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Incompatibility of Polymer Solutions. II. Concentration and Angle Dependence of the Light Scattering in the System Polystyrene + Polyisobutylene + Toluene

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Synopsis

Light scattering experiments are described on the system polystyrene (PS) + polyisobutylene (PIB) + toluene at constant temperature. At a fixed concentration of the nearly "invisible" PIB the light scattering at various angles was measured as a function of varying PS concentration up to the region of incompatibility. For interpretation of the results use is made of an extension of the classical fluctuation theory for multicomponent systems to finite scattering angles. The experimental data can be described qualitatively with this theory. Addition of a second polymer has little influence on the size of the other polymer. The variation of the light scattering with the wavelength can be explained in terms of the (negative) adsorption of one polymer by the other.

INTRODUCTION

Solutions of two different polymers in a single solvent usually separate into two phases at relatively low percentages of polymer. Numerous studies have been devoted to this so-called incompatibility in order to understand the important theoretical and practical features of this phenomenon.

The structure of the interface between two demixed phases is one of the features we are interested in. Hence, we thought it significant to characterize such systems just beyond the limit of incompatibility in the homogeneous phase by means of light scattering. Light scattering studies of such ternary polymer solutions are very limited in number.[1-4] The most extensive ones have been reported by Hyde and Tanner[2] and Kuhn, Cantow, and Burchard.[3,4] In most cases one of the polymers has been chosen to have a specific refractive index increment near zero so that its light scattering is insignificant.

These studies, particularly that of Hyde and Tanner, were limited to (very) low concentrations of the "visible" polymer. Near the region of incompatibility, however, both polymer concentrations are to be considered as finite, i.e., there is already a considerable overlap of individual polymer molecules although the concentrations are still not more than a few percent. So we have performed light scattering experiments up to concentrations in this region where the systems start to show what is called "critical opalescence."

It will be clear that one has also to use a light scattering theory that is valid at finite concentrations. For this purpose the classical fluctuation theory of Einstein[5] and its extensions for multicomponent systems are available.

This, theory, however, has the drawback that it does not treat the angular dependence of the scattered light, and thus cannot predict the large dissymmetries near the critical solution point and spinodal. In previous papers we incorporated angular-dependent terms up to $\sin^2(\theta/2)$ into the classical fluctuation theory.[6–8] Although it cannot be claimed that this theory is exact it gives very reasonable results for two-component systems.[6,7]

In this paper we give the results of some light scattering experiments on the three-component system polystyrene and polyisobutylene in toluene and discuss these in the context of the theories mentioned above.

LIGHT SCATTERING EQUATIONS

In a previous paper[8] we treated the light scattering of a solution containing a solvent and two polymers. (For our ternary system we let component 1 be the solvent, toluene, and components 2 and 3 be the polymers, polystyrene (PS), and polyisobutylene (PIB), respectively.) Because in our experiments $\nu_3 \ll \nu_2$ we arrived at the following expression

$$\frac{2\pi^2\nu^2 kT(1+\cos^2\theta)}{\lambda_0^4 R_\theta^{\text{excess}}} = \frac{g_{33}(K)[g_{22}(K)g_{33}(K) - g_{23}^2]}{[\nu_2 g_{33}(K) - \nu_3 g_{23}]^2} \tag{1}$$

where R_θ^{excess} is the relative scattering (Rayleigh's ratio) for scattering angle θ of the three-component solution over that of the two-component solution containing components 1 and 3; ν and λ are the refractive index of the solution and the wavelength of light; k and T are Boltzmann's constant and the absolute temperature. Further, ν_i is the refractive index increment $\partial\nu/\partial\phi_i$ in terms of the volume fraction ϕ_i, with $i = 2, 3$; and $g_{ij} = \partial^2 g/\partial\phi_i\partial\phi_j$ with g the free enthalpy of mixing per unit volume. The dependence of g_{ij} on the wavenumber $K = (4\pi\nu/\lambda_0)\sin(\theta/2)$ arises from the fact that the concentration fluctuations in a polymer solution can be split up into a fluctuation in centers of mass of the polymer molecules and a fluctuation in their segments. It was shown that the following expressions could be obtained

$$g_{22}(K) = g_{22} + \frac{kTr_{g_2}K^2}{3\omega_2\phi_2} \tag{2a}$$

and

$$g_{33}(K) = g_{33} + \frac{kTr_{g_3}K^2}{3\omega_3\phi_3} \tag{2b}$$

where r_{g_i} is the radius of gyration of the polymer molecule i and ω_i is the partial molecular volume, which is assumed constant with composition and equal to the molecular volume.

Substituting eqs. (2) into eq. (1) and neglecting terms of higher order than K, we obtain for the right-hand side of eq. (1):

$$\frac{g_{33}(g_{22}g_{33} - g_{23}^2)}{(\nu_2 g_{33} - \nu_3 g_{23})^2} + \left\{\frac{(g_{33}^2 R_2 - g_{23}^2 R_3)(\nu_2 g_{33} - \nu_3 g_{23}) + 2g_{23}g_{33}(\nu_2 g_{23} - \nu_3 g_{22})R_3}{(\nu_2 g_{33} - \nu_3 g_{23})^3}\right\} K^2 \tag{3}$$

with

$$R_i = \langle r_{g_i}^2 \rangle / (3\omega_i \phi_i)$$

Since $\nu_3/\nu_2 \approx 0.02$ in our experiments, we can drop ν_3 in eq. (3) and write

$$\frac{2\pi^2 \nu^2 \nu_2^2 (1 + \cos^2 \theta)}{\lambda_0^4 R_\theta^{\text{excess}}} = (g_{22} - g_{23}^2/g_{33})/kT + \{R_2 + R_3(g_{23}/g_{33})^2\}K^2 \qquad (4)$$

For practical purposes we can write eqs. (3) and (4) as a series expansion in the concentration of the visible polymer (component 2), and the wavenumber K:

$$\frac{\mathcal{K} c_2 (1 + \cos^2 \theta)}{R_\theta^{\text{excess}}} = M_2^{*-1} + A_2^* c_2 + D^* K^2 + E^* K^2 c_2 \qquad (5)$$

Here, $c_2 = \phi_2 M_2/\omega_2 N_{Av}$; M_2^* is an apparent molecular weight of component 2; $\frac{1}{2}A_2^*$ is an apparent second virial coefficient; D^* contains the radius of gyration of component 2; and E^* is a term containing the radii of gyration of components 2 and 3. For $\nu_3 = 0$: $M_2^* \rightarrow M_2$; $A_2^* \rightarrow A_2$; $D^* \rightarrow D$; and $E^* \rightarrow E$. Further, $\mathcal{K}$ is the usual optical constant $2\pi^2 \nu^2 (d\nu/dc_2)^2/(\lambda_0^4 N_{Av})$; c_i is the concentration in g cm^{-3}; and $\omega_i = M_1 \bar{v}_1/N_{Av}$, with $\bar{v}_i$ the partial specific volume (cm^3 g^{-1}). Equation (5) differs from prior theories in the appearance of the term $E^* K^2 c_2$.

METHODS AND MATERIALS

For PS, three standard commercial samples with narrow distribution were used: Pressure Chemical Co. (batches 1c, 5a, and 14b with the reported weight average molecular weights of 2×10^5, 5.07×10^5, and 2.05×10^6, respectively) and for PIB we used three specially prepared PIB samples kindly supplied to us by Dr. A. Schuller of BASF (reported viscosity average molecular weight of 1.9×10^5, 5.2×10^5, and 2.7×10^6). Toluene was analytical-grade reagent from BDH, Liverpool.

Molecular Weights

Molecular weight of PS was determined by light scattering in toluene with the Sofica Photo-Gonio-Diffusomètre model 40.000 B. Molecular weight of PIB was determined in the theta-solvent *n*-ethylcaprylate (Merck) (θ = 22°C)[9] with the Fica 50 photometer.

The solutions were filtered through Millipore filters (100 nm or 450 nm) directly into light scattering cells and centrifuged in a Beckman Spinco L preparative centrifuge at 15,000 rpm for 1 hr.

The calibration of the light scattering instruments has been described elsewhere.[10]

Density Increment

Densities of PS and PIB solutions in toluene were measured with a digital density measuring device DMA-02/c from Anton Paar (Graz). Plots of density versus concentration were linear up to 2% polymer. From the ratio of the volumes of polymers and solvent we calculated the number of segments, $m_i = \omega_i/\omega_1$

TABLE I
Characterization of Polymers

	PS(I)	PS(II)	PS(III)	PIB(I)	PIB(II)	PIB(III)
$\langle M \rangle_w \times 10^{-6}$ (g mole^{-1})	0.194^{a}	0.526^{a}	2.40^{a}	0.156^{b}	0.670^{b}	2.44^{b}
$d(\bar{v})^{-1}/dc$	0.200^{a}	0.200^{a}	0.200^{a}	0.051^{b}	0.053^{b}	0.055^{b}
$\bar{v}^{-1}$ (g cm^{-3})	1.050	1.050	1.050	0.915	0.915	0.915
$\langle m \rangle_w \times 10^{-3}$	1.69^{a}	4.57^{a}	20.9^{a}	1.60^{b}	6.90^{b}	25.0^{b}
$d\nu/dc$ (λ_0 = 546 nm) (cm^3 g^{-1})		0.109^{a}			0.008^{a} 0.097^{b}	
$\langle r_g^2 \rangle_z^{1/2}$ (nm)	—	31.4^{a}	97.1^{a}	— $19.2^{b,c}$	35.3^{b} $32.4^{b,c}$	70.0^{b} $72.0^{b,c}$

[a] In toluene (ρ = 0.8657 g cm^{-3})

[b] In n-ethyl caprylate

[c] Calculated from diffusion coefficient. Concentrations of PIB are $C_{\mathrm{PIB(I)}} = 4.18 \times 10^{-3}$ g cm^{-3}, $C_{\mathrm{PIB(II)}} = 2.04 \times 10^{-3}$ g cm^{-3}, and $C_{\mathrm{PIB(III)}} = 1.49 \times 10^{-3}$ g cm^{-3}.

$= M_i\bar{v}_i/M_1\bar{v}_1$. Throughout all calculations we used constant densities for the components.

Refractive Index Increments

Refractive index increments of PS in toluene and PIB in n-ethylcaprylate were measured with a Rayleigh interferometer (Jena) at λ_0 = 546 nm, whereas the refractive index increment of PIB in toluene was measured with a Brice Phoenix differential refractometer by Dr. H. Breuer of BASF.

Radii of Gyration

The z-average radii of gyration in several solvents at zero polymer concentration were determined from Zimm plots in the usual manner. For PIB in n-ethylcaprylate we also determined the translational diffusion coefficients D_t by Rayleigh spectroscopy.[11] In this experiment a 100 mW Spectra Physics Model 165 Ar$^+$ ion laser was used to illuminate the samples and the autocorrelation functions of the intensity of the scattered light were calculated as function of angle with a Nova 1200 computer (Data General Corporation). To convert the obtained diffusion coefficients to the radii of the random coil we neglected the concentration dependence of the diffusion coefficient D_t at the concentrations used and made use of the relation[13,14] $D_t = kT/0.665f_0$ with the friction coefficient $f_0 = 6\pi\eta_0\langle r_{g3}^2\rangle_z^{1/2}$ and η_0 the viscosity of the solvent. Results are given in Table I.

Three-Component Systems

In Part I of this series[14] we reported binodals for three combinations of polymer pairs with comparable molecular weights as obtained from phase separation studies. We also combined binary stock solutions to obtain a homogeneous composition in the neighborhood of the phase-separation boundary.

From these solutions dilutions were made by adding as "solvent" a toluene

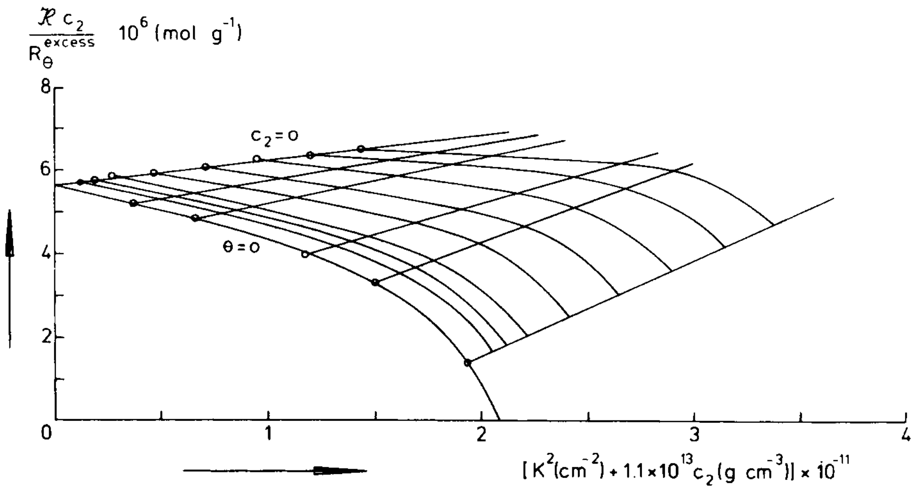

Fig. 1. Zimm plot for the system PS(I) + PIB(I) + toluene at λ_0 = 436 nm and constant volume fraction ϕ_{PIB} = 0.0132.

solution of PIB with the same concentration as the original stock solutions. For the case PS(II) + PIB(II) + toluene scattering of unpolarized incident light was measured at λ_0 = 546 and 436 nm in the Sofica photometer and for all other cases vertically polarized light was used and the scattering measured with the Fica 50 photometer with λ_0 equal to 578, 546, and 436 nm. In the experiments, normal precautions were made to minimize dust contamination. All experiments in toluene were carried out at 21.0°C.

RESULTS

The values of the properties of the individual polymers described in the last section are summarized in Table I. Here we discuss some of these values in comparison with literature data and with data obtained in the three-component systems.

For the three-component systems only experiments with a constant PIB concentration c_3 and a varying PS concentration c_2 are reported. Some typical examples of Zimm plots are given in Figures 1 and 2 for two sets of polymer pairs of comparable molecular weight. The general features of these plots are as follows.

(*1*) Lines of constant c_2 and varying angle θ (K^2) are straight to rather high values of K^2, even for the highest molecular weight pair, PS(III) + PIB(III). This is shown in all cases at constant c_3. We also investigated some cases where c_3 was varied at constant c_2. These Zimm plots showed very strong curvature as a function of K^2 in some cases (at constant c_2, c_3) and require a separate analysis (which will be given in a later paper).

(*2*) Lines of constant K^2 and varying c_2 are also straight, except in the case of the low molecular weight pair PS(I) + PIB(I). This is shown in more detail in Figure 3 for several values of c_3 at θ = 0. One observes a gradual change from convexity to concavity upon changing c_3.

(*3*) Consequences of the variation of the wavelength of the light used are shown in Figure 4 for the PS(III) + PIB(III) system where the lines c_2 = 0 and θ = 0 are

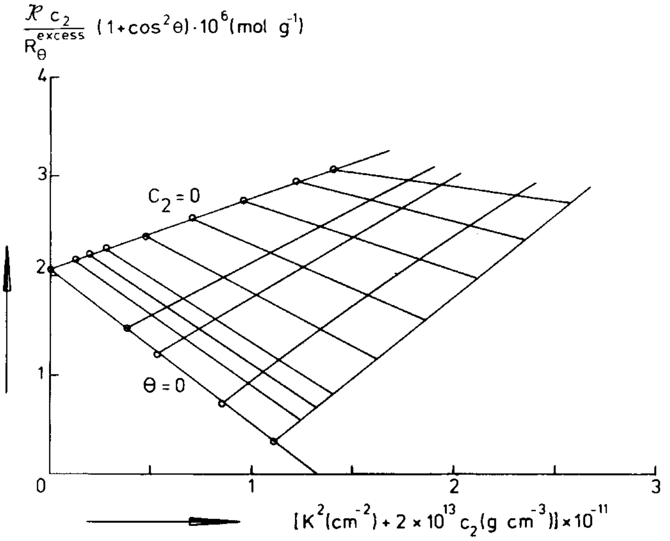

Fig. 2. Zimm plot for the system PS(II) + PS(II) + toluene at $\lambda_0 = 436$ nm and constant volume fraction $\phi_{PIB} = 0.0100$.

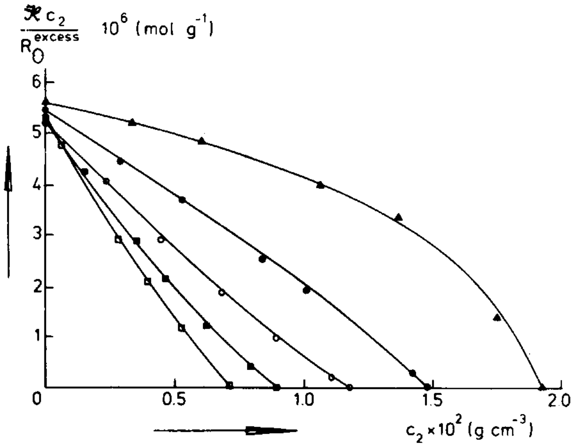

Fig. 3. Lines $\theta = 0$ from Zimm plots ($\lambda_0 = 436$) for the system PS(I) + PIB(I) + toluene at various volume fractions of PIB: (▲) $\phi_{PIB} = 0.0132$; (●) $\phi_{PIB} = 0.0191$; (○) $\phi_{PIB} = 0.0243$; (■) $\phi_{PIB} = 0.0302$; (□) $\phi_{PIB} = 0.0353$.

plotted for $\lambda_0 = 578$, 546, 436 nm. The intercepts on the vertical axis differ considerably depending on the wavelength of the light. In Table II these intercepts, expressed as the apparent molecular weight M_2^*, are given together with the corresponding intercepts on the horizontal axis. The latter intercepts constitute the spinodal composition at the fixed concentration of PIB as follows from eq. (1); and because they are independent of λ_0, as expected, only one value is given.

(*4*) The slopes of the lines $\theta = 0$ are always negative, indicating that in the solvent the concentration of PIB is sufficiently high to make the "solvent" poor and that the system tends to phase separation. In Table II the slopes of the θ

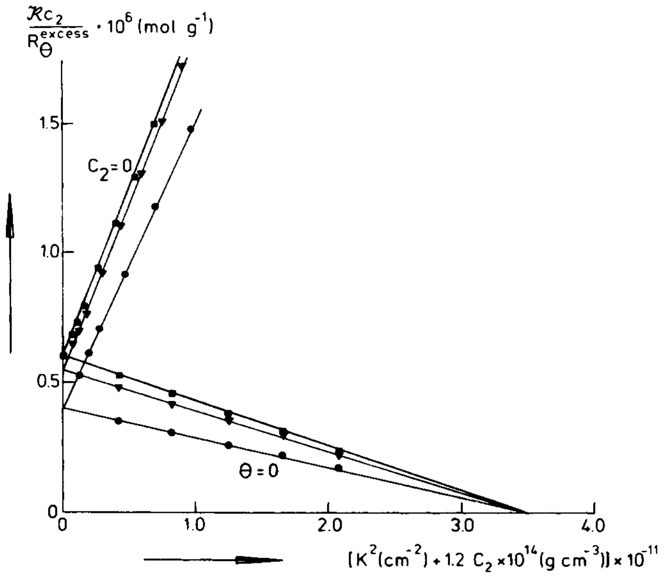

Fig. 4. Lines $\theta = 0$ and $c_2 = 0$ of Zimm plots for the system PS(III) + PIB(III) + toluene at three different wavelengths and constant volume fraction $\phi_{PIB} = 0.0041$. (●) $\lambda_0 = 436$ nm; (▼) $\lambda_0 = 546$ nm; (■) $\lambda_0 = 578$ nm.

= 0 lines are collected, expressed as the second virial coefficients $A_2 = A_2{}^*$ (for $\lambda_0 = 436$ nm where $\mu_3 \approx 0$). Also in Table II, the slopes of the $c_2 = 0$ lines are expressed as the root-mean-square radius of gyration, $\langle r_{g2}{}^2\rangle_z{}^{1/2}$, of PS at $c_2 \rightarrow 0$ in the presence of a finite concentration of PIB.

DISCUSSION

Intercepts on the Vertical Axis

The values of $M_2{}^*$, the reciprocal of the intercept of the Zimm plot, as given in Table II, depend on the wavelength of the light, but are independent of the concentration of PIB. From eqs. (3) and (5) it follows that

$$M_2{}^* = M_2(1 - \nu_3 g_{23}/\nu_2 g_{33})^2 \qquad (6)$$

where M_2 is the true molecular weight of component 2. This variation in $M_2{}^*$ with ν_3 (which depends on λ_0) is a consequence of selective adsorption and is equivalent to the preferential adsorption of one solvent on the polymer in a solution of a polymer in a solvent mixture.[15] This can easily be seen when the factor $\nu_3 g_{23}/\nu_2 g_{33}$ is rewritten in the following way:

$$\frac{\nu_3 g_{23}}{\nu_2 g_{33}} = -\frac{(\partial\nu/\partial c_3)_{\phi_2}}{(\partial\nu/\partial c_2)_{\phi_3}}\left(\frac{\partial c_3}{\partial c_2}\right)_{g_3} \qquad (7)$$

This equation allows us to calculate $\partial c_3/\partial c_2$ if $d\nu/dc_3$ and $d\nu/dc_2$ are known. However, because PIB is nearly "invisible" in toluene it is difficult to measure $d\nu/dc_3$ with sufficient accuracy. So we can only make an estimate of $\partial c_3/\partial c_2$, which was done as follows. The measured $d\nu/dc_3$ of PIB in toluene at 546 nm was 0.008 cm^{3}g^{-1}. The dispersion of $d\nu/dc_3$ with λ was calculated from the molar

TABLE II
Spinodal Compositions, Apparent Molecular Weights at Different Wavelengths, Radii of Gyration, and Second Virial Coefficients

System	$\phi_3 \times 10^2$	$\phi_2 \times 10^2$	$M_2^* \times 10^{-5}$ (436 nm) (g mole^{-1})	$M_2^* \times 10^{-5}$ (546 nm) (g mole^{-1})	$M_2^* \times 10^{-5}$ (578 nm) (g mole^{-1})	$\langle r_{g_2}^2 \rangle_z^{1/2}$ (nm)	$-A_2^* \times 10^4$ (mole cm^3 g^{-2})	$E \times 10^9$ (cm^5 g^{-1})
PS(I)	0	—	1.94	1.94	1.94	—	−9.80	—
+	1.32	1.88	(1.77)	(1.41)	(1.36)	17.8	1.21	0.147
PIB(I)	1.91	1.41	1.83	1.37	1.28	19.3	3.54	0.154
	2.43	1.12	1.94	1.39	1.32	19.1	5.10	0.150
	3.02	0.85	1.91	1.40	1.31	19.1	7.26	0.129
	3.53	0.68	1.89	1.36	1.25	18.5	8.36	0.126
PS(II)	0	—	5.26	5.26	—	31.4	−7.52	—
+	1.00	0.62	4.81	3.76	—	31.4	3.14	0.83
PIB(II)	1.30	0.48	5.09	3.83	—	30.8	4.08	0.88
	2.00	0.36	5.20	3.87	—	31.0	4.90	0.81
PS(III)	0	—	24.0	24.0	24.0	97.1	−4.86	—
+	0.30	0.46	22.7	17.5	16.0	87.8	1.00	12.6
PIB(III)	0.41	0.27	25.0	18.4	16.7	90.7	1.38	12.4
	0.51	0.22	24.4	17.2	17.2	94.2	1.88	9.9
	0.60	0.16	23.8	(15.0)	(14.9)	90.3	2.46	10.0
	0.68	0.13	24.4	17.9	16.1	88.8	3.20	12.0

refractions of the constituent groups of PIB as devised earlier.[16] In this way we found: $d\nu/dc_3 = 0.002 \pm 0.002$ at $\lambda_0 = 436$ nm and $d\nu/dc_3 = 0.009 \pm 0.002$ for $\lambda_0 = 578$ nm.

From the ratios M_2^* (546)/M_2^* (436) and M_2^* (578)/M_2^* (436) $\partial c_3/\partial c_2$ was calculated. The results are plotted in Figure 5. It can be seen that $\partial c_3/\partial c_2$ is ca. 2.2 to 2.8; i.e., that each gram of added PS expels 2.2–2.8 g of PIB from its environment. The dependence on ϕ_3 is rather small.

From the experiments of Hyde and Tanner[2] for PS + PIB + cyclohexane at 30°C we can calculate a linear relation between the negative adsorption and c_3 that gives ca. 0.15 molecules per molecule at $c_3 = 5 \times 10^{-4}$ g cm^{-3}. However, their highest PIB concentration is much smaller than the lowest one we use. It seems reasonable to suppose that on increasing the concentration of PIB the

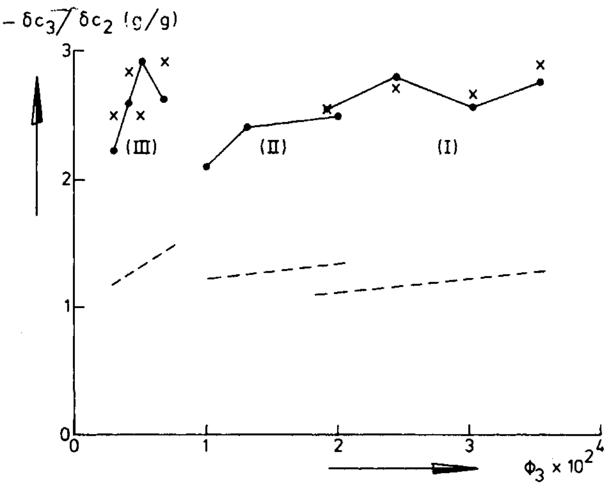

Fig. 5. Values of $\partial c_3/\partial c_2$ from the ratios M^* (546)/M^* (436) (O) and M^* (578)/M^* (436) (×) for PS(III) + PIB(III), PS(II) + PIB(II), PS(I) + PIB(I), from left to right. Dotted lines are calculated from eq. (10) using Ψ_{ij}^0 from ref. (14).

negative adsorption eventually levels off. (This also follows from eq. (10) below.)

It is of interest to determine whether we can predict the factor $\partial c_3/\partial c_2$ from theory. To this end we use the Flory–Huggins model for polymer solutions and write for the free enthalpy (free energy) of mixing per unit volume (cf. Part I of this series[14])

$$\frac{g}{kT} = \sum_{i=1}^{3} n_i \ln \phi_i + \Psi/\omega_1 \tag{8}$$

where n_i is the number of molecules of component i per unit volume and Ψ is a free enthalpy excess function depending on ϕ_2 and ϕ_3 at constant temperature.

$$\Psi = \Psi_2{}^0\phi_2 + \Psi_3{}^0\phi_3 + \tfrac{1}{2}\Psi_{22}{}^0\phi_2{}^2 + \tfrac{1}{2}\Psi_{33}{}^0\phi_3{}^2 + \Psi_{23}{}^0\phi_2\phi_3 \tag{9}$$

with $\Psi_{ij}{}^0 = \partial^2\Psi/\partial\phi_i\partial\phi_j$ and $\Psi_{ij}{}^0$ independent of $\phi_{i,j}$ (in a more familiar form, $\Psi_{22}{}^0 = -2\chi_{12}$; $\Psi_{33}{}^0 = -2\chi_{13}$; $\Psi_{23}{}^0 = \chi_{23} - \chi_{12} - \chi_{13}$).

From eqs. (8) and (9) it follows that

$$\Gamma = -\left(\frac{\partial\phi_3}{\partial\phi_2}\right)_{g_3} = \frac{g_{23}}{g_{33}} = \frac{\dfrac{1}{\phi_1} + \Psi_{23}{}^0}{\dfrac{1}{\phi_1} + \dfrac{1}{m_3\phi_3} + \Psi_{33}{}^0} \tag{10}$$

Using the values for χ_{ij} reported in part I of this series[14] (at the respective M and ϕ_3) one finds the broken lines in Figure 5. The insensitivity to the PIB concentration is correct but our experimental values are appreciably larger than the calculated ones.

Intercepts on the Horizontal Axis

For $\theta = 0$ and $\mathcal{K}c_2/R_\theta = 0$, it follows from eq. (1) that $g_{22}g_{33} - g_{23}{}^0 = 0$, which is the equation for the spinodal.[17]

In the preceding paper[14] we gave experimentally determined spinodals together with the thermodynamic quantities obtained by solving the spinodal equation. The spinodal compositions are summarized in columns 2 and 3 of Table II.

Limiting Angular Dependence of Scattering for $c_2 = 0$

In the following we discuss only the results at $\lambda_0 = 436$ nm, where ν_3 is nearly zero. The slope of the line $c_2 = 0$ gives the root-mean-square radius of gyration of the PS molecule in the absence of PIB and at finite concentration of PIB. It is evident that there is scarcely any change of the radius in the presence of PIB. Only for the highest molecular weight pair, PS(III) + PIB(III), does r_{g2} appear lower (about 7%) in toluene containing PIB than in pure toluene. This results is in good accordance with the results of Hyde and Tanner[2] who did not find a change in the radius of gyration. Kuhn and Cantow[3] find, in their system polystyrene + polymethylmethacrylate + benzene, a decrease in the radius of gyration of up to 30% but they cover a much larger concentration range. In the concentration region of our experiments they find a decrease of nearly 5%.

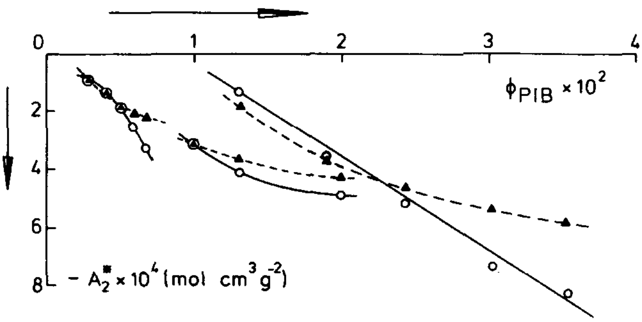

Fig. 6. Second virial coefficients of PS as a function of the volume fraction of PIB [(○) experimental; (▲) calculated from eq. (11)].

We note that our values of the radius of gyration in pure toluene are somewhat higher (about 20%) than values found in the literature.[18] This might be ascribed to the polydispersity of the PS, which increases the z-average value of the radius, as has been observed for PS(III).[19]

It should be noted that although for the pair PS(I) + PIB(I), r_g of PS is too small to be measured in the good solvent, toluene, it can be measured in the very poor "solvent" PIB + toluene. This follows immediately from eq. (5). In a very good solvent A_2^* is large and positive so that the sum $M_2^{*-1} + A_2^* c_2$ is large compared to the term D^*K^2 that contains r_{g2}^2. In a very poor solvent the sum $M_2^{*-1} + A_2^* c_2$ can be small enough that D^*K^2 becomes measurable.

Limiting Concentration Dependence of Scattering for $\theta = 0$

From the initial slope of the line $\theta = 0$ on a Zimm plot the apparent second virial coefficient, $\frac{1}{2}A_2^*$, can be obtained [see eq. (5)]. As can be seen in Table II and Figure 6, A_2^* becomes more negative with increasing PIB concentration, indicating a worsening of the "solvent" with increasing PIB content. The origin of a negative A_2 is here due to the pushing together of neighboring molecules of polymer 2 by the surrounding molecules of polymer 3.

From eqs. (4), (5), (8), and (9), it follows that A_2 can be written as

$$A_2 = \frac{\dfrac{1}{\phi_1} - 2\chi_{12} - (g_{23}^2/g_{33})_{\phi_2=0}}{\bar{v}_1 M_1/\bar{v}_2^2} \tag{11}$$

We can now calculate A_2 and compare the results with experiment. For the χ_{ij} we used the values at the critical point (see Ref. 14). The results are given in Figure 6.

The A_2 found experimentally always has a greater dependence on c_3 than theory predicts (at constant χ_{23}). This can be expected, because in the Flory–Huggins model the interactions are calculated by smearing out the segments of component 2 over the whole volume, thus predicting a less dramatic effect on adding component 3.

If χ_{23} is calculated from the spinodal equation at that particular c_3, experimental and theoretical values of A_2 should only be the same if the $\theta = 0$ line is straight over the whole concentration range of c_2. A discrepancy could arise from

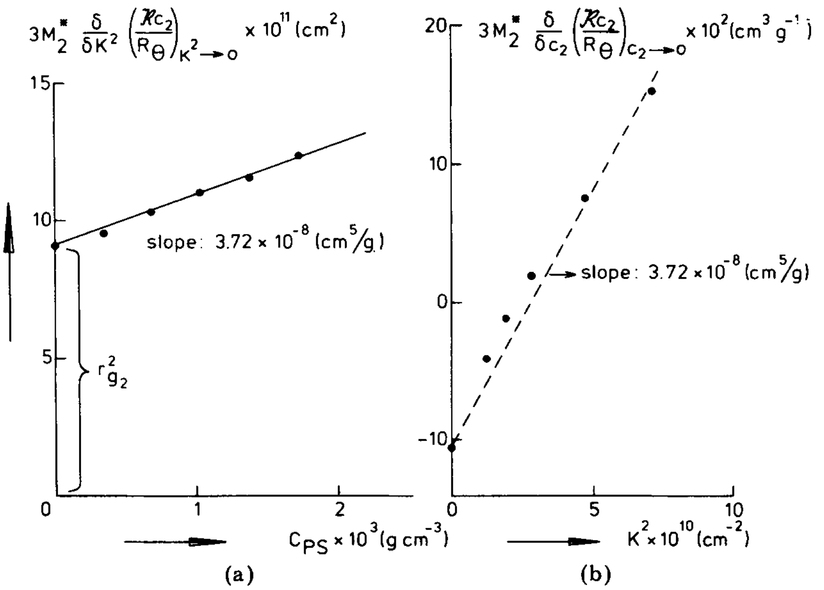

Fig. 7. (a) Variation of the initial slope of lines of varying wavenumber K^2 with c_2. (b) The slope of this line is replotted on to the graph at the right, where the variation of the initial slope of lines of varying c_2 with K^2 is plotted. (Data from Figure 2 of part I of this series[14]).

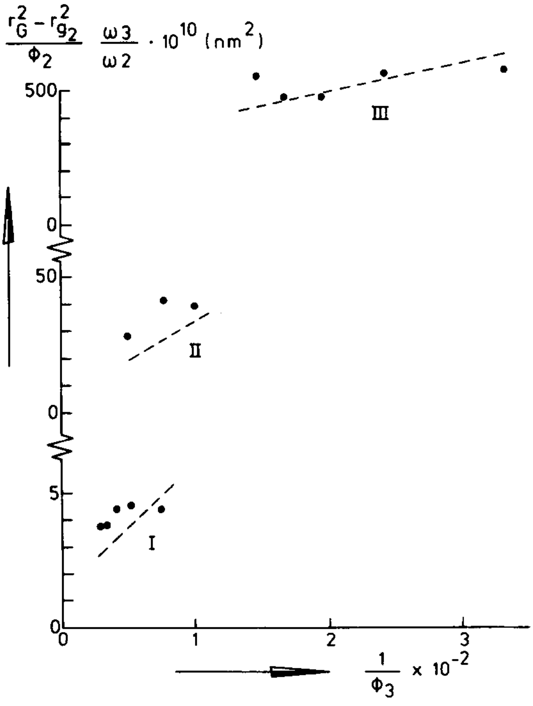

Fig. 8. Values of $(r_G{}^2 - r_{g2}{}^2/\phi_2)(\omega_3/\omega_2)$ versus $1/\phi_3$ for three molecular weight pairs [cf. eq. (13)]. Dotted lines are obtained by calculating $(r_{g3}{}^2\Gamma^2)/\phi_3$ assuming r_{g3} equal to r_{g3} in pure toluene and Γ calculated with eq. (10).

inadequacy of the linear dependence on c_2 in eq. (5). This is the case only for the low molecular weight pair PS(I) + PIB(I), as is obvious from Figure 4. However, a calculation of Kc/R_0 for this case does not predict the experimental dependence c_2 at constant c_3. The reason is not clear.

The Change in Slopes of θ and c_2 Dependences

The Zimm plots obtained with these ternary solutions show peculiar behavior. The slopes of the constant-c_2 lines increase with increasing concentration of PS; and the slopes of the constant-θ lines increase with increasing angle. It can be shown that the increase of both slopes must be coupled if the Zimm plots are to be internally consistent.

In Figure 7a and b an example of this consistency is given. In Figure 7a the slopes of the lines at a constant PS concentration are plotted against that concentration and the slope of this line is transformed to Figure 7b where the slopes of the lines at a constant angle are plotted against that angle. It appears that the transformed slope fits very well with the latter results. This transformed slope is equal to E^* in eq. (5). At $\lambda_0 = 436$: $E^* \approx E$ because $\nu_3 \approx 0$.

The equation of the line in Figure 7a can be written

$$r_G{}^2 = r_{g2}{}^2 + r_{g3}{}^2\Gamma^2 \frac{\omega_2\phi_2}{\omega_3\phi_3} \tag{12}$$

In Figure 8 we have plotted values of $(r_G{}^2 - r_{g2}{}^2)\omega_3/\omega_2\phi_2 = 3EM_2(\bar{v}_3/\bar{v}_2{}^2)$ versus $1/\phi_3$ as obtained from E of the Zimm plots (Table II). According to eq. (12) these should be equal to $(r_{g3}{}^2\Gamma^2)/\phi_3$ if we neglect the dependence of $r_{g2}{}^2$ on ϕ_2. Taking for r_{g3} the values in pure toluene (the values for PIB were assessed from measurements in the theta-solvent n-ethyl caprylate using the Flory expansion factor[20]) and for Γ those calculated with eq. (10), one finds the dotted lines in Figure 8. This looks rather satisfactory. However, it will be apparent that taking the experimental values for Γ, as determined from $M_2{}^*/M_2$, will give results that are much too large.

Of course we have neglected the dependence of r_{g2} and r_{g3} on the increasing concentration of PIB. It would alleviate the discrepancy if either or both decreased. This cannot be expected to be a large effect, however, because the decrease of r_{g2} (at $\phi_2 = 0$) with increasing ϕ_3 is rather small in the concentration ranges we use. Better agreement can only be achieved by assuming a much larger, seemingly unreasonable, value for ν_3 at $\lambda_0 = 546$ and 578 nm.

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