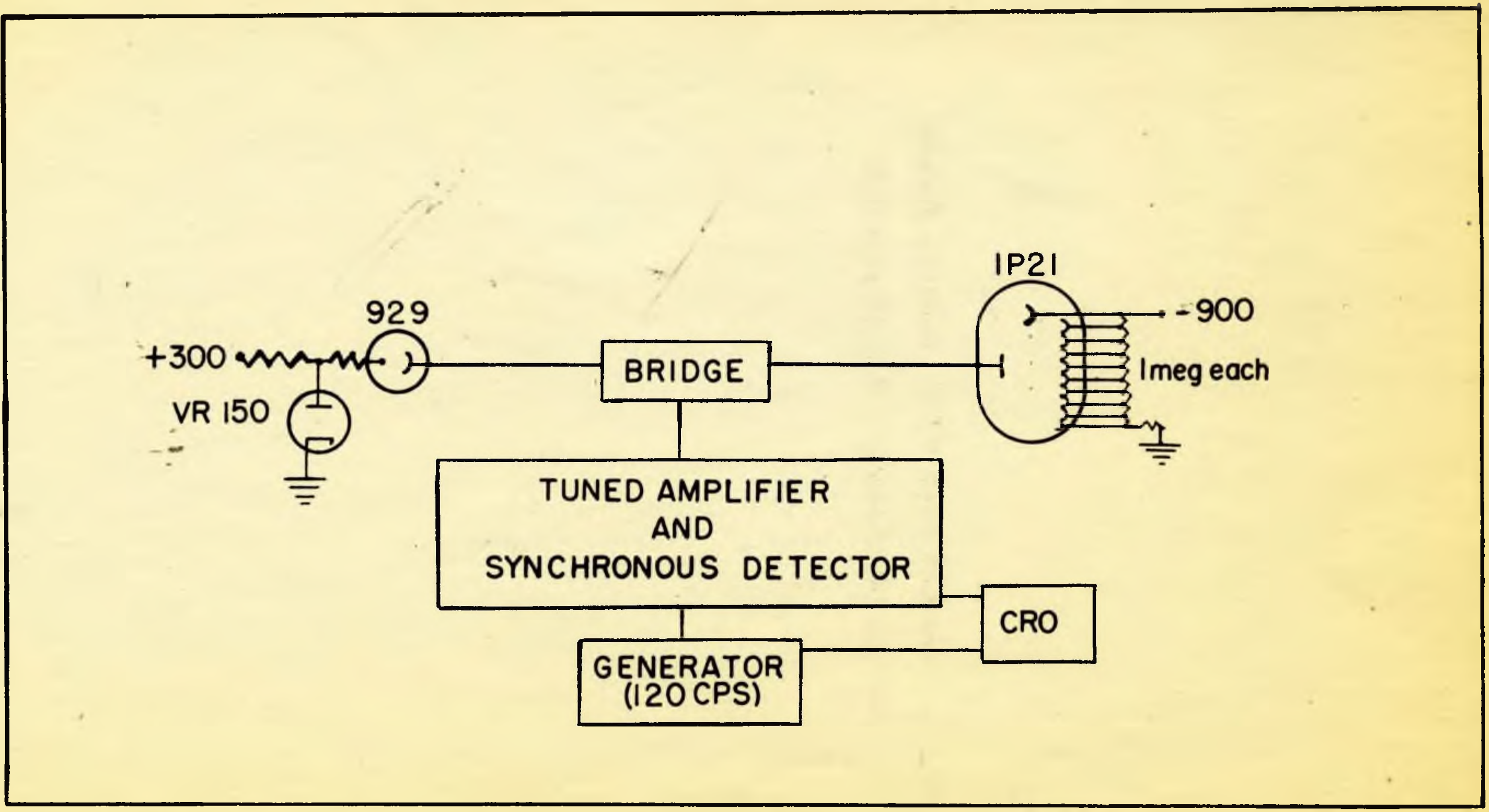

1P21
929
-900
+300
BRIDGE
1meg each
VR 150
TUNED AMPLIFIER
AND
SYNCHRONOUS DETECTOR
CRO
GENERATOR
(120 CPS)

Fig. 5. Circuit Diagram for Null Detector

Components

1.0×10^6 ohm - R_7, R_{11}, R_{15}, R_{19}, R_{20}
2.7×10^5 ohm - R_4, R_5
5.0×10^5 ohm - R_{25}
2.2×10^5 ohm - R_6
7.5×10^4 ohm - R_9, R_{13}
4.7×10^4 ohm - R_{10}, R_{14}, R_{17}
2.5×10^4 ohm - R_{23}
1.0×10^4 ohm - R_1, R_2, R_{18}
4.7×10^3 ohm - R_3, R_{21}, R_{24}
3.0×10^3 ohm - R_{16}
1.0×10^3 ohm - R_8, R_{12}
5.0×10^2 ohm - R_{22}

100 µf - C_5, C_8, C_{11}
20 µf - C_{14}, C_{15}
10 µf - C_3(oil), C_6, C_9, C_{12}
0.1 µf - C_2, C_4, C_7, C_{10}, C_{13}

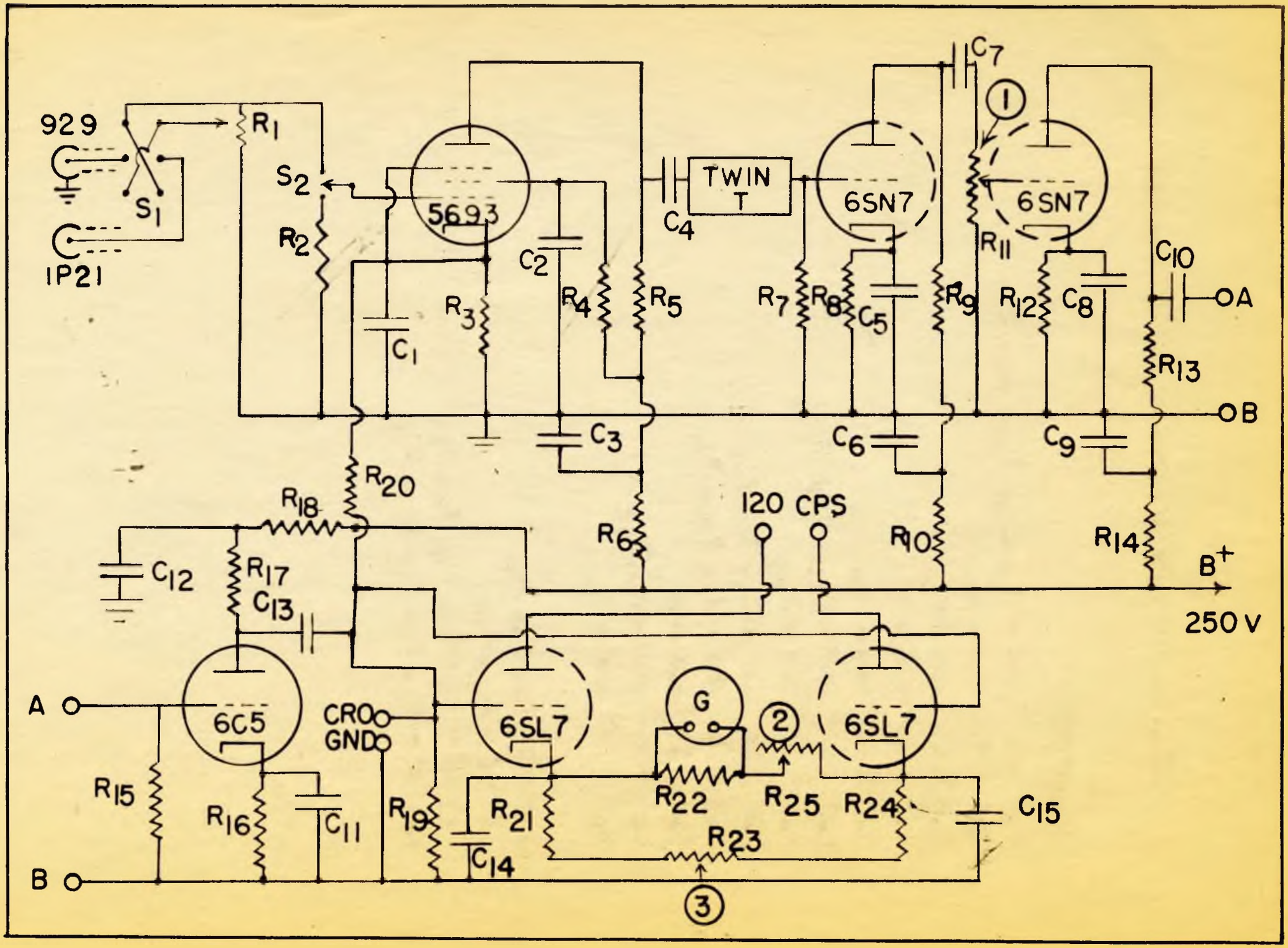

929
1P21
S1
R1
S2
R2
5693
R3
C1
C2
R4
R5
C3
C4
TWIN T
6SN7
C7
①
6SN7
R7
R8
C5
R9
R11
R12
C8
C10
A
R13
B
C6
C9
R20
R18
R6
120 CPS
R10
R14
B+
250 V
C12
R17
C13
A
6C5
CRO
GND
6SL7
G
②
6SL7
R15
R16
C11
R19
R21
C14
R22
R25
R24
C15
R23
③
B

Fig. 6. Circuit Diagram for 120-cycle Generator

Components

10×10^6 ohm - R_{19}
1.0×10^6 ohm - R_2, R_8, R_{12}, R_{16}
3.3×10^5 ohm - R_{18}
7.5×10^4 ohm - R_{10}, R_{14}
4.7×10^4 ohm - R_{15}
4.0×10^4 ohm - R_{11}
1.5×10^4 ohm - R_4
1.3×10^4 ohm - R_5, R_6
1.0×10^4 ohm - R_7
3.7×10^3 ohm - R_{13}
3.3×10^3 ohm - R_9
1.0×10^3 ohm - R_3
2.5×10^2 ohm - R_{17}
2.2×10^2 ohm - R_1

100 µf - C_2, C_6, C_9, C_{12}
20 µf - C_{10}, C_7
8 µf - C_{13}
2 µf - C_3
1 µf - C_4
0.1 µf - C_1, C_5, C_8, C_{11}

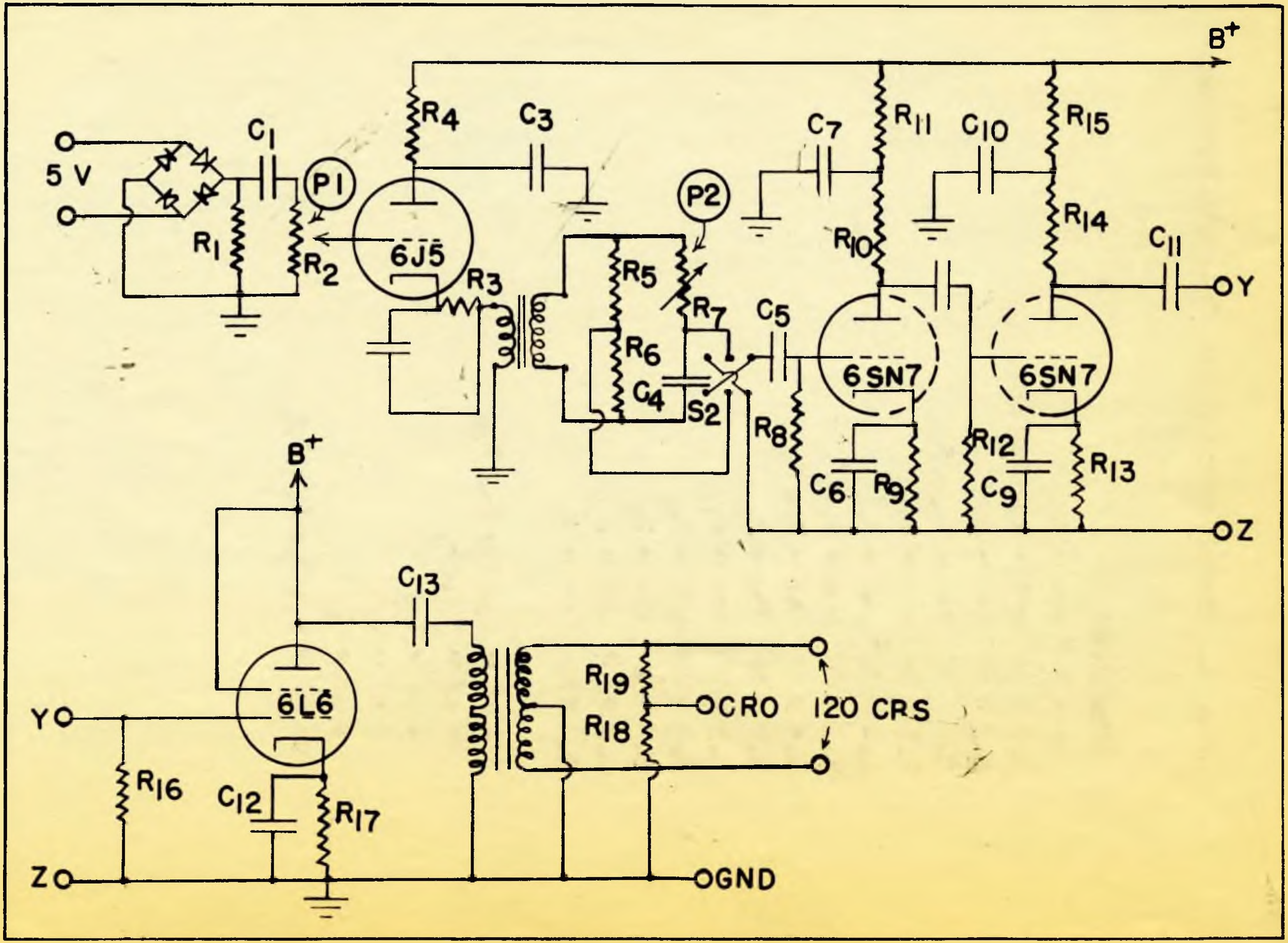

B+
5 V
C1
P1
R1
R2
R4
C3
6J5
R3
R5
R6
C4
S2
R7
P2
C5
C7
R11
C10
R15
R10
R14
C11
Y
6SN7
6SN7
R8
C6
R9
R12
C9
R13
Z
B+
C13
6L6
Y
R16
C12
R17
Z
GND
R19
R18
CRO
120 CPS

Fig. 7. Typical Calibration Curve
for Original Light-Scattering Photometer

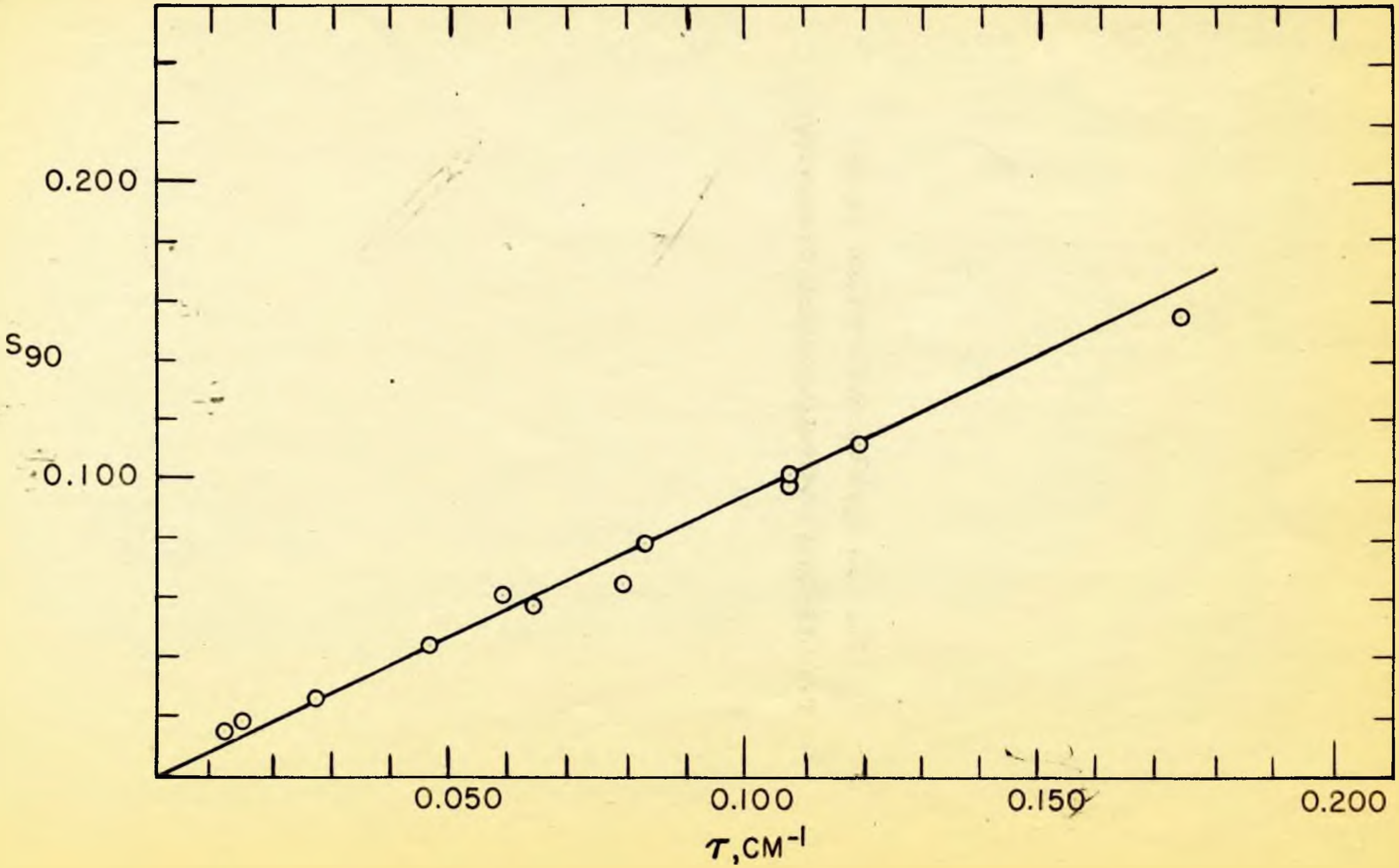

0.200
0.100
S_{90}
0.050
0.100
0.150
0.200
τ, CM^{-1}

Fig. 8. Calibration Curve
for Modified Light-Scattering Photometer

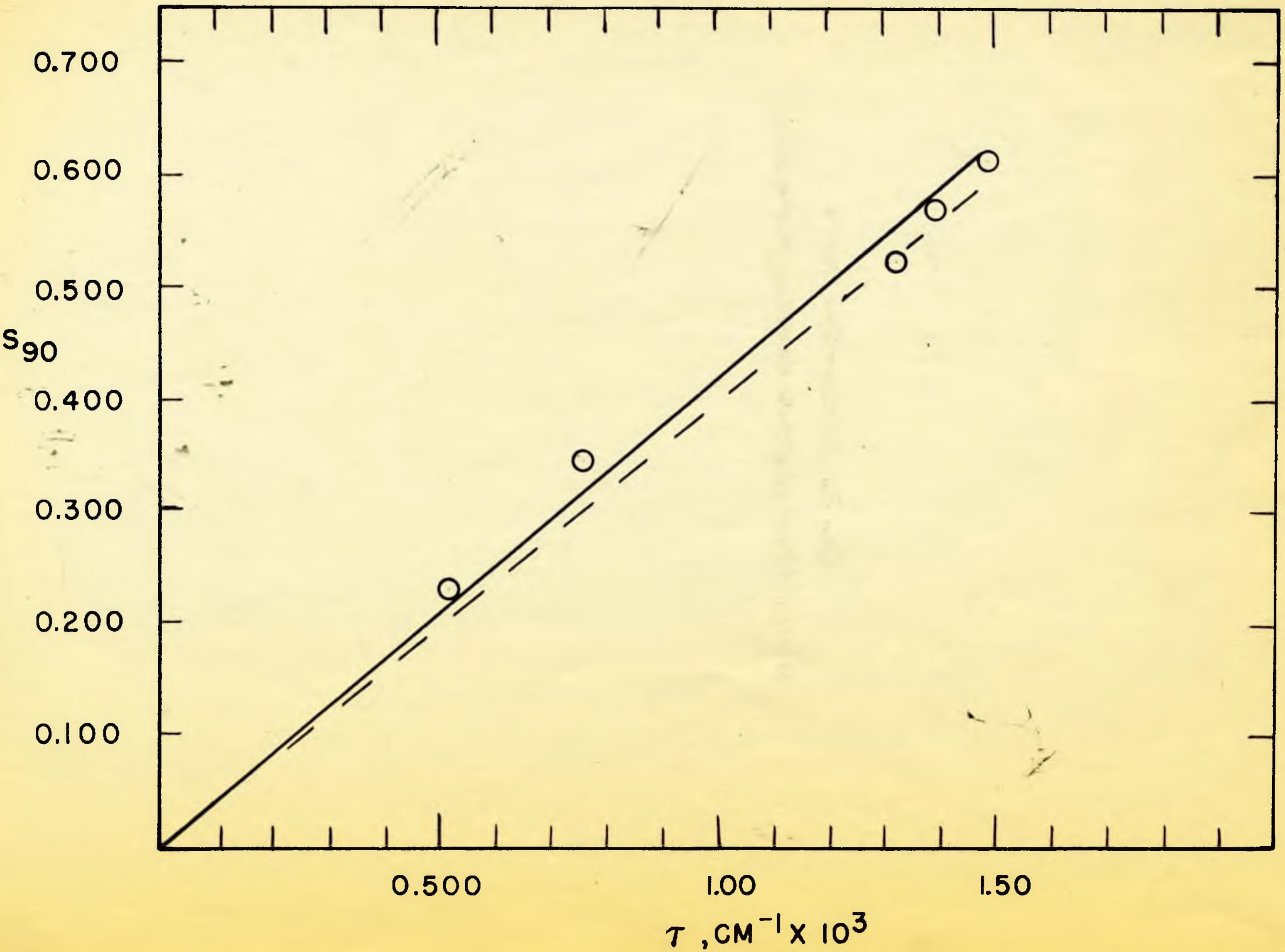
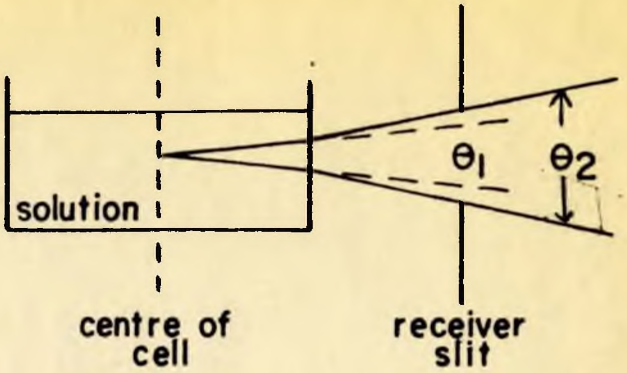
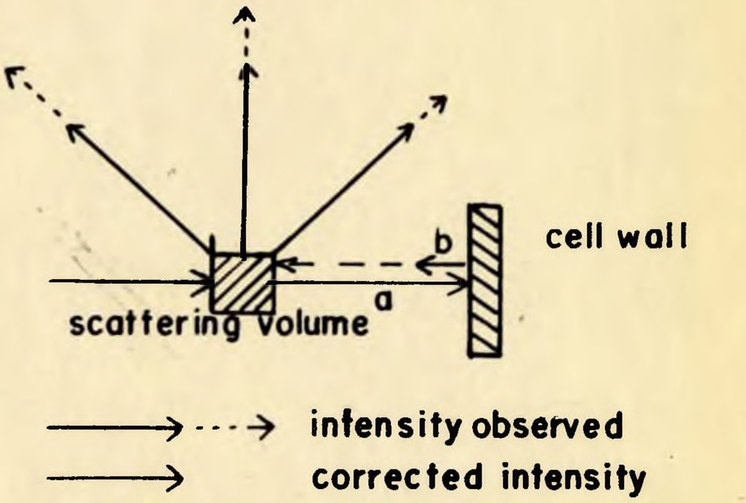

0.700
0.600
0.500
S_{90}
0.400
0.300
0.200
0.100
0.500
1.00
1.50
τ , CM^{-1} X 10^3

Fig. 9. Diagrams Illustrating Corrections for Refractive Index and Backward Reflection of the Incident Beam

REFRACTIVE INDEX EFFECT

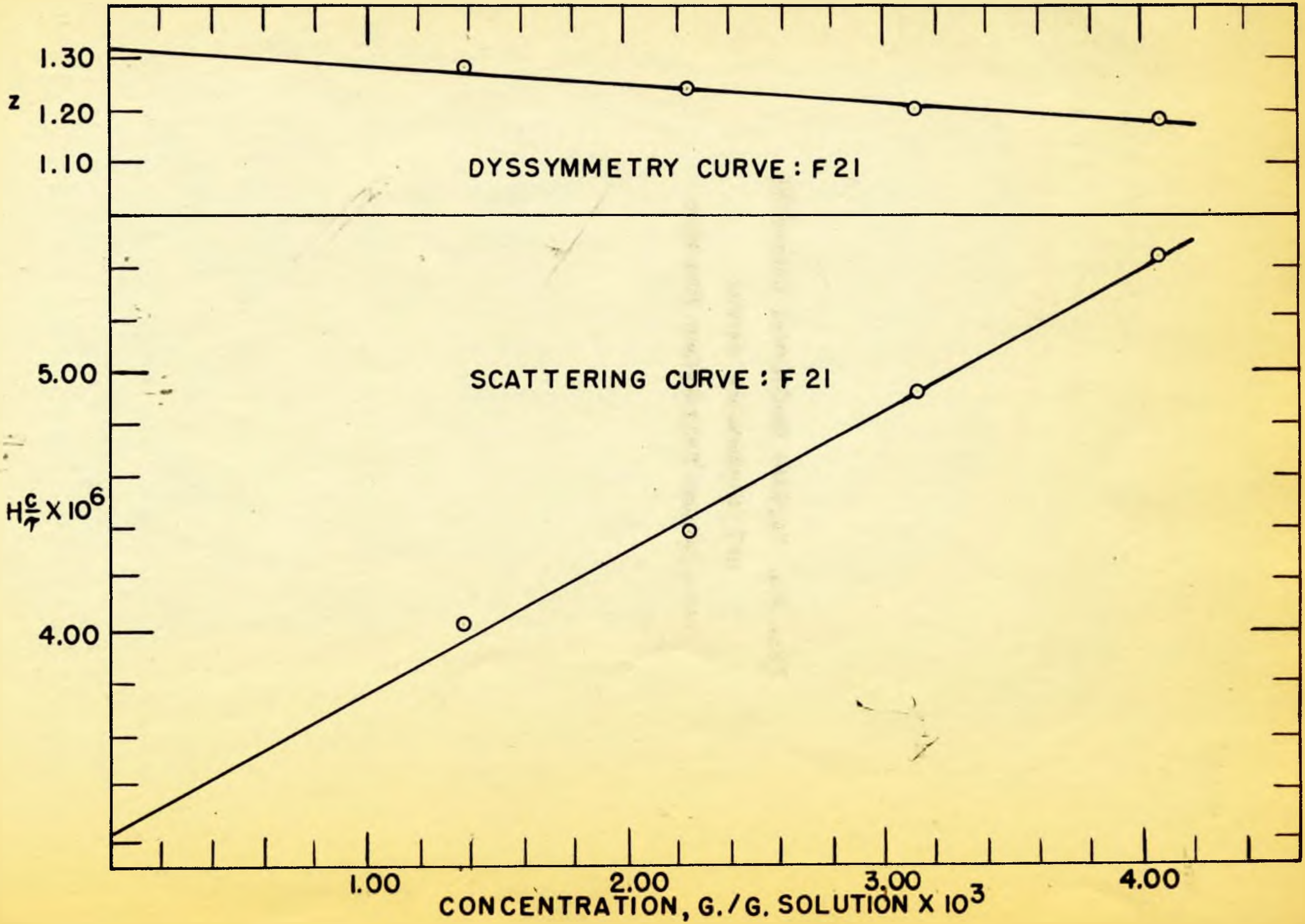


EFFECT OF BACKWARD SCATTERING



Intensity of reflected beam b is
4.7 % of the intensity of incident beam a

Fig. 10. Typical Reciprocal Intensity
and Dyssymmetry Curves
for a Linear Polystyrene Fraction



1.30
z
1.20
1.10
DYSSYMMETRY CURVE : F21
5.00
SCATTERING CURVE : F 21
$H\frac{c}{\tau} \times 10^6$
4.00
1.00
2.00
3.00
4.00
CONCENTRATION, G./G. SOLUTION X 10^3

Fig. 11. Typical Viscosity Curves
for Graft Polymers

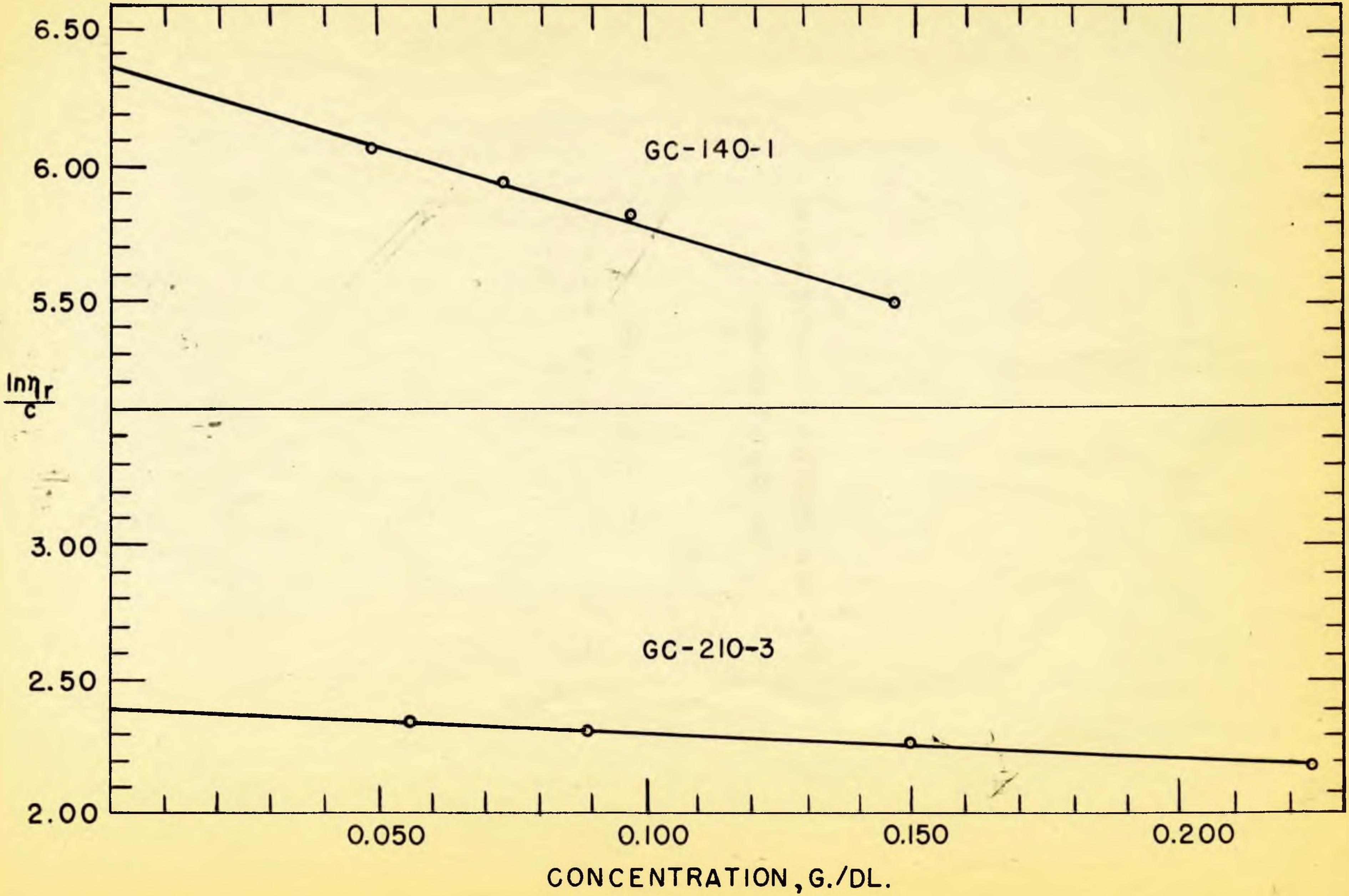

6.50
6.00
5.50
3.00
2.50
2.00
$\frac{\ln \eta_r}{c}$
GC-140-1
GC-210-3
0.050
0.100
0.150
0.200
CONCENTRATION, G./DL.

Fig. 12. Calibration Curve
for Brice-Phoenix Light-Scattering Photometer

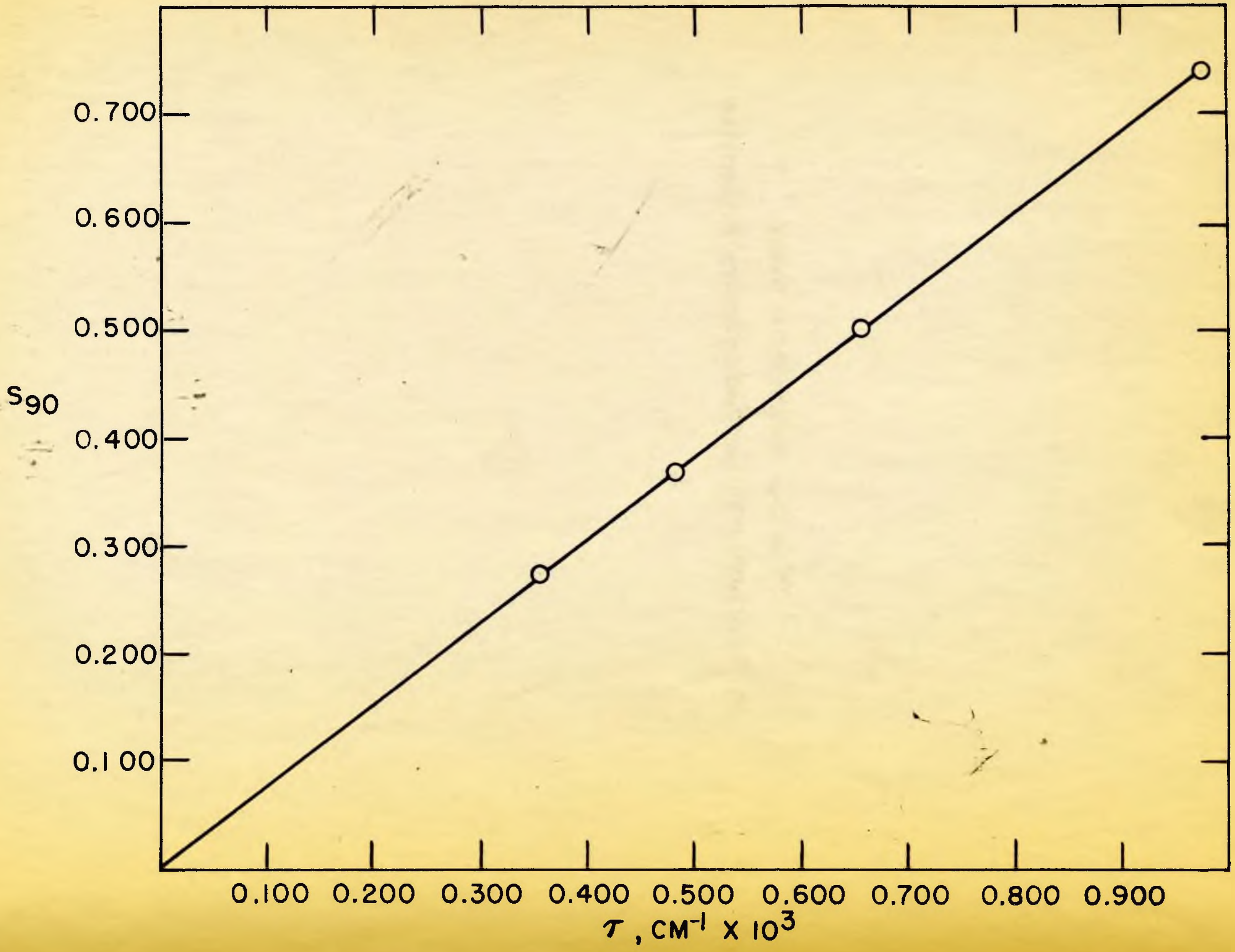
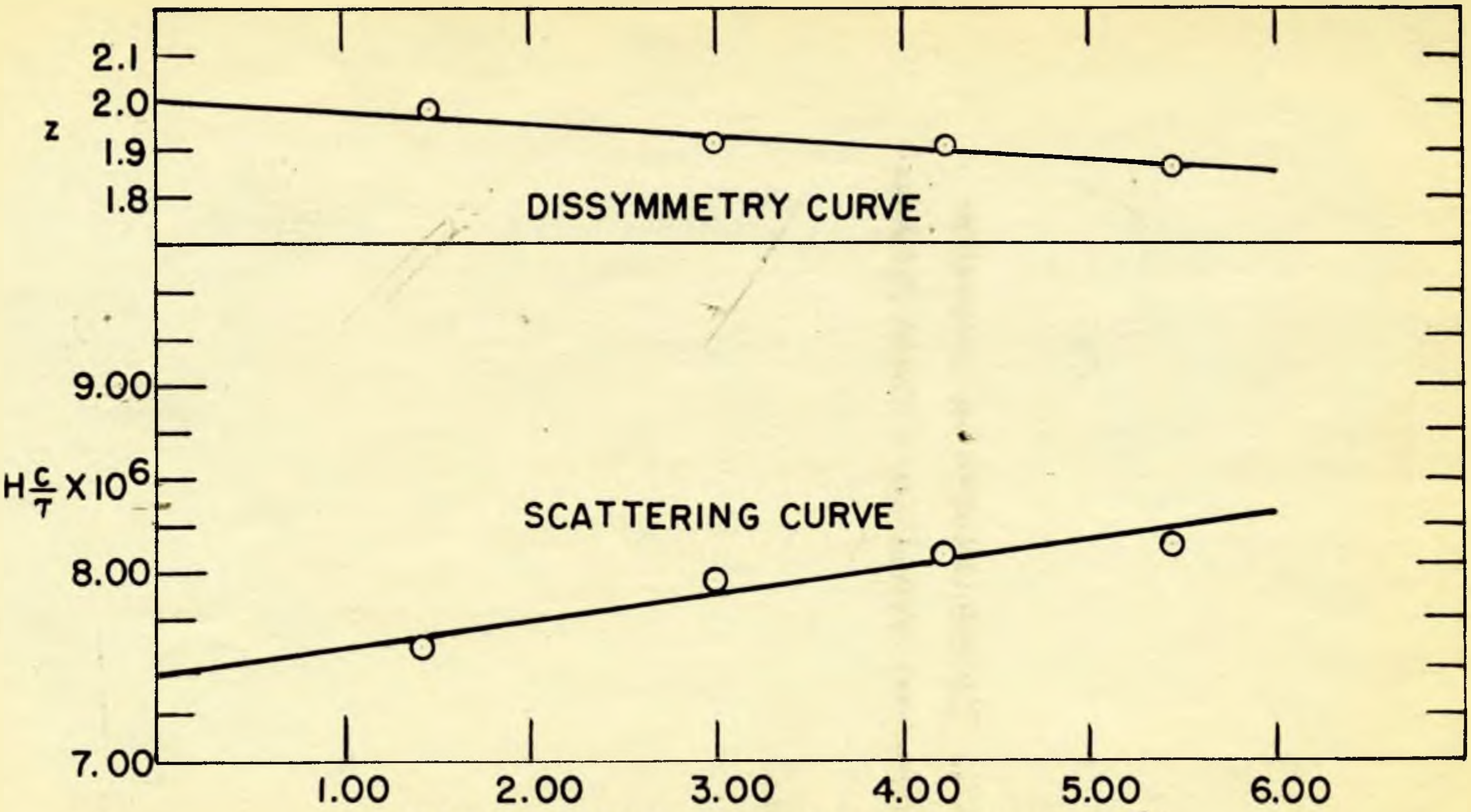

0.700
0.600
0.500
0.400
0.300
0.200
0.100
s_{90}
0.100
0.200
0.300
0.400
0.500
0.600
0.700
0.800
0.900
τ, CM^{-1} X 10^3

Fig. 13. Typical Reciprocal Intensity
and Dyssymmetry Curves for a Graft Polymer



CONCENTRATION, G./G. SOLUTION X 10^4
(SAMPLE: GC-210-3)

Fig. 14. Dependence of Molecular Dimensions in Benzene on Molecular Weight

○ Linear
◑ GC - 140 series
◒ GC - 210 series
◐ GC - 211 series
◓ GC - 230 series
● GC - 621

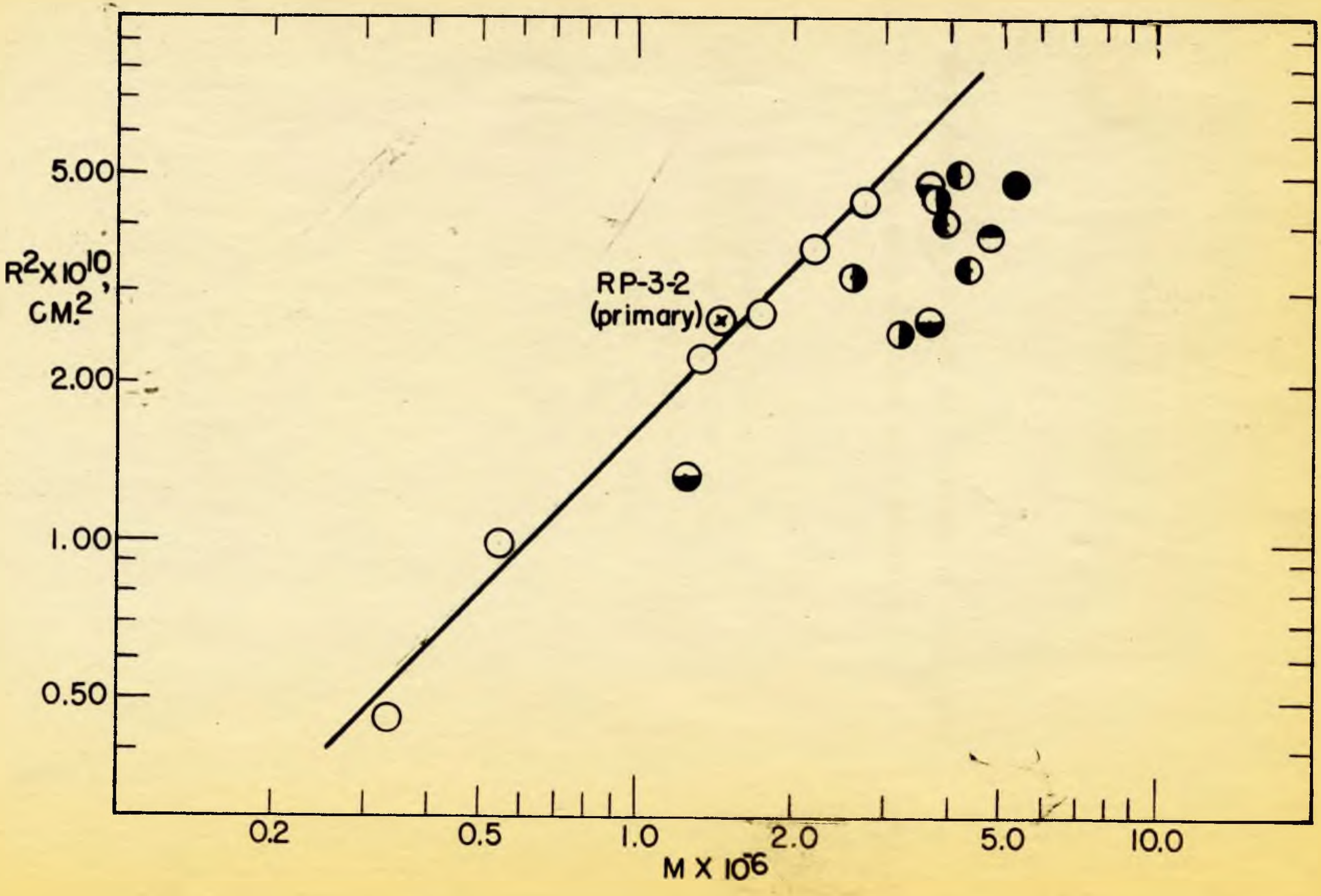
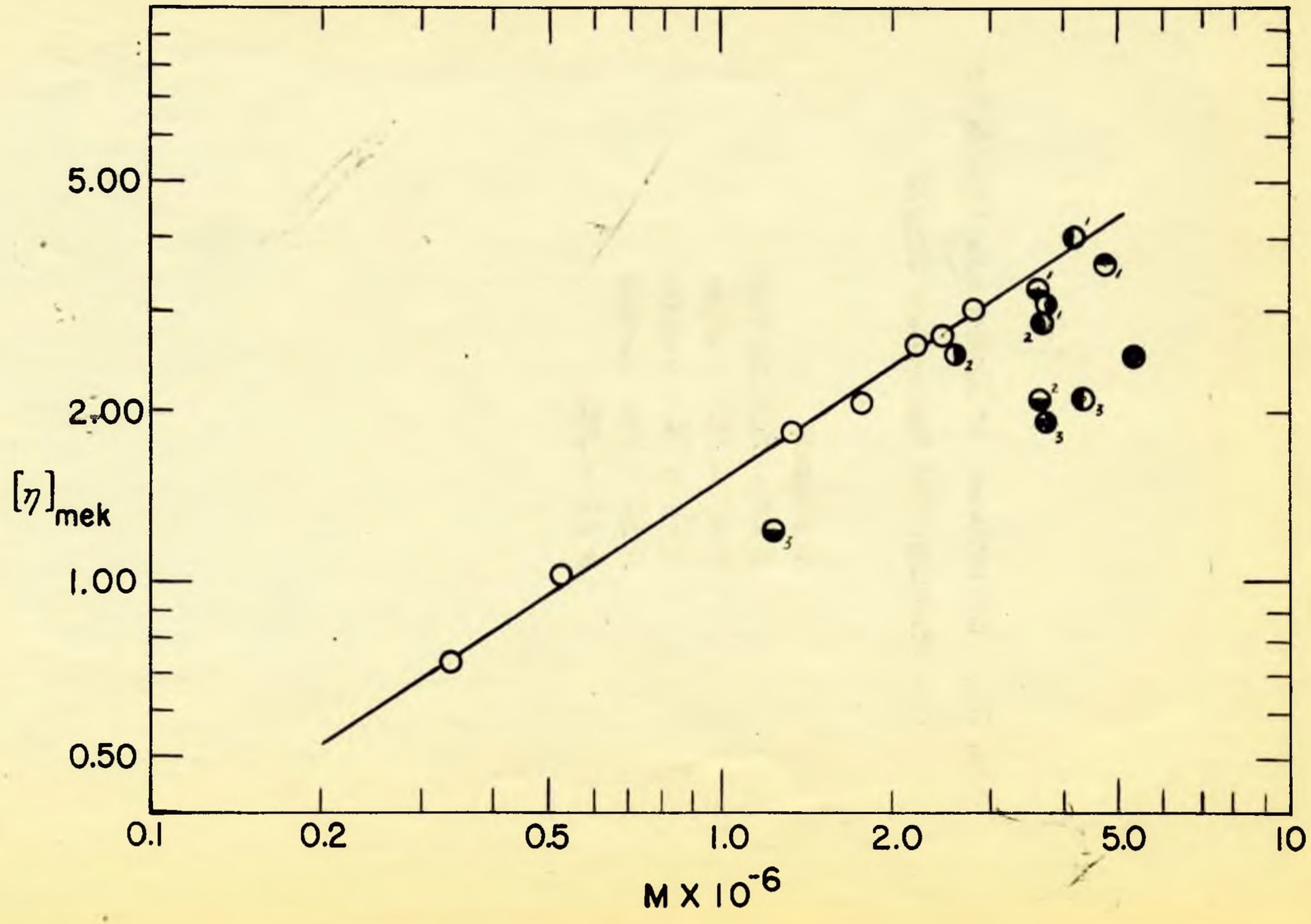

5.00
2.00
1.00
0.50
$R^2 \times 10^{10}$, CM.^{2}
RP-3-2
(primary)
0.2
0.5
1.0
2.0
5.0
10.0
$M \times 10^{-6}$

Fig. 15. Dependence of Intrinsic Viscosity in Butanone on Molecular Weight

○ Linear
◐ GC - 140 series
◒ GC - 210 series
◑ GC - 211 series
◓ GC - 230 series
● GC - 621



5.00
2.00
1.00
0.50
$[\eta]_{mek}$
0.1
0.2
0.5
1.0
2.0
5.0
10
$M \times 10^{-6}$
1
2
3

Fig. 16. Relationship between Intrinsic Viscosities
in Benzene
and Butanone

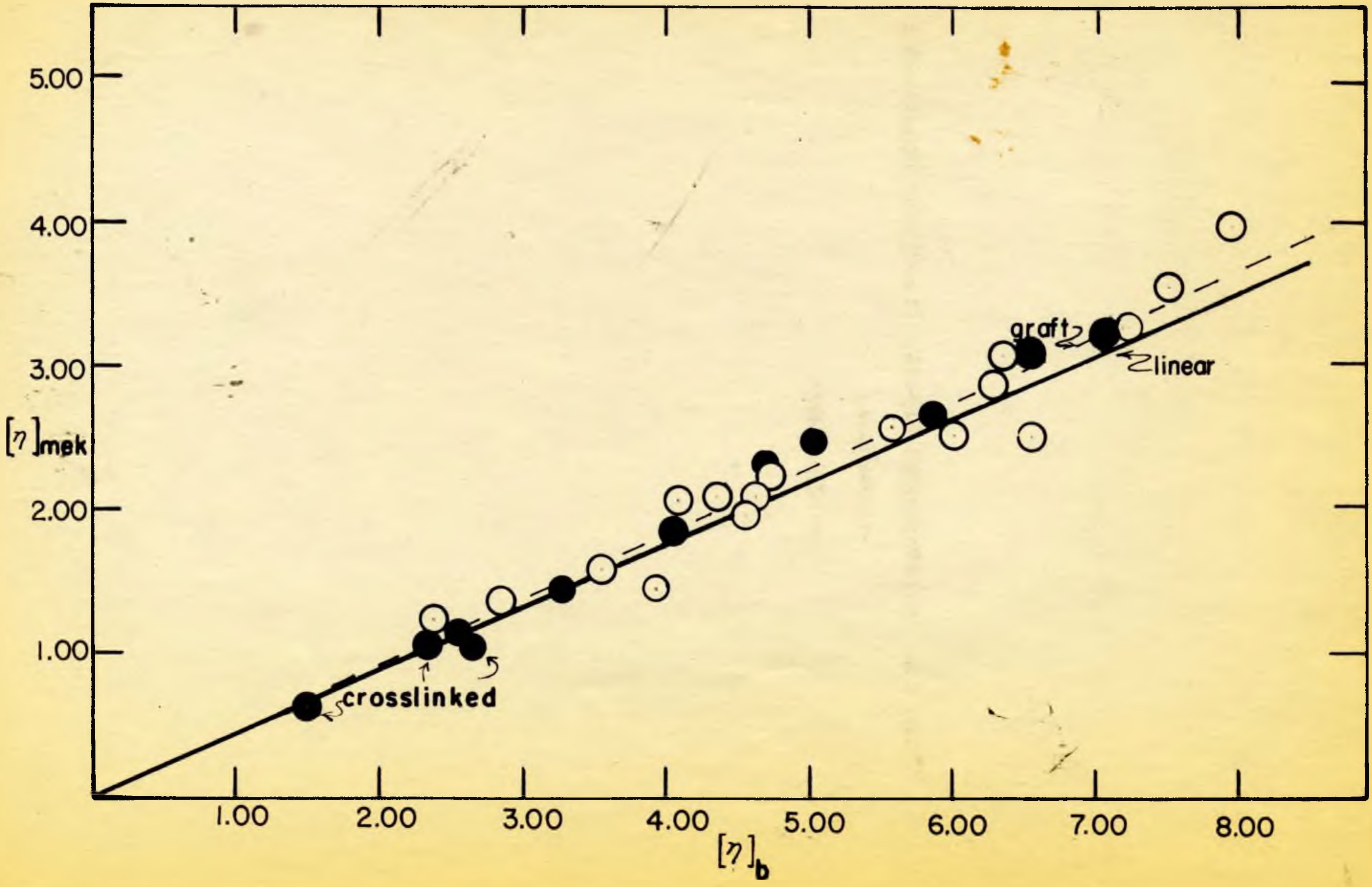
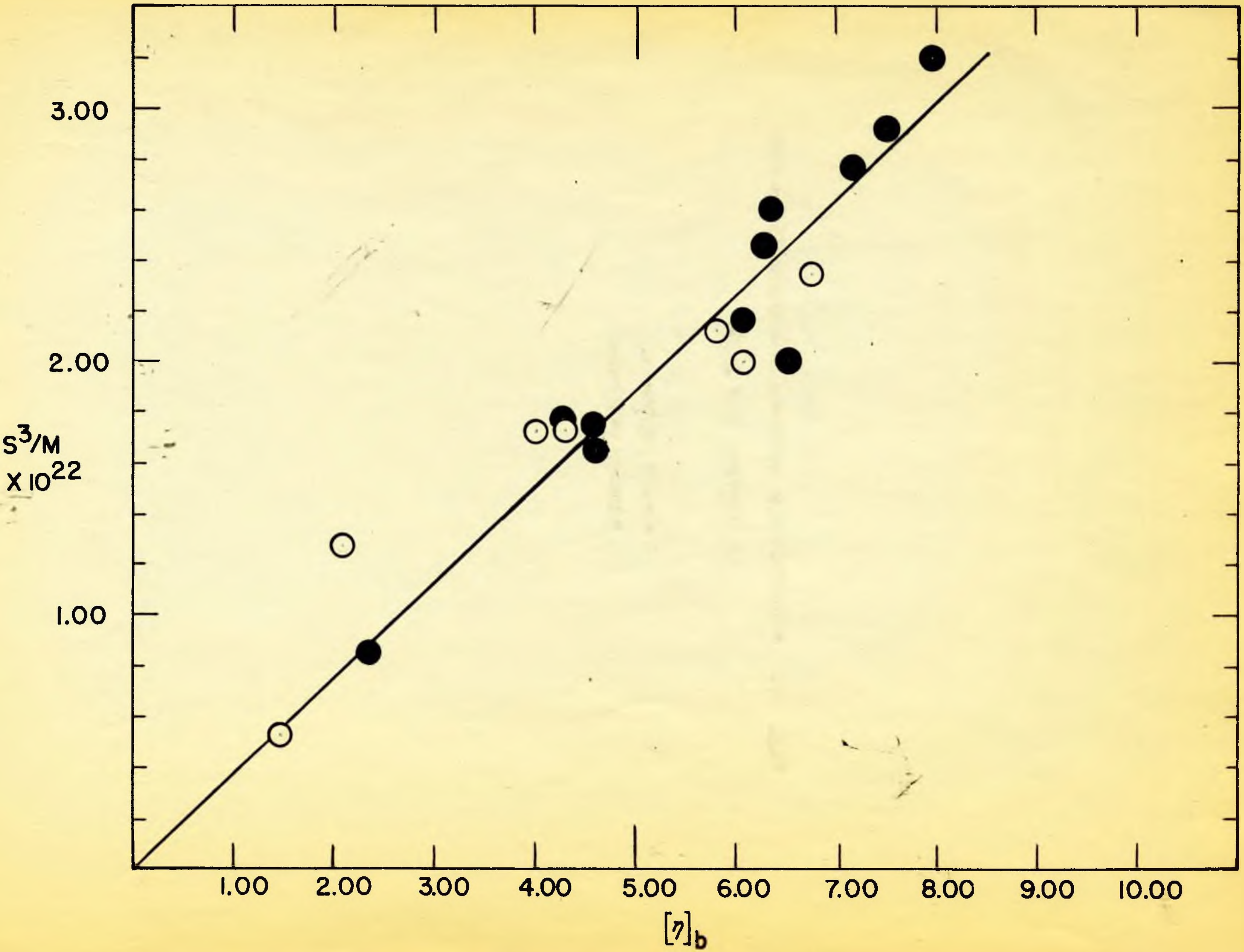

5.00
4.00
3.00
2.00
1.00
[η]mek
1.00
2.00
3.00
4.00
5.00
6.00
7.00
8.00
[η]b
graft
linear
crosslinked

Fig. 17. Relationship between Intrinsic Viscosity in Benzene and S^3/M

● Graft polymers
O Linear polymers



3.00
2.00
1.00
S³/M X 10²²
1.00
2.00
3.00
4.00
5.00
6.00
7.00
8.00
9.00
10.00
[η]b

APPENDIX C

Report to the International Union of Chemistry on Cooperative Viscosity Study

REPORT* ON INTRINSIC VISCOSITY DETERMINATIONS WITH STANDARD POLYSTYRENE SAMPLE 11-26-52

J. A. Manson and L. H. Cragg
McMaster University
Hamilton, Ontario

June 1, 1953

SUMMARY

As reported below, measurements of intrinsic viscosity were made in toluene and methyl ethyl ketone (two different samples of each) by three observers using three different viscometers. Differences in the solvents and in the viscometers were responsible for slight differences in value, the variations being of the order of ±1 ml./g.

"Best" values for intrinsic viscosity at 25.0°C at a shear rate of ca. 2 x 10^3 sec^{-1} are as follows:

toluene	151 (±1) ml./g.
methyl ethyl ketone	84 (±1) ml./g.

(At zero rate of shear the value for toluene is ca. 1 ml./g. higher, viz., 152 ml./g.; for methyl ethyl ketone the shear effect is considerably less.)

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*Except for the omission of graphs and of data such as flow times, this report is a copy of the original one submitted.

STANDARD POLYMER REPORT

Apparatus

The viscometers used, U-14-3 and U-14-12, were of the Ubbelohde type and belonged to a series of viscometers all with diameter of capillary = 0.014 in. modified to permit dilution in the viscometer itself. Designed to have negligible kinetic energy corrections, these viscometers gave almost identical values (within 1 ml./g.) of intrinsic viscosity for the same polymer sample. An Ostwald-type viscometer, SV-1, which calibration showed to have a zero kinetic energy correction, was used in conjunction with a constant pressure apparatus to study the effect of shear rate on viscosity. Viscometer U-14-3 gave $[\eta]$ values from 0.6 to 1 ml./g. lower than did U-14-12. In turn, values determined with U-14-3 are not more than 1 ml./g. lower than with SV-1., the "standard" viscometer.

Special clamps made it possible to mount the viscometers reproducibly in the constant-temperature bath, which operated at 25.0_2 (± 0.01)°C.

For this work, dilutions were made with the same 10 or 5-ml. pipet. Although the 5-ml. pipet delivered 0.006 ml. less solvent than half that delivered by the 10-ml. pipet, this deviation is too small to affect concentrations significantly.

To ensure the removal of dust, all viscometers, pipets and volumetric flasks were cleaned thoroughly with acid-dichromate cleaning solution, rinsed first with filtered distilled water, then with filtered acetone, and dried. (All the volumetric flasks used had a maximum calibration error of ±0.05 ml./50 ml.)

Solvents

Toluene:- (1) British Drug Houses, Sulfur-free; dried over sodium; negative isatin test; n_D^{25} = 1.49253, B.P. = 110.8°C. (corr.)

(2) Steel Company of Canada, nitration grade; washed 3 times with concentrated sulfuric acid, distilled, and dried over sodium. n_D^{25} = 1.49348, B.P. = 110.5°C. (corr.)

Methyl Ethyl Ketone:- Shell Oil Company, dried over Drierite, and redistilled.
Sample 1: laboratory stock; n_D^{25} = 1.37628, B.P. = 79.8°C. (corr.)
Sample 2: freely distilled; n_D^{25} = 1.37631, B.P. = 79.9°C. (corr.)

Preparation of Solutions

The desired weight of polymer (0.18 - 0.20 g.) was weighed into a calibrated 50-ml. volumetric flask, to which was then added enough solvent to dissolve the polymer. Gentle swirling of the flask and contents resulted in rapid solution. The solution was then made up to 50 ml. at 25.0_2°C.

Since the solutions appeared quite clean, only one sample was filtered before making the viscosity measurements; no significant effect on viscosity was noticed.

Concentrations were calculated directly from the weight of polymer used. To check against concentration errors, the two operators made up separate solutions. Exchange of solutions between operators revealed no detectable variation in viscosity curves.

Technique

Before work was begun with the standard polymer, solutions of another polystyrene fraction were used for practice. Randomization of sample, operator, viscometer, and day of run led to the conclusion that either operator, using either viscometer, obtained the same result as the other.

While the standard polymer solution was being made up, the viscometers were placed in the constant temperature bath for 10-15 minutes to allow temperature equilibrium to be reached.

Flow times for filtered pure solvent were then determined; they were measured to the nearest hundredth of a second. Five to ten readings were taken and averaged.

After drying, the viscometers were again placed in the bath, and filled with 10 ml. of solution. Flow times were determined as before; usually 4 or 5 readings were made. When satisfactory agreement as shown by a maximum deviation from the average of ±0.05 sec. had been obtained, 5 or 10 ml. of filtered solvent were added from a pipet, and mixed with the solution already in the polymer bulb by gentle swirling. The solution with the new concentration was then drawn by suction gently up and down the capillary and bulb twice to ensure complete mixing. Flow times were determined again, and the procedure above repeated.

No appreciable evaporation, which would cause a progressive increase in flow time for a given concentration, was noticed. Frequent checking of t_o also indicated no accumulation of polymer on the wall of the capillary.

Results for each run were calculated as $\frac{\eta sp}{c}$ and $\frac{\ln \eta r}{c}$ and plotted on the same graph sheet. Both curves were extrapolated to a common point; the use of both curves made the extrapolation to zero concentration less ambigous.

Viscosity determinations were also made in toluene at various rates of shear. Extrapolation to zero rate of shear indicates a slight shear effect.

Errors

From careful consideration of variations in values of intrinsic viscosity owing to errors in the calibration of flasks, pipets, and viscometers, to variations in concentration or temperature, and to variations in solvents and observers, it was concluded that the probable precision of our values of intrinsic viscosity should be within ±1 ml./g.

TABLE 1

SUMMARY: MEK

Observers: O_1 = Manson; O_2 = Wiles
Viscometers: V_1 = U-14-3; V_2 = U-14-12
Solvent Samples: S_1 = stock MEK; S_2 = fresh MEK
(S_2 = filtered)

	$O_1V_1S_1$	$O_2V_2S_1$	$O_1V_1S_2$	$O_2V_2S_2$[1]
$[\eta]$(ml./g.)	82.6	83.0	83.8	84.2
β	0.10	0.12	0.08	0.08
k'	0.42	0.40	0.44	0.44

Average, stock MEK: $[\eta]$ = 82.8 ± 0.2
k' = 0.41 ± 0.01
β = 0.11 ± 0.01

Average, fresh MEK: $[\eta]$ = 84.0 ± 0.2
k' = 0.44
β = 0.08

TABLE 2

SUMMARY: TOLUENE

Observers: O_1 = Manson; O_2 = Wiles; O_3 = Waugh
Viscometers: V_1 = U-14-3; V_2 = U-14-12; V_3 = SV-1
Solvent Samples: S_1 = BDH S-free toluene; S_2 = purified Stelco toluene

	$O_1V_1S_1$	$O_1V_2S_1$	$O_2V_2S_1$	$O_1V_1S_2$	$O_2V_1S_2$	$O_3V_3S_2$ (free fall)	$O_3V_3S_2$ (D = 0)*
$[\eta]$(ml./g.)	$149._3$ $150._5$ av. $149._9$	$151._5$ $150._5$ av. $151._0$	$150._8$	$151._8$	$152._1$	$151._3$	$152._3$
k'	0.35 0.31 av. 0.33	0.31 0.33 av. 0.32	0.32	0.32	0.30	0.31	
β	0.16 0.19 av. 0.17_5	0.18 0.17 av. 0.17_5	0.17	0.18	0.18	0.18	

Averages:
(at free fall
with V_1 & V_2)

$[\eta] = 150._5 \pm 1$ (S_1)
$[\eta] = 152._0 \pm 1$ (S_2)
$k' = 0.32 \pm 0.01$ (S_1)
$k' = 0.31 \pm 0.01$ (S_2)
$\beta = 0.17_3 \pm 0.00_2$ (S_1)
$\beta = 0.18_0$ (S_2)

---

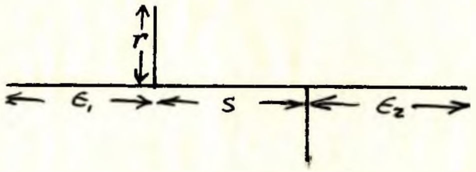
*Results extrapolated to D = 0, that is, to zero rate of shear.

APPENDIX D

Calculation of the Branching Ratio, g, for a Polymer Model

Calculation of the Branching Ratio, g, for a Polymer Model

The model chosen consists of a linear backbone chain carrying simple, trifunctional branches of uniform length, that are equally spaced along the main chain (see diagram).



The effect of branching on the molecular dimensions of the model may, as usual, be expressed in terms of the parameter g; the following expression was obtained by Wales, Marshall, and Weissberg (46) for g:

$$g = \frac{6}{N^3}\left\{ \sum_{i=1}^{\epsilon_1} i(N-i) + \sum_{i=1}^{\epsilon_2} i(N-i) + k\sum_{i=1}^{i=r} i(N-i) + \sum_{p=1}^{p=k+1} \sum_{i=\epsilon_1+pr+(p-1)s+p}^{i=\epsilon_1+pr+ps+p} i(N-i) \right\}$$

where k is the number of branches, ϵ_1, ϵ_2, r, and s have the same significance as in the diagram, and N is the total number of segments in the molecule (conveniently expressed as $M_{polymer}/M_{styrene}$).

This summation has been reduced to a convenient form by Dr. P. R. Beesack*, Department of Mathematics, McMaster

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*The author is grateful to Dr. Beesack for deriving the simpler expression.

University. The following expression was obtained:

$$g = \frac{6}{N^3}\left\{\frac{\epsilon_1(\epsilon_1+1)}{6}(3N-2\epsilon_1-1) + \frac{\epsilon_2(\epsilon_2+1)}{6}(3N-2\epsilon_2-1) + \frac{kr(r+1)}{6}(3N-2r-1) + \sum_4\right\}$$

$$= \sum_1 + \sum_2 + \sum_3 + \sum_4 .$$

where $\sum_4$ is given by

$$\sum_4 = \frac{k-1}{2}\left[N-(k-2)\alpha\right]\left\{\gamma(\gamma+1)-\beta(\beta+1)\right\} - \frac{k-1}{6}\left\{\gamma(\gamma+1)(2\gamma+1)-\beta(\beta+1)(2\beta+1)\right\}$$

$$+ \frac{(k-1)(k-2)}{2}(\gamma-\beta)\alpha\left[N-\alpha\frac{(2k-3)}{3}\right] .$$

The terms α, β, and γ are given as

$\alpha = r + s + 1$

$\beta = \epsilon_1 + r$

$\gamma = \epsilon_1 + r + s + 1$

For convenience, it is assumed that

$\epsilon_1 = \epsilon_2 = s$

If, as with the cases of interest here, $\sum_1$ is very small with respect to $\sum_3$ (less than 1 percent of $\sum_4$), the terms $\sum_1$ and $\sum_2$ may be omitted from the calculations.