DIFFUSION COEFFICIENTS OF POLYSTYRENE AND ACRYLONITRILE COPOLYMERS IN DILUTE SOLUTIONS BY LIGHTBEATING SPECTROSCOPY

Dissertation for the Degree of Ph. D.
MICHIGAN STATE UNIVERSITY
STEVEN WILLIAM GYESZLY
1974

This is to certify that the

thesis entitled

DIFFUSION COEFFICIENTS OF POLYSTYRENE
AND ACRYLONITRILE COPOLYMERS IN
DILUTE SOLUTIONS BY LIGHTBEATING SPECTROSCOPY

presented by

STEVEN WILLIAM GYESZLY

has been accepted towards fulfillment
of the requirements for

Ph. D. degree in Materials Science

Robert Summitt
Major professor

Date February 22, 1974

O-7639

ABSTRACT

DIFFUSION COEFFICIENTS OF POLYSTYRENE AND ACRYLONITRILE COPOLYMERS IN DILUTE SOLUTIONS BY LIGHTBEATING SPECTROSCOPY

By

Steven William Gyeszly

Self-diffusion coefficients (D) were measured of polystyrene (PS) and polystyrene-acrylonitrile copolymer (SAN) in a range of molecular weights and in several solvents in order to demonstrate the effectiveness and reliability of the light beating spectroscopic technique as well as to extend the diffusion coefficient data for these systems.

Agreement between D values determined by lightbeating spectroscopy and calculated from Stokes-Einstein equation for PS spheres in water showed useability and reliability of the used instrumentation. The determined values of D for PS in methylethylketone (MEK) and benzene were in agreement with literature values obtained by other methods proving validity of the new technique and calculation originated by this work.

The diffusion of SAN in different solvents was determined for the first time in this work.

Steven William Gyeszly

It was found that the diffusion coefficient for PS and SAN is the highest in MEK compared with benzene and dimethylformamide (DMF). The value of D for PS is lowest in decalin compared to MEK, DMF and benzene.

Concentration dependence of diffusion of PS and SAN are varied in different solvents. Lower values of D were obtained for higher molecular weights.

All of determined values of D generally agree with the theoretical expectation except for PS-decalin system. The very low diffusion for PS in decalin can be explained by a relatively simple hypothesis dealing with agglomeration of PS molecules.

DIFFUSION COEFFICIENTS OF POLYSTYRENE AND ACRYLONITRILE COPOLYMERS IN DILUTE SOLUTIONS BY LIGHTBEATING SPECTROSCOPY

By

Steven William Gyeszly

A DISSERTATION

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

Department of Metallurgy, Mechanics,
and Materials Science

1974

To my parents and
to my wife.

ACKNOWLEDGMENTS

The author wishes to express his sincere gratitude to his major thesis advisor Dr. Robert F. Blanks for his generous assistance and guidance which ultimately led to the completion of the work reported in this dissertation.

The author is also grateful to the chairman of his doctoral committee Dr. Robert Summitt and members thereof Dr. James W. Goff and Dr. Gary L. Cloud, who with their helpful and understanding attitude greatly encouraged him in the course of his research.

Grateful acknowledgement is also extended to the Chemistry Department, and especially for the cooperation of Dr. Jack B. Kinsinger who provided needed laboratory and equipment without which this thesis could not have been completed.

Thanks are also due Dr. Jerry A. Cowen for the use of his instrument, and to Edward F. Grabowski and Edwin L. Doak for their assistance, and deep appreciation to Dr. Wayne H. Clifford for his valuable advice.

Finally, and above all, I wish to express my deep felt thanks and gratitude to my wife, Zsuzsanna, for her understanding, help, and encouragement, throughout the course of this study. Without her help this work would not have been started nor finished.

TABLE OF CONTENTS

TABLE OF CONTENTS--Continued

LIST OF TABLES

LIST OF FIGURES

LIST OF FIGURES--Continued

FIGURE

LIST OF FIGURES--Continued

FIGURE Page

I. INTRODUCTION

Lightscattering, first discussed theoretically by Rayleigh (1871), has become an important tool in polymer science in the last few decades. From measurements of lightscattering on dilute polymer solutions, the molecular weights of the polymers can be calculated and important information about the size and shape of polymer molecules can be obtained.

The use of the laser as a light source made it possible to determine the motion of polymer molecules in solution by lightbeating spectroscopy. This measurement method is relatively new. Pecora (1964) gave the theoretical relationship between the spectral distribution of light scattered from a polymer solution and the diffusion coefficient of the polymer molecules in the same solution.

In the last seven years a number of experimental studies have been published which verify this theory. The simplest way to do it is by measuring the lightbeating spectrum of light scattered from polystyrene spheres in water, and calculating the diffusion coefficient from this measurement based on the theory. The calculated diffusion coefficient from the lightbeating spectroscopy measurement

can be compared with the calculated diffusion coefficient from the Stokes-Einstein's diffusion equation, if the diameter of the polystyrene spheres is known. This was done by several researchers (Cummin, 1964; Arecchi, 1967; Dubin, 1967; Dunning, 1970; Reed, 1970; Kramer, 1971; Ohbayoshi, 1972; Lee, 1972; and others). Good agreement was found, hence, this method may be used as a calibration procedure for lightbeating spectroscopy measurements.

Most diffusion measurements by lightbeating spectroscopy have involved biological macromolecules (Dubin, 1967; Cummins, 1969; Carew, 1969; Dubin, 1969; Wada, 1969; and others). Only a few experiments have been done in studying the diffusion of synthetic polymers in solution.

Lightbeating spectrum measurements of light scattered from polystyrene molecules in dilute solutions of cyclohexane were made by White (1966) and Chu (1969). Determination of the diffusion coefficient of polystyrene in cyclohexane by lightbeating was reported by French (1969), Reed (1970), and for the polystyrene-methylethylketone system by Ford (1970) and by Kramer (1971).

Stutesman and Blanks (1973) have reported the diffusion constant of polyacrylamide in aqueous solution measured by this method.

All of the diffusion coefficients reported in these works were in good agreement with diffusion coefficients

measured by other methods. Therefore it is assumed in this work that the theoretical relationship between the lightbeating spectrum of the light scattered from polymer molecules in dilute solution and their diffusion in the same solution is valid. Hence this work uses this relationship to obtain information about the diffusion of different synthetic macromolecules in various solvents.

Because lightbeating spectroscopy is a relatively new measurement method for the determination of the diffusion coefficient of macromolecules in dilute solution, one of the main purposes of this study was to establish a standard procedure, including calculations, which can be used as the basis for further investigations.

As was mentioned earlier, only a few diffusion measurements have been made by lightbeating spectroscopy for synthetic polymers. They were mostly for polystyrene in two solvents, methylethylketone and cyclohexane. Therefore another main purpose of this study is to obtain data for other polystyrene in solvent systems (benzene is a good, decalin is a poor, and dimethylformamide is a polar solvent). The fourth system, polystyrene-methylethylketone, was used for comparison with previous data. Five different molecular weights of polystyrene were used to investigate the relationship between the diffusion constant and the molecular weight.

Because of a general lack of data of diffusion coefficients of copolymers in dilute solution in the literature and the fact that no diffusion measurements of copolymers had been made by lightbeating spectroscopy, this work extends the technique to copolymers in dilute solution. Considering that this gives the opportunity to compare the diffusion of polystyrene and its copolymers polystyrene-acrylonitrile copolymer was chosen in three solvents, methylethylketone, benzene, and dimethylformamide. Six different molecular weight polystyrene-acrylonitrile copolymers with different acrylonitrile contents were used to examine the relationship between the diffusion coefficient and the molecular weight or acrylonitrile content of the copolymer.

II. THEORY

A. RELATIONSHIP BETWEEN THE SPECTRAL DISTRIBUTION OF THE INTENSITY OF SCATTERED LIGHT FROM A DILUTE POLYMER SOLUTION AND THE DIFFUSION COEFFICIENT

Lightscattering by a dilute solution of particles can be discussed briefly based on Cummins's (1970) view. If a large volume of solvent containing N identical scattering particles is illuminated by a beam of monochromatic radiation and the scattered light is observed at an angle Θ from the incident beam and at a given point, then the observed field E_j for j^{th} scatterer is equal to $A_j(t)e^{i\phi_j}e^{-\omega_o t}$, where A_j is the scatterer orientation dependent amplitude, ω_o is the frequency of the incident light and t is the time.

If the phase ϕ is zero for the scatterer at the origin and the position of the j^{th} scatterer is $\bar{r}_j$, then $\phi_j \approx (\bar{K}_o - \bar{K}_s)r_j = \bar{Q}\cdot\bar{r}_j$, where $\bar{K}_o$ and $\bar{K}_s$ are the wave vectors of the incident and scattered light, respectively. Considering the fact that the scatterer moves very slowly compared with velocity of the light $|K_o| \approx |K_s|$, we have

$$|\bar{Q}| \approx 2|\bar{K}_o| \sin\frac{\Theta}{2} = (4\pi n_o/\lambda)\sin\frac{\Theta}{2}, \qquad 1.$$

where Q is the scattering vector, n_o is the refractive index of solvent and λ is the wavelength of the light.

The total scattered field E_s at the given point of observation is

$$E_s = \sum_{j=1}^{N} E_j = \sum_{j=1}^{N} A_j(t)[\exp\{iQ\cdot r_j(t)\}][\exp\{-i\omega_o t\}] \quad 2.$$

The average total intensity I_s of the scattered light is equal to the time average of the square of the absolute value of field. Squaring Equation 2 and considering the fact that the scatterers are not correlated so all cross terms average to zero, we obtain $I_s = N<|A|^2>$. (Angular brackets denote a time average.)

Using the autocorrelation function of the optical field with the following assumptions--the scatterers are statistically independent and identical, position and orientation are statistically independent and identical, position and orientation are statistically independent therefore factor amplitudes and phases also are independent--the optical spectrum of the scattered light is given by

$$I(\omega) = (N/2\pi) \int_{-\infty}^{+\infty} [\exp\{i(\omega-\omega_o)\tau\}][C_A(\tau)][C_\phi(\tau)]d\tau, \quad 3.$$

where the amplitude correlation function for spherical scatterers is $[C_A(\tau)] = A^2$ and the phase autocorrelation function $[C_\phi(\tau)]$ is given as $<[\exp\{-i\bar{Q}\cdot\bar{r}(t)\}][\exp\{i\bar{Q}\cdot\bar{r}(t+t)\}]>$.

The phase autocorrelation function was analyzed by Pecora (1964) for lightscattering of dilute solutions of macromolecules.

As a result of thermal motion, the local density of a polymer solution is not equal to its average macroscopic density at a given point in time and at a given position in the fluid. This density fluctuation results in a spectral distribution of the intensity of the light scattered from a polymer solution. The density fluctuation is related to the change of the dielectric constant of the medium. The study of change of the dielectric constant of the medium leads to results analogous to Van Hove's (1954) space time correlation function. This space time correlation function can be divided into two parts: a self and a distinct correlation.

The self-correlation function for the center of mass of a polymer molecule can be calculated from Langevin's equation of Brownian motion,

$$\frac{d\bar{u}}{dt} + \beta\bar{u} = A_f(t), \qquad 4.$$

where $\bar{u}$ is velocity of the center of the polymer molecule, β is the friction coefficient per unit mass and $A_f(t)$ is the fluctuating acceleration of molecule.

The relationship between the diffusion coefficient of a molecule and its friction coefficient is given by

Einstein's diffusion equation,

$$D = \frac{k\,T}{\beta m}\,, \qquad 5.$$

where D is the diffusion coefficient of the molecule, k is the Boltzman constant, T is the absolute temperature, m is the mass of molecule and β is the friction coefficient per unit mass. The basic assumptions of light scattering from dilute polymer solution are the following: Scattering from a single molecule does not depend on the presence of other molecules; the internal rearrangements of polymer molecules do not influence the movement of the mass; and no interaction exists among the polymer molecules in the solution. Considering the above assumptions Pecora (1964) gives the following relationship between the spectral distribution of intensity of scattered light and the translational diffusion coefficient of the polymer molecules in their solution:

$$I(\omega) \sim 2Q^2D/(\omega^2+Q^4D^2), \qquad 6.$$

Where I is the intensity of the scattered light, Q is the scattering vector; ω is the light frequency, and D is the translational diffusion coefficient.

Analysis of Equation 6 shows that a plot of intensity against frequency is Lorentzian and that its half-width at half of maximum intensity $\Delta\omega_{\frac{1}{2}}$ is equal to Q^2D. A similar result is given by Cummins et al. (1964).

The half-width at half of maximum intensity is given in units of radian/sec. Changing this to Hertz and using Equation 1 and the relationship between $\Delta\omega_{\frac{1}{2}}$ and D we can obtain

$$\Delta V = 16\pi(n/\lambda_0)^2 D \sin^2(\frac{\Theta}{2}) \qquad 7.$$

Where ΔV is the full width at half maximum height of the Lorentzian curve in Hertz. From Equation 7 it can be seen that plotting ΔV against $\sin^2(\frac{\Theta}{2})$ results in a straight line which goes through the origin. For a given light source and solution, $(n/\lambda_0)^2$ is constant, therefore the direction tangent, $16\pi(n/\lambda_0)^2 D$ is directly proportional to the translational diffusion coefficient of polymer molecules in their solution. This equation has been verified adequately by the experiments of a number of investigators as mentioned earlier.

Pecora (1964 and 1968a) gave the spectral distribution of light scattered from a dilute solution of monodisperse optically isotropic rigid rods. It was found that rotational diffusion becomes an important part along with the translational diffusion for scattering from long rods at large scattering angles. Pecora (1969) has also investigated theoretically the spectral distribution of light scattered from once broken rods. His results are not discussed here, since the polymer molecules being dealt with

in this work do not exist in solution as either rigid or once broken rods.

Pecora (1965b and 1968b) has developed a theoretical expression to predict the Rayleigh spectrum of light scattered from flexible macromolecules in dilute solutions considering intramolecular effects, which are related to the size of the macromolecules.

Pecora and Tagami (1969a and 1969b) have discussed the effects of polydispersity of polymers on the Rayleigh spectrum. It was shown that if $X = K^2\langle S^2\rangle$ is small, particularly smaller than 0.5, the Rayleigh spectrum consists of a single Lorentzian only, which is related to translational diffusion. There K is the scattering vector and $\langle S^2\rangle$ is the radius of gyration. In dilute solution it is assumed that the polymer molecules are acting independently. Each molecule can be considered to be a string of beads with a tendency to coil itself to form a spherical cloud of chain segments having radial symmetry (Rodriguez, 1970). The diameter of this spherical cloud is not known, but the root mean square distance of elements of the chain from its center of gravity can be calculated

$$\langle S^2\rangle = \frac{Na^2}{6}, \qquad 8.$$

where $\langle S^2\rangle$ is the root mean square distance of elements of chain from its center of gravity, which is called "radius of gyration", N is the number of links in the chain which

can be calculated from the molecular weight of each segment, and a is the length of links, which for molecules with carbon backbone is equal to the C-C single bond distance. Considering the bond angle and the rotation of the segments of polymer molecules, the right side of Equation 8 should be multiplied by corresponding values, approximately two to four, to obtain a more realistic result. If X is larger than 1.0, then the Rayleigh spectrum consists of terms other than the translational one, which are related to intramolecular effects or polydispersity.

Values of X were calculated for all polymer-solvent and copolymer-solvent systems which have been used in this work. It was found that X is always smaller than 0.1 if the scattering angle is equal to or less than 45°. Therefore the Rayleigh spectrum which is obtained should consist of only one Lorentzian, so intramolecular effects and polydispersity of macromolecules are not discussed here.

B. LIGHTBEATING SPECTROSCOPY

An excellent review of light beating spectroscopy was published by Cummins and Swinney (1970), so this subject will be discussed only briefly here. The first demonstration of lightbeating was done by Forrester et al. (1955).

Photoelectric mixing, called lightbeating, is similar to mixing of alternating current electrical signals in non-linear circuit elements. In the above mentioned experiment, a Mercury vapor lamp was used as the light source.

A major improvement in the light source came with the introduction of the laser, which made the technique a relatively common laboratory procedure. Two approaches were applied to develop standard laboratory techniques; namely, heterodyne and homodyne detection. Cummins et al. (1964) used heterodyne detection for studying diffusion of polystyrene latex spheres in a dilute solution by Rayleigh line broadening. With the laser a light source the unscattered light was mixed with the scattered light on the detector. The unscattered light was used as a local oscillator.

Ford and Benedek (1965) utilized homodyne detection for the examination of light scattering in sulfur hexafluoride, SF_6. Homodyne detection is different than heterodyne detection in that no local oscillator is used, which means the scattered light is detected alone on the photodetector.

Considering the view of Forrester (1961), Cummins and Swinney (1970) give an analysis of homodyne and heterodyne detection. Because this work is based on homodyne detection only their final results for homodyne detection will be

given below. For an optical field which is a narrow band Gaussian random process, the following equations are valid.

The optical spectrum of a field is given by

$$I(\omega) = \langle I \rangle \frac{\gamma/\pi}{\gamma^2 + (\omega-\omega_0)^2}, \qquad 9.$$

a Lorentzian function, where γ is $\Delta\omega_{\frac{1}{2}}$ (optical) half width at half maximum height; ω_0 is the center, $\langle I \rangle$ is the total intensity, I is the intensity, and ω is the frequency. The photocurrent spectrum for the same field is

$$P_i^+(\omega)\omega \geq_0 = \frac{e\langle i \rangle}{\pi} + \langle i \rangle^2 \sigma(\omega) + 2\langle i \rangle^2 \frac{2\gamma/\pi}{\omega^2 + (2\gamma)^2}, \qquad 10.$$

where $\frac{e\langle i \rangle}{\pi}$ is the shot noise term from instrumentation, $\langle i \rangle^2 \sigma(\omega)$ is the d.c. component, $2\langle i \rangle \frac{2\gamma/\pi}{\omega^2 + (2\gamma)^2}$ is the beating part of Lorentizian spectrum, $\langle i \rangle^2$ is the total power centered at $\omega = 0$, and 2γ is the $\Delta\omega_{\frac{1}{2}}$ (photocurrent) halfwidth. It can be seen that the halfwidth of a Lorentzian spectrum is equal to twice the halfwidth of the original optical spectrum, i.e., it is equal to the full width of the optical spectrum. Therefore, if one measures the halfwidth of the Lorentzian spectrum, one may obtain diffusion coefficients from Equation 7. It is important to note that these equations are valid only for fields with Gaussian statistics, otherwise in the photocurrent spectrum, Equation 10, no lightbeating term exists.

The development of the theories of light scattering and lightbeating is based on several assumptions: (1) the scattered radiation field on the surface of a photodetector is spatially coherent; (2) a pure monochromatic field is given by the light source; (3) the time period of the photocurrent spectrum measurement is long enough so that the average value of the total effect of the photocurrent spectrum can be measured at any frequency.

Cummins and Swinney (1970) made a theoretical investigation of how the experimental results will be affected when the above assumptions are not quite true during the actual experiment. Their conclusions briefly are the following:

1. The ratio of the photocurrent signal to the square of some constant total photocurrent is inversely proportional to the area of the detector when the area is much larger than λ^2/Ω, where λ is the wavelength of the light and Ω is the solid angle which the source subtends at the detector. If the area of detector is much smaller than λ^2/Ω, then this ratio approaches a constant value, which is independent of the area of the detector. Since Ω is proportional to the scattering volume, it is important to minimize the scattering volume. In practice this can be done if the light beam is focused into the scattering volume.

2. Phase fluctuations of the exciting source have no effect on the result.

3. There is no difference in the light beating spectrum if we compare a multimode laser source to a monochromatic source of the same intensity.

III. EXPERIMENTAL

A. INSTRUMENTATION

A schematic illustration of the instrumentation which was used is shown in Figure 1. The spectrometer was designed and constructed for Brillouin spectrum analysis in the Chemistry Department at Michigan State University by Gaumer (1972), and used by Toth (1973), Nordhaus (1973), and Kumar (1973). Only one analysis of Rayleigh spectra was made previously with this spectrometer by Stutesman (1973), who analyzed the Rayleigh spectrum with a General Radio 1900-A swept-frequency spectrum analyzer. This analyzer measures only one bandwidth at a time and does not analyze all of the signal simultaneously. This method is very time-consuming and the reading of the data points from the spectra is very difficult and has a high probability of error. Another problem with this approach is that the use of high laser power for obtaining a high signal to noise ratio is not possible because the sample may be heated by the laser beam during the lengthy exposure, about 45 minutes, which is required to obtain a spectra with the General Radio 1900-A analyzer. This heating effect results in an unwanted diffusion process due to thermal gradients

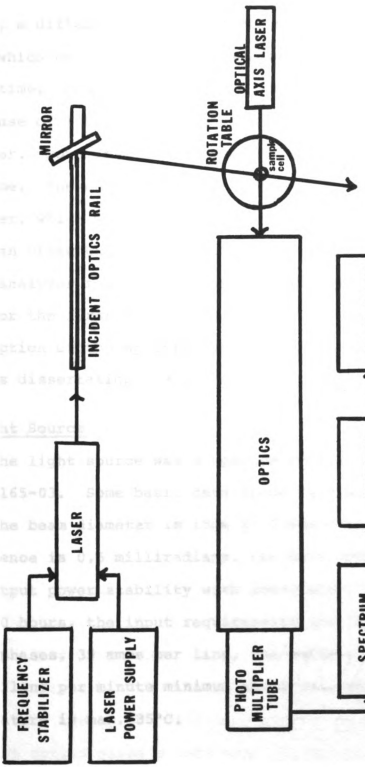


Figure 1. Lightbeating spectrometer.

inside the solution, so low laser power must be used, which gives a low signal to noise ratio. To avoid any heat affect, a different kind of spectrum analyzer should be used, which measures the full spectrum during a relatively short time. At the present time there are two possibilities, use of a corrlation function computer or a "real time" analyzer. Both instruments analyze all of the signal at one time. The choice for this work was a "real time" analyzer, which was borrowed from the Physics Department of Michigan State University. The spectrometer with a "real time" analyzer for analysis of the Rayleigh spectrum was used for the first time at Michigan State University. The description of the spectrometer is given in detail in Gaumers dissertation (1973) so it is not repeated here.

1. Light Source

The light source was a Spectra-Physics Argon ion laser model 165-03. Some basic data about this Argon ion laser are; the beam diameter is 15mm at 5145A wavelength, the beam divergence is 0.5 milliradians, the bore material is BeO, the output power stability with power stabilizer on is $\pm$0.5% over 10 hours, the input requirements are 190 to 225V, three phases, 35 amps per line, the water flow required is 2.2 gallons per minute minimum at 25 psi, and the water temperature is max. 35°C.

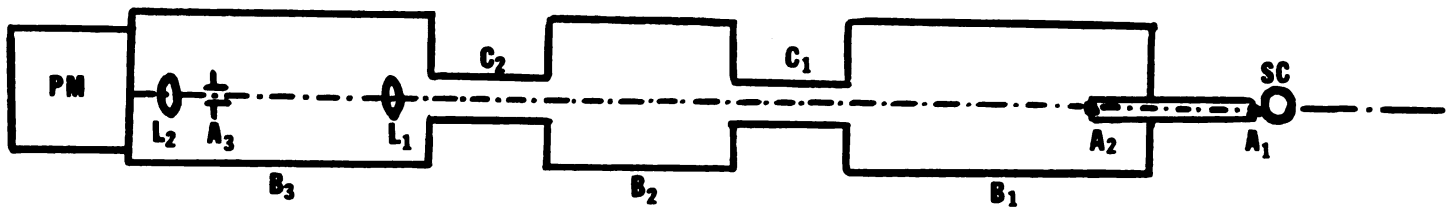
2. Incident Optics

The incident optical system includes a tiltable mirror and a 100mm focal length lens. The mirror can be positioned in order to send the incident light beam into the sample from different angles.

As mentioned earlier for the photocurrent, the signal to shot noise ratio of the photocurrent is inversely proportional to the solid angle which the source subtends at the detector. This angle is directly proportional to the scattering volume, which means a minimum scattering volume results in a maximum signal to shot noise ratio. The scattering volume can be minimized if the laser beam is focused into the sample by a short focal length lens.

3. Collection Optics

Part of the light scattered by the sample has been collected and focused onto the surface of photomultiplier by the collection optics, which are illustrated in Figure 2. The diameters of aperture A_1 and A_2 were about 1mm which determined the cone angle in which the scattered light was collected. The lens L_1 focused the scattered light into the A_3 pinhole, which diameter was approximately 0.01mm. The scattered light which passed through the pinhole was focused by lens L_2 onto the surface of the photomultiplier tube. This system of collection optics combined with the incident optics gives a very high signal to shot noise ratio.



SC	Sample cell	$B_1B_2B_3$	Aluminium boxes
A_1A_2	Variable apertures	C_1C_2	Camera bellows
A_3	Pinhole	PM	Photomultiplier tube
L_1L_2	Lenses		

Figure 2. Optical detection train.

4. Photomultiplier

An EMI 9558B tube was employed as a photomultiplier. Excitation of the photomultiplier was done by a power supply. To reduce the thermionic emissions which result in a high dark current, the photomultiplier tube was placed inside a Products for Research, Inc. Model TE-104 refrigerated chamber.

5. Spectrum Analyzer

The Signal Analysis Industries Corp. Model SAI-51A real spectrum analyzer/digital integrator was used for spectrum analysis. This analyzer is able to measure ten frequency scales from 0-20Hz to 0-1MHz. Flat weighting is 200 lines. With no signal applied the noise level is 60dB below the full scale. The fast display made to an oscilloscope is 40 msec and the slow one to a recorder is 8 sec.

The output of the spectrum analyzer was a logarithmic current power which was connected to a Hewlett-Packard recorder. The spectrum was recorded on 2 cycle semilog graph paper. The output of the analyzer was connected also to an oscilloscope which showed the full spectrum immediately.

B. CALIBRATION

The calibration of any system can be done either by calibration of each element of the system or calibration of the total system at once. If possible the calibration should be done in both ways. In this work the alignment procedure of the spectrometer followed the procedure given by Gaumer (1972) and Nordhaus (1973). The spectrum analyzer was calibrated following the procedure given by its instruction manual. The calibration of the total system was done by use of polystyrene latex as a scattering sample.

Dunning (1970), Reed (1970), Bloomfield (1972), Chu et al. (1972), and Ohbayashi (1972), have measured the diffusion constants of different polystyrene spheres in water by lightbeating spectroscopy. They have found very good general agreement between the calculated diffusion coefficients from the Stokes-Einstein equation and the experimentally determined one from lightbeating spectroscopy. The Stokes-Einstein equation gives a relationship between the diffusion coefficient of spheres in a liquid and their sizes:

$$D = \frac{kT}{6\pi\eta_s r} \qquad 11.$$

Where k is the Boltzman constant, T is the absolute

temperature, η_s is the viscosity of the system, and r is the radius of the spheres. If each element of Equation 11 is known, the diffusion coefficient can be calculated. The calculated diffusion coefficient from the Stokes-Einstein equation for polystyrene latex (diameter of 1090A) is equal to 4.1×10^{-8} $cm^2/sec.$ at 21°C temperature.

The angular dependence of the halfwidth of the light-beating spectrum of scattered light from polystyrene latex is shown in Figure 3. It can be seen that the halfwidths ("best fit") are on a straight line which goes through the origin as the theory predicts. But the direction tangent of this line is about 20% larger than the predicted one from the combination of Equations 7 and 10. This difference can not have arisen from the dust effect (to be discussed in the next section), because the dust effect results in a decrease in the diffusion coefficient instead of an increase. The diffusion coefficient is inversely proportional to the radius of the spheres, a smaller radius gives a higher diffusion coefficient, which means a higher halfwidth in the lightbeating spectrum. This does not seem to be the problem however, because Reed (1970) and others used the same latex and they claimed good agreement between the calculated and measured diffusion coefficient. There is a possibility that the polystyrene latex sample was too old, so the suspension agent did not work satisfactorily which possibly

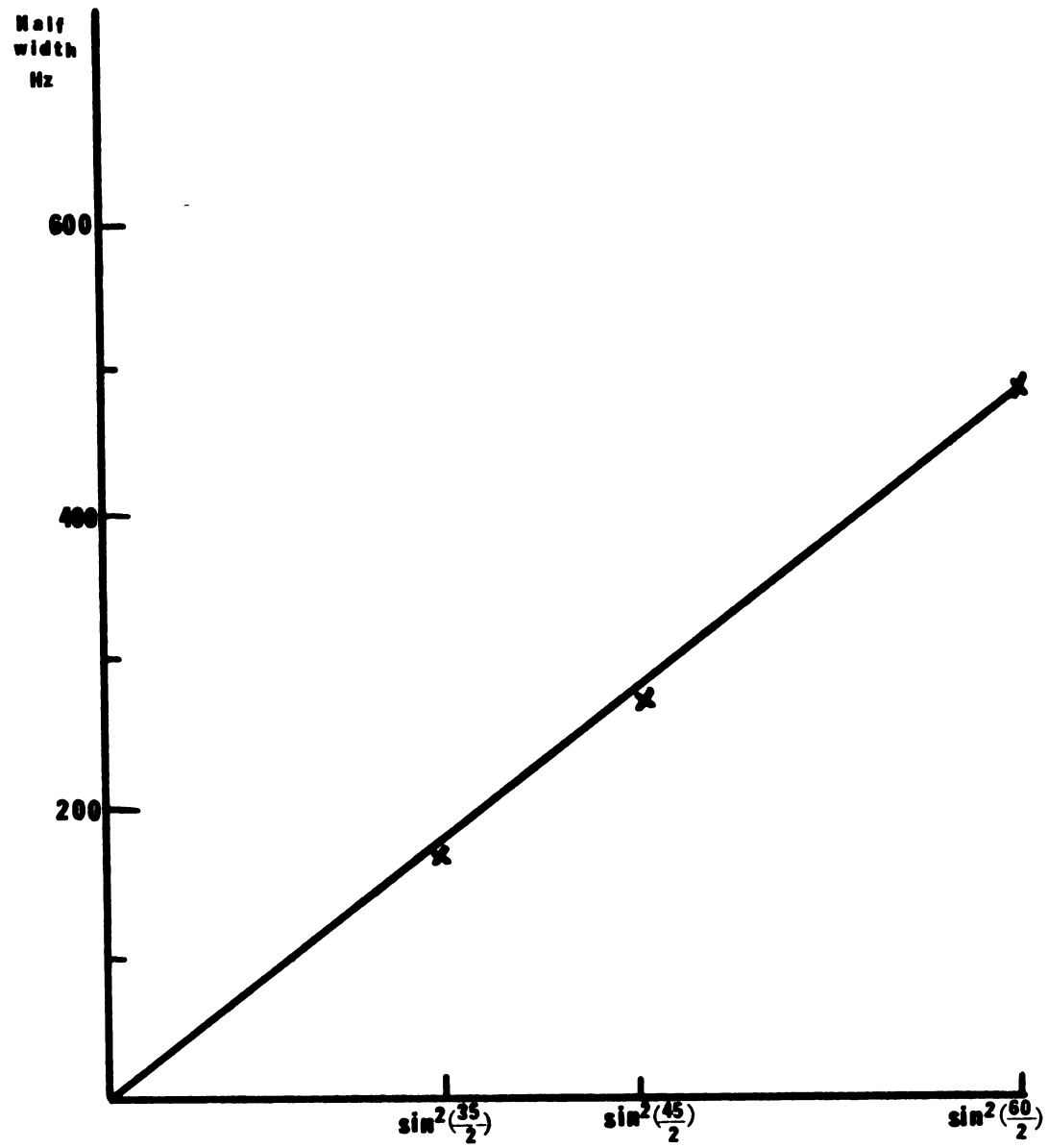


Figure 3. Angular dependence of halfwidth of the light-beating spectrum of polystyrene spheres (d = 1090A).

caused sedimentation of the polystyrene spheres, which means the concentration of spheres in upper regions in the sample decreased and, considering the polydispersity of the latex, smaller spheres stayed in upper region of the sample. Both effects would increase the diffusion coefficient. The concentrated polystyrene latex was purchased from Dow Chemical Company about ten months before its usage. It was kept in a refrigerator. The final solution was made four weeks in advance and it was kept at a constant temperature of 21°C.

Estimating an average of 3% reading error for each reading point (this is reasonable because of sharp changes in the curve), a range of halfwidth of lightbeating spectrum can be given (Table 1 and Figure 4). The calculation method is explained in its own section. Each Lorentzian curve with halfwidth in the ranges given in Table 1 fits the lightbeating spectrum curve, so that the average error for each reading point is less than 3%. It can be seen in Table 1 that the range of the total noise is very narrow, for each scattering angle, so the halfwidth ranges with almost constant error do not come from the difference of the "total noises". (The photocurrent of a lightbeating spectrum to the "total noise" ratio is about 2-35 depending on the frequency.)

Considering the above facts, especially that using the halfwidth method range brings together the values of the

Table 1. Range of halfwidths of lightbeating spectra of light scattered from polystyrene spheres in water.

Scattering angle (°)	Range of halfwidth (Hz)	Range of "total noise"	"Best fit" halfwidth (Hz)
35	140-190	0.65-0.69	165
45	230-310	0.95-1.14	270
60	390-530	0.63-1.11	470

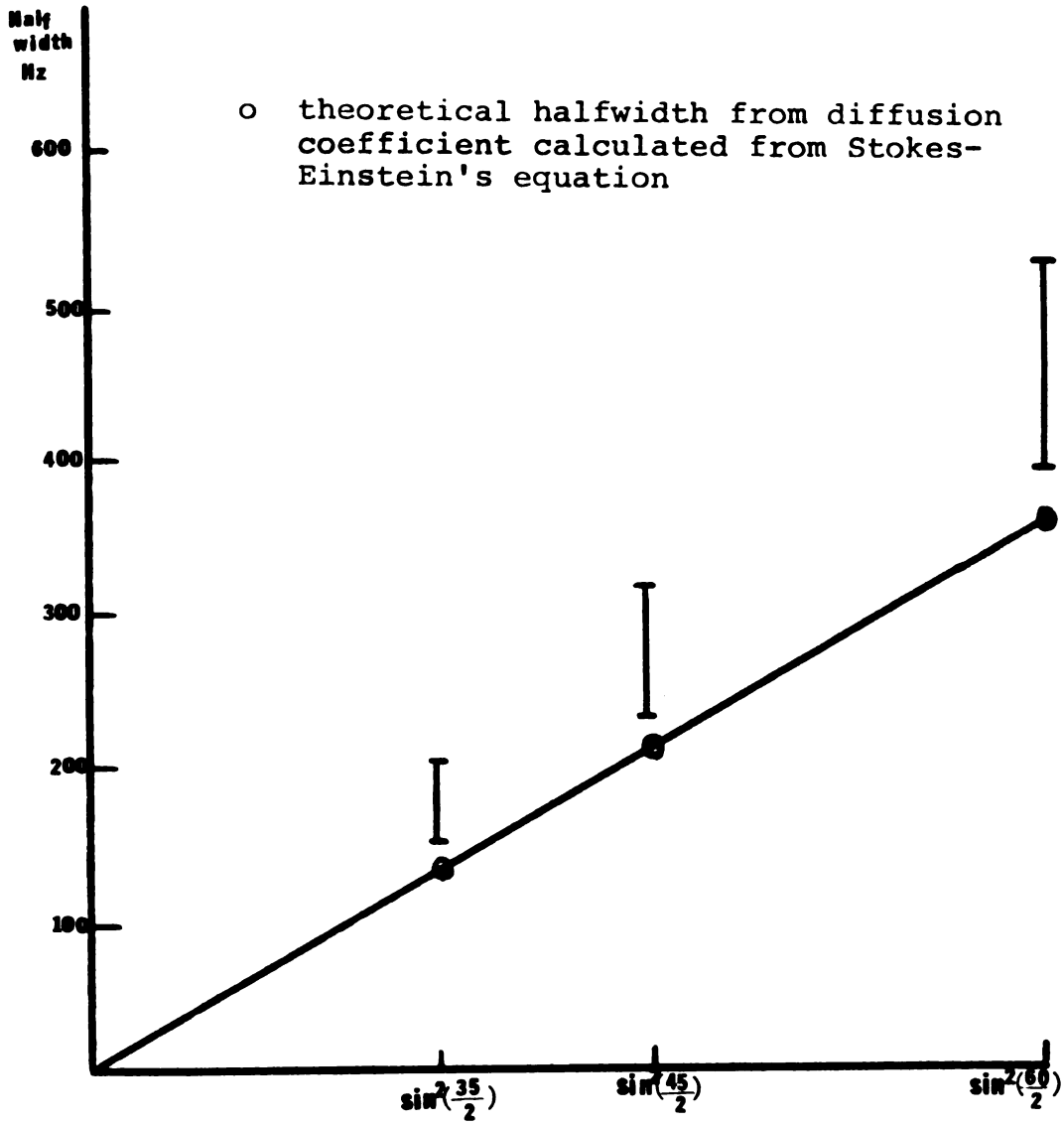


Figure 4. Angular dependence of halfwidth of the light-beating spectrum of polystyrene spheres (d = 1090A).

calculated and the experimental diffusion coefficients, it was assumed that the lightbeating spectrometer described earlier with the spectrum analyzer can be employed for diffusion measurements of polymers in dilute solution.

C. SAMPLE PREPARATION--DUST PARTICLES IN THE DILUTED POLYMER SOLUTION

It is believed that for accurate lightbeating measurements, a "dust free" solution is required. Dust may be introduced into solution in three ways: from the solvent; from the surface of the polymer; and during the solution preparation. The solvent can be distilled under special conditions, it can be microfiltered or it can be centrifuged to make it presumably dust free. The procedure of preparing the solution may be done in principle in a "dust free" environment. These methods are not practical, they are very time-consuming and the results are doubtful. To remove the dust from the surface of a polymer (meaning commercial polymers) is possible only by making a dilute solution and either centrifuging or microfiltering it. This means a cleaning procedure for the solvent alone is not necessary, and the "dust free" environment is not important, because all of the dust particles can be removed from the final solution.

... Reed (1970) used 0.45μ pore size Millipore filters for filteration of polystyrene/cyclohexane solutions. Kramer (1971) reported that he removed dust particles by centrifugation.

The author of this work recognizes the problem of the presence of dust particles in the solution during a light-beating experiment but he argues that the filtration or centrifuging of the solution is not a practical answer to this problem.

The argument is the following: The pore size of the microfilter must be large enough to pass the largest of the polymer molecules, otherwise some polymer molecules would be filtered out. The exact size of polymer molecules in solution can only be estimated because accurate methods--either experimental or calculation--for their determination do not exist. Therefore, it is necessary to use some kind of safety factor to determine the minimum size of the filter pore. Particles with a much larger size than polymer molecules remain in the solution after filtration. It means that the solution is not "dust free". Only the average size of the dust particles is reduced by the filtration. In this way, to assume the solution to be "dust free" and give no consideration to the particles in the solution leads to error.

This work follows another, new approach to overcome the problem of the presence of dust particles in the solution. It was mentioned earlier that the dust can be introduced

into the solution by the solvent, polymer or the environment.

In the environment two factors, air and glassware, should be considered. An air filtered room minimizes the dust in the air. Good cleaning procedures combined with rinses by solvents should provide "dust free" glassware, or more exactly, the dust concentration should be related to the dust concentration in the solvent. The other possibility of introducing dust into the solution is from the polymer. Dust particles cover the surface of the polymer grains. (Commercial polymers, used in this work, were in granular form.) Therefore the surface to volume ratio is small, which means the volume of dust particles, which is directly proportional to the surface of polymer, is also small compared with the volume of polymer. The copolymers were made at the Chemical Engineering Department of Michigan State University, they were kept away from dust during the preparation process, hence only a very low amount of dust was present. The process of solution of polymers and dilution of the solutions reduced the concentration of dust originating from the polymer.

The weighed polymers were put into about 80 cc of solvent and were shaken well in a volumetric flask. The polymer solution was then left to stand overnight and then it was diluted to 100 cc and shaken well. After shaking,

the solution was not moved for a minimum of 24 hours to permit the sedimentation of any larger dust particles which might be present. The required solution volumes were carefully withdrawn using a pipette so that the solution on the bottom (about 25% of total volume) was not disturbed or moved into the other flasks where the final diluted solutions were made. The original solutions were further diluted by solvents 2 to 25 times depending on the required concentration. The final solutions in the sample cells were left undisturbed for a minimum of 24 hours prior to the light scattering measurements so that additional particle sedimentation might take place. The height of the scattered volume from the bottom of a sample cell was the same for each measurement--about 10% below top level of the solution. According to Stoke's sedimentation law for non-uniform size particles, the smaller ones would be found in the top layers of the solution.

Because of the two effects--sedimentation and dilution--it may be assumed that the volume of the particles of dust in the solution which came from the polymers was negligible compared with the volume of dust particles coming from the solvents, and that the dust particles in the scattering volume came from the solvents. Therefore, it would seem that solvent filtration would reduce the problem of dust particles in the scattering volume. But since absolute

filtration does not exist, filtration of the solvent is not the best answer to the dust problem.

The author's feeling is that the following situation during centrifuging of the polymer solution will result in changes in the polymer-solvent system: During centrifuging sedimentation of both dust particles and polymer molecules can occur as a result of dragging. The probability that this will happen depends on the relative sizes of the dust particles and polymer molecules. For a given size of dust particle the probability would be higher for larger polymer molecules. Therefore for solutions of polydisperse polymer, molecules with lower molecular weights might be expected in the higher region of the solution after centrifuging, hence the measured diffusion coefficient will be higher than that which corresponds to the average molecular weight. In the following, the method is shown which was used in this work to compensate for the presence of dust particles in the scattering volume. Using unfiltered pure solvents without any polymer as a scattering sample, the total photocurrent spectra have been obtained, and they are shown in Figures 5, 6, 7, and 8 for different solvents. It can be seen that for benzene and decalin, except below 100 Hz, the photocurrent spectrum is approximately a horizontal line. In the same way for methylethylketone and dimethylformamide the

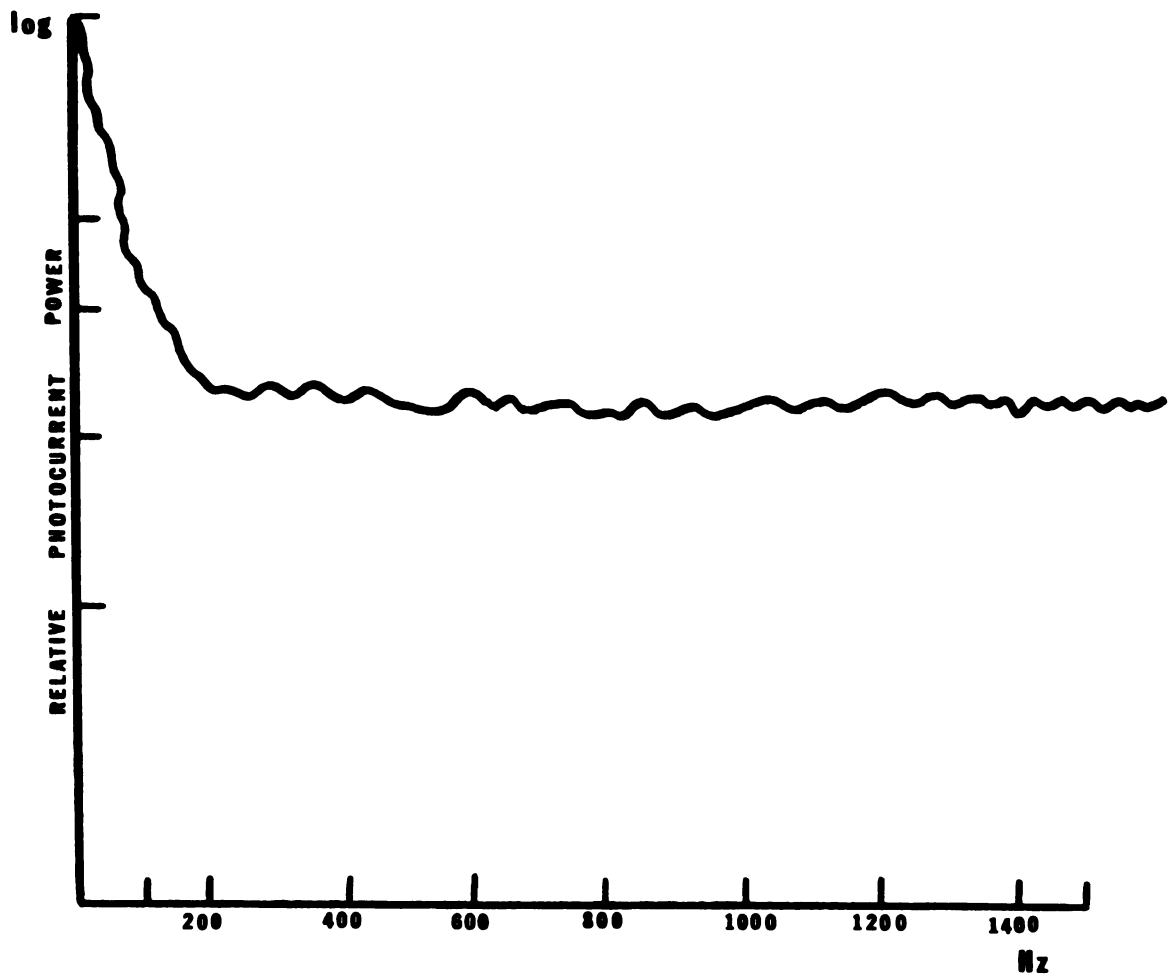


Figure 5. Photocurrent spectrum of light scattered in benzene (scattering angle 25°).

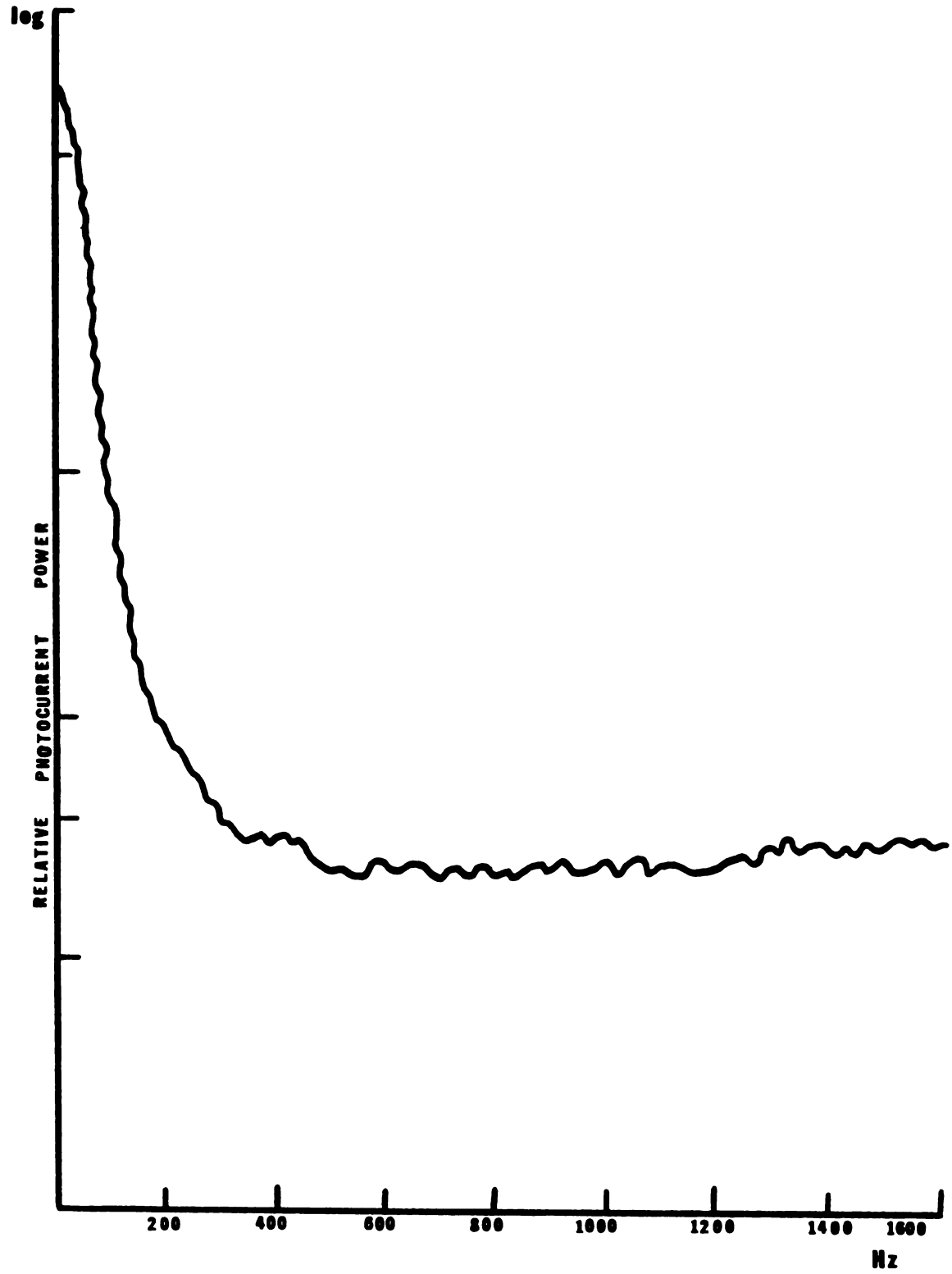


Figure 6. Photocurrent spectrum of light scattered in methylethylketone (scattering angle 25°).

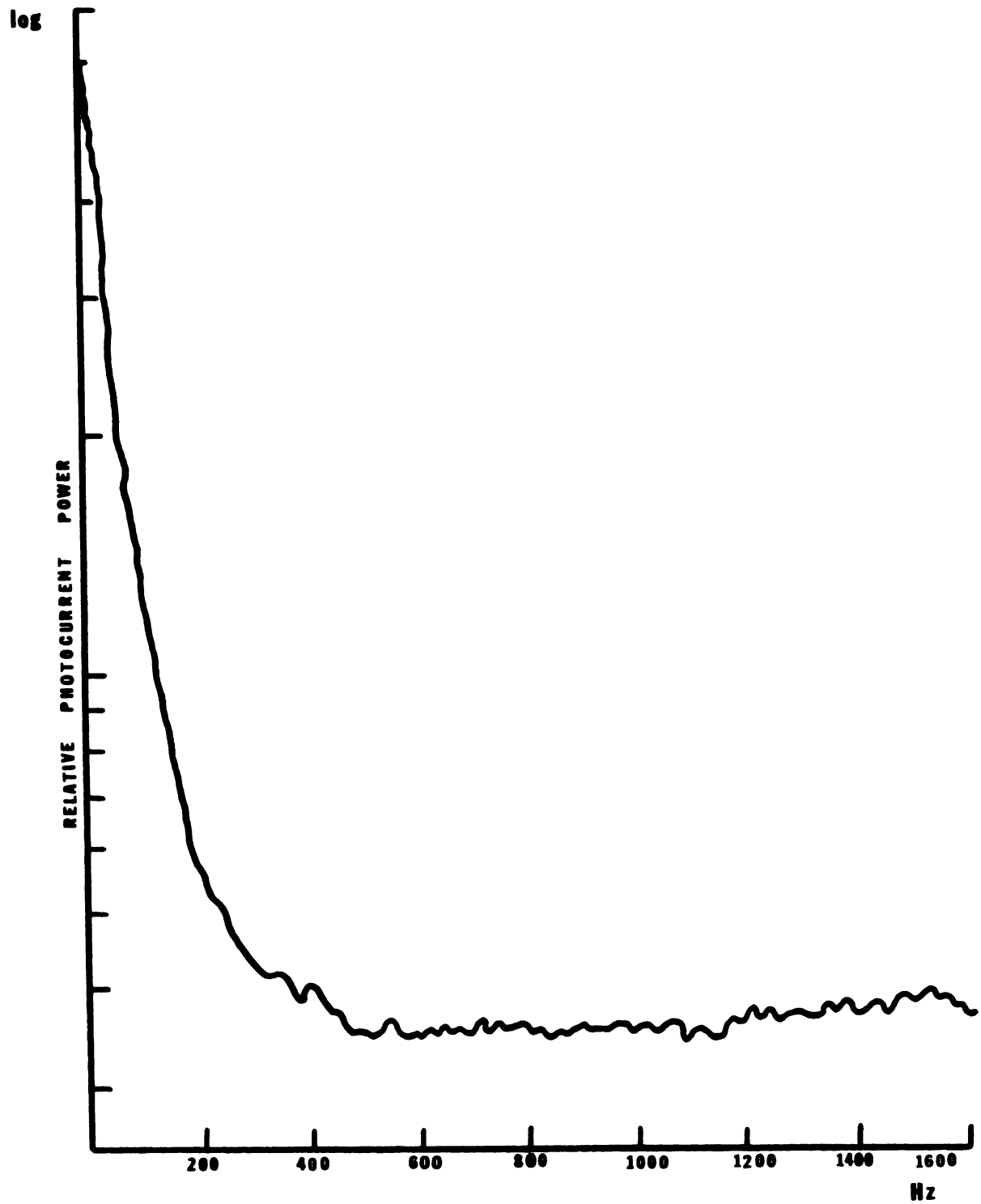


Figure 7. Photocurrent spectrum of light scattered in dimethylformamide (scattering angle 25°).

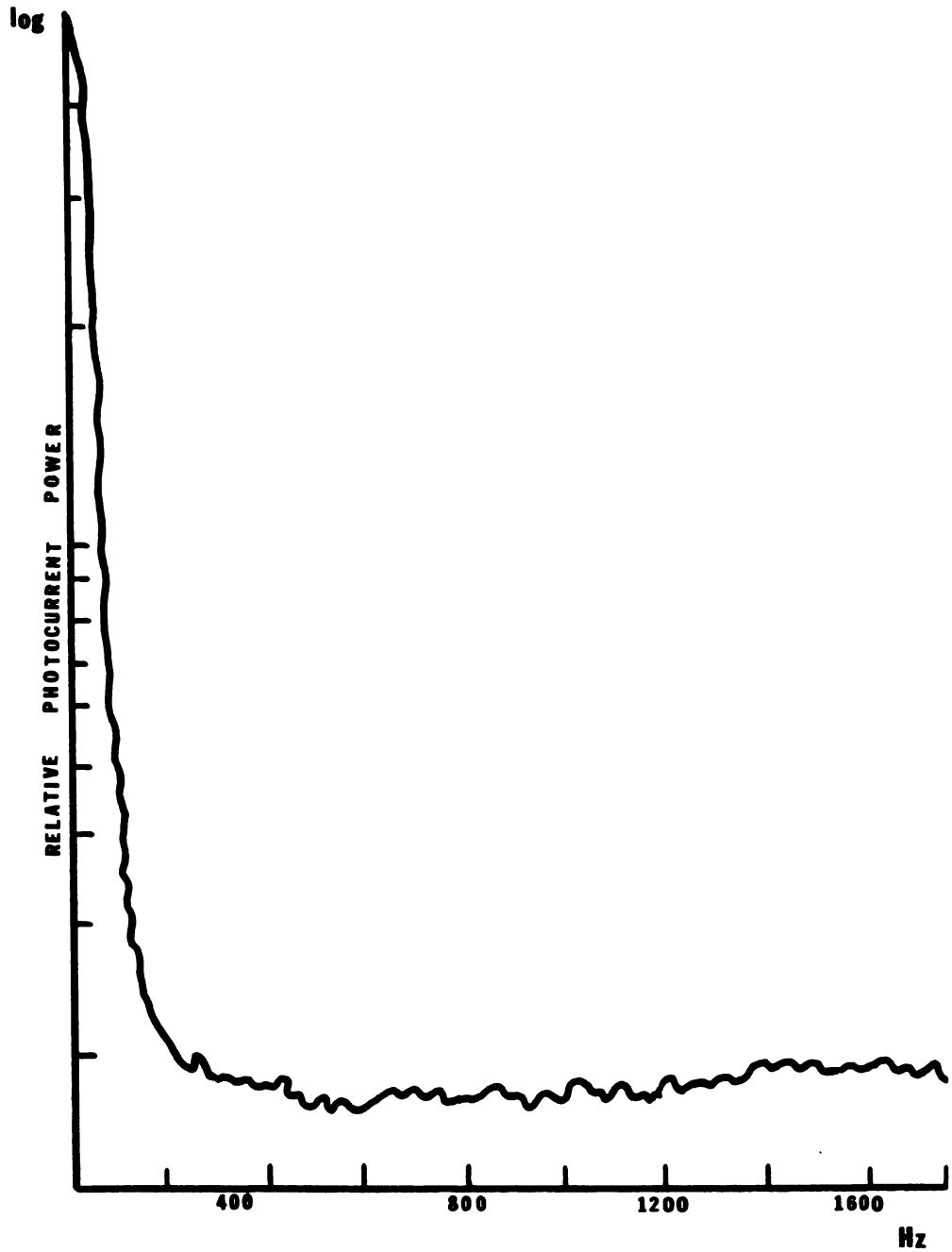


Figure 8. Photocurrent spectrum of light scattered in decalin (scattering angle 25°).

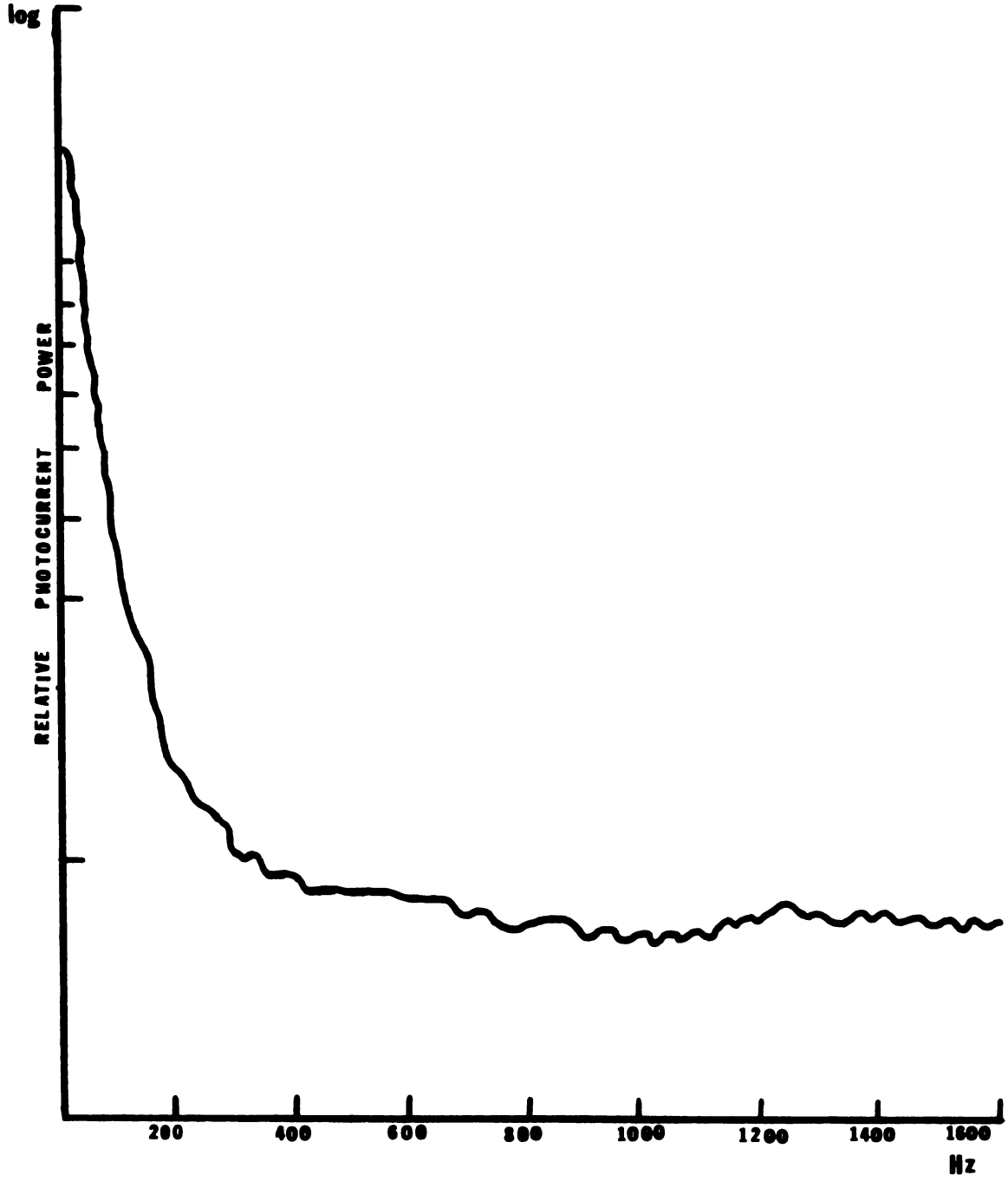


Figure 9. Photocurrent spectrum of light scattered in water (scattering angle 25°).

photocurrent spectrum is approximately a horizontal line at frequencies above 200 Hz. This means the total photocurrent spectrum is constant over 200 Hz for all the solvents of interest here, even with the assumed presence of dust particles. Earlier, it was explained that the dust particles in solution come mostly from the solvent. Hence, those horizontal line spectra of the solvents can be considered as "total shot noise" which arises from the instrumentation and the solvent. Therefore, to subtract this "total shot noise" from the photocurrent spectrum of scattered light of the polymer solution, the lightbeating term of the spectrum can be obtained.

Kramer (1971) has investigated the presence of dust particles in methylethylketone. He measured the total photocurrent spectrum of scattered light from unfiltered, filtered, and centrifuged methylethylketone, and found that the microfiltered (4500Å pore size filter) methylethylketone has a spectral component below 200 Hz, which cannot be recorded for centrifuged (2 hours at 100 x G) samples. His data shows agreement to data of this work. For unfiltered, uncentrifugated methylethylketone no spectral component over 300 Hz was found in the total photocurrent.

The subtraction of "total noise" from the total photocurrent spectrum is not simple for the following reasons.

The absolute value of the photocurrent spectrum is not known, it depends on the intensity of the laser beam, the power current of the photomultiplier and the attenuation of the input to the spectrum-analyzer for a constant scattering angle for a given sample. Input and output limitation of spectrum-analyzer require changes in photomultiplier current and the input attenuator of the spectrum-analyzer for each measurement. It is not necessary to know the absolute value of the photocurrent spectrum, because the information desired the shape, and thus the halfwidth of the spectrum, does not depend on the absolute value of the spectrum. Therefore, the calculation of the halfwidth and the estimation of "total noise" can be done by computer which is discussed later.

D. CALCULATION

As mentioned earlier the photocurrent spectrum for homodyne detection of a Lorentzian optical spectrum consists of three terms: shot noise, the d.c. component and the lightbeating spectrum. If the resulting current in the load resistor is fed through a capacitor, then the d.c. component is blocked out, and the photocurrent spectrum is the sum of the lightbeating spectrum and shot noise. To obtain the lightbeating spectrum, shot noise must be subtracted from the total photocurrent spectrum. The shot

noise level, sometimes called white shot noise level, can be determined in two ways:

(1) By measuring the spectrum at high frequencies, i.e., frequencies beyond which the signal level is significant. The shot noise level is independent of frequency, therefore, practically, measurement of the photocurrent spectrum at high frequencies where the photocurrent is constant gives the level of shot noise.

(2) The sample is replaced by a light bulb, which is used as a light source. The light bulb serves as a white noise generator because the signal spectrum for the light bulb as a light source is negligible compared to the shot noise.

In the following the method used to calculate the diffusion coefficient in this work is discussed.

It can be seen in Figures 5, 6, 7, and 8 that the spectral component below 300 Hz is a smooth curve. Assuming uniform dust particles size (which is a reasonable assumption for a small scattering volume considering the process of sedimentation), this spectral component could arise from light scattered from dust particles. These dust particles are present in the polymer solution also. Therefore, the spectrum of light scattered from a polymer solution consists of the sum of two single Lorentzians; one corresponds to

the polymer, the other to the dust particles. If the spectrum of the scattered light consists of the sum of two single Lorentzians for homodyne detection the lightbeating part of the photocurrent spectrum consists of the sum of three Lorentzians. Cummins et al. (1969) present the equation

$$P_{LB} = 2\langle i\rangle^2 \frac{1}{(B_0+B_2)^2}\left(B_0^2\,\frac{2\Gamma_0/\pi}{\omega^2+4\Gamma_0^2} + 2B_0B_2\frac{(\Gamma_0+\Gamma_2)/\pi}{\omega^2+(\Gamma_0+\Gamma_2)^2} + B_2{}^2\,\frac{2\Gamma_2/\pi}{\omega^2+4\Gamma_2{}^2}\right) \qquad 12.$$

where P_{LB} is the photocurrent of the lightbeating part of the spectrum Γ_0 and Γ_2 are the spectral halfwidths of the two Lorentzians in the scattered light spectrum and B_0 and B_2 are the corresponding intensities.

It can be seen that there are four variables B_0, B_2, Γ_0, and Γ_2 in Equation 12. Considering the total photocurrent spectrum which is the sum of the lightbeating spectrum and the "total noise" there is a fifth variable, the "total shot noise". Hence to calculate the halfwidth of the scattered light from the polymer molecules the curve-fitting computer program must include five unknown parameters. Using only 15-20 data points, the uncertainty of these parameters would be very high and a large error in

the analysis of polymer diffusion would result. Before this difficult problem can be discussed, a simple case should be investigated; viz., a single Lorentzian in the spectrum of the scattered light. In this case, the total photocurrent spectrum of scattered light is given by Equation 10, which may be written

$$P(\omega) = \frac{A}{1 + \frac{\omega^2}{B^2}} + D, \qquad 13.$$

where A is a constant, ω is the frequency, B is the halfwidth of the lightbeating spectrum, and D is the "total shot noise". The photocurrent is known for each frequency from the experimental spectrum, so there are only three unknown parameters: A, B, and D.

The least squares estimate of halfwidth of the lightbeating spectrum of scattered light can be calculated by the computer program given in the Appendix, provided the scattered light spectrum consists only of a single Lorentzian. Assuming that a uniform size of dust particle is present in the scattering volume, the spectrum of light scattered from dust particles will consist of only a single Lorentzian, provided the sample consist of solvent and dust only. It means the halfwidth of the lightbeating spectrum of scattered light from the dust particles can be calculated, so the number of the unknown variables in Equation 12 is reduced from five to four. But four variables still

are too many to calculate an accurate halfwidth of the lightbeating spectrum of light scattered from polymer molecules. (Kramer [1971] was unable to obtain reasonable halfwidths by fitting the lightbeating spectrum of filtered [dust remained] dilute methylethylketone solution of polystyrene.) Therefore, the number of variables should be reduced from four to three. The simplest way to do this is to calculate the halfwidth of the lightbeating spectrum of light scattered from polymer molecules without considering the presence of dust particles. The question is--how much error is introduced by this simplification? In other words, what is the difference between the halfwidth calculated using Equation 12 and that which is calculated by Equation 10, considering the same shot noise? It can be calculated by setting the two equations equal to each other. It means calculating the halfwidths from each equation at a point of the spectrum, which is obtained by actual measurement. Dividing both sides by $2\langle i\rangle^2/\pi$

$$\frac{1}{(B_0+B_2)^2}\left(B_0^2\frac{2\Gamma_0}{\omega^2+4\Gamma_0^2}+2B_0B_2\frac{\Gamma_0+\Gamma_2}{\omega^2+(\Gamma_0+\Gamma_2)^2}+B_2^2\frac{2\Gamma_2}{\omega^2+4\Gamma_2^2}\right)$$

$$=\frac{2\gamma_0}{\omega^2+4\gamma_0^2} \qquad 14.$$

Where $2\Gamma_0$ and $2\gamma_0$ are the halfwidths of the lightbeating spectra of the light scattered from polymer molecules calculated from the different equations.

Equation 14 may be simplified by use of the following assumptions:

1. The intensity of the light scattered from polymers, B_0, is much higher than the intensity of the light scattered from dust particles, B_2. This is true because the intensity is a function of the concentration and is independent of the halfwidth of the spectrum. It was mentioned earlier, that the dust concentration is much lower than the concentration of polymers. This conclusion was supported by observation of the relative intensity and analyzer attenuator settings while recording the spectra of solvent and polymer solution.
2. The frequencies under consideration are much higher than the halfwidth of the lightbeating spectrum of the light scattered from dust particles. For frequencies over 300 Hz, the light beating spectrum of light scattered from dust particles is essentially zero, as shown earlier.

Using these assumptions $B_2^2 \frac{2\Gamma_2}{\omega^2+4\Gamma_2^2}$ becomes negligibly small compared with other terms in Equation 14. If $B_2 = \beta B_0$, $\Gamma_2 = \alpha\Gamma_0$ and $\omega = \delta\Gamma_0$ then Equation 14 is reduced to

$$\frac{1}{(1+\beta)^2}\left(\frac{1}{(\delta^2+4)\Gamma_0} + \frac{\beta(1+\alpha)}{(\delta^2+(1+\alpha)^2)\Gamma_0}\right) = \frac{\gamma_0}{\delta^2\Gamma_0^2+4\gamma_0^2} \qquad 15.$$

Next it is necessary to determine the maximum values for α β and δ.

Using a relatively very low diffusion constant, $D = 1.0 \times 10^{-7}$ cm^2/sec in methylethylketone at 25° scattering angle, the theoretical halfwidth of the lightbeating spectrum of light scattered from polymers is about 200 Hz. The estimated halfwidth of the lightbeating spectrum of light scattered from dust particles in methylethylketone is about 20 Hz at 25° scattering angle, so the value of α is not larger than 0.1.

To obtain the same photocurrent a minimum of 6 dB attenuation had to be used, when the sample was a dilute polymer solution, compared with dust so the input was reduced at least by a factor of four. Therefore, the intensity of light scattered from a polymer solution is at least 16 times larger than the intensity of light scattered from dust particles only hence so β is less than 0.1. δ can be varied between 0.5 and 8, depending on the value of the halfwidth of the lightbeating spectrum of the light scattered from the polymer molecules.

The γ_0/Γ_0 ratio was calculated using the above assumption, and typical values are shown in Table 2. It was found that the halfwidth calculated from Equation 10 is smaller by less than 5% than the halfwidth calculated from Equation 12. It was concluded therefore that the experimental light spectrum of light scattered from dilute polymer solution can be fitted by a single Lorentzian,

Table 2. Ratio of halfwidth of lightbeating spectra calculated from single and three Lorentzians.

α	β	δ	$\frac{\gamma_0}{\Gamma_0}$
0.05	0.02	0.5	0.972
		1.0	0.984
		3.0	0.968
		5.0	0.977
		7.0	0.979
0.05	0.05	0.5	0.939
		1.0	0.966
		3.0	0.925
		5.0	0.946
		7.0	0.950
0.10	0.02	0.5	0.974
		1.0	0.985
		3.0	0.970
		5.0	0.978
		7.0	0.980
0.10	0.05	0.5	0.943
		1.0	0.967
		3.0	0.930
		5.0	0.949
		7.0	0.953
0.50	0.10	0.5	0.959
		1.0	0.971
		3.0	0.928
		5.0	0.944
		7.0	0.947

without a significant loss in precision. In this way all of the spectra were fitted by Equation 10, using a FORTRAN program for the CDC 6500 Computer. This conclusion is further justified by the reasonably good answers obtained for the polystyrene latex calibration runs using only a single Lorentzian calculation.

The computer printout, Table 3, gives the different halfwidths, with the "total shot noise", which results in a minimum for the function

$$\sum_{i=1}^{i} \left(\frac{PT_i - PE_i}{PE_i} \right)$$

where PE_i is the experimental photocurrent at the i^{th} frequency and PT_i is the value calculated from Equation 13. Most authors average the diffusion coefficients obtained from measurements at different scattering angles. Each diffusion coefficient for a given scattering angle is calculated from Equation 7, using the halfwidth of the best fitting curve calculated by computer. This work follows another approach to calculate the diffusion coefficient from the halfwidth of the lightbeating spectrum of light scattered from polymer molecules. The reason for using the alternative approach will become apparent below.

Using 2 cycle semilog graph paper to record the total photocurrent spectra, an average of $\pm 2\%$ reading error is

Table 3. A typical computer printout used for calculation.

Columns from left to right: 1. halfwidth, 2. photocurrent power at zero frequency, 3. "total noise", 4. sum of the least square errors.

OMEGA = frequency
1-EXP = experimental photocurrent power
1-CALC = calculated photocurrent power
E(1) = the least square error

20.0000	3360.9901	1.297518	.016137
50.0000	543.1131	1.289961	.014905
80.0000	216.0151	1.276117	.012815
110.0000	117.2141	1.256311	.010196
140.0000	74.7367	1.230973	.007453
170.0000	52.6567	1.200602	.005017
200.0000	39.7183	1.165724	.003286
230.0000	31.4811	1.126860	.002590
260.0000	25.9074	1.084502	.003172
290.0000	21.9555	1.039088	.005178
320.0000	19.0484	.991002	.008665
350.0000	16.8453	.940563	.013621
380.0000	15.1347	.888037	.019972
410.0000	13.7794	.833634	.027610
440.0000	12.6875	.777517	.036399
470.0000	11.7953	.719813	.046191
500.0000	11.0578	.660613	.056837

24 = NO. OF GOLD SEARCHES AT EACH OF... 230.000

232.0650	31.0277	1.124051	.002587

OMEGA	I-EXP	I-CALC	F(I)
400.00	9.10	8.94	-.017839
500.00	6.50	6.62	.018971
600.00	5.10	5.16	.012087
700.00	4.10	4.20	.023541
800.00	3.60	3.53	-.018805
900.00	3.10	3.06	-.013427
1000.00	2.75	2.71	-.014678
1100.00	2.45	2.45	-.001561
1200.00	2.25	2.24	-.003281
1300.00	2.10	2.08	-.008448
1400.00	1.95	1.95	.001944
1500.00	1.85	1.85	-.000353
1600.00	1.73	1.76	.019264

reasonable. Therefore for 13 data points the total error

$$\sum_{i=1}^{13} \left(\frac{PT_i - PE_i}{PE_i} \right)^2$$

can be as much as 0.0052. This means that if an experimental spectrum is a perfect match to the theoretical spectrum, reading the points and calculating the halfwidth can cause an error as great as 0.0052. Therefore, each and any halfwidth with error equal to or less than 0.0052 for 13 data points may be the required halfwidth; more exactly, instead of one value of halfwidth a range of values of halfwidth should be used. Of course, when the total error is larger than 0.0052 for all of the calculated halfwidth the halfwidth with minimum error should be used. As was explained in a previous chapter, plotting the halfwidths of lightbeating spectra of light scattered from polymer molecules against the sine squared of half of their corresponding scattering angle should give a straight line which goes through the origin.

Figure 10 shows the first step of a typical calculation. The halfwidth with minimum total error is 392 Hz. But between 340 and 440 Hz the total error is less than 0.0052; therefore, this is the range of the halfwidth. Figure 11 shows the next step in the calculation. The ranges at 25° and 35° were plotted and a range was found

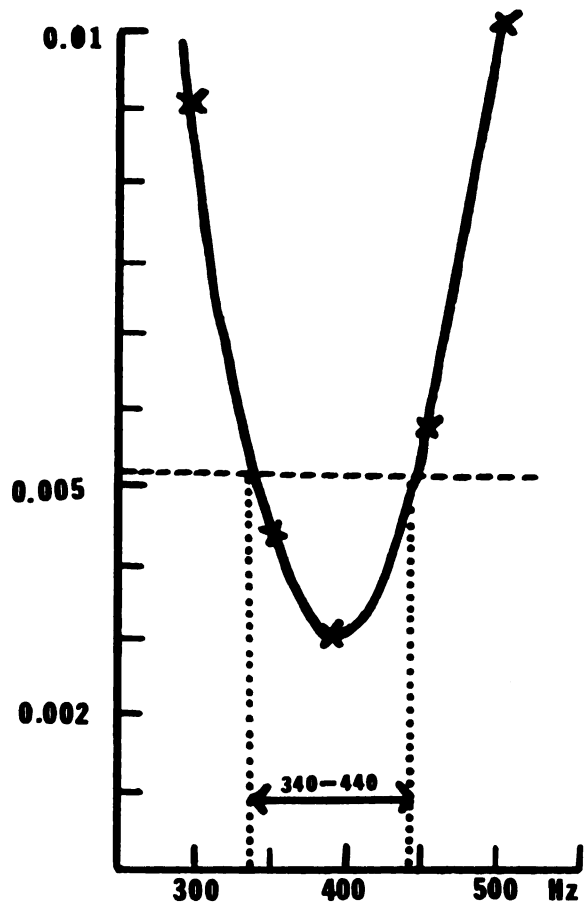


Figure 10. Sum of the square error of calculated halfwidths. Monsanto SAN copolymer M_W = 250,000 in methylethylketone (C = 0.3 g/100g) scattering angle is 25°C.

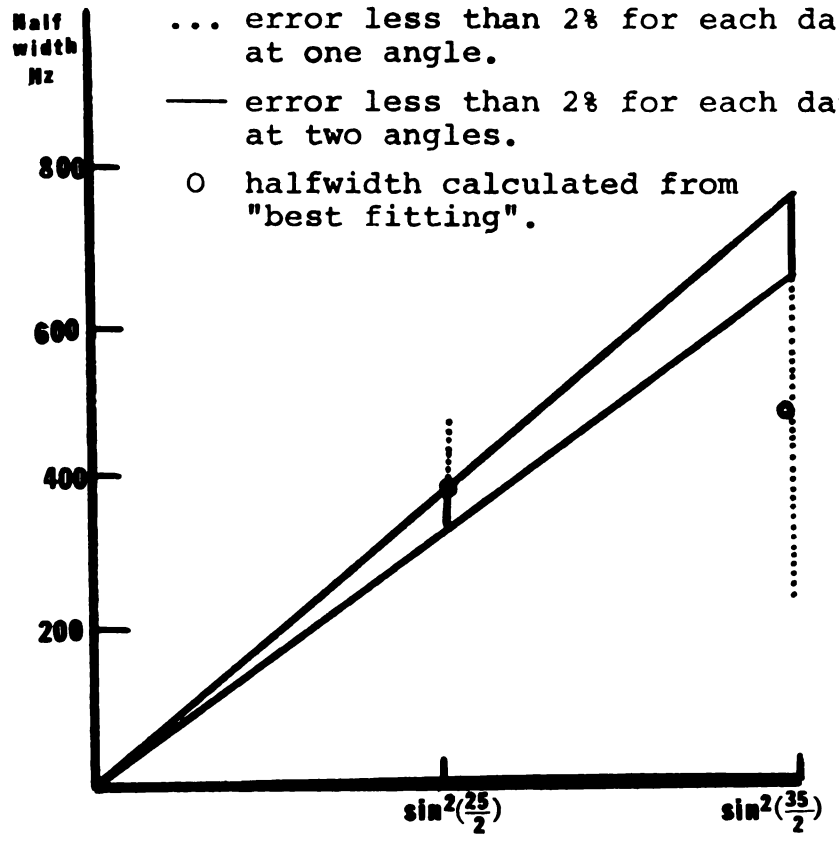


Figure 11. Angular dependence of calculated halfwidth. Monsanto copolymer (M_w = 250,000) in methylethylketone.

for which the average error for each point at both angles was no greater than 2%. The range was 340-410 Hz for 25° scattering angle and 680-790 for 35°. The calculated range for diffusion coefficient was 1.68-2.05 x 10^{-7} cm^2/sec. The diffusion coefficients calculated from the "best fitting" halfwidth minimum error) were 1.28 x 10^{-7} cm^2/sec for 35° and 1.92 x 10^{-7} cm^2/sec for 25° scattering angle, and the average is 1.60 x 10^{-7} cm^2/sec. The original value differ from the average by $\pm$ 20%.

The author feels that using this range method where it is possible, gives more realistic results. Therefore, a range is shown for most of the diffusion coefficients. Where this is not possible, because of reasons mentioned earlier, only the average diffusion coefficients are given. In these cases the difference between the average diffusion coefficient and the original one is less than $\pm$8%.

To eliminate the possibility of error arising from the optical anisotropy of the sample cell (dirt or fault) each measurement was done twice, with the cell turned between measurements. (This changed the horizontal position of the scattering volume also a little bit, so different polymer molecules were in the scattering volume during the second measurement.) Both spectra were recorded and the two curves were matched. Only those spectra have been used in this work which matched each other perfectly.

E. DIFFUSION CONSTANTS OF THE POLYMER MOLECULES IN DILUTE SOLUTION

Investigating the concentration dependence of the diffusion coefficient of polystyrene (M_W = 3.5 x 10^6 and 5 x 10^6) in tetrachloromethane and methylethylketone Tsvetkov and Klenin (1958) obtained an S shaped curve plotting the diffusion constant against concentration. They found for very low concentration (lower than 0.07 g/100g) there is no change in the diffusion coefficient. In the region of concentrations from 0.012 to 0.6 g/100g, the diffusion coefficient shows a very sharp increase. For higher concentrations the rate of growth decreases and the curve approaches a constant value. The concentration dependence of the diffusion coefficient is much less for poor solvents such as methylethylketone than for good solvents such as tetrachloromethane.

Ford *et al.* (1970) found that the diffusion coefficient of polystyrene in methylethylketone above a concentration of about 0.35 g/100g is approximately constant. Below this the concentration dependence of the diffusion coefficient is described by the equation,

$$D(c) = D_o \ (1 + K_D c) \qquad 16.$$

Where D_o is the value of the diffusion coefficient at the limit of zero polymer concentration and K_D is a molecular

weight dependent constant. The K_D was found to be positive for molecular weights above 100,000 and negative for lower molecular weights.

Schick and Singer (1950) published negative values of K_D for $M_W = 9.5 \times 10^4$ and $M_W = 2.4 \times 10^5$, and positive values for M_W equal or higher than 5.6×10^5 for polystyrene-methylethylketone systems. Using the same sample of polystyrene in tetrachloromethane, K_D was found to be negative for $M_W = 9.5 \times 10^4$, zero for $M_W = 2.4 \times 10^5$ and $M_W = 5.6 \times 10^5$, and positive for $M_W = 6.8 \times 10^5$ and $M_W = 9.1 \times 10^5$. Schick and Singer (1950) observed negative K_D values for polystyrene of $M_W = 6.8 \times 10^5$ in decalin. Meyerhoff (1960) reported positive K_D for polystyrene of $M_W = 5.28 \times 10^5$ in methylethylketone.

Both Singer and Tsvetkov show the theoretical derivation of Equation 16. Ford et al. (1970) derived a theoretical relationship between K_D and the molecular weight for polystyrene-methylethylketone systems, but the agreement between the theoretically calculated K_D and that calculated from actual measurement was very poor.

The diffusion coefficient at the limit of zero polymer concentration, D_o, for polymers with different molecular weights was investigated by Ford et al. (1970). They showed a relationship between D_o and the molecular weight in the form of

$$D_o = K_o M^{-b} \qquad 17.$$

Where K_o is a constant and M is the molecular weight. For polystyrene-methylethylketone systems K_o was found to be equal to $3.1 \pm 0.2 \times 10^{-4}$ $cm^2/sec.$ and b was found to be equal to 0.53 ± 0.02 at 298°K (average molecular weights were used).

Equation 17 is similar in form to Staudinger intrinsic viscosity equation

$$[\eta] = KM^{\alpha} \qquad 18.$$

Where $[\eta]$ is the intrinsic viscosity, and K and α are constants. But because the coefficient of b is -1, D_o is inversely proportion to $[\eta]$. For polystyrene-methylethylketone systems α is in the range of 0.58 to 0.635. Schick and Singer (1950) found b equal to 0.53 for a methylethylketone system which is in exact agreement with the b value found by Ford *et al.* (1970), and for polystyrene-tetrachloromethane b was reported to be 0.59 by Schick and Singer (1950). Reed (1970) gave a value of b = 0.51 and K_o = 1.20 for a polystyrene-cyclohexane system.

Ford *et al.* (1970) showed a method to calculate the unperturbed dimensions of polymer molecules in dilute solutions. Two equations are given (the difference is whether the expansion factor molecular weight dependence is calculated by the Flory (1953) or the Kurata and Stockmayer

(1960) equation). Plotting $(D_o M)^{-1}$ against $D_o^3 M^2$ or $g(\alpha_f) M D_o$ the solvent independent ratio $(\frac{\bar{r}_o^2}{M})^{\frac{1}{2}}$ can be calculated, ($g(\alpha_f)$ is a function of the expansion factor), $(\bar{r}_o^2)$ is called the unperturbed dimensions of the polymer molecules. The $(\frac{\bar{r}_o}{M})^{\frac{1}{2}}$ ratio was calculated for a polystyrene-methylethylketone solution and was found to be $(800 \pm 40) \times 10^{-11}$ cm at 298°K. This value is higher than, but of the same order of magnitude as, the result calculated from viscosity measurements which was 670×10^{-11} cm.

IV. RESULTS

The principal goal of this study was to investigate the diffusion coefficient for different polymer solvent and copolymer-solvent systems but without a detailed study of any of them, and to develop the measurement procedure and calculation method for lightbeating spectroscopy, which could be a base for further investigation. Therefore, the diffusion coefficients of five concentrations for each of five specific monopolymer and six copolymer samples each in three or four solvents were determined. Although complete calculations, such as a determination of the diffusion coefficient at the limit of zero concentration could not be done, estimated values for certain systems are given. All of the measurements were done at 21°C temperature. The necessary basic information about the polymers and solvents are given in Tables 4 and 5. All of the measured diffusion coefficients are given in Tables 6, 7, and 8.

Polystyrene-Methylethylketone

Below a concentration of 0.2 g/100g the diffusion coefficient in methylethylketone definitely increases with increasing concentrations of polystyrene in the solution

Table 4. Molecular weights of polystyrene and polystyrene-acrylonitrile copolymer used in this work.

	$M_n \times 10^{-3}$	$M_W \times 10^{-3}$*
Polystyrenes		
UC 000	57.7	130.0
UC 010	37.9	80.0
UC 030	102.7	271.0
UC 040	117.8	338.0
MS-190	103.0	185.0
Polystyrene-acrylonitrile copolymers		
MS-14	141.0	275.0
MS-23	120.0	203.0
MS-37	205.0	332.0
MS-22	339.0	634.0
MoI-25	80.0	247.0
MoII-25	107.0	325.0

* = from Gel Permeation Chromatography
UC = Union Carbide
MS = Michigan State University
Mo = Monsanto
M_n = Number average molecular weight
M_W = Weight average molecular weight

Table 5. Density and refractive index of the solvents used in this work.

Solvent	Density g/cm^3 20°C	Refractive Index
Benzene[1]	0.879	1.501
Methylethylketone[2]	0.805	1.380
Dimethylformamide[3]	0.944	1.427
Decalin (cis/trans)[4]	0.896	1.475

[1]Baker (Reagent)
[2]Fisher (Certified)
[3]Mallinckrodt (Reagent)
[4]Mateson-Coleman (Practical)

Table 6. Diffusion coefficient of polystyrene in different solvents.

	Concentration (g/100g)	Diffusion coefficient x 10^{-7} cm^2/sec. Benzene	MEK	DMF
	0.02		3.60	
	0.05		4.35	
UC 010	0.10		3.89	2.47
	0.20	2.65	4.90	2.30
	0.50	3.84	4.65	2.58
	0.12	2.80	3.02	1.38-1.89
	0.30	2.12	2.44	1.88
UC 000	0.60	2.22	2.84	2.00
	1.20	2.25	2.85	2.08
	3.00	3.10	2.46	2.25
	0.02		1.01-1.18	
MS-190	0.10	2.18	1.74-3.80	
	0.20	1.40-3.10	1.94-3.42	
	0.50	1.60	1.89-3.05	
	0.12	1.23-2.12	1.68-2.05	1.15
	0.30	1.28-1.87	1.31-1.89	1.31
UC 030	0.60	2.68	1.47-2.22	
	1.20	1.92	1.31-1.95	1.34
	3.00	1.42-2.46	1.31-1.93	1.38-1.78
	0.02		1.46	0.55-0.97
	0.05	1.18	1.58-1.80	1.15-1.18
UC 040	0.10	1.01-1.48	1.43-1.55	1.07-1.36
	0.20	1.14-1.42	1.88-2.13	
	0.50	1.14-1.34	1.88-2.19	1.01-1.16

Table 7. Diffusion coefficient of polystyrene-acrylonitrile in different solvents.

	Concentration (g/100g)	Diffusion coefficient x 10^7 cm^2/sec. Benzene	MEK	DMF
	0.02		1.60-1.90	1.34
	0.05		2.38-3.05	1.02-1.38
MS-14	0.10	0.90-1.89	2.62-3.20	1.24-2.00
	0.20	1.10-2.10	2.74	0.95-1.66
	0.50	1.40-1.80	2.79-3.37	1.51
	0.02		2.24	
	0.05		2.22	1.67
MS-23	0.10	1.86	2.84-3.66	1.34-1.57
	0.20	1.71	4.20	1.12-1.33
	0.50	1.84	3.61	1.93
	0.04		2.30-2.95	1.25-1.67
	0.10		2.08	1.48
MS-37	0.20		2.24-3.06	0.84-1.70
	0.40		1.98	1.40
	1.00		2.93	1.45
	0.10	1.42		
MS-22	0.50	1.57-1.73		
	0.04		1.15-1.52	0.64-1.15
	0.10		1.37-1.98	0.43-1.15
MS-22	0.20		1.67-2.56	0.78-1.21
	0.40		1.64-2.56	0.61-1.98
	1.00		2.40	1.30-1.84
	0.06	1.59-2.08		
	0.15	1.38-2.90		
MoI-25	0.30	1.68-2.09		
	0.60	1.72		
	1.50	1.78		
	0.12		3.25	1.01-1.56
	0.30		3.70	1.64
MoI-25	0.60		3.66	2.03
	1.20		3.41	2.28
	3.00		4.00	2.80

continued

Table 7--continued

	Concentration (g/100g)	Diffusion coefficients x10^7 cm^2/sec. Benzene	MEK	DMF
	0.02	1.55-1.75		
	0.05	1.44-1.50		
MoII-25	0.10	1.65-1.80		
	0.20	1.75-2.30		
	0.12		2.21	1.13-2.00
	0.30		2.70-3.12	2.18
MoII-25	0.60		2.39	1.42
	1.20		2.58	1.95
	3.00			3.02-3.18

Table 8. Diffusion coefficient of polystyrene in decalin.

Concentration (g/100g)	Diffusion coefficient x 10^7 cm^2/sec.			
	UC 000	UC 010	UC 030	UC 040
0.05	0.8-1.37		0.91	
0.10	1.02	1.23	0.96	0.50
0.20	0.56	0.56	0.76	0.37-0.73
0.50	0.63	0.75	0.66	0.32-0.68

(Figures 12, 13, and 14). Over 0.2 g/100g concentration the diffusion coefficient of polystyrene in methylethylketone seems to be approximately constant (Figures 15 and 16). The exact determination of the diffusion coefficient at the limit of zero polystyrene concentration, D_o is very difficult because only five concentrations were used, and the extrapolation to zero concentration involves a large uncertainty. An estimated range of D_o can be given:

Polystyrene	M_W	$D_o \times 10^7$ cm^2/sec
UC 010	80,000	3.60-4.00
UC 000	130,000	2.70-3.00
UC 030	271,000	1.65-1.85
UC 040	338,000	1.30-1.60

Plotting log D_o against log M_W, the directional tangent range is 0.63-0.66 with a negative sign, which is equivalent to -b in Equation 17. This value is higher than the value of b reported in the literature (0.53), but considering the small amount of data and the use of D_o ranges instead of fixed values, the agreement probably is satisfactory.

Polystyrene-Benzene

It may be concluded that the diffusion constant is not a function of the concentration for the polystyrene-benzene system in the range 0.12 to 3.0 g/100 g concentration (Figures 13, 14, 15, and 16). D_o may be estimated only for

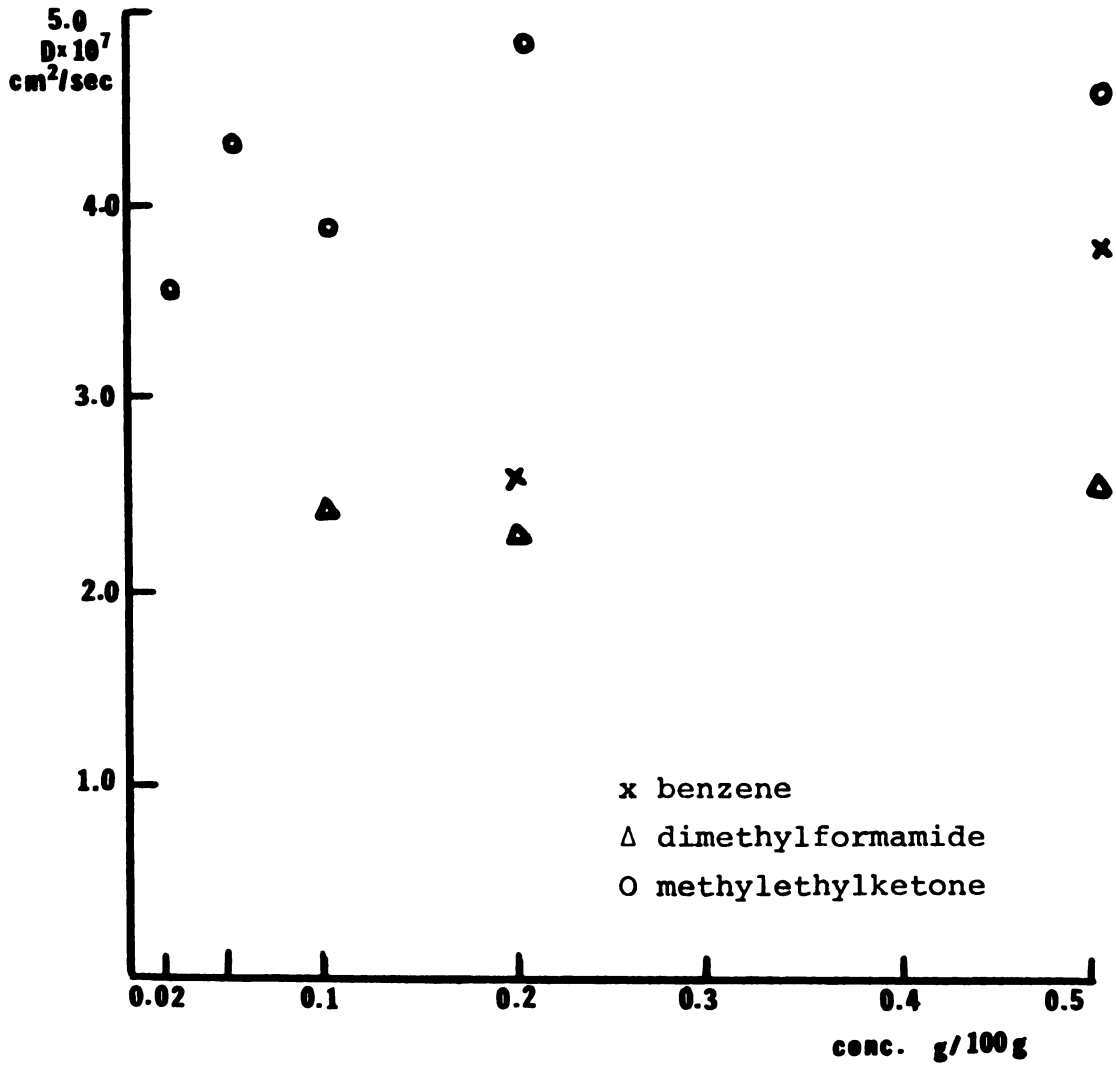


Figure 12. Diffusion coefficient of polystyrene (M_W = 80,000) in different solvents.

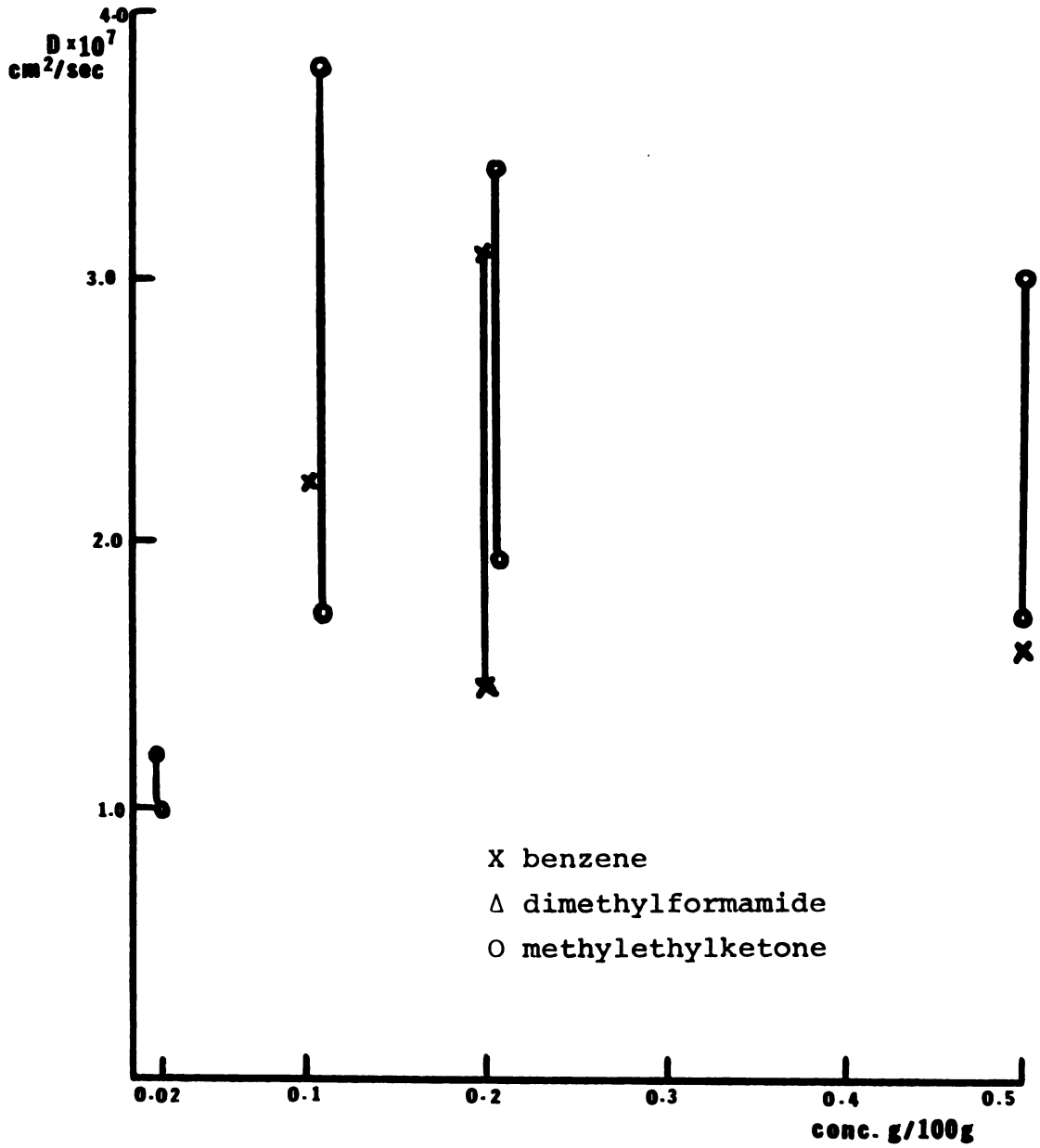


Figure 13. Diffusion coefficient of polystyrene (M_W = 185,000) in different solvents.

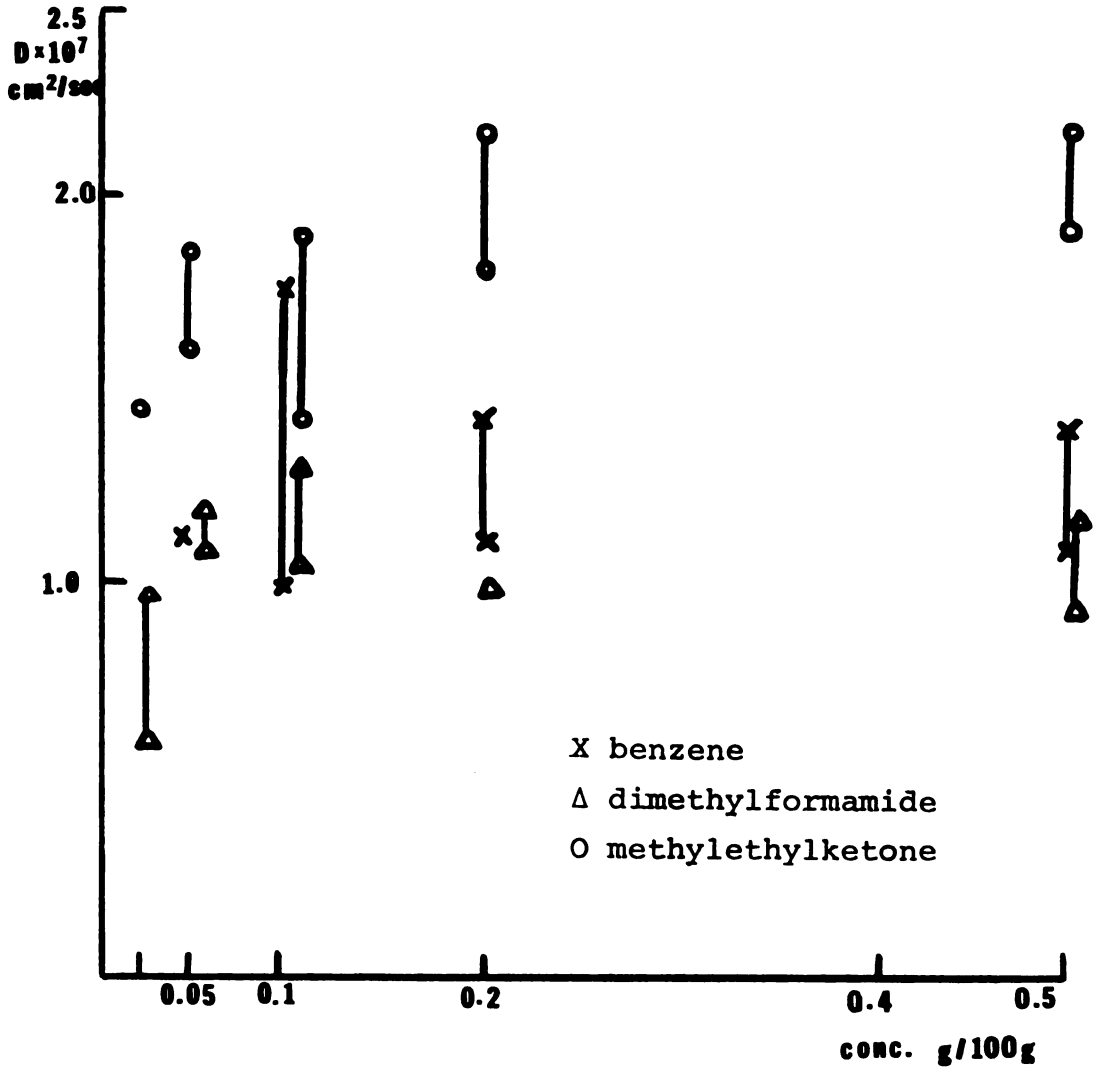


Figure 14. Diffusion coefficient of polystyrene (M_W = 338,000) in different solvents.

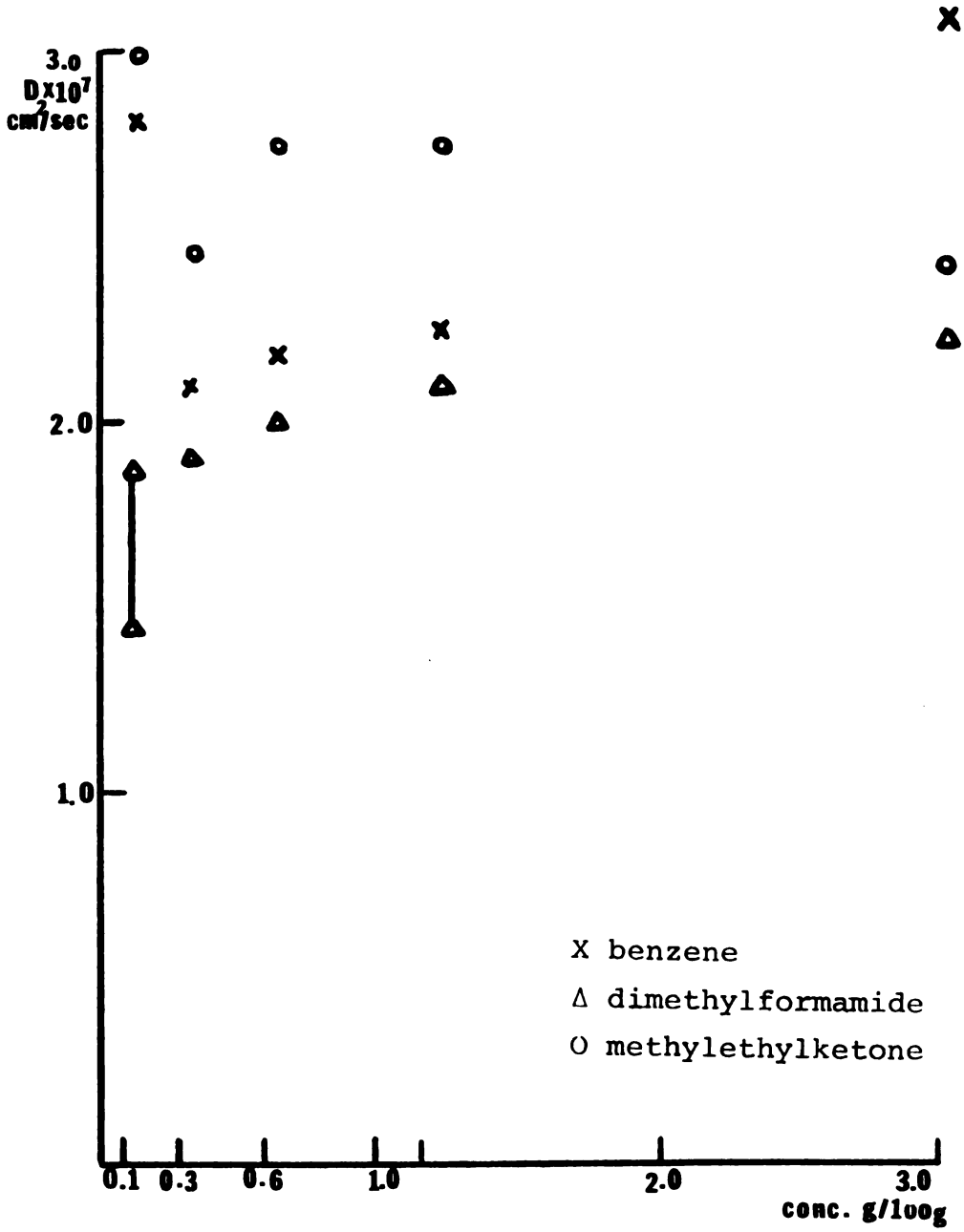


Figure 15. Diffusion coefficient of polystyrene (M_W = 130,000) in different solvents.

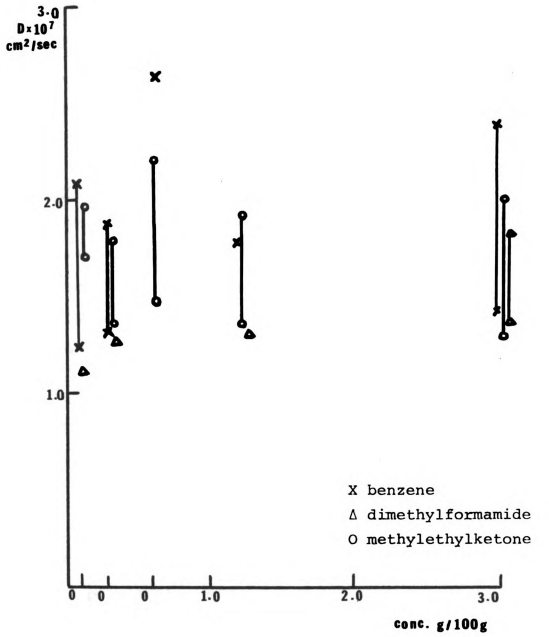


Figure 16. Diffusion coefficient of polystyrene (M_W = 271,000) in different solvents.

UC 040 which is about 1.15-1.35 x 10^{-7} cm^2/sec. and for UC 030 which is about 1.60-1.90 x 10^{-7} cm^2/sec. In this case the exact molecular weight dependence of D_o cannot be obtained but it does decrease with increasing molecular weight as expected.

Polystyrene-Dimethylformamide

The data show that the diffusion coefficient for polystyrene-dimethylformamide tends to increase with increasing concentration below 3.0 g/100g (Figures 15 and 16), but for M_W = 3.38 x 10^5 it is nearly constant (Figure 14). Ranges of D_o which can be estimated

Polystyrene	M_W	D_o x 10^7 cm^2/sec
UC 000	130,000	1.65-1.85
UC 030	271,000	1.00-1.25
UC 040	338,000	0.75-1.00

Polystyrene-Decalin

The available data indicate the diffusion coefficient for the polystyrene-decalin system is unchanged or decreases with increasing concentration, and definitely does not increase in the range of concentration from 0.05 g/100g to 0.5 g/100g (Figure 17). A precise determination of D_o is not possible, but the data show positively that D_o is decreasing with an increase of molecular weight. The range of D_o is about 0.5-1.3 x 10^{-7} cm^2/sec. for the molecular weight range of 80,000 to 338,000.

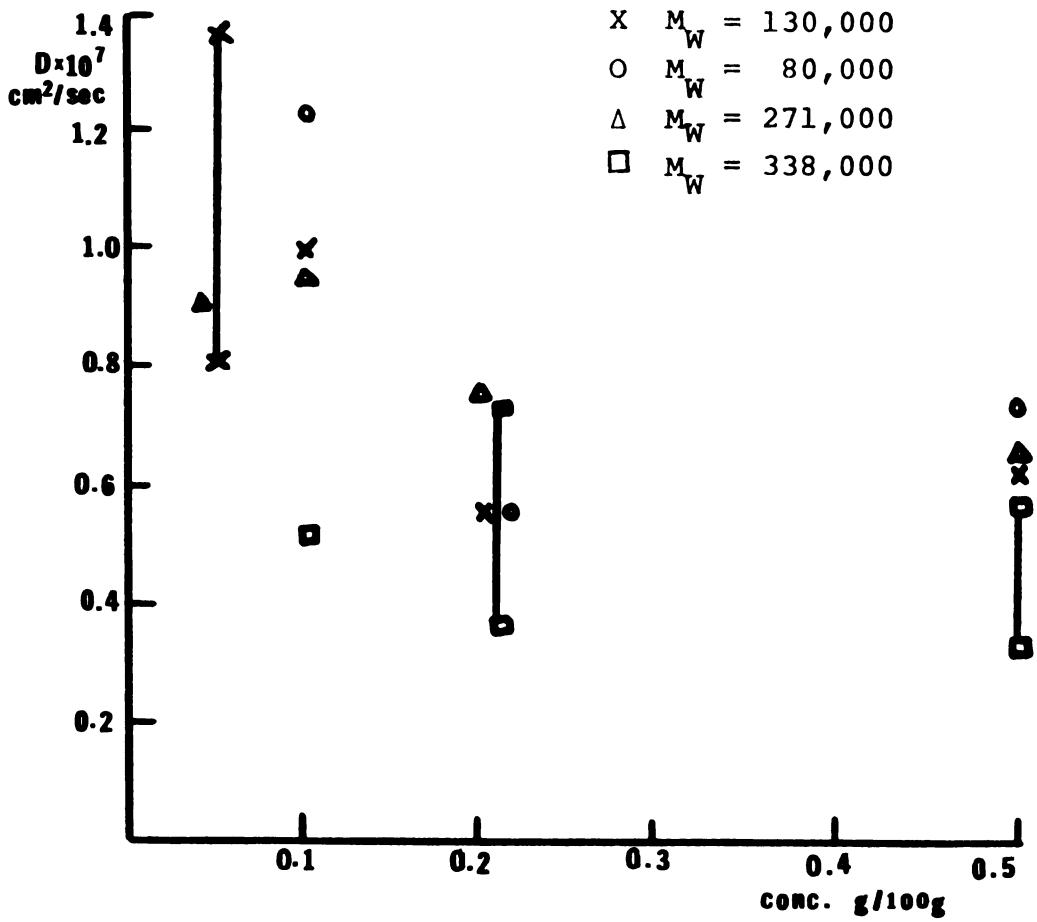


Figure 17. Diffusion coefficient of polystyrene in decalin.

Polystyrene-Acrylonitrile in Methylethylketone

As in the polystyrene-methylethylketone system the diffusion coefficient for the polystyrene-acrylonitrile in methylethylketone below of 0.2 g/100g concentration increases with increasing concentration of copolymer and over 0.2 g/100g concentration approaches some constant value as can be seen in Figures 18, 19, 20, 21, and 22. The molecular weight dependence of D_o cannot be given because D_o cannot be estimated with the required accuracy.

Polystyrene-Acrylonitrile Copolymer in Benzene

It seems that below 1.5 g/100g concentration the diffusion coefficient for polystyrene-acrylonitrile copolymer in benzene does not change with increasing concentration (Figures 18, 19, 20, and 21). Although a precise D_o determination is not possible because of the small number of data points, it can be seen that D_o is decreasing with increases of molecular weight. But because of the relatively small range of molecular weights (2.03×10^5 - 6.34×10^5) this decrease seems small.

Polystyrene-Acrylonitrile Copolymer in Dimethylformamide

The diffusion coefficient slightly increases with increasing polystyrene-acrylonitrile copolymer concentration (Figures 18, 19, 20, 21, 22, and 23). The molecular weight dependence of D_o can be estimated using the ranges of D_o.

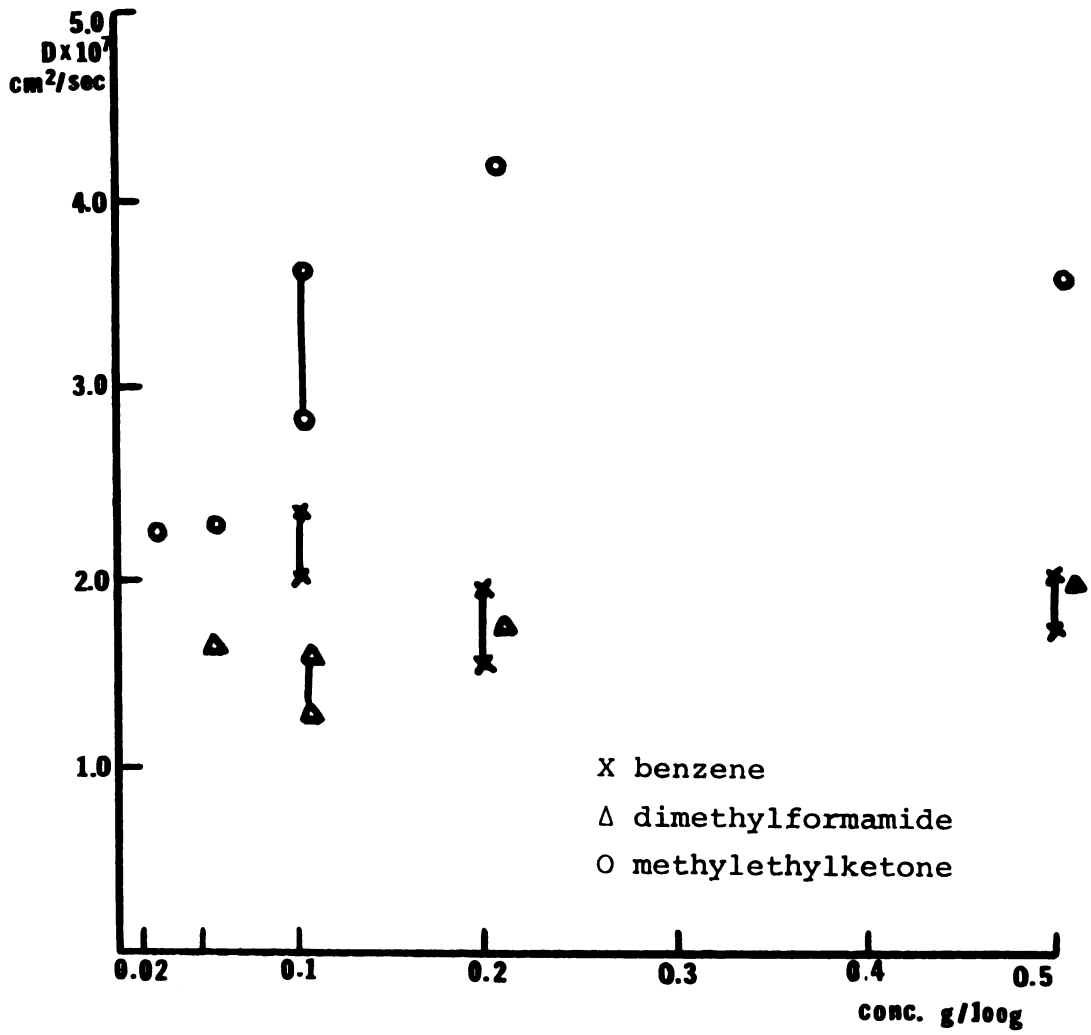


Figure 18. Diffusion coefficient of polystyrene-acrylonitrile copolymer (M_W = 203,000, 23% acrylonitrile content) in different solvents.

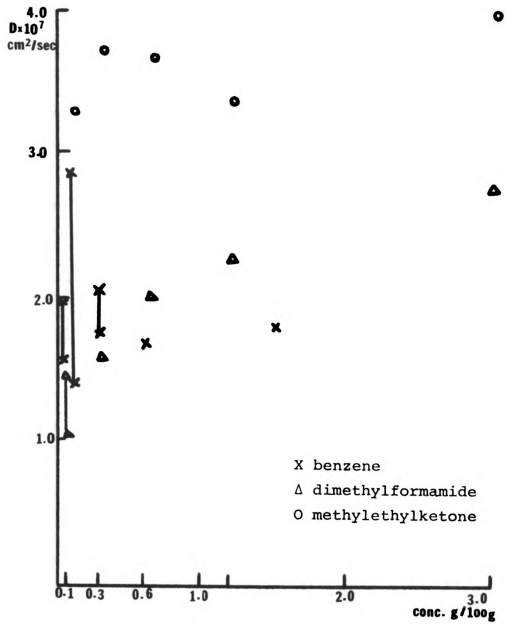


Figure 19. Diffusion coefficient of polystyrene-acrylonitrile copolymer (M_w = 247,000, 25% acrylonitrile content) in different solvents.

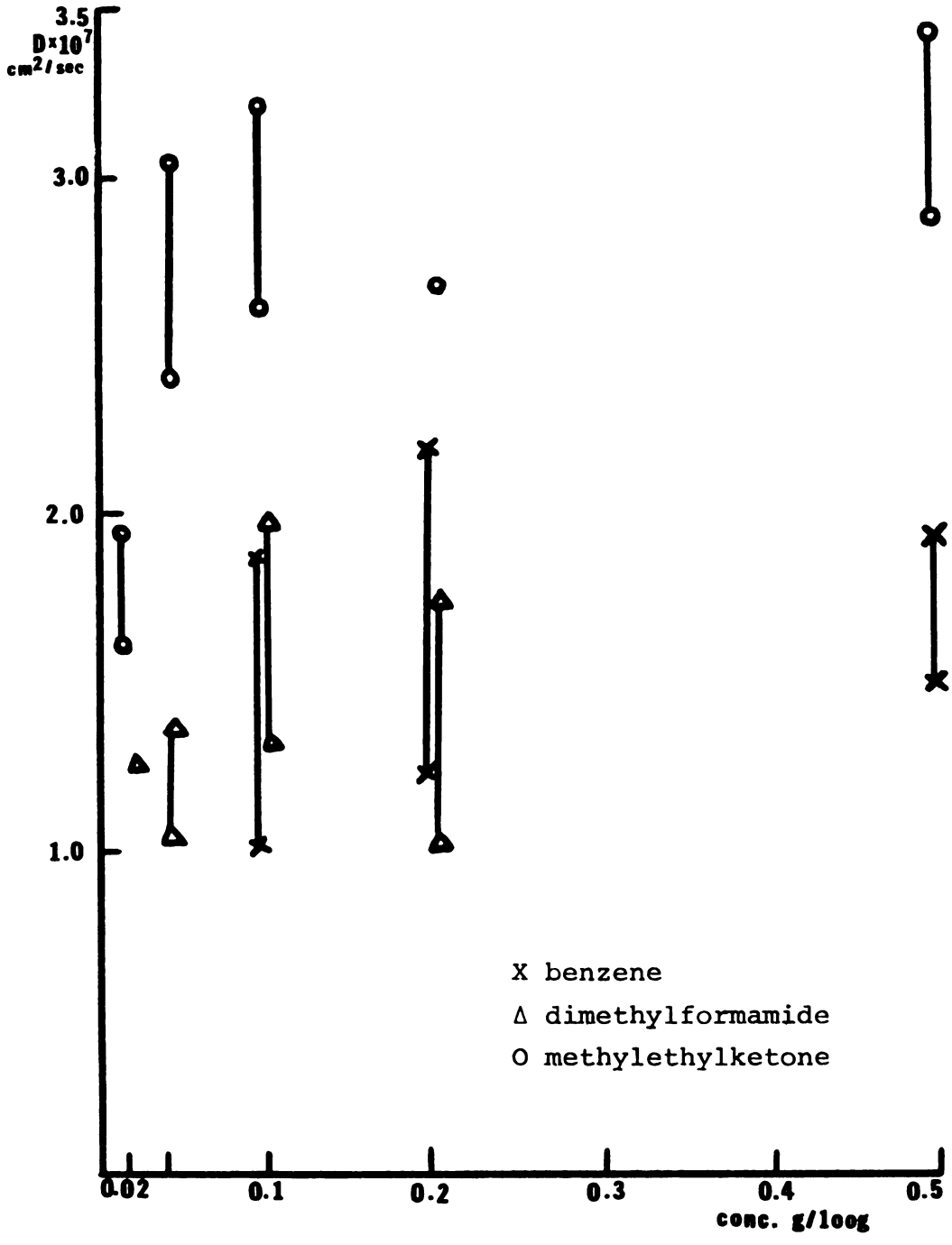


Figure 20. Diffusion coefficient of polystyrene-acrylonitrile copolymer (M_W = 275,000, 14% acrylonitrile content) in different solvents.

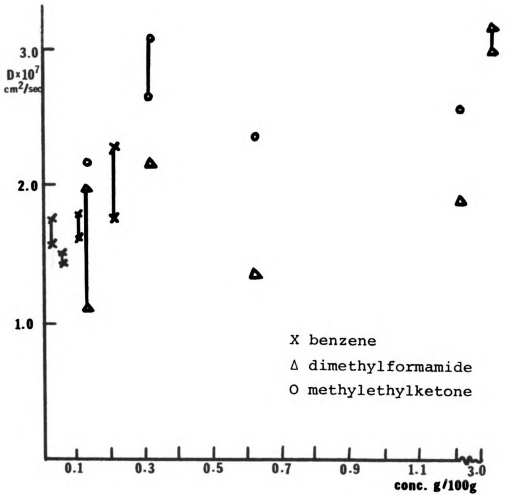


Figure 21. Diffusion coefficient of polystyrene-acrylonitrile copolymer (M_w = 325,000, 25% acrylonitrile content) in different solvents.

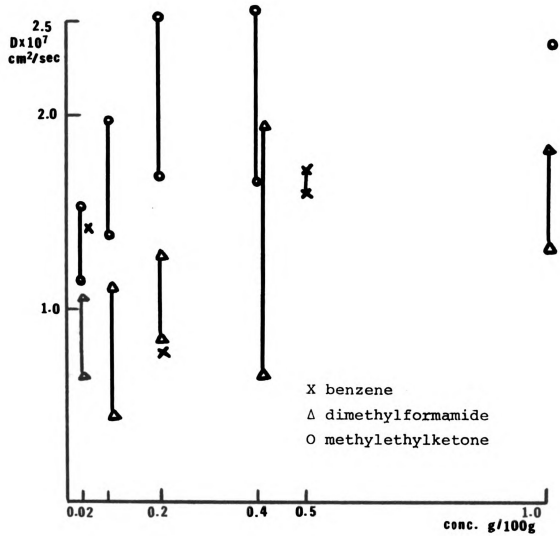


Figure 22. Diffusion coefficient of polystyrene-acrylonitrile copolymer (M_w = 634,000, 22% acrylonitrile content) in different solvents.

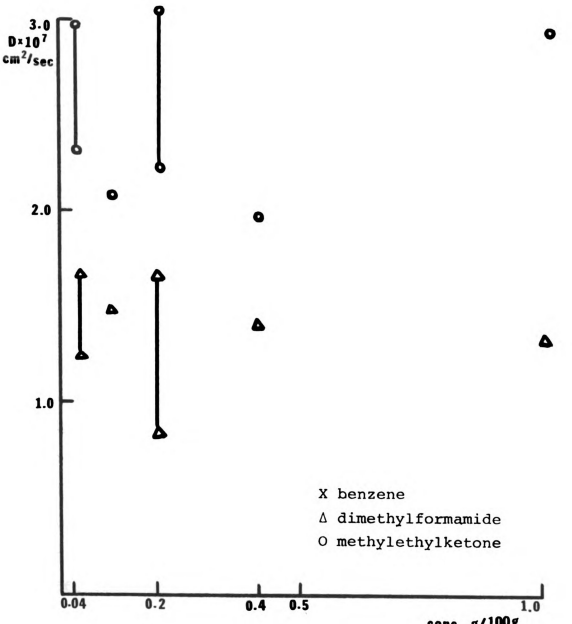


Figure 23. Diffusion coefficient of polystyrene-acrylonitrile copolymer (M_w = 332,000, 38% acrylonitrile content) in different solvents.

	M_W	D_o
MS-14	275,000	1.10-1.30
MS-23	203,000	1.40-1.60
MS-22	634,000	0.70-1.00
MoI-25	247,000	1.20-1.50

Comparison of the Diffusion Coefficients for a Constant Concentration of a Given Polymer (molecular weight is constant) in Different Solvents

Considering the four solvents benzene, decalin, dimethylformamide, and methylethylketone, it can be seen in Figures 12, 13, 14, 15, and 17 that the diffusion coefficient for a given molecular weight and concentration of polystyrene is always the highest in methylethylketone and definitely the smallest in decalin. The second highest diffusion coefficient was measured in benzene and a slightly smaller diffusion constant was found in dimethylformamide. For acrylonitrile-polystyrene copolymer the diffusion coefficient is also highest in methylethylketone. The diffusion coefficients measured in benzene and dimethylformamide are approximately equal.

Comparison of Diffusion Coefficient of Polystyrene and Polystyrene-acrylonitrile (the same concentration and molecular weight) in Different Solvents

Figure 24 shows the diffusion coefficient of polystyrene and polystyrene-acrylonitrile as a function of molecular

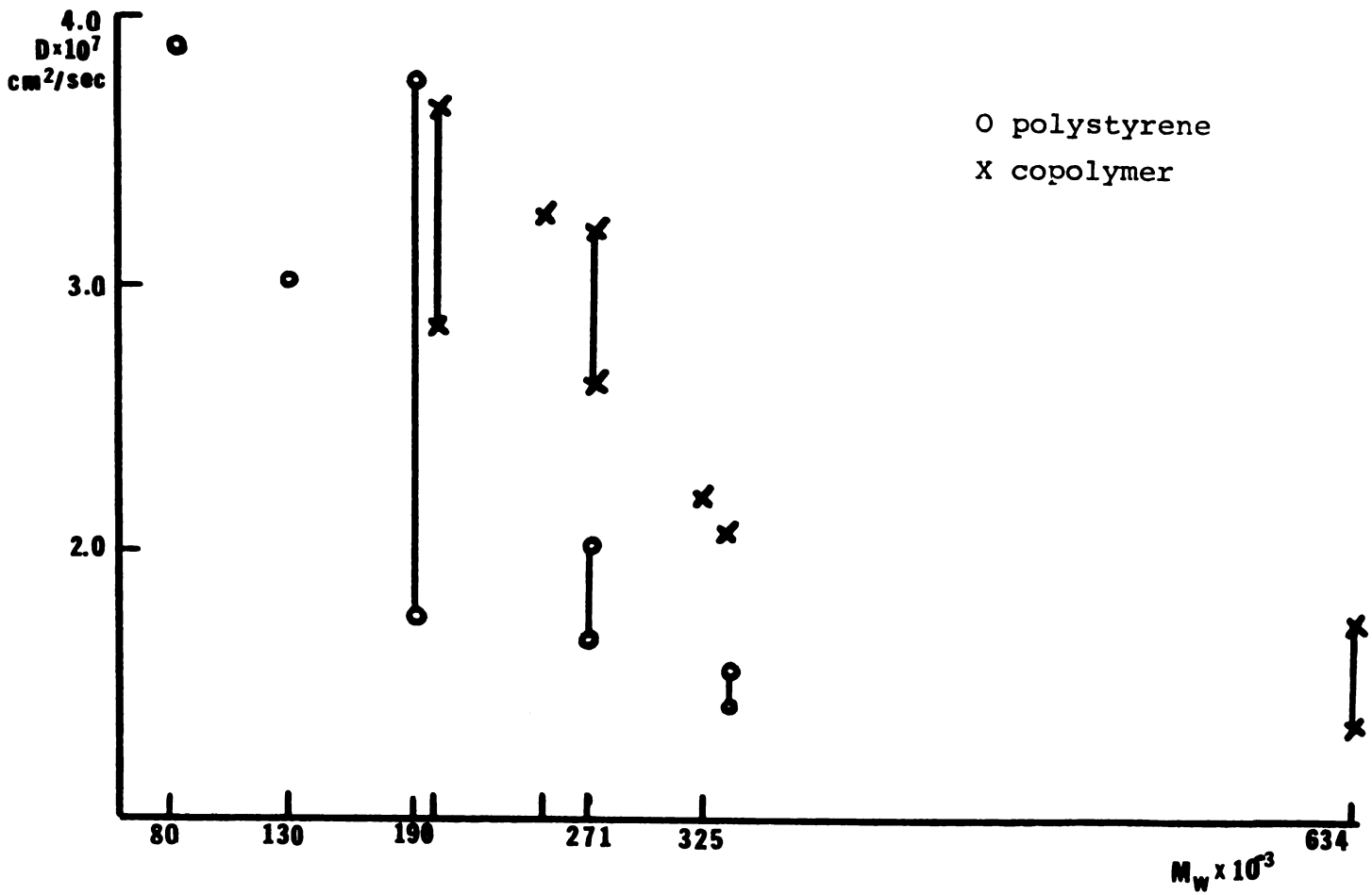


Figure 24. Comparison of diffusion coefficient of polystyrene and polystyrene-acrylonitrile copolymer as function of molecular weight in methyl-ethylketone at 0.1 g/100g concentration.

weight for one concentration (0.1 g/100g) in methylethylketone. It can be seen that the diffusion coefficient of the copolymer is higher by about 40-60% than the diffusion coefficient of the polystyrene. In Figure 25 it can be seen that the diffusion coefficient of the copolymer and polystyrene are about the same in benzene. While the copolymer exhibits only a slight decrease in its diffusion coefficient with increasing molecular weight, the change is much larger for polystyrene.

In dimethylformamide (Figure 26), the diffusion coefficient seems to be a little bit higher for the copolymer than for polystyrene.

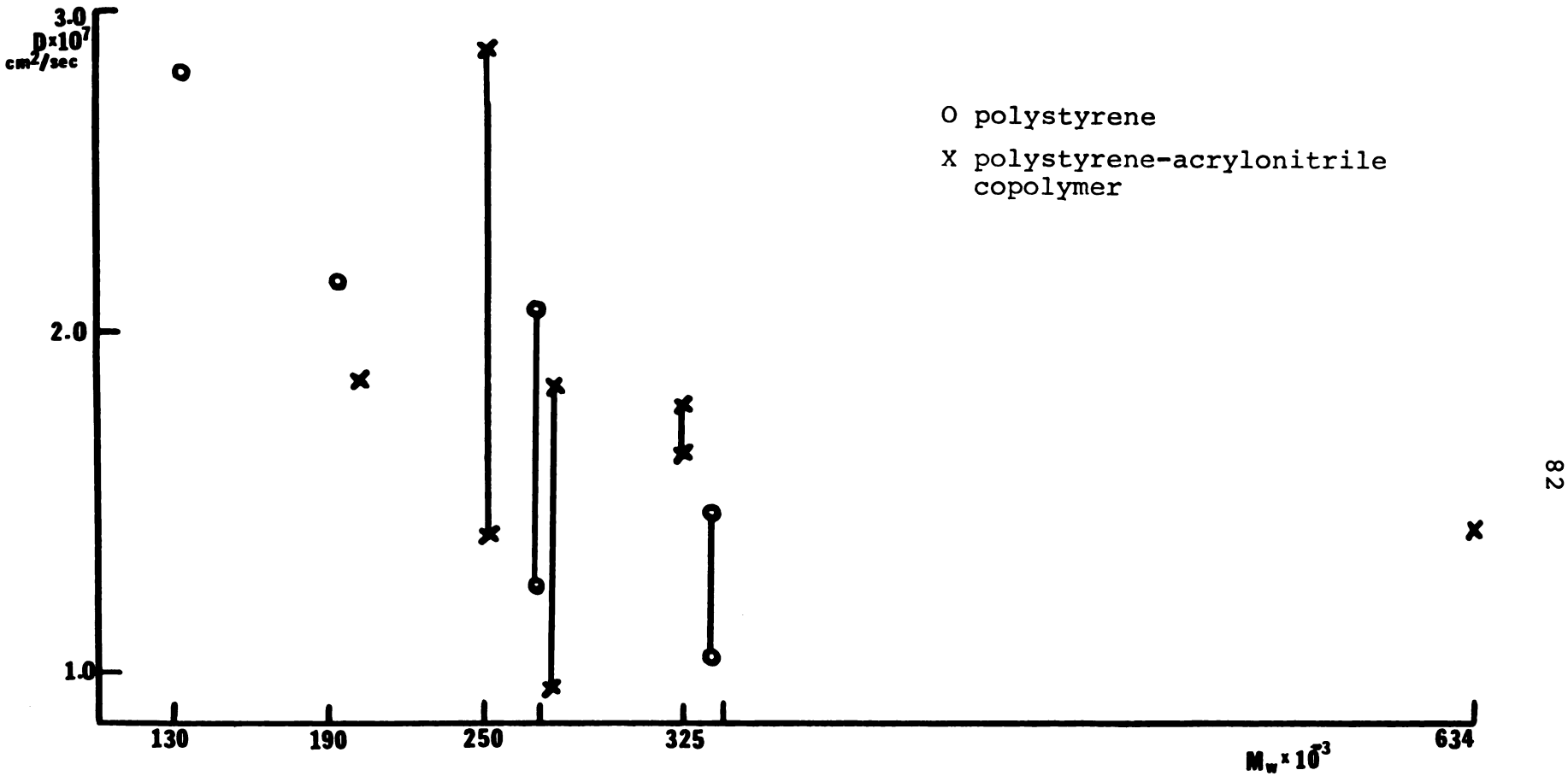


Figure 25. Comparison of diffusion coefficients of polystyrene and polystyrene-acrylonitrile copolymer as function of molecular weight in benzene at 0.1 g/100g concentration.

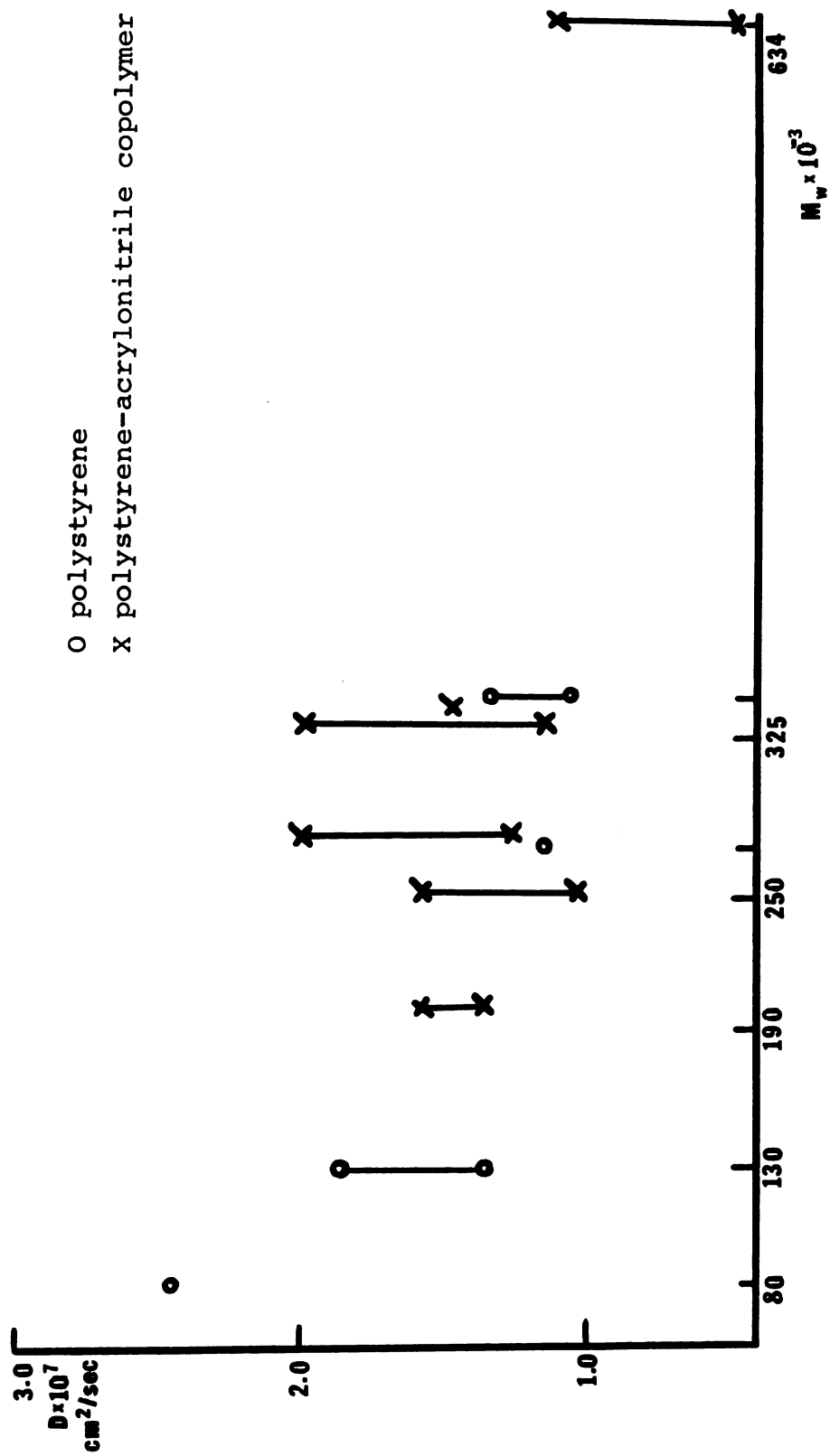


Figure 26. Comparison of diffusion coefficients of polystyrene and polystyrene-acrylonitrile copolymer as function of molecular weight in dimethylformamide at 0.1 g/100g concentration.

V. DISCUSSION

The presence of dust particles in dilute polymer solutions and their effects on lightbeating spectroscopy measurements have been discussed in detail in a previous section. The calibration procedure was also covered earlier. This discussion focuses on the results of these measurements and their comparison with published data.

As mentioned earlier, it was not the purpose of this study to obtain a precise determination of the diffusion coefficient at the limit of zero polymer or copolymer concentration, but rather to develop a standard measurement procedure and calculation technique for the diffusion coefficient in order to give a base for further investigation. To the author's best knowledge no measurement of the diffusion coefficient of polystyrene-acrylonitrile copolymer by lightbeating spectroscopy has been made prior to this work.

As was mentioned in the previous section, the diffusion coefficient of polystyrene decreases or remains constant with increasing concentration in decalin (Figure 17). This result shows similarity to the data published by Schick and Singer (1950), who found the diffusion coefficient

concentration dependence of polystyrene at $M_W = 6.8 \times 10^5$ can be described by the equation

$$D(c) = 0.5\ (1 - 0.15c)$$

where D(c) is the diffusion coefficient at a given concentration and c is the concentration of polystyrene in decalin in units of g/100 cm^3. It can be seen because the coefficient of concentration (-0.15) is negative and small, the diffusion coefficient decreases very slowly with increasing concentration. The results of this work also show that K_D in equation 16 is negative for a range of small molecular weights (80,000 to 332,000). This is similar to the concentration dependence of the diffusion coefficient of polystyrene in methylethylketone found by Schick and Singer (1950) and Ford (1970). However, the sign of K_D turns out to be positive at molecular weight larger than 5×10^5 in methylethylketone according to Schick and Singer (1950), Meyerhoff (1960), and Ford (1970) but remains negative in decalin according to Schick and Singer (1950) and this work.

When a polymer molecule is dissolved in a solvent the molecule will be extended depending on the degree of association between the solvent and the polymer. Dissolving the polymer in a "good" solvent causes the segments of the polymer to associate better with the solvent molecules than

with each other, so the total volume occupied by a single polymer cloud will be extended according to Rodriguez (1970). The intrinsic viscosity is directly proportional to the volume of the polymer molecule in solution according to Flory (1953), and D_o is inversely proportional to the volume of the polymer in solution according to Tsetkov and Klenin (1958). These facts lead to the commonly known conclusion that the intrinsic viscosity is inversely proportional to D_o. Schick and Singer (1950) give the intrinsic viscosity and D_o of polystyrene (M_w = 680,000) in different solvents. It can be seen that if values of $[\eta]$ are plotted against D_o, the points are in a line for four solvents, but the point for decalin is considerably off the line (Figure 27).

An examination of the diffusion coefficients of polystyrenes with different molecular weights, which is part of this work, reveals that higher values are found in methylethylketone (relatively poor solvent) than in benzene (good solvent for polystyrene). A determination of the rank of the solvent (good or bad) can be based on a comparison of the solubility parameters of the polymers and solvents. A smaller absolute value of the difference between the solubility parameter of polymer and solvent means a better solvent. Hansen (1967) reported solubility parameter values for different solvents. A comparison of the

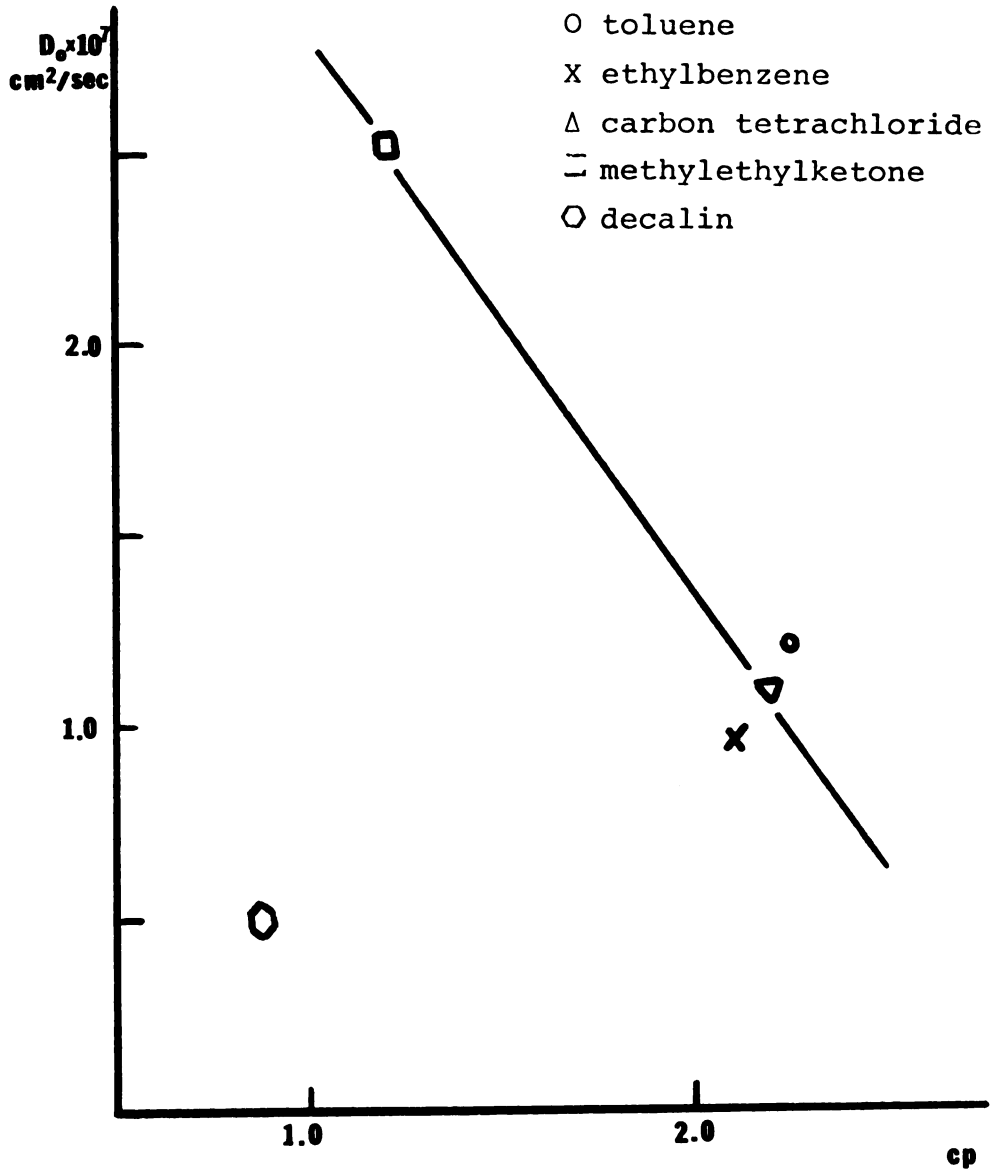


Figure 27. Relationship between the diffusion coefficient and the intrinsic viscosity of different polystyrene solutions (M_W = 680,000).

solubility parameters of polystyrene and methylethylketone and benzene shows that benzene is a very "good" solvent and methylethylketone is a relatively "poor" solvent.

The dissolved polymer molecules in "good" solvents are expanded more than in "poor" solvents, because the segments of polymers associate better with the solvent molecules than with each other. This expansion can be defined as:

$$\alpha = \left(\frac{\bar{r}^2}{\bar{r}_o^2} \right)^{\frac{1}{2}} , \qquad 19.$$

where $(\bar{r}^2)^{\frac{1}{2}}$ is the actual root-mean-square end-to-end distance, $(\bar{r}_o^2)^{\frac{1}{2}}$ is the root-mean-square end-to-end distance for the unperturbed or unswollen dimension, and α is the expansion factor (Rodriguez, 1970). A relationship between the intrinsic viscosity and the expansion factor is given by Flory (1953):

$$[\eta] = \Phi \left(\frac{\bar{r}_o^2}{M} \right)^{\frac{3}{2}} M^{\frac{1}{2}} \alpha^3 , \qquad 20.$$

where $[\eta]$ is the intrinsic viscosity, Φ is a universal constant and M is the molecular weight.

It can be seen for a polymer with a given molecular weight, Equation 20 can be written as

$$[\eta] = C \alpha^3 , \qquad 21.$$

where C is constant and independent of the solvent.

Therefore, the ratio of two intrinsic viscosities measured in two different solvents at the same temperature is equal to the cube of the ratio of the corresponding expansion factors. Using the intrinsic viscosity data for polystyrene published by Kurata (1963), it was found that α in benzene is about 1.2 times larger than in methylethylketone, which means the volume of a polymer molecule in benzene is about 1.7 times larger than in methylethylketone. The diffusion coefficient is inversely proportional to the volume of the polymer molecules (similar to Stokes-Einstein equation shown earlier), so a higher diffusion coefficient is expected for polystyrene in methylethylketone than in benzene. The data of this work agree with this expectation. Generally speaking, the diffusion coefficient in a "poor" solvent for a given polymer is larger than in a "good" solvent.

Decalin is a poor solvent for polystyrene. The theta temperature of a mixture of trans and cis decalin, 19.3°C, is given by Okada et al. (1963). (The theta temperature, sometimes called the Flory temperature, is approximately the temperature at which a polymer of infinite molecular weight would precipitate from the solvent.) Close to the Θ temperature the volume of the polymer molecules in solution is the smallest (unperturbed or unswollen dimensions). The experimental temperature of this work was 21°C, which

is very close to the Θ temperature, so it can be said that the volumes of the polystyrene molecules in decalin had to be a minimum. Therefore, the diffusion coefficient of polystyrene measured in decalin at that temperature should have been the highest among the diffusion coefficients obtained from measurements in different solvents. Looking at Tables 6 and 8, it can be seen that this is not true, the diffusion coefficient of polystyrene measured in decalin is extremely low, the lowest one among all of the diffusion coefficients measured in different solvents, which seems to be contradictory to the theoretical interpretation of the diffusion of polymers in dilute solution.

Considering the fact that two diffusion measurements of polystyrene in decalin, based on different test methods (diffusion cell, Schick, 1950; lightbeating spectroscopy, this work) gave approximately the same results, the probability of error in the measurements is reduced. Therefore, a simple hypothetical explanation of this problem will be given here without detailed proof, future study may improve our understanding of this phenomenon.

The extremely low diffusion coefficient of polystyrene in decalin may have arisen from the fact that the volume of polystyrene molecules is large in decalin. But this is the opposite of what the theory says: the volume of a polymer molecule is the smallest in a poor solvent or very

close to the Θ temperature. However, this is true for one polymer molecule only. It is proposed that agglomeration occurs in polystyrene-decalin system, so the total volume of an average agglomerate is greater than the volume of one molecule in the best solvent. This results in a very low diffusion coefficient for polystyrene in decalin. Many polystyrene molecules stick together (the solvent molecules are not able to separate them), so they move much slower, and their slow movement gives a very low diffusion coefficient. Increasing the concentration of polystyrene results in an increase in the number of the molecules per agglomerate, which leads to a lower diffusion constant and results in a negative K_D. The low viscosity also can be explained. Any viscosity measurements unlike the diffusion measurement, are related to the solution properties instead of those of one polymer molecule itself. Comparing two solutions, polystyrene-benzene and polystyrene-decalin (close to Θ temperature) for the same concentration the number of polymer molecules is the same in both solutions. Regardless of whether the polymer molecules may agglomerate, their total volume in decalin is equal to the number of molecules times their minimum volume. In benzene the polystyrene molecules are extended, so their total volume is equal to number of molecules times the extended volume of each molecule and this total volume is much greater than

the total volume in decalin. Since the viscosity is related to the solution, this higher total volume of polymer molecules in benzene results in a higher viscosity. This means that the simple model given here, which says the polystyrene molecules agglomerate in decalin, explains the extraordinary behavior of dilute decalin solutions of polystyrene close to the Θ temperature. Furthermore, the external shearing imposed upon the system, when measuring viscosity, would tend to break up the polymer agglomerates.

General comments about the relationship between solvents and diffusion coefficients of polymers were given earlier, so the results of this work will now be compared with literature data. The diffusion coefficient of polystyrene in decalin was discussed earlier.

In the previous section a range of D_o of 1.15 to 1.35 x 10^{-7} cm^2/sec is given for polystyrene M_w = 3.38 x 10^5 in benzene. Elias (1961) reported D_o = 1.50 x 10^{-7} cm^2/sec for M_w = 6.06 x 10^5 for the same system. A comparison of the two values shows the D_o from the literature considering the molecular weight difference is a little bit higher than the value calculated in this work. D_o data for polystyrene in methylethylketone at 20°C given by Gralen and Lagermalin (1952), Mayerhoff (1960), and Schick and Singer (1950) compared with the D_o range of this work are shown below:

$D_o \times 10^7$ cm^2/sec.	$M_w \times 10^{-5}$	Source
3.25	5.28	Meyerhoff
6.40	1.8	Gralen
5.14	2.4	Schick
2.70-3.00	1.3	This work

It can be seen that the D_o given by this work is lower than the literature data. This difference may have arisen from the fact that lower concentrations were used in this work than in others, which means to determine D_o, points closer to zero concentration were used. In other studies in the future the diffusion coefficient below 0.01 g/100g concentration should be measured for a more accurate determination of D_o.

Duffusion coefficient data for polystyrene-dimethylformamide were not found in the literature. According to the author's best knowledge no diffusion coefficient measurements have been made for polystyrene-acrylonitrile copolymer in dilute solution. Therefore the data of this work cannot be compared with others.

The exact relationship between the diffusion coefficient of polystyrene-acrylonitrile copolymer in dilute solution and the acrylonitrile content of the copolymer cannot be established based on this study, because of the difference in molecular weights of the samples. But comparing

diffusion data for polystyrene and copolymer, as was mentioned in the previous chapter, it can be concluded that the arcylonitrile content of the copolymer increases the diffusion in dilute solutions of methylethylketone. In benzene the acrylonitrile content of the copolymer reduces the molecular weight dependence of the diffusion coefficient of polystyrene.

It is very interesting to compare the value of D_o for polystyrene, polystyrene-acrylonitrile copolymer and polyacrylonitrile in dimethylformamide.

	$D_o \times 10^7$ cm^2/sec.	Molecular Weight	Source
Polystyrene	1.00-1.25	271,000	This work
Polyacrylonitrile	1.25	270,000	Bisschops (1955)
Polystyrene/acrylonitrile copolymer	1.10-1.30	275,000	This work

It can be seen that D_o is about the same for polystyrene and polyacrylonitrile in dimethylformamide and D_o remains about the same for their copolymer. Of course there is a possibility of a coincidence, and this problem can be the subject of future work.

Figure 28. Photocurrent spectrum of light scattered from polystyrene latex at 35° scattering angle.

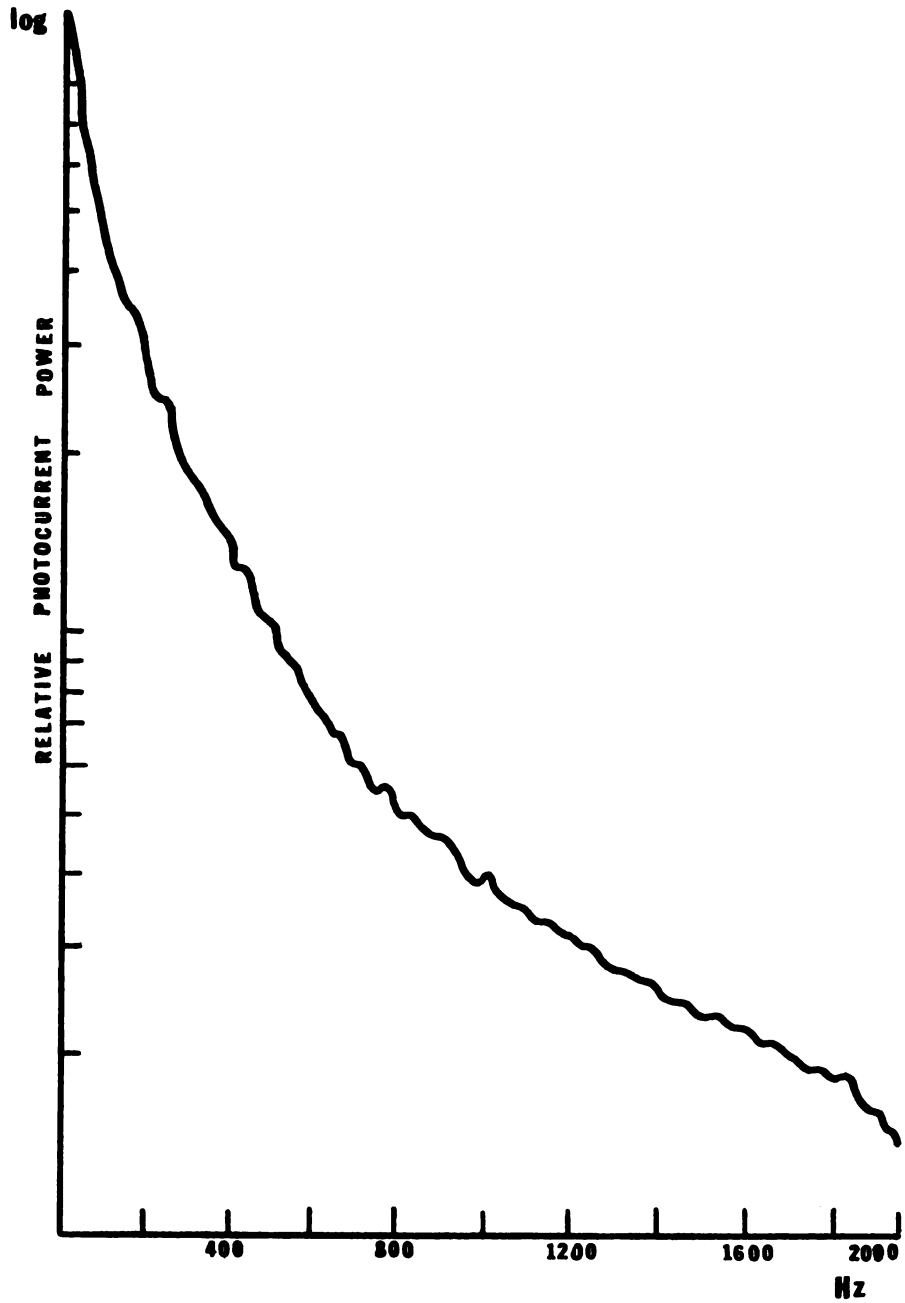


Figure 29. Photocurrent spectrum of light scattered from polystyrene-acrylonitrile copolymer (M_W = 332,000, acrylonitrile content 38%) in dimethylformamide (c = 1.0 g/100g). Scattering angle 25°. Halfwidth 255 Hz. (D = 1.44 x 10^{-7} cm^2/sec)

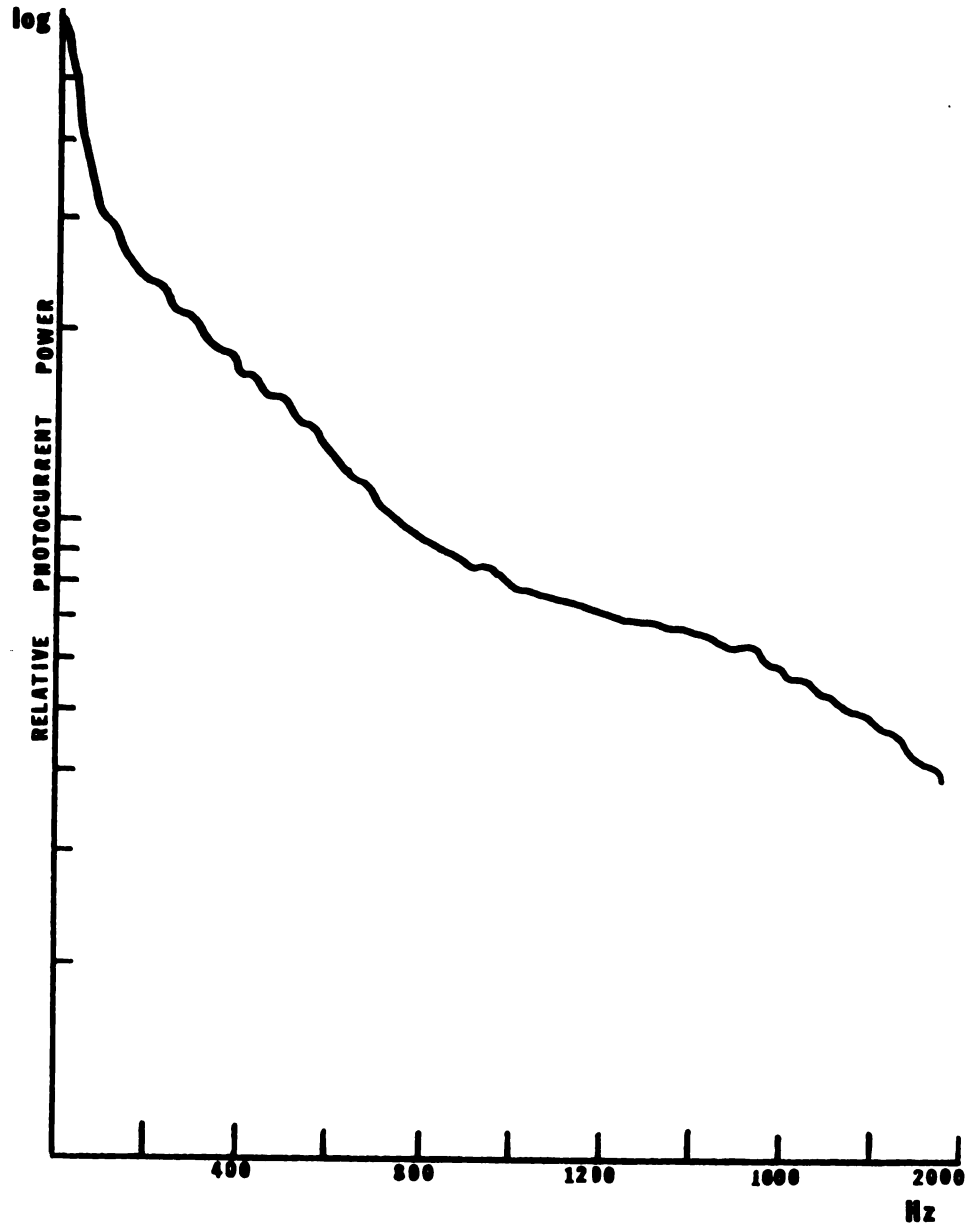


Figure 30. Photocurrent spectrum of light scattered from polystyrene-acrylonitrile copolymer (M_W = 332,000, acrylonitrile content 38%) in dimethylformamide (c = 1.0 g/100g). Scattering angle 35°. Halfwidth 496 Hz. ($D = 1.46 \times 10^{-7}$ $cm^2/sec.$)

APPENDIX

APPENDIX

Program IG4 is used to determine the best values of A, B, and D in Equation 13 from a set of photocurrent power versus frequency data. Briefly, a simple algebraic technique was devised to find the least squares solution for A and D given a specific value of B, the halfwidth. This is done in subroutine FUNC. The program steps through the whole range of possible B values to bracket the optimum, and then goes into a golden search, using subroutine GOLD, to find the best value of B to any desired precision.

```
      PROGRAM IG4(INPUT,OUTPUT,TAPE2=INPUT,TAPE3=OUTPUT)
C
      DIMENSION BMIN(10)
      COMMON AI(50), W(50), N
      CALL NOBLANK
C
      READ(2,300) NSETS
      WRITE(3,310) NSETS
      DO 190  ISET=1,NSETS
C
      READ(2,320) BMIN
      READ(2,300) N,WZR, DELW
      WRITE(3,330) BMIN
      WRITE(3,340) N,WZR, DELW
C
      N2=(N+96)/49
      IF(N2 - 2) 80,90,80
   80 CALL EXIT
   90 READ(2,350) (AI(I),I=1,N)
      DO 100  I=1,N
      W(I)=WZR + DELW*(I-1)
  100 CONTINUE
C
      READ(2,210)  BZ,BM,DB,PRINT
      BMX=BM
C
  105 WRITE(3,240)
      WRITE(3,220) BZ,BM,DB,PRINT
      WRITE(3,240)
C
      B=BZ-DB
      BM=BM + 0.5*DB
      FLAG=1.0
      E=1.0E6
      I=1
C
  110 B=B + DB
      EP=E
      IF(B-BM) 115,160,160
  115 CALL FUNC(B,A,D,E)
      IF(PRINT) 125,125,120
  120 WRITE(3,230)  B,A,D,E
  125 IF(FLAG*(EP-E)) 130,110,110
  130 FLAG=-FLAG
      IF(FLAG) 140,110,110
  140 BMIN(I)=B - DB
      I=I+1
      IF(I-11) 110,150,150
  150 WRITE(3,370) BMIN
      I=1
```

```
      GO TO 110
  160 K=I-1
      WRITE(3,240)
      M=2.0*ALOG(2000.0*DB) + 2.0
      WRITE(3,390) M, (BMIN(J),J=1,K)
      DO 185  J=1,K
      BM=BMIN(J)
      BL=BM - DB
      BH=BM + DB
      CALL GOLD(BL,BH,BM,E,M)
      WRITE(3,240)
      DEL=(BH-BL)*0.5
      BM=BL + DEL
      CALL FUNC(BM,A,D,E)
      WRITE(3,230)  BM,A,D,E,DEL
      WRITE(3,360)
      E2=0.0
      DO 170  I=1,N
      X=W(I)/BM
      STAR=A/(1.0 + X*X) + D
      EX=(STAR - AI(I))/AI(I)
      E2=E2 + EX*EX
      WRITE(3,370) W(I), AI(I), STAR, EX
  170 CONTINUE
      IF(ABS(E2-E) - 1.0E-5) 185,180,180
  180 WRITE(3,380) E2, E
  185 CONTINUE
  190 CONTINUE
      CALL EXIT
C
  210 FORMAT(8F10.3)
  220 FORMAT(10X,4F10.3)
  230 FORMAT(10X,2F15.4,3F15.6)
  240 FORMAT(/)
  300 FORMAT(I3,7X,2F10.3)
  310 FORMAT(////,I10,13H SETS OF DATA)
  320 FORMAT(10A8)
  330 FORMAT(1H1,//,10X,10A8)
  340 FORMAT(//,I9,21H POINTS FROM OMEGA = ,F6.1,
     4  14H    IN STEPS OF,F8.1)
  350 FORMAT(10F6.2)
  360 FORMAT(///,15X,5HOMEGA,5X,5HI-EXP,4X,
     6  6HI-CALC,5X,4HE(I))
  370 FORMAT(10X,3F10.2,F12.6)
  380 FORMAT(//,10X,15HERROR IN E-CALC,2F15.10)
  390 FORMAT(/,10X,I5,24H = NO. OF GOLD SEARCHES ,
     9  13HAT EACH OF...,5F14.3,1,49X, 5F14.3)
C
      END
```

LIST OF REFERENCES

LIST OF REFERENCES

Angus, J. C., D. L. Morrow, J. W. Dunning, and M. J. French, 1969. Ind. Eng. Chem., 61-2, 8.

Arecchi, F. T., M. Giglio, and V. Tartari, 1967. Phys. Rev., 163, 186.

Bandrup, J. and E. H. Immergut, 1966. "Polymer Handbook," John Wiley & Sons, New York.

Billmeyer, F. W., 1971. "Textbook of Polymer Science," Wiley-Interscience, New York.

Bisschops, G., 1955. J. Polym. Sci., 17, 81.

Carew, E. G., J. T. Hicmott, and L. Rimai, 1969. Biophys. J., 9, A212.

Chu, B., N. Kuwahara, and M. Tansky, 1969. J. Chem. Phys., 51, 2449.

Clifford, W. H. Private communications.

Cummins, H. Z. and H. L. Swinney, 1970. In "Progress in Optics," Vol. 8., E. Wolf, Ed., North Holland, Amsterdam-London.

Cummins, H. Z., N. Knable and Y. Yen, 1964. Phys. Rev. Letters, 12, 150.

Cummins, H. Z., F. D. Calcon, T. J. Herbert and G. Woods, 1969. Biophys. J., 9, 518.

Dubin, S. B., J. H. Lunacek, and G. B. Benedek, 1967. Proc. Natl. Acad. Sci., U.S., 57, 1164.

Dubois, M., P. Berge, and C. Laj, 1970. Chemical Physics Letters, 6, 227.

Elias, H. G., 1961. Makromol. Chem., 50, 1.

Flory, P. J., 1953. "Principles of Polymer Chemistry," Cornell, Ithaca, ch. 16.

Ford, N. C. and G. B. Benedek, 1965. Phys. Rev. Letters, 15, 649.

Ford, N. C., W. Lee, and F. E. Karasz, 1969. J. Chem. Phys., 50, 3098.

Forrester, A. T., 1961. J. Opt. Soc. Am., 51, 253.

Frank, H. P. and H. F. Mark, 1955. J. Polymer. Sci., 17, 1.

Frederick, J. E., T. F. Reed, and O. Kramer, 1971. Macromolecules, 4, 242.

French, M. J., J. C. Angus, and A. G. Walton, 1969. Science, 163, 345.

Gaumer, S. J., 1972. Ph.D. Thesis, Michigan State University.

Gralen, N. and G. Lagermalm, 1952. J. Phys. Chem., 56, 514.

Hansen, C. M., 1967. J. Paint Techn., 39, 104.

Kramer, O., 1971. Ph.D. Thesis, University of Akron.

Kumar, A., 1973. Ph.D. Thesis, Michigan State University.

Kurata, M. and W. H. Stockmayer, 1963. Fortschr. Hockpolymer.-Forsch., 3, 196.

Lee, S. P., W. Tcharnuter, and B. Chu, 1972. J. Polym. Sci., 10, 2453.

Meyerhoff, G., 1964. Makromol. Chem., 72, 214.

Morawetz, H., 1965. "Macromolecules in Solution," Interscience, New York.

Nordhaus, D., 1973. Ph.D. Thesis, Michigan State University.

Ohbayashi, K., S. Kagoshima, and A. Ikushima, 1972. Japanese J. of Applied Phys., 11, 808.

Pecora, R., 1964. J. Chem. Phys., 40, 1604.

Pecora, R., 1965. J. Chem. Phys., 43, 1562.

Pecora, R., 1968a. J. Chem. Phys., 48, 4126.

Pecora, R., 1968b, J. Chem. Phys., 49, 1032.

Pecora, R. and Y. Tagami, 1969a. J. Chem. Phys., 51, 3293.

Pecora, R. and Y. Tagami, 1969b. J. Chem. Phys., 51, 3298.

Rayleigh, Lord (J. W. Strutt), 1871. Phil. Mag., 41, 107, 274, 447.

Reed, T. F., 1970. Ph.D. Thesis, University of Akron.

Reed, T. F. and J. E. Frederick, 1971. Macromolecules, 4, 72.

Rimai, L., J. T. Hickmott, T. Cole, and E. B. Carew, 1970. Biophys. J., 10, 20.

Rodriguez, F., 1970. "Principles of Polymer Systems," McGraw-Hill, ch. 7.

Scheflan, L. and J. B. Jacobs, 1953. "The Handbook of Solvents," D. Van Nostrand.

Stiso, S. N., 1972. Ph.D. Thesis, Michigan State University.

Stutesman, W. D., 1972. M.S. Thesis, Michigan State University.

Stutesman, W. D. and R. F. Blanks, 1973. Unpublished work.

Thompson, D. S., 1971. J. Chem. Phys., 54, 1411.

Toth, W., 1973. Ph.D. Thesis, Michigan State University.

Van Hove, L., 1954. Phys. Rev., 95, 249.

Wada, A., N. Suda, T. Tsuda, and K. Soda, 1969. J. Chem. Phys., 50, 31.

Williams, C. S. and O. A. Becklund, 1972. "Optics," Wiley-Interscience, New York.