DETERMINATION OF DIFFUSION COEFFICIENTS OF POLYSTYRENE AND POLYETHYLENE OXIDE IN DILUTE SOLUTIONS BY LIGHT BEATING SPECTROSCOPY

> Thesis for the Degree of M. S. MICHIGAN STATE UNIVERSITY THOMAS JOHN NELSON 1974

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THESIS

ABSTRACT

DETERMINATION OF DIFFUSION COEFFICIENTS OF POLYSTYRENE AND POLYETHYLENE OXIDE IN DILUTE SOLUTIONS BY LIGHT BEATING SPECTROSCOPY

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Thomas John Nelson

The diffusion coefficients of polystyrene and polyethylene oxide in several solvents were measured as a function of molecular weight and concentration using the light beating spectroscopic method. The measurements were made using an optical homodyne spectrometer which incorporated a single mode ion laser as a light source.

Diffusion coefficients determined by light beating spectroscopy and those calculated from the Stokes-Einstein equation for polystyrene spheres in water were found to be in good agreement. The average experimentally determined value for the diffusion coefficient of polystyrene spheres in water was $4.33 \times 10^{-8} \text{ cm}^2/\text{sec}$. The diffusion coefficient of polystyrene spheres in water calculated from the Stokes-Einstein equation at a temperature of 21°C was found to be $4.1 \times 10^{-8} \text{ cm}^2/\text{sec}$. This agreement between the theoretically and experimentally determined diffusivity values of polystyrene spheres in water demonstrated the reliability of the light beating spectroscopic technique, and was the basis for calibration of the instrumentation.

Values determined for the diffusion coefficients of polystyrene in benzene and decalin were found to agree with values reported in other works. Diffusion coefficients of polystyrene were also measured in toluene. The diffusivity of polyethylene oxide in water and carbon tetrachloride was determined for the first time in this work using the light beating technique.

The diffusivity of polystyrene in benzene was found to be generally higher than that of polystyrene in either toluene or decalin. Diffusion coefficients for polystyrene in toluene ranged from 5% to 40% lower than those determined in benzene. The lowest values for the diffusion coefficients of polystyrene were found in decalin. Diffusion coefficients of polyethylene oxide were found to be approximately 15% higher in carbon tetrachloride than in water.

The experimental measurements did not provide a clear determination of the concentration dependence of the diffusion coefficients for the polymer-solvent systems studied. The results were varied for different solvents and polymer molecular weights over the concentration ranges which were examined. In many cases, the diffusion coefficient increased with a decrease in polymer concentration. Lower values of diffusivity were generally obtained for systems with a higher polymer molecular weight. The results obtained in this work agreed with theoretical expectations concerning the behavior of polymer molecules in dilute solution as presented in other works.

DETERMINATION OF DIFFUSION COEFFICIENTS OF POLYSTYRENE AND POLYETHYLENE OXIDE IN DILUTE SOLUTIONS BY LIGHT BEATING SPECTROSCOPY

By

Thomas John Nelson

A THESIS

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

MASTER OF SCIENCE

Department of Chemical Engineering

To my family, and to my fiancee, Sherry, and her family.

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INTRODUCTION

The technique of light beating spectroscopy has its origin in the work of A. Forrester in 1947 and 1948. (1, 2) He proposed that if two light waves of nearly the same frequency were superimposed an electromagnetic beat signal would be produced which could be detected by a nonlinear detector. Useful applications of this concept came with the development of the modern laser. The extremely narrow linewidth of the laser allowed the detection of very small frequency shifts. This high level of sensitivity made possible the study of the motion of solute particles in solution through the use of a laser light beating spectrometer.

In 1963, Cummins, Knable, and Yeh reported the development of an optical heterodyne spectrometer, in which light scattered from a solution was mixed with unscattered laser light. (3) An optical homodyne or self-beat spectrometer was later developed by Ford and Benedek. (4) This instrument consisted of a laser, a photoelectric detector, and a wave analyzer. The scattered light reflected on the photoelectric detector has a frequency distribution. The components of this spectrum beat with each other causing fluctuations in the output of the photoelectric detector which can be analyzed by the wave analyzer. Thus it is possible to study such

phenomena as the fluctuations of the dielectric constant of a solution caused by the Brownian motion of solute molecules in the solution using a laser light beating spectrometer.

These light beating systems have already been used for many applications such as measuring the translational diffusion coefficient of monodisperse polystyrene spheres in dilute solutions (5, 6, 7, 8, 9), measurements on biological macromolecules (6, 9, 10) and polystyrene solutions (6, 7, 11). Diffusion coefficients have also been obtained for polyacrylamide in aqueous solution (12), and for copolymers of styrene and acrylonitrile (13) using the light beating technique.

The diffusion coefficients which have been reported in these works were found to be in good agreement with values obtained for diffusivity using other methods. The theoretical relationship between the spectral distribution of light scattered from a polymer solution and the diffusion coefficient of the polymer molecules in the solution was provided by Pecora in 1964. (14) He has developed theories predicting the analytical form of the spectrum of light scattered from spheres, rods, flexible-coil macromolecules in the free draining approximation of the pearl-necklace model, and Gaussian coils (14-21).

The aforementioned models have become important in the theoretical treatment of the diffusion of polymer molecules in dilute solution. The frictional properties of polymer

chain molecules in solution have been examined through the use of a pearl necklace model of the polymer chain, in which rigid beads are imagined to be connected by infinitely thin linkages. (22) As an approximation to the true behavior of the polymer chain in solution, limiting cases of this model have been considered. In the first case, the beads are relatively far from one another, so that the disturbances of the flow caused by the individual beads may be considered not to interact. This model is generally referred to as the free draining coil. If such a coil is forced to move through a viscous liquid, the frictional resistance to which it will be subjected will be proportional to the number of units composing it.

The second limiting case of the pearl necklace model is known as the hydrodynamically equivalent sphere. (22, 26) In this model, the interactions between flow disturbances are so large that the solvent is effectively trapped within the coil, which may be treated as a rigid sphere. The radius of this equivalent sphere, R, controlling the frictional resistance to linear translation, will be proportional to some characteristic dimensions of the coil, such as the root-mean-square radius of gyration $\langle s^2 \rangle^{1/2}$. Using the equation of Stokes for the frictional coefficient of spheres moving through a fluid,

$$f_{coil} = 6\pi\eta_0 R = 6\pi\eta_0 C < s^2 > 1/2$$

where n_0 is the solvent viscosity and C is a characteristic constant. In a O-solvent (a poor solvent), where $\langle s^2 \rangle^{1/2}$ is proportional to the chain length of the molecule, this equation predicts that the frictional coefficient of chain molecules should increase as the square root of their molecular weight. In better solvents, where the molecular coil is more expanded, the frictional coefficient assumes correspondingly higher values.

The diffusion coefficient can be related to the frictional coefficient, the concentration, and the activity coefficient of the solution by: (12, 22)

$$D = \frac{KT}{f} \left(1 + \frac{\alpha \ln \gamma_i}{\alpha \ln C_i}\right)$$

Y_i = activity coefficient
C_i = concentration
f = frictional coefficient
K = Boltzmann's constant

This equation relates deviations in solution ideality to the effect of concentration changes on the diffusion coefficient, and is valid if the solution is sufficiently dilute. Good agreement has been demonstrated between measured diffusion coefficients of small spherical molecules and those calculated by the above equation.

In this work, the polymer molecule will be treated as an isolated hydrodynamically equivalent sphere whose motion

consists of translational diffusion alone. The purpose of this investigation was to use the light beating spectroscopic method to measure the translational diffusion coefficients of polystyrene in benzene, toluene, and decalin, and polyethylene oxide in water and carbon tetrachloride for a variety of polymer concentrations and molecular weights. The diffusion coefficients of polystyrene were measured to compare with previously reported values. The diffusion coefficients of polyethylene oxide determined by light beating spectroscopy are reported for the first time in this work.

THEORY

The phenomenon of light scattering occurs as a result of inhomogeneities in the optical properties of the scattering medium. This type of scattering is termed Rayleigh scattering. (23) In solutions these inhomogeneities are due to time dependent random molecular motions which produce local fluctuations in the dielectric constant. The frequency of light scattered by these fluctuations exhibits a spectrum characteristic of the time dependence of the fluctuation.

The spectrum of the scattered light may be related to the autocorrelation function, $C(\tau)$, of the electric field of the light. (24) This autocorrelation function is the time average of the product of the signal, at any time t, with the signal at any time t + τ .

 $C(\tau) = \langle E^*(t) E(t+\tau) \rangle$

 $E^{*}(t)$ = electric field at time t $E(t+\tau)$ = electric field at time t+ τ

An optical field may be characterized by such a function assuming random Gaussian statistics of the scattered field. For monochromatic light scattered by a dilute solution of scatterers, the Gaussian statistics have been shown to apply. (24)

Concentration fluctuations do not propagate through the medium, but decay exponentially with time. Assuming that the light source is perfectly monochromatic, such as light produced by an ideal single mode laser, the electric field of the light reaching the photomultiplier tube of an optical homodyne, or self-beat, spectrometer is defined by

$$E(t) = E_0 e^{-iw_0 t}$$

E_o = amplitude of incident electric field
w_o = frequency of incident electric field
t = time

The expression for the amplitude of the electric field, E_0 , may be found from continuum theory. (25)

Using the Wiener-Khintchine theorem, (12, 23, 24)and the expression obtained for the electric field E(t), the power spectrum of the scattered light may be obtained from the autocorrelation function of the scattered field by a Fourier transform relationship

$$P(w) = (2\pi)^{-1} \int_{-\infty}^{\infty} C(\tau) e^{iwt} d\tau$$

P(w) = power spectrum of the scattered light
 falling on the photomultiplier tube

This expression results in a Lorentzian-shaped spectrum centered at w=w_o. The detailed expressions for $C(\tau)$ and E(t) may be found in other works. (12, 23)

The autocorrelation function of the scattered field (24) may be expressed as

$$C(\tau) = \langle I \rangle g^{(1)}(\tau)$$

 $\langle I \rangle$ = total intensity of the scattered light g⁽¹⁾(τ) = correlation function of scattered field

The correlation function of the scattered field is an expression which characterizes the optical field incident upon the surface of the photomultiplier tube. Similarly, the correlation function of the photocurrent, $g^{(2)}(\tau)$, characterizes the photocurrent power spectrum which results from the response of the photomultiplier tube to the incident scattered optical field. The correlation function of the photocurrent, $g^{(2)}(\tau)$, is related to the correlation function for the scattered field, $g^{(1)}(\tau)$, by

$$g^{(2)}(\tau) = 1 + |g^{(1)}(\tau)|^2$$

The relationships shown above may be used to obtain an expression for $C_i(\tau)$, the autocorrelation function written in terms of the photocurrent. (24)

The normalized correlation function of the scattered field, $\bar{g}^{(1)}(\tau)$, for monochromatic light scattered by a dilute solution of scatterers, will have the form

$$\bar{g}^{(1)}(\tau) = e^{-iw_o\tau}e^{-\gamma|\tau|}$$

Then the optical power spectrum of this field is given by

$$I(w) = \frac{\langle I \rangle}{2\pi} \int_{-\infty}^{\infty} e^{i(w-w_0)\tau} e^{-\gamma|\tau|} d\tau$$
$$= \langle I \rangle \frac{\gamma/\pi}{\gamma^2 + (w-w_0)^2}$$

which is a Lorentzian of half width at half-maximum $\Delta w_{1/2}$ (optical) = γ , centered at $w=w_0$, with total intensity <I>.

The photocurrent power spectrum associated with this field may be found from the previously mentioned relation-ships for P(w), $C_i(\tau)$, and $\bar{g}^{(1)}(\tau)$: (24)

$$P_{i}(w) = \frac{1}{2\pi} e^{\langle i \rangle} + \frac{\langle i \rangle^{2} f(w)}{\sqrt{w^{2} + (2\gamma)^{2}}} + \frac{2\gamma/\pi}{\sqrt{w^{2} + (2\gamma)^{2}}}$$

The photocurrent spectrum contains three components. The first, $\frac{e \langle i \rangle}{\pi}$, is a shot noise term which arises from the random emission of electrons from the photomultiplier tube surface when illuminated. The second, $\langle i \rangle^2 f^1(w)$, represents the d.c. portion of the photocurrent which is filtered out before spectral analysis. The third component is the light beating spectrum. This term is a Lorentzian of half width $\Delta w_{1/2}$ (photocurrent) = 2 γ and total power $\langle i \rangle^2$ centered at w=0. The original optical spectrum of half width $\Delta w_{1/2}$ (optical) = γ has produced a Lorentzian photocurrent spectrum of twice the optical width centered at w=0. The experimentally measured half width, $\Delta w_{1/2}$, is equal to $\frac{\gamma}{\pi}$ cycles per second. Measurement of the low frequency photocurrent spectrum (from w=0 to w $\approx 20\gamma$) permits an accurate determination of the width of the original optical line.

The parameter γ may be related to the translational diffusion coefficient by the continuum theory of scattering.(25) By assuming that concentration fluctuations in solution may be described by Fick's second law of diffusion, an expression may be found for γ . (12)

$$\gamma = D \left(\frac{2\pi}{\lambda_{f}}\right)^{2} = D\kappa^{2}$$

$$\kappa = \frac{2\pi}{\lambda_{f}}, \text{ the scattering vector}$$

$$D = \text{ translational diffusion coefficient}$$

The parameter λ_{f} can be related to the light beam incident on the sample and the scattering angle by Bragg's law,

 $\frac{\lambda o}{n} = 2\lambda_{f} \sin \left(\frac{0}{2}\right)$ $\lambda o = \text{wavelength of incident laser beam}$ 0 = scattering angle n = refractive index of the sample solution

The value γ can now be expressed as

$$\gamma = 1) \left[\frac{4\pi n \sin\left(\frac{0}{2}\right)}{\lambda o}\right]^2$$

Solving this expression for 1) and substituting $\Delta w_{1/2}$ for γ/π ,

. . .

$$D = \frac{\Delta w_{1/2} \left(\frac{\lambda o}{n}\right)^2}{16\pi \sin^2\left(\frac{\Theta}{2}\right)}$$

Therefore, it may be seen that the translational diffusion coefficient of macromolecules in solution can be determined with a homodyne spectrometer by measuring the half width of the Lorentzian photocurrent power spectra produced at a specific scattering angle. This expression for the diffusion coefficient assumes that the half width of the spectrum is due only to translational diffusion.

Pecora (15-21) has developed the expressions for the spectral distribution of light scattered from a dilute solution of rigid rods. His theory predicts a light spectrum consisting of a series of Lorentzians. The first term in the spectral distribution expression is equivalent to the results for spherically shaped macromolecules and gives a translational diffusion coefficient. The additional terms depend upon both translational and rotational diffusion. It was found that the rotational diffusion terms become increasingly important for light scattering from rigid rod macromolecules as the scattering angles become large (greater than 60°). Similarly, the spectral distribution of light scattered from macromolecules analyzed by the free draining coil model was found to consist of a series of Lorentzian terms. The relative importance of contributions to the light spectra of macromolecules in solution is given by Pecora in terms of a parameter from Gaussian chain statistics, χ , which is given by

$$\chi = \kappa^2 \quad <_{\rm S}^2 >$$

As χ increases, the relative importance of the second term in the spectral distribution expression increases. It has been shown that if χ is small, in particular smaller than 0.5, the Rayleigh spectrum consists of only a single Lorentzian related to the translational diffusion coefficient. If the value of χ is sufficiently small, the equation which has been presented for the translational diffusion coefficient,

$$D = \frac{\Delta w 1/2 (\frac{\lambda o}{n})^2}{16\pi \sin^2 (0/2)}$$

may be used in the analysis of dilute macromolecular solutions.

The mean square radius of gyration $\langle s^2 \rangle$ is given by the expression (27)

$$\langle s^2 \rangle = \frac{Nb^2}{6}$$

N = number of links in the chain in the pearl necklace model of polymer molecules

. . .

b = length of one link

For molecules with a carbon backbone, b is equal to the bond distance between two carbon atoms. The actual value of $\langle s^2 \rangle$, and therefore χ , will be larger than predicted by the above equation due to bond angle restrictions and rotation of segments of the polymer molecule. If χ is larger than 1.0 the Rayleigh spectrum consists of a series of Lorentzians which may be related to intra-molecular effects or polydispersity as well as to pure translational diffusion. In general, χ is small for small scattering angle and for typical polymer molecular weights. In this situation, the translational diffusion coefficients of macromolecules in dilute solution may be calculated using the expression for J which has been presented.

EXPERIMENTAL

Apparatus

The instrument used in this work to measure the diffusion coefficients of polystyrene and polyethylene oxide was a laser homodyne spectrometer. A schematic of this spectrometer is shown in Figure 1. The system consists of a laser light source, the sample scattering cell, light collecting optics, a spectrum analyzer and averager, and an X-Y recorder.

The laser which was used was a Spectra-Physics 'lodel 165 argon ion laser which operated with a single mode at 5145 Å. The laser light beam was reflected from its incident path by a mirror and directed through the center of a cylindrical sample cell. The sample cell was placed on a rotating table which was used to select the desired scattering angle. The incident laser light beam could be redirected through the center of the sample cell at any scattering angle by rotation and translation of the reflecting mirror on its moveable mount. All scattering angles from 0° to 180° were possible with this arrangement.





A Spectra-Physics Model 132 sighting laser was used to properly align the sample cell and light collection optics of the system. The optical collection system for the scattered light is shown in Figure 2. The light scattered from the sample cell at the desired angle was collected by a series of apertures, lenses, and pinholes and focused upon the surface of the photomultiplier tube. The photomultiplier tube which was employed was an EMI 9558 B tube. The photomultiplier tube was placed in a refrigeration chamber to reduce the level of dark, or background current. This system was chosen because of its high gain and low noise operation.

The photomultiplier tube was connected to the spectrum analyzer-averager system. The system which was chosen for use in this work was the Federal Scientific Corporation Model UA-14A spectrum analyzer and Model 1014 spectrum averager. This system provided "real time" analysis of the scattered light spectrum, analyzing the entire signal at one time. This spectrum analyzer is capable of measuring spectra on 12 frequency scales from 0-10 Hz to 0-50,000 Hz. In this work, spectra were measured in the frequency range of 0-5000 Hz. The spectrum analyzer provided 400 line resolution and a variety of output options. The analyzer was connected to the spectrum averager in order to improve the stability of the fluctuating signals of the scattering spectrum. The averager also provided



Figure 2. Light Collection Optics

signal to noise enhancement by increasing the amplitude of the signal relative to randomly fluctuating noise. The maximum number of successive spectra received from the spectrum analyzer which could be averaged in real time was 1924. All experimental measurements in this work were recorded at this level of averaging.

The output of the spectrum analyzer-averager system was a linear current voltage which was connected to an oscilloscope, for instantaneous display of the full spectrum, and to a Varian Associates F-80 X-Y recorder. The spectrum, which required approximately 45 seconds to be plotted, was recorded on linear graph paper.

Calibration

To insure the reliability of the data provided by the laser light beating homodyne spectrometer used in this work, the system was evaluated using a polystyrene latex as a scattering sample. A number of researchers have measured the diffusion coefficients of different sizes and concentrations of polystyrene latex spheres in water. (5, 28, 29) They have, in general, found good agreement between the calculated diffusion coefficients from the Stokes-Einstein equation

$$D = \frac{KT}{6\pi n_s R}$$

K = Boltzmann's constant^{...}
T = absolute temperature
n_s = solvent viscosity
R = radius of spheres

and the experimentally determined diffusion constants obtained from light beating spectroscopic analysis. The Stokes-Einstein relationship applies to the diffusion of small spheres in a liquid. (22)

The theoretical relationship between the translational diffusion coefficient of macromolecules in solution and the half width of the Lorentzian photocurrent power spectrum predicts that a plot of half width vs. $\sin^2(0/2)$, where 0 is the scattering angle, will result in a straight line through the origin. (12) In order to test this theoretical relationship, the light beating spectra of a solution of polystyrene latex spheres were measured at different scattering angles. The polystyrene spheres used in this work were obtained in latex form from the Dow Chemical Company. The latex material was 10% (by weight) polystyrene in water, with a polystyrene sphere diameter of 1090 \AA . The concentration of the latex was reduced to .01% solids by adding distilled and de-ionized water. Similar concentrations have been used in other works. (29) It has been

proposed that such a concentration is low enough to allow the individual particles to diffuse without any particle interference effects.

The results of measurements made on the sample of polystyrene latex spheres are shown in Table 1 and Figure 3. The value for the diffusion coefficient of the polystyrene spheres obtained from the Stokes-Einstein equation was $4.1 \times 10^{-8} \text{ cm}^2/\text{sec}$ at 21°C. The average value of the diffusion coefficient which was experimentally determined for the spheres was $4.33 \times 10^{-8} \text{ cm}^2/\text{sec}$. This value was obtained from the average of the diffusion coefficients calculated from the half widths at each scattering angle.

The half widths which were measured satisfied the theoretical relationship of linearity which was previously mentioned (Figure 3). The data analysis technique will be discussed in the data reduction portion of this work. The linearity of the results, and the good agreement between calculated and experimental diffusion constant values were used to establish the calibration of the light beating spectrometer.

Sample Preparation

I. Dust Particles in the Polymer Solution

The accuracy of the light beating spectroscopic measurements made on dilute solutions of macromolecules

light scattered from polystyrene spheres in water.									
Scattering angle	Halfwidth (Hz)	Diffusion Coefficient (x 10 ⁸ cm ² /sec)							
30°	92	4.09							
45°	227	4.62							
60°	360	4.29							

Table 1.--Halfwidths, and corresponding diffusion coefficients, of light beating spectra of light scattered from polystyrene spheres in water.

. . .



Figure 3. Angular dependence of half width of the lightbeating spectrum of polystyrene spheres in water.

is dependent to a great extent on the amount of dust in the sample solution. Dust is a very effective scatterer of light, and will introduce error into the measurement of the scattered light spectrum of polymer molecules. Dust may be introduced into the solution by the polymer or the solvent, or may become a problem during solution preparation.

The most common previously used methods of dust removal from macromolecular solutions analyzed by light beating spectroscopy were filtration and centrifugation. (12, 29) Both methods have been subjected to the criticism that, along with dust particles, polymer molecules are also removed during the process. (13) The pore size of the filter used in filtration of a polymer solution is critically important because the exact size of the polymer molecule in solution is unknown. Large polymer molecules may be filtered out of solution with dust particles. Similarly, centrifugation may tend to remove the larger polymer molecules, as well as large dust particles, from the polymer solution.

In order to determine an acceptable sample preparation procedure in this work, different dust removal techniques were used on samples which were otherwise identical. Three sets of samples of polystyrene in benzene were prepared and processed with different dust removal methods. Each set consisted of four samples: polystyrene of two different

molecular weights and two concentrations in benzene. The first set of samples was centrifuged at 40,000 RPM for 2 hours using a Beckman Model L2-65B ultracentrifuge. The second set of samples was filtered with a 5 micron pore size Millipore filter. The third sample set was left unprocessed after the solutions were made.

The results of this analysis are presented in Table 2. While agreement between diffusion coefficients of samples which had been prepared by the three different dust removal methods varies throughout the table, a general agreement between the values may be observed. Furthermore, there is no evidence that any dust removal technique results in consistently lower or higher diffusion constant values than any other technique.

Therefore, it was concluded that centrifugation and filtration did not have a significant effect on the level of dust present in the samples under study. Given this conclusion, the unprocessed method of sample preparation was adopted for the samples in this work.

II. Preparation of Samples

The solutions of polystyrene and polyethylene oxide were made by diluting a stock solution with measured quantities of solvent. The concentrations of the stock solutions prepared were determined by the maximum concentration of each polymer in a particular solvent which was

le	chilques.		
Polystyrene Sample	Concentration (g/100g)	Diffusion Constant (x 10 ⁷ cm ² /sec)	Dust Removal Method
UC 010	3.0 0.5 3.0 0.5 3.0 0.5	1.66 2.06 1.70 2.10 1.73 2.09	CEN CEN IIF MF UN UN
UC 040	3.0 0.5 3.0 0.5 3.0 0.5 5	1.38 1.05 1.34 1.15 1.32 1.13	CEN CEN MF MF UN UN

Table 2.--Diffusion coefficients of polystyrene in benzene using different dust removal techniques.

CEN = Centrifugation
MF = Millipore filtration
UN = Unprocessed
desired for that polymer-solvent system. After being prepared, the stock solutions were mixed by an automatic shaking device, and then allowed to stand untouched for approximately a day. It was hoped that sedimentation of dust particles would occur during the period in which the samples were not moved.

The required solution volumes were then withdrawn from the stock solution with a pipette so that the lower portion of the stock solution was not disturbed or transfered into the final sample cells. These withdrawn solutions were then diluted with appropriate quantities of solvent in order to obtain the desired concentrations for the final samples The final solutions in the sample cells were also left undisturbed for approximately a day so that additional dust sedimentation might take place. The volume of liquid in which the light was scattered in the light beating experiments was always located in the upper 25% of the sample cell, in order to take advantage of any dust sedimentation which might have occurred. All samples which were used in the dust technique evaluation reported in the previous section were prepared in this manner before centrifugation or filtration.

The glassware and sample cells used were kept as clean as possible with acetone, distilled water, and appropriate solvents. Reagent and practical grades of solvent were used without additional purification. Water which was used as a solvent was distilled and deionized.

All samples were run within two days of preparation to minimize the effects of any polymer degradation with time. It was necessary to manually shake the stock solutions of polyethylene oxide in carbon tetrachloride while the solution flasks were run under warm to hot water. This was done in order to promote effective dissolution of the polymer in the solvent. The heating process was discontinued as quickly as possible to prevent the occurrence of polymer degradation.

EXPERIMENTAL PROCEDURE

The laser homodyne spectrometer system was carefully aligned before measurements were made. (12) The light beam from the sighting laser was aimed into the light collection system. A series of mounted pinholes and apertures was utilized to insure the definition of a straight optical path from the sighting laser to the surface of the photomultiplier tube. A lens was then placed along the optical path at a distance from the photomultiplier tube surface equal to its focal length. The lens was adjusted to focus the light on a pinhole placed immediately in front of the surface of the photomultiplier tube (shown in Figure 2).

The path of the main ion laser beam was then adjusted so the desired scattering angle could be measured. The position of the reflecting mirror was adjusted until the main laser beam was directed through the two pinholes on the rotating sample cell table. The position of the sample cell was adjusted until the sighting laser beam and the main laser beam passed directly through the center of the sample cell, with both beams in the same horizontal plane.

After the system was aligned, measurements were made with the room lights turned off to prevent stray

light from entering the system. The power supply to the laser was adjusted to 200mW. This level of power was large enough to result in a high signal to noise ratio in the recorded spectra. The high intensity of the laser was not, however, expected to produce any undesired thermal diffusion in the sample cells due to the short amount of time required by the real time analyzer. Samples were exposed to the laser light for a maximum of 3 to 4 minutes.

The spectrum analyzer-averager system was calibrated according to the operating instructions. The spectra were recorded on linear graph paper with the slowest writing speed available.

A single run consisted of measuring the spectra of a sample at a fixed scattering angle over two frequency ranges: 0-5000 Hz and 0-50,000 Hz. The latter range was used to estimate the background or shot noise term which was the major spectral component at high frequency. All solutions were measured at scattering angles of 30°, 45°, and 60°. Samples which were run were 3 molecular weights of polystyrene, each at concentrations (grams polymer/ 100 grams solvent) of 3.0, 1.0, 0.5, and 0.1 in benzene and toluene, and at concentrations of 0.5, 0.2, 0.1, and 0.05 in decalin. Also run were two molecular weights of polyethylene oxide at concentrations of 0.1, 0.05, 0.025, and 0.01 in water, and at concentrations of 0.05, 0.02, 0.01, and 0.005 in carbon tetrachloride. The molecular weights of the polymers used are given in Table 3.

	$M_{n} \times 10^{-3}$	M _w x 10 ⁻³
Polystyrene		
UC 010 UC 030 UC 040	37.9 102.7 117.8	80.0 271.0 338.0
Polyethylene Oxide		
WSR-205 WSR-301	-	627.58 3657.19

Table 3.--Molecular weights of polystyrene and polyethylene oxide used in this work.

UC = Union Carbide WSR = Union Carbide designation M_n = number average molecular weight M_w = weight average molecular weight

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DATA REDUCTION

The spectrum at a fixed scattering angle and frequency range was recorded on chart paper as a linear voltage amplitude. This amplitude was squared to obtain the desired photocurrent power spectrum P(w). The form P(w)is a Lorentzian centered at w=0 which can be described by the equation

$$P(w) = \frac{v(1)}{1 + \frac{w^2}{[v(2)]^2}}$$

Using the squared voltage amplitudes and the corresponding frequency values from the recorder plot, i.e., P(w) and w, values for the parameters v(1) and v(2) were determined. This was done by a least square computer fit of the data to the above equation, using a program Kinfit, which was developed by the Department of Chemistry at Michigan State University. The half width of the photocurrent spectrum, $\Delta w_{1/2}$, is equal to the parameter v(2). Therefore, the value obtained for v(2) was used in the equation for the translational diffusion coefficient

$$D = \frac{\Delta w_{1/2} (\frac{\lambda o}{n})^2}{16\pi \sin^2(\frac{O}{2})}$$

replacing $\Delta w_{1/2}$. With the refractive index of the solvents and the incident laser beam wavelength of 5145 Å the diffusion coefficient was calculated for each sample at a particular scattering angle.

In order to obtain an accurate fit of the data to the Lorentzian equation, the shot noise amplitude provided by the 0-50,000 Hz spectra for each sample was subtracted from each voltage amplitude (before squaring).

The average values of the diffusion coefficients of the samples were calculated by averaging the coefficients obtained from all the scattering angles for a particular sample. RESULTS

The average values of the measured diffusion coefficients for all polymer-solvent systems studied in this work are presented in Tables 4 and 5. The range of the diffusivities as a function of scattering angle is presented in graphic form in Figures 4 through 8. The complete set of half widths and diffusion coefficients calculated at each scattering angle for all polymer-solvent systems in this work may be found in the Appendix. The concentration and solvent dependence of the diffusion coefficients of polystyrene and polyethylene oxide at a particular molecular weight may also be determined from Figures 4 through 8. The molecular weight dependence of the diffusion coefficients of polystyrene and polyethylene oxide in different solvents is shown in Figures 9 and 10.

Polystyrene-Benzene

The largest values for the diffusion coefficient of polystyrene in the three solvents used in this work were found in benzene (see Figures 4 to 6). The differences between diffusion coefficients measured at different scattering angles for given samples of polystyrene in benzene were generally less than 20% of the corresponding average diffusivity values reported in Table 4. It is

Polystyrene Sample	Concentration (g/100g)	Diffusion Benzene	Constant x 10 ⁷ Toluene	cm ² /sec Decalin
UC 010	3.0 1.0 0.5 0.2 0.1 0.05	1.75 2.01 2.10 2.56	1.39 1.20 2.00 2.18	0.80 0.73 0.89 0.94
UC 030	3.0 1.0 0.5 0.2 0.1 0.05	1.39 1.46 1.41 1.42	1.33 1.06 0.93 1.17	0.68 0.78 0.83 0.85
UC 040	3.0 1.0 0.5 0.2 0.1 0.05	1.30 1.14 1.12 1.29	1.28 1.06 1.07 1.11	0.58 0.60 0.72 0.77

Table 4.--Diffusion constants of polystyrene in different solvents.

Polyethylene Oxide Sample	Concentration (g/100g)	Diffusio Water	n constant x 10 ⁷ cm ² /sec Carbon tetrachloride
WSR-205	$\begin{array}{c} 0.10 \\ 0.05 \\ 0.025 \\ 0.02 \\ 0.01 \\ 0.005 \end{array}$	0.23 0.27 0.25 0.33	- 0.35 0.40 0.44
WSR-301	$\begin{array}{c} 0.10 \\ 0.05 \\ 0.025 \\ 0.02 \\ 0.01 \\ 0.005 \end{array}$	0.24 0.24 0.26 0.28	0.28 - 0.34 0.38

Table 5.--Diffusion constants of polyethylene oxide in different solvents.



Figure 4. Range of diffusion coefficients of UC 010 polystyrene in different solvents calculated at different scattering angles.



Figure 5. Range of diffusion coefficients of UC 030 polystyrene in different solvents calculated at different scattering angles.



Figure 6. Range of diffusion coefficients of UC 040 polystyrene in different solvents calculated at different scattering angles.



Figure 7. Range of diffusion coefficients of WSR-205 polyethylene oxide in different solvents calculated at different scattering angles.



Figure 8. Range of diffusion coefficients of WSR-301 polyethylene oxide in different solvents calculated at different scattering angles.



Figure 10. Diffusion coefficient of polyethylene oxide as a function of molecular weight in different solvents and at different concentrations.



Figure 9. Diffusion coefficient of polystyrene as a function of molecular weight in different solvents and at different concentrations.

this range of diffusivities measured at different scattering angles which appears for all samples in Figures 4 to 8.

The diffusion coefficient of polystyrene in benzene tended to increase with a decrease in polymer concentration for the smallest molecular weight polystyrene sample examined (see Figure 4). For the remaining polystyrene samples the concentration dependence of the diffusion coefficient was not precisely defined by the experimental results (see Figures 5 and 6). The diffusion coefficient of polystyrene in benzene tended to decrease with increasing molecular weight in the concentration range which was used (see Figure 9).

Polystyrene-Toluene

The diffusion coefficients of polystyrene in toluene were consistently lower than those recorded in benzene (see Figures 4 to 6). Diffusivity values of polystyrene measured in toluene ranged from 5% to 40% below the values of the diffusion coefficients of polystyrene measured in benzene for corresponding concentrations and molecular weights.

The diffusion constants of polystyrene in toluene tended to decrease with increasing polystyrene molecular weight (see Figure 9). The relationship between diffusivity and concentration in toluene was not apparent from the data, although the diffusion coefficient at the lowest molecular weight polystyrene appeared to increase with decreasing concentration (see Figures 4 to 6).

The differences between diffusion coefficients measured at different scattering angles for given samples of polystyrene in toluene were generally less than 15% of the corresponding average diffusivity values reported in Table 4.

Polystyrene-Decalin

The smallest values for the diffusion coefficient of polystyrene were found in decalin (see Table 4). Although the changes were slight in many cases, the diffusion constants of polystyrene in decalin tended to decrease with increasing polystyrene molecular weight and with increasing concentration (see Figures 4, 5, 6, 9).

The differences between diffusion coefficients measured at different scattering angles for given samples of polystyrene in decalin were generally less than 25% of the corresponding average diffusivity values reported in Table 4.

Polyethylene Oxide-Water

The diffusion coefficients of polyethylene oxide in water appeared to be slightly smaller, in general, than the diffusivity values of polyethylene oxide recorded in carbon tetrachloride (see Figures 7 and 8). The diffusivities which were measured for polyethylene oxide in water decreased with increasing concentration, although the changes were slight (see Figures 7 and 8). The molecular weight dependence of the diffusion coefficients of polyethylene oxide in water was not apparent from the data (see Figure 10).

Polyethylene Oxide-Carbon Tetrachloride

The diffusion coefficients of polyethylene oxide in carbon tetrachloride appeared to be slightly larger than the values determined for polyethylene oxide in water, although the differences in the diffusivities measured in the two systems were small (see Figures 7 and 8). Some difficulty was encountered in obtaining useful spectra for two of the samples in this group (see Table 5). The polyethylene oxide would not remain dissolved in the carbon tetrachloride in these two samples, invalidating the experimental results. The remaining samples showed diffusion coefficients which tended to decrease with increasing concentration and with increasing molecular weight, although the changes were extremely slight (see Figures 7, 8, 10).

ERROR ANALYSIS

The major sources of error in this work were the preparation of samples and the method of obtaining and analyzing data.

Although good cleaning procedures were used at all times, it was inevitable that some level of dust concentration was present in the sample solutions. However, different dust removal techniques were found to have little effect upon the spectra which were recorded. Therefore, the total dust level, especially within the small scattering volume of solution, was assumed to be small. The failure of the dust removal techniques to affect the results of the measurements may indicate that the dust particle size was small. Small dust particles would, nevertheless, introduce error into the measurements and distort the results.

Difficulty was encountered in preparing acceptable solutions of polyethylene oxide in carbon tetrachloride at some of the higher concentrations used in this work. In preparing stock solutions of polyethylene oxide in carbon tetrachloride, the polymer tended to adhere to the sides of the container. The polymer and solvent were shaken under warm to hot water in a closed container for approximately

two hours in order to dissolve the polymer in the solvent. In some cases it was not possible to completely remove polymer from the container walls, and new solutions had to be prepared. This difficulty certainly led to uncertainty in the exact concentrations of polyethylene oxide in carbon tetrachloride.

A major problem in reporting accurate results from light beating spectroscopic measurements is the available method of data analysis. Spectra must be recorded on paper, and the corresponding values of voltage amplitude vs. frequency must be visually read from the plot. The real time analyzer-averager system greatly enhances the signal to noise ratio of the spectra. However, it is not possible to remove all irregularities from the spectra. A typical recorded spectra is shown in Figure 11. Amplitude data is limited to two significant figures, and obtaining an accurate value for the shot noise (amplitude of plot at very high frequency, representing system noise) is not simple. The values which were used for the shot noise term, which was subtracted from the total spectra, were obtained from spectra recorded at a frequency range of 0-50,000 Hz. However, uncertainty in the reading of these values was again a problem.

Alignment of the optical system was also an important procedure for insuring accurate results. Lining up the incident beam so that the scattering angle was precisely





known, centering the sample cell directly in the beam, and good alignment of the receiving optics so as to define a rigidly straight path were all necessary to minimize the error in the data. Early sets of data were found to have been run when the system was not properly aligned. This may have resulted in an error in the scattering angles which were used. These data were repeated, after proper alignment of the system.

The errors of the total measurement-data analysis system were reflected in the differing values obtained for the diffusion coefficients of a sample at different scattering angles. Most of the values used in this work show good agreement with the linearity condition imposed by the equation relating half width to diffusion coefficient; that is, a straight line resulted from a plot of half width vs. $\sin^2(0/2)$ for most of the data. Some data initially provided nonlinear results, and were retaken to assure linearity. Difficulty was especially noticed in obtaining linear results at a scattering angle of 60°. Some data for polystyrene in benzene and toluene could not be fit satisfactorily to a Lorentzian equation, and values were not reported for the half width or the diffusion constant for such samples. The effect of polydispersity of polymer samples and the appearance of multiple Lorentzian data might have been responsible for this difficulty.

DISCUSSION

One of the purposes of this work was to measure the diffusion coefficients of polystyrene in various solvents and at different polymer concentrations and molecular weights in order to compare the experimental values with previously reported diffusivities in similar systems. The samples of polystyrene which were used in this work were obtained from the Michigan State University Department of Chemical Engineering. Gyeszly (13), in his dissertation, reported the measurement of diffusion coefficients of polystyrene samples of the same molecular weight as those used in this work, and obtained from the same source.

In both works, the diffusion coefficients of polystyrene were measured in benzene and decalin. Values for the diffusion constants obtained in both works are shown in Table 6.

The diffusivities reported in the two studies were in relatively good agreement. Differences in the concentration ranges of the polystyrene solutions used in the two works made absolute comparison difficult. However, a much closer agreement between the two works was observed for polystyrene diffusivities measured in decalin than for diffusion constants measured in benzene. An examination

Solvent			Gyeszly's Work	This Work	
	Polystyrene Sample	1)x10 ⁷ cm ² /sec	Conc. Range (g/100g)	Dx10 ⁷ cm ² /sec	Conc. Range (g/100g)
Benzene	UC 010 UC 030 UC 040	2.65-3.84 1.23-2.68 1.01-1.48	.52 3.012 .505	1.75-2.56 1.39-1.46 1.12-1.30	3.01 3.01 3.01
Decalin	UC 010 UC 030 UC 040	0.56-1.23 0.66-0.96 0.32-0.73	.51 .505 .51	0.73-0.94 0.68-0.85 0.58-0.77	.505 .505 .505

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Table 6.--Comparison of diffusion coefficients of polystyrene in benzene and decalin in two works.

of Table 6 will show that the polystyrene concentration ranges in decalin which were studied in the two works were very similar. The differences in concentration ranges in benzene which were used in the two works were much more significant.

The data reduction methods employed in the two works were also different. The Gyeszly data was generally reported as a range of values at each concentration. This was attributed to a data analysis system which attempted to place bounds on the diffusivity values according to estimates of inherent error in analyzing the data. The diffusivities in this work were reported as average values which were calculated from data which satisfied the linearity condition with respect to scattering angle (see CALIBRATION).

In addition, the Gyeszly data was produced from a spectrum with a frequency range of 0-2000 Hz, as compared with the 0-5000 Hz range used in this work.

In consideration of these differences, the agreement between the two works is quite good for the polystyrene systems. As was noted by Gyeszly, the lower diffusion constants obtained in decalin were not previously predicted by theory. Schick obtained approximately the same results for polystyrene diffusion in decalin by a diffusion cell technique in 1950. Nevertheless, the theoretical concept of the polymer molecule in solution results in a prediction of higher polystyrene diffusion constants in decalin than in benzene. (22)

Decalin is a poor solvent for polystyrene. As in Gyeszly's work, the decalin used in this study was a mixture of cis and trans isomers of decalin. At the experimental temperature of approximately 21°C employed in this work, cis and trans decalin is very close to the theta condition. The theta condition is the point at which a polymer of infinite molecular weight would precipitate from the solvent. Close to the theta condition the volume of the polymer molecules in solution is the smallest (unperturbed or unswollen dimensions). This is because the polymer molecules do not tend to interact with the solvent molecules in a solvent near the theta condition (poor solvent). Therefore, the theoretically small molecular size of the polystyrene molecule in decalin should result in a higher diffusion coefficient than that measured for polystyrene in a good solvent (in which the molecular chain is more expanded and diffuses with less ease) such as benzene.

An agglomeration theory proposed by Gyeszly explains the apparent contradiction between theory and experiment. The occurrence of agglomeration of polymer molecules in decalin is suggested as a means of increasing particle size, and therefore decreasing the polystyrene diffusion coefficient in decalin. This proposal accounts for the behavior of polystyrene in decalin near the 0-temperature in terms of diffusivity and viscosity measurements which have been recorded. It satisfactorily explains the behavior of the

polystyrene-decalin system used in this work. The theory would suggest that an increase in either polymer concentration or molecular weight would tend to increase the size of the particles formed by agglomeration, and therefore decrease the diffusion coefficient. This behavior was generally noted in the measurements which were made on the polystyrene-decalin system used in this work.

As was mentioned earlier in this work, the diffusion coefficient of polystyrene decreases with increasing concentration in decalin. This result is similar to that reported by Schick and Singer (1950), who found that the diffusion coefficient concentration dependence of polystyrene in decalin at a weight average molecular weight (M_w) of 6.8 x 10⁵ 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 grams /100 cm³. Since the coefficient of concentration (-0.15) is negative and small, the diffusion coefficient decreases slowly with increasing concentration. The lower molecular weight polystyrene used in this work explains the higher diffusivities reported in this work as compared to the values predicted by the above equation.

Theoretical considerations also predict a decrease in diffusion coefficient with increasing concentration of polymer. (12, 22) As has been stated previously in this work, the diffusion coefficient can be related to the frictional coefficient, the concentration, and the activity coefficient of the solution by the equation

$$D = \frac{KT}{f} \left(1 + \frac{\alpha \ln \gamma_i}{\alpha \ln C_i} \right)$$

Y_i = activity coefficient
C_i = concentration
f = frictional coefficient
K = Boltzmann's constant

For a polymer in any solvent better than a theta solvent, the solution will exhibit a negative deviation from ideality, $\alpha Ln \gamma_i$ $\frac{1}{\alpha \ln C_i}$ will be positive, and this factor will tend to increase the diffusion coefficient as the solution concentration increases. The equation above is based on the assumption that the hydrodynamic resistance to the motion of a particle is independent of the presence of other similar particles. This is a good assumption only if the diffusing particles are far apart. At higher concentrations, the hydrodynamic disturbances created by their motion will interact causing a change in the frictional coefficient. As a result, an increase in concentration will, in general, cause an increase in the frictional coefficient which will, in turn, decrease the diffusion coefficient. In a number of cases in this work, the diffusion coefficient decreased with

increasing concentration, although the results for many systems did not indicate a trend.

In general, the diffusion coefficients measured in this work were found to decrease with increasing molecular weight. While no specific equation for a particular polymer-solvent system was found, a general relationship has been known to apply to many systems of polymers in solution. The equation

 $D = K M^{-b}$

- D = diffusion coefficient
- K = constant
- M = molecular weight of polymer
- b = constant

has been applied to many polymer solutions, as well as to extrapolations to zero polymer concentration. (11) This equation predicts a decrease in the diffusion coefficient with increasing molecular weight.

The diffusion coefficients of polystyrene were also measured in toluene. The relationship between the intrinsic viscosity of a polymer in solution and the expansion factor, α , was used to compare the diffusivities reported in toluene to those in benzene. (27) The expansion factor can be defined as

$$\alpha = \left(\frac{\bar{r}^2}{\bar{r}_0^2}\right)^{1/2}$$

$$\bar{r}^2 = \text{actual mean square end to end distance of a polymer chain}$$

$$\bar{r}_0^2 = \text{mean square end to end distance for unperturbed dimensions}$$

A relationship between the intrinsic viscosity and the expansion factor is given by Flory (1953) as

$$[n] = \Phi(\frac{\bar{r}_{0}^{2}}{M})^{3/2} M^{1/2} \alpha^{3}$$

which, for a given molecular weight of polymer, M, may be written as

$$[n] = C \alpha^3$$

C = constant which is independent of 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. Values for K and a in the equation

$$[n] = KM^a$$

were found in data published by Kurata, (31) and were used to compare the intrinsic viscosity of polystyrene in toluene to that in benzene. For similar molecular weight ranges, a number of pairs of values of K and a were reported for polystyrene in both benzene and toluene. Most values which were reported for these two solvents, in the molecular weight range used in this work, were quite similar. This indicated that the intrinsic viscosities, and therefore, the expansion factors of polystyrene in benzene and toluene were similar. This, in turn, would indicate that the polystyrene molecules in benzene and toluene were of comparable size. Therefore, the diffusion coefficients in benzene and toluene should be similar in magnitude.

The experimentally determined values for the diffusion coefficient of polystyrene in benzene and toluene were similar, although the diffusivities in toluene were consistently lower than those in benzene. More precise intrinsic viscosity data in the appropriate molecular weight range might confirm these results. This would suggest that use of experimentally determined diffusion coefficients from light beating spectroscopy provides a more accurate and precise method of studying macromolecular behavior in solution than use of available intrinsic viscosity data. The differences in reported parameters for intrinsic viscosity relationships make comparisons of macromolecular behavior in similar systems, such as benzene and toluene, very difficult. With the use of the light beating technique, the ability to compare polymer behavior in similar systems appears to be greatly enhanced.

The validity of the assumption that only translational diffusion occurred in the polymer solutions was examined by use of the Gaussian parameter, χ , (12, 22) which is given by

$$\chi = \kappa^{2} \langle s^{2} \rangle$$

$$\kappa = \text{scattering vector}$$

$$\langle s^{2} \rangle = \text{mean square radius of gyration}$$

The values of χ characteristic of this work were determined to discover the existence of multiple Lorentzian data or polydispersity effects. The scattering vector, κ , is given by

$$\kappa = \frac{16\pi n^2}{\lambda o^2} \sin^2 \left(\frac{\Theta}{2}\right)$$

n = refractive index of solvent
λo = incident laser wavelength
Θ = scattering angle

In order to determine the largest χ value occurring in this work, the largest value of κ was found by maximization of the refractive index (benzene, 1.501) and the scattering angle (0=60°) in the scattering vector equation. A value for $\langle s^2 \rangle$ was found from published experimental data. (27) Using these results, the largest value obtained for the parameter, χ , for polystyrene was approximately 0.05. This value was multiplied by a factor of 12 to estimate the contribution of bond angle restrictions and rotational effects in increasing the size of the polymer in solution (increasing $\langle s^2 \rangle$). This produced a χ value of 0.60. This value of χ was found to be below 1.0, which was mentioned earlier in this work as a transition point for the appearance of multiple Lorentzian spectra. This value of χ of 0.60 is apparently high enough to cause some deviation of the single Lorentzian shape due to intramolecular motion, but not high enough to invalidate the isolated sphere approximation of the polymer molecule in solution, or the assumption of translational diffusion effects occurring alone. Therefore, the equation relating the translational diffusion coefficient to the experimentally determined half width, which was used in this work, would appear to be a valid relationship in the analysis of the light beating spectroscopic data of this work.

The diffusion coefficients of polyethylene oxide were measured for the first time by the method of light beating spectroscopy in this work. Diffusion coefficient data for polyethylene oxide in water and carbon tetrachloride were not found in the literature.

Experimentally determined values for the expansion factor, α , were used to compare the behavior of polyethylene oxide in water and carbon tetrachloride. (30) For polyethylene oxide of molecular weight (\mathfrak{A}_{w}) 6.2758 x 10⁵, the

value of α for polyethylene oxide in water was found to be 1.684, while that in carbon tetrachloride was given as 1.274. These values indicated that the polyethylene oxide molecule was in a more expanded form in water than in carbon tetrachloride. Using the previously discussed theories of macromolecules in solution, the diffusion coefficient of polyethylene oxide in water would be expected to be smaller than the diffusivity of polyethylene oxide in carbon tetrachloride.

Expansion factor data also predicts a higher polyethylene oxide diffusion coefficient in carbon tetrachloride for polyethylene oxide of molecular weight (M_W) 3.65719 x 10⁶. Expansion factors from different sources also tend to support this finding. (30)

The experimentally determined diffusion coefficients of polyethylene oxide in water and carbon tetrachloride appear to support the conclusions derived from expansion factor data. Although the differences tended to be small, the diffusion coefficient of polyethylene oxide in water tended to be smaller than that in carbon tetrachloride. Since water is a good solvent for polyethylene oxide and carbon tetrachloride is a poor solvent, the results agree with theoretical predictions concerning polymer behavior in solution. The polymer molecules are more extended in the good solvent (water) offering greater frictional resistance to diffusion. In the poor solvent (carbon tetrachloride), the smaller polymer particle size results in greater diffusion of the particles.
The experimental diffusivities of polyethylene oxide in water and carbon tetrachloride emphasize the unusual character of the behavior of polystyrene in the poor solvent decalin. Different theoretical treatments are required to explain the behavior of polystyrene in decalin and polyethylene oxide in carbon tetrachloride.

CONCLUSIONS

The results of this work appear to reaffirm the reliability of the light beating spectroscopic technique in the measurement of diffusion coefficients of macromolecules in dilute solution. Available theoretical development is able to account for the behavior of macromolecules in solution under differing conditions of solvent media, polymer concentration, and molecular weight as determined by light beating spectroscopy.

In order to improve the accuracy of the light beating technique, the areas of sample preparation and data analysis must be examined. An improved method of dust removal from the polymer samples would provide better assurances of the accuracy and true Lorentzian form of the spectra which are measured. The use of direct computer analysis of spectra, avoiding the error involved in translating data from the recorded spectra, would greatly enhance the accuracy and reliability of the light beating method.

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NOMENCLATURE

- b = Length of one link in pearl necklace model of polymer molecule
- $C_i = Concentration$
- C(\u03c4) = Autocorrelation function of electric field of scattered light
- $C_i(\tau)$ = Autocorrelation function written in terms of the photocurrent
 - D = Translational diffusion coefficient
- E(t) = Electric field of scattered light at time t

$$E(t+\tau)$$
 = Electric field of scattered light at time t + τ

- E_{o} = Amplitude of electric field
 - f = Frictional coefficient
- $g^{(1)}(\tau)$ = Correlation function of scattered light field
- $g^{(2)}(\tau)$ = Correlation function of photocurrent
 - <l>Total intensity of scattered light
 - K = Boltzmann's constant
 - M = Molecular weight
 - N = Number of links in chain of polymer molecule
 - n = Refractive index
 - R = Radius of sphere

 $(s^2)^{1/2}$ = Root-mean-square radius of gyration of polymer molecule in solution

T = Temperature

t = Time

- w = Frequency of scattered light
- w_0 = Frequency of light source

 $\Delta w_{1/2}$ = Half width of scattered light spectrum

Greek Symbols

- α = Expansion factor for polymer molecule in solution
- γ_i = Activity coefficient
 - γ = Half width of optical scattered spectrum of light
 - κ = Scattering vector
 - Θ = Scattering angle
- λ_{o} = Wavelength of incident laser beam
 - η = Viscosity
- [n] = Intrinsic viscosity
 - τ = Time

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APPENDIX

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Scattering Angle	Polystyrene Sample	Concentration (g/100g)	Halfwidths (Hz)	$D \times 10^7$ cm ² /sec
30°	UC 010	3.0 1.0 0.5 0.1	508 564 612 680	1.77 1.97 2.14 2.37
45°	UC 010	3.01.00.50.1	1184 1347 1290 1716	1.89 2.15 2.06 2.74
60°	UC 010	$3.0 \\ 1.0 \\ 0.5 \\ 0.1$	1711 2054 -	1.60 1.92
30°	UC 030	$3.0 \\ 1.0 \\ 0.5 \\ 0.1$	395 400 373 404	1.38 1.40 1.30 1.41
45°	UC 030	$3.0 \\ 1.0 \\ 0.5 \\ 0.1$	890 883 927 821	1.42 1.41 1.48 1.31
60°	UC 030	$3.0 \\ 1.0 \\ 0.5 \\ 0.1$	$ 1465 \\ 1668 \\ 1540 \\ 1658 $	1.37 1.56 1.44 1.55
30°	UC 040	$3.0 \\ 1.0 \\ 0.5 \\ 0.1$	406 330 319 378	1.41 1.15 1.11 1.32
45°	UC 040	$3.0 \\ 1.0 \\ 0.5 \\ 0.1$	702 664 689 789	1.12 1.06 1.10 1.26
60°	UC 040	$3.0 \\ 1.0 \\ 0.5 \\ 0.1$	$ 1476 \\ 1294 \\ 1230 \\ 1380 $	1.38 1.21 1.15 1.29

Polystyrene in Benzene

Scattering Angle	Polystyrene Sample	Concentration (g/100g)	Halfwidth (Hz)	$D \ge 10^7$ cm ² /sec
30°	UC 010	3.0 1.0 0.5 0.1	397 348 567 740	1.40 1.22 1.99 2.60
45°	UC 010	$3.0 \\ 1.0 \\ 0.5 \\ 0.1$	803 753 1251 1250	1.29 1.21 2.01 2.01
60°	UC 010	$3.0 \\ 1.0 \\ 0.5 \\ 0.1$	1572 1243 2061	1.48 1.17 1.94
30°	UC 030	3.0 1.0 0.5 0.1	395 296 262 322	1.39 1.04 0.92 1.13
45°	UC 030	$3.0 \\ 1.0 \\ 0.5 \\ 0.1$	859 647 535 747	1.38 1.04 0.86 1.20
60°	UC 030	$3.0 \\ 1.0 \\ 0.5 \\ 0.1$	1286 1169 1073 1253	1.21 1.10 1.01 1.18
30°	UC 040	3.0 1.0 0.5 0.1	370 289 288 315	1.30 1.02 1.01 1.11
45°	UC 040	3.01.00.50.1	784 722 684 697	1.26 1.16 1.10 1.12
60°	UC 040	$3.0 \\ 1.0 \\ 0.5 \\ 0.1$	$ 1349 \\ 1049 \\ 1179 \\ 1158 $	1.27 1.00 1.11 1.09

Polystyrene in Toluene

Scattering Angle	Polystyrene Sample	Concentration (g/100g)	Halfwidth (Hz)	$D \times 10^7$ cm ² /sec
30°	UC 010	0.5 0.2 0.1 0.05	230 202 261 251	0.83 0.73 0.94 0.91
45°	UC 010	0.5 0.2 0.1 0.05	448 478 563 490	0.74 0.79 0.93 0.81
60°	UC 010	0.5 0.2 0.1 0.05	847 702 846 1136	0.82 0.68 0.82 1.10
30°	UC 030	0.5 0.2 0.1 0.05	181 220 221 244	0.65 0.79 0.80 0.88
45°	UC 030	0.5 0.2 0.1 0.05	466 484 502 478	0.77 0.80 0.83 0.79
60°	UC 030	0.5 0.2 0.1 0.05	640 785 878 919	0.62 0.76 0.85 0.89
30°	UC 040	0.5 0.2 0.1 0.05	156 170 205 225	0.56 0.61 0.74 0.81
45°	UC 040	0.5 0.2 0.1 0.05	369 339 472 471	0.61 0.56 0.78 0.78
60°	UC 040	0.5 0.2 0.1 0.05	578 661 733 754	0.56 0.64 0.71 0.73

Polystyrene in Decalin

Scattering Angle	Polyethylene Oxide Sample	Concentration (g/100g)	Halfwidth (Hz)	$D \times 10^7$ cm ² /sec
30°	WSR-205	$\begin{array}{c} 0.10 \\ 0.05 \\ 0.025 \\ 0.01 \end{array}$	61 65 70 74	0.27 0.29 0.31 0.33
45°	WSR-205	$\begin{array}{c} 0.10 \\ 0.05 \\ 0.025 \\ 0.01 \end{array}$	89 128 84 148	0.18 0.26 0.17 0.30
60°	WSR-205	$\begin{array}{c} 0.10 \\ 0.05 \\ 0.025 \\ 0.01 \end{array}$	207 228 221 299	0.25 0.27 0.26 0.36
30°	WSR-301	$\begin{array}{c} 0.10 \\ 0.05 \\ 0.025 \\ 0.01 \end{array}$	52 58 63 76	0.23 0.26 0.28 0.34
45°	WSR-301	$\begin{array}{c} 0.10 \\ 0.05 \\ 0.025 \\ 0.01 \end{array}$	123 108 124 103	0.25 0.22 0.25 0.21
60°	WSR-301	$\begin{array}{c} 0.10 \\ 0.05 \\ 0.025 \\ 0.01 \end{array}$	208 190 199 243	0.25 0.23 0.24 0.29

Polyethylene Oxide in Water

Scattering Angle	Polyethylene Oxide Sample	Concentration (g/100g)	Halfwidth (Hz)	$D \times 10^7$ cm ² /sec
30°	WSR-205	$\begin{array}{c} 0.05 \\ 0.02 \\ 0.01 \\ 0.005 \end{array}$	92 108 127	0.34 0.40 0.47
45°	WSR-205	$\begin{array}{c} 0.05 \\ 0.02 \\ 0.01 \\ 0.005 \end{array}$	2 0 2 2 4 3 2 4 3	0.34 0.41 0.41
60°	WSR-205	0.05 0.02 0.01 0.005	- 386 390 436	- 0.38 0.39 0.43
30°	WSR-301	$\begin{array}{c} 0.05 \\ 0.02 \\ 0.01 \\ 0.005 \end{array}$	87 - 98 108	0.32 - 0.36 0.40
45°	WSR-301	$\begin{array}{c} 0.05 \\ 0.02 \\ 0.01 \\ 0.005 \end{array}$	1 3 0 - 2 0 1 1 8 4	0.22 - 0.34 0.31
60°	WSR-301	$ \begin{array}{c} 0.05\\ 0.02\\ 0.01\\ 0.005 \end{array} $	317 - 335 433	$0.31 \\ - \\ 0.33 \\ 0.43$

Polyethylene Oxide in Carbon Tetrachloride

