Mesophase formation and polymer compatibility: 3. Poly(γ-benzyl-L-glutamate)/poly(n-hexyl-isocyanate)/diluent system

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This paper reports a study of a phase equilibrium for a ternary system involving a rigid polymer poly(γ-benzyl-L,glutamate, PγBLG) a semirigid polymer poly(n-hexyl-isocyanate, PHIC) and a diluent chloroform ($CHCl_3$), at 20°C. This ternary system exhibits a single isotropic phase only when the combined volume fraction is below 0.02. When (v_2+v_3) is between 0.02 and 0.08, two isotropic phases exist; one containing prevailing PHIC and the other PγBLG. Above a critical volume fraction there is a composition range, which corresponds to the biphasic gap of the corresponding binary systems, in which three phases coexist. All compositions are invariant inside this area of the diagram. For higher volume fractions, two anisotropic phases are stable, each containing pure polymer. It appears that the incompatibility between the polymer, already evident, in the isotropic phase, does not allow the formation of a single anisotropic phase.

(Keywords: liquid crystals; ternary systems; compatibility)

INTRODUCTION

The phase behaviour of ternary systems comprising two polymers and a solvent has been discussed in previous papers[1,2]. The two systems investigated comprised:

(1) A rodlike polymer (poly(*p*-benzamide) (PBA)) and a flexible polymer (poly(acrylonitrile) (PAN)) plus *N,N* dimethylacetamide, (DMAc) + 3% LiCl.

(2) Two semirigid polymers and a solvent (cellulose acetate, CA)–(hydroxypropylcellulose, HPC)–DMAc.

The results obtained with the former system were in line with theoretical predictions[3]. We observed the exclusion of the flexible polymer (PAN) from the mesophase formed above a critical concentration of the two polymers. In fact the flexible polymer was found only in the conjugate isotropic phase. This behaviour is due to the entropy effect related to the interference of random coils with the mutual orientation of the rodlike molecules. In the latter system (CA, HPC, DMAc), we observed, at variance with theoretical expectations[4,5], that the two semirigid polymers were incompatible in both isotropic and anisotropic mesophases. As in the case with low molecular weight compounds, the theory predicts a single nematic phase containing the two polymers. The two polymers, CA–HPC, formed two phases at very low (isotropic) and very high (anisotropic) concentrations and three coexisting phases at intermediate concentrations. We never observed a single anisotropic phase. The lack of compatibility in the anisotropic phase of the two polymers was attributed to the unfavourable enthalpic interactions of the two polymers responsible also for the incompatibility in the isotropic phase.

In the present paper we describe the behaviour of the poly(γ-benzyl-L-glutamate, PγBLG)–poly(n-hexyl-isocyanate, PHIC)–chloroform ($CHCl_3$) system. With respect to the CA–HPC–DMAc system previously reported, the present system exhibits some differences in the conformation of the two polymers. In fact while the high molecular weight PHIC can be considered a semirigid polymer, PγBLG, due to its low molecular weight, can be regarded as a rod-like polymer. As in the case of the CA–HPC–DMAc system, we found that PγBLG and PHIC are not compatible in both the isotropic and anisotropic solutions. Three coexisting phases were observed at intermediate polymer concentrations.

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EXPERIMENTAL

Materials

The PHIC sample is similar to that used and described in a previous investigation[6]. The molecular weight was determined from the intrinsic viscosity in toluene at 25°C, using Berger's and Tidswell's relation[7]. The intrinsic viscosity was 13.28 dl/g corresponding to a molecular weight of 285 000. The PγBLG was supplied by Sigma Chemical Company and its molecular weight was 30 000. The solvent was analytical grade chloroform. Ternary mixtures were prepared by dissolving weighed amounts of the polymers in the solvent. The concentration C_p of the overall system was calculated from the weight of PHIC and PγBLG and solvent present in the mixture and is given by the sum of PHIC [(g of PHIC)/(g of PHIC + g of PγBLG + g of solvent)] × 100 and PγBLG [(g of PγBLG)/(g of PγBLG + g of PHIC + g of solvent)] × 100. The concentrations expressed as polymer volume fractions, v_2 and v_3 were calculated from the corresponding values of C_p using the partial specific volumes of PHIC ($\bar{v}_{PHIC}$), PγBLG ($\bar{v}_{P\gamma BLG}$) and the specific volume of the solvent (V_1), and assuming additivity. These quantities were determined pycnometrically at 25°C. $\bar{v}_{PHIC}$ was found to be equal to 0.952 ml/g and $\bar{v}_{P\gamma BLG} = 0.754$ ml/g ($V_1 = 0.681$ ml/g). The mixtures were highly viscous and were stirred with very slow rotation at room temperature for about one month. The phases were separated by centrifugation following a technique identical to that reported in a previous investigation[2]. To determine the individual phase compositions in the polyphase regions we first evaluated the overall C_p by drying a sample aliquot, *in vacuo* at 50°C. The ratio between the amounts of the two polymers was determined by quantitative infrared analysis[8], using a Perkin Elmer spectrophotometer, model 983. We measured the absorbance of films (thickness 45 μm) obtained by evaporation of a series of PHIC/PγBLG mixtures containing known amounts of the two polymers. We observed that the best correlations between the relative amounts of the two polymers and their absorbance was between the ratio of the absorbances at a frequency of $\nu_1=3289\,\mathrm{cm}^{-1}$ and $\nu_2=2895\,\mathrm{cm}^{-1}$ when PγBLG was less than $\sim 20\%$. When PHIC was less than $\sim 30\%$ the best correlation was given by the ratio of the absorbances at a frequency of $\nu_3=2957\,\mathrm{cm}^{-1}$ and ν_1. These calibration curves allow us to determine the composition of the polymer mixtures using i.r. absorbance measurements. A very good reproducibility was shown by the analytical data. The critical concentration C_p^* for the appearance of the anisotropic phase at room temperature, for binary solutions of PHIC or PγBLG in $CHCl_3$, was determined with a polarizing microscope (Reichert Zetopan) using a technique similar to that described previously[2]. The occurrence of anisotropy within the ternary systems was likewise monitored with the polarizing microscope.

RESULTS AND DISCUSSION

Optical determination, on binary PHIC/$CHCl_3$ and PγBLG/$CHCl_3$ solutions, yielded $C'_p=6.8\%$ ($\bar{v}'_3=0.092$) and $C'_p=6.4\%$ ($\bar{v}'_2=0.070$) respectively, as the critical concentration at which an anisotropic phase appears.

In terms of the original Flory theory

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

the data would correspond to the axial ratio of $\simeq 85$ and $\simeq 110$ respectively. These axial ratios are substantially greater than those that can be calculated for PγBLG from the relationship[11] $x=(DP\times 1.5)/15.5\simeq 13$; and for PHIC from $x=2q/16.4\simeq 30$ where the persistence length ($q=250$ Å) was evaluated using the values of $|\eta|$ in $CHCl_3$ for different molecular weights reported by Berger[7]. Similar discrepancies have already been observed although not as extensively[6]. The width of the biphasic gap for the binary PγBLG/$CHCl_3$ system was measured by the variation of the volume fraction of the isotropic phase with the overall concentration. The results are reported in *Figure 1*. These data show that the composition C_p'' of the conjugated anisotropic phase is $\sim 8.5\%$ ($v''=0.092$) and that $C''_p/C'_p=1.3$. The biphasic width gap determination of the binary PHIC/$CHCl_3$ system is complicated by the difficulty of isolating the conjugated phases even after extensive centrifugation. This is probably due to the very high viscosity of this system. A series of ternary mixtures, covering an overall C_p range between 1% and 9%, were prepared. The overall composition of the mixtures is given in *Table 1* (see *Figures 2* and *3*). The phase diagram has been constructed by using the same approach and the same symbols described in a previous article[1]. All mixtures contained more or less equal amounts of the two components with the exception of mixtures 8, 9, 11 and 12. When the overall C_p is $\sim 1\%$ (cf. mixture 1 in *Figures 2* and *3*) a single isotropic phase containing both polymers is observed. When the overall C_p is between $\sim 1.5\%$ and 6.5%, isotropic phases I and II are observed. The compositions of these isotropic phases are given in *Table 2* and in *Figures 2* and *3*.

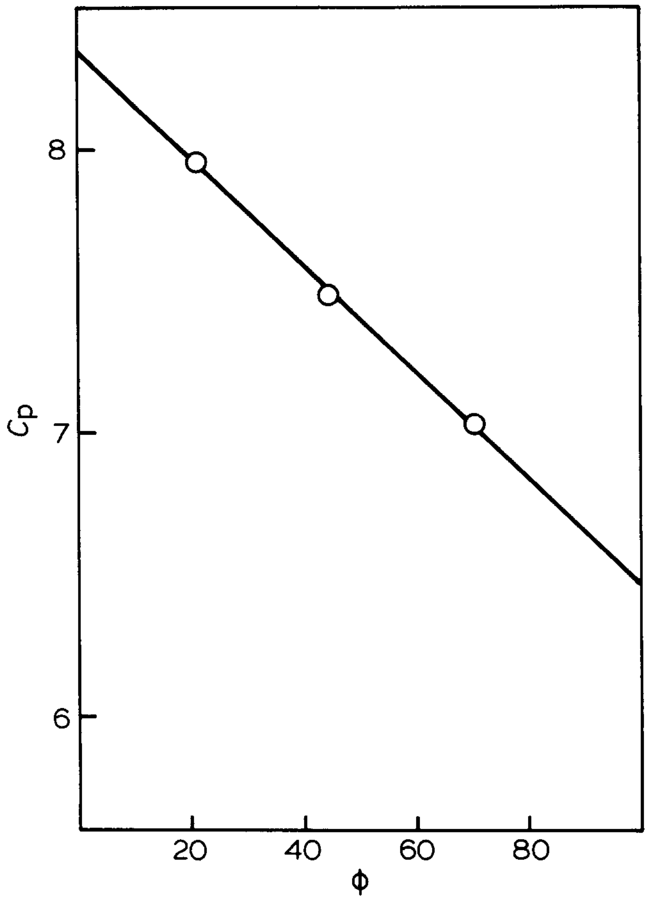

Figure 1 Overall composition C_p vs. the volume fraction of the isotropic phase (ϕ) for PγBLG–$CHCl_3$ binary system

Table 1 Overall composition of ternary mixture

	PγBLG		PHIC		
Mixture	C_{p2}	v_2	C_{p3}	v_3	$C_{p2}+C_{p3}$
1	0.5	0.0055	0.5	0.0070	1.0
2	1.0	0.0110	1.1	0.0153	2.1
3	1.5	0.0165	1.6	0.0222	3.1
4	2.1	0.0230	2.0	0.0277	4.1
5	2.5	0.0273	2.5	0.0345	5.0
6	3.0	0.0327	2.9	0.0399	5.9
7	3.5	0.0381	3.5	0.0481	7.0
8	7.0	0.0768	0.4	0.0055	7.4
9	4.5	0.0491	2.5	0.0344	7.0
10	4.0	0.0434	4.0	0.0548	8.0
11	1.0	0.0107	7.3	0.0990	8.3
12	2.4	0.0259	6.0	0.0817	8.4
13	4.5	0.0487	4.6	0.0628	9.1

We have observed that the exclusion of the PHIC from phase I and of the PγBLG from phase II increases when the overall concentration is increased. The exclusion of the PγBLG is practically complete above an overall

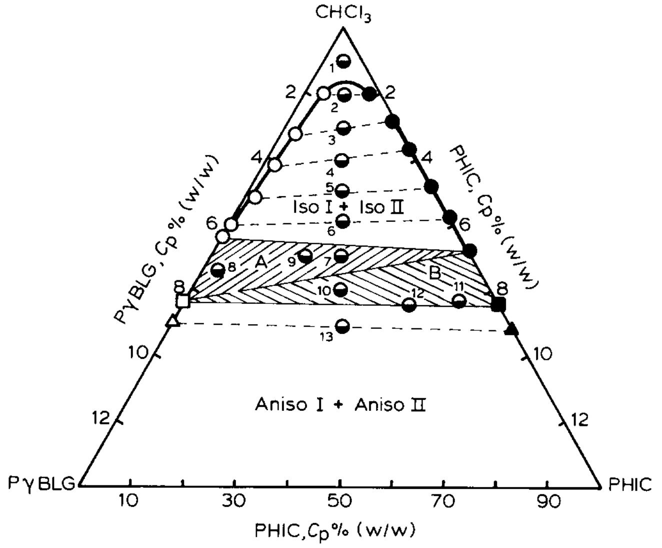

Figure 2 Ternary phase diagram for the system PγBLG/PHIC/CHCl$_3$ at 20°C: (◑) overall composition of polyphasic mixture; (○) composition of isotropic phase I; (●) composition of isotropic phase II; (□) composition of anisotropic phase I in region A; (■) composition of anisotropic phase II in region B; (△) composition of pure anisotropic phase I; (▲) composition of pure anisotropic phase II

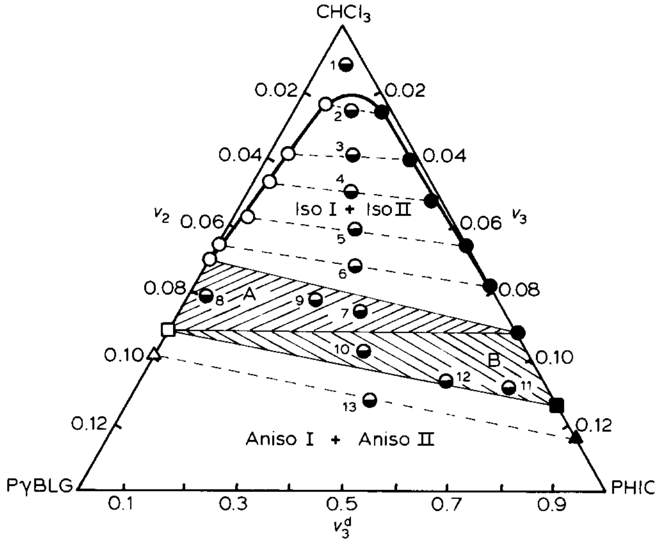

Figure 3 Some data comprising *Figure 3* with composition given as volume fraction

Table 2 Composition of conjugate isotropic phases

	Isotropic I				Isotropic II			
	PγBLG		PHIC		PγBLG		PHIC	
Mixture	C_{p2}	v_2	C_{p3}	v_3	C_{p2}	v_2	C_{p3}	v_3
2	1.45	0.0160	0.55	0.0077	0.27	0.0030	1.70	0.0236
3	2.89	0.0318	0.40	0.0056	0.13	0.0014	2.75	0.0380
4	3.92	0.0432	0.32	0.0044	0.13	0.0014	3.64	0.0501
5	4.91	0.0540	0.29	0.0040	0.07	0.0008	4.85	0.0665
6	6.00	0.0660	nd*	nd*	0	0	5.80	0.0792

*nd = insufficient amount to perform determination

Table 3 Volume fraction of each phase within the three phase region

Mixture	ϕ iso II, %	ϕ iso I, %	ϕ aniso I, %
7	53	29	18
8	5	50	45
9	38	38	24

$C_p \sim 6\%$ (mixture 6). Furthermore, we observed a small amount of PHIC detected by i.r. qualitative analysis, even in samples of higher concentration. Extensive centrifugation of mixtures with C_p between $\sim 6.5\%$ and 7.5% (area A, in *Figures 2* and *3*) resulted in the separation of three phases (see *Figure 4*) containing, isotropic PHIC at the top, anisotropic PγBLG in the middle, and iso PγBLG containing a small trace of PHIC at the bottom. The iso PγBLG phase is at the bottom with respect to the aniso PγBLG phase because the density of PγBLG ($1.283\ \mathrm{g\,cm^{-3}}$)[9] is lower than that of the solvent ($1.47\ \mathrm{g\,cm^{-3}}$). This situation has already been observed in other systems[10].

The volume fraction, ϕ, of each of these phases (ϕ = volume phase/total volume) is given in *Table 3* and the corresponding compositions are included in *Table 4*. The compositions of these three phases observed with mixtures 7, 8 and 9 do not change in spite of the variation of their volumes. When the overall C_p is greater than 7.5% upon extensive centrifugation we observed two phases,

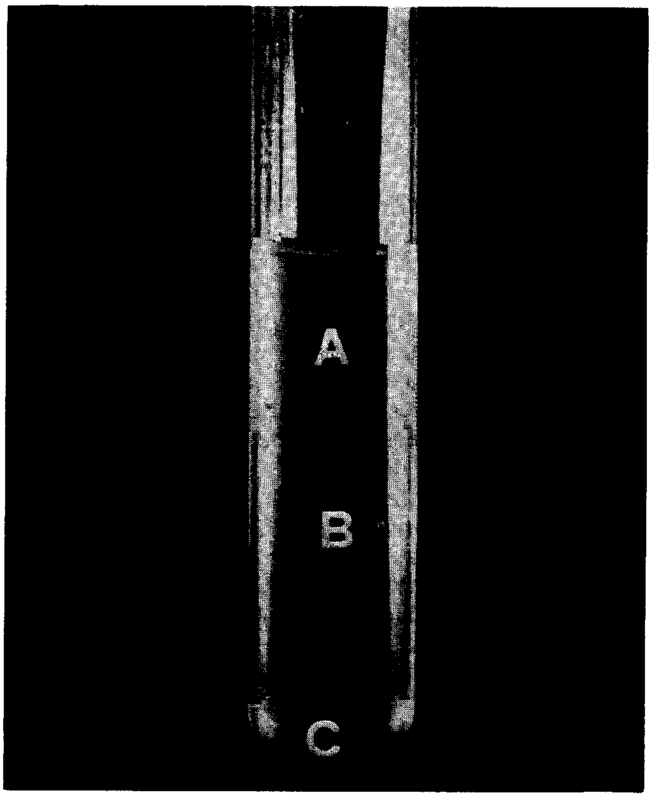

Figure 4 Photograph of coexisting phases at the phase equilibrium (area A). A = isotropic (PHIC), B = anisotropic (PγBLG), C = isotropic (PγBLG)

Table 4 Composition of conjugate isotropic and anisotropic phases in region A

	Isotropic I				Anisotropic I				Isotropic II			
	PγBLG		PHIC		PγBLG		PHIC		PγBLG		PHIC	
Mixture	C_{p2}	v_2	C_{p3}	v_3	C_{p2}	v_2	C_{p3}	v_3	C_{p2}	v_2	C_{p3}	v_3
7	6.4	0.070	nd*	nd*	8.2	0.089	0	0	0	0	6.8	0.092
8	nd*	nd*	nd*	nd*	8.4	0.092	0	0	0	0	nd*	nd*
9	6.5	0.071	nd*	nd*	nd*	nd*	0	0	0	0	6.9	0.093

*nd = insufficient amount to perform determination

Table 5 Composition of conjugate anisotropic phases

	Anisotropic I				Anisotropic II			
	PγBLG		PHIC		PγBLG		PHIC	
Mixture	C_{p2}	v_2	C_{p3}	v_3	C_{p2}	v_2	C_{p3}	v_3
10	8.4	0.0921	0	0	0	0	7.7	0.1044
11	8.3	0.0911	0	0	0	0	8.3	0.1123
12	8.3	0.0911	0	0	0	0	8.5	0.1149
13	9.0	0.0987	0	0	0	0	9.2	0.124

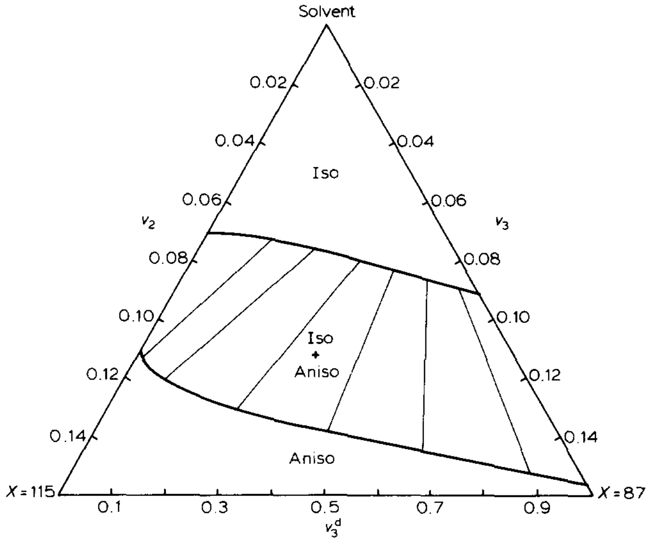

Figure 5 Theoretical phase diagram for an athermal system with $x_1 = 115$; $x_2 = 87$. The polymer with $x = 87$ is composed of ten segments jointed together

the aniso PγBLG at the bottom and aniso PHIC at the top (area B, mixtures 10, 11 and 12). The composition of the PγBLG phase is the same for all three samples and is given in *Table 5*. The composition of the PHIC phase is between 7.7% and 8.5%. These values fall within the biphasic gap of the PHIC/CHCl$_3$ system (considering a ratio C_p''/C_p' equal to 1.3, and being $C_p' = 6.8$, we obtain $C_p'' = 8.8\%$). We think that in area B we have three phases: aniso PγBLG, iso PHIC and aniso PHIC. However, we cannot observe them because the high viscosity of the system prevents a separation of the two PHIC phases, as was the case of the binary system PHIC/CHCl$_3$. For any overall C_p greater than 8.2%, the system consists of two anisotropic phases: aniso I and aniso II. The data in *Table 4* for mixture 13 show that the composition of the two anisotropic phases increases with the overall composition C_p.

Figure 5 shows a theoretical phase diagram calculated, according to the Flory–Matheson theory[5] for an athermal system formed by a rigid polymer and a semirigid polymer. The axial ratios used were $x_1 = 115$ and $x_2 = 87$. These values coincide with the experimental values of v_2' and v_3'. The semirigid polymer was considered to be formed by ten segments joined together in line with the conformation of our PHIC sample. The diagram predicts the existence of three areas:

(a) A homogeneous isotropic phase with complete miscibility between the polymers.

(b) A biphasic area composed of an isotropic phase and an anisotropic phase, each of them containing both polymers.

(c) A homogeneous anisotropic phase with complete miscibility between the polymers.

Thus, even the introduction of partial flexibility does not alter the expectation of complete miscibility within the anisotropic phase for two rodlike polymers[4]. In order to explain the difference between theoretical and experimental results, we have evaluated the Hildebrand solubility parameters 'δ' for the two polymers. The approach is similar to that described in a previous paper[2]. From these data the χ_{23} interaction parameter for the PγBLG–PHIC pair and $\chi_{23}^{\mathrm{crit.}}$ were calculated at room temperature. Data obtained were as follows:

χ_{23}	$\chi_{23}^{\mathrm{crit.}}$
0.80	0.035

Since $\chi_{23}^{\mathrm{crit.}} < \chi_{23}$ the two polymers are expected to demix at some percentage composition in the undiluted system. In solution, assuming ($\chi_{12} = \chi_{13}$) the maximum polymer volume fraction at which the two polymers should be compatible is evaluated to be $v_p \sim 0.004$. This value is higher than the one obtained experimentally, $v_1 \sim 0.02$, which indicates a somewhat greater incompatibility between the two polymers. We think that this incompatibility counteracts the formation of a homogeneous phase which would be predicted by theory.

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