related T_0 to the conformational entropy.[4] A higher B value corresponds to higher steric hindrance and a higher T_0 value, to greater configurational entropy. It should be pointed out that the effect on the glass transition temperature due to branching in PPG is quite similar to that found in poly(ethyl acrylate), in which the methyl substitution causes T_g to shift higher by 80 °C. The $\bar{\tau}$ value found for poly(ethyl methacrylate) is also greater than that found in the acrylate polymer.[5]

In conclusion, we have shown that branching of the side group in PPG has a pronounced effect on the dynamics of the density fluctuations. The density–density correlation function relaxes slower in the branched than in the linear PPG.

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Registry No. PPG, 25322-69-4; PPG glycerol ether, 25791-96-2.

References and Notes

(1) Wang, C. H.; Fytas, G.; Lilge, D.; Dorfmüller, Th. *Macromolecules* **1981**, *14*, 1363.
(2) Stockmayer, W. H.; Burke, J. J. *Macromolecules* **1969**, *2*, 647.
(3) Helfand, E. *J. Chem. Phys.* **1971**, *54*, 4651.
(4) Miller, A. *Macromolecules* **1978**, *11*, 859.
(5) Fytas, G.; Patkowski, A.; Meier, G.; Dorfmüller, Th. *Macromolecules* **1982**, *15*, 214; submitted.

Light Spectroscopy in Polymer Solutions at Θ Conditions in the Crossover Concentration Domain between the Dilute and Semidilute Regimes

Jean-Pierre Munch,[†] Gerard Hild,[‡] and Sauveur Candau*[,†]

Laboratoire d'Acoustique Moleculaire, Université Louis Pasteur, Institut de Physique, 67070 Strasbourg Cedex, France, and Centre de Recherches sur les Macromolécules, CNRS, 67083 Strasbourg Cedex, France. *Received March 5, 1982*

ABSTRACT: The concentration dependence of the diffusion constant has been measured by light spectroscopy for solutions of polystyrenes of molecular weight ranging from 20 000 to 2 × 10^6 at Θ conditions. In the concentration domain extending from the very dilute limit to slightly beyond the crossover concentration c^* between the dilute and semidilute regimes, the data can be represented in the form of a universal normalized hydrodynamic plot. The temperature dependence of the diffusion constant has been investigated in the vicinity of the critical point and compared to the predictions of the critical phenomena theory.

Introduction

The functional dependence upon temperature and monomer concentration of the microscopic and thermodynamic parameters describing solutions of flexible polymers has been derived by Daoud and Jannink[1] on the basis of the analogy between the Θ point in polymer solutions and the tricritical point.[2] This dependence was represented in the form of a molecular weight independent diagram of $\tau M^{1/2}$ vs. $cM^{1/2}$, where c is the polymer concentration (expressed in g cm^{-3}), M the molecular weight of the polymer, and τ the reduced temperature: $\tau = (T - \Theta)/\Theta$ (T, absolute temperature; Θ, theta temperature). Experimental verification of such a diagram was provided by both small-angle neutron scattering experiments[3] and precipitation curves obtained earlier by Schultz and Flory.[4]

Also, scaling approaches have been used to predict dynamic properties of polymer solutions at temperatures equal to the Θ temperature.[5] However, the experimental studies did not provide clear evidence of the theoretically predicted behavior.[6–13] For instance, the concentration dependence of the cooperative diffusion constant in the semidilute regime could not be verified from light spectroscopy experiments because of complications arising from the superposition of several modes in the spectrum of scattered light.[6,7] On the other hand, sedimentation[8–11] and concentration gradient diffusion (CGD)[12] experiments performed over a rather limited range of concentrations provided results in good agreement with the scaling predictions. Also, the sedimentation behavior in the dilute range at the Θ temperature could be approximately represented on a "hydrodynamic normalized plot" by a single curve in the molecular weight range 110 000–950 000.[11] In order to examine whether a similar behavior is observed for the diffusion constant, we have investigated by light spectroscopy solutions of polystyrene of weight-average molecular weights ranging from $\bar{M}_w = 20\,000$ to $\bar{M}_w = 2 \times 10^6$ in two Θ solvents (cyclohexane at 34.5 °C and cyclopentane at 20.4 °C) and at concentrations extending from the very dilute limit to slightly beyond the crossover concentration c^* between the dilute and semidilute regimes. We have also measured the diffusion constants of a cross-linked polystyrene network swollen at equilibrium either in cyclohexane at 34.5 °C or in cyclopentane at 20.4 °C, in order to compare the behavior of linear and cross-linked polymeric systems at the Θ conditions. Finally, we present some measurements of the temperature dependence of the diffusion constant of Θ solutions in the crossover concentration domain. The results are compared with the theoretical predictions for the critical phase separation of binary mixtures.

Experimental Section

A. Samples. Linear polystyrenes of low polydispersity ($\bar{M}_w/\bar{M}_n$ < 1.15) were prepared under an inert atmosphere by anionic polymerization in an aprotic solvent (THF) with an efficient initiator such as α-methylstyrene tetramer or potassium naphthalenide. The polydispersity of the samples was checked by GPC and the molecular weights were determined by light scattering measurements in THF. The obtained values of $\bar{M}_w$ are 20 000, 130 000, 570 000, and 10^6. The sample with $\bar{M}_w = 2 \times 10^6$

[†] Laboratoire d'Acoustique Moleculaire, Université Louis Pasteur.
[‡] Centre de Recherches sur les Macromolécules, CNRS.

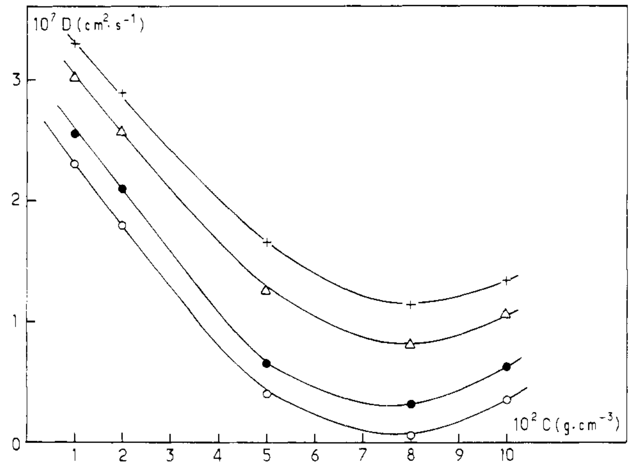

Figure 1. Concentration dependence of D of polystyrene solutions ($\bar{M}_w$ = 130 000) in cyclohexane: (+) T = 34.5 °C; (△) T = 30.5 °C; (●) T = 25 °C; (○) T = 22 °C.

was purchased from Dow Chemical Co.

Polymer solutions of different concentrations in cyclohexane or in cyclopentane (Θ solvent of polystyrene at 34.5 °C and 20.4 °C, respectively) were freed from dust by centrifugation for 2 h at 17 000 rpm.

The investigated network was prepared by anionic block copolymerization of styrene and divinylbenzene.[14] The length of the elastic chains between chemical branch points corresponds to a "precursor" polystyrene of molecular weight 128 000. The equilibrium volume swelling degree of this sample is 7 in cyclohexane at 34.5 °C and 6.4 in cyclopentane at 20.5 °C.

B. Correlation Time Measurements. A Spectra Physics argon ion laser (λ = 488 nm) was used in conjunction with a 72-channel clipped digital autocorrelator (Precision Devices and Systems LTD Malvern) for measuring the autocorrelation function of the scattered light intensity. The scattering angle was varied from 20° to 120°. The temperature was held constant to within ±0.01 °C. The cube-shaped gel samples were put in standard glass cells containing an excess of swelling liquid. They were allowed to stand for at least 1 day to attain stability.

Intensity correlation data were routinely processed, using the method of cumulants[15,16] to provide the average decay rate $\langle\Gamma\rangle$ and the variance v. The latter parameter is a measure of the width of the distribution of decay rates and is given by

$$v = (\langle\Gamma^2\rangle - \langle\Gamma\rangle^2)/\langle\Gamma\rangle^2 \qquad (1)$$

where $\langle\Gamma^2\rangle$ is the second moment of the distribution.

The diffusion coefficient D was determined from the average decay rate $\langle\Gamma\rangle$ according to

$$\langle\Gamma\rangle = 2k^2D \qquad (2)$$

The magnitude of the scattering vector k is given by

$$k = [4\pi n \sin(\theta/2)]/\lambda \qquad (3)$$

where θ is the scattering angle, λ is the wavelength of the incident light in a vacuum, and n is the index of refraction of the scattering medium.

Results and Discussion

A. Crossover between the Dilute and Semidilute Regimes at the Θ Temperature. Figures 1 and 2 illustrate, respectively, the influence of the temperature and of the molecular weight on the concentration dependence of the diffusion constant D for polystyrene solutions in cyclohexane and cyclopentane. The $D(c)$ curves exhibit a smooth minimum at a concentration approximately independent of temperature, but which increases as the molecular weight decreases. This minimum, first observed by Rehage et al.,[13] has been correlated to the crossover concentration c^* between the dilute and semidilute regimes.[7,17] This smooth transition is accompanied by an increase of the variance as illustrated in Figure 3. Beyond the concentrations considered in this paper, the autocorrelation function becomes strongly nonexponential and contains components having very long decay times. Such a behavior has already been observed in both good and Θ solvents.[7,17-21] The origin of the observed nonexponentiality is still unclear and the exact shape of the autocorrelation function is not yet established. Some authors have used the cumulant method to analyze the data,[19,21] whereas a bimodal distribution was reported in other studies.[7,18,20] In this paper we have restricted ourselves to a range of concentrations where the variance is relatively low so that the application of eq 2 to determine D seems to be a reasonable assumption even though it does not have a theoretical basis. The self-consistency of the results provides some a posteriori justification of this assumption. However, for higher concentrations the D values obtained from a cumulant fit seem to be meaningless.

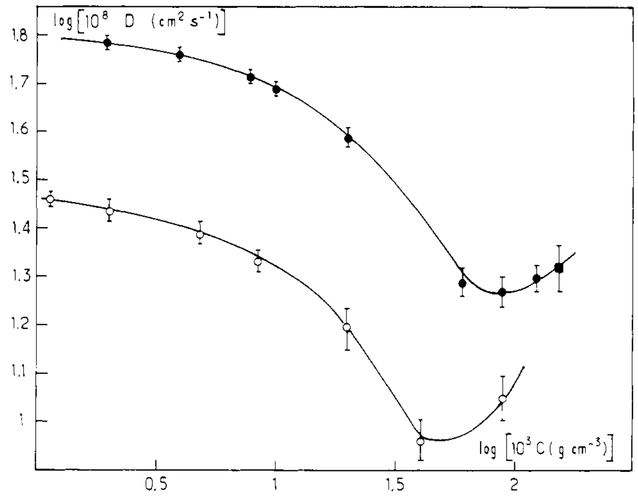

Figure 2. Concentration dependences of D of polystyrene solutions in cyclopentane: (●) $\bar{M}_w$ = 130 000; (○) $\bar{M}_w$ = 570 000.

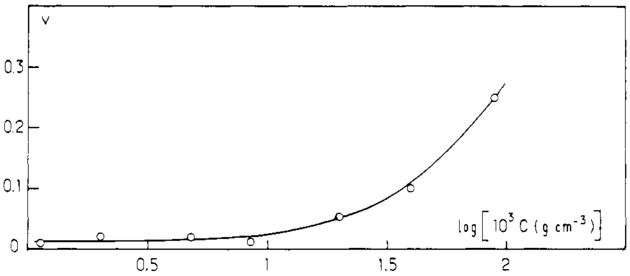

Figure 3. Concentration dependence of the variance of polystyrene solutions of molecular weight $\bar{M}_w$ = 570 000 in cyclopentane at 20.4 °C.

The observed behavior of the diffusion constant can be inferred from the theoretical predictions made for the two limiting concentration ranges $c \ll c^*$ and $c \gg c^*$ (but still in the semidilute regime).

For dilute solutions $D(c)$ can be approximated as

$$D(c) = D_0(1 + \phi c) \qquad (4)$$

D_0, which is obtained by extrapolation of $D(c)$ to zero concentration, is related to the hydrodynamic radius R_H through the relationship

$$D_0 = k_BT/6\pi\eta_0R_H \qquad (5)$$

where k_B is the Boltzmann constant and η_0 the viscosity of the solvent. The interaction parameter ϕ is given by[22]

$$\phi = 2mNA_2 - \phi_f - \bar{v} \qquad (6)$$

m is the mass of monomer, $\bar{v}$ is the partial specific volume of the polymer, N is the number of monomer units in a chain, A_2 is the second virial coefficient, and ϕ_f is the hydrodynamic interaction parameter of the friction coefficient.

At the Θ temperature, A_2 vanishes. Furthermore $\bar{v}$ is small, compared to ϕ_f, which is strongly negative. As a consequence, ϕ can be approximated as ϕ_f, which is proportional to the intrinsic viscosity $[\eta]$,[17,23] that is, to the square root of the molecular weight M:

$$\phi_f \sim [\eta] \sim M^{1/2} \qquad (7)$$

Then using eq 4 and 7, we obtain

$$D(c)/D_0 = 1 + \alpha c M^{1/2} \qquad (8)$$

where α is a constant for a given polymer.

In the semidilute regime ($c \gg c^*$) both static and dynamic features have been discussed in terms of scaling approaches. The behavior of the static correlations near the Θ temperature has been analyzed by Daoud and Jannink, who derived the following expression for the total density–density correlation function:[1]

$$g(r) = \langle \rho(0)\rho(r) \rangle - \rho^2 \equiv \langle \delta\rho(0)\delta\rho(r) \rangle = (\text{constant})\rho^2 \frac{a}{r} e^{-r/\xi} \qquad (9)$$

where ρ is the monomer density, a^3 the volume of a monomeric unit, and ξ a correlation length inversely proportional to ρ:

$$\xi \sim 1/\rho a^2 \sim c^{-1} \qquad (c > c^*) \qquad (10)$$

Dynamical scaling for polymers in Θ solvents has been theoretically investigated by Brochard and de Gennes.[5] Assuming that hydrodynamic interactions between monomers due to backflow is dominant, these authors establish the following relation between the diffusion constant $D(c)$ and the static correlation function $g(\vec{r})$:

$$D(c) = \int g(\vec{r}) \frac{k_B T}{6\pi\eta_0 r} \, d\vec{r} \Big/ \int g(\vec{r}) \, d\vec{r} \qquad (11)$$

Equations 9 and 11 lead to the following expression for $D(c)$:[24]

$$D(c) = k_B T / 6\pi\eta_0\xi \propto c \qquad (12)$$

Therefore, taking into account that D_0 varies like $M^{-1/2}$, we obtain the following concentration dependence of D/D_0 in the semidilute regime:

$$D/D_0 = \beta c M^{1/2} \qquad (c \gg c^*) \qquad (13)$$

where β is a numerical constant.

The crossover between dilute and semidilute regimes occurs at $c \simeq c^*$, that is, at a concentration such that

$$cM^{1/2} = \text{constant} \qquad (14)$$

The above considerations explain the experimentally observed behavior of $D(c)$. The initial decrease of D is associated with the hydrodynamic interactions of the friction coefficient, which produce a slowing down of the translational self-diffusion of the chain in the dilute regime. On the other hand, in the entangled solution, the long-wavelength fluctuations involve cooperative chain motion, characterized by a cooperative diffusion constant that increases linearly with the concentration. As a consequence, $D(c)$ must exhibit a minimum at a concentration close to c^*.

Furthermore, eq 8, 13, and 14 predict that for $T = \Theta$, the concentration dependence of D should be represented in the form of a molecular weight independent diagram of D/D_0 vs. $cM^{1/2}$. In Figure 4a, we have reported the data corresponding to linear polymer samples of molecular weight ranging from 20 000 to 2×10^6 dissolved either in cyclohexane at 34.5 °C or in cyclopentane at 20.4 °C. On the same figure, we have plotted the results of CGD experiments performed by Roots and Nyström[12] on a solution of polystyrene of molecular weight 10^6 in cyclohexane. It can be seen that the experimental points gather around a unique curve showing a rather flat minimum. The deviation observed for the data corresponding to the highest concentration investigated by light spectroscopy is likely to be connected with the rather large variance ($v \sim 0.25$) of the autocorrelation function obtained for this sample (cf. Figure 3).

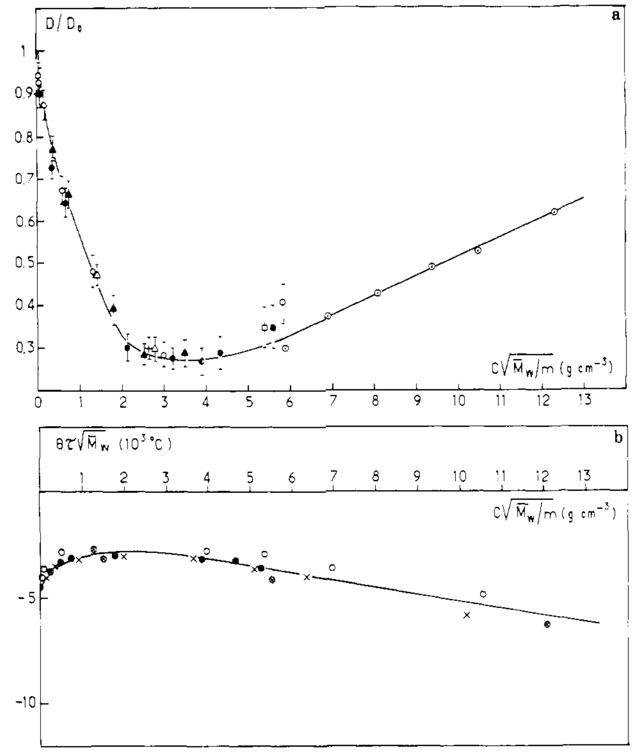

Figure 4. (a) Normalized hydrodynamic diagram of polystyrene solutions at the Θ temperature; $m = 104$ represents the molecular weight of the styrene. Cyclohexane at 34.5 °C: (△) $\bar{M}_w = 20\,000$; (▲) $\bar{M}_w = 130\,000$; (+) $\bar{M}_w = 2 \times 10^6$; (□) network. Cyclopentane at 20.4 °C: (●) $\bar{M}_w = 130\,000$; (⊙) $\bar{M}_w = 570\,000$; (◐) $\bar{M}_w = 10^6$; (■) network. (b) Normalized phase diagram of polystyrene solutions in cyclohexane (from Daoud and Jannink[1]). The data were taken from ref 4. Lines are guides for the eye.

It is also interesting to remark that data relative to the two networks swollen at equilibrium lie also on the same curve. This tends to prove that the restoring force associated with the long-wavelength fluctuations in networks swollen in a Θ solvent is determined by the free energy of mixing of polymer and solvent alone and that the elasticity associated with the presence of cross-links does not play any role. This is contrary to what is observed for networks swollen at equilibrium in good solvents, which exhibit systematically a higher value of D than the corresponding semidilute solutions.[20,25]

Figure 4b, which represents the normalized coexistence curve of the polystyrene–cyclohexane systems in the phase diagram $\Theta\tau(\bar{M}_w/m)^{1/2}$ derived by Daoud and Jannink,[1], illustrates the correlation between the minimum of $D(c)$ and the critical solution concentration. It must be remarked that the c^* concentration calculated by Daoud and Jannink corresponds roughly to the concentration where D/D_0 starts to increase with $c(\bar{M}_w/m)^{1/2}$.

B. Critical Behavior Associated with Phase Separation. The critical phase separation of a binary fluid mixture occurs for a concentration corresponding to the maximum of the coexistence curve where both coexistence and spinodal curves have a common horizontal tangent. For polymer systems, the critical concentration c_c and temperature T_c are dependent on the molecular weight of the polymer according to[1,26,27]

$$c_c = M^{-1/2}w^{-1}$$

$$(T_c - \Theta)/T_c = -2wM^{-1/2} \qquad (15)$$

where w is the third virial coefficient of the osmotic pressure.

The phase diagrams of such systems are not easy to establish because of some complications arising from the macromolecular nature of the solute. More specifically, the polydispersity of the samples broadens the coexistence curve. Moreover, the phase separation for systems of compositions located between the spinodal curve and the coexistence curve is very slow, leading possibly to some errors in the determination of the latter, mainly in the high polymer concentration range. As a consequence, the critical concentration is rather difficult to locate and several studies report values of c_c larger than the concentration at the maximum of the coexistence curve.[28,29]

The range of the critical fluctuations is characterized by a correlation length ξ_c, which diverges at the critical temperature according to the following law:[27]

$$\xi_c \cong R_0\left(\frac{\Theta - T_c}{T - T_c}\right)^{\nu_c} \qquad (16)$$

where ν_c is an exponent close to $^2/_3$.

The form of eq 16 is such that at $T = \Theta$, the correlation length is equal to the size R_0 of the unperturbed chain.

By combining eq 15 and 16 and taking into account that $R_0 \sim M^{1/2}$, we obtain

$$\xi_c \propto M^{1/6}[(T - T_c)/T_c]^{-2/3} \qquad (17)$$

The relation (11) between the diffusion constant and the static correlation function enables the prediction of the temperature dependence of D close to the critical temperature[27] in the hydrodynamic limit:

$$D = k_BT/6\pi\eta_0\xi_c \qquad \text{with } k\xi_c < 1 \qquad (18)$$

In the nonlocal hydrodynamic region ($k\xi_c \geq 1$), the diffusion coefficient has the more general form derived by Kawasaki:[30]

$$D \simeq \frac{k_BT}{6\pi\eta_0\xi_c}\left(1 + \frac{3}{5}k^2\xi_c^{\,2}\right) \qquad (19)$$

The above derivation of the temperature dependence of the diffusion coefficient does not take into account hydrodynamic interactions of the friction coefficient. It was shown in the preceding paragraph that these interactions considerably slow down the translational diffusion.

From the relation

$$D = k_BT/6\pi\eta_0\xi_H \qquad (20)$$

one measures a hydrodynamic correlation length which, at the Θ temperature and critical concentration, greatly exceeds the hydrodynamic radius obtained at infinite dilution. However, although $\xi_H \gg \xi_c$, one expects that both correlation lengths for solutions at critical concentration scale with temperature as $(T - T_c)^{-2/3}$ in the vicinity of T_c. As a matter of fact, one is never sure that the polymer concentration is exactly the critical concentration, in which case the correlation length diverges at the spinodal temperature $T_{sp} \leq T_c$. However, the behavior of ξ_H in the vicinity of the critical concentration should still be described by eq 17, in which T_c is replaced by T_{sp}.

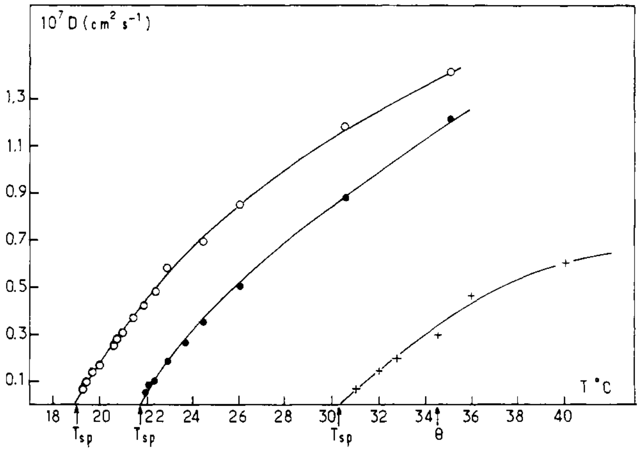

Figure 5. Temperature dependences of the diffusion coefficient of polystyrene solutions in cyclohexane: (○) $\bar{M}_w$ = 130 000, $c(\bar{M}_w/m)^{1/2}$ = 2.83 g cm^{-3}; (●) $\bar{M}_w$ = 130 000, $c(\bar{M}_w/m)^{1/2}$ = 3.53 g cm^{-3}; (+) $\bar{M}_w$ = 2 × 10^6, $c(\bar{M}_w/m)^{1/2}$ = 2.73 g cm^{-3}.

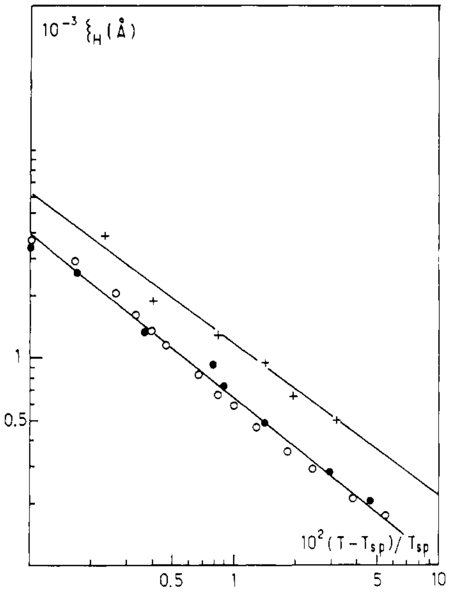

Figure 6. Temperature dependences of the hydrodynamic correlation length of polystyrene solutions in cyclohexane. Symbols are the same as in Figure 5.

In Figure 5 are reported the temperature dependences of D of polystyrene solutions of molecular weights 130 000 and 2 × 10^6 at concentrations located in the region of the minimum of $D(c)$. The extrapolations at $D = 0$ give the corresponding spinodal temperature.

Figure 6, which shows a log–log plot of the hydrodynamic correlation length as a function of $(T - T_{sp})/T_{sp}$ for the same systems, reveals several interesting features:

(a) For a given molecular weight, the data relative to two slightly different concentrations close to the critical concentration lie on the same curve when plotted as a function of $(T - T_{sp})/T_{sp}$. This behavior, also observed for the static correlation length ξ_c,[31] shows that the fluctuations can be described in the first approximation by the same laws in the vicinity of both critical temperature and spinodal temperature.

(b) The exponents of the power laws describing the temperature dependence of the hydrodynamic correlation length for critical fluctuations (0.73 and 0.79 for $\bar{M}_w$ = 2 × 10^6 and $\bar{M}_w$ = 130 000, respectively) are larger than the theoretically predicted value 0.66. This result, in good agreement with earlier observations of Kuwahara et al.,[29] may be due to the uncertainty arising from the rather large variance (0.25–0.5) of the autocorrelation function close to the critical point.

(c) The hydrodynamic correlation length ξ_H is much larger than the critical correlation length measured from the angular disymmetry of the scattered light, which does not exceed 500 Å in the domain of $T - T_{sp}$ investigated here.[29,31] This explains that no deviation from the k^2 dependence was observed for the rate constant $\langle \Gamma \rangle$ in our experiments.

(d) The two straight lines of Figure 6, relative to samples of molecular weights 130 000 and 2×10^6, respectively, are shifted on the vertical scale by a factor of the order of 1.8, which is in reasonable agreement with the prediction 1.58 in eq 17.

Conclusion

The main result of this paper concerns the concentration and molecular weight dependences of the diffusion constant, which can be represented on the form of a normalized hydrodynamic plot showing a minimum in the crossover region between the dilute and semidilute regimes.

The temperature dependence of the diffusion constant in the crossover region has also been analyzed in terms of the theories of critical fluctuations. The hydrodynamic correlation length measured in the vicinity of the critical point exceeds considerably the critical static correlation length because of virial effects on the friction coefficient. This difference between static and correlation length is likely to be also observed in the semidilute concentration range.

Registry No. Polystyrene, 9003-53-6; styrene–divinylbenzene copolymer, 9003-70-7.

References and Notes

(1) Daoud, M.; Jannink, G. *J. Phys. (Orsay, Fr.)* **1976**, *37*, 973.
(2) de Gennes, P.-G., *J. Phys. Lett. (Orsay, Fr.)* **1975**, *36*, L 55.
(3) Cotton, J. P.; Nierlich, M.; Boue, F.; Daoud, M.; Farnoux, B.; Jannink, G.; Duplessix, R.; Picot, C. *J. Chem. Phys.* **1976**, *65*, 1101.
(4) Schultz, A. R.; Flory, P. J. *J. Chem. Phys.* **1953**, *74*, 4760.
(5) Brochard, F.; de Gennes, P.-G. *Macromolecules* **1977**, *10*, 1157.
(6) Chu, B.; Nose, T. *Macromolecules* **1980**, *13*, 122.
(7) Nose, T.; Chu, B. *Macromolecules* **1979**, *12*, 590.
(8) Roots, J.; Nyström, B. *J. Polym. Sci., Polym. Phys. Ed.* **1981**, *19*, 979.
(9) Nyström, B.; Roots, J. *J. Macromol. Sci., Rev. Macromol. Chem.* **1980**, *C19*, 35.
(10) Roots, J.; Nyström, B. *Polymer* **1979**, *20*, 148.
(11) Nyström, B.; Roots, J.; Bergman, R. *Polymer* **1979**, *20*, 157.
(12) Roots, J.; Nyström, B. *Macromolecules* **1980**, *13*, 1595.
(13) Rehage, G.; Ernst, O.; Fuhrmann, J. *Discuss. Faraday Soc.* **1970**, *49*, 208.
(14) Weiss, P.; Hild, G.; Herz, J.; Rempp, P. *Makromol. Chem.* **1970**, *135*, 249.
(15) Koppel, D. E. *J. Chem. Phys.* **1972**, *57*, 4814.
(16) Brown, J. C.; Pusey, P. N.; Dietz, R. *J. Chem. Phys.* **1975**, *65*, 1101.
(17) Lempert, W.; Wang, C. H. *Ferroelectrics* **1980**, *30*, 107.
(18) Mathiez, P.; Mouttet, C.; Weisbuch, G. *J. Phys. (Orsay, Fr.)* **1980**, *41*, 519.
(19) Schaeffer, D. W.; Joanny, J. F.; Pincus, P. *Macromolecules* **1980**, *13*, 1280.
(20) Munch, J. P.; Lemarechal, P.; Candau, S.; Herz, J. *J. Phys. (Orsay, Fr.)* **1977**, *38*, 1499.
(21) Munch, J. P.; Herz, J.; Boileau, S.; Candau, S. *Macromolecules* **1981**, *14*, 1370.
(22) Yamakawa, H. "Modern Theory of Polymer Solutions"; Harper and Row: New York, 1971.
(23) Adam, M.; Delsanti, M. *J. Phys. (Orsay, Fr.)* **1980**, *41*, 713.
(24) Actually, the Brochard–de Gennes theory predicts a bimodal decay behavior for the autocorrelation function but the amplitude of the fast mode, associated with the elasticity of the entangled solution, is too small to be detected. Similar behavior is also predicted by a more recent approach (Reihanian, H.; Jamieson, A. M. *Macromolecules* **1979**, *12*, 684).
(25) Munch, J. P.; Candau, S.; Herz, J.; Hild, G. *J. Phys. (Orsay, Fr.)* **1977**, *38*, 971.
(26) Flory, P. J. "Principles of Polymer Chemistry"; Cornell University Press: Ithaca, NY, 1953.
(27) de Gennes, P.-G. "Scaling Concepts in Polymer Physics"; Cornell University Press: Ithaca, NY, 1980.
(28) Koningsveld, R.; Kleintjens, L. A.; Schultz, A. R. *J. Polym. Sci., Part A-2* **1970**, *2*, 1261.
(29) Kuwahara, N.; Fenby, D. V.; Tamsky, M.; Chu, B. *J. Chem. Phys.* **1971**, *55*, 1140.
(30) Kawasaki, K. *Phys. Lett. A* **1969**, *30A*, 325.
(31) Kojima, J.; Kuwahara, N.; Kaneko, M. *J. Chem. Phys.* **1975**, *63*, 332.

A Study of the Behavior of Water in Nafion Membranes

Noel G. Boyle,[†] Vincent J. McBrierty,[*,†] and Dean C. Douglass

Bell Laboratories, Murray Hill, New Jersey 07974. *Received April 15, 1982*

ABSTRACT: This paper reports NMR data for perfluorosulfonate acid Nafion membranes containing various amounts of water. Results are also presented for Fe^{3+}- and Na^+-exchanged salts. The glasslike behavior at low temperatures is discussed. The data indicate that there is a distribution of heterogeneous water sites in the membranes and that fast exchange, on the NMR time scale, occurs between sites near room temperature and above. The presence of paramagnetic species in samples containing water, implied by the magnitude of the NMR relaxation times, is confirmed by X-ray fluorescence measurements, which reveal iron (and potassium) in significant amounts.

Introduction

Many studies[1-13] have revealed the complex behavior of water associated with diverse solid media. Whether isolated in the vitreous or amorphous state[11] or incorporated in certain biological systems[5,8] or porous materials,[6,7,13] water manifests behavior essentially different from that observed in the bulk state. At low temperatures glasslike character is often observed.

Of interest in this paper is the behavior of water in the perfluorosulfonate membranes developed by the Du Pont company under the tradename Nafions. A preliminary report[14] has shown that water in Nafions also exhibits glasslike behavior at low temperatures and that data from NMR and neutron scattering experiments can be described

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[†] Department of Pure and Applied Physics, Trinity College, Dublin 2, Ireland.