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HUGGINS' k' AS A MEASURE OF NON-LINEARITY
IN NORMAL AND CROSS-LINKED POLYSTYRENE

by

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A Thesis

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Abstract

Polystyrene samples prepared in emulsion at 55° C. were carefully fractionated. The resulting fractions were in turn fractionated, combined in groups having similar intrinsic viscosities, and re-fractionated. As the intrinsic viscosity of these fractions increased, the value of Huggins' k' in methyl ethyl ketone was found to increase slightly (from 0.39 to 0.41). Polystyrene samples prepared in exactly the same way except for the addition of small amounts of divinylbenzene, a cross-linking agent, were similarly fractionated. The value of k' in methyl ethyl ketone for these fractions increased considerably (from 0.41 to 0.68) as the intrinsic viscosity increased, even though the amount of divinylbenzene added was very small (from 0.003 to 0.05%). Relations were then established for these cross-linked fractions between k' and the proportion of divinylbenzene present, and between k' and the intrinsic viscosity of the fractions.

It was concluded that polystyrene prepared in emulsion at 55° C. is essentially linear in structure, and that the value of Huggins' k' seems to provide a convenient and sensitive test for the presence of any appreciable branching that might occur in polystyrene.

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INTRODUCTION

1. Statement of the Problem

During the course of an investigation into a long-range problem concerning the precipitation of polystyrene from solution, it was found necessary to obtain polystyrene fractions having a distribution of molecular weights as narrow as possible and having an essentially linear structure. These requirements arose because a sharp precipitation point can be found only with a narrow distribution of molecular weights, and because, on the basis of certain evidence (35, 45, 46), the precipitation point might be sensitive to small changes in structure. Accordingly, polystyrene samples were carefully fractionated, and the fractions in turn were fractionated and refractionated (with suitable recombination of fractions each time); however, further fractionation failed to give any better separation of fractions with respect to molecular weight. In view of the warning of Bamford and Dewar (9), who claim that the polymerization of styrene to high conversions such as the 96% conversion used in this study results inevitably in branching, an investigation, reported in this thesis, was undertaken to determine whether or not branching had occurred. According to the rate constants of Bamford and Dewar (9), confirmed by Melville and Valentine (69), the rate of chain transfer is approximately 1/1000 times the rate of propagation of the monomer units. Now the process of chain transfer results in the formation of a branch; therefore one might expect that branching should occur to at

least some extent. On the other hand, Outer, Carr, and Zimm (78) found by light scattering methods that no detectable branching existed in some normal polystyrene samples. This apparent contradiction made it impossible to decide, without further experimental evidence, whether or not a significant and detectable amount of branching was present in the polystyrene fractions already prepared.

Since Simha (86) predicted that an increase in Huggins' k' , a constant characteristic of a given polymer-solvent system (58), should indicate branching, and since this prediction had been substantiated by Baker (7), Speiser and Whittenberger (89), and Walker and Winkler (106), the values of k' were calculated for the fractions. A slight but definite trend was noted in k' (from 0.39 to 0.41) as the molecular weight increased. This increase might have meant that the laboriously prepared fractions were useless for their original purpose because of branching in the higher molecular weight range, for there was no way of determining the amount of branching indicated by this trend.

The next logical step was suggested by the work of Walker and Winkler (106), who were at that time completing a study of variations in k' of bulk-polymerized polystyrene cross-linked by adding varying amounts of divinylbenzene to the polymerization mixture. Accordingly, it was decided to copolymerize styrene and divinylbenzene in an emulsion system to discover whether or not the values of k' for the artificially cross-linked polymer differed significantly from those for the normal polystyrene fractions.

As soon as work began, it became evident that the copolymer prepared in an emulsion system had very different characteristics from

that prepared in a bulk system. For example, no sharp "gel point" could be found for the emulsion-polymerized polystyrene, while a very definite one exists for the bulk-polymerized polymer (106). Furthermore, the polymers used in this study were very difficult to study by normal viscosity methods because of unusual solubility properties.

For these reasons, it was decided that a suitable thesis problem would be a comparison of the viscosity behaviour in dilute solution of normal polystyrene fractions with those of polystyrene cross-linked to various degrees with divinylbenzene.

2. Definitions of Branching and Cross-linking

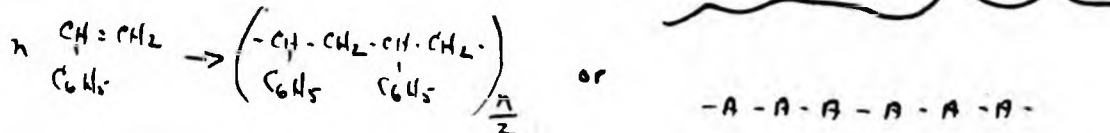
If we represent a bifunctional monomer, that is, one which can form two primary valence bonds with another monomer molecule, by $-A-$, a trifunctional monomer by $-B-$, and a tetrafunctional monomer by $-C-$, it is easy to predict the type of structure formed by the polymerization of each monomer type. Thus, polymerization of $-A-$ should obviously result in a product having the structure $-A-A-A-A-A-A-A-A-A-$. However, if $-A-$ were copolymerized with $-B-$ or $-C-$, it is evident that the resulting molecules should have possibilities for growth in more than one dimension, e.g. $-A-A-B-A-A-B-$, or $-A-A-C-A-A-A-C-A-A-$. In other words, these molecules can grow in several directions to form a number of branches on the main chains.



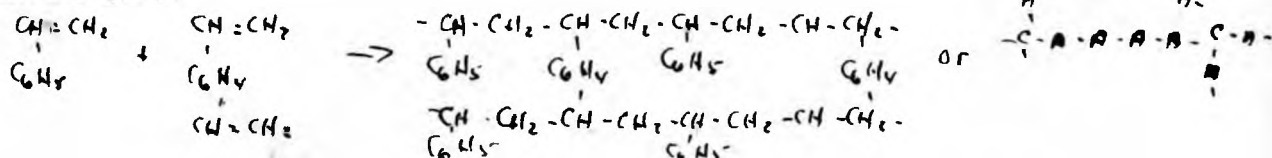
If two or more long molecules become linked through one or more branches, the molecules are said to be crosslinked.



Hence, if styrene, a bifunctional monomer, is polymerized, a linear chain should result.

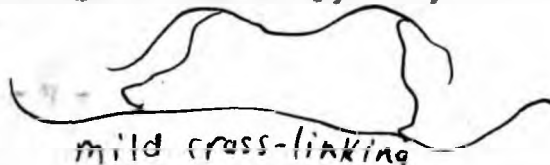


If a small amount of divinylbenzene, a tetrafunctional monomer, is copolymerized with styrene, a branched, or rather cross-linked chain should result. Though there is a possibility of the occurrence of cyclization with divinylbenzene, cyclization occurs to only a very small extent (98).



A few polyfunctional units can by branching and crosslinking increase the average molecular weight of a polymer very considerably. Eventually the process of cross-linking, if continued in three dimensions, leads to infinitely large insoluble molecules which are then said to possess a netted structure and to form a gel (40, 41, 42, 97, 98, 99).

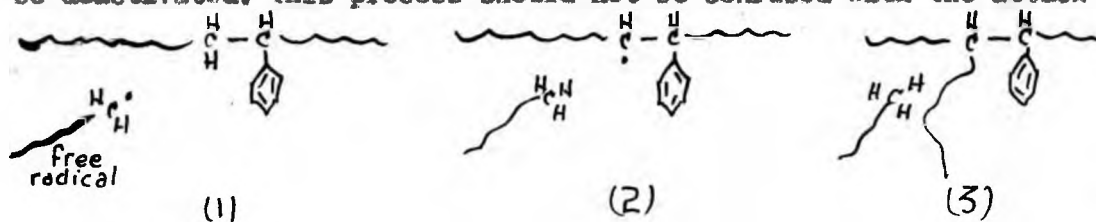
Since cross-linking can be seen from the above description to be an extreme case of branching, a small amount of cross-linking would be practically equivalent to branching. In this study, then, the results



for the mildly cross-linked samples should apply to branched structures as well.

Now the picture of simple styrene polymerization (p. 4) is complicated by the fact that branching or cross-linking might take place during polymerization in several ways (9, 66, 77).

With normal polystyrene a free radical may attack a growing or dead (terminated) polymer chain. In this case, the abstraction of a hydrogen atom from the chain by the free radical activates the chain, which can then grow from the point of activation. Thus a branch could develop on the polymer chain attacked, while the free radical would be deactivated. This process should not be confused with the attack



of a free radical on an unreacted vinyl group of a divinylbenzene molecule in a chain of styrene and divinylbenzene units. In this case, the free radical activates the vinyl group in the usual way.

Another possibility suggested is the formation of a quinoid structure in the styrene molecule (66, p. 220). Though this structure could lead to extensive branching, it should produce a highly coloured



polymer. Since polystyrene is always colourless, or at most only slightly coloured, this suggestion has not been favoured.

Whenever the behaviour of a given polymer sample deviates from that of a standard sample having a structure known to be linear (66), the possibility of the presence of such branching or cross-linking should be investigated. For example, the solubility and the rheology of a polymer may vary widely, depending on the degree of cross-linking.

3. Historical: Cross-linking of Polymers

Staudinger and his coworkers (93, 94, 95, 96) were the first to notice that the addition of small amounts of divinylbenzene to a styrene polymerization mixture had a profound effect upon the properties of the polymer produced. Instead of the usual soluble polystyrene, they obtained a product which, while insoluble, swelled almost infinitely in the common polystyrene solvents such as benzene. Though Staudinger investigated in considerable detail the viscosity and swelling behaviour of these cross-linked polymers, and though a number of patents, such as those of D'Alelio (25, 26), were taken out for copolymers of styrene and divinylbenzene, interest was not great in these unusual polymers which are rather difficult to experiment with. Norrish and Brockman (77) found results similar to those of Staudinger and his workers.

More recent work with these copolymers has been done by Breitenbach and his group, who, in a series of papers (16, 17, 18, 19), discuss the swelling properties of such gels in binary liquid mixtures, and the formation of unusual cauliflower-like gels with divinylbenzene concentrations ranging from 0.4 to 1.5%.

In 1941, Flory began a series of studies on copolymers of styrene and divinylbenzene and on gelation and crosslinking in general. Having calculated the conditions under which gelation should occur (40), he found that these gel points (points at which gelation takes place) determined experimentally agreed fairly well with the theoretical critical points for the formation of infinite chain networks, that is,

of an infinite three-dimensional structure.¹ Flory showed the simultaneous presence of sol and gel in a cross-linked system to be a consequence of the random distribution of branches, and not of any differences in chemical properties of the polymerization ingredients (41). According to the same study, since highly branched species are preferentially converted to gel as the extent of polymerization approaches that corresponding to the gel point, the average complexity of the sol decreases beyond the gel point. Up to this point the intrinsic viscosity should increase, for the polymer, though having an increased molecular weight, is still soluble; after this point the insoluble gel formed is removed by precipitation so that the intrinsic viscosity of the soluble portion decreases. Flory continued his calculations in later papers (42, 43) to show that as polymerization proceeds past the gel point, the disparity between the degrees of cross-linking in the sol and gel portions of a cross-linked polystyrene sample increases. However, Flory's theories were restricted to certain functional units and to a restricted range of molecular weights.

Stockmayer (97, 98) confirmed Flory's theory qualitatively and extended it to cover chains of any length and branch units of any functionality. In another mathematical paper, Stockmayer predicted the amount of divinylbenzene required to cause gelation in copolymers of styrene and divinylbenzene (99). While his gel point equation failed to

¹ It should be noted that the gel point for a given polymer system may be reached either by increasing the degree of conversion, or extent of polymerization, or by increasing the proportion of an added cross-linking agent. In either case, the degree of crosslinking will be increased, for there will be a higher probability for chain transfer.

hold quantitatively because of the higher reactivity of divinylbenzene as compared to styrene (66), he predicted that gelation should occur when the concentration of divinylbenzene reached 0.03 %, or less.²

Another equation for predicting gel points was developed by Walling (110), though he showed it to be equivalent to Stockmayer's equation. Walling suggested that gelation should take place when from 13 to 23% of a polymerization mixture consists of highly swollen particles.

In Boyer's experiments on the thermodynamic properties of copolymers of styrene and divinylbenzene immersed in polystyrene solutions, he found gelation to occur when 0.033% divinylbenzene was present (13, 14). This value is very close to the 0.03% predicted above by Stockmayer (99). Boyer and Spencer (14) noted that in general gels contain an appreciable amount of soluble material, and that the proportion of soluble material varies inversely with the concentration of divinylbenzene. Also, since divinylbenzene is more reactive than styrene, it may be used up quite soon in the polymerization process. Thus the final polymer would contain a higher proportion of soluble material than would the initial polymer.

Janssen and Caldwell (62), investigating the gelation of Vinylite VYNW in methyl ethyl ketone, found that a few polymer-polymer contacts caused by the presence of a small amount of very high molecular weight material could tie the molecules into a network structure. This network could trap low molecular weight material which might dissolve later if the whole polymer were placed in a standard-type solvent(67).

²Compare the gel point values found by Boyer and Spencer (14), Staudinger et.al. (93, 94, 95, 96), Valyi, Janssen, and Mark (105), and Walker and Winkler (106).

In 1945, Valyi, Janssen, and Mark (105) carried out a very interesting study of the molecular weight distributions of fractions of polystyrene cross-linked by copolymerization in bulk to 95% conversion with divinylidiphenyl and diisopropenyldiphenyl—vinyl compounds which are more stable than divinylbenzene. They found that gelation occurred at a divinyl compound concentration of 0.025%, as compared with the 0.023% noted by Staudinger et.al. (93, 94, 95, 96), the 0.033% reported by Boyer (13), the 0.03% predicted by Stockmayer (99), and the 0.10% found by Frank et.al. (47).

An excellent discussion of branching and cross-linking may be found in another paper by Flory(45). He pointed out that the experimental determination of the molecular weight distribution is very difficult to carry out and has a rather dubious significance. Since the solubility of two molecules with the same average molecular weight but with different degrees of cross-linking will be different, Flory predicted that fractionation of cross-linked polymers might reveal variations from normal fractionation behaviour. These variations will be discussed in more detail in later sections.

Recently, after this study was begun, Walker and Winkler (106) published the results of their study of the viscosity behaviour of fractions of styrene-divinylbenzene copolymers, prepared to a conversion just below the gel point. In contrast to Valyi et.al. (104), who had found the viscosity behaviour to be normal for similar fractions, they noticed deviations from normal¹ behaviour, which will be discussed in the next section.

However, there was still need for a simple experimental method

for the qualitative and quantitative detection of branching in polystyrene -- a. i., of course, in other polymers. While Wall (107) described a mathematical method of detecting cross-linking by analysing such data as intrinsic viscosities at various stages of conversion, his method is laborious, and applies only to the detection of cross-linking during the polymerization reaction. The application of light scattering techniques has not been very satisfactory either. Though Outer et.al. (78) have recently studied cross-linked polystyrene by such methods, the haze due to structural heterogeneity (33) hinders investigation.

However, after ^{the} ^{of} considering certain evidence, to be presented in the following pages, it seemed possible that a simple method for the detection of branching in polystyrene might be based on determinations of Huggins' k' .

4. Historical: The Relation of Huggins' k' to Branching

In 1943, Huggins showed that various viscosity-concentration relations for polymer solutions (58) may be reduced to the form:

$$\frac{\eta_{sp}}{c} = [\eta]c + k[\eta]^2 c^2 \quad \left(\begin{array}{l} + \text{higher powers neglected} \\ \text{at low concentrations} \end{array} \right)$$

or

$$\frac{\eta_{sp}}{c} = [\eta] + k' [\eta]^2 c \dots \dots$$

where k' is a constant characteristic of a given polymer-solvent system.

Though recently Eirich and Edsman (36) have urged that Huggins' k' be redefined, Huggins' interpretation will be used throughout this work.¹ According to Huggins, the value of k' depends on the sizes, shapes, and cohesional properties of both solvent and solute molecules.

In 1942, Alfrey, Bartovics, and Mark (3) suggested that the degree of coiling or uncoiling of polymer molecules depends on whether or not the solvent is energetically favourable to the solute. Similar conclusions were reached by Flory (44) and Huggins (59), and were supported by such workers as Cragg and Rogers (24).

This theory leads to several conclusions regarding k' . First, it would be reasonable to expect that polymer molecules should be more coiled in a poor solvent than in a good one — that the molecules would tend towards aggregation more in a poor solvent. Now, since a branched polymer should have a moderate to strong tendency towards aggregation because of the entanglement of branches, the effect of branching should be to produce a tendency towards aggregation comparable to that produced by moving from a good to a poorer solvent with a given linear polymer. If, then, this coiling increases the solute-solute interaction, k' should be higher in a poor solvent than in a good one.² Similarly, if branching leads to an increase in solute-solute interaction or attraction,

¹In this thesis k' will refer to the Huggins k' , and not to any other constant, such as Wissler's k' (112).

²Indeed, Huggins (60, 61), in disagreement with some conclusions of Alfrey, Bartovics, and Mark (4), who reported a dependence of k' on the temperature of polymerization, suggested that the decrease observed in k' might have been due to differences in the degree of coiling. However, an increase in branching might be expected at high temperatures; this increase should be, but was not, reflected in higher k' values.

and thus in the total interaction in a given solvent (for the solute-solvent attraction should remain approximately constant), then branching should lead to an increase in k' .

Working with cellulose acetate fractions, Bartovics and Mark (11) found evidence that supported the views about good and poor solvents discussed above, and Huggins' conception of k' as an interaction constant. Spurlin's views (91, 92) are also in accord with these ideas, for he suggested that the abnormally high value of the slope (and hence of k') of specific viscosity curves for cellulose in various solvents indicates a poor solvent (with the same tendency towards aggregation as that caused by branching).³

However, an element of doubt regarding the constancy of k' with respect to heterogeneity of molecular weight became troublesome.

To account for apparent variations in k' for cellulose acetate (11), Coppick (22) proposed a heterogeneity coefficient q such that $q = \frac{\text{apparent } k'}{\text{true } k'}$. Coppick justified this step by pointing out that a given solvent, if good for short molecules, would be poorer for longer molecules. Thus k' would vary with the molecular weight heterogeneity -- a conclusion similar to those drawn by Howlett *et.al.* (57), whose experimental accuracy was, however, rather low. Coppick gained further support from Spencer and Boyer (90), who claimed that, in contrast to data of Hansen (53) indicating the constancy of k' both for fractions

³Recently, Evans and Spurlin (37) noted that the presence of bound metal ions in ethylcellulose caused a marked increase in the slope of the specific viscosity curves (and hence in k') from that for the normal polymer. Apparently the effect of the bound metal ions is to produce large electrostatic forces between the chains to which they are attached. Thus the polymer-polymer interaction should become quite high.

and for original polymer, k' was higher for the unfractionated sample of polystyrene than for its fractions. But, as was the case with Howlett et.al. (57), their experimental accuracy was not very high. Though Barry (10) claimed that k' decreased with increasing molecular weight, his results had an inherent error of about $\pm 2\%$ -- an error of the same magnitude as the variations claimed for k' .

Goldberg, Hohenstein, and Mark (49) found k' approximately constant for polystyrene in benzene, but slightly variable with molecular weight for polystyrene in methyl ethyl ketone (from 0.42 to 0.63). Though branching might have caused such an increase, one would expect branching to affect the values in benzene as well.

Fortunately, Davis later proved that, contrary to Coppick (22), Howlett et.al. (57), and Spencer and Boyer (90), k' is actually independent of the molecular weight distribution of the polymer (27). More recently, graphs of specific viscosity drawn by Tremenozzi (103) show the unfractionated polymer to have a viscosity behaviour similar to that of the fractions.

So far, then, k' seems independent of molecular weight and of molecular weight distribution. Variations of k' must arise from some other source.

Predictions made by Simha (86) and by Speiser and Whittenberger (89) that k' should increase as the degree of branching increases have been fulfilled by considerable experimental evidence.

One of the first indications of such a relation was found by Davis and Elliott (28), who reported that the slope constant k (where $2.303 k = k'$) varied for cellulose and cellulose nitrate from 0.16 to

0.20 (corresponding to a change in k' from 0.37 to 0.46) as molecular weight increased.

In 1945, Speiser and Whittenberger (89) found that the k' for amylopectin, the branched isomer of starch, was much greater than the k' for amylose, the unbranched or linear isomer. Similar results have been obtained by Wolf et al. (113).

Another example of widely different values of k' may be found in a paper by Naidus and Mark (76), who found that the lower five fractions of polyvinyl *n*-butyl ether had an average k' value of 0.50, as compared to an average value of 0.80 for the upper five fractions, in which branching might be suspected. Also, when Merz (70) polymerized polycyclohexylmethacrylate in two stages -- one stage thermal, at 330° C. for 15 minutes and then at 25° C., and the other catalyzed with benzoyl peroxide at 80° C. -- he found two peaks in the molecular weight distribution curve corresponding to k' values of 0.35 and 0.68. Again, it would be reasonable to suspect that branching may have occurred, particularly during the second stage. Working with polystyrene, Gralen and Lagermalm (51) found two peaks in the distribution curve -- an observation suggesting that one peak might represent a cross-linked species of polymer.

Considerable experimental work carried out with diene polymers believed to be partly branched led Henderson and Legge (54), Switzer (100), and Brown (20) to conclude that k' increases with the degree of branching or cross-linking. These radical changes in k' (say, from 0.40 to 0.70) show up in a positive slope for the inherent viscosity curves (8), for $k' = 0.50 - \beta$. Normally the slope is negative, and hence β is

positive. With Neoprene GN, Moehel et.al. (72) found an increase in k' from 0.37 to 0.92 as the intrinsic viscosity of fractions increased.^{4,5} Since osmotic pressure measurements showed a slightly lower μ for the top fractions, Moehel concluded that they were possibly branched or cross-linked. In fact, he estimated that about 25% of the polymer was branched or cross-linked.

The ageing of polymers provides another clue to the effect of cross-linking or branching on k' . Morrison, Holmes, and McIntosh (75) noted that with polyvinyl acetate containing a little ferric ion, which is known to effect cross-linking in polyvinyl acetate, the k' of solutions in bis(2-chloroethyl)ether changed from 0.34 to 0.39 after ageing for three days. This change could have been due only to changes in the average molecular weight or in the chemical nature of the polymer. Since molecular weight does not apparently affect k' appreciably, (38), Morrison concluded that the change was caused by a change in the chemical structure such as that brought about by branching. On the other hand, Sirianni, Wise, and McIntosh (87) found no noticeable variation in k' when polymethyl methacrylate was aged at 100°C.

Thus certain variations in k' have been noted in materials known or believed to be branched or cross-linked. The next logical step

⁴Moehel also found that the whole polymer behaved just as another fraction in the sequence of fractions would behave. Compare the findings of Spencer and Boyer (92) and Davis (27).

⁵As a matter of interest, Sheffer (85), working with high polymeric aluminum soaps, noted k' values greater than unity. However, since k' has no real thermodynamic basis, Sheffer did not try to relate this unusual magnitude of k' to structure.

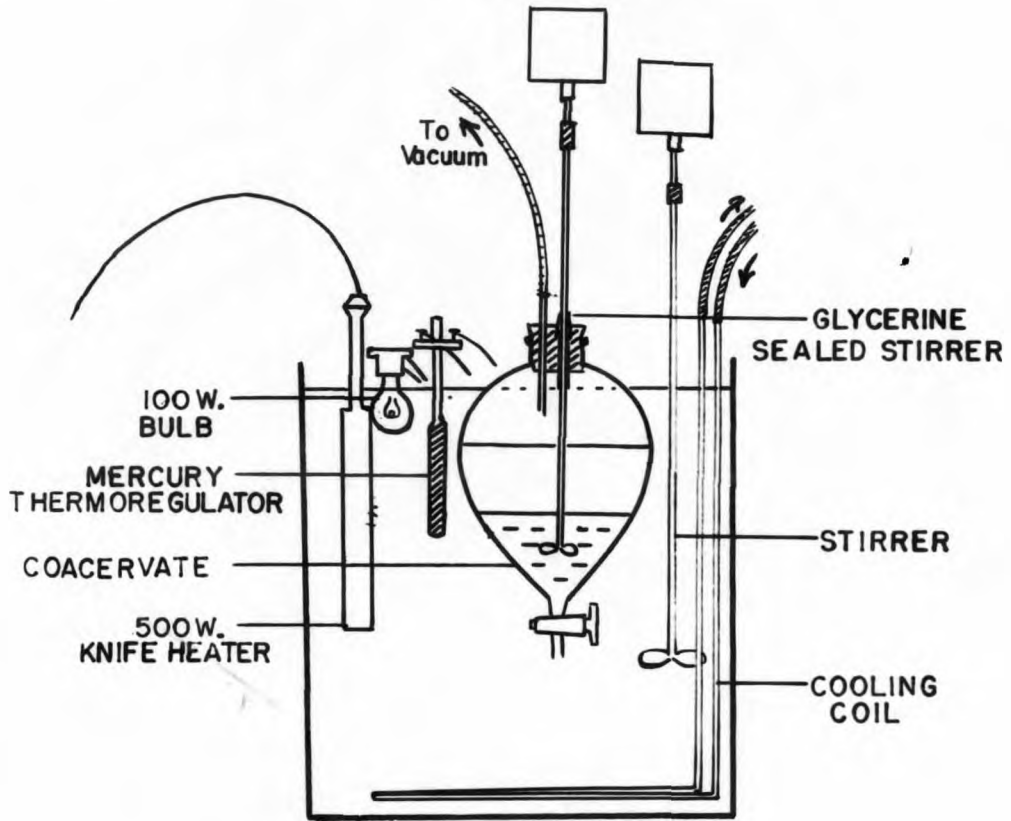
is to examine values of k' for polymers which have been cross-linked deliberately.

Schaeffgen and Flory (82) synthesized multichain polymers with one, two, four, and eight branches per molecule. While k' values from their data have a rather large relative error, there does seem to be a slight trend towards an increase in k' as the degree of branching increases.— from 0.31 for the linear polymer to 0.40 for the most highly branched material. Youngson and Melville (68, 114), predicting a change in k' with branching, synthesized branched molecules from polyethylene adipate and such polyfunctional compounds as pentaerythritol. Unfortunately, reliable values of k' could not be calculated.

Though Valyi (104) determined the intrinsic viscosities for fractions of polystyrene cross-linked with divinylbenzene, calculations of k' show no variations from normal. However, Walker and Winkler (106) found unusually high values of k' (e.g., 0.80) for fractions of soluble copolymers of styrene and divinylbenzene. They concluded that normal polystyrene prepared in bulk has an essentially linear structure, for the amount of divinylbenzene required to cause large variations from the usual value of k' , about 0.38, was quite small -- about 0.4%.

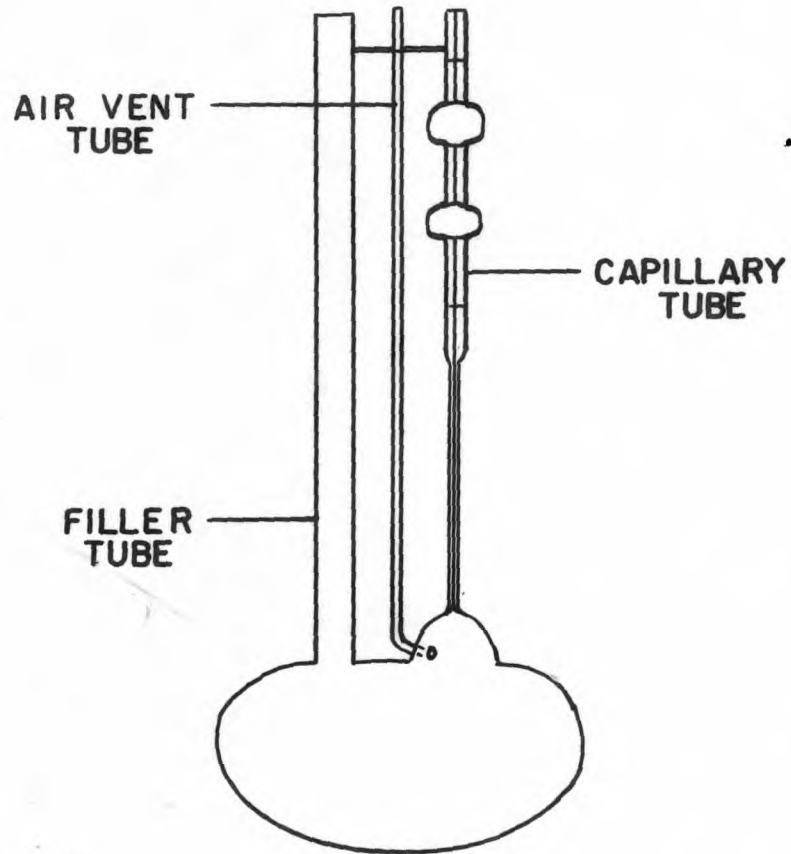
Hence there have been good indications that k' should vary with the degree of cross-linking of a polymer. Since the polystyrene to be used in the long-range precipitation problem was prepared in emulsion -- in contrast to the bulk-polymerized materials used by Walker and Winkler (106) -- this study was begun.

DIAGRAM I



APPARATUS FOR FRACTIONATION

DIAGRAM 2



MODIFIED UBBELOHDE VISCOMETER, SERIES U 14

EXPERIMENTAL

1. Apparatus

Polymerizations were carried out at $55.0(\pm 0.1)^{\circ}\text{C}$. in 250-ml. glass-stoppered bottles. The bottles, clamped in a motor-driven steel frame, were rotated end over end in the steel constant-temperature bath at a rate of 33 r.p.m.

Temperatures required for fractionation and intrinsic viscosity determinations were maintained in glass constant-temperature baths regulated to $55.0(\pm 0.2)$ and $25.00(\pm 0.02)^{\circ}\text{C}$., respectively.

The most convenient vessel for primary fractionations was found to be a 3-l. separatory funnel with stem out short, and fitted with a stopper providing for a glycerine-sealed paddle stirrer and a vacuum outlet. For subsequent fractionations, other separatory funnels of appropriate sizes were used. With a separatory funnel, the coacervate may be drawn off quite neatly and easily, though great care must be taken to keep the stopcock vacuum-tight. After the open tube at the bottom of the stopcock has been plugged tightly with a greased cork or rubber stopper, it is best to apply a thick coat of grease to the outside of the stopcock, stem, and plug to prevent the leakage of water into the vessel when a vacuum is applied.

The viscometers used, U14-3 and U14-11 of a modified Ubbelohde series, which had a large bulb to permit the making of dilutions in the viscometer itself, were obtained from Polymer Corporation (55). The diagram facing this page illustrates the general appearance of this

type of viscometer. Designed to have negligible kinetic energy corrections, these viscometers gave almost identical intrinsic viscosity values (within ± 0.02 units) for a given polystyrene dispersion, or, to use a more common term, solution. Mountings were made reproducible by using specially designed viscometer clamps incorporating standard taper pins. Thus the viscometers were clamped in a given standard position each time they were used.

2. Materials

(a) Solvents and Non-solvents

Benzene (Steel Company of Canada), ASTM Industrial Grade, redistilled and dried over sodium; B.P. 80.5°C. , $\eta_{\text{D}}^{20} = 1.4972$

Toluene (Steel Company of Canada), Nitration Grade, treated with concentrated sulfuric acid to remove sulfur compounds, redistilled and dried over sodium; B.P. 110°C. , $\eta_{\text{D}}^{20} = 1.4926$.

Ethanol (Canadian Industrial Alcohol Company), unmatured spirits, 95%.

n-Butanol (Baker and Adamson), Technical Grade, 95%.

Methyl Ethyl Ketone (Shell Oil Company), Technical Grade, dried over calcium chloride (115) and redistilled; B.P. 79.8°C. , $\eta_{\text{D}}^{20} = 1.3754$.

According to Doyle et.al.(34) and Toms (102), the quality of solvents used in viscometric work is very important. For example, Dumitru (35) has noted wide variations of refractive index, flow time, and solvent power with different samples of purified methyl ethyl ketone. Occasionally similar variations were noticed while work for this thesis was being carried out; results concerning the solvent at fault were discarded. Accordingly, solvents were checked continually for refractive index and flow time, and a given "batch" of solvent was used throughout a given series of intrinsic viscosity determinations.

(b) Reagents

Styrene (Polymer Corporation), inhibited with *t*-butylcatechol.

Divinylbenzene (Polymer Corporation), 50% solution in ethylbenzene.

Potassium persulfate, Dodecyl Mercaptan, and Soap Flakes,
(obtained from Polymer Corporation).

3. Preparation of Polymers

(a) Linear Polystyrene

Samples were prepared by polymerizing, at 55°C., an emulsion having the following composition per 250-ml. bottle (except for certain variations in the proportion of mercaptan which are noted in sample descriptions):

Styrene	50.0 gm.
Oxygen-free distilled water	90.0 gm.
Soap flakes	2.5 gm.
Potassium persulfate	0.15 gm.
Dodecyl mercaptan	0.025 gl. ¹

The styrene was washed, in an atmosphere of nitrogen, with 10% sodium hydroxide solution, and then rinsed with water, to remove inhibitor; nitrogen was then bubbled through the washed styrene to remove any dissolved oxygen that might still remain. After the reactants had been thoroughly mixed -- again in an atmosphere of nitrogen -- in 250-ml. glass-stoppered bottles, the resulting emulsion was rotated in the bottles at 55^o C. until the desired percentage conversion was reached. Coagulation of the final mixture by pouring into an excess of ethanol yielded a granular polymer which was filtered off, washed with ethanol, and dried at 50 C. for from 15 to 20 hours. Since, according to Mesrobian and Tobolsky (71), the intrinsic viscosity of a polystyrene film changes very little on prolonged heating at 100^o C., it would seem that 50^o C. is a safe temperature for drying.²

(b) Cross-linked Polystyrene

Polymerization of the cross-linked polymer was carried out in the same manner as that for the linear polystyrene, except that

¹Incidentally, according to Hohenstein and Mark (56), the use of a modifier reduces the amount of branching in a polymer.

²However, Lewis and Mayo (64) claim that drying should be carried out under vacuum at low temperatures. See also Mark (65), and Werkin (111).

varying amounts of divinylbenzene were added to the emulsion. Though, drying was carried out under the same conditions as used for the linear polystyrene -- 50 C. for from 15 to 20 hours -- the dried samples were fractionated as soon as possible to minimize any variations in molecular weight caused by polymerization after precipitation.

3. Fractionation

The method of fractional precipitation by means of the preferential evaporation of solvent from a solution of a polymer in a solvent-nonsolvent mixture was found to be convenient and efficient. Used by Badgley, Frilette, and Mark (6), Goldberg, Hohenstein, and Mark (49), and by Gralen and Lagermalm (51) to yield fractions having a distribution curve similar to that for fractions prepared by conventional precipitation methods (23). Following the procedure of Goldberg et.al.(49), a 3% solution of polystyrene in a mixture of methyl ethyl ketone and n-butanol was used. While Switzer (100) strongly recommends the use of initial concentrations not greater than 1% for the efficient fractionation of GB-S, higher concentrations seem permissible with other polymers. For example, Morey and Tamblin (74) found a 2% solution satisfactory for cellulose acetate, and Billmeyer and Stockmayer (12) used 4% solutions of polymethyl methacrylate. Enough n-butanol had been added, slowly, with stirring, to a solution of the polymer in methyl ethyl ketone to just bring the solution to the precipitation point, as judged by the

obscuring of an incandescent lamp filament placed behind the bath.

After enough methyl ethyl ketone had been added to just redissolve and hence reclarify the mixture, and a vacuum, supplied by a Bunsen filter pump, had been applied, the methyl ethyl ketone was evaporated until the precipitation point was reached again. Evaporation was continued until it was considered, on the basis of experience, that a fraction of suitable size should result. When this point, which can be found easily only after considerable practice at observing turbidities, was reached, the mixture was stirred for 30 minutes to ensure the attainment of equilibrium, and then allowed to settle. After removal of the coacervate (or precipitated fraction), the vacuum was applied once more, and the evaporation procedure was repeated as above to yield the second, third, and further fractions.

While the first fraction usually required from 12 to 15 hours of settling for good phase separation to occur, later fractions usually required less time.³ If the settled fraction was too large or too small, the fraction was redissolved by the addition of methyl ethyl ketone, if necessary, and the evaporation procedure was repeated until a fraction of the desired size was obtained. With an initial weight of 30 grams of polystyrene, the maximum volume of coacervate that can be handled readily is about 100 ml.

The coacervate was drawn off into a small flask; in fact, a little supernatant liquid was drawn off as well. The flask was kept

³The suggestion of Morey and Tamlyn (73) that the addition of a little dilute hydrochloric acid to a fractionation mixture was tried, but enough results, using the dilute acid, to allow the drawing of any definite conclusion were not obtained.

at 45⁰ C. until good phase separation occurred. This operation served two purposes -- it flushed out the stopcock, and, if phase separation in the large vessel had not been clean-cut, it allowed the supernatant liquid to separate from the coacervate faster than if both were kept in the large vessel. Any supernatant liquid obtained was poured back into the fractionation vessel. Since the coacervate was dissolved in methyl ethyl ketone and reprecipitated in n-butanol or ethanol (by pouring in dropwise with vigorous stirring) the coacervate was not washed, as suggested by Switzer (100). According to Scott (84), such a reprecipitation should be sufficient to remove the lower molecular weight "tail" accompanying each fraction. This reprecipitation should be equivalent to washing the fraction with a solvent-nonsolvent mixture having a composition the same as the composition at the time of precipitation. The method of reprecipitation used -- very similar to methods recommended by Werbin (111) or Alfrey (2) -- yielded a fluffy, fibrous fraction, which was filtered off, drained, washed with water, and partially dried at room temperature.⁴

These primary fractions were each refractionated; groups of the resulting secondary fractions having similar intrinsic viscosities were refractionated. The final tertiary fractions were carefully dried at 50⁰ C. to constant weight.⁴ Further fractionations failed to result in any consistent improvement in the separation of fractions with respect to intrinsic viscosity.

⁴ Since according to Mark (65) the drying of polymers is the most important part of the purification procedure, this step was always carried out in exactly the same manner.

4. Intrinsic Viscosity Determinations

Preparation of Solutions

Solutions were prepared by allowing the desired amount of polystyrene to stand away from direct light in a 50-ml. volumetric flask with solvent at room temperature until equilibrium was reached. To loosen swollen coalescing particles, the flasks were swirled gently (102), but not shaken vigorously. If, as was the case with the dissolution of cross-linked polystyrene, all the solid did not dissolve, only the soluble portion was used for the intrinsic viscosity determinations. Having been made up at 25.00° C. to 50 ml. -- if all the polymer was soluble -- the solutions were filtered through a fritted glass disc to remove dust and other extraneous matter. If some solid remained undissolved, the soluble portion was decanted, filtered, and made up to volume at 25.00° C. To eliminate dust in the flasks used for the final solutions, all such flasks were boiled in concentrated nitric acid, rinsed with filtered distilled water, and dried at 110° C.

Concentration Determinations

Since with tertiary fractions there was no significant change in concentration after filtration, concentrations were calculated directly from the amount of polymer weighed out. On the other hand, with preliminary fractions, which frequently contain some foreign matter such as dust, concentrations had to be determined by evaporation of aliquot samples of solution at 50° C. to constant weight. Tests confirmed the accuracy and precision of the latter method to be ±1%. Concen-

trations were calculated either directly in gm. solute/100 ml. solution, or by multiplying the weight percent (gm. solute/100 gm. solution) by the density of the solution at the temperature desired.⁵ A typical result for a concentration might be 0.404(±0.04)gm./100 ml.

Flow Times

Flow times were measured in duplicate or, more usually, in triplicate (or, if flow times remained reasonably constant, until agreement to ±1% was obtained). However, with concentrated solutions in methyl ethyl ketone of high molecular weight fractions or even with more dilute solutions in benzene (103) the flow times were too great to yield the maximum precision of ±1%. Furthermore, with such solutions of high molecular weight polymers, evaporation of even a small amount of solvent causes a steady increase in flow time. Hence the use of methyl ethyl ketone as a solvent for routine determinations of intrinsic viscosity is preferable to the use of benzene, which involves flow times of inconvenient magnitude. Also, with high molecular weight fractions, the initial concentration should be lower than with lower molecular weight fractions — say, 0.2% instead of 0.4%. With high concentrations or with very high molecular weight fractions, inherent viscosities may be anomalously high or low, owing to the critical concentration effects noted by Boyer and Spencer (15). Quite recently Trementozzi (103) has noted such deviations with high molecular weight

⁵Though actually the density of solvent was used instead of the density of solution, the error involved is negligible.

polystyrene in toluene.⁶

Calculation of Intrinsic Flow Time, or Intrinsic Viscosity

Values of intrinsic flow time were determined from values of flow time and concentration as follows:

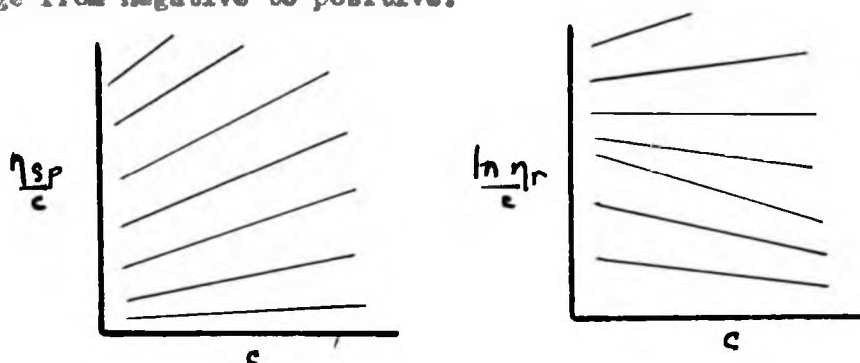
Flow times were obtained for the polystyrene solutions, and, if possible, for three or more dilutions — with a concentration range of from 0.4 to 0.05%. Corresponding values for $\frac{\ln t_r}{c}$, the inherent flow time, were calculated, the inherent flow time was plotted against concentration, and the intrinsic flow time $[t]$, or $\lim_{c \rightarrow 0} \left(\frac{\ln t_r}{c} \right)$, was determined by extrapolation of the curve to zero concentration. Since the viscometers used have negligible kinetic energy corrections (55), $[t] \equiv [\eta]$, with an accuracy of $\pm 2\%$.

The intrinsic viscosity may also be obtained by plotting the curve of $\frac{\eta_{sp}}{c}$, the specific viscosity, (or, in this case, $\frac{t_{sp}}{c}$), against concentration, and again extrapolating to zero concentration. Though this latter plot is probably the one which has been used most often, it has some serious disadvantages. While a more accurate value of $[\eta]$ for low molecular

⁶To account for these deviations in viscosity behaviour at high concentrations, Boyer and Spencer(15) calculated tentative critical concentrations for polystyrene in benzene and methyl ethyl ketone. Pointing out that these values probably were not quantitatively correct, they found that for a molecular weight of 10^4 the critical concentration was 0.3 gm./100 ml. in benzene, and 0.7 gm./100 ml. in methyl ethyl ketone. For a molecular weight of 10^5 the corresponding critical concentrations were 0.02 and 0.08 gm./100 ml., respectively. While Doty and Steiner (31) point out that critical concentrations may be experimentally inaccessible, the concept seems reasonable enough. At any rate, the investigator should certainly be wary about giving equal weight to points on a viscosity graph corresponding to a wide range of concentrations.

weight polymers may be found by extrapolating both the inherent viscosity and the specific viscosity curves plotted on the same sheet, the slope of the specific viscosity curve is often too great, with higher molecular weights, for plotting a curve with sufficient accuracy.⁷

However, the most serious disadvantage of the specific viscosity curve in connection with the work reported here is that it does not emphasize visually changes in the value of k' as does the inherent viscosity curve. Even with large changes in k' the slopes of the specific viscosity curves remain positive, while the slopes of the inherent viscosity curves change from negative to positive.



Calculation of k'

The two equations

$$\frac{\eta_{sp}}{c} = [\eta] + \kappa [\eta]^2 c \dots$$

and

$$\ln \eta_r = [\eta] - \beta [\eta]^2 c \dots$$

⁷In order to plot both graphs on one sheet, the scale must be so reduced that the advantage of obtaining higher accuracy by finding the $[\eta]$ at which both curves intersect is lost. Also, Coppick (21) claims that the specific viscosity curve is not as linear as the inherent viscosity one as concentration increases. See also Howlett et. al. (57), and Rothman et. al. (80), who claim that the $\frac{\eta_{sp}}{c}$ curves are linear ordinarily.

are mathematically related by the expression $k' = 0.50$.

$$\frac{\eta_{sp}}{c} = [\eta] + \kappa' [\eta]^2 c \dots$$

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

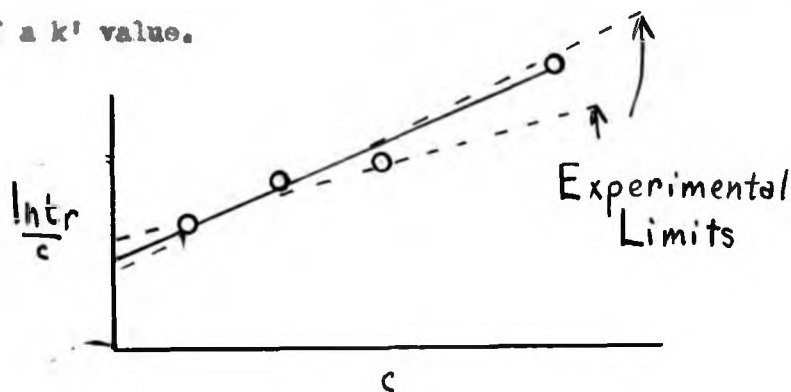
Now $\eta_{sp} = \eta_r - 1$, or $\eta_r = 1 + \eta_{sp}$

$$\begin{aligned} \therefore \frac{\ln \eta_r}{c} &= \frac{1}{c} \left\{ \ln (1 + \eta_{sp}) \right\} \\ &= \frac{1}{c} \left\{ \eta_{sp} - \frac{\eta_{sp}^2}{2} + \frac{\eta_{sp}^3}{3} \dots \right\} \\ &= \frac{\eta_{sp}}{c} - \frac{1}{2} \frac{\eta_{sp}^2}{c^2} \cdot c \dots \\ &= [\eta] + \kappa' [\eta]^2 c + \frac{1}{2} c \left\{ [\eta]^2 + \kappa' [\eta]^3 c \dots \right\} \\ &= [\eta] + (\kappa' + 1/2) [\eta]^2 c + \dots \\ &= [\eta] + \beta [\eta]^2 c \dots \end{aligned}$$

$$\therefore \kappa' + \beta = 0.50$$

In this work, the constant actually evaluated was β ; k' was then calculated from β . Now $\beta = - \frac{[\eta] - \ln \eta_r / c}{[\eta]^2 c}$ and when determined experimentally may vary considerably from case to case. Thus an error of ± 0.02 when $\beta = 0.10$ means a relative error of $\pm 20\%$. If, however, k' is used instead of β when one wishes to compare the behaviour of various fractions, k' would equal 0.40 ± 0.02 ; in this case, the relative error would be only $\pm 4\%$. Thus, while β is determined experimentally, it is best to calculate k' in order to avoid being misled by apparent changes in β which are really only values scattered within the rather wide limits of error.

In any case, it seems that k' values are accurate to the second decimal place only. The investigator might be justifiably cautious about accepting apparently accurate values having more than two significant figures (51). In this work, the extreme values of k' possible were calculated by using the experimental limits possible for the slope and intrinsic viscosity of a given inherent viscosity curve. It would seem advisable to perform similar calculations with data given whenever doubt arises as to the reliability and accuracy of a k' value.



RESULTS AND DISCUSSION

1. Physical Properties of the Polymers

The normal polystyrene, that is, the polystyrene prepared without the addition of divinylbenzene, exhibited the general physical properties expected of linear high polymers. White amorphous solids, the whole polymer and fractions could be dissolved easily in benzene, toluene, and the poorer solvents acetone and methyl ethyl ketone, though the higher molecular weight fractions naturally required considerable time to dissolve completely. In each case, after swelling to a very high degree, the polymer dissolved to form a viscous solution with the pale bluish haze characteristic of a colloidal dispersion. From these solutions, the polystyrene could be precipitated quite readily by the addition of such non-solvents as water, ethanol, or n-butanol.

Though the cross-linked polystyrene had an appearance similar to that of the normal polymer, its solubility characteristics and its optical properties were rather unusual when it was dissolved in any of the above solvents.

As might be expected (16, 17, 19, 28, 77, 99, 104), the slightly cross-linked polymer showed a very high capacity for swelling along with a low solubility -- at a concentration of, say, 0.4% -- in benzene or toluene. However, the bluish sol, or soluble portion, did have a fairly high viscosity. Apparently the cross-links, while permitting considerable swelling, tend to resist rupture by benzene or toluene (66, p.348). Nevertheless, enough material must be dissolved

by the good solvents to yield a viscous solution. Attempts to dissolve the cross-linked polystyrene -- at a concentration of 0.4% -- in acetone or methyl ethyl ketone gave very different results. Practically all the polymer dispersed rapidly, after standing with either solvent, to form a turbid dispersion with a very low viscosity. If the polystyrene was rotated end over end in a bottle with benzene, a turbid, only moderately viscous solution or dispersion resulted -- very much the same result as the one obtained using methyl ethyl ketone. The agitation may have broken up or disentangled clumps of macrogel, or agglomerated gel particles, into smaller gel particles termed microgel particles (7). According to Baker (7), a polar environment aids dispersion considerably by colloidal peptization or by disentangling particles. Certainly methyl ethyl ketone, a rather poor solvent, could tend to disentangle large agglomerations of gel by coiling the components of the large mass. Thus cross-linked polystyrene gels may be dispersed by physical or chemical means.

Attempts to remove the insoluble gel in the benzene dispersion by filtration through a sintered glass disc resulted in an apparently hopelessly clogged filter. Repeated immersions and washings with benzene had no beneficial effects; even benzene alone would not pass through the filter under any degree of agitation. If, however, a very small amount of acetone or methyl ethyl ketone was added to the clogged filter, it passed through the filter immediately. Then if benzene was poured in, it passed readily through the filter.

This interesting observation lends strong support to the current theory (3) of the coiling and uncoiling of polymer molecules in solution.

If the solvent is an energetically favorable one, the mean statistical shape of the molecule should be extended, or uncoiled; if the solvent is energetically unfavorable, the mean shape should be coiled (24, 30). With benzene as a solvent, it must attract the polystyrene molecules and extend the polymer chain to such an extent as to hinder diffusion of solvent into the interior of the polymer mass and to prevent the passage of the resulting bulky solvated chains through the pores of the filter. In methyl ethyl ketone, a poorer solvent, the chains must coil up sufficiently tightly to reduce the effective diameter of the chain to a size that will allow free passage through the filter disc.

These solutions (this more usual term being used instead of the more correct dispersion) in benzene and methyl ethyl ketone seem to be examples of a lyophilic and a lyophobic dispersion. Presumably, if an ideal, or indifferent solvent -- one in which the chain would assume its most probable configuration, intermediate between the two extremes mentioned above -- were used, the solution would be of neither one type nor the other.

The optical properties of the cross-linked polystyrene solutions were very different from those of normal polystyrene solutions. A definite and visually evident increase in the turbidity of dilute solutions of the cross-linked polymer as the degree of cross-linking was increased was found for methyl ethyl ketone as solvent. But the most striking optical effect was noted in concentrated solutions (2-3%). While a solution of a normal polystyrene fraction in methyl ethyl ketone exhibits a bluish tinge caused by light scattering, the concentrated solutions of cross-linked polystyrene in methyl ethyl ketone

displayed a vivid combination of reddish and bluish tints -- they seemed almost fluorescent, and retained this property even in a fairly dark place. This property was much more evident in solutions of the polymer in methyl ethyl ketone than in benzene; it seemed also to be associated with fractions having an abnormally high value of k' . Since the fractions having such high k' values should contain the highest percentages of divinylbenzene -- for at high conversions cross-linking is not uniform (45) -- the proportion of cross-linking agent appears to be involved. The effect of concentration was examined; the property was much more noticeable at a concentration of 0.2% than at one of 0.4%. The "batch" of methyl ethyl ketone was checked for purity, and various other samples of that solvent were tried. The results of the tests showed that the property was not caused by the methyl ethyl ketone itself, but by the solution.

The explanation for this unusual optical behaviour is not apparent. Though solid polystyrene fluoresces under ultraviolet irradiation, no one has ever reported fluorescence in the visible range for polystyrene solutions. It is interesting to note that a quinoid structure, such as that postulated by Schulz (66, p.220), is often associated with colour or fluorescence; the quinoid structure is now, however, believed to be rather improbable. While Doty, Wagner, and Singer (30) explained an opalescence noted in polymer solutions near their precipitation points as being due to increased association, Ewart et.al. (39) claim the explanation lies rather in a selective absorption of solvent. The most probable explanation of this phenomenon might be simply based on a great increase in scattered light caused by cross-linking.

2. Inherent Flow Time Curves and Intrinsic Flow Time

Tables 1 to 8, inclusive, give the $[\eta]_s'$, or intrinsic flow times, (and the data necessary for their determination) for primary, secondary, and tertiary fractions of normal polystyrene, and for unfractionated and primary fractions of cross-linked polystyrene.

In Fig. 1 are shown the inherent viscosity curves, that is, curves of $\frac{\ln t_r}{c}$ vs. c , for several normal polystyrene fractions and for one unfractionated sample. These curves, typical of the many obtained in this study, illustrate the degree of accuracy obtainable in the calculation of $[\eta]$. If for each curve the two most extreme curves possible representing the data are drawn, the deviation of $[\eta]$ from that obtained from the curve already drawn and judged best is at most about ± 0.02 units. This calculated value of the error depends upon the fact that the size of the circles represents the approximate error involved in the measurement of $\frac{\ln t_r}{c}$ and c . The approximate error in $\frac{\ln t_r}{c}$ is ± 0.01 units (the error caused by a variation in flow time of 0.1 sec.), while the error in concentration is ± 0.05 gm./ 100 ml. of solution. Fig. 1 also shows no very great difference between the curves for an unfractionated sample and its tertiary fractions; the slight difference noted is within the experimental variation for a given curve. Fig. 5 illustrates such experimental variations; it shows that the viscosity behaviour of the fractions studied is independent of heterogeneity of molecular weight -- a conclusion identical with that of Davis (27), and contradicting the claim of Spencer and Boyer (90) that viscosity behaviour is a function of heterogeneity.

Fig. 2 contrasts the inherent viscosity curves for normal polystyrene with those of cross-linked polystyrene. As the degree of cross-linking increases — as indicated by the increase in the percentage of cross-linking agent — the deviations from behaviour predicted on the assumption that the curves would be similar to those for the normal polymer become more and more marked. The predicted "normal" curves are indicated by a short line leading to the $[\eta]$ of a given fraction. A startling change of slope from negative to positive — a change which does not show up in specific viscosity curves — such as noted by Baker (7), Brown (20), and Switzer (100) is seen for the more highly cross-linked polymers, that is, for those having a divinylbenzene content greater than 0.003%. It may also be noted that the separation of fractions with respect to $[\eta]$ becomes poorer as the degree of cross-linking increases; in other words, the efficiency of fractionation varies inversely with the degree of cross-linking. In fact, with one highly cross-linked sample (see Table 7), the fraction having the highest $[\eta]$ did not precipitate first. An effect of cross-linking on solubility has been predicted by Flory (46), who suggested that the solubility of two molecules having the same average molecular weight could be very different, depending on their respective structures. Indeed, Baker, Fuller, and Weiss (8) reported an anomalously high solubility for branched molecules. Thus K₃ and H₂, or K₁, though highly cross-linked, might have remained in solution until after H₁, or K₂ and F₃, more linear fractions, precipitated. There is no obvious explanation for such behaviour, especially since the more cross-linked fractions had the higher intrinsic flow times.

3. Intrinsic Flow Times and Molecular Weights

Since there was no method available for the determination of molecular weights, directly, molecular weights were calculated by means of the following relationship:

$$M^{0.53} = [\eta] \times 7.0 \times 10^{-4} \quad (49)$$

The calculated values ranged from 6×10^3 , for fraction E4-AC, to 7×10^6 , for fraction G1A1. No calculations were made for cross-linked samples, for results obtained would be meaningless (8, 29, 46, 48).

In Fig. 3 the intrinsic flow time data from Tables 2, 3, 5, 6, 7, and 8 are plotted — $[t]$ in benzene against $[t]$ in methyl ethyl ketone(63). With the normal and cross-linked polystyrene samples good and fair curves, respectively, are obtained, though the two curves do not coincide. This result should mean that the data are reasonably reliable and accurate; an error in one of the intrinsic flow time values will cause a noticeable deviation from the curve drawn.

4. Intrinsic Flow Time and Percent Divinylbenzene

It may be seen from Fig. 4 that as the percent divinylbenzene and therefore the degree of cross-linking increases, the $[t]$ of the unfractionated polymer, after rising slightly at first above the value

for the normal polystyrene made from a similar "recipe", falls off quite smoothly. The curve for benzene has a shape identical with that for methyl ethyl ketone; it is merely shifted to a higher range of intrinsic flow times.

This steady decrease after a maximum has been reached is analogous to the increase and decrease in the intrinsic flow time of QR-S as the percent conversion, and therefore the degree of cross-linking (83), increases discussed by Baker (7), Flory (41), Schulze and Crouch (83), and Wall et.al. (108, 109). In each case the real variable is the degree of cross-linking, though the method of changing the variable differs. That is, the degree of cross-linking may be varied by changing either the percent conversion or the percent of cross-linking agent.

The initial increase of the intrinsic flow time may be explained as being due to the increase of the average molecular weight of the polystyrene molecules. As this molecular weight increases, that is, as the molecule grows in three dimensions, the flow resistance, the viscosity, and the intrinsic flow time must increase. However, at a certain point, the peak of the curve drawn, the more highly branched species begin to become entangled with one another to form relatively insoluble gel particles. The preferential removal of high molecular weight molecules from solution by precipitation of this gel effectively reduces the viscosity of the soluble portion¹ -- thus causing a decrease in intrinsic flow time (105). As the degree of cross-linking increases

¹ This study deals only with soluble portions.

further, the average complexity of the soluble portion decreases still further (41), so that the intrinsic flow time of the soluble portion decreases steadily.

Another factor contributing to the decrease in intrinsic flow time after a certain point has been reached could be the formation of microgel (7), small aggregates of gel which, though still in solution, have a low intrinsic flow time. In fact, with the polystyrene samples studied, this effect might very well be the dominant one, for no definite gel point was noticed at which macrogel, or large insoluble aggregates of gel, became evident. One would certainly expect to notice a sharp gel point at the curve maximum if the removal of gel from solution were the main factor responsible for the decrease in intrinsic flow time of the soluble portion. Furthermore (see section 5), the k' of the sol continues to increase even though the intrinsic flow time decreases; this increase in k' would, according to Baker (7), indicate the formation and presence of microgel. Similar reasoning could also explain the fact that Schulze and Crouch (83) found that intrinsic viscosities of sol portions of GR-S often decrease before the presence of macrogel becomes apparent. It seems likely, then, that the formation of microgel is, in this case at least, the chief factor causing the decrease of intrinsic flow time when the degree of cross-linking is increased.

5. Huggins' Constant, k'

Huggins' constant, k' , was calculated by using the relationship $k' = 0.50 - \beta$ (as in Introduction), where β is the slope constant in the equation

$$\ln \frac{t_r}{c} = \frac{[t]}{or} - \beta [t]^2 c \dots\dots$$

$$\ln \frac{\eta_r}{c} = \dots\dots \text{etc.}$$

which can be transformed into the equivalent equation

$$\frac{t_{sp}}{c} = \frac{[t]}{or} + k' [t]^2 c \dots\dots$$

$$\frac{\eta_{sp}}{c} = \dots\dots \text{etc.}$$

Now in practice the theoretical relationship $k' = 0.50 - \beta$ is found to be only approximately true; values of k' and β determined directly from experimental inherent flow time and specific flow time curves for normal and cross-linked fractions lead to the more accurate relationship $k' = 0.55 - \beta$. However, this latter equation does hold for a range of intrinsic flow times from 0.96 to at least 1.73. The error involved by using the theoretical relationship, being constant, would not affect qualitatively any graphs drawn using the k' values calculated indirectly from β values; it would merely shift the graphs a little higher, not change their shape.

β may be determined by calculating the slope of the curve resulting when - slope of the inherent flow time curve is plotted against $[t]^2$, for

$$\beta = \frac{[t] - \ln \frac{t_r}{c}}{[t]^2 c} = \text{- Slope } \frac{\ln t_r / c \text{ curve}}{[t]^2}$$

It should be noted that the curves in Fig. 5, which illustrates this type of graph, show an appreciably wide scatter of points around the curve drawn. Because of this scatter, it would seem definitely preferable to calculate β from the complete curve rather than from a point representing an individual fraction. Otherwise, especially with lower molecular weight fractions, erroneous conclusions may be drawn from apparent differences in k' which are really within the large experimental error for an individual calculation. Another point to note is that values of β and of k' are reliable to only two decimal places -- even the second place being somewhat in doubt. One should, therefore, be cautious about accepting values of β or k' for which accuracy is claimed to more than two decimal places (81).

From Fig. 5 k' was calculated to be 0.40 ± 0.01 in methyl ethyl ketone, and to be 0.38 ± 0.01 for at least the medium molecular weight fractions in benzene.² These values agree closely with those reported by Ewart (38) -- $k' = 0.38$ for polystyrene in benzene, and slightly greater in methyl ethyl ketone. This slightly higher value in methyl ethyl ketone, a poorer solvent than benzene³, is in accord with the results of many investigators (5, 9, 52, 79, 91, 92). There is no evidence of any very significant change in k' as molecular weight increases such as Goldberg et.al. (49) claimed, though k' does

²Since intrinsic flow times are very much greater in benzene than in methyl ethyl ketone, an enormous and unwieldy graph would be required to deal with the high molecular weight fractions.

³Incidentally, Owens et.al. (79), working with solutions of pectinic acid in aqueous sodium chloride, noticed a decrease in k' from 0.42 to 0.38 as temperature, and thus solvent power, was increased.

increase from 0.40 to 0.41.

It may be seen from Fig. 5 that the points for unfractionated polystyrene and for primary and secondary fractions fall well upon the curves drawn. This fact supports the conclusions of Davis (27) that the viscosity behaviour of polymer solutions is independent of the heterogeneity of molecular weight. It tends to refute the claims of Spencer and Boyer (90), Coppick (22), and Howlett et.al. (57) that molecular weight heterogeneity affects the slope of the viscosity curves, though perhaps the cellulose derivatives studied by Coppick and Howlett had a very unusual distribution of molecular weights.

Furthermore, the points for polystyrene samples made to low conversions (30%), or with a different percentage of modifier (as was the case with fraction B1) all fall upon the same curve as do the points for the high-conversion polystyrene samples having the lowest percentage of modifier. Now Bamford and Dewar (9) predicted a considerable increase in branching for polymers made to high conversions. If such an increase took place, then, the value of k' would be no criterion of the degree of branching; if the value of k' is a dependable criterion of branching, then no appreciable branching took place in the samples of high-conversion polystyrene studied.

Finally, the points for cross-linked polystyrene containing 0.003% divinylbenzene, or about one divinylbenzene molecule to 30,000 styrene molecules, also fall upon the curve. Again, either k' is no criterion of branching, or else there is very little branching in normal high molecular weight polystyrene, whether or not it is prepared to a high conversion.

Fig. 6, in which $-slope$ of the inherent viscosity curve is plotted against $[t]^{1/2}$ for cross-linked samples and their fractions, shows marked changes of β in methyl ethyl ketone occurring with cross-linked polystyrene. Data of Brown (20), Naidus and Mark (76), and Switzer (100) yield similar results for GR-S. For comparison with the normal polystyrene curve, the line representing $k' = 0.40$ as in Fig. 5 is drawn as well. With 0.01% divinylbenzene, corresponding to one molecule of divinylbenzene to 10,000 molecules of styrene (67), the curve is very different from the one for 0.03% divinylbenzene, or for any other proportion of the cross-linking agent. Thus a small amount of artificially induced cross-linking in polystyrene results in a dramatic increase in k' .

It seems reasonable, then, to conclude that polystyrene prepared in emulsion at 55°C . has an essentially linear structure. This conclusion supports the view of Outer et.al.(78) that chain transfer, or branching, is not of appreciable importance in a catalyzed polymerisation system having, of course, no cross-linking agents present.

6. Variation of k' with Divinylbenzene Content

Fig. 7 illustrates the variation of k' of the filtered soluble portion of cross-linked polystyrene dissolved in methyl ethyl ketone and benzene as the degree of cross-linking is increased. As might be expected from the previous sections, the k' curve for methyl ethyl

ketone is shifted higher than the one for benzene. At high degrees of cross-linking, however, the difference between the two curves becomes more marked. Apparently when considerable cross-linking exists, the total interaction of the cross-linked molecules with each other and with solvent molecules must be very much greater with a poor solvent such as methyl ethyl ketone than with a better solvent such as benzene. Such a picture seems reasonable, for, while the solvating effect of benzene on branches certainly inhibits coiling and reduces polymer-polymer contact, the tendency toward a higher k' caused by the normal coiling effect of methyl ethyl ketone would likely be considerably enhanced by the probability of the formation of microgel, with an attendant great increase in polymer-polymer interaction.

The shape of either curve is very similar to that of the curve in which k' is plotted against conversion of GR-S (7, 108, 109) — even more similar than is the corresponding curve in this study, k' plotted against percentage of divinylbenzene (p.37).

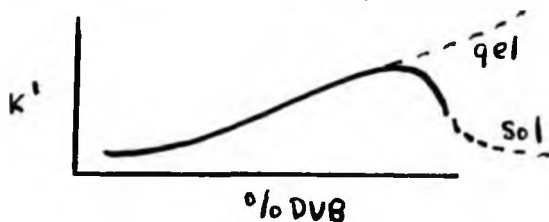
As suggested before, the formation of microgel (7) seems to provide a probable explanation of the shape of the curve. As the average molecular weight increases at first, the intrinsic flow time rises until microgel begins to form. From this point on, intrinsic flow time decreases steadily, for the inherent flow time, or viscosity, of the small particles of microgel (200-3,000 Å) is low. Since Baker associates positive slopes of the inherent viscosity curves (and hence any value of k' greater than 0.50) with the presence of microgel, k' should rise at this point, as is the case here, while the intrinsic viscosity of the soluble portion is decreasing. Thus, with microgel, the gel point, or

the point at which macrogel begins to form, is not near the maximum of the $[\eta]$ - $\%DVB$ curves, as expected from Wall's results with GR-S (108, 109), but is near the maximum of the k' - $\%DVB$ curve. At the intrinsic flow time peak, which would ordinarily indicate the beginning of the precipitation of macrogel, the incipient macrogel must be dispersed into microgel. However, at the k' peak, the degree of cross-linking is so high that macrogel does form in appreciable quantities -- with any divinylbenzene concentration greater than 0.01%. all polystyrene samples contained considerable insoluble gel. In comparison, Walker and Winkler (106) found the gel point for their cross-linked polystyrene samples at 0.05% divinylbenzene, and Boyer and Spencer (14) found their gel point to be at about 0.03% divinylbenzene, while they noted complete solubility when the divinylbenzene concentration was between 0.01 and 0.02%.

An explanation of the increase in k' with cross-linking, particularly when microgel is present, may be found by considering solute-solute and solute-solvent interactions.⁴ As the intrinsic viscosity, and hence molecular weight, increases, the interaction between the polymer chain and solvent increases slightly; since the chain is longer, there is a greater opportunity for interaction. When the intrinsic viscosity begins to decrease owing to the formation of microgel, considerable interaction will take place between the portions of a given chain which begin to coil. Thus the total interaction, and

⁴According to the interpretation of Huggins (58), k' represents the total interaction between polymer, polymer, and solvent.

hence k' , keeps increasing until a maximum k' value is reached. At this point, which is probably the true macro-gel point at which the microgel particles begin to interact with one another or agglomerate -- resulting in a very high value for k' , the macrogel begins to precipitate. As it does so, the average molecular weight of molecules left in solution begins to decrease (41, 43)⁵. This decrease should result in a sharp reduction in both types of interaction -- a reduction indicated by the sudden drop in the value of k' . The value of k' then tends towards that for the linear polymer, for as the degree of cross-linking increases, more and more of the cross-linked material is found in the gel portion so that the proportion of linear polymer in the sol portion increases (43). Incidentally, by this same reasoning, a soluble portion showing some increase in k' should certainly indicate a considerably greater increase in the k' for the gel phase. Therefore, it seems likely that, at the peak in Fig. 7, the k' of the gel phase would increase to infinity, while the k' of the sol phase would decrease till it approaches the value for the linear polymer. Also, the use of the filtered soluble



portion for the k' test for branching is justified; if any branching shows up in the sol, it will certainly be present in the gel phase.

⁵As the degree of cross-linking increases, the disparity between sol and gel viscosity characteristics increases also.

7. Variation of k' with Intrinsic Flow Time

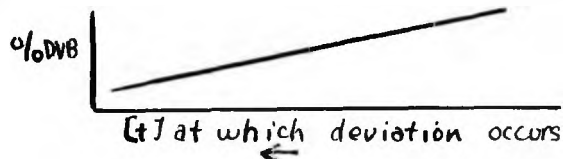
If the average k' for normal polystyrene fractions is represented by the horizontal line in Fig. 8, deviations from this straight line occur only at high values of intrinsic flow time. If k' values for polystyrene cross-linked by copolymerization with 0.03% divinylbenzene and its fractions are plotted in a similar fashion, the deviations at high molecular weights are still rather slight. But when the k' values of the other cross-linked samples and their fractions are plotted, the curves show marked deviations from the horizontal line; they form a family of lines (at least in methyl ethyl ketone) -- the individual position depending on the percentage of divinylbenzene. Admittedly, the accuracy of the k' values is low for the more highly cross-linked polymers; in fact, for divinylbenzene concentrations greater than 0.05%, the curves apparently merge into a sort of continuum. However, when the percentage of divinylbenzene is fairly low, the curves are quite distinct and characteristic of a given degree of cross-linking. Such a graph should provide, then, a sensitive means of detecting cross-linking in its early stages. Since a high degree of cross-linking, with the divinylbenzene concentration greater than 0.1%, is detectable anyway by means of solubility tests, the lower degrees of cross-linking are the ones of chief interest in this study.

It is significant to note that deviation of k' occurs at a much lower intrinsic flow time with the highly cross-linked polymers than with the mildly cross-linked ones. Indeed, the $[t]$ intercepts

of the curves with the line representing a k' of 0.40 are in rough proportion to the percentage of divinylbenzene. Thus

$$\frac{3.8}{0.05} \sim \frac{2.4}{0.003}$$

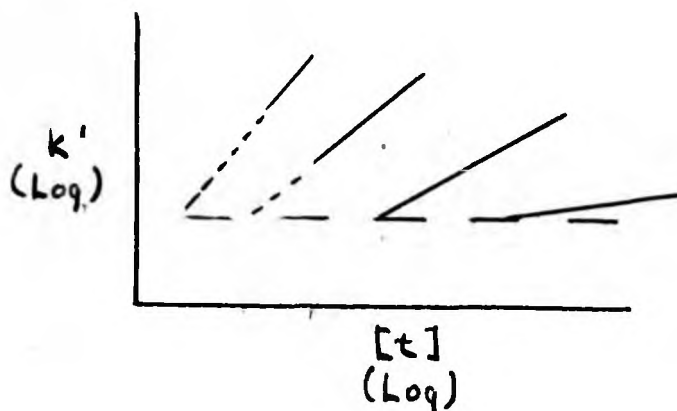
and so on. Statistically, one might expect such a result, for the more



divinylbenzene present, the shorter should be the chains which contain enough divinylbenzene to cross-link sufficiently to affect k' .

A similar type of curve may be obtained ^{by plotting} values of k' and intrinsic viscosity noted by Mochel et.al. (72) for Neoprene GN. Also, values of k' determined by Brown (20) for GR-S gave a similar curve when plotted against intrinsic viscosity. Interestingly enough, however, he found only one such curve no matter what conversion he used. It seems, then, that with percentage conversion of GR-S as the analogue of percentage of divinylbenzene in cross-linked polystyrene in this type of graph, cross-linking does not occur until a certain intrinsic viscosity is reached -- regardless of the percentage of conversion. With percentage conversion as the cross-linking variable, there seems to exist a critical chain length, as indicated by a certain intrinsic viscosity, which must be exceeded before the molecules can cross-link.

If the graph of k' and intrinsic flow time is plotted on log-log paper, straight lines may be obtained instead of the curves found above. Such a graph could be quite useful, especially if one wished to find accurate values for the intercepts of the curves with the normal k' line.



8. Suggestions for further work

(a) Work was begun on a study of the flexibility of polystyrene in solution by comparing the ratios of intrinsic flow times in benzene to those in methyl ethyl ketone. This work could easily be extended by using a wider range of molecular weights and by using synthetic poor solvents, such as mixtures of benzene and butanol.

(b) This study of the variation of k' could be extended by obtaining good values for k' in benzene and other solvents, including synthetic poor solvents. The fractionation of other cross-linked polystyrene samples containing other proportions of divinylbenzene had been

begun at the time of writing; this work should certainly be completed so that data for divinylbenzene concentrations intermediate between the ones used here might be obtained.

(c) It should be very interesting to discover whether or not cross-linked polystyrene samples prepared to various conversions would yield identical curves of k' plotted against intrinsic flow time -- as was the case with GR-S (20). The author predicts that identical curves would be found. Some work was begun on the preparation of cross-linked polystyrene to several conversions.

(d) Light scattering and precipitability data for both the normal and cross-linked polystyrene would be extremely helpful. Mr. E. Dumitru had begun the task of obtaining such data when this work was completed.

(e) Investigations into the optical properties noted for the solutions of cross-linked polystyrene samples, into the size of cross-linked polystyrene molecules in methyl ethyl ketone and benzene, and into microgel formation should prove to be quite interesting.

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TABLES

Explanation of Fraction Code Numbers

The first letter of the code number refers to the particular polystyrene "batch" which was fractionated, and stands for a certain percentage of modifier and a certain percent conversion, as follows:

B	-	0.050%	modifier,	and	97%	conversion,
C	-	0.025%	"		96%	"
D	-	0.025%	"		30%	"
E	-	3.00 %	"		100%	"
and F	-	0.025%	"		96%	"

The first number refers to the order in which the fraction precipitated; the second letter refers to the order in which the secondary fraction of the given primary fraction precipitated, and so on. Thus ClA represents the first fraction to precipitate when the first primary fraction, Cl, of batch C is fractionated, and ClA2 represents the second tertiary fraction obtained by the fractionation of ClA. However, various secondary fractions having similar intrinsic flow times were combined before refractionation so that tertiary fractions are really named after the major constituent of the mixture. Thus we have

	F3A1	from	F1A, F1A1, F3A, F3B,
	F7B1	from	F1A3, F1C, F5C, F7B, F7C, F8A,
	F3C1	from	F3C, F8B, F8C,
and	F5A1	from	F5A, F5B, F6, F7A.

TABLE I

INTRINSIC FLOW TIMES AND SLOPE CONSTANTS OF NORMAL UNFRACTIONATED POLYSTYRENE, AND NORMAL PRIMARY AND SECONDARY FRACTIONS, IN METHYL ETHYL KETONE

Fraction code no.	% Conversion	Conc., gm./100 ml.	$\ln t / c$	$[\eta]$ - slope	β	k'	
B1	99	0.399	1.79	1.96	0.42 ₅	0.11	0.39
		0.200	1.88				
		0.133 ₀	1.91				
		0.100	1.91.				
C	99	0.396	1.86	2.04	0.45 ₀	0.11	0.39
		0.198	1.95				
		0.132	1.99				
		0.099 ₀	2.01				
C1	99	0.458	2.48	2.82	0.72 ₆	0.09 ₁	0.41
		0.242	2.65				
		0.162	2.71				
		0.121	2.74				
C2C	99	0.423	1.16	1.24	0.18 ₈	0.12	0.38
		0.212	1.20				
		0.141	1.20				
		0.106	1.24				
C4	99	0.396	1.37	1.48	0.28 ₀₀	0.13	0.37
		0.198	1.42				
		0.132	1.44				
		0.099	1.45				
C4A	99	0.485	1.28	1.37	0.17 ₅	0.09	0.41
		0.242	1.34				
		0.162	1.35				
		0.121	1.35				
D1	30	0.400	1.50	1.63	0.30 ₀	0.11	0.39
		0.200	1.57				
		0.133	1.60				
		0.100	1.60				
D1A	30	0.375	1.85	2.00	0.42 ₅	0.11	0.39
		0.188	1.92				
		0.125	1.95				
		0.094	1.97				

TABLE II

INTRINSIC FLOW TIMES OF LOW MOLECULAR WEIGHT NORMAL POLYSTYRENE FRACTIONS IN METHYL ETHYL KETONE AND BENZENE

Solvent	Fraction no.	Conc., g./100 ml.	$\ln t_r/c$	$[\eta]$
Methyl ethyl ketone	E1A	0.443	0.19 ₀	0.19
	E2B	0.477	0.14 ₈	0.15
	E4Ac ¹	0.484	0.06 ₇	0.07 ₀
Benzene	E1A	0.487	0.27 ₃	0.27
		0.244	0.27 ₀	
	E2B	0.490	0.20 ₁	0.20
		0.295	0.20 ₂	
	E4Ac	0.492	0.07 ₇	0.07 ₇

¹This fraction consists of the portion of E4 which was soluble in acetone.

TABLE III

INTRINSIC FLOW TIMES AND SLOPE CONSTANTS OF NORMAL POLYSTYRENE
TERTIARY FRACTIONS IN METHYL ETHYL KETONE

Fraction code no.	Concn., gm./100 ml.	$\ln t_r/c$	$[\eta]$	- slope	β
G1A1	0.467	3.09	3.55	1.11	0.08 ₃
	0.293	3.33			
	0.156	3.38			
	0.117	3.42			
G2A1	0.436	2.49	2.82	0.75 ₀	0.09 ₅
	0.218	2.66			
	0.145	2.72			
	0.109	2.78			
G4A3	0.424	0.97	1.00	0.08 ₀	0.08 ₀
	0.212	0.99			
	0.141	0.90			
	0.106	0.98			
G4B2	0.383	0.66	0.69	0.08 ₀	0.16 ₆
	0.192	0.67			
	0.128	0.69			
	0.096	0.69			
F1A1A1	0.426	2.50	2.80	0.72 ₅	0.09 ₃
	0.213	2.64			
	0.142	2.68			
	0.107	2.72			
F3A2	0.421	1.24	1.31	0.16 ₀	0.09 ₃
	0.210	1.28			
	0.140	1.29			
F3A3	0.413	1.11	1.19	0.19 ₀	0.13 ₃
	0.206	1.14			
	0.138	1.15			
	0.103	1.17			
F3C1	0.374	0.74	0.77	0.10 ₀	0.17 ₀
	0.187	0.75			
	0.125	0.77			

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TABLE III
(Continued)

Fraction code no.	Conc., gm./100 ml.	$\ln \eta/c$	$[\eta]$	- Slope	β
F3C2	0.388	0.59	0.59	$[\eta]$	$[\eta]$
	0.194	0.59		too	too
	0.129	0.60		low	low
F5A1	0.415	1.86	2.01	0.35 ₀	0.08 ₇
	0.208	1.94			
	0.138	1.95			
	0.104	1.97			
F5A3	0.385	1.23	1.26	0.15 ₀	0.09 ₄
	0.193	1.25			
	0.128	1.26			
F7B1	0.370	1.32	1.39	0.19 ₀	0.09 ₈
	0.185	1.35			
	0.123	1.36			
	0.092	1.36			
F7B2	0.381	1.15	1.21	0.14 ₀	0.09 ₆
	0.190	1.18			
	0.127	1.18			
	0.095	1.19			
F7B3	0.378	0.99	1.03	0.11 ₀	0.10 ₀
	0.189	1.01			
	0.126	1.02			

TABLE IV

INTRINSIC FLOW TIMES AND SLOPE CONSTANTS OF NORMAL POLYSTYRENE
TERTIARY FRACTIONS IN BENZENE

Fraction code no.	Conc., gm./100 ml.	$\ln t_r/c$	$[\eta]$	- Slope	β
G1A1	0.147	7.27	8.37	7.6	0.11
	0.098	7.64			
	0.073 ₅	7.80			
	0.058 ₈	7.93			
G2A1	0.207	5.43	6.39	4.7	0.12
	0.138	5.72			
	0.104	5.91			
	0.069	6.06			
G4A3	0.344	1.83	2.06	0.60	0.14
	0.172	1.94			
	0.115	1.98			
	0.086	1.99			
G4B2	0.412	1.21	1.37	0.40	0.21
	0.206	1.28			
	0.137	1.32			
	0.103	1.35			
F1A1A1	0.221	5.22	6.33	5.1	0.13
	0.147	5.59			
	0.110	5.78			
	0.074	5.96			
F3A2	0.339	3.57	4.37	2.4	0.12
	0.180	3.98			
	0.120	4.00			
	0.090	4.26			
F3A3	0.359	2.47	2.87	1.1	0.14
	0.169	2.67			
	0.113	2.73			
	0.068	2.78			
F3C1	0.400	1.42	1.58	0.40	0.16
	0.200	1.50			
	0.133	1.54			
	0.100	1.54			

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TABLE IV
(Continued)

Fraction code no.	Conc., gm./100 ml.	$\ln t_w/c$	$[\eta]$	- slope	β
F3C2	0.405	1.02	1.12	0.25	0.20
	0.203	1.07			
	0.135	1.09			
	0.101	1.10			
F5A1	0.217	3.84	4.44	2.7	0.14
	0.144	4.04			
	0.108	4.14			
	0.072	4.27			
F5A3	0.339	2.42	2.80	1.2	0.16
	0.169	2.64			
	0.113	2.71			
	0.085	2.90			
F7B1	0.430	2.42	2.95	1.4	0.16
	0.215	2.65			
	0.143	2.75			
	0.107	2.80			
F7B2	0.380	2.34	2.71	0.98	0.13
	0.190	2.56			
	0.127	2.62			
	0.095	2.64			
F7B3	0.412	1.81	2.10	7.3	0.17
	0.206	1.96			
	0.137	2.01			
	0.103	2.03			

TABLE V

INTRINSIC FLOW TIMES AND SLOPE CONSTANTS OF UNFRACTIONATED CROSS-LINKED POLYSTYRENE IN METHYL ETHYL KETONE

%DVB	Conc., gm./100 ml.	ln t_{sp}/c	$[\eta]$	Slope	β	k'
0.00300	0.386	2.19	2.38	-0.48	0.09	0.41
	0.193	2.28				
	0.129	2.32				
	0.097	2.32				
0.00625	0.404	2.28	2.55	-0.68	0.10	0.40
	0.202	2.42				
	0.135	2.46				
	0.101	2.48				
0.0125	0.400	1.74	1.82	-0.20	0.06	0.44
	0.200	1.80				
	0.133	1.80				
	0.100	1.78				
0.0250	0.418	1.00	0.95 ₅	0.09 ₅	-0.11	0.61
	0.209	0.97				
	0.139	0.96				
	0.105	0.96				
0.0500	0.392	0.68 ₄	0.63	0.12 ₅	-0.31	0.81
	0.196	0.65 ₈				
	0.131	0.64 ₅				
	0.098	0.62 ₇				
0.100	0.392	0.38 ₆	0.34	0.12 ₅	-0.64	1.14
	0.196	0.37				
	0.131	0.36 ₄				
	0.098	0.34 ₃				
0.120	0.376	0.34 ₀	0.32	0.01 ₅	-0.49	0.99
	0.188	0.33 ₃				
	0.125	0.31 ₇				
	0.094	0.31 ₃				
0.140	0.432	0.29 ₁	0.29	0.02 ₅	-0.30	0.80
	0.216	0.30 ₀				
	0.144	0.29 ₀				
0.150	0.460	0.26 ₆	0.26	0.01	-0.15	0.65
	0.230	0.27 ₀				
	0.153	0.26 ₄				

TABLE VI

INTRINSIC FLOW TIMES AND SLOPE CONSTANTS OF UNFRACTIONATED CROSS-LINKED POLYSTYRENE IN BENZENE

$\%DVB$	Conc., gm./100 ml.	$\ln t_w/c$	$[t]$	Slope	β	k'
0.00300	0.202	3.24	4.67	-7.1	0.35	0.15
	0.135	3.72				
	0.101	4.03				
	0.068	4.36				
(Because of the great deviation of these values from those expected, they have been omitted from graphs and calculations.)						
0.00625	0.266	5.05	5.57	-1.15	0.04	0.46
	0.133	5.42				
	0.089	5.47				
	0.067	5.49				
0.0125	0.243	4.17	4.31	-0.22	0.03	0.47
	0.122	4.24				
	0.081	4.27				
	0.061	4.27				
0.0250	0.252	2.50	2.34	0.62	-0.11	0.61
	0.126	2.41				
	0.084	2.40				
	0.063	2.38				
0.0500	0.400	1.47	1.35	0.30	-0.16	0.66
	0.200	1.42				
	0.133	1.39				
	0.100	1.38				
0.100	0.418	1.05	0.93	0.28	-0.32	0.82
	0.209	0.99				
	0.139	0.98				
	0.105	0.96				
	0.070	0.94				
0.120	0.403	0.69	0.85	0.10	-0.14	0.64
	0.202	0.87				
	0.134	0.86				
	0.101	0.86				
00.140	0.341	0.70	0.73	-0.03	0.06	0.44
	0.171	0.70				
	0.114	0.70				
0.150	0.212	0.518	0.52	0.00	0.00	0.50
	0.106	0.514				
	0.071	0.550				
	00.053	0.524				

TABLE VII

INTRINSIC FLOW TIMES AND SLOPE CONSTANTS OF CROSS-LINKED POLYSTYRENE
PRIMARY FRACTIONS IN METHYL ETHYL KETONE

Fraction no.	%DVB	Conc., gm./100 ml.	$\ln t_w/c$	$[\eta]$	Slope	β	k'
G1	0.0030	0.390	2.86	3.19	-0.82	0.08	0.42
		0.195	3.02				
		0.130	3.09				
		0.098	3.11				
G2	"	0.403	2.76	3.10	-0.85	0.09	0.41
		0.202	2.94				
		0.134	2.98				
G4	"	0.406	1.32	1.42	-0.28	0.12	0.38
		0.203	1.37				
		0.135	1.40				
		0.102	1.40				
H1	0.0250	0.396	1.21	1.12	0.19	-0.15	0.65
		0.198	1.15				
		0.132	1.14				
		0.099	1.14				
H2	"	0.400	0.465	0.48	-0.05	0.04	0.46
		0.200	0.472				
		0.133	0.473				
		0.100	0.499				
H3	"	0.414	1.06	1.02	0.11	-0.11	0.61
		0.207	1.05				
		0.138	1.04				
		0.104	1.03				
J1	0.0125	0.416	2.68	2.61	0.13	-0.02	0.52
		0.208	2.66				
		0.139	2.63				
		0.104	2.63				
J2	"	0.420	2.46	2.46	0.00	0.00	0.50
		0.210	2.46				
		0.140	2.46				
		0.105	2.45				

(Continued next page)

TABLE VII
(Continued)

Fraction code no.	%DVB	Conc., gm./100 ml.	ln t_r/c	$[t]$	Slope	β	k'
J3	0.0125	0.417	1.32	1.40	-0.28	0.10	0.40
		0.209	1.36				
		0.139	1.37				
		0.104	1.38				
K1	0.0500	0.322	1.27	0.725	0.10	-0.18	0.68
		0.161	0.74				
		0.107	0.73				
		0.081	0.72				
K2	"	0.494	1.08	0.725	0.075	-0.14	0.64
		0.247	0.74				
		0.165	0.73				
		0.124	0.74				
K3	"	0.380	0.77	0.730	0.075	-0.14	0.64
		0.190	0.76				
		0.127	0.75				
		0.095	0.74				

TABLE VIII

INTRINSIC FLOW TIMES AND SLOPE CONSTANTS OF CROSS-LINKED POLYSTYRENE
PRIMARY FRACTIONS IN BENZENE

Fraction code no.	%DVB	Concn., gm./100 ml.	$\ln t_w/c$	$[\eta]$	Slope	β	k'
Q1	0.0030	0.201	5.85	7.10	-6.53	0.13	0.37
		0.134	6.20				
		0.101	6.45				
		0.081	6.58				
Q2	"	0.190	5.33	6.54	-6.10	0.15	0.35
		0.127	5.65				
		0.095	5.88				
		0.076	6.06				
Q4	"	0.380	3.13	3.96	-1.13	0.07	0.43
		0.190	3.53				
		0.127	3.68				
		0.095	3.74				
H1	0.0250	0.140	2.79	2.57	0.85	-0.12	0.62
		0.093	2.64				
		0.070	2.63				
		0.056	2.62				
H2	"	0.157	2.80	2.66	0.62	-0.09	0.59
		0.104	2.75				
		0.076	2.74				
		0.066	2.74				
H3	"	0.306	3.00	2.66	4.62	-0.11	0.61
		0.153	2.80				
		0.102	2.75				
		0.077	2.76				
J1	0.0125	0.148	5.57	5.90	-1.15	0.03	0.47
		0.099	5.70				
		0.074	5.68				
		0.059	5.79				
J2	"	0.150	4.57	4.94	-2.06	0.08	0.42
		0.100	4.63				
		0.075	4.63				
		0.0600	4.78				

(Continued next page)

TABLE VIII
(Continued)

Fraction code no.	%DVB	Conc., ga./100 ml.	$\ln t_r/c$	$[\eta]$	Slope	β	k'
J3	0.0125	0.300	2.71	3.30	-2.17	0.07	0.43
		0.150	2.91				
		0.100	3.04				
		0.075	3.11				
H4	0.0250	0.404	2.33	2.57	-0.58	0.01	0.49
		0.202	2.47				
		0.131	2.58				
		0.101	2.57				

GRAPHS

Representation of Inherent Errors

The diameters of the circles drawn represent approximately the errors inherent in the determination of the quantities concerned. Where the errors involved have been large, vertical lines have been drawn to represent the experimental limits of error.

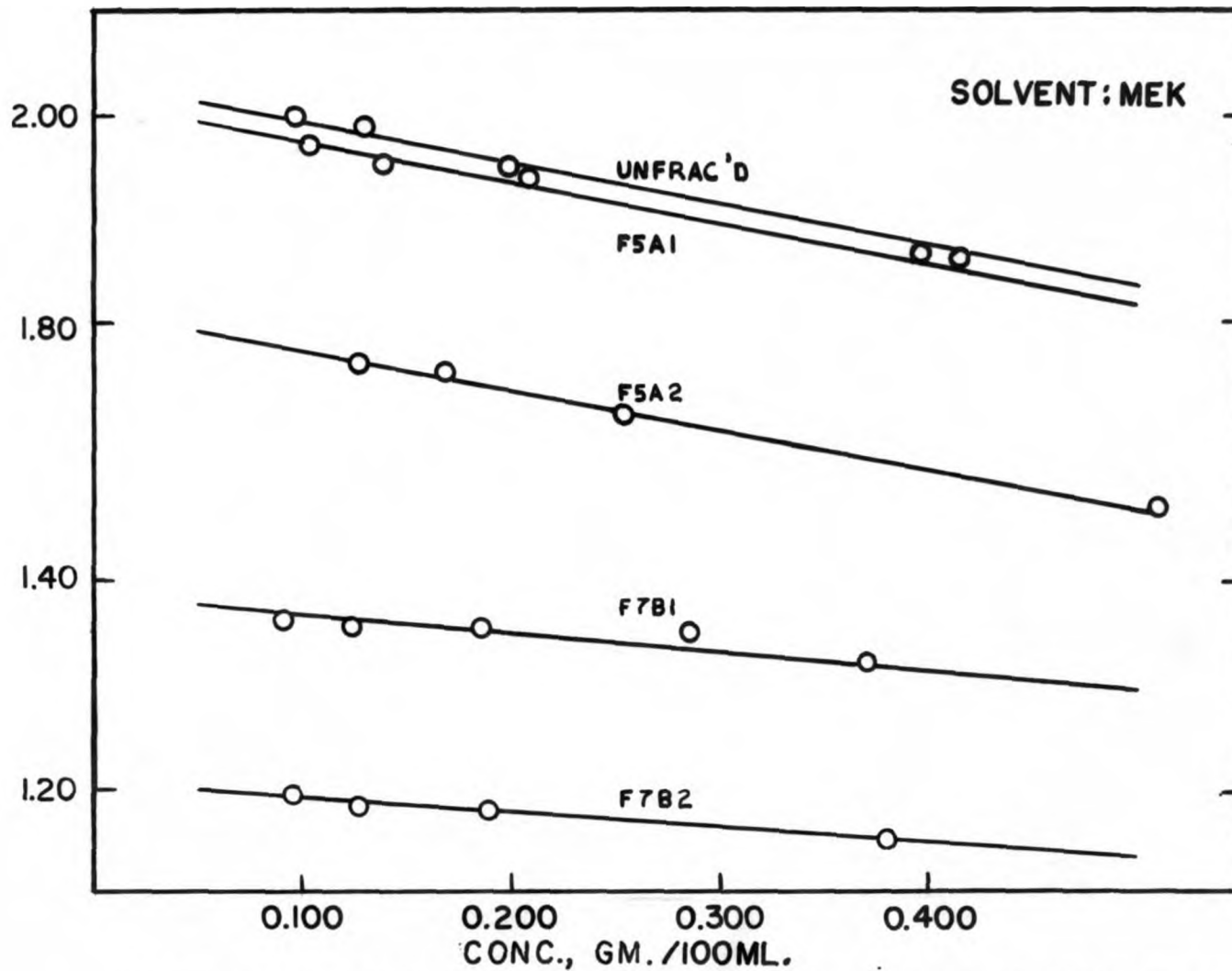
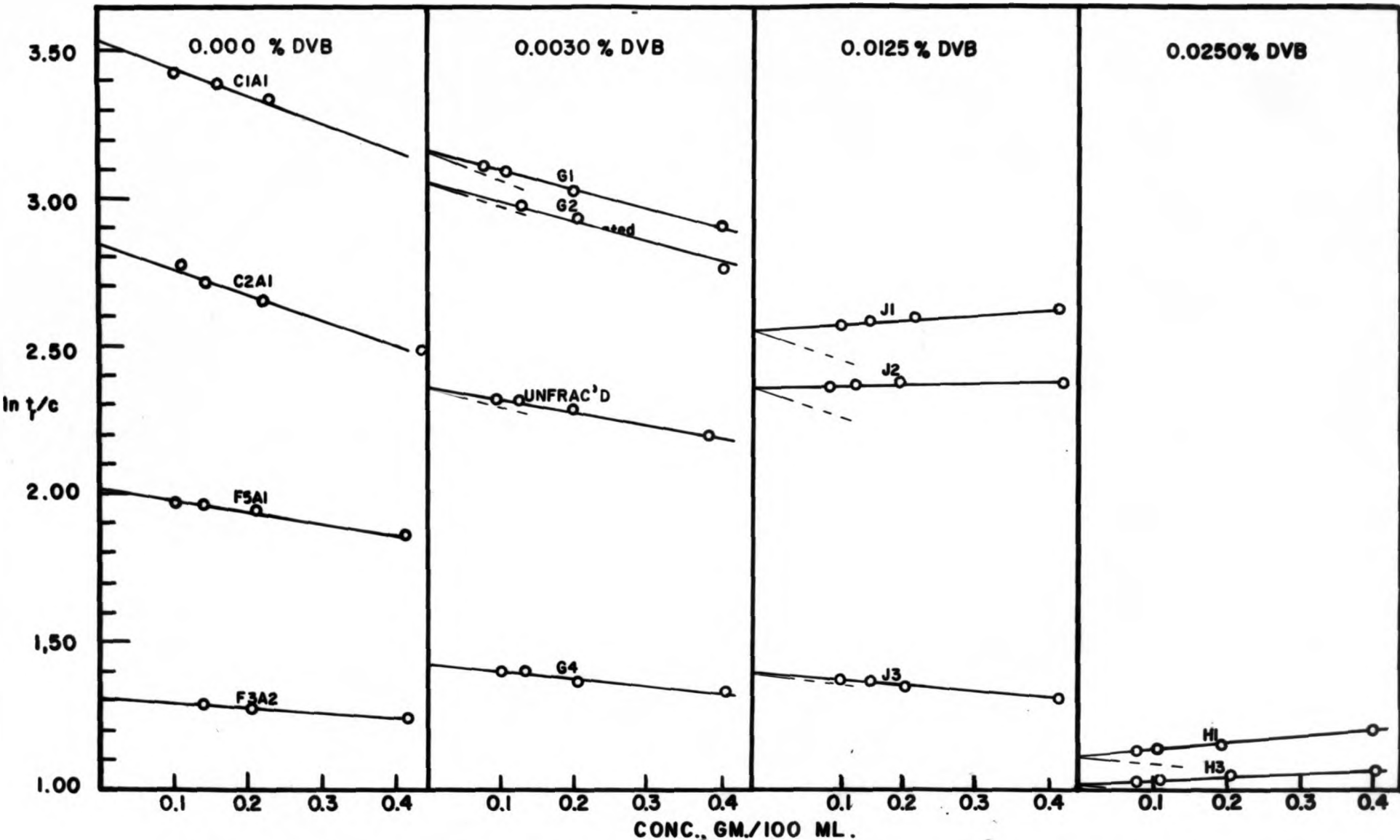
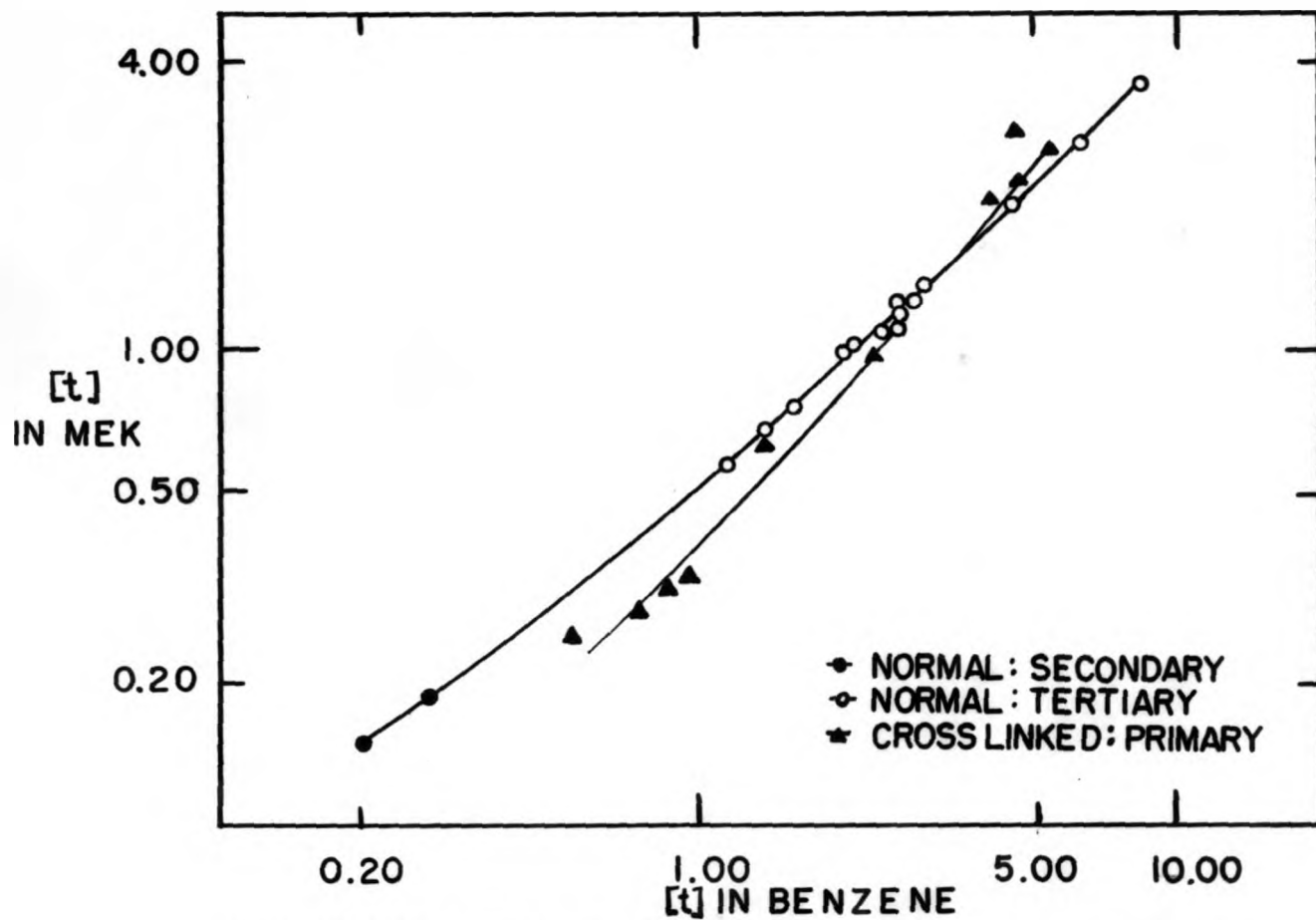


FIG. 1

TYPICAL INHERENT FLOW TIME CURVES
FOR POLYSTYRENE

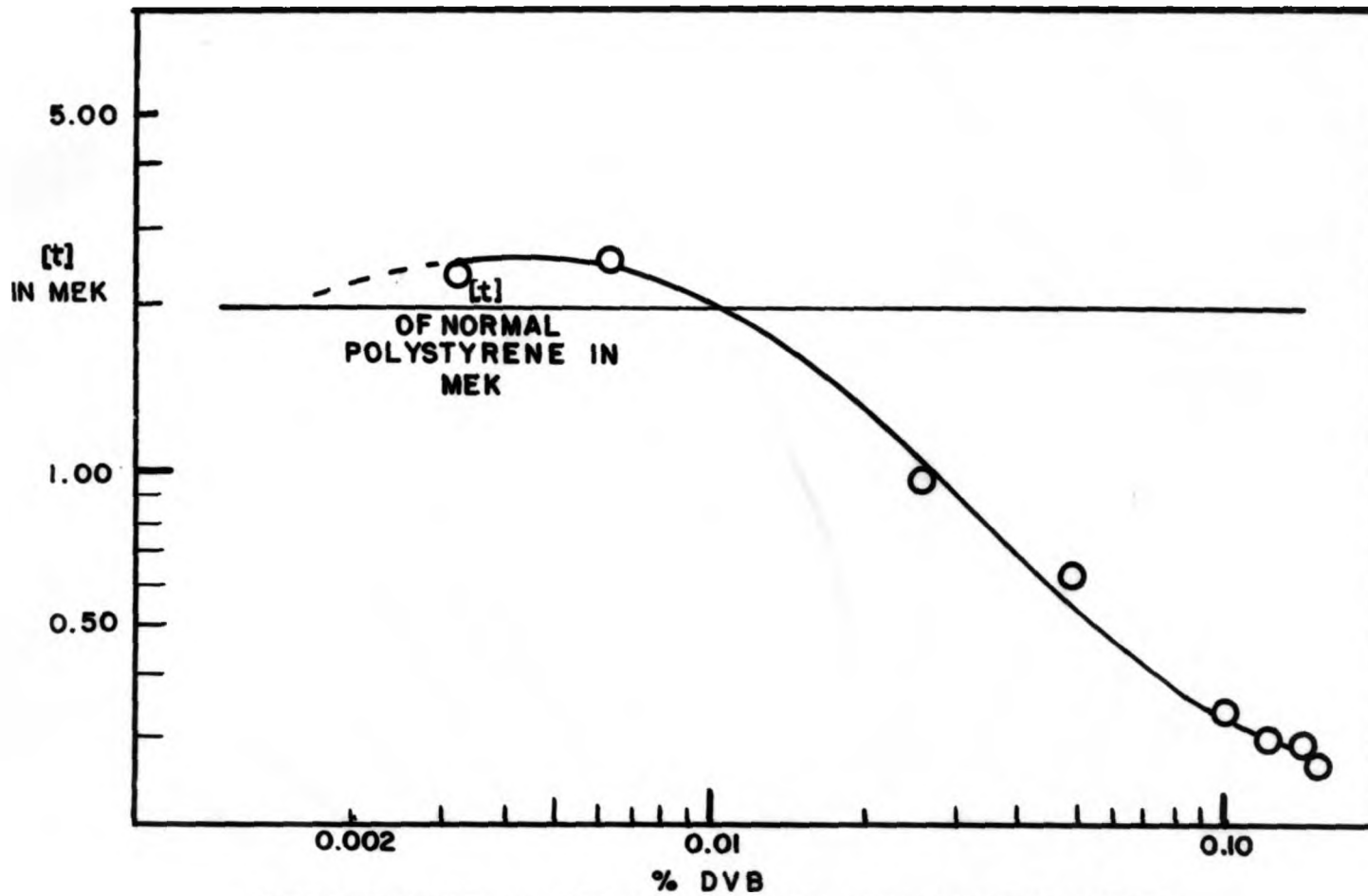


A COMPARISON OF INHERENT FLOW TIME CURVES FOR NORMAL AND CROSS-LINKED POLYSTYRENE FRACTIONS IN MEK



RELATION BETWEEN $[\eta]$ IN MEK AND $[\eta]$ IN BENZENE FOR NORMAL AND CROSS-LINKED POLYSTYRENE FRACTIONS

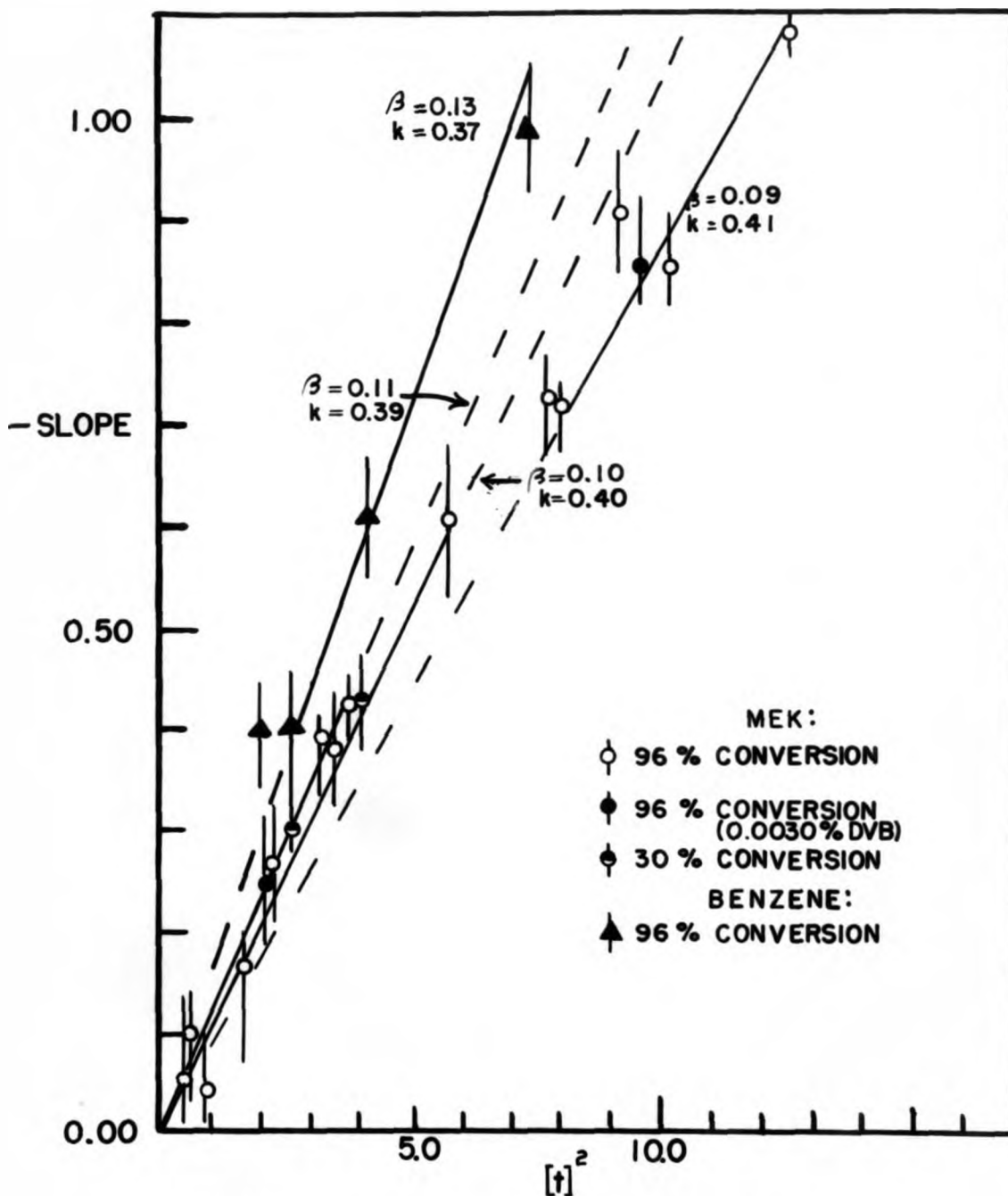
FIG. 3



DEPENDENCE OF $[\eta]$ IN MEK OF UNFRACTIONATED
CROSS-LINKED POLYSTYRENE ON % DVB

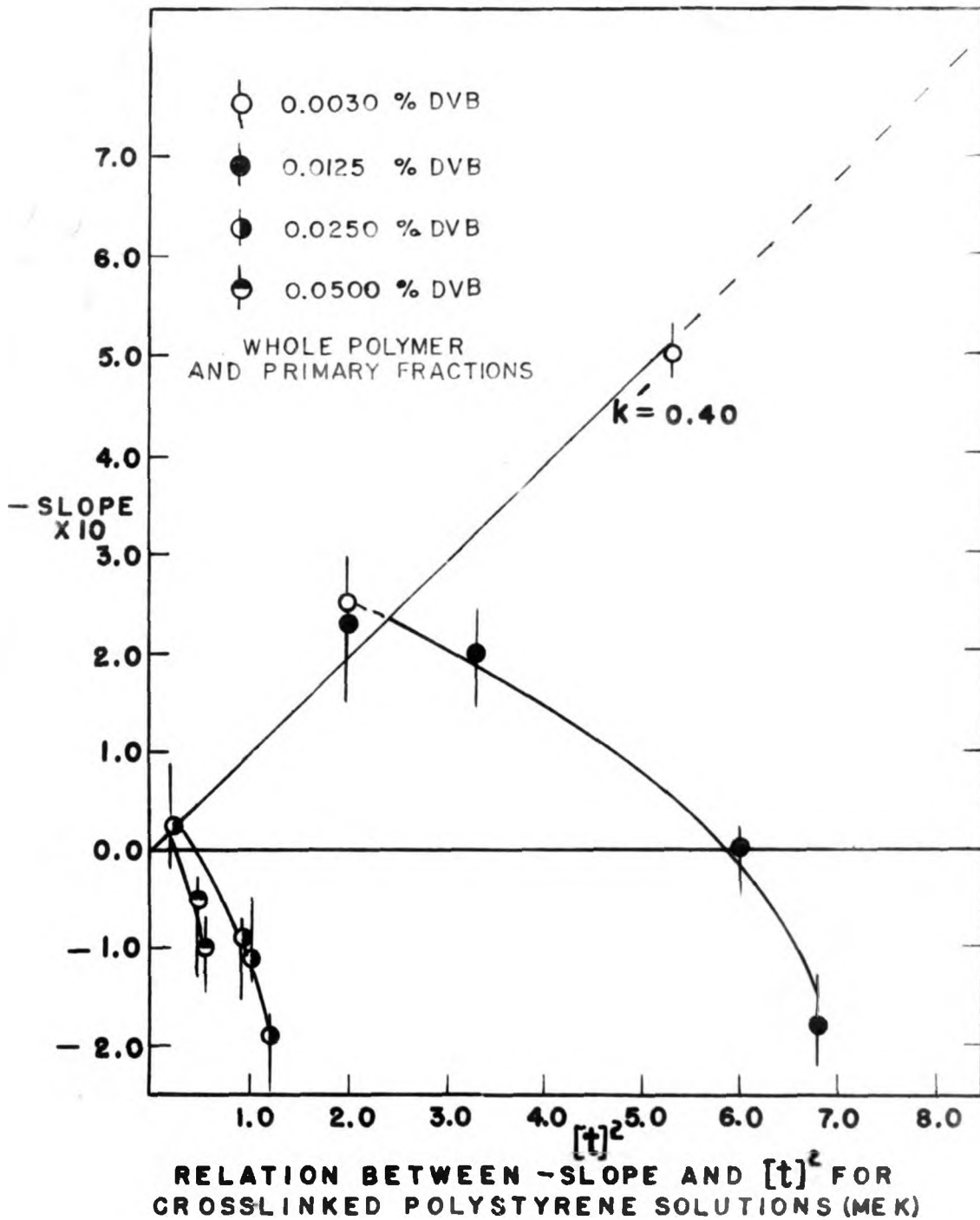
FIG. 4

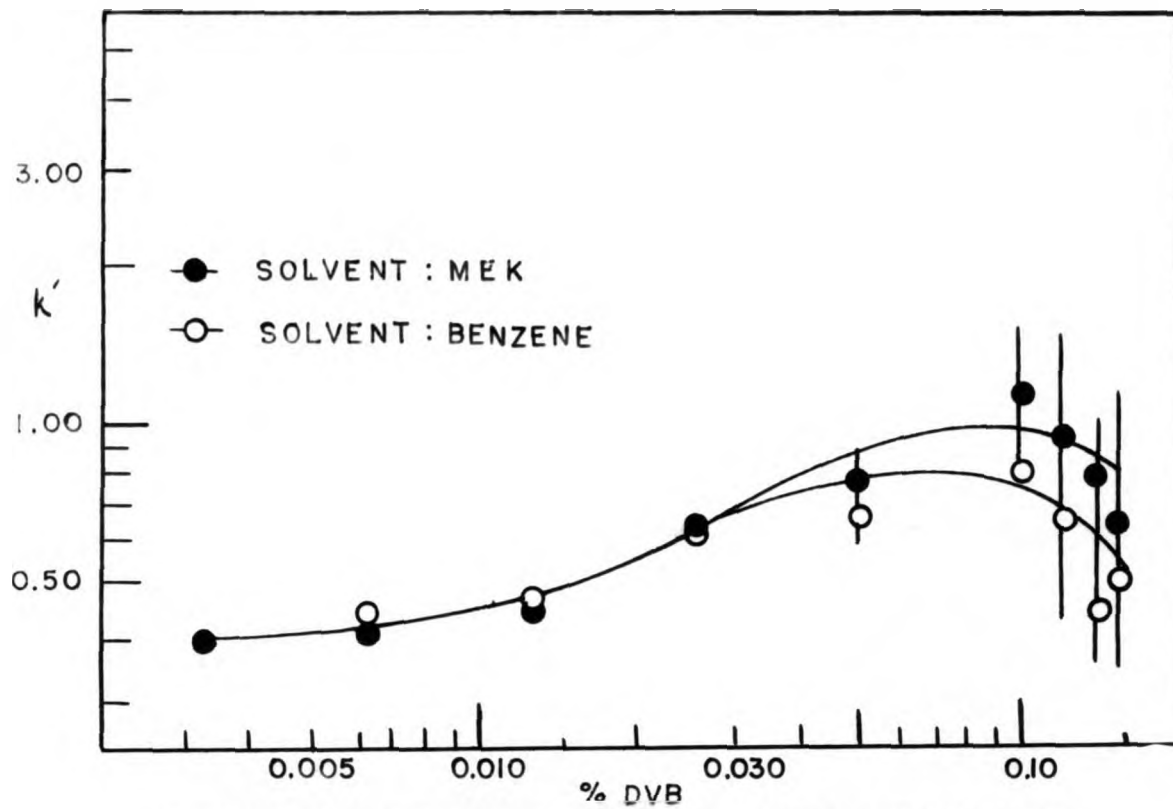
FIG. 5



RELATION BETWEEN SLOPE OF INHERENT FLOW TIME CURVES AND $[t]^2$ FOR POLYSTYRENE FRACTIONS

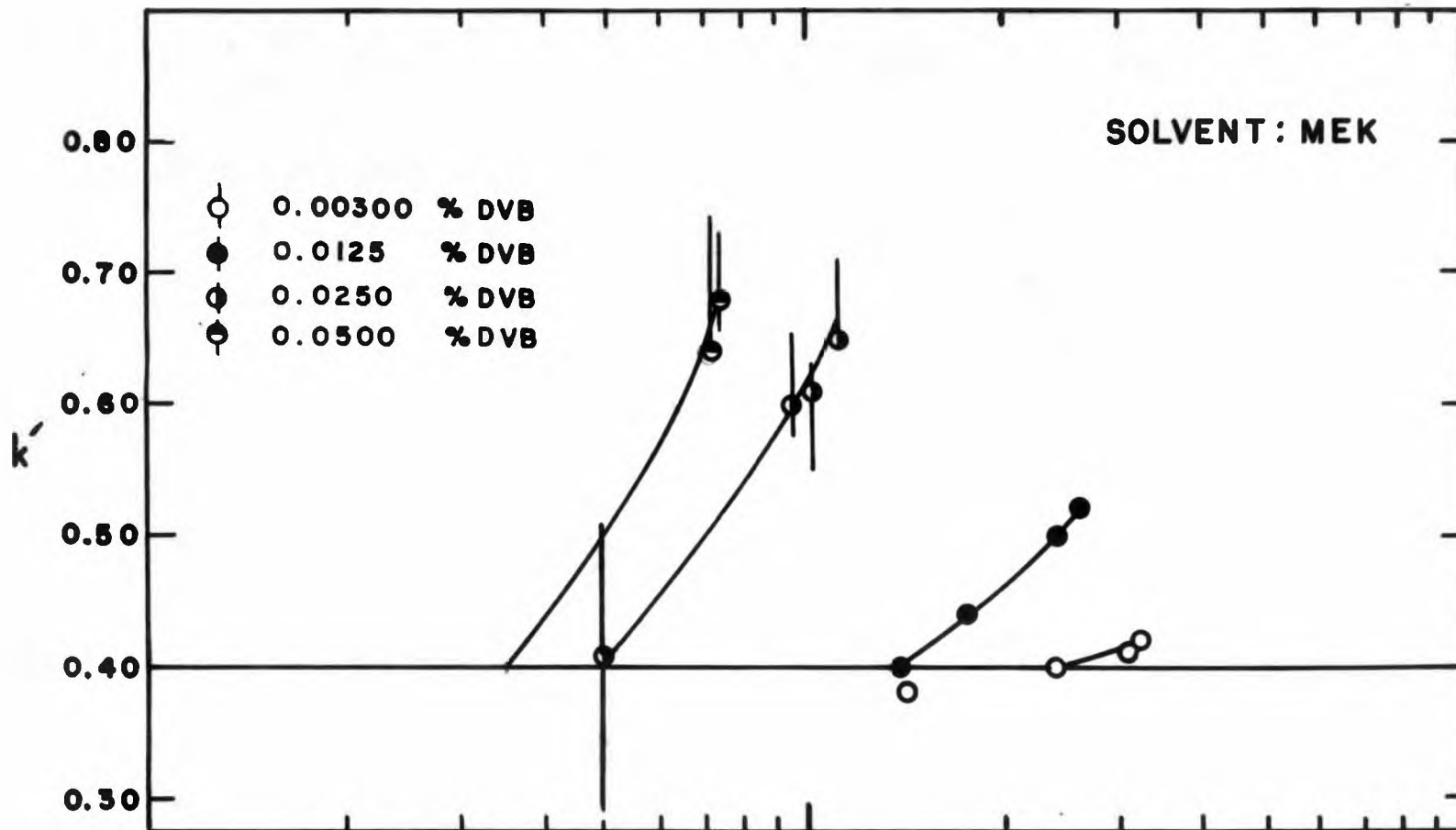
FIG. 6





RELATION BETWEEN k' OF UNFRACTIONATED CROSS-LINKED POLYSTYRENE SOLUTIONS AND % DVB

FIG. 7



RELATION OF k' OF CROSS-LINKED POLYSTYRENE
FRACTIONS TO $[t]$

FIG. 8