Light scattering from dilute diblock copolymers in semidilute homopolymer solutions

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We investigate the small-angle light scattering from dilute polystyrene (PS)–poly(dimethylsiloxane) (PDMS) diblock copolymers in semidilute isorefractive PDMS/tetrahydrofuran (THF) solutions. We compare the results with those obtained on PS/PDMS homopolymer mixtures and analyse the data quantitatively in terms of the only available theoretical results based on the mean-field approach. We also obtain measurements of diffusion coefficients of probe PS molecules and probe PS–PDMS diblock molecules in semidilute PDMS/THF solutions by dynamic light scattering and show the different coupling that occurs between the probe molecule and the semidilute matrix.

(Keywords: light scattering; diblock copolymers; diffusion coefficients)

INTRODUCTION

We obtain small-angle light scattering results from ternary solutions of polystyrene (PS)–poly(dimethylsiloxane) (PDMS) diblock copolymers in semidilute PDMS/tetrahydrofuran (THF) solutions. The two components of the PDMS/THF mixture (species 3 and 1, respectively) are nearly isorefractive and have been used previously in the study of optically labelled ternary solutions with PS (species 2) as the probe molecules[1,2]. The purpose of this study of light scattering from block copolymers is to estimate the change in interaction (or excluded volume) parameter between the two types of segments, 2 and 3, when segments 2 belong to a diblock copolymer as opposed to a homopolymer. To make the conditions in the two cases as nearly identical as possible, we examine solutions where species 2 (PS) is dilute and species 3 (PDMS) is in the semidilute regime. In semidilute PDMS/THF solutions, addition of PS segments in the form of homopolymer PS chains or of diblock PS–PDMS molecules will only have a negligible effect on the total PDMS segment concentration. We analyse the results in terms of the mean-field formulation of the scattering theory[3,4] and find that under similar conditions for homopolymers and copolymers, quite different values of the excluded volume parameter v_{23} are obtained. We ascribe the difference to the local environment of the PS segment, which must be quite different in the mixtures of homopolymers from that in the copolymer/homopolymer mixtures despite the fact that the average concentrations in the two cases are the same.

We also report measurements of diffusion coefficients of the PS–PDMS diblock copolymer in the nearly isorefractive mixture of PDMS/THF solutions by dynamic light scattering. The tracer diffusion of the diblock chain, $D(0)$, is obtained by an extrapolation procedure of the measured mutual diffusion coefficient $D(c)$ in the limit of zero diblock concentration, c. The effect of the interaction between the probe molecule and the semidilute matrix solution is illustrated again by comparing results from the diblock polymers to those of PS homopolymers in the same matrix solution. The entanglement of the PDMS block of the probe diblock chain with the semidilute PDMS matrix affects both $D(0)$ and k_D, the concentration coefficient of diffusion.

LOW-ANGLE ELASTIC LIGHT SCATTERING

A general equation giving the light scattered by a solution of homopolymers and copolymers in a solvent at arbitrary concentrations was recently presented by Benoît and co-workers[3,4]. Their approach of extending the Ornstein–Zernike theory of direct and indirect interactions to polymer solutions was shown to be equivalent to a random phase approximation. At very small or zero scattering angle the scattering intensity can be expressed as the Rayleigh factor ΔR_0 given by:

$$\frac{\Delta R_0}{N_A K}=\frac{a_2^2X_2+a_3^2X_3+2a_2a_3X_{23}+(a_2^2v_{22}+a_3^2v_{22}-2a_2a_3v_{23})(X_2X_3-X_{23}^2)}{1+v_{22}X_2+v_{33}X_3+(v_{22}v_{33}-v_{23}^2)(X_2X_3-X_{23}^2)} \tag{1}$$

where N_A is Avogadro's number and K is a constant equal to $4\pi^2n^2\lambda_0^{-4}N_A^{-1}$, with n being the refractive index of the solution and λ_0 the wavelength of incident light *in vacuo*. The vs represent concentration-dependent

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excluded-volume parameters. The *a*s are contrast factor of the polymers with the solvent and are defined by:

$$a_i = v_i m_i / N_{\mathrm{A}} \qquad (2)$$

where m_i is the molecular weight of a monomer of polymer *i*, and v_i is the refractive index increment of species *i* with the solvent at its concentration c_i' in the solution, i.e.

$$v_i = c_i \overset{\lim}{\rightarrow} c_i' \left(\frac{\partial n}{\partial c_i}\right)_{T,P,c_j} \qquad (3)$$

with *T* being the temperature and *P* the pressure. The *X*s are normalized concentrations which, for the general case of N_2 homopolymer 2, N_3 homopolymers 3, and N_{23} block copolymers 2–3 having chain length P_2, P_3 for the homopolymers and P_2', P_3' for the blocks of the diblock chains, can be expressed as[4]:

$$X_2 = N_2 P_2^2 + N_{23} P_2'^2; \quad X_3 = N_3 P_3^2 + N_{23} P_3'^2;$$
$$X_{23} = N_{23} P_2' P_3' \qquad (4)$$

For simplicity, we have dropped here summations over different chain lengths P_i and P_i' that take into account the polydispersity of the polymer samples. We now consider some special limiting cases relevant to the experimental results to be presented below. We note that in the absence of copolymers, $X_{23} = 0$ and equation (1) reduces to the case of mixtures of homopolymers[3]. (The term $a_2 a_3 x_{23}$ is missing in equation (34) of ref. 4.)

Copolymer/solvent solutions

In the case of a monodisperse solution of diblock chains which are homogeneous in composition (i.e. constant P_2' and P_3') we have:

$$X_2 = N_{23} P_2'^2; \quad X_3 = N_{23} P_2'^2; \quad \text{and } X_{23} = N_{23} P_2' P_3' \qquad (5)$$

In that case, $X_2 X_3 - X_{23}^2 = 0$ and the Rayleigh factor in equation (1) simplifies to:

$$\frac{\Delta R_0}{N_{\mathrm{A}} K} = \frac{a_2^2 X_2 + a_3^2 X_3 + a_2 a_3 X_{23}}{1 + \upsilon_{22} X_2 + \upsilon_{33} X_3} \qquad (6)$$

Use of equation (2) and inversion of equation (6) leads to the following scattering result expressed in standard form:

$$\frac{K v_2^2 c_2}{\Delta R_0} = \frac{1}{\mathscr{M}_2'} + \left[\upsilon_{22} + \upsilon_{33}\left(\frac{P_3'}{P_2'}\right)^2\right] \frac{N_{\mathrm{A}}}{m_2^2} \frac{M_2'}{\mathscr{M}_2'} c_2 \qquad (7)$$

where c_2 is the concentration in mass/volume of block 2 in the solution, M_2' is the molecular weight of block 2, and $\mathscr{M}_2'$ is a modified molecular weight given by:

$$\mathscr{M}_2' = M_2'\left[1 + \left(\frac{v_3}{v_2} \frac{M_3'}{M_2'}\right)^2 + \frac{2 v_3 M_3'}{v_2 M_2'}\right] \qquad (8)$$

For a homogeneous, monodisperse block copolymer, the concentration *c* of the copolymer is given by:

$$c = c_2 / w_2 = c_2 M / M_2' \qquad (9)$$

where w_2 is the weight fraction of 2 in the block copolymer and *M* is the molecular weight of the copolymer equal to $M_2' + M_3'$. In the limit of zero concentration, equation (7) reduces to:

$$\frac{K_c}{\Delta R_0} = \frac{1}{v_2^2 M_2' w_2 + v_3^2 M_3' w_3 + v_2 v_3 (M_2' w_3 + M_3' w^2)} = \frac{1}{v^2 M^*} \qquad (10)$$

where *v* is the refractive index increment of the copolymer which can be taken as $v_2 w_2 + v_3 w_3$. M^* is the apparent molecular weight of the copolymer which is defined by equation (10) and is thus solvent dependent. Equation (10) is a classical result in the scattering from dilute copolymer solutions[5,6].

For the PS–PDMS system investigated here the PDMS (3) is nearly isorefractive with the solvent, THF (1), and v_3/v_2 was found to be 3.47×10^{-2}. Because M_3'/M_2' is of order one for the copolymer sample investigated, we have to a good approximation (7% error):

$$\mathscr{M}_2' = M_2' \qquad (11)$$

and

$$\frac{K v_2^2 c_2}{\Delta R_0} = \frac{1}{M_2'} + \left(\upsilon_{22} + \upsilon_{33} \frac{P_3'}{P_2'}\right) \frac{N_{\mathrm{A}}}{m_2^2} c_2 \qquad (12)$$

Knowledge of the weight fraction of styrene (2) in the PS–PDMS block copolymers will allow us to plot the right-hand side of equation (12) *versus* c_2 to obtain $1/M_2'$ as the intercept and an apparent second virial coefficient that depends on υ_{22}, υ_{33}, P_2' and P_3'.

Dilute copolymer in semidilute homopolymer solutions

For the case of dilute copolymers 2–3 in semidilute homopolymer solution 1/3 with $N_{23} \ll N_3$ and $P_3' < P_3$, equations (5) simplify to:

$$X_2 = N_{23} P_2'^2; \quad X_3 \cong N_3 P_3^2; \quad \text{and } X_{23} = N_{23} P_2' P_3' \qquad (13)$$

Under these conditions, X_{23}^2 is much smaller than the product $X_2 X_3$ since $N_{23} P_3'^2 / N_3 P_3^2 \ll 1$. The neglect of X_{23}^2 term in equation (1) reduces this expression to that of a homopolymer mixture except for the $a_2 a_3 X_{23}$ term. The excess scattering of the copolymer over that of the semidilute homopolymer solution can then be written in exactly the same form as that used previously for the homopolymer mixture:

$$\frac{K v_2^2 c_2}{\Delta R_0} = \frac{1}{\Omega^2}\left(\frac{1}{M_2'} + 2 A_{2,\mathrm{app}} c_2\right) \qquad (14)$$

where Ω^2 is now defined as:

$$\Omega^2 = \left(1 - \frac{\upsilon_{23} X_3}{1 + \upsilon_{33} X_3} \frac{a_3}{a_2}\right)^2 + \frac{2 a_3 X_{23}}{a_2 X_2 (1 + \upsilon_{33} X_3)^2} \qquad (15)$$

Equation (15) differs from the case of the homopolymer mixture previously considered[1] by the presence of the second term on the right-hand-side involving X_{23} that we show below to be negligible. The apparent second virial coefficient $A_{2,\mathrm{app}}$ is unchanged from its previous definition in homopolymer mixtures, i.e.

$$2 A_{2,\mathrm{app}} c_2 = \frac{1}{M_2'}\left(\upsilon_{22} X_2 - \frac{\upsilon_{23}^2 X_2 X_3}{1 + \upsilon_{33} X_3}\right) \qquad (16)$$

A simplification occurs when species 3 is in semidilute concentration. We have previously verified[1] that for a 15% PDMS/THF solution[1], $\upsilon_{33} X_3 \gg 1$; this result is anticipated since one would expect $A_{2,\mathrm{app}}$ to be independent of M_3, the molecular weight of component 3, and hence independent of X_3. In this case it is easy to show that the last term in equation (15) is also negligible as it is the product of $2 v_3 M_3' / v_2 M_2'$ with $1/\upsilon_{33}^2 X_3^2$, both of which are small. The expressions for Ω and $A_{2,\mathrm{app}}$ then reduce to:

$$\Omega = 1 - \frac{v_{23}}{v_{33}}\frac{a_3}{a_2} \tag{17}$$

$$2A_{2,\mathrm{app}} = \left(v_{22} - \frac{v_{23}^2}{v_{33}}\right)\frac{N_A}{m_2^2} \tag{18}$$

which are the same as in a ternary homopolymer solution[1]. Equation (14) with equations (17) and (18) are therefore applicable to dilute block copolymer 2–3 in semidilute homopolymer solution 1/3 as well as dilute homopolymer 2 in semidilute homopolymer solution 1/3. Hence, we will analyse our data in terms of equation (14) and obtain the experimentally accessible quantities Ω and $A_{2,\mathrm{app}}$ from both PS homopolymer and PS–PDMS copolymer in a given semidilute PDMS/THF solution. In the mean-field approximation used in deriving equation (1), which is the basis of the above results, no change in Ω and $A_{2,\mathrm{app}}$ should be observed, in principle, since the concentration of the polymeric species 3 remains practically identical in the two cases considered (dilute PS and dilute PS–PDMS in semidilute PDMS/THF). Any difference is due to the inappropriateness of the mean-field approach and can be interpreted in terms of changes of v_{23} that can be ascertained from equations (17) and (18) assuming the form of equation (14) still holds.

DYNAMIC LIGHT SCATTERING

The electric field correlation function for a ternary solution containing a dilute probe polymer and a refractive index matched solvent consists of two decay rates[7,8]. However, when the probe is dilute and the host polymer is in semidilute concentration, the amplitude of the decay rate related to the host is negligible and only one decay rate corresponding to the diffusion of the probe is observed[7]. The tracer diffusion coefficient of the probe at infinite dilution, $D(0)$, and the concentration coefficient of diffusion, k_D, may be obtained from the experimental decay rates by fitting the diffusion data to:

$$D(c) = D(0)(1 + k_D c) \tag{19}$$

We have demonstrated previously that equation (19) is applicable to homopolymer ternary mixtures of PS probes in PDMS/THF solutions and investigated a range of PS molecular weights when R_H/ξ is of order unity, where R_H is the hydrodynamic radius of PS in pure THF and ξ is the dynamic correlation length of semidilute PDMS matrix. Here, we show that equation (19) is equally applicable when the probe molecule is a diblock copolymer (PS–PDMS) and observe a very different behaviour of k_D for the diblock probe as a function of the semidilute (PDMS/THF) polymer concentration as compared to the behaviour of k_D for the homopolymer PS probe. In the case of a homopolymer probe, the reduced diffusion coefficient, $D(0)/D_0(0)$ (where $D(0)$ and $D_0(0)$ are the diffusion coefficient of the probe in semidilute solutions and in the pure solvent, respectively), has often been interpreted in terms of models for the transport of Brownian spherical particles in random inhomogeneous media when $R_H/\xi \leqslant 1$. It has been observed by forced Rayleigh scattering[9] that the theoretical result[10]:

$$D(0)/D_0(0) = \exp(-R_H/\xi) \tag{20}$$

is obeyed by small PS chains diffusing in semidilute PS chains of much higher molecular weights for $R_H/\xi \leqslant 3$. On the other hand, when the diffusing probe is a different species from the matrix solution, studies made in polyacrylamide gels indicated that the smaller probes diffused relatively more slowly than the larger ones[11]. In that case, an empirical modification of equation (20) was used to represent the data. In this paper, we present measurements of the diffusion coefficient of block copolymers (PS–PDMS) where one of the blocks is of the same species as the homopolymer of the PDMS/THF matrix solution and compare the results with those of PS chains in the same semidilute matrix solutions. The results provide some information on the nature of the coupling that occurs between the probe molecule and the matrix.

EXPERIMENTAL

The semidilute matrix PDMS/THF solutions were prepared from a fractionated sample of polydisperse, trimethylsiloxy-terminated PDMS. The original unfractionated sample was obtained from Petrarch Systems, Inc. The fractionation procedure used is described in ref. 1. The molecular weight distribution of the fractionated sample was obtained using h.p.l.c. and indicated a polydispersity of 1.6 and a weight average molecular weight, $M_w = 175\,000$. Narrow-distribution PS samples were obtained from Polysciences, Inc. and from the Pressure Chemical Co. The PS–PDMS sample used was sample 15 of ref. 12 and was provided by Dr J. Roovers. This sample had $M_w = 100\,000$, a polydispersity of 1.15 and a weight fraction of styrene of 0.471 (ref. 12). The PS samples, the PS–PDMS sample and the solvent THF (Aldrich Chemical Co., 99.9+%, h.p.l.c. grade, inhibitor-free) were all used as received.

Ternary solutions consisting of the semidilute PDMS/THF matrix and the PS or PS–PDMS probes were prepared by weight. Concentrations were calculated assuming additivity of volumes. The densities at 25°C were taken[1] to be $\rho_{\mathrm{PDMS}} = 0.9697\ \mathrm{g\,cm^{-3}}$, $\rho_{\mathrm{PS}} = 1.0711\ \mathrm{g\,cm^{-3}}$ and $\rho_{\mathrm{THF}} = 0.884\ \mathrm{g\,cm^{-3}}$. For the low-angle light scattering (LALS), the solutions were filtered directly into the scattering cell; for the dynamic light scattering (d.l.s.), the mixtures were filtered through 0.45 μm pore size filters into dust-free Pyrex 13 mm i.d. centrifuge tubes. The mixtures were then centrifuged as a further precaution for cleanness and the centrifuge tubes were immersed in a refractive index matched glycerol, both contained in a Brice-Phoenix C-105 cylindrical light-scattering cell. The LALS photometer and the d.l.s. set-up used have been described previously[1].

RESULTS AND DISCUSSION

Low-angle light scattering

Scattering intensities were measured at scattering angles of less than 5° and were taken as intensities at $\theta = 0°$ because corrections were negligible[1]. ΔR_0 in the equations for LALS described earlier represents the increase in scattered intensity of a solution dilute in polymer 2 over that of the solvent, and is proportional to $c_2 M_w v_2^2$. Ideally, in the comparison of the scattering from homopolymer PS and block copolymer PS–PDMS, we would like to have had a homopolymer PS of the same molecular weight as the PS block of the PS–PDMS copolymer. However, such a molecular weight (~47 000)

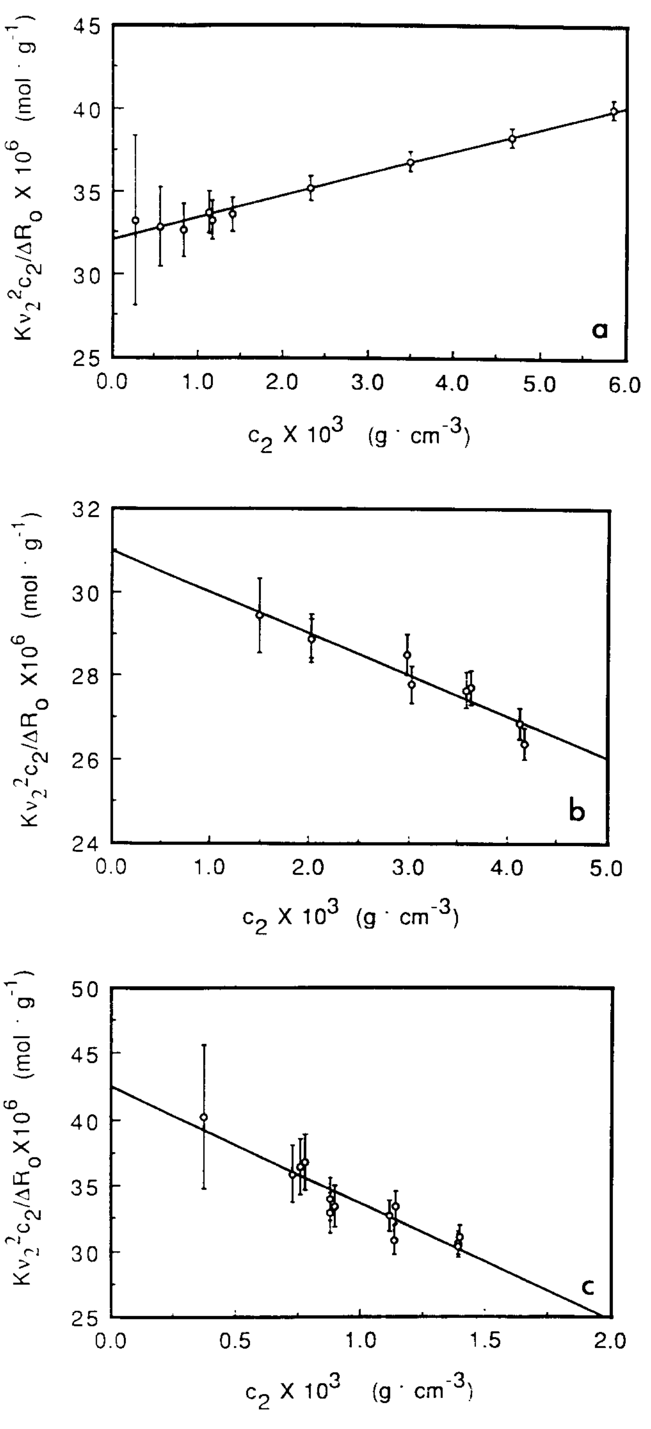

Figure 1 $K\nu_2^2c_2/\Delta R_0$ *versus* c_2 for homopolymer PS at 25°C in: (a) THF; (b) 7.5 vol% PDMS/THF solution; (c) 15 vol% PDMS/THF solution

was too high to be sufficiently soluble in the 15% volume PDMS/THF solution used as solvent to cover a range of c_2 broad enough to calculate reliably the slope and y-intercept of the data, so that apparent molecular weights and second-virial coefficients could be determined. In *Figure 1*, the results of excess scattering intensities of a PS homopolymer with $M_w = 32\,100$ are plotted as $K\nu_2^2c_2/\Delta R_0$ *versus* c_2 for the three different solvents: a, pure THF; b, 7.5 vol% PDMS/THF; and c, 15 vol% PDMS/THF. The values of $M_w = 32\,100$ and polydispersity = 1.02 of the sample were determined by h.p.l.c. The molecular weight obtained from the intercept of the best-fit line in *Figure 1a* (PS in solvent a) gave 31 200 ± 1100 g mol^{-1}, in good agreement with the h.p.l.c. measurement. The excluded-volume parameter v_{22} can be obtained from:

$$N_A v_{22} = 2A_2 m_2^2 = 14.49 \text{ cm}^3 \text{ mol}^{-1} \tag{21}$$

where $2A_2 = 1.34 \times 10^{-3}$ mol cm^3 g^{-2} from the slope of the line in *Figure 1a* and $m_2 = 104$ for styrene. In terms of an interaction parameter, we have:

$$N_A v_{22} = v_1(1 - 2\chi_{12}) \tag{22}$$

Using the result of equation (21) and taking $v_1 = 81.4$ cm^3 mol^{-1} for THF, we find $\chi_{12} = 0.411$. The intercept for the best-fit line in *Figure 1b* (PS in solvent b) gives an apparent molecular weight, $M_{w,app}$, of 32 270 ± 1700 g mol^{-1} which is, within experimental error, identical to the value in pure THF. Since, from equation (14):

$$M_{w,app} = \Omega^2 M_w \tag{23}$$

and $M_{w,app} = M_w$, the value of Ω is indistinguishable from unity for solvent b and this solution indeed behaves as perfectly isorefractive. For Ω to be close to unity, we must have from equation (17):

$$v_{23} \ll a_2 v_{33}/a_3 \tag{24}$$

From values of ν_2 and ν_3 previously determined to be 0.1885 cm^3 g^{-1} and 0.00654 cm^3 g^{-1}, respectively[1], and taking $m_2 = 104$ and $m_3 = 74$, we find using equation (2) that $a_2/a_3 = 40$. Thus, for the effect of refractive index mismatch to be detectable ($\geqslant 10\%$) in equation (17), we must have $v_{23}/v_{33} \geqslant 4$. A negative apparent second virial coefficient implies from equation (18) that v_{23} is relatively large since from equation (18) we have in this case $v_{23}^2 > v_{22}v_{33}$. However, the magnitude of $A_{2,app}$ in solvent b (*Figure 1b*) is relatively small compared to that observed in solvent c (see *Table 1*). The scattering results in the latter solution, shown in *Figure 1c*, give an intercept corresponding to $M_{w,app} = 23\,460 \pm 2900$ g mol^{-1}, which is markedly different from that in the previous two solvents. The parameter Ω takes on a value of 0.87 and solvent c can no longer be assumed to be a perfectly isorefractive solution. We note that this change from solvent b is not brought about by any change in refractive index properties but rather by a change in the excluded-volume parameters. From equation (17) one calculates that in solvent c one has $v_{23} \cong 5v_{33}$. The large increase of v_{23} relative to v_{33} is also seen in the second virial coefficient, which decreases by almost an order of magnitude from its value in solvent b (see *Table 1*).

The scattering results from the diblock copolymer sample in the same three solvents, a, b and c, are shown in *Figure 2*. In pure THF, the intercept of the best-fit line to the data in *Figure 2a* corresponds to a $M_w = 46\,800$ g mol^{-1}, in good agreement with the expected value of 47 000 for the PS block as anticipated

Table 1 LALS results for PS and PS–PDMS in various solvents at 25°C

Polymer	Solvent	$M_{w,app} \times 10^{-3}$ (g mol^{-1})	$A_{2,app} \times 10^3$ (cm^3 mol g^{-2})	Ω^2
PS	THF	31.2 ± 1.1	0.671	
PS	7.5 vol% PDMS	32.3 ± 1.7	−0.511	1.04
PS	15 vol% PDMS	23.5 ± 2.9	−3.37	0.75
PS–PDMS	THF	46.8 ± 5.1	2.38	
PS–PDMS	7.5 vol% PDMS	53.8 ± 2.3	−0.0805	1.15
PS–PDMS	15 vol% PDMS	45.0 ± 3.4	−1.17	0.96

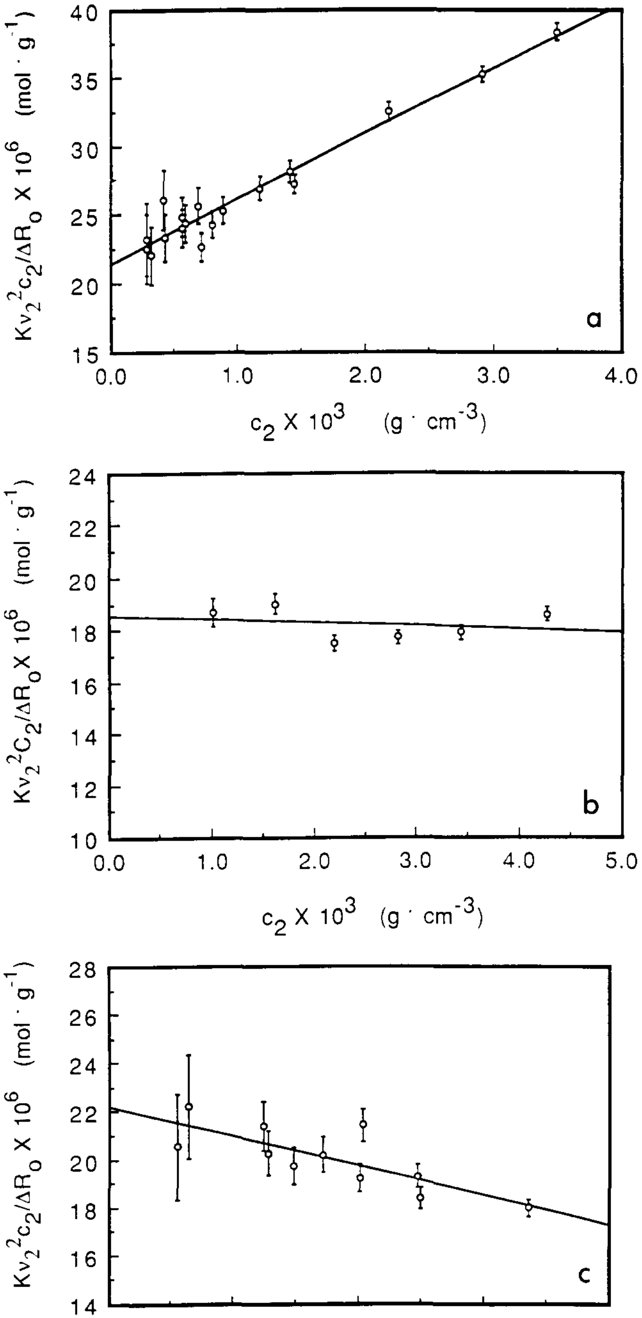

Figure 2 $Kv_2^2c_2/\Delta R_0$ *versus* c_2 for diblock copolymers PS–PDMS at 25°C in: (a) THF; (b) 7.5 vol% PDMS/THF solution; (c) 15 vol% PDMS/THF solution

in equation (11). The correction terms in equation (8) were not detectable. In semidilute PDMS/THF solutions, one expects a decrease in the apparent molecular weight from equations (14) and (17). In *Figure 1b*, we seem to obtain a slight increase in the apparent molecular weight whereas in *Figure 1c* the molecular weight is unchanged within experimental error (see *Table 1*). We note that in solvent b, the last term in equation (15) is more appreciable due to the lower concentration of PDMS (X_3) in the solution and will tend to partially offset the decrease in Ω from unity in the first term. In both solvents b and c, Ω is very close to unity (*Table 1*) and relation (24) must apply. This is also confirmed by the values of the apparent second virial coefficient. In solvent b, $A_{2,\mathrm{app}}$ is almost zero for the copolymer sample and we must have from equation (18):

$$v_{23}^2 \cong v_{22} v_{33} \qquad (25)$$

For the homopolymer sample, however, we found that $v_{23}^2 > v_{22}v_{33}$. Since the concentrations of species 2 (PS) and 3 (PDMS) are identical in both cases, we can assume that v_{22} and v_{33} are the same in both cases and that v_{23} is appreciably smaller in the block copolymer than in the homopolymer, in contrast to expectations based on the mean-field approximation. From $A_{2,\mathrm{app}}$ of the copolymer in solvent c, v_{23}^2 is now larger than $v_{22}v_{33}$, but still smaller than its value for the homopolymer in the same solvent. These results are consistent with the idea of a local THF concentration around a homopolymer PS chain that is larger than the average THF concentration in solution and that is often quantified in terms of a preferential adsorption parameter[1,13]. In the block copolymer, where the PS block is chemically attached to a PDMS block, preferential adsorption of THF molecules on the PS chain is less pronounced, as indicated by our scattering results. Assuming that v_{22} and v_{33} are the same for both dilute homopolymer and dilute copolymer at a given concentration of species 3, we find that the difference between the two values of v_{23}, for the diblock and for the homopolymer, is larger in solvent b than in solvent c. This is consistent with the fact that as polymer 3 concentration increases, the concentration around a homopolymer chain (2) becomes more uniform and less distinguishable from the copolymer (2–3) case. The preferential adsorption described above to explain the difference in v_{23} between the homopolymer and block copolymer samples is an indication of the limitations of the mean-field approach which ignores local concentration variations[4]. In the system investigated here, one will have to go to higher concentrations in PDMS than used here (equivalent to $1.5c^*$ and $3c^*$, where c^* is the overlap concentration) to achieve a certain degree of equivalence between the scattering results of a homopolymer and those of a copolymer, implied in the theoretical results for LALS, described above.

Dynamic light scattering

The results of the reduced diffusion coefficient, $D(0)/D_0(0)$, of homopolymer PS probes in a 15 vol% PDMS/THF solution reported earlier[1] are plotted in *Figure 3* on the basis of equation (20). The hydrodynamic radius, R_H, of PS in pure THF was determined from $D_0(0)$ by using the Stokes–Einstein relation. The dynamic correlation length, ξ, of the semidilute PDMS solution was estimated from d.l.s. measurements of the cooperative diffusion[1]. We see from *Figure 3* that the exponential dependence on R_H in equation (20) is not a good representation of the data for a given ξ, as the slope of the best-fit line is close to 0.5 rather than unity. Furthermore, results obtained with a different semidilute solution (the 7.5 vol% PDMS/THF solution) do not fall on the same curve as the data from the more concentrated semidilute solution, as shown in *Figure 3*. The range of molecular weights of the PS probes examined in the 7.5 vol% solution is shown in *Table 2* and did overlap with that of the 15 vol% solution studied earlier. Comparison of $D(0)/D_0(0)$ of different probes as a function of R_H/ξ agrees with the earlier observation that at a given

R_H/ξ, smaller probes diffuse relatively more slowly than larger ones[11]. For instance, a PS probe of $M_w = 30\,000$ is more retarded by a semidilute PDMS solution than a PS probe of $M_w = 60\,000$ in an equivalent solution (same R_H/ξ). We note that the value of R_H used here is that obtained in pure THF and not in the semidilute solutions. However, we have argued previously that this difference is expected to be negligible for low molecular weight probes, as R_H scales as $M_w^{-0.51}$ for PS in THF and the coils are not expanded[1]. The model for transport of particles that leads to the simple dependence on ξ in equation (20) ignores the coupling between the concentration fluctuations of the matrix solution and the probe diffusion. Such a coupling is difficult to model, but a recent stochastic model of the dynamics of flexible chains has been successfully applied to the tracer diffusion in homopolymer melts[14,15]. Here, we illustrate experimentally the effect of this coupling on the diffusion of PS–PDMS block copolymer in semidilute PDMS solutions.

The diffusion coefficients $D(c)$ of the PS–PDMS diblock copolymer studied above were obtained from d.l.s. measurements in three solvents: a, pure THF; b, 7.5 vol% PDMS/THF solution; and c, 12.5 vol% PDMS/THF solution. The data are plotted in *Figure 4* and can be analysed in terms of equation (19), where the tracer diffusion coefficients at infinite dilution $D(0)$ and the concentration coefficients of diffusion, k_D, can be extracted from the data. The values of $D(0)$ and k_D obtained from a least-squares fit to the data are listed in *Table 3*. The values of the reduced tracer diffusion coefficients of the block copolymers *versus* R_H/ξ are shown in *Figure 3* along with the homopolymer data.

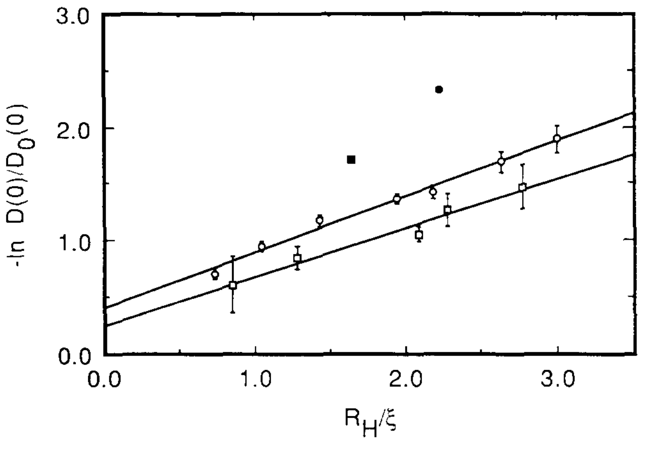

Figure 3 Reduced diffusion coefficients data at 25°C: ○, PS in 15 vol% PDMS/THF solution reported in ref. 1; □, PS in 7.5 vol% PDMS/THF solution; ●, PS–PDMS sample in 7.5 vol% PDMS/THF solution; ■, PS–PDMS sample in 12.5 vol% PDMS/THF solution

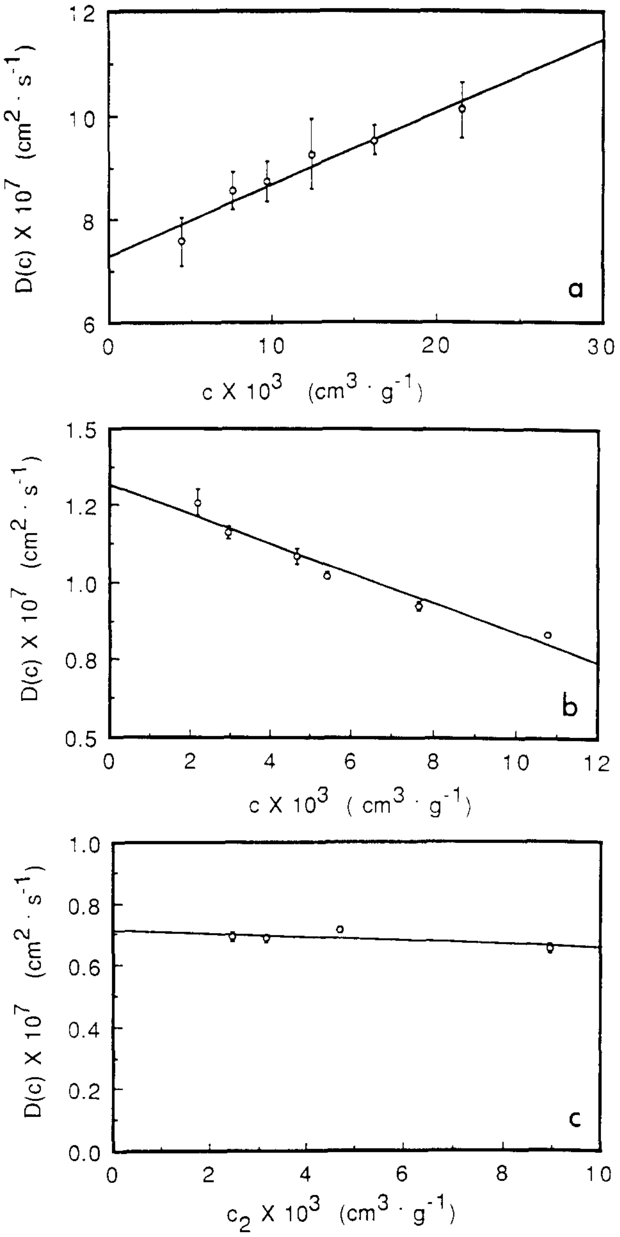

Figure 4 Mutual diffusion coefficient, $D(c)$ *versus* diblock copolymer PS–PDMS concentration, c, at 25°C in: (a) THF; (b) 7.5 vol% PDMS/THF solution; (c) 12.5 vol% PDMS/THF solution

Table 3 D.l.s. results from PS–PDMS diblock in various solvents at 25°C

Solvent	$D(0) \times 10^7$ (cm^2 s^{-1})	K_D (cm^3 g^{-1})
THF	7.280 ± 0.900	19
7.5 vol% PDMS/THF	1.320 ± 0.030	−36
15 vol% PDMS/THF	0.715 ± 0.024	−8.4

Table 2 Hydrodynamic properties of PS in solution with THF and mixtures of 7.5 vol% PDMS and THF at 25°C

$M_w \times 10^{-3}$ (g mol^{-1})	$D(0) \times 10^7$ (cm^2 s^{-1})	K_D (cm^3 g^{-1})	$D_0(0) \times 10^7$ (cm^2 s^{-1})	R_H (nm)	$D(0)/D_0(0)$
14.1	7.728 ± 0.900	−48.6	14.20	3.40	0.5442
31.2	4.030 ± 0.210	−78.6	9.395	5.15	0.4290
46.7	2.695 ± 0.175	−91.5	7.733	6.24	0.3485
99.6	1.475 ± 0.090	−136	5.201	9.18	0.2837
152	0.989 ± 0.160	−333	4.307	11.20	0.2297

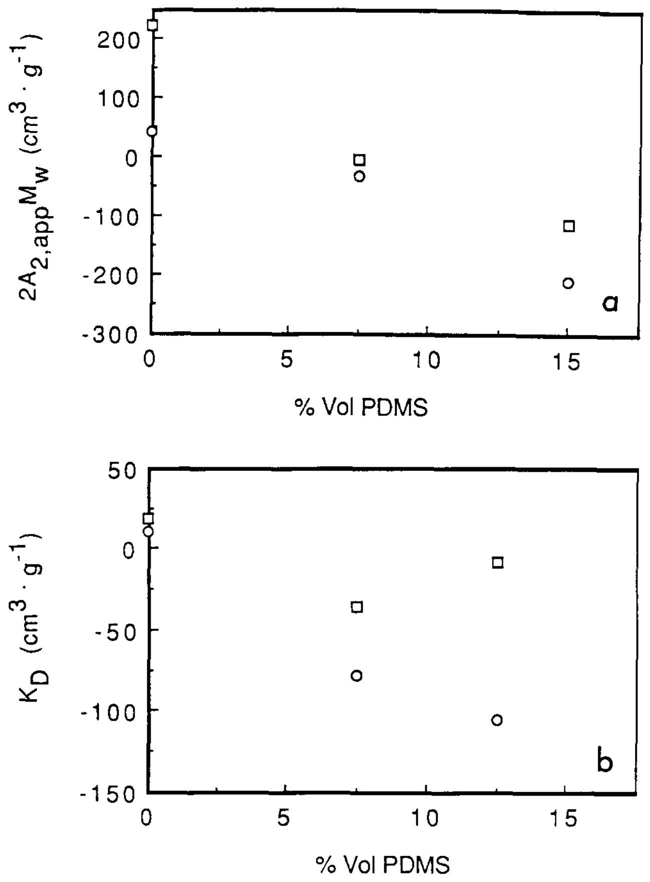

Figure 5 (a) Variations of $2A_{2,\mathrm{app}}M_w$ as a function of the PDMS concentration in the solvent; (b) variations of k_D as a function of PDMS concentration in the solvent. ○, PS; □, PS–PDMS

The PDMS block on the probe significantly retards its diffusion in comparison to a PS homopolymer of the same R_H/ξ. We note that for solvent c the correlation length ξ has become smaller than the PDMS block size, making the probe likely to entangle with the PDMS semidilute matrix. Such entanglement is less likely to occur for the homopolymer PS probes in view of the LALS results, suggesting strong THF preferential adsorption around the PS chains. The role of the thermodynamic interaction between the probe and the matrix can also be seen by comparing the variations of k_D and $2A_2M_w$ (obtained from LALS) as a function of the polymer matrix concentration shown in *Figure 5*. The basis of this comparison lies in the relation[16]:

$$k_D = -k_f + 2A_2M_w \qquad (26)$$

applicable to dilute binary polymer solutions and previously extended to the type of pseudobinary solutions considered here[1]. For the homopolymer PS probe, both $2A_2M_w$ and k_D show a marked decrease with the polymer matrix concentration, whereas for the diblock probe we notice a slight increase in k_D at the 12.5 vol% matrix concentration as compared to its value at 7.5 vol% matrix concentration. As noted earlier, at this polymer matrix concentration, the PDMS block of the probe molecule may be entangled with the matrix and subject to the much faster concentration fluctuations of the semidilute solution, leading to the observed result.

CONCLUSIONS

Low-angle light scattering results from ternary polymer solutions of dilute homopolymer PS and dilute diblock PS–PDMS chains in semidilute isorefractive PDMS/THF solutions are compared. By analysing the results using expressions based on a mean-field approach, we show that the excluded volume (or interaction) parameter v_{23} between PS segments and PDMS segments differ in the two cases, assuming that the self-excluded volume parameters remain unchanged. The results are consistent with a larger local THF concentration around the segments of the homopolymer PS chain than around the PS segments of the diblock chain. Higher concentration of PDMS in the PDMS/THF matrix solution lead to greater homogeneity in concentrations and a greater degree of equivalence of v_{23} between the two types of ternary solutions. Our results show the usefulness and limitations of the mean-field expressions. Another aspect of the interaction between the probe and the matrix is revealed by dynamic light scattering through the measurement of the probe diffusion coefficient.

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