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MESOMORPHIC POLYMORPHISM IN SOME DISC-LIKE COMPOUNDS

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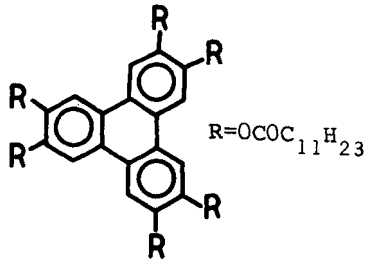
ABSTRACT: A complex mesomorphic polymorphism is shown in a hexa-n-dodecanoate of triphenylene. Both by calorimetric measurements and optical textures, evidence of three different mesophases are given. Two of these transitions are practically second order ones.

Two homologous series of disc-like molecules, recently described, exhibit thermotropic mesomorphism; benzene hexa-n-alkanoates[1] and hexasubstituted ethers or esters of triphenylene.[2] At first, the possibility of this mesophase being a birefringent plastic crystal was considered,[1] taking into account the large enthalpies measured at the isotropic transition. This ambiguity has been partly removed by our own results. Binary phase diagrams[2,3] and heats of transition were obtained for two homologous series of hexasubstituted triphenylenes and are very similar to those encountered in usual liquid crystals. At last, to prove definitively that these new compounds are true liquid crystals in the accepted sense of the term, mesomorphic polymorphism has to be found; we did it with some hexa-n-esters with long alkyl chains[4] where we have found two mesomorphic phases. In fact, this polymorphism was found before we thought; we have just found that the hexa-n-dedocanoate of triphenylene exhibits three different thermotropic phases.

EXPERIMENTAL RESULTS



The hexa-n-dodecanoate of triphenylene has been synthesized following the method we recently published.[2,5] It consists of coupling the corresponding acid chloride with hexahydroxy-2,3,6,7,10,11-triphenylene. We have prepared a large quantity of this compound to allow several studies and to obtain more

precise physical properties

Temperature and heat of transitions are given below:

T^oC	C	$\xrightarrow{80^o}$	D_0	$\underset{92^o}{\overset{93^o}{\rightleftarrows}}$	D_1	$\underset{109.8^o}{\overset{111^o}{\rightleftarrows}}$	D_2	$\underset{120.9^o}{\overset{122.3^o}{\rightleftarrows}}$ I
$\Delta H(mole^{-1})$	14.2 Kcal		~ 0 cal.		35 cal.		577 cal.	

C = crystal; I = isotropic; $D_{0,1,2}$ = mesophase 1,2,3

These enthalpies have been measured by differential scanning calorimetry using a Du Pont 990 thermal analyzer.

The D_0D_1 transition cannot be observed, at the higher sensibility of the thermal analyzer even by repetitive scanning to avoid noise. This new transition is practically a second order one.

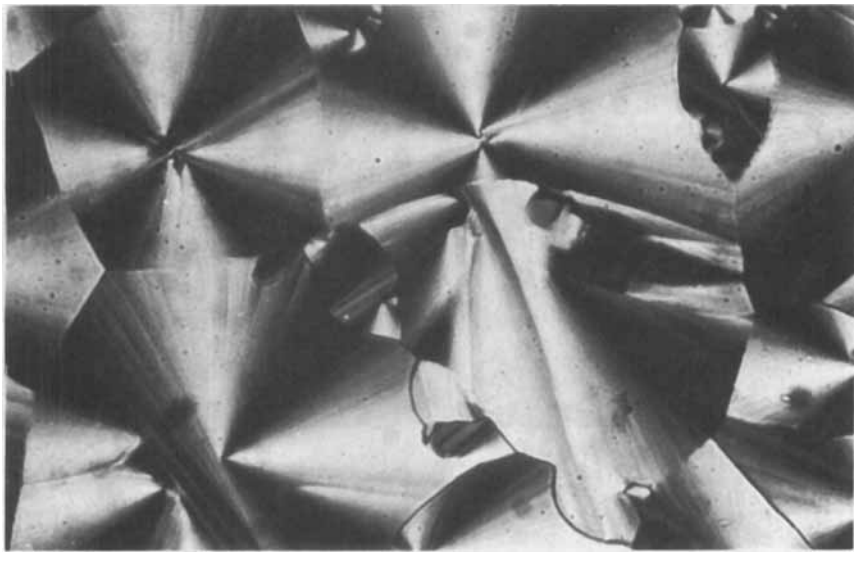
Optical textures where observed with a polarizing microscope equipped with a heating and cooling stage (Mettler FP5).

The higher temperature phase (Fig. 1a) is characterized, in some areas of the preparation, by big focal conics very similar to those observed with smectics A.[6,7] On cooling one can observe the D_1 phase (Fig. 1b); this original texture makes its appearance with concentric rings which look like "finger prints". At last, near 92°C the D_0 phase is observed (Fig. 1c). At first sight, the texture seems strictly superimposable on D_2 at a higher temperature (Fig. 1a) we are led to the idea of a re-entrant phase! Careful examination of the picture shows the presence of longitudinal and radial striation lines in the smectic E.[6,7] On heating the sample again, we obtain the textures of Figures 2a and 2b for the D_1 and D_2 phases. At last, we show in Figure 3 a picture of the crystalline phase taken in the same area of the sample at 50°C.

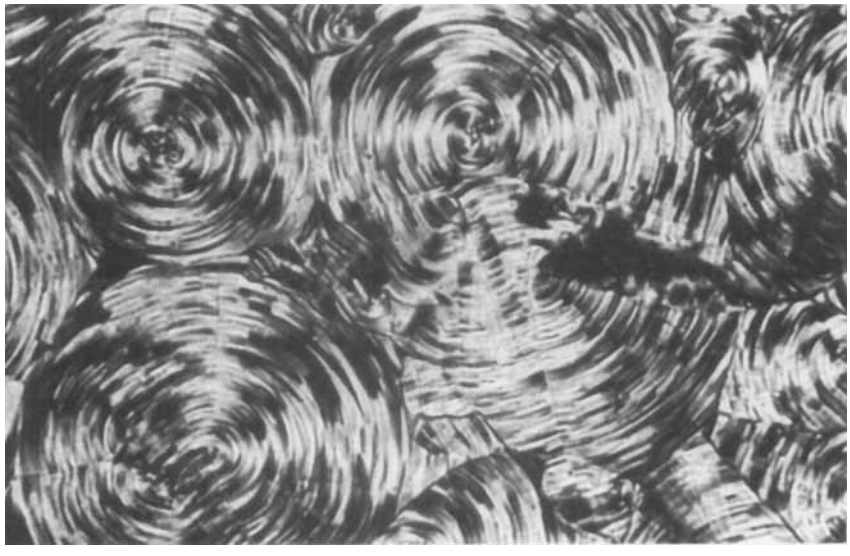
We must point out that on heating, we find again exactly the same texture for the D_2 phase (compare Figs. 1a and 2b). Further, we must point out that for the intermediate phase D_1 the consideration is now just between the focal conics of D_2 or D_0 and the "finger print" texture (Fig. 2a).

Figure 1 Textures of the compound : hexa-n-dodecanoate of triphenylene on cooling

1a D_2 phase at 112°C



1b D_1 phase at 108°C



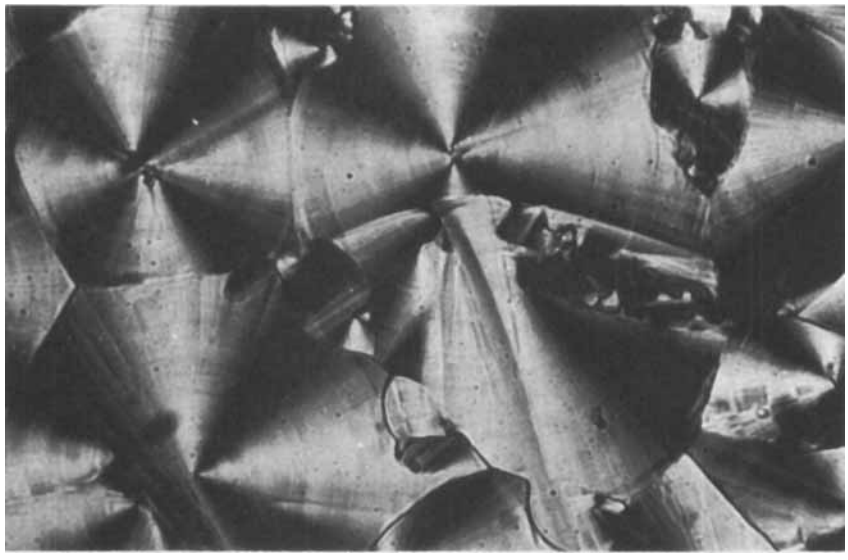
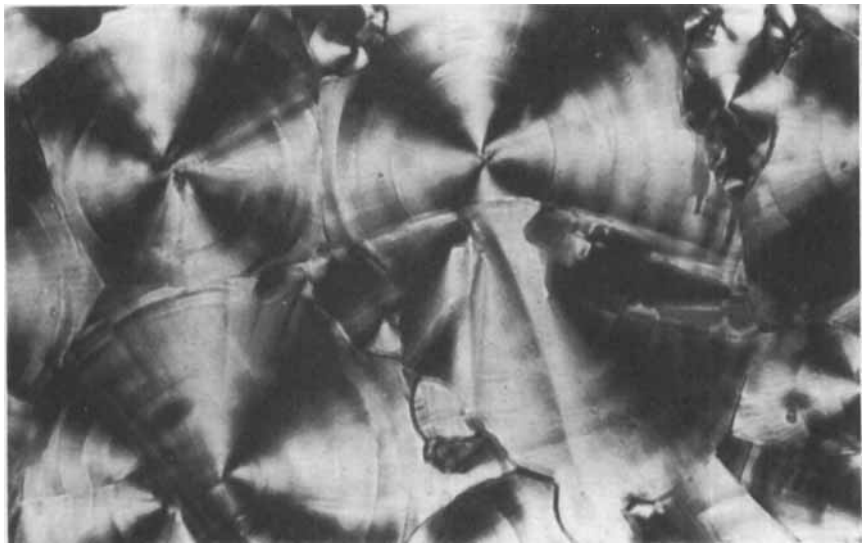


Figure 2 Textures of the hexa n-dodecanoate of triphenylene one heating

2a D_1 phase at 110°C



2b D_2 phase at 111°C

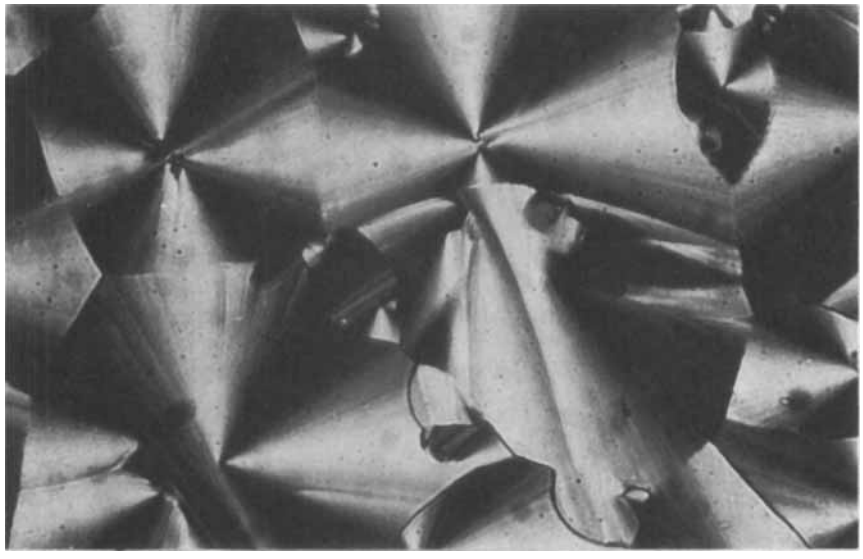
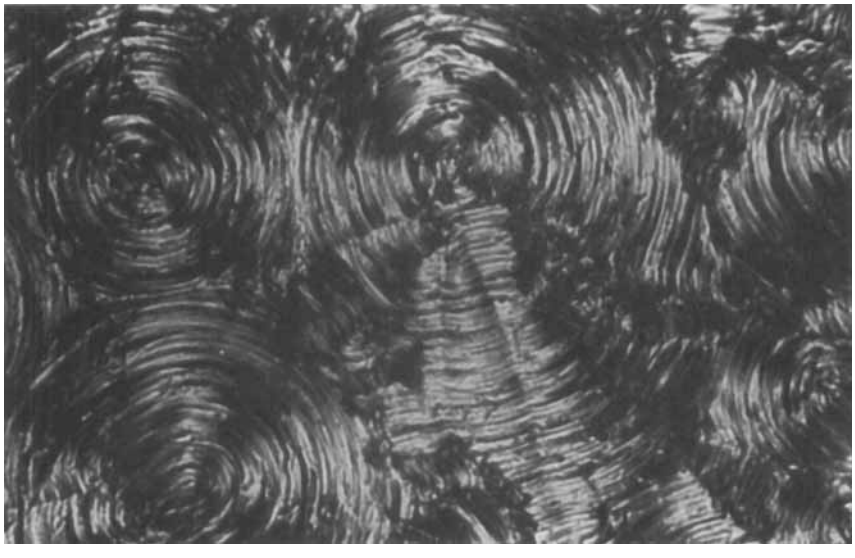


Figure 3 Crystalline phase at 50°C



We must note that in other domains of the preparation another type of texture can be observed for the D_1 phase; there are convergent rods with the angles between rods roughly 60°; this shows a hexagonal short range order.

CONCLUSION

We have shown, for the first time, the existence of three different mesophases in a disc-like mesogen; one of the transitions is essentially second order. A systematic study of this polymorphism is in progress by the well known technique of isomorphism and will be published elsewhere. Anyway, this polymorphism confirms clearly the real mesomorphic nature of this new kind of liquid crystal with physical properties very similar to a rod-like mesogen but with a drastically different molecular organization which we found.

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