

Co-operative diffusion of semi-dilute solutions, concentrated solutions and swollen networks for polystyrene in dibutylphthalate

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The diffusion constant of solutions of polystyrenes of molecular weight ranging from 110 000 to 3.6×10^6 in straight-chain-dibutylphthalate has been measured by photon correlation spectroscopy as a function of polymer volume fraction and temperature. In the semi-dilute range the co-operative diffusion constant D_c exhibits a much smaller increase with the polymer volume fraction Φ than theoretically predicted, except at high temperatures ($T \geq 100^\circ\text{C}$) where it follows a $\Phi^{1/2}$ law characteristic of a marginal solvent. This effect can be described to an enhancement of the friction factor, which is also demonstrated by a decrease in D_c occurring at a volume fraction which increases with temperature. The same effect is observed in swollen networks but it is strongly reduced for swelling equilibrium conditions.

Keywords Semi-dilute; spectroscopy; diffusion; networks; photon correlation spectroscopy; polystyrene

INTRODUCTION

The static and dynamic properties of polymer solutions have aroused a great deal of interest in the last few years, due to both experimental progress and new theoretical approaches. Thus, small-angle neutron scattering techniques have elucidated some problems relative to the local conformation of the chains whereas photon correlation spectroscopy (PCS) has provided information on the collective motions.

The application of new theoretical techniques, mainly based on scaling methods, led to important predictions concerning the asymptotic long-chain power law of solution properties. Of particular interest is the so-called semi-dilute regime corresponding to solutions where the coils do overlap but where the polymer volume fraction is still low. In such systems the measurement of the autocorrelation function of scattered light provides a measure of the co-operative diffusion constant D_c which is related to the hydrodynamic correlation length ξ_H through^{1,2}:

$$\xi_H = \frac{k_B T}{6\pi\eta_0 D_c} \quad (1)$$

where k_B is the Boltzmann constant, T the absolute temperature and η_0 the viscosity of the solvent. The concentration dependence of ξ_H depends mainly on the quality of the solvent. For good solvents, de Gennes identified ξ_H with the average distance ξ_p between nearest chain contacts and derived the following scaling law as a function of monomer concentration, ρ ^{1,2}:

$$\xi_H \sim \rho^{-3/4} \quad (2)$$

At theta conditions, the interaction pair vanishes and the correlation length is associated with ternary contacts, in which case³:

$$\xi_H \sim \rho^{-1} \quad (3)$$

The cross-over between good and theta solvent has been investigated in detail by Daoud and Jannink⁴⁻⁶ who defined a theta domain, which is a function of both concentration and molecular weight of the chains.

However, several PCS studies demonstrated that the concept of a sharp cross-over between good and theta solvents was unrealistic and that the notion of marginal solvents should also be taken into account. More specifically the variations of ξ_H with ρ were generally described by power laws with an exponent larger than $-3/4$ ⁷⁻¹¹. This can be qualitatively understood from the fact that ξ_H is sensitive to short polymeric sequences which are less swollen than larger ones. As a matter of fact, there is a characteristic length ξ_c beneath which the chain is ideal. The influence of this scale dependence of the swelling on the hydrodynamic correlation length has been treated in two different ways. The first approach is similar to that used by Weill and des Cloizeaux¹² for the single-chain problem and assumes that the monomer-monomer correlation function changes abruptly from Gaussian to excluded volume statistics at a temperature dependent cut-off value of the number of monomers. This leads to apparent dynamical exponents^{5,13}.

However, Schaeffer *et al.*¹⁰ assume that for a marginal solvent, the hydrodynamic screening is inefficient, and that the binary contacts are still dominant; this is typically a mean field situation. The temperature concentration diagram for the semi-dilute regime is then subdivided into good, marginal and theta domains, separated by cross-over lines. More specifically, starting from a good solvent

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solution at a given temperature and increasing the concentration, leads to the following sequence of scaling laws:

$$\xi_H \sim \rho^{-3/4} \text{ (good)}, \xi_H \sim \rho^{-1/2} \text{ (marginal)}, \xi_H \sim \rho^{-1} \text{ (theta)}$$

The ensemble of collected data support this analysis¹⁴. However, several points remain to be clarified. For most investigated semi-dilute systems the autocorrelation function of scattered light was found to be strongly non-exponential with evidence of slow decaying modes^{8,15-19}. These modes have been attributed to either the presence of locally undissolved polymer¹⁸ or to the self diffusion of entangled polymer coils¹⁶. The exact origin of these modes and their influence on the determination of D_c are still undetermined. Also, the concentration dependence of D_c for volume fractions >0.1 is not well understood. In some cases, a maximum has been reported for D_c at a volume fraction Φ varying from 0.15 to 0.5^{20,21}. Again, the origin of this maximum and its dependence on the quality of diluent are not established.

This paper reports a study of the diffusion coefficient of polystyrene in dibutylphthalate solutions over a large range of temperature and concentration. This system presents some interesting features. First the dissolutions can be carried out at relatively high temperatures which ensures the homogeneity of the solutions. Secondly, dibutylphthalate is a marginal solvent for polystyrene over all the investigated temperature range (4.5–140°C), the quality of the solvent decreasing as the temperature increases. It is then possible to separate the respective influences of temperature as such and of the quality of the diluent. Thirdly, the possible correlation between the position of the maximum of $D_c(c)$ and temperature can be investigated over a large range of temperatures.

Also in this paper are reported measurements of the co-operative diffusion coefficient for a series of crosslinked networks swollen in the same diluent. The temperature and concentration dependences of D_c are compared with those obtained for the solutions.

EXPERIMENTAL

Materials

The polystyrene samples used for the PCS experiments originated from Pressure Chemical Co and had the following weight average molecular weights and indices of polydispersity:

$$M_w = 110000 (<1.06), 670000 (<1.15), \\ 2 \times 10^6 (<1.2) \text{ and } 3.6 \times 10^6 (<1.2)$$

The temperature dependences of the second virial coefficient and of the radius of gyration were established using an anionically prepared sample of molecular weight 680000 and polydispersity index $M_w/M_n \leq 1.05$. This sample was kindly made available by Dr Strazielle of Centre de Recherches sur les Macromolécules, Strasbourg.

The polystyrene networks were obtained by radical copolymerization of styrene and divinylbenzene in benzene solution in the presence of azo-2-2'-isobutyronitrile as the initiator, at 60°C over a period of 48 h. Five networks of various degrees of crosslinking have been prepared using different concentrations of styrene and

divinylbenzene; their characteristics have been given in a previous paper²².

The straight-chain dibutylphthalate was purchased from BDH Co and used without further purification. The solutions of linear polystyrenes were allowed to stand for a few days at 100°C to ensure complete dissolution of the polymer. The networks were swollen by various amounts of straight-chain dibutylphthalate at 120°C. Swelling equilibrium conditions were obtained by placing the sample at 120°C in an excess of solvent. The polymer concentration at the swelling equilibrium was determined by a weighing technique. When the temperature is lowered, the swelling degree does not change appreciably. Furthermore, the time required by the gel to reach a new equilibrium is of the order of weeks because of the high viscosity of the diluent and the large volume ($\sim 1 \text{ cm}^3$) of the sample²³. In this study the temperature range was scanned in less than a day so that the polymer concentration within the gel could be considered as constant.

Light scattering experiments

The scattered intensities have been measured by means of a Sofica photogoniometer operating at a wavelength of 546 nm on dilute solutions [$\Phi < 10^{-3}$] previously freed of dust by centrifugation. The refractive index increment of the polystyrene straight-chain dibutylphthalate was determined with a Brice-Phoenix differential refractometer, at 25°C it was found equal to 0.114.

A Spectra-Physics argon-ion laser ($\lambda = 488 \text{ nm}$) was used in conjunction with a 48 channel clipped digital autocorrelator (Malvern Instruments) for measuring the autocorrelation function of the scattered light intensity. The scattering angle was varied from 20° to 120°. The temperature was constant to within $\pm 0.1^\circ\text{C}$. The experimental data were routinely processed using a new multi-exponential sum fitting program realized in the laboratory²⁴. This analysis provides the average decay rate $\bar{\Gamma}$ and the variance, v . The latter parameter is a measure of the width of the distribution of decay rates and is given by:

$$v = (\overline{\Gamma^2} - \bar{\Gamma}^2) / \bar{\Gamma}^2 \quad (4)$$

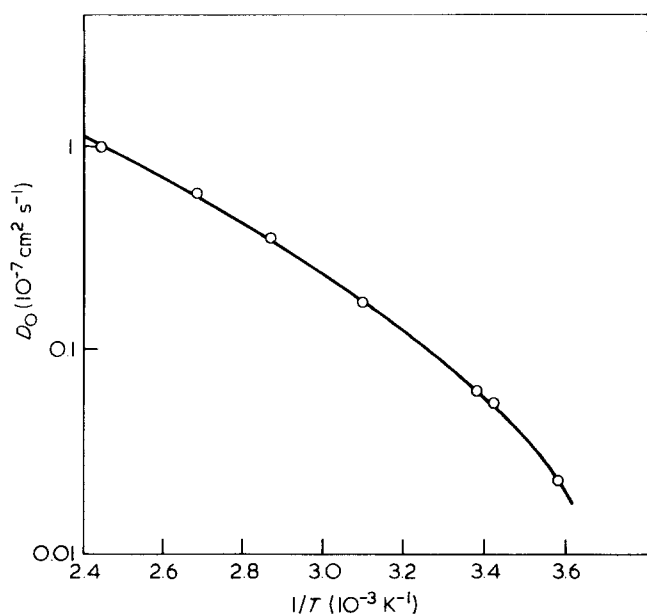
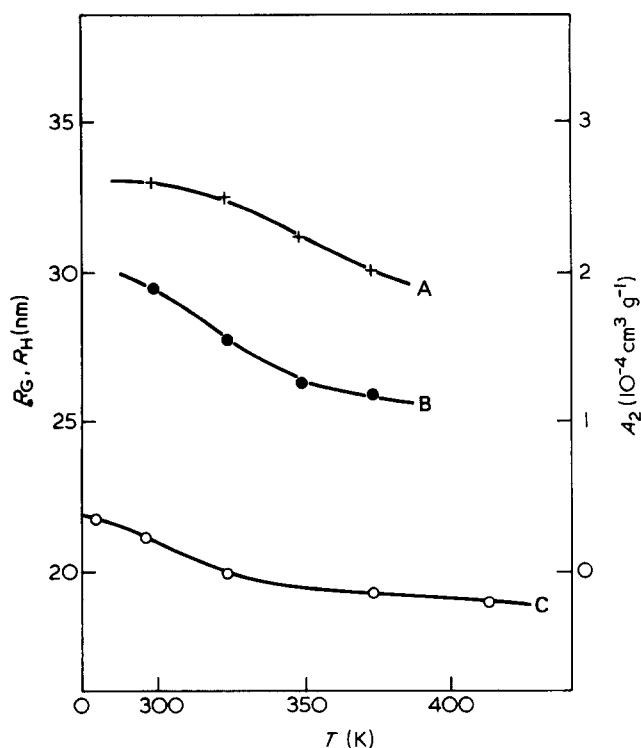
where $\overline{\Gamma^2}$ is the second moment of the distribution. The detection scheme was either homodyne or heterodyne. In the latter case, the scattered signal was mixed with an external oscillator using a Michelson type interferometer.

Samples at volume fractions up to 0.1, 0.03 and 0.37×10^{-2} for molecular weights of 670000, 2×10^6 and 3.6×10^6 , respectively, were freed of dust by centrifugation of the scattered cells at 40°C. More concentrated samples contained dust and possibly local inhomogeneities resulting in a quasistatic scattered intensity. This strong signal heterodyned to some extent the signal associated with the dynamic fluctuation concentrations. Measurements made with and without an external oscillator allowed a check of the nature (homodyne or heterodyne) of the detection regime. The signals scattered from samples at concentrations larger than the upper limits given previously as well as from swollen networks were found to be fully heterodyned.

RESULTS

Thermodynamic characteristics of the PS-N-dibutylphthalate systems

Light scattering and PCS measurements in dilute solutions provide a determination of the single particle


 Figure 1 Temperature dependence of D_0 for $M_w=670\,000$

 Figure 2 Temperature dependences of A, R_G ; B, A_2 ; C, R_H . The R_G and A_2 measurements have been made on a sample of $M_w=680\,000$, the R_H measurements on a sample $M_w=670\,000$

characteristics. Thus, the translational diffusion coefficient is obtained from the average decay time $\bar{\Gamma}$ of the autocorrelation function through the following relation, valid for homodyne detection:

$$\bar{\Gamma} = 2DK^2 \quad (5)$$

where K is the magnitude of the scattering vector given by:

$$K = (4\pi n \sin(\theta/2)) / \lambda \quad (6)$$

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.

In the heterodyne regime, that is when a static reference signal is superimposed on the dynamic scattering, $\bar{\Gamma}$ is given by²⁵:

$$\bar{\Gamma} = DK^2 \quad (7)$$

The extrapolation of D to zero concentration, D_0 , is related to the hydrodynamic radius R_H of the molecule through the Stokes-Einstein relation:

$$D_0 = \lim_{c \rightarrow 0} D = \frac{k_B T}{6\pi\eta_0 R_H} \quad (8)$$

The concentration dependence of D for a PS sample of molecular weight $M_w=670\,000$ in the dilute regime ($\Phi < 0.25 \times 10^{-2}$) is negligible over the whole range of temperature investigated, this behaviour is typical of a marginal solvent¹⁹. The variation of D_0 with $10^3/T$ for this sample is shown in Figure 1. The temperature dependence of the hydrodynamic radius of this sample, as determined by combining D_0 measurements and the variation of the viscosity of the dibutylphthalate with temperature^{26,27} is shown in Figure 2. In the same Figure are plotted the variations of the radius of gyration R_G and the second virial coefficient A_2 obtained for a PS sample of molecular weight $M_w=680\,000$. The three parameters R_H , R_G and A_2 decrease slightly as the temperature increases indicating the occurrence of a lower critical solution temperature $> 140^\circ\text{C}$. Table 1a compares the values of R_G , R_H and A_2 obtained for solutions in straight-chain dibutylphthalate with those characteristic of a good solvent (benzene) and a theta solvent (cyclohexane), respectively. It is evident that the ratio $R_H/R_G=0.625 \pm 0.015$ over the whole range of temperature. The results demonstrate that straight-chain dibutylphthalate is a marginal solvent for polystyrene in the temperature range 22–140°C.

This conclusion is also supported by the equilibrium swelling degree measurements of the PS networks. In Table 1b are reported the polymer volume fractions at the swelling equilibrium for PS networks in dibutylphthalate,

Table 1 (a) Thermodynamic characteristics of linear PS samples in straight-chain dibutylphthalate

Solvent	Dibutylphthalate		Benzene $T=25^\circ\text{C}$	Cyclohexane $T=34.5^\circ\text{C}$
	$T=25^\circ\text{C}$	$T=100^\circ\text{C}$		
R_G (nm) ^a	33.0	30.5	36.0 ^c	24.0 ^d
R_H (nm) ^b	21.2	19.3	26.7 ^e	17.2 ^f
$10^4 A_2$ (cm ³ g ⁻¹) ^a	1.9	1.2	3.4 ^c	0

^a $M_w=680\,000$

^b $M_w=670\,000$

^c From ref. (28)

^d From ref. (29)

^e From ref. (30)

^f From ref. (31)

(b) Polymer volume fraction in networks swollen at equilibrium in different diluents

Samples	Solvent	Dibutylphthalate	Benzene	Cyclohexane
		$T=120^\circ\text{C}$	$T=25^\circ\text{C}$	$T=34.5^\circ\text{C}$
R 43		0.077	0.037	0.17
R 42		0.15	0.063	0.26
R 36		0.21	0.12	0.36
R 35		0.21	0.12	0.37
R 20		0.33	0.18	—

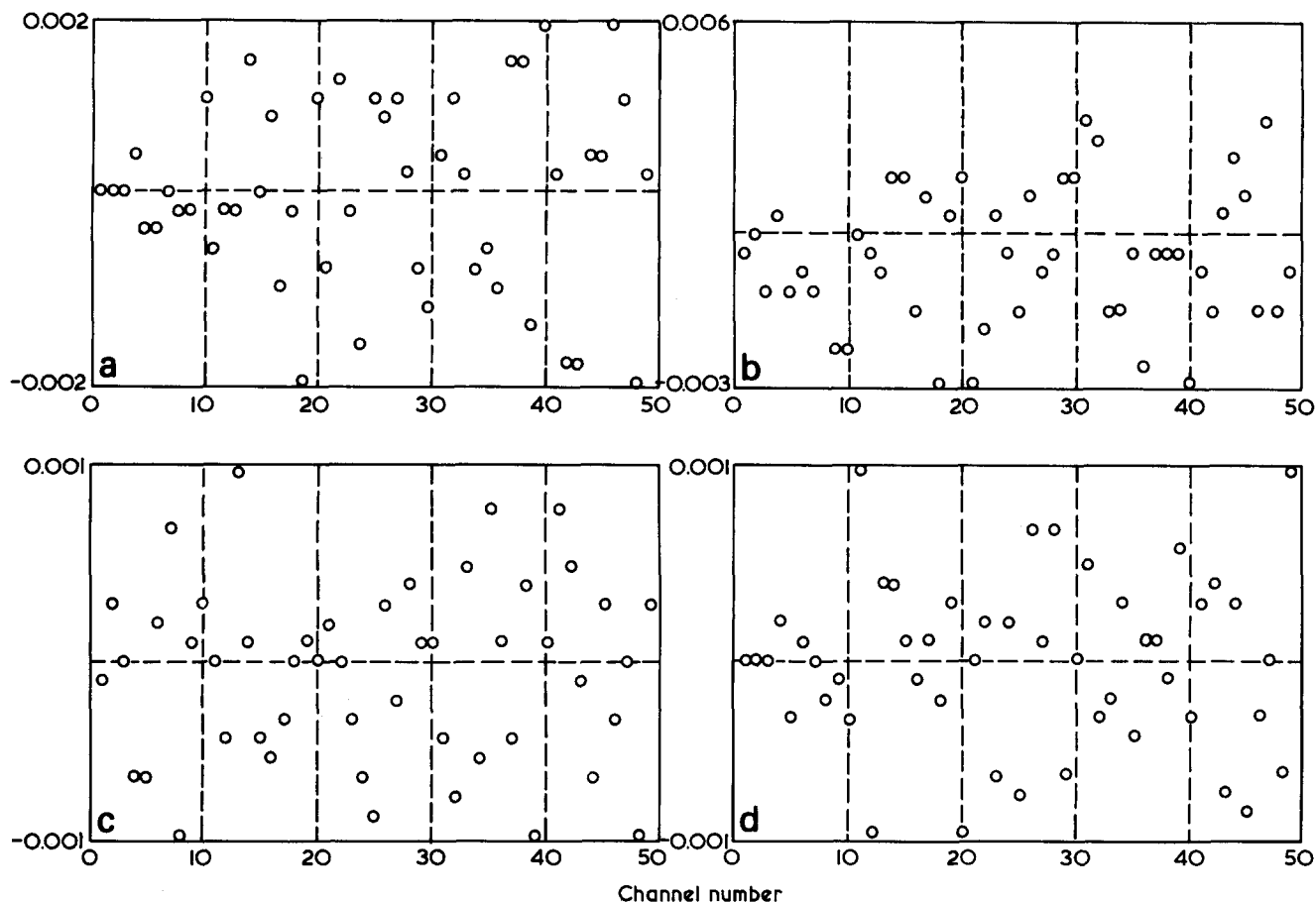


Figure 3 Residuals from computer fitting with results summarised in Table 2. Sample temperature, 292K; and scattering angle, 90°

at 120°C, benzene at 25°C and cyclohexane at 34.5°C. The values obtained are intermediate between those characteristic of a good and a theta solvent, respectively.

Characteristics of the autocorrelation function of scattered light in the semi-dilute and concentrated regimes

The shape of the autocorrelation function of light scattered from semi-dilute solutions, i.e. in the range $3.7 \times 10^{-4} \leq \Phi \leq 0.11$, depends on the method of preparation. More specifically, solutions prepared at room temperature and maintained at this temperature for more than three weeks exhibited autocorrelation functions characterized by a bimodal decay. When these samples were heated to 100°C, a progressive decrease of both the amplitude and the decay time of the slow mode was observed until the mode eventually vanished. Once cured by this procedure, the samples scattered light in the homodyne regime as ascertained from measurements made with and without a reference beam (cf Experimental). Similar observations have been made on various other systems. For instance PS-ethylacetate semi-dilute solutions exhibit a bimodal autocorrelation the characteristics of which vary with the time elapsed from the preparation of the solution^{8,18}. The variance of the autocorrelation function of light scattered from semi-dilute polydimethylsiloxane solutions in marginal solvents was found to decrease as the temperature increases¹⁹. It was also noted recently that freeze drying of the samples prior to the dissolution could lead to an anomalous behaviour of the autocorrelation function³²⁻³³. It is likely that all these effects originate from the presence of local concentration inhomogeneities

which have also been indicated by neutron and conventional light scattering^{34,35}.

For more concentrated solutions ($\Phi > 0.11$) and swollen networks, no slow mode was detected but the scattered signal was fully heterodyned. Very slow drifts of the direct photocurrent were often observed leading to reduced accuracy in the determination of the decay time. For all the investigated systems, the autocorrelation function was found to follow either a single exponential decay or a narrow distribution with a characteristic variance ≤ 0.12 . The residuals from computer fitting the correlation functions were small and in Figure 3 some representative examples are shown. The characteristic features of the examples and the computer fit are summarised in Table 2. The average decay time $\bar{\Gamma}$ varies rectilinearly with K^2 as illustrated in Figure 4.

Temperature, molecular weight and concentration dependences of the co-operative diffusion constant in semi-dilute and concentrated solutions

From the decay time or average decay time $\bar{\Gamma}$ of the autocorrelation function, the co-operative diffusion constant D_c can be obtained through the relation:

$$\bar{\Gamma} = DK^2$$

with

$$D = D_c(1 - \Phi) \quad (9)$$

where a heterodyne detection scheme is assumed. The factor $(1 - \Phi)$ which is generally neglected in the dilute or semi-dilute range is associated with the solvent displacement^{1,36}.

Table 2 Characteristic features of typical autocorrelation functions

Samples	M_w	Φ	Scattering mode	Variance	$(g^{(1)}(0) - 1)(\alpha)$	$(g^{(1)}(\infty) - 1)(\beta)$
a	$3.6 \cdot 10^6$	0.014	homodyne clipped	0.09	0.28	0.002
b	670 000	0.11	homodyne clipped	0.03	0.36	0.009
c	670 000	0.31	heterodyne clipped	0.08	0.04	0.005
d	670 000	0.54	heterodyne scaled	0.05	0.06	—

(α) Amplitude of the normalized autocorrelation function (cf ref. 25)

(β) Excess baseline

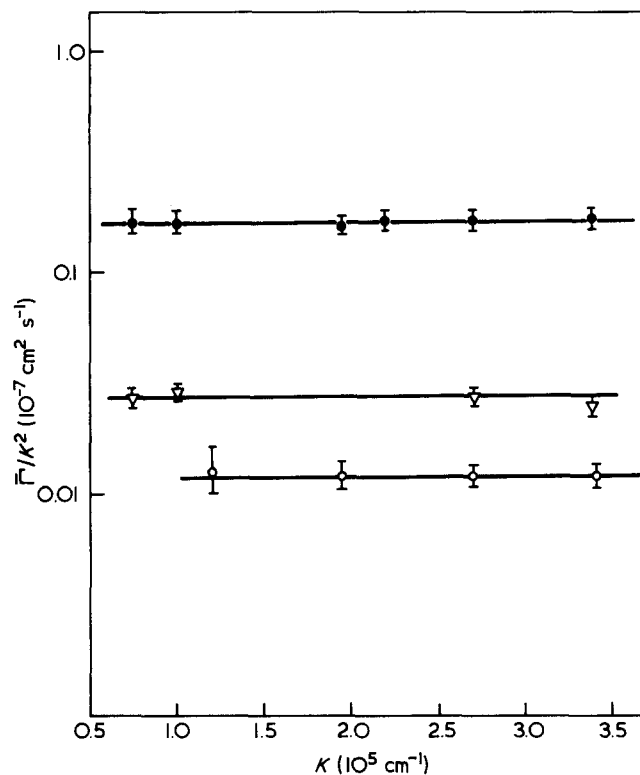


Figure 4 Average decay time divided by K^2 versus K . ●: M , 2×10^6 ; Φ , 0.19; $T=297.7\text{K}$. ▽: M , 670 000; Φ , 0.37; T , 293K. ○: M , 670 000; Φ , 0.54; T , 292K

The variations of the co-operative diffusion constant of semi-dilute and concentrated solutions as a function of temperature, molecular weight and polymer volume fraction are shown in Figures 5–8 which indicate that:

- (1) The variations of D versus the inverse of temperature show a non-Arrhenius behaviour which is strongly enhanced at high concentration (cf Figures 5 and 6).
- (2) The co-operative diffusion constant is independent of the molecular weight of the polystyrene sample as specifically illustrated by Figure 7 which shows the data obtained for three samples of molecular weights 110000, 670000 and 2×10^6 , respectively, at a polymer volume fraction of ≈ 0.3 .

The curves of Figure 8 representing the polymer volume fraction dependence of D_c indicate three different behaviours depending on the concentration range. In the dilute range, the diffusion constant is independent of the

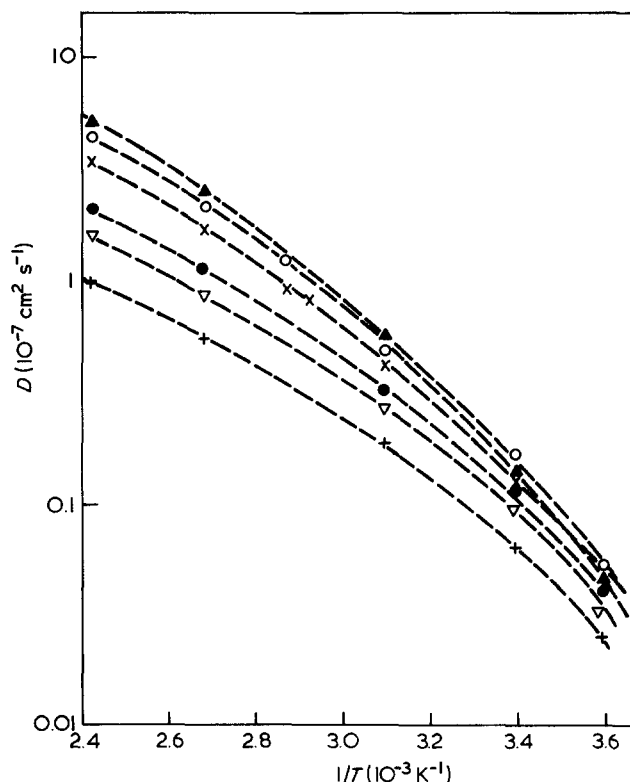


Figure 5 Temperature dependences of D . +: M , 3.6×10^6 ; Φ , 0.37×10^{-2} . ▽: M , 3.6×10^6 ; Φ , 0.75×10^{-2} . ●: M , 3.6×10^6 ; Φ , 1.4×10^{-2} . ×: M , 670 000; Φ , 3×10^{-2} . ○: M , 670 000; Φ , 6.7×10^{-2} . ▲: M , 670 000; Φ , 11×10^{-2}

concentration as mentioned previously. In the semi-dilute domain D_c increases with Φ . The high concentration range is still characterized by an increase of D_c with Φ at high temperature but as the temperature is lowered, an inversion in the sign of the variation of $D_c(\Phi)$ is observed, resulting eventually at the lower temperatures investigated in a large decrease in D_c . The maximum of $D_c(\Phi)$ is reasonably flat and therefore difficult to locate accurately. However, it can be inferred qualitatively from the graphs of Figure 8 that the volume fraction of $D_{c,max}$ is shifted towards the high values of Φ as the temperature is increased.

Polymer volume fraction and temperature dependences of swollen networks

The polymer volume fraction dependence of a network can be investigated in two different ways.

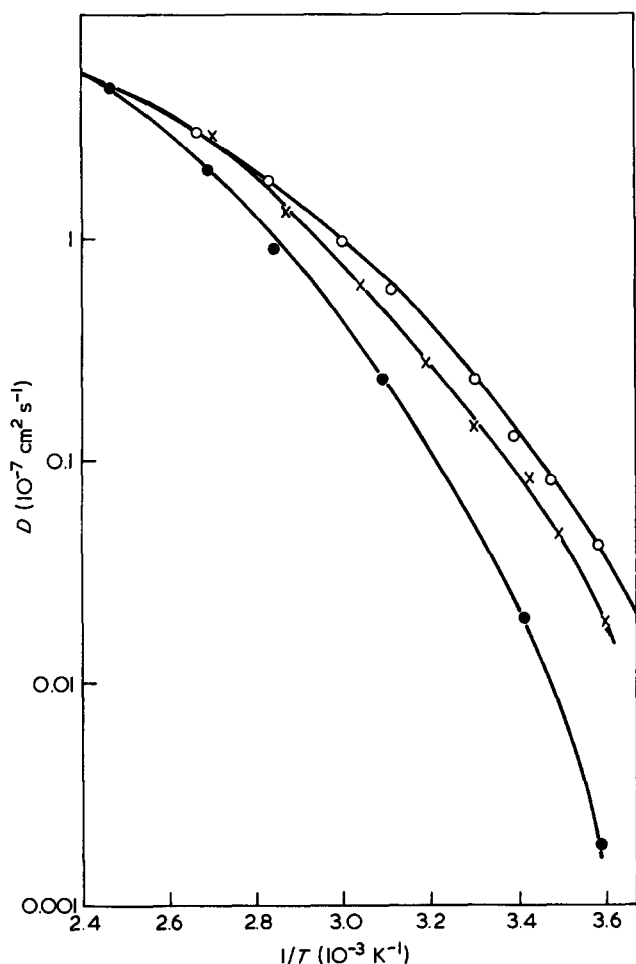


Figure 6 Temperature dependences of D for $M_w=670\,000$. \circ : $\Phi=0.23$; \times : $\Phi=0.32$; \bullet : $\Phi=0.54$

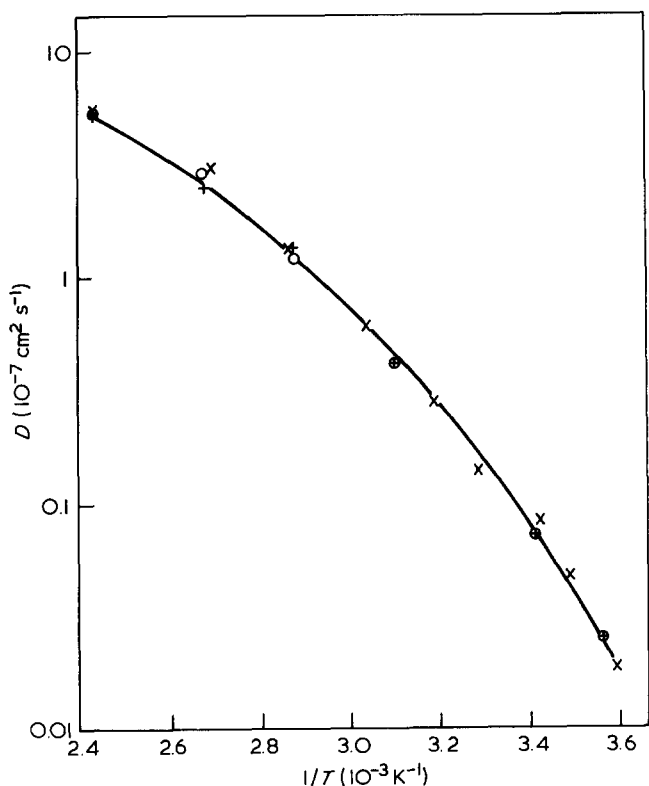


Figure 7 Temperature dependence of D for three different molecular weights. \circ : $M, 110\,000$; $\Phi, 0.3$. \times : $M, 670\,000$; $\Phi, 0.32$. $+$: $M, 2 \times 10^6$; $\Phi, 0.33$

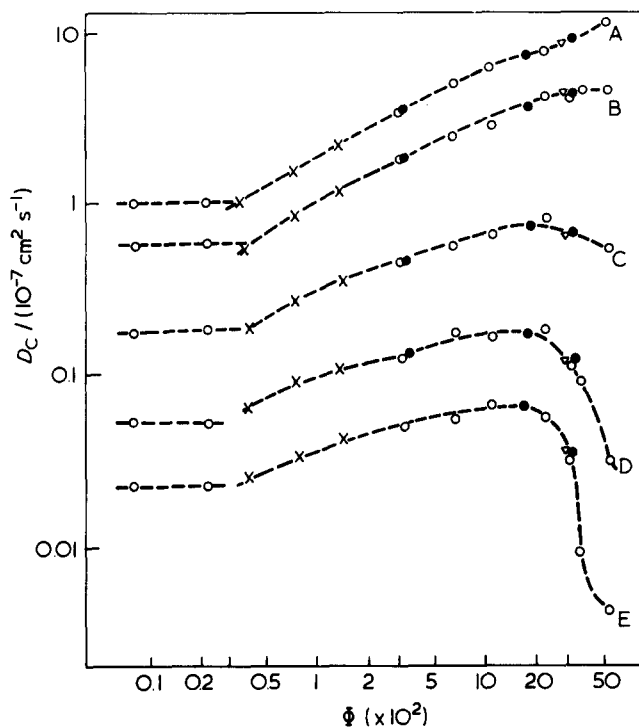


Figure 8 Concentration dependence of D_c for different temperatures. \times : $M, 3.6 \times 10^6$; \circ : $M, 670\,000$; \bullet : $M, 2 \times 10^6$; ∇ : $M, 110\,000$. A, 413; B, 373; C, 323; D, 292; E, 279K. The lines are guides for the eye

- (1) Several networks of different crosslinking densities are swollen in an excess of solvent until the equilibrium is reached.
- (2) A given network is swollen with various amounts of diluent.

Previous studies have shown that the two swelling procedures are not equivalent from the point of view of the elasticity or the collective motions of the gels. It was shown that D_c was slightly larger for networks swollen at equilibrium than for the corresponding semi-dilute solutions of large macromolecules⁸. However, the concentration dependences of both systems were similar. The deswelling of a given network produces a smaller variation of D_c which eventually becomes less than the value of the corresponding semi-dilute solution.

Figure 9 illustrates the comparison between the polymer volume fraction dependences of D_c for networks swollen at equilibrium and semi-dilute solutions at different temperatures, in the case of PS-dibutylphthalate systems. All but the most dilute (R 43) networks exhibit values of D_c larger than those of the solutions.

In Figure 10 the behaviour of the networks deswollen with respect to the equilibrium conditions is compared with that of the solutions. Also are reported the results obtained for the networks swollen at equilibrium. It can be seen that at high volume fractions the co-operative diffusion constant tends to be equal to or smaller than that of semi-dilute solutions. This is also observed in Figure 11 which shows the temperature dependences of D_c for a network swollen at equilibrium and deswollen, respectively, and for solutions at the same volume fractions.

DISCUSSION

An analogy between the permanent network in cross-linked swollen gels and the transient network in semi-

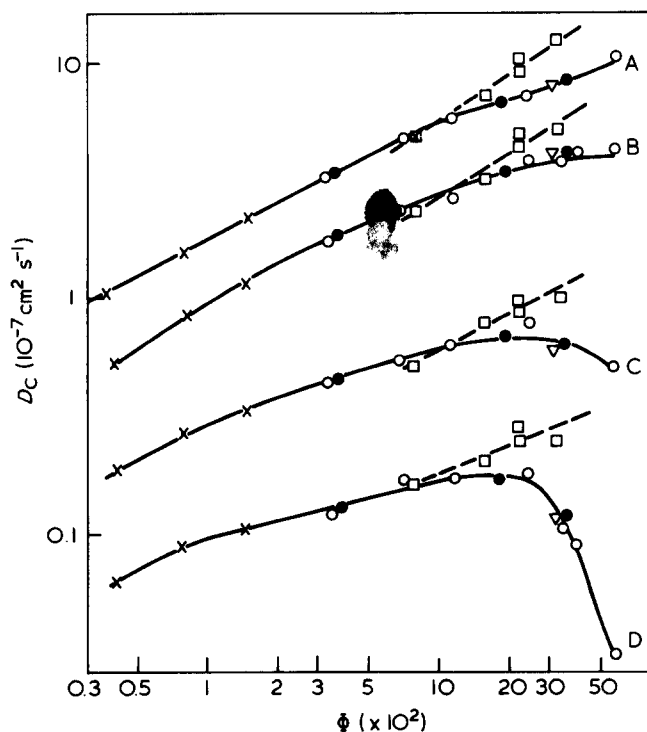


Figure 9 Comparison between polymer volume fraction dependences of D_c for networks swollen at equilibrium (\square) and semi-dilute solutions at A, 413; B, 373; C, 323; D, 292K. The symbols are the same as in Figure 8. The lines are only as guides for the eye

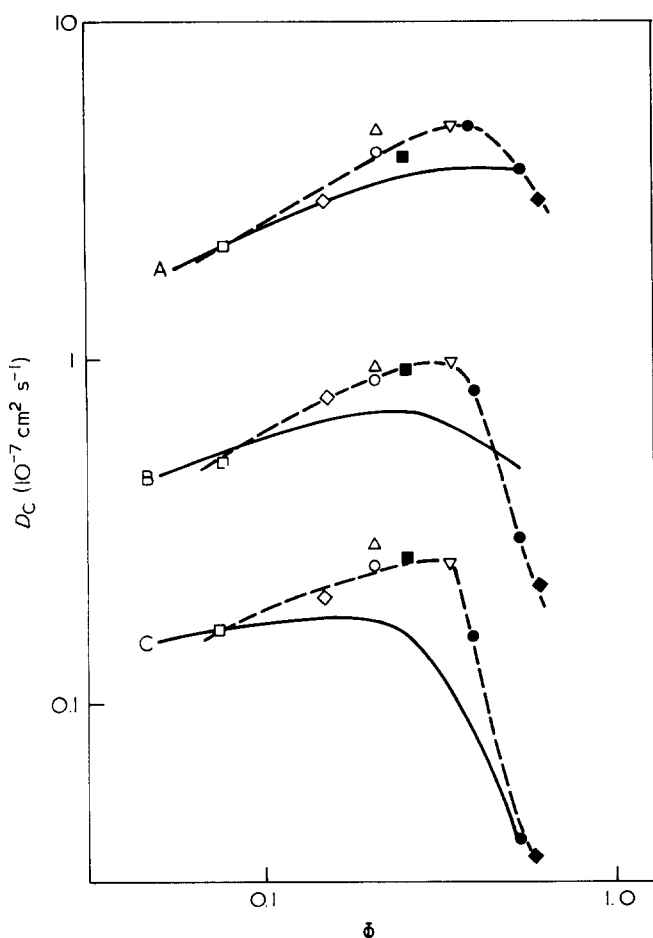


Figure 10 Concentration dependences of D_c for networks swollen at equilibrium (open symbols), deswollen networks (filled symbols) and solutions (continuous lines). \square , R 43; \diamond , R 42; \circ , R 35; \triangle , R 36; ∇ , R 20; A, 373; B, 323; C, 292K. The dotted lines are guides for the eye

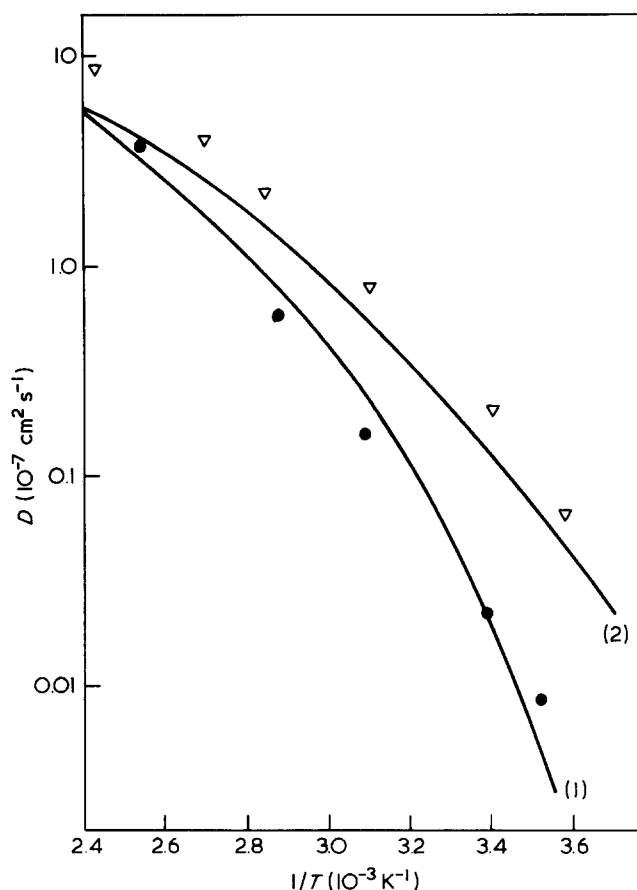


Figure 11 Temperature dependences of D for the network R 35 at the swelling equilibrium volume function $\Phi=0.21$ (∇) and deswollen at $\Phi=0.52$ (\bullet). The curves (1) and (2) represent the variation of D versus Φ for solutions at the same volume fractions

dilute solutions has been developed by de Gennes to describe the dynamic properties of the latter systems^{1,2}. The hydrodynamic screening length ξ_H was identified with the average size ξ_p of either the strands of the permanent network or the so called 'concentration blob' of the solution, that is the part of the chain between two consecutive interchain contacts. The dynamical regime of interest in this study is the pseudo-gel regime which is characterised by a range of scattering wavevectors such as $k\xi_p \ll 1 \ll kR_G$. In this range, photon correlation spectroscopy experiments probe the motion of the centre of mass of a concentration blob. The equation of motion for the time-dependent distribution function for the centre of mass of the blob is obtained from a balance of osmotic and frictional forces. Solving this equation leads to the following expression for the intermediate scattering function $S(K, t)$ which is directly related to the intensity correlation function:

$$S(K, t) = \rho g_p e^{-D_c(1-\Phi)K^2 t} \quad (10)$$

where ρ/g_p is the density of blobs and the co-operative diffusion constant D_c is given by^{3,7}:

$$D_c \approx \frac{M_{os}}{(\rho/g_p)6\pi\eta\xi_p} \quad (11)$$

$M_{os} = K_{os} + \frac{4}{3}\mu$ (K_{os} = osmotic compressional modulus, μ = shear modulus) is the longitudinal osmotic modulus and $6\pi\eta\xi_p$ is the blob friction constant. Generally it is assumed that $M_{os} \approx K_{os}$ although it has been shown recently that the contribution of the shear modulus was

not negligible for swollen networks^{38,39}. However, for good or marginal solvents, both K_{os} and μ depend on the probability of binary contacts and, therefore, follow the same power dependence with ρ .

Equation (11) reduces to Equation (1) if M_{os} is taken proportional to the blob density, i.e.:

$$M_{os} \simeq k_B T (\rho/g_\rho) \quad (12)$$

and with $\xi_\rho \simeq \xi_H$.

For good solvent conditions scaling analysis predicts the following power laws for ξ_ρ and D_c :

$$\xi_\rho \sim \rho^{-3/4} \sim \Phi^{-3/4} \text{ which leads to } D_c \sim \Phi^{3/4} \quad (13)$$

In marginal solvents, that is when the chains are nearly ideal on all length scales and the binary interactions are weak, the analysis of Schaeffer *et al.* predicts^{10,14}:

$$\xi_\rho \sim \rho^{-1/2} \text{ and } D_c \sim \Phi^{1/2} \quad (14)$$

In theta systems the three body interactions dominate two-body effects. Therefore, the compressional osmotic modulus K_{os} is proportional to the probability of ternary contacts while μ remains proportional to the probability of binary contacts. A scaling approach, derived by Brochard and de Gennes, predicts a bimodal decay behaviour for $S(K, t)$, the two modes being associated with K_{os} and μ , respectively⁴⁰. However the amplitude of the fast mode, controlled by the elastic rigidity, is too small to be detected and the autocorrelation function of scattered light is dominated by the component due to the three body interactions. The corresponding correlation length varies with ρ according to:

$$\xi_\rho \sim \rho^{-1} \sim \Phi^{-1} \text{ which leads to } D_c \sim \Phi \quad (15)$$

The above volume fraction dependence of ξ_ρ and D_c is expected to apply to semi-dilute theta systems for all concentrations and to other systems for sufficiently high values of ρ so that ξ_ρ is less than the distance ξ_c beneath which the chain is ideal. As a consequence, for semi-dilute solutions in a good solvent a $\Phi^{3/4}$ dependence of D_c would be expected at low concentration (but still above the cross-over concentration) and a linear variation with Φ at high concentration with a possible intermediate marginal regime where D_c varies as $\Phi^{1/2}$. This theoretical summary shows that in any case, the co-operative diffusion constant D_c of semi-dilute solutions should show an increase with Φ equal or larger than that described by a $\Phi^{1/2}$ power law.

The results obtained in this study and illustrated in Figure 8 are in accordance with such conclusions only in the high temperature range where the experimental values of D_c can be fitted to a straight line in a log-log plot, for a reasonable range of polymer volume fraction $0.0037 \leq \Phi \leq 0.11$. At $T=413$ K, $D_c \sim \Phi^{0.52 \pm 0.02}$.

This result is in good agreement with the theoretical predictions for marginal solvents. In the case investigated here, the quality of the diluent improves as the temperature is lowered and correlatively an increase of the overall variations of $D_c(\Phi)$ due to a larger exponent of the power law is expected at least in the low polymer volume fraction limit. However, it is the opposite behaviour which is observed, the increase of D_c with Φ becoming less pronounced when T decreases. This behaviour must be correlated with the slowing of the fluctuation occurring at higher volume fractions, as shown by the decrease in D_c . Obviously this slowing appears progressively when Φ is

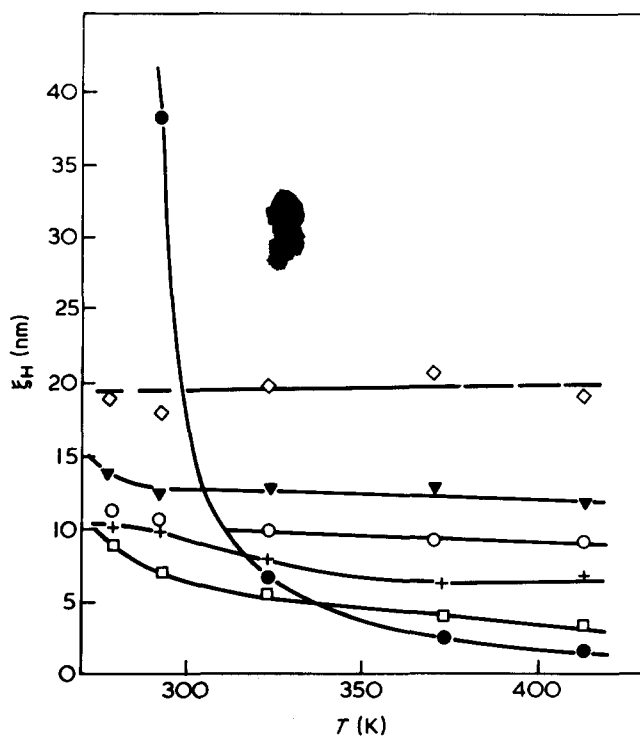


Figure 12 Variation of ξ_H versus T for different concentrations. \diamond : $\Phi, 0.37 \times 10^{-2}$; ∇ : $\Phi, 0.75 \times 10^{-2}$; \circ : $\Phi, 1.4 \times 10^{-2}$; $+$: $\Phi, 3 \times 10^{-2}$; \square : $\Phi, 0.11$ and \bullet : $\Phi, 0.54$

increased, producing a maximum in $D_c(\Phi)$ which is shifted towards higher volume fraction when T is increased.

The temperature dependence of D_c also provides confirmatory evidence of anomalous behaviour. As the radius of gyration R_G decreases when the temperature increases, ξ_H might be expected to increase with temperature¹³. The opposite behaviour is observed in Figure 12 where the values of ξ_H calculated from equation (1) for different polymer volume fractions are plotted as a function of T . It must be noted, however, that the decrease of ξ_H becomes less pronounced when Φ decreases and/or T increases.

The origin of the effect responsible for the slowing of the fluctuations is difficult to assess. Structural relaxation mechanisms associated with the glass transition can be discarded because the autocorrelation function decays according to a single exponential and the decay time varies as K^2 (cf Figures 3 and 4).

Referring back to equation (11), it is apparent that D_c is defined as the ratio of the longitudinal osmotic modulus over a friction factor. It is unlikely that the modulus could decrease as the concentration is increased. Therefore, the most plausible interpretation is in terms of an enhancement of the friction factor. Such enhancement is expected at high polymer volume fraction when the monomer-monomer friction becomes non-negligible compared to the monomer solvent friction. However, as indicated previously, the phenomenon is sensible for the systems investigated here, even in the low concentration range where other systems show a normal behaviour. It appears then that the observed supplementary friction involves specific polymer-solvent interactions as well. In this respect some recent experiments by Tan *et al.*⁴¹ are noteworthy. They succeeded in preparing thermoreversible gels by cooling moderately concentrated solutions of atactic polystyrene in some specific solvents, the higher the polymer concentration, the higher the gelation temperature. Although the nature and the origin of this

phenomenon is not yet understood, the results of Tan *et al.* suggest that interchain junctions can form. If such interchain junctions occur, they must be relatively weak so that they should not affect considerably the longitudinal modulus. However, they might introduce a supplementary friction between polymer chains, producing a decrease of D_c .

Inspection of the results obtained for swollen networks also reveals interesting features. In particular, the co-operative diffusion constant of networks swollen at equilibrium still increases with Φ in a range of Φ when it decreases or tends to level off for semi-dilute solutions. Such behaviour could be due to the fact that at swelling equilibrium the strands of the network are mostly interspersed so that the interchain contacts are mainly permanent crosslinks. Therefore, the supplementary friction associated with labile junctions would be strongly reduced. However, the strands of deswollen networks are strongly interspersed, favouring the formation of temporary contacts between chains. This would explain why such gels tend to behave similarly to solutions (*cf Figures 11 and 12*).

CONCLUSION

The results of this study show that the collective motions of semi-dilute polymer solutions cannot always be described by a one parameter theory taking into account only the quality of the diluent. Although for polystyrene the dibutylphthalate is a marginal solvent in the whole investigated temperature range with a slight decrease of the quality of the diluent as the temperature increases, the typical marginal solvent behaviour has only been observed in the high temperature range ($T \geq 373$ K). The polymer volume fraction dependence of the co-operative diffusion constant D_c indicates an anomalous enhancement of the friction factor even for moderately concentrated solutions. This enhancement, the nature of which is not yet understood, becomes increasingly pronounced as the temperature is lowered and the volume fraction is increased. There is a possible correlation between these observations and the physical gelation properties recently discovered⁴¹, which would be worthy of further investigation.

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