A study of the phase behaviour of blends of side-chain liquid crystal polymers

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The phase behaviour of mixtures of acrylate based side-chain liquid crystal polymers is examined. The constituent polymers differ only in the number of alkyl units in the coupling chain between the mesogenic units and the polymer backbone. Mixtures composed of such materials exhibit both a lower critical solution temperature in the isotropic phase range and a upper critical solution temperature in the nematic phase range. The miscibility gap for 50/50 mixtures is of the order of ~30°C but there is minimal miscibility in the nematic phase range. This behaviour is observed for both mixtures involving nematic phases with the same sign of orientational coupling between the mesogenic units and the polymer chains and mixtures involving polymers with opposite signs of coupling. There is an asymmetry in the miscibility curve for a mixture containing polymers of opposite signs of coupling.

(Keywords: phase behaviour; blends; liquid crystal polymers)

INTRODUCTION

The study of mixtures of known and unknown liquid crystal compounds is a powerful classic technique for phase identification[1]. Miscibility is a direct indication of a common phase type, whereas the observation of phase separation conveys no positive information. Traditional polymers of different chemical composition rarely show miscibility, even over a limited composition range due principally to the low entropy of mixing. This paper is concerned with the phase behaviour of mixtures or blends of side-chain liquid crystal polymers with different chemical configurations. Such side-chain liquid crystal polymers are composed of three main structural units. These are the polymer backbone, the mesogenic unit and the spacer chain which attaches the mesogenic units to the polymer backbone. In the liquid crystal phase these individual components have antagonistic tendencies since the polymer backbone is entropically driven towards a random coil type configuration, while the mesogenic units stabilize with long range orientational ordering. The chemical connectivity of the system leads to a coupling of the behaviour of the polymer chain and the mesogenic units in which the polymer chain is orientationally ordered. The polymer chain may be arranged preferentially parallel to the mesogenic units, a phase labelled as N_{III} by Warner *et al.*[2,3] or preferentially perpendicular to the mesogenic units labelled as N_I (*Figure 1*). We have shown that for a series of acrylate-based side-chain liquid crystal polymers, in which only the number of alkyl units in the coupling chain was varied, that both types of nematic phases may be observed experimentally[4,5]. In this study we examine the phase behaviour of mixtures of polymers in which the two parent polymers exhibit either N_I and N_{III} or N_{III} and N_{III} phases. Studies of low molar mass liquid crystal mixtures and polymer/liquid crystal systems have attracted attention in recent years[6–10], however there appear to be few, if any, reports in the literature of mixtures of side-chain liquid crystal polymers. Mixing of side-chain liquid crystal polymers involves additional interactions to those observed in conventional polymer blends because of the presence of the long range orientational order of the side-chain mesogenic units and their inherent connectivity with the polymer backbone. Therefore mixtures of side-chain liquid crystal polymers offer potential for new effects, such as the interaction between the nematic miscibility and the polymer backbone miscibility, and a system which is rich in phase behaviour.

EXPERIMENTAL

Materials

The basic materials used in these studies were acrylate-based side-chain copolymers in which the

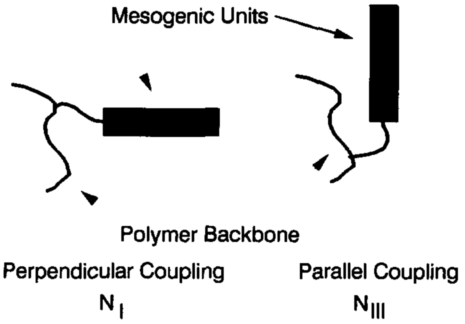

Figure 1 Schematic representation of the different coupling arrangements between the mesogenic side chains and the polymer backbone in a nematic side-chain liquid crystal polymer

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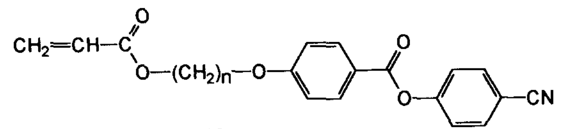
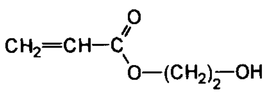
Table 1 Characteristics of the copolymers used

Polymer	Number of alkyl units in spacer unit *n*	I:II (mol%)[a]	M_w[b]	*DP*[c]	T_g (°C)	T_{NI} (°C)	Sign of coupling[d]
P3	3	94:6	8.4×10^4	249	58	100	−
P4	4	94:6	9.3×10^4	265	48	119	+
P5	5	94:6	1.0×10^5	275	33	114	−
P6	6	94:6	8.6×10^4	228	29	125	+

[a] Confirmed by proton n.m.r.
[b] Determined using g.p.c. with polystyrene standards
[c] *DP*, degree of polymerization
[d] Taken from reference 4



[I]



[II]

Figure 2 Chemical configuration of the monomers

mesogenic monomer (I) in each copolymer differed only in the number of alkyl units in the coupling chain (*Figure 2*). The other comonomer in each copolymer was a 'non-mesogenic' monomer (II) albeit at a low concentration. These copolymers were prepared using well established methods[11–15] and the basic characteristics of these copolymers are shown in *Table 1*. Each copolymer forms a single liquid crystal phase with an enantiotropic nematic–isotropic phase transition. The sign of the orientational coupling between the mesogenic units and the polymer backbone which has been established from parallel studies on crosslinked materials formed from this series of copolymers[5] is also shown in *Table 1*. A positive coupling indicates a preferential parallel alignment of the polymer backbone and the mesogenic unit while a negative coupling sign refers to a perpendicular arrangement. The glass transition temperature (T_g) falls as the number of alkyl units in the spacer chain is increased, reflecting the greater conformational freedom of the system. In contrast, the nematic–isotropic phase transition temperature (T_{NI}) fluctuates with spacer length probably as a consequence of the well known odd–even effect in liquid crystal systems[16].

Mixtures of copolymers P3 and P4 were prepared at compositions of 25/75, 50/50, 37/63 and 25/75% w/w by dissolving the two components in the required proportions in dichloromethane to form a 5% (w/w) solution. The prepared solutions were cast on a Kapton film placed inside a Petri dish. The solvent was allowed to evaporate at room temperature. When most of the solvent had evaporated, the cast film was held at 50°C for 24 h under reduced pressure to completely remove all traces of the solvent. Similar mixtures of copolymers P3 and P5 and P4 and P6 at a composition of 50/50 were prepared using the same procedure. The liquid crystal mixtures were annealed at different temperatures in the range 30–180°C using a temperature controlled oven (±1°C) for periods of ~36 h to ensure complete equilibration. These thin film samples were then quenched into air in order to freeze-in the structure of the mixtures.

Methods

The phase behaviour of the mixtures was examined between cover slips in a polarizing optical microscope equipped with a heating stage. The constituent polymer systems were very similar, particularly with regard to their optical properties, and hence it was not straightforward, especially in the liquid crystal phase, to determine whether a single phase or multiple phases were present. Since the various polymer systems exhibited somewhat different T_g values, thermal analysis was used to determine the extent of miscibility in these mixtures in a similar manner to that used for isotropic glasses formed by more traditional polymers. A single glass transition is considered as a suitable criterion for determining that a mixture forms a single miscible phase in the case of isotropic polymers[17,18]. Application of that approach to this study of side-chain liquid crystal polymers assumes that the rapid cooling which follows the annealing procedure inhibits the diffusion of chain segments and hence the quenched room temperature structure is a static replica of the molecular arrangements at the annealing temperature especially on the structural scale effectively probed by the glass transition measurements. This appears to be a reasonable assumption in the light of the relaxation times in the nematic phase range, typically ~10^5 s, measured for similar side-chain liquid crystal polymers using electro-optic procedures[19,20]. Moreover, following the quenching procedure each sample was held at temperatures well below the glass transition thereby inhibiting any further structural reorganization. The annealed mixtures were examined using a differential scanning calorimeter (Perkin–Elmer DSC-2C) equipped with a sub-ambient temperature facility employing a heating rate of 10°C min^{-1} and using a sample weight of ~5 mg. Due to the fact that subsequent cooling and heating cycles may lead to structural reorganization only one d.s.c. run was employed each time to obtain the data reported here.

BACKGROUND

The general behaviour of liquid crystal polymer mixtures has been outlined by Brochard *et al.*[21]. In their approach for a mixture of mesogens A and B the free energy of mixing (per site) may be partitioned as follows:

$$G = G_{\text{iso}} + G_{\text{nem}} \tag{1}$$

where G_{iso} describes the system without nematic order, whereas G_{nem} involves the anisotropic interactions. For the isotropic part of the free energy of mixing the Flory–Huggins approach is used and G_{iso} is given by[21]:

$$G_{\text{iso}} = kT\left[\frac{1-\phi}{n_A}\ln(1-\phi) + \frac{\phi}{n_B}\ln\phi\right] + \phi(1-\phi)\chi \tag{2}$$

where ϕ is the volume fraction of B and $n_{A,B}$ are the degrees of polymerization of each component. The first two terms represent the entropy of mixing and χ is the interaction parameter between the two components. For temperatures above the nematic–isotropic phase transition only this term needs to be considered since the long range orientational parameters S_A and S_B will be zero. For such a system the miscibility is determined by the value of χ. For a polymer system it is expected that in the isotropic phase, we shall observe a lower critical solution temperature (*LCST*), above which the mixtures exhibit almost total phase separation.

A mean field model, essentially the Maier Saupe model is used to describe the nematic part of the free energy of mixing[21]:

$$\begin{aligned} G_{\text{nem}} = {} & -T\textstyle\sum(S_A)(1-\phi) - T\sum(S_B)\phi - \frac{1}{2}U_{AA}S_A^2(1-\phi)^2 \\ & -\tfrac{1}{2}U_{BB}S_B^2\phi^2 - U_{AB}S_AS_B\phi(1-\phi) \end{aligned} \tag{3}$$

Here $\sum(S)$ is the decrease in the entropy due to the alignment of the molecules and the last three terms describe the gain in energy through orientational correlations and involve the three nematic interaction parameters U_{AA}, U_{BB} and U_{AB} and the nematic order parameters S_A and S_B. The strength of the interaction parameters for each component is directly related to the clearing temperature of that component and hence the values of U_{AA} and U_{BB} differ for the pairs of polymers considered here by ~5%. In the theoretical evaluation of Brochard *et al.*[21] only systems in which $U_{AA} = U_{BB}$ were considered. Clearly if $U_{AB} > U_{AA,BB}$ then mixing leads to enhanced order, if the reverse is true, phase separation or the suppression of the nematic phase is favoured. For typically rod-like low molar mass systems these interaction parameters may be represented by a simple anisotropic potential. For a side-chain liquid crystal polymer, the interactions involve both mesogen–mesogen and mesogen–backbone components. The mutual orientation of the polymer chain and the mesogenic units vary according to the precise chemical configuration of the coupling chain (*Table 1*). It might be expected, therefore, that systems involving different signs of coupling between the mesogenic side chain and the polymer backbone may have reduced interaction parameters, U_{AB}, compared to systems with the same sign of coupling. Of course the nature of the mesogens themselves may play the dominant role in determining the values of U_{AB}. In this study the constitution of the rigid portion of the mesogenic unit of the side-chain liquid crystal polymers remains constant, it is only the coupling chain which is varied. Moreover, we have chosen a set of polymers in which there is minimal variation in the degree of polymerization for the series of parent polymers.

RESULTS

The first set of results relate to mixtures of the side-chain liquid crystal copolymers P3 and P4. P3 has a coupling chain consisting of three alkyl units and previous studies have shown that it exhibits a N_I phase while P4 has a coupling chain with four alkyl units in it and it exhibits a N_{III} phase[4]. Optical microscopy shows that these mixtures exhibit nematic phases across the complete composition range, although there is a broad biphasic region as revealed in the phase diagram shown in *Figure 3*.

Figure 4 shows the glass transition data recorded for a series of 50/50 mixtures of P3 and P4 prepared at various annealing temperatures. It is clear that at both high and low annealing temperatures two glass transitions were recorded, which indicate the existence of phase separated structures. However, over a limited span of ~30°C, a single glass transition was recorded, the signature of a homogeneous single phase. In the temperature range over which a single glass transition was recorded, the T_g was constant. Similar profiles of the

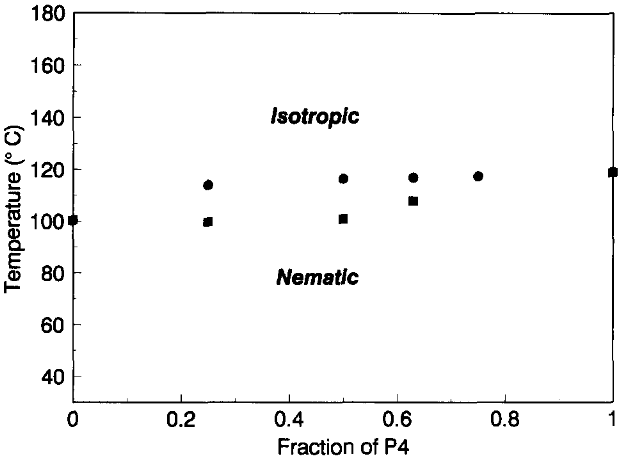


Figure 3 Nematic–isotropic phase transitions observed by optical microscopy for mixtures of P3 and P4 plotted against the mixture composition

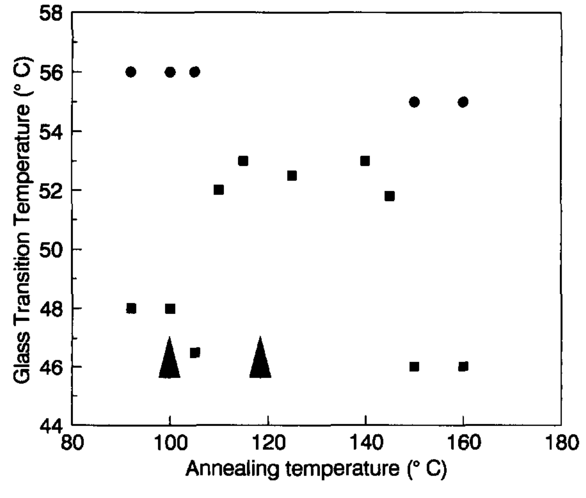


Figure 4 Glass transition temperatures recorded by d.s.c. for a series of samples of a 50%/50% mixture which had been annealed at various temperatures and then quenched to room temperature prior to the d.s.c. scan plotted against the annealing temperature. The arrows correspond to the liquid crystal–isotropic transitions observed in the optical microscope

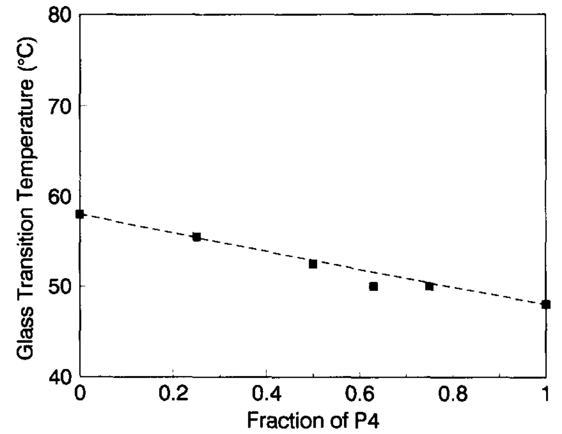


Figure 5 Glass transition temperatures recorded by d.s.c. for a series of mixtures of P3 and P4 which had been annealed at particular temperatures corresponding to the single phase region and quenched to room temperature prior to the d.s.c. scan plotted against the mixture composition

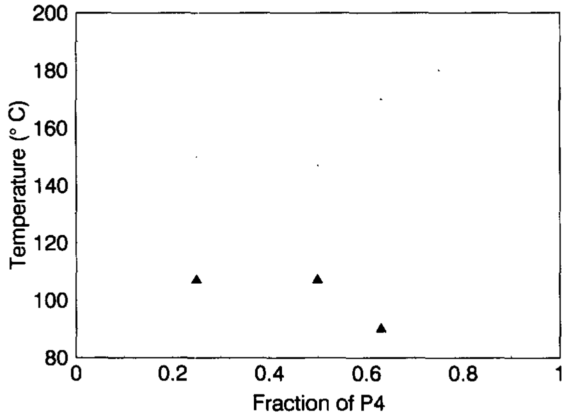


Figure 6 Plot of the upper (▲) and lower (*) critical solution temperatures derived from a study of the glass transition behaviour for a series of mixtures of P3 and P4

glass transition data against annealing temperature were recorded for mixtures of P3 and P4 at a range of compositions. *Figure 5* shows the T_g for the single phase region obtained from a series of samples annealed at different temperatures plotted against the mixture composition. For an intimate mixture of polymers the T_g is predicted by Fox[22]:

$$\frac{1}{T_g}=\frac{w_1}{T_{g1}}+\frac{w_2}{T_{g2}} \qquad (4)$$

where $T_{g1,g2}$ are the glass transition temperatures and $w_{1,2}$ are the concentrations of the two components in the mixture. The broken line in *Figure 5* shows the values expected for a miscible molecular mixture based upon the values obtained for the T_gs for the parent polymers and using equation (4). The excellent agreement confirms that in that temperature range the mixtures do indeed exhibit a single phase system.

In *Figure 6* the miscibility component of the phase diagram for the P3/P4 mixtures obtained from an analysis of the glass transition data for each composition of the mixture is presented. The diagram shows that the mixtures exhibit limited miscibility. At high temperatures clear phase separation is observed and the system exhibits a *LCST* curve which is strongly composition dependent as shown in *Figure 6*. Such behaviour is typical of many polymeric systems. Comparison of the temperature range of the *LCST* curve with the T_{NI} values shown in *Figure 3* confirms as expected that this phase separation takes place in the isotropic phase range. In fact we can use the T_g data to evaluate the composition of the two phases. Using data such as that shown in *Figure 4* and equation (3) it is clear that the mixture has separated more or less completely into the pure components. Such a complete phase separation into the pure components is a strong characteristic of polymer systems.

There is a single phase region below the *LCST* curve with a temperature span of ~30°C. At lower temperatures the mixtures exhibit a further phase separation and a composition dependent upper critical solution temperature (*UCST*) type curve is observed. Comparison of the temperature ranges with the T_{NI} values shown in *Figure 3* shows that this lower phase separation takes place at a temperature which lies in the biphasic region between the nematic and isotropic phases. Analysis of the T_g data reveals that below the *UCST* the mixture separates largely into the pure components. We have superimposed on the T_g plot for the 50/50 mixture of P3/P4, the phase transition temperatures observed in the polarizing microscope. This shows that the extent of miscibility in the nematic phase range is minimal for this composition. In contrast the mixture of P3/P4 with a composition of 25/75 does not exhibit any phase separation over the experimentally accessible temperature range which lies above the glass transition.

In order to determine whether the phase separation in the nematic phase range is due to the difference in the sign of coupling between the mesogenic unit and the polymer backbones in the two constituent copolymers, mixtures of the other copolymers shown in *Table 1* were considered. The use of the glass transition as a probe of molecular mixing is most straightforward when there is a significant difference between the T_gs of the two component copolymers. For the range of copolymers studied here, P3 and P4 may be considered ideal for this purpose, while the other copolymer pairs exhibit smaller differences between their T_gs. For this reason only the 50/50 compositions of the mixtures involving P3/P5 and P4/P6 were considered. *Table 2* shows the *LCST* and *UCST* values obtained by examination of the glass transition data for samples of those mixtures annealed at different temperatures. Essentially similar behaviour was observed for the mixtures of P3 and P5 and P4 and P6 as detailed above for the P3/P4 mixture although in both cases a reduced miscibility range was observed. In all cases miscibility in the nematic phase range was severely limited in the 50/50 mixtures.

DISCUSSION

The fact that these pairs of almost identical copolymers exhibit immiscibility in the isotropic phase is not

Table 2 *LCST* and *UCST* values for 50/50 mixtures

Polymers in 50%/50% mixture	*LCST* (°C)	*UCST* (°C)	Miscibility range (°C)
P3/P4	150	107	43
P3/P5	135	110	25
P4/P6	140	110	30

surprising. It is well established that complementary chemical structures are required to compensate for the limited contribution of the entropy of mixing in polymer mixtures. For chemically similar polymers the only interactions between chain segments of the different polymers are those arising from van der Waals type forces. These in general give rise to a positive enthalpy of mixing which would lead to immiscibility. Certainly polymers of a similar structure to those considered here but without the mesogenic side groups, such as poly(n-butyl acrylate) and poly(ethyl acrylate) and other n-alkyl acrylates and methacrylates are both immiscible in the solid state[23] and in solution[24]. The addition of the polar mesogenic units has to a certain extent stabilized the homogeneous mixtures as shown in *Figure 6*. This may be due either to the fact that such large side groups render the differences between the two polymers with various coupling chain lengths proportionally smaller, or perhaps to a stabilizing dipolar coupling between the mesogenic groups.

The theoretical study of Brochard *et al.*[21] predicts that the polymeric nature of side-chain liquid crystal polymers will severely limit the extent of miscibility in the ordered phases even for chemically similar systems. That expectation is borne out by the results reported here for the nematic phases of the acrylate-based liquid crystal polymers. If we utilize the classic view of a side-chain liquid crystal polymer as mesogenic units attached to a polymer backbone, essentially the model employed by Brochard *et al.*, then in this work the mesogenic units are equivalent. For non-polymer-based mesogens with alkyl terminal chains of broadly similar length, considerable miscibility is shown, usually a eutectic phase system is exhibited at the nematic–crystal transition, but above that a single nematic phase is observed[25]. The fact that the formation of the ordered nematic phase leads to phase separation in the side-chain liquid crystal polymer systems considered here suggests that we must consider at least the complete side chain as the mesogen, rather than simply the rigid portion although of course the differences between the mesogenic units are effectively amplified by the low entropy of mixing of the polymer backbones.

The miscibility range in the differing pairs of copolymers varies largely as a consequence of shifts in the *LCST* curve observed in the isotropic phase. These shifts appear to be a consequence of the chemical differences in the side chain rather than the small molecular weight variations. The system with the smallest difference between the spacer lengths of the constituent copolymers exhibits the highest *LCST* temperature.

It would appear that the phase behaviour as a function of composition is not symmetrical (*Figure 6*). Mixtures with a high fraction of P4 exhibit an extended miscibility range in both the nematic and isotropic phases. A similar asymmetry was observed in random copolymers formed from the same mesogenic units considered here but with either two or three alkyl units in the spacer chain[26,27]. It was found that there was a null coupling between the mesogenic units and the polymer backbone at a composition of 25/75 in terms of units with $n=2/n=3$. In other words in a random copolymer system, in which the chemical connectivity inhibits phase separation, the coupling between the mesogenic units and the polymer backbone may be considered as the weighted sum of the component couplings. At a suitable concentration systems involving units of opposite signs of coupling will exhibit a null coupling. The fact that such a null coupling composition is not at a 50/50 composition indicates that the strengths of the coupling are not equivalent, indeed it is clear that the coupling in systems with an even number of alkyl units in the coupling chains exhibits a higher level of coupling[26,27]. This arises since in a parallel configuration between the mesogenic unit and the polymer backbone, the nematic field coupling between the two adds to the influence of the chemical configuration of the coupling chain. For a perpendicular arrangement, the nematic field must reduce the strength of the coupling which arises through the spacer unit. In the mixtures studied in this work, although a miscible mixture but with a null coupling between the mesogenic units and the polymer backbones is possible, the decreased stability of the nematic phase for such a configuration might be expected to result in a phase separated structure in which the different opposing couplings may be retained. It is tempting to associate the asymmetry in the *LCST* curve with a similar null coupling composition but where the absence of any differences in the sign of ordering of the polymer backbones leads to an enhanced miscibility for the two side-chain polymers. This would suggest that there are additional contributions to the free energy of mixing over and above those considered by Brochard *et al.*[21] which take account of the mixing of differently ordered polymer chain trajectories. However, the studies on the mixtures of copolymers with the same signs of coupling, which also reveal phase separated structures in the nematic phase range for the 50/50 mixtures, demonstrate that straightforward chemical differences are as responsible for the phase separation as the differences in the coupling. This is not unreasonable given the very low level of orientational order of the backbone chain in the nematic phases of these polymers[4,5].

CONCLUSIONS

These studies have shown that even for chemically rather similar side-chain liquid crystal polymers the development of long range orientational ordering leads to almost complete phase separation in the nematic phase as predicted by the work of Brochard *et al.*[21]. This phase separation takes place whether the two component polymers have similar or dissimilar signs of coupling between the polymer backbones and the mesogenic side chains.

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