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Liquid Crystals

Publication details, including instructions for authors and subscription information:

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To cite this Article Chen, Fu-Lung and Jamieson, A. M.(1993) 'Odd-even effect in miscibility of main-chain liquid crystal polymers with low molar mass nematogens', *Liquid Crystals*, 15: 2, 171 – 183

To link to this Article: DOI: 10.1080/02678299308031948

URL: <http://dx.doi.org/10.1080/02678299308031948>

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Odd-even effect in miscibility of main-chain liquid crystal polymers with low molar mass nematogens

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(Received 22 December 1992; accepted 18 March 1993)

Qualitative phase diagrams were constructed using the contact method for binary mixtures of several chemically-distinct low molar mass nematogens (LMMN) with a main chain liquid crystal polymer (TPB- x) which has a mesogenic group, 1-(4-hydroxy-4'-biphenyl)-2-(4-hydroxy phenyl) butane, separated by flexible alkyl spacers of variable length, x . Several interesting effects were observed. TPB- x was found to exhibit an odd-even variation in miscibility in the nematic state ($2n + 1 =$ miscible, $2n =$ immiscible) with 4'-pentyl-4-cyanobiphenyl (5CB), but not with 4'-pentyloxy-4-cyanobiphenyl (5OCB) in which most polymers were completely miscible. On prolonged isothermal annealing in the biphasic region in 5CB, TPB- $2n$ exhibited spherulitic crystallization of the liquid crystal polymer. These observations are shown to be qualitatively consistent with a modification of the Flory-Huggins theory by Brochard *et al.*

1. Introduction

The fact that a single chemical compound cannot fulfil the liquid crystal materials specifications for even the simplest type of electro-optic display makes it of interest to understand the thermodynamic properties, specifically the phase diagrams or miscibility behaviour of mixtures of mesogens. The features of such phase diagrams can be elucidated either by using the technique of thermal optical analysis [1-4] or by the contact method [5]. The major advantage of the latter technique is that the quantity of material needed is very small. However, only the qualitative features of the phase diagram can be obtained by this approach. Recently, the contact method has been successfully used to identify mesophases in liquid crystal mixtures [6], to measure the critical temperatures in nematic-nematic phase separation [7, 8], to characterize the upper stability limit of an induced smectic A phase [9], and to determine the Flory interaction parameters of solutions of liquid-crystalline side chain polymers in low molecular weight liquid crystals [10]. Concerning the thermodynamics and phase behaviour of liquid crystal mixtures, several theories have been proposed. Among these, Flory and co-workers [11-16] first provided a theoretical framework for the thermodynamics of mixtures of rod-like polymer molecules of varying flexibility. Brochard *et al.* [17] extended the Flory-Huggins theory to mixtures of flexible nematic chains dissolved in a low molar mass nematogen (LMMN), by incorporating additional enthalpic contributions which took the form of Maier-Saupe potential terms [18].

The odd-even effect in the clearing temperatures of mesogenic molecules containing linear alkyl spacers is a well-known phenomenon [19, 20] resulting from differences

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in conformations between the odd and even spacers [21]. However, only one brief report [22] of an odd–even effect in the miscibility of nematic mixtures is known to the authors. In the investigation described here, we apply the contact method to explore the miscibility of a class of mainchain liquid crystal polymers (LCP), TPB- x , which consist of rigid mesogens separated by flexible alkyl spacers of variable length, x , in several chemically distinct LMMNs. This class of main chain LCP was discovered and extensively characterized by Percec *et al.* [23], and shows a strong odd–even effect in the clearing temperatures. From our experiments, we find that this main chain LCP also exhibits an odd–even effect in its miscibility with 4'-pentyl-4-cyanobiphenyl (SCB), but not with 4'-pentyloxy-4-cyanobiphenyl (5OCB). We demonstrate that these observations can be qualitatively interpreted by a modification of the Flory–Huggins theory developed by Brochard *et al.* [17] for LCP–LMMN mixtures. Furthermore, information on the LCP–LMMN nematic interaction energy can also be extracted from our results using this theory.

2. Experimental

2.1. Materials

The main chain LCP, TPB- x , consists of a mesogenic unit, 1-(4-hydroxy-4'-biphenyl)-2-(4-hydroxyphenyl) butane, separated by flexible alkyl spacers of variable length, x . Specimens of this main chain LCP were supplied to us by Professor Virgil Percec (Case Western Reserve University). The chemical structure, phase transition temperatures and molecular weights are shown in figures 1 and 2 and table 1,

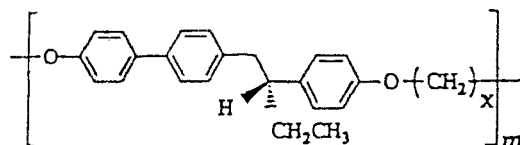


Figure 1. The chemical structure of TPB- x . A racemic mixture of this species was studied.

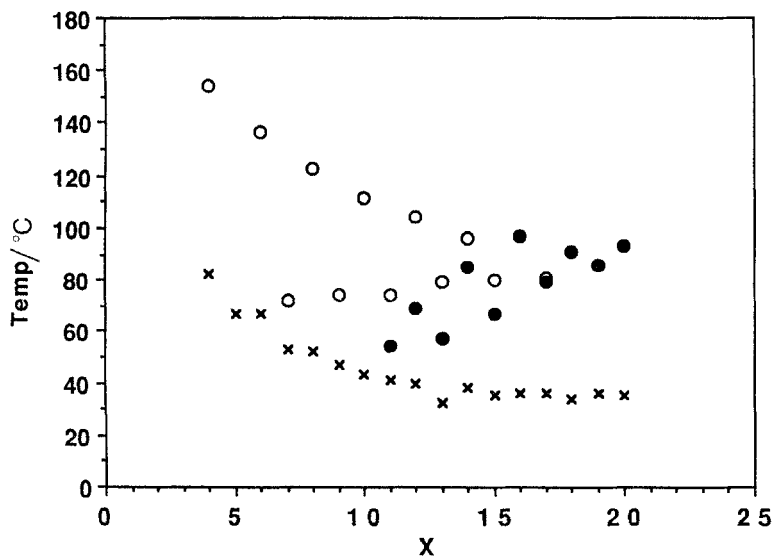


Figure 2. Phase transition temperatures of TPB- x . Data were from the second heating scan (after [23]). \circ , T_{NI} ; \bullet , T_C ; \times , T_g .

Table 1. Molecular weights of TPB-x. These data were measured by GPC using chloroform as a solvent and polystyrene as a standard [23].

X	4	6	7	8	9	10	11	13	14	15
$M_n \times 10^{-4}$	1.5	1.7	1.5	2.2	2.6	2.9	2.0	3.4	3.0	3.0
M_w/M_n	1.8	1.7	2.4	2.5	3.0	2.9	2.1	2.3	2.2	2.1

respectively [23]. 4'-Pentyl-4-biphenylcarbonitrile (5CB, $T_{NI}=35^\circ\text{C}$) and 4'-octyl-4-biphenylcarbonitrile (8CB, $T_{NI}=40^\circ\text{C}$) were from BDH chemicals. 4'-Pentyloxy-4-biphenylcarbonitrile (5OCB, $T_{NI}=67^\circ\text{C}$) and *N*-(4-methoxybenzylidene)-4'-butylaniline (MBBA, $T_{NI}=40^\circ\text{C}$), were from the Aldrich Chemical Company. All the materials were used as received without further purification.

2.2. Contact method

The procedures used to characterize the phase diagrams of the mixtures were as follows. (1) A small amount of the LCP was placed between a polyimide-treated cover glass slide and a clean glass slide as substrate in a hot stage. (2) The temperature was raised above the clearing temperature of the LCP and the sample temperature maintained until the LCP became sufficiently thin. (3) The LMMN was introduced via capillary action to form a mixing zone at its nematic temperature. (4) The mixing zone was observed with an optical polarizing microscope. The equipment used consisted of a Carl Zeiss optical polarizing microscope, a Mettler FP 82 hot stage and a Mettler FP 80 central processor. By varying temperature while observing the mixing zone, the evolution of different phases could then be observed. More specifically, the specimen was heated to above the LCP clearing temperature at a heating rate of $10^\circ\text{C min}^{-1}$, followed by cooling to 2°C above the lower bound of the nematic phase of the LMMN at the maximum cooling rate of the hot stage. To increase the width of the mixing zone for immiscible mixtures which exhibit more complex morphology, the specimen was held for 10 min above the LCP clearing temperature. For miscible mixtures, the heating rates used to observe phase evolutions were $0.2^\circ\text{C min}^{-1}$ below and 1°C min^{-1} above the LMMN clearing temperature. For immiscible systems, the heating rates were the same except for 2°C min^{-1} above the LMMN clearing temperature. After quenching from above the LCP clearing temperature, specimens which exhibited immiscibility were also annealed at temperatures in the biphasic region to ensure reaching the equilibrium state. Such experiments showed that LCP crystallization occurs in the biphasic region on prolonged annealing.

3. Results and discussion

Four classes of phase diagram, summarized by photographs of the mixing zone under the cross-polarizing microscope, shown in figures 3–6, were observed in our study. Note that the positions of specimens in figures 3–5 remain unchanged when comparing micrographs at different temperatures. In case 1 (see figure 3), no miscibility gap can be found over the entire nematic range and the nematic–isotropic transition boundary moves continuously from the right polymer-poor side toward the left polymer-rich side as the temperature is increased. On the left hand side of figure 3, the pure LCP shows as a dark domain under cross polarizers since its birefringence is very weak. Also, the boundary between the LCP and the nematic mixture moves to the left

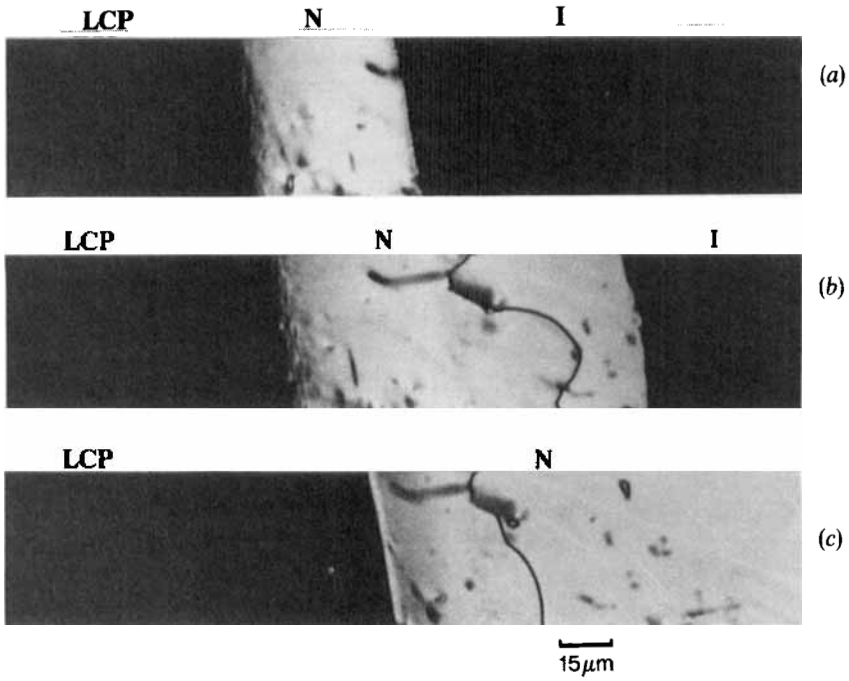


Figure 3. Phase evolution corresponding to case 1 for the binary mixture of TPB-7/5CB, viewed by optical microscopy under cross polarizers. (a) $T = T_3 = 45^\circ\text{C}$, (b) $T = T_2 = 38.1^\circ\text{C}$, (c) $T = T_1 = 26.0^\circ\text{C}$.

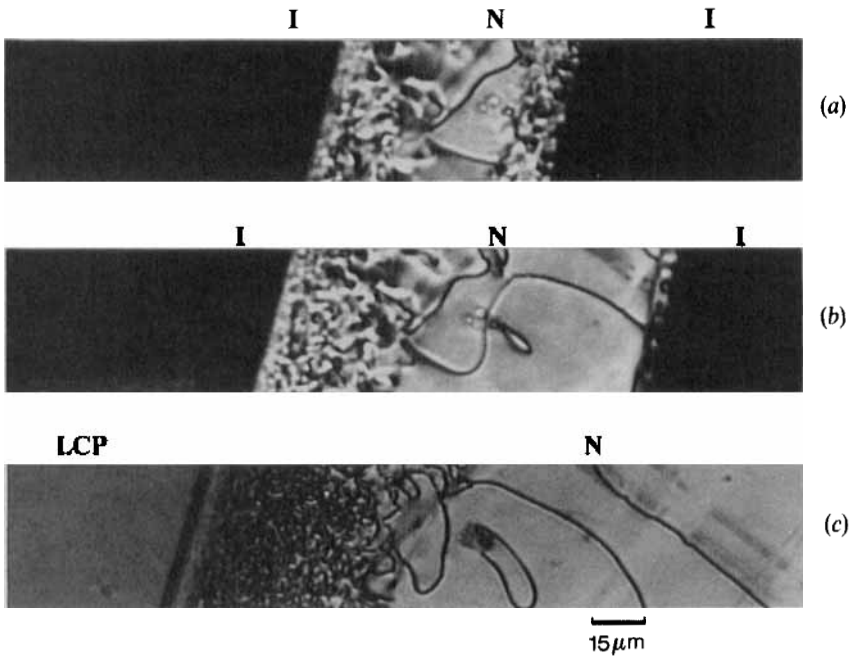


Figure 4. Phase evolution corresponding to case 2 for the binary mixture of TPB-7/5OCB, viewed under cross polarizers. (a) $T = T_3 = 68.3^\circ\text{C}$, (b) $T = T_2 = 67.9^\circ\text{C}$, (c) $T = T_1 = 50.0^\circ\text{C}$.

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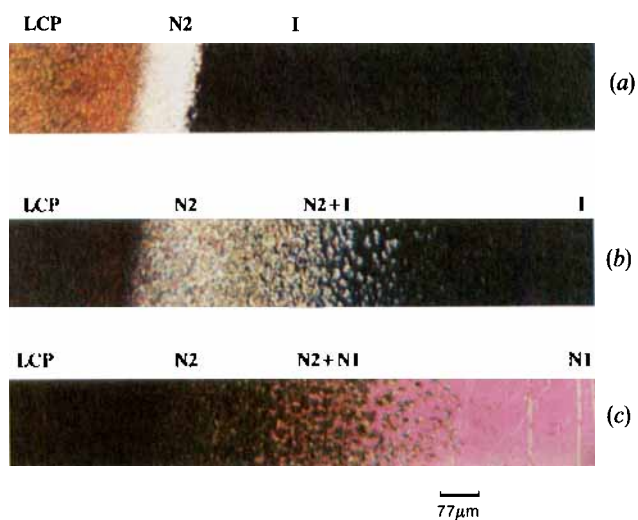


Figure 5. Phase evolution corresponding to case 3 for the binary mixture of TPB-4/5OCB, prior to annealing viewed under cross polarizers. (a) $T = T_3 = 110.0^\circ\text{C}$, (b) $T = T_2 = 79.5^\circ\text{C}$, (c) $T = T_1 = 63.1^\circ\text{C}$.

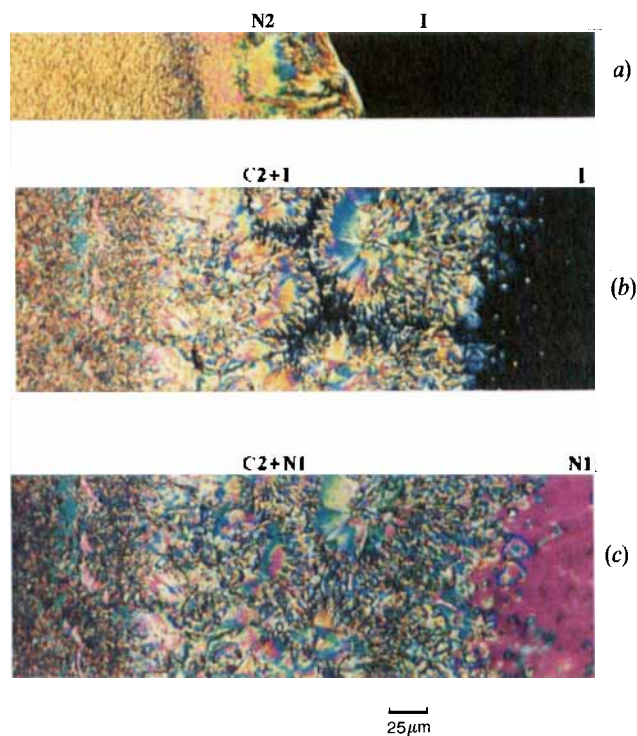


Figure 6. Phase evolution corresponding to case 4 for the binary mixture of TPB-8/5CB, annealed for 50 h at 28°C , viewed under cross polarizers. (a) $T = T_3 = 100.0^\circ\text{C}$, (b) $T = T_2 = 50.0^\circ\text{C}$, (c) $T = T_1 = 34.0^\circ\text{C}$.

as the temperature is raised because of continuous interdiffusion. Above the clearing point of the LMMN, a dark region appears on the right-hand side of figure 3(b), corresponding to isotropic LMMN, and gradually moves to the left-hand side (see figure 3(a)) as the temperature increases. By observing the evolution of these phases with temperature, and invoking the phase rule, the qualitative features of the corresponding phase diagram can be constructed and are shown in figure 7 where T_1 , T_2 and T_3 indicate schematically the temperatures at which figures 3(c), (b) and (a) were recorded respectively. In case 2 (see figure 4), again no miscibility gap can be observed over the entire nematic range. However, in this system the nematic mixture is stable, over a certain range of compositions, above the clearing point of the LCP. Thus, we see two nematic-isotropic transition boundaries which move toward each other as the temperature is raised further. This situation corresponds to the formation of an azeotrope. The corresponding phase diagram is displayed in figure 8 where again T_1 , T_2 , and T_3 indicate temperatures where figures 4(c), (b) and (a) were recorded.

In case 3 (see figure 5), a miscibility gap is found in which two nematic liquid crystal phases coexist, and which intercepts but does not cross the nematic-isotropic spindle. N1, the polymer-poor nematic phase, is visible in figure 5(c) as the purple field on the right-hand side. On raising the temperature, the N1-isotropic boundary appears on the right-hand side and moves to the left, invading the region where domains of the polymer-rich, N2, nematic phase exist, visible as bright birefringent particles in figure 5(b). At still higher temperatures, in figure 5(a), the N2-isotropic boundary moves to the left. The corresponding phase diagram is shown in figure 9. In case 4 (see figure 6), spherulites can be observed in the biphasic zone. The boundaries of the spherulites are clearly evident in figure 6(b). If we use an untreated cover glass slide instead of the polyimide-treated cover glass slide, as shown in figure 10, the Maltese cross patterns of the spherulites under crossed polarizers can be observed. In principle, these spherulites could be either pure polymer or a solid solution of LCP with LMMN. However, because of the chemical dissimilarity of the LCP and the LMMN, and since we find that in fact these solution-grown crystals have higher melting temperatures than those of the bulk crystallized LCP, we deduce that the spherulites must be pure

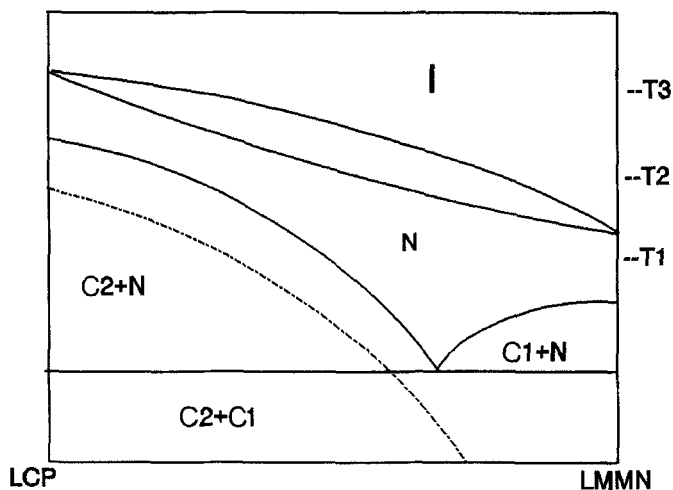


Figure 7. The case 1 phase diagram. The presence of the glass transition, shown as a dashed line, will prohibit the phase evolution.

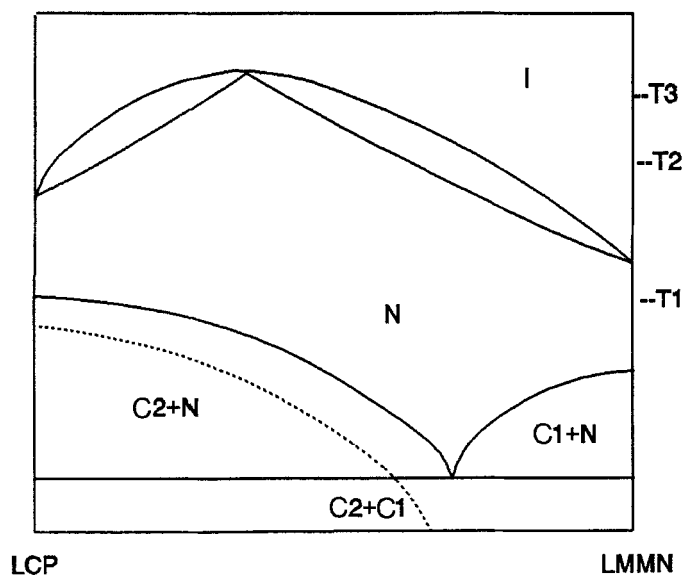


Figure 8. The case 2 phase diagram. The presence of the glass transition, shown as a dashed line, will prohibit the phase evolution.

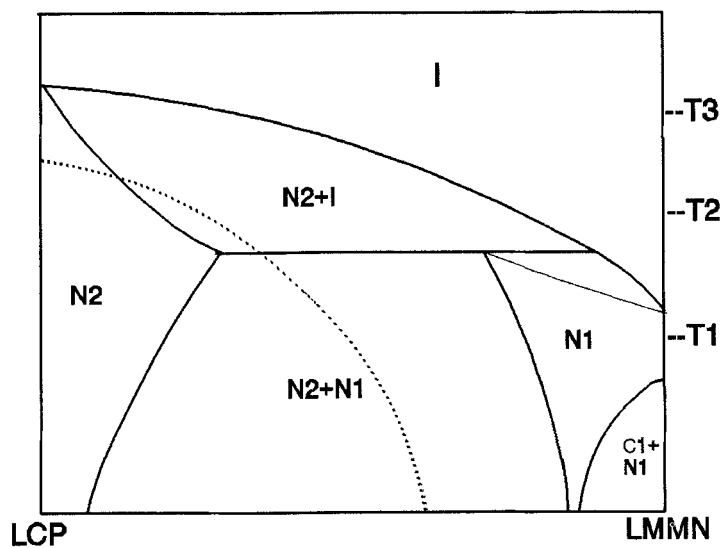


Figure 9. The case 3 phase diagram. The presence of the glass transition, shown as a dashed line, will prohibit the phase evolution.

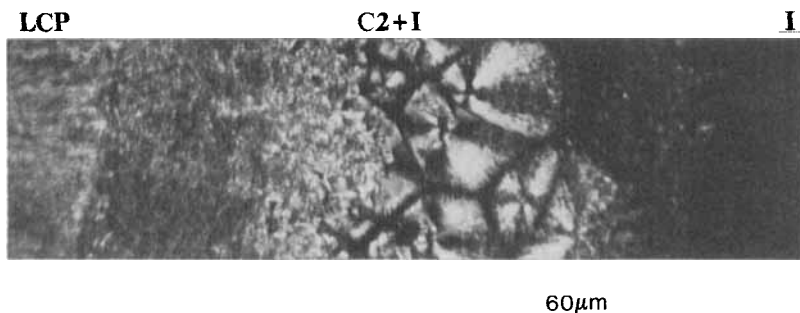


Figure 10. The Maltese cross patterns of the spherulites viewed between clean cover glass slides under cross polarizers in TPB-8/5CB at 45°C after being annealed for 50 h at 28°C.

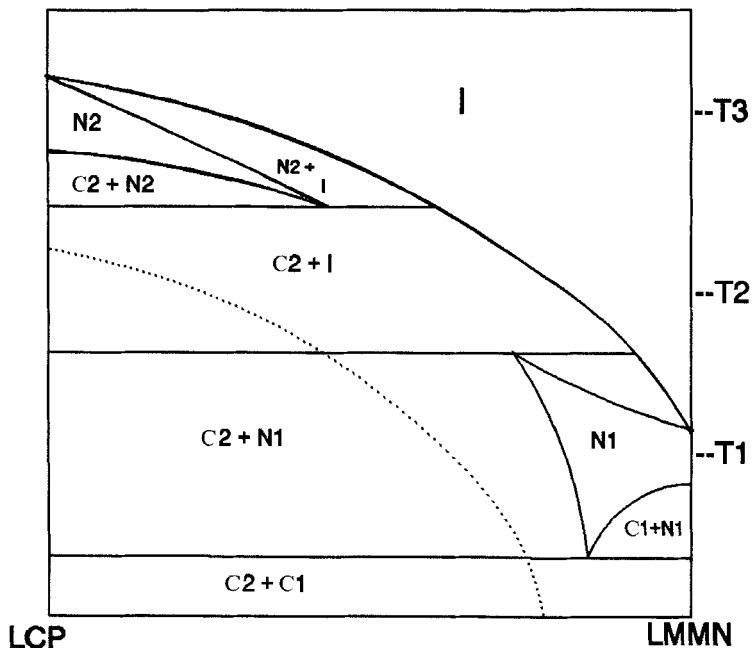


Figure 11. The case 4 phase diagram. The presence of the glass transition, shown as a dashed line, will prohibit the phase evolution.

LCP. Figure 11 shows the corresponding phase diagram. Note that, in addition to the distinctive evidence for formation of spherulites, the larger super heating effect, and the inability to mechanically deform the crystalline domains, enable us to clearly distinguish between nematic and crystal phases.

In table 2, we list the various LCP/LMMN combinations that belong to each class of phase diagrams. First, we note that case 4 diagrams are generally obtained from case 3 diagrams on annealing. As expected, we find that the annealing conditions are strongly dependent upon the LCP spacer length. For example, we were unable to see any crystals formed when TPB-4/5OCB was annealed at 51°C for 12 hours, but we did see spherulites appear when it was annealed at 100°C for 4 hours. The most difficult

Table 2. Classification of phase diagrams of TPB-*x* in LMMN mixtures. Brackets denote without annealing.

Phase diagram	System
Case 1	TPB-7/5CB, TPB-9/5CB, TPB-11/5CB TPB-13/5CB, TPB-15/5CB, TPB-6/5OCB TPB-8/5OCB, TPB-10/5OCB TPB-14/5OCB, TPB-7/8CB, TPB-11/MBBA
Case 2	TPB-7/5OCB, TPB-9/5OCB, TPB-11/5OCB TPB-13/5OCB, TPB-15/5OCB
Case 3	(TPB-4/5CB), (TPB-4/5OCB) (TPB-6/5CB), (TPB-8/5CB), (TPB-10/5CB) (TPB-14/5CB), (TPB-10/MBBA) (TPB-8/8CB)
Case 4	TPB-4/5CB, TPB-4/5OCB, TPB-6/5CB, TPB-8/5CB TPB-10/5CB, TPB-14/5CB

Table 3. The annealing conditions to reach the equilibrium state of case 4.

System	Annealing conditions	
	Temperature/°C	Time held/h
TPB-4/5CB	85	14
	100	4
	110	2
TPB-4/5OCB	85	14
	100	4
	110	2
TPB-6/5CB	50	30
	70	24
TPB-8/5CB	28	50
	45	21
TPB-10/5CB	40	48
TPB-14/5CB	35	48

system to crystallize is TPB-14/5CB in which spherulites can only be obtained from 5CB-rich compositions in the biphasic region, and the annealing temperature must be below 50°C. Typical annealing conditions, at which crystallization occurs, are summarized in table 3. Note from this table that the annealing temperature must be raised as the spacer length decreases. This is consistent with the decreasing flexibility of the LCPs at shorter spacers, manifested in the higher glass transition temperatures (T_g) (see figure 2). Thus, for each mixture which exhibits a case 4 phase diagram, we always find a precursor (metastable) case 3 phase diagram because of the kinetic retardation of the crystallization process due to the high viscosity of the concentrated N2 nematic phase. Note also, that TPB-4, TPB-6, TPB-8 and TPB-10, which do not crystallize in the

bulk state due to the proximity of T_g (see figure 2), do crystallize from the mixtures since T_g is lowered in the presence of the LMMN. Furthermore, table 3 indicates that the melting point of the solution-crystallized LCP's are higher than those of the bulk-crystallized, as evidenced by the fact that the crystallization temperature, 110°C, of TPB-4 in 5CB or 5OCB, is higher than the melting point of TPB-4 in the bulk state, 85°C. A further point to be made here is that we find the miscibility of TPB-2*n* in 5OCB decreases as the spacer length decreases such that the C2+N boundary of TPB-6/5OCB (case 1, figure 7) is very close to the nematic-isotropic spindle and hence the eutectic temperature is comparatively high (>40°C). A further comment about this will be made later.

Of particular interest is our observation that this main chain LCP shows a strong odd-even effect in its miscibility with 5CB but not with 5OCB. Specifically, in 5CB, *x*-odd shows case 1 while *x*-even shows case 3/case 4. In 5OCB all TPB-*x* species show case 1 or case 2, with the sole exception of TPB-4 which shows case 3/case 4. Note that all these polymers are miscible in the isotropic state, therefore we deduce that demixing occurs because of a change in free energy in the nematic state. Initially, it seems inexplicable that such a dramatic difference should exist between TPB-4/5OCB (immiscible) and TPB-6/5OCB (miscible), or between TPB-*x*/5CB (odd-even) and TPB-*x*/5OCB (all miscible). However, recent studies in the literature find large differences, ranging up to 30°C, in the critical temperatures for nematic-nematic phase separation of LCP/LMMN mixtures, which merely result from a change in aliphatic carbon content in the LMMN solvent, $C_7H_{15}O-p-C_6H_4CO_2-C_{10}H_6-OC_nH_{2n+1}$, from *n* = 10 to 11 [10]. Thus, the phase diagram behaviour is in fact very sensitive to small changes in LMMN and, presumably also in LCP structure. It follows, therefore, that our results are, in fact, not so surprising as will now be discussed in detail.

To interpret our experimental observations, we use an extension of the Flory-Huggins theory by Brochard *et al.* [17]. We first recall the essential features of this theory and then we derive criteria of miscibility applicable to our systems. Brochard *et al.* [17] derived the following expression for the excess free energy of mixing of an LCP/LMMN mixture, identifying A=LMMN and B=LCP

$$\delta G_m/RT = (\phi/N_B) \ln \phi + ((1-\phi)/N_A) \ln(1-\phi) + (\bar{U}_0/RT)\phi(1-\phi), \quad (1)$$

where $N_A = 1$ and $N_B = N = \text{LCP degree of polymerization}$, ϕ is the LCP volume fraction, and the A-B exchange interaction energy in the nematic phase, \bar{U}_0 , is given by

$$\bar{U}_0 = U + 0.5U_{AA}S_A^2 + 0.5U_{BB}S_B^2 - U_{AB}S_AS_B. \quad (2)$$

Here U_0 is the A-B exchange interaction energy in the isotropic phase, and the remaining terms are the corresponding exchange interaction in the nematic phase, consisting of a sum of Maier-Saupe interaction terms, such that S_A and S_B are the order parameters of A and B respectively, and U_{AA} , U_{BB} and U_{AB} are the binary contact interaction energies in the nematic state of A to A, B to B and A to B, respectively. As shown by Brochard *et al.* [17], U_{AA} and U_{BB} can be expressed as $4.54RT_A$ (where $T_A = T_{NI}$ of pure A) and $4.54RT_B$ (where $T_B = T_{NI}$ of pure B), respectively. S_A and S_B are functions of T/T_A , T/T_B , U_{AB}/U_{AA} , U_{AB}/U_{BB} and the LCP volume fraction, ϕ , and can be evaluated by minimization of the excess nematic free energy. Note that equation (1) formally neglects any contribution to configurational entropy due to changes in polymer chain anisotropy in the nematic state. For our experiments in which demixing occurs at very low polymer volume fraction, ϕ , such contributions are unimportant.

For dilute mixtures, where $\phi \approx 0$ and when $T \approx T_A$, S_A and S_B can be expressed by the following equations [17]:

$$S_A = 0.429 = \text{order parameter of pure A at } T_A, \quad (3)$$

$$S_B = S_A U_{AB}/U_{AA} \quad \text{if} \quad U_{AB} \lesssim U_{AA}. \quad (4)$$

Under these conditions, we can write down criteria for miscibility at $\phi \approx 0$ and $T \approx T_A$. First, we define the gain in enthalpy due to mesogen alignment as

$$\Delta = \bar{U}_0 - U_0 = 0.5 U_{AA} S_A^2 + 0.5 U_{BB} S_B^2 - U_{AB} S_A S_B. \quad (5)$$

Inserting the relations of equations (3) and (4), equation (5) becomes

$$\Delta = 1.9477R [0.5 T_A - (U'_{AB}/T_A)(1 - 0.5 T_B/T_A)], \quad (6)$$

where U'_{AB} is $U_{AB}/4.54R$. For TPB- x /5CB, which shows a change from miscibility to immiscibility as the spacer length changes from odd to even, the only difference between even and odd polymers in equation (1) is the magnitude of Δ . Therefore it is quite clear that Δ plays the key role in determining the miscibility of LCP/LMMN mixtures. From the requirement that, for miscibility, $\bar{U}_0/RT \leq \chi_c$, and, for immiscibility, $\bar{U}_0/RT > \chi_c$, where

$$\chi_c = 0.5 + 1/N^{0.5} \quad (7)$$

and N is the polymer degree of polymerization, we have the criterion for miscibility

$$\Delta \leq \chi_c R T_A - U_0. \quad (8)$$

Equations (6) and (8) indicate that an odd-even effect in miscibility can occur at $\phi \approx 0$ and $T \approx T_A$ if there is an odd-even effect in T_B . For our systems, the value of T_B/T_A is less than 2. Therefore, if U'_{AB} is too small (≈ 0), no odd-even effect in miscibility will be found. Likewise, if U'_{AB} is too large, an odd-even effect in miscibility will not be possible. In summary, to have an odd-even effect in miscibility, a certain combination of T_A , U'_{AB} and T_B is necessary. In addition to equations (6) and (8), the criteria, $U'_{AB} > U'_{AA}$ and $U'_{AB} > U'_{BB}$, must be added for those systems which show an azeotrope (case 2 phase diagram) [17].

Our experimental results show that immiscibility occurs in very dilute solution, at $\phi < 0.01$. Also, the nematic-isotropic transition temperatures of the N1 phase of highest LCP concentration in the phase diagrams for case 3 and case 4 are almost identical to that of the pure LMMN. These facts make it reasonable to interpret our results by criteria of miscibility at $\phi \approx 0$ and $T \approx T_A$. Under these conditions, upper or lower bounds for the LCP-LMMN nematic interaction energy, U'_{AB} , can be extracted for each system provided we specify χ_c and U_0 in equation (8). For illustrative purposes, and since solubility parameter calculations, by the method of Small [24], indicate similar values for 5CB and 5OCB, we set $U_0 = 0.5RT_A$ (5CB) for both mixtures. Also, since all TPB- x polymers used have similar N , we set $\chi_c = 0.5$. With these assumptions, we find miscibility when $\Delta \leq 0$ and immiscibility when $\Delta > 0$ for TPB- x /5CB. In contrast, we find miscibility when $\Delta \leq 16R$ and immiscibility when $\Delta > 16R$ for TPB- x /5OCB. Based on these criteria, values of U'_{AB} for TPB- x /5CB and TPB- x /5OCB can be computed and are listed in table 4. From table 4, it is clear that we can choose a single value for U'_{AB} of TPB- $2n$ /5CB and TPB- $2n+1$ /5CB, viz. $333 \leq U'_{AB} < 344$, and the odd-even effect can be rationalized solely on the basis of the odd-even variation of the LCP clearing temperature, T_B . Likewise, complete miscibility of all TPB- x in 5OCB, including immiscibility for $x=4$, can be explained by

Table 4. The TPB- x /LMMN nematic interaction energy, U'_{AB} , of TPB- x /5CB and TPB- x /5OCB.

System	U'_{AB}/K	System	U'_{AB}/K
TPB-4/5CB	< 393	TPB-4/5OCB	< 385
TPB-6/5CB	< 377	TPB-6/5OCB	≥ 372
TPB-7/5CB	≥ 328	TPB-7/5OCB	> 345
TPB-8/5CB	< 364	TPB-8/5OCB	≥ 363
TPB-9/5CB	≥ 330	TPB-9/5OCB	> 347
TPB-10/5CB	< 356	TPB-10/5OCB	≥ 356
TPB-11/5CB	≥ 330	TPB-11/5OCB	> 347
TPB-13/5CB	≥ 333	TPB-13/5OCB	> 352
TPB-14/5CB	< 344	TPB-14/5OCB	≥ 347
TPB-15/5CB	≥ 333	TPB-15/5OCB	> 353

choosing a single larger value of U'_{AB} , $372 \leq U'_{AB} < 385$. We thus infer U'_{AB} for TPB- x with 5OCB is larger than for TPB- x with 5CB, which implies that the gain in enthalpy, Δ , is smaller for TPB- x with 5OCB than with 5CB, i.e. the absence of an odd–even effect in TPB- x /5OCB occurs because TPB- x is more compatible in the nematic state with 5OCB than with 5CB. Finally, it is appropriate to explain why the miscibility of TPB- $2n$ with 5OCB decreases as the spacer length decreases, whereas the miscibility decreases as the spacer length increases for TPB- $2n + 1$ with 5CB [22]. For TPB- $2n$, the clearing temperature, T_B , decreases significantly with the spacer length so that Δ diminishes with spacer length (see equation (6)), i.e. the miscibility in 5OCB increases with the spacer length. In contrast, for TPB- $2n + 1$, the clearing temperature slightly increases, and hence there is an increase in Δ , leading to a decrease in the miscibility as the spacer length increases.

4. Conclusion

We have provided further evidence that the contact method can be applied to elucidate the qualitative features of the phase diagrams of LCP–LMMN mixtures. The main chain liquid crystal polymer, TPB- x , was found to exhibit an odd–even effect with respect to x in miscibility with 5CB but was completely miscible with 5OCB, except for $x = 4$. All of these observations are in agreement with criteria of miscibility at $\phi \approx 0$ and $T \approx T_A$ derived from an extension of the Flory–Huggins theory by Brochard *et al.* [17]. From these criteria, we conclude that three parameters, namely the clearing temperatures of LMMN and LCP, T_A and T_B , and the nematic interaction energy, U'_{AB} , control the miscibility of LCP in LMMN. Furthermore, upper and lower bounds to U'_{AB} can be extracted using our experimental results and the theoretical miscibility criteria. From the computed U'_{AB} , we find that the odd–even effect can be interpreted simply as resulting from the odd–even variation of the LCP clearing temperature, if we choose a single value for U'_{AB} of TPB- $2n$ /5CB and TPB- $2n + 1$ /5CB. Likewise, the miscibility characteristics of TPB- x for all x in 5OCB can be explained if we choose a single value U'_{AB} of TPB- x /5OCB which is larger than that of TPB- x /5CB.

We would like to thank Professor Virgil Percec, at Case Western Reserve University, for kindly supplying the main chain LCP. Also, we thank Mr Pat Dunn, at Kent State University, for the courtesy of polyimide-coated glass. Finally, financial support from the NSF Science and Technology Center (ALCOM) DMR 89-20147 and NSF Materials Research Group DMR 01845 is gratefully acknowledged.

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