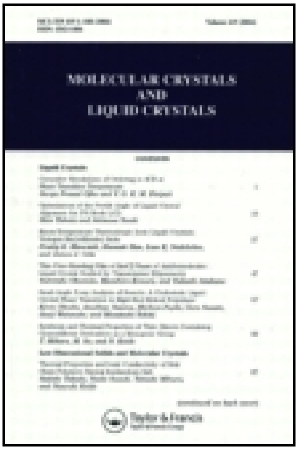

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Electric Field Effects and Miscibility in Cybotactic Micellar Nematic and Ordinary Nematic Polyesters

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ELECTRIC FIELD EFFECTS AND MISCIBILITY IN CYBOTACTIC MICELLAR NEMATIC AND ORDINARY NEMATIC POLYESTERS

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ABSTRACT

Miscibility behavior and electro-optical instabilities are reported for two main chain thermotropic nematic polyesters formed by regularly alternating a disubstituted azoxybenzene mesogen with a flexible spacer containing either 7 or 10 methylene units (HEPTA-9 and DDA-9, respectively). Polymer HEPTA-9 displays an ordinary nematic organization and polymer DDA-9 forms a cybotactic nematic phase. Both are totally miscible with each other, and with PAA, in the nematic phase. Williams domains and dynamic scattering modes are observed in both cases.

We have recently reported the existence of two distinct levels of order in a homologous series of flexible thermotropic nematic polyesters (1,2). The structure of the repeating units is based on the 4,4'-dioxy-2,2'-dimethylazoxybenzene moiety

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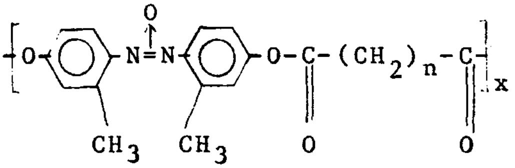
*Present address: Institute of Organic Chemistry, University of Mainz, D-6500 Mainz, Federal Republic of Germany (mesogen 9) and is represented by the formula:



with n=4-12. We have shown that a relatively high level of molecular order exists in the nematic phase for n=4,6,8,10 and 12 (n=even), while a significantly lower degree of molecular order prevails for n=5,7,9 and 11 (n=odd). This intense and sustained odd-even effect is reflected by the oscillation of the nematic-isotropic temperatures, T_{NI}, and transition entropies, $\triangle S_{NI}$ (3). Quenched oriented samples show a distinct small angle X-ray diffraction pattern for n=even; this SAXS pattern is absent in the case of n=odd (1,2). The nematic order parameter S was measured by NMR for n=10 (polymer DDA-9) and n=7 (polymer HEPTA-9); for DDA-9 the value of S is substantially higher than for HEPTA-9, in agreement with calorimetric and X-ray diffraction results (1,2). A considerable degree of orientational correlation between repeating units is observed in the case of DDA-9: a rapid cooperative build-up of order is reflected in the steep increase of $\triangle S_{NI}$ (4) and S(5) with increasing molecular mass M, in contrast to the relatively small influence of M on the values of $\triangle S_{NI}$ and S in HEPTA-9 (1).

In analogy to the term coined by deVries (6) to describe the special molecular organization of some low molecular mass nematics, we have termed the organization of the n=even series "micellar cybotactic nematic", as contrasted with the "ordinary nematic" organization of the n=odd samples.

The cybotactic nematic phase is considered as composed of clusters of molecules aligned with the director and confined to tilted layers. This arrangement of molecules is closely related to a smectic of low order, but considerably more fragmented.

In this letter we report on the miscibility of polymers DDA-9 (n=even) and HEPTA-9 (n=odd) with a low molecular mass nematic and with each other, as well as on the behavior of these polymers in an electric field. This study was undertaken in order to investigate a possible influence of the cybotactic nematic organization in polymeric liquid crystals on their miscibility behavior and alignment in an electric field.

EXPERIMENTAL

The mixtures were prepared by slow evaporation of solvent from solutions in chloroform, followed by heating of the nematic melt in a vacuum oven. The phase diagrams were obtained by microscopy using a Leitz Ortholux II Polarizing Microscope. The results were in agreement with DSC measurements performed by means of a Perkin Elmer 2C instrument, with sample thermal history as described previously (4).

The conducting glass slides coated with SnO_2 were arranged into a sandwich cell. A temperature resistant polymeric film of 25 μm. thickness was used as a spacer. Provision for the sample was made by cutting out a small piece of spacer at the center. The cell was then placed in a metal holder on a hot-stage. The AC voltage was applied by means of a variable amplifier coupled with a voltmeter.

A constant frequency of 60 Hz was used in all cases. All measurements were made at a reduced temperature $T_{red} \approx 0.95$. A Leitz Ortholux II Polarizing Microscope was used to monitor the electro-optical effects.

RESULTS AND DISCUSSION

Both polymers display under the polarizing microscope classical schlieren nematic textures. Spontaneous homeotropic alignment was observed in both systems for values of $\overline{M}_n \lesssim 5{,}000$. Figure 1 shows the phase diagram obtained by mixing polymer DDA-9 with 4,4'-methoxyazoxybenzene (PAA), a standard low molecular mass nematic. The polymer is unfractionated, with a polydispersity index $\overline{M}_w/\overline{M}_n \approx 2$. The polydispersity of this sample is reflected in the wide biphasic gap, N + I, observed by polarizing microscopy. Total miscibility in the nematic phase is observed on heating and cooling, and similar results are observed for the system PAA - HEPTA-9. Figure 2 shows the phase diagram obtained by mixing DDA-9 with HEPTA-9. Sample DDA-9 is polydisperse, whereas the HEPTA-9 sample is a fairly narrow fraction, with a correspondingly narrow biphasic gap. Total miscibility between the two polymers is observed in the nematic phase.

Figures 3 and 4 show the Williams domains patterns and dynamic scattering modes in polymers HEPTA-9 and DDA-9, respectively, with a magnification of 320x. The molecular weight of both samples was $\overline{M}_n$=2500 g/mole and, in order to avoid the homeotropic alignment which spontaneously occurs in this range of molecular weights, we have pretreated the slides by rubbing to achieve homogeneous textures prior to application of

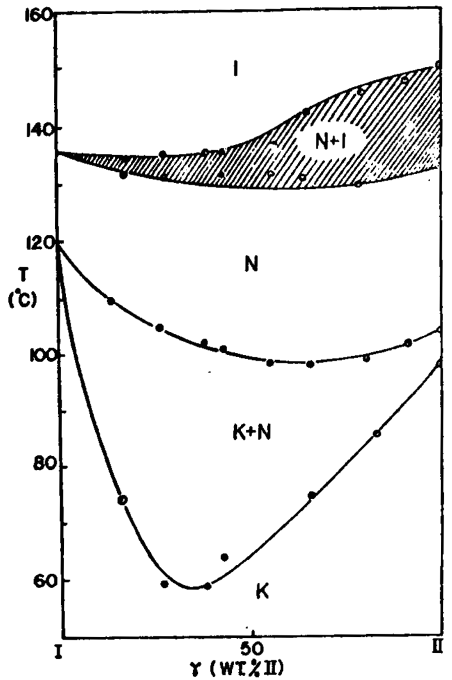


FIGURE 1 Phase Diagram (Temperature, T, Vs. Composition, γ) of the System PAA(I, M=258.3)/DDA-9 (II, $\bar{M}_n$=4000)

Microscopy (Heating rate 10°/Min.)

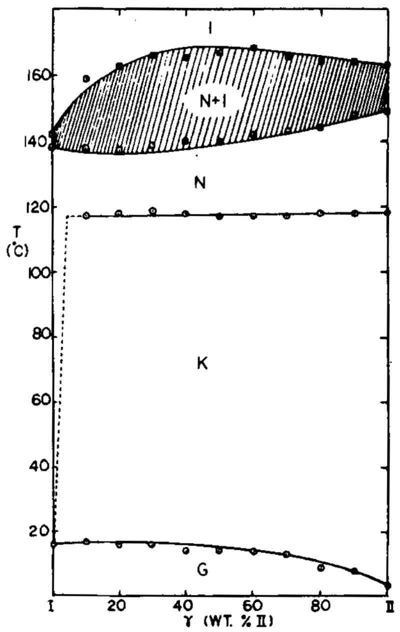
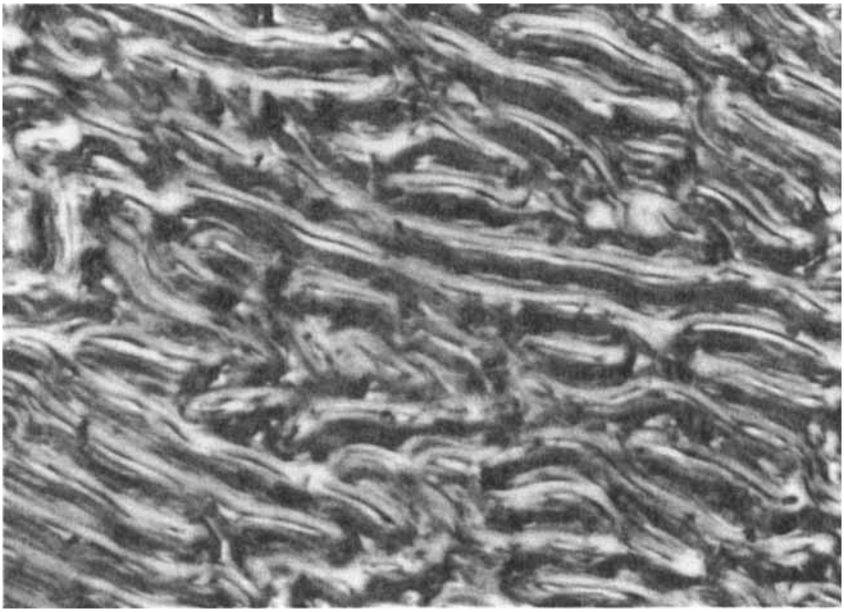


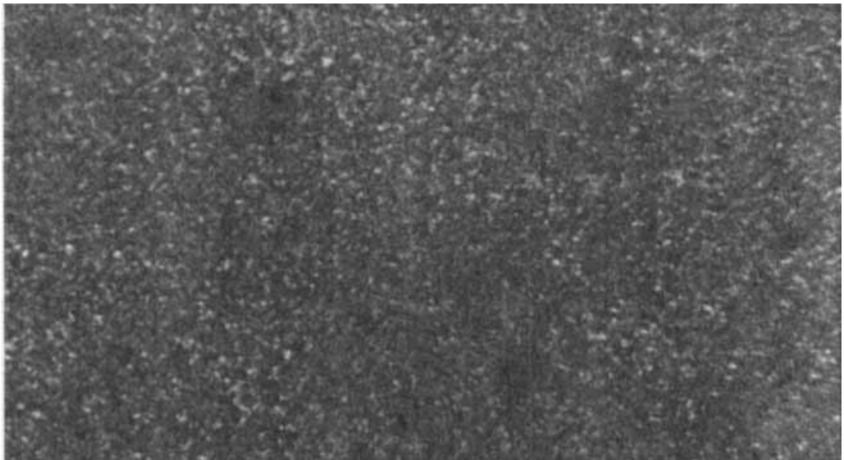
FIGURE 2 Phase Diagram (Temperature, T, Vs. Composition, γ) of the System HEPTA-9 (I, M_n=4000)/DDA-9(II, M_n=4000).

⊙ DSC (Heating rate, 20°/Min.)

⊡ Microscopy (Heating rate, 3°/Min.)

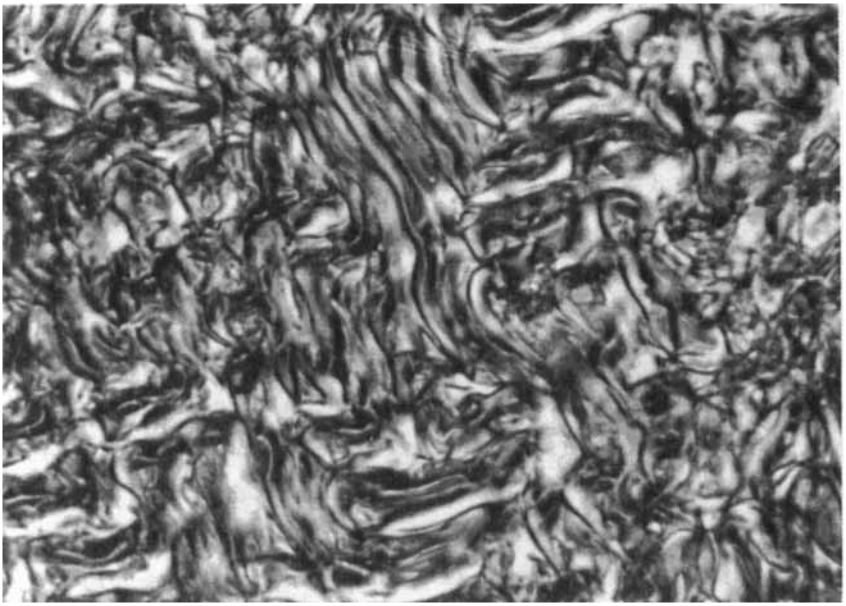


(a) Williams Domains (15 V)

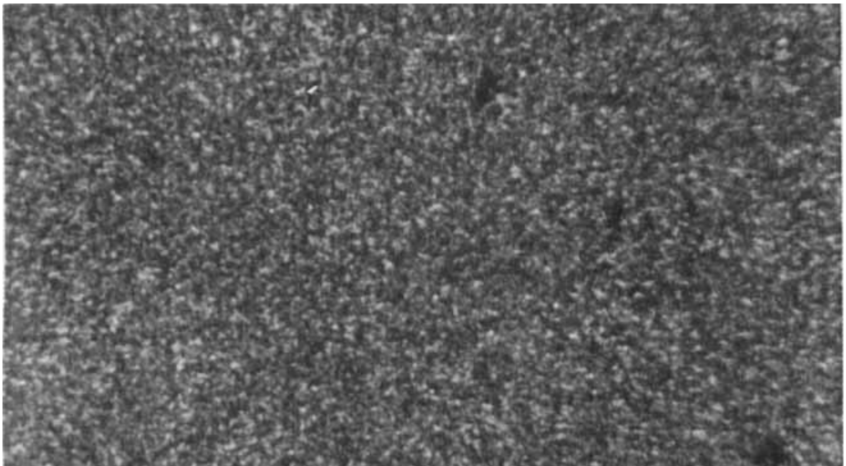


(b) Dynamic Scattering Mode (100 V)

FIGURE 3 POLYMER HEPTA - 9



(a) Williams Domains (20 V)



(b) Dynamic Scattering Mode (100 V)

FIGURE 4 POLYMER DDA-9

electric field. Dynamic scattering modes were observed above 60 volts. We can see that both polymers display the same type of electro-optical instabilities. Similar behavior was reported by Krigbaum et al. (7) in the case of a nematic main chain polymer based on a substituted stilbene mesogen.

In conclusion, it is clear from our results that both types of liquid-crystalline polyesters, "micellar-cybotactic nematic" and "ordinary nematic", although different with respect to local molecular ordering, display similar electric field effects and miscibility. Consequently, in analogy to low molecular mass cybotactic and noncybotactic nematics, they can be classified as belonging to the same type of mesophase.

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