

THE FRACTIONATION AND MOLECULAR WEIGHT DETERMINATION OF EMULSION POLYMERIZED POLYSTYRENE

> Thesis for the Degree of M. S. MICHIGAN STATE COLLEGE Max Wallace Krell 1949

This is to certify that the

thesis entitled

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presented by

Max Wallace Krell

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Palph Line Major professor

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Date_

THE FRACTIONATION AND MOLECULAR

WEIGHT DETERMINATION OF ETULSION POLYMERIZED POLYSTYREME

By

MAX WALLACE KRELL

A THESIS

Submitted to the School of Graduate Studies of Michigan State College of Agriculture and Applied Science in partial fulfillment of the requirements for the degree of

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INTRODUCTION

During the past few years the emulsion polymerization of styrene has been investigated extensively in this laboratory. 1,2,3,4,5 These investigations, for the most part, have been concerned with the various phases of the reaction. Determinations of the average molecular weight have been made in conjunction with this work, and some preliminary efforts have been made on the fractional precipitability of the polystyrene from a solvent system by a non-solvent.

This paper reports the results of the first work in this laboratory to establish some relationship between the molecular weight distribution of a given sample of polystyrene and the "precipitability" of that polymer from solution. The fractionation of the polymer samples, and the determination of their molecular weights are necessarily an integral part of this investigation.

The term "precipitability" as used in this work is defined as the extinction of light caused by the turbidity of a polymer solution, which is due to the precipitation of the polymer from solution by a non-solvent.

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HISTORICAL

Styrene was first produced in 1831 by Bonastre as a distillation product of storax, which was obtained from Liquidambar Orientalis, a tree native to Asia Minor. Eight years later, Eduard Simon obtained (upon heating the monomer) what was thought to be an oxide of styrene, but which in reality was polystyrene.

It was not until 1845 that the polymeric nature of the material was recognized by two Englishmen, Hofmann and Blyth. In 1869 Berthelot reported the preparation of monomeric styrene from ethyl benzene.

The first patents on polystyrene were granted to Dr. F. E. Matthews of London, England in 1911. Two French chemists, Dufraisse and Moreu were responsible for a great deal of development work on the polymer, and in work published in 1933 they discussed agents which retarded styrene polymerization.

Commercial production of polystyrene was attempted in Germany about 1930, and by the Naugatuck Chemical Company in the United States in 1933. However, it was not until 1937, when the Dow Chemical Company perfected the ethylbenzene method for the production of the monomer that large scale production of the polymer could begin. Since 1937, many other companies have taken up polystyrene production, many of them obtaining their monomer from Dow Chemical Company.

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The Dow method for the production of monomeric styrene consists of the pyrolytic dehydrogenation of ethylbenzene which is produced by a liquid phase reaction of benzene with ethylene under atmospheric pressure at 88° C. Any polyethylbenzenes produced are disproportionated by recycling so that the yield of ethylbenzene is high. The ethylbenzene is then catalytically dehydrogenated to styrene at temperatures of 600 to 800° C. Yields of 50 to 80 percent are reported.

Styrene will polymerize slowly on standing at room temperature but its polymerization may be inhibited by numerous antioxidants, hydroquinone and tertiary butyl catechol being the most important commercially. They may be removed by distillation of the styrene over solid caustic.

Styrene polymerization is accelerated both by heat and catalysts, average chain length of the polymer decreasing with increasing temperature and increasing concentration of the catalyst used. Air must be excluded in the polymerization, otherwise yellowing of the product will occur. The polymerization of styrene is thought to be a chain reaction which is initiated by the activation of the double bonds of a small number of molecules. These activated molecules provide muclei for polymerization, adding monomer molecules with which they come in contact, and transmitting their energy of activation to the larger molecules as they grow.

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As is often the case with commercial products, scientific research has lagged far behind the commercial development. Determination of average molecular weight began in 1930 when Staudinger and Heuer⁶ reported finding some relationship between viscosity of polymeric solutions and molecular weight of the polymer. In subsequent papers Staudinger^{7,8} published data on the relationship between viscosity of polymeric solutions and chain length of the polymers. The Staudinger method, made use of extensively in this thesis for the determination of molecular weight, will be discussed in a later portion of this work.

In 1926, Svedberg⁹ reported the derivation of the formula for obtaining molecular weights by sedimentation data using a high speed or "ultra" centrifuge. This first report was followed by several later ones along the same line, in which molecular weights were determined, and size distribution, sedimentation, and dispersion studies were made.

Later developments brought applications of these methods of determination of molecular weight into the field of high polymeric materials. In 1935 Signer¹⁰ reported his work with the ultracentrifuge, and the following year published results on the direct determination of the molecular weight of polystyrene with this instrument.¹¹

In 1936 Schulz's work¹² appeared, in which he had developed an equation for the molecular weight determination of highly polymerized compounds from osmotic pressure measurements. The following

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year Dobry¹³ applied the osmotic pressure method for the determination of the molecular weight of polystyrene.

The latest method to be devised for the determination of the molecular weight of polystyrene is the method of light scattering. The work of Debye¹⁴ is probably the most outstanding in this field.

Because of the simplicity of the apparatus, and the ease of manipulation, the viscosity method is still the most widely used of the methods mentioned.

All of the methods discussed give average molecular weights rather than absolute values. Quite often molecular weight values determined with the ultracentrifuge vary markedly from those obtained by viscosity methods. Probably the ultracentrifuge gives more nearly an absolute value, but the viscosity molecular weight of a typical polymer would not be seriously in error unless the polymer is extensively branched. In the case of polystyrene this error would not be large.

Much work has been done on the molecular weight distribution of polystyrene, but little has been published on the actual fractionation of the polymer into components of different molecular weight. In an article appearing in 1936 Schulz and Husemann¹⁵ published their work in which they fractionally precipitated a butanone solution of polystyrene by adding methanol as a non-solvent. This was followed by a later article by Schulz and Dinglinger¹⁶ in which essentially the same method was used.

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Since these articles were published, little has appeared on the subject of polystyrene fractionation. The Dow Chemical Company is working on the problem from a commercial standpoint, but has not published any work regarding it. An article by Morey and Tamblyn¹⁷ confirms, for the most part, the work of Schulz.

Only a few studies on the precipitability of a polymer solution by a non-solvent have been made. Schulz¹⁸ published an article in 1937 in which he tried to relate solubility and molecular weight of high molecular compounds. Adams and Powers¹⁹ studied the polymer distribution of varnish resins. Morgan¹, of this laboratory, was the first to apply the method of Adams and Powers to polystyrene samples.

REAGENTS

Styrene The styrene used in this work was obtained from the Dow Chemical Company. Before use, the monomer was distilled under reduced pressure (20 m.m.) and that portion having a refractive index of 1.544 collected for use in the emulsion polymerization.

Water The water used for the aqueous phase of the emulsion was distilled from alkaline potassium permanganate (300 grams potassium hydroxide, 8 grams potassium permanganate per liter of solution) under an atmosphere of air or nitrogen, depending on which atmosphere was to be used for the polymerization. Two liters of water were added to 50 mls. of the alkaline permanganate, the mixture refluxed for thirty minutes, and then allowed to distil. The first 200 mls. of distillate were discarded, the receiver flushed with steam from the distilling system, and the distillate again collected. If a nitrogen atmosphere was used, the water was kept under nitrogen pressure until used.

Potassium Persulfate Merck's reagent grade was recrystallized from purified water (see above), filtered off, and dried at room temperature for 48 hours.

<u>Dupanol</u> <u>G</u> This material, manufactured by DuPont, was used as the emulsifying agent. It is reported as being lauryl amine sulfate. The Dupanol G was stored as a liquid at 50° C. to provide for an easy method of handling the reagent.

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Aluminum Chloride Baker's C. P. (AlCl₃·6H₂O)

<u>Toluene</u> Baker's C. P. This reagent was redistilled under atmospheric pressure and the fraction having a refractive index of 1.498 collected for use in viscosity measurements.

Ethanol U. S. P. 95% (B. P. 76 - 77°C.)

Methanol Merck's C. P.

Butanone Eastman's C. P.

<u>Nitrogen</u> Water pumped. The nitrogen, before use, was passed through alkaline pyrogallol solution. This solution consisted of fifty grams of potassium hydroxide in 100 mls. of water, to which was added five grams of pyrogallic acid.

PREPARATION OF POLYMER SAMPLES

The method of emulsion polymerization employed for the preparation of polystyrene used in this work was adapted from the methods of co-workers in this laboratory.^{1,2,3,4,5} The polymerization was carried out in a three necked, round bottom, one liter flask with standard taper ground glass joints. The flask was fitted with a mercury sealed swivel stirrer, thermometer, nitrogen addition tube, (when using a nitrogen atmosphere) and a reflux condenser. The condenser was attached to a small double water trap to permit nitrogen to escape and prevent air from entering the reaction vessel. The reaction flask was immersed in a constant temperature bath at $60^{\circ}C.-0.2^{\circ}C.$ throughout the polymerization. Polymerizations were carried out under both nitrogen and air atmospheres, with and without stirring.

The emulsion was composed of eight parts of water to one part of styrene, with one percent Dupanol G emulsifier, based on the aqueous phase. The catalyst, potassium persulfate, was used at a concentration of 0.0017 M. based on the aqueous phase.

In carrying out a polymerization, the Dupanol G and water were added to the reaction vessel which had previously been flushed out with nitrogen if a nitrogen atmosphere was to be used. The styrene was then added, and the reaction mixture stirred until it reached operating temperature. At this time the calculated amount

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of catalyst was added and timing begun. In the case where the reaction was not stirred, the stirrer was turned off two minutes after addition of the catalyst. Where partial stirring was employed, the stirrer was turned off at the same time, and then turned on for two minute periods at one-half hour intervals. Reaction times varied from 55 minutes to $14\frac{1}{2}$ hours, depending on the atmosphere used and whether or not the emulsion was stirred after the addition of the catalyst.

At a recorded time, the polymer was precipitated from the emulsion by pouring the emulsion into approximately twice its volume of 95% ethanol to which had been added a trace of aluminum chloride. After complete precipitation had occurred, the polymer was filtered off by the use of suction, washed twice with 95% ethanol, and then six times with distilled water. After final washing, the polymer was filtered off and allowed to dry at 50° C. for 48 hours.

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| Sample | Length of Run (Hrs.) | Atmosph ere | Stirring | Actual Yield | Percent Yield |
|--------|-------------------------|--------------------|----------|-----------------|------------------|
| 1 | 3:20 | Nitrogen | None | 59.0 g. | 78.6 |
| 2 | 6:30 | Air | Complete | 89.5 g. | 89.5 |
| 3 | 14:30 | Air | Complete | 66.3 g. | 88.4 |
| 4 | 0:55 | Nitrogen | Complete | 78.8 g. | 87.6 |
| 5 | 1:40 | Nitrogen | Partial | 81.6 g. | 90 .7 |
| 6 | 3:00 | Air | Complete | 80.9 g. | 89 .9 |

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DETERMINATION OF "PRECIPITABILITY"

"Precipitability" curves were obtained by utilization of the method of Adams and Powers¹⁹ with modifications. Solutions of the polymer samples in butanone, 0.02 molar, were prepared. The molarity referred to is that of the "Grundmol", which is a molarity based on the weight of the recurring group in the polymer. In the case of polystyrene, a molar solution would be one containing 104 grams of polymer per liter of solution.

To 125 mls. of this solution, methanol was added with stirring at 20°C. and the extinction of light passing through the solution measured by means of a photoelectric cell and galvanometer. (See diagram on following page.) Methanol was added until further addition brought about no further extinction of light. Graphs were then plotted with percent methanol (based on total weight of solution) as the abscissa and extinction $\begin{bmatrix} \text{Log} & \text{incident light}(I_0) \\ \text{transmitted light}(I) \end{bmatrix}$ as the

ordinates. In all cases incident light was equal to 100.

The tangent or differential curves from the extinction curves were also plotted. The tangents were calculated between successive points on the extinction curves, and the values obtained plotted opposite the average percent methanol between these successive pairs of points.

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TABLE II - POLYMER # 1

| м1. СН ₃ ОН | %СН 3 ОН | ·I | I°/I | logI ₀ /I | А ▼. %СН _З ОН | Tangent |
|------------------------|-----------------|-----------------------|---------------|----------------------|---------------------------------|-----------------|
| 2.0 | 1.55 | 100.0 | 1.000 | 0.0000 | 0 . 78 | 0.0000 |
| 4.0 | 3.05 | 100.0 | 1.000 | 0.0000 | 2.30 | 0.0000 |
| 6.0 | 4.51 | 100.0 | 1.000 | 0.0000 | 3 .78 | 0.0000 |
| 8.0 | 5.92 | 99.5 | 1.005 | 0.0022 | 5.21 | 0.0015 |
| 10.0 | 7.30 | 99.0 | 1.010 | 0.0043 | 6.61 | 0.0016 |
| 12.0 | 8.63 | 98 •5 | 1.015 | 0.0065 | 7.96 | 0.0016 |
| 14.0 | 9.93 | 98 . 0 | 1.020 | 0.0086 | 9.28 | 0.0016 |
| 15.5 | 10.87 | 87.0 | 1.150 | 0.0607 | 10.40 | 0 .0555 |
| 16.0 | 11.18 | 78.0 | 1.282 | 0.1079 | 11.02 | 0.1522 |
| 16.5 | 11.50 | 71.0 | 1.410 | 0.1492 | 11.34 | 0 .1290 |
| 17.0 | 11.80 | 65.0 | 1.540 | 0.1875 | 11.65 | 0 .1270 |
| 17.5 | 12.11 | 59.5 | 1.680 | 0.2253 | 11.96 | 0.1220 |
| 18.0 | 12.41 | 55.0 | 1.820 | 0 .2601 | 12.26 | 0 .1159 |
| 18.5 | 12.71 | 53.0 | 1.888 | 0.2760 | 12.56 | 0 .0531 |
| 19.0 | 13.01 | 50.0 | 2.000 | 0.3010 | 12.86 | 0.0834 |
| 20.0 | 13.63 | 45.5 | 2.198 | 0.3420 | 13.32 | 0 .0662 |
| 21.0 | 14.18 | 41.5 | 2.410 | 0.3820 | 13.90 | 0.0727 |
| 22.0 | 14.73 | 38.5 | 2.600 | 0.4148 | 14.46 | 0.0595 |
| 23.0 | 15.33 | 36.5 | 2.742 | 0.4381 | 15.03 | 0 .03 88 |
| 25.0 | 16.44 | 33.5 | 2.987 | 0.4752 | 15.88 | 0.0335 |
| 27.0 | 17.53 | 31.0 | 3.206 | 0.5060 | 16.98 | 0.0282 |
| 30.0 | 19.10 | 2 9.5 | 3.390 | 0.5302 | 18.32 | 0.0154 |
| 3 5.0 | 21.60 | 27.5 | 3.640 | 0.5611 | 20.35 | 0.0124 |
| 4 0.0 | 23.94 | 2 6 . 5 | 3 .775 | 0 .5769 | 22.77 | 0.0068 |
| 45.0 | 26.16 | 26.0 | 3.847 | C.5851 | 25.05 | 0.0037 |
| 50.0 | 28.24 | 2 5.5 | 3.925 | 0 .5938 | 27.70 | 0.0042 |
| 55.0 | 30.21 | 25.0 | 4.000 | 0.6021 | 29.22 | 0.0040 |
| 60.0 | 32.08 | 24.5 | 4.085 | 0.6112 | 31.14 | 0 .0049 |
| 65.0 | 33.84 | 24.0 | 4.165 | 0 .6196 | 32. 96 | 0 .0048 |
| 70.0 | 35.52 | 24.0 | 4. 165 | 0 .6196 | 34. 68 | 0.0000 |

TABLE III - POLYMER # 2

| Ml. | сн _з он | %СН ОН 3 | I | I /I | logI _o /I | Av. %CH ₃ OH | Tangent |
|-----|--------------------|--------------------|---------------|---------------|----------------------|-------------------------|-----------------|
| | 4.0 | 3. 05 | 100.0 | 1.000 | 0.0000 | 1.52 | 0.0000 |
| | 8.0 | 5.92 | 100.0 | 1.000 | 0.0000 | 4.49 | 0.0000 |
| | 12.0 | 8.63 | 100.0 | 1.000 | 0.0000 | 7.28 | 0.0000 |
| | 14.0 | 9.93 | 100.0 | 1.000 | 0.0000 | 9.28 | 0.0000 |
| | 16.0 | · 11.18 | 98 . 0 | 1.021 | 0.0090 | 10.56 | 0 .0072 |
| | 16.5 | 11.50 | 96.0 | 1.042 | 0.0179 | 11.34 | 0.0276 |
| | 17.0 | 11.80 | 92.5 | 1.081 | 0.0338 | 11.65 | 0.0532 |
| | 17.5 | 12.11 | 89.0 | 1.124 | 0.0508 | 11.96 | 0.0546 |
| | 18.0 | 12.41 | 84.9 | 1.191 | 0 .0759 | 12.26 | 0 •0838 |
| | 18.5 | 12.71 | 78 . 0 | 1.282 | 0 . 1079 | 12.56 | 0 .1066 |
| | 19.0 | 13.01 | 72.0 | 1.390 | 0 .1430 | 12.86 | 0.1171 |
| | 19.5 | 13.31 | 67.0 | 1.494 | 0.1744 | 13.16 | 0.1045 |
| | 20.0 | 13.63 | 63.5 | 1.575 | 0 .1973 | 13.47 | 0.0716 |
| | 20.5 | 13.89 | 60.5 | 1.654 | 0.2185 | 13.76 | 0 •0819 |
| | 21.0 | 14.18 | 58. 0 | 1.725 | 0 .23 68 | 14.04 | 0.0630 |
| | 22.0 | 14.73 | 53.5 | 1.870 | 0.2718 | 14.46 | 0 •0637 |
| | 23.0 | 15.33 | 50 . 0 | 2.0 00 | 0.3010 | 15.03 | 0 .04 86 |
| | 24.0 | 15.89 | 47.5 | 2.106 | 0.3235 | 15.61 | 0 .0401 |
| | 25.0 | 16.44 | 45.0 | 2.224 | 0.3471 | 16.16 | 0.0431 |
| | 27.0 | 17.53 | 42.0 | 2.382 | 0 .3 769 | 16.98 | 0 .0274 |
| | 29.0 | 18.59 | 40.0 | 2.500 | 0 .3979 | 18.06 | 0 .0198 |
| | 32.0 | 20.12 | 37.5 | 2.670 | 0.4265 | 19.36 | 0 .0187 |
| | 35.0 | 21.60 | 3 6.0 | 2.780 | 0.4440 | 20.86 | 0.0118 |
| | 40.0 | 23.94 | 3 4.5 | 2.900 | 0.4624 | 22.77 | 0.0078 |
| | 45 .0 | 26.16 | 33.0 | 3 .030 | 0.4814 | 25. 05 | 0 .008 6 |
| | 50.0 | 28.24 | 32.5 | 3 .078 | 0 •4883 | 27.20 | 0 .0033 |
| | 55.0 | 30.21 | 31.75 | 3.150 | 0 .4983 | 29.22 | 0.0052 |
| | 60.0 | 32. 08 | 31.50 | 3.178 | 0.5022 | 31.14 | 0 .0020 |
| | 65.0 | 33.84 | 31.25 | 3.200 | 0 .5052 | 32.96 | 0.0017 |
| | 70.0 | 35.52 | 31.0 | 3.225 | 0 •5085 | 34.68 | 0.0020 |
| | 75.0 | 37.12 | 31.0 | 3.225 | 0 .5085 | 36.32 | 0.0000 |
| | | | | | | | |

TABLE IV - POLYMER # 3

| Ml. | CH ₃ OH | %сн _з он | I | I_/I | logI /I | Av.%CH3OH | Tangent |
|-----|--------------------|---------------------|---------------|-------|-------------------------|-----------|-----------------|
| | 4.0 | 3 •05 | 100.0 | 1.000 | 0.0000 | 1.52 | 0.0000 |
| | 8.0 | 5.92 | 100.0 | 1.000 | 0.0000 | 4.49 | 0.0000 |
| | 12.0 | 8.63 | 100.0 | 1.000 | 0.0000 | 7.28 | 0.0000 |
| | 14.0 | 9.93 | 100.0 | 1.000 | 0.0000 | 9.28 | 0.0000 |
| | 16.0 | 11.18 | 100.0 | 1.000 | 0 .0000 | 10.56 | 0.0000 |
| | 16.5 | 11.50 | 98.5 | 1.015 | 0 .0065 | 11.34 | 0.0202 |
| | 17.0 | 11.80 | 96.5 | 1.037 | 0.0158 | 11.65 | 0.0300 |
| | 17.5 | 12.11 | 94.5 | 1.058 | 0.0245 | 11.96 | 0.0281 |
| | 18.0 | 12.41 | 92.5 | 1.081 | 0.0338 | 12.26 | 0.0311 |
| | 18.5 | 17.71 | 90.5 | 1.105 | 0 . 04 34 | 12.56 | 0.0318 |
| | 19.0 | 13.01 | 87.5 | 1.142 | 0•057 7 | 12.86 | 0 .0477 |
| | 19.5 | 13.31 | 82.5 | 1.211 | 0.0831 | 13.16 | 0 .0649 |
| | 20.0 | 13.63 | 77.5 | 1.290 | 0.1106 | 13.47 | 0.0858 |
| | 20.5 | 13.89 | 72.5 | 1.380 | 0.1399 | 13.76 | 0 .1128 |
| | 21.0 | 14.18 | 69.0 | 1.449 | 0.1611 | 14.04 | 0.0728 |
| | 21.5 | 14.47 | 66.0 | 1.515 | 0.1804 | 14.32 | 0.0667 |
| | 22.0 | 14.73 | 63.5 | 1.575 | 0.1973 | 14.60 | 0.0649 |
| | 22.5 | 15.04 | 61.5 | 1.627 | 0.2114 | 14.88 | 0 .045 5 |
| | 23.0 | 15.33 | 60.0 | 1.667 | 0.2219 | 15.18 | 0.0364 |
| | 24.0 | 15.89 | 5 7. 0 | 1.755 | 0.2443 | 15.61 | Q•0398 |
| | 25.0 | 16.44 | 54.5 | 1.835 | 0 .263 6 | 16.16 | 0 .0352 |
| | 26.0 | 16.99 | 52.5 | 1.905 | 0 .27 99 | 16.72 | 0 .02 95 |
| | 28.0 | 18.06 | 49.5 | 2.020 | 0 .3054 | 17.52 | 0 .023 8 |
| | 30.0 | 19.10 | 47.0 | 2.126 | 0.3276 | 18.58 | 0.0214 |
| | 32.9 | 20.12 | 45.0 | 2.221 | 0.3466 | 19.61 | 0.0186 |
| | 35.0 | 21.60 | 4 4.5 | 2.298 | 0.3614 | 20.86 | 0.0100 |
| | 40.0 | 23.94 | 44.25 | 2.381 | 0 .37 68 | 22.77 | 0.0066 |
| | 45.0 | 26.16 | 44.0 | 2.470 | 0.3927 | 25.05 | 0.0072 |
| | 50.0 | 28.24 | 4 4.0 | 2.470 | 0 .3927 | 27.20 | 0.0000 |

TABLE V - POLYMER # 4

| м1. СН ₃ ОН | %сн ₃ он | I | I_/I | logI ₀ /I | A ▼ •%CH ₃ OH | Tangent |
|------------------------|---------------------|---------------|---------------|----------------------|---------------------------------|------------------|
| 6.0 | 4.51 | 100.0 | 1.000 | 0.0000 | 2.26 | 0.0000 |
| 8.0 | 5.92 | 100.0 | 1.000 | 0.0000 | 5.22 | 0.0000 |
| 10.0 | 7.30 | 99.5 | 1.005 | 0.0022 | 6.61 | 0.0016 |
| 12.0 | 8.63 | 99.0 | 1.010 | 0.0043 | 7.96 | 0.0016 |
| 14.0 | 9,93 | 98 . 5 | 1.015 | 0 .00 65 | 9.28 | 0 .0017 |
| 16.0 | 11.18 | 88.0 | 1.137 | 0.0558 | 10,56 | 0.0392 |
| 16.5 | 11.50 | 74.5 | 1.342 | 0 .12 78 | 11.34 | 0 .2250 |
| 17.0 | 11.80 | 63.0 | 1.589 | 0,2011 | 11.65 | 0.2446 |
| 17.5 | 12.11 | 55.5 | 1.802 | 0 .25 58 | 11.96 | 0 .1760 |
| 18.0 | 12.41 | 50 .0 | 2.000 | 0.3010 | 12.26 | 0.1843 |
| 18.5 | 12.71 | 46.0 | 2.175 | 0.3375 | 12.56 | 0 . 12 14 |
| 19.0 | 13.01 | 43.0 | 2. 326 | 0 .3666 | 12.86 | 0 .0972 |
| 19.5 | 13.31 | 41.0 | 2.441 | 0.3876 | 13.16 | 0 .0697 |
| 20.0 | 13.63 | 39.5 | 2.534 | 0,4038 | 13.47 | 0.0508 |
| 21.0 | 14.18 | 36.5 | 2.740 | 0.4378 | 13.90 | 0 .0617 |
| 22.0 | 14.73 | 34 .5 | 2,900 | 0.4624 | 14.46 | 0 .0449 |
| 23.0 | 15.33 | 33.5 | 2.985 | 0 •474 9 | 15.03 | 0.0209 |
| 25.0 | 16.44 | 31.5 | 3.176 | 0.5019 | 15.88 | 0.0242 |
| 27.0 | 17.53 | 30.0 | 3.333 | 0 •52 28 | 16,98 | 0.0192 |
| 30.0 | 19.10 | 28.5 | 3.510 | 0.5453 | 18.32 | 0.0143 |
| 35.0 | 21.60 | 26.5 | 3.775 | 0.5769 | 20.35 | 0.0126 |
| 40.0 | 23.94 | 25.0 | 4.000 | 0.6021 | 22.77 | 0,0107 |
| 45.0 | 26. 16 | 24.5 | 4.080 | 0.6107 | 25.05 | 0.0039 |
| 50.0 | 28.24 | 24.25 | 4.120 | 0 .6149 | 27.20 | 0,0020 |
| 55 .0 | 30.21 | 24.0 | 4.166 | 0 .6197 | 29.22 | 0.0024 |
| 60.0 | 32.08 | 23.75 | 4.210 | 0 .6243 | 31.14 | 0.0030 |
| 65.0 | 33.84 | 23.75 | 4.210 | 0 .6243 | 33.46 | 0.0000 |

TABLE VI - POLYMER # 5

| Ml.CH ₃ OH | %СН ОН 3 | I | I°\I | logI ₀ /I | Av.%CH OH 3 | Tangent |
|-----------------------|--------------------|-------|---------------|----------------------|----------------|-----------------|
| 4 .0 | 3 .05 | 100.0 | 1.000 | 0.0000 | • 1.52 | 0.0000 |
| 8.9 | 5.92 | 100.0 | 1.000 | 0.0000 | 4.49 | 0.0000 |
| 10.0 | 7.30 | 100.0 | 1.000 | 0.0000 | 6.61 | 0.0000 |
| 12.0 | 8.63 | 100.0 | 1.000 | 0.0000 | 7.92 | 0.0000 |
| 14.0 | 9.93 | 99.5 | 1.005 | 0.0022 | 9.28 | 0.0017 |
| 15.5 | 10.87 | 95.0 | 1.052 | 0.0220 | 10.40 | 0.0211 |
| 15.0 | 11.18 | 90.0 | 1.111 | 0.0457 | 11.02 | 0 .07 65 |
| 16.5 | 11.50 | 84.0 | 1.190 | 0.0756 | 11.34 | 0 .093 5 |
| 17.5 | 12.11 | 77.5 | 1.290 | 0.1106 | 11.82 | 0.0740 |
| 18.0 | 12.41 | 69.5 | 1.439 | 0.1581 | 12.26 | 0.1582 |
| 18.5 | 12.71 | 63.5 | 1.575 | 0.1973 | 12.56 | 0.1307 |
| 19.0 | 13.01 | 58.0 | 1.725 | 0.2368 | 12.86 | 0.1322 |
| 19.5 | 13.31 | 54.5 | 1.834 | 0.2634 | 13.16 | 0.0882 |
| 20.0 | 13.63 | 52.0 | 1.923 | 0.2840 | 13.47 | 0.0643 |
| 21.0 | 14.18 | 48.0 | 2.084 | 0.3189 | 13.90 | 0.0635 |
| 22.0 | 14.73 | 44.5 | 2.225 | 0.3473 | 14.46 | 0.0517 |
| 24.0 | 15.89 | 40.0 | 2.500 | 0.3979 | 15.31 | 0.0436 |
| 26.0 | 16.99 | 38.0 | 2.632 | 0.4203 | 16.44 | 0.0203 |
| 30.0 | 19.10 | 34.5 | 2.900 | 0.4624 | 17.04 | 0.0200 |
| 35.0 | 21.60 | 32.5 | 3. 080 | 0.4886 | 20.35 | 0.0105 |
| 40 .0 | 23.94 | 31.0 | 3.225 | 0.5085 | 22.77 | 0.0085 |
| 45.0 | 26.16 | 30.0 | 3.333 | 0.5228 | 25.05 | 0.0064 |
| 50.0 | 28.24 | 29.5 | 3. 390 | 0.5302 | 27.20 | 0.0036 |
| 55.0 | 30.21 | 29.0 | 3.450 | 0.5378 | 29.22 | 0.0039 |
| 60.0 | 32. 08 | 28.75 | 3.480 | 0.5416 | 31.14 | 0.0020 |
| 65.0 | 33.84 | 28.5 | 3.510 | 0.5453 | 33.46 | 0.0021 |
| 70.0 | 35.52 | 28.5 | 3.510 | 0.5453 | 34. 68 | 0.0000 |

TAPLE VII - POLYMER # 6

| Ml.CH ₃ OH | %CH_OH | I | I_/I | logI /I | Ат.%СН_ОН | Tangent |
|-----------------------|--------|----------------|---------------|----------------|-----------|-----------------|
| 2.0 | 1.55 | 100.0 | 1.000 | 0.0000 | 0.72 | 0.0000 |
| 4.0 | 3.05 | 100.0 | 1.000 | 0.0000 | 2.30 | 0.0000 |
| 6.0 | 4.5] | 99.75 | 1.002 | 0.0009 | 3.78 | 0.0006 |
| 8.0 | 5.92 | 99.5 | 1.005 | 0.0022 | 5.22 | 0.0009 |
| 10.0 | 7.30 | 99 .2 5 | 1.008 | 0.0035 | 6.61 | 0.0010 |
| 12.0 | 8.63 | 99.0 | 1.011 | 0.0048 | 7.96 | 0.0010 |
| 14.0 | 9.93 | 98.75 | 1.013 | 0.0056 | 9.28 | 0.0006 |
| 16.0 | 11.18 | 98.5 | 1.016 | 0.0069 | 10.56 | 0.0010 |
| 16.5 | 11.50 | 98 •0 | 1.021 | 0.0090 | 11.34 | 0.0067 |
| 17.0 | 11.80 | 89.0 | 1.124 | 0.05 08 | 11.65 | 0.1391 |
| 17.5 | 12.11 | 78.5 | 1.275 | 0.1055 | 11.96 | 0.1765 |
| 18.0 | 12.41 | 70,5 | 1.420 | 0,1523 | 12.26 | 0.1559 |
| 18.5 | 12.71 | 63.0 | 1.589 | 0.2011 | 12.56 | 0.1628 |
| 19.0 | 13.01 | 58.5 | 1.710 | 0.2330 | 12.86 | 0.1063 |
| 19.5 | 13.31 | 53.5 | 1.870 | 0.2718 | 13.16 | 0 .12 95 |
| 20.0 | 13.63 | 50.5 | 1.980 | 0.2967 | 13.47 | 0.0776 |
| 21.0 | 14.18 | 46.0 | 2.075 | 0.3170 | 13.90 | 0.0370 |
| 22.0 | 14.73 | 42.5 | 2.353 | 0.3716 | 14.44 | 0.0994 |
| 23.0 | 15.33 | 40.0 | 2.500 | 0.3979 | 15.03 | 0.0439 |
| 24.0 | 15.89 | 38.5 | 2.600 | 0.4150 | 15.61 | 0.0304 |
| 26.0 | 16.99 | 35.5 | 2.820 | 0.4502 | 16.44 | 0.0321 |
| 28.0 | 18.06 | 34.0 | 2.942 | 0.4686 | 17.52 | 0.0169 |
| 30.0 | 19.10 | 32.5 | 3. 078 | 0 .4883 | 18.58 | 0 .0189 |
| 35.0 | 21.60 | 30.0 | 3.333 | 0.5228 | 20.35 | 0.0138 |
| 40.0 | 23.94 | 28.5 | 3.510 | 0.5453 | 22.77 | 0.0096 |
| 45.0 | 26.16 | 27.5 | 3.638 | 0.5609 | 25.05 | 0.0070 |
| 50 . 0 | 28.24 | 26.5 | 3. 775 | 0.5769 | 27.20 | 0.0077 |
| 55.0 | 30.21 | 26.0 | 3. 850 | 0.5855 | 29.22 | 0.0043 |
| 60.0 | 32.08 | 25.75 | 3.885 | 0.5894 | 31.14 | 0.0021 |
| 65.0 | 33.84 | 25.5 | 3.922 | 0.5935 | 32.96 | 0.0023 |
| 70.0 | 35.52 | 25.25 | 3.960 | 0 .5977 | 34.68 | 0 .0025 |
| 75.0 | 37.12 | 25.0 | 4.000 | 0.6021 | 36.32 | 0.0027 |





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FIGIRE S

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FRACTIONATION

Fractionation was accomplished by stepwise precipitation of the polymer from solution. Ten grams of polystyrene were dissolved in one liter of butanone, and methanol added, with stirring at 20° C., to a predetermined percentage of nonsolvent. The mixture was allowed to stand in a 20°C. constant temperature bath until complete sedimentation occurred. The supernatant liquid was then decanted off, the polymer fraction washed with methanol, and dried at 50° C. for 48 hours. Methanol was again added to the liquid mixture, and the process repeated. In this manner, each original polymer sample was divided into from four to seven fractions. After drying, the fractions were weighed, and the molecular weight determined by the viscosity method. The process of fractionation consumed approximately two weeks. Recovery of the original polystyrene sample ran from 92.74 to 99.33 percent.

TABLE VIII - POLYMER # 1

FRACTIONATION

| Fraction | Percentage Range of Nonsolvent | Weight of Fraction |
|---------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------|
| 1 2 3 4 5 6 7 | 00.0 - 11.0 $11.0 - 12.0$ $12.0 - 13.0$ $13.0 - 14.0$ $14.0 - 16.0$ $16.0 - 20.0$ $20.0 - 35.0$ | 2.3887 g. 5.1883 g. 0.9154 g. 0.4532 g. 0.2341 g. 0.1308 g. 0.0287 g. |
| | Percent Recovery - 93.39 | |
| | TABLE IX - POLYMER # 2 | |
| | FRACTIONATION | |
| | | |
| Fraction | Percentage Range of Nonsolvent | Weight of Fraction |
| Fraction 1 2 3 4 5 6 7 | Percentage Range of Nonsolvent 00.0 - 11.5 11.5 - 12.0 12.0 - 13.0 13.0 - 14.0 14.0 - 15.0 15.0 - 20.0 20.0 - 36.0 | Weight of Fraction 4.0013 g. 1.5293 g. 2.2351 g. 0.7259 g. 0.3313 g. 0.30249 g. |
| Fraction 1 2 3 4 5 6 7 | Percentage Range of Nonsolvent 00.0 - 11.5 11.5 - 12.0 12.0 - 13.0 13.0 - 14.0 14.0 - 15.0 15.0 - 20.0 20.0 - 36.0 Percent Recovery - 93.12 | Weight of Fraction 4.0813 g. 1.5293 g. 2.2351 g. 0.7259 g. 0.3313 g. 0.3844 g. 0.0249 g. |
| Fraction 1 2 3 4 5 6 7 | Percentage Range of Nonsolvent 00.0 - 11.5 11.5 - 12.0 12.0 - 13.0 13.0 - 14.0 14.0 - 15.0 15.0 - 20.0 20.0 - 36.0 Percent Recovery - 93.12 TABLE X - POLYMER # 3 | Weight of Fraction 4.0813 g. 1.5293 g. 2.2351 g. 0.7259 g. 0.3313 g. 0.3844 g. 0.0249 g. |

| Percentage Range | Weight of | | |
|--------------------|--------------------------------------------------------------------------------------------------------------------------------------------|--|--|
| of Nonsolvent | Fraction | | |
| 00.0 - 11.5 | 2.5040 g. | | |
| 11.5 - 12.0 | 2.5523 g. | | |
| 12.0 - 13.0 | 2.2915 g. | | |
| 13.0 - 14.0 | 0.8037 g. | | |
| 14.0 - 15.0 | 0.4974 g. | | |
| 15.0 - 16.5 | 0,5248 g. | | |
| 16.5 - 28.0 | 0.7597 g. | | |
| | Percentage Range of Nonsolvent 00.0 - 11.5 11.5 - 12.0 12.0 - 13.0 13.0 - 14.0 14.0 - 15.0 15.0 - 16.5 16.5 - 28.0 | | |

Percent Recovery - 99.33

`
FRACTIONATION

| Fraction | Percentage Range | Weight of |
|----------|--------------------------|-------------------|
| | Of Nonsolvent | Fraction |
| 1 | 00.0 - 10.8 | 4. 6539 g. |
| 2 | 10.8 - 11.5 | 3.5409 g. |
| 3 | 11.5 - 12.0 | 0.7781 g. |
| 4 | 12.0 - 34.0 | 0.5357 g. |
| | Percent Recovery - 95.09 | |
| | | |

TABLE XII - POLYMER # 5

FRACTIONATION

| Fraction | Percentage Range | Weight of |
|----------|------------------|-------------------|
| | of Nonsolvent | Fraction |
| 1 | 00.0 - 11.0 | 3.2 298 g. |
| 2 | 11.0 - 11.5 | 3.4147 g. |
| 3 | 11.5 - 12.0 | 1.2267 g. |
| 4 | 12.0 - 13.0 | 1.0298 g. |
| 5 | 13.0 - 14.0 | 0.3823 g. |
| 6 | 14.0 - 35.0 | 0.3221 g. |

Percent Recovery - 96.05

TABLE XIII - POLYMER # 6

FRACTIONATION

| Fraction | Percentage Range of Nonsolvent | Weight of Fraction |
|----------|-----------------------------------|-----------------------|
| 1 | 00.0 - 12.5 | 2.7341 g. |
| 2 | 12.5 - 13.0 | 3.023E g. |
| 3 | 13.0 - 14.0 | 1.9893 g. |
| 4 | 14.0 - 15.0 | 0.7555 g. |
| 5 | 15.0 - 16.0 | 0.4096 g. |
| 6 | 16.0 - 40.0 | 0.3620 g. |

Percent Recovery - 92.74

DETERMINATION OF MOLECULAR WEIGHTS

Average molecular weights of the samples were determined by the viscosity method, using a Cannon - Fenske - Ostwald pipette. Data obtained from these measurements was used in the Staudinger equation:

$$M_{\bullet}W_{\bullet} = \frac{h_{sp}}{K_{m} \times C_{m}}$$

where M.W. = average molecular weight $K_m = 1.8 \times 10^{-4}$ $C_m =$ molar concentration of polymer in toluene solution $h(sp) = \frac{\text{time of efflux of solution at } 20^{\circ}C_{\bullet}}{\text{time of efflux of solvent at } 20^{\circ}C_{\bullet}} - 1$

The molecular weight of the fractionated samples of polystyrene was determined in the same way. In all cases C_m was approximately 0.01 M. based on the weight of the recurring unit in the polymer. Efflux time of pure toluene was 53.5 sec.

TABLE XIV - MOLECULAR WEIGHT DETERMINATION

| Polymer | Concentration | Efflux time | Molecular Weight |
|---------|---------------|-------------|------------------|
| 1 | 0.0101 M. | 84.1 sec. | 312,200 |
| 2 | 0.0101 | 72.9 | 198,700 |
| 3 | 0.0102 | 74.8 | 215,400 |
| 4 | 0.0102 | 101.7 | 486,500 |
| 5 | 0.0100 | 87.9 | 354,700 |
| 6 | 0.0102 | 70.2 | 167,900 |

TABLE XV - POLYMER # 1

MOLECULAR WEIGHT DETERMINATION

| Fraction | Concentration | Efflux Time | Molecular Weight |
|----------|---------------|---------------|------------------|
| 1 | 0.0099 M. | 107.0 sec. | 559 ,0 00 |
| 2 | 0.0103 | 93 . 7 | 404,000 |
| 3 | 0.0099 | 75.4 | 228,500 |
| 4 | 0.0103 | 69.1 | 156,800 |
| 5 | 0.0103 | 63.3 | 98,800 |
| 6 | 0.0103 | 60 .3 | 68,400 |
| 7 | 0.0110 | 60 .2 | 63,000 |

TABLE XVI - POLYMER # 2

MOLECULAR WEIGHT DETERMINATION

| Fraction | Concentration | Efflux Time | Molecular Weight |
|----------|---------------|---------------|------------------|
| 1 | 0.0102 M. | 90.9 sec. | 381,900 |
| 2 | 0.0102 | 81.3 | 284,100 |
| 3 | 0.0101 | 73.3 | 203,200 |
| 4 | 0.0102 | 65.9 | 125,900 |
| 5 | 0.0102 | 63 . 3 | 100,100 |
| 6 | 0.0101 | 60.9 | 75,900 |
| 7 | 0.0088 | 56.2 | 31.800 |

TABLE XVII - POLYMER # 3

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MOLECULAR WEIGHT DETERMINATION

| Fraction | Concentration | Efflux Time | Molecular Weight |
|----------|------------------------|--------------|------------------|
| 1 | 0.0103 M. | 83.3 sec. | 300,700 |
| . 2 | 0.0102 | 75.1 | 219,900 |
| 3 | 0.0101 | 67.5 | 144,200 |
| 4 | 0.0101 | 62.6 | 93,700 |
| 5 | 0. 010 4 | 60.6 | 71,100 |
| 6 | 0.0103 | 58 .4 | 49,500 |
| 7 | 0.0100 | 55.7 | 22,700 |

TABLE XVIII - POLYMER # 4

MOLECULAR WEIGHT DETERMINATION

| Fraction | Concentration | Efflux Time | Molecular Weight |
|----------|---------------|--------------|------------------|
| 1 | 0.0101 M. | 111.3 sec. | 593,100 |
| 2 | 0.0103 | 93.8 | 406,300 |
| 3 | 0.0101 | 78.7 | 259,100 |
| 4 | 0.0100 | 69 .3 | 164,100 |

TABLE XIX - POLYMER # 5

MOLECULAR WEIGHT DETERMINATION

| Fraction | Concentration | Efflux Time | Molecular Weight |
|----------|---------------|--------------|------------------|
| 1 | 0.0101 M. | 121.1 sec. | 693,000 |
| 2 | 0.0101 | 102.5 | 504,800 |
| 3 | 0.0103 | 88.3 | 349,500 |
| 4 | 0.0101 | 78 .7 | 259,900 |
| 5 | 0.0102 | 70.3 | 170.700 |
| 6 | 0.0103 | 64.9 | 114.900 |

TABLE XX - POLYMER # 6

MOLECULAR WEIGHT DETERMINATION

| Fraction | Concentration | Efflux Time | Molecular Weight |
|----------|---------------|-------------|------------------|
| 1 | 0.0102 M. | 82.1 sec. | 290,000 |
| 2 | 0.0102 | 73.9 | 207,300 |
| 3 | 0.0103 | 65.9 | 125,500 |
| 4 | 0.0100 | 62.0 | 88,200 |
| 5 | 0.0101 | 59.6 | 62,500 |
| 6 | 0.0103 | 57.6 | 41,400 |

GRAPHICAL REPRESENTATION OF MOLECULAR WEIGHT DISTRIBUTION DATA

The molecular weight distribution curves for the six samples used in this work were constructed by plotting the average molecular weight of the fractions obtained versus the weight fractions (based on the original sample weight of 10 grams) up to and including the fraction of the molecular weight being plotted. For the last weight fraction only, one-half of the weight of the last fraction was added to the cumulative weight, since this was the last point to be plotted on the curve.

The tangent or differential curves from the molecular weight distribution curves were also plotted. The tangents were calculated between successive points on the molecular weight distribution curves, and the values obtained plotted opposite the average molecular weight corresponding to the midpoint between these successive pairs of points.

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TABLE XXI - POLYMER # 1

| Fraction | Weight of | Average Molecular | Weight | Tangent |
|----------|-----------|-------------------|--------------------------|-------------------------|
| | Fraction | Weight | Fraction \mathbf{x} 10 | |
| l | 2.3887 g. | 559,000 | 8.1449 | 0.0771×10^{-4} |
| 2 | 5.1883 | 404,000 | 6.9505 | 0.2940 |
| 3 | 0.9154 | 228,50 0 | 1.7622 | 0.1275 |
| 4 | 0.4532 | 156,800 | 0.8468 | 0.0781 |
| 5 | 0.2341 | 98,800 | 0.3936 | 0.0768 |
| 6 | 0.1308 | 68,300 | 0.1595 | 0.2465 |
| 7 | 0.0287 | 63,000 | 0.0287 | •••••••••• |

TABLE XXII - POLYMER # 2

| Fraction | Weight of Fraction | Average Molecular Weight | Weight Fraction x 10 | Tangent |
|----------|-----------------------|-----------------------------|------------------------|-------------------------|
| 1 | 4. 0813 g. | 381,900 | 7.2715 | 0.2090×10^{-4} |
| 2 | 1.5293 | 284,100 | 5.2309 | 0.1890 |
| 3 | 2.2351 | 203,200 | 3 .7 016 | 0.2890 |
| 4 | 0.7259 | 125,900 | 1.4665 | 0.2815 |
| 5 | 0.3313 | 100,100 | 0.7406 | 0.1370 |
| 6 | 0.3844 | 75,900 | 0.4093 | 0.0872 |
| 7 | 0.0249 | 31,800 | 0.0249 | |
| | | | | |

TABLE XXIII - POLYMER # 3

| Fraction | Weight of | Average Molecular | Weight | Tangent |
|----------------|-----------|-------------------|-------------------------|-------------------------|
| | Fraction | Weight | Fraction x 10 | |
| 1 | 2.5040 g. | 300,700 | 8 . 68 14 | 0.1553×10^{-4} |
| 2 | 2.5523 | 219,900 | 7.4294 | 0.3370 |
| 3 | 2.2915 | 144,200 | 4.8771 | 0.4285 |
| 4 | 0.8037 | 90,700 | 2.5856 | 0.4100 |
| ⁻ 5 | 0.4974 | 71,100 | 1.7819 | 0.2300 |
| 6 | 0.5248 | 49,500 | 1.2845 | 0.1955 |
| 7 | 0.7597 | 22,700 | 0.7597 | |

TABLE XXIV - POLYMER # 4

| Fraction | Weight of Fraction | Average Molecular Weight | Weight Fraction x 10 | Tangent |
|----------|-----------------------|-----------------------------|-------------------------|-------------------------|
| 1 | 4.6539 g. | 593,100 | 7.1816 | 0.1241×10^{-4} |
| 2 | 3.5409 | 406,300 | 4.8547 | 0.2400 |
| 3 | 0.7781 | 259,100 | 1.3138 | 0.0819 |
| 4 | 0.5357 | 164,100 | 0.5357 | |

TABLE XXV - POLYMER # 5

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| Fraction | Weight of Fraction | Average Molecular Weight | Weight Fraction x 10 | Tang ent |
|----------|-----------------------|-----------------------------|-------------------------|-------------------------|
| 1 | 3.2298 g. | 693,000 | 7.9905 | 0.0858×10^{-4} |
| 2 | 3.4147 | 504,800 | 6.3756 | 0.2195 |
| 3 | 1.2267 | 349,500 | 2.9609 | 0.1368 |
| 4 | 1.0298 | 259,900 | 1.7342 | 0.1153 |
| 5 | 0.3823 | 170,700 | 0.7044 | 0.0686 |
| 6 | 0.3221 | 114,900 | 0.3221 | |

TABLE XXVI - POLYMER # 6

| Fraction | W ei ght of | Average Molecular | Weight | Tangent |
|----------|--------------------|-------------------|------------------------|-------------------------|
| | Fraction | Weight | Fraction x 10 | |
| 1 | 2.7341 g. | 290,000 | 7. 907 2 | 0.1651×10^{-4} |
| 2 | 3.0238 | 207,300 | 6.5402 | 0.3660 |
| 3 | 1.9893 | 125,500 | 3.5164 | 0.5330 |
| 4 | 0.7555 | BB ,2 00 | 1.5271 | 0.2942 |
| 5 | 0.4096 | 62,500 | 0.7716 | 0.1895 |
| 6 | 0.3620 | 41,400 | 0.3620 | |



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GRAPHICAL DETERMINATION OF INTRINSIC VISCOSITY

Intrinsic viscosities for the first three fractions of polymer # 2 were obtained by determining the specific viscosities of these samples at three different concentrations, dividing the specific viscosities obtained by the concentration (in grams of polymer per 100 ml. of solvent) and plotting this value of $N_{sp/C}$ versus the concentration. The points plotted approximated straight lines. The y-axis intercepts of these lines were the intrinsic viscosities of the polymer samples used.

TABLE XXVII

Determination of Intrinsic Viscosities of Three Fractions of Polymer # 2

| Fraction | Concentration (g./100 ml.) | Time of Efflux (sec.) | hsp | ¶sp∕C |
|----------|----------------------------|--------------------------|--------|-------|
| 1 | 0.1058 | 90.9 | 0.700 | 6.52 |
| | 0.0529 | 69.4 | 0.297 | 5.62 |
| | 0.0264 | 60 .2 | 0.125 | 4.84 |
| 2 | 0.1056 | 81.3 | 0.520 | 4.93 |
| | 0.0528 | 65.3 | 0.221 | 4.18 |
| | 0.0264 | 58.4 | 0.094 | 3.54 |
| 3 | 0.1052 | 73.3 | 0.370 | 3.51 |
| | 0.0526 | 62.2 | 0.166 | 3.15 |
| | 0.0263 | 57.1 | 0.0673 | 2.56 |

The intrinsic viscosities as determined by extrapolation were 4.40 for fraction #1, 3.14 for fraction # 2, and 2.30 for fraction # 3.



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DETERMINATION OF "PRECIPITABILITY" OF FRACTIONATED SAMPLES

"Precipitability" was determined on certain of the polystyrene fractions in the manner described on page 11. The differential (tangent) curves were plotted. These results are shown in the following tables and graphs.

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TABLE XXVIII - POLYMER FRACTION 3-1

PRECIPITABILITY

| м1. СН ₃ ОП | %CH_OH | I | I_/I | logI ₀ /I | Av.%CH_OH | Tangent |
|------------------------|--------|-------|---------------|----------------------|-----------|---------|
| 00.0 | 00.00 | 100.0 | 1.000 | 0.0000 | 0.00 | 0.0000 |
| 15.0 | 10.56 | 100.0 | 1.000 | 0.0000 | 5.28 | 0.0000 |
| 16.0 | 11.18 | 100.0 | 1.000 | 0.0000 | 10.87 | 0.0000 |
| 16.5 | 11.50 | 87.0 | 1.149 | 0.0603 | 11.34 | 0.1883 |
| 17.0 | 11.80 | 72.0 | 1.389 | 0.1427 | 11.65 | 0.2747 |
| 17.5 | 12.11 | 68.0 | 1.471 | 0.1676 | 11.96 | 0.0804 |
| 18.0 | 12.41 | 63.5 | 1.575 | 0.1973 | 12.26 | 0.0990 |
| 18.5 | 12.71 | 60.0 | 1.667 | 0.2219 | 12.56 | 0.0820 |
| 19.0 | 13.01 | 57.5 | 1.739 | 0.2403 | 12.86 | 0.0613 |
| 20.0 | 13.63 | 52.0 | 1.923 | 0.2840 | 13.32 | 0.0706 |
| 21.0 | 14.18 | 48.0 | 2.082 | 0.3185 | 13.90 | 0.0628 |
| 23.0 | 15.33 | 43.0 | 2.325 | 0.3664 | 14.76 | 0.0416 |
| 25.0 | 16.44 | 40.0 | 2.500 | 0.3979 | 15.88 | 0.0284 |
| 30.0 | 19.10 | 36.0 | 2.775 | 0.4433 | 17.77 | 0.0170 |
| 35.0 | 21.60 | 33.5 | 2 .985 | 0.4749 | 20.35 | 0.0126 |
| 40.0 | 23,94 | 32.5 | 3.075 | 0.4878 | 22.77 | 0.0059 |
| 45.0 | 26.16 | 31.5 | 3.174 | 0.5016 | 25.05 | 0.0062 |
| 50.0 | 28.24 | 31.0 | 3.225 | 0.5085 | 27.20 | 0.0033 |
| 55.0 | 30.21 | 30,5 | 3.278 | 0.5156 | 29.22 | 0.0036 |
| 60.0 | 32.08 | 30.0 | 3.333 | 0.5228 | 31.14 | 0.0038 |
| 65.0 | 33.84 | 30.0 | 3.333 | 0.5228 | 32.96 | 0,0000 |

TABLE XXIX - POLYMER FRACTION 3-3

PRECIPITABILITY

| Ml.CH ₃ OH | %СН 3 ОН | I | I /I | logI /I | Av.%CH OH 3 | Tangent |
|-----------------------|-----------------|-------|---------------|----------------|----------------|---------|
| 00.0 | 00.00 | 100.0 | 1.000 | 0.0000 | 0.00 | 0.0000 |
| 15.0 | 10.56 | 100.0 | 1.000 | 0.0000 | 5.28 | 0.0000 |
| 17.0 | 11.80 | 100.0 | 1.000 | 0.0000 | 11.18 | 0.0000 |
| 18.0 | 12.41 | 74.0 | 1.351 | 0.1307 | 12.10 | 0.2142 |
| 18.5 | 12.71 | 58.0 | 1.725 | 0.2368 | 12.56 | 0.3537 |
| 19.0 | 13.01 | 51.0 | 1.961 | 0.2925 | 12.86 | 0.1890 |
| 19.5 | 13.31 | 47.0 | 2.126 | 0.3276 | 13.16 | 0.1170 |
| 20.0 | 13.63 | 44.0 | 2.272 | 0.3564 | 13.47 | 0.0900 |
| 21.0 | 14.18 | 40.0 | 2.500 | 0.3979 | 13.90 | 0.0755 |
| 22.0 | 14.73 | 37.0 | 2.702 | 0.4317 | 14.46 | 0.0615 |
| 23.0 | 15.33 | 35.5 | 2.818 | 0.4499 | 15.03 | 0.0303 |
| 25.0 | 16.44 | 33.0 | 3. 030 | 0.4814 | 15.88 | 0.0284 |
| 30.0 | 19.10 | 29.5 | 3.390 | 0.5302 | 17.77 | 0.0190 |
| 35.0 | 21. 60 | 27.5 | 3.635 | 0.5605 | 20.35 | 0.0121 |
| 40.0 | 23.94 | 26.5 | 3.776 | 0.5770 | 22.77 | 0.0070 |
| 45 .0 | 26.16 | 25.5 | 3.920 | 0.593 3 | 25 .05 | 0.0073 |
| 50.0 | 28.24 | 24.5 | 4.085 | 0.6112 | 27.20 | 0.0086 |
| 55.0 | 30.21 | 24.5 | 4.085 | 0.6112 | 29.22 | 0.0000 |

TABLE XXX - POLYMER FRACTION 3-5

PRECIPITABILITY

| Ml.CH ₃ OH | %СН _З ОН | I | ı^ı | logI /I | Av.%CH_OH | Tangent |
|-----------------------|---------------------|-------|-------|---------|-----------|---------|
| 00.0 | 00.00 | 100.0 | 1.000 | 0.0000 | 0.00 | 0.0000 |
| 19.0 | 13.01 | 100.0 | 1.000 | 0.0000 | 6.00 | 0.0000 |
| 20.0 | 13.63 | 100.0 | 1.000 | 0.0000 | 13.32 | 0.000 |
| 20.5 | 13.89 | 98.O | 1.020 | 0.0086 | 13.76 | 0.0330 |
| 21.0 | 14.18 | 91.0 | 1.099 | 0.0410 | 14.04 | 0.1117 |
| 21.5 | 14.47 | 82.0 | 1.220 | 0.0864 | 14.32 | 0.1562 |
| 22.0 | 14.73 | 72.0 | 1.389 | 0.1427 | 14.60 | 0.2162 |
| 22.5 | 15.04 | 62.0 | 1.612 | 0.2074 | 14.88 | 0.2085 |
| 23.0 | 15.33 | 55.5 | 1.801 | 0.2555 | 15.18 | 0.1660 |
| 24.0 | 15.89 | 48.0 | 2.082 | 0.3185 | 15.61 | 0.1125 |
| 25.0 | 16.44 | 44.0 | 2.272 | 0.3564 | 15.16 | 0.0690 |
| 27.0 | 17.53 | 40.0 | 2.500 | 0.3979 | 16.98 | 0.0381 |
| 30.0 | 19.10 | 36.5 | 2.740 | 0.4378 | 18.32 | 0.0254 |
| 35.0 | 21.60 | 34.0 | 2.940 | 0.4684 | 20.35 | 0.0122 |
| 40.0 | 23.94 | 32.0 | 3.124 | 0.4947 | 22.77 | 0.0112 |
| 45.0 | 26.16 | 31.5 | 3.175 | 0.5017 | 25.05 | 0.0032 |
| 50 . 0 | 28.24 | 31.0 | 3.224 | 0.5984 | 27.20 | 0.0032 |
| 55.0 | 30.21 | 31.0 | 3.224 | 0.5084 | 29,22 | 0.0000 |

TABLE XXXI - POLYMER FRACTION 4-1

PRECIPITABILITY

| Ml.CH ₃ OH | %сн _з он | I | ı°\i | logI_/I | Av.%CH_OH | Tangent |
|-----------------------|---------------------|--------------|-------|---------|-----------|---------|
| 0.0 | 0.00 | 100.0 | 1.000 | 0.0000 | 0.00 | 0.0000 |
| 5.0 | 3.81 | 100.0 | 1.000 | 0.0000 | 1.90 | 0.0000 |
| 10.0 | 7.30 | 100.0 | 1.000 | 0.0000 | 5.56 | 0.0000 |
| 15.0 | 10,56 | 98.0 | 1.020 | 0.0086 | 8.93 | 0.0026 |
| 15.5 | 10.87 | 97.0 | 1.031 | 0.0133 | 10.72 | 0.0152 |
| 16.0 | 11.18 | 71.0 | 1.408 | 0.1486 | 11.02 | 0.4364 |
| 16.5 | 11.50 | 63.0 | 1.588 | 0.2008 | 11.34 | 0.1630 |
| 17.0 | 11.80 | 57.5 | 1.739 | 0.2403 | 11.65 | 0.1317 |
| 17.5 | 12.11 | 53. 0 | 1.886 | 0.2755 | 11.96 | 0.1135 |
| 18.0 | 12.41 | 50.0 | 2.000 | 0,3010 | 12.26 | 0.0850 |
| 19.0 | 13.01 | 45.5 | 2.198 | 0.3420 | 12.70 | 0.0683 |
| 20 .0 | 13.63 | 42.5 | 2.355 | 0,3720 | 13.32 | 0.0484 |
| 21.0 | 14.18 | 40.0 | 2.500 | 0.3979 | 13.90 | 0.0471 |
| 23.0 | 15.33 | 37.5 | 2.665 | 0.4257 | 14.76 | 0.0242 |
| 25.0 | 16.44 | 36.0 | 2.778 | 0.4437 | 15.88 | 0.0162 |
| 30.0 | 19.10 | 33.0 | 3.030 | 0.4314 | 17.77 | 0.0142 |
| 35.0 | 21.60 | 31.5 | 3.175 | 0,5017 | 20.35 | 0.0081 |
| 40.0 | 23.94 | 30.5 | 3.280 | 0.5159 | 22.77 | 0.0061 |
| 45.0 | 26.16 | 30.0 | 3.333 | 0.5228 | 25.05 | 0.0031 |
| 50.0 | 28.24 | 30.0 | 3.333 | 0.5228 | 27.20 | 0.0000 |

TABLE XXXII - POLYMER FRACTION 4-3

| PRECIPITABLL | LTY. |
|--------------|------|
|--------------|------|

| Ml.CH ₃ OH | %сн ₃ он | I | I°\I | logI ₀ /I | Av.%CH_OH | Tangent |
|-----------------------|---------------------|--------------|-------|----------------------|--------------|----------------|
| 0.0 | 0.00 | 100.0 | 1.000 | 0.0000 | 0.00 | 0.0000 |
| 10.0 | 7.30 | 100.0 | 1.000 | 0.0000 | 3 .65 | 0.0000 |
| 15.0 | 10,56 | 100.0 | 1.000 | 0.0000 | 8.93 | 0.0000 |
| 16.0 | 11.18 | 99.0 | 1.010 | 0.0043 | 10.87 | 0.0069 |
| 16.5 | 11.50 | 98.0 | 1.020 | 0.0086 | 11.34 | 0.0134 |
| 17.0 | 11.80 | 54.0 | 1.851 | 0.2674 | 11.65 | 0.8627 |
| 17.5 | 12.11 | 42.0 | 2.380 | 0.3766 | 11.96 | 0 .3850 |
| 18.0 | 12.41 | 37.0 | 2.701 | 0.4315 | 12.26 | 0 .1830 |
| 18.5 | 12.71 | 34.5 | 2.900 | 0.4624 | 12.56 | 0.1030 |
| 19.0 | 13.01 | 32.5 | 3.075 | 0.4878 | 12.86 | 0.0847 |
| 20.0 | 13.53 | 30.0 | 3.333 | 0 .5228 | 13.32 | 0.0565 |
| 22.0 | 14.73 | 2 6•5 | 3.774 | 0.5768 | 14.18 | 0.0491 |
| 25.0 | 16.44 | 23.5 | 4.252 | 0.6286 | 15.58 | 0.0303 |
| 30.0 | 19.10 | 21.0 | 4.755 | 0.6772 | 17.77 | 0.0183 |
| 35.0 | 21.60 | 19.0 | 5.258 | 0,7208 | 20.35 | 0.0214 |
| 40.0 | 23.94 | 18.0 | 5.555 | 0.7447 | 22.77 | 0.0102 |
| 45.0 | 26.16 | 17.0 | 5.885 | 0.7698 | 25.05 | 0.0113 |
| 50.0 | 28.24 | 16.5 | 6.055 | 0.7821 | 27.20 | 0.0059 |
| 55.0 | 30.21 | 16.0 | 6.250 | 0.7959 | 29.22 | 0.0070 |
| 60.0 | 32.08 | 16.0 | 6.250 | 0.7959 | 31.14 | 0.0000 |

TABLE XXXIII - POLYMER FRACTION 4-4

PRECIPITABILITY

| Ml.CH ₃ OH | %Сн ₃ ОН | I | I°\I | logI_/I | Av.%CH3OH | Tangent |
|-----------------------|---------------------|-------|---------------|----------------|-----------|----------------|
| 0.0 | 0.00 | 100.0 | 1.000 | 0.0000 | 0.00 | 0.0000 |
| 15.0 | 10.56 | 100.0 | 1.000 | 0.0000 | 5.28 | 0.0000 |
| 16.0 | 11.18 | 100.0 | 1.000 | 0.0000 | 10.87 | 0.0000 |
| 16.5 | 11.50 | 99.5 | 1.005 | 0.0022 | 11.34 | 0.0069 |
| 17.0 | 11.80 | 99.0 | 1.010 | 0.0043 | 11,65 | 0.0070 |
| 17.5 | 12.11 | 98.5 | 1.015 | 0.0065 | 11.96 | 0.0071 |
| 18.0 | 12.41 | 54.5 | 1.835 | 0.2636 | 12.26 | 0.8570 |
| 18.5 | 12.71 | 42.5 | 2.352 | 0.3714 | 12.56 | 0.3593 |
| 19.0 | 13.01 | 37.0 | 2.702 | 0.4317 | 12.86 | 0.2010 |
| 19.5 | 13.31 | 34.5 | 2.898 | 0.4621 | 13.16 | 0 .1013 |
| 20.0 | 13.63 | 32.5 | 3.075 | 0.48 78 | 13.47 | 0 .0803 |
| 21.0 | 14.18 | 30.0 | 3.333 | 0.5228 | 13.90 | 0.0636 |
| 22.0 | 14.73 | 28.5 | 3.508 | 0.5451 | 14.46 | 0.0406 |
| 23.0 | 15.33 | 27.0 | 3.7 05 | 0.5688 | 15.03 | 0.0395 |
| 25.0 | 16.44 | 25.0 | 4.000 | 0.6021 | 15.88 | 0.0300 |
| 30.0 | 19.10 | 22.5 | 4.4 45 | 0.6479 | 17.77 | 0.0172 |
| 35.0 | 21.60 | 20.5 | 4.880 | 0.6884 | 20.35 | 0.0162 |
| 40 .0 | 23.94 | 19,5 | 5.130 | 0.7101 | 22.77 | 0.0092 |
| 45.0 | 26.16 | 18.5 | 5.405 | 0.7328 | 25.05 | 0.0102 |
| 50.0 | 28.24 | 18.0 | 5.555 | 0.7447 | 27.20 | 0.0057 |
| 55.0 | 30.21 | 18.0 | 5.555 | 0 .7447 | 29.22 | 0.0000 |



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DISCUSSION

Polymer samples used in this work were made by emulsion polymerizing styrene under carefully controlled conditions. A considerable quantity of polymer prepared by a known and reproducible method was necessary for each sample. Conditions of polymerization were chosen so that the samples would vary in characteristics, yet be obtainable by procedures studied by other workers 1,2,3,4,5 within this laboratory.

The measurement of "precipitability" by light extinction required that the total amount of polymer in solution remain suspended as the non-solvent addition occurred. Sedimentation of polymer would result in a discontinous "precipitability" curve. Trials with solutions of different concentration indicated that the use of a two-hundredths molar solution of polystyrene in butanone was most satisfactory. The use of a more concentrated polymer solution resulted in sedimentation of the solid polymer during the determination, and solutions of lesser concentration did not give a suitable extinction of light.

Fractionation of the polymer samples was based on the work of Schulz and Dinglinger,¹⁶ who gave no specifications for actual procedure. Morey and Tamblyn¹⁷ stated that concentration of the polymer solution had little effect on the quality of the fractionation. It was necessary to develop a suitable procedure, and in its development it was discovered that the fractionation

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was simpler if carried out in dilute solutions containing approximately ten grams of polystyrene in one liter of butanone.

The precipitation by methanol of concentrated solutions of polystyrene resulted in instantaneous precipitation in the area where the methanol entered the solution. With vigorous agitation, the precipitated polymer returned to solution, but further addition of methanol gave the same result, leading to a slow, laborious procedure.

With the dilute solution mentioned above, precipitation occurred gradually. Addition of methanol turned the polymer solution milky white as precipitation occurred, and sedimentation of the polymer took place in twenty-four hours or less. The polymer separated as a gelatinous mass, which upon washing with methanol quickly solidified.

The quality of the fractionation varied with the original polystyrene samples used. The molecular weight range of a given polymer determined how easily it could be fractionally precipitated, and into how many fractions it could be separated.

As an example, the fractionation of polymer # 4 is compared to the fractionation of polymer # 3. Polymer # 4 was separated into four fractions with distinctly different average molecular weights, i.e. the "precipitability" tangent curves for three of the four fractions obtained each showed distinctly different maximum. (Figure 17) The areas under the "precipitability"

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tangent curves for the three fractions were very small laterally, which indicated that these polymer fractions had a narrow range of molecular weight. The lateral width of the area under the "precipitability" tangent curve for polymer # 4 (Figure 6) was quite small, which indicated that the original sample had a narrow range of molecular weight. The conditions of polymerization for this sample were such that a polymer with a limited range of molecular weight was expected.

The lateral width of the area under the "precipitability" tangent curve for polymer # 3 (Figure 5) was much greater than that for polymer # 4, which indicated a greater range in molecular weight. The "precipitability" tangent curves for three fractions of polymer # 3 (Figure 16) each showed a distinct maximum, and lateral width of area under the curves indicated a much narrower range of molecular weight than in the original sample. Comparison of the "precipitability" tangent curves for fractions of polymer # 4 (Figure 17) and polymer # 3 (Figure 16) indicated a greater homogeneity of molecular weight in the fractions of polymer # 4.

The samples obtained by fractionation might be fractionated a second time. A second fractionation into constituents of different molecular weight would be possible on samples where the lateral width of the area under the "precipitability" tangent curve for the sample in question was large. Some overlapping

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of molecular weight between the last and first fractions from two successive samples would occur in the second fractionation. Where the lateral width of the area under the "precipitability" tangent curve was very small, little could be gained by a second fractionation, as almost complete precipitation would occur suddenly, giving little, if any, separation.

In recent years controversy has arisen concerning the proper approach to methods of molecular weight determination of polymers. The values of average molecular weights determined by use of the ultracentrifuge and osmometer are more nearly absolute values than those determined by viscosity, but the length of time required for these determinations, and the inaccessibility of the necessary equipment often forces workers in this field to use other methods.

The determination of average molecular weight by viscosity measurements has been the subject of more controversy than the determination of molecular weight by other methods. It is quite certain that the original Staudinger equation

should be modified, but investigators in this field cannot agree upon what the modification should be. Two other versions of the Staudinger equation have been proposed:

(1)
$$\left[h\right] = KM \neq constant$$

(2) $\left[h\right] = KM^{0}$

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At the present time equation (2) holds the greatest promise. It is quickly apparent that the original Staudinger equation is a special case of equation (2) with beta equal to one.

As a comparison of the usefulness of these equations viscosity measurements were made on solutions of certain polymer samples at different concentrations, and their intrinsic viscosities obtained (Figure 13). These values of [N] were used in equation (2) along with values of K and beta obtained by Goldberg, Hohenstein and Mark.²¹ In certain cases molecular weights obtained from the Staudinger equation and equation (2) were in fair agreement, in other cases they varied widely. The determination of K and beta for equation (2) is still in the experimental stage and values available are not too reliable.

As an example, the values of K and beta for polystyrene polymerized at 60° C. are 1.28 x 10^{-4} and 0.7, respectively. These constants, according to Goldberg, Hohenstein, and Mark,²¹ cover a molecular weight range of 550,000 to 2,000,000. On the first fraction from polymer # 7 the intrinsic viscosity was 4.4. Using equation (2)

$$4.4 = 1.28 \times 10^{-4} \times M^{0.7}$$

a value of 3,022,000 was obtained, which was approximately eight times the value obtained by the use of the Staudinger equation.

Since this pair of values for K and beta do not cover the molecular weight range of the polymer in question, good correlation was not expected. According to Goldberg, Hohenstein and Mark,²¹ the values of K and beta covering this range of molecular weight are for polystyrene polymerized at 120° C. and are 5.5 x 10^{-3} and 0.8, respectively. Using these values and the same value of 4.4 for the intrinsic viscosity in equation (2)

$$4.4 = 5.5 \times 10^{-3} \times M^{0.8}$$

a value of 4255 was obtained, which was just slightly over one percent of the value obtained by use of the Staudinger equation.

Many factors affect the determination of the values of K and beta, and separate constants must be determined experimentally for polystyrene polymerized under various conditions. Type of system used in the polymerization, catalyst, catalyst concentration, temperature, and time allowed for polymerization could all exert an influence on these constants.

Another method for the determination of molecular weight of polystyrene from viscosity measurements has been proposed by Kemp and Peters.²³ It is based on the Arrhenius relation:

$$\frac{\log \eta_r}{C} = K$$

where η_{Y} is the relative viscosity.

Kemp and Peters proposed equation is

$$M = \log \eta_r \times K$$

They determined the value of K to be .45 x 10^4 for low molecular weight polystyrene in benzene or chloroform. Price and Adams²⁴ modified K for toluene solutions of high molecular weight

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polystyrene, and determined the value of the constant to be $.74 \times 10^4$.

Using this value of K for the determination of the average molecular weight of polymer # 1

$$M = \frac{\log \frac{84.1}{53.5} \times .74 \times 10^4}{.0101}$$

a value of 144,000 is obtained, as compared to a value of 312,200 obtained from the Staudinger equation. The values obtained for the average molecular weights of the six polymers used in this work are listed below.

| | Sample | Molecular weights by | |
|---------|--------|----------------------|--------------------------|
| Polymer | | Kemp-Peters | Staudinger |
| | | Equation | Equation |
| 1 | | 144,000 | 312,200 |
| 2 | | 98,500 | 198,700 |
| 3 | | 105,100 | 215,400 |
| 4 | | 202,000 | 4 86 , 500 |
| 5 | | 159,000 | 354,700 |
| 6 | | 85,500 | 167,900 |
| | | | |

The values for the average molecular weight as determined by the Kemp-Peters equation vary from 41 to 51 percent of the value obtained for the value of the average molecular weight as determined by the Staudinger equation. This correlation is a great improvement over that obtained in the case of the modified Staudinger equation.

In this work the primary objective was to obtain molecular weight comparisons rather than absolute molecular weight determinations. Therefore, the use of the Staudinger equation is justified

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because it is as suitable as other proposed equations for comparative purposes. The same method for the determination of molecular weight is used in all instances, therefore, comparisons may be made with reasonable accuracy. The constant used in the Staudinger equation is one which was determined experimentally for polystyrene, and which has been used extensively.

The molecular weight distribution curves obtained from the fractionation data were the typical S-shaped curves (Figures 9 and 10) comparable to those published in work by other investigators. Before comparison with "precipitability" curves it should be noted that the distribution curves should be reversed. On the distribution curves the molecular weight increases from left to right on the "precipitability" curves the equivalent of molecular weight, i. e., solubility of polymer, decreases from left to right as the high molecular weight polymer was the first to be precipitated. This same characteristic was carried through to the tangent curves derived from the "precipitability" and molecular weight distribution curves.

Actual point by point comparison of these tangent curves was not possible, as it was impossible to use the same units and scales as ordinates and abscissas. The comparison of the maxima of the tangent curves was made possible by a method based on average molecular weight in the following fashion: The maximum on the molecular weight distribution tangent curve for polymer # 3 (Figure 11)

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occurred at a molecular weight of 64,000. The average molecular weights of the fractions obtained from polymer $\frac{\pi}{T}$ 3 showed that this value was included between fractions four and five. (Table XVII). These two fractions were precipitated from solutions between thirteen and fifteen percent non-solvent concentration (Table X). Interpolation for the value of 64,000 between the values of 71,100 (fraction 5) and 93,700 (fraction 4) gave a percent non-solvent concentration of 13.86%. This value is onetenth of one percent from the value obtained for the maximum of the tangent curve as calculated from the "precipitability" curve (Table IV).

The same use of data from the other five curves gave corresponding results. The agreement of percentage values was not as good in all cases as it was with polymer # 3, but all of the comparisons were close to the values calculated from the "precipitability" curve. Better agreement could be obtained by more extensive fractionation, which would result in more exact curves.

| Polymer Sample | Maximum Percent Non-solvent "Precipitability" Tangent Curves | Maximum Percent Non-solvent Calculated from Distribution Tangent Curves | Difference |
|-------------------|-----------------------------------------------------------------------|-------------------------------------------------------------------------------------|------------|
| 1 | 11.02 | 11.99 · | 0.97 |
| 2 | 12.86 | 13.54 | 0.68 |
| 3 | 13.76 | 13.86 | 0.10 |
| 4 | 11.65 | 11.42 | 0.23 |
| 5 | 12.26 | 11.43 | 0.83 |
| 6 | 11.96 | 12.99 | 1.03 |

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As the maxima of the two types of tangent curves are comparable, it is reasonable to assume "precipitability" tangent curves could serve as an approximation to the distribution tangent curve with proper mathematical treatment. The tangent curves as derived in this work are graphical differentiations of the "precipitability" and molecular weight distribution curves. If the equations of the "precipitability" and molecular weight distribution curves could be determined, actual point by point comparison could be made and these equations might then be differentiated mathematically. If this were possible, a useful tool for fast approximations of molecular weight distribution of a given polymer sample would be provided, eliminating the slow laborious procedure of fractionation. This method would necessarily be limited to polystyrene, but further work might extend it to other types of polymers.

Several extensions of this work are possible. There are many possibilities in the field of molecular weight, as present inconsistencies are extensive. As considerable equipment is necessary for work with the ultracentrifuge, the osmometer would be the logical choice for continuation in this work. Data and results obtained in this manner could be compared with data and results obtained from viscosity measurements. There is still a great deal to be done in the calculations of K values, as well as values of beta, providing it is proven that the equation using beta is the proper one.

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The fractionation procedure could be improved by developing some type of container which would facilitate separation of the precipitated polymer sample and the supernatant solution. It is also possible that fractionation could be carried out in conjunction with the "precipitability" apparatus, resulting in a more uniform separation.

As has been mentioned previously, a mathematical treatment of this work could lead to a valuable shortcut in determining molecular weight distribution of polymers. It is difficult to say how extensive this work would have to be to obtain the proper correlation between these two types of curves.

SUMMARY

- A new and simpler method based on "precipitability" is proposed for determination of integral average molecular weight distribution curves of emulsion polymerized polystyrene.
- 2. The above method has been applied to differential distribution curve maxima and the differential "precipitability" curve maxima with suitable agreement. In no case was the variation equal to more than the equivalent value of 1.03%.
- 3. Fractional precipitation of polystyrene is possible using butanone as a solvent and a lower member of the alcohol series as a non-solvent. The choice of alcohol has little effect upon the fractionation.
- 4. The extent and quality of fractionation of a given polymer is dependent upon the individual sample, and the conditions under which it was prepared.
- 5. It is advantageous to use relatively dilute solutions in the fractional precipitation, and still more dilute solutions in "precipitability" measurements.

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