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PHASE DIAGRAMS OF CHOLESTERIC AND NEMATIC THERMOTROPIC LIQUID-CRYSTALLINE POLYMERS

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ABSTRACT

Linear mesogenic polyesters with flexible spacers (molecular weight ranging from 9,000 to 20,000) are studied by polarized microscopy. The nematic and cholesteric mesophases are identified by means of the contact method. Two enantiomers form perfect solid, cholesteric and liquid solutions. The sign of the twist of the cholesteric phases are determined.

Since the earlier work of Sackman and Demus (1) miscibility criteria are used in assigning the type of mesophase of low molecular weight liquid crystals. In the case of polymers the high viscosity of the fluid phases hampers the diffusion and defect relaxation. This last factor increases the difficulty to observe clear textures. Nevertheless Cser et al (2) claim miscibility of p-alkyl-p'acryloyloxyazoxybenzene with the corresponding polymers in the nematic state and Noel

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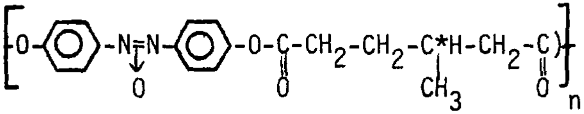
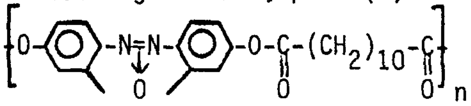
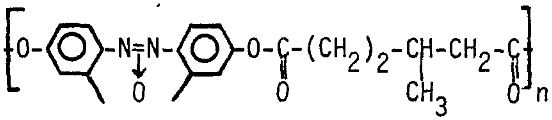
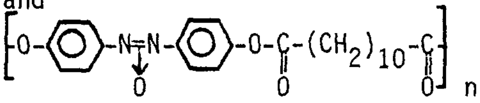
+ Equipe associee au C.N.R.S.

TABLE I (Studied Compounds)

Compounds	Abbreviation	$[\eta]^{30°}$ (dl/g)	$\overline{M}_n$ (dalton)	Phase Transition
 racemic mixture	MAA-8	.39		$K221N296I$
Preceeding formula, pure (+) enantiomer	MAA*-8	.38		$K221N_{\ell}296.5I$
	DDA-9L	.25	4000	$K109N146I$
Preceeding formula, higher n	DDA-9H	.80	18000 to 20000	$K118N153I$
 (+) enantiomer	MAA*-9	.62	7800	$K151N_{\ell}201I$
Statistical copolymer of repeat unit of MAA*-8 and  (equimolecular)	MAA*/DDA*-8 (50/50)	.50	10800	$K162N_{\ell}278.5I$
Statistical copolymer of repeat units of DDA-9 and MAA*-9 (equimolecular)	MAA*/DDA-9 (50/50)	.58	10800	$K81N_{\ell}180I$

The phases exhibited by a compound are K for solid, N for nematic, N_{ℓ} for left handed cholesteric and I for isotropic liquid.

and Billard (3,4) have also reported complete miscibility of poly(azomethine) with three nematic reference solvents as well as a nematic phase of a co[poly(ethyleneterephtalate) p-oxybenzoate] and a smectic phase of a copolyester belonging to a series of terphenyl derivatives. In most cases the polymers were of a rather low molecular weight. In this paper we present some more data concerning nematic and cholesteric thermotropic polyesters based on 4,4'azoxybenzene (mesogene-8) and 4,4'-azoxy2,2'-methylbenzene (mesogene-9) with a number average molecular weight exceeding 10,000, studied recently (5,6,7). The molecular weights $\overline{M}_n$ are obtained from Vapor Pressure Osmometry (VPO) in $CHCl_3$. The limited solubility of the MAA-8 polymer does not allow a precise determination of $\overline{M}_n$ by V.P.O., but the value of the inherent viscosity [η] suggests a $\overline{M}_n$ between 6000 and 8000. The transition temperatures are determined from D.S.C. (Perkin - Elmer, IIB) and microscopic studies (Table I).

The binary phase diagrams are established by microscopic (Leitz, Pamphot) observations of contact preparations (8). To identify the mesophases we have used as reference compounds bis(benzylidene-p.methylaniline) with a nematic mesophase identified in turn by mixing it with n,n'-terephthalylidene-bis-(4-n-butylaniline) (T.B.B.A: K190N265I); the p-azoxyanisol (PAA: K118N135I) and the p-azoxyphenetol (PAP: K138N169I).

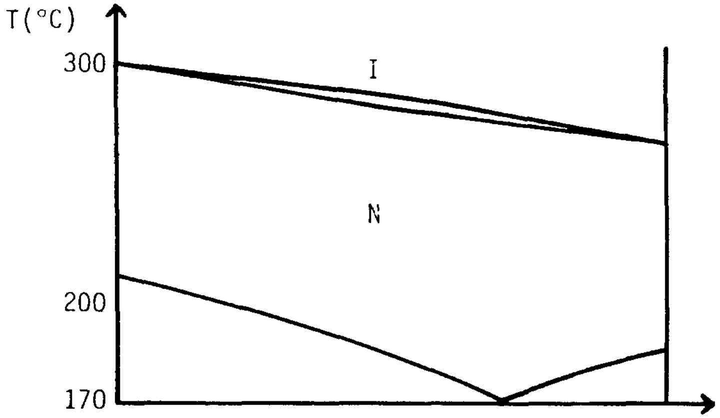


FIGURE 1 - Binary phase diagram of the mixtures of MAA-8 (on the left) and bis(benzylidene-p.methylaniline) (on the right).

The Figure 1 gives the phase diagram of the mixtures of MAA-8 with the bis(benzylidene-p.methylaniline) as reference compound. This polymer exhibits a mobile nematic phase with schlieren-like texture and threads. The mesophase of MAA*-8 obtained by melting is also very fluid and exhibits small size focal conics. By pressing the cover slip a homogeneous texture with beautiful colors (due to the dispersion of a very high rotatory power) appears.

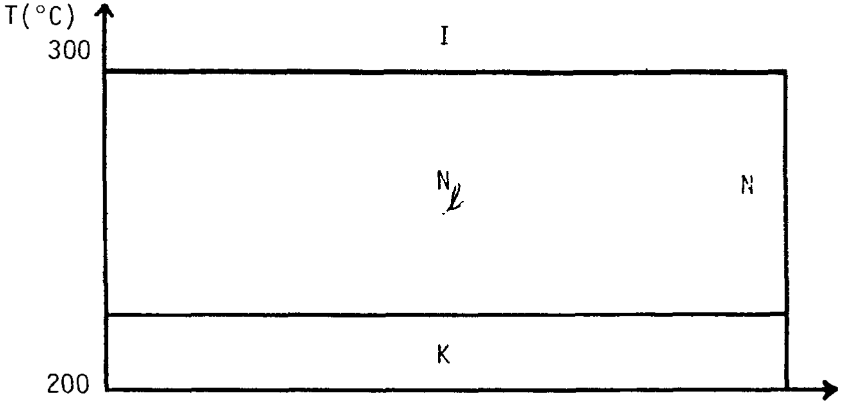


FIGURE 2 - Binary phase diagram of the mixtures of MAA*-8 (on the left) and MAA-8 (on the right).

In the phase diagram of MAA-8 and MAA*-8 (Figure 2) the spindles are reduced to horizontal straight lines. Consequently the mixtures of the two enantiomers of MAA*-8 form perfect solid, cholesteric and liquid solutions. This situation has been already encountered for the case of low molecular weight mesogens (9). The sign of the twist of the cholesteric phase is determined from the displacement of the isochromatic lines (10) in the mixtures. This sign is left handed. The MAA*/DDA-8 gives also a fluid mesophase with similar textures. To identify the phase of the copolymer the MAA-8 polymer is used as a reference compound (Figure 3).

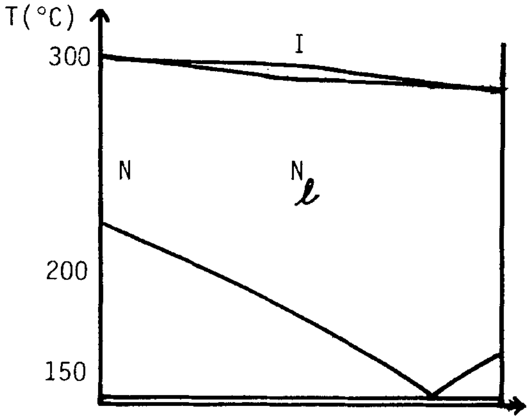


FIGURE 3 - Binary phase diagram of the mixtures of MAA-8 (on the left) and MAA*/DDA*-8 (50/50) (on the right).

The MAA*/DDA-8 copolymer exhibits also a left handed cholesteric mesophase.

The DDA-9L polymer gives a mobile mesophase. This polymer is totally miscible with the p-azoxyanisole in the nematic state. The higher molecular weight analogue, DDA-9H is fibrous. The nematic phase is very viscous and exhibits a schlieren-like texture. The chiral MAA*-9 polymer gives a viscous mesophase with small sized focal conics. Identified by mixing with the p-azoxyphenetol it appears as a left handed cholesteric. Similar results are obtained with MAA*/DDA-9 (50/50). The mesophase viscosity of the polymers described above increases with the molecular weight. However the mobility of their mesophases remains sufficient to use successfully the contact method and the obtained binary phase diagrams allow to establish the nematic or cholesteric nature through the application of miscibility rules (11). The observation of the isochromatic line displacement allows to establish the sign of the twist of the cholesteric phases.

This work gives an example of perfect solid, cholesteric and liquid solutions formed by polymeric enantiomers.

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