Experimental investigations of light scattering by a solution of two polymers

L. Ould Kaddour and Cl. Strazielle
Institut Charles Sadron (CRM-EAHP), CNRS-ULP, 6 rue Boussingault, 67083 Strasbourg, France
(Received 21 April 1986; revised 23 July 1986)

The elastic light scattering intensity was measured for a mixture of two polymers, a and b, in tetrahydrofuran (THF) (a: polystyrene (PS); b: polydimethylsiloxane (PDMS)), as a function of all concentrations and wavevectors for four systems (S_I: $M_a = 230000$, $M_b = 280000$; S_{II}: $M_a = 1.4 \times 10^6$, $M_b = 1.22 \times 10^6$; S_{III}: $M_a = 1.4 \times 10^6$, $M_b = 4.2 \times 10^6$; S_{IV}: $M_a = 3 \times 10^6$, $M_b = 4.2 \times 10^6$). The concentrations were varied from dilute solution to the onset of phase separation. The experiments were done at constant polymer composition in certain cases, and at constant polydimethylsiloxane concentration in others. The experimental results are compared with recent theories which predict the scattered intensity for these same conditions. A thermodynamic analysis was performed by evaluating the incompatibility of this ternary system and by determining the polymer–polymer interaction parameter under three conditions: at the spinodal composition, at the binodal point, and also in some solvents under the optical 'theta' conditions.

(Keywords: mixture of two polymers; polystyrene/polydimethylsiloxane; light scattering; thermodynamic properties)

INTRODUCTION

Until recently, the description of light scattering from three components, with two polymers a and b in a solvent s, was considered as a thermodynamic problem[1-4]. This means that, for both small and large molecules, the only theoretical approach was based on the study of thermodynamic fluctuations and the scattered intensity was evaluated as a function of the derivatives of the free energy of mixing[1,5].

Recently, Benoît and Benmouna[6,7] proposed a new theory based on the application of the Ornstein–Zernicke formalism[8] or equivalently on the use of the random-phase approximation (RPA)[9]. Their theory gives the scattered intensity at any concentration and angle if one assumes that the form factors of polymers are known. One point of interest of this theory for experimentalists is that the angular dependence of the scattered light cannot be explained by a simple generalization of Zimm's procedure[10]. In the new theory, the angular dependence does not come from the form factors P_a and P_b only, but also from quadratic terms involving the product P_aP_b.

It is interesting to check whether this theory (which is a type of mean-field approximation) is useful for the interpretation, at least qualitatively, of experimental results. It has been shown by neutron scattering[11] in the case of two component systems that this approximation is reasonably good in the high concentration domain. It is also interesting to see if it can be applied to more dilute solutions and to mixtures of two polymers. This is the purpose of the present work which is based on the study of a mixture of two well known polymers, polystyrene (PS) and polydimethylsiloxane (PDMS), in solution with tetrahydrofuran (THF) and other solvents. These two polymers are incompatible ($\chi_{ab} > 0$), and therefore the range of accessible concentrations is rather limited to avoid phase separation.

Furthermore, since the refractive index of PDMS is practically the same as that of THF, the corresponding refractive index increment, dn/dc_b, in the mixture is zero. Therefore, one 'sees' only the PS and this fact makes data interpretation simpler.

In the first part of this paper, the theoretical formalism to be used for data interpretation is summarized in a form more suitable for experimentalists. In the second part, the samples and experimental techniques are described. In the last section, the results and their interpretations are presented.

The experiments described here were made under various conditions:

(a) constant composition by weight ($y = c_a/(c_a + c_b)$) of PS in the mixture;

(b) constant concentration c_b in PDMS;

(c) the so-called optical 'theta' conditions as explained later. Finally, the results for the interaction parameter χ_{ab} obtained by three different methods are presented.

THEORETICAL

General equations

The mean-field theory developed by Benoît and Benmouna[6,7] leads to the general relation for the scattering intensity $\Delta I(q)$ for a mixture of two polymers a and b in a solvent s:

$$I(q) = \frac{a^2 x_a + b^2 b_b + (a^2 v_b + b^2 v_a - 2ab v_{ab}) x_a x_b}{1 + v_a x_a + v_b x_b + (v_a v_b - v_{ab}^2) x_a x_b} \qquad (1)$$

In light scattering experiments, the contrast factors a and b should be identified with the refractive index increments

0032-3861/87/030457-10\$03.00

$\nu_a = dn/dc_a$ and $\nu_b = dn/dc_b$ respectively. The other quantities appearing in equation (1) are defined as:

$$x_i = N_i n_i^2 P_i(q) \qquad (i = \text{a,b}) \qquad (2)$$

where N_i is the number of chains of i per unit volume and n_i the number of elements (or monomers) per chain of i. We have $n_i = M_i \tilde{v}_i / V_s$ where M_i and $\tilde{v}_i$ are the molecular weight and specific volume of polymer i respectively and V_s the molar volume of solvent. $P_i(q)$ is the form factor of polymer i normalized as $P_i = 1$ for $q = 0$ ($q = (4\pi/\lambda)\sin(\theta/2)$ where λ is the wavelength of the incident beam in the medium, and θ the scattering angle).

The quantity v_{ij} is the excluded volume parameter relative to monomer i and j defined by the relationship:

$$v_{ij} = \int_0^\infty dr\, 4\pi r^2 \{1 - \exp[-u_{ij}(r)/k_\beta T]\}$$

where $u_{ij}(r)$ is the potential of the mean force between monomers i and j at a distance r and $k_\beta T$ the temperature in units of the Boltzmann constant k_β. It is important to note that $u_{ij}(r)$ may depend on monomer concentration and hence also v_{ij}, since the interaction between monomers i and j, in the presence of others, is strongly affected as the concentration increases. If j refers to solvent, it is suppressed in the formula.

Equation (1) is valid for any value of the concentration of both polymers a and b. In the dilute region, it gives the result obtained by using the single contact approximation. In the bulk limit, it gives the correct result of the random-phase approximation. It is also valid for arbitrary molecular weights M_i and form factors P_i of the chains. Furthermore, the thermodynamic conditions themselves can be chosen arbitrarily, since one can treat either compatible or incompatible polymers by adjusting v_{ab}, and one can select either good or bad solvents by adjusting the excluded volume parameters v_a and v_b.

In order to understand better the meaning of these parameters and the usefulness of equation (1), it is worth while at this stage to write these results in terms of standard experimental quantities. First, one can define the contrast factors (a and b) as:

$$a = \nu_a m_a / N_A \qquad \text{and} \qquad b = \nu_b m_b / N_A \qquad (3)$$

where N_A is Avogadro's number and m_i ($i =$ a or b) the molecular weight of monomer i. The concentrations c_i are expressed (in g cm^{-3}) as

$$c_i = N_i M_i / N_A \qquad i = \text{a or b} \qquad (4)$$

with $M_i = m_i n_i$.

The thermodynamic properties are expressed in terms of generalized second virial coefficients $A_{2,ij}(c)$ which are allowed to be concentration-dependent and which are introduced through the excluded volume parameters v_{ij} as follows:

$$A_{2,ij} = v_{ij} N_A / (2 m_i m_j)$$

i.e. $$v_a = 2A_{2,a} m_a^2 / N_A \qquad v_b = 2A_{2,b} m_b^2 / N_A$$

$$v_{ab} = 2A_{2,ab} m_a m_b / N_A \qquad (5)$$

Following Benoît and Benmouna[12], the generalized virial coefficient can be defined in terms of the enthalpy of mixing G_E per unit cell (i.e. V_s) and consequently in terms of Flory's interaction parameters χ_{is} ($i =$ a or b) and χ_{ij} ($i =$ a and $j =$ b). If it is assumed that the Flory–Huggins theory is valid for these systems, one can write:

$$A_{2,a} = \frac{\tilde{v}_a^2}{2V_s}\left(\frac{1}{\phi_s} - 2\chi_{as}\right) \qquad A_{2,b} = \frac{\tilde{v}_b^2}{2V_s}\left(\frac{1}{\phi_s} - 2\chi_{bs}\right)$$
$$A_{2,ab} = \frac{\tilde{v}_a \tilde{v}_b}{2V_s}\left(\frac{1}{\phi_s} - \chi_{as} - \chi_{bs} + \chi_{ab}\right) \qquad (6)$$

where ϕ_s is the volume fraction of solvent: $\phi_s = 1 - \phi_a - \phi_b$ with $\phi_a = c_a \tilde{v}_a$ and $\phi_b = c_b \tilde{v}_b$.

On the other hand, the form factors $P_i(q)$ should be understood here as generalized concentration-dependent form factors, namely those characterizing the chains in the actual system under investigation. The implicit dependence of the virial coefficients and the form factors upon concentration was justified formally by Benoît and Benmouna using a renormalization argument involving contacts of all orders between polymers in the system. Finally, substituting equations (3), (4) and (5) into equation (1) leads to:

$$(K')^{-1}\Delta I(q) =$$
$$\frac{a^2 c_a M_a P_a + b^2 c_b M_b P_b + 2(a^2 A_{2,b} + b^2 A_{2,a} - 2ab A_{2,ab}) c_a c_b M_a M_b P_a P_b}{1 + 2A_{2,a} M_a c_a P_a + 2A_{2,b} M_b c_b P_b + 4(A_{2,a} A_{2,b} - A_{2,ab}^2) c_a c_b M_a M_b P_a P_b} \qquad (7)$$

In this relation, a and b now directly represent the refractive index increments $\nu_a = dn/dc_a$ and $\nu_b = dn/dc_b$, and $\Delta I(q)$ the scattering intensity expressed as the Rayleigh ratio. $(K')^{-1}$ is an optical constant, $K' = 2\pi^2 n^2 / \lambda_0^4 N_A$, with λ_0 the wavelength of the incident radiation in vacuum, and n the refractive index of the solution.

This equation will be used as the theoretical basis for interpretation of our data in the forthcoming sections. Several remarks are in order here, which will help with the understanding of our experimental observations.

Equations of the spinodal. The spinodal equations can be obtained from equation (7) by noting that at $q = 0$, the scattered intensity diverges (i.e. $\Delta I(q \to 0) \to \infty$) if

$$1 + 2A_{2,a} M_a c_a + 2A_{2,b} M_b c_b$$
$$+ 4(A_{2,a} A_{2,b} - A_{2,ab}^2) c_a c_b M_a M_b = 0 \qquad (8)$$

This equation can be used to determine $A_{2,ab}$ and hence χ_{ab} (see equation (6)) assuming that $A_{2,a}$ and $A_{2,b}$ are known for given values of c_a and c_b. It may be convenient to introduce the parameter:

$$\beta = A_{2,ab}^2 / A_{2,a} A_{2,b}$$

in terms of which equation (8) becomes:

$$1 + 2A_{2,a} M_a c_a + 2A_{2,b} c_b M_b + 4A_{2,a} A_{2,b} c_a c_b M_a M_b (1 - \beta) = 0 \qquad (9)$$

Obviously β may depend on concentration, as we discussed earlier. Furthermore, if it is assumed that $A_{2,\mathrm{a}}$ and $A_{2,\mathrm{b}}$ remain positive as the concentration increases, equation (9) is satisfied if $\beta > 1$, which implies that the polymers a and b are incompatible. Finally, one must note that the spinodal equation as well as the forward-scattering intensity ($q \to 0$) were obtained before from a purely thermodynamic point of view by Stockmayer in 1955[1], and used since then extensively for experimental interpretations.

Asymptotic behaviour of $\Delta I(q)$ *in the intermediate* q *range*. In the range of q where $qR_{\mathrm{g},i} \gg 1$ ($i = \mathrm{a,b}$), the form factors $P_i(q)$ tend to an asymptotic limit proportional to $1/q^2(b'^2)^{1/\nu}$ when b' is the element length and ν the exponent of the power law ($R_\mathrm{g} \sim n^\nu$). The substitution of this limit in equation (7) indicates that the scattered intensity from the mixture is simply the superposition of the intensities corresponding to the constituents a and b. Therefore, in the high q range, the scattered intensity is not affected by the interaction properties of the polymers in solution.

The case where $b = \mathrm{d}n/\mathrm{d}c_\mathrm{b} = 0$. In our experimental investigation, the case of a PS–PDMS–THF mixture is considered in which the refractive indices of PDMS and THF are practically the same. If PDMS is denoted b, one has $b = v_\mathrm{b} = 0$, and therefore equation (7) written in the reciprocal form after some straightforward manipulations gives:

$$\frac{Kc_\mathrm{a}M_\mathrm{a}}{\Delta I(q)} = \frac{1}{P_\mathrm{a}} + 2A_{2,\mathrm{a}}c_\mathrm{a}M_\mathrm{a} - \beta\frac{4A_{2,\mathrm{a}}A_{2,\mathrm{b}}M_\mathrm{a}M_\mathrm{b}c_\mathrm{a}c_\mathrm{b}P_\mathrm{b}}{1 + 2A_{2,\mathrm{b}}M_\mathrm{b}P_\mathrm{b}c_\mathrm{b}} \tag{10}$$

with $K = K'a^2$. Since equation (10) is one of the main equations used in the experimental interpretation in the form of Zimm plots, it is worthwhile discussing briefly some of its limits.

First, in the dilute range, the third term on the right-hand side is quadratic in the concentration and hence it makes a vanishingly small contribution; this means that one should expect a regular Zimm plot in this concentration range.

Secondly, in the small q limit, one observes an apparent radius of gyration of the 'visible' polymer a which is strongly affected by the properties of the mixture, and in particular by the values of β, c_b and $R_{\mathrm{g,b}}$. Setting $P_i(q) = 1 - q^2R^2_{\mathrm{g},i}/3$, equation (10) gives:

$$\frac{Kc_\mathrm{a}M_\mathrm{a}}{\Delta I(q)_{q\to 0}} = A + \tfrac{1}{3}q^2R^2_{\mathrm{g,app}} \tag{11}$$

where A and $R_{\mathrm{g,app}}$ are obtained as:

$$A = 1 + 2A_{2,\mathrm{a}}M_\mathrm{a}c_\mathrm{a} - B$$

$$R^2_{\mathrm{g,app}} = R^2_{\mathrm{g,a}}\left(1 + \frac{R^2_{\mathrm{g,b}}}{R^2_{\mathrm{g,a}}}\,\frac{B}{(1 + 2A_{2,\mathrm{b}}c_\mathrm{b}M_\mathrm{b})}\right) \tag{12}$$

with

$$B = \beta\frac{4A_{2,\mathrm{a}}A_{2,\mathrm{b}}M_\mathrm{a}M_\mathrm{b}c_\mathrm{a}c_\mathrm{b}}{(1 + 2A_{2,\mathrm{b}}c_\mathrm{b}M_\mathrm{b})}$$

This clearly shows that the apparent radius of gyration is strongly affected by the properties of the mixture in the small q region, in contrast to that found for the high q region as we have noticed above. This behaviour tends to distort the Zimm plots, and produces curvature as q increases. This point will be clarified in the discussions of the experimental part.

Furthermore, at the zero q limit, equation (10) becomes:

$$\frac{Kc_\mathrm{a}M_\mathrm{a}}{\Delta I(q=0)} = 1 + 2A_{2,\mathrm{a}}M_\mathrm{a}c_\mathrm{a} - \beta\frac{4A_{2,\mathrm{a}}A_{2,\mathrm{b}}M_\mathrm{a}M_\mathrm{b}c_\mathrm{a}c_\mathrm{b}}{1 + 2A_{2,\mathrm{b}}M_\mathrm{b}c_\mathrm{b}} \tag{13}$$

This quantity is plotted in *Figure 1* as a function of c_a assuming that $A_{2,\mathrm{a}}$, $A_{2,\mathrm{b}}$ and $A_{2,\mathrm{ab}}$ do not depend on concentration: in this figure $2A_{2,\mathrm{a}}M_\mathrm{a} = 2A_{2,\mathrm{b}}M_\mathrm{b} = 240\,\mathrm{ml\,g^{-1}}$ with $M_\mathrm{a} = M_\mathrm{b}$. Assuming $c_\mathrm{a} = c_\mathrm{b}$, one chooses three values of β (i.e. $\beta = 0.6$, 1 and 1.7) to illustrate the fact that for $\beta > 1$, $\Delta I(q = 0)$ diverges at a given concentration c_a which shows that one is on the spinodal.

The optical 'theta' conditions

Coming back to the original form of the scattering intensity as given by equation (1) and keeping terms up to second order in concentration gives:

$$\Delta I(q) \simeq [a^2x_\mathrm{a} + b^2x_\mathrm{b} + (a^2v_\mathrm{b} + b^2v_\mathrm{a} - 2abv_\mathrm{ab})x_\mathrm{a}x_\mathrm{b}] \times (1 - v_\mathrm{a}x_\mathrm{a} - v_\mathrm{b}x_\mathrm{b}) \tag{14}$$

Rearranging this equation slightly leads to:

$$\Delta I(q) \simeq (a^2x_\mathrm{a} + b^2x_\mathrm{b}) - 2abx_\mathrm{a}x_\mathrm{b}v_\mathrm{ab} - a^2{x_\mathrm{a}}^2v_\mathrm{a} - b^2{x_\mathrm{b}}^2v_\mathrm{b} \tag{15}$$

and assuming, following Flory, that:

$$v_\mathrm{a} + v_\mathrm{b} - 2v_\mathrm{ab} = (V_\mathrm{s}/N_\mathrm{A})^2\chi_\mathrm{ab} \tag{16}$$

one obtains from equation (15) after rearrangement:

$$\Delta I(q) \simeq a^2x_\mathrm{a} + b^2x_\mathrm{b} - [(ax_\mathrm{a} + bx_\mathrm{b})(av_\mathrm{a}x_\mathrm{a} + bv_\mathrm{b}x_\mathrm{b}) + 2\chi_\mathrm{ab}(V_\mathrm{s}/N_\mathrm{A})abx_\mathrm{a}x_\mathrm{b}] \tag{17}$$

One sees that if the refractive index increments of the two polymers and their relative concentration are

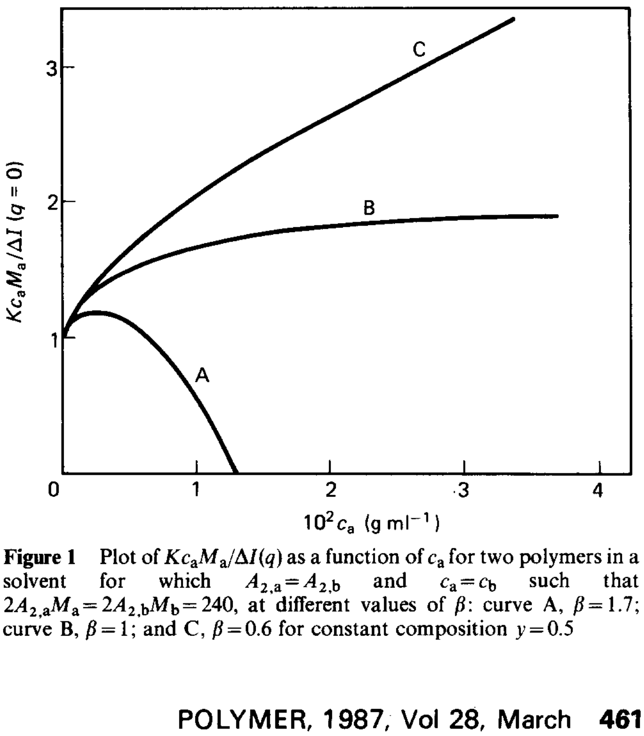

Figure 1 Plot of $Kc_\mathrm{a}M_\mathrm{a}/\Delta I(q)$ as a function of c_a for two polymers in a solvent for which $A_{2,\mathrm{a}} = A_{2,\mathrm{b}}$ and $c_\mathrm{a} = c_\mathrm{b}$ such that $2A_{2,\mathrm{a}}M_\mathrm{a} = 2A_{2,\mathrm{b}}M_\mathrm{b} = 240$, at different values of β: curve A, $\beta = 1.7$; curve B, $\beta = 1$; and C, $\beta = 0.6$ for constant composition $y = 0.5$

adjusted in order to have:

$$ax_a + bx_b = 0 \tag{18}$$

one obtains:

$$\Delta I(q) \simeq a^2 x_a + b^2 x_b - 2\chi_{ab}(V_s/N_A)abx_a x_b \tag{19}$$

Equation (18) is known as the optical 'theta' condition[13].

Unfortunately, the quantity $ax_a + bx_b$ is a function of q if the form factors of polymers a and b are different. Equation (18) can therefore only be satisified for one angle and the best value will be at $q = 0$. Under these conditions, equation (19) written for $q = 0$ is:

$$\Delta I(q=0) \simeq a^2 c_a M_a + b^2 c_b M_b - 2\chi_{ab}(V_s/N_A)abc_a c_b M_a M_b \tag{20}$$

which allows the determination of χ_{ab} without knowledge of $A_{2,a}$ and $A_{2,b}$ (or χ_{as} and χ_{bs}).

EXPERIMENTAL

Samples

Polystyrene (PS) samples were prepared by anionic polymerization following the classical procedure used in the laboratory[14]. The PS sample with the highest molecular weight, however, was prepared using a special method developed by Lapp and described elsewhere[15]. The polydispersity for these samples was in the range of 1.1 to 1.3. Polydimethylsiloxane (PDMS) samples are either commercial samples or obtained in our laboratory by cationic polymerization[16]. These polymers were fractionated using toluene as the solvent and methanol as the precipitant. The polydispersity of the fractions is of the order of 1.2. The highest molecular weight PDMS sample was not fractionated ($M_w/M_n \simeq 2$). All solvents were purified by distillation.

The samples were characterized by light scattering and size exclusion chromatography. The main parameters such as molecular weight M_w, radius of gyration and second virial coefficients are given in *Table 1*. The second virial coefficients for PS were determined in dilute THF solution. For PDMS, this procedure is not possible in THF since the refractive index increment $\nu_b = 0$. Therefore, we tried to select a solvent whose thermodynamic properties are as close as possible to those of THF but with a convenient value of ν_b. These conditions are fulfilled by toluene, in which the parameters K and α of the Mark–Houwink equation $[\eta] = KM^{\alpha}$ are close to those of THF. Moreover, if one uses the Stockmayer–Fixman[17] representation for viscosity results, one can evaluate the thermodynamic parameter B, which is proportional to the second virial coefficient. The values obtained for THF and toluene differ by about 10%.

Techniques

The light scattering apparatus used was a Fica 50 with a vertically polarized incident beam of wavelength $\lambda_0 = 546$ nm (or 436 nm). The scattering angle was varied from 30° to 150°. The solutions were centrifuged at an acceleration of 25 000 g for 2 h. The unknown refractive index increments were measured using a Brice Phoenix differential refractometer. In *Table 2*, we give these quantities for PS and PDMS in the various solvents used in this work.

The cloud point was obtained by direct visual observation. For the determination of binodal, solutions with known amounts of the two polymers in THF were placed in calibrated tubes. After intensive shaking, the mixtures were left to separate into two phases for one or two days. The volumes of both phases were measured. The total polymer concentrations in these phases were determined by weighing the residues after extraction and drying. These residues were dissolved in chloroform and the PS concentrations determined by u.v. absorption. All experiments were performed at room temperature (22°C).

RESULTS AND DISCUSSION

The first series of experiments were performed in THF where only PS is 'visible'. Four polymer mixtures were studied differing in their molecular weights. They are defined by:

System I: PS ($M_w = 230\,000$) + PDMS ($M_w = 280\,000$)
System II: PS ($M_w = 1.4 \times 10^6$) + PDMS ($M_w = 1.22 \times 10^6$)
System III: PS ($M_w = 1.4 \times 10^6$) + PDMS ($M_w = 4.2 \times 10^6$)
System IV: PS ($M_w = 3 \times 10^6$) + PDMS ($M_w = 4.2 \times 10^6$)

Each system is characterized by the total concentration, $c_T = c_a + c_b$, and the weight composition of PS, $y = c_a/(c_a + c_b)$, where a is PS and b is PDMS respectively. Two cases were considered. In the first one, y is kept constant and the measurements are made for different values of c_a. In the second case, the PDMS concentration c_b is constant and c_a varies as well as y.

Table 1 Molecular weight M_w, radius of gyration R_g and second virial coefficient A_2 for PS and PDMS samples

System	M_w		$A_2 \times 10^4$ (mol ml g^{-2})	R_g (Å)
I	PS	230 000	5.7	190
	PDMS	280 000	2.8^a	220^a
II	PS	1.4×10^6	2.8	660
	PDMS	1.22×10^6	2.6^a	540^a
III	PS	1.4×10^6	2.8	660
	PDMS	4.2×10^6	1.66^a	1310^a
IV	PS	3.0×10^6	1.94	1120
	PDMS	4.2×10^6	1.66^a	1310^a

^{a} Results obtained in toluene for PDMS

Table 2 The refractive index increments, dn/dc, of PS and PDMS in different solvents at $\lambda = 546$ nm

Solvents	n_0	$\left(\frac{dn}{dc}\right)_{PS}$ (ml g^{-1})	$\left(\frac{dn}{dc}\right)_{PDMS}$ (ml g^{-1})
THF	1.404	0.152	0
	(1.411)^a	(0.202)^a	
Cyclohexane	1.424	0.168	−0.025
Chloroform	1.444	0.157	−0.045
CCl_4	1.459	0.142	−0.052
Toluene	1.496	0.111	−0.094
Dichlorobenzene	1.551	0.052	−0.145
Styrene	1.545	0.065	−0.138

^{a} Values at $\lambda = 436$ nm

The composition of the polymer mixture is constant: y = constant

Light scattering measurements were made on systems I, II and IV at different concentrations up to phase separation and for different values of y. Some of the results are illustrated in *Figures 2*, *3* and *4* where the classical Zimm representation[10] is used by plotting $Kc_aM_a/\Delta I(q)$ as a function of c_a + constant × $\sin^2(\theta/2)$.

Figure 2 shows the results for system I with $y = 0.75$ and c_a concentrations ranging from 0.053×10^{-2} to 2.4×10^{-2} g ml^{-1}. *Figure 3* corresponds to system II with $y = 0.5$ and a maximum concentration $c_a = 4.5 \times 10^{-3}$ g ml^{-1}. *Figure 4* is for system IV for $y = 0.75$, and a maximum concentration $c_a = 3.8 \times 10^{-3}$ g ml^{-1}.

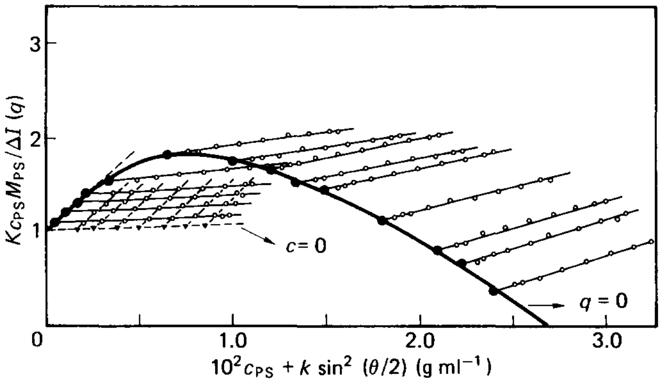

Figure 2 Zimm plot, $Kc_{PS}M_{PS}/\Delta I(q)$ as function of c_{PS} + constant × $\sin^2(\theta/2)$ for system I, PS–PDMS–THF at $y = 0.75$

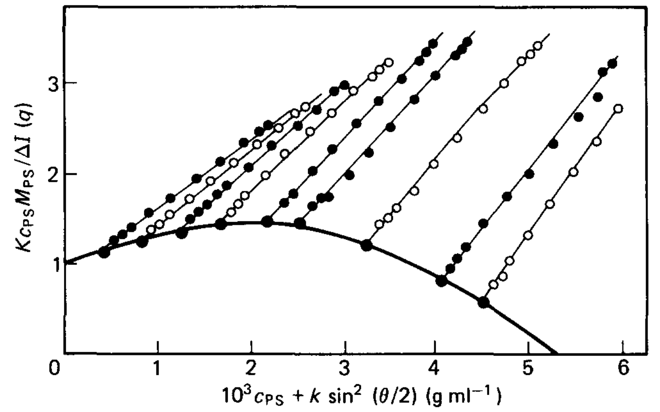

Figure 3 Zimm plot, $Kc_{PS}M_{PS}/\Delta I(q)$ as function of c_{PS} + constant × $\sin^2(\theta/2)$ for system II at $y = 0.5$

For these three systems, the low angle range of the Zimm plots have approximately the same shape. The curve at $q = 0$ goes through a maximum and decreases afterwards. It can be easily extrapolated to $Kc_aM_a/\Delta I(q = 0) = 0$, indicating an infinite scattered intensity, which means that spinodal has been reached. The corresponding concentration gives a point on the spinodal curve represented by equation (8). These curves are very similar to the theoretical one shown in the first part with $\beta > 1$ (see *Figure 1*). This behaviour is characteristic of an incompatible mixture and will be discussed later.

On the other hand, as opposed to the case where the solvent does not contain any polymer, i.e. $c_b = 0$ or $y = 1$, the initial slopes of the curves $Kc_aM_a/\Delta I$ *versus* q at constant c_a giving the apparent radii of gyration $R_{g,app}$ are not identical. These slopes are increasing when c_a increases to reach a limiting value. This can be understood by examining equations (11) and (12). From these, the apparent radius of gyration as a function of c_a, expressed in units of c_a^s, the concentration of PS at spinodal, is calculated. For the quantities appearing in the B term of equation (12), the values used for $A_{2,a}$ and $A_{2,b}$ were obtained in dilute solution (in good solvents such as THF and toluene respectively) and the value for β was obtained from the spinodal equation: equation (8) and quoted in the thermodynamic part (see *Table 3*). It is important to note that the apparent radii of gyration defined here differ from the classical apparent radii of

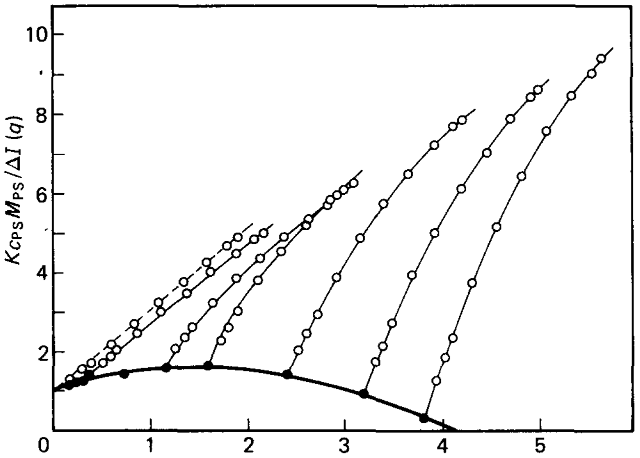

Figure 4 Similar Zimm plot for system IV at $y = 0.75$

Table 3 Values of $A_{2,ab}$ and the ratio β for the four systems studied, and their spinodal composition

System (M_a–M_b)	Experimental conditions	$c_a^s \times 10^2$ (g ml^{-1})	$c_b^s \times 10^2$ (g ml^{-1})	y (at spinodal)	$A_{2,ab} \times 10^4$ (mol ml g^{-2})	β
I (230 000–280 000)	constant y	0.47_7	3.585	0.117	5.82	2.10
		0.72_5	2.17	0.25	5.61	1.97
		1.6	1.6	0.50	5.26	1.73
		2.7	0.9	0.75	5.58	1.95
		3.2	0.702	0.82	5.83	2.11
II (1.4×10^6–1.22×10^6)	constant y	0.53	0.53	0.50	3.43	1.62
III (1.4×10^6–4.2×10^6)	constant c_b	0.315	0.469	0.40_2	2.74	1.62
IV (3.10^6–4.2×10^6)	constant c_b	0.153	0.500	0.23_5	2.39	1.77
	constant y	0.160	0.480	0.25	2.38_5	1.76
	constant c_b	0.250	0.293	0.46	2.32	1.67
	constant y	0.270	0.350	0.43_7	2.31	1.65
	constant y	0.410	0.137	0.75	2.43_6	1.84

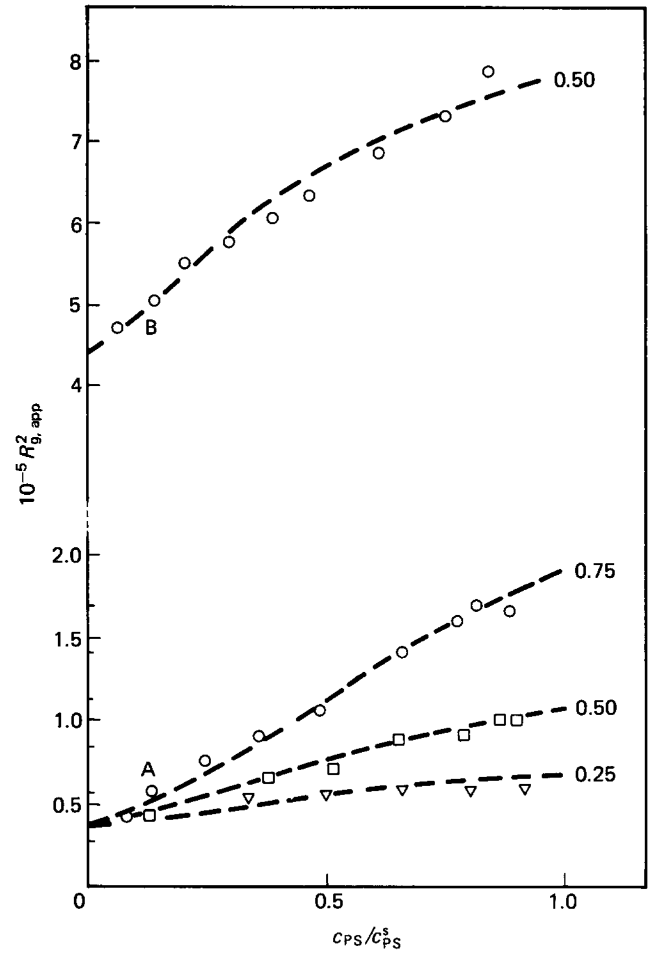

Figure 5 Evolution of $R^2_{g,app}$ *versus* c_{PS}/c^s_{PS}: curves A, for system I at $y=0.25$, 0.5, 0.75; curve B, for system II at $y=0.5$ (---, calculated curves)

gyration obtained by normalization to unity from the $q=0$ values[18].

Figure 5 represents the variations of $R^2_{g,app}$ as a function of the ratio c_a/c^s_a for system I (*Figure 5a*) at different compositions, i.e. $y=0.25$, 0.5 and 0.75, and for system II (*Figure 5b*) at $y=0.5$. The broken curves are theoretical results given by equation (12). The agreement between theory and experiment is surprisingly good for these systems.

Let us come back to *Figure 4* which corresponds to system IV with the highest molecular weight at $y=0.75$. One observes a peculiar behaviour in the angular dependence of the scattered light. The curves are straight lines at low c_a concentration and bend as the concentration increases. One can explain these distortions by considering the general equation applied in the case where $b=v_b=0$, i.e. equation (10), and observing that, in the intermediate q range, the effect of interaction between polymers disappears when $q^2R^2_{g,a}$ increases, whereas the slope at low q values is increased due to these interactions as has already been noted. In our experiments, however, even with the highest molecular weight systems, one does not reach the intermediate q range where the scattered intensity is given by the limiting value of $P_a(q)$. Therefore, it would be audacious to try to make a quantitative determination; one can observe only that the trend is in good agreement with the theoretical predictions.

The solvent is a mixture of THF and PDMS at a constant concentration c_b

Experiments were performed on systems II, III and IV choosing either low or high PDMS concentrations. Some of the results are displayed in *Figures 6* and *7*. These figures represent the ratio $Kc_aM_a/\Delta I(q)$ as a function of c_a + constant × $\sin^2(\theta/2)$. *Figure 6* corresponds to system III with $2A_{2,b}c_bM_b \simeq 1$ ($c_b=7.4\times10^{-3}\,\mathrm{g\,ml^{-1}}$) and for concentrations c_a ranging from 1.5×10^{-3} to $7.5\times10^{-3}\,\mathrm{g\,ml^{-1}}$. *Figure 7* represents the case of system IV with $2A_{2,b}c_bM_b=6.5$ ($c_b=4.84\times10^{-3}\,\mathrm{g\,ml^{-1}}$).

The Zimm plots are very different, in particular for $2A_{2,b}M_bc_b=1$; the angular dependence contains distortions which are more pronounced than found when increasing the c_a concentration.

To understand these diagrams, equation (10) is written in the form:

$$\frac{Kc_aM_a}{\Delta I(q)}=\frac{1}{P_a}+2A_{2,a}c_aM_a\left(1-\beta\frac{2A_{2,b}M_bc_bP_b}{1+2A_{2,b}M_bc_bP_b}\right) \qquad (21)$$

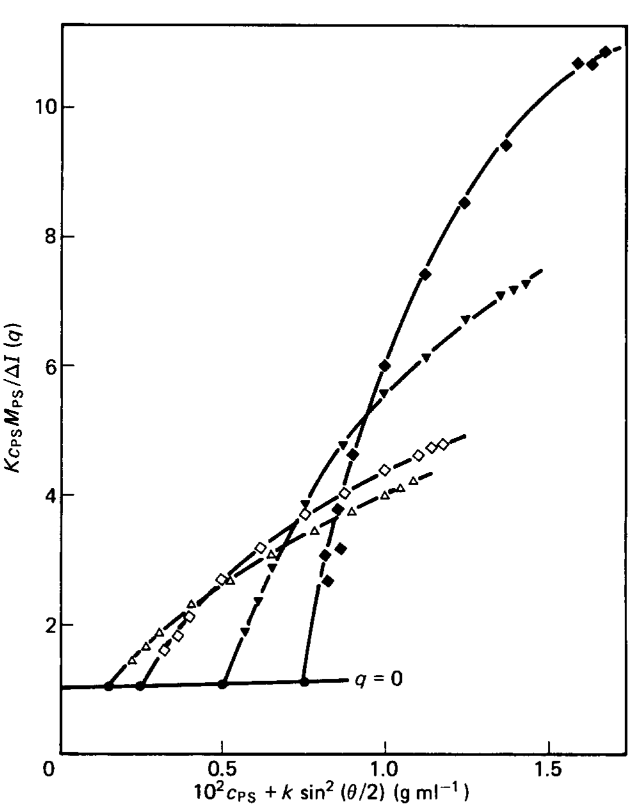

Figure 6 Zimm plot, $Kc_{PS}M_{PS}/\Delta I(q)$ as a function of c_{PS}+constant × $\sin^2(\theta/2)$ for system III at constant c_b such that $2A_{2,b}M_bc_b=1$, at $\lambda=436$ nm

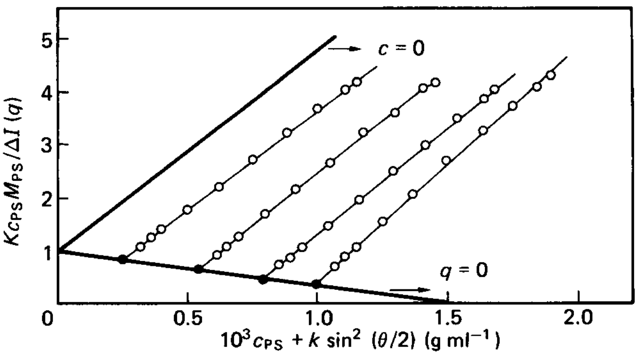

Figure 7 Zimm plot for system IV at constant concentration c_b, such that $2A_{2,b}M_bc_b=6.5$ at $\lambda=546$ nm (b is PDMS)

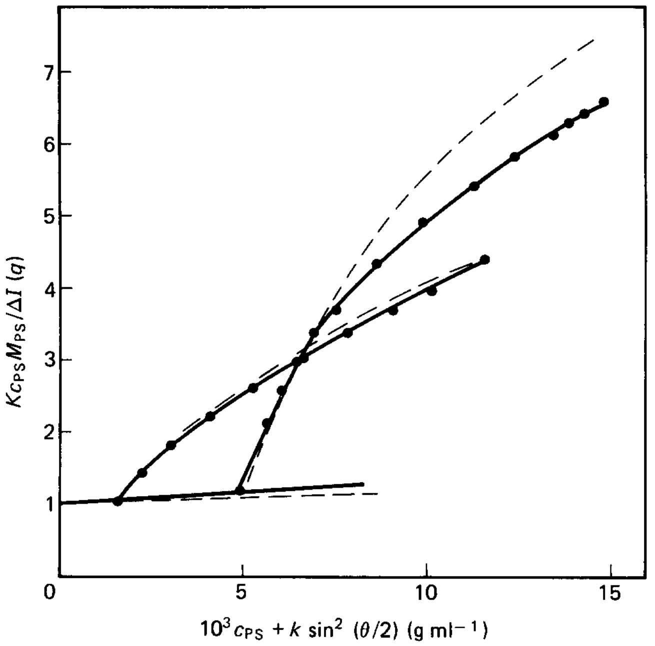

Figure 8 Comparison between the calculated curves, $Kc_{PS}M_{PS}/\Delta I(q)$ as a function of c_{PS}+constant × $\sin^2(\theta/2)$ (-----), and experimental results for system III at two concentrations of PS, such that $2A_{2,b}c_bM_b = 1$

One observes that if $2A_{2,b}c_bM_b$ is much higher than 1, one can neglect 1 as compared to $2A_{2,b}c_bM_b$, and write:

$$\frac{Kc_aM_a}{\Delta I(q)} = \frac{1}{P_a} + 2A_{2,a}(1-\beta)M_ac_a \tag{22}$$

which leads to an ordinary Zimm plot showing an apparent second virial coefficient equal to $A_{2,a}(1-\beta)$ which is negative for $\beta > 1$. This is, indeed, what the experiments show in *Figure 7*.

On the other hand, if one chooses c_b such that $2A_{2,b}M_bc_b = 1$, equation (21) reads:

$$\frac{Kc_aM_a}{\Delta I} = \frac{1}{P_a} + 2A_{2,a}M_ac_a\left(1 - \beta\frac{P_b}{1+P_b}\right) \tag{23}$$

One observes that, at $q = 0$, this equation becomes independent of c_a if $\beta = 2$, which is consistent with the behaviour illustrated by *Figure 6*. To demonstate this behaviour not only at $q = 0$ but also as a function of q, *Figure 8* compares experimental and theoretical results for two c_a concentrations. The theoretical curves (broken curves) are obtained from equation (23) with $\beta = 1.9$ (see the variation of β with y composition: *Figure 9* and *Table 3*) and by choosing the experimental values in dilute solution with good solvents for the form factors P_a and P_b. The agreement is fairly good except fot the highest concentration c_a in the intermediate q range. Other experiments are necessary to explain this point.

Analysis of the thermodynamic limit (i.e. $q = 0$)

For most of these systems, the ratio $Kc_aM_a/\Delta I(q = 0)$ tends to zero as the concentration c_a increases, which means that we approach the spinodal represented by the relation (9):

$$1 + 2A_{2,a}c_a^sM_a + 2A_{2,b}M_bc_b^s + 4A_{2,a}A_{2,b}M_aM_bc_a^sc_b^s(1-\beta) = 0$$

This relation shows that, if one assumes $A_{2,a}$ and $A_{2,b}$ are positive, β has to be higher than 1. In *Table 3* we give the concentrations c_a^s and c_b^s obtained experimentally at the spinodal for various systems. Knowing c_a^s and c_b^s one can deduce β from the previous equation by assuming that $A_{2,a}$ and $A_{2,b}$ are constant (*Table 1*). The results are displayed in both *Table 3* and *Figure 9* which shows β as a function of the y composition. We note that β, which is a function of y, is independent of molecular weight, because practically the same values are observed for different systems at a given composition.

It is customary to interpret second virial coefficients in terms of the interpenetration function which is defined as[19]

$$A_2 = \psi\frac{(R_g^2)^{3/2}}{M^2}4\pi^{3/2}N_A \tag{24}$$

where R_g is the radius of gyration of the chain in dilute solution. In the case of a mixture, we define ψ_a and ψ_b in terms of $A_{2,a}$ and $A_{2,b}$ and ψ_{ab} as follows:

$$A_{2,ab} = \psi_{ab}\frac{(R_{g,a}^2R_{g,b}^2)^{3/4}}{M_aM_b}4\pi^{3/2}N_A \tag{25}$$

This shows immediately that:

$$\beta = \psi_{ab}^2/\psi_a\psi_b \tag{26}$$

Recent theories[20] have shown that, regardless of the solvent quality and the nature of the polymers, ψ should depend on molecular weight according to the relation of the type:

$$\psi = \psi_0 + kM^{-a}$$

where ψ_0 is a universal number, k is a constant and a is the critical exponent. In these experiments, β seems to be independent of molecular weight, which implies that the

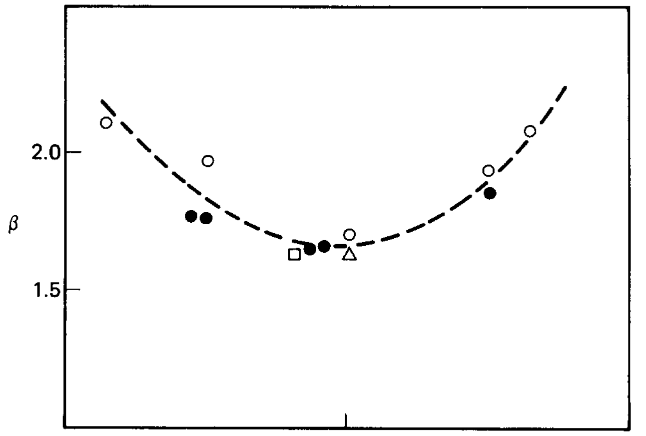

Figure 9 Variation of parameter $\beta = A_{2,ab}^2/A_{2,a}A_{2,b}$ *versus* y for the different systems: ●, system I; △, system II; □, system III; ○, system IV

exponents for ψ_a, ψ_b and ψ_{ab} are close to each other. The same observation has been made with the PS–PMMA mixture in toluene or benzene[21]. However, if one considers the result obtained by Van den Esker and Vrij[3] on the system PS–PIB (polyisobutylene) in toluene and deduces β as a function of y from the χ_{ij} parameters, one obtains different curves for different molecular weights: at a given composition, β decreases when the molecular weights of both polymers increase, in contradiction with our observations.

Expressing the scattered intensity at zero angle *versus* c_a by writing $c_b = c_a(1-y)/y$, one obtains:

$$\frac{Kc_aM_a}{\Delta I(q=0)} = 1 + 2A_{2,a}M_ac_a\left(1 - \beta\frac{2A_{2,b}M_bc_a(1-y)}{y + 2A_{2,b}M_bc_a(1-y)}\right) \qquad (27)$$

This equation is plotted in *Figure 10* together with the experimental results for system I at various compositions: $y = 0.25$, 0.50 and 0.75. Although the second virial coefficients $A_{2,a}$, $A_{2,b}$ and β are assumed to be independent of concentration, good agreement is obtained between the experimental and theoretical curves.

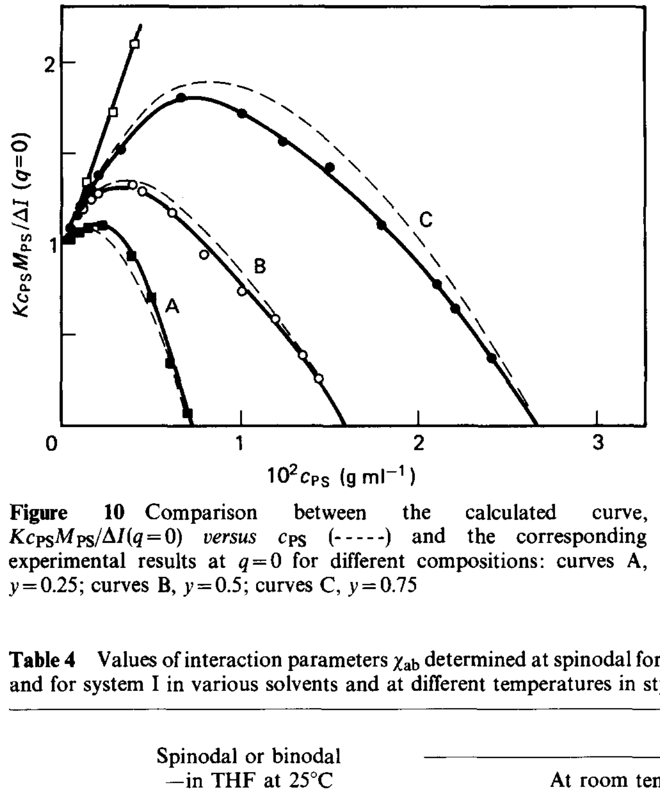

Figure 10 Comparison between the calculated curve, $Kc_{PS}M_{PS}/\Delta I(q=0)$ *versus* c_{PS} (-----) and the corresponding experimental results at $q=0$ for different compositions: curves A, $y=0.25$; curves B, $y=0.5$; curves C, $y=0.75$

Determination of the interaction parameter χ_{ab}

Until now, the interaction between unlike polymers has been characterized using the β parameter, which has the advantage of being independent of any specific model. In order to compare these results with those obtained by classical methods, one needs to apply the same model and mainly use the Flory–Huggins interaction parameters χ_{ab}. From its definition, the parameter β does not depend on χ_{ab} alone but also χ_{as} and χ_{bs}. Therefore, it is interesting to evaluate χ_{ab} from the results of β, using equation (6) to define the relation between the second virial coefficients and the interaction parameters χ_{ij}.

The values of χ_{ab} obtained in this way (at the spinodal) are reported in the first part of *Table 4*. These results, which are for systems I and IV, can be compared with those obtained by other methods. This has been done using, on the one hand, the optical 'theta' conditions as suggested by Fukuda and Inagaki[13] and, on the other hand, by measuring phase equilibria.

Optical 'theta' conditions. It has been seen, in the theoretical part, that if equation (18), expressed now in terms of concentrations c_i and molecular weights M_i of both polymers, is verified, i.e. $a\bar{v}_aM_ay + b\bar{v}_bM_b(1-y) = 0$ (where a and b are the refractive index increments, v_i the specific volumes of polymers and y the composition of the mixture), equation (20) valid for dilute solution at $q=0$ reduces to:

$$\frac{K'c_T}{\Delta I(q=0)} = A + BA^2c_T\chi_{ab} \qquad (28)$$

where $c_T = c_a + c_b$ is the total concentration. A and B are given by:

$$A = [a^2M_ay + b^2M_b(1-y)]^{-1}$$

and

$$B = 2abM_aM_by(1-y)\bar{v}_a\bar{v}_b/V_s$$

Table 4 Values of interaction parameters χ_{ab} determined at spinodal for systems I and IV, and at the optical theta conditions for system IV in toluene and for system I in various solvents and at different temperatures in styrene and in cyclohexane

	Spinodal or binodal —in THF at 25°C		Theta optical conditions in various solvents					
			At room temperature			Temperature dependence		
System	y	χ_{ab}	Solvent	y	χ_{ab}	t (°C)	χ_{ab}[b]	χ_{ab}[c]
I	0.117	0.025	Toluene	0.538	0.032	19	0.063	
	0.250	0.0210	Chloroform	0.216	0.028 ± 0.002	25	0.053	0.051
	0.500	0.015	CCl_4	0.296	0.036 ± 0.003	30		0.041
	0.750	0.021	Cyclohexane	0.149	0.050	40		0.039
	0.820	0.025	Styrene	0.687	0.053	50	0.039	
	–	0.021[a] ± 0.003				52		0.036
						62	0.036	
						35	0.047	
IV	0.235	0.0096	Toluene	0.556	0.0122			
	0.250	0.0095						
	0.460	0.0084						
	0.437	0.0074						
	0.750	0.0105						

[a] Values from phase separation experiments (binodal). [b] In styrene for IV. [c] In cyclohexane for IV.

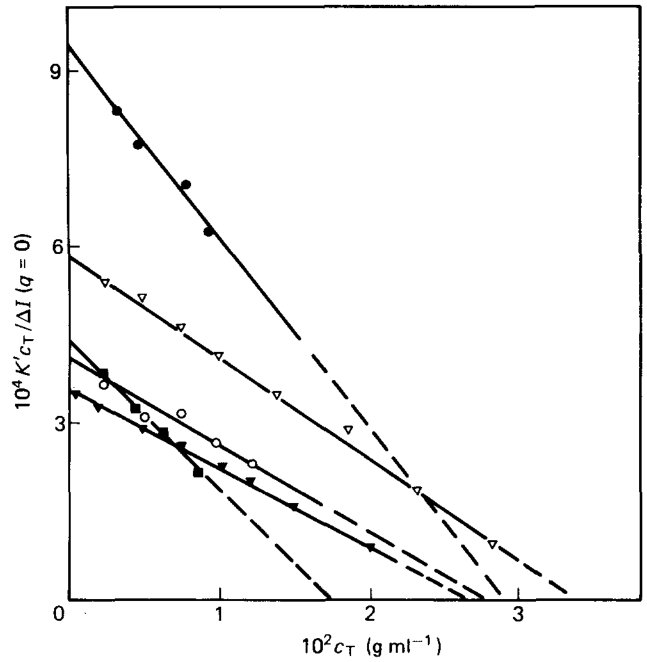

Figure 11 Plots of $K'c_T \times 10^4/\Delta I(q=0)$ *versus* c_T, concentration of polymers, for system I in optical theta conditions, $a\tilde{v}_a y M_a + b\tilde{v}_b(1-y)M_b = 0$, in different solvents: △, toluene; ○, carbon tetrachloride; ▽, chloroform; ■, styrene; ●, cyclohexane

This shows that the slope of $K'c_T/\Delta I(q=0)$ as a function of c_T (or apparent second virial coefficient) is proportional to χ_{ab} independently of the parameters χ_{as} and χ_{bs}. This allows the determination of χ_{ab} with a higher accuracy. Note that for the above so-called optical 'theta' conditions to be fulfilled, one has to have $ab<0$, i.e. to find a solvent in which a and b are of opposite sign; such solvents are easily found for the mixture PS–PDMS. Other solvents such as toluene, chloroform, CCl_4, cyclohexane or styrene have been used. *Table 4* gives the composition at which these solvents fulfil this condition together with the values of χ_{ab} obtained from equation (28). *Figure 11* shows $K'c_T/\Delta I(q=0)$ as a function of c_T for various optical 'theta' solvents of system I.

Furthermore, for two solvents (styrene and cyclohexane), the effect of the temperature on χ_{ab} was studied. A strong decrease of χ_{ab} was observed as the temperature increased, which indicates the existence of an upper critical solution temperature (*UCST*). This result, however, must be viewed with caution. It is known that cyclohexane[22] and styrene[23] are 'theta' solvents for PS and PDMS around 35°C, respectively. Therefore $A_{2,a}=0$ in the first solvent and $A_{2,b}=0$ in the second one, and one should introduce in these cases higher-order terms in the expansion of A_2 as a function of the concentration in order to have meaningful results. In this paper we have interpreted the data assuming $A_{2,i}$ to be constant but this approximation is obviously invalid when the first term of the expansion is zero or near to zero. For a correct explanation of the results, one has to take triple contacts into account using a more elaborate theoretical analysis.

Phase equilibrium (binodal). The other method which was used to determine χ_{ab} for system I was based on the equilibrium studies between two phases. If we have reached true thermodynamic equilibrium, one can write χ_{ij} as a function of c_i (phase 1) and c_i' (phase 2), $i=$ a or b, as[24]:

$$\chi_{ab}=\chi_{as}+\chi_{bs}+(\phi_a-\phi_a'+\phi_b'-\phi_b)^{-1}\left[\frac{1}{n_a}\ln\left(\frac{\phi_a}{\phi_a'}\right)+\frac{1}{n_b}\ln\left(\frac{\phi_b'}{\phi_b}\right)\right.$$
$$\left.-2\chi_{as}(\phi_a-\phi_a')-2\chi_{bs}(\phi_b'-\phi_b)\right] \quad (29)$$

where ϕ_i (or ϕ_i') are the volume fractions, i.e. $\phi_i=c_i\tilde{v}_i$, and n_i the number of elements in the chain, i.e. $n_i=M_i\tilde{v}_i/V_s$ (with $i=$ a or b).

Since the concentrations were determined at phase equilibrium or at the binodal (see experimental part) and χ_{as} and χ_{bs} are known from the second virial coefficients, it is easy to obtain χ_{ab}. The value for system I reported in *Table 4* is a mean value obtained from four experiments. One can see that χ_{ab} determined from the binodal ($\chi_{ab}=0.021$) and the spinodal (χ_{ab} ranging from 0.025 to 0.015) are in agreement. It has to be noted that the χ_{ab} parameter determined in the same range of molecular weights ($M_a \sim M_b \sim 2\times10^5$) for another system such as PS–PIB[3] or PMMA–PDMS[25] is comparable to the χ_{ab} value for the PS–PDMS mixture, whereas for the PS–PMMA system[13] the χ_{ab} parameter is lower ($\chi_{ab}=0.004$).

The thermodynamic results are summarized in *Figure 12*. On this figure the spinodals for systems I and IV and the binodal for system I are plotted. Some cloud points are also reported. What is surprising is that the difference between the spinodal and the binodal is not striking. The same behaviour has already been indicated for the system PS–PI (polyisoprene) in THF[26].

CONCLUSIONS

In this paper, we have presented the results of a systematic investigation by light scattering from ternary mixtures of PS–PDMS in THF and in other solvents, starting from low concentrations up to the precipitation threshold. Our aim was to see if the simple mean-field theory proposed by Benoît and Benmouna could explain the results. Remembering that such a mean field is not expected to apply to dilute solutions because of the strong concentration fluctuations in this region, the agreement with the theory is found to be much better than expected. Even if one makes the strong assumption that all thermodynamic quantities do not depend on concentration, we obtained reasonable, and in many

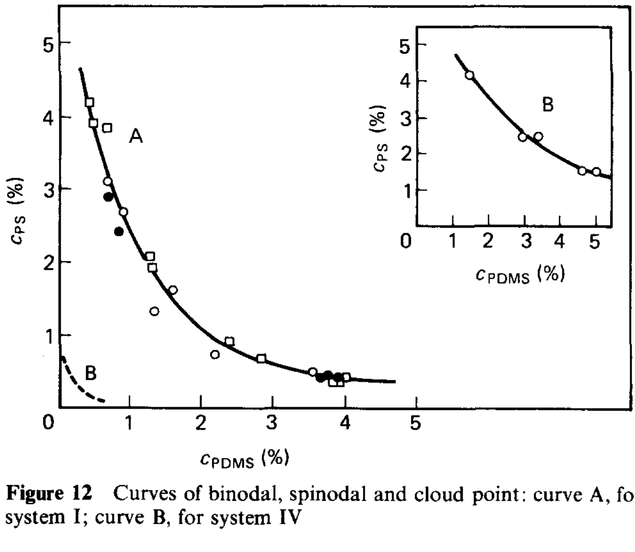

Figure 12 Curves of binodal, spinodal and cloud point: curve A, for system I; curve B, for system IV

cases, quantitative agreement. We were also able to explain the distortion of the experimental angular distribution of light. Furthermore, we obtained values for the interaction parameter χ_{ab} which are in reasonable agreement with those obtained by classical methods. Very precise experiments are needed if one wants to evaluate the variation of the thermodynamic parameters with concentrations and to see what could be gained using a more refined theory.

ACKNOWLEDGEMENTS

The authors express their gratitude to Professor H. Benoît and M. Benmouna for fruitful discussions and help in preparing the manuscript.

This work has been done within the framework of scientific collaboration between the Universities of Tlemcen and Strasbourg. The first author wants to thanks Professor G. Weill, Director of the Institute Charles Sadron, for giving her the possibility of working in Strasbourg.

REFERENCES

1 Stockmayer, W. *J. Chem. Phys.* 1950, **18**, 58

2 Kratochvil, P., Vorlicek, J., Strakova, D. and Tuzar, Z. *J. Polym. Sci., Polym. Phys. Edn.* 1975, **13**, 2321

3 Van den Esker, M. W. J. and Vrij, A. *J. Polym. Sci., Polym. Phys. Edn.* 1976, **14**, 1943; Van den Esker, M. W. J., Laven, J., Broeckman, A. and Vrij, A. *J. Polym. Sci., Polym. Phys. Edn.* 1976, **14**, 1953

4 Kratochvil, P. and Vorlicek, J. *J. Polym. Sci., Polym. Phys. Edn.* 1976, **14**, 1561

5 Kirkwood, J. G. and Goldberg, R. J. *J. Chem. Phys.* 1950, **18**, 54

6 Benoît, H. and Benmouna, M. *Polymer* 1984, **25**, 1059

7 Benoît, H. and Benmouna, M. *Macromolecules* 1984, **17**, 535

8 Ornstein, L. and Zernike, F. *Proc. Acad. Sci. Amsterdam* 1914, **17**, 793

9 de Gennes, P. G. 'Scaling Concepts in Polymer Physics', Cornell University Press, Ithaca, New York, 1967

10 Zimm, B. H. *J. Chem. Phys.* 1948, **16**, 1093

11 Ullman, R., Benoît, H. and King, J. S. *Macromolecules* 1986, **19**, 183

12 Benoît, H., Wu, W., Benmouna, M., Mozer, B., Bauer, B. and Lapp, A. *Macromolecules* 1985, **18**, 986

13 Fukuda, T., Nagata, M. and Inagaki, H. *Macromolecules* 1984, **17**, 548

14 Szwarc, M. 'Carbanions, Living Polymers and Electron Transfer Processes', Interscience, New York, 1968

15 Lapp, A., Beinert, G. and Picot, C. *Makaromol. Chem.* 1984, **185**, 453

16 Lapp, A., Herz, J. and Strazielle, C. *Makromol. Chem.* 1985, **186**, 1919

17 Stockmayer, W. H. and Fixman, M. *J. Polym. Sci.* (*C*) 1963, **1**, 137

18 Lapp, A., Picot, C. and Strazielle, C. *J. Physique Lett.* 1985, **46**, 1031

19 Yamakawa, H. 'Modern Theory of Polymer Solutions', Harper and Row, New York, 1971, p. 168

20 des Cloizeaux, J. *J. Physique* 1981, **42**, 635; Joanny, J. F., Leibler, L. and Ball, R. *J. Chem. Phys.* 1984, **81**, 4640

21 Ould Kaddor, L. and Strazielle, C., in preparation

22 Brandrup, J. and Immergut, E. H. (Eds.) 'Polymer Handbook', Wiley, New York, 1967, Ch. IV, p. 161

23 Lapp, A. and Strazielle, C. *Makromol. Chem. Rapid Commun.* 1985, **6**, 591

24 Allen, G., Gee, G. and Nicholson, J. P. *Polymer* 1960, **1**, 56

25 Anasagasti, M., Katime, I. and Strazielle, C., to be published

26 Maconnachie, A. Preprint, IUPAC Symp. on Macromolecules, Strasbourg, 1981