MOLECULAR WEIGHT INVESTIGATION OF POLYSTYRENE

BY LIGHT SCATTERING, OSMOMETRY, AND VISCOSITY MEASUREMENTS

A THESIS

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LIST OF SYMBOLS

I. MISCELLANEOUS

M molecular weight

M_w weight average molecular weight

M_n number average molecular weight

M_v viscosity average molecular weight

W.P.   whole polymer (unfractionated)

θ theta solvent

χ polymer-solvent interaction constant

x segment number

F fraction number of polystyrene

II. VISCOSITY

η_o viscosity of solvent

η viscosity of polymer solution

η_{sp} specific viscosity

η_{sp}/c reduced viscosity

$[\eta]$ intrinsic viscosity

c concentration g/100ml or g/dl

a constant for polystyrene 0.69

k constant for polystyrene 1.7×10^{-4}

III. OSMOMETRY

π osmotic pressure in cm and atm

R ideal gas constant, 0.082 (1-atm/°K mole)

T temperature in degrees Kelvin, 298° K

c concentration g/l

$(\pi/c)_o$ reduced osmotic pressure

IV. LIGHT SCATTERING

τ turbidity

H combination of many factors reducing to 6.18×10^{-5} $n^2 (n-n_o/c)^2$

n refractive index of polystyrene solution

n_o refractive index of toluene 1.515

c concentration in g/ml

a periodically derived constant relating the opal glass reference standard to that of the working standard, 0.531

TD   correction factor for the reference standard, 0.321

F neutral filters used in the instrument, 0.500, 0.250, 0.123 and 0.0462

G_w galvanometer deflection for the light beam with the working standard (at 0°)

G_s galvanometer deflection for scattered light (at 90°)

R_w/R_c 1.035 for the 40 x 40 mm semioctagonal cell (λ =546nm) wave length of monochromatic light used, 546 nm

N Avogadro's number

h width of light beam, 1.20 cm

ABSTRACT

Polystyrene can be precipitated from a toluene solution by the addition of methanol as the non-solvent. This procedure executed step by step will cause the polymer to precipitate into fractions in order of decreasing molecular weight. Seven fractions were obtained in the above manner with an eighth one being recovered by evaporation of the solution.

All synthetic polymer samples have broad distributions of molecular weights. The number average molecular weight, M_n, for this polystyrene sample was 96,000. The M_n for fractions 1-6 ranged from 189,000 to 89,000. The M_n was determined by osmotic pressure measurements. Light Scattering from the polymer solution gave the weight average molecular weight, M_w, of 219,000 for the whole polymer. The fractions had M_w from 613,000 down to 22,700. The ratio of M_w/M_n for the whole polymer was 2.28, and that of the first six fractions ranged from 3.24 to 1.29. The viscosity average molecular weight, M_v, for the whole polymer was found to be 201,000 and those of the fractions ranged from 447,000 to 14,100.

Analysis of the data revealed partial reverse order fractionation in the first fraction. There was also some diffusion of low molecular weight polymer across the membrane in the osmometry determinations of the later fractions.

CHAPTER I

INTRODUCTION

This study was undertaken to characterize a sample of polystyrene by its molecular weight distribution. This investigation also included fractionation of the polystyrene into various fractions to assess its molecular weight distribution.

Of the many different techniques presently available, three methods were selected because of their ease or the availability of equipment. Light Scattering measurements were used to obtain weight average molecular weights; Osmometry was selected to obtain number average molecular weights; Viscosity measurements gave viscosity average molecular weights, the values of which fall between weight average and number average molecular weight.

CHAPTER II

REVIEW OF LITERATURE

I. CHARACTERISTICS OF POLYSTYRENE

Atactic polystyrene is a colorless, transparent thermoplastic polymer resistant to many chemicals. Yet, it is readily soluble in aromatic solvents such as toluene and softens above 100° C. It is a common polymer with a wide variety of uses, particularly in the injection molding process. It is composed of styrene monomers in long, unbranched chains, the structure of which is given by Figure I (13,21).

II. FREE RADICAL FORMATION

The atactic polystyrene used for this study was prepared by polymerization of styrene. In this polymerization process the reaction was catalyzed by means of benzoyl peroxide – a free radical initiator (13,15). The mechanism involves the following steps.

1. **FREE RADICAL FORMATION—BREAKDOWN OF BENZOYL PEROXIDE**

$$C_6H_5-\overset{\overset{O}{\|}}{C}-O-O-\overset{\overset{O}{\|}}{C}-C_6H_5 \longrightarrow 2\ \ C_6H_5-\overset{\overset{O}{\|}}{C}-O^{\bullet} \longrightarrow C_6H_5-\overset{\overset{O}{\|}}{C}-O^{\bullet}\ +\ C_6H_5^{\bullet}\ +\ CO_2$$
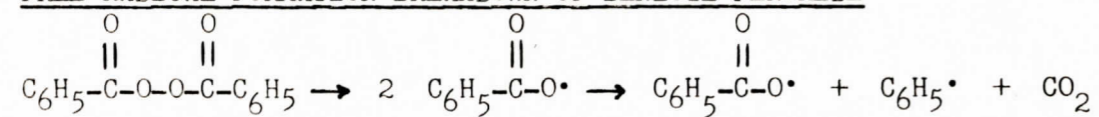
BENZOYL PEROXIDE

2. **CHAIN INITIATION**

$$C_6H_5-\overset{\overset{O}{\|}}{C}-O^{\bullet}\ +\ \underset{\underset{C_6H_5}{|}}{CH_2=CH} \longrightarrow C_6H_5-\overset{\overset{O}{\|}}{C}-O-CH_2-\overset{\overset{H}{|}}{\underset{\underset{C_6H_5}{|}}{C}}{}^{\bullet}$$

STYRENE

$$-CH-CH_2-CH-CH_2-CH-CH_2-CH-CH_2-CH-CH_2-CH-CH_2-CH-CH_2-CH-$$
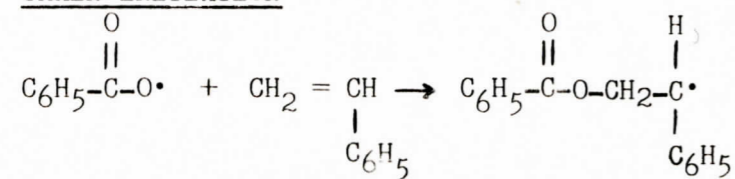
FIGURE I

STRUCTURE OF ATACTIC POLYSTYRENE (13)

3. <u>PROPAGATION OF CHAIN-SEQUENTIAL ADDITION OF MONOMERS TO THE CHAIN</u>

$$C_6H_5-\overset{\overset{O}{\|}}{C}-O-CH_2-\overset{\overset{H}{|}}{\underset{\underset{C_6H_5}{|}}{C}}\cdot \quad + \quad X \ CH_2=\overset{H}{\underset{\underset{C_6H_5}{|}}{C}} \quad \longrightarrow$$

$$C_6H_5-\overset{\overset{O}{\|}}{C}-O-CH_2-\overset{\overset{H}{|}}{\underset{\underset{C_6H_5}{|}}{C}}-\left(CH_2-\overset{H}{\underset{\underset{C_6H_5}{|}}{C}}-\right)_{X-1} CH_2-\overset{H}{\underset{\underset{C_6H_5}{|}}{C}}\cdot$$

4. <u>CHAIN TERMINATION</u>

$$C_6H_5-\overset{\overset{O}{\|}}{C}-O-CH_2-\overset{\overset{H}{|}}{\underset{\underset{C_6H_5}{|}}{C}}-\left(CH_2-\overset{H}{\underset{\underset{C_6H_5}{|}}{C}}-\right)_{X-1} CH_2-\overset{H}{\underset{\underset{C_6H_5}{|}}{C}}\cdot \quad + \quad R-CH_2-\overset{H}{\underset{\underset{C_6H_5}{|}}{C}}\cdot \quad \longrightarrow$$

$$C_6H_5-\overset{\overset{O}{\|}}{C}-O-CH_2-\overset{\overset{H}{|}}{\underset{\underset{C_6H_5}{|}}{C}}-CH_2-\overset{H}{\underset{\underset{C_6H_5}{|}}{C}}-CH_2-\overset{H}{\underset{\underset{C_6H_5}{|}}{C}}-\overset{H}{\underset{\underset{C_6H_5}{|}}{C}}-CH_2-R$$
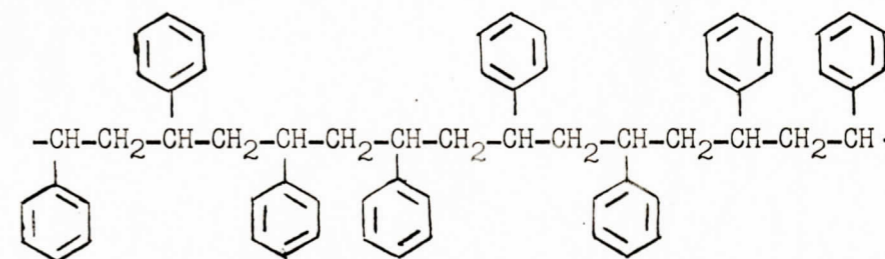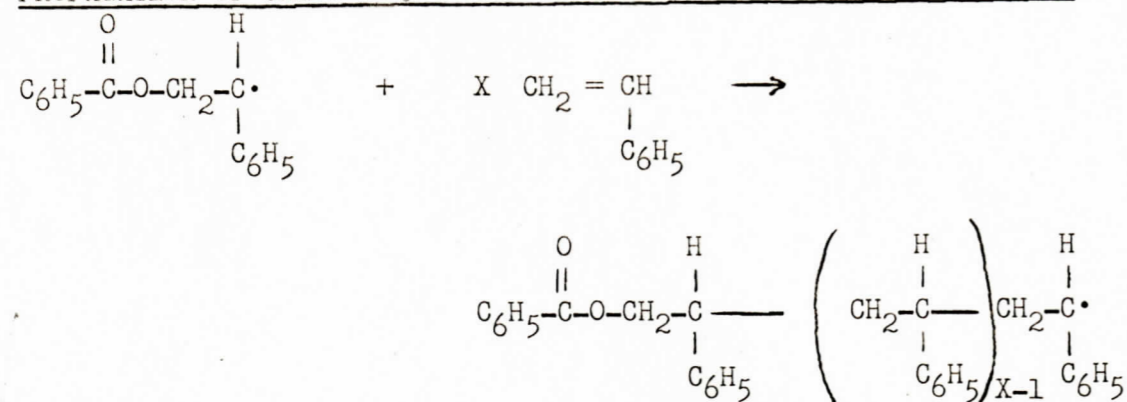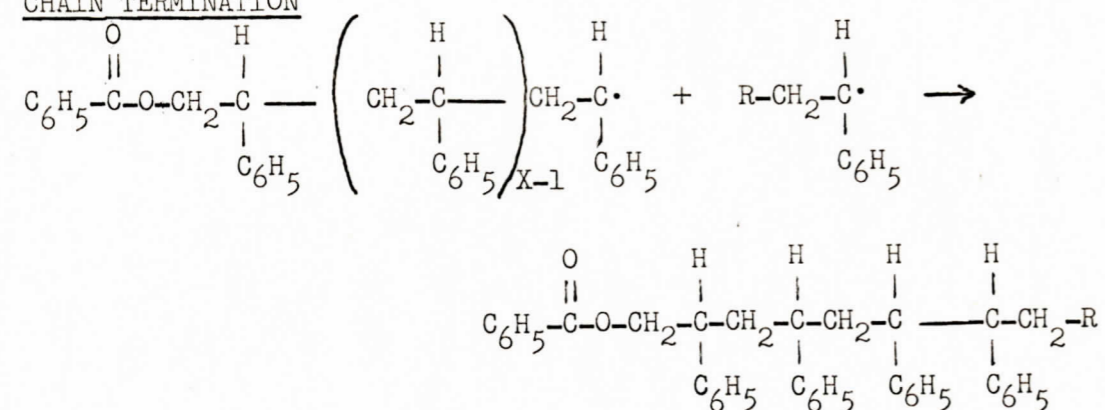
The chain termination steps can occur in several ways:

(a) two free-radical chains can unite or

(b) a free-radical chain can unite with a small free-radical such as $C_6H_5\cdot$ (15).

III. THEORY OF SOLUBILITY

Polymers when dissolved in a solvent will have interactions with the solvent as well as other portions of the polymer molecule. If the solvent is a good one, then the solvent-polymer attractive forces are larger than the intra-polymer or intra-solvent forces. Also, when the solvent is a good one, the polymer molecule expands or swells, allowing

the solvent molecules close association with all portions of the polymer. The polymer tends to be stretched out in a rod. In the Mark-Houwink equation (see Page 10), which relates intrinsic viscosity to molecular weight, the constant "a" will have a certain value depending on the solvent. In good solvents, "a" is above 0.5. In poor solvents the intra-polymer and intra-solvent forces are greater, and the molecule remains in a tightly coiled arrangement. There is, in most solvents, a constant interplay between the osmotic effect of the solvent trying to extend the polymer, and the elastic intra-polymer forces trying to return it to a minimal energy state. In poor solvents the value of "a" is below 0.5 with the extreme being zero. The polymer also exhibits a tightly coiled spherical condition when "a" is zero. A theta solvent is one in which the polymer is allowed to achieve a perfectly randomly kinked configuration or coil. There are no long range intra-polymer attractions: only short range ones between neighboring groups. The constant "a" in a θ solvent is exactly 0.5 (4)(5)(13)(15)(19).

IV. MOLECULAR WEIGHT DISTRIBUTION

Most synthetic macromolecules, during the polymerization process, grow to varying lengths depending on the experimental conditions. This random growth leads to a broad distribution of molecular weights. Since the polymer has chains of many different molecular weights, there is no one, single method of defining the molecular weight of the polymer. The three weights measured in this investigation are the weight average, M_w, the viscosity average, M_v, and the number average, M_n. A typical distribution of molecular weights is given in Figure II (4)(19).
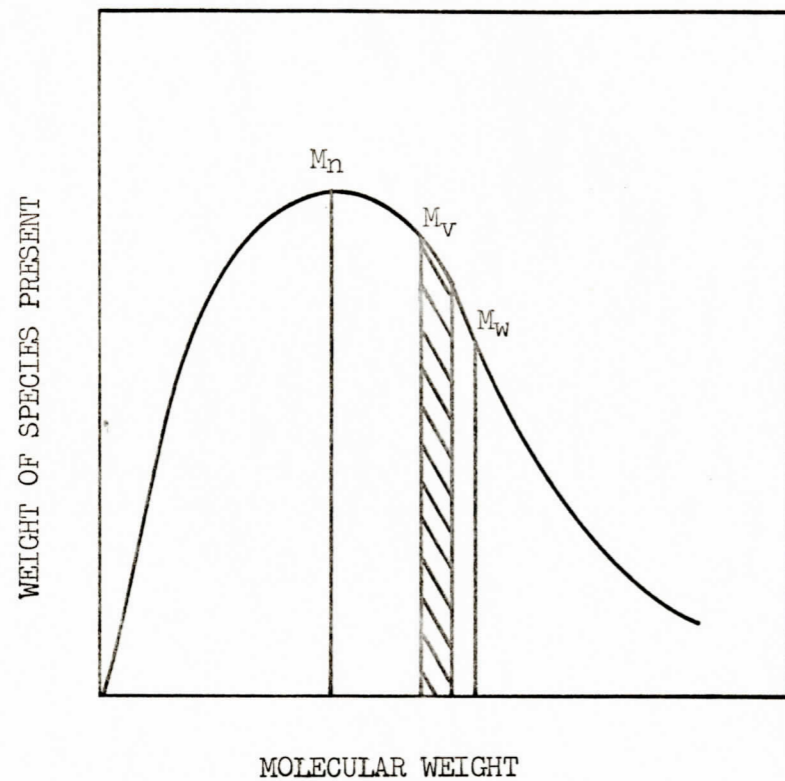
FIGURE II

TYPICAL DISTRIBUTION OF MOLECULAR WEIGHTS IN A POLYMER SAMPLE (4)(19)

The number average molecular weight, M_n, is defined as the sample weight divided by the number of moles, n:

$$M_n = \frac{\text{sample weight}}{n}$$

Each sample can be considered to be composed of many fractions of different molecular weight M_1, M_2, M_3, etc. There are certain numbers of moles of each fraction n_1, n_2, n_3, etc. The M_n then becomes:

$$M_n = \frac{n_1 M_1 + n_2 M_2 + n_3 M_3 \cdots}{n_1 + n_2 + n_3 \cdots}$$

$$M_n = \frac{\sum n_i M_i}{\sum n_i}$$

The colligative properties of polymers in solution are dependent on M_n (2)(4)(13).

The weight average molecular weight, M_w, is an average wherein each molecule makes a contribution according to its size.

$$M_w = \frac{n_1 M_1^2 + n_2 M_2^2 + n_3 M_3^2 \cdots}{n_1 M_1 + n_2 M_2 + n_3 M_3}$$

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

The turbidity is dependent on the size distribution of the molecules of M_w (4)(13).

The viscosity average molecular weight, M_v, is obtained from viscosity measurements with the constant "a" described by the weight average measurements.

$$M_v = \left[\frac{\sum n_i M_i^{a+1}}{\sum n_i M_i} \right]^{\frac{1}{a}}$$

The constant "a" depends upon solvent-polymer interaction. The M_v is between M_n and M_w. When "a" becomes unity then the M_v becomes M_w (13). For a monodispersive polymer

$$M_n = M_v = M_w$$

since all the polymer chains are the same length. When the polymers are of different lengths, there is a distribution of molecular weights. The ratio most often used to describe this breadth of distribution is the M_w/M_n. This ratio is usually large for most polymers, being in the range of 1.5-5 (1)(4)(19)(23). The ratio M_w/M_v can also give information about the distribution (28).

V. FRACTIONAL PRECIPITATION OF POLYSTYRENE

Fractional precipitation from solution is one of the more common batch fractionation procedures available. It can be accomplished by one of the following three methods:

1. non-solvent addition

2. evaporation of solvent

3. temperature decrease

This study will limit discussion to that involving the step by step addition of a non-solvent to a polymer solution to precipitate successively the higher molecular weight fractions first and the lower ones last (4)(17).

The synthetic polymers available today are not homogeneous molecules of identical weight, but mixtures of many different molecular weights often over a wide range. The poly-dispersed polymer is in a single liquid phase with a good solvent. The solvent power is decreased past the critical point, to cause a second phase to separate.

The fractionation of polymers depends on the principle that the lower molecular weight ones tend to be more soluble in the phase of greater solvent power. The phase of lower solvent power is either a viscous liquid or a gel containing the higher molecular weight fractions. The ratio of solvent to non-solvent as well as the molecular weight distribution is quite different in each phase (8)(14).

Solvent power can be expressed as polymer-solvent interaction constant, χ. A good solvent should have an χ under 0.5 and a non-solvent a value above 0.5. If χ_c (critical value), something over 0.5, is reached by non-solvent addition, then a second phase forms. The χ_c is dependent on molecular size. The fact that the system is multicomponent leads to incomplete separation of the molecules (17).

The advantages of this system of fractionation are the simple procedure, and no need for elaborate equipment. The vessel has to be large enough to contain the polymer solution plus the final amount of non-solvent. The vessel must also be of the proper shape so that the second phase can fall to the bottom for easy collection. A syringe with a long cannula can be used to remove the lower phase (17).

The selection of solvent and nonsolvent for atactic polystyrene precipitation has few limitations. The non-solvent should be chosen so as to cause precipitation within a reasonable volume. A nonsolvent

with a relatively weak precipitating power will lead to large volumes of solution. However, if a non-solvent of great precipitating power is used, poor control of fractionation can occur. Also the solvent-non-solvent mixture should not produce a better solvent than the pure solvent. The solvent-non-solvent pair should lead to an easily handled precipitate. Reverse-order fractionation occurs when intermediate molecular weight polymers precipitate in the early fractions. The possibility of reverse order fractionation in some systems can occur if the precipitating power of the non-solvent used is too great or if the initial polymer concentration is too great. Either possibility should be avoided if possible (17).

Another condition which may be involved in fractional precipitation procedure is the phenomenon of "tailing." This is the condition whereby every fraction contains a certain percentage of lower molecular weight polymers. This, too, is enhanced by a greater precipitating power of the non-solvent used (17).

VI. METHODS OF MOLECULAR WEIGHT DETERMINATIONS

Molecular Weight By Viscosity. The viscosity average molecular weight, M_v, may be determined by the Mark-Houwink equation (2)(9)(24):

$$[\eta] = KM_v^a$$

$[\eta]$ is the intrinsic viscosity, and K and "a" are empirical constants dependent on the polymer-solvent system. The values of the constants used for polystyrene in toluene at $25^{\circ}C$ are: (9)(21)

a = 0.69   K = 1.7 x 10^{-4}

The viscosity average molecular weight, M_v, will be intermediate between the number average and weight average molecular weights (9)(13)(24).

Actually, the M_v is a range depending on the polymer-solvent interaction (23).

The constant "a" usually has values between 0.5 and 0.8 in a good solvent, although values have been higher. A θ solvent is one in which "a" exactly equals 0.5 and the molecule is perfectly flexible.

For values higher than 0.5 and lower than 0.8, the polymer will be a linear and partially flexible chain. A value of 1.0 for "a" indicates a rather rigid rod. The values used in this study were obtained by light scattering of a polystyrene sample with a molecular weight range similar to the molecular weight range of this sample (4)(5)(6)(13)(18)(21).

The specific viscosity, η_{sp}, is defined as:

$$\eta_{sp} = \frac{\eta - \eta_o}{\eta_o}$$

where η and η_o are viscosities of the solution and solvent, respectively. The specific viscosity can now be determined from the flow time of the polymer solution, t, and comparing it to that of the solvent, t_o:

$$\eta_{sp} = \frac{\eta}{\eta_o} - 1 = \frac{\rho\, t}{\rho_o t_o} - 1$$

Using the same viscometer and considering the densities, ρ and ρ_o of both solvent and dilute polymer solution to be essentially equal, the specific viscosity becomes: (2)(6)(9)(24)

$$\eta_{sp} = \frac{t}{t_o} - 1$$

The reduced viscosity, $\dfrac{\eta_{sp}}{c}$, is calculated by dividing the specific viscosity by the concentration (2)(9).

Finally, the intrinsic viscosity can be determined by extrapolating the reduced viscosity to an infinite dilution (9)(13)(24).

$$[\eta] = \lim_{c \to o} \frac{\eta_{sp}}{c}$$

Concentration is measured in g/100ml and the units of intrinsic viscosity are deciliters per gram (24).

Molecular Weight By Osmometry. Osmotic pressure, π , develops across any membrane in which the solvent can pass but the solute can not. The basic equation which relates osmotic pressure to molecular weight is:

$$\frac{\pi}{c} = \frac{R\,T}{M} + B\,c$$

Concentration c, is in g/l, and T is temperature in degrees Kelvin. R is the ideal gas constant and B is a constant related to the polymer-solvent interaction. Since the molecular weight in this equation is solely dependent upon the number of molecules and not the size, M is a number average. Plotting $\frac{\pi}{c}$ versus c for a number of dilute solutions and extrapolating to infinite dilution, the second term becomes zero and gives:

$$\lim_{c \to o} \frac{\pi}{c} = \left(\frac{\pi}{c}\right)_o = \frac{R\,T}{M}$$

This equation now can be used to determine M_n. The term $\left(\frac{\pi}{c}\right)_o$ is called the reduced osmotic pressure (2)(9)(13)(19)(21).

There are many types of semipermeable membranes available. In this study cellophane membranes were used. In practice most membranes are not truly semipermeable, which leads to a major problem — the diffusion of smaller polymers across the membrane into the solvent. The lower limit of polymer impermeability varies with the type of membrane, but it is generally considered to be somewhere around 25,000. Errors can arise with samples of a molecular weight range of 40,000–50,000, if there is an appreciably wide distribution (4)(13)(19)(27).

Molecular Weight By Light Scattering. The M_w can be determined from methods such as light scattering which depends on the size or weight of the molecule. Light scattering can be used to measure polymer molecular weights from approximately 5,000 and up (2)(13).

The light scattered at 90° to the incident beam can be defined in classical terms as the turbidity, τ , and is expressed by the equation:

$$\tau = \frac{32\,\pi^3}{3} \cdot \frac{n_o^2\,(n - n_o)^2}{\lambda^4} \cdot \frac{1}{n_s}$$

The index of refraction of the solution is n and that of the solvent is n_o. The wave length, λ , is that of the irradiating light in a vacuum expressed in cm. The term n_s, number of molecules per cm^3, can be replaced with cN/M where N is Avogadro"s number, M is the molecular weight, and c is the concentration in g/cm^3. τ now becomes:

$$\tau = \frac{32\,\pi^3\,n_o^2\,\left(\dfrac{n - n_o}{c}\right)^2\,Mc}{3\,\lambda^4\,N}$$

In the above equation several terms can be combined into a single one and given the designation H:

$$H = \frac{32\,\pi^3\,n_o^2}{3N\,\lambda^4}\,\left(\frac{n - n_o}{c}\right)^2$$

The term $\left(\dfrac{n - n_o}{c}\right)^2$ is the refractive index increment and is measured by a differential refractometer (3)(10)(22).

The above equation reduces to:

$$\frac{\tau}{c} = HM$$

for infinitely dilute solutions. For solutions of higher concentrations,

the equation becomes:

$$\frac{Hc}{\tau} = \frac{1}{M} + 2Bc$$

where B is a constant dependent on solvent-polymer interaction. It is the same constant which appears in the osmotic equation. By plotting $\frac{Hc}{\tau}$ versus c, the weight average molecular weight can be determined from the intercept (3)(10)(22).

The turbidity, τ, is measured from polymer solutions by the ratio of scattered light at 90°, Gs, to the transmitted light at 0°, Gw, as previously mentioned. In practice a complex formula involving many corrections and factors is used:

$$\tau = \frac{16\ T\ D}{3\ (1.049)\ h} \left[n^2 \left(\frac{R_w}{R_c} \right) \right] \left[aF \left(\frac{Gs}{Gw} \right) \right]$$

In order to measure the ratio of light more accurately, the instrument introduces neutral filters, F, into the primary beam to bring it into the range of the scattered light. The constant, "a", is determined periodically and relates the working standard to the opal glass reference standard. The term R_w/R_c is a correction for the incomplete compensation for refractive effects. The "h" term is the width of the diaphragm of the incoming light, and TD is a correction factor in order for the reference standard to be a perfect reflecting diffusor (22).

One major problem of the light scattering method is the presence of large colloidal particles which, nevertheless, can be removed by the use of a fine sintered glass filter (4)(26).

EXPERIMENTAL PROCEDURES

I. CHEMICALS

The solvents used in these experiments were purified by distillation. The solvent for the polystyrene was toluene, Mallinckrodt, analytical reagent. The non-solvent used in fractionation was anhydrous methanol, Mallinckrodt, analytical reagent. The atactic polystyrene sample was obtained from Monsanto Chemical Company.

The polystyrene was weighed on a Voland 100 analytical balance by using weights which were previously calibrated on a Mettler balance. The original sample of polystyrene was weighed on the Mettler balance.

Polystyrene solutions for all molecular weight determinations were prepared by the dilution of a 1% (w/v) stock solution of each fraction and of the whole polymer to the desired concentration.

All intercepts were determined from the least square lines. No attempt was made to calculate the slope of the various lines as all the desired data could be derived from the intercepts.

II. FRACTIONATION PROCEDURES

Fractionation was accomplished by the step by step addition of methanol to a 2% (w/w) polystyrene - toluene solution. This concentration was chosen to give the maximum quantity of each fraction with the least amount of solvent. Enough methanol was added to cause approximately 10% of the polystyrene to precipitate. The solution was then placed in a cold box at 0°C for 24 hours. The lower phase containing the

precipitated polystyrene fraction was removed, dried for at least one week on a warm water bath and weighed. The procedure was repeated six more times. The eighth fraction was obtained by evaporating the solvent. The schedule of the methanol addition and the fraction weights are given in Table I.

III. VISCOSITY PROCEDURES

Viscosity measurements were made on each fraction and on the whole polymer with a Cannon-Fenske viscometer, size 100. The temperature was maintained at 25.0°C ± 0.1 by means of a thermoregulated water bath. Ten milliliters of each solution was used for each concentration. The efflux times were measured by means of a stopwatch. Repeated trials were made until the results of three procedures agreed, within 0.2 sec (24). To help reduce errors, two viscometers were used with each solution concentration, and a 4X magnifying glass aided in observing the passage of the meniscus.

The maximum concentration used was 1%. As the molecular weight of each fraction decreased, the efflux times of the lower concentration were too small for reliability. Therefore, as the molecular weight of each fraction decreased the lowest concentration was increased. Between each fraction, the viscometers were cleaned with toluene followed by potassium dichromate cleaning solution.

IV. OSMOMETRY PROCEDURES

A Hellfritz rapid, double-chambered, osmometer manufactured by Carl Schleichier and Schuell Co. was used in these experiments. The

osmometer was assembled according to established procedures (7). The only change made was that the assembling was carried out under a layer of toluene to prevent the membrane from drying (20). After filling, the capillary tubes were sealed with meta phosphoric acid since it is not soluble in toluene. The entire apparatus was placed in a cuvette containing toluene. The cuvette was then placed in a constant temperature bath at 25.0°C ± 0.1. The time needed for equilibrium to occur was between 3 and 24 hours. Periodic readings were made until the same reading was obtained over a 30-minute period. Height differences in centimeters were recorded.

The cellophane membrane (filter type 07, thickness 80-90 μ, and diameter 65 mm) used had an osmotic permeability which allowed molecular weight determinations down to 25,000.

The membranes were conditioned by daily washes with distilled water for a period of one week, then soaked for 24 hours in each of these solutions: 30% acetone-70% water, 50% acetone-50% water, 70% acetone-30% water, and 100% acetone. The membranes were then placed in acetone for three days with daily acetone changes. Conditioning to toluene was next accomplished by soaking in 30% toluene-70% acetone, 50% toluene-50% acetone, 70% toluene-30% acetone and finally 100% toluene. Finally, the membranes were soaked in toluene for two more days with daily toluene changes. Any improperly prepared membranes were detected by the appearance of white spots (16)(20).

V. LIGHT SCATTERING PROCEDURES

The light scattering was performed with a Brice-Phoenix Universal 2000 Light Scattering Photometer equipped with a Honeywell recorder. The light of wavelength 546 nm was obtained from a mercury lamp.

The procedure and equation for determining M_w were those given in the light scattering operating manual (22). The scattering ratio, G_s/G_w, was measured five times for each sample concentration and then averaged, and the turbidity was calculated. The turbidity of the solvent, toluene, was then determined and subtracted to give actual turbidity, τ , of the polystyrene solution (22). No dissymmetry corrections were made as the molecular weights were not extremely large and did not justify these corrections (1)(26).

The corrections for incomplete compensation for refraction effects (R_w/R_c) were obtained from the Brice-Phoenix light scattering manual. The constant "a", which relates the working standard to the opal glass reference standard, was determined by the procedures in the operation manual (22). No additional corrections were necessary.

The solutions of polystyrene used for the light scattering measurements were prepared separately and filtered under pressure through a fine sintered glass filter. The toluene was also filtered in the same filter (26).

The refractive index increment, $\left(\dfrac{n-n_o}{c}\right)$, was determined by using a Brice-Phoenix differential refractometer and by using the procedures outlined in the Brice-Phoenix Differential Refractometer manual. A KCl solution was used to determine the constant, k, as specified by the above operation manual.

CHAPTER IV

RESULTS AND DISCUSSION

I. FRACTIONATION

The attempt to arrive at exactly 10% fractional weights was not achieved because of the unpredictability of the fractionating system (Table I). This unpredictability was probably due to small variations in the cooler box temperatures. The weights, the percentages of each fraction and the cumulative percentages are given in Table I.

The combined weight of the fractions was 5% greater than the original polystyrene weight. This was due to solvent which was not evaporated during the drying of each fraction. Even extended drying time over a warm water bath and air drying failed to reduce the weight (17). In an effort to obtain adequate amounts of each fraction, the toluene-polystyrene solution was probably too concentrated, which resulted in a partial reverse order fractionation of the first fraction (17).

II. VISCOSITY

The viscosity average molecular weights, Table IV, are in proper order and agree reasonably well with the other molecular weight averages. There is some difficulty in timing the lower molecular weight fractions, Table II , and lower concentrations of other fractions. This is due to small differences in efflux times between solvent and solution. This small error in timing leads to a corresponding larger error in η_{sp}/c, Table III. This did not, however, appear to be a major problem in obtaining the final results.

TABLE I

FRACTIONATION OF POLYSTYRENE IN TOLUENE (2%)[a] BY METHANOL

FRACTION NUMBER	CUMULATIVE CH3OH ml	WEIGHT OF FRACTIONS g	CUMULATIVE FRACTIONS			
			WEIGHT g	% BASED ON 40 g	% BASED ON 42 g	CUMULATIVE %
1	570	6.240	6.240	15.6	14.9	14.9
2	580	3.805	10.045	9.5	9.1	24.0
3	592	4.793	14.838	12.0	11.4	35.4
4	608	4.328	19.166	10.8	10.3	45.7
5	650	6.894	26.060	17.2	16.4	62.1
6	749	7.440	33.500	18.6	17.7	79.8
7	824	2.099	35.599	5.3	5.0	84.8
8	from evaporation of solution	6.406	42.005	16.0	15.3	100.0
TOTAL	—	—	—	105.0	100	—

[a] 40 g of Polystyrene in 1960 g (2240 ml) of Toluene

TABLE II

THE AVERAGE VISCOSITY EFFLUX TIMES OF EACH CONCENTRATION
FOR EACH FRACTION OF A TEN ml SAMPLE

CONCENTRATION g/100 ml	W.P.	TIME IN SECONDS FRACTION NUMBER							
		1	2	3	4	5	6	7	8
1.00[a]	85.4	—[d]	117.2	102.2	90.2	76.8	62.5	55.0	47.8
1.00	85.4	135.1	117.3	102.5	90.5	77.2	62.6	55.1	47.9
0.75	72.6	104.5	93.2	83.8	75.6	66.9	56.6	51.2	46.0
0.75	72.6	104.8	93.2	83.9	75.7	66.9	56.7	51.3	46.0
0.60	—[b]	—	—	—	—	—	—	—	45.2
0.60	—	—	—	—	—	—	—	49.2	45.2
0.50	60.9	79.0	72.8	67.6	62.8	57.1	51.2	47.8	44.6
0.50	60.9	79.1	73.1	67.5	62.8	57.1	51.1	47.9	44.7
0.40	—	—	—	—	—	—	—	46.6	44.0
0.40	—	—	—	—	—	—	—	46.6	44.2
0.30	—	—	—	—	—	50.5	47.6	45.3	43.3
0.30	—	—	—	—	—	50.7	47.3	45.3	43.4
0.25	50.6[c]	58.2	55.6	53.5	51.4	48.8	46.3	—	—
0.25	50.6[c]	58.2	55.7	53.5	51.4	48.8	46.3	—	—
0.20	—	54.5	52.5	=	49.3	—	—	—	—
0.20	—	54.6	52.5	=	49.3	—	—	—	—

[a] Each concentration is listed twice since two viscometers were used. Times for solvent passage of both were 41.8 seconds.
[b] Indicates no solution prepared
[c] The concentration for this fraction was 0.248 g/100 ml
[d] The values for these solutions were in error and disregarded.

TABLE III

REDUCED VISCOSITY, $\dfrac{\eta_{sp}}{c}$

CONCENTRATION g/100 ml	W.P.	1	2	3	4	5	6	7	8
						FRACTION NUMBER			
1.00	1.043	=	1.804	1.452	1.158	0.837	0.495	0.316	0.144
1.00	1.043	2.232	1.806	1.452	1.165	0.846	0.498	0.318	0.146
0.75	0.981	2.000	1.640	1.340	1.079	0.800	0.472	0.300	0.134
0.75	0.981	2.009	1.649	1.342	1.081	0.800	0.475	0.303	0.134
0.60	-	-	-	-	-	-	-	0.295	0.136
0.60	-	-	-	-	-	-	-	0.295	0.136
0.50	0.912	1.780	1.484	1.234	1.004	0.732	0.450	0.288	0.134
0.50	0.912	1.784	1.498	1.230	1.004	0.732	0.444	0.292	0.139
0.40	-	-	-	-	-	-	-	0.288	0.132
0.40	-	-	-	-	-	-	-	0.288	0.144
0.30	-	-	-	-	-	0.693	0.430	0.279	0.120
0.30	-	-	-	-	-	0.710	0.440	0.279	0.128
0.25	0.846	1.568	1.320	1.120	0.920	0.668	0.432	-	-
0.25	0.838	1.568	1.332	1.120	0.920	0.668	0.432	-	-
0.20	-	1.520	1.280	=	0.895	-	-	-	-
0.20	-	1.530	1.280	=	0.895	-	-	-	-

TABLE IV

INTRINSIC VISCOSITY $[\eta]$, AND VISCOSITY AVERAGE MOLECULAR WEIGHT, M_v

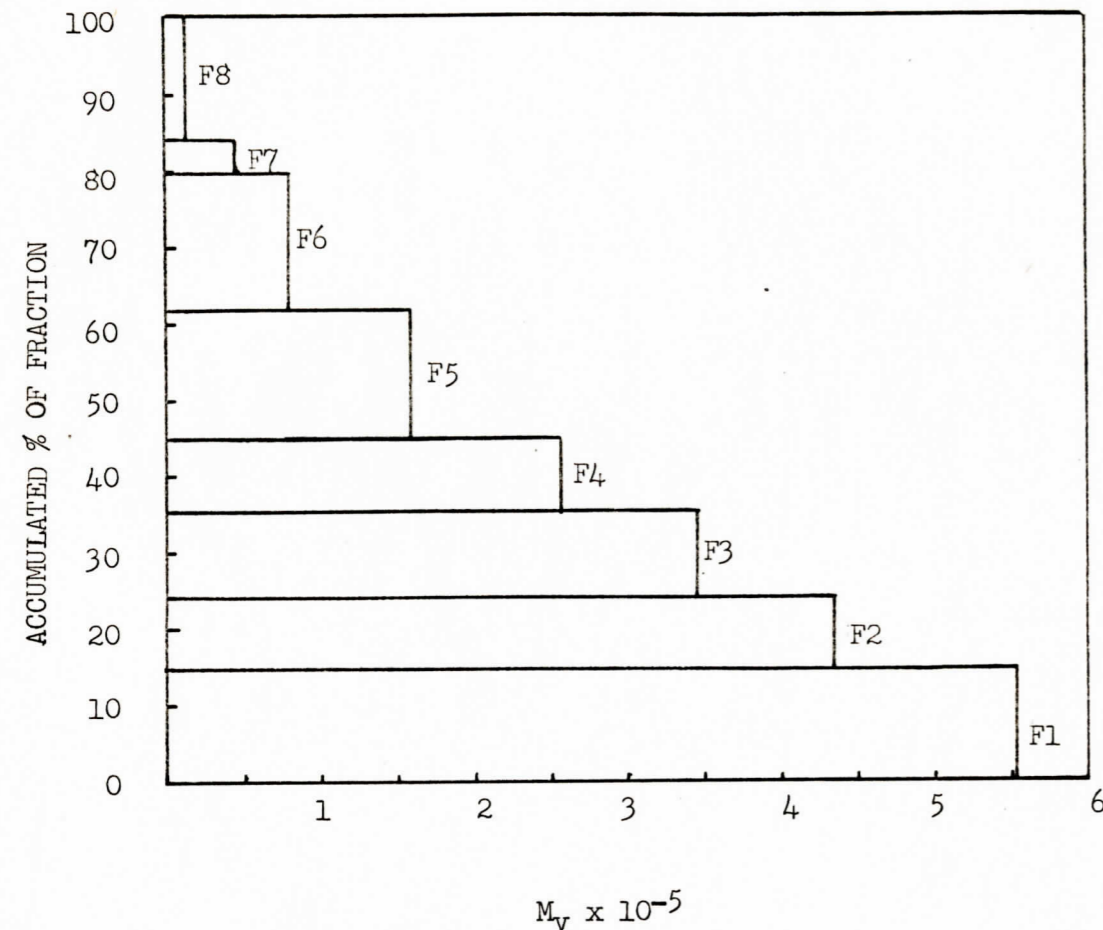| FRACTION NUMBER	$[\eta]$ dl/g	M_v
W.P.	0.776	228,000
1	1.35	554,000
2	1.16	435,000
3	1.01	348,000
4	0.835	256,000
5	0.622	159,000
6	0.408	80,000
7	0.266	40,000
8	0.124	11,000

FIGURE III

INTEGRAL DISTRIBUTION OF M_v FOR THE POLYSTYRENE SAMPLE

The molecular weight of each fraction, Table IV, is successively less than the previous value. This seems to indicate that no appreciable molecular weight inversion occurred during fractionation. The integral distribution for M_v is given in Figure III. However, when comparing M_w to M_v, the ratio, 1.37, of fraction 1 appears larger than the ratio for the whole polymer or its neighboring fractions. This points to the possibility that some increased amount of low molecular weight polymer is, indeed, precipitated in the first fraction step leading to a large spread of average molecular weights.

III. OSMOMETRY

The M_n of the first six fractions and the whole polymer were in reasonable agreement (see Table VIII and Figure IV). In the lower molecular weight fractions, there was probably diffusion of the smaller polymers across the membrane leading to higher molecular weights than should have been obtained. This is especially true in fraction 6 where the M_n exceeded the M_v. Diffusion is also apparent in the M_w/M_n and M_v/M_n ratios as they are decreasing with an increase of fraction number. Fractions 7 and 8 were not tested because of a shortage of suitable membranes. This diffusion of a small polymer has been observed in many other cases (4)(11)(12)(25). The cellophane membranes were recommended only down to a molecular weight of 25,000 (7). This diffusion may be decreased by reducing the time for equilibrium to occur (4)(7)(25). To help decrease time for equilibrium to be reached, a long needle was inserted into a capillary tube and the liquid

height adjusted (7)(25). This procedure did not prove successful; it caused a hole in the membrane probably by ballooning the membrane against a sharp edge of the osmometer.

Tables V and VI give the osmotic pressures in centimeters and in atmospheres. Table VII lists the osmotic pressure per concentration for each fraction.

The high M_w/M_n and M_v/M_n, as given in Table X, in fraction 1 is due to partial reverse order fractionation. The M_n is dependent upon the number of particles whereas M_v and M_w are more dependent on the size. This in turn would lead to the spread. The reverse order fractionation also would cause the lower M_n in fraction 1 compared to the rest of the fractions.

The metaphosphoric acid used as a capillary tube sealant had a detrimental effect on the membranes which limited the effective life to no more than three trials. There seemed to be one concentration in each fraction which gave values out of line with others or where the osmometer repeatedly leaked. Repeated trials were attempted. After a period of time, a switch to a solution of a different concentration was necessary in view of the limited supply of membranes. These are indicated by a double line in Tables V-VIII. Leakage from the osmometer was detected by a deviation in total height of liquid in both capillary tubes.

VI. LIGHT SCATTERING

The values obtained for τ were in agreement for all solutions (see Table IX). The refractive index increments (Table X)

TABLE V

OSMOTIC PRESSURE-HEIGHT-DIFFERENCE IN CENTIMETERS
BETWEEN SOLVENT AND SOLUTION

CONCENTRATION		FRACTION NUMBER					
g/l	W.P.	1	2	3	4	5	6
10.0	3.80	2.30	2.30	2.50	2.50	2.95	3.80
7.5	2.60	1.40	1.70	1.70	1.80	=	2.65
5.0	=a	0.90	0.95	=	=	1.20	1.80
3.0	-	-	-	-	-	0.85	=
2.5	0.85	=	0.45	0.55	0.65	0.65	0.85
2.0	-	0.35	=	0.40	0.45	-	-
1.5	0.45	-	-	-	-	-	-

aValues with large deviation from the other values of that fraction

TABLE VI

OSMOTIC PRESSURE, π (10^4 atm)

| CONCENTRATION | | FRACTION NUMBER | | | | | |
g/l	W.P.	1	2	3	4	5	6
10.0	31.92	13.31	19.32	21.01	21.00	24.78	31.92
7.5	21.85	11.76	14.28	14.28	15.12	=	22.26
5.0	=a	7.56	7.98	=	=	10.08	15.12
3.0	-	-	-	-	-	7.14	=
2.5	7.14	=	3.78	4.62	5.46	5.46	7.14
2.0	-	2.94	=	3.36	3.78	-	-
1.5	3.77	-	-	-	-	-	-

aValues with large deviations from the other values in that fraction

TABLE VII

OSMOTIC PRESSURE PER CONCENTRATION, $\dfrac{\pi}{c}$ $10^4 \left(\dfrac{\text{l-atm}}{\text{g}}\right)$

| CONCENTRATION | | FRACTION NUMBER | | | | | |
g/l	W.P.	1	2	3	4	5	6
10.0	3.19	1.93	1.93	2.10	2.10	2.48	3.19
7.5	2.91	1.57	1.90	1.90	2.02	=	2.97
5.0	=a	1.51	1.60	=	=	2.02	3.02
3.0	-	-	-	-	-	2.38	=
2.5	2.86	=	1.51	1.85	2.18	2.18	2.86
2.0	-	1.47	-	1.68	1.89	-	-
1.5	2.51	-	-	-	-	-	-

aValues with large deviations from the other values of that fraction

TABLE VIII

REDUCED OSMOTIC PRESSURE, $\left(\frac{\pi}{c}\right)_o$ $10^4\left(\frac{\text{1-atm}}{g}\right)$ AND

NUMBER AVERAGE MOLECULAR WEIGHT, M_n

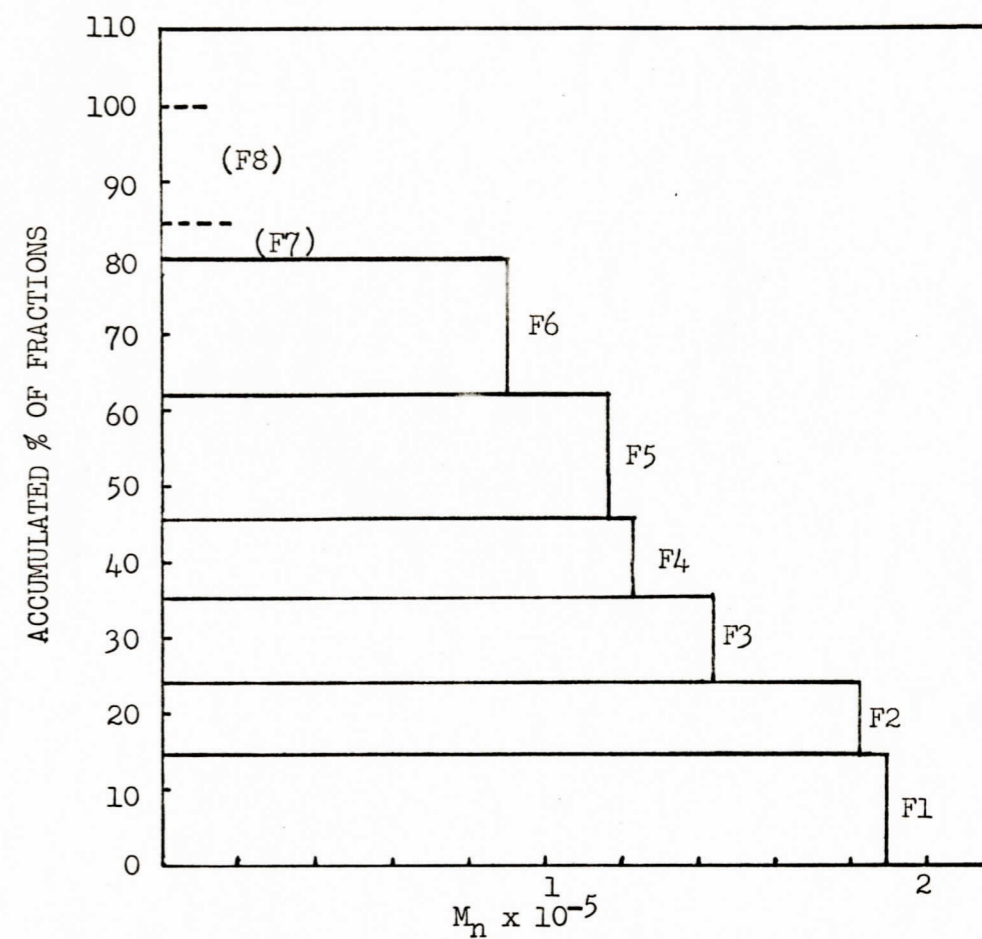| FRACTION NUMBER	$\left(\frac{\pi}{c}\right)_o$	M_n
W.P.	2.54	96,000
1	1.29	189,000
2	1.34	182,000
3	1.70	144,000
4	1.98	123,000
5	2.10	116,000
6	2.72	89,000
7	$-^a$	-
8	-	-

[a]Fractions 7 and 8 were not tested

FIGURE IV

INTEGRAL DISTRIBUTION OF M_n FOR POLYSTYRENE

seemed to increase as the solutions became more dilute. They were in agreement with published values (5). In only three solutions were reasonable refractive index increments not obtained. They were the 1% for fraction 8 and the 0.4% for fractions 7 and 8. Since these latter two were the only fractions with the 0.4% concentration they were omitted. Values for the square of the refractive index increment are given in Table XI.

The values for $\frac{Hc}{\tau}$ are listed in Table XII for each fraction. The limiting $\frac{Hc}{\tau}$ and M_w are given in Table XIII. Figure V shows the integral distribution for M_w.

The M_w values obtained from the light scattering data indicate that no reverse order fractionation occurred.

V. RATIOS OF THE VARIOUS MOLECULAR WEIGHTS

Comparison of the M_v, M_n, and M_w of each fraction, Table XIV, shows certain relationships not seen in the evaluation of a single set of results. The ratio of M_w/M_n is in the range of 2.2 for the whole polymer and fractions 2-4. The extremely high value 3.24 for the first fraction shows a very broad distribution of molecular weights. The relative low M_n of 189,000 for this fraction indicates the presence of an excess amount of intermediate molecular weight components—more than the tailing effect can explain. The fractionation solution was a fairly concentrated solution which probably caused this partial reverse order fractionation.

It should be emphasized that complete reverse order precipitation did not occur, but only some of the intermediate molecular weight components precipitated in the first fraction.

TABLE IX

TURBIDITY, τ (10^3)

CONCENTRATION g/ml x 10^2	W.P.	FRACTION NUMBER 1	2	3	4	5	6	7	8
1.00	1.21	1.46	1.47	1.32	1.30	1.10	0.843	0.137	=a
0.75	1.17	1.42	1.38	1.29	1.18	0.996	0.789	0.595	0.244
0.50	1.02	1.40	1.30	1.19	1.06	0.859	0.617	0.432	0.184
0.30	-	-	-	-	-	0.676	0.419	0.279	0.112
0.25	0.701	1.11	1.00	0.894	0.751	0.585	0.381	-	-
0.20	0.601	0.964	0.890	0.781	0.664	-	-	-	-

[a] The value for this solution was in error and disregarded

TABLE X

REFRACTIVE INDEX INCREMENT, $\left(\dfrac{n-n_o}{c}\right)$

CONCENTRATION g/ml x 10^2	W.P.	FRACTION NUMBER							
		1	2	3	4	5	6	7	8
1.00	0.0978	0.110	0.105	0.107	0.106	0.103	0.105	0.105	=a
0.75	0.0980	0.108	0.108	0.107	0.111	0.105	0.110	0.104	0.103
0.50	0.108	0.109	0.110	0.108	0.109	0.107	0.109	0.101	0.109
0.30	-	-	-	-	-	-	0.106	0.101	0.110
0.25	0.114	0.114	0.116	0.116	0.112	0.113	0.112	-	-
0.20	0.113	0.117	0.114	0.121	0.116	0.114	-	-	-

[a]The value for this solution was in error and disregarded

TABLE XI

REFRACTIVE INDEX INCREMENT SQUARED, $\left(\dfrac{n-n_o}{c}\right)^2$ (10^3)

CONCENTRATION g/ml x 10^2	W.P.	FRACTION NUMBER							
		1	2	3	4	5	6	7	8
1.00	9.56	12.1	10.99	11.4	11.2	10.7	11.0	11.2	=a
0.75	9.60	11.7	11.7	11.4	12.3	11.1	12.1	10.8	10.6
0.50	11.7	11.9	12.1	11.7	11.9	11.5	11.9	10.1	11.9
0.30	-	-	-	-	-	-	11.2	10.1	12.0
0.25	12.1	13.0	13.5	13.5	12.5	12.8	12.5	-	-
0.20	12.8	13.7	13.0	14.6	13.5	13.0	-	-	-

[a]The value for this solution was in error and disregarded

TABLE XII

$$\frac{Hc}{\tau}(10^6) \text{ FOR EACH FRACTION AND CONCENTRATION}$$

CONCENTRATION g/ml x 10^2	FRACTION NUMBER								
	W.P.	1	2	3	4	5	6	7	8
1.00	10.9	11.5	10.6	12.0	12.0	13.4	18.0	21.0	=a
0.75	8.53	8.53	8.80	9.21	10.9	11.6	16.0	18.9	45.2
0.50	7.94	5.98	6.46	6.82	7.81	9.25	13.4	16.2	44.8
0.30	-	-	-	-	-	7.86	11.1	15.1	44.5
0.25	5.99	4.05	4.68	5.23	5.76	7.69	11.4	-	-
0.20	5.89	3.94	4.04	5.17	5.63	-	-	-	-

aThe value for this solution was in error and disregarded

TABLE XIII

$$\text{LIMITING } \left(\frac{Hc}{\tau}\right)_0 (10^6) \text{ AND WEIGHT AVERAGE}$$
$$\text{MOLECULAR WEIGHT, } M_W$$

FRACTION NUMBER	$\left(\frac{Hc}{\tau}\right)_0$	M_W
W.P.	4.51	219,000
1	1.63	613,000
2	2.45	408,000
3	3.04	329,000
4	3.77	265,000
5	5.52	181,000
6	8.64	116,000
7	12.1	82,600
8	44.1	22,700
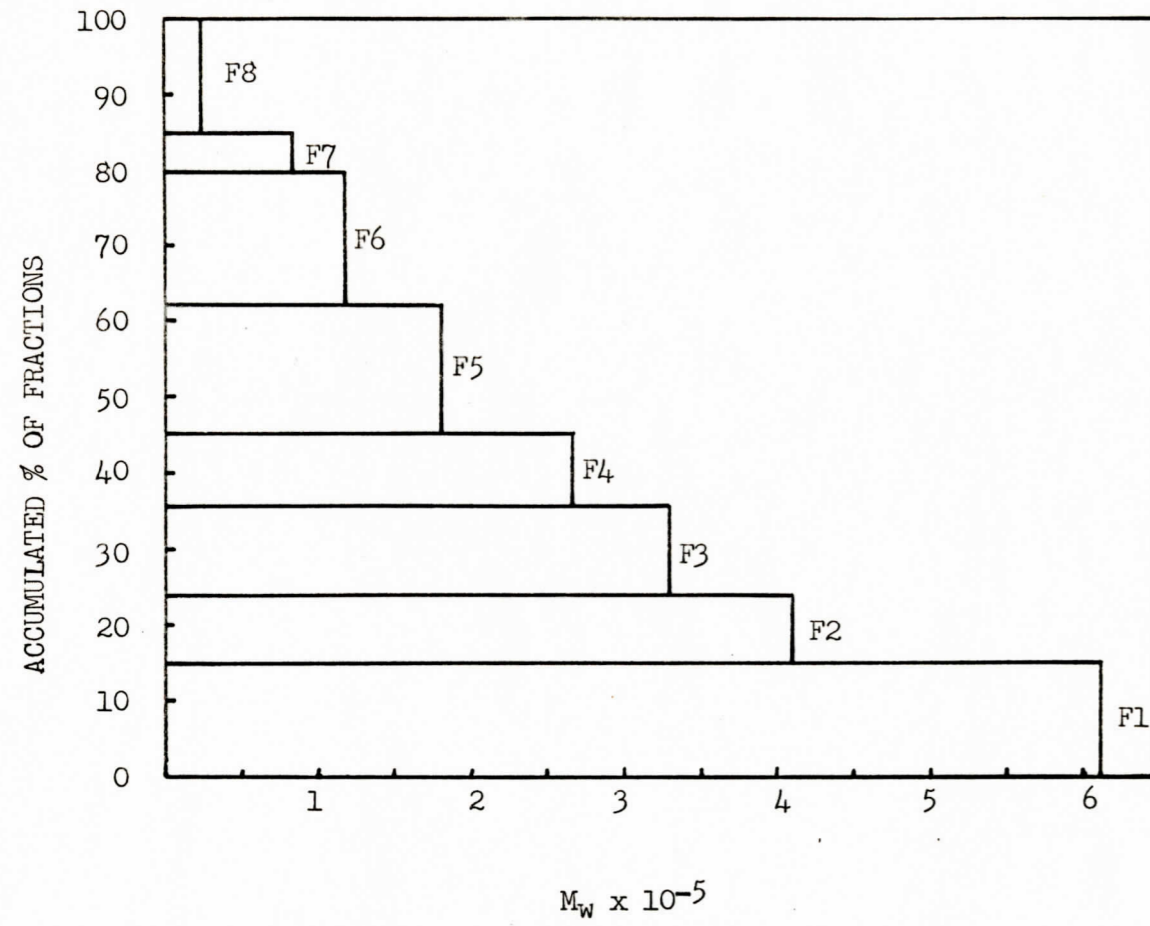
FIGURE V

INTEGRAL DISTRIBUTION OF M_w FOR POLYSTYRENE

(y-axis: ACCUMULATED % OF FRACTIONS; x-axis: $M_w \times 10^{-5}$; fractions F1–F8)

TABLE XIV

MOLECULAR WEIGHT RATIOS

FRACTION NUMBER	M_n	M_v	M_w	M_v/M_n	M_w/M_n	M_w/M_v
W.P.	96,000	201,000	219,000	2.09	2.28	1.09
1	189,000	447,000	613,000	2.37	3.24	1.37
2	182,000	360,000	408,000	1.98	2.24	1.13
3	144,000	295,000	329,000	2.05	2.28	1.12
4	123,000	224,000	265,000	1.82	2.15	1.18
5	116,000	146,000	181,000	1.26	1.56	1.24
6	89,900	79,200	116,000	0.88	1.29	1.46
7	-	42,600	82,600	-	-	1.94
8	-	14,100	22,700	-	-	1.61

Although the small M_w/M_n, 1.29, of the sixth fraction indicates a narrow distribution, the large M_w/M_v, 1.46, demonstrates that the distribution is, in fact, large. The small M_w/M_n may be due to diffusion of small polymer across the membrane.

CHAPTER V

CONCLUSION

The whole polymer has a M_w of 219,000, while the M_n is 96,000. The fractions have M_w values which range from 613,000 to 22,700, M_v values which range from 447,000 to 14,100, and fractions 1-6 have M_n values which range from 189,000 to 89,000 (Table XIV). The whole polymer and the fractions are poly-dispersed. Definite fractionation of polystyrene occurred from the 2% solution and there was some reverse order fractionation in the first fraction. Finally, there was diffusion of low molecular weight molecules across the osmotic membrane.

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