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# INVESTIGATION OF POLYMER MESOPHASES BY OPTICAL MICROSCOPY

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► **To cite this version:**

B. Fayolle, C. Noel, J. Billard. INVESTIGATION OF POLYMER MESOPHASES BY OPTICAL MICROSCOPY. Journal de Physique Colloques, 1979, 40 (C3), pp.C3-485-C3-489. 10.1051/jphyscol:1979397 . jpa-00218794

**HAL Id: jpa-00218794**

**<https://hal.science/jpa-00218794>**

Submitted on 4 Feb 2008

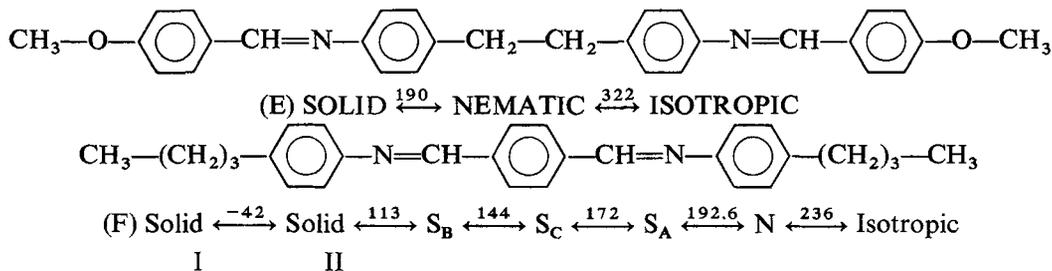
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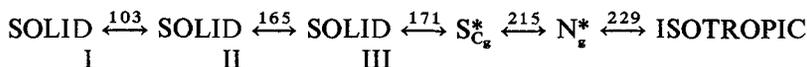
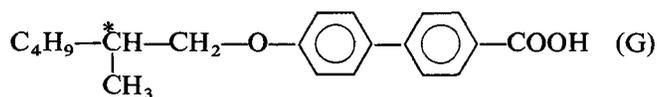


It has an inherent viscosity at 25 °C of 0.6 dl/g at a concentration of 0.5 g/dl in dichloroacetic acid.

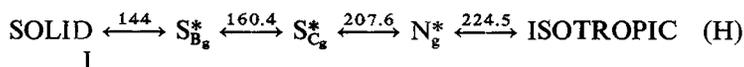
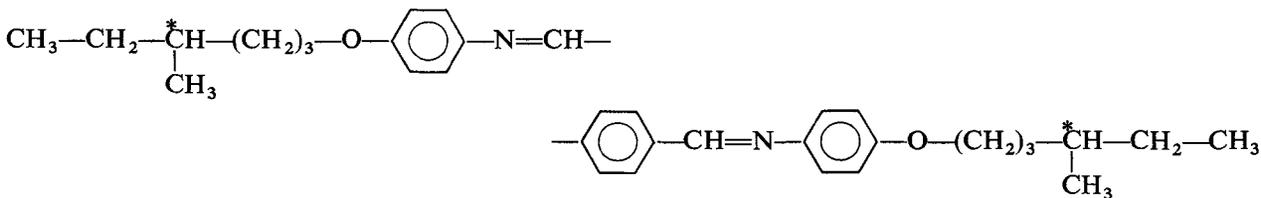
The reference compounds used to identify the polymeric mesophases are the N,N'-di(p-methoxybenzylidene)  $\alpha,\alpha'$ -bi-p-toluidine (E) (Eastman Organic Chemicals) for the copolyester B and the terephthal-bis-(p-butyl-aniline) (F) (12) for the copolyester C



The conversion of polymeric mesophases to the cholesteric or the twisted smectic C form is performed by the addition of the following optically active solutes : the 4'-(2-methyl hexyloxy) biphenyl-4-carboxylic acid (G) [13],



and the terephthalylidene-bis-4-(+)-4'-methylhexyloxy)-aniline (14) (H)



Phase transition temperatures and enthalpies are measured using a differential thermal analyzer (Du Pont 990). The samples are examined under dry nitrogen flow. Scanning rates of 10 K/min are used. The transition temperatures are taken as the endotherm maximum point. For the evaluation of the transition enthalpies an indium sample is used as reference standard.

The textures of the phases are observed between cover slips with a polarizing microscope (Leitz, Panphot) equipped with a heating stage [Mettler FP5 or Leitz 1377].

**3. Results.** — The transition enthalpies and temperatures are given in the table I.

**3.1 Co[POLY(ETHYLENE TEREPHTHALATE)-p-OXYBENZOATE].** — DSC scans show a first order transition at 298 °C. No upper transition is observed up to 350 °C. Observations with the polarizing microscope indicate the formation of a birefringent melt at the same temperature. As shown in figure 1, the copolyester mesophase has a typical threaded Schlieren texture. It is isomorphic with the nematic phase of the reference compound E. The isobaric phase diagram of mixtures of the copolyester B and the substance E shows a nematic eutectic point at 160 °C. The equilibrium spindle between the nematic and liquid phases is regular.

The copolyester mesophase is also isomorphic with the nematic phase of the copolyazomethine A which is itself isomorphic with the nematic phases of known reference compounds [10]. The isobaric phase

lyester mesophase has a typical threaded Schlieren texture. It is isomorphic with the nematic phase of the reference compound E. The isobaric phase diagram of mixtures of the copolyester B and the substance E shows a nematic eutectic point at 160 °C. The equilibrium spindle between the nematic and liquid phases is regular.

TABLE I

Transition temperatures (°C) and enthalpies (kcal/monomer unit)

Polymers	C	S <sub>c</sub>	N	L
A	•	258- ~ 0.48	•	> 341 °C •
B	•	298- 0.13	•	> 350 °C •
C	•	112-5.22 •		247-6 •

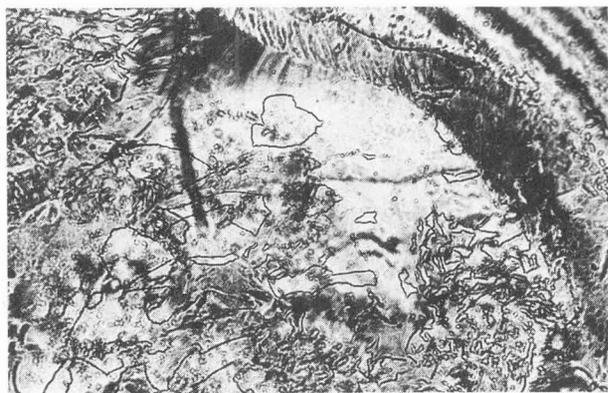


FIG. 1. — Typical threaded Schlieren texture of the nematic phase.

diagram of mixtures of the copolyester B and the copolyazomethine A shows an eutectic at 239 °C.

It is worthwhile to note that the nematic phases of B and A can be transformed to cholesteric ones by dissolving an optically active compound in them. The figure 2 shows that the copolyazomethine A is totally miscible with the optically active compound H in the nematic-cholesteric state. This chiral compound, on addition to the copolyazomethine mesophase, causes the formation of the typical planar texture of cholesterics. In the range of small content of the chiral compound parallel lines are formed as shown in figure 3a. As the content of H increases moiré fringes appear (Fig. 3b). The planar texture exhibits typical colours of rotatory power's dispersion.

Similar results are observed with the copolyester B. The isobaric phase diagram of this copolyester and the chiral compound G shows an eutectic at 149 °C. The cholesteric mesophase appears at 209 °C. The

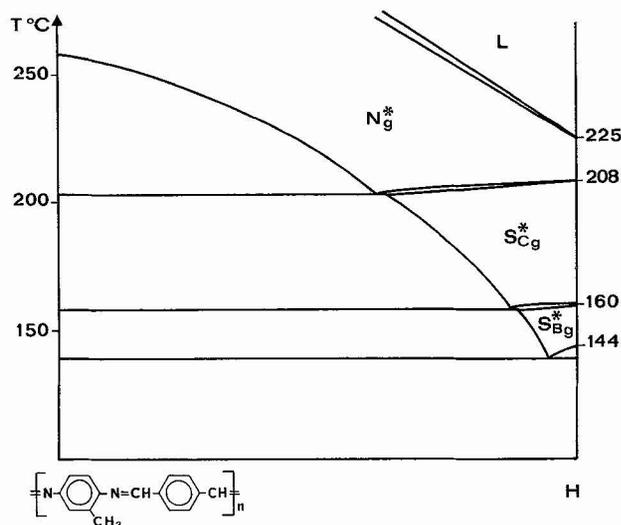
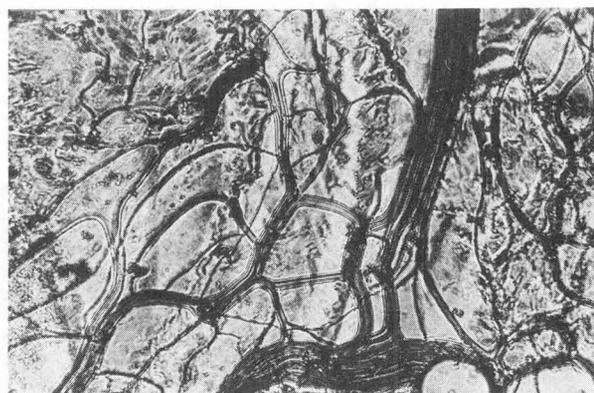


FIG. 2. — Isobaric phase diagram of the copolyazomethine A and the chiral compound H.



a)



b)

FIG. 3. — Typical plane texture obtained at 260 °C by the addition of the optically active compound H to the copolyazomethine A ; (a) parallel lines, (b) moiré fringes.

equilibrium spindle between the cholesteric and liquid phases shows a minimum at 223 °C.

**3.2 COPOLYESTER C.** — DSC scans show that two first order transitions separated by 135 °C are found in sample C. As observed for different polymers exhibiting mesophasic behavior [2, 8, 10, 15], the melting endotherm of the original sample, which appears at 112 °C, is broadly shouldered on the low temperature side. Another interesting observation is the high enthalpy change involved in the liquid crystal-isotropic liquid transition as compared to the melting enthalpy (Table I).

On cooling from the amorphous isotropic liquid, the copolyester C gives rise to an anisotropic liquid that exhibits a texture with focal conics (Fig. 4). The smectic C phase of the copolyester C is identified by isomorphy with the smectic C phase of the reference compound F (Fig. 5). Besides the smectic C phase of the copolyester C is miscible with the left handed twisted smectic C phase ( $S_{C_g}^*$ ) of either the chiral compound G or the optically active substance H (Fig. 6a and b). In the figure 6, the abbreviation TS is used to indicate the domains which exhibit the twisted smectic textures shown in figures 7a and b.

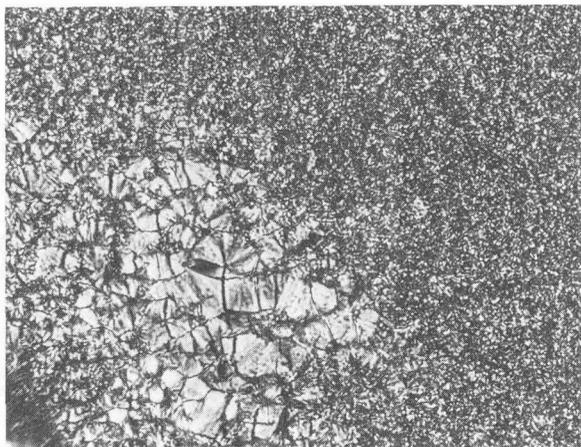


FIG. 4. — Texture of the smectic C phase of the copolyester C.

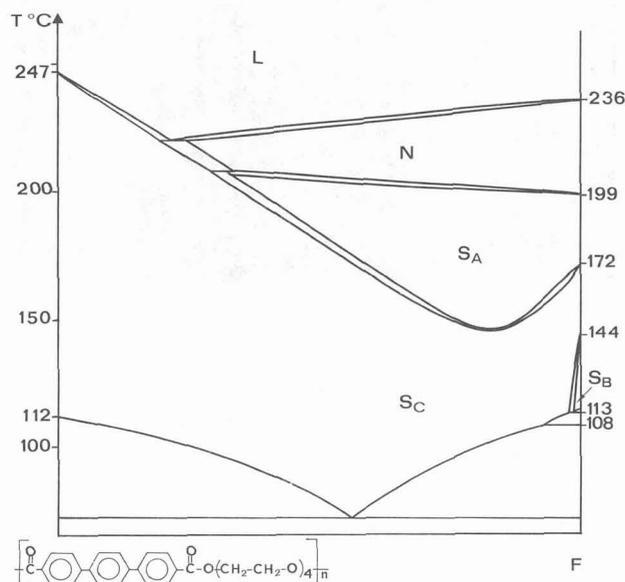
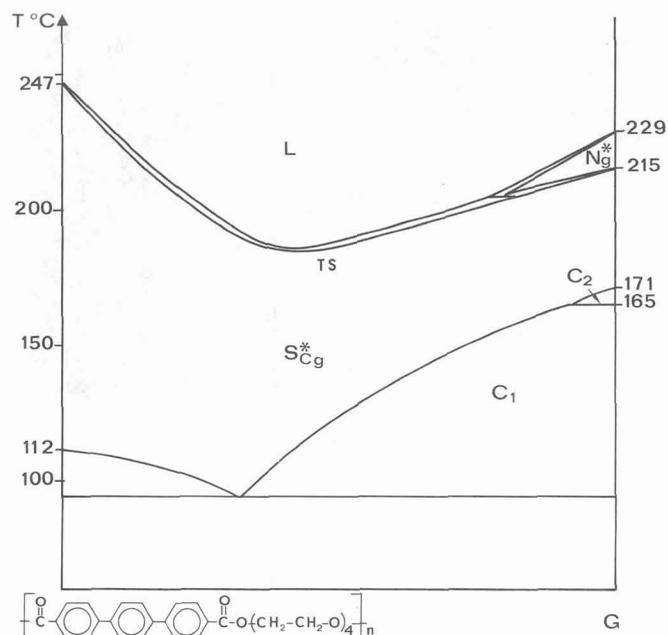


FIG. 5. — Isobaric phase diagram of the mixtures of the copolyester C and the reference compound F.

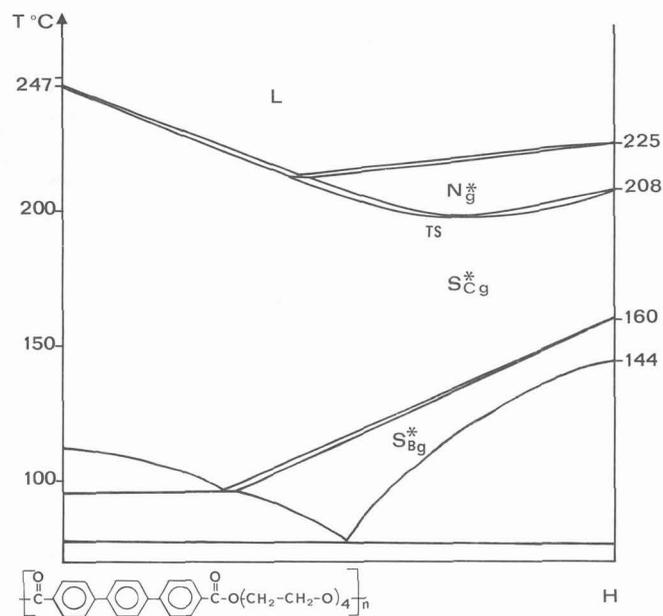
**4. Conclusion.** — In this study, by using the contact method, we have been able to identify the nematic phase of a co[poly(ethylene terephthalate)-p-oxybenzoate] and the smectic C phase of a copolyester belonging to series of terphenyl derivatives. However, as to the macromolecule organization in the smectic strata, a model is still hypothetical and needs further experimental confirmation.

The conversion of the liquid crystalline polymer phases to the cholesteric or the twisted smectic C form can be performed by the addition of optically active solutes.

**Acknowledgments.** — The authors acknowledge Pr. G. W. Gray (University of Hull, HUG 7RX,



a)



b)

FIG. 6. — Isobaric phase diagram of the mixtures of the copolyester C and the chiral compound G (a); H (b).

England), MM. Strzelecki and Liebert (Laboratoire de Physique des Solides, Université de Paris Sud, Centre d'Orsay) and Mrs Leclercq (Laboratoire de Chimie Organique des Hormones, Collège de France, Paris) for the reference compounds H, F and G. The authors are also indebted to Professor L. Monnerie (Laboratoire PCSM, 10, rue Vauquelin, 75231 Paris Cedex 05) who suggested this work.

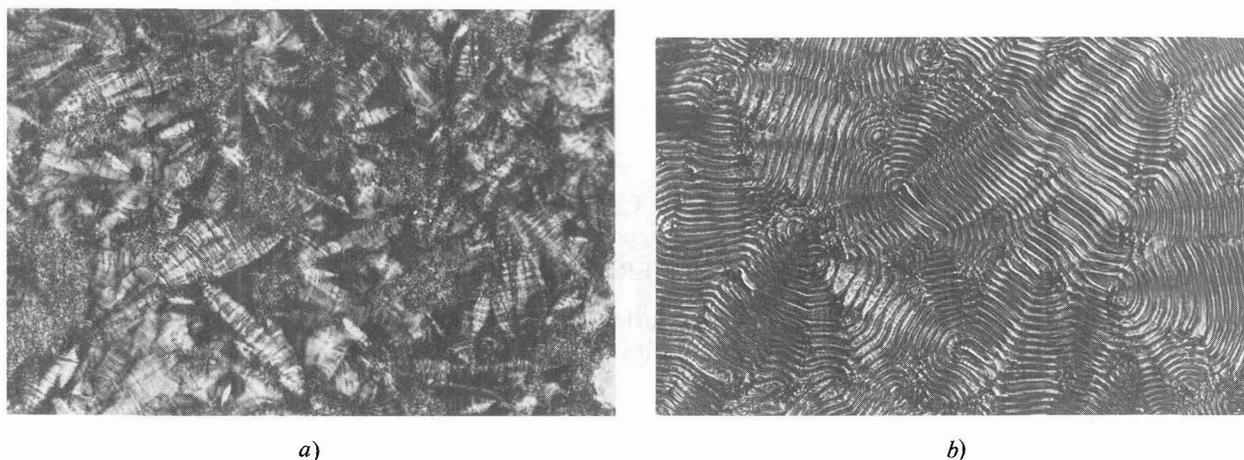


FIG. 7. — Twisted smectic C textures obtained by the addition of G (a) or H (b) to the smectic C phase of the copolyester C.

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