pressure for 18 hr. Polymer, PMT of 270°, with η_{inh} 0.50, was obtained.

Preparation of XII. A small polymer tube containing 4.38 g (0.011 mol) of VI, 1.10 g (0.010 mol) of hydroquinone, and 0.005 g of triphenylphosphene was treated as in the previous example. Polymer, PMT of 310°, with η_{inh} 0.53, was obtained.

Preparation of XIII. A small polymer tube containing 4.38 g (0.11 mol) of VI, 1.58 g (0.01 mol) of III, and 0.005 g of triphenylphosphene was treated as in a previous experiment. Polymer, PMT 256°, with η_{inh} 0.70, was obtained.

Preparation of XIV. To a Waring Blendor containing 125 ml of water, 2.65 g (0.0275 mol) of sodium carbonate, 2.63 g (0.0125 mol) of bis(4-aminocyclohexyl)methane (53% *trans,trans* isomer), and 25 ml of ethylene dichloride was added, with rapid stirring, a solution of 3.53 g (0.0125 mol) of V in 50 ml of ethylene dichloride. The reaction mixture was stirred 5 min and poured into hot water. The ethylene dichloride was boiled off and the precipitated polymer washed three times with water, three times with methanol, and dried at 70° *in vacuo* overnight. The yield was 4.8 g of polymer with η_{inh} of 1.80 and a PMT of 312°.

Preparation of XV. To a Waring Blendor containing 125 ml of water, 2.65 g (0.0275 mol) of sodium carbonate, 2.63 g (0.0125 mol) of bis(4-aminocyclohexyl)methane (70% *trans,trans* isomer) and 25 ml of ethylene dichloride was added, with rapid stirring, a solution of 3.53 g (0.0125 mol) of V in 50 ml of ethylene dichloride. The reaction mixture was stirred for 5 min and poured into hot water. The ethylene dichloride was boiled off and the precipitated polymer was washed three times with water, three times with methanol, and dried at 70° *in vacuo* overnight. The yield was 4.8 g of polymer with η_{inh} 1.66 and a PMT of 39°.

Preparation of XVI. To a Waring Blendor containing 125 ml of water, 2.65 g (0.0275 mol) of sodium carbonate, and 1.08 g (0.0125 mol) of piperazine was added, with rapid stirring, a solution of 3.53 g (0.0125 mol) of V in 75 ml of ethylene dichloride. After stirring for 5 min, the reaction mixture was poured into water and the precipitated polymer washed three times with water, three times with methanol, and dried at 70° *in vacuo* overnight. Yield was 3.6 g of polymer with η_{inh} 2.25 and a PMT of 388°.

Preparation of XVII. A solution of 2.37 g (0.015 mol) of III and 3.75 g of bis(4-isocyanotophenyl)methane in 20 ml of dry dimethyl sulfoxide was heated for 4 hr. The solution was poured into water, and the precipitated polymer washed three times with water and dried at 70° *in vacuo* overnight. The yield was 5.9 g of polymer with η_{inh} 0.7 and a PMT of 285°.

Preparation of XVIII, XIX, XX, and XXI. The above polymers were prepared by the catalyst and procedure used for the preparation of XIII.

Infrared spectra were recorded on a Perkin-Elmer Model 21 with a sodium chloride prism, thin films being obtained by melting samples on the prism. The pertinent bands for the previously mentioned compounds, between 9 and 10 μ, are given in Table IV.

On the Shape of the Intramolecular Scattering Function for Chain Molecules in Good and Poor Solvents[1,2]

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ABSTRACT: A light-scattering study of the intramolecular scattering function was conducted using very narrow fractions of polystyrene and poly(dimethylsiloxane) in both Θ solvents and good solvents. By combining the angular and the wavelength dependence of the data it was possible to study the scattering function over a wide range of values and to make meaningful comparison of the results with the theoretical equations of Debye and Isihara for Θ solvents, and of Ptitsyn and others for good solvents. For the Θ systems it was found that the equations of Debye and Isihara, which were found by numerical calculations to be experimentally indistinguishable for cases of practical interest, accounted well for the results. On the other hand, for good solvents the Ptitsyn equation overestimated the influence of the excluded volume effects on the scattering function. In fact, as long as the molecular weight of the polymer was less than a few million, the Debye equation fit the results very well. For molecular weights greater than a few million it was necessary to use the Ptitsyn function to fit the data, but with an excluded volume parameter ϵ smaller than the *a priori* value calculated from the Mark–Houwink viscosity–molecular weight exponent.

Debye's[4] classical equation for $P(\theta)$, the intramolecular scattering function for chain molecules, has been criticized from two different points of view. Since 1957, one group of workers[5–9] has maintained that his equation should be valid at the Θ condition, but not in good solvent systems, where non-Gaussian chain statistics become operative due to long-range intramolecular interactions. A more recent criticism has

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(1) Taken in part from a thesis presented by T. E. S. in partial fulfillment of the requirements for the Ph.D. degree, Georgia Institute of Technology, 1967.

(2) Presented in part at the 153d National Meeting of the American Chemical Society, Division of Polymer Chemistry, Miami Beach, Fla., April 1967; *cf. Polym. Preprints*, **8**, 616 (1967).

(3) To whom all correspondence should be addressed.

(4) P. Debye in "Light Scattering from Dilute Polymer Solutions," D. McIntyre and F. Gornick, Ed., Gordon and Breach, New York, N. Y., 1964, p 139.

(5) O. B. Ptitsyn, *Zh. Fiz. Khim.*, **31**, 1091 (1957); see ref 4, p 231, for English translation.

(6) H. Benoit, *Compt. Rend.*, **245**, 2244 (1957).

(7) C. Loucheux, G. Weill, and H. Benoit, *J. Chim. Phys.*, **55**, 540 (1958); see ref 4, p 243, for English translation.

(8) A. J. Hyde, J. H. Ryan, and F. T. Wall, *J. Polym. Sci.*, **33**, 129 (1958).

(9) A. J. Hyde, *Trans. Faraday Soc.*, **56**, 591 (1960).

been made by Isihara,[10] who claims that Debye's equation is an approximation which is valid only at low angles, even at the Θ condition. In both instances, refinements of the Debye theory yielded new equations.

In this paper we shall examine the validity of these proposed improvements of the Debye theory. Experimental scattering data are presented for fractions of polystyrene (PS) and poly(dimethylsiloxane) (PDMS) in both Θ solvents and good solvents.

Theoretical

The intramolecular scattering function can be represented by eq 1, where $P(\theta)$ is the scattered intensity at

$$P(\theta) = \frac{1}{N^2}\sum_i\sum_j \left\langle \frac{\sin \mu r_{ij}}{\mu r_{ij}} \right\rangle \qquad (1)$$

an angle θ, $\mu = (4\pi/\lambda')\sin(\theta/2)$, N is the number of segments in the chain, λ' is the wavelength of the light in the medium, and r_{ij} is the distance between segments i and j. If the Gaussian distribution function is used for r_{ij}

$$W(r_{ij}) = (3/2\pi\overline{r_{ij}^2})^{3/2}\exp(-3r_{ij}^2/2\overline{r_{ij}^2})4\pi r_{ij}^2 \qquad (2)$$

then performing the average over the intramolecular distance indicated in eq 1 gives the result

$$\left\langle \frac{\sin \mu r_{ij}}{\mu r_{ij}} \right\rangle = \exp(-\mu^2\overline{r_{ij}^2}/6) \qquad (3)$$

Thus eq 1 becomes

$$P(\theta) = \frac{1}{N^2}\sum_i\sum_j \exp(-\mu^2\overline{r_{ij}^2}/6) \qquad (4)$$

Debye[4] made the assumption, consistent with Gaussian statistics, that

$$\overline{r_{ij}^2} = |i - j|b^2 \qquad (5)$$

where b is the length of a segment. He thus obtained from eq 4 the result

$$P(\theta) = (2/x^2)(e^{-x} - 1 + x) \qquad (6)$$

where $x = 16\pi^2R^2\{\sin(\theta/2)/\lambda'\}^2$. Here R^2 is the mean-square radius of gyration. Although eq 6 has been used extensively, its range of applicability is not yet certain. Perhaps the most immediate difficulty to face is one which Isihara has noted,[10] namely, that eq 2 is only valid for sufficiently large distances r_{ij}. By a more refined treatment which avoids the Gaussian assumption, Isihara derived eq 7, which should be superior to eq 6 for large values of x and small values of N,

$$P(\theta) = (N + 1)^{-1} + 2[1 - \Phi/(N + 1)]\{\Phi - 1 + [1 - \Phi/(N + 1)]^{N+1}\}/\Phi^2 \qquad (7)$$

where $\Phi = [N + 1][1 - \sin(\mu b)/\mu b)]$. Equation 7 reduces to eq 6 for $N = 0$ and also for the case of small angles and very large values of N. The disagreeable feature of eq 7 is that N, the number of scattering segments, appears explicitly. The same is true of the bond length b. The magnitudes of these parameters depend on the manner in which the real chain is divided into segments. Debye's equation (eq 6) does not have this difficulty because there N and b appear together as the quantity $Nb^2/6$, which for Gaussian chains is R^2, an experimentally measurable quantity. Thus, the relative status of eq 6 and 7 is of some importance, since the complications introduced by Isihara should obtain even at the Φ condition.

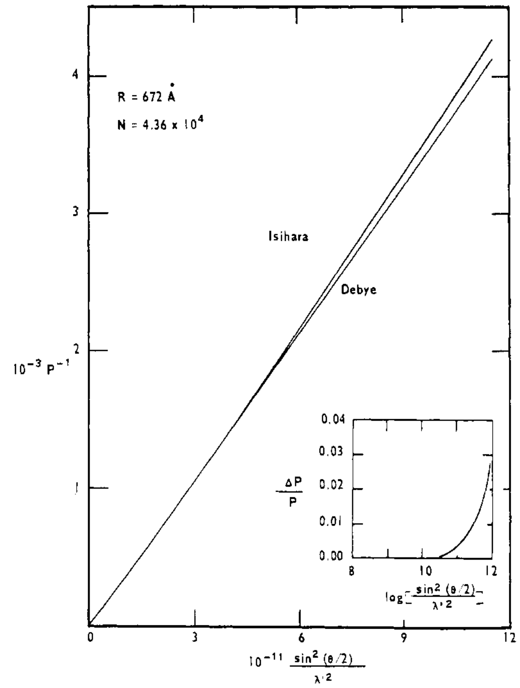

Figure 1. Comparison of the Isihara and Debye scattering functions. Insert gives the relative error of the Debye function.

We have compared eq 6 and 7 by numerical calculations. In Figure 1 some of the results are shown for the case $R = 672$ Å, and $N = 4.36 \times 10^4$ (these values are taken to be representative of fraction PS-III in cyclohexane, *cf.* below). Note that the two functions for P^{-1} are numerically indistinguishable for P^{-1} values less than 1000. Since P^{-1} seldom exceeds *ca.* 20, for practical purposes we may say that although Isihara's equation is more general than Debye's, it does not differ from it at all for values of the abscissa variable $(\sin(\theta/2)/\lambda')^2$ which are accessible in visible light scattering. From the insert to Figure 1, which gives the relative error of the Debye equation as a function of the logarithm of the abscissa variable, it can be seen that the error is almost nil for realistic abscissa values. In fact, even for a scattering angle as high as 140°, a 0.1% error would require a value of λ' of about 500 Å.

In another set of calculations a constant value of 1.5×10^9 was assigned to $[\sin(\theta/2)/\lambda']^2$, which is at the upper limit of the experimentally accessible values. Keeping b constant at 7.9 Å, N was varied from unity to 10^{10}. Here the relative error was zero for $N = 0$ (as it must since $P = 1$ for both cases), passed through a slight maximum at $N = 4 \times 10^3$ and then leveled off for high values of N. Even at the maximum, however, the relative error was less than 0.01%. The picture remains unchanged if other values of b are chosen. Thus, the general features of Figure 1 are applicable to a wide range of values of N and R.

In the light of these calculations we conclude that the refinements and complications of the Isihara theory do

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(10) A. Isihara, *J. Chem. Phys.*, **40**, 1137 (1964).

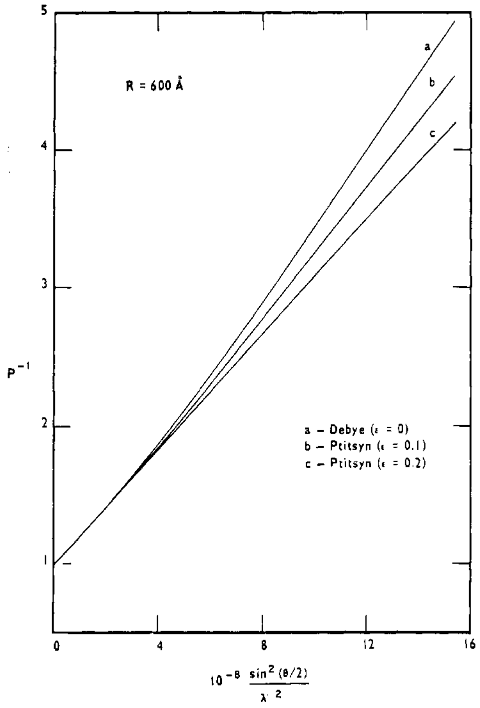

Figure 2. Comparison of the Debye and Ptitsyn scattering functions for different values of ϵ; $R = 600$ Å.

not produce any numerical distinctions from the simpler Debye equation for visible light scattering.

A different criticism of Debye's equation is based on on the failure of Gaussian statistics in good solvent media. Ptitsyn,[5] Benoit, *et al.*,[6,7] and Hyde, *et al.*,[8,9] continue to use eq 3 which is itself a consequence of the Gaussian distribution, eq 2. However, instead of eq 5, they use eq 8, where ϵ is a parameter which is zero

$$\overline{r_{ij}^2} = |i - j|^{1+\epsilon}b^2 \tag{8}$$

in a Θ solvent and greater than zero in a good solvent. Following substitution of eq 8 into eq 4 and replacing summation by integration, $P(\theta)$ becomes

$$P(\theta) = 2\int_0^1 (1 - y)\exp\left[-x\left(1 + \frac{5\epsilon}{6} + \frac{\epsilon^2}{6}\right)y^{1+\epsilon}\right]dy \tag{9}$$

where $y = |i - j|/N$. Of course when $\epsilon = 0$, eq 9, referred to hereafter as the Ptitsyn equation, reduces to eq 6, the Debye equation. The approximation in eq 9 is that the solvent effects influence merely the mean square distances between segments but not the statistical distribution of these distances. A more appropriate procedure would be to use a better distribution than eq 2 in good solvents. Preliminary notice of this type of approach has been given for a distribution function which was deduced from Monte Carlo calculations, but the details are not yet available.[11]

In Figure 2 are shown reciprocal scattering functions P^{-1} calculated from eq 6 and 9 for the values of ϵ and R indicated. From these results it is clear that the refinements of the Ptitsyn theory certainly must be considered for visible light scattering. Although appreciable differences between the two functions are present for the value of R equal to 600 Å, they become even more pronounced for higher values.

In order to fit experimental data with curves like those in Figure 2 the parameter ϵ must be known. Loucheux, *et al.*,[7] have suggested two methods for its evaluation. The first of these makes use of the Flory–Fox equation for the intrinsic viscosity[12]

$$[\eta] = \Phi(\overline{r^2})^{3/2}/M \tag{10}$$

and the empirical Mark–Houwink equation

$$[\eta] = K'M^a \tag{11}$$

If eq 8 is now substituted into eq 10 for the case $|i - j| = N$, there results

$$[\eta] = K'M^{(1+3\epsilon)/2} \tag{12}$$

Comparing with eq 11

$$\epsilon = (2a - 1)/3 \tag{13}$$

Since Mark–Houwink exponents generally lie in the range $0.5 \leq a \leq 0.8$, the corresponding values of ϵ are expected to range from 0 to 0.2. To anticipate the discussion of our experimental results, we find that use of eq 13 seriously overestimates the value of ϵ which is required to fit eq 9 to the data.

The second method for estimating values of ϵ utilizes the actual light-scattering data by plotting log P^{-1} *vs.* log [sin $(\theta/2)/\lambda'$]^2. According to Loucheux, *et al.*,[7] such a plot should be linear at high values of the abscissa with a slope equal to ϵ. Although they obtained for their system a value of ϵ compatible with the viscosity exponent, this method in general overestimates the appropriate value of ϵ. Hyde[9] has proposed an improved but elaborate method for evaluating ϵ which we have not used.

There are very few investigations reported in the literature which are suitable for testing the validities of eq 6 and 9. This is partly due to the fact that these equations apply only to monodisperse polymers. As Figure 2 shows, the effect of the non-Gaussian statistics is to impart downward curvature to the reciprocal scattering function P^{-1}, an effect which is also caused by polydispersity. Also, the investigations to date have utilized a single wavelength, a restriction which we shall show to be unfavorable if the shape of the function P^{-1} is desired over as wide a range of values as is possible.

Eskin[13] made measurements on two polystyrene fractions in cyclohexane and toluene, using 5460-Å incident light. He found that the Debye equation fits the data in cyclohexane (a Θ solvent) as expected, but that for a sample of $M = 20 \times 10^6$, downward curvature was observed at large angles. He concluded that eq 9 provided a better fit to his data than eq 6, but, in fact, we conclude that his data for this fraction are better fit by eq 6 than by eq 9. His rejection of eq 6 is based on an *a priori* assignment of a value of R^2 (obtained from a viscosity measurement) whereas by using a reasonable value of R^2 his data for P^{-1} can be represented very well

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[11] D. McIntyre, J. Mazur, and A. Wims, *Bull. Amer. Phys. Soc.*, **11**, 165 (1966).

[12] P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953, Chapter 14.

[13] V. E. Eskin, *Vysokomol. Soedin.*, **1**, 138 (1959).

by eq 6 except at the very highest angles. Similar data were also reported for seven fractions of poly(2,5-dichlorostyrene) in dioxane, a good solvent,[14] but no attempt was made to use the angular data to test eq 6 and 9.

Loucheux, Weill, and Benoit[7] studied the angular dependence of scattering of a single polystyrene fraction ($\overline{M}_w = 9 \times 10^6$) in benzene, a good solvent, and in cyclohexane, a Θ solvent, using 5460-Å incident light. This polymer had a rather broad distribution of molecular weight ($\overline{M}_w/\overline{M}_n = 1.8$) and thus a polydispersity correction was necessary. Because of this complication, their evidence favoring the Ptitsyn function in good solvents is of an indirect rather than a direct nature. Their method, which utilizes the low- and high-angle data to predict the width of the molecular weight distribution, depends upon reaching the asymptotic region of $P^{-1}(\theta)$ instead of comparing the actual angular data with a theoretical function. As we have discussed elsewhere,[15] it is more profitable to consider the shapes of scattering functions in the experimentally accessible range of values of $\sin(\theta/2)/\lambda'$ than to depend upon conclusions which are based on the asymptotic behavior expected theoretically, since true asymptotic behavior is very difficult to observe.

Hyde, *et al.*,[8] made independent measurements on essentially the same sample as Loucheux, *et al.*, using benzene and butanone as solvents and 5460-Å radiation. Their conclusion favoring the Ptitsyn function was likewise based upon the failure of eq 6 to predict properly the breadth of the molecular weight distribution.

Prud'homme and Sicotte[16] studied six sharp polystyrene fractions with molecular weights ranging up to 1.1×10^6 in toluene with 5460-Å light. Although these workers did examine the actual angular dependence of the scattering, their molecular weights were too low to discriminate between eq 6 and 9, which fit their data equally well.

Debye, *et al.*,[17] studied a PS polystyrene fraction ($\overline{M}_w = 1.5 \times 10^6$) in benzene and found the angular data to be well fit by eq 6. Since their measurements were made with 4358-Å incident light and since the molecular weight was moderately high, the values of x obtained were high enough to make a distinction between eq 6 and 9; however, these authors made no mention of either the Ptitsyn theory or the theoretical objections to using eq 6 in good solvent systems.

It was our purpose to study the angular dependence of the light scattered by different polymer–solvent systems and by this to know better the experimental regions of applicability of the equations of Debye, eq 6, and of Ptitsyn, *et al.*, eq 9. In order to progress beyond the previous studies, we have (1) made measurements on two linear polymers differing in chain flexibility; (2) used several very sharp fractions of moderately high molecular weight; and (3) extended the range of the variable x and verified the high-angle data by the use of more than one wavelength for each experiment.

The two linear polymers chosen for study were atactic polystyrene (PS) and poly(dimethylsiloxane) (PDMS). The characteristic unperturbed ratios, $\overline{r_0^2}/Nb^2$, for these polymers are 10.6 for PS[18] and 6.3 (in butanone) or 7.7 (in a low cohesive energy density mixture) for PDMS.[19] Thus PS is a slightly less flexible chain than PDMS.

The fractions, with the exception of PS-II (*cf.* below), possessed very sharp molecular weight distributions, and hence the polydispersity problems associated with some of the former investigations were mostly eliminated. By using Θ solvents as well as good solvents, the polydispersity effect was examined and evaluated without any excluded volume complications.

Finally, as we have recently pointed out,[15] the fact that $P(\theta)$ is a function of wavelength as well as angle can have considerable experimental significance. Although this double functional dependence is obvious upon inspection of eq 1, experimental workers have evidently failed to appreciate its advantages. All the investigations noted above fully utilized only one wavelength, often 5460 Å. If incident radiation of 3650 Å is also used and the values of P^{-1} are plotted *vs.* $[\sin(\theta/2)/\lambda']^2$, the range of the abscissa values is approximately twice that obtained using the green wavelength alone. In view of the fact that departures from the Debye equation are greatest at large abscissa values (*cf.* Figure 2), this extension has great importance for our present purposes. In all the experiments of this study, measurements were made using both 4358- and 3650-Å incident light, and for several systems 5460-Å radiation was also used.

Experimental Section

Photometer. A modified Brice–Phoenix photometer was used. The slits were replaced with rectangular slits made from razor blades, blackened with a benzene flame. The slit immediately in front of the cell was 2.0 × 5.0 mm. The angular range covered was extended from 25 to 140° by removing part of the working standard shield and by moving the limit stop for the photomultiplier housing. The scattering compartment was insulated with foamed polystyrene and painted black. Partial temperature control was accomplished by circulating either heated or cooled air through the scattering compartment by an external blower. The photomultiplier housing was cooled by two copper coils through which tap water was circulated. Further control of temperature was accomplished by circulating water from an external constant temperature bath through a jacket which surrounded the cylindrical scattering cell. This jacket was fabricated from a brass pipe about which was 0.25-in. copper tubing tightly coiled and soldered. This in turn was covered with polystyrene foam and black tape. A section of the pipe about 2 in. in height and subtending an angle of about 200° was removed to permit unobstructed passage of light through the cell. An insulated brass lid was placed on top of the glass cell cover. The temperature was determined by thermometers immersed in the water entering and leaving the jacket. Temperatures remained constant to within ±0.05° when using this arrangement for measurements in Θ solvents. In good solvent systems, where less precise temperature control was required, the cell jacket was not used, and the tem-

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(14) V. E. Eskin and T. Volkov, *Vysokomol. Soedin.*, **5**, 614 (1963); *J. Polym. Sci. USSR*, **5**, 1292 (1963).

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(16) J. Prud'homme and Y. Sicotte, *Can. J. Chem.*, **42**, 2078 (1964).

(17) P. Debye, B. Chu, and H. Kaufmann, *J. Polym. Sci., Part A*, **1**, 2387 (1963).

(18) W. R. Krigbaum and D. K. Carpenter, *J. Phys. Chem.*, **59**, 1166 (1955).

(19) J. E. Mark and P. J. Flory, *J. Amer. Chem. Soc.*, **86**, 138 (1964).

peratures remained constant to ±0.5°. The cell alignment was checked using fluorescein solutions, for which the intensities were constant to ±1% over the range of $30° \leq \theta \leq 135°$ after multiplying by the sin θ volume correction. For pure benzene, the readings were constant to ±1% after multiplying by $\sin\theta/[1 + \cos^2\theta(1 - \rho)/(1 + \rho)]$ over the range of $25° \leq \theta \leq 140°$ at 3650 and 4358 Å, where ρ is the 90° depolarization. For 5460 Å this criterion was met for the range $35° \leq \theta \leq 140°$. Unpolarized incident light was used.

An unmodified Brice–Phoenix differential refractometer was used for the specific refractive increment measurements.

Viscometers. Several Ubbelohde types were used, one of which was a four-bulb rate of shear instrument. Kinetic energy and rate of shear corrections were applied when needed.

Polymer Samples. The four PDMS fractions were supplied by Mr. Robert Buch.[20] Characterization by light scattering and osmometry of other fractions from the same fractionation led to an estimated value of $\overline{M}_w/\overline{M}_n$ for the four fractions of 1.10 or less.

PS-I was an anionically polymerized polystyrene sample supplied by Dr. F. Wenger.[21] Although the $\overline{M}_w/\overline{M}_n$ ratio was already 1.02, further fractionation was effected by fractional precipitation from benzene by methanol. The first 10% of the material to precipitate was discarded and 90% of the remaining material was used in this study. PS-II was an anionically polymerized sample supplied by Dr. H. McCormick. His characterization[22] by sedimentation velocity yielded the results $\overline{M}_w = 3.22 \times 10^6$ and $\overline{M}_w/\overline{M}_n = 1.29$. PS-III was an anionically polymerized sample supplied by Dr. G. Berry.[23]

Solvents. All four solvents used (benzene, cyclohexane, carbon tetrachloride, and bromocyclohexane) were reagent grade and were distilled. Except for bromocyclohexane, all liquids were redistilled just before use.

Procedures. Solutions were prepared separately and filtered through sintered glass filters into the scattering cell, which was itself freed of dust by repeated rinsing with the condensed vapors of a refluxing liquid (usually the same as the solvent used in the measurements). Filtration was repeated until visual examination with the aid of a mirror of the light scattered using unfiltered mercury radiation showed dust to be absent. Concentrations were measured by dry weight analysis of the solutions after the scattering or viscosity data were obtained except when bromocyclohexane was the solvent. In this case the solvent decomposed to give a gummy residue, so the concentrations were taken to be those of the solutions as originally prepared. Intensity data were obtained in the usual manner except in one respect. Because of the large dissymmetries encountered, it was difficult to relate the readings for the lowest angles (highest readings) with those angles around 90° (lowest readings) if the same photomultiplier voltage was used throughout the angular scan. Therefore the data were obtained for the low angular range, *e.g.*, up to 50° at one voltage, and then the voltage was increased so that the 50° reading would be approximately full scale. The high-angle data were obtained at this higher voltage and related to the low-angle data by means of the two readings at the overlap angle of 50°.

Data were obtained at 5° intervals for each of the wavelengths used. The angular data were corrected for back reflection through the cell of the transmitted beam by using the equation[24]

$$i(\theta) = \frac{1}{1 - 2f}[i'(\theta) - fi'(180 - \theta)] \qquad (14)$$

where $i'(\theta)$ and $i'(180 - \theta)$ are excess scattering intensities, and $f = [(n_1 - n_2)/(n_1 + n_2)]^2$ is the Fresnel relation giving the fraction of the transmitted beam reflected back into the cell. Here n_1 and n_2 are refractive indices of the glass and of air, respectively. Based upon the known value of the refractive index of Pyrex, 1.474 at the sodium D line, and dispersion data estimated from that of other glasses, the values of f were calculated to be 0.0370 (5460 Å), 0.0380 (4358 Å), and 0.0394 (3650 Å).

The absolute calibration of the instrument was based upon benzene, for which the values adopted for $10^6 \times$ Rayleigh's ratio were 17.2 (5460 Å), 48.7 (4358 Å), and 112.0 (3650 Å), all at 30°. The first two values were obtained by averaging the results given by Tomimatsu and Palmer at 25°[25] and by making the temperature correction suggested by Ehl, *et al.*[26] The third value was calculated from the first two by using the dispersion relation given by Cantow.[27] The n^2 refractive index correction was used.

Results and Discussion

The intrinsic viscosities $[\eta]$, the weight average molecular weights $\overline{M}_w$, and the second virial coefficients A_2 are recorded in Table I. The values of $\overline{M}_w$ were obtained in the customary manner by double extrapolation of Kc/R to $c = 0$ and $\theta = 0$. The concentration extrapolations were performed first at each angle, using linear extrapolations for measurements in Θ solvents, and square root extrapolations for measurements in good solvents. The values of $(Kc/R)_{c=0}$ were then extrapolated graphically to zero angle to give $(Kc/R)_{\substack{c=0\\ \theta=0}}$. The values of $\overline{M}_w$ shown in Table I are the averages of those found at each wavelength. For each sample, these values agreed to within ±3%. However, the average $\overline{M}_w$ values for a given fraction which were obtained in different solvents show poorer agreement, particularly for the higher molecular weights. This is due partly to uncertainties involved in the absolute calibration and in dn/dc values and partly to the unavoidable difficulties involved in the extrapolation of the angular envelope for high molecular weight polymers to zero angle. We point out, however, that our main interest in this paper is in the angular dependence of scattering and not in absolute intensities.

We will not discuss the virial coefficient data other than to note that the normal decrease of A_2 with increasing M is exhibited by the system PS–C_6H_6, whereas the A_2 values are essentially independent of M for the system PDMS-CCl_4.

Intramolecular scattering functions P^{-1} were constructed from the infinite dilution data obtained at the different wavelengths and then plotted as a function of the variable $[\sin(\theta/2)/\lambda']^2$. In Figure 3 the data for PDMS-III in benzene (a good solvent) are represented in this way. It is to be particularly noted that the data points obtained at the three wavelengths overlap smoothly, thus imparting confidence to the important region of the high abscissa values. Also it should be noted that the range of abscissa values accessible to

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(20) Dow Corning Corp.

(21) Mellon Institute.

(22) H. McCormick, Dow Chemical Co., private communication.

(23) Mellon Institute.

(24) J. P. Kratohvil, *J. Colloid. Sci.*, **21**, 498 (1966).

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(26) J. Ehl, C. Loucheux, C. Reiss, and H. Benoit, *Makromol. Chem.*, **75**, 35 (1964).

(27) H. Cantow, *ibid.*, **18/19**, 367 (1956).

TABLE I
EXPERIMENTAL RESULTS

System	Temp, °C	[η]	$10^{-6}\overline{M_w}$	10^4A_2	R_{LT}, Å	R, Å
PS-I, C_6H_6	35.0 ± 0.5	3.42[a]	1.30	2.82	556 ± 16	546
PS-I, CCl_4	30.0 ± 0.5	2.89	1.40	2.30	547 ± 13	534
PS-II, CCl_4	30.0 ± 0.5	5.35	4.35	2.05	1205 ± 24	. . .
PS-III, C_6H_6	30.0 ± 0.5	9.00	5.72	1.97	1471 ± 69	1400[b]
PS-I, C_6H_{12}	$34.9_4 \pm 0.05$	1.03	1.30	0.00	344 ± 12	348
PS-II, C_6H_{12}	$34.7_6 \pm 0.05$	1.77	3.19	0.17	725 ± 10	. . .
PS-III, C_6H_{12}	$34.4_9 \pm 0.05$	2.06	4.53	0.08	682 ± 43	672
PDMS-I, CCl_4	30.0 ± 0.5	2.30	0.588	2.97	368 ± 12	375
PDMS-II, CCl_4	30.0 ± 0.5	3.00	0.815	2.97	453 ± 21	454
PDMS-III, CCl_4	30.0 ± 0.5	4.11	1.46	3.01	664 ± 24	647
PDMS-III, C_6H_6	30.0 ± 0.5	2.45	1.63	1.55	551 ± 13	544
PDMS-IV, CCl_4	30.0 ± 0.5	4.95	1.72	2.90	700 ± 33	692
PDMS-IV, $C_6H_{11}Br$	$29.1_2 \pm 0.05$	. . .	2.16	0.03	453 ± 15	443

[a] At 30.0°. [b] From eq 9, $\epsilon = 0.11$.

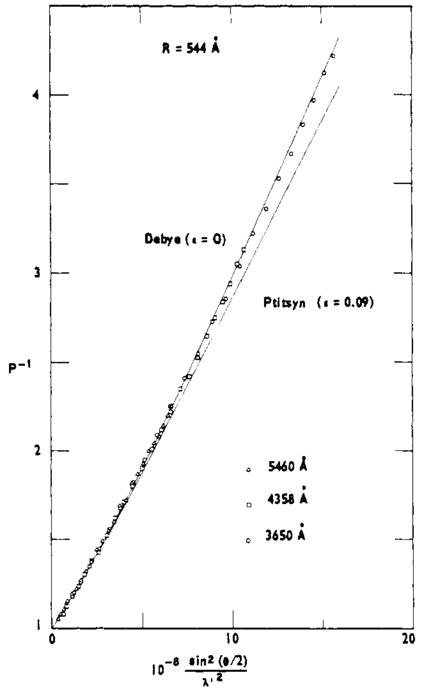

Figure 3. P^{-1} data for PDMS-III in benzene at 30.0°. Demonstrates overlapping of data for three wavelengths.

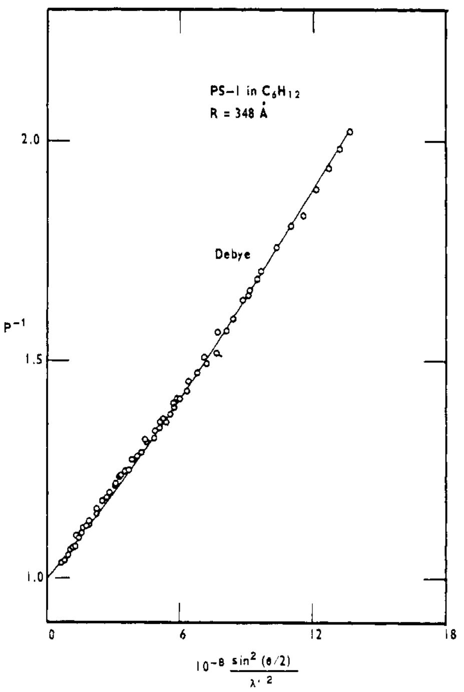

Figure 4. P^{-1} data for PS-I in cyclohexane at 34.9₄°.

measurement by an angular scan has been doubled by extending the wavelength of the incident radiation from 5460 down to 3650 Å.

From the initial tangents of curves such as Figure 3, the root-mean-square radius of gyration can be obtained. These values are designated R_{LT} in Table I. The error limits indicated are typical of the precision of molecular dimensions determined in the manner where the stress is on the low-angle data, which are the most difficult to obtain precisely. It would be preferable to determine a value for the radius of gyration by fitting experimental data over a wide range of values to an expression for P^{-1} which includes R^2 as a parameter. It is for this reason that it is important to know about the ranges of validity of eq 6 and 9.

First we shall discuss the behavior of P^{-1} in Θ solvents, since the Ptitsyn and Debye functions are identical under these conditions. Furthermore, as the numerical calculations show (*cf.* Figure 1), the Isihara and Debye functions are indistinguishable.

For the Θ temperature for the PDMS–$C_6H_{11}Br$ system we adopted the value of $\Theta = 29.0°$, as determined by Schulz and Haug.[28] For PS–C_6H_{12}, Θ was taken to be 34.8°,[18] although an attempt to determine the Θ temperature from the temperature coefficient of A_2 from our fraction PS-I gave a value $\Theta = 33.9°$. This uncertainty in Θ is unimportant for our purposes inasmuch as the P^{-1} curves for PS-I in C_6H_{12} at four temperatures in the range 33–36° exhibited essentially the same shape. Therefore, although any one of these four PS-I in C_6H_{12} measurements would have served equally well for the purpose of testing the Debye function, that for 34.94° was chosen. Figure 4 shows the data along with the Debye curve for R = 348 Å, which agrees well with the value $R_{LT} = 344 \pm 12$ Å. The good fit, obtained to

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(28) G. V. Schulz and A. Haug, *Z. Phys. Chem.* (Frankfurt an Main), **34**, 328 (1962).

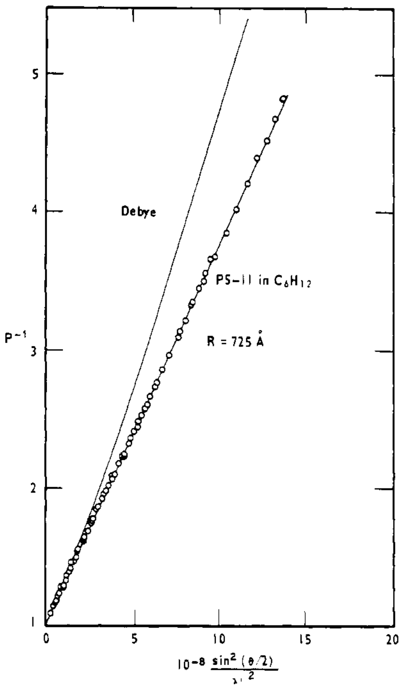

Figure 5. P^{-1} data for PS-II in cyclohexane at $34.7_6°$ with straight line drawn through the data.

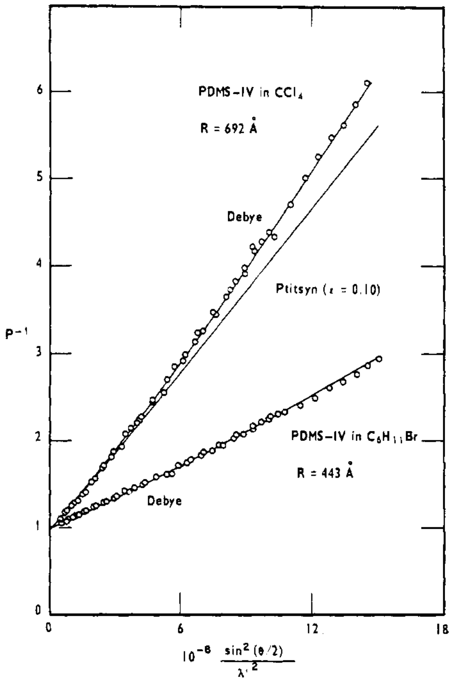

Figure 6. P^{-1} data for PDMS-IV in carbon tetrachloride at 30.0° and in bromocyclohexane at $29.1_2°$.

TABLE II
VALUES OF a AND ϵ FOR GOOD SOLVENT SYSTEMS

System	a	ϵ
PDMS–CCl_4	0.65	0.10[a]
PDMS–C_6H_6	...	0.09[b]
PS–C_6H_6	0.74	0.16[a]
PS–CCl_4	...	0.15[b]

[a] Calculated from eq 13. [b] Estimated from ratios of $[\eta]$ in different solvents.

within 1%, is of course the result expected for the Θ solvent. In this figure and in those to follow, the data points obtained at the different wavelengths will not be distinguished by different symbols.

Similar data are shown for PS-III in C_6H_{12} at 34.49° (Figure 10) and for PDMS-IV in $C_6H_{11}Br$ at 29.12° (Figure 6). In both these cases the fit by the Debye function is good, and the values of R used agree within experimental error with the values R_{LT} obtained from the limiting tangents.

As pointed out in the Experimental Section, the molecular weight distribution of fraction PS-II was broader than the others. Therefore the results shown in Figure 5 for this sample are not surprising. The data cannot be fit by the Debye function, eq 6, which applies to a monodisperse polymer. The upward curvature inherent in the Debye function precludes its use as a good approximation to the data, which in this case are best fit by a straight line. Thus R was calculated from the slope of the straight line drawn through the data, and that value, 725 Å, was employed in the calculation of the Debye curve.

Since this experiment on PS-II was conducted at the Θ temperature, excluded volume effects were absent and the results can be interpreted in terms of the polydispersity of the sample. Benoit[29] has shown that for a polydisperse collection of Gaussian coils, the ratio $\overline{M}_z/\overline{M}_w$ is given by 1.5 times the ratio of the initial slope of P^{-1} to the slope of its asymptote. Therefore, if it can be assumed that the straight line in Figure 5 represents both the initial and asymptotic behavior, $\overline{M}_z/\overline{M}_w = 3/2$ for this fraction. Furthermore, the ratio $\overline{M}_w/\overline{M}_n = 2$, also by Benoit's analysis. Thus the light-scattering results indicate a distribution such that $\overline{M}_z:\overline{M}_w:\overline{M}_n = 3:2:1$. Since McCormick's sedimentation velocity analysis gave a result $M_w/M_n = 1.29$ for this sample, attempts were made using this value and several different molecular weight distribution functions f(N) to calculate numerically values of the polydisperse scattering function

$$P(\theta) = \int_0^\infty N f(N) P_N(\theta)\, dN \Big/ \int_0^\infty N f(N) dN \qquad (15)$$

Using for f(N) the Schulz–Zimm, the log normal, and the experimental function obtained from the sedimentation velocity analysis, respectively, the calculated values of P^{-1} each showed upward curvature. From this we conclude that the ratio $\overline{M}_w/\overline{M}_n = 1.29$ is indeed too small for function PS-II, and we adopt the values $\overline{M}_z:\overline{M}_w:\overline{M}_n = 3:2:1$ as the better description of the sample.

The measurements of P^{-1} for PS and PDMS in Θ solvents served a dual purpose: (1) they established the validity of the Debye equation (eq 6) for Θ systems; (2) they allowed any departures from the Debye equation for measurements in good solvents to be attributed to excluded volume rather than to polydispersity effects, the exception to this being fraction PS-II.

Turning to a discussion of the data obtained in good solvents, we recall (*cf.* Figure 2) that the Ptitsyn equation (eq 9) requires an assignment for the parameter ϵ.

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(29) H. Benoit, *J. Polym. Sci.*, 11, 507 (1953).

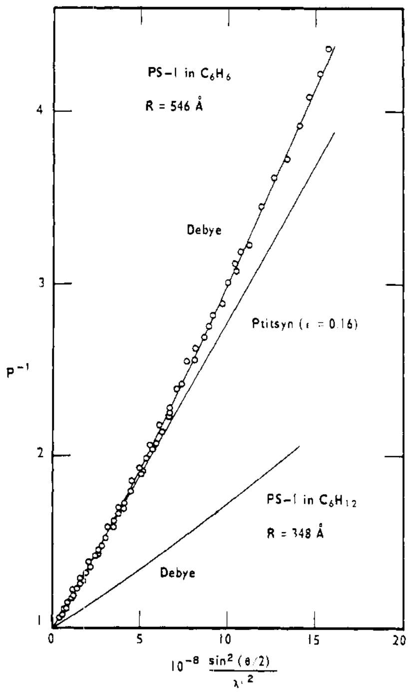

Figure 7. P^{-1} data for PS-I in benzene at 35.0°. Also Debye curve for PS-I in cyclohexane at 34.94°.

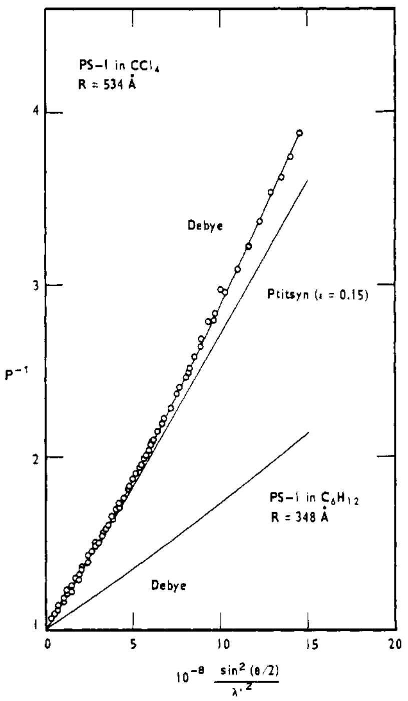

Figure 8. P^{-1} data for PS-I in carbon tetrachloride at 30.0° Also Debye curve for PS-I in cyclohexane at 34.44°.

Equation 13 was used for this purpose. To obtain Mark–Houwink exponents *a*, our intrinsic viscosity data were utilized. The values in Table II resulted.

The data of Figure 3 for PDMS in benzene are characteristic of all of the data obtained with PDMS in good solvents. The data exhibit more upward curvature than is permitted by the Ptitsyn equation with $\epsilon = 0.09$. In fact, the Debye equation with $R = 544$ Å is seen to provide an excellent fit to the data. If it is attempted to force a better fit with eq 9 at high angles with the same value of ϵ, then there is poor agreement at low angles, and the value of R exceeds the error limits of the R_{LT} value. If R is kept within these limits the only way in which eq 9 can be made to fit the data is to use a much smaller value of ϵ, but then for practical purposes one is dealing with the Debye equation (eq 6), for which $\epsilon = 0$.

In Figure 6 the data for fraction PDMS-IV in CCl_4 are shown along with the data for the same fraction in the Θ solvent, bromocyclohexane. This fraction has the highest molecular weight of the PDMS samples studied, $\bar{M}_w = 1.7 \times 10^6$, and is therefore the one for which deviations from the Debye equation for good solvent systems are most likely. However, not only in the Θ solvent but also in the good solvent are the data fit very well by eq 6. As in Figure 3, the upward curvature in the good solvent precludes a fit using eq 9 and the *a priori* value of ϵ from eq 13. The data for PDMS-I and PDMS-II in CCl_4 (not shown) also are fit very well by eq 6.

For each of the PDMS systems the value of R recorded in Table I was determined by fitting the data over the entire angular range with the Debye function; in all cases, it is seen that these values agree well with those determined by the limiting tangent method, R_{LT}. However, the precision of the values of R is *ca.* five times better than those of R_{LT}.

Since the first polystyrene fraction to be discussed, PS-I, was essentially the same sample as that used by Debye, Chu, and Kaufmann,[17] it had particular significance. As pointed out in the Theoretical Section, their results in benzene, using a single wavelength, were adequately fit by eq 6, but they did not discuss eq 9. Our results are shown in Figure 7, along with the Debye curve which fits the data obtained in cyclohexane at the same temperature (the points are omitted to avoid congestion). Even though benzene is a very good solvent and the molecular weight of the fraction is moderately high, the Ptitsyn function with $\epsilon = 0.16$ overestimates the downward curvature at high angles, and the Debye equation fits very well. Realization that the conclusions of Debye, *et al.*, were reached by utilizing data extending up to an abscissa value of only *ca.* 11×10^8 Å^{-2} reemphasizes the importance of going to shorter wavelengths and overlapping the data.

Figure 8 displays the results for the same sample, this time in CCl_4 at 30.0°. The higher refractive increment of this system (0.148 ml/g at 5460 Å) compared to PS in benzene (0.109 ml/g at 5460 Å) is evidenced by the decrease in the scatter of the data points. Again the Debye curve fits the data. Because of the small extent of scatter of these data points it is worthwhile to ascertain how well the Ptitsyn function fits the data if the fit is forced at high angles. It turns out that a good fit can be obtained using eq 9 if $R = 544$ Å and $\epsilon = 0.05$. Thus, the more elaborate theory can be used to fit the data, but not with the *a priori* value of ϵ calculated from eq 13. The value of ϵ required is so nearly zero that, as mentioned above in the case of PDMS in C_6H_6, the difference between eq 9 and 6 is inconsequential.

Turning to the results on polystyrene PS-II, it was pointed out above in the discussion on Θ solvent systems that this sample appears to have a molecular

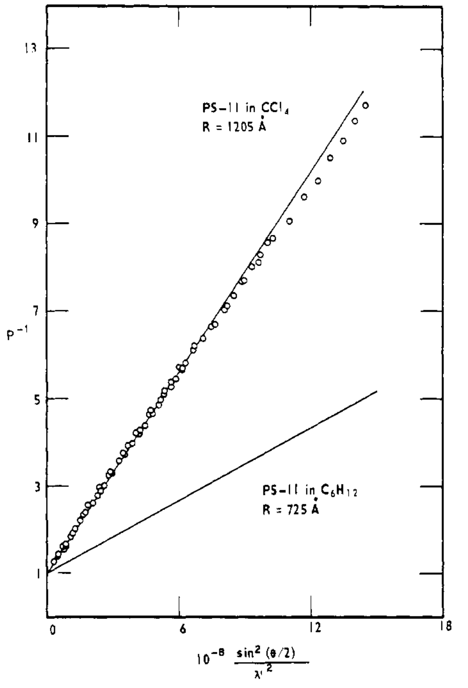

Figure 9. P^{-1} data for PS-II in carbon tetrachloride at 30.0°, with straight line giving initial slope. Also straight line for PS-II in cyclohexane at 34.7$_6$°.

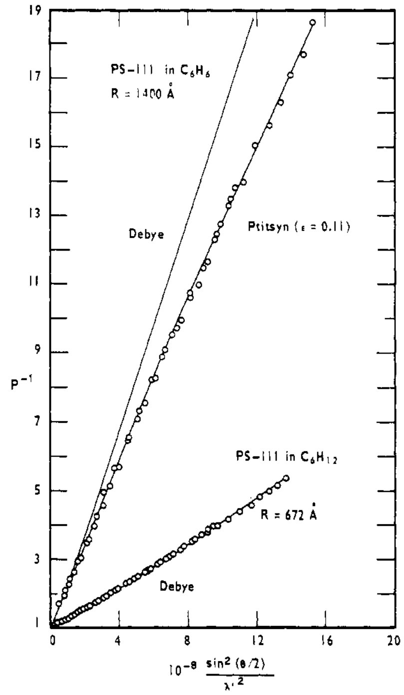

Figure 10. P^{-1} data for PS-III in benzene at 30.0° and in cyclohexane at 34.4$_9$°.

weight distribution characterized by $\overline{M}_z:\overline{M}_w:\overline{M}_n$ = 3:2:1. Consequently, if excluded volume effects do not appreciably affect the results in a good solvent, a straight line is to be expected for P^{-1}, which, however, exhibits a larger slope than at the Θ condition. Figure 9 shows the data for PS-II in CCl_4 at 30.0°. For comparison, the straight line from Figure 5 is included. Although the effect is small, the data in CCl_4 do exhibit some downward curvature which is to be attributed to the excluded volume effect.

A more clear-cut example of the excluded volume effect is found in the case of PS-III, the sample having the highest molecular weight, $\overline{M}_w = 5.7 \times 10^6$ in benzene at 30.0°. Figure 10 shows that the data exhibit pronounced downward curvature in benzene and cannot be fit by the Debye equation. This is not due to polydispersity, since the data in cyclohexane show upward curvature and are fit well by the Debye equation. The Ptitsyn function, eq 9, with $R = 1400$ Å and $\epsilon = 0.11$, fits the benzene data well. It must be pointed out, however, that this value of ϵ, obtained by trial and error, is considerably less than the value of 0.16 predicted by eq 13.

It is thus seen from Figures 9 and 10 that the excluded volume effect does produce downward curvature relative to the Debye equation provided that the molecular weight is sufficiently large. On the other hand, for the systems investigated, although large values of ϵ were predicted by eq 13, a value of $\epsilon = 0$ or some other small number quite satisfactorily accounts for the results; and even in the system where excluded volume effects were clearly manifested, the value of ϵ required to fit the data is considerably smaller than the value required by eq 13.

Thus, although eq 9 becomes preferable to the simpler eq 6 for very high molecular weight polymers in good solvents, the parameter ϵ must be regarded as adjustable, and will invariably be smaller than the value predicted by eq 13.

The reason that eq 13 seriously overestimates ϵ is related to an inadequacy of eq 8, which states that the excluded volume effects for a pair of segments i and j can be treated in a manner equivalent to the effects involving the end segments of a chain, since eq 8 is a generalization of the empirical evidence for the dependence of $\bar{r}^2$ upon M in good solvents. In fact, the effective value of ϵ for small values of $|i - j|$ is smaller than for large values. Equation 13, however, correlates ϵ with the Mark-Houwink exponent a, which is related *via* eq 10 to the largest of the intramolecular contour separations, namely, $|i - j| = N$. Thus the ϵ of eq 9 is some average, intermediate between the extremes of zero and the value predicted by eq 13.

Examination of eq 1 shows that in the high angle region (large μ), where deviations between the Debye and Ptitsyn functions can become pronounced, it is the smaller values of r_{ij} that contribute most effectively to the scattered intensity. Therefore, the effective value of ϵ in this region should be lower than that which obtains at low angles (low μ). In this range, however, the magnitude of ϵ is unimportant, *cf.* Figure 2.

As a last point of possible interest we note that the benzene data in Figure 10 appear to exhibit an inflection point. This feature is required by eq 9,[8] or any other equation which has positive curvature at low angles and eventually exhibits downward curvature.

Conclusion

Debye's formula for the intramolecular scattering function, eq 6, is valid not only for Θ systems, but also for good solvent systems if the molecular weight is not too high, *e.g.*, less than several million. Under these conditions the value of ϵ in eq 9 required to fit the data is essentially zero. When the molecular weight exceeds several million it is no longer valid to use the Debye approximation in good solvent systems. However, if the Ptitsyn equation is then used, ϵ must be adjusted to give the best fit rather than using the *a priori* value calculated from the Mark–Houwink exponent.

As a practical consequence of the wide range of validity of the Debye equation we suggest that chain dimensions of sharp fractions of polymers in the intermediate range of molecular weights be measured by fitting the entire angular envelope to this equation instead of attempting to draw the initial tangent to the low angle data. A gain in precision is thereby effected of approximately fivefold. We also direct attention to the desirability of measuring the scattering intensity as a function of both angle and wavelength and expressing the results as a function of the variable $[\sin(\theta/2)/\lambda']^2$ in order to increase the range of experimental values of P^{-1}.

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Nuclear Magnetic Resonance Studies of Polymer Solutions. IV. Polyethylene Glycols

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ABSTRACT: The intramolecular structure of poly(ethylene glycol) (PEG) in solution was studied by a high resolution nmr technique. Most of the experiments were carried out on highly purified oligomeric PEG's, ranging from a trimer to an octamer. The nmr spectra were measured as a function of the chain length. In concentrated solutions, the PEG's are all in states of association, which differ from the individual molecular species. Valuable nmr information concerning the dependence of the intramolecular structure of PEG on its molecular weight may only be obtained from dilute solutions. The protons of the internal ethylenes (E_i) of all PEG'S of various chain length resonate at an identical frequency in their dilute chloroform and aqueous solutions. With the exception of the two outer symmetrical E_i groups, the remaining E_i protons of PEG resonate also at an identical frequency in pyridine. No definite structural information about the chain molecule has been derived from these results alone. In benzene or α-chloronaphthalene, a drastic change in the nmr spectrum of PEG was observed for the hexamer, at which there exist two well-resolved peaks of equal size for the E_i protons, and below which only a single peak was seen. A further change in the nmr spectrum of PEG in benzene or α-chloronaphthalene was observed for the heptamer, at which a new nmr peak appears. This new nmr peak may be referred to as a polymeric peak, which increases with the chain length and, eventually, becomes a predominant peak for high molecular weight PEG. A similar conclusion may also be applied to the nmr results obtained for PEG in carbon tetrachloride. The interaction of the solvent with the E_i groups of the PEG's is generally stronger for the lower PEG's than for the higher members. However, if some specific solvation and complexation are involved, the results may be reversed.

The structure of polyethylene glycol (PEG) has been extensively studied by a number of authors, by various experimental methods, such as X-ray, ir, and dipole moment measurements.[1–7] By measuring the dipole moments of PEG's, ranging from a monomer to a heptamer, in solutions, Kubo, *et al.*,[7] found that the dipole moment of PEG increased progressively with the degree of polymerization. A free rotational model with *trans* and *gauche* minima of equal importance was suggested for these low members of PEG.[7] On the other hand, according to the ir spectra of PEG (mol wt 6000) in the molten and crystalline states, Davison[3] concluded that the conformations of the O(–CH_2-CH_2–)O portion in PEG are all in the *gauche* form. This conclusion is consistent with the highly crumpled helical structure suggested by X-ray diffraction measurements.[1,2] The higher stability of the *gauche* conformation of PEG was also supported by Mark and Flory from their calculations based on the attractive and repulsive interactions between neighboring segments.[8] Further ir studies of PEG's of various degrees of polymerization revealed that the helical structure of the high members of the PEG series changed into less regular structures of the lower members.[4] Recently, Tadokoro[9] reviewed the structural studies of PEG and stated that the 7/2 helix conformation for high PEG polymer is the most reasonable one at present.

The high resolution nmr technique was used to study the chain conformation of PEG by Connor and McLauchlan.[10] They measured the temperature dependence of the couplings in the C^{13}–H proton satellite side

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