

Phase Behavior and Order in Mixtures of Main-Chain Nematic Polyesters with Small Molecules: A Combined Proton and Deuterium NMR Study

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ABSTRACT: Thermotropic-lyotropic phase behavior is investigated in two mixtures composed of a perdeuterated small molecule and a protonated thermotropic nematic main-chain polyester. Each component can be independently followed by combining deuterium and proton NMR spectroscopy: width of the nematic-isotropic (N + I) biphasic, temperature dependence of composition of the coexisting N and I phases, and the orientational order of each component are measured. In the mixture *p*-azoxyanisole- (PAA14-) (poly[oxy(chloro-1,4-phenylene)oxycarbonyl][(trifluoromethyl)-1,4-phenylene]carbonyl), the polymer has a fully aromatic para-linked structure and the small molecule is itself nematic below 135 °C; above the clearing temperature of PAA14 athermal lyotropic phase behavior is observed, at least within the experimentally accessible temperature range. In the mixture nitrobenzene-(NBd5-) poly([oxy(3-methyl-1,4-phenylene)-azoxy(2-methyl-1,4-phenylene)oxy(1,12-dioxo-1,12-dodecanediyl)], the polymer chain is inherently flexible; the nematic phase is destabilized upon addition of NBd5, and the N + I biphasic drastically broadened. Orientational order of the polymer is decreased, but the basic conformational characteristic of the chain, namely, spacer extension, is retained.

Introduction

Complete experimental characterization of binary mixtures where at least one component is mesomorphic requires delineation of the coexistence curve for the isotropic and anisotropic phases and independent determination of orientational order of both components. Nuclear magnetic resonance combining proton (¹H NMR) and deuterium (²H NMR) spectroscopy may provide this detailed analysis in mixtures where one of the components is deuterated, as long as order parameters can be reliably extracted from the ¹H and ²H NMR spectra. Not surprisingly, such comprehensive studies are few.¹⁻⁴

The ²H NMR splittings of perdeuterated *p*-azoxyanisole (PAA14), a low molecular mass (LMM) nematic, have been thoroughly analyzed in terms of structure, conformation, and orientational order.^{5,6} Main-chain nematic polyesters synthesized from mesogen 4,4'-dihydroxy-2,2'-dimethylazoxybenzene and alkanedioic acids have similarly been studied in terms of their orientational and conformational order via the ¹H NMR spectrum of the mesogen and the ²H NMR spectrum of the aliphatic spacer, respectively.^{7,8} Nematic poly([oxy(3-methyl-1,4-phenylene)azoxy(2-methyl-1,4-phenylene)oxy(1,12-dioxo-1,12-dodecanediyl)], subsequently called polymer DDA9, has been investigated in detail. Binary mixtures of PAA14 with DDA9 and PAA14 with 4,4'-acetoxy-2,2'-dimethylazoxybenzene, a nonmesomorphic model of the mesogenic core of DDA9, have been studied via a combined ¹H NMR and ²H NMR approach.¹ The following information can be extracted for every composition:

(1) Delineation of the width of the nematic-isotropic (N + I) biphasic comprised between T_N and T_I , respectively, the temperature of appearance of the isotropic and disappearance of the nematic component of the biphasic.

Temperature T_N is associated with the appearance in the NMR spectrum of the sharp central line characteristic of the I phase, and T_I with the disappearance of the dipolar or quadrupolar splittings characteristic of an aligned nematic phase.

(2) Temperature dependence of f_N^D and f_N^H , the mass fractions of deuterated and protonated components present within the nematic portion of the biphasic. Both f_N^D and f_N^H are deduced from the intensity of the sharp central line belonging to the I component relative to the total intensity.

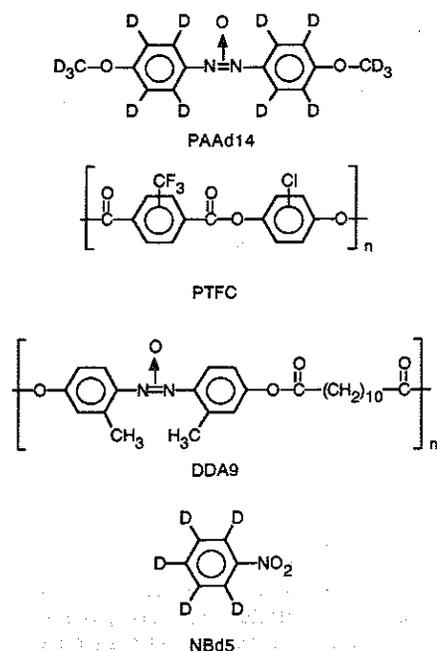
(3) Order parameter of each component, from the appropriate dipolar and quadrupolar splittings.

We now use the same approach to investigate thermotropic-lyotropic phase behavior in the following two binary systems: PAA14-PTFC (poly[oxy(chloro-1,4-phenylene)oxycarbonyl][(trifluoromethyl)-1,4-phenylene]carbonyl), a para-linked fully aromatic polyester;⁹ DDA9-NBd5 (perdeuterated nitrobenzene), a nonmesomorphic diluent.

In the first case, both components are thermotropic nematics and form nematic solutions below the clearing temperature of PAA14. Above this temperature, the LMM component may be considered as an isotropic solvent and the system is found to display nearly athermal lyotropic phase behavior upon addition of PTFC. The phase diagram is established and order parameters of both components are deduced. In the second system, phase transition temperatures as well as temperature dependence of f_N^D and f_N^H are deduced and the order parameter of the PLC component is measured; temperature dependence of quadrupolar splittings of NBd5, roughly proportional to its order parameter is reported. The nematic phase of DDA9 is drastically destabilized by addition of NBd5, to the benefit of a broadly enlarged N + I biphasic.

The experimental results are briefly discussed in terms of solvent structure and conformational characteristics of

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the LCP chains, one rigid and the other inherently flexible.

Experimental Section

Materials. PTFC belongs to a family of fully aromatic para-linked polyesters synthesized at the Polaroid Corp. and our sample is designated as structure XXII in reference.⁹ It is a noncrystalline material with a nematic glass transition at 71 °C and onset of a fluid phase at 127 °C. No clearing point is found on scanning until 450 °C. Decomposition in air is reported at 460 °C. Inherent viscosity measured at 30 °C is 0.79 dL/g (at a concentration of 0.5 g/dL in 1/1 (v/v) tetrachloroethane-*p*-chlorophenol). Degree of polymerization is estimated at DP ≈ 21.¹⁰

DDA9 was prepared and characterized as previously described.¹¹ The DSC peak minima on cooling from the I phase (scanning rate 20 K/min) are 115 (I - N) and 66 °C (N - K). $M_n = 2900$ with a polydispersity of ≈ 1.2.

Methods. Six PTFC-PAAAd14 samples were prepared in standard 5-mm NMR tubes, each containing 100 mg of material: pure PTFC and the mixtures, characterized by the value of ϕ_0^M , the mass fraction of PTFC ($\phi_0^M = 0.07, 0.15, 0.24, 0.30, \text{ and } 0.45$). The two powders were mixed in the tubes, heated to the liquid state, degassed, and sealed under primary vacuum. The samples were then equilibrated for 10–20 days in an oil bath maintained at 133 °C, a temperature at which both components are in the fluid nematic state. Very long annealing times are indeed required to ensure compositional equilibrium in nematic PLC mixtures.¹²

The mixtures were examined successively by ²H NMR and ¹H NMR with a CXP90 Bruker spectrometer working at 13.8 and 90.1 MHz, respectively. The sample tubes were rapidly transferred from the thermostat to the spectrometer probe also set at 133 °C and kept at this temperature until well-resolved ²H NMR spectra of PAAAd14 were obtained. The samples were then heated by steps of 1–2 °C and kept 1–2 h at each step, and the ²H NMR spectra recorded with a repetition rate sufficiently long compared to spin-lattice relaxation times. ¹H NMR experiments were performed by following exactly the same procedure.

Onset of the biphasic region is revealed by appearance of a sharp central line at temperature T_N . Complete isotropization could not be observed. Thermal degradation of PAAAd14, starting at ≈ 185 °C, limits the experimentally accessible temperature range.

The DDA9-NBd5 mixture ($\phi_0^M = 0.07$) was examined on cooling from the I phase and f_N deduced from the relative intensity of the central I line, taking as reference the peak intensity in the pure I phase (see ref 2 for experimental details).

As mentioned above, the mixture PAAAd14-PTFC was examined on heating from the pure N phase, since the pure I phase could not be reached within our experimental temperature range. Estimation of f_N^H and f_N^D from the relative intensity of the I

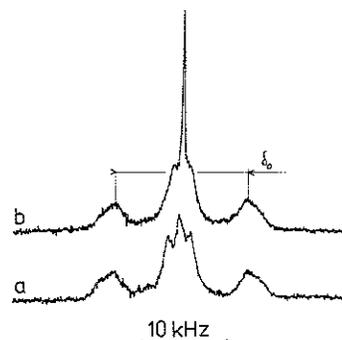


Figure 1. ¹H NMR spectra of PTFC in PAAAd14 (0.07 mixture). (a) pure N phase at 122.5 °C; (b) N + I biphasic at 138 °C. Note the sharp peak corresponding to the I component of the biphasic.

peak is delicate under these conditions because it is achieved by comparing intensities of spectral components with very different widths; this may introduce a large systematical error, especially in the ²H NMR experiments, where the signal to noise ratio is not very good. In fact, this error results from just a scaling factor, which can be adjusted experimentally. Alternatively, f_N and $f_I = 1 - f_N$ can be deduced from the area (determined by a “cut and weigh” approach) of the peaks corresponding to the aligned N component, taking as reference the area in the pure N phase. A calibration curve relating isotropic peak height and peak area can thus be obtained.

Results and Discussion

PTFC-PAAAd14. PTFC polymer readily forms nematic solutions with PAAAd14. Two representative ¹H NMR spectra of PTFC dissolved in PAAAd14 are illustrated in Figure 1a and b, showing the polymer aligned within the pure N phase and the N + I biphasic, respectively. The dipolar splitting represented as δ_0 is related to the main order parameter S_H via the relation

$$2\delta_0/\text{kHz} = 22.6S_H \quad (1)$$

as deduced from spectral simulation.¹³ Within the biphasic region, the value of f_N^H , fraction of polymer present in the N component, is deduced as described in the Experimental Section. The ²H NMR spectra of PAAAd14 within the pure N phase as well as in the N + I biphasic are analyzed as described in previous studies^{5,6} and are not shown here. The fraction of PAAAd14 present in the N component is represented as f_N^D . The mass fractions ϕ_N^M and ϕ_I^M of PTFC in the N and I components are deduced from eqs 2 and 3.

$$\phi_N^M = \frac{f_N^H \phi_0^M}{f_N^H \phi_0^M + f_N^D (1 - \phi_0^M)} \quad (2)$$

$$\phi_I^M = \frac{(1 - f_N^H) \phi_0^M}{(1 - f_N^H) \phi_0^M + (1 - f_N^D) (1 - \phi_0^M)} \quad (3)$$

While PTFC dissolved in PAAAd14 aligns readily for all mixtures studied, the neat polymer could not be macroscopically aligned under our experimental conditions. From the knowledge of the aligned spectra one can easily see that the ¹H NMR spectrum of neat PTFC (Figure 2) is typical of a “powder” N phase. The transition to a fluid nematic phase occurring at 127 °C⁹ is revealed by a general narrowing (compare spectra a and b of Figure 2). The order parameter of neat PTFC is estimated by comparing the shape and width of the experimental “powder” spectrum with the theoretical powder spectrum calculated by taking as reference the aligned spectrum of the 0.24 mixture.

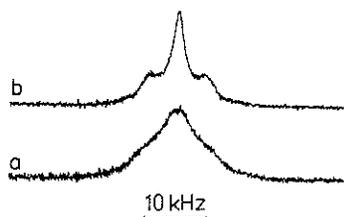


Figure 2. ^1H NMR spectra of neat PTFC. (a) 120 °C; (b) 160 °C.

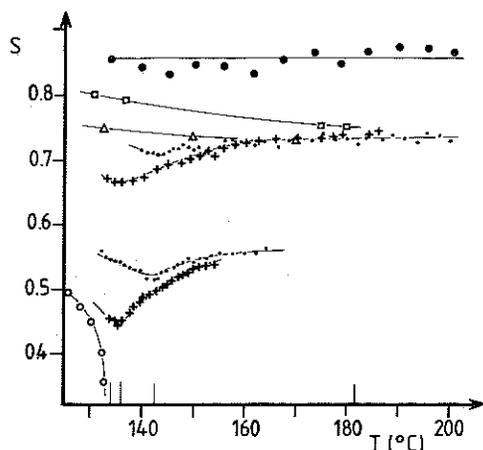


Figure 3. Temperature dependence of order parameters. Key: ●, neat PTFC; □, PTFC in 0.45 mixture; Δ, PTFC in 0.30 mixture; ·, top PTFC in 0.15 mixture, bottom PAA in 0.15 mixture; +, top PTFC in 0.07 mixture, bottom PAA in 0.07; ○, neat PAA. Vertical bars (from left to right): T_{NI} of PAA; T_{NI} of 0.07, 0.15, and 0.30 mixtures. The 0.45 mixture did not reach N + I biphasic within experimental range.

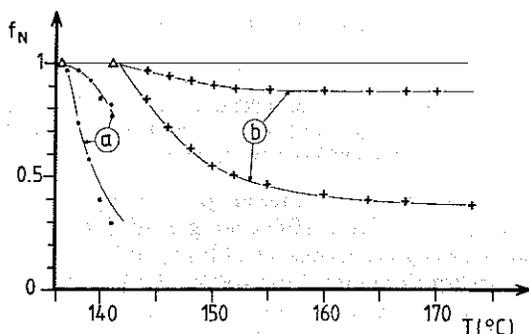
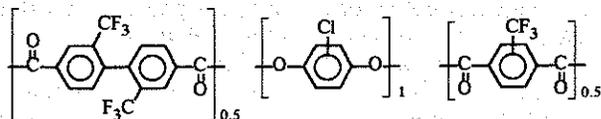


Figure 4. Temperature dependence of nematic fraction f_N in the N + I biphasic region. (a) 0.07 mixture; (b) 0.15 mixture. Upper curves refer to PTFC (f_N^H). Lower curves refer to PAA (f_N^D).

Within the temperature interval that was experimentally accessible to us, the value of S_H for the neat polymer remains constant at $S_H \approx 0.85$ as illustrated in Figure 3 (top curve). This value is slightly higher than the maximum value deduced from IR dichroism in an oriented film of a related polymer,⁹ terpolymer



Temperature dependence of f_N^H and f_N^D is illustrated in Figure 4 for the 0.07 and 0.15 mixtures, the remaining mixtures displaying a behavior similar to that of mixture 0.15. The nematic phase of PAA is stabilized by addition of PTFC, as might be expected. At a given temperature, f_N^D is much smaller than f_N^H , as PAA is preferentially transferred into the I component of the biphasic. Although

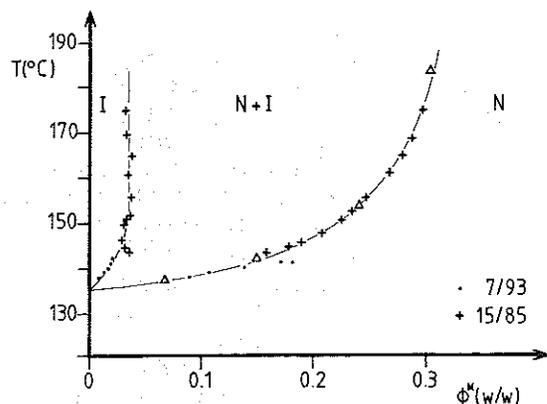


Figure 5. Phase diagram for the PTFC-PAA14 system. Key: ·, from data for 0.07 mixture; ×, from data for 0.15 mixture; Δ, experimental T_N values for the 0.07, 0.15, 0.24, and 0.30 mixtures.

f_N^D decreases faster than f_N^H with increasing temperature, both values level off to reach athermal behavior at higher temperatures.

Similarly, the temperature dependence of order parameter for the various mixtures, which is plotted in Figure 3, also develops a plateau as the temperature is increased. The value of S_H , which gives the order parameter of guest PTFC, is shown for mixtures 0.07, 0.15, and 0.30. The value of S_D for the host PAA is shown for mixtures 0.15, 0.07, and for pure PAA. The order of the LMLC host is increased and that of the PLC guest is decreased with respect to the pure components, as expected on theoretical grounds.¹⁴

$S(T)$ for the 0.07 and 0.15 mixtures displays a minimum related to the appearance of the I phase and the selective partitioning of chain lengths between the I and N components of the biphasic (appearance of the first I droplets is indicated by vertical bars on the abscissa of Figure 3). Let us first examine the evolution of $S_D(T)$ in these relatively dilute solutions. As temperature increases through the biphasic, the concomitant decrease of S_D is reversed due to expulsion of PAA from the N component. Order parameters eventually level off. The shape of $S_H(T)$ is similar, but the minima are more shallow.

In the range of temperatures where the values of f_N display athermal behavior, values of S_H are located on the same plateau (within experimental error) for mixtures 0.07, 0.15, and 0.30. This suggests that, at a given temperature within the plateau, the composition of coexisting phases is the same for all three mixtures, as would be expected for a purely binary system. In the 0.45 mixture, the pure N phase is preserved until the upper limit of our experimental temperature range and the $S_H(T)$ plateau is not reached within that range (data not shown in Figure 3).

The phase diagram built from eqs 2 and 3 and Figure 4 is illustrated in Figure 5. The nematic phase is stabilized by addition of PTFC chains. Over our experimental temperature range the coexistence curves for the I and N components display a "chimney-like" behavior above ≈ 145 °C. For the 0.15 mixture the first I drop appears at 142 °C. If PTFC were monodisperse, the N component evolved from the 0.07 mixture would have exactly the same composition and the same order parameter as the 0.15 mixture. A glance at Figure 3 reveals that this is not quite the case, as polydispersity in chain lengths undoubtedly broadens the biphasic region.

As mentioned previously, PTFC belongs to a family of para-linked polyesters based on trifluoromethyl substitution in a phenyl and/or biphenyl moiety. These

structural features preserve molecular rigidity, but the polymers fail to exhibit expected lyotropic behavior in conventional organic solvents even at polymer concentrations as high as 50% (w/v).⁹ These results, as yet unexplained, are in analogy to observations reported for similarly substituted polyamides¹⁵ and in contrast to the phase behavior observed here, at least in the range of temperatures experimentally accessible to us (below the temperature of thermal decomposition of PAA).

The data illustrated in Figures 3–5 clearly suggest athermal lyotropic behavior, in agreement with the relatively rigid conformation of PTFC chains.⁹ The biphasic gap, as measured by the ratio of experimentally determined mass fractions for the coexisting anisotropic and isotropic phases within the athermal region, is

$$\phi_N^M / \phi_I^M \approx 0.33/0.03 \quad (4)$$

This can be converted to a ratio of volume fractions via

$$\phi^V = \frac{\phi^M}{\phi^M + \frac{\rho_{\text{PTFC}}}{\rho_{\text{PAA}d14}}(1 - \phi^M)} \quad (5)$$

By estimating the density of PAA_{d14} from literature data¹⁶ and computing the density of PTFC from the length and cross section of the repeating unit we get

$$\phi_N^V / \phi_I^V \approx 0.40/0.05 \quad (6)$$

a value characteristic of a very broad biphasic region.

For a solute consisting of monodisperse rods, Onsager's theoretical treatment¹⁷ predicts $\phi_N^V / \phi_I^V = 1.3 \pm 0.1$ and Flory's¹⁸ α value approaching 1.46 in the limit of infinite chain length. In polydisperse systems, selective transfer of longer chains into the anisotropic component significantly broadens the biphasic region, in a manner depending on average chain length and the ratio of volumes of the two phases. If we assume a most probable distribution of chain lengths in PTFC,¹⁰ our results are found to be in general agreement with Flory and Frost's¹⁹ prediction based on the lattice approach to mixtures of rodlike particles in athermal systems with most probable distribution and $DP \approx 20$. Let us note, however, that a more quantitative comparison of experimental data and theory must await a more thorough study of PTFC chain conformation in this mixture (in particular relation between persistence length and chain length, the latter being ≈ 250 Å).

The broad biphasic region observed here is in contrast to most experimental data reported for unfractionated polypeptides, polyaramides, and other rigid polymers,^{20,21} where the ratios of coexisting volume fractions are often much smaller than predicted. Since diffusion of polymer chains is a slow process, compositional equilibration over domains large enough to allow a clean separation of macroscopic I and N domains may be difficult to achieve and experiments relying on physical fractionation of the two components may be subject to error. NMR, on the other hand, does not suffer from such limitations and may provide a more accurate picture of partitioning between the coexisting components.

DDA9–NBd₅. In contrast to PTFC, DDA9 is an inherently flexible polymer whose persistence length in the isotropic state is of the order of a single repeating unit.²² Orientational and conformational ordering of chains upon cooling through the I/N transition is well documented and need not be restated here. Let us mention that both levels of order are coupled and, at a given reduced temperature, increase with increasing chain length; e.g.,

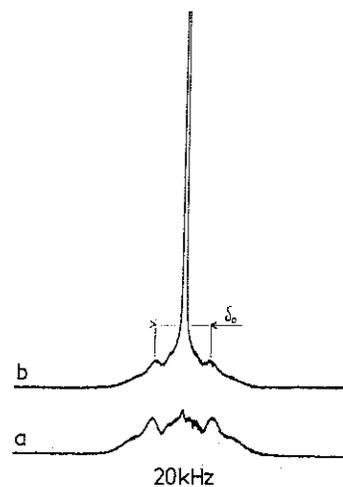


Figure 6. ¹H NMR spectra of DDA9. (a) neat DDA9 at 91 °C; (b) in mixture with 7.4% NBd₅ at 78 °C. Note the sharp peak corresponding to the I component of the biphasic.

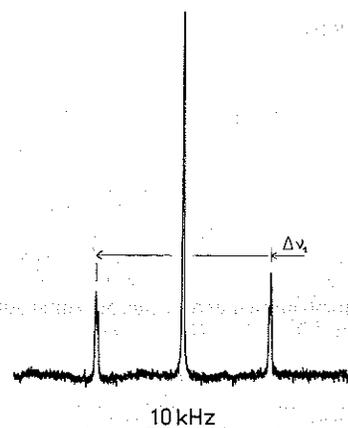


Figure 7. ²H NMR spectrum of NBd₅ in the 0.074 NBd₅–DDA9 mixture at 87 °C. The sharp central peak corresponds to the NBd₅ in the I component of the biphasic.

the chains become more ordered upon cooling and/or upon increasing DP, the latter effect being operative well beyond the customarily cited "plateau" level of $DP \approx 10$.

In a preliminary investigation of DDA9 with nitrobenzene as diluent carried out for \bar{M}_n values in the range 8000–18000 amu,²³ the crystallization and isotropization DSC peak maxima were observed to fall drastically (≈ 120 °C) upon addition of as little as 1–2% nitrobenzene. At the same time, NMR showed that the N + I biphasic was broadened to the extent that crystallization took place before the pure N phase could be reached. Furthermore, we did not observe alignment of the N component in the spectrometer field, probably because sample viscosity was too high, due to the drastic reduction in transition temperatures. Consequently, a DDA9 of mass $\bar{M}_n = 2900$ amu was used in the present study and we are thus describing a sample with a level of order and biphasic width characteristic of the oligomeric range ($DP \approx 7$).

Results are presented for a solution containing 7.4% nitrobenzene-*d*₅ (w/w). Representative ¹H NMR spectra of pure DDA9 (Figure 6a) and DDA9 in the mixture (Figure 6b) as well as part of a ²H NMR spectrum of NBd₅ in the mixture (Figure 7) are illustrated. A sharp line corresponding to the I component is always present in the mixtures.

The value of S_H is deduced from the dipolar splitting δ_0 via the relation

$$2\delta_0/\text{kHz} = 24.08S_H \quad (7)$$

as previously described.⁷ The rather high value of the

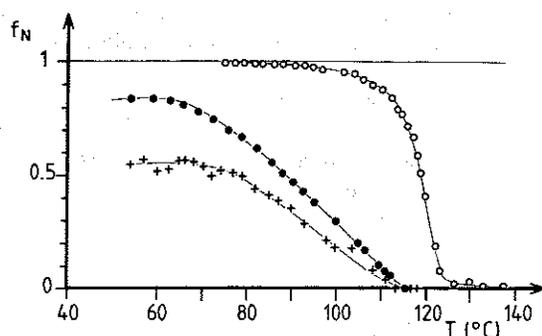


Figure 8. Temperature dependence of the nematic fraction, f_N . Key: \circ , pure DDA9, f_N^H ; \bullet , DDA9 in mixture, f_N^H ; $+$, NBd5 in mixture, f_N^D .

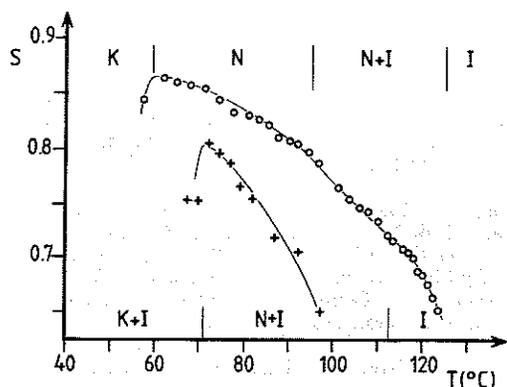


Figure 9. Temperature dependence of order parameter of DDA9. Key: \circ , neat DDA9; $+$, DDA9 in mixture.

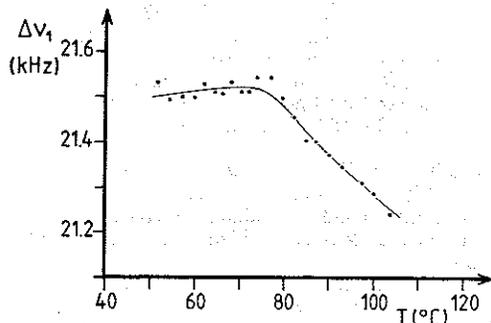


Figure 10. Temperature dependence of the quadrupolar splitting, $\Delta\nu_1$, of NBd5 in the N component of the mixture.

quadrupolar splitting $\Delta\nu_1$ (Figure 10) suggests that guest NBd5 is aligned, but characterization of its order requires knowledge of complete ^2H NMR spectra (important lines indeed fall outside our spectral range).

Temperature dependence of the nematic fraction is shown in Figure 8, with f_N^H and f_N^D as defined above for the PTFC system. Both f_N^H and f_N^D in the mixture increase in perfectly linear fashion before leveling off. Depression of T_I is modest, but T_N is depressed to the point that crystallization takes place from the biphasic. Comparison of f_N^H and f_N^D shows that NBd5 prefers to concentrate in the I component, as might be expected. In contrast, PAAd14 added to DDA9 in approximately the same concentration acts as a "probe" molecule ($f_N^H \approx f_N^D$).²

Order parameter values are plotted in Figure 9 for pure DDA9 and DDA9 in the mixture. Selective partitioning of chain lengths in the biphasic, with progressive incorporation of ever shorter and less ordered chains into the N component, is reflected by an undulation of S in pure DDA9.²⁴ As a consequence of chain fractionation within the biphasic, molecular morphology of the pure N phase

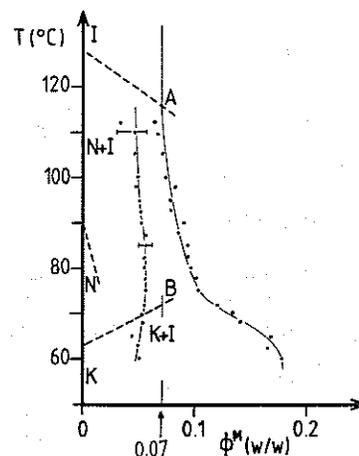


Figure 11. Temperature dependence of ϕ_N^M and ϕ_I^M in the DDA9-NBd5 mixture. The phase diagram is delineated by the dashed lines. Note the broad N + I biphasic of pure DDA9, strongly broadened by addition of small amounts of NBd5. Point A is T_I of the 0.07 mixture. Point B is the appearance of the crystallization of the 0.07 mixture. The two lines going through the black points (ϕ_N^M and ϕ_I^M) are not part of the phase diagram, but represent the NBd5 mass fraction in the N (or K) component (left) and the I component (right) of the biphasic in the 0.07 mixture.

is heterogeneous with regions segregated by chain length and level of order.^{15,22} Incipient crystallization induces collapse of macroscopic alignment and concomitant apparent decrease of S .

$S_H(T)$ of DDA9 rises more steeply in the mixture, presumably because the shorter, more poorly ordered chains, are never incorporated into the N component.

The mass fractions of NBd5 of the N and I components in equilibrium at a given temperature are given by eq 8 and 9, respectively, where $\phi_0^M = 0.074$ is the initial concentration.

$$\phi_N^M = \frac{f_N^D \phi_0^M}{f_N^D \phi_0^M + f_N^H (1 - \phi_0^M)} \quad (8)$$

$$\phi_I^M = \frac{(1 - f_N^D) \phi_0^M}{(1 - f_N^D) \phi_0^M + (1 - f_N^H) (1 - \phi_0^M)} \quad (9)$$

Temperature dependence of ϕ_N^M and ϕ_I^M is plotted in Figure 11. The value of ϕ_N^M is reasonably constant, while ϕ_I^M decreases as the proportion of I component increases and the value of ϕ_0^M is recovered upon disappearance of the N component at $\approx 115^\circ\text{C}$. Crystallization takes place in the vicinity of $70\text{--}75^\circ\text{C}$, as indicated by the collapse of S (Figure 9). At the same time, the quadrupolar splitting $\Delta\nu_1$ levels off to a value of ca. 21.5 kHz and f_N^D to ≈ 0.55 . In the region where K, N, and I phases coexist, the "chimney" broadens, probably because NBd5 tends to be expelled from the crystalline phase. Below 65°C , approximately 25% of the total material still remains in the I phase.

Although the two curves ϕ_N^M and ϕ_I^M form a fairly straight chimney, the strong temperature dependence of S_H and f_N indicates that we do not observe athermal behavior. Furthermore, lines ϕ_N^M and ϕ_I^M in Figure 11 do not represent the phase diagram for this system. Pure DDA9 itself displays a broad N + I biphasic, delineated in Figures 9 and 11. Thus, a pure N phase in the mixtures

must necessarily be a narrow strip limited to very low concentrations (represented by a dashed line in Figure 11).

As illustrated in Figure 8, NBd5 prefers to concentrate in the I phase. However, the relative independence of ϕ_N^M on temperature (Figure 11) may suggest that, within the nematic component, it does not appear to concentrate preferentially in regions dominated by the shorter polymer chains.

Figure 11 shows that in the DDA9-NBd5 mixture it is not possible to construct a phase diagram from a single composition (in contrast to the PTFC-PAAd14 system in which polydispersity effects could be neglected in first approximation). Thus, composition dependence of transition temperatures should be established for several different values of ϕ_0^M . As noted previously, NMR experiments lead to accurate delineation of the phase diagram. On the other hand, when composition dependence of transition temperatures is extracted from DSC peak maxima or by polarizing microscopy, the width of the N + I biphasic region may be drastically underestimated. This is especially true in the vicinity of T_N , where small isotropic domains dispersed in a nematic matrix are easily overlooked. In addition, the presence of a T_{NK} peak on DSC may mask persistence of an I component at temperatures well below onset of crystallization.

In summary, the following qualitative conclusions can be made concerning the mixture DDA9-NBd5:

(1) Although the order parameter of DDA9 in the presence of NBd5 is depressed, as might be expected, inspection of its ^1H NMR line shape reveals that the principal conformational characteristics of pure DDA9 are present in the mixture. A similar conclusion was recently suggested by Viney and et al.,²⁵ who have established (from visual observation) the phase diagram for a combined main- and side-chain nematic PLC formed of mesogens connected by aliphatic spacer groups. Experimental results were compared with the prediction of Flory and Warner²⁶ for rodlike segments connected by free joints and incorporating orientation-dependent interactions. Theory and experiment could not be reconciled.

(2) The diluent NBd5 molecules appear to be rather highly ordered within the N component.

(3) The pure N phase is destabilized to the benefit of a drastically broadened N + I biphasic region.

The strong effect observed upon dilution of the N phase with NBd5 molecules may be understood qualitatively when one considers the influence of 4-4'-acetoxy-2,2'-dimethylazobenzene on the nematic order in PAAd14. In this binary system of small molecules investigated by Esnault et al.,¹ the solute is a potential nematic, with a virtual clearing temperature estimated at ≈ 220 K. Yet, despite its highly anisotropic shape, the molecule acts as a perturbation of the local orientational order of PAA. The authors proposed a model of the system in which an isolated solute molecule produces a perturbation over a mean volume equivalent to roughly 10 times its own molecular volume. This perturbation is characterized by a correlation length whose concentration dependence diverges at T_N . This indicates that orientational order is strongly affected throughout the system and it is to be expected that NBd5, a nonnematogenic structure, will strongly amplify this behavior.

In conclusion, we have investigated thermotropic-lyotropic phase behavior in two very different systems. The

experimental approach common to both studies, combining ^1H NMR and ^2H NMR spectroscopies, provides a means to accurately identify and "weigh" the phases present at a given temperature without resorting to physical fractionation. Molecular order of both components can be established. Success of this approach, however, is predicated upon the macroscopic alignment of the nematic component.

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References and Notes

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Registry No. PAAd₁₄, 39750-11-3; PTFC (copolymer), 109977-42-6; PTFC (SRU), 102819-40-9; DDA9 (copolymer), 132775-40-7; DDA9 (SRU), 79079-27-9; NBd₅, 4165-60-0.