Solubility of liquid crystalline side-chain polymers in smectic A solutions

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We describe and analyse in this paper the behaviour of solutions of side-chain liquid crystalline polymers (LCP) in molecular compounds in their smectic A phases. We give evidence for a straight correlation between phase separation and the difference in smectic layer spacings of the components of the binary system. In addition, making use of materials containing fluorinated segments, we show that fluorocarbon moieties greatly enhance the incompatibility of the mixture.

1. Introduction

For a long time, electro-optical applications of liquid crystals have involved the use of mixtures of several molecular compounds for which a requisite property is the compatibility of the components, such that the system is homogeneous over the largest range of temperature. (The term molecular is used in opposition to macromolecular to differentiate these non-polymeric mesogens.) In contrast, in the new generation of displays developed from the concept of polymer dispersed liquid crystals (PDLC) [1, 2], the liquid crystal has to phase separate from a polymer based mixture in order to form micro-sized droplets. The analysis of the instability of solutions of mesogens is thus appealing in both practical and fundamental aspects (for example, the study of the dynamics of phase separation in an anisotropic medium is also of current interest [3, 4]).

So far, a limited number of systems is available on which to conduct such a study of phase separation between two mesophases of the same nature, but of different composition. Gaps of miscibility in nematic solutions of a liquid crystalline polymer (LCP) in a molecular nematogenic solvent have been the very first to be reported in thermotropic binary mixtures [5, 6, 7]. More recently, the combination of two molecular compounds has provided the first example of a gap of miscibility in a smectic A solution [8] of molecular mesogens. In the former case, the drop in the entropy of mixing associated with the macromolecular nature of the solute explains the occurrence of limited solubility [9]. Otherwise the components have not to be chemically unlike [7]. In contrast a clear difference in the chemical nature of the two molecular components seems necessary in the latter case: one of them is a so-called polar mesogen with a cyano head and the second contains a perfluorinated extremity in lieu of the usual aliphatic flexible tail [8, 10].

Making use of a set of tailor-made LCPs [11, 12] which all give a smectic A phase, in this paper, we extend these studies to the investigation of the compatibility of

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LCP-LMW pairs in a smectic A solution. The occurrence of smectic A–smectic A phase separations in these systems will be discussed with respect to (i) the role of the proportion of mesogenic side-groups, which appeared important to the solubility of a LCP in previous studies of nematic or isotropic solutions [13, 14], (ii) the role of the fluorine content of the LCP in comparison with the behaviour of fluorinated–non-fluorinated pairs of molecular mesogens, and (iii) the structure of the layers, which we reveal is strongly coupled to this type of phase separation.

2. Materials

Different types of comb-like LCPs based on a polysiloxane backbone have been prepared and used as the polymeric component in the binary systems. Their molecular structures are summarized in figure 1.

In polymers of type **1** in figure 1, the side-groups differ only in the extremity R. For each R, two compounds have been prepared, depending on the proportion of mesogenic groups and characterized by the ratio $(a/a + b) \times 100 = x$ per cent. Either x per cent = 100 per cent ($\overline{DP}_n \approx 37$) (the resulting material is a so-called 'undiluted' homopolymer) or x per cent = 30 per cent ($\overline{DP}_n \approx 29$) (the resulting material is a so-called 'diluted' copolymer). As for the variations in the end groups R these are:
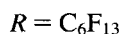
$R = C_6F_{13}$ the corresponding polymer is labelled P6, F_6 100 per cent (the polymer with x per cent = 30 per cent is not mesomorphic).
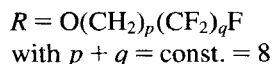
$R = O(CH_2)_p(CF_2)_qF$ the corresponding polymers are labelled P6, H_pF_q x per cent
with $p + q = \text{const.} = 8$ depending on the values x per cent.

$R = O(CH_2)_8H$ the corresponding polymers are labelled Pn, 8 x per cent. They are the analogous non-fluorinated polymers isometric with the previous ones.
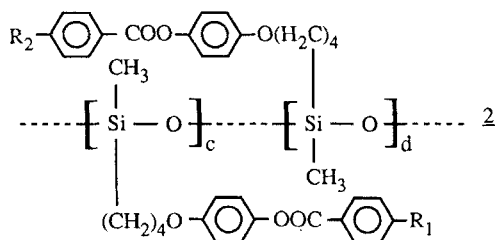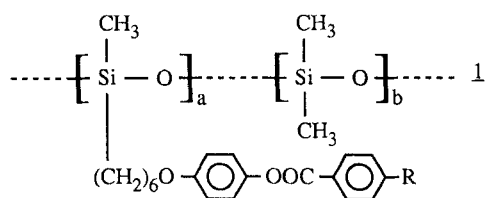

Figure 1.   Chemical structures of the two series of liquid crystalline polymers. Top: series **1** in the text; bottom: series **2** in the text.

The type **2** macromolecule in figure 1 is a copolymer combining two kinds of side-groups, a non-fluorinated one $R_1 = O(CH_2)_8H$ and a fluorinated one $R_2 = O(CH_2)_5(CF_2)_3F$. The corresponding polymers are labelled P4, $(8/H_5F_3)$ *y* per cent. The ratio *y* per cent $= (d/c + d) \times 100$ refers to the proportion of fluorinated groups in the copolymer.

All polymers share the requisite property of giving a convenient range of smectic A phase and direct clarification from the smectic A to the isotropic liquid phase. The preparation and complete characterization of the polymorphism for most of these polymers can be found in a previous paper [12] in which we also studied the structure of the layers in their smectic A phases through the measurement of the layer spacings.

Finally, we have used various non-polymeric solvents, which will be specified as needed, for the sake of obtaining a comparison of the miscibility of fluorinated LCPs and of common non-fluorinated LCPs in either fluorinated or non-fluorinated S_A solvents.
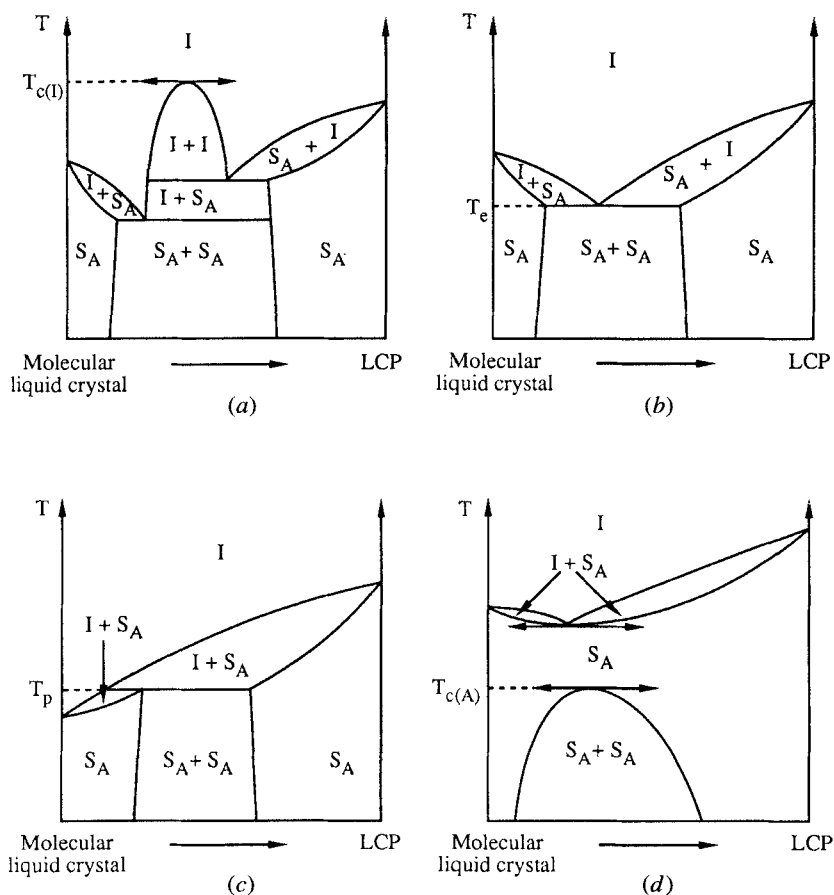

Figure 2. The four topologies leading to a gap of miscibility in the smectic A phase. (*a*) consolute point in the isotropic phase (characteristic temperature: $T_{c(I)}$); (*b*) eutectic point (characteristic temperature: T_e); (*c*) peritectic point (characteristic temperature: T_p); (*d*) consolute point in the smectic A phase (characteristic temperature: $T_{c(A)}$).

3. Experimental

To investigate the phase diagrams we have applied the classical contact method (as described in [7]) involving the use of a polarizing microscope (Olympus BH-2) equipped with long working distance objectives and a hot stage (Mettler FP 82). As for the phase separation which is of special interest in this work, this is clearly indicated by a phase line in the isotropic state and in the smectic A phase as well, provided that it occurs in a homeotropic area. It is then simple to spot precisely the temperature at which this phase line disappears, i.e. the critical temperature of the consolute point. From these observations we have been led to classify the different cases of phase separation in our systems according to four topologies which are sketched in figure 2. Each one is especially characterized by one temperature above which the two components become compatible. In two cases, this corresponds to a consolute point, either in the isotropic phase (see figure 2 (*a*)) or in the smectic A phase (see figure 2 (*d*)). In the two others, this defines either a eutectic point (see figure 2 (*b*)) or a peritectic point (see figure 2 (*c*)). Note that no composition scale is given on these diagrams, as is usual for the contact method. Consequently a few samples with fixed concentrations have been further analysed for one selected binary system, in order to obtain some information about the critical composition.
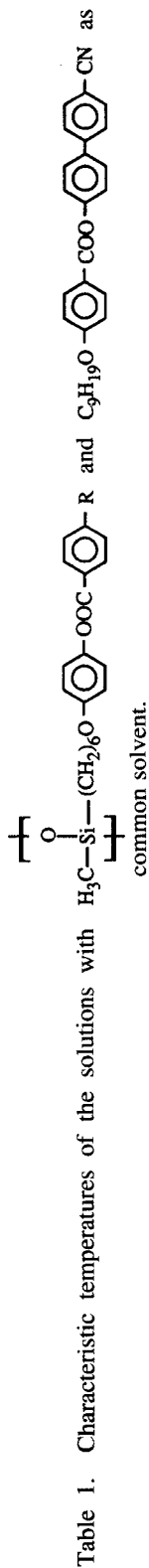
4. Results and discussion

4.1. *Influence of fluorination on the miscibility of the LCP*

This can be discussed using the temperatures at which the LCPs, x per cent = 100 per cent, with decreasing fluorine content, become compatible with the same LMW solvent, as defined above. Table 1 provides this comparison and also gives additional information about the topology of the corresponding phase diagrams. Obviously an increased content of fluorine is unfavourable to the miscibility. More generally, we observed that most systems involving a fluorinated polymer phase separate in the isotropic phase or immediately when they become smectic A. Even the occurrence of a consolute point in the smectic A phase is very rare. This comment extends also to the 'diluted' fluorinated polymers which are the first of this kind to display such a high incompatibility with a low molecular weight solvent ('dilution' was observed to improve greatly the solubility in nematic solutions [13]). This is why it becomes convenient to consider only the binary systems involving the non-fluorinated P6,8 x per cent polymers in order to discuss the other issues of this study.

4.2. *Influence of the proportion of side-groups on the miscibility of the LCP*

Qualitatively it appears that 'diluted' polymers are more soluble in a smectic A solvent than 'undiluted' polymers, whatever the nature of the mesogenic group. For example, the $P6,H_pF_q$ 30 per cent polymers show mostly eutectic topologies (see figure 2 (*b*)), whereas the analogous polymer with x per cent = 100 per cent phase separates in the isotropic phase (see figure 2 (*a*)). This greater solubility could be attributed, at least in part, to the diminishing polymer size when x decreases. Indeed if one assumes that the Flory–Huggins theory of regular solutions (zero excess entropy) applies, T_c would depend only on the molar volume v of the polymer for a given solvent

$$T_c = \lambda \frac{v_{\text{polymer}} v_{\text{solvent}}}{[v_{\text{polymer}}^{1/2} + v_{\text{solvent}}^{1/2}]^2}.$$

Table 1. Characteristic temperatures of the solutions with $H_3C-Si-(CH_2)_6O-\bigcirc-OOC-\bigcirc-R$ and $C_3H_{19}O-\bigcirc-COO-\bigcirc-CN$ as common solvent.

R	Notation	Highest temperature for phase separation/°C	Comment
$-C_6F_{13}$	P6, F₆ 100 per cent	> 250	No consolute point obtained prior to decomposition
$-O(CH_2)_4-(CF_2)_4-F$	P6, H₄F₄ 100 per cent	237	Temperature of consolute point in the isotropic phase (see figure 2(a))
$-O(CH_2)_5-(CF_2)_3-F$	P6, H₅F₃ 100 per cent	180	Temperature of eutectic point (see figure 2(b))
$-O(CH_2)_8-H$	P6,8 100 per cent	—	Full miscibility down to crystallization

Table 2.   Critical temperatures at the consolute point in solutions with

$$C_6F_{13} \text{—}\langle O \rangle\text{—} COS \text{—}\langle O \rangle\text{—} OC_6H_{13}$$
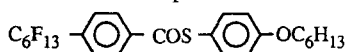
as common solvent.

Polymer notation	$T_c/^\circ C$
P6,8 100 per cent	101
P6,8 30 per cent	95

The variation of the solubility with the variation in the proportion of mesogenic groups would thus appear qualitatively analogous to a simple change in volume, provided that the interaction λ is little affected; this seems reasonable, since the chemical nature of the polymer is not fundamentally modified.

One can discuss further the modification of the solubility of a polymer in relation to 'dilution' thanks to the P6,8 100 per cent and P6,8 30 per cent polymers when employing the same solvent. A consolute point is detected in both systems in the smectic A phase (topology figure 2 (*d*)) and the critical temperature decreases with decreasing *x* per cent as shown in table 2. According to the above equation, and taking equal densities for the solvent and the polymer, we expect T_c, *x* per cent = 30 per cent = 0·8 T_c, *x* per cent = 100 per cent, i.e., T_c, *x* per cent = 30 per cent ≈ 300 K for T_c, *x* per cent = 100 per cent = 374 K. These values show a significant difference from the 6°C change actually measured.

The variation of T_c connected with a change in the size of the polymer can be qualitatively interpreted by analogy with the variation of the critical temperature with the degree of polymerization (that is the size) in Flory's theory of real macromolecular solutions. Since we have

$$\frac{1}{T_c} = \frac{1}{\theta}\left(1 + \frac{1}{\psi}\left(\frac{1}{2N} + \frac{1}{\sqrt{N}}\right)\right),$$

in which θ and N are respectively Flory's temperature characteristic of the solvent–solute interaction and the average number of repeat units in the polymer chain, a weak dependence of T_c on N means a large value of the entropic term ψ in the generalized interaction parameter χ, $\chi = (\frac{1}{2} - \psi) + (\psi\theta/T)$. In nematic solutions of side-chain LCPs, the value of ψ was previously reported to be doubled as a consequence of a coupling with the nematic order parameter [9]. Yet our miscibility studies of these nematic solutions have also shown that the drop in the critical temperature from *x* per cent = 100 per cent to *x* per cent = 30 per cent was large enough to prevent the observation of a gap of miscibility for the 'diluted' polymers [13, 15] (the available temperature range of the nematic phase of the solution, typically 30–40°C, is usually limited by crystallization well above room temperature).

One can thus infer from the above discussion that the excess entropy term is much larger in smectic A solutions and that an additional coupling with the smectic order parameter must explain this further increase of ψ in smectic A systems, as discussed in the following section.

4.3. *Influence of the layer spacings on the miscibility of the LCP*

In table 3 we have reported the values of the temperatures at the consolute point for the polymer P6,8 30 per cent combined with three homologous alkyloxy-

Table 3. Critical temperatures for P6,8 30 per cent in cyanobiphenyl solvents. See text for the definition of $|\Delta d|/d$.

nOCB	$d_{(n\text{OCB})}$/Å	T_c/°C	$|\Delta d|/d$
10OCB	34·8	57	$8·7 \times 10^{-3}$
11OCB	36·6	63	6×10^{-2}
12OCB	38·6	83	0·12

cyanobiphenyls (nOCB from Merck Ltd). There is clearly a regular increase with the number of carbons n of the aliphatic chain and consequently with the layer thickness in the smectic A phase of the cyanobiphenyl compound.

At this point it is of special interest to recall the model of microsegregation which can be applied to 'diluted' side-chain polysiloxanes [16]. We have shown for our polysiloxanes that the values of the layer spacings are consistent with this model which supposes a separation between two sublayers, one containing the non-mesogenic backbone and the other the mesogenic side-groups [12] (see figure 3).

Now let us plot, in figure 4, T_c as a function of the ratio $|\Delta d|/d$ as defined below:

$$\frac{|\Delta d|}{d} = \frac{|S_A \text{ layer spacing of } n\text{OCB} - S_A \text{ mesogenic sublayer spacing of P6,8 30 per cent}|}{S_A \text{ mesogenic sublayer spacing of P6,8 30 per cent}}$$

$$= \frac{|d_{(n\text{OCB})} - 34·5|}{34·5}.$$

The value of the sublayer spacing of P6,8 30 per cent is obtained from the X-ray measurements in [12]. It is striking from this representation that T_c approaches a minimum at $|\Delta d|/d \neq 0$, which strongly suggests that the difference in the smectic A layer spacings of the two components brings about a specific contribution to the phase separation. But it is unfortunate that decreasing further the value of n to check experimentally the existence of this minimum is impossible because of the occurrence of crystallization of the nOCB compound ($n \leq 9$).

However, such a minimum has been observed in a second set of measurements involving P6,8 100 per cent as the common polymer paired with three homologous fluorinated solvents (see table 4). The layer structures of these compounds are all monomolecular; since the mesogenic cores have same lengths in the molecular and polymeric compounds, one therefore expects the layer spacings to be comparable when $m = (6 + 8)/2 = 7$. Assuming full control of the solubility by the parameter $|\Delta d|/d$ in this series would lead to the lowest value of T_c for this value of m, instead of $m = 6$. However, we have to take into account that from one molecular solvent to the other we change not only the layer spacings, but also the number of perfluorinated methylenes. Consequently the LCP–solvent interaction is also modified in such a way that the miscibility is poorer for larger values of m. The shift of the minimum of T_c towards a lower value of m thus seems well explained by an interaction parameter involving an isotropic term (sensitive to the fluorine content) and a coupling term with the smectic A order parameter (sensitive to the difference in layer spacing).

To support further the above assumptions, we propose a last set of results obtained with the copolymers of type **2** as defined in the Materials Section. From the values in table 5, we have plotted in figure 5 on the same graph:

    (i) (full circles) the temperatures of phase separation for the polymers in a given solvent and
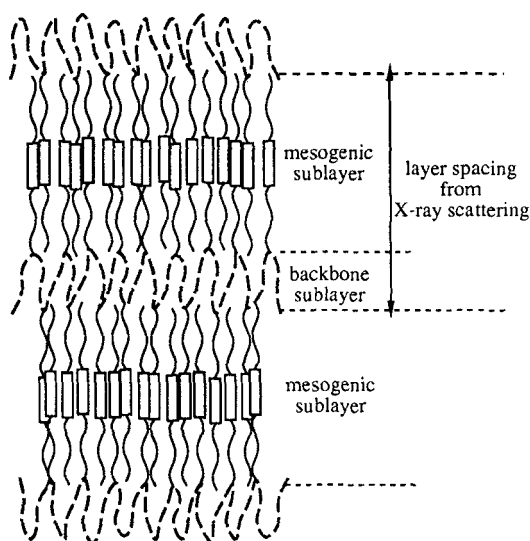
Figure 3.   Model of microsegregated layers in 'diluted' liquid crystalline side-chain polymers.
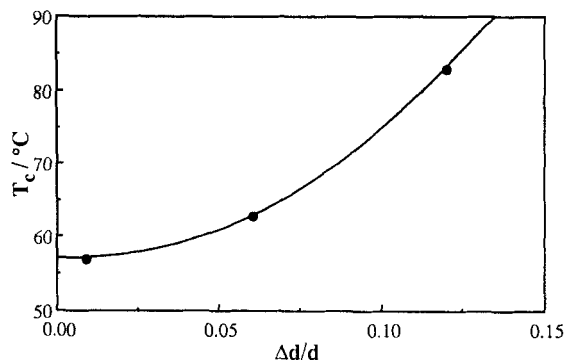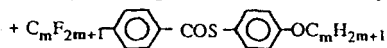

Figure 4.   Critical temperatures for P6,8 30 per cent in cyanobiphenyl solvents as a function of the reduced difference in layer spacings between the solvents and the polymer.

Table 4.   Temperatures of S_A–S_A phase separation for the binary systems P6,8 100 per cent

$$+ C_mF_{2m+1}\text{-}\bigcirc\text{- cos -}\bigcirc\text{-}OC_mH_{2m+1}$$

m	Temperature for phase separation/°C	Comment
4	114	Temperature of peritectic point (see figure 2 (c))
6	101	Temperatures of consolute points (see figure 2 (d))
7	117	

Table 5. Critical temperatures for the solutions of the copolymers with $R_1 = O$–$(CH_2)_5$–$(CF_2)_3$–F and $R_2 = O$–$(CH_2)_8$–H with

$$C_6F_{13} -\!\!\bigcirc\!\!- \cos -\!\!\bigcirc\!\!- OC_6H_{13}$$
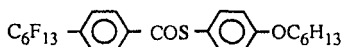
as common solvent. y per cent: proportion of R_1 versus R_2. See text for the definition of $|\Delta d|/d$.

Copolymer composition, y per cent	Sublayer spacing of copolymer/Å	$T_c/°C$	$|\Delta d|/d$
0	26·9	108	$9·1 \times 10^{-2}$
25	27·6	80	$6·7 \times 10^{-2}$
50	26·1	94	$1·18 \times 10^{-1}$
75	N.A.	107	N.A.
100	49·4	129	$6·69 \times 10^{-1}$

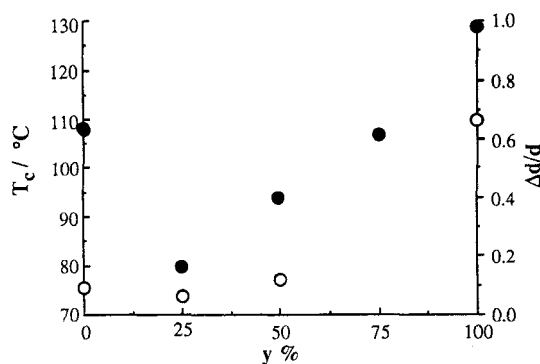N.A.: not available (see also text).

Figure 5. Left axis, full circles: temperatures of phase separation in binary systems of copolymers with variable proportion, y per cent, of fluorinated side-groups and a common fluorinated solvent. Right axis, open circles: reduced difference in layer spacings between the copolymers and the solvent as a function of y per cent.

(ii) (open circles) the parameter $|\Delta d|/d$ for the same binary systems as a function of the common variable y per cent, which represents the proportion of fluorinated side-groups in the copolymers.

Since the solvent is now the unchanged component in these mixtures, the values of $|\Delta d|/d$ are obtained as follows:

$$\frac{|\Delta d|}{d} = \frac{|S_A \text{ mesogenic sublayer spacing of P4, } (8/H_5F_3) \ y \text{ per cent} - S_A \text{ layer spacing of the solvent}|}{S_A \text{ layer spacing of the solvent}}$$

One must also emphasize that the values of the sublayer spacings of the copolymers involve some uncertainties. These arise from a very low intensity of X-rays scattered by the copolymers, ascribable to a levelling of the electron densities with the layers associated with the fluorine atoms (no Bragg scattering could be detected at all for the y per cent $= 75$ copolymer following several hours of exposure; this explains the missing values in table 5).
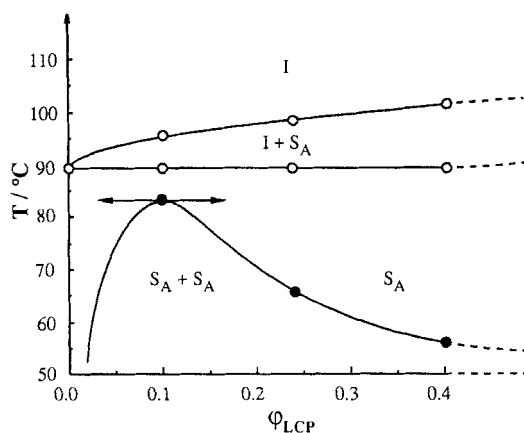
Figure 6.   Part of the composition–temperature phase diagram between 12OCB and P6,8 30 per cent. ϕ_{LCP}: volume fraction of liquid crystalline polymer.

As discussed earlier, a combination of the differences in fluorine content and in layer spacings of the components seems qualitatively to account for the evolution of the two curves. Starting from y per cent $= 0$, one observes a significant decrease in the temperature of phase separation around y per cent $= 25$, which is consistent with an improvement of the interaction between a copolymer containing fluorinated side-groups and the fluorinated solvent, together with a weak and almost constant difference in layer spacings. Approaching y per cent $= 100$, the term depending on the difference in layer spacings becomes largely dominant and the increase of T_c parallels the increase of $|\Delta d|/d$.

Altogether, these observations suggest that the best miscibility can be obtained for components having the same layer spacing in their smectic A phases. The incompatibility is enhanced either when the LCP has a larger layer thickness than the molecular solvent or the reverse case. Although these smectic A systems are fluid, obtaining homogeneous mixtures appears to be strongly dependent on this parameter which characterizes the liquid crystalline structure, in the same way that solid solutions depend on the closeness of the crystalline parameters.

4.4. Evaluation of the critical composition

We have chosen the system P6,8 30 per cent–12OCB to observe the phase separation in a few mixtures with low polymer content. The resulting portion of the phase diagram is shown in figure 6. It allows location of the critical composition, expressed in volume fraction of polymer, at $\phi_{c, exp} \approx 0.1$. Using again Flory's theory, we can evaluate the critical volume fraction from $\phi_{c, FH} = 1/\{1 + [\nu_{LCP}/\nu_{solvent}]^{1/2}\}$. Considering the densities of the LCP and the mesogenic solvent to be similar leads to $\phi_{c, FH} = 1/\{1 + [M_{LCP}/M_{solvent}]^{1/2}\} \approx 0.20$. This value is significantly larger than the experimental result. Such a discrepancy did not appear for nematic solutions of liquid crystalline polymers [17] which confirms that this model conceived for isotropic solutions is definitely not suitable for smectic A solutions.

Finally, one can discuss briefly the boundary of the gap of miscibility, narrow at the top and wider at lower temperatures. The fabric-like pattern observed when the phases separate in these mixtures, analogous to the texture described in [4] for the

spinodal decomposition in molecular smectics, strongly suggests that we actually observe a spinodal line, and not the binodal line, which would explain this unusual shape.

5. Conclusions

It is now clear that solutions of a liquid crystalline polymer in a molecular mesogen are more likely to phase separate in the smectic A phase than in the isotropic or nematic states. Indeed, we have shown that a major parameter in the phase separation process is the difference in layer spacings of the smectic A phases of the two components of the mixture. Adding a strong coupling with the smectic order parameter is obviously unfavourable to the solubility.

We can also propose that the confinement of the backbone in the smectic A state is certainly relevant in order to explain the discrepancies arising in the comparison with Flory's theory is isotropic macromolecular solutions.

The differences in the solubility parameters due to chemical differences between the side-group and the molecular solvent are also important to phase separation. This is especially true when the LCP (or to a lesser extent the molecular solvent) contains fluorinated segments; this often causes the components to phase separate at high temperature in the isotropic phase or at least to be fully immiscible in the smectic A state. In this situation gaps of miscibility can exist despite equal layer spacings.

Finally we confirm that the macromolecular nature of one component makes it easier to observe smectic A–smectic A phase separation in macromolecular solutions than in molecular solutions. For example, as described above, phase separation occurs in mixtures combining a cyano-substituted molecular compound and a LCP with a classical non-polar side-group, but this behaviour has never been reported so far for similar solutions between two molecular compounds, although large differences in layer spacings might exist in these systems as well. (Note however that phase separation between a fluorinated and a cyano compound is common to either case.) From this point of view, some phase diagrams of this type could usefully be revisited.

References

[1] DOANE, J. W., WEST, J. L., WHITEHEAD JR, J. B., and FREDLEY, D. S., 1990, *SID 90 Digest*, p. 224.

[2] See also DOANE, J. W., 1991, *Liquid Crystals, Applications and Uses*, edited by B. Bahadur (World Scientific Singapore), Chap. 14. DOANE, J. W., 1991, *MRS Bull.*, **16**, 22.

[3] CASAGRANDE, C., VEYSSIE, M., and KNOBLER, C. M., 1987, *Phys. Rev. Lett.*, **58**, 2079.

[4] SIGAUD, G., GARLAND, C. W., NGUYEN, H. T., ROUX, D., and MILNER, S. T., 1993, *J. Phys. II*, **3**, 1343.

[5] RINGSDORF, H., SCHMIDT, H. W., and SCHNELLER, A., 1982, *Makromolek. Chem., Rap. Commun.*, **3**, 745.

[6] CASAGRANDE, C., VEYSSIE, M., and FINKELMANN, H., 1982, *J. Phys. Lett.*, **43**, L-371.

[7] SIGAUD, G., ACHARD, M. F., HARDOUIN, F., MAUZAC, M., RICHARD, H., and GASPAROUX, H., 1987, *Macromolecules*, **20**, 578.

[8] SIGAUD, G., NGUYEN, H. T., ACHARD, M. F., and TWIEG, R. J., 1990, *Phys. Rev. Lett.*, **65**, 2796.

[9] SIGAUD, G., ACHARD, M. F., HARDOUIN, F., COULON, C., RICHARD, H., and MAUZAC, M., 1990, *Macromolecules*, **23**, 5020.

[10] TWIEG, R. J., BETTERTON, K., DIPIETRO, R., GRAVERT, D., NGUYEN, C., NGUYEN, H. T., BABEAU, A., DESTRADE, C., and SIGAUD, G., 1992, *Molec. Crystals liq. Crystals*, **217**, 201.

[11] LAFFITTE, J.-D., 1992, Ph.D. Thesis, Université Bordeaux I, No. 856.

[12] LAFFITTE, J.-D., MAUZAC, M., TWIEG, R. J., NGUYEN, H. T., and SIGAUD, G., 1994, *Liq. Crystals*, **16**, 223.

[13] HARDOUIN, F., SIGAUD, G. KELLER, P., RICHARD, H., NGUYEN, H. T., MAUZAC, M., and ACHARD, M. F., 1989, *Liq. Crystals*, **5**, 463.

[14] NGUYEN, H. T., ACHARD, M. F., HARDOUIN, F., MAUZAC, M., RICHARD, H., and SIGAUD, G., 1990, *Liq. Crystals*, **7**, 385.

[15] RICHARD, H., MAUZAC, M., SIGAUD, G., ACHARD, M. F., and HARDOUIN, F., 1987, *Liq. Crystals*, **9**, 679.

[16] DIELE, S., OELSNER, S., KUSCHEL, F., HISGEN, B., RINGSDORF, H., and ZENTEL, R., 1987, *Makromolek. Chem.*, **188**, 1993.

[17] CASAGRANDE, C., GUEDEAU, M. A., and VEYSSIE, M., 1987, *Molec. Crystals liq. Crystals, Lett.*, **4**, 107.