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Thermotropic Liquid Crystalline Polymers Smectic "C" Phase in a Liquid Side-Chain Poly α Chloroacrylate

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SUMMARY

Microscopic observations, thermal studies, dielectric relaxation measurements and X-Ray diffraction experiments on magnetically aligned samples of a mesogenic side-chain poly 4 - butoxy-phenyl - 4 (α chloro-acryloyloxyhexyloxy) benzoate are presented.

INTRODUCTION

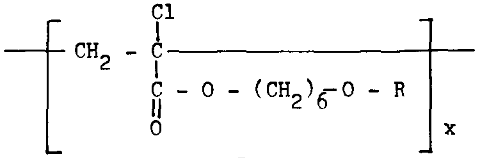
Many studies in the field of mesogenic side-chain polymers have been carried out during last years. They now allow to find some reports of existence of thermotropic liquid-crystalline (LC) states for such polymeric system (1, 2, 3). In the liquid crystalline states, the motions of the polymer main chain have to be decoupled from those of the anisotropically oriented mesogenic side chains by flexible spacers. The synthesis and identification of nematic, cholesteric and some smectic such as S_A, S_B polymeric liquid crystals have already been reported (4, 5). Some authors claimed formation of Sc tilted smectic phase (6, 7).

In this communication, we report direct information about the structural state of the smectic C phase of a polyα chloroacrylate by means of optical microscopy, differential scanning calorimetry, dielectric relaxation measurements and X-Ray diffraction experiments on magnetically aligned samples.

RESULTS AND DISCUSSION

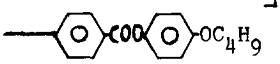
N and Sc phases were discovered in the poly α chloroacrylate of general formula (1)

(1)



$$-\!\!\left[\, CH_2 - \underset{\underset{\underset{\displaystyle O}{\|}}{C - O - (CH_2)_6 - O - R}}{\overset{Cl}{C}} \,\right]_x\!\!-$$

with R =



Experimental Part

The synthesis of polymer (1) has been described earlier (8) ($M_w = 5.10^4$). Preparation of p - n butyloxyphenol was made following the procedure of Klarman et al. (9). Optical studies with polarized light were performed using a microscope (Leitz Orthoplan) equipped with a heating stage. The DSC curve was obtained with a DSC4 Perkin-Elmer and the frequence and temperature dependent dielectric measurements were made with a LCR Meter HP 4262A (temperature range : - 70° C + 210° C, frequency range 100 Hz - 10 kHz)

Results

The characteristic DSC-curve with two endothermal peaks corresponding to $S_c \longrightarrow N$ and $N \longrightarrow$ isotropic melt transitions are given in fig. 1. The glass transition temperature was observed on the DSC curve at 30° C.

Both N and S_c phases display a very fine "Schlieren" texture at temperatures below the clearing temperature T_{cl} (fig. 2). Increasing the temperature up to 388K leads to full disappearance of the anisotropy, i.e. to the transition into the isotropic melt.

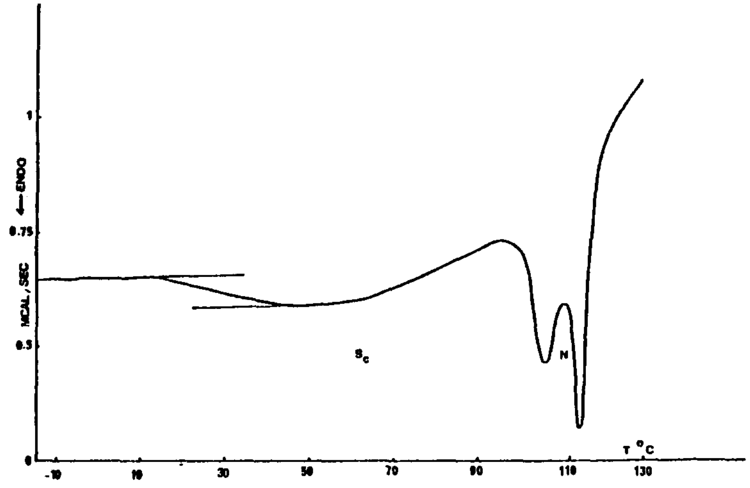


Fig. 1 : DSC-curve of polymer 1
scan rate : 20° C/mn
weight of the sample : 7 mg

Thermal data of polymer (1) (Tg :glass transition temperature : T_{cl} : clearing temperature : T_1 : temperature of $S_c \longrightarrow N$ transition are :

Tg/° C	T_1/° C	T_{cl}/° C
30	105	112

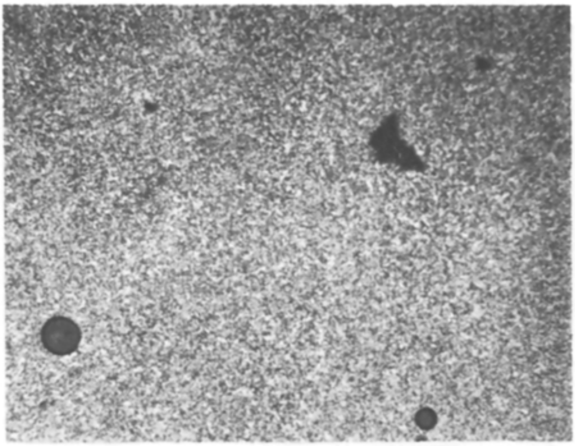


Fig. 2 : Optical texture photograph of LC Polymer 1 at 383K (crossed polarizers, enlargement 200X)

This polymer was also studied by frequency and temperature dependent dielectric measurements. in the dielectric relaxation spectrum (Fig. 3) three motions are observed (β, α, γ) (Tab. I)

TABLE I : Temperature of α, β, γ relaxations at different frequencies (°C)

T_β	T_α	T_γ
10^3Hz -20	40	120
10^4Hz -30	45	120
DSC 1Hz (unfound)	30	

The relaxation seems to be due to internal movements of the mesogenic groups : the ester bridge ($-\mathrm{C}(=\mathrm{O})\mathrm{O}-$) between the two aromatic rings (6, 10).

At the glass transition (α relaxation), the centers of gravity of the mesogenic groups and the polymer chain become mobile and dipole reorientations are possible.

The relaxation can be correlated with the clearing phenomenon (6, 10)

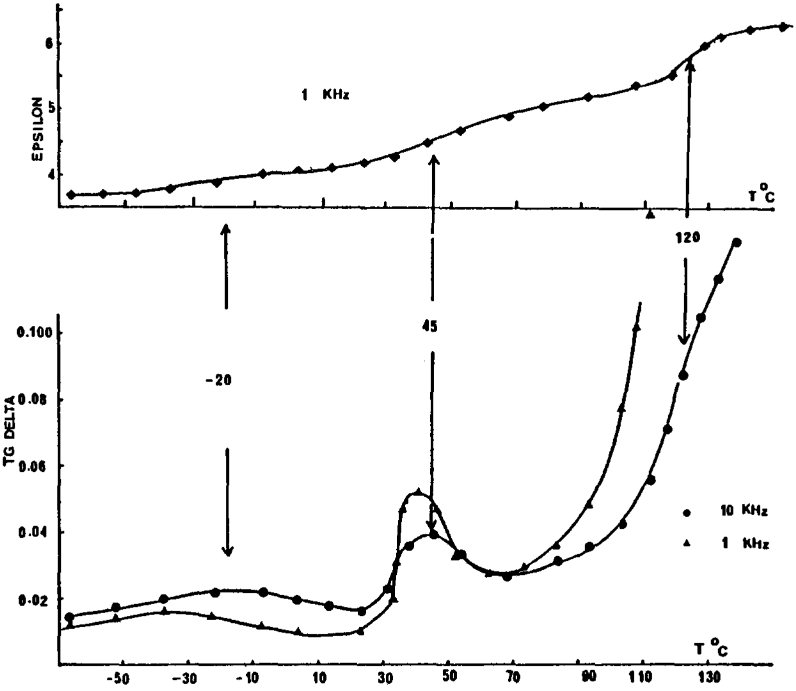


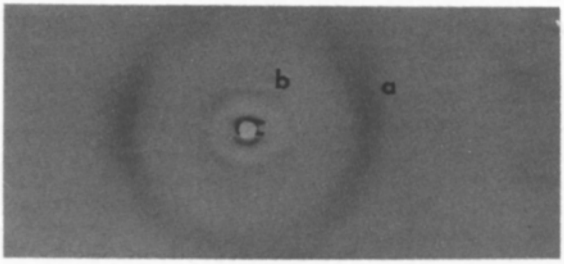
Fig. 3 : Dielectric Relaxation Spectrum

X-Ray Diffraction Experiments on Magnetically Aligned Samples.

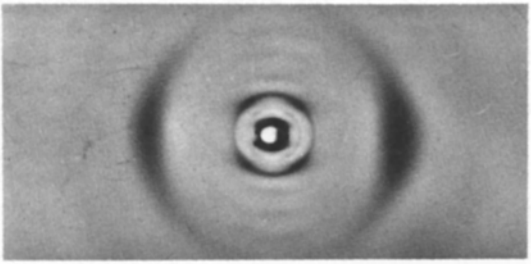
Oriented X-ray diffraction patterns were obtained on aligned samples by applying a field of 1,7 T for a few hours at a temperature just below the N-I transition (K_{α} (Cu) = 1,54 A ; diameter of the lindeman glass tube = 1,5 mm).

The magnetic field (along the Z axis) is perpendicular to the X-ray beam (along the Y axis) and to the capillary tube (along the X axis).

Fig. 4a and b show oriented diffraction patterns in the nematic (4a) and smectic phases (4b) for polymer (1).



4a



4b

In fig. 4a, two symetrical wide angle crescents (a) are located in a direction (equater) perpendicular to the field direction. They are due to the lateral interferences between the mesogenic cores and they show that these moities are aligned by the magnetic field. The radial and angular extension of the crescents (a) are similar to those of low molecular weight calamitic mesogens (S order parameter $\sim$ 0,6-7). At low angles, along the meridian field direction and perpendicular to it, we find curved diffusion lines (b) (1st and 3rd orders).

When cooling down the sample, these lines (b) condense into Bragg spots (fig. 4b). The glassy state of the polymer is reached without any significant change. Going from the nematic to the smectic phase, the angular extension of the wide angle crescents (a) decrease, showing an increase of the order parameter.

The diffraction pattern represented on fig. 4b and 4c is characteristic of a smectic C phase (11).

The occurence of this smectic C phase was already mentioned by R. Zentel in a drawn fiber of the same polymer (12).

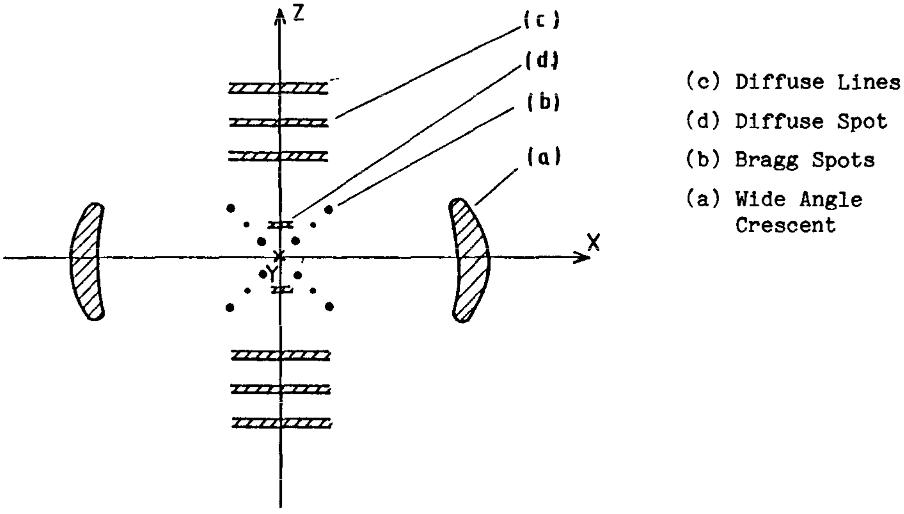


fig.4c

Schematic Representation

Two sets of Bragg spots (b) are aligned on straight lines making an angle of 40° with respect to the magnetic field (three orders of reflection are visible on the photograph).

These spots actually form the intersection of a ring with the Ewald sphere, since we have a cylindrical symmetry aroud Oz. Such a ring shows the existence of tilted layers making an angle of $\alpha \sim 40°$ with the director. Cooling the aligned nematic phase into the smectic phase, the appearance of such spots is, thus, characteristic of a smectic C phase. Table II gives some numerical values for the smectic periodicity.

TABLE II

	Periodicity along Oz	Periodicity along Ox
(a)	-	4,6 A
(b) 1st order	56,0 A	67,2 A
2nd order	27,8 A	34,2 A
3rd order	18,5 A	21,3 A
(c) 6th order	9,8 A	-
8th order	7,0 A	-
10th order	5,6 A	
(d)	28,3 A	

Tilt angle 40°

If we compare the length of a monomer ($\sim$28 A) measured on Dreiding stereomodels) with the smectic periodicity ($B_{1z} \sim 56$ A) along the z axis, we find that we need two monomers stretched and aligned along Oz to obtain a thickness of 56 A. This means that the smectic lamellar are bilayer (cf. ref. 13). We have two possible structures for such bilayer lamellar. The mesogenic cores need to make the tilt angle $\alpha = 40°$ with the perpendicular to the layer. Let us consider a pair of mesogenic cores associated together end to end : such two cores either may be strictly antiparallel (cf. Fig. 5a) or they may form an angle $\rho = \pi - 2\alpha$ (cf. Fig. 5b). The X-ray photograph shown in Fig. 4b allows us to rule out this second hypothesis because, in such a case, the outer ring would be split into 4 crescents showing the two possible orientations of the aromatic moieties. We do not observe any effect of this kind and may thus conclude that Fig. 5a is the thermodynamically stable arrangement for our bilayer lamellar.

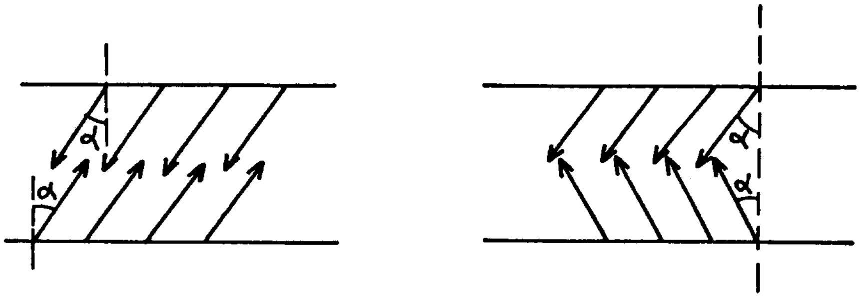


fig.5a fig.5b

Fig.5 : Possible arrangements for bilayer lamellar

Conclusion : Microscopic observations, DSC, dielectric relaxation and X-ray diffraction patterns on magnetically aligned samples have clearly shown that Polymer (1) basically presents a smectic C bilayer lamellar organization usually found with a cyano end group on the mesogenic core. High exposure patterns have demonstrated that slow recrystallization takes place and that smectic A fluctuations exist in the sample.

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