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Binary Contacts in Semidilute Solution: Good and Θ Solvents

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ABSTRACT: In this paper we show that the concentration dependence of the plateau shear elastic modulus and of the viscosity can be understood if two lengths, the correlation length of concentration fluctuations and the tube diameter, are considered. To interpret the temperature variation of the viscosity and of the self-diffusion coefficient with the solvent quality, one has to take into account the local viscosity to which monomers are sensitive. This concentration dependent local viscosity, deduced from neutron spin−echo measurements, is independent of the polymer molecular weights, solvent viscosities and Θ temperatures. The local viscosity decreases to reach the solvent viscosity value at high temperature, that is, under good solvent conditions. The role of the macroscopic concentration on a local scale, seems to indicate that, in semidilute Θ solutions, the polymers are transparent to each other, as far as dynamic properties are concerned.

Introduction

The polymer conformations, in semidilute solution, are well understood whatever the solvent quality. Scaling laws are well established and are found to be universal, that is, valid for any polymer molecular weight and polymer species.[1,2] These concentration scaling laws are expressed as functions of the overlap ratio C/C^*, independent of local properties. C^*, the overlap concentration, corresponds to the polymer close packing condition: $C^* \propto N/R^3$. The dilute size R and degree of polymerization N are linked by $R \propto N^{\nu}$, with $\nu = 0.588$ and 0.5 for good solvent and for Θ solvent conditions, respectively. Temperature scaling laws have been established to account for the variation of polymer properties as the solution is brought from Θ to good solvent condition.[3,4]

Recently[5] it was shown that the viscosities of semidilute good solvent solutions obey the universal scaling law only if the reduced concentration used is the entanglement ratio C/C_e. For polymer species as different as polystyrene, polybutadiene and polyisoprene, in good solvent conditions, the entanglement ratio depends both on the overlap ratio C/C^* and on the number N_e of binary contacts necessary to make an entanglement. Measurements of the osmotic modulus K and of the plateau elastic modulus G allow this number $N_e = K/G$, to be determined.[5] It is independent of the concentration and proportional to the number of monomers necessary to make an entanglement in the melt ($G \approx kT\rho/N_e$ where ρ is the polymer density). Thus, in the following, we will consider that, in the semidilute regime, the number N_e of binary contacts necessary to make an entanglement is identical for good solvents and Θ solvents.

In this paper we focus on how the presence of two lengths, the correlation length ξ of concentration fluctuation and the tube diameter A, influences the dynamic properties.

I. Definitions

The correlation length ξ of the concentration fluctuations is, both in good solvents and in Θ solvents, a function of concentration only ($\xi \propto C^{\nu/(1-3\nu)}$); this was well verified experimentally by small angle neutron scattering[6] (SANS) and light scattering.[7] ξ is predicted to be also the screening length of hydrodynamic interactions;[1,8,9] this is confirmed by measurements of the sedimentation coefficient[10,11] and of the diffusion coefficient.[12] Within part of the polymer of size ξ, often referred to as the "blob", most monomers belong to the same chain. The number of monomers g in ξ is a function of concentration ($g \propto C^{1/(1-3\nu)}$) as g and ξ are linked by $\xi \propto g^{\nu}$. The number of blobs per chain N/g increases with the overlap ratio as $N/g = (C/C^*)^{1/(3\nu-1)}$. However, in good solvents, the blob size ξ_{GS} corresponds to the mean distance between two consecutive binary contacts between two different chains. However, in Θ solvent, ξ_{Θ} corresponds to the mean distance between ternary contacts of monomers belonging to different chains.

Under Θ conditions, there are two nonproportional lengths: ξ_{Θ} and the mean distance between binary contacts. Binary contacts do not show up in properties linked to the polymer conformation because the second virial coefficient is zero. Brochard and de Gennes[13] have considered that the mean distance between self-knots l_s occurring inside the blob. For a single chain the number of self-knots[1] is proportional to $\sqrt{N}$. As the chain is Gaussian at all scales, $R^2 = l_s^2\sqrt{N}$ and $R^2 \propto N$, and hence $l_s \propto N^{1/4}$. In semidilute Θ solutions the number N of monomers in the chain must be replaced

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by the number of monomer in the blob g_Θ ($g_\Theta \propto C^{-2}$), hence l_s ($\propto C^{-1/2}$) decreases as the concentration increases. Colby and Rubinstein have considered the intermolecular binary contact. If l is the mean distance between two intermolecular binary contacts their density ($1/l^3$) is proportional to C^2 ($l \propto C^{-2/3}$). Thus, the number n of monomers within l is $n \propto l^2 \propto C^{-4/3}$. Here one has to note that l as well as l_s are smaller than ξ_Θ.

Under both solvent conditions, the tube diameter A is proportional to $\sqrt{N_e}$ times the mean distance between binary contacts.[14] Thus, in good solvents, $A_{GS} = \xi\sqrt{N_e} \propto C^{-0.77}\sqrt{N_e}$, and $A_\Theta = l\sqrt{N_e} \propto C^{-2/3}\sqrt{N_e}$ in Θ solvents. Note that as in ref 8, A_Θ is taken proportional to l because intermolecular binary contacts are required for formation of entanglements. In semidilute solutions where chains interpenetrate ($C > C^*$), two concentration regimes are to be distinguished for dynamic properties: the nonentangled ($C < C_e$) and the entangled ($C > C_e$) regime.[15] The crossover concentration C_e corresponds to the concentration for which the tube diameter A is equal to the radius of gyration of the interpenetrated chain, i.e.:

$$\begin{aligned} C_{eGS} &\propto (N/N_e)^{1-3\nu} \propto (N/N_e)^{-0.76} \quad \text{in good solvents} \\ C_{e\Theta} &\propto (N/N_e)^{-3/4} \quad \text{in } \Theta \text{ solvents} \end{aligned} \tag{1}$$

Here we note the following points

- The dependence of the entanglement concentration C_e with the degree of polymerization N is similar under Θ and good solvent conditions.
- While in a good solvent C_e and the overlap concentration C^* are proportional, this is not the case in Θ solvents ($C^* \propto N^{-1/2}$).

Under Θ as well as under good solvent conditions, for $C < C_e$, polymers are interpenetrated but not entangled. The longest relaxation time, the viscosity, and the self-diffusion coefficient are those of a Rouse chain of blobs because there is no hydrodynamic interaction between blobs:

$$\begin{aligned} \tau_{\text{Rouse}} &= \tau_{\text{blob}}(\text{N/g})^2 \approx \tau_{\text{Zimm}}(C/C^*)^{(2-3\nu)/(3\nu-1)} \\ \eta_{\text{Rouse}} &= \eta_s N/g \approx \eta_s (C/C^*)^{1/(3\nu-1)} \\ D_{\text{selfRouse}} &= R^2/\tau_{\text{Rouse}} \propto N^{-\nu}(C/C^*)^{(\nu-1)/(3\nu-1)} \end{aligned} \tag{2}$$

Here τ_{blob} and τ_{Zimm} are the characteristic times of the blob ($\propto \xi^3$) and of the dilute polymer($\propto R^3$), η_s is the viscosity of the solvent.

To establish the laws governing the temperature dependence as the system is brought from a Θ to a good solvent condition, it was assumed[16] that there is only one reduced temperature variable, τ/τ^{**}, influencing the two nonproportional lengths ξ_Θ and A. τ is the relative temperature ($\tau = (T - \Theta)/\Theta$) and $\tau^{**}(\propto C)$ is the crossover between Θ and good solvent condition temperatures. The scale on which the polymer is Gaussian decreases as τ increases,[4] for $\tau = \tau^{**}$ it is equal to the correlation length of concentration fluctuations ξ, while it becomes smaller as $\tau > \tau^{**}$.

In the entangled regime ($C > C_e$), we first consider the influence of the two lengths, ξ and A, on the concentration and temperature dependence of the plateau elastic modulus where only entanglements come into play. Then we will investigate the viscosity behavior in which friction has to be considered.

II. Role of Entanglements: The Plateau Modulus

II.1. Theoretical Expectations. The plateau elastic modulus G is proportional to the number of entanglements per unit volume ν_e. Following Colby and Rubinstein[8] this is the volume occupied by N_e blobs included in the entanglement strand; thus, $\nu_e = 1/(N_e\xi^3)$. As the chain is Gaussian on a length scale larger than ξ, the square of the tube diameter is expressed as $A^2 = N_e\xi^2$ and

$$G = \frac{kT}{A^2\xi} \tag{3}$$

Thus, using for ξ and A the equations given previously, we find for the plateau shear elastic modulus

$$\begin{aligned} G_{GS} &\propto \frac{kT}{N_e}C^{3\nu/(3\nu-1)} \quad \text{with} \quad \frac{3\nu}{3\nu-1} = 2.31, \\ G_\Theta &\propto \frac{kT}{N_e}C^{7/3} \end{aligned} \tag{4}$$

As for the number of binary contacts N_e and the number of blobs N_e in the entanglement strand, one has to distinguish between good and Θ solvent conditions. In the former case, they are proportional to the number of monomers between two successive entanglements in the melt.[5] In the latter case, the ratio depends on concentration as $N_e/N_e \propto C^{2/3}$.

Using eqs A 6 and 4 one obtains, for $\tau/\tau^{**} > 1$, for the temperature dependence (see Appendix 2)

$$G_{GS} = G_\Theta(\tau/\tau^{**})^{(7/3-4\nu)/(1-3\nu)} \tag{5}$$

The exponent is equal to 0.024 (with $\nu = 0.588$), and the plateau elastic modulus can be considered to be independent of the solvent quality and thus of the temperature.[17]

II.2. Experimental Results. Most of the results analyzed in this paper were given in refs 18 and 19. Thus no details will be given on the different experimental arrangements used. The polymers studied are polystyrene (PS) from Tosoh Corp., polybutadiene (PB) from Polymer Laboratories, and polyisoprene (PI) kindly provided by L. Fetters (Exxon Research & Engineering Co.). Their characteristics are given in Table 1.

In Figure 1 the plateau elastic modulus is plotted as a function of the concentration. The semidilute PS solutions are dissolved either in benzene or in cyclohexane (Θ solvent for PS at 35 °C). The values of the plateau shear elastic modulus are corrected for the density differences between the two solvents.[20] Within experimental precision the plateau elastic modulus is independent of the solvent quality. Best fits of the data points, measured on PS in the good solvent and the Θ solvent, give

$$\begin{aligned} G_{GS} &= (1.3 \pm 1) \times 10^6 C^{2.36\pm0.3} \\ G_\Theta &= (7 \pm 3) \times 10^5 C^{2.26\pm0.2} \end{aligned} \tag{6}$$

Table 1. Characteristics of the Sample Used for Viscoelastic Measurements[a]

M_w	m_0	$[\eta]_{GS}$ (cm^3/g)	$[\eta]_{\Theta_s}$ (cm^3/g)	N_e	$C_{e_{GS}}$ (g/cm^3)	$C_{e\Theta_s}$ (g/cm^3)
			PS			
2.06×10^7	104	2380	402	185	0.00484	0.00534
6.77×10^6		1035	231		0.0113	0.0123
3.84×10^6		680	174		0.0175	0.0188
			PI			
9.4×10^5	68	470		112	0.0252	0.0271
			PB			
9.6×10^5	54	600		38	0.00912	0.01

[a] Weight averaged (M_w) and monomer (m_0) molecular weights, intrinsic viscosities $[\eta]$ (values taken from PS in good solvent,[54] PS in Θ solvent,[33] and PI and PB[38]), and number of binary contacts (N_e) between two successive entanglements, were measured in semidilute solution.[5] Entanglement concentration values C_e are deduced from eq 1.

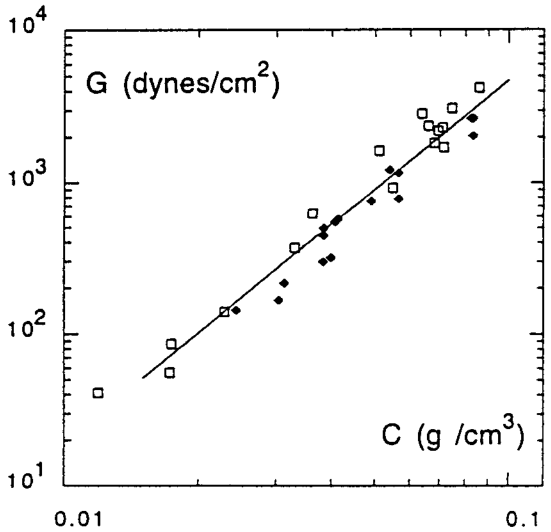

Figure 1. Variation of the plateau shear elastic modulus as a function of the concentration (log−log scale): (□) PS in benzene (GS) and (◆) PS in cyclohexane (Θ solvent). The full line corresponds to the best fit of combined data measured under good and Θ solvent conditions.

The plateau elastic modulus is expressed in dyn/cm^2 and the concentration in g/cm^3. This result is in good agreement with those obtained on high molecular weight polybutadiene.[21]

As expected, the modulus is found to be independent of the temperature as the system is brought from the Θ to the good solvent condition. In Figure 2, the plateau elastic modulus at a given temperature T divided by its value at the Θ point, $G(T)/G_\Theta$, is plotted as a function of the reduced temperature τ/τ^{**}. $\Theta\tau^{**}$ that is the distance to the Θ temperature of the crossover between Θ and good solvent, is taken to be equal to 35C from ref 3. For $0.15 < \tau/\tau^{**} < 45$, $G(T)/G\Theta$ is, within experimental accuracy (15%), independent of the temperature:

$$G(T)/G_\Theta = 1.05 \pm 0.08$$

In the same temperature range the bulk osmotic modulus, which is sensitive to the correlation length ξ, increases by more than a decade.[22]

The independence of the plateau elastic modulus of the solvent quality indicates that the description of entanglements as done in refs 8 and 16 is correct. Now we will consider the concentration and temperature dependence of the viscosity, where the role of friction has to be taken into account.

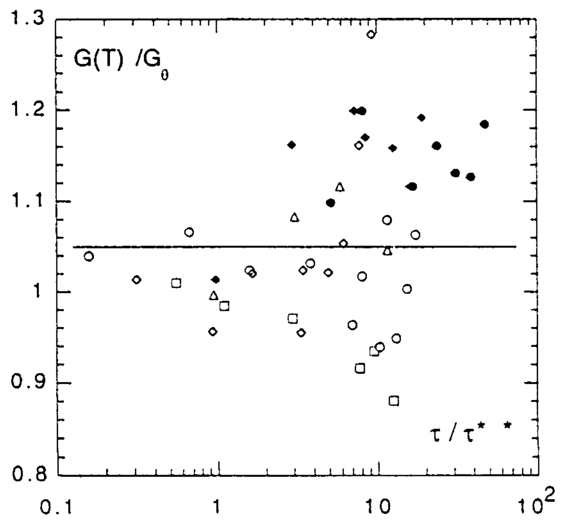

Figure 2. Variation of the plateau shear elastic modulus divided by its value at the Θ temperature as a function of the reduced temperature τ/τ^{**}. τ is the reduced temperature = $(T - \Theta)/\Theta$ and $\tau^{**} = 35C$ (from ref 3). As predicted by theory, the plateau shear elastic modulus is, within experimental precision, temperature independent. Symbols have the following meaning: M = 20.6 × 10^6, C(g/cm^3) = 0.0553 (□), 0.040 (○), 0.024 (△) $M = 6.77 \times 10^6$, C(g/cm^3) = 0.0821 (◇), 0.0304 (◆), and 0.016 (●).

III. Role of Friction

Following de Gennes[23] Rubinstein, Colby, and Daoud[8,16] we recall the laws governing the concentration and temperature dependence of the viscosity and of the self-diffusion coefficient.

III.1. Theoretical Background. The viscosity is equal to the product of the plateau elastic modulus (eq 4) and the longest viscoelastic relaxation time T_r (see appendix eq (A4). In semidilute entangled solutions ($C > C_e$), in good solvents and in Θ solvents, respectively

$$\eta_{GS} \approx \frac{\eta_S}{{N_e}^2}\left(\frac{N}{g}\right)^3 \propto \eta_s \frac{N^3}{{N_e}^2} C^{3/(3\nu-1)} \approx \eta_{Rouse}\left(\frac{C}{C_e}\right)^{2/(3\nu-1)}$$

$$\eta_\Theta \approx \frac{\eta_S}{{N_e}^2}\left(\frac{N}{g}\right)\left(\frac{N}{n}\right)^2 \propto \eta_s \frac{N^3}{{N_e}^2} C^{14/3} \approx \eta_{Rouse}\left(\frac{C}{C_e}\right)^{8/3} \tag{7}$$

Thus η/η_{Rouse} as a function of the entanglement ratio C/C_e is expected to be independent of the solvent Equality ($2/(3\nu - 1) = 2.62$ while $8/3 = 2.66$).

For $\tau/\tau^{**} > 1$, the temperature dependence of the viscosity is obtained using eqs 7 and A 6:

$$\eta_{GS} = \eta_\Theta \left(\frac{\tau}{\tau^{**}}\right)^{(14/3)-(3/(3\nu-1))} \quad \text{with} \quad \frac{14}{3} - \frac{3}{3\nu - 1} = 0.74 \tag{8}$$

Thus an increase of the viscosity is expected as the temperature is increased from the Θ point. However this increase is mainly due to the temperature variation of η_{Rouse}:

$$\eta_{RouseGS} = \eta_{Rouse\Theta}\left(\frac{\tau}{\tau^{**}}\right)^{3(2\nu-1)/(3\nu-1)} \quad \text{with} \quad \frac{3(2\nu - 1)}{3\nu - 1} = 0.69$$

The self-diffusion coefficient, proportional to

$$D_{\mathrm{self}} \approx R^2/T_{\mathrm{r}} \approx GR^2/\eta \qquad (2)$$

is, in a good solvent and in a Θ solvent, equal to

$$D_{\mathrm{selfGS}} \propto \frac{N_{\mathrm{e}}}{\eta_{\mathrm{s}}(N/g)^2\xi} \propto \frac{N_{\mathrm{e}}}{\eta_{\mathrm{s}}N^2}C^{-(2-\nu)/(3\nu-1)} \propto D_{\mathrm{Rouse}}(C/C_{\mathrm{e}})^{-1/(3\nu-1)}$$

$$D_{\mathrm{self}\Theta} \propto \frac{N_{\mathrm{e}}}{\eta_{\mathrm{s}}(N/g)(N/n)\xi} \propto \frac{N_{\mathrm{e}}}{\eta_{\mathrm{s}}N^2}C^{-7/3} \propto D_{\mathrm{Rouse}}(C/C_{\mathrm{e}})^{-4/3} \qquad (10)$$

Thus $D_{\mathrm{self}}/D_{\mathrm{Rouse}}$ as a function of the entanglement ratio C/C_{e} is expected to be independent of the solvent quality ($1/(3\nu - 1) = 1.31$ while $4/3 = 1.33$).

For $\tau/\tau^{**} > 1$, the diffusion coefficient is expected to decrease as the temperature is increased from Θ:

$$D_{\mathrm{selfGS}} = D_{\mathrm{self}\Theta} \times \left(\frac{\tau}{\tau^{**}}\right)^{(13/3-8\nu)/(3\nu-1)} \quad \text{with} \quad \frac{(13/3 - 8\nu)}{(3\nu - 1)} = -0.48 \qquad (11)$$

However, this decrease is mainly due to the variation of D_{Rouse} with temperature.

In this model, as the plateau elastic modulus is temperature independent, the following ratio is equal to the square of the expansion factor, α

$$\frac{D_{\mathrm{selfGS}}\eta_{\mathrm{GS}}}{D_{\mathrm{self}\Theta}\eta_{\Theta}}\,\frac{G_{\Theta}}{G_{\mathrm{GS}}} = \frac{R^2(T)}{R^2{}_{\Theta}} = \alpha^2 \qquad (10)$$

In semidilute solutions, i.e., at polymer concentrations much smaller than the solvent concentration, in this theoretical approach, the following hypotheses have been made.

•A single reduced temperature variable τ/τ^{**} has been introduced while there exists two pertinent lengths at Θ.

•The local viscosity, i.e., the viscosity to which a monomer is subjected, is the solvent viscosity, whatever the solvent quality.

•Even in Θ semidilute solutions, in a blob, due to their space-filling nature ($g = c\xi^3$), most monomers belong to the same chain.

III.2. Local Friction. Small-angle neutron spin−echo[24] (NSE) experiments yield measurements of the dynamics on a scale $8 < 1/q(\text{Å}) < 70$ where q is the wave vector transfer. It has been shown[25] that, at the Θ point, measurements performed on PS cyclohexane at $q\xi_{\Theta} > 1$, are concentration and q dependent. To scale measurements performed at different concentrations the dimensionless length to be used is ql_{s}, with $l_{\mathrm{s}} = \sqrt{20.5\times5.5/C} = 10.6/\sqrt{C}$ (l_{s} in Å and C in g/cm^3). The l_{s} expression is consistent with the mean distance between self-knots. However, due to the narrow concentration range over which experiments can be performed, it cannot be excluded that the length observed by NSE is not proportional to $C^{-2/3}$; i.e., it is not the intermolecular binary contact distance.

For $ql_{\mathrm{s}} > 1$ the dynamic structure factor is sensitive to internal modes.[26] As at length scales smaller than ξ or l_{s}, monomers are subjected to hydrodynamic interactions[9] (Zimm dynamics); the dynamic structure factor is

$$S(q,t) = \int_0^{\infty}\mathrm{d}u\, \exp[-u - (\Gamma_q t)^{2/3}\, h(u(\Gamma_q t)^{-2/3})]$$

$$\text{with} \quad \Gamma_q = \frac{kT}{6\pi\eta_{\mathrm{loc}}}\,\mathrm{q}^3 \quad \text{and} \qquad (13)$$

$$h(u) = \frac{2}{\pi}\int_0^{\infty}\mathrm{d}x\, \frac{\cos(xu)}{x^2}[1 - \exp(-x^{3/2}/2)]$$

where η_{loc} is the viscosity to which a monomer is subjected. A simplified expression for $S(q,t)$ is

$$S(q,t) = \exp[-B(\Gamma_q t)^{2/3}] \qquad (14)$$

the prefactor value B is 1.35 from ref 27. Note that the dimensionless variable $\Gamma_q t$ also allows one to take into account the temperature and the local viscosity dependence of the dynamic structure factor. If the local viscosity η_{loc} is the solvent viscosity η_{s} then the dynamic structure factor must be independent of concentration, of temperature, and of solvent quality for $ql_{\mathrm{s}} > 1$.

$\Gamma_q t$ is, whatever the solvent quality, the correct time reduced variable for the dynamic structure factor, indicating that hydrodynamic interaction prevails in this q range. Actually, for a given sample, $S(q,t)$ is independent of the transfer vector when plotted as a function of $\Gamma_q t$.[28] $S(q,t)$ measured either on PS dissolved in a good solvent, deuterated benzene (Figure 3a), or on PS dissolved in a Θ solvent, deuterated cyclohexane at 39 °C (Figure 3b), are plotted as a function of $(\Gamma_q t)^{2/3}$. In this representation, Figure 3a shows that, $S(q,t)$ is independent of temperature and slightly concentration dependent in good solvent, while Figure 3b demonstrates that $S(q,t)$ is strongly concentration dependent in Θ solvent. The full lines in the figure correspond to the best fit of the data using eq 14, assuming $\eta_{\mathrm{loc}} = \eta_{\mathrm{s}}$, and the prefactors B so determined are given in Table 2. In good solvent, B is independent of the concentration, a monomer is subjected to the solvent viscosity. The value of the prefactor is equal to 0.8 ± 0.05 rather than 1.35.[29] In Θ solvent, the values of the prefactor B are concentration dependent (Table 2): the solvent viscosity η_{s} is not that to which a monomer is subjected under Θ conditions ($\eta_{\mathrm{loc}} \neq \eta_{\mathrm{s}}$). It should be noted that, as for $ql_{\mathrm{s}} > 1$, $\Gamma_q t$ is the reduced time for $S(q,t)$ measured at different q values; this indicates that first Zimm dynamics is observed, and second η_{loc} is independent of q.

To find the parameter that could influence η_{loc}, we investigated PS of different molecular weights ($4 \times 10^4 \leq M \leq 2 \times 10^7$) dissolved in different Θ solvents having different viscosities ($0.15 \leq \eta(\mathrm{cp}) \leq 2.6$) and different Θ temperatures ($22 \leq \Theta$ (°C) ≤ 155). We have also studied a different polymer (PI) dissolved in dioxane at Θ = 38 °C. In Table 3 are listed the molecular weights and the concentrations of the samples studied. Note that, the lowest molecular weight is not interpenetrated ($C/C^* < 1$) and unentangled ($C/C_{\mathrm{e}} < 1$). In Table 4 are listed the solvents used and their Θ temperatures, as well as their viscosities (see Appendix 3).

In Figure 4 we plot, as a function of the concentration, the relative local viscosity $\eta_{\mathrm{loc}}/\eta_{\mathrm{s}}$ measured on PS and PI Θ solutions. $\eta_{\mathrm{loc}}/\eta_{\mathrm{s}}$ is deduced from $1/\eta_{\mathrm{s}}(\Gamma_{\mathrm{cq}})^{3/2}$ where the characteristic frequency Γ_{cq} is determined by fitting the spectra to eq 13. On both polymer species (PS and

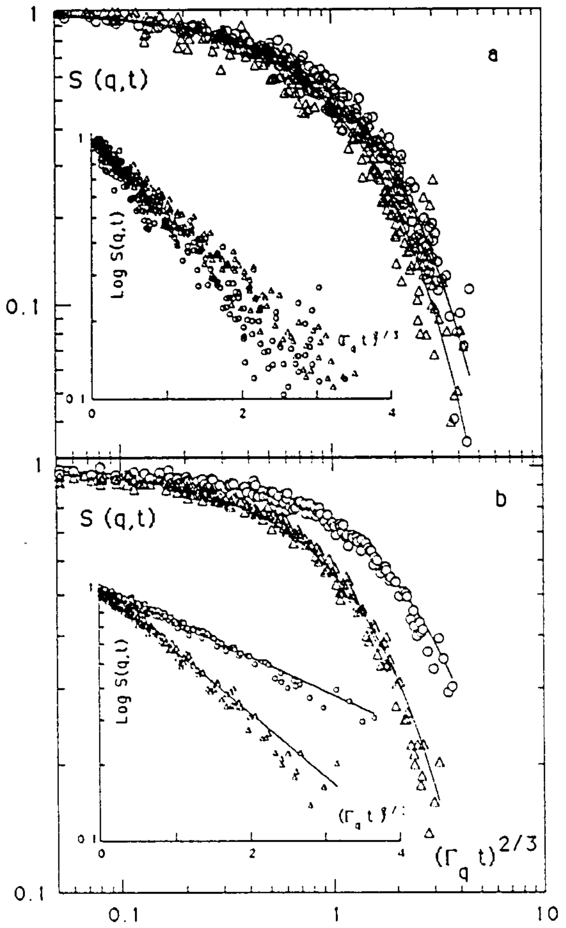

Figure 3. Dynamic structure factor as a function of the dimensionless time $\Gamma_q t$ where $\Gamma_q = kTq^3/6\pi\eta_s$. The log−log scales, used allow a presentation of data points equally spaced. The X axis $(\Gamma_q t)^{2/3}$, as well as log−ln scales used in the inset allow one to display the stretched exponential line shape. Full lines correspond to best fits by eq 14. (a) Good solvent (PS/benzene $M = 6.77 \times 10^6$) semidilute solution, $T = 30$ and 64 °C (C(g/cm^3) = 0.072 (○) and 0.016 (△). (b) Θ solvent (PS/cyclohexane $M = 3.84 \times 10^6$) semidilute solution, $T = 39$ °C (C(g/cm^3) = 0.117 (○) and 0.022 (△).

Table 2. Prefactor Values Found by Fitting the Dynamic Structure Factors in Good and Θ Solvents to Eq 14

C (g/cm^3)	$B_{\Theta\ \text{solvent}}$	$B_{\text{good solvent}}$
0.072		0.74 ± 0.05
0.016		0.84 ± 0.05
0.117	0.46 ± 0.03	
0.022	0.69 ± 0.03	

PI) the relative local viscosity is dependent on the concentration

$$\frac{\eta_{\text{loc}}}{\eta_s} = (1.3 \pm 0.1)[1 + \beta C] \qquad (15)$$

The numerical value 1.3 is, within experimental precision, found to be identical for PI and for PS in good[30] and Θ solvents. However if the same data treatment is done on $S(q,t)$ measured by light scattering on a very dilute (C (g/cm^3) ≈ 10^{-4}) high molecular weight (20.6×10^6) PS/benzene solution, the numerical value is found to be equal to 1. We do not understand the origin of this discrepancy.

From the concentration dependence, β values are found to be equal to β_{PI}(cm^3/g) = 10 ± 2.8 for PI samples and β_{PS}(cm^3/g) = 17 ± 2 for PS samples. In the later case, β_{PS} is independent of the molecular weight, the Θ temperatures and the solvent viscosities. This concentration dependence is, within experimental error, in good agreement with that measured for a single PS molecular mass dissolved in one solvent.[25] Note that $\beta_{\text{PS}}/\beta_{\text{PI}}$ (=1.7) is on the same order of magnitude as the concentration ratio determined either on the Kuhn length having a mass m_k and a length l_k[31] ($C_k \approx m_k/l_k^3$, $C_{k\text{PI}}/C_{k\text{PS}} = 1.6$) or on the persistence length[32] ($C_l \approx$ ml/la^2 where m is the mass per unit length, l the persist-

Table 3. Molecular Weight M_w, Concentration C, Relative Overlap Concentration C/C^*, and Entanglement Ratio C/C_e for Samples on Which Neutron Spin−Echo Experiments Were Performed

M_w	C(g/cm^3)	C/C^*	C/C_e
	PS		
4.4×10^4	0.111	0.776	0.206
	0.0400	0.280	0.0744
3.86×10^6	0.117	7.66	6.24
	0.0811	5.31	4.32
	0.0575	3.77	3.06
	0.0221	1.45	1.18
8.4×10^6	0.0708	6.84	6.76
2.06×10^7	0.0515	7.79	9.64
	PI		
9.4×10^5	0.0946		3.50
	0.0744		2.76
	0.0413		1.53

Table 4: Θ Temperatures of PS and PI in Different Solvents, and Solvent Viscosities (η_s) in Centipoise[a]

	Θ (°C)	η_s(cp)
PS/deuterated Decalin (*a*)	22.0 ± 0.2	2.531
PS/deuterated cyclopentane (*b*)	25.50 ± 0.5	0.4419
PS/hydrogenated cyclopentane[43]	154.5	0.1589
PS/deuterated cyclohexane[52]	40 ± 1	0.7450
PI/deuterated dioxane[53]	38	0.9744

[a] *a* and *b* are explained in Appendix 3.

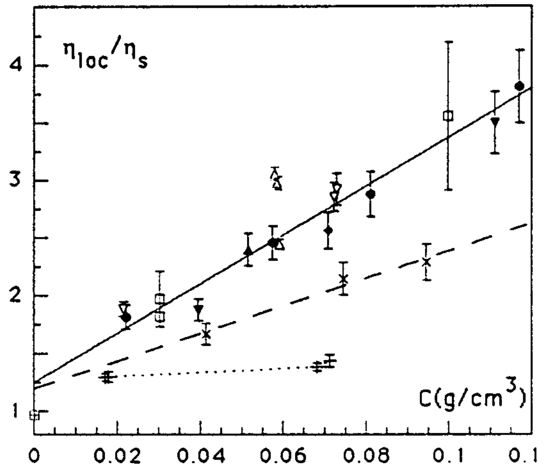

Figure 4. Variation as a function of the concentration C of the relative local viscosity η_{loc}/η_s measured on PS and PI semidilute Θ solutions. Full symbols correspond to different molecular weights of PS/cyclohexane (▲) 2.06×10^7; (◆) 8.4×10^6; (●) 3.84×10^6; (▼) 4.4×10^4). Open symbols correspond to $M = 3.84 \times 10^6$ in different Θ solvents ((□ PS/Decalin at 22 °C; (▽) PS/cyclopentane at 25 °C (Θ_U); (△) PS/cyclopentane at 150, 155, and 160 °C (close to Θ_L); (×) PI/dioxane; (+) PS/benzene (good solvent)). Note the points ● and △ at $C \approx 0.06$ g/cm^3 are measured at 39 °C for PS in cyclohexane and at 150 °C for PS in cyclopentane. The full line corresponds to the best fit combined PS data points $\eta_{\text{loc}}/\eta_s = 1.25\ (1 + 17C)$ and the dotted line corresponds to the best fit PI data points $\eta_{\text{loc}}/\eta_s) = 1.2\ (1 + 10C)$.

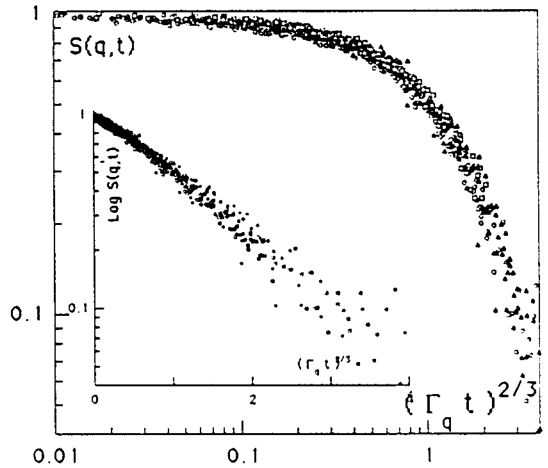

Figure 5. Dynamic structure factor as a function of the dimensionless time $\Gamma_q t$. Here $\Gamma_q = kTq^3/6\pi\eta_{loc}$ with $\eta_{loc} = \eta_s(1 + 17C)$. The axes used are explained in the legend of Figure 3. The spectra measured on PS in different Θ solvents superimpose when the concentration dependence of the local viscosity is taken into account. The different systems exemplified are PS/cyclohexane, PS/cyclopentane (Θ_U = 22 °C), PS/cyclopentane (Θ_L = 155 °C), and PS/Decalin.

ence length, and *a* the axial radius of the polymer and $C_{lPI}/C_{lPS} = 1.7$). C_l being independent of the persistence length, this could explain why β_{PS} is independent of the Θ temperature while *l* varies as $1/T$.

In Figure 5 the structure factors $S(q,t)$, measured for PS dissolved in cyclohexane (Θ = 39 °C), Decalin (Θ = 22 °C), cyclopentane (Θ_U = 25.2 °C and Θ_L = 155 °C) are plotted, as a function of $(\Gamma_q t)^{2/3}$ in which η_{loc} is taken equal to be to $\eta_s(1 + 17C)$. The excellent superposition confirms that the concentration dependence given by eq 15 with $\beta_{PS}(\text{cm}^3/\text{g}) = 17$ is independent of the data treatment (spectra fitted using either eq 13 or eq 14). The concentration dependence of η_{loc} becomes obvious when Figure 3b and Figure 5 are compared.

As found for PS in cyclohexane,[25] η_{loc}/η_s decreases as the temperature is increased from the Θ point for the two PS Decalin solutions studied (C (g/cm^3) = 0.03 and 0.10). In Figure 6, the relative local viscosity η_{loc}/η_s is plotted as a function of the distance to the Θ temperature for PS Decalin and PS cyclohexane. Note that τ/τ^{**} ($=(T - \Theta)/35C$) is not the reduced temperature variable for the relative local viscosity. Actually, in the Figure 6 inset, it is shown that the relative variation of the local viscosity, $\eta_{rloc}/\eta_{rloc\Theta}$ (with $\eta_{rloc} = \eta_{loc}/\eta_s$) scales with $(T - \Theta)C^{1/2}$.

To check the influence of η_{loc} on the dynamics of the polymer center of mass, we performed light scattering experiments. The low molecular weights ($9.1 \times 10^3 \leq M \leq 1.9 \times 10^5$) used give dilute solutions in the same range of concentration as that in which neutron scattering experiments were performed ($0.02 < C$ (g/cm^3) < 0.1). In Figure 7 the diffusion coefficient divided by its value at zero concentration, $D/D_{C=0}$, is plotted as a function of the reduced concentration $[\eta]C$. For the intrinsic viscosity $[\eta]$, the limit to zero concentration of $(\eta - \eta_s)/C\eta_s$, its values are taken from ref 33. One can see that the diffusion coefficient decreases as the reduced concentration increases, as expected.[34] In this representation $D/D_{C=0}$ is independent of molecular weight, and for $[\eta]C < 1$

$$D/D_{C=0} = 1 - 0.46[\eta]\text{C}$$

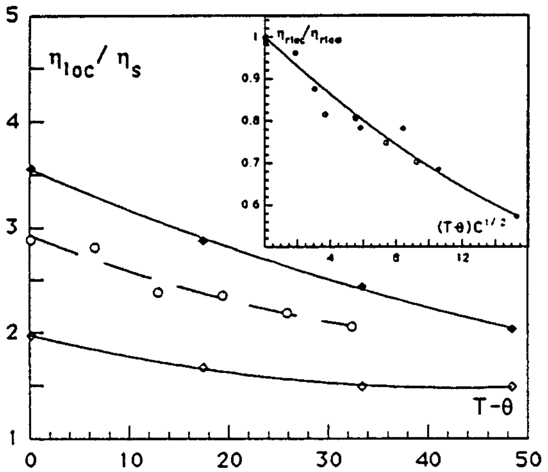

Figure 6. Variation of the local viscosity divided by the solvent viscosity η_{loc}/η_s as a function of the distance to the Θ temperature. Data were obtained on PS/Decalin (C (g/cm^3) = 0.030 (◇), 0.1 (◆)) and on PS/cyclohexane (C (g/cm^3) = 0.081 (○). Lines are guide for the eyes. η_{loc}/η_s have the same temperature dependence in both solvents. In the inset is shown the relative variation of the local viscosity, $\eta_{rloc}/\ \eta_{rloc\Theta}$ (with $\eta_{rloc} = \eta_{loc}/\eta_s$) as a function of $(T - \Theta)C^{1/2}$.

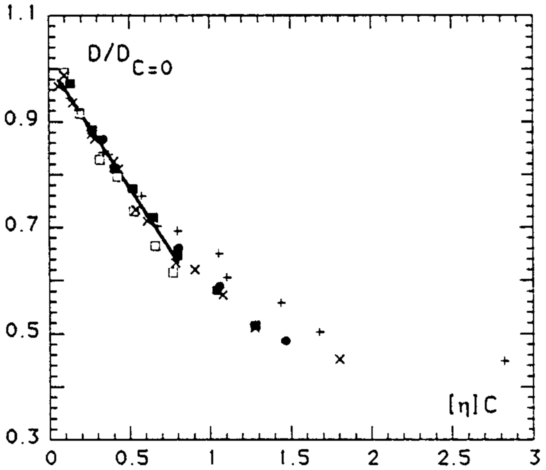

Figure 7. Variation, as a function of the reduced concentration $[\eta]C$ of the reduced diffusion coefficient $D/D_{C=0}$, measured by light scattering on dilute solutions. $[\eta]$ is the intrinsic viscosity[33] and $D_{C=0}$ the zero concentration limit of the diffusion coefficient. The range of concentration studied is $0.01 < C$ (g/cm^3) < 0.1. The different symbols correspond to different molecular weights and different solvents: for PS/cyclohexane, M = 9.1×10^3 (□), 1.84×10^4 (■), 4.39×10^4 (×), 1.9×10^5 (+); for PS/Decalin $M = 1.84 \times 10^4$ (●). The line corresponds to the fit of the combined data points: $D/D_{C=0} = 1 - 0.46C[\eta]$.

The value 0.46 is in good agreement with the value measured under Θ conditions at much lower concentration ($C < 0.01$) either by light scattering[34] (0.64) or by sedimentation[10] (0.58). In good solvent, comparison between the concentration dependence of the sedimentation coefficient[35] and the intrinsic viscosity[36] leads to a higher prefactor value (0.85). Note that if η_{loc} had an influence on D, $D/D_{c=0}$ should have been dependent on the molecular weight in the Figure 7 representation and the prefactor should have been smaller in good solvent than in Θ solvent. This indicates that any fraction of the polymer moves as if it was in uniform translational motion in a medium having the viscosity of the solution.

Thus, one can conclude that for PS and PI in a Θ solvent, the concentration dependent local viscosity affects only the local dynamics. When the temperature

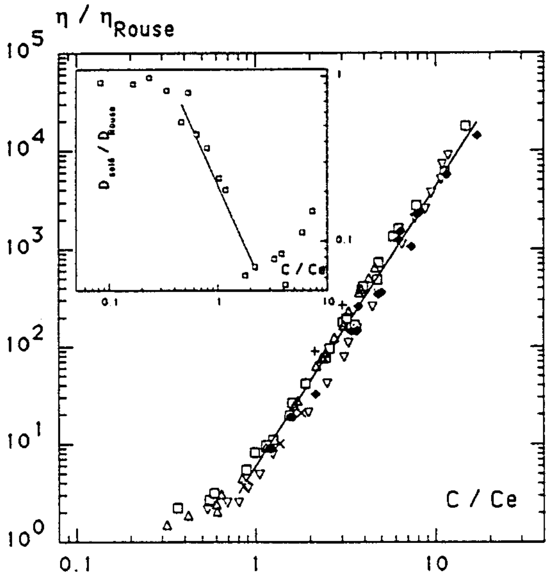

Figure 8. Variation of $\eta/\eta_{\rm Rouse}$, as a function of the entanglement ratio C/C_e. The measured viscosity is divided by the Rouse viscosity deduced from eq 2 (see Table 1) in which the overlap concentration C^* is replaced by the intrinsic viscosity $[\eta]$ (see Table 1). C_e is deduced from the measured number of binary contact (see Table 1 and eq 1. Symbols have the following meaning: (□) PS in benzene (GS) and (◆) PS in cyclohexane (Θ solvent), (▽ and ▲) PB and PI in cyclohexane (GS). Experimental results, obtained in PI dissolved in toluene[55] (GS), are also plotted (M = 4.9 × 10^5 (+), 5.6 × 10^5 (×), 1.1 × 10^6 (●)). The full line corresponds to the fit of combined data points: $\eta/\eta_{\rm Rouse} = 6(C/C_e)^{2.9}$. In the inset is shown the variation of $D_{\rm self\Theta}/D_{\rm Rouse}$ as a function of the entanglement ratio C/C_e. The Θ self-diffusion coefficient $D_{\rm self\Theta}$ is taken from ref 39 and the Rouse diffusion coefficient determined from the lowest molecular weight measurements. Measurements are performed on different molecular weights ($5 \times 10^4 \leq M_w \leq 9.65 \times 10^6$) and at $C = 0.04$ g/cm^3. The full line corresponds to the $C/C_e^{-1.5}$ dependence.

is raised above Θ, the local viscosity decreases and reaches the solvent viscosity in good solvent.

III.3. Macroscopic Viscosity. III.3.1. Concentration Dependence. Following eq 7 the reduced viscosity $\eta/\eta_{\rm Rouse}$ is expected to be a unique function of the entanglement ratio C/C_e whatever the solvent quality and the polymer species (PS, PI, and PB). This is actually observed in Figure 8 where $\eta/\eta_{\rm Rouse}$ is plotted as a function of C/C_e. $\eta_{\rm Rouse}$ is determined from eq 2, where $1/C^*$ is replaced by $[\eta]$ to ensure continuity of the viscosity between dilute and semidilute solutions (see discussion in ref 5). In good solvents $\eta_{\rm Rouse}/\eta_s = (C[\eta])^{1.3}$ and in Θ solvents $\eta_{\rm Rouse}/\eta_s = (C[\eta])^2$ (the intrinsic viscosity values, $[\eta]$, are given in Table 1). C_e is calculated from N/N_e values (given in Table 1) $C_{\rm eGS} = (N/N_e)^{-0.76}$ and $C_{\rm e\Theta} = (N/N_e)^{-3/4}$. Under good solvent conditions, the entangled concentration was determined in ref 5, using measured values of the second virial coefficient MA_2 and of the number of binary contacts per entanglement N_e ($C_e' = N_e^{0.76}/MA_2$). C_e'/C_e is independent of the polymers species (for PS, PI, PB: $C_e'/C_e = 2.5 \pm 0.2$). The viscosity measured in the Θ solvent is divided by the local viscosity (eq 15). Note that if C/C^* is used as the reduced concentration variable, the reduced viscosity is dependent on the polymer species under the good solvent condition[5] but also dependent on the molecular weight in the Θ solvents.[19] The observed superposition is evidence for the influence of the correlation length ξ and of the tube diameter A on the macroscopic viscosity.[37] The full line corresponds to the fit to the combined data points

$$\eta/\eta_{\rm Rouse} = 6(C/C_e)^{2.9\pm0.1} \tag{16}$$

As in the melt,[38] the exponent is larger than the expected value (2.6). This corresponds to the molecular weight dependence of the viscosity (3.4) which is found experimentally to be stronger than predicted by reptation theory (3).

We are indebted to P. T. Callaghan for sending us his experimental data on the self-diffusion coefficient.[39] Measurements were performed at a concentration of 0.04 g/cm^3 for a wide range of molecular weight[40] ($5 \times 10^4 \leq M_w \leq 9.65 \times 10^6$). For $5 \times 10^4 \leq M_w \leq 3.3 \times 10^5$, the molecular weight dependence of $D_{\rm Rouse}$ is found to be inversely proportional to the molecular weight: $D_{\rm Rouse} = 0.026/M^{1.0\pm0.03}$ (with D in cm^2/s). $D_{\rm self\Theta}/D_{\rm Rouse}$ decreases with the entanglement ratio as $C/C_e^{-1.5}$ (see inset in Figure 8), in the range $0.5 \leq C/C_e \leq 2$, but it increases for $C/C_e > 2$ (corresponding to $M > 4 \times 10^6$). The quantity $D_{\rm self}\eta/(GR_g^2)$ can also be deduced from self-diffusion and viscosity measurements. At $C = 0.04$ g/cm^3, the value of the plateau shear elastic modulus G, is 570 dyn/cm^2 while the radius of gyration at the Θ temperature[41] is $R_{\rm g\Theta}$ (cm) $= 2.9 \times 10^{-9}\sqrt{M}$. For $1 \times 10^6 \leq M \leq 4 \times 10^6$, $D_{\rm self}\eta/GR_{\rm g\Theta}^2$ is found to be constant and equal to 0.37 ± 0.08, while this quantity increases for higher molecular weights. Both these increases may be due to a polymer relaxation time that is too long compared to the maximum delay time in the pulse gradient spin−echo technique (see Experimental Section in ref 39 p 3312). The independence of $D_{\rm self}\eta/(GR_{\rm g\Theta}^2)$ with molecular weight is consistent with measurements performed on PS in dibutyl phthalate in the concentrated regime ($w = 0.4$ g/g).[42]

Since the theoretical scaling laws for the concentration dependence of the viscosity are confirmed experimentally, we now focus on the temperature dependence of the macroscopic viscosity and the self-diffusion coefficient.

III.3.2. Temperature Dependence. From a theoretical point of view, the viscosity is expected to increase and the self-diffusion coefficient to decrease as the temperature is increased from the Θ point (see eqs 8 and 11). Experimentally, the opposite behavior is observed. In Figure 9, it can be seen that the relative viscosity ($\eta_r = \eta/\eta_s$) divided by its value at the Θ temperature ($\eta_r/\eta_{r\Theta}$) decreases as $T - \Theta$ increases.[43,44] The empty circles in Figure 9 correspond to the full circles in which the viscosity is divided by the temperature-dependent local viscosity instead of the solvent viscosity. In Figure 9 experimental results are also plotted for PB dissolved in dioxane (Θ = 25 °C). In this system the decrease with temperature of $\eta_r/\eta_{r\Theta}$ is smaller than for PS in cyclohexane. This fact could be linked to the smaller influence of the concentration on the local viscosity of PI dissolved in dioxane, as compared to PS in various Θ solvents (eq 15 and β values). From the self-diffusion coefficient experimental data,[39] $D_{\rm rself}/D_{\rm rself\Theta}$ ($D_{\rm rself} = D_{\rm self}\eta_s/T$ with T in K) is plotted as a function of $T - \Theta$ in Figure 10. Contrary to the theoretical expectation, this quantity increases with temperature. We will show that these temperature variations are due to the decrease of the local viscosity (measured by NSE) as the temperature is increased.

Since the macroscopic viscosity and the self-diffusion coefficient[39] have been measured on two similar molec-

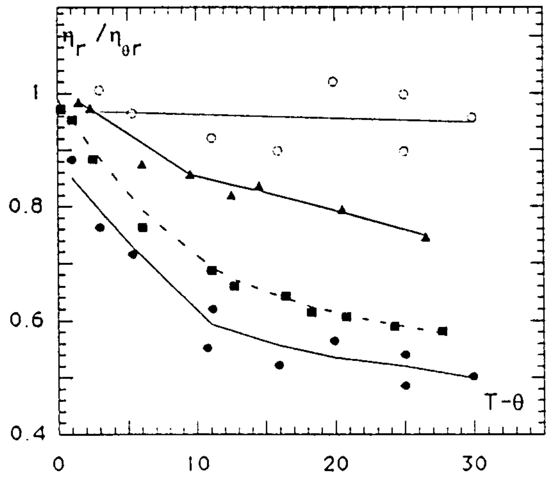

Figure 9. Decrease of the relative viscosity $\eta_r/\eta_{r\Theta}$ as a function of distance to the Θ temperature $T - \Theta$. Theoretically the opposite behavior is expected. Measurements performed on 6.77×10^6 molecular weight PS in cyclohexane at two concentrations (C (g/cm^3) = 0.04 (■), 0.082 (●) and on 9.65×10^5 molecular weight PB in dioxane (C (g/cm^3) = 0.076 (▲)). ○ correspond to ● in which the viscosity is divided into the local viscosity instead of the solvent viscosity. Lines are guides for the eyes.

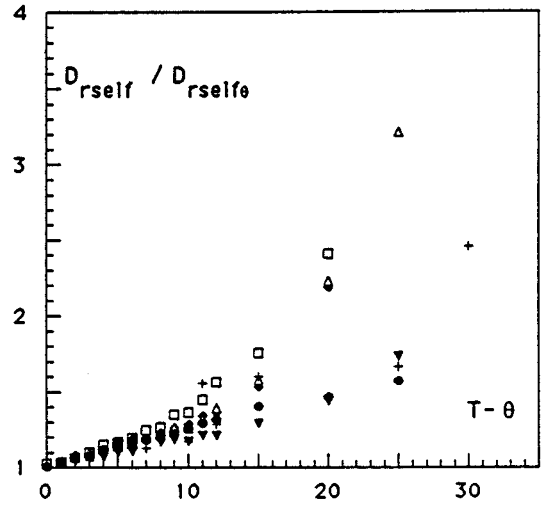

Figure 10. Increase of the self-diffusion coefficient (from ref 39). D_{rself} was reduced by its value at Θ temperature ($D_{\text{rself}} = D_{\text{self}}\eta_s/T$ with T in K) as a function of the distance to the Θ temperature $T - \Theta$. Theoretically, the opposite behavior is expected. Experiments were performed at C (g/cm^3) = 0.04 and for different molecular weights: M = 1.03×10^6 (□), 1.45×10^6 (◆), 1.75×10^6 (△), 3.04×10^6 (▼), 4.0×10^6 (●), 6.85×10^6 (+).

ular weights 3.86×10^6 (4.0×10^6) at a concentration of $C \approx 0.04$ g/cm^3, their temperature variation can be compared. In Figure 11 the square of the expansion factor α^2 is plotted as a function of the reduced temperature variable τ/τ^{**}. Here α^2 is deduced from the product of the self-diffusion coefficient and the viscosity in good solvent ($\tau > \tau^{**}$) divided by the same quantity at Θ (see eq 12). The square of the expansion factor so deduced is constant for $0 < \tau/\tau^{**} < 10^{45}$, while for $10 < \tau/\tau^{**} < 20$, it increases by 20% as the reduced temperature is increased by a factor of 2 as expected theoretically (see eq A7). Although the macroscopic viscosity and the self-diffusion coefficient vary with temperature contrary to the theoretical predictions, their product increases with temperature as expected. This product is independent of the friction. Thus the local viscosity influences the viscosity as much as the self-diffusion coefficient.

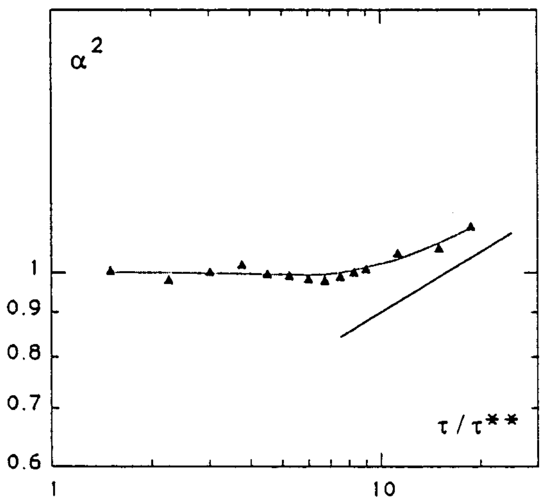

Figure 11. Variation as a function of the reduced temperature τ/τ^{**} of the square of the expansion factor α^2. τ is the reduced temperature $\tau = (T - \Theta)/\Theta$ and τ^{**} is the crossover temperature equal to $35C$ (for PS in cyclohexane). α^2 is deduced from the ratio of the product of the viscosity by the self-diffusion coefficient at different temperatures divided by its value at Θ (see eq 12). Experiments were performed at C (g/cm^3) = 0.04 and $M = 3.86 \times 10^6$ (4.0×10^6). The mass in parentheses was used for self-diffusion coefficient measurements. The straight line is a guide for the eyes corresponding to the expected temperature dependence of the square of the size expansion factor $\alpha^2 \approx \tau/\tau^{**0.23}$.

It is tempting to compare this deduced square expansion factor with that actually measured experimentally by SANS experiments. The variation with temperature of the radius of gyration of a few labeled PS chains in a semidilute solution of unlabeled chains[3,46] provides a direct measurement of the expansion factor $\alpha_R{}^2$. The increases of $\alpha_R{}^2$ was found to agree with theoretical expectation ($\tau/\tau^{**0.23}$). However, $\alpha_R{}^2$ increases with τ/τ^{**} faster than the square expansion factor deduced from eq 12. As noted in reference,[47] this may be due, to the fact that $\alpha_R{}^2$ found in semidilute solutions is larger than in that in dilute solutions ($C \rightarrow 0$). In fact the experiments were performed with too low molecular weights ($<2 \times 10^5$) with the consequence that, to be in semidilute solution, the concentration is too high (>14 g/cm^3).

Experimental confirmation of the temperature dependence of the viscosity can be done if experiments are performed at low enough concentration such that the local viscosity is that of the solvent (see Figure 4). The macroscopic viscosity was measured on the highest molecular weight PS ($M = 20.6 \times 10^6$) in the entangled regime[48] but at very low concentration ($5.9 \times 10^{-3} \leq C$ (g/cm^3) ≤ 0.0108). Figure 12, shows a plot as a function of the reduced temperature τ/τ^{**}, of the relative viscosity divided by its value at Θ, $\eta_r/\eta_{r\Theta}$, measured on PS dissolved in cyclohexane (empty symbols) and on PS dissolved in transdecalin[49] (full triangles). The reduced viscosity $\eta_r/\eta_{r\Theta}$ increases with reduced temperature. The line in Figure 12, which is not a fit, is the theoretically expected dependence $\tau/\tau^{**0.74}$ (eq 8). This result is an indication that if the local viscosity were the solvent viscosity, the temperature dependence of the macroscopic viscosity would follow the theoretical expectation. To measured the temperature exponent, however, a PS of molecular weight of 2×10^8 must be used in order to

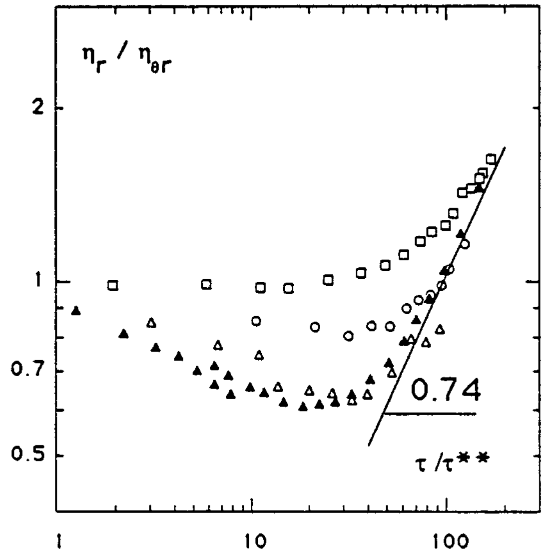

Figure 12. Variation of the reduced viscosity $\eta_r/\eta_{r\Theta}$ as a function of the reduced temperature τ/τ^{**} (defined in Figure 11), measured on PS 20.6×10^6 molecular weight for $C \le 0.01$ g/cm^3. Empty symbols correspond to PS cyclohexane (C (g/cm^3) $= 5.9 \times 10^{-3}$ (□), 6.8×10^{-3} (○), 1.08×10^{-2} (△); solid triangles to PS transdecalin (C (g/cm^3) $= 8.87 \times 10^{-3}$). To superimpose the cyclohexane and transdecalin data measured at high reduced temperature, $\Theta\tau^{**}$ for transdecalin was taken as equal to 565 °C.

access the range $C_e < C \ll 0.01$. Such high molecular weight samples are not at present available.

Conclusion

The dynamic properties of semidilute solutions are fully described by theory if two lengths, namely the tube diameter A and the correlation length of concentration fluctuation ξ, are considered. Under both Θ and good solvent conditions, the hindrance to movement encountered by one chain due to the presence of the others, i.e., the tube, is defined by binary contacts. This implies that in a Θ solvent A and ξ are not proportional, the latter being the mean distance between ternary contacts. This theory provides an understanding of two important experimental features.

- The plateau elastic modulus is independent of the solvent quality.
- Whatever the polymer species and the solvent quality, the ratio of the viscosity to its value in the unentangled regime, $\eta/\eta_{\mathrm{Rouse}}$, scales with the entanglement ratio C/C_e. At the entanglement concentration C_e, the tube diameter is equal to the polymer size.

One problem remains puzzling, namely the temperature dependence. We show by NSE measurements that the discrepancy in the temperature behavior between theory and experiment (viscosity and self-diffusion coefficient) is due to a variation of the local viscosity, with temperature and concentration. If, in good solvent, the local viscosity is the solvent viscosity, in Θ solvent, neither the solvent viscosity, nor the Θ temperature, nor the molecular weight of the polymer affects the relative local viscosity. It varies as $\eta_{\mathrm{loc}}/\eta_s = 1 + \beta C$ where β depends on the polymer species. Note that for the two polymer species studied $\beta_{\mathrm{PS}}/\beta_{\mathrm{PI}} \approx C_{l\mathrm{PS}}/C_{l\mathrm{PI}}$, where C_l is the concentration on the scale of the persistence length. These results rule out the following possible causes of the origin of this local friction: proximity of the glass transition temperature, because experiments performed on PS at 39 and 155 °C have the same local viscosity $\eta_{\mathrm{loc}}/\eta_s$; coupling between solvent and polymer relaxation times[50] or individual bead contribution to local viscosity.[51] These effects are strongly dependent on the temperature, on the solvent, and on the nature of the polymer. Moreover none of these authors consider the Θ point as peculiar.

This concentration-dependent local viscosity is due to a competition between monomer-monomer friction f_m and monomer-solvent friction f_s, which leads to a total friction per monomer: $f = f_s(1 - \phi) + f_m\phi$, where ϕ, the monomer volume fraction, is proportional to the concentration. The reduced local viscosity can then be expressed as $\eta_{\mathrm{loc}}/\eta_s = 1 + \phi\ ((f_m/f_s) - 1)$. As $\eta_{\mathrm{loc}}/\eta_s$ is independent of the solvent viscosity, f_m as well as f_s are proportional to the solvent viscosity. This local viscosity could be a precursor sign of phase separation.

The role of concentration on the local viscosity is also difficult to understand. In the blob model (in ξ most monomers belong to the same chain) the concentration that could play a role, at a length scale much shorter than the blob size, is the internal concentration. This is independent of the concentration in dilute solutions ($C_{\mathrm{int}} \propto N/R_g^3$), but concentration dependent in semidilute solutions ($C_{\mathrm{int}} \propto g/\xi^3 \propto C$). Thus, if C_{int} were the pertinent concentration affecting the local viscosity, one would find a local viscosity that is concentration independent for the lower molecular weight studied by NSE ($M = 4 \times 10^4$), for which $C/C^* < 1$. The only possible explanation for the influence of the macroscopic concentration C on the local viscosity is that friction can occur between two monomers belonging to any polymer present in the solution. Hence, for dynamic properties, the polymers are transparent to each other in dilute as well as in semidilute Θ solutions.

However, the mechanism which causes the concentration-dependent local viscosity under Θ conditions remains to be explained.

Acknowledgment. We would like to thank M. Milas as well as M. Rinaudo for the deuterated Decalin viscosity measurements and C. Lartigue, who helped us with the light scattering experiments performed in Grenoble. We would like also to thank R. Colby, E. Geissler, A. Halperin, M. Rawiso, and M. Rubinstein for permanent and fruitful discussions. We are indebted to P. T. Callaghan for sending us his experimental data on the self-diffusion coefficient.

Appendix 1: Concentration Dependence of the Longest Relaxation Time

The tube length L is equal to the degree of polymerization N divided by the number of monomers in an entanglement strand, multiplied by the length of the strand. Thus

$$L_{\mathrm{BS}} \propto \frac{N}{N_e g} N_e^{1/2} \xi \quad \text{and} \quad L_\Theta \propto \frac{N}{A} \qquad \text{(A1)}$$

As ξ is the screening length for hydrodynamic interactions, the diffusion coefficient of the polymer in the tube is expressed by the same equation in good and Θ solvents. The chain is considered to be a Rouse chain of N/g blobs whose friction is proportional to their size ξ and to the solvent viscosity η_s:

$$\frac{1}{D_{\text{tube}}} \propto \frac{N}{g}\eta_s\xi \tag{A2}$$

As usual, the reptation time T_r is the time needed for the chain to escape from the tube:

$$T_r = \frac{L^2}{D_{\text{tube}}} \tag{A3}$$

Thus using eqs A1−A3, we find, in good solvent and in Θ solvent

$$\begin{aligned} T_{\text{rGS}} &\propto \frac{\eta_s}{N_e}\left(\frac{N}{g}\right)^3\xi^3 \approx T_{\text{RouseGS}} \times \left(\frac{C}{C_e}\right)^{1/(3\nu-1)} \\ T_{\text{r}\Theta} &\propto \frac{\eta_s}{N_e}\left(\frac{N}{g}\right)\xi\frac{N^2}{n} \approx T_{\text{Rouse}\Theta}\left(\frac{C}{C_e}\right)^{4/3} \end{aligned} \tag{A4}$$

where n, the number of monomers within l, the mean distance between two intermolecular binary contacts, is $n \propto l^2 \propto C^{-4/3}$.

Appendix 2: Temperature Dependence

We take as an example the radius of gyration R, for which the scaling law is, as usual

$${R_{\text{GS}}}^2 = {R_\Theta}^2\left(\frac{\tau}{\tau^{**}}\right)^Y \tag{A5}$$

$$\text{with} \quad \Theta\tau^{**} \propto \mathrm{C} \tag{A6}$$

Y is determined such that:

for $\tau < \tau^{**}$, $R = R_\Theta$ independent of the concentration and

$$\text{for } \tau > \tau^{**},\ R^2 = {R_{\text{GS}}}^2 \approx \frac{N}{g}\xi^2 \propto C^{(1-2\nu)/(3\nu-1)} \propto C^{-0.23}$$

This yields $Y = 0.23$, and the temperature scaling law, for $\tau/\tau^{**} > 1$, becomes

$${R_{\text{GS}}}^2 = {R_\Theta}^2 \times \left(\frac{\tau}{\tau^{**}}\right)^{0.23} \tag{A7}$$

Appendix 3: Characterization of the Θ Solvents

For PS/deuterated Decalin the Θ temperature was measured by light scattering. It was taken as the temperature for which the second virial coefficient vanishes (a in Table 4). The viscosity of the deuterated Decalin was measured with a Low Shear 30 viscosimeter (Contraves), its variation with temperature given in ref 20. For PS/deuterated cyclopentane, difficulties were encountered in measuring the upper Θ temperature by light scattering (perhaps owing due to the solvent high volatility), and we therefore measured the phase separation temperature of a PS sample of molecular weight 20.6 × 10^6 at $C \approx C^* = 7 \times 10^{-3}$. Phase separation occurs at 24.2 ± 0.3, and we estimate the upper Θ temperature to be 1 °C higher ($\Theta_U = 25.2$ °C) (b in Table 4). Its was not possible to measure the lower Θ temperature, and measurements were therefore made at 5 °C below and above the lower Θ temperature for PS in hydrogenated cyclopentane[43] (Θ_L =154.5 °C). The Θ temperature for PS in deuterated cyclohexane is taken from ref 52. The Θ temperature for polyisoprene dioxane is 34.1 °C.[53] The Θ temperature in deuterated solvent was not measured but chosen 4° higher than the hydrogenated solvent (by similarity with H and D cyclohexane).

References and Notes

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