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Mesophase Formation and Polymer Compatibility. The Poly(*p*-benzamide)–Polyacrylonitrile–Diluent System

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ABSTRACT: We report a study of phase equilibria for a ternary system involving a rigid polymer, unfractionated poly(*p*-benzamide) (PBA), a random coiled polymer, unfractionated polyacrylonitrile (PAN), and a diluent composed of *N*,*N*-dimethylacetamide + 3% LiCl. Three different PAN samples were used, covering a range of molecular weight between 60000 and 160000. Above a critical concentration of the two polymers, one observes a biphasic region composed of a nematic and an isotropic phase. Separation of the two phases by centrifugation, analysis of phase volume and composition, separation of PBA from PAN, and determination of the partition according to molecular weight were performed. The nematic phase contains the high molecular weight fraction of PBA, and the isotropic phase contains PAN + the low molecular weight fraction of the rigid polymer. Increasing the molecular weight of PAN causes an increase of the PAN/PBA ratio in the isotropic phase. The results are in satisfactory agreement with the theory of ternary systems composed of a rigid and a random coiled polymer. Minor deviations from theory involve a greater rejection of PBA by the flexible polymer and a lower amount of diluent in the isotropic phase than predicted. The role of polymer compatibility in the isotropic state is discussed.

In a previous paper[1] we reported the phase behavior of the system poly(*p*-benzamide) (PBA)–polyterephthalamide of *p*-aminobenzhydrazide (X-500)– *N*,*N*-dimethylacetamide (DMAc) + 3% LiCl. The results showed complete exclusion of X-500 from the mesophase that was formed above a critical concentration of the two polymers. X-500 was found only in the conjugate isotropic phase, which contained also the low molecular weight components of PBA. The segregation of X-500 in the isotropic phase was in qualitative agreement with Flory's theory of phase equilibria involving monodisperse rodlike and random coiled polymers.[2] The fractionation of PBA was also expected from the theory of mixtures of rodlike molecules[3,4] and from previous results obtained with binary systems.[5]

Some aspects of the behavior of the ternary systems remained, nevertheless, unclarified. The theoretical basis for incompatibility[2] rests on entropy considerations based on the interference of the random coil with the mutual orientation of the rodlike molecules in the mesophase. Compatibility between rodlike molecules is assisted by the lack of such an interference. We were concerned by the possible role of the degree of flexibility of the nonrodlike component and of the polymer "compatibility", as usually defined in the case of isotropic mixtures of two random coiled polymers.[6] In the latter case, compatibility is prevalently based on enthalpy parameters that reflect favorable interaction between molecules. A contribution from such an effect is not included in the above theories.[2-4] Therefore, we considered of interest the comparison of phase diagrams involving polymers with large differences in their chemical constitution. Furthermore, theory[2-4] only describes the behavior of two extremes: rigid rods and random coils. Are polymers of intermediate rigidity (e.g., wormlike chains) expected to enter the mesophase or the isotropic solution? The study of these problems is relevant not only to the thermodynamics of liquid crystalline solutions but also to the processing of two-polymer systems.

In the present paper we describe the behavior of the PBA–polyacrylonitrile (PAN)–DMAc + 3% LiCl systems. With respect to the PBA–X-500–DMAc + 3% LiCl system previously reported, the present system exhibits a much greater difference between the chemical constitution of the rigid and the flexible polymers. Moreover, while X-500 exhibits a partial degree of rigidity,[7-9] PAN conforms with the random coil model. We also study the role of the

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Table I
Characteristics of Samples Investigated

sample	$[\eta]$, dL/g	$\bar{M}_v$	C_p, % stock soln
PBA	1.65[a]	12 000	8.91/8.52
PAN-A	1.32[b]	59 500	20.6
PAN-B	1.99[b]	102 000	20.6
PAN-C	2.80[b]	160 000	20.5

[a] 96% H_2SO_4, 25 °C; $[\eta] = 1.9 \times 10^{-7}\bar{M}_w^{1.7}$. [b] DMAc, 20 °C; $[\eta] = 30.7 \times 10^{-5}\bar{M}_w^{0.761}$

molecular weight of the flexible polymer and perform a more detailed comparison with theory[2] than previously done.[1]

Experimental Section

Materials and Stock Solutions. The PBA sample is similar to that used in the previous investigation[1] and was synthesized following the method of Yamazaki et al.[10] Its intrinsic viscosity in 96% H_2SO_4 at 25 °C was 1.65 dL/g, corresponding to a molecular weight of ~12 000 in terms of the $[\eta]$–molecular weight relationship given by Schaefgen et al.[11] Three PAN samples covering a range of molecular weight from 160 000 to 59 000 were used. The molecular weight was determined from the intrinsic viscosity in DMAc at 20 °C by the relationship of Fujisaki et al.[12] Sample characteristics are collected in Table I. Intrinsic viscosities were determined as previously described.[1] PAN-B was supplied by BASF. It was purified by washing with boiling water for 1 h, rinsing with methanol and acetone, and drying at 50 °C under vacuum. PAN-A and PAN-C were synthesized by us following the method described by Price et al.[13] In the case of PAN-A, cupric sulfate was used as a chain-terminating agent.[14] The solvent was analytical grade DMAc containing 3 g of LiCl/100 mL of DMAc + LiCl solution.

The samples were separately dissolved in the solvent by slow stirring at room temperature. Concentrations of filtered solutions were determined by precipitating the polymer with water and eliminating LiCl by washing. Polymer concentration, C_p, is given as grams of polymer per 100 g of solution. The composition of binary stock solutions of PBA and PAN thus prepared is included in Table I. Concentrations are alternatively given as polymer volume fraction. These were calculated from the corresponding C_p by using the partial specific volumes of PBA ($\bar{v}_{PBA}$) and PAN ($\bar{v}_{PAN}$) and the specific volume of the diluent (V_1) and assuming additivity. These quantities were determined pycnometrically at 25 °C. As previously reported,[1] $\bar{v}_{PBA} = 0.7542$ mL/g and $V_1 = 1.0356$ mL/g. $\bar{v}_{PAN}$ was found equal to 0.8768 mL/g. The solubility limit of PAN in DMAc + 3% LiCl at 20 °C was determined by gradually increasing C_p above 20%.

Phase Diagrams. We followed the technique previously described.[1] The ternary mixtures were prepared by mixing weighed amounts of pairs of binary stock solutions. From the weight of PBA, PAN, and diluent present in the mixtures, C_p of the overall system is given as $[g_{PBA}/(g_{PBA} + g_{PAN} + g_{Dil})] \times 100$ for PBA and as $[g_{PAN}/(g_{PBA} + g_{PAN} + g_{Dil})] \times 100$ for PAN. Mixtures were stirred by slow rotation at room temperature (~20 °C) for about 15–20 days to reach apparent equilibrium. Separation of the coexisting phases was achieved by centrifugation at 3000 rpm for 3–4 h. The volume fraction of the isotropic phase ϕ (volume iso/total volume) was obtained from the phase volume determined by calibration of the centrifuge tube. The composition of the individual isotropic and anisotropic phases in the biphasic region was determined by using weighed aliquots of each phase. The aliquot was diluted with diluent and the polymer precipitated with water. The precipitate was washed with water at 90 °C for 1 h in order to eliminate LiCl. The dried and weighed polymer was extracted with dimethylformamide at 80 °C. The latter is a good solvent for PAN but does not dissolve PBA (a test performed with a known mixture of the two polymers gave quantitative separation). From the results of the extraction, the composition in grams of *each* polymer per 100 g of ternary solution of *each* phase was determined. The partition of molecular lengths of PBA in the two phases was determined on the isolated PBA by measuring its intrinsic viscosity. LiCl disproportion was not investigated in the present work. However, in previous investigations it was demonstrated that LiCl concentration was essentially the same in the two phases[1,15] (one-component diluent approximation).

Table II
Composition of Coexisting Phases for PAN Sample B

soln	$C_{p,PBA}$, %	v_2	$C_{p,PAN}$, %	v_3	(PBA + PAN), %	PAN/(PAN + PAB)	ϕ
			Overall (Biphasic)				
1	5.080	0.0375	1.243	0.0107	6.323	0.20	0.70
2	8.158	0.0609	1.738	0.0151	9.896	0.18	0.35
3	3.873	0.0286	3.153	0.0271	7.026	0.45	0.75
4	4.329	0.0321	3.813	0.0329	8.142	0.47	0.69
5	6.298	0.0471	5.462	0.0475	11.760	0.46	0.61
			Isotropic				
1	4.567	0.0337	1.385	0.0120	5.952	0.23	1
2	3.762	0.0279	4.703	0.0405	8.465	0.55	1
3	2.804	0.0207	3.726	0.0320	6.530	0.57	1
4	2.344	0.0173	4.944	0.0425	7.288	0.68	1
5	1.772	0.0131	8.671	0.0748	10.443	0.83	1
			Anisotropic				
1	7.120	0.0529	0	0	7.120	0	0
2	10.638	0.0800	0	0	10.638	0	0
3	8.346	0.0620	0	0	8.346	0	0
4	9.514	0.0711	0	0	9.514	0	0
5	13.333	0.1007	0	0	13.333	0	0

Optical anisotropy of the solutions was determined with a Reichert-Zetopan polarizing microscope.

Results

Optical determinations on binary PBA–DMAc/LiCl solutions yielded $C_p' = 5.6\%$ as the critical concentration at which an anisotropic phase appears. On the basis of previous results,[15] the conjugate nematic solution has $C_p'' \sim 7.5\%$, and the solubility limit of PBA occurs at $C_p \simeq 12\%$. C_p' is somewhat larger for the present sample than for the PBA previously used,[1] which had a slightly higher molecular weight.[15] The binary PAN–DMAc/LiCl solutions exhibited a solubility limit at $C_p \sim 21\%$.

In no case was a single anisotropic phase observed with the ternary systems. Eventually, at C_p greater than ~13%, crystallization occurred (cf. seq.). As observed with the PBA–X-500 system,[1] the two phases were homogeneous and stable, ϕ did not change after apparent equilibrium was reached, and separation by centrifugation was easily achieved. The compositions of the ternary systems in the biphasic region with PAN-B (8.91% stock) are collected in Table II. For a given mixture, labeled in column 1, the table indicates the overall composition and the corresponding compositions of pure isotropic and anisotropic phases separated by centrifugation (overall solution no. 1 corresponds to isotropic and anisotropic solutions no. 1, and so on). The measured volume fraction of the isotropic phase is indicated in the last column. ϕ could also be calculated from the balance of the various compositions, with an agreement within the experimental error. Columns 2 and 4 give the composition of ternary systems as grams of each polymer per 100 g of biphasic, isotropic, and anisotropic solution. Columns 3 and 5 indicate the corresponding compositions given as polymer volume fraction; the indexes 1, 2, and 3 refer to diluent, PBA, and PAN, respectively. The remaining columns indicate the total solid and the weight fraction of PAN in each mixture. Note that all data indicate complete absence of PAN from the anisotropic phase.

The data in Table II were used to construct the phase diagrams of Figures 1 and 2 based on compositions expressed, respectively, as C_p and as volume fraction. The sides of the diagrams[1] represent binary mixtures PBA–diluent ($v_2 = 1 - v_1$), PAN–diluent ($v_3 = 1 - v_1$), and PBA–PAN ($v_3^d = 1 - v_2^d$) (the superscript d indicates that

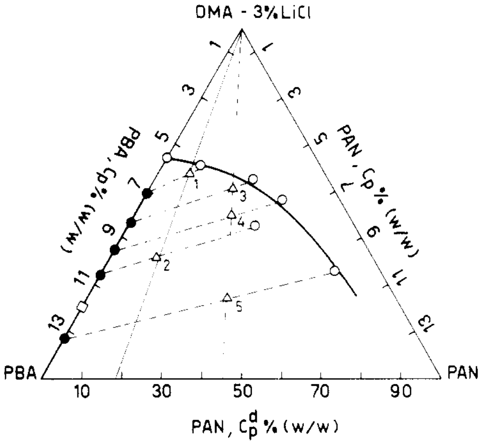

Figure 1. Ternary phase diagram for the system PBA–PAN (sample B)–DMAc + 3% LiCl at 20 °C: (○) composition of conjugated isotropic phase; (●) composition of nematic phase; (□) solubility limit for PBA in binary mixture;[15] (△) overall composition of biphasic mixture (cf. Table II).

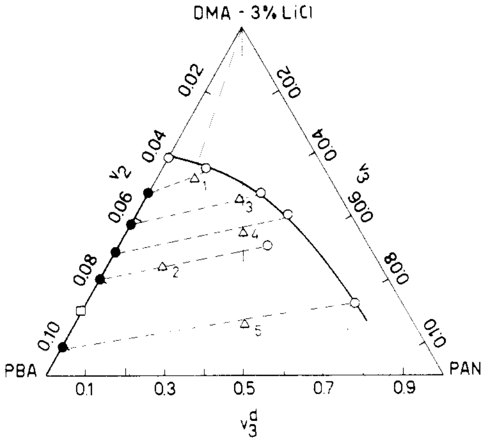

Figure 2. Same data in Figure 1 with compositions given as volume fraction.

Table III
PBA Fractionation Data[a]

				isotropic soln		anisotropic soln	
soln	C_p overall	PAN/(PAN + PBA)	ϕ	$[\eta]$, dL/g	$\bar{M}_v$	$[\eta]$, dL/g	$\bar{M}_v$
1	6.323	0.20	0.70			2.07	13800
2	9.896	0.18	0.35	1.32	10600	1.83	12800
3	7.026	0.45	0.75	1.60	11000	2.02	13600
4	8.142	0.46	0.69	1.13	9700	1.86	12950
5	11.760	0.47	0.61			2.00	13500

[a] $[\eta]$ in 96% H_2SO_4 at 25 °C; original PBA: $[\eta]$ = 1.65 dL/g, $\bar{M}_v$ = 12000.

Table IV
Effect of PAN Molecular Weight on Composition of Coexisting Phases

$\bar{M}_v$	$C_{p,PBA}$, %	v_2	$C_{p,PAN}$, %	v_3	(PBA + PAN), %	PAN/(PAN + PBA)	ϕ
			Overall (Biphasic)				
59500	4.371	0.0324	0.757	0.0328	8.128	0.47	0.73
102000	4.329	0.0321	3.813	0.0329	8.142	0.47	0.69
160000	4.312	0.0320	3.805	0.0328	8.117	0.47	0.69
			Isotropic				
59500	2.682	0.0198	4.809	0.0413	7.491	0.64	1
102000	2.344	0.0173	4.944	0.0425	7.288	0.68	1
160000	2.099	0.0155	5.163	0.0443	7.262	0.71	1
			Anisotropic				
59500	10.081	0.0755	0	0	10.081	0	0
102000	9.514	0.0711	0	0	9.514	0	0
160000	9.247	0.0691	0	0	9.247	0	0

no diluent is present). Dotted lines are the tie lines linking the compositions of conjugate phases that fall in the binodal curves. The strong inclination of the tie lines with respect to the vertex-to-base line reflects the disproportion of solutions having the overall composition $v_2 + v_3 = 1 - v_1$, indicated by the triangles, into anisotropic solutions richer in PAN. The binodal for the anisotropic phase actually coincides with the binary PBA–diluent axis, illustrating the complete exclusion of PAN from the pure nematic phase of the rigid polymer. We note that mixture no. 1 exhibits a pure nematic phase having a PBA concentration (7.12%) somewhat lower than that ($C_p'' \sim$ 7.5%) corresponding to the biphasic gap of the binary PBA/diluent system.

The binodal for the isotropic phase reveals an increase of the combined PBA + PAN concentration at which an anisotropic phase appears (downtrend of the $(v_2 + v_3)'$ line) when the total solid (PBA + PAN) or the PAN/(PBA + PAN) ratio is increased. The isotropic binodal should[2] be extrapolated to 100% PAN. However, already with mixture no. 5, it was noticed that the pure nematic phase began to crystallize upon standing for periods of over 1 month (cf. also ref 15). In fact, the composition of the nematic phase of the latter mixture is slightly larger than the solubility limit of PBA previously reported.[1,15] Obviously then, also the composition of the conjugate isotropic phase corresponds to a metastable situation. Also in other cases[15–18] it has been noticed that the smaller nucleation rate of crystals vs. liquid crystals allows the observation of the mesophase under metastable conditions. For compositions significantly larger than ~13% crystallization prevents the determination of the binodals for the present system.

The amount of PBA in the isotropic phase decreases with increasing total solid at a given v_3^d, but, simultaneously, there is a fractionation effect, which is illustrated by the data in Table III. In analogy with the situation discussed for the PBA–X-500 system,[2] $\bar{M}_v$ in the anisotropic phase is consistently larger than in the isotropic one. However, the efficiency of fractionation for the present system appears lower than in the previous case.[1] The partition of molecular lengths is affected by the value of ϕ at a given weight fraction of PAN, in line with previous results.[1]

The effect of the molecular weight of PAN on the biphasic equilibria is illustrated in Table IV and in the lower part of Figure 3. The variation of composition of conjugated phases with molecular weight was measured for the same overall C_p and v_3/v_2. The mixture with PAN-B is the same mixture indicated by no. 4 in Table II (overall C_p = 8.14). An increase of PAN molecular weight causes a decrease of PBA concentration in both phases and an increase of PAN in the isotropic phase. The plot in Figure 3 illustrates the variation of tie lines with molecular weight. It is seen that upon increasing molecular weight the inclination of the lines with respect to the vertex to base line is increased (the tie lines become more nearly parallel to the base line). Simultaneously, the PBA + PAN concentration in the isotropic phase decreases. These effects are, however, rather small ones.

Discussion

The phase diagram of the PBA–PAN–diluent system (Figure 2) is qualitatively similar to that expected from

Table V
Comparison between Theory and Experiment

system	theor = exp	theor		exp		theor	exp	Δ slope,[b]
	v_2''	v_2'	v_3'	v_2'	v_3'	slope[a]	slope[a]	%
PBA-PAN[c]	0.08	0.022	0.0266	0.016[e]	0.050[e]	0.65	0.17	74
PBA-PAN[c]	0.10	0.012	0.043	0.013	0.075	0.61	0.14	77
PBA-X-500[d]	0.075	0.032	0.008	0.016	0.027	1.16	0.64	45
PBA-X-500[d]	0.085	0.029	0.014	0.008	0.037	1.06	0.62	42

[a] Slope of tie line with respect to 2–3 base line. [b] [(theor slope − exp slope)/theor slope] × 100. [c] x_2 = 191, x_3 = 1097. [d] x_2 = 220, x_3 = 70. [e] Extrapolated.

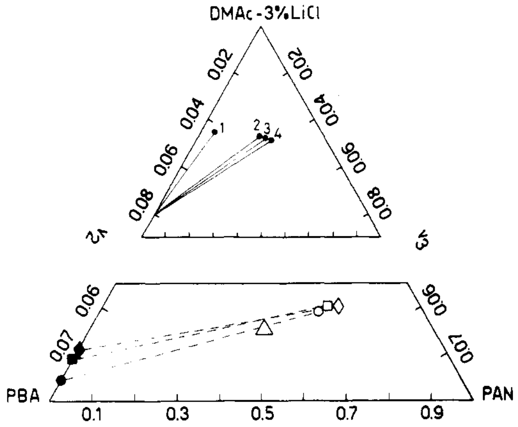

Figure 3. Upper part shows theoretical tie lines calculated[2] for x_2 = 191 and x_3 = 70 (1), 640 (2), 1097 (3), and 1721 (4). Lower part shows variation of tie lines with PAN molecular weight: (○, ●) sample A (MW = 59 500); (□, ■) sample B (MW = 102 000); (◇, ◆) sample C (MW = 160 000). Overall C_p is 8.13% in all cases.

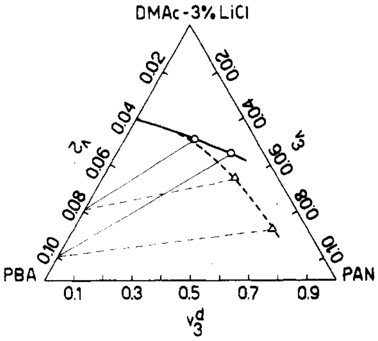

Figure 4. Comparison between theoretical (full lines) and experimental (broken lines) diagrams for the PBA–PAN–diluent system (cf. Table V).

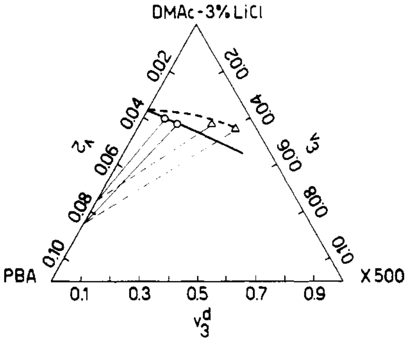

Figure 5. Comparison between theoretical (full lines) and experimental (broken lines) diagrams for the PBA–X-500–diluent system[1] (cf. Table V).

theory.[2] A similar conclusion was reached with the previously investigated PBA–X-500–diluent system.[1] A more detailed quantitative comparison between theory and experiment for the two systems is presented in Figures 4 and 5 and in Table V. The broken tie lines are typical experimental lines derived from Figure 2 for the PBA–PAN–diluent systems and from Figure 2 of ref 1 for the PBA–X-500–diluent system. The broken isotropic binodals are the experimental lines. The unbroken binodals and tie lines were calculated from Flory's theory.[2] For clarity only two tie lines are shown, calculated for the same v_2'' value (composition of conjugated anisotropic phase) corresponding to the experimental tie lines. (The same trend is exhibited by the comparison at constant v_3/v_2.) The axial ratios (x_2) of the two PBA samples were obtained from the equation[19]

$$v_2' = \frac{8}{x}\left(1 - \frac{2}{x}\right)$$

using the experimental values of the critical concentration for the binary PBA–diluent system. In this way the theoretical line is fitted to the experimental one at v_3 = 0. Previously[15] discussed deviations of the behavior of binary systems, with respect to the above equation, are reflected in a larger value of x_2 than expected on the basis of the persistence length. x_3 for PAN and X-500 was calculated from the ratio of the molar volume of polymer and diluent (alternative calculation of x_3[20] produced no significant variation of final results). Data are collected in Table V. Considering the PBA–PAN–diluent case (Figure 4), the experimental tie lines are more nearly parallel to the base line than theoretically expected. The experimental binodal for the isotropic phase is below the theoretical one, indicating that phase separation begins at higher overall concentration (smaller v_1) than expected. Hwang et al.[21] determined the critical concentration for a ternary system involving a rigid and a flexible polymer. They also observed that phase separation begins at a larger overall concentration than theoretically expected. Considering the PBA–X-500 diluent case (Figure 5), the experimental tie lines are also more nearly parallel to the base line than expected, but the deviation is less severe than in Figure 4. The slope of the tie lines is larger than for the system containing PAN, and at variance with the latter system, the isotropic binodal is above the theoretical curve. The data in Table V reveal that, in all cases, the isotropic phase contains less of the rigid polymer and more of the flexible one than predicted.

The PBA–PAN–diluent system differs from the one previously investigated[1] because of differences in the chemical constitution, degree of flexibility, and molecular weight of PAN and X-500. On the other hand, the molecular weight distributions of the polymers we have used should not be greatly different from each other. Moreover, experiments[15,20] with one-polymer systems show that the width of the biphasic region for polydisperse systems conforms to the theory for monodisperse systems better than to the theory that accounts for polydispersity. Therefore, we first consider the compatibility of the PBA–PAN and PBA–X-500 pairs in terms of the conventional analysis of enthalpy parameters in isotropic solutions. We have calculated the Hildebrand solubility parameter δ at room temperature of PBA, PAN, and X-500 according to[6]

$$\delta = \rho(\sum F_i / M_u)$$

where $\sum F_i$ is the sum over the molar attraction constants of all chemical groups in the repeating unit, M_u is the molecular weight of the unit, and ρ is the polymer density. The interaction parameters χ_{23} for the pairs PBA–PAN and PBA–X-500 were calculated according to[6]

$$\chi_{23} = \frac{V_R}{RT}(\delta_2 - \delta_3)^2$$

where V_R is a reference volume, taken as 100 mL/mol.[6] Finally, the critical $\chi_{23}{}^c$ was calculated according to[6]

$$\chi_{23}{}^c = \frac{1}{2}\left(\frac{1}{(x_2)^{1/2}} + \frac{1}{(x_3)^{1/2}}\right)^2$$

where x_2 and x_3 are the degrees of polymerization in terms of the volume V_R. Data thus obtained are as follows:

pair	χ_{23}	$\chi_{23}{}^c$
PBA-X-500	6×10^{-4}	0.014
PBA-PAN	0.101	0.01

For the PBA–X-500 pair, $\chi_{23}{}^c \gg \chi_{23}$, suggesting that the two amorphous polymers should mix in the undiluted state and therefore be compatible in a common solvent over the whole composition range.[6] For the PBA-PAN pair, $\chi_{23}{}^c < \chi_{23}$ and, therefore, the two polymers should demix at some percentage composition in the undiluted state. In solution, the maximum polymer volume fraction at which the two polymers should be compatible turns out to be[6] $v_2 \sim 0.10$ (assuming $\chi_{12} = \chi_{13}$). In conclusion, the crude evaluation of compatibility of the two polymer pairs in the isotropic solution suggests that no demixing should have been expected in the concentration range ($v_2 < \sim 0.1$) in which we have operated. Thus, the phase separation observed with both the PBA–PAn–diluent and the PBA–X-500–diluent systems is triggered by entropy effects related to the formation of the mesophase.[2] The differences in the compatibility of the two systems may therefore only be analyzed in terms of deviations from athermal behavior (χ parameters = 0), assumed by the theory of mesophase formation.[2] The reduced inclination of the tie line for the PAN-containing system may be in line with the larger positive χ_{23} of the PBA–PAN pair. However, it is not simple to explain on this basis why the smaller slope corresponds to greater values of $(v_2 + v_3)'$ and vice versa. It should be interesting to explore other systems in which a liquid–liquid separation due to incompatibility in the isotropic state occurs within the concentration range of mesophase formation.

Turning to the role of partial flexibility, we note that the persistence length of PAN is on the order[22] of 7 Å, similar to that of typical flexible polymers. The contour length of our sample B (~3000 Å) corresponds to ~400 persistence lengths or ~200 Kuhn segments. Therefore, our PAN sample can be described as a random coil. Since the lattice model was used[2] for the partition function of the random coil, one might be concerned by the slight deviation from unity of the axial ratio (~4) of the Kuhn segment of PAN. However, if Flory's calculations[2] are repeated by using in place of the above partition function the expression valid for a semirigid chain composed of rods connected by flexible joints,[23] we obtain a result identical with that described by the theoretical curve in Figure 4, provided the axial ratio of the rods is ≤6. Infact, it is well-known[24] that when $x \leq 6$ no mesophase can be formed in the absence of soft interactions. Thus, the deviation between theory and experiment observed in Figure 4 cannot be attributed to the small rigidity of PAN.

More complex is the case of X-500. Its persistence length, ~50 Å,[7,8] while about 8 times smaller than that of PBA,[9] corresponds to an axial ratio of the Kuhn segment of ~10. The contour length of the X-500 sample previously used[1] is equivalent to ~5 Kuhn segments. The chain is certainly a semirigid one, although X-500 never attains a mesophase at rest.[9] The simplest approach, that of regarding the X-500 chain as a collection of independent Kuhn segments, turns out to be untenable. In fact, we have calculated the ternary diagram for two rodlike polymers having axial ratios in the ratio 1:4 using the Abe and Flory theory.[4] The diagram reveals a slope of tie lines even greater than that indicated by the theoretical result in Figure 5. A more refined approach would be that using the chemical potentials corresponding to various models of semirigid chains,[25,26] i.e., the wormlike chain,[27] or rods connected by various types of flexible joints.[23,28] We plan to present these calculations in a forthcoming publication dealing with mesophase formation for solutions of *two* semirigid polymers (having $x > 6$).

We now turn to the role of molecular weight of the random coil on the ternary equilibria. The experimental data in the lower part of Figure 3 indicate that an increase of molecular weight from 60 000 to 160 000 produces about a 32% decrease of the inclination of the tie lines with respect to the 2–3 base line. The total composition $(v_2 + v_3)'$ in the isotropic phase decreases by a small 2% in the corresponding molecular weight range. These results may be compared with theoretical predictions[2] for a system composed of a isodiametrical solvent, a rodlike polymer with axial ratio x_2, and a random coiled chain with contour length x_3. In the upper part of Figure 3 we report tie lines calculated from theory[2] for $x_2 = 191$ (axial ratio fitted to the present PBA sample) and for $x_3 = 640$, 1097, and 1721 (corresponding to PAN-A, -B, and -C, respectively; we also include a tie line calculated for $x_3 = 70$, which approximates x_3 of the previously used X-500 sample). The data show a decrease of ~11% of the slope of the lines when x_3 increases from 640 to 1721. This decrease favorably compares with the decrease shown by the experimental lines, although theory somewhat underestimates the effect. The theoretical lines also show a small increase (~2%) of the total composition $(v_2 + v_3)'$ for x_3 between 640 and 1721. However, if the restriction of a constant v_2'' is eliminated (calculation at given v_3/v_2), $(v_2 + v_3)'$ actually decreases by ~2%, in excellent agreement with experiments in the same molecular weight range. The theoretical calculation predicts that in all cases the isotropic binodal for a higher molecular is above the binodal for a lower molecular weight.[2]

The theoretical tie lines in the upper part of Figure 3 reveal that the effect of molecular weight on the slope is a rather large one when low molecular weight (corresponding to X-500) is included. This is the reason for the large difference in the theoretical slopes reported in Table V for the two systems at $v_2'' = 0.08$ (the increase of x_2 from 191 to 220 has slightly reduced the difference expected at given x_2). It was noted above that the experimental decrease of the slope of the tie lines with molecular weight is even larger than predicted. If the theoretical slope for the PAN-containing system (0.65) is revised on this account, the greater part of the *difference* in Δ slope (cf.

Table V) for the two systems is explained. Remaining deviations from theory are the findings that slopes are generally smaller than expected and that the binodal for the PAN-containing system falls below that for the X-500 system.

The foregoing analysis has failed to provide an explanation for the remaining discrepancies between theory and experiment. The study of additional systems exhibiting even greater differences in chemical constitution and conformation (as noted above) might help in clarifying said discrepancies. It is, in any case, important to appreciate that the differences exhibited by the two systems, both with respect to each other and with respect to theory, are relatively minor ones. The theory appears to be on a very sound basis.

Registry No. PBA, 24991-08-0; PAN, 25014-41-9; DMAc, 127-19-5; 4-aminobenzoic acid homopolymer, 25136-77-0.

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Effect of Block Copolymers at a Demixed Homopolymer Interface

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ABSTRACT: A statistical thermodynamic theory is used to derive the mean-field equations for the fundamental probability distribution functions characterizing a system of two immiscible homopolymers (A and B), diluted with solvent, in the presence of a diblock copolymer (AB). The equations are solved numerically in a "*computer experiment*" and the various contributions to the free energy and interfacial tension are evaluated to determine their relative importance. For a symmetric diblock copolymer and homopolymers of infinite molecular weight (as well as a symmetric solvent), we find that the reduction in interfacial tension, $\Delta\gamma$, with increasing copolymer molecular weight and concentration arises mainly from the energetically preferred orientation of the blocks at the interface into their respective compatible homopolymers. The main counterbalancing term in the expression for $\Delta\gamma$ is the entropy loss of the copolymer which localizes at the interface. The loss of conformational or "*turning-back*" entropy of both copolymers and homopolymers at the interface is shown to contribute little to $\Delta\gamma$. Keeping only the two main terms in $\Delta\gamma$, we find an exponential dependence on the parameter $Z_C\chi\varphi_P$, where Z_C is the degree of polymerization of the symmetric copolymer, χ is the interaction parameter between A and B, and φ_P is the volume fraction of homopolymer.

1. Introduction

The use of block copolymers has led to the design of polymer blends with remarkably versatile mechanical properties.[1-5] In particular, when added in small amounts to immiscible homopolymers, the block copolymers are found to behave as classical surfactants, similar to soap molecules at an oil-water interface.[6-8] The additive facilitates mixing by dramatically lowering the interfacial tension between the two normally immiscible phases.

Although there is now a great deal of experimental information available,[9-12] our theoretical understanding has not kept up with the latest practical developments. The purpose of this series of papers is to apply our recently developed general theory of polymeric alloys to study the emulsifying behavior of block copolymers in immiscible homopolymer blends.

In an earlier paper[13] we set up and solved numerically the mean-field equations for a quaternary system consisting of two highly incompatible homopolymers, along with the associated diblock copolymer, and diluted with a good solvent. In the absence of detailed microscopic information about the modified interphase region between the homopolymers, we performed what was essentially a computer experiment, in which the interfacial polymer