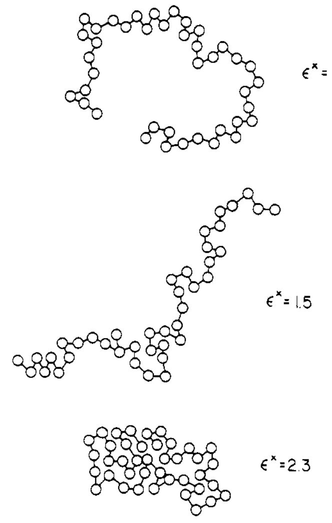

Figure 6. Snapshot configurations of 40-bead polymers from Monte Carlo simulations. These were hand drawn; thus some of the distances between beads appear unequal.

and is unlikely to exhibit any very extended shapes.

Conclusion

We conclude that a free energy consisting of two parts, an elastic part and a liquid-like part, in the spirit of Flory's mean field theory, describes a two-dimensional polymer very well in both the excluded volume and collapsed regimes. This theory predicts a sharp transition but does not predict ideal coil behavior at the transition, which distinguishes it from three dimensions, where is is thought that there is quasi-ideal behavior at the Θ temperature. Consistent with this prediction our Monte Carlo data give no indication of a crossover from excluded volume behavior to ideal coil behavior as found in the three-dimensional simulation.[5] Although our data are not sufficient to rule out other exponents than those derived by Flory, it is clear that these exponents are very close to the correct values.

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Photon Correlation Spectroscopy on Polystyrene Solutions under High Pressure

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ABSTRACT: The diffusion coefficient D of a narrow-fraction polystyrene ($\bar{M}_w = 111\,000$, $\bar{M}_w/\bar{M}_n \le 1.06$) in toluene has been studied as a function of pressure from 1 up to 5000 atm for both dilute and semidilute solutions by using the photon correlation spectroscopy technique. In dilute solution the value of the coefficient k_D, representing the concentration dependence of D, was found to be independent of pressure. Likewise, the hydrodynamic radius R_H, obtained from the value of D at infinite dilution, was observed to be independent of pressure. The observed decrease in D with increasing pressure is, for all concentrations, completely correlated to the pressure dependence of the solvent viscosity.

Introduction

Although there are a number of total intensity light scattering investigations[1-9] dealing with the effect of pressure on, for example, the second virial coefficient and the radius of gyration of polymer chains in dilute solution, little attention[10] has been paid to the pressure dependence of dynamical properties in polymer systems. The main objective of the present paper is to study the effect of pressure on the diffusion features in dilute and semidilute polymer solutions.

In recent years photon correlation spectroscopy (PCS) has been extensively used to study dynamic features of

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flexible macromolecules in solution. There has been a great deal of current interest in the behavior of the mutual diffusion coefficient as a function of concentration and temperature. However, up to now all investigations have been conducted at atmospheric pressure. To gain a more detailed picture of transport phenomena in macromolecular solutions it is desirable to perform measurements at elevated pressures.

In the present work, the pressure dependence of the diffusion coefficient of dilute and semidilute solutions of polystyrene in toluene is studied over a pressure range of 1–5000 atm by utilizing the PCS technique. The system polystyrene/toluene was chosen because static properties (e.g., the second virial coefficient and the radius of gyration) at elevated pressures are fairly well-known for this system.

Experimental Section

Materials and Preparation of Solutions. A polystyrene sample (Pressure Chemical Co., Pittsburgh, Pa.) characterized by $\bar{M}_w = 111\,000$ and $\bar{M}_w/\bar{M}_n \leq 1.06$ was used as received. The solvent toluene (pa, Merck AG) was used without further purification.

Solutions of five different concentrations were prepared by weighing. The solutions were filtered through 0.22-μm Millipore filters directly into precleaned light scattering cuvettes of 16-mm path length in an atmosphere of filtered air.

High-Pressure Cell. The design and operation of the high-pressure equipment used in this work has been described in detail elsewhere.[11] Only a brief description will be given here.

The pressure vessel consists of a steel cylinder with a central axial hole and a smaller radial channel, both of which can be closed at the ends with O-ring-sealed pistons supported by screws. The central hole forms the main pressurized volume. The two side pistons and the bottom piston are channeled and provided with synthetic sapphire windows which are tightened by using the conventional unsupported area technique.

The solution to be studied is enclosed in a cylindrical quartz cuvette having an optically flat bottom and two, oppositely placed, optically flat windows. The cuvette was closed with a movable black-oxidized aluminum plunger, equipped with two Viton O-rings. The plunger transmits the pressure and isolates the sample solution from the pressure-transmitting fluid. The sapphire windows of the high-pressure vessel are provided with apertures of appropriate size and the entire sample cuvette, except for the windows, is painted black to minimize the effect of stray light.

The cuvette containing the solution is centered in the vessel by means of a black specially designed holder and surrounded by the pressure-transmitting medium glycerol (~87%, Merck AG). The cell is then placed under vacuum, and a steel piston is laid on the surface of the glycerol. The vessel is then attached to a small hydraulic press and the top piston is pressed down by a steel rod passing through a central hole in the upper supporting screw; the pressure is transmitted to the sample solution by the downward movement of the aluminum plunger in the cuvette. When the desired pressure in the cell has been reached, it is locked in by turning the top screw down against the top piston. The high-pressure vessel can now be removed from the press and placed in the light scattering apparatus. The hydraulic press is equipped with a Bourdon gauge that has been accurately calibrated by a piezometric method[12] so the pressure inside the vessel is known with ±2.5% inaccuracy.

The high-pressure vessel is surrounded by a copper coil through which water could be circulated. During the experiment the vessel with the coil was kept under an insulating hood. By this arrangement the temperature in the sample cuvette could be controlled within ±0.1 °C. All measurements were carried out at 25 °C.

Photon Correlation Spectroscopy. In this work a Coherent Radiation Model CR-4 argon ion laser was operated at a wavelength of 488 nm with a quartz etalon frequency stabilizer in the cavity to ensure single-mode operation. The stability of the system was continuously monitored during the course of the experiment by a spectrum analyzer connected to an oscilloscope. The laser beam was focused at the center of the cuvette, and the light scattered at 90° was imaged on the photocathode of an ITT FW130 photomultiplier tube; a 100-μm pinhole in front of the photocathode effectively defined the scattering volume. After amplification and discrimination (Nuclear Enterprises NIM modules), the resulting standardized photovoltage pulses were fed into a 128-channel digital correlator (Langley-Ford Instruments) which was set to generate the *full* autocorrelation function of the scattered intensity; the buildup of the correlation function was displayed on an oscilloscope.

The correlator is equipped with a device so that the last 8 channels can be delayed in time in such a way that the last channel corresponds to a delay time of 256 channels. The average value of the last 8 channels which form the "base line" was consistently equal to or insignificantly larger than that obtained from the monitoring channels of the correlator.

The correlator was interfaced to a Luxor ABC 80 microcomputer, which was programmed to calculate the normalized *full* photon counting time correlation function and to analyze and store the data. The data analysis procedure employed to evaluate the relaxation times will be discussed below; basically the methods of data analysis of Pusey et al.[13] and Koppel[14] were used.

Correlation Functions. In the homodyne configuration, which was used in this study, the (normalized) experimental intensity autocorrelation function was obtained as

$$C(iT) = \langle n(t)n(t+iT)\rangle / \langle n(t)\rangle^2 \qquad (1)$$

where $n(t)$ and $n(t + iT)$ are the number of photon counts at times t and $t + iT$ over a short time interval T and i is an integer. The correlation function is obtained at 120 values of $\tau = iT$. The relationship between the intensity correlation function $g^{(2)}(\tau) \equiv C(iT)$ $(\tau \neq 0)$ and the electric field correlation function $g^{(1)}(\tau)$ has been shown to be

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

The number β is a factor related to the "efficiency" of the experiment and is treated as an adjustable parameter in the data-fitting procedure.

For a polydisperse sample with a continuous distribution of sizes and in the absence of internal motions or for a system exhibiting a distribution of collective motions that can be represented by a superposition of exponential decays, $g^{(1)}(\tau)$ has the form

$$|g^{(1)}(\tau)| = \int_0^\infty G(\Gamma)\exp(-\Gamma\tau)\,\mathrm{d}\Gamma \qquad (3)$$

where $G(\Gamma)$ is the normalized distribution of decays. By using the method of cumulants, one may write eq 2 as

$$\ln|g^{(2)}(\tau) - 1| = \ln\beta + 2|-\bar{\Gamma}\tau + \frac{\mu_2}{\bar{\Gamma}^2}\frac{\bar{\Gamma}^2}{2!}\tau^2 - ...| \qquad (4)$$

where the average decay rate $\bar{\Gamma}$ and its variance $\mu_2/\bar{\Gamma}^2$ are defined as

$$\bar{\Gamma} \equiv \int_0^\infty G(\Gamma)\Gamma\,\mathrm{d}\Gamma \qquad (5)$$

$$\frac{\mu_2}{\bar{\Gamma}^2} \equiv \frac{1}{\bar{\Gamma}^2}\int_0^\infty G(\Gamma)(\Gamma - \bar{\Gamma})^2\,\mathrm{d}\Gamma \qquad (6)$$

The correlation data were fitted, according to eq 4, to a quadratic polynomial in τ and the results were discarded when $|\mu_2/\bar{\Gamma}^2|$ exceeded 0.03; the latter quantity constitutes a crude measure of the nonexponentiality of the correlation function.

The first cumulant of the scattered electric field time correlation function of flexible linear chains is predicted by the theory to depend on the scattering angle θ or the magnitude of the corresponding scattering vector $q = (4\pi n/\lambda)\sin(\theta/2)$, where λ is the wavelength of the incident light and n is the index of refraction of the solution. Under the condition $qL \ll 1$, where L is a characteristic length, it has been shown that

$$\bar{\Gamma} = \bar{D}q^2 \qquad (7)$$

where $\bar{D}$ is a z-average translational diffusion coefficient in the dilute regime and similar weighting factors apply for the collective motions; in the present work $qL < 0.3$. The index of refraction

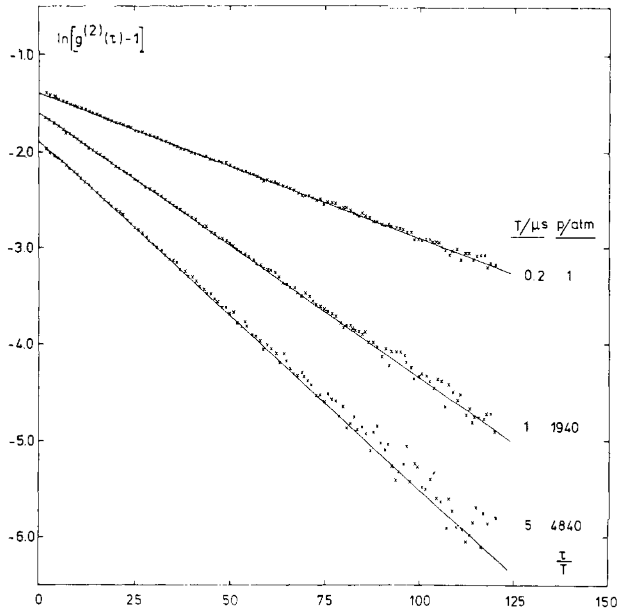

Figure 1. Semilog plot of $g^{(2)}(\tau) - 1$ vs. channel number (τ/T) for polystyrene in toluene at a concentration of 4.43 kg m^{-3} (the value at atmospheric pressure) and at the pressures (p) and sample times (T) indicated. The solid line represents the best fit to the experimental data.

of the solution was estimated from the measured refractive index of the solution (the measurements were carried out in a refractometer of the Abbê type at 488 nm) and the known[15] pressure dependence of the index of refraction of toluene. The diffusion coefficients could accordingly be evaluated by means of eq 7.

Figure 1 shows typical plots of $\ln|g^{(2)}(\tau) - 1|$ vs. channel number (τ/T) for the system polystyrene/toluene at the pressures and sample times indicated. This illustration clearly demonstrates that the experimental points representing the three different pressures are well fitted to straight lines; the electric field autocorrelation function of the scattered light decays as a single exponential. It was consistently found that the correlation data could be described adequately by a single exponential.

Results and Discussion

It is well-known from the pioneering work of Bridgman[16,17] that pressure may have a considerable effect on the viscosity of a liquid. Furthermore, static light scattering measurements[1-9] on dilute polymer solutions have shown that the hydrostatic pressure may affect quantities such as the second virial coefficient and the radius of gyration. Questions related to these factors will be discussed below in connection with the interpretation of the observed features.

The translational diffusion coefficient D for dilute polymer solutions can be expanded to first order in concentration as

$$D = D_0(1 + k_D c + ...) \tag{8}$$

where D_0 is the diffusion coefficient at infinite dilution and k_D determines the concentration dependence of D.

Figure 2 depicts linear extrapolations of the diffusion coefficient to infinite dilution for PS ($\bar{M}_w$ = 111 000) in toluene for six different pressures. The values of D_0 and k_D are listed in Table I. The observed decrease in D_0 with increasing pressure is directly correlated (vide infra) to the change in viscosity of the solvent with pressure.

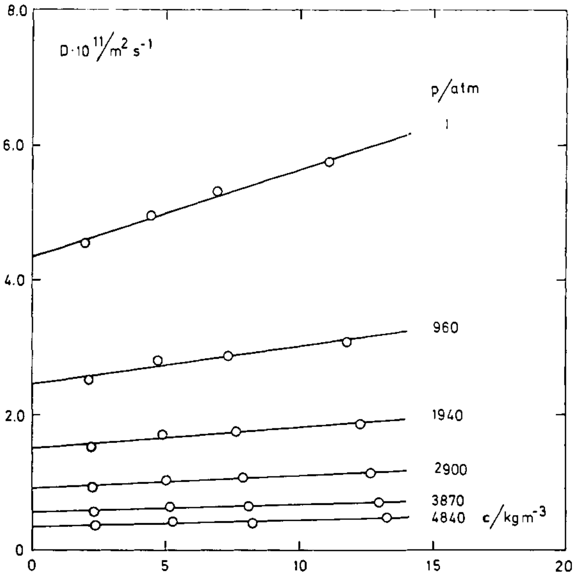

Figure 2. Concentration dependence of the diffusion coefficient for polystyrene in toluene at the pressures indicated.

Table I
Characteristic Data for Polystyrene in Toluene at Various Pressures

p/atm	$10^{11} \times D_0/(\mathrm{m^2\ s^{-1}})$	$10^{10} \times R_H/\mathrm{m}$	$k_D/(\mathrm{m^3\ kg^{-1}})^a$
1	4.3_5	91	0.030 ± 0.003
960	2.4_8	85	0.022 ± 0.006
1940	1.5_2	83	0.020 ± 0.006
2900	0.9_2	87	0.020 ± 0.005
3870	0.5_6	90	0.020 ± 0.006
4840	0.3_5	91	0.023 ± 0.010

[a] Standard deviation given.

The concentration dependence of D is governed by thermodynamic and hydrodynamic factors; irreversible thermodynamics shows that[18,19]

$$k_D = 2A_2M - k_f - v_2 \tag{9}$$

where M is the molecular weight, A_2 is the second virial coefficient, k_f (or equivalently k_s in sedimentation coefficient terminology) is the first-order friction coefficient concentration dependence, and v_2 is the partial specific volume of the solute. According to the theory of Yamakawa[19] for a coiled linear chain in a good solvent, k_f can be expressed as

$$k_f = 1.2A_2M + N_A V_H/M \tag{10}$$

Here N_A is Avogadro's constant and V_H is the chain hydrodynamic volume given by

$$V_H = \tfrac{4}{3}\pi R_H^3 \tag{11}$$

where R_H is the hydrodynamic radius. From eq 9–11 it follows that

$$k_D = 0.8A_2M - \frac{4}{3}\pi\frac{N_A}{M}R_H^3 - v_2 \tag{12}$$

Static light scattering measurements on the present polymer–solvent system have shown[6] that A_2 is practically independent of pressure over the range covered here. Likewise, the present PCS measurements indicate (vide infra) that the hydrodynamic radius is independent of pressure. Thus the two first terms on the right-hand side of eq 12 should not vary with pressure for the system under study. The partial specific volume, on the other hand, has been observed[12] to decrease (for this system) by approximately 10% in the pressure interval studied here. However, the value of v_2 is *very* small in comparison with the difference of the two other terms; hence ~10% change in v_2 is not expected to be reflected in the experimental value of k_D. We may conclude that the observed constancy of k_D (see Table I) is consistent with the theoretical conjecture (eq 12).

In order to discuss coil dimensions it is convenient to consider the hydrodynamic radius, which can be estimated

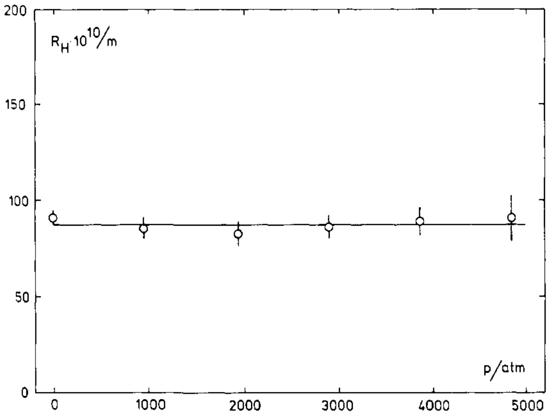

Figure 3. Plot of the hydrodynamic radius for polystyrene in toluene as a function of pressure. The error bars indicate twice the standard deviation.

from the diffusion coefficient extrapolated to zero concentration by using the Stokes–Einstein relation:

$$R_H = kT/6\pi\eta D_0 \qquad (13)$$

Here k is Boltzmann's constant, T is the absolute temperature, and η is the solvent viscosity. Values of η at different pressures were determined from data in ref 16. It was found that the viscosity of toluene increased by a factor of ~12 in the pressure range studied in this paper.

In Figure 3 R_H is plotted as a function of pressure. We note that, within experimental error, R_H is independent of pressure (see also Table I). In this context it is interesting to note that a recent light scattering investigation[9] on the same polymer–solvent system showed that the radius of gyration decreased by ~12% over the pressure interval 1–1800 atm. These findings seem to indicate that the hydrodynamic radius is less sensitive to pressure than the radius of gyration.

Figure 4 shows a plot of the ratio D^p/D^1 vs. pressure for the concentrations indicated. The concentrations represent both the dilute region and the semidilute regime (where the polymer chains overlap each other). The solid curve represents the relative change in solvent viscosity (η^1/η^p) with pressure. The consistency between the experimental points and the curve shows that the pressure dependence of the diffusion coefficient is entirely correlated to the change in solvent viscosity with pressure. Consequently, the pressure dependence of D for this system may be expressed as

$$D^p \simeq D^1(\eta^1/\eta^p) \qquad (14)$$

where the superscripts 1 and p indicate atmospheric and the considered pressure, respectively.

Finally, let us make some remarks concerning the diffusion process in an ultracentrifuge. This apparatus is now and then employed to measure diffusion coefficients. Frequently, a synthetic boundary cell is utilized, where the diffusing interface between solvent and solution is formed while the rotor is accelerating. By following the broadening of the boundary with time the diffusion coefficient can be evaluated. The thickness of the solvent layered onto the solution and the angular velocity of the rotor regulate the pressure. In this kind of experiment the pressure on the boundary may amount to 50 atm. Judging from the results in Figure 4, a pressure of this magnitude may cause a decrease of the diffusion coefficient of about 10%. Thus it may be necessary for certain polymer–solvent systems to correct the diffusion data obtained in an ultracentrifuge for the induced pressure. Pressure effects on sedimentation boundary are often interpreted theoretically by employing the Lamm differential equation.[20] Due to lack of experimental data it has been assumed that the incorporated diffusion coefficient is independent of pressure. However, experiments of the type presented in this study provide a basis for a rigorous analysis where the pressure dependence of the diffusion coefficient can be taken into account in the numerical solutions to the Lamm equation.

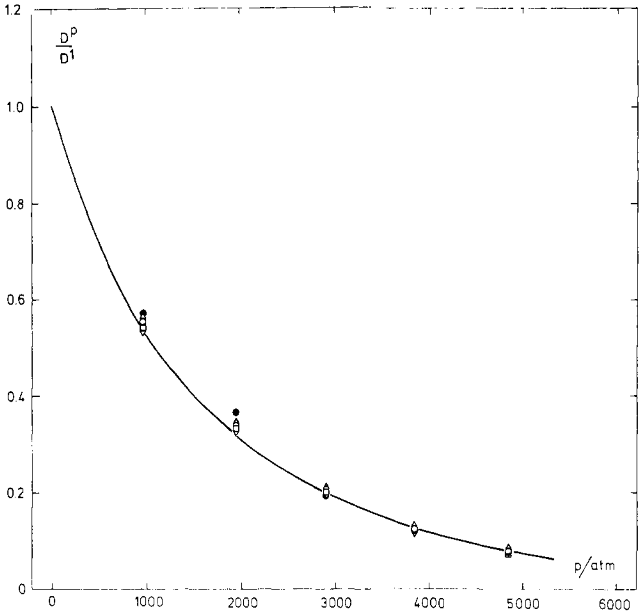

Figure 4. Plot of the ratio D^p/D^1 vs. pressure for the concentrations (kg m^{-3}) indicated (the values refer to atmospheric pressure): (○) 1.99; (△) 4.43; (□) 6.94; (▽) 11.1; (●) 53.0. The solid curve represents the relative change in solvent viscosity (η^1/η^p) with pressure.

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