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A STUDY OF THE IRRADIATION METHOD IN THE MEASUREMENT OF MOLECULAR WEIGHT DISTRIBUTION IN POLYSTYRENE

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SUMMARY

The object of this investigation was to study the radiation crosslinking-solubility characteristics of polystyrene. The purpose was to determine whether properties of the molecular weight or size distribution of a polymeric system can be measured experimentally from its subsequent crosslinking-solubility behavior.

A series of samples of polystyrene were used ranging in weight average molecular weight, $\overline{M}_w$, from about 1,000,000 to 5,000,000; in number average molecular weight, $\overline{M}_n$, from about 300,000 to 3,000,000; in z-average molecular weight from about 1,600,000 to 7,500,000; and with distribution breadth ranging from very narrow ($\overline{M}_w/\overline{M}_n = 1.06$) to fairly broad ($\overline{M}_w/\overline{M}_n = 3.7$). Each sample was irradiated in vacuum by Cobalt-60 gamma radiation for various total doses, and the resulting solubility for each dosage was determined by solvent extraction of the partially gelled solid films. From existing theories of random crosslinking and chain scission, equations were developed, relating the measurable properties of gel curves (solubility as a function of radiation dose) to the initial molecular weight distribution of the sample, and two properties of the

distribution ($\bar{M}_w/\bar{M}_n$ and $\bar{M}_z/\bar{M}_w$) were computed for each sample.

From the dependence of gel point dosage upon $\bar{M}_w$, it was concluded that crosslinking density is proportional to radiation dose. Likewise, chain scission density is proportional to radiation dose, as shown by the constancy of the chain scission parameter (chain scissions per crosslinked unit) from sample to sample, and the ability of a single value of this parameter to fit over the entire dose range in samples with most-probable distribution ($\bar{M}_w/\bar{M}_n = 2$).

The gel curves themselves were reproducible and were experimentally accurate enough to allow unambiguous measurement of the quantities required for the computation of $\bar{M}_w/\bar{M}_n$ and $\bar{M}_z/\bar{M}_w$. With few exceptions, the values of $\bar{M}_w/\bar{M}_n$ and $\bar{M}_z/\bar{M}_w$ obtained from the gel curves are in good agreement with those obtained from light scattering measurements, ultracentrifuge-sedimentation studies, and by the known compositional makeup of the samples.

Subsidiary tests indicate that 1) oxygen has a considerable effect on apparent crosslinking behavior, 2) such variables as radiation dose rate (over a range of nine) and film thickness (over a range of two) produce no effect on the results, 3) extraction solvents such as benzene, toluene, and cyclohexane, give identical solubility results, but methyl ethyl ketone gives higher

and unstable solubilities, and 4) pre-irradiation conditioning, such as film-casting solvent, can produce a considerable effect on apparent crosslinking behavior.

An anomalous solubility behavior in the vicinity of the gel point is noted, indicating a discrepancy between gel point dosage deduced from extrapolation of the main body of the gel curve to 100% solubility on the one hand, and the minimum dose at which insolubility first occurs on the other. This may account for the high value of crosslinking efficiency derived from gel point measurements in this study using the former criterion (1700 electron volts per crosslinked unit), and those of some other investigators using the latter criterion (850-1100 e.v.).

Two conclusions can be drawn from the results: 1) for polystyrene, the basic assumptions of statistically random crosslinking and chain scission are well met in the range of chain lengths covered, and 2) the resulting gel structures are stable and reproducible enough to allow accurate computation of the distribution parameters desired.

I. INTRODUCTION

A. General Objectives

High polymers possess many interesting properties which are unique to molecules built up by the consecutive linking together of many identical sub-units. A characteristic of great importance is the distribution of molecular weights or sizes resulting from the polymerization process, and much effort has been exerted, with varying degrees of success, to develop methods capable of measuring this distribution. The purpose of this study is to investigate the interrelation between the initial molecular weight distribution possessed by a high polymer and its subsequent crosslinking-solubility behavior, in order to determine whether it is experimentally possible to deduce information about the distribution from this behavior. The polymer selected for this purpose was polystyrene; the agency used to introduce crosslinks into the solid polymer was gamma radiation. The basic approach used in this study is to prepare, by various methods, samples of polymer with known distribution and to compare the experimental solubility behavior with that predicted by the theory. This is developed more fully in the later sections covering experimental procedure and results.

The main purpose of this introduction is to present the theoretical structure developed by various investigators upon which the method is based. The importance and general characteristics of distribution functions as generally applied to polymer systems are described. The common methods used to predict theoretically and measure experimentally distribution, are outlined in some detail. The concept of gel formation due to random crosslinking, along with the solubility characteristics of crosslinked systems are discussed; and the general arguments used in the development of equations relating initial distribution to resultant crosslinking-solubility characteristics are presented. Finally, the meaning of these equations in terms of irradiation crosslinking, and their subsequent modification due to the effect of simultaneous chain scission are discussed.

B. Distribution Functions

1. Definitions and Examples

A polymeric system is composed of molecules formed by the linking together of a large number of monomeric units through chemical bonds. Conceptually the resulting molecule is a chain, the links of which are the repeating units derived from the monomer. Structurally the chain may be linear (units connected to form a linear sequence), branched (possessing side chains of varying length), or highly crosslinked (where linear sequences have become joined by chemical

linkages to form a network-like macrostructure extending throughout the system).

Polymers in the first two categories above are called soluble in the sense that they are capable of dissolving in a suitable solvent without the destruction of chemical bonds, to form a true solution. They can be characterized either by their molecular weight, M, or by the number of monomeric sub-units, or mers, comprising each polymer molecule, called the degree of polymerization, D.P.

A system which contains molecules all with the same D.P. is termed monodisperse or homogeneous. Due to the statistical nature of polymerization processes, the resulting polymer molecules do not all have the same D.P. and thus there always is a range or distribution of molecular weights represented in the system. Such systems are termed polydisperse or heterogeneous. In order to treat the polydispersity of a system in a quantitative manner, mathematical functions are defined which describe the distribution of molecular weights present. One such relation is W(n), the weight distribution function, which describes the fraction of the total <u>weight</u> of the sample which is contributed by the n-mer molecules present. Another is F(n) the number distribution function, which describes the fraction of the total <u>number</u> of polymer molecules present which are n-mer molecules. Since molecular weight, m, is given by the product of the degree of polymerization, n, and the repeating unit (mer)weight, m_o, alternate expressions can be

defined for the above functions in terms of molecular weight instead of D.P.:

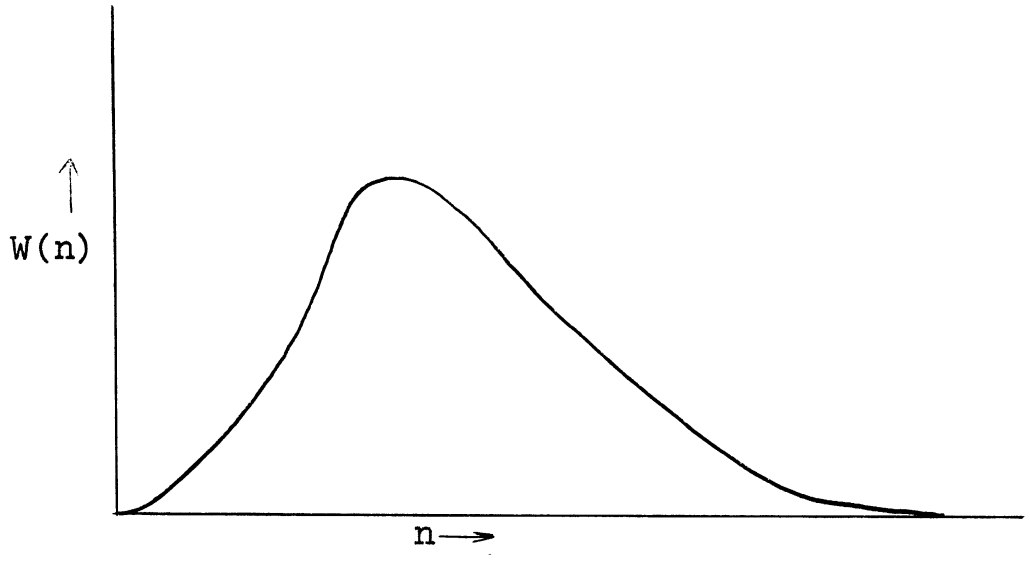
$$W(m) = W(nm_o)$$

$$F(m) = F(nm_o)$$

Likewise there is a simple relationship between W(n) and F(n):

$$W(n) = \frac{m_o n\, F(n)}{\sum_{n=1}^{\infty} m_o nF(n)} = \frac{n\, F(n)}{\sum_{n=1}^{\infty} nF(n)}$$

For purposes of discussion, only W(m) or W(n) will generally be used henceforth. The following sketch shows an example of the sort of function one might expect for W(n):



Degree of Polymerization

From the definition of W(n) and from properties common to all distribution functions, the following restrictions must hold:

1.) $W(n)$ is defined for all positive integral values for n.

2.) $W(n) \geqslant 0 \qquad (n \geqslant 1)$

3.) $\sum_{n=1}^{\infty} W(n) = 1$

4.) $W(n) = f_1 W_1(n) + f_2 W_2(n) + \text{------} + f_k W_k(n)$

This last expression is a linear mixing law which states that if k samples are mixed together, the resulting distribution is given by adding together the products of each sample distribution, $W_i(n)$, by its respective weight fraction, f_i, of the resultant sample.

One method of characterizing polymers is by their molecular weight, necessarily an average due to the distribution of sizes present. The average degree of polymerization, $\overline{DP}$, or the average molecular weight, $\overline{M}$, obtained depends upon the averaging process used. Several different averages are commonly used in the polymer field. $\overline{DP}_n$, the number-average degree of polymerization, is simply the total number of mers in the system divided by the total number of polymer molecules and is the value obtained from colligative property measurements (osmotic pressure, freezing point depression). $\overline{DP}_w$, the weight-average degree of polymerization, is the value resulting from a molecular weight measurement by light-scattering and is always larger than $\overline{DP}_n$. $\overline{DP}_z$, the so-called z-average degree of polymerization, results from molecular weight measurements from the migration of the molecules in

an intense centrifugal field (sedimentation and diffusion) and is in turn larger than both $\overline{DP}_n$ and $\overline{DP}_w$.

These various average D.P.'s are defined in terms of the moments of the distribution W(n). For high polymers, the main contributions to these averages are yielded by n's much greater than one, so it has become customary to treat W(n) as a continuous function and replace summation by integration.

$$\overline{DP}_n = \frac{1}{\sum_{n=1}^{\infty} \frac{W(n)}{n}} = \left[\int_0^{\infty} \frac{W(n)}{n}\, dn\right]^{-1} \qquad (1\text{-a})$$

$$\overline{DP}_w = \sum_{n=1}^{\infty} nW(n) = \int_0^{\infty} nW(n)\,dn \qquad (1\text{-b})$$

$$\overline{DP}_z = \frac{\sum_{n=1}^{\infty} n^2W(n)}{\sum_{n=1}^{\infty} nW(n)} = \frac{\int_0^{\infty} n^2W(n)\,dn}{\int_0^{\infty} nW(n)\,dn} \qquad (1\text{-c})$$

By extending the above results, higher average D.P.'s such as $\overline{DP}_z + 1$, $DP_z + 2$, etc., can be defined, in an analogous way, as the ratio of two successive moments of W(n). Of course, since molecular weight is given by the product of mer weight, m_o, and degree of polymerization, then: $\overline{M}_n = m_o\overline{DP}_n$, $\overline{M}_w = m_o\overline{DP}_w$, and $\overline{M}_z = m_o\overline{DP}_z$.

The particular expression for W(n) to which a polymer system conforms is related to the mechanisms and relative rates of the successive reactions which produce the

building up of the final chains from monomer molecules. It is possible, having postulated what reactions are involved, to predict the form of W(n) for a particular resultant polymer system. An example of this approach is afforded by the case of free-radical type polymerization to give linear polymers in which termination of chain growth is by disproportionation and, thereby, mutual deactivation between two growing radicals. The resultant weight distribution function of the polymer is the so-called "most-probable" distribution:*

$$W(n) = a^2 n e^{-an} \qquad (2)$$

The parameter, a, is equal to the reciprocal of $\overline{DP}_n$.

This is a very common type of distribution function for polymers, being characteristic also of radical-type polymerizations where termination is by chain transfer to neutral molecules, and to difunctional polycondensations.*

Most-probable distribution also arises in connection with chain scission, another process of importance. In this circumstance, some of the bonds which bind the monomeric units into the chainlike polymer molecules are broken, causing a net decrease in average molecular weight.

Consider a system with an arbitrary distribution function, W(n). If scission occurs at random in the polymer chains, the distribution will, in general, change, and

*P. J. Flory "Principles of Polymer Chemistry". Pp. 317-346. Cornell University Press, Ithaca, New York, 1953.

with sufficient scissions, will approach symptotically the most-probable distribution, irrespective of W(n). For linear polymers, possessing initially most-probable distribution, the effect of chain scission will appear only in the average chain length parameter, a. The full significance of this result with regard to this study will be discussed in a later section.

Bamford and Tompa (1) have presented a general method by which it is possible to calculate successive moments of a distribution function from considerations of the mechanisms of polymerization.

Following are other examples of distribution functions found in certain polymeric systems and which are either empirical or derived from polymerization mechanism considerations.

Beasley (2) has derived an expression for the weight distribution of a polymer in which long-chain branching occurs due to chain transfer with dead polymer:

$$W(n) = \frac{(1 - B)n}{n_o^2 \left(1 + \frac{Bn}{n_o}\right)^{\left(1 + \frac{1}{B}\right)}}$$

B is a parameter related to the frequency of branching, and n_o is the number-average number of monomeric units in the primary linear chains forming the branched molecules.

Wesslau (3) found empirically that the weight distribution of Zeigler type (low pressure) polyethylene conformed to a log-normal distribution:

$$W(n) = \frac{1}{B' \pi^{\frac{1}{2}} n} \exp \left\{ - \frac{1}{(B')^2} \ln^2 \frac{n}{n_o} \right\} \quad (4)$$

The significance of the parameters B' and n_o is not clear, except for the fact that n_o is some sort of average chain length and B measures the distribution breadth.

Zimm (4), in his discussions of the light scattering characteristics of polymer solutions and their dependence on the distribution function uses as a model the following distribution, commonly termed the Schulz distribution:

$$W(n) = \frac{a^{Z+1} n^Z e^{-an}}{\Gamma(Z + 1)} \quad (5)$$

Here, as above, the two parameters, a and Z, are related respectively to an average chain length and the breadth of the distribution.

A characteristic of the distributions presented above, and in fact, of all polymeric distribution functions, is the presence of a parameter (a, n_o, -----) which is related to some average chain length.

$$\overline{DP}_n = \frac{1}{a}, \quad \overline{DP}_w = \frac{2}{a}, \quad \overline{DP}_z = \frac{3}{a}$$

Furthermore, the ratio of any two average molecule weights should then be independent of this parameter, and should depend only on the form of the particular distribution function and on the other parameters present:

Most-probable: $$\frac{\overline{DP}_w}{\overline{DP}_n} = 2, \quad \frac{\overline{DP}_z}{\overline{DP}_w} = \frac{3}{2}$$

Beasley: $\frac{\overline{DP}_w}{\overline{DP}_n} = 2\frac{(1 - B)}{(1 - 2B)}$, $\frac{\overline{DP}_z}{\overline{DP}_w} = \frac{3}{2}\frac{(1 - 2B)}{(1 - 3B)}$

Wesslau: $\frac{\overline{DP}_w}{\overline{DP}_n} = \frac{\overline{DP}_z}{\overline{DP}_w} = \exp\left\{\frac{(B')^2}{2}\right\}$

Schulz: $\frac{\overline{DP}_w}{\overline{DP}_n} = \frac{Z + 1}{Z + 2}$, $\frac{\overline{DP}_z}{\overline{DP}_w} = \frac{Z + 2}{Z + 3}$

The result is that any form for the distribution function implies the existence of a family of distributions, any two members of which may have different values for a particular D.P. (depending upon the chain length parameter), but all members of which must yield the same value for ratios of two different average D.P.'s. Samples which belong to the same family of distributions (for example, all most-probable distribution samples, all Wesslau distribution samples with $B' = 0.3$, etc.) arbitrarily will be said to have the same distribution or type of distribution.

The distribution function is of considerable importance both from both the practical and scientific point of view. The properties of polymeric systems which are important technologically, such as tensile strength, melt viscosity, and stiffness, all depend on some average molecular weight. In order to evaluate different samples in terms of their expected mechanical properties it is common practice to measure their molecular weights (necessarily an average). The conclusion that two samples will behave the same way because, for instance, their weight-average

molecular weights are the same, is not really justified if the property in question depends primarily on the number-average molecular weight, unless the samples have essentially the same distribution. Likewise, when several batches of polymer are blended together to produce improved properties, complicated distributions can be produced whose effects upon properties are difficult to predict from a single molecular weight measurement.

From the research point of view, the distribution function represents one path to verify or even predict the types of chemical mechanisms by which the polymer is built up. For example, the experimental verification that certain types of radical-type polymerizations produced most-probable distribution yielded an additional, even if indirect, bit of evidence that the mechanisms postulated from other results were indeed correct. Likewise, any series of mechanisms which ultimately arise to explain the Zeigler-type polymerizations should be consistent with the log-normal type distribution function (equation 4) found experimentally.

2. Common Methods Used to Measure Distribution

a. General Considerations

One unambiguous method for determining the breadth of distribution in a sample is to measure by different experiments two or more of its various average molecular weights. Thus, osmotic pressure gives a number-average

value ($\bar{M}_n$), light scattering gives a weight-average value ($\bar{M}_w$) and the ratio, ($\bar{M}_w/\bar{M}_n$), gives a measure of the breadth of distribution (being 1.0 for a monodisperse system, 2.0 for a sample with most-probable distribution, etc.). It is apparent however, that, except for a monodisperse system, a simple ratio cannot produce the entire distribution function. What is required is a method which operates on the polymer molecules in some systematic manner according to their molecular weights to give a measurable function which, in principle at least, can be inverted to obtain the distribution function.

Several methods have been brought forth as a means of determining the distribution of a polymer from a single type of experiment. None are ideal and all are plagued with difficulties, both experimental and theoretical, which limit their usefulness, but under the proper conditions, they can yield valuable information on the distribution.

b. Fractionation

Fractionation is a general term applied to any process wherein a polydisperse polymer is separated into a series of relatively homogeneous samples or fractions by using the fact that the solubility of polymer molecules decreases with increasing molecular weight. One common technique is to make a dilute solution of the polymer in a suitable solvent and then to add slowly a miscible non-solvent. With sufficient non-solvent added, a second,

polymer-rich, liquid phase is formed, and all molecular weight species present distribute themselves between the two phases: the largest molecules present show a significant preference for the second phase, while the smaller molecules show relatively less discrimination. This selective migration of the larger molecules into a second phase and the subsequent removal of the phase from the system can be repeated many times by adding fresh increments of non-solvent, the result being that the initially broad distribution sample is divided into a number of narrow fractions, the molecular weight of each new fraction being lower than the preceding. A common procedure is then to divide each fraction in sub-fractions by the same method to refine the separation. The molecular weights of these fractions are measured, and the distribution function is constructed from the weights of the fractions and their respective molecular weights.

One of the advantages of fractionation methods lies in the directness and simplicity of interpretation of the results. It is the only available general method for producing a series of narrow distribution samples and thereby separating the distribution into its component parts. It has several drawbacks, which limit its usefulness, at least insofar as distribution information is concerned.

First of all, distribution between the phases during fractionation depends upon branching and crystallinity

in the polymer as well as molecular weight, so the method is applicable with certainty only to linear, amorphous polymers. Secondly, good separations are obtained only when the solution is very dilute (less than 1% polymer and preferably about 0.1%), necessitating the handling of large quantities of solvent if reasonably sized fractions are to be obtained. In addition, it is quite time consuming and even with careful work, does not always produce fractions narrow enough to give meaningful distribution data. Fractionation is extensively used, however, as a means of producing samples which are much narrower than the usual, as polymerized, samples.

c. Light Scattering

Light scattering techniques have come into very prominent usage in recent years for the characterization of polymers. Basically, they involve passing a beam of light through dilute solutions of the polymer in a suitable solvent, and measuring the relative intensities of the light scattered both as a function of angle to the incident beam and as a function of concentration. The angular scattering intensities due to the polymer molecules alone are obtained by subtracting the scattering due to pure solvent, and these quantities, together with the concentrations of the solutions, are used to obtain the weight-average molecular weight for the polymer $\overline{M}_w$.

The dependence of scattered intensity both upon angle and upon concentration has been extensively investigated

both theoretically and experimentally with the result that additional information is attainable. One specific result is that under certain conditions proper treatment of the scattering data can yield information on the molecular weight distribution function of the polymer. The method has been used mainly on samples obtained from the fractionation process alluded to previously, to ascertain semi-quantitatively, the narrowness of the fractions obtained. The application of light scattering in this investigation will be described more fully in the section describing experimental procedures.

d. Sedimentation methods

Another method for obtaining distribution information involves the use of the ultracentrifuge in which a dilute solution of the polymer is centrifuged at rates high enough to cause actual migration of the polymer molecules through the solution in analogy to the settling of particles in a suspension. It depends upon the fact that the molecules sediment at a rate proportional to the square root of their mass.

At the onset of centrifugation, the polymer molecules are dispersed throughout the solution uniformly, but under the influence of the field they all tend to move outward from the center of rotation. This gives rise to a boundary, separating solvent and solution, which moves at a rate equal to the sedimentation velocity of the polymer

molecules (again in analogy to the settling of a suspension). At the onset, the boundary coincides with the meniscus of the solution in the centrifuge cell and is very sharp, but as centrifugation proceeds, the boundary tends to spread as it moves due to the superimposed effects of diffusion and polydispersity.

The usual in situ optical methods (Lamm scale method or schlerien optics) depend on refractive index changes between pure solvent and solution in the region of the boundary and are capable of giving a photographic record of refractive index gradient (and therefore concentration gradient, since refractive index is linear in concentration) as a function of position in the cell. Such records are obtained as a function of time for each of a series of concentrations, and the results extrapolated by well known techniques to zero concentration to eliminate interaction effects and to infinite time to eliminate diffusional effects. The result, after insertion of the relation tion of sedimentation velocity to molecular weight, produces the weight distribution of the polymer. The application of this method to polystyrene is described in a recent paper by McCormick (5), which also contains a list of references describing the modern advances in the theory and results treatment of molecular sedimentation.

An objection to sedimentation methods in general is the exceeding complexity in interpretation when measurements are made at experimentally reasonable concentrations,

due to non-ideal thermodynamic behavior. Even with suitably defined activity coefficients, this non-ideality makes interpretation of the results very difficult. However, it is possible to choose solvents which minimize this thermodynamic problem and, in fact, the careful choice of a solvent is imperative since the accuracy of the results are improved by large refractive index and density differences between solvent and polymer.

At the present time, in spite of interpretation difficulties and cost of the specialized equipment required, sedimentation stands as the only method capable of routine use in research laboratories to obtain a molecular weight distribution by a single series of experiments and in a reasonable amount of time.

C. Crosslinking-Gel Theory

1. Concepts and General Results with Regard to Distribution

Many polymers occur as linear or slightly branched chains. These primary chains by and large are soluble in the sense that the molecules of polymer, when added to a suitable solvent, will become solvated and disperse themselves throughout the solvent to form a true solution. The larger is the chain length of the polymer, the more it will expand in the solution. If crosslinks, i.e. chemical bonds between the chains, are added to the solid system in sufficient numbers, a portion of these

chains become interconnected to form a ramified network structure whose solution properties vary considerably from those of the primary molecules. The crosslinks can be (arbitrarily) classified according to their two functions. Some serve to link together primary chains into very large molecules extending throughout the system while others serve as intramolecular crosslinks to interconnect various segments of these large molecules back upon themselves. If the resulting system is then placed in a solvent, the primary molecules imbedded in, but not connected to, the network will diffuse out and distribute themselves uniformly through the solvent. The network or gel structure itself will imbibe solvent but will expand only to a limited extent due to the intramolecular crosslinks which, by acting as elastic connections between various portions of the large molecule, resist the solvating or swelling action of the solvent. Clearly then, there is a sharp demarcation between the behavior of soluble molecules and this "insoluble" gel structure. If more solvent is added to the system, a soluble molecule with the same molecular weight as the gel structure would expand to distribute itself more or less uniformly through the larger volume of solvent. The gel's sphere of influence on the contrary, is governed not by the amount of solvent present but by the balance between solvation (osmotic) forces tending to expand the molecule and intramolecular chemical bond forces resisting the expansion.

The extent of crosslinking, or crosslinking density, α, for a system is commonly defined as the number of monomeric repeating units which participate in crosslinks divided by the total number of these repeating units present in the system. It is apparent that as α is increased for the system, the fraction of the primary chains connected to the gel will increase and the structure itself will become more tightly bound. Also since the number of crosslinking sites for a molecule is proportional to its molecular weight, it follows that the larger chains are statistically more likely to become a part of the gel during the early stages of gel formation.

In connection with the sharp demarcation between gel networks and soluble molecules, it is necessary to inquire into the conditions necessary for the onset of gel formation, that is, for the transition of a slightly crosslinked but totally soluble polymer to a material which contains a finite amount of gel. Considering a system of primary polymer molecules, having an initial molecular weight distribution W(n) and a weight-average degree of polymerization of $\overline{DP}_w$, Stockmayer (6) has shown that under the conditions of random crosslinking and negligible intramolecular crosslinking, the onset of gel formation (gel point) is reached when an average of one crosslink for every two weight-average primary molecules present in the system has been added independently of W(n). Thus, having defined the crosslinking, α, as the fraction of the

monomeric units comprising the primary molecules which participate in crosslinks, and since there are two crosslinked units per crosslink, the criterion for gelation is that $\alpha \overline{DP}_w \geq 1$, independently of W(n), the gel point being the limiting condition:

$$\alpha \overline{DP}_w = 1 \qquad (6)$$

Each crosslink added to a system at or beyond its gel point will serve one of three purposes. It may bind together two primary molecules which are each already part of the gel, it may unite two soluble molecules to form a larger but still soluble molecule, or it may serve to attach a soluble molecule to the gel, in which case it increases the fraction of the total polymer which is gel. Each of the above possibilities is amenable to a statistical treatment to ascertain the inter-relationship between crosslinking density, gel fraction, and the molecular weight distribution of the primary molecules initially present in the system.

This treatment was accomplished first by Flory (7) and independently by Charlesby (8) and Baskett (9), and the following result was obtained:

$$1 - x = \sum_{n=1}^{\infty} W(n)\left[1 - \alpha x\right]^n \qquad (7)$$

x = fractional weight of gel in the system

α = crosslinking density

W(n) = weight distribution function of the primary molecules

The assumptions used in the derivation are that α is very small ($\ll 1$) and that random statistics apply to the crosslinking process.

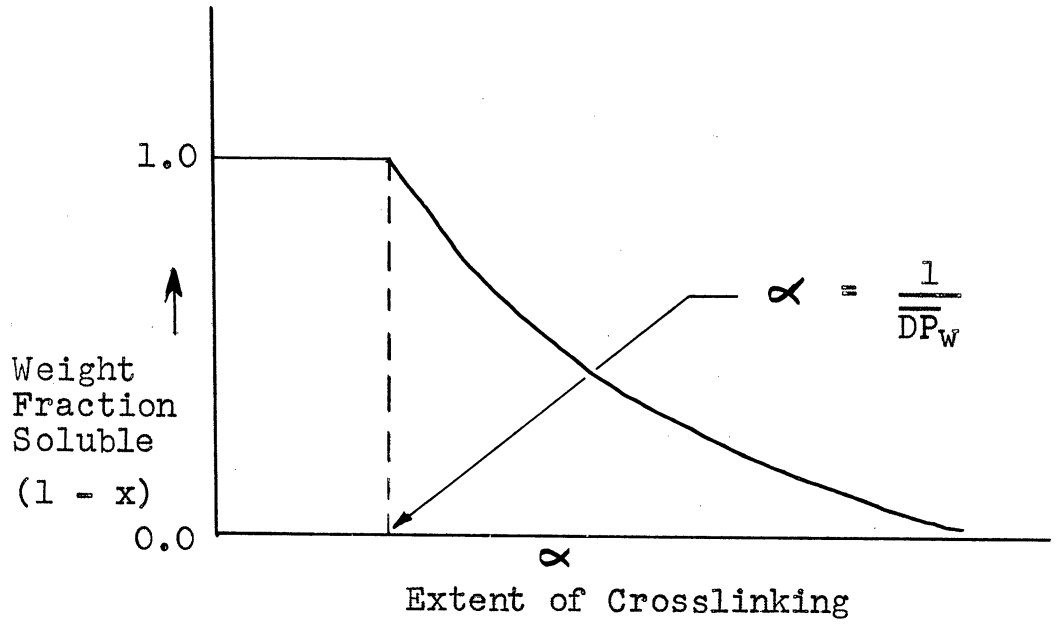
Baskett used the fact that, since αx is very small, $(1 - \alpha x)^n$ is very close to $e^{-\alpha xn}$, and showed that by replacing the summation by integration (treating n as continuous), the following modified LaPlace transform expression is obtained:

$$1 - x = \int_0^\infty W(n) e^{-\alpha xn} \, dn \qquad (8)$$

The important point in the result is that, when crosslinking is random, a selective, albeit statistical, removal of the chains from the soluble portion of the sample according to molecular weight occurs. This forms the basis for the inter-relationship between crosslinking-solubility behavior on one hand, and the primary molecular weight distribution function on the other. It also suggests that the gel curve (gel fraction as a function of crosslinking density, α), will yield information about the primary distribution through inversion of the transform. The sketch on the following page shows a typical gel curve.

2. Crosslinking by High Energy Radiation

It has been found that high polymers in the solid state undergo a number of reactions when exposed to high energy radiation. The initial step is the interaction between the incident high energy electrons or photons and

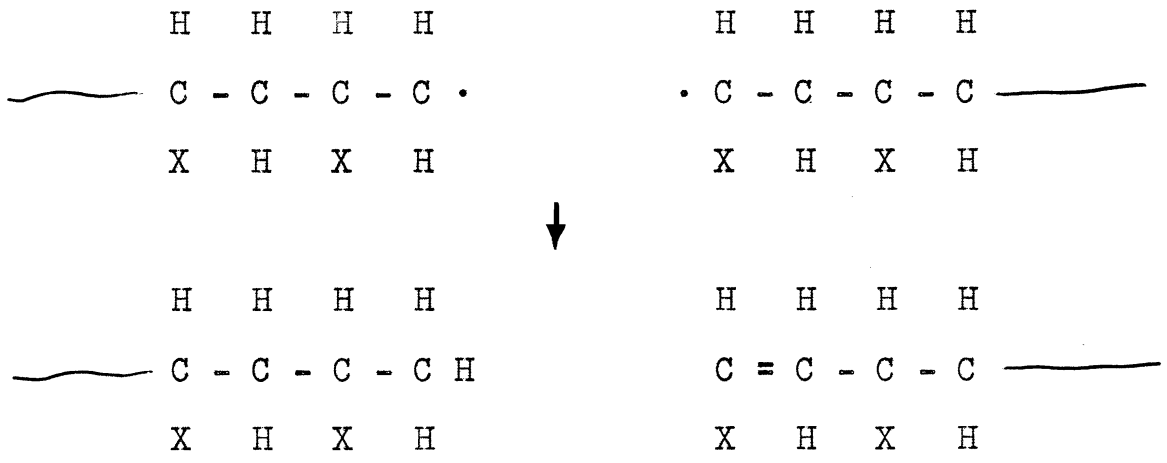


and the electron clouds around the atoms composing the polymer resulting in ionization and disruption of chemical bonds.

In the case of a vinyl type polymer, such as polyethylene, polystrene, or polymethyl methacrylate, these ions quickly decompose to form free radicals which may then undergo a number of reactions. They may be neutralized by a radical acceptor such as oxygen (10). The radical may attack a proton on an adjacent chain producing a chemical bond or crosslink between the chains with the ejection of the proton (11). Alternately, a crosslink may be formed by the mutual reaction between radicals created independently on adjacent chains.

An important parallel reaction, chain scission, is found to accompany crosslinking, whose frequency, compared to crosslinking, varies from polymer to polymer.

As a result of this reaction, permanent main chain (carbon to carbon) fracture occurs. This result is generally thought to involve the opening of a main chain bond by the radiation with the production of a radical on both ends (10). If a simple recombination occurs, no permanent effect results but a second reaction between the radicals, disproportion, is possible in which case the break becomes permanent.



Likewise, if a radical acceptor such as oxygen is present, one or both of the radicals may be neutralized making recombination impossible (10).

Secondary effects, such as hydrogen evolution and various types of unsaturation also can occur and the behavior of a particular polymer with respect to crosslinking and chain scission may range from polymethyl methacrylate where chain scission predominates overwhelmingly (12) to certain silicone materials which undergo only crosslinking (13). In addition there is evidence indicating that certain semi-crystalline polymers undergo

radiation-induced reactions in the crystalline regions at different rates than in the amorphous regions (14). Reference (14) contains a good bibliography to work which has been done in clarifying the mechanisms of reactions occuring during irradiation of polymers in the solid state.

It is postulated that, in the absence of crystallinity effects, the extent of crosslinking and of chain scission will both be proportional to the radiation dose in the range of interest (that is, where the fraction of units participating in crosslinks and the fraction of primary bonds broken is small compared to one). It is further asserted that, since each primary chain is composed of hundreds of thousands of identical repeating units connected by identical bonds, all repeating units and all primary bonds are equivalent with regard to capability for crosslink participation or for chain-scission. These are all physically quite reasonable assumptions.

The attainment of random crosslinking depends not only upon this random disposition of crosslinked units, but also upon a random combination of the two units to form the crosslink. Generally the location of chains in an amorphous solid is presumed to be random with uniform distribution of all molecular weight species throughout the solid. Thus, with regard to crosslinks between repeating units from <u>different</u> adjacent primary molecules, the selection is certainly random. A question arises,

however, concerning crosslinks between units in the same primary molecule. It is possible, and in fact highly probable, that the primary chain, in its tortuous path through the tangled array of chains in the matrix, could "cross" itself many times such that units from the same chain are in a position suitable for crosslinking. This type of intermolecular crosslinking would be sterile, in the sense that it would not contribute to the formation of gel. As long as the proportion of sterile to effective crosslinks is a constant, and not dependent upon the molecular weight of the particular chains, the randomness and proportionality of effective crosslinks to radiation dose is valid.

Within the limitations mentioned then, high energy radiation furnishes a means of systematically adding random crosslinks to a solid polymer system, and as such, has received some attention in recent years as a means of analyzing initial molecular weight distribution through application of the crosslinking-gelation-solubility theories developed in the previous section I-C-1. The fact that random chain scission accompanies the crosslinking requires modification of the gel theory to incorporate this effect into the general formulas relating the gel curve to the distribution function.

3. Modification of Equations to Account for Chain Scission

In analogy with the definition of α, the extent of chain scission, β, is defined as the number of chain

scissions per monomeric unit present in the system. As asserted previously, this process, like crosslinking, is taken to be random in nature all bonds in the system have an equal probability of undergoing fracture (ignoring the possibility, for instance, that the presence of a crosslink in a chain allows the bonds near it to undergo scission more easily). Thus the two processes are uncoupled in the sense that a polymeric system undergoing a certain extent of simultaneous chain scission, β_o, and crosslinking, α_o, would reach the same state of affairs if it first underwent pure scission exclusively to the extent of β_o, and this resulting system subsequently underwent pure crosslinking to the extent of α_o.

It is seen that the effect of the chain scission will be an alteration of the primary molecular weight distribution function. That is to say, the primary molecular weight distribution, or the distribution which would prevail if all the crosslinks were removed, will continually change during the crosslinking process due to the simultaneous random chain scission. This instantaneous primary distribution $W(n,\beta)$ will be a function of the initial primary distribution $W(n,o)$, the structure of the primary molecules, and β, the extent of chain scission. Using the independence of the crosslinking and scission processes, it can be seen that modifying equation 8 by the substitution of $W(n,\beta)$ for $W(n)$ will account completely for the effect of scission

upon the gel curves. The modification of a distribution function by random chain scission has been treated by several authors (15-17) and is, in theory, calculable using random statistics. In practice, tractable expressions are obtained only when the structure of the initial molecules is known. For linear molecules, and for small β , the result is comparatively simple (18):

$$W(n,) = e^{-\beta n}\left\{ W(n,o) + \beta n \sum_{\lambda = n+1}^{\infty} \frac{W(\lambda,o)}{\lambda} \left[2 + \beta(\lambda - n)\right] \right\} \quad (9)$$

Again replacing summation by integration, the final equation relating the initial distribution, gel fraction, and extent of crosslinking and chain scission, obtained by substituting $W(n,\beta)$ into equation 8, is (18):

$$1 - x = \left(\frac{x}{x+\delta}\right)^2 w(s') + \left(\frac{\delta}{x+\delta}\right)^2 + 2\,\frac{\delta x}{(x+\delta)^2}\,\frac{1}{s'}\int_0^{s'} w(\lambda)\,d\lambda \quad (10)$$

where: $\delta = \beta/\alpha$ = chain scission parameter

$$s' = \alpha(x + \delta)$$

$$w(s') = \int_0^{\infty} W(n,o)e^{-s'n}dn$$

It was proposed earlier that high energy radiation produces random crosslinking and chain scission in many solid state polymers in proportion to the total radiation dose. For any particular polymer this implies the existence

of two constants, one a proportionality constant between radiation dose, R, and crosslinking density, α ; the other equal to the chain scission parameter, δ , defined as random chain scissions introduced per crosslinked unit. These constants presumably will be independent of molecular weight and molecular weight distribution.

At this point it is convenient to introduce an alternate expression for the crosslinking present in a system. The definition of the crosslinking density, α , was presented earlier as the fraction of monomeric units present in the system which participate in crosslinks; there being two crosslinked units per crosslink. Another commonly used definition is the crosslinking index, γ , defined by the equation:

$$\gamma = \alpha \overline{DP}_w \qquad (11)$$

Thus the crosslinking index is the number of monomeric units participating in crosslinks per initial weight-average polymer molecule. Note that the criterion for gel formation (equation 8) becomes $\gamma \geq 1$ and that γ is expressable as:

$$\gamma = \frac{\alpha}{\alpha_o} \qquad (12)$$

α_o = crosslinking density at the gel point on the absence of chain scission

γ can then be expressed without the proportionality constant between α and R:

$$\gamma = \frac{R}{R_o} \qquad (13)$$

R_o = radiation dose required to reach the gel point in the absence of chain scission.

Equation 12 may be rewritten in terms of γ and in this way samples with the same type of distribution (equal in all respects except for the chain length parameter) will all yield the same gel curve as a function of γ. Thus expressing equation 12 in this manner:

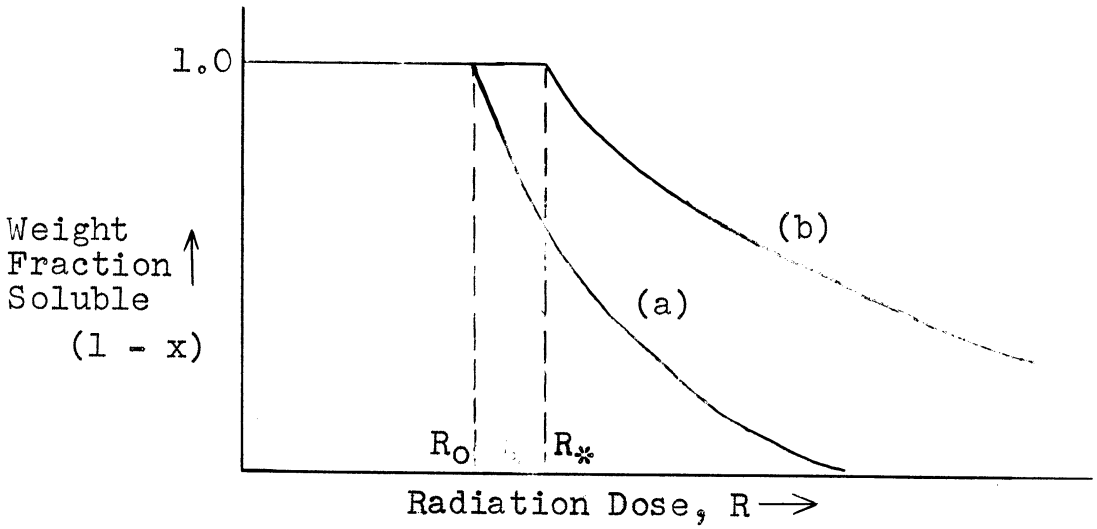
$$1 - x = \left(\frac{x}{x+\delta}\right)^2 w(s) + \left(\frac{\delta}{x+\delta}\right)^2 + \frac{2\delta x}{(x+\delta)^2} \frac{1}{s} \int_o^s w(\lambda) d\lambda \qquad (14)$$

where $$w(s) = \int_o^\infty W(n) \exp\left\{-\frac{sn}{\overline{DP}_w}\right\} dn$$

and where $$s = \gamma(x+\delta) = \frac{R}{R_o}(x+\delta)$$

Since chain scission is occurring during the crosslinking process, then R_o, termed the virtual gel point dose, will be less than R_*, the actual or measured gel point dose. The relation between these two quantities will be covered in a later section. The following sketch shows a relative comparison between a) a gel curve for pure crosslinking by radiation and b) a gel curve on the same sample with simultaneous chain scission.

The experimentally available quantity then is a gel curve such as (b) in the sketch. The crosslinking theory, as culminated by equation 10 or equation 14, defines the relationship of this measurable function to the



initial molecular weight distribution function, W(n); and through these equations, one is presented with a method for determining properties of the distribution such as $\overline{M}_n$, $\overline{M}_w$, and $\overline{M}_z$.

II. EXPERIMENTAL PROCEDURES

A. General Considerations

As stated in the introduction, the object of this study is to investigate the crosslinking-solubility behavior of irradiated polymers to determine the effect of initial molecular weight and, more particularly, initial molecular weight distribution on the gel curves produced. The ultimate goal is the evaluation of this method as a tool to measure distribution, both from the point of view of experimental accuracy and reproducibility, and of interpretability of the results in terms of the distribution. The purpose of this particular section is to outline the general experimental considerations; the following sections will cover each technique in detail.

Broadly speaking, the approach was to choose a suitable polymer for the study, prepare and characterize a number of samples of this polymer with various molecular weight distributions and then to determine gel curve on the samples and compare the results with those predicted from the theory. To this end, a series of samples of polystyrene were prepared in such a manner as to produce in each of them a most-probable or nearly most-probable distribution, each sample having a different average molecular weight. One of these was then fractionated by

partial precipitation to yield a second series of samples possessing different average molecular weights, but with a much narrower distribution than most-probable. Samples having distributions broader than most-probable could then be easily produced by mixing together two samples which have a wide disparity in average molecular weight.

Polystyrene has several characteristics which make it particularly well suited to a study of this kind. In the first place, due to the technological importance of the polymer, polymerization conditions to yield a known product have been thoroughly investigated, such that a polystyrene of almost any desired average molecular weight less than about two million can be easily obtained. It has also been demonstrated (38) that under all but the most severe polymerization conditions, a linear polymer, non-crystalline, thermally stable, and easily soluble in common organic liquids, is produced. Likewise, the solution properties, used to determine average molecular weight, are well known for polystyrene, simplifying the characterization of the samples used in the study. Finally the radiation properties of polystyrene have been investigated somewhat, and crosslinking effects (19, 20, 21), accompanied by chain scission to a lesser extent (12), have been established.

Bulk thermal polymerization, in which pure styrene is induced to polymerize by thermally generated free

radicals, was chosen as the means of polymer formation, since by this technique, in contrast to peroxide or photo-initiation, no foreign atoms are introduced into the polymer chains. As mentioned in section I-B-1 the distribution function to which a polymerized system conforms is directly dependent upon the sequence of reactions by which the polymer molecules grow and cease to grow (terminate). The growth steps, the attack upon a monomer molecule by the free radical on the end of a partially grown chain and the subsequent incorporation of the monomer into the chain, repeated until termination, is common to all types of free radical polymerization. The termination step however may be either by coupling, in which two growing chains join to form a single inactive chain; or by disproportionation in which mutual deactivation of two growing chains occurs without joining. The distinction is important because the latter termination mechanism leads to most-probable distribution ($\overline{M}_w/\overline{M}_n = 2$), whereas the former results in a somewhat narrower distribution ($\overline{M}_w/\overline{M}_n = 1.5$). For most vinyl-type polymers, termination by disproportionation occurs, but a mechanism study of polystyrene (22) seemed to indicate that in this case, both reactions occur, with coupling predominating. This situation would indicate that the resulting distribution would be a rather complex superposition of the two distributions mentioned above.

Measurements performed to determine directly the distribution for thermal polystyrene (23, 24) indicate, however, that it conforms very closely to most-probable distribution; at least, insofar as fractionation data is concerned, deviations from most-probable distribution are difficult to detect, and the ratio, $\overline{M}_w/\overline{M}_n$, is found to range between 1.9 to 2.0. The result is that, although there may be some deviation from most-probable distribution in the case of bulk-polymerized polystyrene, it is small and difficult to detect experimentally.

As a control, the molecular weights of some of the samples were approximated by intrinsic viscosity measurements. Firm values for the molecular weights of all samples used in the study were obtained by light scattering techniques.

All irradiations were carried on in vacuo to eliminate effects due to oxygen (section I-C-2).

Gamma radiation was used for all the irradiations, mainly because of the availability on the campus of a high flux source. It is, however, well suited to a study of this kind because of its high penetrating power. In contrast to high energy electron or deuteron radiation, which decrease in intensity rapidly on passing through matter, the attenuation of a gamma field upon traversing the pyrex irradiation tubes and the films is negligible, and thus the samples are irradiated uniformly throughout their thickness.

Low temperature solvent extraction was used throughout as a means of determining the soluble fraction in the irradiated samples without modifying the solubility behavior by thermal or oxidative degradation. The polymer samples used in the experiments were cast from solution in the form of thin films. The purpose of this is twofold: a high specific surface during evacuation facilitates the removal of oxygen dissolved in the film, and, during the solvent extraction step, diffusion of the soluble polymer out of the gel matrix is also hastened.

B. Polymerization and Characterization of Samples

1. Polymerization Methods

The polystyrene samples used in the experiments came from four sources. One sample, labeled O, was formed by the thermal polymerization of a sample of styrene obtained from the Dow Chemical Company. The polymerization was carried on at room temperature over a period of several years, and although the bottle was unopened, no particular precautions were observed concerning oxygen or inhibitors present. Before use, it was precipitated twice from methyl ethyl ketone solution using methanol.

The samples labeled A, 53TH, 65TH, and 75TH were obtained by the thermal polymerization of styrene at elevated temperatures with suitable precautions as to impurities. Styrene, 99.6% pure, obtained from Union Carbide Corp., was vacuum distilled (40 mm Hg, 60°C) in

an all-glass still through a 20" column of glass helices. A precondensor was used to control the reflux. After operating at total reflux for about 30 minutes, the styrene was allowed to distill over at a rate of 300 cc per hour with a reflux ratio of approximately ten. The first quarter of the distillate was discarded and the succeeding two quarters were collected in suitable receivers as purified styrene with a boiling range of approximately 0.1°C.

The styrene was further treated by degassing prior to polymerization. The receivers from the distillation were connected to a vacuum line and given a slight preliminary pump down. The styrene was then cooled by a dry ice - isopropyl alcohol mixture to its freezing point and the gasses above the crystallizing liquid - solid mixture were pumped out by the vacuum system (liquid air - trapped mercury diffusion pump with mechanical fore-pump). The crystals of frozen styrene formed nucleation sites for the dissolved gases which bubbled out of the mixture rapidly. When this procedure caused no more bubbling, the container was sealed off under vacuum and stored in a deep freeze at -20°C, prior to polymerization.

The polymerization was carried on by placing the container in a stirred water bath maintained at the desired temperature. After the time necessary to cause 10-15% conversion of styrene to polymer, the container was removed from the bath, opened, and the contents poured with rapid stirring into an excess of methanol, miscible with

styrene but causing the polymer formed to precipitate. The polymer was then redissolved in methyl-ethyl ketone and reprecipitated by adding the solution dropwise to a stirred excess of methanol. The polymer was finally removed into fresh methanol, allowed to stand overnight and then air dried at room temperature for several days. In final form the polymer was fluffy and pure white.

For one sample, labeled 1-B, the monomer was purified in the same manner as described above, but a photoinitiator, azo-bis-isobutyryl-nitrile (ABBN), was added to a concentration of 3.0×10^{-4} moles per liter, and the monomer was photopolymerized at 25°C by using a mercury vapor light, placed at a suitable distance from the polymerization tube.

The sample labeled D-2 was a narrow-distribution polystyrene sample ($\bar{M}_w/\bar{M}_n = 1.04$) obtained through the courtesy of the Dow Chemical Company.

Polymerization Data

Sample	Type of Polymerization	Polymerization Temperature	Polymerization Time	Conversion
A	Thermal	60°C	160 hr.	17.0%
53TH	"	53°C	265 hr.	15.0%
65TH	"	65°C	94.5 hr.	15.5%
75TH	"	75°C	40.5 hr.	13.5%
1-B	Photo	25°C	165 hr.	11.5%
O	Thermal	Room Temp.	5 years	80-90

2. Fractionation

The fractionation procedure used in this investigation as a means of obtaining a series of narrow molecular

weight distribution samples is the partial precipitation method described in section I-B-2-b.

Two hundred grams of sample A polystyrene were dissolved in approximately 18 liters of commercial grade methyl ethyl ketone contained in a large pyrex container suspended in a water bath maintained at 34.3 ± .01°C. Sufficient methanol was added to bring the system to the point of precipitation (about 4 liters) and then a slight excess was added dropwise, with stirring, causing the solution to become increasingly cloudy. When the turbidity indicated that 10-20 grams of polymer had separated, addition of the methanol was stopped and the bath temperature was raised several degrees to redissolve this second phase. The bath temperature was then allowed to cool slowly back to the original temperature so that, with continued stirring, the phase separation would occur under nearly equilibrium conditions. With the initial temperature re-established, the stirrer was turned off and the polymer-rich second phase allowed to settle overnight. After settling, the supernatant phase was siphoned off and the lower phase, containing the fraction, was removed, re-dissolved in methyl ethyl ketone, and precipitated in an excess of methanol. The supernatant liquid was then replaced in the bath, a fresh increment of methanol added, and a new fraction obtained. This process was repeated until the initial polymer had been divided into ten primary fractions.

The volume of solution was maintained at between 20 and 22 liters during most of the process, and hence the concentration of polymer at precipitation ranged from an initial value of 0.9 gm per 100 cc. for the first fraction down to less than 0.5 gm per 100 cc. in the later fractions. Since the efficiency of fractionation is enhanced by lowering the polymer concentration, the sharpness of the cuts should improve for the later fractions.

In order to obtain narrower distribution samples, several of the primary fractions were subjected to refractionation, and five of the resulting samples were used in the crosslinking study.

The first two secondary fractions from primary fraction number two, totaling 11 grams in weight, were found to possess the same intrinsic viscosity. They were recombined and fractionated into three tertiary fractions, the middle tertiary fraction being labeled F-22.

Samples F-32 and F-33 represent the second and third secondary fractions respectively of primary fraction three.

Sample F-50 is the fifth primary fraction, not refractionated.

Sample F-61 is the first secondary fraction of primary fraction number six.

The weights of these samples are in the following table:

Sample	Yield (grams)
F-22	7.1
F-32	3.5
F-33	3.0
F-50	13.7
F-61	6.1

3. Intrinsic Viscosity Measurements

The relationship between dilute solution viscosity and average molecular weight is a well-known property of polymers, and is commonly used as a quick and convenient means of approximating molecular weight for control purposes.

It is found that the viscosity-weight concentration relationship is represented fairly well by the following equation for dilute solutions.

$$\frac{1}{c}\left[\frac{\eta}{\eta_o} - 1\right] = [\eta] + k'[\eta]^2 c \qquad (15)$$

η = solution viscosity

η_o = solvent viscosity

c = solution concentration

k' = a constant of polymer-solvent system, independent of $[\eta]$

$[\eta]$ = intrinsic viscosity

The value of $[\eta]$ for linear polymers, and for a given solvent and temperature, has been found to be related to the molecular weight of the polymer by the relation:

$$[\eta] = K M^a \tag{16}$$

K and a are constants, characteristic of the polymer-solvent system. For polystyrene these constants are known for a number of different solvents, so that a measurement of $[\eta]$ for a sample allows estimation of its molecular weight. For a polydisperse system, the molecular weight obtained is the so-called viscosity average, involving the exponent a;

$$\bar{M}_V = \left[\int_0^\infty m^a W(m)\,dm\right]^{1/a} \tag{17}$$

The viscosity measurements were made at 34.8°C using reagent grade cyclohexane as solvent. A modified Ubbelohde suspended-level viscometer, manufactured by Canadian Laboratory Supplies, Ltd., Montreal, Quebec, according to a design developed at the Polymer Corporation, Sarnia, Ontario, was used in all the experiments.

Standard methods were used to obtain solution viscosities and to treat the results to obtain intrinsic viscosity, see reference 25 for instance. The intrinsic viscosities were converted to viscosity-average molecular weights by (26, 27):

$$[\eta] = 8.1 \times 10^{-4} (\bar{M}_V)^{\frac{1}{2}} \tag{18}$$

For samples with most-probable distribution, the ratio of weight-average to viscosity-average molecular weight depends upon the viscosity exponent. In this case,

where the exponent is 0.5, the ratio of 1.20, and hence for this distribution weight-average molecular weight may be estimated. For samples of narrower distribution this ratio approaches 1.0. The following table contains the resulting data.

Sample	$[\eta]$ $\frac{dl}{gm}$	$\bar{M}_v \times 10^{-6}$	$\bar{M}_w \times 10^{-6}$ (est.)
0	1.73	4.55	5.45
53TH	1.07	1.74	2.08
A	1.00	1.52	1.82
1-B	0.903	1.24	1.49
65TH	0.952	1.36	1.63
75TH	0.805	0.985	1.18
F-50	1.035	1.63	----
F-32	1.215	2.25	----
F-33	1.200	2.19	----

4. Light-scattering

Light scattering measurements were performed on all samples used in the crosslinking studies. The purpose was to measure the weight-average molecular weight, $\bar{M}_w$, of each sample, and, for the samples prepared by fractionation, to obtain some information on molecular weight distribution.

The scattering measurements were performed with a Brice-Phoenix light scattering photometer, model number 1410, using monochromatic light with wave length 4360A isolated from a mercury vapor lamp. The characteristics of the photometer, along with the calibration of the photometer and scattering cell are described in the photometer manual (28), and in two publications (25, 29).

Reagent-grade benzene was used as solvent for all light-scattering runs. Stock solutions were prepared by dissolving the polymer in benzene to the desired concentration. To eliminate scattering due to dust, the solvent and solutions were filtered through sintered glass, then centrifuged at 20,000 g. in a Servall angle centrifuge for about three hours. After centrifugation, they were removed carefully by hypodermic syringes, preparatory to being added to the scattering cell.

For each sample, galvanometer readings were recorded for the scattering intensity with pure solvent and with four concentrations of solution. The angles measured were 28, 30, 45, 60, 75, 90, 105, 120, and 135 degrees. In addition, a measurement of primary beam intensity was made at the exit to the cell and recorded as zero angle intensity. Measurement on pure solvent was for the purpose of obtaining the background scattering which must be subtracted from the solution scattering values, and also as a means of testing for the presence of dust. Benzene-polystyrene solutions, being quite non-polar, are relatively easy to obtain dust free by centrifugation. Solvent dissymmetry, defined as the ratio of scattering intensity at 45° to that at 135° and equal to 1.0 for completely dust-free solvent, was seldom greater than 1.02 and never greater than 1.03.

After the pure solvent scattering envelope was determined, small aliquots of the stock solution were added

to the solvent in the cell, the cell being weighed before and after each addition. The scattering envelope was obtained for each concentration and the last concentration in the cell was determined by evaporation to dryness of a measured portion of the residual solution, which allowed calculation of the other concentrations from the weighings.

Standard light scattering procedures were used to correct the galvanometer readings for filter transmittance, for modifications to the observed intensity due to internal cell reflections, for background (solvent) scattering, for changes in the scattering volume with angle, and for an angular effect sometimes known as the unpolarized light correction. These corrections are covered in detail in one of the references (25).

The resulting data was analysed using the method of Zimm (4), by which a double extrapolation plot is constructed, allowing calculation of the weight-average molecular weight, $\overline{M}_w$. This same plot allows the measurement of other quantities relating to the polymer. The second virial coefficient, A_2, relating to solvent-polymer interaction energy, results, as well as a quantity, $\overline{S}_z^2$, the z-average mean-square radius of gyration of the polymer molecules in solution.

In addition, under the proper conditions it is possible to analyse the scattering behavior of the polymer to obtain information on the distribution. Curve fitting

methods (30, 31) have been developed wherein measured scattering curves are compared with scattering properties of a theoretical sample with various model distributions (equation 5). In theory the proper choice of the breadth parameter, Z, allows superposition of the scattering curves. In practice the scattering is somewhat insensitive to distribution, and, in terms of determining distribution, the method is only semi-quantitative at best. Only three values of Z have been considered for the samples in this study. A Z of one corresponds to most-probable distribution ($\bar{M}_w/\bar{M}_n = 2$), a Z of four corresponds to a narrower distribution ($\bar{M}_w/\bar{M}_n = 1.2$), and a Z of 19 corresponds to a very narrow distribution ($\bar{M}_w/\bar{M}_n = 1.05$). Due to measurement errors, limitations in the theory, and insensitivity, further refinement was not deemed worthwhile.

The values obtained for $\bar{M}_w$, $\bar{A}_2$, $\bar{S}_z^2$, and Z are listed in the following table.

Light Scattering Data

Sample	$\bar{M}_w \times 10^{-6}$	$S_z^2 \times 10^{-6}$ (cm^2)	$A_2 \times 10^2$ $\frac{cm^3}{mole\text{-}gm}$	Z
0	4.93	2.43	2.98	1
53TH	2.05	0.932	3.98	1
A	1.75	0.709	3.52	1
1-B	1.52	0.587	3.52	1
65TH	1.44	0.604	2.98	1
75TH	1.15	0.451	4.47	1
F-22	3.36	1.34	3.10	4
F-32	2.69	0.919	3.07	4
F-33	2.42	0.787	3.22	19
F-50	1.82	0.619	3.75	4
F-61	1.77	0.539	3.53	19
D-2	0.226	0.064	4.25	--

The validity of these data were checked by comparing $\overline{S}_z^2$ and A_2 with values obtained by other investigators using polystyrene in benzene. They check very well with values obtained by Manson (32), and also with a value by Wall (33). The dependence of $\overline{S}_z^2$ on $\overline{M}_w$ should be related to the intrinsic viscosity exponent (see equation 18) for the polystyrene-benzene system (34). The data yield a value of 0.75 compared to literature values of 0.715 (35), 0.72 (36), 0.73 (37), and 0.85 (29). The values of Z for the fractions correspond reasonably well to what might be expected on the basis of the fractionation procedure; that is, F-50, being a primary fraction is relatively broader than F-61, a secondary fraction; and F-22 and F-32, being higher molecular weight and coming from relatively concentrated precipitating solution, are not overly narrow in spite of being tertiary and secondary fractions respectively. Finally, the molecular weights agreed very closely with those found by sedimentation measurements or those computed from the intrinsic viscosity. (Table 8 contains a comparison of $\overline{M}_w$ obtained by the three methods.)

5. Formulation of Mixtures Used

To extend the range of distribution breadths investigated, two mixtures were prepared. For one, M-0, equal portions of two most-probable distribution samples, samples 0 and 75TH, were dissolved in benzene and the resulting 3% solution was allowed to mix on a paint roller for three days. Results cast some doubt on the ability of

this method to produce the random mixing on a molecular scale necessary, so mixture M-1 was prepared, constitutionally identical to M-0 but using a 0.75% benzene mixing solution and rolled for ten days.

The other mixture, M-2, was prepared from equal proportions of fractions F-32 and D-2, mixed as a 2% solution for eight days. (The lower chain lengths of this mixture's constituents alleviate this random mixing problem since the shorter chains untangle more rapidly in solution.)

The various average molecular weights for a mixture can be calculated from the average molecular weights of the components of the mixture. For equal weight proportions of two components, a and b, the equations are:

$$\bar{M}_n = \frac{2}{\frac{1}{(\bar{M}_n)_a} + \frac{1}{(\bar{M}_n)_b}}$$

$$\bar{M}_w = \frac{(\bar{M}_w)_a + (\bar{M}_w)_b}{2}$$

$$\bar{M}_z = \frac{(\bar{M}_z)_a(\bar{M}_w)_a + (\bar{M}_z)_b(\bar{M}_w)_b}{(\bar{M}_w)_a + (\bar{M}_w)_b}$$

These formulas follow directly from the definitions of the various averages and the linear mixing law property of distributions (see section I-B-1).

For application to mixture M-1, the various average molecular weights were computed using $\overline{M}_w$ for samples 0 and 75TH from light scattering measurements and assuming a most-probable distribution for each. For the mixture M-2, the molecular weights of sample D-2 were estimated from the light scattering $\overline{M}_w$ and from average molecular weight ratios obtained from the sedimentation measurements (see Table 8). For sample F-32, they were estimated from the light scattering $\overline{M}_w$ and the breadth parameter Z, also obtained from the light scattering. The computed molecular weights for M-1 and M-2 are listed in Table 8.

C. Crosslinking-Solubility Measurements

1. Film Casting

Samples suitable for irradiation and extraction were prepared as follows: The polymer was dissolved in a solvent (reagent grade benzene in almost all cases) to form about a 4% solution. This solution was then pulled by vacuum slowly through a coarse sintered glass filter to remove dust and then poured onto the freshly cleaned surface of mercury contained in a pyrex dish. The dish was covered, allowing the solution to spread itself uniformly over the surface,

and then the cover was shimmed up slightly to allow slow evaporation of the solvent. The formation of the solid film generally required two to four days. (More rapid evaporation of solvent caused wrinkling and a rough-surfaced, non-uniform film.)

The resultant films, ranging in thickness from two to three mils except in special cases, peeled away from the sides of the container easily, were of reasonably uniform thickness ($\pm$0.3 mil), and were smooth, clear, colorless, stiff but not to brittle and almost completely dust-free. They were then cut into small sheets approximately 2" x 3", weighing roughly 200 mgms.

2. Evacuation

The films to be irradiated were rolled up and placed, generally in pairs, inside pyrex tubes. A short pyrex tube, having a 10/30 ₸ joint at one end, and containing a seal-off joint, was sealed on the open end of the tube containing the films and the entire assembly was placed on a vacuum line manifold and exhausted by a liquid nitrogen-trapped mercury diffusion pump with a mechanical forepump, capable of vacuums the order of 10^{-6} mm. of mercury.

Oxygen has a considerable effect upon the radiation properties of polymers, presumably through its

radical acceptor characteristics (12, 39). This should be particularly true under the conditions of thin polymer films and the relatively low dose rates used in these experiments, since oxygen reactions in polymers are apparently diffusion controlled (39). For this reason, a series of experiments were carried on to determine the evacuation time required to reduce the amount of oxygen present in the tube and dissolved in the films below the level where it has measurable effects on the solubility characteristics of the polymer. The results of these experiments are summarized in the following table:

Polymer-Sample 0, Irradiation Dose - 15.1×10^6 reps. Casting Solvent - Benzene

Dose Rate - 0.9×10^6 reps/hour

Evacuation Time (hours)	Soluble Fraction
0.00	1.000
0.25	0.397
1.0	0.414
6.0	0.390
21.0	0.386
68.5	0.381
168.3	0.380

From these results it is apparent that, although even very short evacuation times lead to a high insoluble fraction, evacuations the order of three days to a week are required to reach a steady value.

In view of the above effect, all samples used in these experiments were subjected to a total evacuation

time ranging from six to eight days. As an added precaution, the tubes were heated twice during the evacuation, usually on the second and third days, to approximately 70°C for about an hour to aid in the removal of adsorbed and absorbed gases and traces of the casting solvent. After this treatment and subsequent cooling to room temperature, the tubes showed no discharge with a Tesla coil, indicating a pressure of less than 10^{-3} mm. of mercury. After completion the samples were sealed off under vacuum at a pressure of less than 10^{-5} mm. of mercury.

3. Irradiation Techniques

The high energy radiation for all the experimental work in this investigation was supplied by a cobalt-60 gamma source. The source, located in the Phoenix Memorial Laboratory on the north campus of the University, consists of 5000±300 curies of cobalt-60. The source material is in the form of cylinders of cobalt metal, each weighing 7.1 grams, incased in an aluminum sheath 1/16" thick. There are 350 such slugs in the source arrangement. The slugs are placed, ten per tube, in 35 aluminum tubes approximately 12" long, and these "pencils" of cobalt are positioned in a hollow cylindrical arrangement with an inside diameter of four inches.

This source assembly is on an elevator which allows it to be moved between the radiation cave and a

water well below, into which the source is lowered when entry into the cave is desired for placing samples.

Two types of measurements are possible as a means of determining the effect of a particular radiation source on matter. Since the effect is directly related to the energy dissipation within matter, one method is to determine, by various means, the energy dissipated in the material of interest during irradiation. Another, much more common method, is to calibrate the source of radiation by the energy dissipation in some standard material, and to use this as a measure of the field intensity.

Units have been devised to define quantity of radiation for various uses. The roentgen (r) is that quantity of gamma radiation which dissipates 83 ergs in a gram of air. The roentgen-equivalent-physical (rep) is that quantity of radiation which dissipates 93 ergs in a gram of living tissue, about the same amount as produced by one roentgen of gamma rays. A third unit used frequently is the rad, which is the amount of radiation required to produce 100 ergs per gram of material.

The standard unit of measure in this laboratory for defining gamma field intensity or dose rate is rep per hour. The doses rates prevailing around the outside of the source and within the source center were measured by members of the Phoenix Laboratory staff using ferrous-ferric dosimetry as described by Weiss (40).

Except for a series of experiments to determine the effect of dose rate on the results, all irradiations were carried on in the center of the source. This has several advantages. For one, this is the region of maximum dose rate, so that shorter irradiation times are required here than outside the center. Even more important, the center of the source affords a region of very uniform dose rate both radially and longitudinally with respect to the cobalt cylinder. By placing the evacuated irradiation tubes so that the rolled up films are located near the source center line and symmetrically about its midplace, reproducible dose rates with a variation of less than 1% over the films are easily attained.

Exposure times are measured by an electric timer connected, through a relay, to the elevator such that time is recorded only when the source elevator is "up" and actual irradiation of the samples is taking place. There is an additional increment of radiation not recorded on the clock, occurring while the source is being raised and lowered and amounting to 2670 reps in the source center. Compared to the total doses given the samples, this correction was negligible and was omitted in all calculations.

At the time of installation in May, 1958, the dose rate in the source center at midplace was 0.91×10^6 rep per hour. This dose rate decreases slowly with time (about 12% per year) due to the Cobalt-60 half life of

of 5.3 years and must be accounted for in the calculation of total dose for runs performed on dates after May, 1958.

Some evidence has been found for the presence of reactive species long after irradiation has ceased (14,41, 42). It is thought that this is caused by free radicals trapped in the solid polymer matrix. Due to the relative immobility of the chain segments in most solid polymers, diffusion of segments bearing the free radicals into positions which allow mutual deactivation is slow, and these species can persist for long periods of time.

To test the effect of this phenomenon on the measured solubility, three tubes of films were irradiated with equal doses. For one set (a) the tube was opened for extraction in benzene 24 hours after completion of the irradiation, the second set (b) was heated in its tube for 24 hours at 100°C and then opened for extraction, the third set (c) was allowed to set for one week at room temperature, then opened for extraction. The results are in the following table:

Sample - A, Radiation Dose - 39.4×10^6 reps

Set	Soluble Fraction	Treatment
a	0.373	24 hour holdup
b	0.366	24 hour holdup and heat treatment
c	0.352, 0.352	1 week holdup

The effect is seen to be small, but by no means negligible. Subsequent experiments indicated that the

soluble fraction given by set c checked well with samples allowed to "age" for a month or more. On this basis, irradiated samples were allowed to age in the evacuated tubes for at least a week, and generally for two weeks or more, before extraction.

4. Solvent Extraction Methods

After removal from the irradiation tube, the films were weighed to the nearest tenth of a milligram and immediately placed in a tube containing approximately 100 cc. of extraction solvent, reagent grade benzene, except in special cases. These extraction tubes were suspended in a water bath maintained at a temperature of 35±1°C. The supernatant liquid contained extracted soluble material was poured off about once a day and replaced with either fresh reagent grade solvent or reagent grade solvent from previous extractions, distilled to remove dissolved polymer.

After several days, when the extraction of soluble material was felt to be almost complete, an aliquot of the supernatant liquid was tested for dissolved polymer by adding to an excess of methanol. The methanol, being a non-solvent for polystyrene, causes any dissolved polymer to precipitate and form a bluish haze in the mixture. The limit of detectability of polymer was found to be about 0.3 mg. per 100 cc. of benzene. When this haze was found to be absent, the supernatant liquid was changed once more, the system allowed to set for two days, and

then retested. If the result was again negative, the extraction was adjudged complete and the extracted film ready for isolation and weighing. Since generally there were two films from each irradiation tube, the extraction was tested further for completeness by continuing the extraction of one film two or three days longer than the other and comparing the resulting gel fraction from each. The results verified that within the precision of measurement, the added extractions produce no effect.

The insoluble material, present in the form of a swollen gel was isolated by being poured into an excess of methanol, which serves the dual purpose of leaching out the extraction solvent and yielding the insoluble material as a white, stiff, coherent mass, a convenient form for handling, drying, and weighing. The material was then placed in an aluminum foil dish and dried overnight at 100°C in a vacuum oven. Longer drying times were found to produce no further weight change in the solid. The material was then allowed to cool in a controlled temperature-humidity room and weighed to the nearest tenth of a milligram.

The above procedure was quite satisfactory for films in which the soluble fraction is about 55% or less. Extraction of films with higher solubles content yielded gel structures which were highly swollen and extremely fragile and which tend to break up into a number of small fragments under the slightest provocation.

Since these gels have imbibed large amounts of solvent, they have net densities very near the solvent itself and tend to be easily dispersed throughout the extraction tube, causing repeated removal of the supernatant liquid, and thereby of the soluble material present, to be difficult. (As the sol content decreases, the gel structure is more tightly bound and mechanically much more stable.)

Several methods were tried to overcome the drawback of gel instability and breakup. In the first, the swollen gel was poured into a weighed ceramic Soxhlet-type extraction thimble. The thimble was placed in an empty covered beaker and the excess solvent allowed to drain out. Due to the "gooey" nature of the high sol-content gels, the pores in the thimble quickly became plugged and generally a waiting period of up to 24 hours was necessary before fresh solvent could be poured into the thimble. This process was repeated until the drained liquid tested negative for dissolved polymer. The thimble and contents were then vacuum dried and weighed to determine the residual solid.

Another method used the same procedure as above with a stainless steel or copper wire basket of various meshes in place of the ceramic thimble in an attempt to avoid plugging and to allow free passage of the solvent through and out of the gel network.

A third method was to place the film directly in a 400 cc beaker filled with solvent at room temperature.

Due to the larger diameter of the beaker compared to the tube, the slightly higher density of the gel allowed it to fall to the bottom of the beaker so that most of the supernatant liquid could be poured off and replaced once a day with a minimum of mechanical disturbance to the gel.

The ceramic thimble method not only required inconveniently long times (three to four weeks) but gave values for the gel fraction which were consistently too high. Subsequent investigation showed that there was an adsorption of the soluble molecules on the ceramic surface which was difficult to remove even with prolonged soaking in pure solvent. The wire baskets, while being more permeable to solvent, had the unfortunate characteristic of allowing passage of small fragments of gel, even for the finest meshes used (200 mesh).

The beaker method was by far the most satisfactory, and allowed unambiguous measurement of gel content for films having as high as 98% solubles present.

Presumably, for doses below the gel point, the film should be completely soluble. That is to say, although the average molecular weight has increased, the crosslinking density is not sufficient to form the macroscopic network required for insolubility. In several instances, samples with doses less than R_* (as deduced by extrapolating the main body of the gel curve) apparently were not completely soluble, and had an entirely different appearance from other swollen gels. Whereas the usual gel

for high solubility films was clear and highly swollen to the point of being almost invisible in the extraction solvent, this insoluble matter was opaque and only slightly swollen. This effect did not occur with all sub-gel point samples and was quite irregular. (For instance it occurred for sample A at a dose of 13.1 megareps, but not for a dose of 13.4 megareps; and for sample 65TH with a dose of 14.0 megareps, it was observed for one film in the set of two, but not for the other.) In all cases the weight of this insoluble matter amounted to less than 1% of the total weight, and because of its irregular and anomalous character, was neglected in the computation of solubility.

III. PRESENTATION OF SOLUBILITY DATA

The solubilities obtained for all samples used in this study, computed as fractional weight loss upon extraction, are listed, together with the corresponding radiation dosages in megareps, in the following tables. The distribution information determined from these data by methods to be described in the next section, is listed in Tables 9 and 10 in the appendix.

The preparation and characterization information on all the samples used in the study, listed under the previous headings of polymerization, fractionation, mixture preparation, light scattering, and intrinsic viscosity; are summarized for convenience in Table 8 in the appendix. Also included in Table 8 is molecular weight distribution information on selected samples, obtained by Dr. H. W. McCormick using ultracentrifuge-sedimentation techniques.

The solubility data for the samples with most-probable distribution (53TH, 65TH, 75TH, 1-B, A, 0) are listed in Table 1. Table 2 contains the same data for the narrow distribution fractions (F-22, F-33, F-50, F-61), while Table 3 contains the solubility data on the broad distribution mixtures (M-1, M-2). Tables 4-7 contain solubility data obtained during isolated experiments

on certain incidental variables of interest, such as a) dose rate, b) film thickness, c) film casting solvent, and d) extraction solvent. The purpose and results of these experiments are described in a later section (IV-E).

TABLE 1

SOLUBILITY DATA FOR SAMPLES WITH MOST PROBABLE DISTRIBUTION

Film Casting Solvent - Benzene

Extraction Solvent - Benzene

Dose Rate - 0.8-0.9 Megareps/hour

Film Thickness - 2-3 mils

Sample	Radiation Dose in Megareps	Soluble Fraction
1-B	24.0	0.795
	25.5	0.638, 0.625
	34.8	0.435
	36.9	0.419, 0.400, 0.427
	44.8	0.363, 0.374
	59.5	0.279, 0.262
	55.9	0.280, 0.296, 0.282
	71.5	0.244, 0.243
	89.9	0.207, 0.207
	127.6	0.154, 0.145
53TH	20.4	0.577, 0.572
	25.5	0.461, 0.468
	29.4	0.395, 0.398
	33.8	0.354, 0.357
	51.7	0.240, 0.245
	55.5	0.250, 0.261
	91.9	0.156, 0.161
	131.0	0.128, 0.133
75TH	14.0	1.000, 1.000
	26.8	0.670, 0.669
	38.0	0.502, 0.512
	59.5	0.321, 0.324
	78.4	0.246, 0.250
	83.7	0.252
	115.8	0.190, 0.194
	142.8	0.157, 0.158
	145.7	0.164, 0.168
65TH	14.0	1.000, 1.000
	26.8	0.575, 0.562
	29.9	0.525, 0.535
	43.0	0.371, 0.385
	49.9	0.350
	73.4	0.245, 0.242
	79.5	0.215, 0.221
	97.9	0.196, 0.196
	141.1	0.162, 0.156
	142.8	0.145, 0.148
0	8.22	0.583, 0.597
	10.2	0.490, 0.506
	11.6	0.429, 0.425
	14.0	0.409, 0.424
	16.0	0.375, 0.384
	16.3	0.342, 0.342
	27.1	0.261, 0.258
	50.5	0.189, 0.193
	82.4	0.168, 0.169
A	13.1	1.000, 1.000
	13.4	1.000, 1.000
	20.6	0.610, 0.613
	21.7	0.615, 0.605
	25.5	0.566, 0.573
	26.2	0.513, 0.505
	33.7	0.409, 0.408
	33.8	0.441, 0.441
	39.4	0.352, 0.352
	39.8	0.333, 0.338
	41.3	0.342, 0.339
	75.0	0.218, 0.223
	79.5	0.217, 0.212
	81.0	0.245, 0.257
	89.0	0.186, 0.184
	131.2	0.161, 0.161

TABLE 2

SOLUBILITY DATA ON NARROW DISTRIBUTION FRACTIONS

Film Casting Solvent - Benzene

Extraction Solvent - Benzene

Dose Rate - 0.8-0.9 megareps/hour

Film Thickness - 2-4 Mils

Sample	Radiation Dose (Megareps)	Soluble Fraction
F-22	6.48	0.937
	7.38	0.785
	8.12	0.700
	9.58	0.561
	10.22	0.562
	10.51	0.515
	13.04	0.384
	14.03	0.372
	16.02	0.321
	16.16	0.307
	20.32	0.228
	26.73	0.190
	39.93	0.143
	73.49	0.114
	91.52	0.111
	116.37	0.102
F-50	14.06	0.932
	16.34	0.756, 0.760
	17.69	0.672
	21.97	0.508, 0.498
	27.06	0.401, 0.401
	35.58	0.298, 0.298
	49.85	0.220, 0.218
	78.69	0.158, 0.160
	142.81	0.111, 0.113

Sample	Radiation Dose (Megareps)	Soluble Fraction
F-33	8.18	1.000
	9.76	0.885
	11.89	0.640
	11.92	0.682
	13.18	0.571
	15.61	0.458
	15.86	0.446
	16.28	0.449
	20.57	0.342
	26.15	0.257
	26.20	0.271
	33.71	0.212
	40.85	0.171
	41.26	0.184
	74.97	0.126
	79.53	0.117
F-61	12.58	0.978
	16.03	0.643
	19.44	0.495
	26.15	0.326
	39.81	0.201
	111.94	0.109
	141.09	0.104

TABLE 3

SOLUBILITY DATA ON BROAD DISTRIBUTION MIXTURES

Film Casting Solvent - Benzene

Extraction Solvent - Benzene

Dose Rate - 0.8-0.9 Megareps/hour

Film Thickness - 2-3 Mils

Sample	Radiation Dose (Megareps)	Soluble Fraction
M-0	11.17	0.711, 0.705
	13.32	0.641
	16.87	0.557, 0.562
	21.22	0.478, 0.493
	27.30	0.402, 0.405
	40.62	0.313, 0.316
	54.84	0.250, 0.252
	99.26	0.170, 0.174
	116.37	0.172, 0.171
M-1	8.18	0.973, 0.958
	10.86	0.740, 0.748
	13.42	0.655, 0.659
	16.74	0.570, 0.571
	20.35	0.511, 0.506
	26.55	0.417, 0.421
	39.32	0.311, 0.316
	73.62	0.209, 0.206
	133.30	0.152, 0.146
M-2	23.41	0.884, 0.884
	29.21	0.743, 0.755
	38.06	0.620, 0.628
	51.29	0.526, 0.521
	67.64	0.457, 0.462
	73.49	0.427, 0.429
	82.36	0.396, 0.398
	116.37	0.306, 0.309
	142.81	0.254, 0.256
	281.70	0.149, 0.150

TABLE 4

EXTRACTION SOLVENT STUDY - FIRST SERIES

Sample Used - 53TH

Film Casting Solvent - Benzene

Film Thickness - 2.5 Mils

Dose Rate - 0.8 Megareps/hour

Soluble Fraction in:

Radiation Dose in Megareps	Benzene	Toluene	Cyclohexane	Methyl Ethyl Ketone
16.0	0.787	0.781	---	1.000
19.4	0.627	0.605	---	0.802
26.2	0.457	0.457	---	0.600
39.8	0.318	0.306	0.313	0.406
111.9	0.147	0.148	0.144	0.183

TABLE 5

FILM THICKNESS STUDY AND EXTRACTION SOLVENT STUDY - SECOND SERIES

Sample Used - 53TH

Film Casting Solvent - Benzene

Film Thickness - 7 Mils

Dose Rate - 0.8 Megareps/hour

Soluble Fraction in:

Radiation Dose (Megareps)	Benzene	Methyl Ethyl Ketone
16.7	0.738	0.813
20.4	0.608	0.691
26.6	0.456	0.503
39.3	0.322	0.358
121.4	0.150	0.168

TABLE 6

FILM CASTING SOLVENT STUDY

Sample Used - A

Film Casting Solvent - Methyl Ethyl Ketone

Film Thickness - 2.5 Mils

Dose Rate - 0.8 Megareps/hour

Extraction Solvent - Benzene

Radiation Dose (Megareps)	Soluble Fraction
20.0	0.851
27.1	0.621
39.7	0.423, 0.426
78.7	0.243, 0.240

TABLE 7

DOSE RATE STUDY

Sample Used - A

Film Casting Solvent - Benzene

Extraction Solvent - Benzene

Film Thickness - 2.5 Mils

Dose Rate - 0.091 Megareps/hour

Radiation Dose (Megareps)	Soluble Fraction
38.3	0.382, 0.387
42.6	0.331, 0.336
56.4	0.258
84.3	0.210, 0.207
175.9	0.135, 0.134

IV. TREATMENT OF DATA

A. Methods of Interpretation

Several general approaches are possible for determining the applicability of random crosslinking-solubility theories to the evaluation of molecular weight distribution. In the first place, the theories are based on very few physical assumptions and are merely the statistical consequences of these assumptions. Hence, if one could demonstrate with certainty that high energy radiation induces truly random crosslinking and chain scission, in proportion to the radiation dose, and that amorphous polymer systems are truly randomly mixed, then all the results of the random statistics analysis must follow, and the theory is "true". These assumptions are much too general to be tested directly, and thus it is necessary to investigate their consequences, such as equations 10 and 14, as to how well the predicted interrelationship between initial molecular weight distribution and solubility properties holds. There is also the question of experimental measurement of the solubility properties and whether precision sufficient for meaningful interpretation of the results in terms of initial distribution is attainable.

The most clear cut method available in theory would be to first measure the gel curve for a sample with known distribution. Equation 10 would then be inverted to express the initial distribution function, W(n) as a function of the gel curve, $x(\alpha, \delta)$. The point-by-point distribution would then be calculated from the measured gel curve and compared to the known distribution. The complexity and non-linearity of equation 10 makes even analytical inversion extremely formidable. This, together with the fact that graphical inversion of LaPlace transform-like equations require experimentally prohibitive accuracy (43), makes this method inapplicable. Generally speaking, all hope of obtaining a graphical distribution function from a graphical gel curve must be abandoned, but, as will be seen, this does not at all eliminate the possibility of obtaining useful information on the properties of the distribution from the gel curve.

Two other techniques are available for accessing the validity and accuracy of the theory. One is to produce samples whose distribution is known by an analytical expression. With the aid of separate measurements to determine the parameters required, the gel curves are calculated from equations 10 or 14 compared with the resulting experimental gel curves. Samples with most-probable distribution yield relatively simple expressions and are well suited for analysis of this sort.

This method is difficult to use in most cases, however, because of the lack of a precise analytical expression (the fractions, for instance), or because the complexity of equation 14 makes the required calculations cumbersome.

A more satisfactory approach, at least for developing methods to determine properties of unknown distributions, is to analyse equation 14 to determine the connection between the properties of an arbitrary distribution and measurable properties of the resultant gel curves, such as limiting slopes and intercepts. It will be shown that, in spite of the apparent complexity of equation 14, some rather simple relationships hold, either approximately or exactly, between ratios of different average molecular weights ($\overline{M}_w/\overline{M}_n$, $\overline{M}_z/\overline{M}_w$) in the initial distribution, and certain properties of the resultant gel curve.

The two procedures used in this study to interpret the results can be summarized as follows. Where simplicity allows it, the form of the gel curve will be predicted (equation 14) from a prior knowledge of the distribution (most-probable distribution samples) and the parameters in the gel equation will be adjusted to see if the theory and results are consistent. The second procedure will seek to interpret the analytical properties of the gel curves (limiting slopes, intercepts, etc.) in terms of average molecular weight ratios in the fractions and mixtures used. The criterion will be the reasonableness of

the resulting values in view of these approximately known distributions.

The succeeding portions of this section will outline in detail the considerations which eventually lead to an interpretation of a gel curve in terms of initial molecular weight distribution, independent of all other information. Early experiments and interpretation on samples with most-probable distribution are described; and, in an effort to measure δ , the chain scission parameter, a useful method for displaying the solubility data is developed. By means of this plot, and through proper consideration of equation 14, the solubility data for the fractions and mixtures are interpreted to give $\overline{M}_w/\overline{M}_n$ and $\overline{M}_z/\overline{M}_n$. The gel point, corrected for the effects of chain scission, is shown to be related to initial weight average molecular weight as gelation theory would predict. Gel swelling results are presented as an independent means for evaluating the crosslinking efficiency of the radiation, and the effect of incidental variables such as radiation dose rate, film casting and extraction solvent, and film thickness.

B. Analysis of Most-Probable Distribution Samples

1. Chain Scission Parameter

The early experiments in this investigation were performed on samples of polystyrene with most-probable

distribution. The gel curve expression predicted from equation 14 for this distribution is the following:

$$1 - x = \left[\frac{2 + \gamma\delta}{2 + \gamma(x + \delta)}\right] = \left[\frac{2 + \frac{R\delta}{R_o}}{2 + \frac{R}{R_o}(x + \delta)}\right]^2 \qquad (19)$$

A plog of log (soluble fraction) versus log (radiation dose) was prepared for the experimental data. By the proper choice of R_o and δ in equation 19, it was possible to get a good fit between calculated and experimental gel curves. Values for these parameters, however, have a certain amount of arbitrariness by this method and thus it seemed worthwhile to look for new ways to evaluate them.

It can be seen that, for δ equal to zero in equation 19, the soluble fraction, 1 - x, approaches zero for large crosslinking densities. It has been shown that, for δ not zero, there is a limiting soluble fraction, the magnitude of which is dependent only upon the value for this chain scission parameter (18):

$$1 - x_\infty + (1 - x_\infty)^{\frac{1}{2}} = \delta \qquad (20)$$

$1 - x_\infty$ = limiting soluble fraction

Therefore, for systems in which δ is less than two, a measurement of this limiting soluble fraction will allow direct calculation of the chain scission parameter. (For systems where δ is greater than two, gel will never

occur at any crosslinking density, and the entire method is inapplicable.)

One way to evaluate the limiting soluble fraction is to perform solubility measurements for various values of R and then extrapolate the results to infinite radiation dose. With this idea in mind, equation 19 was re-examined to see if the data could be plotted in such a manner as to allow linear extrapolation to infinite dose (for instances, to 1/R equal to zero). Rearrangement of equation 19 yields the following useful equation:

$$1 - x + (1 - x)^{\frac{1}{2}} = 2\frac{R_o}{R} + \delta \qquad (21)$$

This form predicts a straight line for gel measurements from a most-probable distribution sample if the data is plotted as $(1 - x) + (1 - x)^{\frac{1}{2}}$ against 1/R. Besides allowing a more direct determination of the parameters, δ and R_o, this predicted straight line form also allows a somewhat more objective judgement as to how well the data fit the theory (that is, how well a straight line represents the data). The extreme usefulness of this type of plot in the analysis of gel curves from samples with distributions other than most-probable will become apparent in the next section.

This straight line form was found to represent the data very well for all most-probable distribution samples investigated in this study. For examples, see Figs. 1 and 2. The values of δ obtained for each sample are

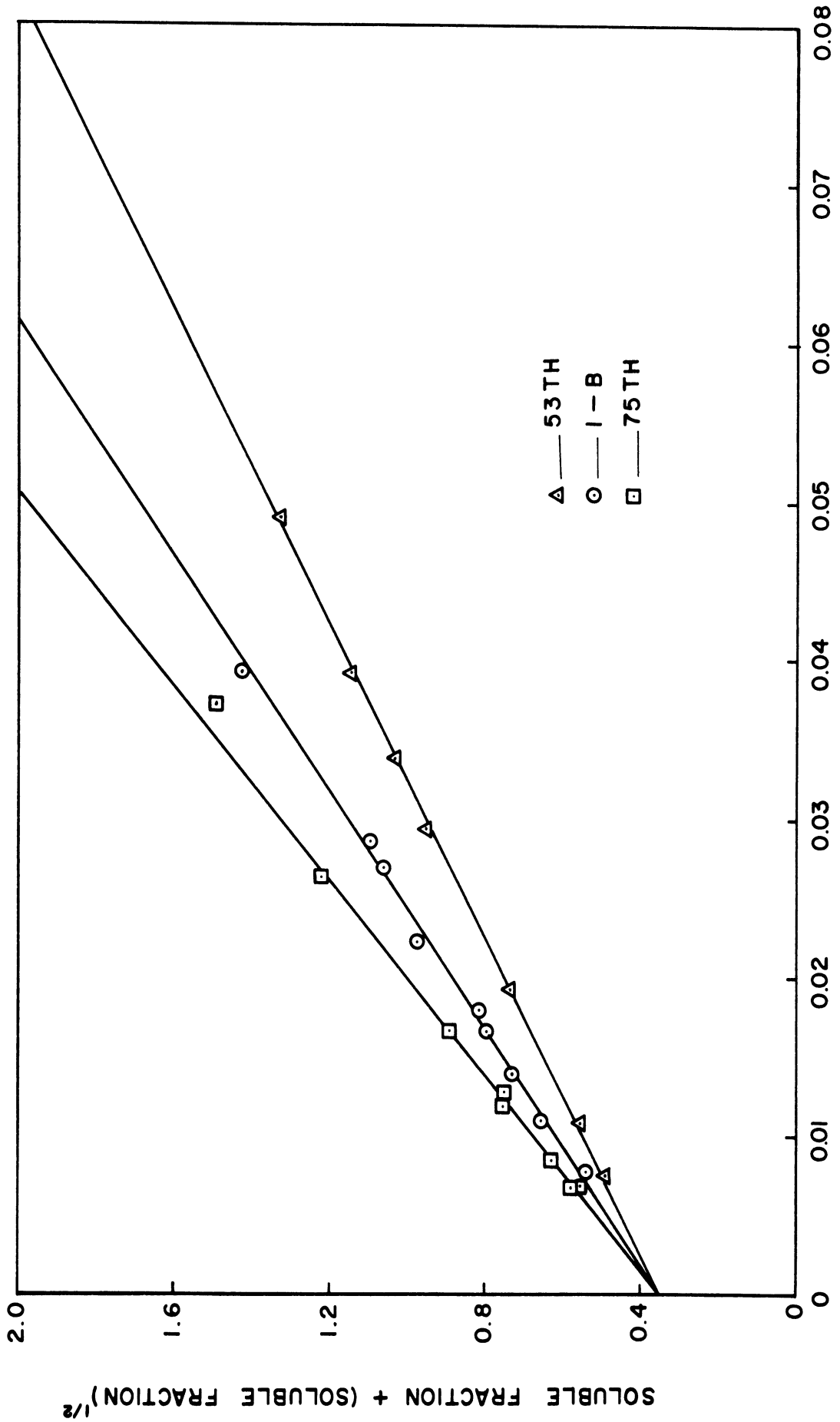


Figure 1. Gel Curves for Some Representative Most-Probable Distribution Samples.

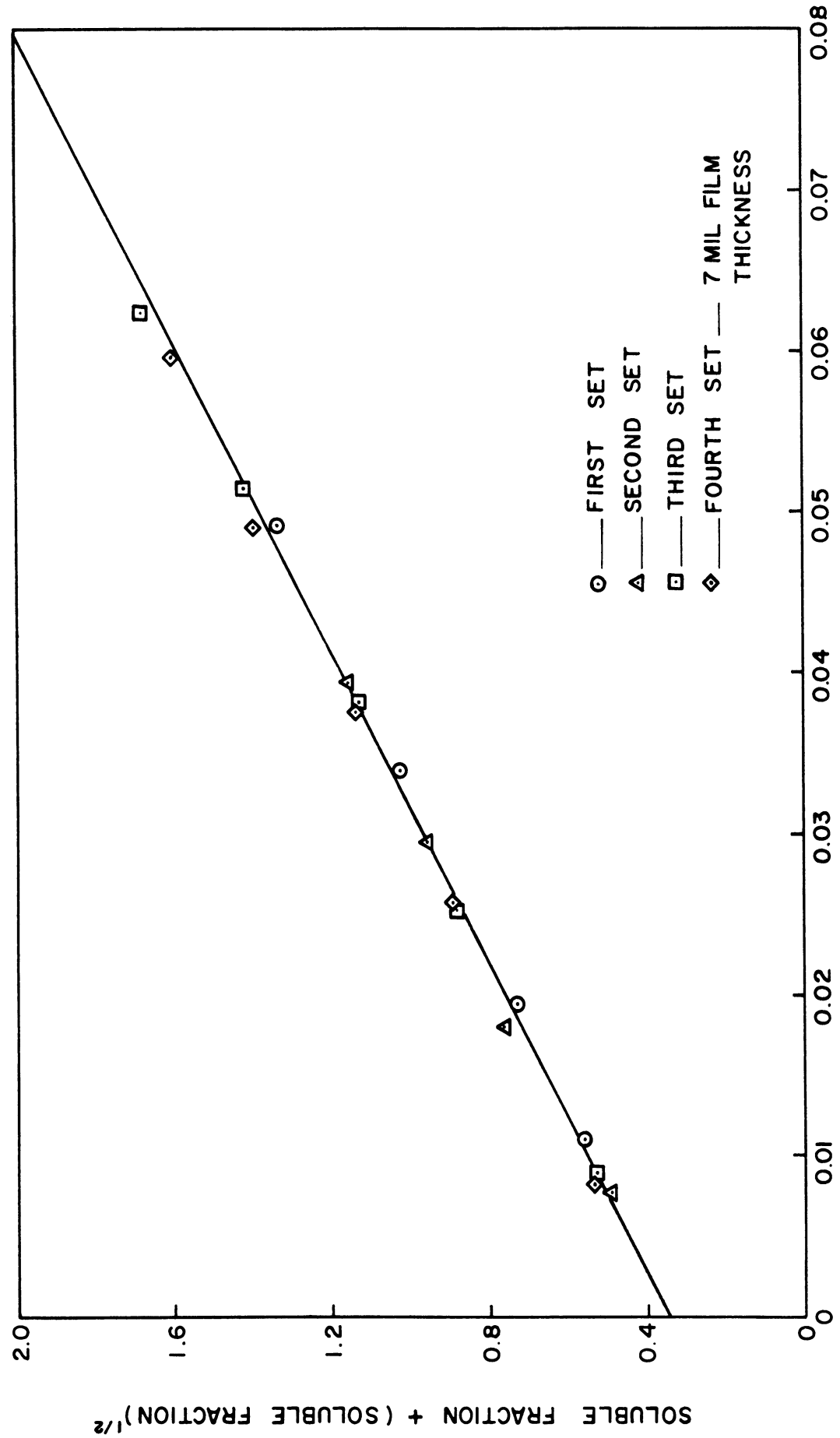


Figure 2. Composite Gel Curve for Most-Probable Distribution Sample 53th, from Several Different Runs.

listed in Table 9. For five of the six samples having most-probable distribution, δ ranges from 0.34 - 0.38, the "0" sample giving a value of 0.49. This anomaly may be due to the lack of precautions taken during polymerization of this sample (see section II-B-1) causing it to be partially oxidized and more susceptible to chain scission. The observed range for δ in polystyrene is in excellent agreement with the value of 0.35 found by Shultz (12), although somewhat higher than the range 0.0 - 0.2 found by Charlesby (19).

Another method for the measurement of the chain scission parameter has been suggested and used in the case of polyethylene (9). A sample is irradiated to produce gel and the soluble material is extracted. Portions of this sample, now totally insoluble, are re-irradiated and thereby, the limiting solubility is approached from the total insolubility side. Measurements of this type were attempted in this study but apparently some degradation of the gel structure occurred during the post-extraction drying since, even without re-irradiation, re-extraction of the supposed totally insoluble material produced an appreciable new soluble fraction.

2. Virtual Gel Point Dose Parameter

The slope of the straight lines obtained for most-probable distributions samples is equal to two times the virtual gel point dosage, R_o. In the absence of chain scission, the crosslinking density required to reach the

gel point, α_o, is equal to $1/\overline{DP}_w$ (equation 6). Since α is presumed to be proportional to the radiation dose, then the product, $\overline{M}_w R_o$, should be a constant. This quantity, computed from the light scattering results and the gel curve slope for each sample is satisfactorily constant and is listed in Table 9 along with R_o.

Thus, the data for the most-probable distribution samples is in good agreement with the three predictions of the theory: a straight line representation for the individual gel curves, the relative constancy of δ determined from various samples, and the correlation of R_o with $\overline{M}_w$.

C. Analysis of Fractions and Mixtures

1. Limiting Behavior of Gel Curves for High Doses

It is well known that under the influence of random chain scission, any initial molecular weight distribution will approach most-probable distribution (17). The primary distribution prevailing during the irradiation-crosslinking process, that is, the distribution which would prevail in the absence of the crosslinks, is undergoing just such a process due to the simultaneously occurring chain scission. Hence for extents of irradiation such that the average number of chain scissions per initial polymer molecule is becoming large compared to one, and yet for which β is still much less than one ($1/\overline{DP}_n \ll \beta \ll 1$), the primary distribution prevailing is approaching

most-probable distribution. This implies that, when plotted as $(1 - x) + (1 - x)^{\frac{1}{2}}$ against $1/R$, all gel curves must approach straight line behavior for sufficiently high irradiation dose, R, irrespective of initial distribution.

For most-probable distribution polymers, where the plot is linear over the entire range of solubility (equation 21), the slope of the line is $2R_o$. It seemed possible that the slope of the limiting straight line for an arbitrary initial distribution might be some simple function of the initial distribution. It can be shown (Appendix A-1) that this is true and the form of the limiting straight line is:

$$1 - x + (1 - x)^{\frac{1}{2}} = \frac{\bar{M}_w}{\bar{M}_n} \frac{R_o}{R} + \delta \qquad (22)$$

where $\bar{M}_w$, $\bar{M}_n$ are the average molecular weights of the initial distribution, and, as before, R_o is the dose required to reach the gel point for the sample with this initial distribution, in the absence of chain scission. The implication is that, if R_o could be determined by some means, then a measurement of this limiting slope would yield directly the ratio of weight to number average molecular weight for a specimen. Recently, Charlesby (44) has derived a result equivalent to equation 22, and applied it in another context.

The range of solubility where this limiting behavior becomes controlling depends upon the magnitude of the chain

scission parameter, and upon the initial distribution to some extent. Gel curves for model distributions, calculated from equation 14 and plotted in this manner, indicate that, for δ equal to 0.35, doses much less than ten times the gel point dosage should be sufficient to produce solubilities lying close to the asymptotic straight line for most distributions.

2. Evaluation of the Virtual Gel Point Dosage, R_o.

The evaluation of R_o requires examination of the gel curve near the measured gel point of the system, R_*. As was mentioned previously, the occurrence of chain scission causes the actual gel point to be displaced to higher doses than would be observed in the absence of chain scission. The ratio R_*/R_o will depend in general upon the magnitude of δ, and also the initial distribution for the sample. For samples with most-probable distribution, for example, the relation is obtained by setting x equal to zero in equation 21:

$$\frac{R_*}{R_o} = \frac{1}{1 - \delta/2} \qquad (23)$$

It can be shown that, for arbitrary but not too broad a distribution and for moderate values of δ, the general effect for linear polymers is approximated by (appendix A-2):

$$\frac{R_*}{R_o} = \frac{1}{1 - \frac{\bar{M}_z}{\bar{M}_w}\frac{\delta}{3}} \qquad (24)$$

where $\bar{M}_Z$ and $\bar{M}_W$ are average molecular weights for the initial distribution. This equation is exact for most-probable distribution samples; in fact, it fits very well for a wide range of distributions. Since R_* is a measurable quantity, R_o is readily obtained if the initial distribution of the sample is known. However, the method is to be applied to samples whose distribution is not known, so it is necessary to find an alternate means for evaluating $\bar{M}_Z/\bar{M}_W$ which depends only on the properties of the experimental gel curve itself.

In an early paper (8), Charlesby pointed out that, for the case of no chain scission, the initial rate of gel formation is directly related to $\bar{M}_Z/\bar{M}_W$ for the primary chains:

$$\frac{dx}{dR} = \frac{2\,R_o}{(\bar{M}_Z/\bar{M}_W)} \qquad (25)$$

This suggests that the slope of the gel curve at the gel point, S_o, on a plot of $(1 - x) \div (1 - x)^{\frac{1}{2}}$ against $1/R$, might be capable of yielding this ratio of $\bar{M}_Z/\bar{M}_W$ if suitable account can be taken of the effects of chain scission. This is indeed true, and the result (see appendix A-3), should hold approximately for linear polymers with arbitrary (but not too broad) distribution and for small δ :

$$\frac{\bar{M}_Z}{\bar{M}_W} = \frac{3\,R_o}{S_o}\left\{1 + \frac{R_*\delta}{S_o}\left[\frac{3}{2}\,\frac{\bar{M}_{Z+1}}{\bar{M}_{Z+1}} - 2\right]\right\} \qquad (26)$$

S_o = slope at the gel point of a plot of $(1 - x) \div (1 - x)^{\frac{1}{2}}$ vs. $1/R$.

Since the correction due to chain scission is small, then for the purpose of equation 24, the effect may be ignored to give the following simple result:

$$\frac{\bar{M}_z}{\bar{M}_w} = \frac{3R_o}{S_o} \tag{27}$$

Making use of this last approximation and equation 24, the expression for R_o becomes:

$$R_o = \frac{1}{\frac{1}{R_*} + \frac{\delta}{S_o}} \tag{28}$$

3. Evaluation of $\bar{M}_w/\bar{M}_n$ and $\bar{M}_z/\bar{M}_w$

Using equations 22 and 28, $\bar{M}_w/\bar{M}_n$ can be written in terms of only the measurable properties of the gel curve: R_*, δ , S_o, and S_∞ (the limiting slope of the gel curve for high dose).

$$\frac{\bar{M}_w}{\bar{M}_n} = \frac{S_\infty}{R_*} + \delta\left(\frac{S_\infty}{S_o}\right) \tag{29}$$

The error in this expression due to the approximations introduced in the derivation of equation 27 should be small due to the relative insensitivity of R_o, computed from equation 24, to $(\bar{M}_z/\bar{M}_w)$.

Equation 26 may be used in a similar way to calculate the ratio $\bar{M}_z/\bar{M}_w$ for the initial sample, subject to the choice of a value for the ratio M_{z+1}/M_z appearing. Generally speaking, the ratios, $\bar{M}_w/\bar{M}_n$, $\bar{M}_z/\bar{M}_w$, $\bar{M}_{z+1}/\bar{M}_z$, etc., form a sequence which behaves in a systematic manner

so that, having a firm value for $\overline{M}_w/\overline{M}_n$ from equation 29 and an approximate value for $\overline{M}_z/\overline{M}_w$ from equation 27, one can "guess" a value for $\overline{M}_{z+1}/\overline{M}_z$ and use it to calculate a better approximation for $\overline{M}_z/\overline{M}_w$ from equation 26. Just as equation 24 is somewhat insensitive to the choice of $\overline{M}_z/\overline{M}_w$, so equation 26 is likewise insensitive to the choice of $\overline{M}_{z+1}/\overline{M}_z$. A sample calculation of $\overline{M}_w/\overline{M}_n$ and $\overline{M}_z/\overline{M}_w$ for sample F-22 is given in the appendix.

In summary, one determines points on a gel curve for a linear sample with arbitrary (within certain limits) distribution and these data are plotted in the form $(1 - x) + (1 - x)^{\frac{1}{2}}$ versus $1/R$. The quantities, δ, R_*, S_o, and S_∞, are measured from the properties of the curve, and using equations 26 and 29, two properties of the initial distribution, $(\overline{M}_w/\overline{M}_n)$ and $(\overline{M}_z/\overline{M}_w)$, are calculated. The necessary restrictions on these formulas are that the initial chains are linear, that the distribution is not too broad, and that δ is not too large.

4. Treatment of Data

The gel curves for the four fractions (F-22, F-33, F-50, F-61) and the two mixtures (M-1, M-2) were plotted in the prescribed manner (Figures 3-8). As predicted by the preceding arguments and found in model gel curves computed from equation 14, the data on the fractions show an upward curvature, characteristic of samples with distributions narrower than most-probable. The mixtures, on the other hand, show the concave downward type of curvature

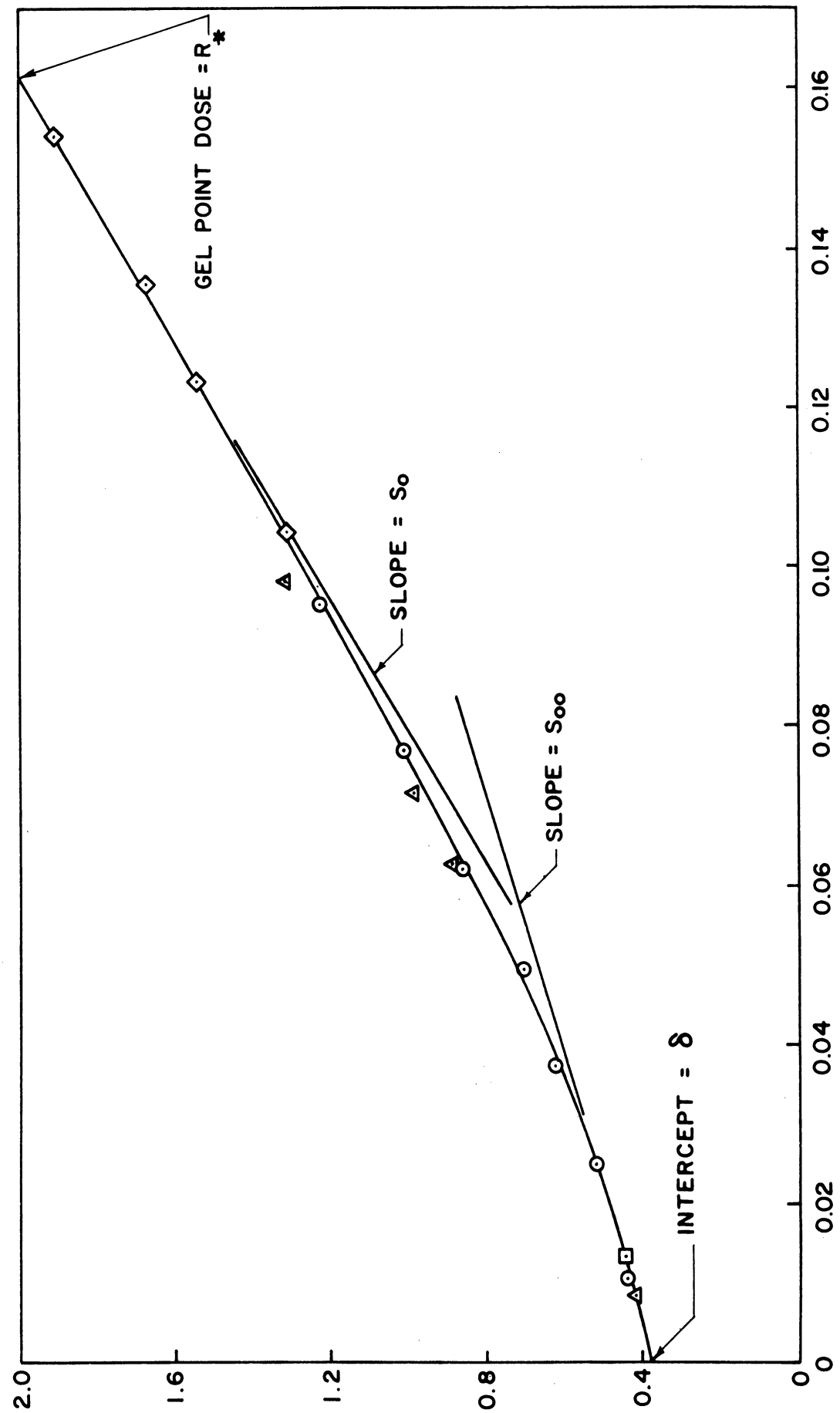


Figure 3. Gel Curve for Narrow Distribution Tertiary Fraction, F-22.

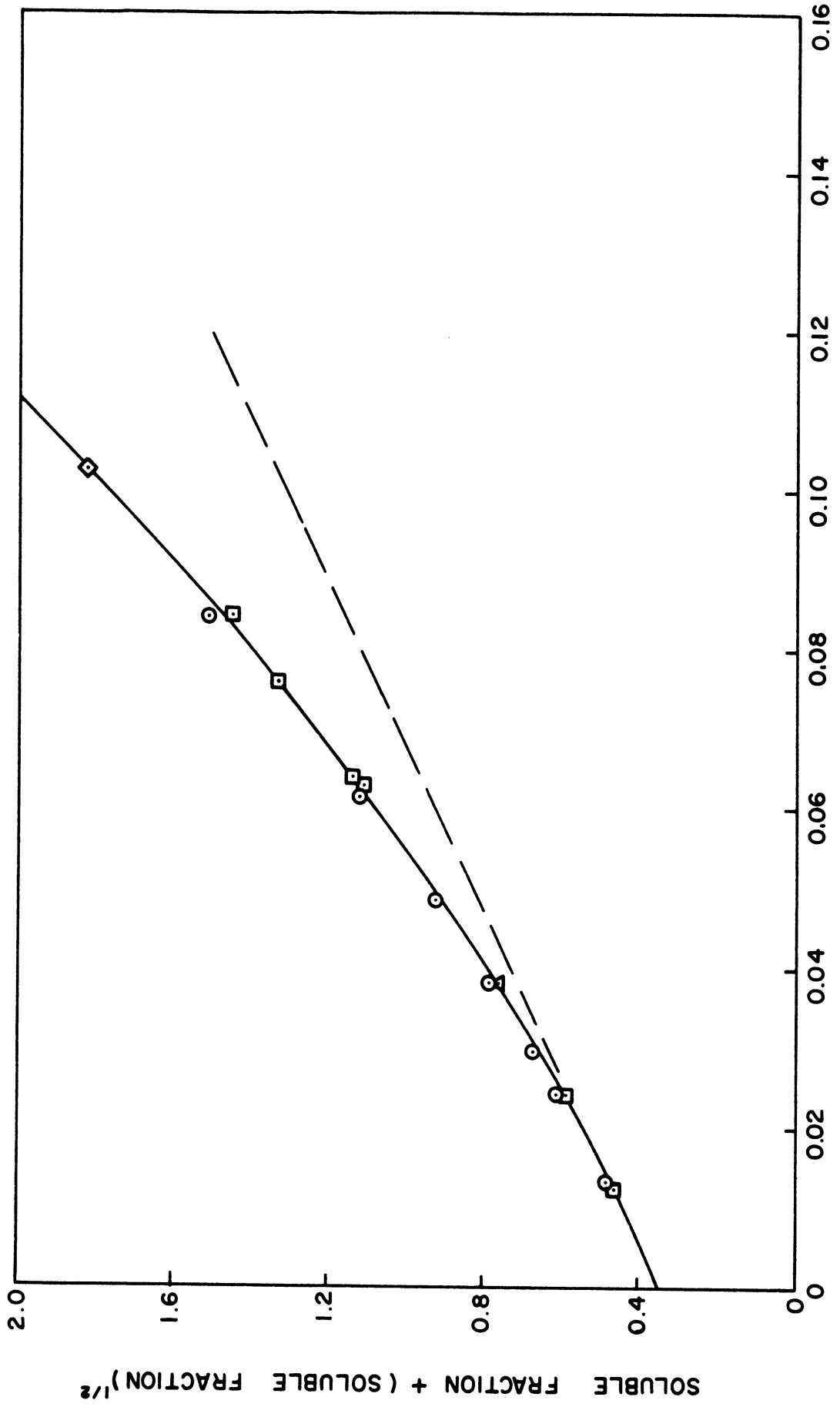


Figure 4. Gel Curve for Narrow Distribution Secondary Fraction, F-33.

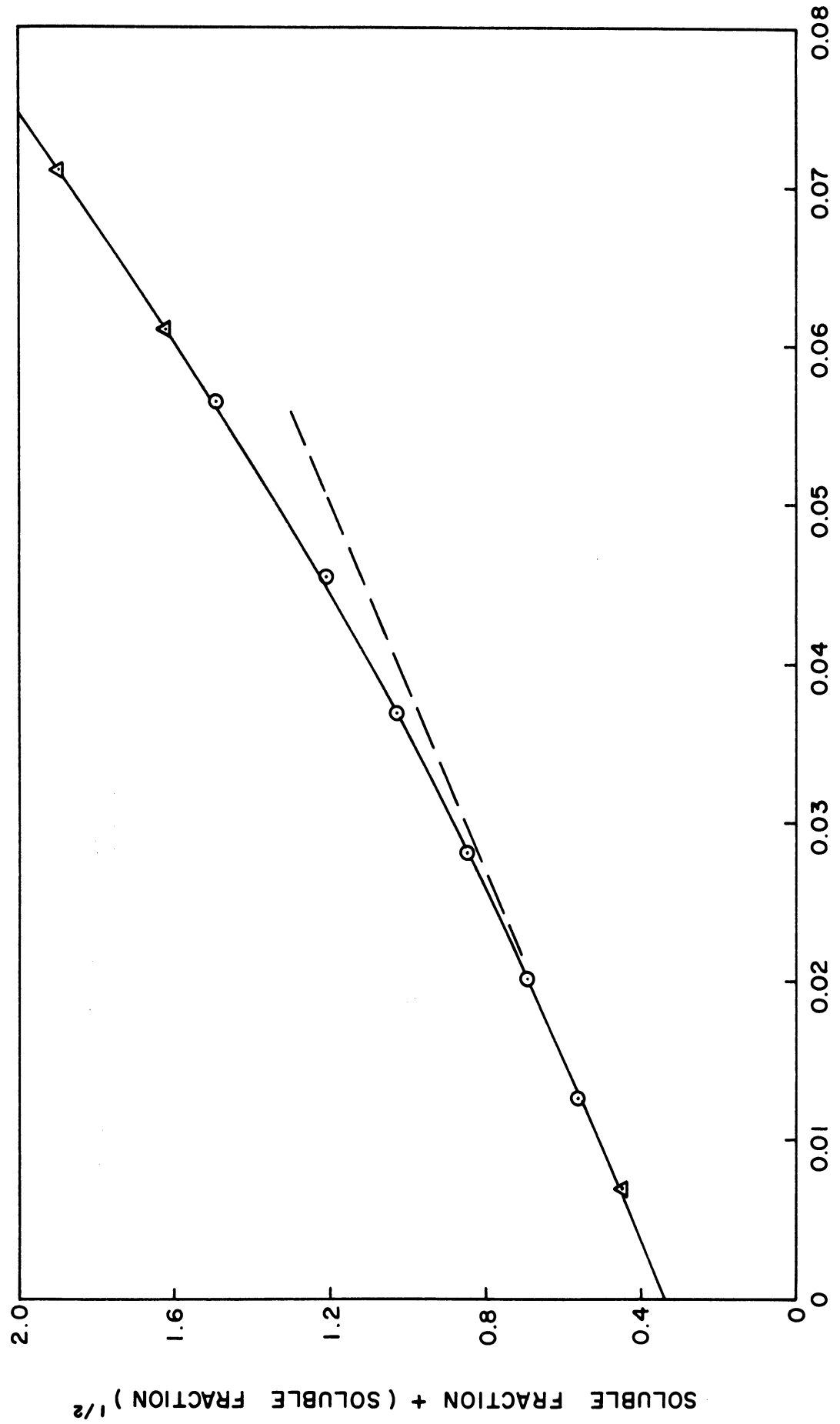


Figure 5. Gel Curve for Narrow Distribution, Primary Fraction, F-50.

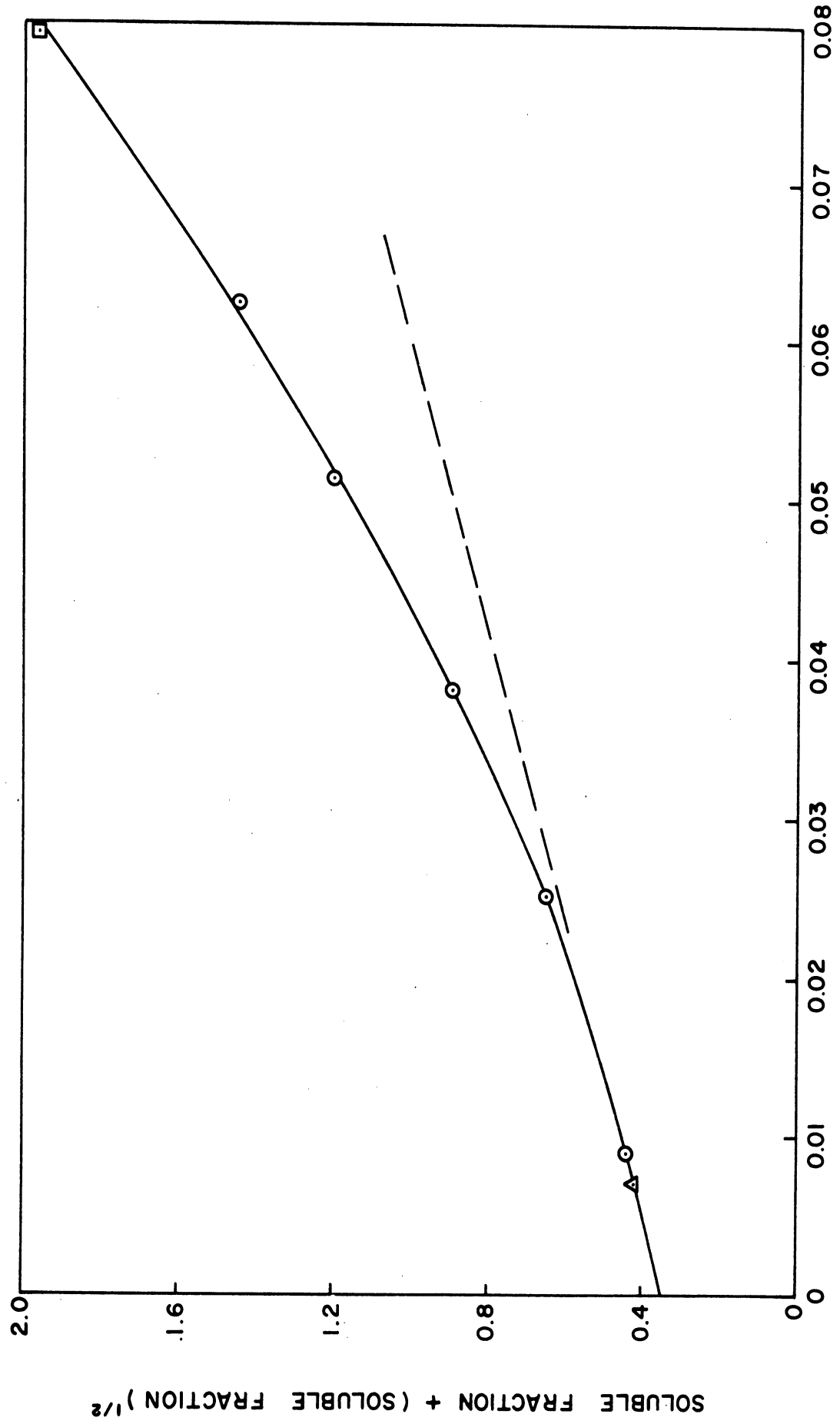


Figure 6. Gel Curve for Narrow Distribution, Secondary Fraction, F-61.

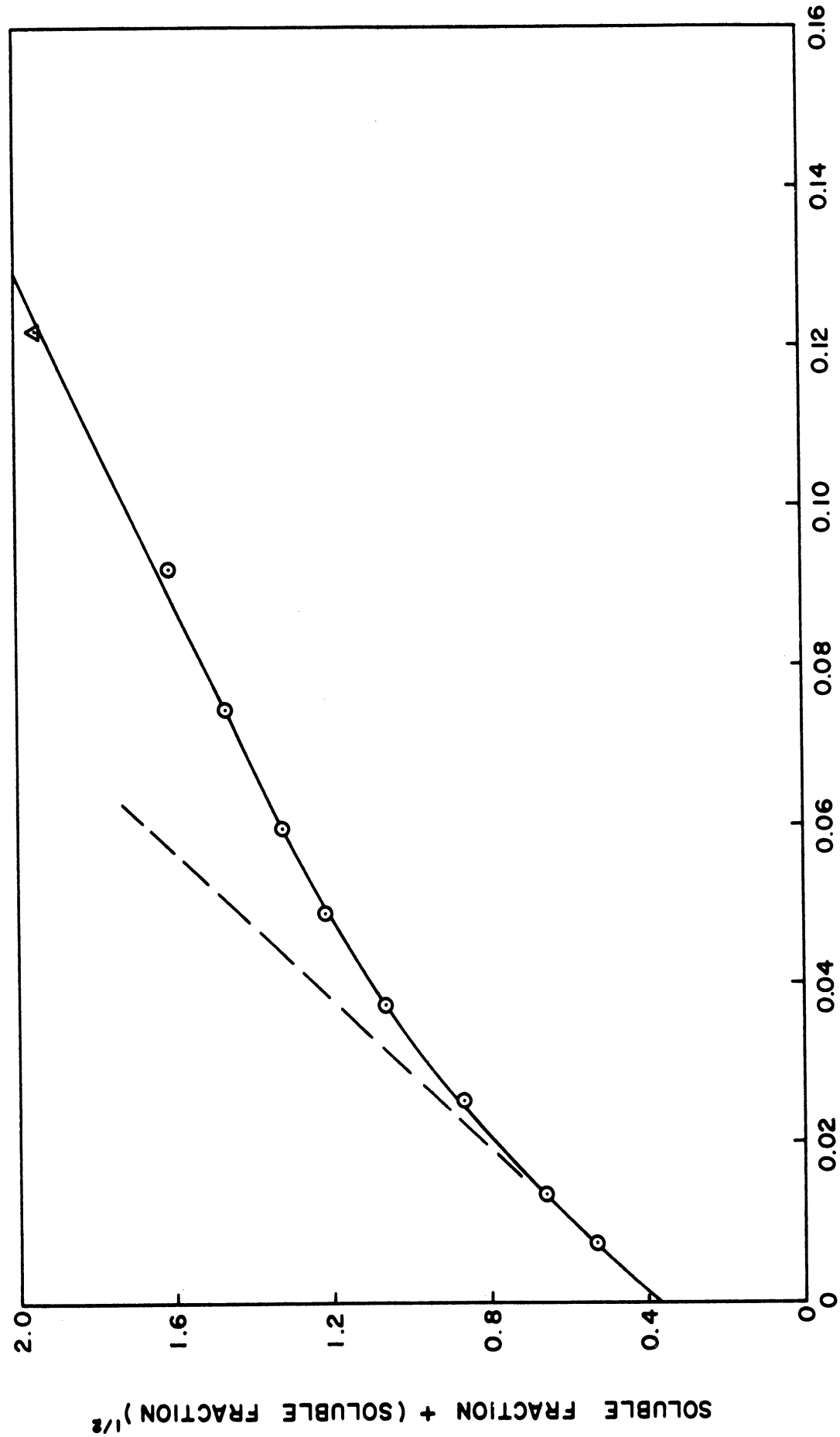


Figure 7. Gel Curve for the Broad Distribution Mixture of Most-Probable Distribution Samples, M-1.

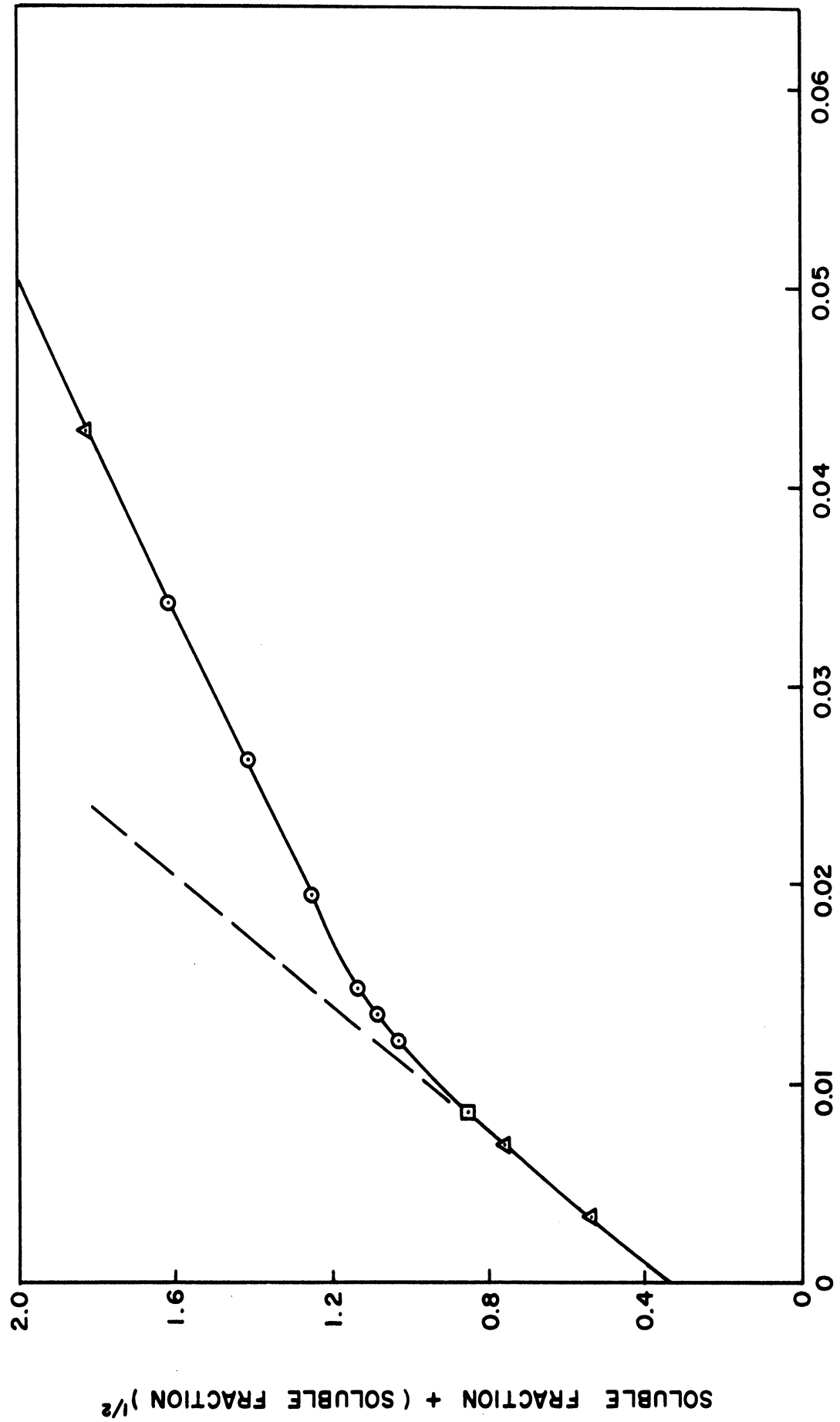


Figure 8. Gel Curve for the Broad Distribution Mixture of Fractions, M-2.

which should occur with samples having distributions broader than most-probable. In addition, all appear to approach the straight line behavior predicted for high doses. This is particularly evident with sample F-22, (Figure 3) where it is seen that the evaluation of the slopes and intercepts required for analysis is fairly unambiguous due to straight line behavior over a considerable range, both for high doses and for doses near the gel point. The values of S_o, S_∞, R_*, and δ, measured from these curves, together with computed values for R_o and $\bar{M}_w R_o$ are listed in Table 9. The values of $\bar{M}_z/\bar{M}_w$ and $\bar{M}_w/\bar{M}_n$, calculated using equations 26 and 29, are presented in Table 10, along with the estimated value of $\bar{M}_{z+1}/\bar{M}_z$ used in the calculation of $\bar{M}_z/\bar{M}_w$ in equation 26.

D. Correlation of R_o - Crosslinking Efficiency

The results obtained from the distribution analysis include a tabulation of R_o's for all samples (Table 9) and the corresponding $\bar{M}_w$'s from light-scattering (Table 8). Each gel point dosage, corrected for chain scission, represents the dose required to produce a crosslinking density, α, in the sample of $1/\overline{DP}_w$. This affords another method for testing the validity of the assumption of proportionality between radiation dose and crosslinking density. A plot of R_o against $1/\bar{M}_w$ should produce a single curve fitting all samples

irrespective of distribution, and with α strictly linear in R, the curve must be a straight line passing through the origin. Figure 9 shows the result. It can be seen here and also in the tabulation of the supposedly constant product, $R_o\bar{M}_w$, (Table 9), that for low values of the R_o's, there is a slight downward trend. In order to preserve the zero intercept property (no crosslinks for zero radiation dose), a "best-fit" line in Figure 9 should probably be a flattened S-shaped curve. However, the absolute error in $\bar{M}_w$ from light scattering increases with increasing $\bar{M}_w$ and a very small systematic error in extrapolation of the scattering results could easily produce this apparent falling off trend. At any rate, the departure from linearity is small and, within the errors to be expected in the measurements, the curve is fit equally well by a straight line. The line put through the data in Figure 9 represents the average of the product, $R_o\bar{M}_w$.

Since $R_o\overline{DP}_w$ is equal to the irradiation dose per mole of crosslinked units formed per gram, then the crosslinking efficiency, defined as energy dissipated per crosslinked unit formed, can be calculated. Using the average value of $R_o\bar{M}_w$ derived from all samples, 19.6 x 10^6 $\frac{\text{megareps - gm}}{\text{mole}}$; the conversion factor, 5.24 x 10^{19} $\frac{\text{electron volts}}{\text{gm - megarep}}$; and Avagadro's number; a value of 1700 $\frac{\text{electron volts}}{\text{crosslinked unit}}$ is obtained for the crosslinking efficiency. Values obtained for polystyrene by other

investigators range considerably below this value. Wall, using a cobalt-60 radiation source benzene-cast film in vacuum found about 1000 e.v. (21), Shultz, using high energy electrons on films in air, cast from methyl ethyl ketone found 855 e.v. (12), and Charlesby, using atomic pile radiation with commercial polystyrene rods in air found about 1000 e.v. (19, 47).

Sources of deviation in these numbers for different investigators include ±10% for differences in light scattering instrument calibration (difference in sample molecular weight obtained); an estimated 5% spread in estimation of the gel point dosage (this should be only about 2% in this study); and a maximum of 15% due to differences in source calibration method, according to staff members in charge of the radiation source used in this study. This would lead to an expected spread of 20-30% while actually, including the value from this study, they cover over a factor of two. This spread is not unique to polystyrene. On the basis of hydrogen evolution studies in polyethylene, Dole (51) computes an equivalence of 109 megareps to the "unit dose" in the B.E.P.O. atomic pile in Harwell, England; whereas Charlesby states a value of 40-50 megareps (45), and later of 54-58 megareps (46).

Three effects may account for this spread. One is the presence of oxygen during irradiation which could on the basis of earlier experiments in this study lead to

high crosslinking efficiency found. This seems unlikely in view of the precautions taken during evacuation, and, at any rate, in view of other investigators' results in the actual presence of air this effect must be small.

A second effect is that noted in the section on extraction technique (II-C-4) where the frequent appearance of small amounts of insoluble matter were noted in films which, from the doses used and in view of the rest of the solubility behavior as a function of dose, should have been completely soluble. As was noted, this insoluble matter did not behave in the manner expected of gels near the gel point, being opaque and only slightly swelled, and amounted to only a few tenths of a percent of the total film extracted. Since gel points by other investigators (12, 21) were taken as initial appearance of insoluble matter whereas those in this study were determined as that extrapolated from the main body of the gel curve, this would possibly account for some of the disparity, and may be a manifestation of the inability of the theory to account for the effect of intra-chain crosslinking in the vicinity of the gel point.

A third possible explanation for the spread in crosslinking efficiency lies in the large effect film conditioning on apparent crosslinking efficiency. A considerable effect due to film casting solvent will be noted in a later section (IV-D-4) which may be due to an effect on the ratio of effective to sterile (non-observable)

crosslinks, or possibly to a "protective" effect due to residual film casting solvent.

Whether any or all of these conjectures are acceptable, Figure 9 demonstrates excellent agreement in the results of this study and indicates that, whatever the explanation for the high crosslinking efficiency obtained, it apparently does not affect the internal consistency of the study. In addition, as an additional check on this crosslinking efficiency, some gel swelling measurements were carried out. This technique, in essence, counts the number of crosslinks which resist the swelling action of the solvent and produced a rough estimate of the crosslinking efficiency of 2000 e.v./crosslinked unit. In addition it gives a value of A_2 in good agreement with that obtained from light scattering (see Appendix C).

E. Investigations of Some Incidental Variables on the Gel Curves

1. Dose Rate Effect

As mentioned before, all irradiations were carried on at dose rates of the order of one megarep per hour. Using sample A, a series of irradiations were carried on outside the source center at a distance such that the dose rate was about 0.1 megareps per hour for all samples. The resultant solubilities are in Table 7. The value for R_0 calculated from this low dose run was 11.3 megareps, compared to 11.0 at the higher rate. This indicates that

within the errors of the dosimetry methods used to calibrate the dose rates (±10%), the effect of dose rate on crosslinking efficiency is very small over the range 0.9 - 0.1 megareps per hour. The constancy of δ (0.37 compared to 0.38) indicates also that over this range, the extent of chain scission is likewise dependent only upon the total dose. Since oxygen is known to have a considerable effect on solubility, and since the effect of oxygen is a diffusion controlled process, one might expect a difference in solubility behavior with dose rate if oxygen were present. The results, indirectly, at least, indicate that the evacuations were quite efficient.

This result is in good agreement with dose rate investigations using other polymers (48) and seem to indicate that the crosslinks are mainly formed between radicals produced by the same photon-matter interaction event.

2. Film Thickness Effect

As mentioned earlier, the films used in most of the experiments ranged in thickness from 2 - 3 mils. On the face of it, one would not expect any effect on solubility due to film thickness. However, there are certain procedures used in the experiments which involve diffusional processes, such as evacuation to remove dissolved oxygen from the films, extraction to remove the soluble material, and the ever-present possibility that some oxygen may be present in the tubes during irradiation.

To investigate the possibility that such an effect might occur, a series of irradiations were carried out for sample 53TH, using films 7 mils thick. The results presented in Table 5, indicate that, if there is such an effect, it is certainly second order (R_o from 10.3 to 10.2, δ from 0.34 to 0.36) and is within the experimental accuracy of the method.

3. Extraction Solvent Effect

The solvent used in most of the work was reagent grade benzene. Since the quantity measured is not a true solubility, but the weight fraction of the polymer which is attached together to form the gel network, it is to be expected that other solvents would produce the same solubility behavior.

Early in the experimental work, it was noticed that when the two films from the same irradiation tube, presumably having the same fraction soluble, were extracted one by benzene as usual, the other in reagent grade methyl, ethyl ketone, large differences in soluble fraction resulted. The film extracted in methyl ethyl ketone invariably gave much higher solubilities. To investigate further this rather unpleasant, apparent dependence of soluble fraction upon solvent, a series of irradiations were carried on in tubes containing four films each of sample 53TH. The four films from each tube were each placed in different solvents, benzene, toluene, methyl ethyl ketone and cyclohexane, so that a series of gel curves could be

obtained for identically irradiated specimens in different solvents. The resulting solubilities from this first series are shown in Table 4. It is apparent that benzene, toluene, and cyclohexane give results which are in good agreement (due to the "poor solvent" character of cyclohexane, the extractions required longer times and only for the high gel content specimens was complete extraction feasible.) The methyl ethyl ketone extractions on the other hand, give a straight line displaced up such that both R_o and δ are higher. It was also noted that complete extraction of these films could not be obtained, as though a constant degradation of the gel was occurring.

In the first series of experiments (Table 4), the computed parameters are:

Extraction Solvent	R_o(megareps)	δ
Benzene, Toluene, Cyclohexane	10.3	0.35
Methyl Ethyl Ketone (MEK)	12.4	0.41

It is seen that R_o is increased by 20% and δ by 17%. Since δ equals the ratio of chain scissions per crosslinked unit, and since R_o is the dose required to add sufficient crosslinks to bring the system to its gel point, the fact that both δ and R_o increase by about 20% for MEK implies that at the time of extracted film recovery, the crosslinking density is less in the MEK extracted films than the others by 20% while the chain scissions are about the same. This, together with the

fact that, in contrast withthe other solvents, extensive extraction never yielded a film free of soluble matter; and the persistence of the straight line gel curve behavior; all implies that the MEK produces a selective rupture of crosslink bonds, kinetically first order with respect to the number of crosslinks present in the gel matrix. This would seem to point to a selective susceptibility of crosslink bonds to attack by this solvent due to some chemical difference from the main-chain bonds.

A possible explanation could lie in the trapped free radicals from the irradiation process (see section II-C-3) which may persist into the extraction stage. It would be expected that contact with the solvent at the onset of extraction would destroy these radicals, and it is conceivable that the solvent effect is some ramification of this radical deactivation. Another series of experiments on sample 53TH were carried out in which films were first extracted for a few days in benzene, then transferred to methyl ethyl ketone. It would be expected that any difference due to trapped radicals would be thus nullified, but again the same effects occurred: the impossibility of complete extraction, and the increase of δ and R_o, (7% and 9% respectively) by about the same ratio over those values for the other solvents (see Table 5).

Except for this anomalous result with methyl ethyl ketone, the soluble fraction is independent of the solvent used.

4. Film Casting Solvent Effect

For almost all the experiments the film casting solvent used was reagent grade benzene. The casting solvent and method were maintained constant to insure a constant chain orientation in the films such that the ratio of sterile to effective crosslinks would be constant (see section I-C-2). Another consideration is the possibility of residual solvent in small amounts even after extensive evacuation and heating, which, if different solvents were used, might lead to different crosslinking effects. (Wall (21), for instance, noted the persistence of casting-solvent benzene in the gases evolved during irradiation even after seemingly thorough degassing.) To determine whether or not there is such an effect, a film of sample A was cast using reagent grade methyl ethyl ketone.

The solubility results were quite striking. The films behaved quite normally in all respects during the extraction process but the results showed an increase in R_o of 28% over results obtained with benzene cast films, with the value of δ (0.38 to 0.37) remaining essentially unchanged. This would indicate, from the definition of R_o and δ, that both the crosslinking efficiency and chain scission efficiency of the radiation has increased by 28%.

Since methyl ethyl ketone is a "poorer" solvent for polystyrene than benzene, the chains in the solid

might be less extended and one might expect a higher proportion of sterile to effective crosslinkages and also of sterile chain scissions (scission occurring in the chain "loop" formed by a sterile crosslinkage), and thereby an increase in the observed radiation efficiencies. The residual methyl ethyl ketone in the film may act as a "protector" also, although its concentration, after prolonged evacuation and heating, must be very small. The amount of additives required to produce effects of this size normally run to 5-10% by weight of the sample and the concentration of methyl ethyl ketone, even before evacuation and heating, is considerably less than this.

V. DISCUSSION OF RESULTS

A. Reproducibility

A series of experiments were carried on to determine the effect of several experiment variables on the solubility results. In the first place, gel curves for all the samples are composites from entirely different runs. That is, a few films for a sample were cast, evacuated, irradiated, and extracted to determine the range of irradiation doses necessary to produce the required curves, then successive runs on the sample were carried out by a different series of film casting, evacuation, irradiation and extraction experiments. Unless otherwise indicated, the different symbols used for the data points (circles, squares, etc.) on the gel curves indicate different runs. The results indicate that the variation in benzene-cast films, and minor differences in evacuation runs, location in the radiation source, and extraction produce no serious effect on solubility properties. See Fig. 2 for instance.

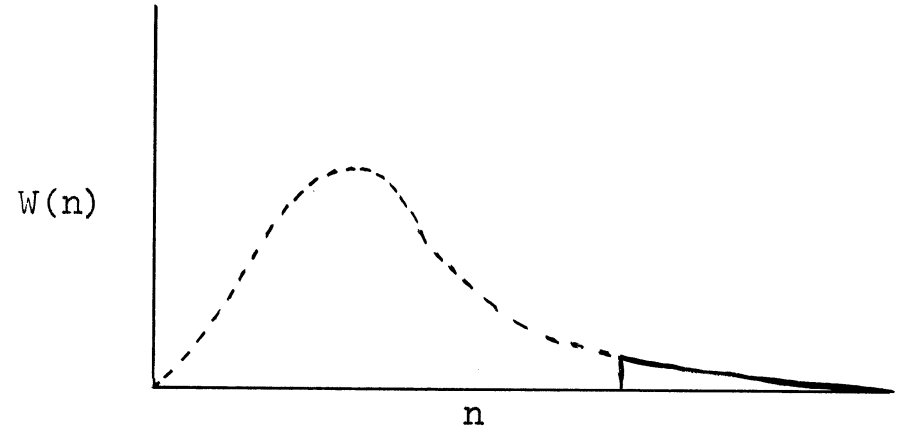
B. Accuracy

Several means are available for determining the accuracy of the distribution parameters obtained from the gel curves. In the first place, there is a qualitative

correctness in the curves, attested to by the concave upward curvature shown by the fractions, corresponding to a narrow distribution (Figs. 3-6); the straight line behavior shown by the as-polymerized samples, corresponding to most-probable distribution (Figs. 1-2); and the concave downward curvature shown by the mixtures, corresponding to broader distribution (Figs. 7-8).

The values for $\bar{M}_w/\bar{M}_n$ and $\bar{M}_z/\bar{M}_w$ obtained for the fractions correspond very well to values which might be expected on the basis of the fractionation techniques. Generally speaking the fraction should be narrower a) the more dilute is the primary fractionating solution, b) the lower the molecular weight of the fraction, and c) the more times it is subjected to refractionation. Thus, F-50, being a primary fraction, shows considerable broadness, and while F-61 and F-33 are both secondary fractions, F-61 is narrower than F-33 because of its lower molecular weight and because it was obtained from a later primary fraction (more dilute primary fractionation solution). Also, the rapid drop in $\bar{M}_z/\bar{M}_w$ compared to $\bar{M}_w/\bar{M}_n$ for F-50 indicates a low molecular weight "tail" with a relatively sharp cutoff on the high molecular weight end of the distribution, which is reasonable to expect from a primary fraction near the middle of the initial distribution. The fact that F-22 shows a ratio of $\bar{M}_z/\bar{M}_w$ higher than $\bar{M}_w/\bar{M}_n$ is somewhat unexpected although not at all impossible; for instance, calculations on a hypothetical

distribution composed of the high molecular "tail" of a most-probable distribution, show a value of $\overline{M}_Z/\overline{M}_W$



higher than M_W/M_n by as much as 4%. As a matter of fact, F-22, derived from the second primary fraction, is related very roughly to such a distribution.

The agreement between expected and measured values of $\overline{M}_W/\overline{M}_n$ and $\overline{M}_Z/\overline{M}_W$ for the mixtures, M_1 and M_2, is reasonably good (Tables 8 and 9) with a spread of 10-12%. Actually, for the case of M-1, the fact that such a well-behaved gel curve was obtained is surprising since one of the components, sample 0, showed the anomalously high value of δ (equal to 0.49) when irradiated separately.

The distributions for the fractions were measured by Dr. H. W. McCormick using the ultracentrifuge. By this method, graphical distributions are obtained by techniques described in a recent paper by Dr. McCormick (5). The distributions for the fractions, F-50, F-61, F-33, and F-22 are shown in Figure 12; the values of

$\bar{M}_w/\bar{M}_n$ and $\bar{M}_z/\bar{M}_w$ computed graphically from these curves are listed in Table 8.

It can be seen that the trend for the values for $\bar{M}_w/\bar{M}_n$ is the same as with the gel curve values. Thus, with regard to $\bar{M}_w/\bar{M}_n$, F-61 < F-22 < F-33 < F-50. It is also apparent however, that the actual values diverge rather rapidly from increasing $\bar{M}_w/\bar{M}_n$, with the sedimentation values predicting relatively narrower distributions. The most serious difference is with sample F-50, and the value of 1.48 obtained from gel measurements for $\bar{M}_w/\bar{M}_n$ does seem rather out of keeping with that expected, even for a primary fraction. Some of the fault may lie with the need for more solubility values at the high doses to establish the limiting slope with more certainty, although a limiting slope corresponding to the value of 1.15 for $\bar{M}_w/\bar{M}_n$ from the sedimentation curve for F-50 definitely does not fit the data.

The tendency of the sedimentation data to show narrower distribution may possibly be due to the inability of the method to "see" tails on the distribution which may be small compared to the total sample weight but which may contribute significantly to $\bar{M}_n$ on one side and $\bar{M}_z$, $\bar{M}_{z+1}$, etc., on the other. It is certainly reasonable that any error which is accrued through use of the distribution in Figure 12 to calculate average molecular weights other than $\bar{M}_w$ will tend to make the samples look slightly narrower than they actually are. On the other hand, the

results obtained on the mixtures (M-1 and M-2) seem to indicate that the values for $\bar{M}_w/\bar{M}_n$ obtained from the gel curves tend to overestimate the breadth of distribution. All in all, except for F-50, the agreement of $\bar{M}_w/\bar{M}_n$ is satisfactory, and the fact that both methods predict the same order of the samples with respect to the size of $\bar{M}_w/\bar{M}_n$ reinforces their validity.

With the possible exception for F-22, the agreement between $\bar{M}_z/\bar{M}_w$ determined by the two methods is very good, although again the values from the gel curves are generally higher than those from sedimentation. Actually, this must be regarded as a check of the method independent of the $\bar{M}_w/\bar{M}_n$ values, since entirely different portions of the gel curve produce the separate values. The peculiar result observed for F-22, a higher value for $\bar{M}_z/\bar{M}_w$ than for $\bar{M}_w/\bar{M}_n$, is probably not real, although the distribution for F-22 in Figure 12 does give some indication of the type of high molecular weight "tail" and low molecular weight "cutoff" required for such an occurrence.

The results indicate that values for the initial distribution parameters, $\bar{M}_w/\bar{M}_n$ and $\bar{M}_z/\bar{M}_w$, can be obtained from gel data which are in reasonably good agreement with values obtained by sedimentation methods (fractions), and calculated for known mixtures, for distributions ranging from very narrow ($\bar{M}_w/\bar{M}_n$ = 1.06) to fairly broad ($\bar{M}_w/\bar{M}_n$ = 3.7).

C. Applicability of Method

1. Distribution Determination

The analysis of a system in terms of the distribution of chain lengths represented presents a problem of considerable importance to polymer chemists. By and large, the usual methods depend upon the solution properties of polymeric systems and are strictly valid only under experimental conditions which are many times difficult to attain. For instance, fractionation requires very dilute solutions and extremely careful handling methods, and is applicable with sureness only for non-crystalline, linear polymers. Light scattering, besides being insensitive to distribution, is applicable only for a relatively narrow range of chain sizes ($0.1\lambda < S < \lambda$). Sedimentation has come to be an excellent method, but it too is exceedingly dependent upon the proper choice of solvent, the use of very dilute solutions, and presents interpretational difficulties; it also requires the use of a specialized and expensive piece of equipment.

The use of crosslinking-solubility methods presents an entirely different approach to the problem, in which the solid polymer is used. It depends upon practically none of the assumptions required for the solution methods, and, although it has its own set of restrictions, it presents a supplemental method for the attack of the problem which, under the proper conditions, could be quite useful.

In one sense, it is not an absolute method, since a single gel curve, in the absence of all other information, cannot produce absolute values for the initial average molecular weights. In another sense, however, it is absolute, since it is capable of yielding ratios of average molecular weights directly. Thus, from the properties of the gel curve, the virtual gel point dosage R_o, and the chain scission parameter, δ , can be computed. These two quantities are all that is required to express the gel curve as it depends on γ and δ in equation 14, which in turn means that in principle, the entire initial distribution is defined, except for the average chain length parameter.

It must be emphasized that this "normalizable" characteristic of gel curves is very important since it means that a wide variety of conditions may be used for the crosslinking step which may produce widely different crosslinking efficiencies, but which for the same sample, should ultimately produce the same values for molecular weight ratios.

The method can be calibrated to produce absolute molecular weights however. The product, $R_o\bar{M}_w$, must be a constant for a given polymer such as polystyrene, and for a given set of experimental conditions such as those used in this study. Thus, this constant can be measured by determining R_o for samples with known values of $\bar{M}_w$; the constant can then be used, together with R_o from the gel

curve, to compute $\bar{M}_w$ for an unknown sample. In this study, for example, the samples with most-probable distribution yield values of R_o in a straight forward manner, from the slopes of the linear gel curves. The average product, $R_o\bar{M}_w$, calculated from light scattering molecular weights for these six samples, is:

$$R_o\bar{M}_w = 19.7 \times 10^6 \text{ megareps}$$

By reference to R_o from their respective gel curves, and using the above constant, values of $\bar{M}_w$ can be calculated for the mixtures (M-1 and M-2) and the fractions (F-22, F-33, F-50, F-61). In the following table values calculated in this manner are shown along with $\bar{M}_w$ obtained from light scattering and sedimentation:

	(gel curve)	(light scattering)	(sedimentation)
Sample	$\bar{M}_w \times 10^{-6}$	$\bar{M}_w \times 10^{-6}$	$\bar{M}_w \times 10^{-6}$
M-1	3.29	3.04	----
M-2	1.28	1.46	----
F-22	3.78	3.36	3.68
F-33	2.55	2.42	2.40
F-50	1.71	1.82	1.81
F-61	1.82	1.77	1.88

The agreement between the three methods is seen to be fairly good.

The one important characteristic which must prevail is that crosslinking and chain scission reactions are random. Almost as important is the requirement of a constant value of the chain scission parameter during

the course of crosslinking which, while not a requirement in the basic theory, certainly makes interpretation much simpler. For polystyrene, the linear behavior of the most-probable distribution samples (Figs. 1 and 2 for instance) certainly suggests that δ remains a constant over a wide range of doses and in fact, for most cases, changes only slightly if at all from one sample to another. This same result has been found to hold for several other vinyl type polymers (49).

Also for simplicity it is very convenient to have extent of crosslinking directly proportional to irradiation dose, although, in principle, the general dependence of crosslinking upon dose is directly attainable from a series of gel point measurements on samples with known weight average molecular weight (Fig. 9).

There is no limitation on the method with regard to maximum average chain length or molecular weight. In fact, the larger are the initial chain lengths represented, the smaller is R_o and thus the lower are the total doses required to produce the limiting solubility behavior necessary for the calculation of $\overline{M}_w/\overline{M}_n$ and δ . There is a lower limit on the initial average degree of polymerization however. The evaluation of $\overline{M}_w/\overline{M}_n$ depends upon the existence of a range such that the chain scissions per initial chain is large compared to one (to obtain the asymptotic linear behavior) and yet such that the fraction of the total bonds in the system which are broken is small

(β , as defined earlier is still small compared to one to avoid saturation effects):

$$\frac{1}{\overline{DP}} \ll \beta \ll 1 \qquad (30)$$

This would require a minimum $\overline{DP}$ of the order of 100 to satisfy both requirements, and, for polystyrene for example, a lower limit of initial average molecular weight about the order of 10,000. The limitation on the determination of $\overline{M}_Z/\overline{M}_W$ is not as severe, but as the initial average molecular weight becomes small, many of the approximations used in the derivations are no longer as valid as with large chains. For instance, the accurate expression for the relation between crosslinking density at the gel point, α_o , and initial weight average degree of polymerization, $\overline{DP}_W$ is actually (6):

$$\alpha_o = \frac{1}{\overline{DP}_W - 1}$$

which obviously differs significantly from equation 6 only for $\overline{DP}_W$ in the order of ten or less. Likewise, for small polymer molecules, crosslinking density, α , no longer remains small compared to one, and serious saturation effects can occur in radiation crosslinking, such as departure from direct proportionality to dose. (The relation between dose and crosslinking would probably take on a first order reaction character such as: $\alpha = 1 - e^{-kR}$, which, for small α , becomes approximately

$\alpha = kR$.) In addition, as the crosslinking and chain scission densities increase, as would be required for the analysis of smaller polymer molecules, reactions such as the scission of previously formed crosslinks begin to become important, invalidating the assumption of independence between crosslinking and chain scission, together with the simplifications this allowed in obtaining the equations used.

With regard to crosslinkability, polystyrene must be considered as an atypical case. Due apparently to the stability of the phenyl ring, polystyrene crosslinks with great difficulty compared to other polymers, and hence doses up to 200 megareps are required to produce a reasonably complete gel curve, even for samples whose $\overline{M}_w$ is relatively high (order of one million). This is brought out by a comparison of crosslinking efficiencies for different polymers. Shultz (49) observed a crosslinking efficiency of roughly 100 electron volts per crosslinked unit for a series of different polyacrylates; for polyethylene, the value is roughly 100 electron volts (50) also; whereas for polystyrene the value ranges from 850-1700 electron volts. Hence, the excessive dosages required for gel curve determination in polystyrene would not be required in a distribution investigation of other polymers.

The method is obviously restricted to polymers in which crosslinking is sufficiently frequent with respect

to chain scission such that gel formation actually occurs ($\delta < 2$). Practically speaking, the restriction on δ is more severe, since the initial characteristics of the distribution become more obscured, the larger the proportion of simultaneous chain scission, and also the equations developed to account for this effect becomes less certain. Probably the upper limit on δ is about 0.5; fortunately, a reasonable proportion of interesting polymers lie in this region:

Polymer	δ
Polyethylene	0.20 (9), 0.35 (44)
Several Polyacrylates	0.13 - 0.25 (49)
Poly Vinyl Acetate	0.10 (44)
Poly Vinyl Chloride	0.35 (44)

It is worth noting that although the approximations used to account to the simultaneous chain scission become more accurate as δ becomes smaller, the effect of smaller δ's is to cause the limiting linear solubility behavior, necessary for the evaluation of $\bar{M}_w/\bar{M}_n$, to occur at higher and higher values of γ. This can be easily seen by dividing equation 30 through by α to give:

$$\frac{1}{\gamma} \ll \delta \ll \frac{1}{\alpha} \qquad (31)$$

That is, the limiting behavior is reached for $\delta\gamma$ somewhat greater than one, which, for small δ, can place excessive requirements on the magnitude of γ (that is, inconveniently large radiation dose).

For δ very close to zero, however another approach is possible. For example, if δ equals zero, equation 7 is valid, and although no simple relationship holds for the limiting slope on the plot of $(1 - x) + (1 - x)^{\frac{1}{2}}$ against 1/R, $\bar{M}_w/\bar{M}_n$ is given by the following result (see Appendix A, equation b):

$$\frac{\bar{M}_w}{\bar{M}_n} = \int_0^\infty (1 - x)\, d(\gamma x)$$

Thus the experimental gel curve, 1 - x as a function of xR, can be graphically integrated to give $R_o(\bar{M}_w/\bar{M}_n)$ if δ is equal to zero; and although this integral does not converge for $\delta > o$, the integrand can undoubtedly be modified for δ very small (say the order of 0.01 - 0.05) to produce an expression whose integral is very close to $R_o\ \bar{M}_w/\bar{M}_n$.

An unfortunate characteristic of this method, as compared to solution methods, is the non-recoverability aspect. This is particularly serious in the case of fractions where only a small sample is available in the first place. A fairly unambiguous gel curve was obtained from fraction F-61 using only seven data points (Figure 6). Single films were used, each weighing about 150 mg, so the total polymer used was roughly one gram. This could probably be cut to less than one-half gram by using smaller films although manipulation then becomes a problem with the small weights involved.

The choice of polystyrene for use in this study allowed a relatively simple analysis due to its chain linearity and amorphous character. In section I-C-2 it was pointed out that semi-crystalline polymers have been found to show different crosslinking rates in the crystalline and non-crystalline regions. This of course would render the analysis of gel curves quite difficult and casts suspicion on the basic assumption of random crosslinking. It is possible to avoid this difficulty, however, by carrying on the irradiations at temperatures above the crystalline melting point of the polymer. Lawton, Balwit, and Powell (14) present gel curves which indicate that there is a considerable effect of crystallinity on gel curve behavior for low-pressure polyethylene. (Gel curves above and below the temperature of crystallization indicate a considerable difference in both apparent crosslinking efficiency and chain scission parameter.)

Crosslinking theory probably could be used for non-linear polymers also but they require modification with regard to the effect of simultaneous chain scission. Equation 9 governing the change in primary distribution due to chain scission is only valid for linear chains, and hence equation 10 and all the succeeding equations deduced from it (except for equation 22 which Charlesby showed to be true even for branched initial primary chains) are no longer valid. If the type and frequency

of branching are known than another equation could be substituted for equation 9, and new equations could be deduced relating measurable properties of the gel curves to initial distribution. Another, more serious, difficulty arises however which reflects seriously on the basic assumption of random crosslinking. Beasley (2) points out, in his derivation of the distribution function for systems which branch due to polymer transfer, that the presence of branches effectively shield units near the middle of the branched molecules for further transfer reactions. In the solid state, these units buried within the branched chains likewise would have no opportunity to form crosslinks with other molecules. It can be seen that in the limiting case, only units on the "surface" of molecules could form effective crosslinks and thus the crosslinking expectancy of a chain would be proportional to $n^{2/3}$ rather than to n as required.

As an example of the usefulness of the crosslinking technique, consider the case of the linear polymers produced using Ziegler-Natta type catalysts. As mentioned earlier, Wesslau found that a two parameter, log-normal distribution fit his fractionation data (equation 4), one parameter being an average chain length parameter, n_o, the other a breadth parameter, B'. Since the fundamental significance of n_o and B' is unknown, it would be worthwhile, in the interest of building

a mechanism theory for this type of polymerization, to investigate their dependence upon polymerization conditions. From a single molecular weight determination, it is impossible to separate the effects since each average molecular weight depends upon both parameters. However, having established the scission parameter, δ , one could calculate a series of gel curves as a function of γ with various values of B', in which case, by superposition, differences in the values of n_o and B' for a series of samples could be easily measured. The straightforward application of the approach outlined in section IV-C-4 would also apply of course, but due to the broadness normally observed with these samples ($\bar{M}_w/\bar{M}_n$ equal to ten is not uncommon), the approximations used in their derivation become less certain. It is worth noting that these "low-pressure" polymers in most cases are soluble only at elevated temperatures ($>100^{\circ}C$) which presents considerable experimental difficulty to the dilute solution methods for measuring distribution, whereas high temperature irradiation (to remove crystallinity difficulties) and solvent extraction are relatively easy, although, for the extraction, precautions must be taken to avoid oxidative gel degradation at these temperatures.

Generally speaking, the simplified method used in this study should produce good distribution results under the following conditions: 1) initially linear chains with $\overline{DP}_n$ the order of at least 100, 2) non-crystalline

structure during irradiation, 3) random crosslinking and chain scission, both proportional to the radiation dosage, 4) a value of δ in the range 0.5 - 0.1 and, 5) a distribution which is not too broad.

2. Effect of Variables on Radiation-Induced Reactions

The plotting method used, which produces straight lines for samples with most-probable distribution, presents a nice way of comparing the effect of variables on the crosslinking process. Examples of this are the two different effects found due to film casting solvent (see section IV-E-4) and due to extraction solvent (see section IV-E-3). It also illustrates the hazards involved in deducing effects from single point solubilities. For example, an increase in solubility for a given dose may be due to a protection effect (as may be the case with the MEK casting solvent experiment), it may be due to decrease in crosslinks with chain scissions relatively constant (as with the MEK extraction solvent effect) or it may be due to enhancement of chain scission reactions with constant crosslinking. Each of these effects produces a different gel curve, still a straight line, but with a different relation between comparative values of δ and R_o.

VI. CONCLUSIONS

The purpose of this study was to test the applicability of radiation crosslinking-insolubility measurements to the general problem of molecular size distribution in a polymeric system.

A simplifying premise, that crosslinking density is directly proportional to radiation dose, was found to be valid for polystyrene from the dependence of gel point dosage upon initial molecular weight. This is further verified by the straight line behavior found in gel curves for samples with most-probable distribution. The chain scission parameter was found to be reasonably constant from sample to sample; and it was likewise found to be independent of radiation dose over wide ranges of dose as shown by the linear gel curves obtained for samples with most-probable distribution.

The theoretical relationship between molecular weight distribution and crosslinking-solubility behavior was reduced to a set of equations accounting for the effect of chain scission, and relating measurable properties of the gel curve to ratios of initial average molecular weights for the samples. With samples of polystyrene ranging in distribution from very narrow ($\bar{M}_w/\bar{M}_n$ = 1.06)

to fairly broad ($\bar{M}_w/\bar{M}_n$ = 3.7), the values of $\bar{M}_w/\bar{M}_n$ and $\bar{M}_z/\bar{M}_n$ were then calculated from the gel curves. They were found to be in good agreement with those expected, either on the basis of sample makeup, or from ultra-centrifuge-sedimentation studies and the conditions of preparation. The gel curves obtained were all very well defined and easily reproducible. The effects of such incidental variables as radiation dose rate, extraction solvent (under most circumstances), and film thickness were negligible. On the basis of the above results, it was concluded that 1) the conditions vital to the theory, statistically random crosslinking and chain scission, are well fulfilled in the case of polystyrene, 2) the experimental accuracy is sufficient to allow measurement of the gel curve properties required for the calculation of $\bar{M}_w/\bar{M}_n$ and $\bar{M}_z/\bar{M}_w$, and 3) the approximate equations developed to account for the effect of chain scission in the computation of $\bar{M}_w/\bar{M}_n$ and $\bar{M}_z/\bar{M}_w$ are reasonably valid for the range of distributions covered.

The value of crosslinking efficiency, computed from gel point dosage is found to be considerably higher than that noted by previous authors. Also observed was the appearance of insoluble matter at doses below the gel point dosage (obtained by extrapolation from the main body of the gel curve). This may represent some manifestation of limitation in the theory, and may

account for the disparity between the crosslinking efficiency calculated from these results and those calculated from the dose at which insolubility first occurs. A considerable effect of pre-irradiation treatment (such as film-casting solvent) on crosslinking efficiency is also noted, indicating the equivocal nature of such values. The important result however, is the fact that the method depends only upon a constant value of crosslinking efficiency under a given set of experimental conditions, and this requirement is borne out very well by the excellent internal consistency of the study.

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APPENDIX A

DERIVATION OF EQUATIONS USED IN GEL CURVE ANALYSIS

1. Relation of Limiting Slope, S_∞, to Initial Distribution

The expression relating the gel curve to the sample distribution is equation 10:

$$1 - x = \left(\frac{x}{x+\delta}\right)^2 w(s') + \left(\frac{\delta}{x+\delta}\right)^2 + \frac{2\delta x}{(x+\delta)2} \frac{1}{s'}\int_0^{s'} w(\lambda)\,d\lambda \quad (14)$$

where, as before $\delta = \beta/\alpha$

$$s' = \alpha(x+\delta)$$

$$w(s') = \int_0^\infty W(n) e^{-s'n}\,dn$$

The following limiting results must be true from the definition of w(s'):

$$\lim_{s' \to \infty} w(s') = 0 \qquad (a)$$

$$\lim_{s' \to \infty} \int_0^s w(\lambda)\,d\lambda = 1/\overline{DP}_n \qquad (b)$$

Thus, for sufficiently large s', the limiting behavior, from equation (14), must be:

$$1 - x = \left(\frac{\delta}{x+\delta}\right)^2 \quad \frac{2\delta x}{(x+\delta)3} \left(\frac{1}{\gamma}\right) \left(\frac{\overline{DP}_w}{DP_n}\right) \qquad (c)$$

This can be rearranged, using the fact that $\delta = 1-x_\infty + (1-x_\infty)^{\frac{1}{2}}$, where $1-x_\infty$ is the limiting soluble fraction, and the expression of γ as R/R_0:

$$(x_\infty - x)\left[1-x_\infty + x + 2(1-x_\infty)^{\frac{1}{2}}\right]\left[1-x_\infty + x + (1-x)^{\frac{1}{2}}\right] = 2\delta\left(\frac{\bar{M}_w}{\bar{M}_n}\right)\frac{R_o}{R} \qquad (d)$$

Under the limiting conditions of interest, x is very nearly x_∞ and the equation simplifies without serious error to:

$$(x_\infty - x)\left[1 + 2(1-x)^{\frac{1}{2}}\right]\left[1 + (1-x)^{\frac{1}{2}}\right] = 2\delta\left(\frac{\bar{M}_w}{\bar{M}_n}\right)\frac{R_o}{R} \qquad (e)$$

Thus:

$$\lim_{R\to\infty}\left\{\frac{d(1-x)}{d\ 1/R}\right\} = 2\delta\left(\frac{M_w}{\bar{M}_n}\right)\frac{R_o}{\left[1 + 2(1-x_\infty)^{\frac{1}{2}}\right]\left[1 + (1-x_\infty)^{\frac{1}{2}}\right]} \qquad (f)$$

and since:

$$\frac{d}{d\ 1/R}\left\{(1-x) + (1-x)^{\frac{1}{2}}\right\} = \frac{d(1-x)}{d\ 1/R}\left[1 + \frac{1}{2(1-x)^{\frac{1}{2}}}\right] \qquad (g)$$

then, again in the limit of x near to x_∞ for g, the final equation is obtained from f and g:

$$\lim \frac{d}{d\ 1/R}\left\{1-x + (1-x)^{\frac{1}{2}}\right\} = \left(\frac{\bar{M}_w}{\bar{M}_n}\right)R_o \qquad (h)$$

Thus defining the left side of equation (h) as the limiting slope, S_∞, it follows that the limiting straight line for arbitrary distribution, in the presence of simultaneous chain scission, must have the form:

$$(1-x) + (1-x)^{\frac{1}{2}} = \frac{S_\infty}{R} + \delta \qquad (i)$$

$$S_\infty = \left(\frac{\overline{M}_w}{M_n}\right) R_o \qquad (j)$$

2. Effect of Chain Scission on Gel Point Dosage

Equation 10 can be rearranged to give the form:

$$x + 2\delta - x^2 - \delta^2 - 2\delta x = x\, w(s') + 2\delta \frac{1}{s'} \int_o^{s'} w(\lambda)\, d\lambda \qquad (k)$$

As the gel fraction, x, approaches zero (gel point), the relation between initial distribution, the chain scission parameter and the crosslinking density results:

$$1 - \frac{\delta}{2} = \frac{1}{\delta \alpha_*} \int_0^{\delta \alpha_*} \int_o^\infty W(n) e^{-s'n}\, dn\, ds' \qquad (l)$$

α_* = crosslinking density at the gel point

Equation l may be simplified by reversing the order of integration to give:

$$1 - \frac{\delta}{2} = \frac{1}{\delta \alpha_*} \int_o^\infty W(n) I(n, \delta \alpha_*)\, dn \qquad (m)$$

$$\text{where } I(n, \delta \alpha_*) = \frac{1 - e^{-\delta \alpha_* n}}{n}$$

For $\delta \alpha_*$ sufficiently small, $I(n, \delta \alpha_*)$ can be expressed by a series about $\alpha_* \delta$ equal to zero:

$$I(n, \delta\alpha_*) = \delta\alpha_* \left[1 - \frac{\delta\alpha_*}{2!} n + \frac{(\delta\alpha_*)^2}{3!} n^2 - .... \right] (n)$$

Using this expression, the integral in equation m may be evaluated in terms of the various initial average $\overline{DP}$'s of the system:

$$1 - \frac{\delta}{2} = 1 - \frac{\delta\alpha_*}{2} \overline{DP}_w + \frac{(\delta\alpha_*)^2}{6} \overline{DP}_w \overline{DP}_z - .... \qquad (o)$$

Introducing γ_*, the crosslinking index at the gel point, defined in the usual way as $\alpha_* \overline{DP}_w$, equation o becomes:

$$1 = \gamma_* - \frac{\delta\gamma_*^2}{3} \left(\frac{\overline{M}_z}{\overline{M}_n}\right) + ... \qquad (p)$$

Thus, rearranging:

$$\gamma_* = \frac{1}{1 - \frac{\delta}{3} \gamma_* \frac{\overline{M}_z}{\overline{M}_w} + \epsilon} \qquad (q)$$

ϵ = error in ignoring higher order terms in the expansion

To the approximation that γ_* is nearly one for δ small, and that ϵ, being positive will tend to cancel the error involved, the equation becomes:

$$\gamma_* = \frac{1}{1 - \frac{\delta}{3} \frac{\overline{M}_z}{\overline{M}_w}} \qquad (r)$$

Since γ_* is also expressable as R_*/R_o, the resulting expression is:

$$R_o = R_* \left(1 - \frac{\delta}{3} \frac{\bar{M}_z}{\bar{M}_w}\right) \qquad (s)$$

3. Relation of Initial Slope, S_o, to Initial Distribution

Equation 14 can be rearranged to give the form:

$$x^2 + 2\delta x + \delta^2 - x\left[1 - w(s)\right] - 2\delta\left[1 - \frac{1}{s}\int_o^s w(\lambda)d\lambda\right] = o \qquad (t)$$

Taking the derivative of this expression with respect to the crosslinking index, γ, and letting x, the gel fraction, go to zero, an expression is obtained for $dx/d\gamma$ at the gel point:

$$\left.\frac{dx}{d\gamma}\right|_{x=o} = \frac{2\delta}{\gamma_*} \frac{\left[\frac{1}{s}\int_o^s w(\lambda)d\lambda - w(s)\right]}{\left[2\delta + 3w(s) - 2\frac{1}{s}\int_o^s w(\lambda)d\lambda + 1\right]} \qquad (u)$$

The quantities, w(s) and $1/s\int_o^s w(\lambda)d\lambda$, have power series expansions for s (equal to $\delta\gamma_*$ at the gel point) sufficiently small (note equations m and o). Proceeding formally:

$$w(s) = 1 - \delta\gamma_* + \left(\frac{\bar{M}_z}{\bar{M}_w}\right)\frac{(\gamma_*\delta)^2}{2} - \left(\frac{\bar{M}_z}{\bar{M}_w}\right)\left(\frac{\bar{M}_{z+1}}{\bar{M}_w}\right)\frac{(\gamma_*\delta)^3}{6} + \ldots \qquad (v)$$

$$\frac{1}{s}\int_o^s w(\lambda) = 1 - \frac{\gamma_*\delta}{2} + \frac{\bar{M}_z}{\bar{M}_w}\frac{(\gamma_*\delta)^2}{6} - \left(\frac{\bar{M}_z}{\bar{M}_w}\right)\left(\frac{\bar{M}_{z+1}}{\bar{M}_w}\right)\frac{(\gamma_*\delta)^3}{24} + \ldots \qquad (w)$$

Substituting these expressions into equation u, this expression is obtained:

$$\left.\frac{dx}{d\gamma}\right|_{x=o} = \frac{3}{\gamma_*^3}\,\frac{\bar{M}_w}{\bar{M}_z}\,\Phi \qquad (x)$$

where $\Phi = \dfrac{1 - \frac{1}{3}\frac{\bar{M}_z}{\bar{M}_w}\,\delta\,\gamma_*^2 + \frac{1}{6}\left(\frac{\bar{M}_z}{\bar{M}_n}\right)\left(\frac{M_{z+1}}{\bar{M}_w}\right)\delta^2\gamma_*^3 - \cdots}{1 - \frac{1}{2}\left(\frac{\bar{M}_{z+1}}{\bar{M}_w}\right)\delta\,\gamma_* + \cdots}$

Since γ_* is equal to R_*/R_o, the relationship between $dx/d\gamma$ and S_o is the following:

$$\frac{d}{d\,1/R}\left\{(1-x) + (1-x)^{\frac{1}{2}}\right\}_{x=o} = S_o = \frac{3}{2}\,R_o\,\gamma_*^2\left(\frac{dx}{d\gamma}\right)_{x=o} \qquad (y)$$

Then from equation x, S_o becomes:

$$S_o = \frac{3R_o\bar{M}_w}{\bar{M}_z}\,\frac{\Phi}{\gamma_*} \qquad (z)$$

From equation r, there is an approximation for γ_*:

$$\frac{1}{\gamma_*} = 1 - \frac{\delta}{3}\left(\frac{\bar{M}_z}{\bar{M}_w}\right)$$

likewise:

$$\frac{1}{1 - \frac{1}{2}\frac{\bar{M}_{z+1}}{\bar{M}_w}\,\delta\,\gamma_*} = 1 + \frac{\bar{M}_{z+1}}{\bar{M}_w}\,\frac{\delta\gamma_*}{2} \qquad (aa)$$

These approximations may be combined into equation z, and discarding terms higher than the first power in δ, the result is:

$$S_o = \frac{3R_o\bar{M}_z}{\bar{M}_w}\left[1 + \left(\frac{\bar{M}_z}{\bar{M}_w}\right)\left(\frac{\delta\gamma_*}{3}\right)\left(\frac{3}{2}\ \frac{\bar{M}_{z+1}}{\bar{M}_z} - 2\right)\right] \qquad \text{(bb)}$$

It can be seen that, except for very broad distributions where $\bar{M}_{z+1}/\bar{M}_z$ becomes large, the slope modification due to chain scission is small for small values of δ . The expression for $\bar{M}_z/\bar{M}_w$ in terms of measurable constants and $\bar{M}_{z+1}/\bar{M}_z$ for small δ is:

$$\frac{\bar{M}_z}{\bar{M}_w} = \frac{3R_o}{S_o}\left\{1 + \frac{R_*\delta}{S_o}\left[\frac{3}{2}\ \frac{\bar{M}_{z+1}}{\bar{M}_z} - 2\right]\right\} \qquad \text{(cc)}$$

APPENDIX B

SAMPLE CALCULATION

Sample Calculation

This section presents a sample calculation to show how the properties of the gel curve are used to compute M_w/M_n and M_z/M_w. The curve from the narrow distribution fraction, F-22, plotted as (soluble fraction) + (soluble fraction)$^{\frac{1}{2}}$ against reciprocal radiation dose in megareps, R^{-1}; is shown in Figure 3. The quantities indicated on the figure: δ , S_o, S_∞, and R_*, are measured from the curve:

$$\delta = 0.37$$

$$S_o = 12.05 \text{ megareps}$$

$$S = 6.00 \text{ megareps}$$

$$R_* = 6.19 \text{ megareps}$$

$\overline{M}_w/\overline{M}_n$ is calculated, using equation 29:

$$\frac{\overline{M}_w}{\overline{M}_n} = \frac{S_\infty}{R_*} + \delta\left(\frac{S_\infty}{S_o}\right) \qquad (29)$$

$$\frac{\overline{M}_w}{\overline{M}_n} = \frac{(6.00)}{(6.19)} + \frac{(0.37)(6.00)}{(12.05)}$$

$$\frac{\overline{M}_w}{\overline{M}_n} = 1.15$$

Since this is a fairly narrow sample, the higher ratios of successive average molecular weights should be near $\bar{M}_w/\bar{M}_n$ and should probably be even closer to one. For the purpose of calculating $\bar{M}_z/\bar{M}_w$ from equation 26, a reasonable value for $\bar{M}_{z+1}/\bar{M}_z$ of 1.10 is chosen:

$$\frac{\bar{M}_z}{\bar{M}_w} = \frac{3R_o}{S_o}\left\{1 + \frac{R_* \delta}{S_o}\left[\frac{3}{2}\frac{\bar{M}_{z+1}}{M_z} - 2\right]\right\} \qquad (26)$$

The value for R_o to be inserted in equation 26 is calculated by equation 28:

$$R_o = \frac{1}{\frac{1}{R_*} + \frac{\delta}{S_o}} \qquad (28)$$

$$R_o = \frac{1}{\frac{1}{(6.19)} + \frac{(0.37)}{(12.05)}}$$

$$R_o = 5.20 \text{ megareps}$$

Substituting numbers in equation 26:

$$\frac{\bar{M}_z}{\bar{M}_w} = \frac{(3)(5.20)}{(12.05)}\left\{1 + \frac{(6.19)(0.37)}{(12.05)}\left[\frac{(3)(1.10)}{(2)} - 2\right]\right\}$$

$$\frac{\bar{M}_z}{\bar{M}_w} = 1.21$$

The relative insensitivity of the resulting value of $\bar{M}_z/\bar{M}_w$ to the choice of $\bar{M}_{z+1}/\bar{M}_z$ is shown by the fact

that other values for $\bar{M}_{Z+1}/\bar{M}_W$ give only slightly different results for $\bar{M}_Z/\bar{M}_W$:

$$\frac{\bar{M}_Z}{\bar{M}_W} = 1.21 \qquad \frac{\bar{M}_{Z+1}}{\bar{M}_Z} = 1.10$$

$$\frac{\bar{M}_Z}{\bar{M}_W} = 1.25 \qquad \frac{\bar{M}_{Z+1}}{\bar{M}_Z} = 1.20$$

$$\frac{\bar{M}_Z}{\bar{M}_W} = 1.17 \qquad \frac{\bar{M}_{Z+1}}{\bar{M}_Z} = 1.00$$

APPENDIX C

GEL SWELLING MEASUREMENTS

Gel Swelling Measurements

In section I-C-1 it was stated that the "insoluble" characteristic of crosslinked gel structures is due to intramolecular crosslinks. A certain number of the crosslinks merely join the primary chains into a giant molecule, the remaining crosslinks (intramolecular) interconnect segments of the giant molecule back upon themselves and it is these bonds which resist the solvating action of the solvent to produce an equilibrium swelling volume. Flory and Rehmer (53) have treated this relationship of swelling ratio (ratio of swelled volume to dry volume) to crosslinking density and have produced the following equation:

$$\frac{v_1 \rho}{M_c} = \frac{\frac{\mu}{V^2} + \frac{1}{V} + \ln\left(1 - \frac{1}{V}\right)}{\frac{1}{V^{1/3}} - \frac{1}{2V}}$$

V = swelling ratio

μ = polymer-solvent interaction coefficient

v = molar volume of solvent

ρ = dry density of polymer

M_c = average molecular weight between effective or intramolecular crosslinks

This equation refers to a "perfect" gel structure where chain entanglements are absent. The coefficient, μ,

is related to the second virial coefficient of the polymer, solvent system, A_2, by the following equation:

$$A_2 = \frac{1}{\rho^2 v_1} (0.5 - \mu) \qquad \text{(ee)}$$

Charlesby has shown (52) that M_c is calculable from the statistics of crosslink formation, and showed that the resulting relationship for samples with most-probable distribution is:

$$M_c = \frac{M_{og} \alpha_g}{(2 - x)\ (M_{og}\alpha_g - 2)} \qquad \text{(ff)}$$

M_{og} = number-average molecular weight of primary molecules composing the gel

α_g = crosslinking density in gel

α = crosslinking density of total system (gel plus soluble molecules)

x = insoluble or gel fraction

and:

$$M_{og}\alpha_g = \frac{2 - x}{(1 - x)^{\frac{1}{2}}} \qquad \text{(gg)}$$

If these last two equations are combined, the result is:

$$M_c = \frac{1}{\alpha\left[2 - x - 2(1- x)^{\frac{1}{2}}\right]} \qquad \text{(hh)}$$

Since α is presumed proportional to irradiation dose, R, and since M_c is a unique function of the swelling ratio, V, then swelling measurements on most-probable

distribution samples, together with solubility results and radiation dose offer an independent check on the proportionality constant between α and R. In addition, since no value for the chain length parameter appears in equation (5), the equation must apply equally well under conditions of simultaneous chain scission, since for samples with most-probable distribution, only the primary chain length parameter (not the distribution type) is affected.

To test the above proposals, swelling volumes were measured for several films during the course of routine determination of soluble fraction. After complete extraction of the soluble material in benzene, the swelled films were isolated by pouring off the supernatant solvent and "tumbling" them in a large dry beaker until the excess solvent was removed. They were then placed in a glass-stoppered, tared bottle and weighed, the swelled volume being directly calculable from this swelled weight. The dry volume was determined from the dried gel weight and the density of polystyrene (1.04). Table 11 contains the values obtained. Figure 10 is a plot of swelling ratio for samples with most-probable distribution (A, 53TH, 65TH) as a function of $R\left[2 - x - 2(1 - x)^{\frac{1}{2}}\right]$. It can be seen that the same curve satisfies the data from all three samples reasonably well.

For swelling ratios large compared to one, equation dd is closely approximated by:

$$\frac{\rho v_1}{M_c} = \frac{V^{-5/3}}{(1 - \frac{1}{2V^{2/3}})}(0.5 - \mu) + \frac{1}{3V} \qquad \text{(ii)}$$

This, together with equation hh, implies that a plot of ϕ (equal to $V^{5/3} R \left[2 - x - 2(1 - x)^{\frac{1}{2}}\right]\left[1 - \frac{1}{2V^{2/3}}\right]$ against 1/V should produce a straight line with an intercept of $\frac{0.5 - \mu}{\rho v_1 k}$ (k is defined by $\alpha = kR$) and a slope of $\frac{1}{3 \rho v_1 k}$. Figure 11 shows such a plot, indicating that, analysed in this manner, the data scatter rather badly. In an effort to get some information from the data, a least-squares slope and intercept were calculated which produced these values:

$$0.5 - \mu = 0.022$$

$$k = 4.5 \times 10^{-6} \frac{\text{fraction of units crosslinked}}{\text{megareps}}$$

The value for μ corresponds to an A_2 equal to 2.3×10^{-4} which agrees well with A_2 values in benzene from light-scattering (see section II-B-4) extrapolated through its weak dispendence on molecular weight to $1/\bar{M}_w = 0$, which should correspond somewhat to the gel condition. The value of k is in reasonable agreement with the value from gel point measurements (5.3×10^{-6} $\frac{\text{fraction of units crosslinked}}{\text{megareps}}$) and corresponds to a crosslinking efficiency of 2000 electron volts/crosslinked unit (1700 from gel point measurements).

Although these values check out quite well, the swelling results are actually open to some skepticism. In the first place, the data scatter is serious enough that the 95% confidence limit on the slope is 50%. Also there is the uncertainty as to whether a straight line is the model to use since it is quite conceivable that

is a function of swelling volume (through a dependence on polymer concentration). In addition, equation dd uses the approximation of no chain entanglements, which is undoubtedly not the case with real swollen gel structures, and the resulting swelling volumes are smaller than would be observed in the absence of this effect. Therefore the value of μ calculated by this method (0.478) is probably high to an extent governed by the relative effect of chain entanglements. Furthermore the method used to obtain the swelling volumes may be questionable since some deswelling during isolation of the gels undoubtedly takes place.

In view of the aforementioned uncertainties, it is probably best to regard the results as only semi-quantitative, and to say that they are, if not an independent check, at least reasonably consistent with results obtained from the gel curve measurements and the light scattering results.

APPENDIX D

TABLES

TABLE 8

COMPOSITE SAMPLE PREPARATION AND CHARACTERIZATION DATA

Sample	Preparation	Light Scattering $\bar{M}_w \times 10^{-6}$	Intrinsic Viscosity $\bar{M}_w \times 10^{-6}$	Sedimentation Study $\bar{M}_w \times 10^{-6}$	$\bar{M}_w/\bar{M}_n$	$\bar{M}_z/\bar{M}_w$
A	Thermal polymerization at 60°C	1.75	1.82	---	2.0[a]	1.5[a]
53TH	Thermal polymerization at 53°C	2.05	2.08	---	2.0[a]	1.5[a]
65TH	Thermal polymerization at 65°C	1.44	1.63	---	2.0[a]	1.5[a]
75TH	Thermal polymerization at 75°C	1.15	1.18	---	2.0[a]	1.5[a]
1-B	Photo polymerization	1.52	1.49	---	2.0[a]	1.5[a]
0	Thermal polymerization Room Temperature	4.93	5.45		2.0[a]	1.5[a]
F-22	Tertiary fraction obtained from second primary fraction of Sample A	3.36	---	3.68	1.075[b] 1.20[c]	1.06[b] 1.17[c]
F-32	Secondary fraction obtained from third primary fraction of Sample A	2.69	---	---	1.20[c]	1.17[c]
F-33	Secondary fraction obtained from third primary fraction of Sample A	2.42	---	2.40	1.12[b] 1.05[c]	1.09[b] 1.04[c]
F-50	Fifth primary fraction of Sample A	1.82	---	1.77	1.15[b] 1.20[c]	1.11[b] 1.17[c]
F-61	Secondary fraction obtained from sixth primary fraction of Sample A	1.77	---	1.87	1.06[b] 1.05[c]	1.05[b] 1.04[c]
D-2	Narrow fraction obtained from Dow Chemical Co.	0.226	---	0.248	1.04[e]	1.02[e]
M-1	Equal weight mixture of Sample 0 and 75TH	3.04[d]	3.31[d]	---	3.26[d]	2.05[d]
M-2	Equal Weight mixture of Samples D-2 and F-32	1.46[d]	---	---	3.72[d]	2.15[d]

a Most-probable distribution values.

b Computed from ultracentrifuge distributions, Figure

c Estimated from light scattering polydispersity parameter, Z.

d Computed from values for the components of the mixtures.

e Computed from sedimentation distribution, data not included.

TABLE 9

PARAMETERS MEASURED FROM GEL CURVES

Sample	R* (Megareps)	S_o (Megareps)	S (Megareps)	δ	R_o	$R_o\bar{M}_w \times 10^{-6}$
M-1	7.73	9.74	21.9	0.37	5.98	18.2
M-2	19.7	23.9	60.7	0.34	15.4	22.5
F-50	13.4	27.6	17.0	0.34	11.5	20.9
F-61	12.3	29.3	11.5	0.34	10.8	19.1
F-33	9.00	19.5	9.55	0.35	7.73	18.7
F-22	6.19	12.2	6.00	0.37	5.20	17.4
0	---	---	---	0.49	3.85	19.0
53TH	---	---	---	0.34	10.3	21.1
A	---	---	---	0.38	11.0	19.3
1-B	---	---	---	0.35	13.5	20.5
65TH	---	---	---	0.36	13.7	19.7
75TH	---	---	---	0.35	16.3	18.7

TABLE 10

DISTRIBUTION DATA COMPUTED FROM GEL CURVES

Sample	$(\bar{M}_w/\bar{M}_n)$	$(\bar{M}_z/\bar{M}_w)$	Estimated $\bar{M}_{z+1}/\bar{M}_z$ Used in Equa. 26
M-1	3.66	1.99	1.5
M-2	3.94	1.89	1.3
F-50	1.48	1.17	1.1
F-61	1.065	1.035	1.0
F-33	1.235	1.12	1.1
F-22	1.15	1.19	1.1

TABLE 11

GEL SWELLING DATA

Sample	Radiation Dose (Megareps)	Swelling Ratio (Swelled/Dry Volume)	Soluble Fraction
A	26.2	133.0	0.513
	33.7	77.3	0.409
	33.8	87.3	0.441
	39.8	60.6	0.333
	41.3	54.9	0.342
	55.5	51.1	0.320
	75.0	34.0	0.218
	81.0	36.0	0.245
	89.0	30.7	0.186
	131.0	25.8	0.181
53TH	25.5	121.0	0.461
	33.8	70.0	0.354
	55.5	44.4, 44.8	0.250, 0.261
65TH	49.9	54.1	0.350
A (Low Dose Rate)	84.3	31.2, 30.6	0.210, 0.207

APPENDIX E

FIGURES

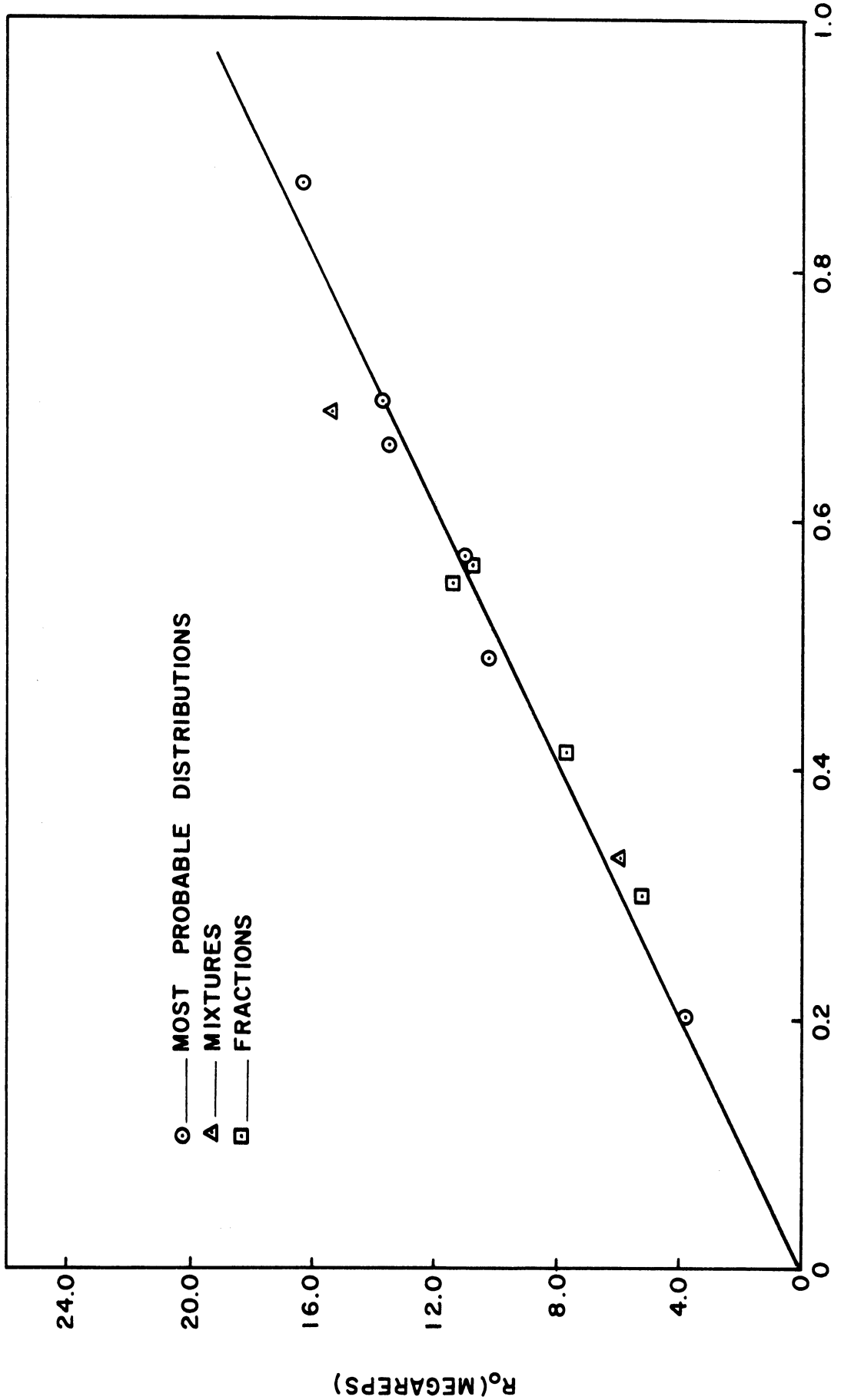

Figure 9. Virtual Gel Point Dosage as a Function of Reciprocal Weight-Average Molecular Weight.

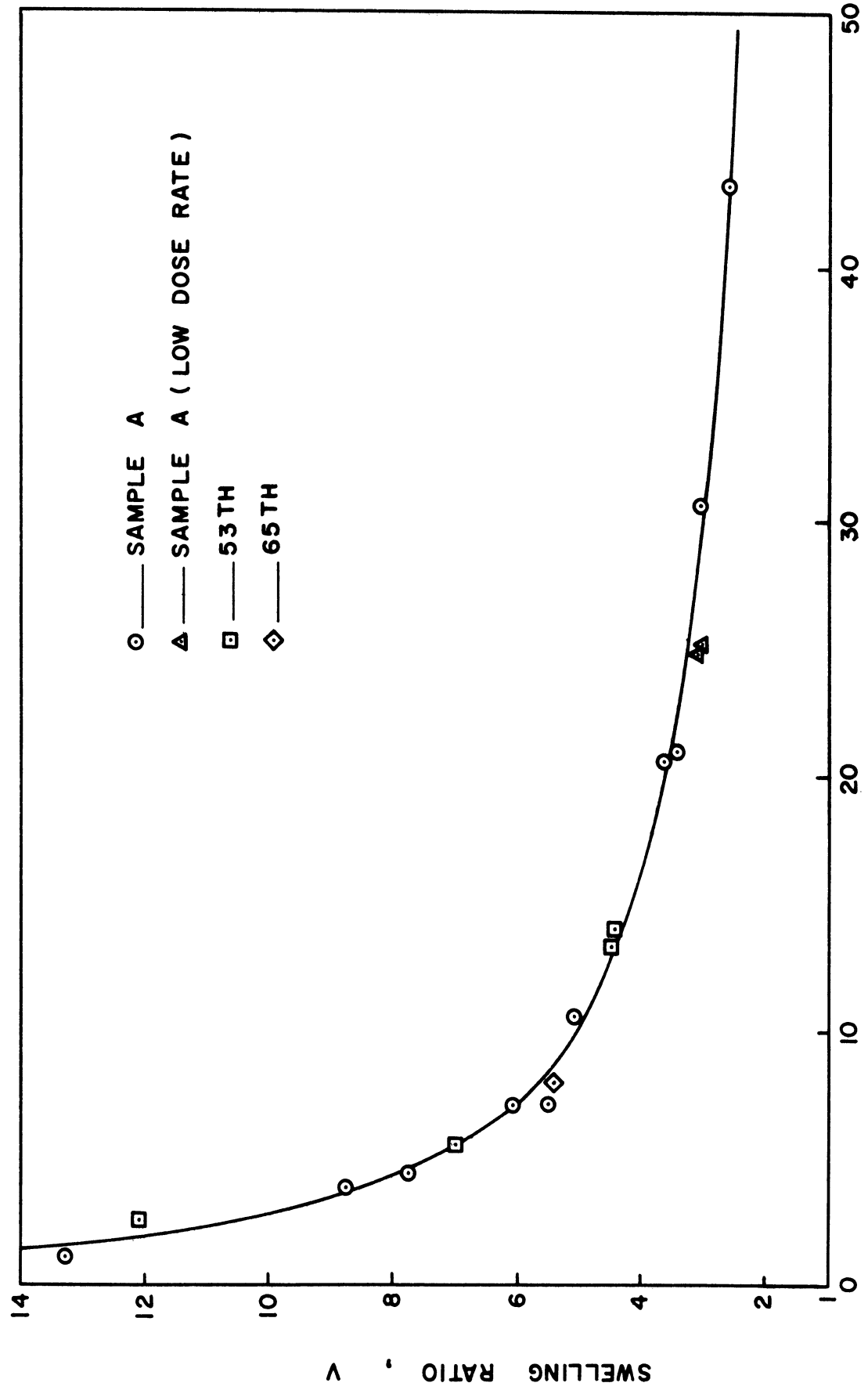

Figure 10. Gel Swelling Ratio Dependence on the Product $R[2-X-(1-X)^{1/2}]$

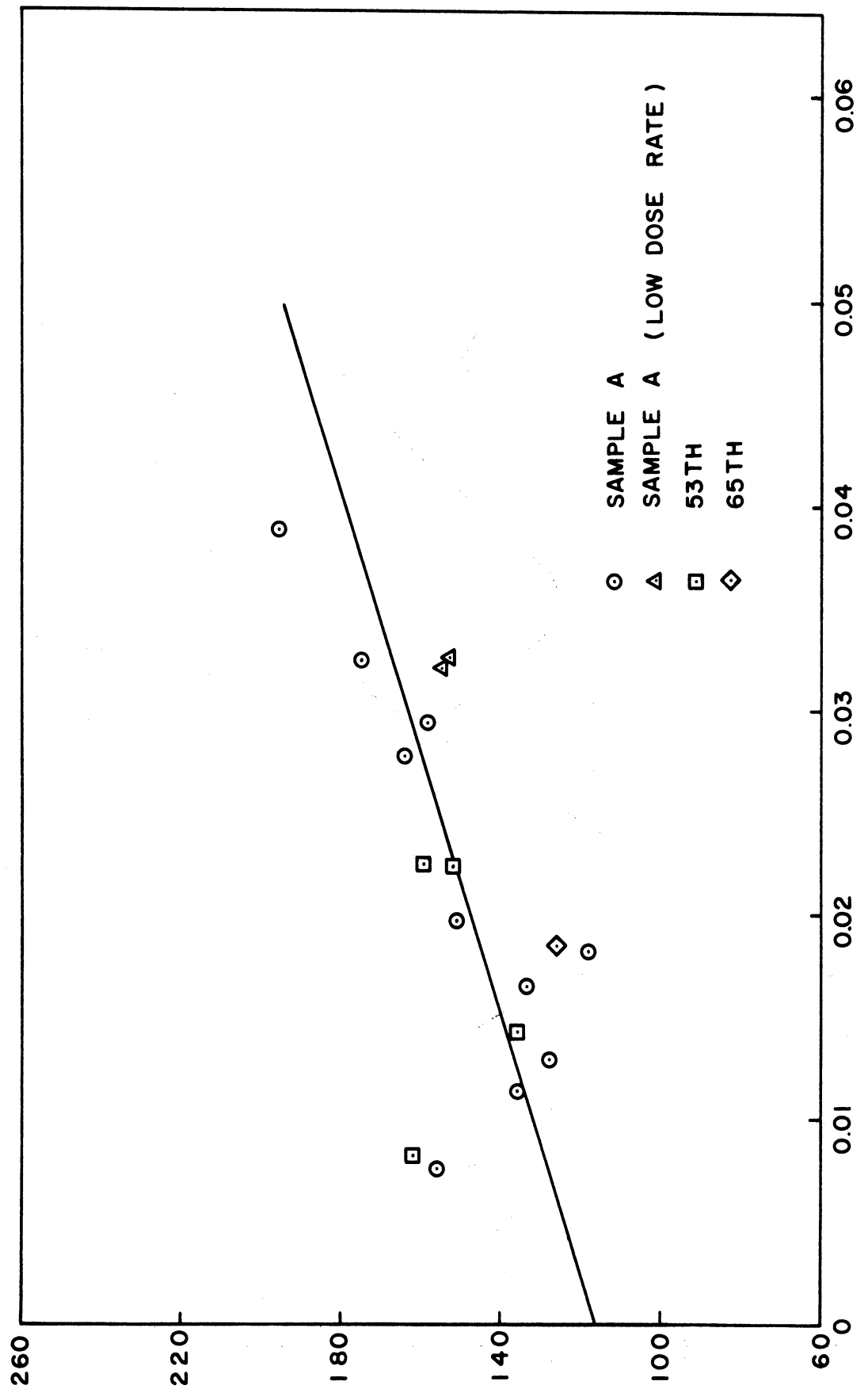

Figure 11. Plot for the Evaluation of Cross Linking Efficiency from Gel Swelling Data.

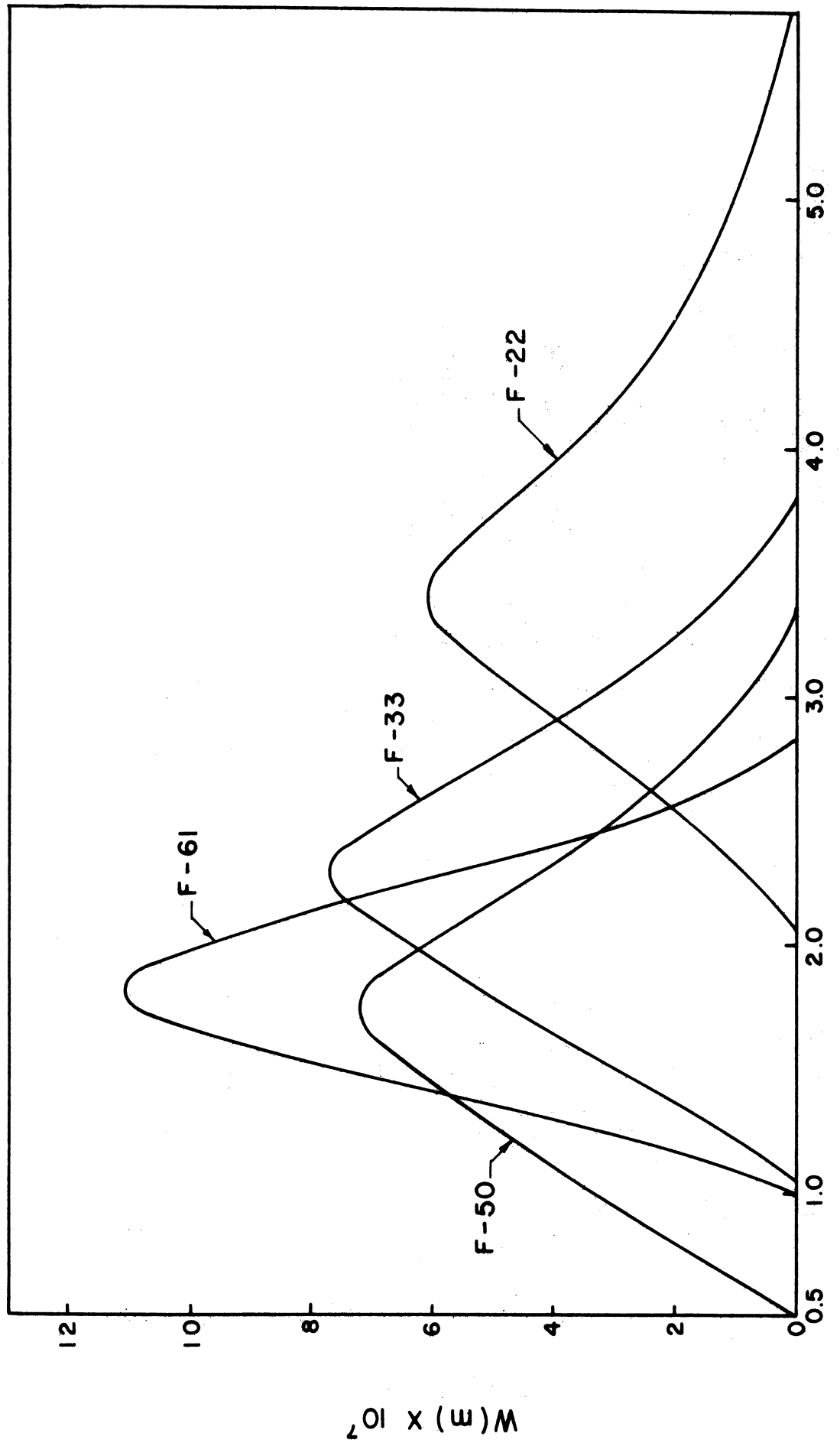

Figure 12. Weight Distribution of Narrow Distribution Fractions as Measured by the

APPENDIX F

NOMENCLATURE AND SYMBOLS

NOMENCLATURE AND SYMBOLS

a	Parameter in most-probable distribution expression
a	Exponent in relationship between intrinsic viscosity and molecular weight
A_2	Second Virial Coefficient
α	Crosslinking density, fraction of monomeric units participating in crosslinks
α_o	Crosslinking density required to reach the gel point in the absence of simultaneous chain scission
α_*	Crosslinking density required to reach the gel point in the presence of simultaneous chain scission
B,B'	Breadth parameters in distribution functions
β	Chain scission density, fraction of primary chain bonds fractured
γ	Crosslinking index, equal to $\alpha \overline{DP}_w$
γ_*	Crosslinking index at gel point in the presence of simultaneous chain scission
D.P.	Degree of polymerization
$\overline{DP}_n$	Number average D.P.
$\overline{DP}_w$	Weight average D.P.
$\overline{DP}_z$	z-average D.P.
δ	Chain scission parameter, primary chain scissions per crosslinked unit
$[\eta]$	Intrinsic viscosity
k	Proportionality constant between crosslinking density and radiation dose, megareps-1
K	Constant in relation between intrinsic viscosity and molecular weight

M,m	Molecular weight
m_o	Monomer, mer, or unit weight
$\overline{M}_n$	Number-average molecular weight
$\overline{M}_v$	Viscosity-average molecular weight
$\overline{M}_w$	Weight-average molecular weight
$\overline{M}_z$	z-average molecular weight
M_c	Average molecular weight between crosslinks in the gel
μ	Solvent-polymer interaction coefficient
n	Degree of polymerization
N	Avagadro's number
R	Radiation dose, megareps
R_o	Virtual gel point dosage, dosage required to reach the gel point in the absence of simultaneous chain scission, megareps
R_*	Actual gel point dosage, dosage required to reach the gel point in the presence of simultaneous chain scission, megareps
s'	Variable defined as $\alpha(x+\delta)$
s	Variable defined as $\beta(x+\delta)$
S_o	Slope of gel curve at the gel point dosage, megareps
S_∞	Slope of gel curve at doses which are large compared to R_*, megareps
$\overline{S_z^2}$	z-average mean-square radius of gyration of polymer molecules in solution, cm^2
V	Gel-swelling ratio, ratio of swelled weight to dry weight for the gels
$W(n),W(m)$	Molecular weight distribution function, the fraction of the sample weight contributed by polymer molecules with a D.P. of n (or of molecular weight m, where $m = m_o n$)
x	Weight fraction of crosslinked sample which is part of the gel (insoluble fraction)
Z	Breadth parameter in distribution function