by Dr. W. J. Jackson and H. F. Kuhfuss.

Registry No. (*p*-Acetoxybenzoic acid)(ethylene glycol)(terephthalic acid) (copolymer), 52237-98-6.

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Relationships between Molecular Structure and Immiscibility of Liquid Crystalline Side-Chain Polymers in Low Molecular Weight Nematic Solvents

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ABSTRACT: The so-called "contact method" is used to investigate the problems of incomplete miscibility newly encountered in binary solutions of liquid crystal side-chain polymers and low molecular weight (LMW) nematogenic compounds. We first demonstrate the possibilities and the limits of this technique applied to the observation of the phenomenon of phase separation in these systems. Then we analyze how the critical demixing temperature is influenced by various modifications of the molecular structure of the polymer solute and of the LMW solvent. The experimental results are interpreted in order to specify the relevant solute–solute, solvent–solvent, and solute–solvent interactions. We infer from this discussion that the solute–solvent interactions are favored by more flexible mesogenic parts in the liquid crystalline polymer and, in contrast, by stiffer LMW molecules.

Introduction

Prior to the discovery of polymers with mesomorphic properties, no example was known of a gap of miscibility in binary mixtures of liquid crystals. Furthermore the properties of easy miscibility have been long and widely applied to characterize the nature of the mesophases by using a reference method.[1,2]

Thus a novel difficulty was introduced in the study of phase diagrams of liquid crystals by the first discovery of a nematic–nematic immiscibility in binary systems of side-chain polymers with low molecular weight (LMW) mesogens by Casagrande et al.[3]

Such an incompatibility does not seem to be really outstanding, and numerous cases of liquid–liquid immiscibility are obvious. One must consider, however, that among the hundreds or even thousands of binary phase diagrams of liquid crystals studied previously this behavior was never before observed. One can contrast the chemical vicinity of the components of most mixtures, but even when two very different nematogens are associated, such as a rodlike mesogen with a disklike one, this usually generates the disappearance of the nematic properties.[4]

The mechanism of this phase separation has been explored experimentally in order to discover whether it is a spinodal decomposition or not.[5] In addition, theoretical calculations varying interactions between the two components have been used to describe the behavior of such binary solutions.[6] We propose an experimental study in which we outline what kinds of interactions would be relevant in this phenomenon.

For this purpose we have first chosen an experimental means of investigation for this peculiar immiscibility property: the phase diagrams are observed by using the contact method in order to determine the critical temperature T_c below which the domain of the homogeneous nematic phase is divided by a gap of miscibility. These choices concerning the method are discussed and substantiated in the Experimental Section. The various classes of binary diagrams are also described in this section.

Starting from a large family of side-chain polysiloxanes with liquid crystalline (LC) properties, we have varied the nature of the low molecular weight (LMW) nematogen used as solvent. In each case the critical demixing temperature is measured. These results are presented in the second part of the paper. Finally, use is made of these results to estimate what chemical parameters are more likely to induce a phase separation.

Experimental Section

To describe the contours of the gap of miscibility, the simplest method would be elaboration of homogeneous binary mixtures with fixed fractions X in polymer units, studying their evolution with decreasing temperature (e.g., by means of light scattering) in order to determine the temperature of the phase separation as performed by Casagrande et al.[3] and Benthack-Thoms and Finkelmann.[7] Such an approach appeared absolutely unthinkable to us: the study under consideration in this paper implies dozens of variations of the constituents of the binary mixture. This would require hundreds of mixtures in order to draw precisely enough the demixtion curve for all the systems. Consequently, one needs a large quantity of each compound (at least 1 g) and a great deal of time because of the difficulties in getting well-homogenized

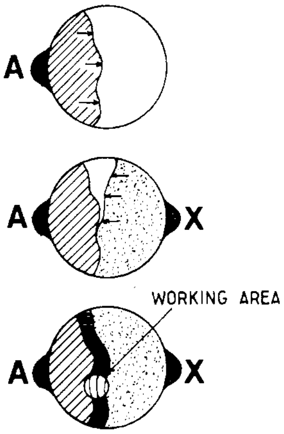


Figure 1. Preparation of a sample in the contact method: (a) melting of compound A at T_{mA} (T_m: melting temperature); (b) melting of compound B at $T_{mB} < T_{mA}$; (c) sample ready to observe. The circled zone is the working area.

samples and the slow kinetics of the phase separation.

Thus we have applied the so-called "contact method"[8] to obtain rapid sketches of phase diagrams of liquid crystals. It provides us with the main characteristic temperatures and rules out most of the drawbacks mentioned above.[9]

In order to describe the binary phase diagram between two compounds (say, A and B), it is necessary to perform a preliminary and separate observation of each one at the polarizing microscope to note the temperatures of the different phase transitions (melting, i.e., crystal to mesomorphic; clearing, i.e., mesomorphic to isotropic liquid; and all other phase changes among the various mesomorphic states that can occur between melting and clearing). The key point of this method is the peculiar preparation of the sample (Figure 1).

A small amount of the compound with the highest melting temperature (A, for instance) is deposited on the edge of a cover slip lying on a glass slide. The compound is gradually heated by moving the slide on a heating bench (Kofler type) up to the melting temperature (T_{mA}, Figure 1, top) at which the viscosity of the mesomorphic state is usually low enough to allow a capillary flow between the cover slip and the glass plate. (In fact, the correct use of the viscosity is very important to obtain a good preparation. In the case of polymers, which are much more viscous in the melt than LMW compounds, this material must be deposited on the glass slide and then squeezed to obtain a sufficiently thin film.) With some experience, one can easily operate in such a way that the space under the cover slip is not completely filled. The sample is removed from heat and cooled to room temperature. Now the same operation is realized on the opposite side of the cover slip with compound B, which has a lower melting temperature (T_{mB}). Once B flows in the free space it meets A (Figure 1, middle), and at that time a slight diffusion of one in the other occurs. This small domain of mixing (Figure 1, bottom) exhibits all the molar fractions for the binary system, and a microscopic investigation of this portion of the sample as a function of temperature is sufficient to obtain the thermodynamic characteristics of the phase diagram. It is only a matter of careful observation of the behavior of the equilibrium lines separating two different phases: the direction of their shifts gives the sign of the slopes and the temperatures at which they join, vanish, or split indicate special locations such as triple points or extrema. The major advantage of this technique for our study lies in the two following points: (1) The quantity of each compound consumed is about 1 mg. (2) Although there exists a continuous diffusion of matter from one side of the sample to the other, which is more or less important according to the temperature and the nature of the phases, the phase lines are fundamentally equilibrium sites at the considered temperature and pressure. Thus the thermal characteristics collected from these lines are the real thermodynamical constants for the studied diagram.

The counterpart of the advantages of this contact method is that we have no scale to measure the corresponding molar fractions. The influence of this parameter cannot be evaluated through these experiments.

How does this technique apply to the specific problem of measuring the critical temperature T_c defining the extremum of the phase separation curve? Experimentally, the phase separation between two nematic domains at $T < T_c$ appears as a domain of perturbed texture extending on both sides of a frontier line (Figure 2a). As the temperature increases, the demixing part gets smaller and the line alone remains (Figure 2b). With further increase of T, this line ultimately vanishes (Figure 2c), resulting in one single homogeneous nematic domain. Now the nematic phases of the polymer and the LMW compound are totally miscible. The temperature at which the line is lost to view is thus taken as the critical temperature T_c. The schematic diagram of Figure 3a depicts this kind of observation.

In some cases the dividing line remains beyond the nematic to isotropic phase change (Figure 2d). Hence it separates two isotropic liquids; in a similar way the critical temperature at which they become totally miscible is picked up when the line disappears. The diagram corresponding to this demixing in the isotropic phase is represented in Figure 3b.

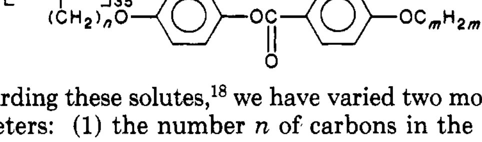
An intermediate case occurs when the gap of miscibility intercepts but does not cross the spindle of nematic–isotropic coexistence. No critical temperature can be assigned to this case, as is obvious in Figure 3c. Mention must be made also of the case with two compounds that are totally miscible over all the range of stability of the nematic phase (Figure 3d). Moreover, only the phase separation between two nematic or isotropic phases can be clearly characterized. We are unable to measure a critical temperature when smectic phases are arising.

We have shown that T_c is readily accessible by this method in most cases, but X_c, the corresponding critical concentration for the polymer at the consolute point, is not. X_c, as estimated from earlier experimental studies[3,7] and our own results on binary mixtures with fixed fractions in polymer units,[10] is about 0.1 and is a barely varying parameter. These observations are consistent with the network theory developed by Brochard et al.[6] in which X_c depends only on the degree of polymerization. Other general models proposed to describe the process of phase separation show similarly the invariability of X_c, its value resulting only from the choice of the entropic term.[11]

Since in our study the polymer compounds all have the same degree of polymerization, the critical molar fraction can be considered constant. X_c being unknown but constant, it becomes clear that T_c is the only relevant parameter accounting for the interactions between the polymer and the LMW compound (solute and solvent, respectively, since around T_c we have seen that $X_{c,pol} = 0.1$) and can be regarded as a quantity related to the solubility of this solute in the solvent: the higher T_c, the poorer the solubility of the polymer and vice versa. This remark is illustrated in Figure 4, where a molecular parameter concerning either the solute or the solvent is specifically and regularly varied.

Results and Discussion

A. Results. Our present work has been done with a family of mesogenic poly(methylsiloxanes) for which we have published the main thermodynamic and structural properties elsewhere.[12]



Regarding these solutes,[18] we have varied two molecular parameters: (1) the number n of carbons in the alkoxy spacer that links each side group to the polysiloxane backbone and (2) the number m of carbons in the "free" alkoxy chain at the other end of the side group (Figure 5a).

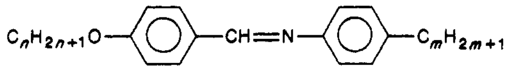
Table I lists these solutes and indicates their polymorphism. Furthermore, the solvents have been chosen in order to evaluate the solubility of the polymer as a function of the typical characteristics of a LMW nematogen, i.e., the number of carbons in the flexible aliphatic chains and their nature (alkyl or alkoxy) and the size and nature of

Table I
Transition Temperatures for the Poly(methylsiloxanes) Substituted with 4-Alkoxyphenyl Esters of *p*-Alkoxybenzoic Acids[12]

			phase transition temp,[a] °C				
$P_{n,m}$	*n*	*m*	S		N		I
$P_{3,1}$	3	1	.	119	—		.
$P_{4,1}$	4	1	.	74	.	104	.
$P_{5,1}$	5	1	.	122	—		.
$P_{6,1}$	6	1	.	109	—		.
$P_{10,1}$	10	1	.	133	—		.
$P_{4,2}$	4	2	.	113	.	127	.
$P_{4,3}$	4	3	.	115	.	122	.
$P_{4,4}$	4	4	.	144	—		.
$P_{4,8}$	4	8	.	133	—		.

[a] I: isotropic phase. N: nematic phase. S: smectic phase. A period (.) indicates the phase exists; a dash (—) indicates the phase does not exist.

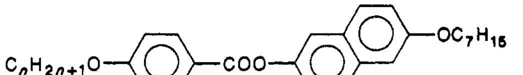
Table II
Transition Temperatures for the Series of Alkoxybenzylidene-*p*-alkylanilines[13]



			phase transition temp,[a] °C				
*n*O*m*	*n*	*m*	S		N		I
304	3	4	.	19.8	.	53.2	.
404	4	4	.	45.8	.	75.2	.
504	5	4	.	52.1	.	68.9	.
604	6	4	.	69.4	.	77.0	.
704	7	4	.	64.0	.	71.4	.
804	8	4	.	80.8	—		.
505	5	5	.	52.6	.	77.4	.
506	5	6	.	61.0	.	72.9	.
507	5	7	.	63.8	.	77.8	.
508	5	8	.	66.5	.	73.9	.
705	7	5	.	80.0	.	83.0	.
707	7	7	.	83.5	.	83.8	.

[a] Symbols have same meaning as in Table I.

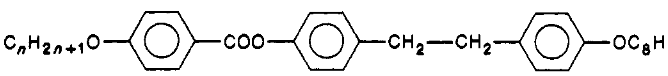
Table III
Transition Temperatures for the Series of 6-(Heptyloxy)-2-naphthyl *p*-Alkoxybenzoates[14]



	phase transition temp,[a] °C				
n	S		N		I
4	—		.	135	.
6	—		.	121.6	.
7	—		.	132.8	.
8	.	77.0	.	132.7	.
9	—		.	129.5	.
10	.	98.4	.	129.5	.
11	.	103.5	.	125.6	.
12	.	107.9	.	125.0	.

[a] Symbols have same meaning as in Table I.

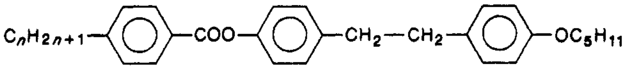
Table IV
Transition Temperatures for the Series of 2-(*p*-(Octyloxy)phenyl)-1-(*p*-((alkoxybenzoyl)oxy)phenyl)ethanes[15]



	phase transition temp,[a] °C				
n	S		N		I
4	.	86.5	.	148.0	.
6	.	109.0	.	143.0	.
7	.	118.0	.	140.0	.
8	.	124.0	.	139.0	.
9	.	133.0	.	141.0	.
10	.	136.0	.	140.0	.

[a] Symbols have same meaning as in Table I.

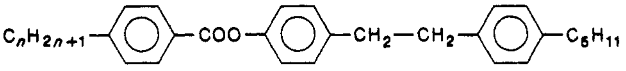
Table V
Transition Temperatures for the Series of 2-(*p*-Pentylphenyl)-1-(*p*-((alkylbenzoyl)oxy)phenyl)ethanes[16]



	phase transition temp,[a] °C				
n	S		N		I
3	—		.	113.0	.
5	.	75.0	.	110.0	.
6	.	84.0	.	103.0	.
7	.	88.0	.	106.5	.
8	.	92.0	.	102.5	.

[a] Symbols have same meaning as in Table I.

Table VI
Transition Temperatures for the Series of 2-(*p*-Pentylphenyl)-1-(*p*-((alkoxybenzoyl)oxy)phenyl)ethanes[16]



	phase transition temp,[a] °C				
n	S		N		I
3	—		.	123.5	.
4	—		.	138.0	.
5	—		.	127.5	.
6	.	59.0	.	122.5	.
7	.	81.0	.	128.0	.
8	.	95.0	.	130.0	.
10	.	111.0	.	125.0	.
11	.	120.0	.	123.0	.

[a] Symbols have the same meaning as in Table I.

the rigid core (Figure 5b). Taking advantage of the hundreds of liquid crystalline materials that have been synthesized the past years in our laboratory,[14–16] we have selected the five series listed in Tables II–VI.

Most of the binary diagrams coupling these solutes and solvents have been analyzed according to the method described above. The critical temperature of the phase separation has been noted when it exists. Tables VII–XI are a condensed picture of these observations: each location in a table corresponds to the behavior observed for one binary system between a polymer solute (columns) and a LMW solvent (rows). D_n stands for a phase separation occurring in the nematic domain (see Figure 3a). The corresponding critical temperature T_c is given. D_i indicates a phase separation in the isotropic state (see Figure 3b) for which a critical temperature is also reported. NA (for not available) corresponds to the third case in the first part (see Figure 3c). M means that both compounds appear totally miscible over all the range of the isotropic and nematic phases (see Figure 3d).

However, these results are not directly meaningful in this form, and the consequences of the chemical variations on the solvents or the solutes can be better evaluated from the following discussion.

B. Discussion. How can we connect the analysis of our experimental results to the theory of Brochard et al.?[6]

Table VII
Miscibility Behavior and Critical Temperatures (°C) for Binary Systems of Polymer P with Compounds of Table II[a]

*n*O*m*	P3,1	P4,1	P5,1
3O4	M	M	M
4O4	D_n 70.5	D_n 50.0	D_n 48.7
5O4	NA	D_n 64.0	D_n 56.8
6O4	NA	D_n 76.0	D_n 74.0
7O4	NA	NA	NA
8O4	NA	D_i 129.0	NA
5O5	NA	D_n 75.0	
5O6	D_i 71.0	D_n 101.6	NA
5O7	D_i 77.9	NA	NA
5O8		D_i 144.0	NA
7O5	NA	D_i 131.0	NA
7O6	D_i 80.3	D_i 152.0	NA
7O7		D_i 177.0	D_i 84.1

[a] D_n: the demixting occurs in the nematic state. D_i: the demixting occurs in the isotropic state. NA: not available (see Figure 3c). M: miscibility over all the isotropic and nematic states.

Table VIII
Miscibility Behavior and Critical Temperatures (°C) for Binary Systems of Polymer P with Compounds of Table III[a]

n	$P_{3,1}$	$P_{4,1}$	$P_{4,2}$	$P_{4,3}$	$P_{4,4}$	$P_{4,8}$	$P_{6,1}$	$P_{10,1}$
4		M						
5	D_n 100	M						
6	D_n 120	D_n 57	M	M	M	M	D_n 81	M
7	D_n 127	D_n 92	D_n 75	D_n 71	M	M	D_n 99	M
8	D_n 139	D_n 108	D_n 91	D_n 86	D_n 83	M	D_n 108	M
9	D_i 150	D_n 121	D_n 104	D_n 99	D_n 94	M	D_n 117	M
10	D_i 162	D_i 133	D_n 113	D_n 109	D_n 104	M	D_n 127	M
11	D_i 191	D_i 149	D_n 122	D_n 116	D_n 108	M	NA	M
12	D_i 225	D_i 180	D_i 133	D_n 124	D_n 116	M	NA	M

[a] Symbols have same meaning as in Table VII.

Table IX
Miscibility Behavior and Critical Temperatures (°C) for Binary Systems of Polymer P with Compounds of Table IV[a]

n	$P_{4,1}$	*n*	$P_{4,1}$
3	M	7	NA
4	D_n 88	8	D_i 140
5	D_n 108	9	D_i 165
6	D_n 118	10	D_i 193

[a] Symbols have same meaning as in Table VII.

Table X
Miscibility Behavior and Critical Temperatures (°C) for Binary Systems of Polymer P with Compounds of Table V[a]

n	$P_{4,1}$	*n*	$P_{4,1}$
3	M	7	D_i 149
5	D_n 95	8	D_i 170
6	NA		

[a] Symbols have same meaning as in Table VII.

Table XI
Miscibility Behavior and Critical Temperatures (°C) for Binary Systems of Polymer P with Compounds of Table VI[a]

n	$P_{4,1}$	*n*	$P_{4,1}$
5	D_n 74	8	D_n 117
6	D_n 88	10	D_i 186
7	D_n 110	11	D_i 209

[a] Symbols have same meaning as in Table VII.

We recall that in this latter work the reduced critical temperature in the nematic phase is expressed as

$$\theta_c^{\text{nem}} = \theta_c \tilde{U}_0 / U_0 \qquad (1)$$

where θ_c is the reduced temperature for the consolute point in the isotropic phase

$$\theta_c = kT_c/U_0$$

$$\tilde{U}_0 = U_0 - U_{AB}S_AS_B + \tfrac{1}{2}U_{AA}S_A^2 + \tfrac{1}{2}U_{BB}S_B^2 \qquad (2)$$

A represents the LMW solvent and B the polymer solute. (The basic mesogenic units A and B are assumed to be of similar size.) S_A and S_B are the corresponding order parameters, and U_{AA}, U_{BB}, and U_{AB} are the nematic interaction parameters. These last three parameters are positive. U_0 is the A–B pair interaction energy which controls the miscibility in the isotropic phase. $\tilde{U}_0$ is the effective interaction parameter which controls the miscibility in the nematic phase. Thus the variation of θ_c^{nem} depends mainly on this last parameter.

In Figures 6–9 we have reported the variations of T_c according to the modifications of the molecular parameters of the LMW solvents and of the polymer solutes. In this form these figures help in the discussion of the evolutions of T_c in two different ways: (1) At constant polymer, i.e., U_{BB} is fixed. (a) Varying the solvent within a given series, we consider that U_{AA} does not vary much from one homologue to the other (this assumption seems reasonable since T_{NI} (temperature of the nematic to isotropic phase transition) does not vary significantly within each family of solvent used (see Tables II–IV). It follows that the driving term in $\tilde{U}_0$ is then $-U_{AB}S_AS_B$. (b) When the solvent is varied from one series to the other, U_{AA} cannot be considered constant, and $\tilde{U}_0$ will be modified according to the set of two terms $-U_{AB}S_AS_B + {}^1/_2U_{AA}S_A^2$. (2) At constant LMW solvent, i.e., U_{AA} is fixed, the polymers which are necessarily taken in the only family that we studied are varied. Therefore U_{BB} will be considered roughly constant for the same reason that led us to consider U_{AA} poorly modified in a given family. So, $-U_{AB}S_AS_B$ is again the most efficient term in this case.

Finally, one can note in every case that switching from a phase separation occurring in the nematic phase to a phase separation occurring in the isotropic phase is smooth (see Tables VII–XI). This can be interpreted as the influence of an anisotropic interaction term in the mixing enthalpy which controls the miscibility in the isotropic phase: in other words, when the phase separation occurs not too far from the nematic phase, the value of the temperature of the consolute point is modified by the nematic fluctuations, which are not taken into account in the theory.

1. **Influence of the Length of the Aliphatic Chains of the Solvent.** Figure 6 represents the evolution of the critical temperature of phase separation as a function of the total number of carbon atoms in the two aliphatic tails of the LMW solvent at constant solute $P_{4,1}$. Full circles correspond to critical temperatures in the nematic phase, and crosses correspond to critical temperatures in the isotropic phase (the same comment will apply to Figures 7–9).

It is conspicuous that, whatever the family of solvent is (U_{BB} is fixed and U_{AA} is slightly modified), the lengthening of the chains leads to a clear increase of the critical temperature (the increment of T_c per additional CH_2 group being similar from one series of solvents to another). Thus this experimental result means that the enlargement of the flexible part of the solvent makes U_{AB} decrease since U_0 increases. That is, the interactions between the solvent and the solute are not favored by an increase of the aliphatic part of the molecules of solvent.

2. **Influence of the Nature of the Core of the Solvents.** The core is essentially a stiff part with regard to the chains. Thus, the results of Figure 6 can be discussed as for the chains, considering a more or less large degree

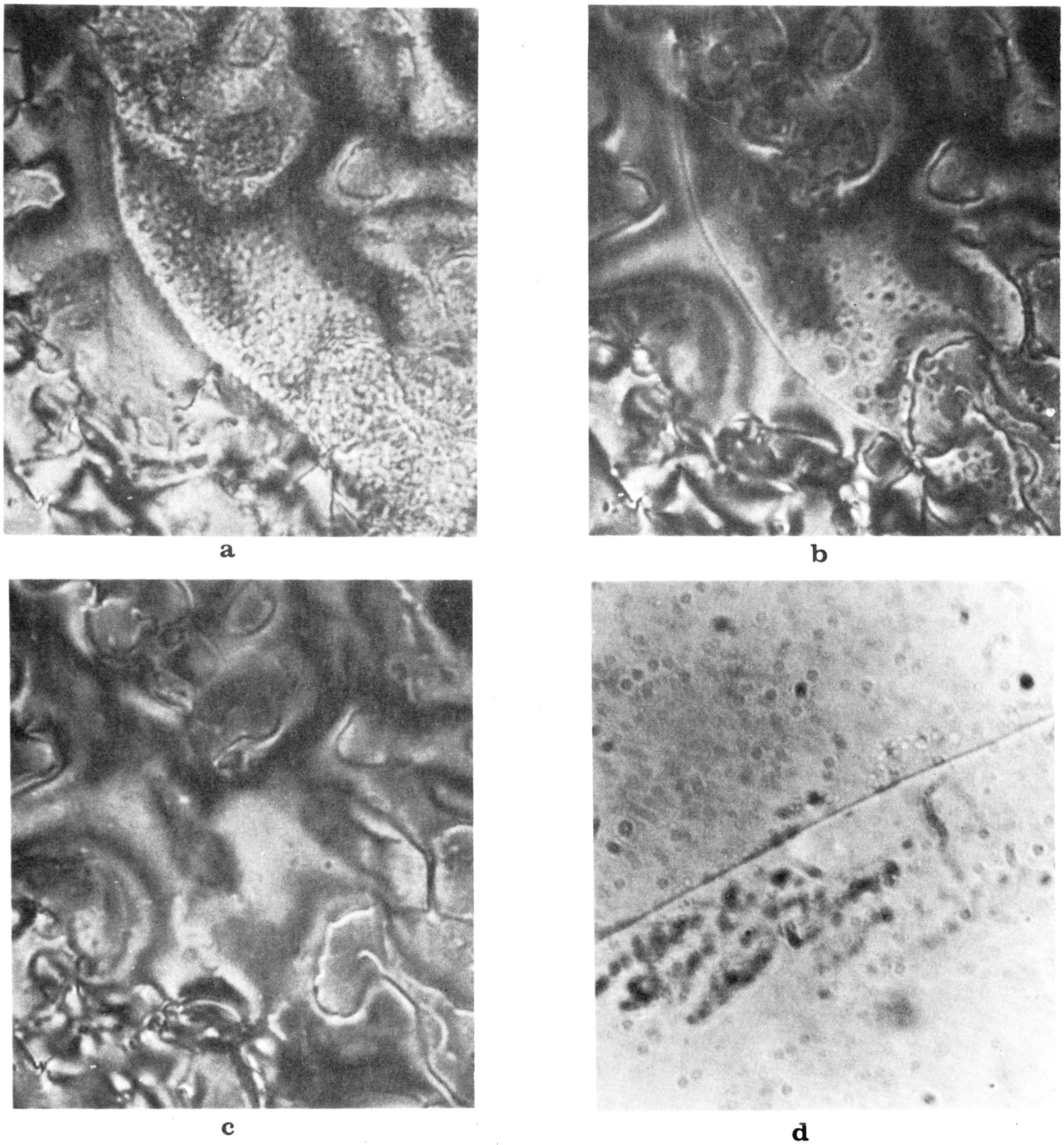


Figure 2. Evolution of phase separation as a function of temperature through the contact method: (a) $T < T_c$, the nematic–nematic phase separation extends on a large domain in the center of the picture; (b) T approaches T_c, the line still indicates the immiscibility between the nematic phases; (c) $T > T_c$, the line has vanished, and both compounds are now totally miscible; (d) LC polymer and LMW mesogen are still immiscible in the isotropic phase. One observes a line of phase separation between two isotropic media. Photographs a, b, c: crossed polarizer and analyzer. Photograph d: polarizer and analyzer not crossed.

of flexibility. For given chain lengths, this degree will decrease with increasing length of the core. In addition, the core itself can be more or less stiff depending on its molecular structure. Stiffer and larger cores induce better pair interactions U_{AA} as noticed from the average values of T_{NI} in Tables II–IV (the degree of flexibility of the molecules can be considered smaller for the "three rings" solvents compared to that for the "two-rings" ones; between the two series with long cores, the CH_2–CH_2 group is obviously more flexible than the naphthalene part). However, T_c decreases clearly with an increasing rigidity of the molecules of solvent (this result appears, for example, in Figure 6 along the vertical line corresponding to constant $n = 13$). So U_0 decreases, which implies that U_{AB} increases sufficiently in order that $-U_{\mathrm{AB}}S_{\mathrm{A}}S_{\mathrm{B}} + {}^1/_2U_{\mathrm{AA}}S_{\mathrm{A}}^2$ decreases. Thus the increase in stiffness of the solvent is strongly favorable to better interactions between the LMW molecules and the molecules of polymer.

3. Influence of the Nature of the Chains of the Solvents. The same discussion applies to the change from alkyl to alkoxy chains for the solvents (Figure 7). Alkoxy chains provide better interactions than alkyl ones for the same number of methylene groups. It is well-known that T_{NI} is usually higher for alkoxy compounds than for alkyl ones, and this is verified in Tables IV–VI. U_{AA} is then likely to increase but the corresponding T_cs decrease, which means that changing from dialkyl to alkyl-alkoxy and eventually to dialkoxy solvents increases $U_{\mathrm{AB}}S_{\mathrm{A}}S_{\mathrm{B}}$ as well.

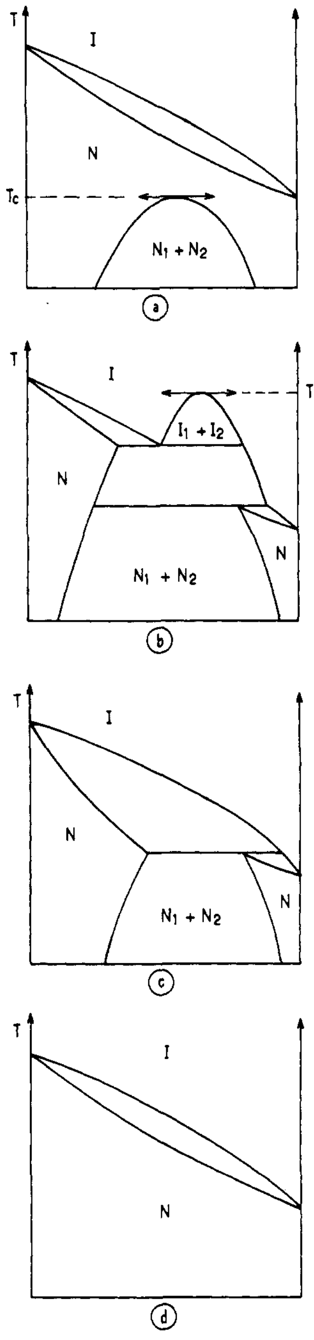


Figure 3. Simplified representation of the different cases of binary diagrams considered in the text: (a) phase separation occurs in the nematic phase (D_n in Tables VII–XI); (b) phase separation occurs in the isotropic phase (D_i in Tables VII–XI); (c) phase separation intercepts but does not cross the nematic–isotropic spindle (no critical temperature can be determined (NA in Tables VII–XI)); (d) no phase separation is observable over the whole nematic domain (M in Tables VII–XI). To ease the drawing the gaps of miscibility have been enlarged. Their actual extension appears in ref 3 and 7.

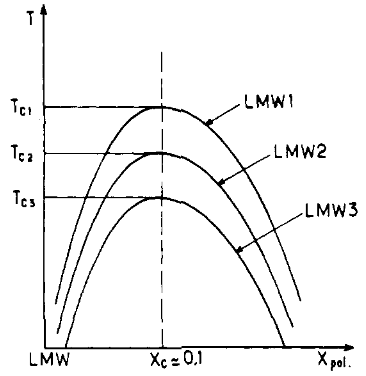


Figure 4. Evolution of the gap of miscibility at constant critical molar fraction in polymer. The lower the critical temperature is, the better the solubility of the polymer in the LMW solvent is.

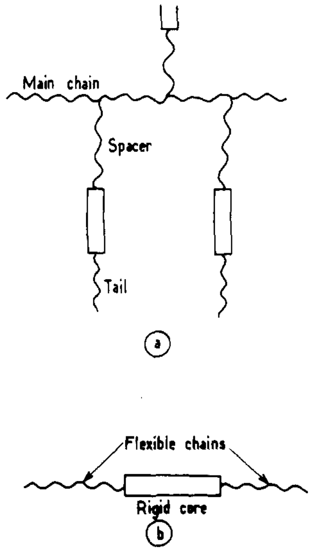


Figure 5. Definition of the molecular parameters that can be varied: (a) in the LC side-chain polymer; (b) in the LMW nematic solvent.

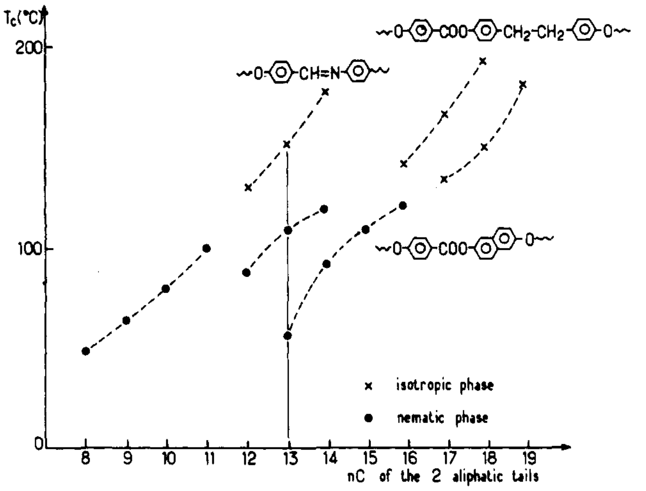


Figure 6. Evolution of the critical temperature of phase separation as a function of the total number of carbons in the flexible chains of the LMW solutes pertaining to the three different families of Tables II–IV. Constant polymer $P_{4,1}$. Full circles: critical temperature in the nematic phase. Crosses: critical temperature in the isotropic phase. The dotted lines are guides for the eye. The full line at $n = 13$ emphasizes the effect of changing the core at constant number of carbons.

4. Influence of the Length of the Spacer of the Polymer Solute. Now the evolution of T_c as a function of the molecular structure of the polymer solute is more difficult to appreciate since we know less about the way in which LC polymer–LC polymer interactions are influenced. But it seems that once more our results can be usefully compared to the theory. In Figure 8 one can follow the evolution of T_c at constant solvent as a function of the lengthening of the spacer of the polymer: in this case U_{AA} is constant, the influence of these changes upon U_{BB} appearing weak (T_{NI} or T_{SI} (temperature of the smectic to isotropic phase transition) barely varies in Table I). However, T_c clearly decreases from $P_{3,1}$ to $P_{4,1}$. Thus U_{AB}

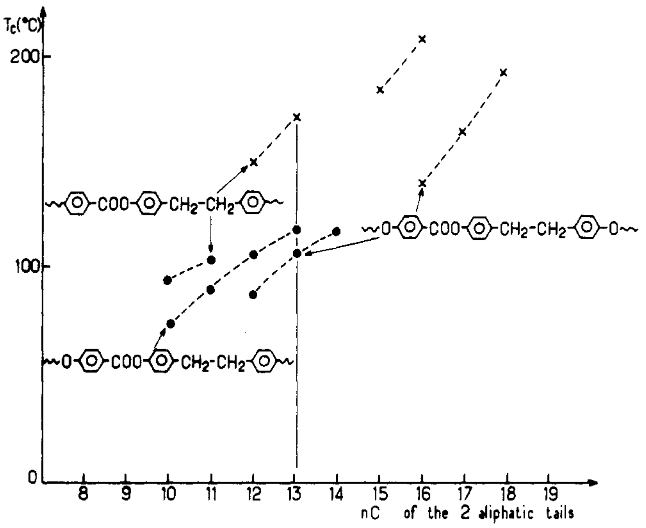


Figure 7. Influence of the nature (alkyl or alkoxy) of the flexible chains of the LMW solutes on the critical temperature of phase separation. Constant polymer $P_{4,1}$. Full circles: critical temperature in the nematic phase. Crosses: critical temperature in the isotropic phase. The dotted lines are guides for the eye.

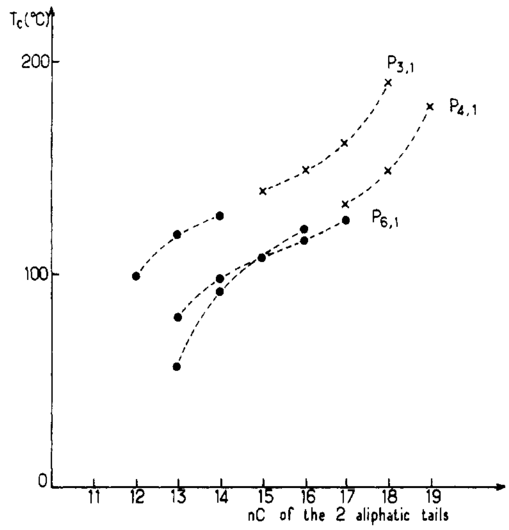


Figure 8. Influence of the length of the spacer of the LC polymer solute on the critical temperature of phase separation. Constant series of LMW solvents (see Table II). Full circles: critical temperature in the nematic phase. Crosses: critical temperature in the isotropic phase. The dotted lines are guides for the eye.

obviously increases owing to a greater decorrelation of the side groups of the solute B with regard to the main chain. For short spacers at least, it appears that the more rigidly linked to the siloxane backbone the mesogenic groups are ($P_{3,1}$), the more difficult the interactions with the nematic solvent are. For long spacers, one can perhaps expect to come back to the usual behavior, i.e., a decrease of the interaction term due to the increasing flexibility of the mesogenic part leading to an increase of T_c. Up to the spacer with 10 methylene groups it appears that this change of regime does not occur since a complete miscibility is observed over all the nematic domain for the binary systems involving $P_{10,1}$ (see Table VIII). Thus one can conclude that the interactions between the solvent and the solute are much more positively influenced by the uncoupling of the mesogenic part from the main chain than they are negatively influenced by the associated increase of the flexibility of the side groups.

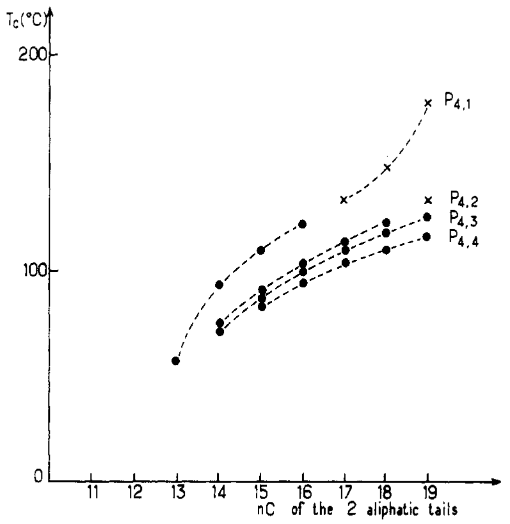


Figure 9. Influence of the length of the tail of the LC polymer solute on the critical temperature of phase separation. Constant series of LMW solvents (see Table II). Full circles: critical temperature in the nematic phase. Crosses: critical temperature in the isotropic phase. The dotted lines are guides for the eye.

5. Influence of the Length of the Tail of the Polymer Solute. More surprising is the case of increasing tails, for in this case one should expect an increase of T_c with m since the strength of the interactions might be regularly decreased (due to higher flexibility). In fact, one finds the opposite, as presented in Figure 9!

This result cannot be explained unless one considers the specific polymer–polymer interactions that we know are present in this polysiloxane series: the structural and density data that we have collected[17] have clearly shown that the side groups induce antiferroelectric interactions with a large overlapping of the cores. The shorter the tail is, the more important these antiparallel associations are. These interactions are gradually destroyed for long tails as proved by the evolution of the molecular area assigned to each side group.[17]

Our result corresponds to a decrease of U_0 when m increases, particularly when one changes from $P_{4,1}$ to $P_{4,2}$. Thus, U_{AB} should increase together with looser core–core interactions in the polymer. In terms of solubility this negative role of the associations of the side groups in this family of polysiloxanes is certainly enhanced by the fact that the molecules of the different series of solvent do not have this tendency to antiparallel pairing.

Conclusion

We have first shown in this paper that the contact method is a convenient technique to evaluate the properties of miscibility of a liquid crystal polymer solute in a nematic LMW solvent. The qualitative comparison of our first results with the "first generation theory" of Brochard et al. is summarized in the following. On one hand, every parameter that increases the anisotropic interactions among the molecules of nematic solvent plays the same role with regard to the interactions between solute and solvent. On the other hand, every parameter that influences the anisotropic interactions among the molecules of polymer solute so that these interactions are closer to those of the solvents used in the study modifies largely the interactions with the solvent as well.

Thus, there seemingly exists a large consistency regarding the nature of the interactions stabilizing a mesomorphic state in a LC side-chain polymer and a usual nematic of LMW molecules. Yet gaps of miscibility arise in binary mixtures of such nonpolar compounds. Among the possible factors responsible for this incompatibility is the special role of unusual structures in the pure polysiloxanes under consideration, and we add that the role of the main chain has been completely ruled out from our discussion, although it does participate in some manner to the solute–solvent interactions.

This work engages us to proceed in order to clarify the different points discussed above. The forthcoming studies will include the change of the nature of the polymer, first, in order to analyze the influence of the backbone and, second, to avoid neighboring core–core overlaps and to evaluate the importance of this factor on the phase separation. In contrast, the strengthening of this antiparallel arrangement can be obtained with polar side groups attached to the poly(methylsiloxane) backbone. With regard to the solvent, we envision the use of polar solvents, which in turn could show a tendency to antiferroelectric interactions.

Acknowledgment. We are greatly indebted to Dr. Nguyen Huu Tinh for the use of the series of mesogenic LMW compounds.

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(18) We will often refer in the following to the polymer as the solute and to the LMW nematogen as the solvent (since $X_c = 0.1$).

Crystal Structure of Isotactic 1,4-*trans*-Poly(2-methylpentadiene). An Application of the Rietveld Method

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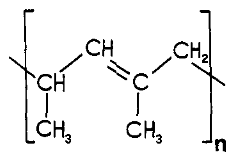
ABSTRACT: The crystal structure of isotactic 1,4-*trans*-poly(2-methylpentadiene) has been determined through best fitting of the X-ray diffraction powder profile (Rietveld method). The final refinement cycles were carried out on 12 structural and 18 nonstructural parameters; three constraints were introduced in the form of Lagrange multipliers. A different half-height width for equatorial and layer reflections was adopted in connection with given crystallite dimensions. The final disagreement factor $R_2 = \sum|I_o - I_c|/\sum I_{net}$ was 0.099. The conformation of the polymer chain can be described as a sequence of TS$^+$TS$^-$ torsions. Crystal packing is described, and no particularly short contact is detected.

Introduction

Crystal structure determinations from powder X-ray diffraction data find at present an increasing number of applications.[1-6] Availability of very accurate experimental data and of efficient computational routines[7,8] that can optimize both structural parameters and parameters that, more generally, depend on experimental conditions of data recording and of sample preparation (e.g., preferred orientation, zero correction, shape of peaks, etc.) is the basis of the recent success of this structural approach, which is usually referred to as the Rietveld[9] whole-fitting method.

In the case of crystalline polymers the analysis of X-ray diffraction data from powders can be convenient when obtaining oriented fibers presents some problem. In fact, in principle, the two-dimensional spreading that characterizes fiber diffraction diagrams allows better resolution among peaks and reveals diffracted intensities at higher 2θ values, thus giving more information. From a practical point of view, however, it is quite often the case that a rigorously quantitative analysis of a powder profile can solve a structural problem in an easier and quicker way, leading to quite reliable results. We have already applied this method to the crystal structure determination of isotactic 1,4-*trans*-poly(1,3-pentadiene) (ITPP),[10] where conflicting conclusions were drawn from an X-ray diffraction analysis from oriented fibers[11] and from a vibrational analysis on a bulk-crystallized sample.[12] Our approach indicated that ITPP assumes different conformations depending on whether crystallization occurs under stretching conditions or not.

The present work is devoted to the study of the crystal structure of isotactic 1,4-*trans*-poly(2-methylpentadiene) (PMPD) (1); Figure 1(II) shows the numbering scheme of



1

carbon atoms. This polymer has been known for many

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