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MESOPHASIC BEHAVIOUR OF SOME POLYCARBONATES OF 4,4' DIHYDROXY-α,α'-DIMETHYLBENZALAZINE

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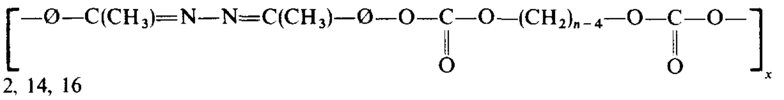
Abstract—Polycarbonates of formula:



$$\left[-\varnothing-C(CH_3)=N-N=C(CH_3)-\varnothing-O-\underset{\underset{O}{\|}}{C}-O-(CH_2)_{n-4}-O-\underset{\underset{O}{\|}}{C}-O-\right]_x$$

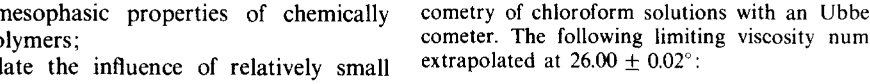
$n = 10, 12, 14, 16$
have been prepared and characterized by DSC thermal analysis and X-ray diffraction methods. They show thermotropic mesophasic behaviour. The melting and clearing temperatures and the thermal stability range of the mesophase decrease with increasing length of the aliphatic part of the polymer chain. The high temperature X-ray diffraction spectra show that the liquid crystal phases are nematic. Three of the four polymers show solid state polymorphism, the observable crystal phase depending on the thermal history of the sample.

INTRODUCTION

We have already reported [1, 2] the mesophasic properties of some polymers having main chains of alternating rigid, highly conjugated atomic groups and flexible aliphatic portions.

For low molecular weight mesophasic compounds, a major point receiving great attention is the detailed analysis of the relation between chemical composition, structure and mesophasic properties. A considerable amount of interesting data and correlations has already been collected [3, 4] but this is not so for polymeric liquid crystals, although the scientific interest on them is rapidly growing.

We refer here to the synthesis and characterization of polymers with formula:



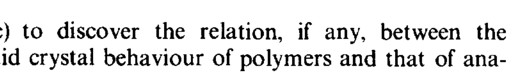
$$\left[-O-\overset{\overset{O}{\|}}{C}-O-(CH_2)_{n-4}-O-\overset{\overset{O}{\|}}{C}-O-\varnothing-C(CH_3)=N-N=(CH_3)C-\varnothing-\right]_x$$

$n = 10, 12, 14, 16$ (Ø = $-C_6H_4-$)

This study was undertaken for the following purposes:

(a) to elucidate the influences of the relative length of the rigid conjugated part and of the aliphatic section on the mesophasic properties of chemically homologous polymers;

(b) to elucidate the influence of relatively small changes in chemical composition on the mesophasic behaviour (comparison with analogous polyesters, containing the group

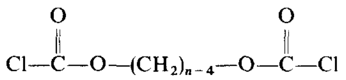


$$-O-\overset{\overset{O}{\|}}{C}-CH_2- \text{ in place of } -O-\overset{\overset{O}{\|}}{C}-O-);$$

(c) to discover the relation, if any, between the liquid crystal behaviour of polymers and that of analogous low molecular weight compounds.

EXPERIMENTAL

Polycarbonates with the above formula were prepared by reaction of 4,4' dihydroxy-α,α'-dimethylbenzalazine (HO—Ø—C(CH$_3$)=N—N=C(CH$_3$)—Ø—OH) in alkaline aqueous solution with a chloroform solution of the appropriate alkylchlorocarbonate



$$Cl-\overset{\overset{O}{\|}}{C}-O-(CH_2)_{n-4}-O-\overset{\overset{O}{\|}}{C}-Cl$$

following a procedure analogous to one already described [1]. The alkylchlorocarbonates were prepared by reaction of the corresponding di-alcohols and phosgene in benzene solution by standard methods. The polymers are designated by the symbol PC*n* (n = 10, 12, 14, 16).

The polymers were examined by NMR spectroscopy in CDCl$_3$ solution and the spectra agreed with the formulae. Quantitative elemental analysis for PC12 gave: C%: 68.99 exp., 68.96 calc.; H%: 7.32 exp., 7.28 calc.; N%: 5.25 exp., 5.36 calc. The polymers were also characterized by viscometry of chloroform solutions with an Ubbelhode viscometer. The following limiting viscosity numbers were extrapolated at 26.00 ± 0.02°:

$$PC10[\eta] = 1.80\,dl\,g^{-1};\ PC12[\eta] = 1.58\,dl\,g^{-1};$$
$$PC14[\eta] = 2.13\,dl\,g^{-1};\ PC16[\eta] = 2.05\,dl\,g^{-1}.$$

Thermal analysis was performed with a DSC-2 Perkin–Elmer differential scanning calorimeter. An indium sample (Fluka 99.999%) was used as standard. The samples were examined under dry nitrogen flow.

X-ray diffraction spectra of the solid samples were recorded both by counter methods, using a Philips powder goniometer, and by photographic means utilizing a flat-film camera. X-ray spectra of the liquid samples were

Table 1. Lattice distances (10^{-10} m) and diffraction intensities on arbitrary scale of samples with different thermal histories

PC10		PC12				PC16		
a	b	a	b	c	d	a	b	c
8.81 vw	15.5 w	8.51 s	8.51 s	6.98 s	8.33 vw	26.4 s	23.2 s	24.7 s
8.15 m	8.51 w	5.83 vw	6.97 vw	5.38 vs	6.98 s	14.3 w	11.6 s	11.3 w
7.24 m	7.67 w	5.37 vs	5.83 w	4.93 vw	5.38 vs	8.33 vw	5.16 m	6.25 w
5.53 vs	6.74 m	4.86 vs	5.23 vs	4.55 vs	4.93 vw	6.97 vw	4.75 vs	5.24 s
4.99 vs	5.11 vs	4.31 s	4.81 vs	4.36 vs	4.55 vs	4.87 vw	4.31 s	4.81 m
4.50 vw	4.19 vw	4.07 s	4.11w	3.86 vs	4.38 vw	4.50 m	3.92 vs	4.32 m
4.24 vw	4.00 s	3.81 vs	3.99 s	3.59 s	3.86 vs	4.32 vs	3.69m	4.21 m
4.11 s	3.70 vs	3.46 w	3.72 vs	3.24 vw	3.59 s	4.08 w	3.43 w	3.76 vs
3.86 m	3.26 m		3.55 s			3.80 m		
3.70 vs			3.41 m			3.56 w		
3.14 w								

PC10—a: Sample annealed 1 hr at 474 K with no previous thermal treatment; b: Sample crystallized from the melt but not annealed.

PC12—a: Sample annealed 1 hr at 448 K after crystallization from the melt; b: Sample annealed 1 hr at 448 K with no previous thermal treatment; c: Sample crystallized from the melt but not annealed; d: Sample previously brought to the isotropic phase and then crystallized from the melt.

PC16—a: Sample annealed 1 hr at 433 K with no previous thermal treatment; b: Sample annealed 1 hr at 433 K after crystallization from the melt; c: Sample previously brought to the isotropic phase and then crystallized from the melt.

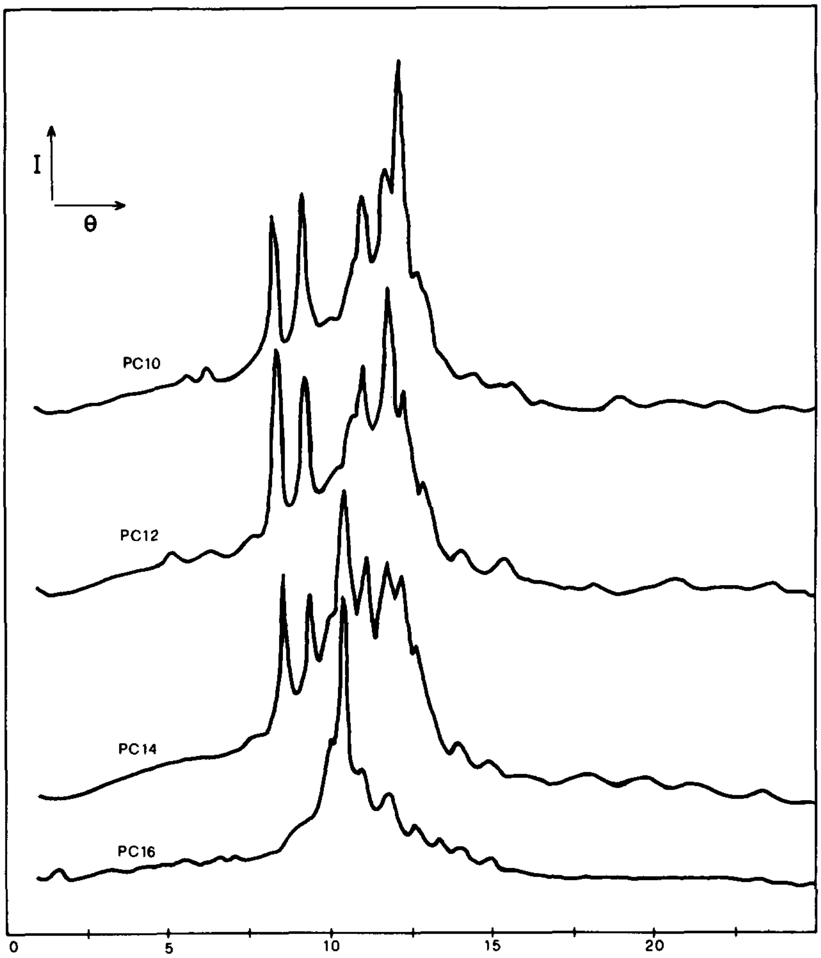


Fig. 1. X-ray diffraction spectra from samples annealed for 1 hr with no previous thermal treatment. Annealing temperatures: PC10; 474 K, PC12: 448 K, PC14: 443 K, PC16: 433 K. Philips powder goniometer, CuKα, $T = 20°$.

recorded only by the photographic method. The samples were kept inside sealed glass capillaries to protect them from extensive oxidation.

Optical observation was performed using a Leitz polarizing microscope fitted with a Mettler FP5 microfurnace.

RESULTS AND DISCUSSION

The polymers are semicrystalline and show polymorphic behaviour both in the solid (with the exception of PC14) and in the liquid state.

The solid state polymorphism of PC10, PC12 and PC16 is clearly revealed by X-ray diffraction techniques. The X-ray diffraction pattern is strongly dependent on the thermal history of the sample. Lattice distances and intensity values on an arbitrary scale, as measured from photographic X-ray spectra of samples having different thermal histories, are reported in Table 1. Figure 1 shows a homogeneous set of X-ray diffraction spectra recorded by counter methods from samples previously annealed at a temperature some degrees lower than the melting temperature. The DSC thermal behaviour of samples with the same thermal history is shown in Fig. 2.

Although each polymer has its own peculiarities, some common features can be pointed out. The X-ray spectra of untreated samples are similar to those given by annealed samples but different from those given by samples crystallized from the melt. Annealed samples of PC12 and PC16 previously crystallized from the melt show X-ray diffraction patterns different from those obtained from melt-crystallized but not annealed samples. No such difference is observed for polymers PC10 and PC14. Samples of PC12 and PC16 show different X-ray diffraction patterns according to whether they have been crystallized by cooling a liquid phase that was or was not previously isotropized. No such differences are shown by similarly treated samples of PC10 and PC14.

It must be pointed out that, in the crystallization from the melt, the liquid crystal phase is always involved. In no case was the crystallization of an undercooled isotropic phase observed. It would therefore be interesting to elucidate how the thermal history of the liquid phase influences the crystallization process.

Polymorphism is very common among crystalline polymers. We have found other examples in mesophasic polymers [2] showing perfectly reversible solid state transitions and with well defined regions of thermal stability for each solid phase. In the present case, the DSC analysis does not afford unequivocal evidence for solid phase transitions. Figures 3, 4 and 5 show the melting endotherms of samples having different thermal histories and corresponding to different solid phases as demonstrated by the X-ray dif-

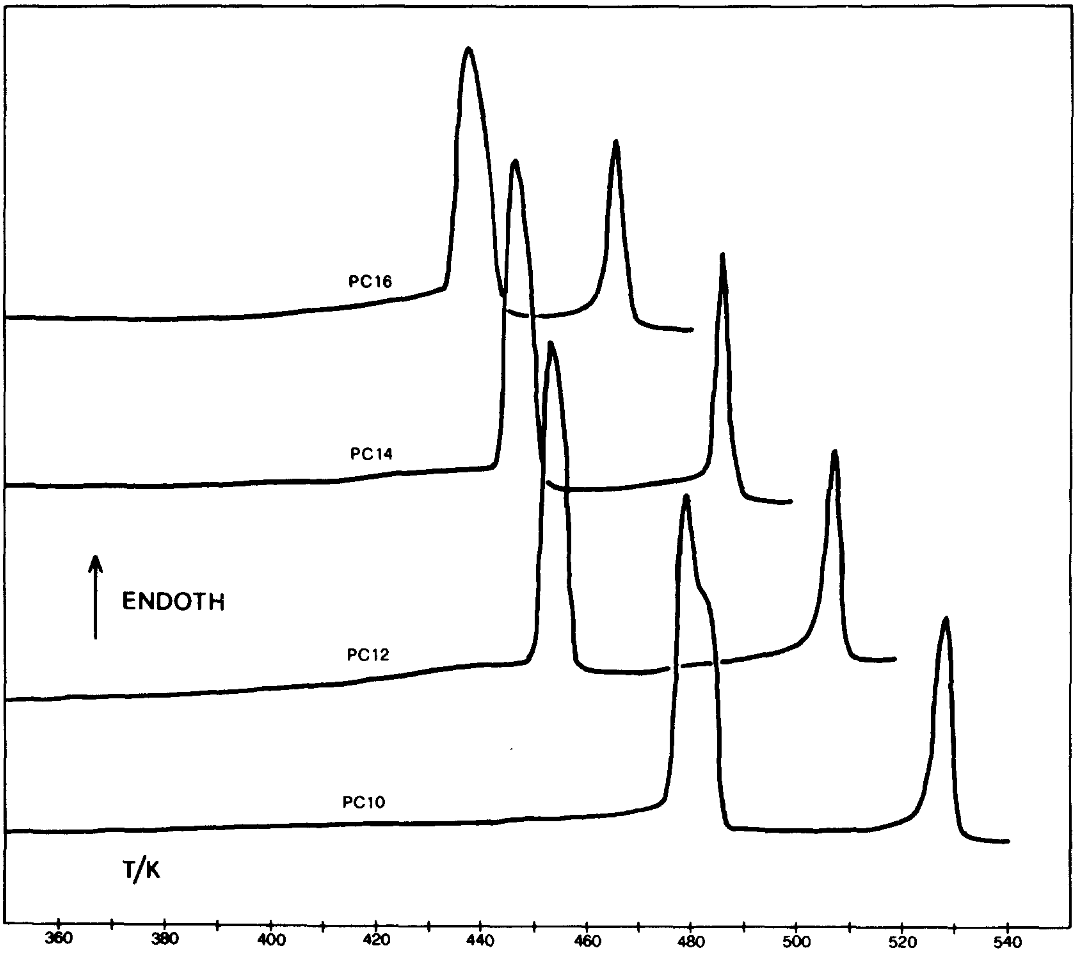


Fig. 2. DSC thermograms of samples treated as indicated in Fig. 1. Heating rate 10 K/min.

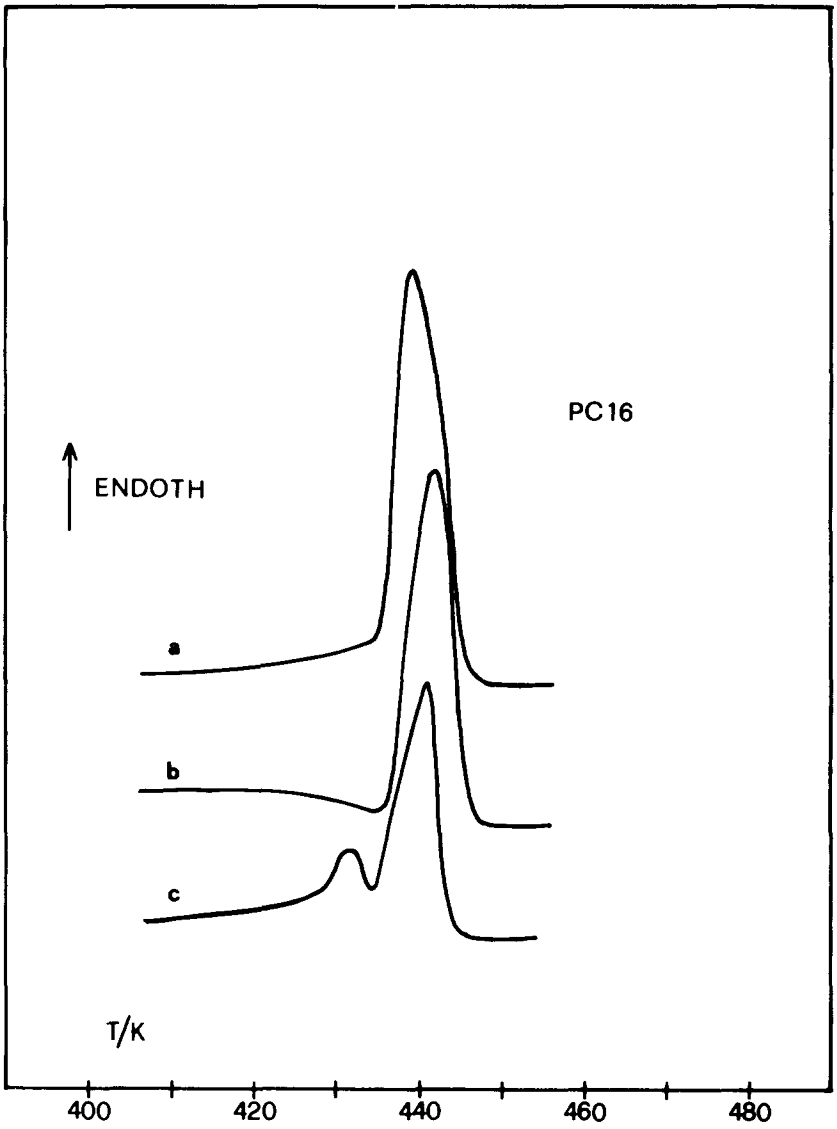


Fig. 3. PC16—Melting endotherms of samples with different thermal histories. Heating rate 10 K/min. a: Sample annealed 1 hr at 433 K with no previous thermal treatment; b: Sample annealed 1 hr at 433 K after crystallization from the melt; c: Sample previously brought to the isotropic phase and then crystallized from the melt.

fraction spectra. Some of the endotherms are in the form of shouldered peaks. This is consistent with the occurrence of solid phase transitions very close to the melting. But, particularly in the case of unannealed samples (Figs 3c, 4c, 4d, 5b), some irregularities of the melting endotherms could be attributed as well to pre-melt crystallization. This phenomenon is quite well detectable in Figs 4(c) and 5(b) from the relevant exothermic deviation of the DSC diagram.

The thermal analysis of the polymers clearly indicates their mesophasic behaviour (Fig. 2). The lower temperature endotherms correspond to the melting of the semi-crystalline polymers while those at higher temperature correspond to the isotropization of the liquid crystal phase.

The X-ray diffraction spectra of the liquid crystal phases are consistent with a nematic structure. Figure 6 shows the X-ray diffraction spectrum of a sample of PC16 at 453 ± 5 K (the spectra of the other polymers are quite similar). The spectrum consists of two haloes peaked around $\theta = 8.9^\circ$ and $\theta = 3.1^\circ$ respectively. No trace of a low angle, relatively sharp Bragg diffraction peculiar to the smectic structure is detectable. This very simple X-ray diffraction pattern is similar to that recorded by us at room temperature from a quenched sample of a mesophasic copolyester of formula:

$$\begin{array}{l}[-\varnothing-C(CH_3)=N-N=(CH_3)\\ \qquad\times\ C-\varnothing-OOC-(CH_2)_n-COO-]_x\end{array}$$

$n = 6$ (50%), 10 (50%) (ref. [5]).

For this polymer a third very broad and faint halo (around $\theta = 22.3^\circ$ for the CuKα radiation) was detected, not visible in the spectra of the polycarbonates. This is most probably caused by the thermal motion that cuts off the diffraction intensity at higher angles. A two halo pattern is normally found with

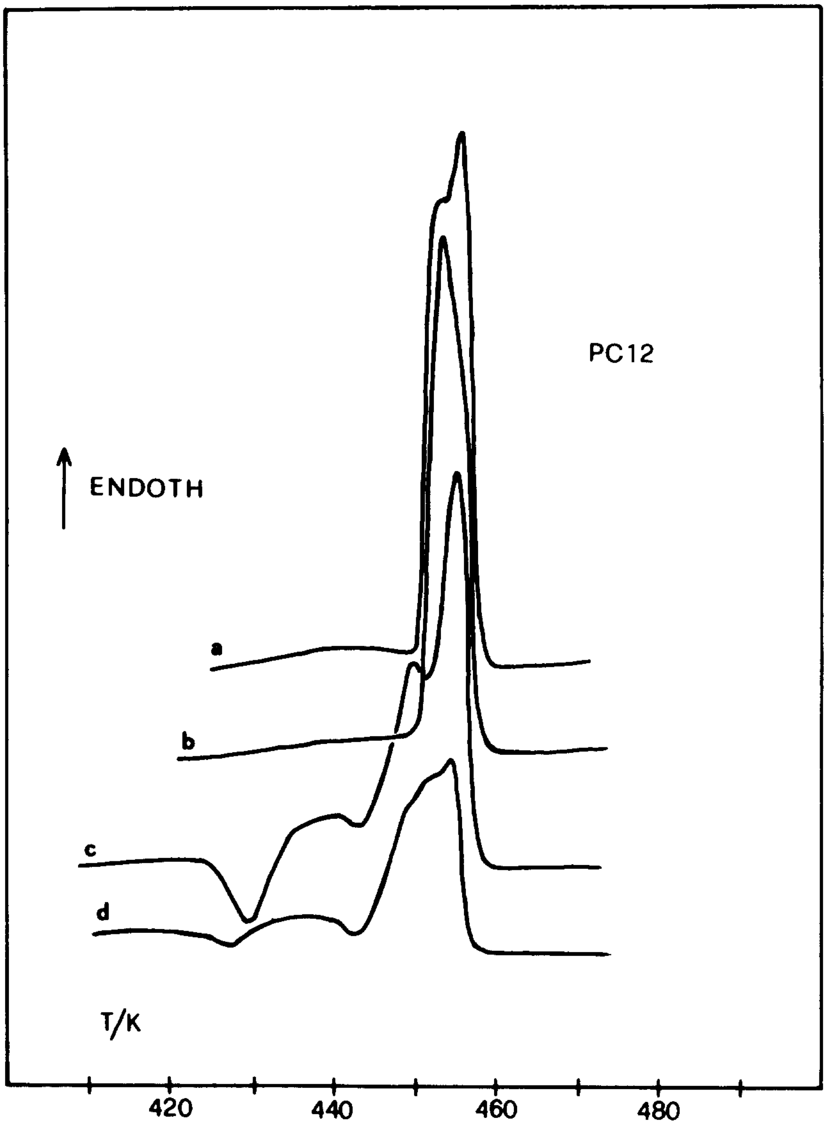


Fig. 4. PC12—Melting endotherms of samples with different thermal histories. Heating rate 10 K/min. a: Sample annealed 1 hr at 448 K after crystallization from the melt; b: Sample annealed 1 hr at 448 K with no previous thermal treatment; c: Sample crystallized from the melt but not annealed; d: Sample previously brought to the isotropic phase and then crystallized from the melt.

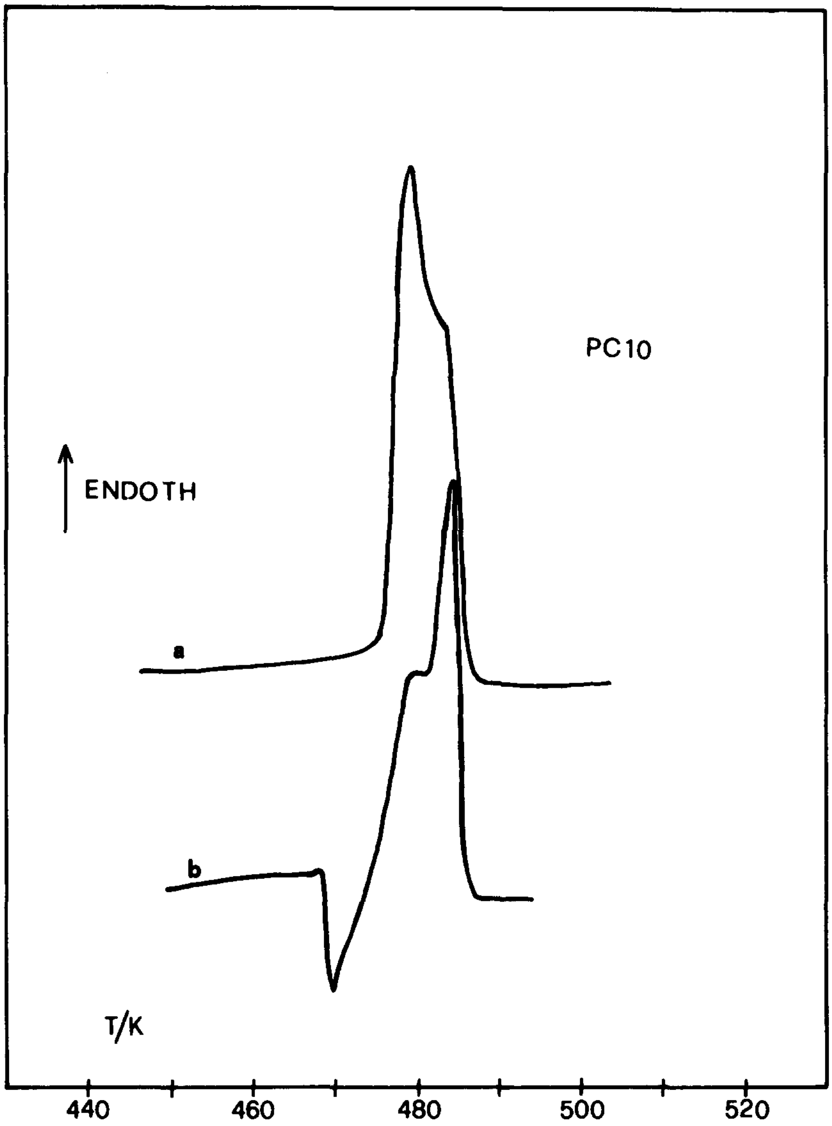


Fig. 5. PC10—Melting endotherms of samples with different thermal histories. Heating rate 10 K/min. a: Sample annealed 1 hr at 474 K with no previous thermal treatment; b: Sample crystallized from the melt but not annealed.

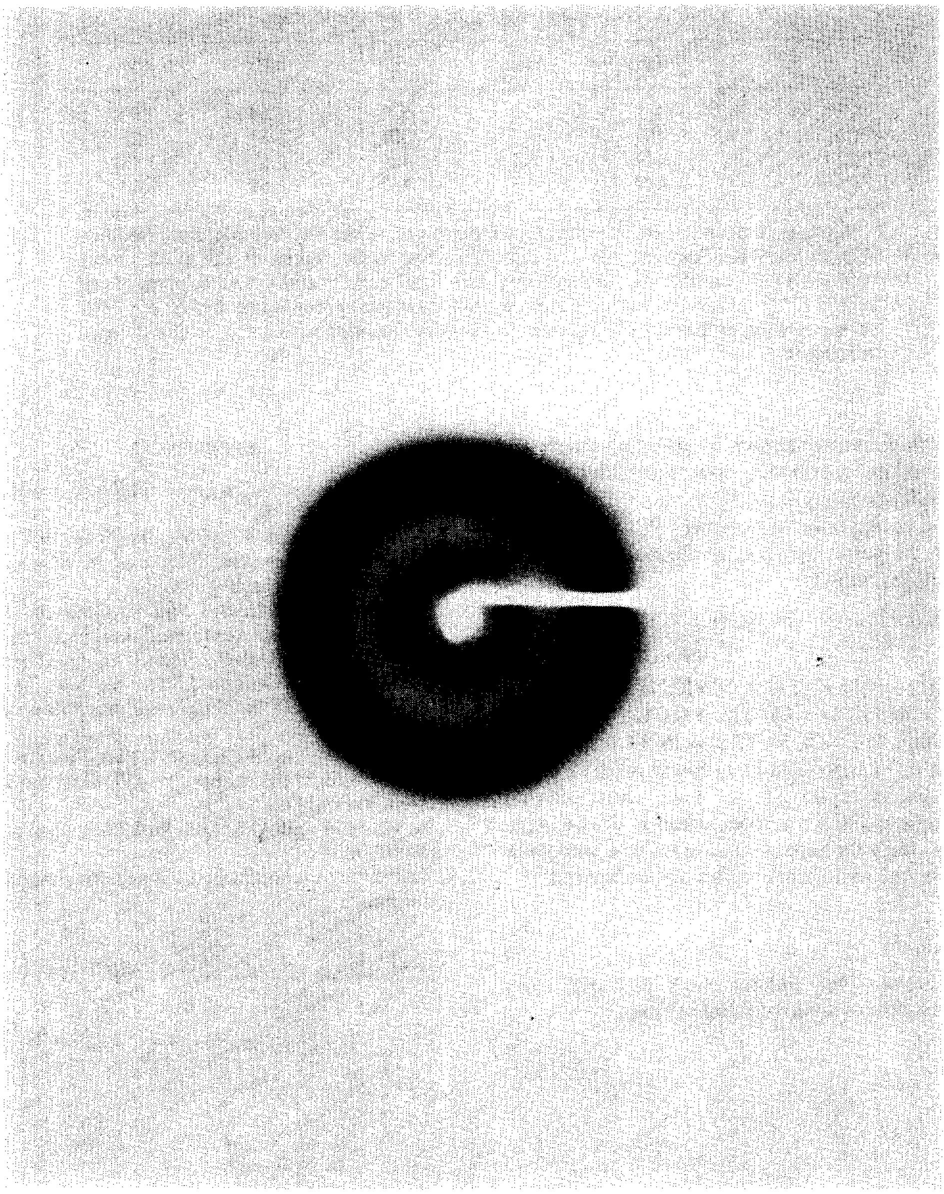


Fig. 6. PC16—X-ray diffraction spectrum of the liquid crystal phase. Flat-film camera, CuKα, $T = 453 \pm 5$ K.

the nematic phases of low molecular weight mesophasic compounds [6].

The observations made with the polarizing microscope confirm the nature of the phase transitions (i.e. melting followed by the isotropization of the liquid phase) but are of no use for defining the nature of the liquid crystal phase. No significant morphological features are recognizable.

Some thermodynamic data for the phase transitions are reported in Table 2. The molar melting enthalpy data are only indicative, since the amounts of crystallinity of the samples are not known. On the contrary, the data referring to the liquid phase transitions are fully significant. They are not dependent on the thermal history of the sample, provided that there is no chemical decomposition caused by excessive heating (> 560 K) and/or oxidation.

The molar isotropization entropy has a fixed value for the four polymers. This feature, when associated with the nematic nature of the polymeric mesophase, is an example of similarity between the behaviour of mesophasic polymers and that of chemically analogous low molecular weight liquid crystal compounds. Attention must be called to the usual behaviour of a homologous series of low molecular weight mesophasic compounds having various number of carbon atoms along the aliphatic chain. The total molar isotropization entropy (including molar entropies from liquid phase transitions such as smectic-smectic or smectic-nematic) shows a marked increase with increasing length of the chain for those members of the series showing smectic mesophases, while only a very small progressive variation is observed, apart from fluctuations due to odd–even effects, when the only liquid crystal phase is nematic [7, 8].

The lowering of the isotropization temperature and the narrowing of the thermal stability range of the mesophase with increasing length of the aliphatic

Table 2. Thermodynamic data for the phase transition

	Tm	ΔHm	Ti	ΔHi	ΔSi
PC10	481	3.7	530	1.64	3.10
PC12	453	3.5	508	1.67	3.29
PC14	448	3.5	486	1.57	3.23
PC16	440	3.3	467	1.59	3.40

Melting (Tm) and isotropization (Ti) temperatures, in the Kelvin scale, are reproducible within 4 K. They are the averages of several values taken at the peak of the relevant DSC endotherms. The enthalpy data (kcal mol^{-1}) and the entropy data (cal mol^{-1} K^{-1}) relative to the liquid phase transition are reproducible within 5%. The molar melting enthalpies (ΔHm) refer to samples annealed with no previous thermal treatment.

chain are other features shown by these polymers and also structurally analogous low molecular weight liquid crystal compounds [7, 8].

Finally, a comparison of polymers PC10, PC12 and PC14 with polyesters of similar formula and corresponding chain length:

$$[-\emptyset-C(CH_3)=N-N=(CH_3) \\ \times\ C-\emptyset-OOC-(CH_2)_{n-2}-COO-]_x$$

($n = 10$, Tm = 483 K; Ti = 529 K, $n = 12$, Tm = 483 K; Ti = 514 K, $n = 14$, Tm = 480 K; Ti = 496 K) corresponding to PC10, PC12 and PC14 respectively, shows that polycarbonates have lower melting points and their liquid crystal phases have wider thermal stability ranges. The same conclusion is drawn when the thermal data for sets of analogous low molecular weight di-esters and dicarbonates are compared.

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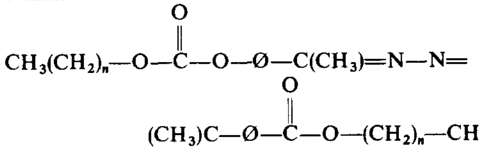
REFERENCES

1. A. Roviello and A. Sirigu, *J. Polym. Sci., Polym. Lett. Ed.* **13**, 455 (1975).
2. A. Roviello and A. Sirigu, IUPAC 5th Discussion Conf. on Phases and Interfaces in Macromolecular Systems C18, Prague (1976).
3. G. W. Gray, *Molecular Structure and the Properties of Liquid Crystals.* Academic Press, New York (1962).
4. *Liquid Crystals 3*, Part 2, (edited by G. H. Brown and M. M. Labes). Gordon & Breach, New York (1972).
5. A. Roviello and A. Sirigu, *Europ. Polym. J.* **15**, 61 (1979).
6. A. De Vries, *Liquid Crystals 3*, Part 1 (edited by G. H. Brown and M. M. Labes), p. 457. Gordon & Breach, New York (1972).
7. A. Roviello and A. Sirigu, *Mol. Cryst. Liq. Cryst.* **33**, 19 (1976).
8. Our data, to be published, on nematic carbonates with formula:



$$CH_3(CH_2)_n-O-\overset{O}{\overset{\|}{C}}-O-\emptyset-C(CH_3)=N-N= \\ (CH_3)C-\emptyset-\overset{O}{\overset{\|}{C}}-O-(CH_2)_n-CH_3$$