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Lyotropic block copolymers of poly(*p*-benzamide) and, poly[2-phenylene (5-benzimidazole)]: the ternary system copolymer/poly(*p*-benzamide)/ dimethylacetamide-lithium chloride†

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New rigid-flexible copolymers based on poly(*p*-benzamide) (PBA) and poly[2-phenylene (5-benzimidazole)] (PABI) were synthesized, varying the molecular weight of the flexible block. Ternary solutions in dimethylacetamide-3% LiCl show the peculiar behaviour expected theoretically for this kind of system. In particular, it was demonstrated that more copolymer enters the anisotropic phase as the PABI chain length becomes shorter. Comparison with homopolymer mixtures shows the usefulness of the copolymer in improving the amount of flexible chains inside the mesophase.

(Keywords: rigid-flexible copolymer; lyotropic polymer; ternary system)

INTRODUCTION

A few years ago we reported’ the phase behaviour of a ternary system based on a rigid lyotropic polymer, a rigid–flexible diblock copolymer and a diluent. The terms ‘rigid’ and ‘flexible’ are obviously related to limit models, suitable for describing the experimental properties of that system. The rigid lyotropic polymer as well as the ‘rigid’ part of the block copolymer were made from poly(*p*-benzamide) (PBA). The contour length of our PBA sample (650 Å) was of the same order as the PEA persistence length, *q* [400 Å^2 to 800 Å^3], the latter condition being sufficient to consider the chain as rigid.

The other part of the diblock was a polyterephthalamide of *p*-aminobenzhydrazide (PABH-T); its persistence length (50 Å) may be considered as being intermediate between those of a semiflexible polymer and a coiled polymer^{4,5}, as evidenced from the lack of anisotropic behaviour at rest.

Dimethylacetamide (DMAc) containing 3% (w/w) of LiCl (DMAc–3LiCl) was the diluent.

The ternary phase diagram was described in terms of the volume fraction, *v*, of the polymeric components and was studied up to the solubility limit of PBA (v = 0.09 ml g^{-1})^6.

Three peculiar areas were identified: tht: first one extends from the pure solvent to the *v*′ line (*v*′ ≅ limit concentration at which the anisotropic phase becomes stable as a function of the polymeric composition). In this area the solutions are isotropic and contain both PBA and copolymer, whatever the proportion is. The second area, extending between the v’ and *v*″ lines (*v*″ ≅ limit concentration for the stability of the isotropic phase at different polymeric compositions), refers to the biphasic solutions: the composition of the iso- and anisotopic conjugated phases fails on the *v*′ and *v*″ line, respectively. Finally, the area under line *v*″ concerns the pure anisotropic phase which contains both PBA and copolymer.

The general features of the diagram agreed qualitatively with the theoretical prediction by Matheson and Flory^7 for athermal and monodispersed systems. The main goal was the demonstration that the copolymer *may* enter the mesophase. However, our system represented a poor approximation to the theoretical model, not only because of polydispersity problems and the existence of solubility limits, but mainly because of the partial flexibility of PABH-T,

Recently a new copolymer based on PBA was synthesized by some of us^8: the flexible part was a new aromatic polyamide, poly[(2-phenylene (5-benzimidazole)] (PABI). Its behaviour as determined by viscometry and light scattering’ corresponds to that of an expanded coil. having a persistence length of ≈ 20 Å. It is completely compatible with PBA in isotropic solutions’“. Moreover, the conditions for varying the molecular weight and, consequently, the ratio between the rigid and flexible parts were assessed’.

In this paper we shall show the phase properties of ternary mixtures comprising PBA, PBA-PABI copolymer and diluent. The influence of PABI length on the ability of the copolymer to enter the mesophase is also considered and discussed.

EXPERIMENTAL

Homopolymers

The sample of PBA was the same used in a previous work’“. Three samples of PABI, –COCl terminated, were synthesized in DMAc–3LiCl according to the route

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Table 1 PBA and PABI characterization data

Sample	$[\eta]^a$ (dl g^{-1})	$\overline{M}_w$	$\overline{M}_n$	v'
PBA	1.580	11 800^b	7400^d	0.044
PABI I	0.335	12 400^c	6200^e	—
PABI II	0.415	15 000	7500^d	—
PABI III	1.150	54 000	27 000^e	—

^{a}Measured in 96% H_2SO_4 at 25°C
^{b}From Schaefgen relationship[11]
^{c}From[9]
^{d}Experimentally determined from chemical titration of terminal groups
^{e}Assuming $\overline{M}_w/\overline{M}_n = 2$ as in the case of sample II

Table 2 Characterization of PBA/copolymer stock samples

Ternary mixture	PABI (w/w %)	Copolymer (v/v %)	v'
PBA/copolymer I/diluent	17	36.1	0.049
PBA/copolymer II/diluent	16	30.5	0.045
PBA/copolymer III/diluent	27	32.0	0.044

described in previous papers[8,9]. A suitable amount of each sample was recovered by precipitation and used for molecular characterization.

Table 1 collects the data for PBA and PABI samples.

Copolymer synthesis

The copolymer synthesis was performed according to the procedure described in [8], using an excess of PABI with respect to PBA (mol/mol). The ratio between the end groups, –COCl of PABI and $-NH_2$ of PBA, was about 2.4:1 mol/mol to maximize the yield of the diblock. The unreacted PABI was extracted after precipitation of the product by using DMAc at 70°C.

The PBA/copolymer mixture was washed with methanol, dried, weighed and analysed by ultraviolet (u.v.) spectrophotometry in DMAc–3% LiCl solution. The PBA and PABI show maximum absorbance at λ = 346 and 370 nm, respectively. By assuming absorbance additivity rules it is possible to write a system of two equations at two different λ:

$$A_\lambda = K_{\lambda,\mathrm{PBA}} c_{\mathrm{PBA}} + K_{\lambda,\mathrm{PABI}} c_{\mathrm{PABI}}$$

where c is concentration expressed in mg ml^{-1} and K_λ are constants evaluated for PBA and PABI solutions at known concentration. From these equations the PABI content, expressed as a weight fraction with respect to the overall amount of polymer (see second column of *Table 2*), can be evaluated.

The percentage of copolymer in relation to the overall polymer content was obtained by mass balance, supposing a diblock structure, and on the basis of the known percentage of PABI and the $\overline{M}_n$ values for PBA and PABI. In order to express w/w concentration as a volume fraction, the specific volumes of PBA (0.754 ml g^{-1}), PABI (0.699 ml g^{-1}) and the diluent (1.036 ml g^{-1}) were used. For the copolymer the specific volume was calculated by assuming the additivity of contributions from the two blocks and a ratio between the weight of the two blocks equal to the ratio of the corresponding $\overline{M}_n$ values (see *Table 1*). The copolymer contents expressed as volume fraction are reported in column 3 of *Table 2*.

The diblocks based on PABI samples I, II and III are called copolymers I, II and III, respectively.

The values of v' for the three mixtures, obtained by increasing the overall polymer concentration up to the appearance of the anisotropic phase, as observed by optical microscopy, are also reported in the last column of *Table 2*.

Phase diagrams

The three PBA/copolymer mixtures were used to prepare some solutions in the biphasic gap. After equilibration for about 3 weeks, conjugated phases were separated by centrifugation at 30 000 rev min^{-1} and analysed according to described procedures[8–10].

RESULTS AND DISCUSSION

Table 3 gives the overall concentration (expressed as volume fraction) and composition of the conjugated phases examined here. Subscripts 2 and 3 indicate PBA and copolymer, respectively (while 1 is the diluent). The use of volume fraction to express the composition of binary and ternary mixtures is consistent with the variables used in the theoretical predictions and makes discussion of the diagram easier.

The data in *Tables 2 and 3* were used to construct the ternary phase diagram of *Figure 1*. The scales on the left and right side represent the binary systems PBA/solvent and copolymer/solvent, respectively. The base axis gives as a percentage the amount of copolymer with respect to the total amount of (PBA + copolymer) (v/v %).

We discuss the diagram starting from the left-hand axis, where the values of v_2' and v_2'' for PBA dissolved in DMAc–3LiCl are reported. The values v_2' and v_2'' were the same as those reported in [10].

Coming now to the inner part of the phase diagram, three peculiar areas (a, b and c) may be identified: at low overall concentration, v_{2+3}, isotropic solutions are stable (region a). This is limited by the line v', obtained by connecting the v_{2+3}' values of the samples PBA/copolymer I, PBA/

Table 3 Summary of data related to the phase behaviour of PBA/copolymer/diluent systems

Sample	overall		isotropic		anisotropic	
	v_{2+3}	100 v_3/v_{2+3}	v_{2+3}'	100 v_3/v_{2+3}'	v_{2+3}''	100 v_3/v_{2+3}''
PBA/copolymer I/diluent	0.065	36.1	0.054	49.2	0.073	21.0
	0.070	36.1	0.057	51.8	0.077	21.0
PBA/copolymer II/diluent	0.061	30.5	0.052	44.7	0.094	10.3
	0.064	30.5	0.052	50.1	0.093	11.2
	0.068	30.5	0.051	47.3	0.098	10.3
PBA/copolymer III/diluent	0.062	32.0	0.053	56.5	0.080	1.70
	0.067	32.0	0.057	62.2	0.085	2.30

Table 4 Highest PABI content (volume fraction) experimentally observed in the mesophase

PABI	$v_{PABI}/v_{tot} \times 100$	
$\overline{M}_w$	Homopolymer mixture	Copolymer mixture
12 400	3.6	10.5
54 000	0	2.0

copolymer II, PBA/copolymer III (*Table 3*) and the v' ($\equiv v_{2+3}'$) values of *Table 2*.

This line is expected to split on the right-hand side into three different lines which should cross the right axis at locations corresponding to the v_3' values of the pure copolymers. According to the theory[7], the critical concentration, v_3', should increase with the length of the flexible block (v_3' of copolymer III $>$ v_3' of copolymer II $>$ v_3' of copolymer I). The experimental test of this prediction entails the preparation of pure copolymers, and will be object of future research.

Under line v' the systems become biphasic (region b) and the compositions of the anisotropic conjugated phases are represented by three different lines. These lines, when extended through the whole diagram, should represent the lower boundary of the biphasic area. Although only the range at low copolymer content has been tested experimentally, we may reasonably conclude that the biphasic area related to copolymer III is the widest, while the area related to copolymer I is the narrowest. The pure anisotropic phase falls in the areas c, under the v'' lines. The amount of copolymer entering the anisotropic phase increases strongly with decreasing length of the PABI chains, PBA being the same in all cases. We believe that this result, theoretically predicted[7], has been demonstrated here for the first time.

A last point concerns the comparison between the amount of PABI accepted in the anisotropic phase when covalently linked to PBA and when in the form of a pure homopolymer.

In a recent paper[10] we described the behaviour of the ternary systems PBA/PABI/DMAc–3LiCl, the rigid component (PBA) being the same as used in the present work. The main conclusion was that the PBA anisotropic phase may accept a little amount of PABI when its contour length, L, is sufficiently short: this was the case for PABI having $\overline{M}_w = 12\,400$ ($L = 613$ Å), while the sample having $\overline{M}_w = 54\,000$ ($L = 2670$ Å) was totally excluded. This result may not be explained by Flory's original theory, which predicts that a flexible polymer of any length when introduced in a mesophase should negatively influence the mesophase stability.

However, Blonski *et al.*[12] recently suggested that the existence of a certain degree of anisotropic interaction between the rigid molecules stabilizes the mesophase, creating the condition to accept a certain amount of the flexible polymer. The previously mentioned results confirmed this prediction, both from a qualitative and a quantitative point of view.

It is now easy to check whether the existence of a chemical link between PABI and PBA (rigid–flexible copolymer) improves the amount of PABI in the mesophase. *Table 4* gives the data for the two kinds of system. Comparison of the last two columns shows that the amount of PABI increases significantly when present as copolymer.

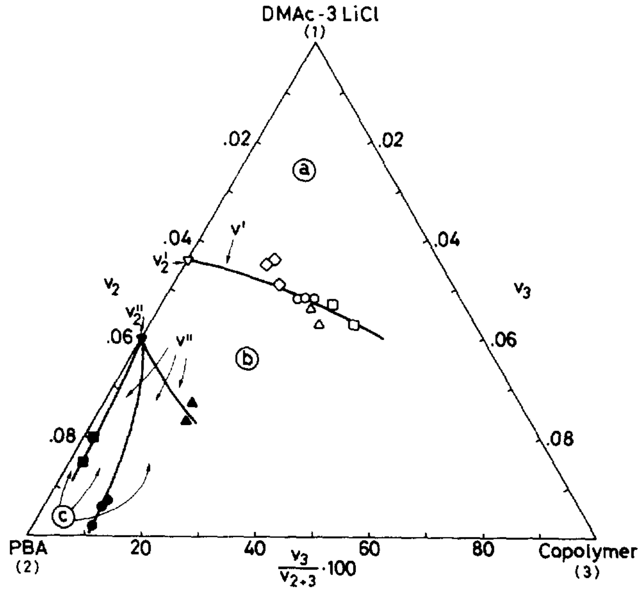

Figure 1 Ternary phase diagram of PBA/copolymer/diluent. Open symbols: v_{2+3}' values for conjugated isotropic phase composition (△, copolymer I; ○, copolymer II; □, copolymer III); ◇, v_{2+3}' for the mixtures in *Table 2*. Solid symbols: v_{2+3}'' values for conjugated anisotropic phase composition. a, b and c represent isotropic, biphasic and anisotropic regions, respectively. ▽, v_2' (PBA/diluent binary system), ▼, v_2'' (PBA/diluent binary system)

CONCLUSIONS

We believe that our results concerning the properties of rigid–flexible lyotropic copolymers qualitatively demonstrate two main points. First of all, it is evident that the copolymers may participate in the lyotropic mesophase as for the system examined previously[1] and that the width of the biphasic gap is progressively reduced as the flexible tail of the diblock becomes shorter. In other words (see *Figure 1*) we may presume that area c, related to the pure anisotropic phase containing both components, becomes as wider as the molecular weight of the flexible component is lowered.

Second, it was also demonstrated that the copolymer allows us to introduce into the mesophase a higher amount of flexible chains with respect to a sample made of a mixture of the homopolymers.

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