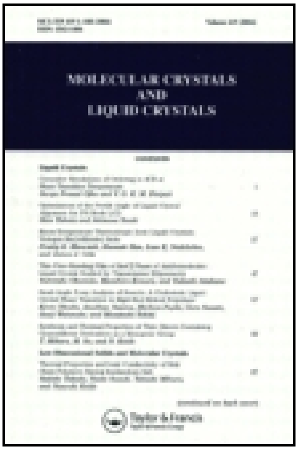

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X-Ray Analysis of Chiral Thermotropic Co-Bipolyesters Based on Linear and Non-Linear Aromatic Units

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X-Ray Analysis of Chiral Thermotropic Co-Bipolyesters Based on Linear and Non-Linear Aromatic Units†

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A series of chiral thermotropic liquid crystalline co-bipolyesters based on linear and non-linear aromatic cores and an optically active (S)-1,2-propanediyl spacer are studied by X-ray diffraction analysis. Complementary differential scanning calorimetry data are presented. It is found that different polymorphs exist in the solid phase, depending on copolymer chemical composition and thermal history. The occurrence of a cholesteric mesophase is demonstrated in copolymers containing non-linear units up to as high as 70%.

INTRODUCTION

In previous work[1,2] some of us have described the synthesis and properties of chiral thermotropic co-bipolyesters derived from an optically active (S)-1,2-propanediol (PG) and linear, mesogenic bis(4-

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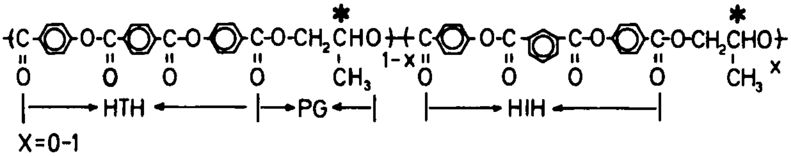
carboxyphenyl) terephthalate (HTH) and non-linear, "non-mesogenic" bis(4-carboxyphenyl) isophthalate (HIH).



The incidence and stability of the polymer mesophase strongly depended on the relative amounts of HTH and HIH residues, the widest temperature ranges (100-140°C) being obtained at intermediate chemical compositions. Therefore, it was shown that polymeric products whose mesomorphic properties could be modulated on the basis of appropriate combinations of structural isomers of aromatic cores with mesogenic and non-mesogenic tendency, respectively, could be realized.

However, in some cases the nature of the liquid crystalline phase could not be unambiguously identified by a combination of differential scanning calorimetry and optical observation of the birefringent textures. Additionally, there was indication that in the solid state the copolyesters displayed different behaviour and degrees of crystallinity, depending on the thermal history. In the present paper we report a detailed investigation by X-ray diffraction analysis in both the solid and liquid crystal phases, and present new thermal analysis data. This work was carried out with the aim of gaining a better insight into the complex polymorphic behaviour of this class of mesomorphic copolyesters.

EXPERIMENTAL PART

The polymer samples were prepared according to the procedure already described.[1,2] Differential scanning calorimetry (DSC) measurements were carried out using a Perkin-Elmer DSC-2 calorimeter at a heating/cooling rate of 10°C/min. Phase transitions were taken as corresponding to the maximum in the enthalpic peaks. Where no transition endotherms could be observed, the transition temperatures were determined by optical microscopy using the hot stage of a Reichert Polyvar microscope. The structural characteristics of the compounds investigated were studied by X-ray diffraction in a transmission geometry. The measurements were carried out by means of a conventional X-ray powder diffractometer. Ni filtered CuKα radiation (λ = 1.54 Å) was used. Photographs were obtained by means of an Elliot toroidal camera mounted on a Rigaku-Denki RU200 rotating anode generator. Heating was achieved by a hot stage whose temperature was controlled to ±0.1°C by an electronic device.

RESULTS AND DISCUSSION

The properties in dilute solution and in bulk of the chiral polyesters investigated are discussed in detail elsewhere,[2] and the same notation is used to identify the copolyesters with different concentrations of aromatic isomeric units. Their physico-chemical characteristics, including phase transition temperatures obtained by DSC and/or optical microscopy, are summarized in Table I. A common characteristic of the investigated polymeric compounds, with exception of homopolymer HTH (run T), is the weak intensity of the diffraction pattern particularly in the small angle region. This is probably due to the influence of concomitant factors such as partial crystallinity of the sample,[3] relatively low spatial modulation along the polymeric chains of the electron density, and incomplete ordered stacking of the molecular repeat units. Another interesting feature generally observed

TABLE I

Physico-chemical properties of bipolyesters based on linear HTH and non-linear HIH aromatic units and (S)-1,2-propanediol[a]

	Composition	$[\eta]$[b]		Thermal properties[d]	
Run	(HIH-%)	(dl/g)	$[\alpha]_D^{25}$[c]	T_m(°C)	T_i(°C)
T	0	0.02[e]	+ 9.5[e]	334	360
TI1	10	0.22	+91.7	222	325
TI2	30	0.18	+81.5	145	285[f]
TI3	50	0.25	+82.2	139	220
TI4	70	0.18	+66.5	112[f]	115[f]
I	100	0.20	+66.5	130[f]	---[g]

[a] Enantiomeric purity ≥ 95%.
[b] Intrinsic viscosity in trifluoroacetic acid at 30°C.
[c] Optical rotatory power in trifluoroacetic acid.
[d] By DSC, if not otherwise indicated.
[e] In fuming sulfuric acid.
[f] By optical microscopy.
[g] Not liquid crystalline.

was the difference in the behaviour of samples with different thermal history. Moreover, all the phase transitions occur gradually with increasing temperature in agreement with the DSC results.

Figure 1 gives the X-ray diffraction profiles for homo-bipolyester HTH/PG. The diffraction pattern obtained at 25°C (Figure 1a) is

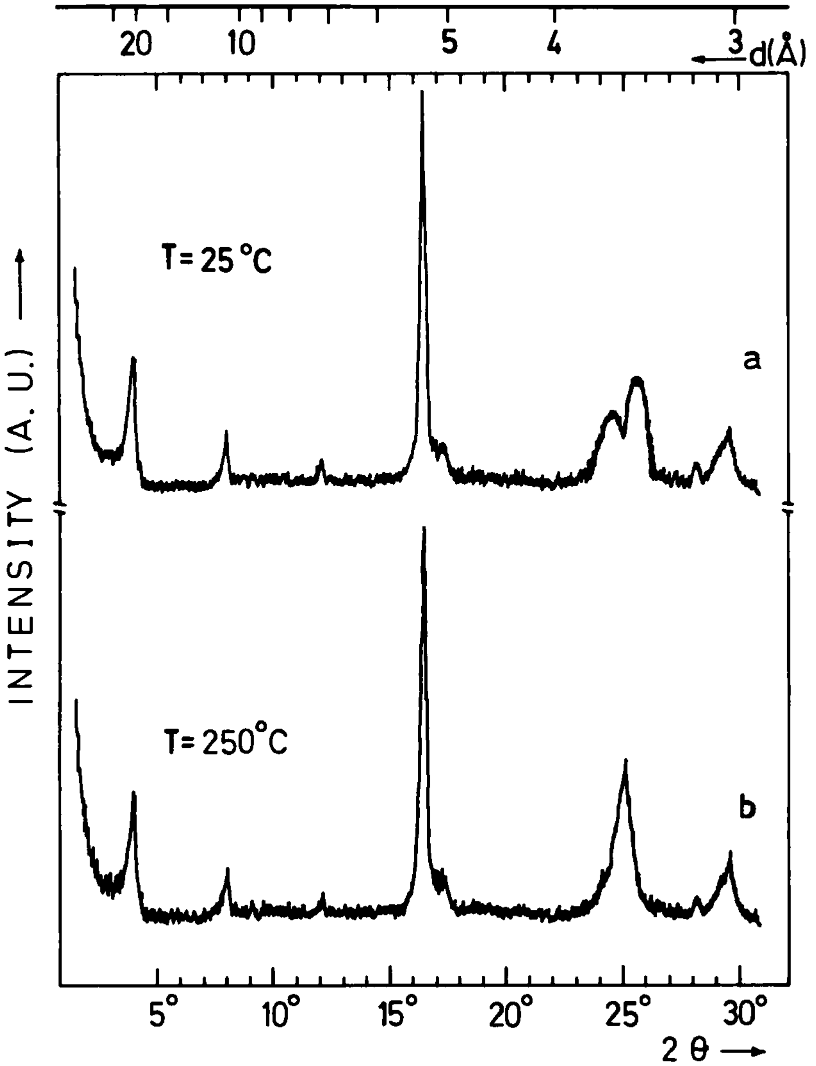


FIGURE 1 X-ray diffraction profiles obtained for homo-bipolyester HTH/PG at (a) T = 25°C and (b) T = 250°C.

characterized by several narrow Bragg peaks, indicating a high degree of crystallinity. In particular, three diffraction peaks are visible in the small angle region corresponding to the first, second, and third order reflection associated with the periodicity $d = 22.4 \pm 0.1$ Å. This value is close to the calculated length of the HTH-PG repeat unit in the fully extended conformation (~22.5 Å), and is also in agreement with previous observations on analogous polyesters based on the same HTH mesogenic unit and various polymethylene spacers.[4] The wide angle region is characterized by several peaks, starting at a periodicity of 5.37 ± 0.05 Å, with a rather narrow and intense signal, and extending down to about 3 Å with signals of progressively smaller intensity. By using the Scherrer equation quoted as (12.2) in ref. 5, a rough evaluation of the linear dimension L of the crystalline domains can be obtained. In fact, a lower limit for L is given by:

$$L = \frac{0.9\lambda}{\Delta(2\theta)\cos\theta_B}$$

where λ is the X-ray wavelength, θ_B is the Bragg angle, and $\Delta(2\theta)$ is the full width at half maximum of the diffraction peak. A value of $L \geqslant 300$ Å was evaluated. Some peaks in the wide angle region appear relatively broad and are due, most likely, to the superimposition of several unresolved peaks. Alternatively, the broadness could be due to an anisotropy of the linear dimensions of the crystalline domains. The described diffraction pattern remained practically unaltered with increasing temperature up to 230°C. At that temperature and above, a modification in the wide angle region was observed, as shown in Figure 1b. The two peaks corresponding to about 3.65 Å and 3.50 Å are replaced by a relatively narrow peak (at 3.55 Å). This result corresponds to an increase of symmetry and, consequently, to a decrease of order as the temperature is increased. However, due to instrumental limitations (i.e. an upper hot stage temperature of 280°C), no observation of the behaviour of the anisotropic melt ($T_m = 334$°C) was possible. Figure 2 shows the diffraction patterns obtained at different temperatures for co-bipolyester containing 10% of non-linear HIH units (run TI1). The diffractograms of the untreated, virgin sample recorded between room temperature and 120°C show a broad peak with a pronounced shoulder (Figure 2a) corresponding approximately to spacings $d = 4.6 \pm 0.1$ Å and 4.1 ± 0.1 Å, respectively, and an inner peak corresponding to $d = 22.7 \pm 0.4$ Å, that is very close to the value observed for HTH/PG homo-bipolyester. The intensity of this peak is comparatively rather weak. This can be essen-

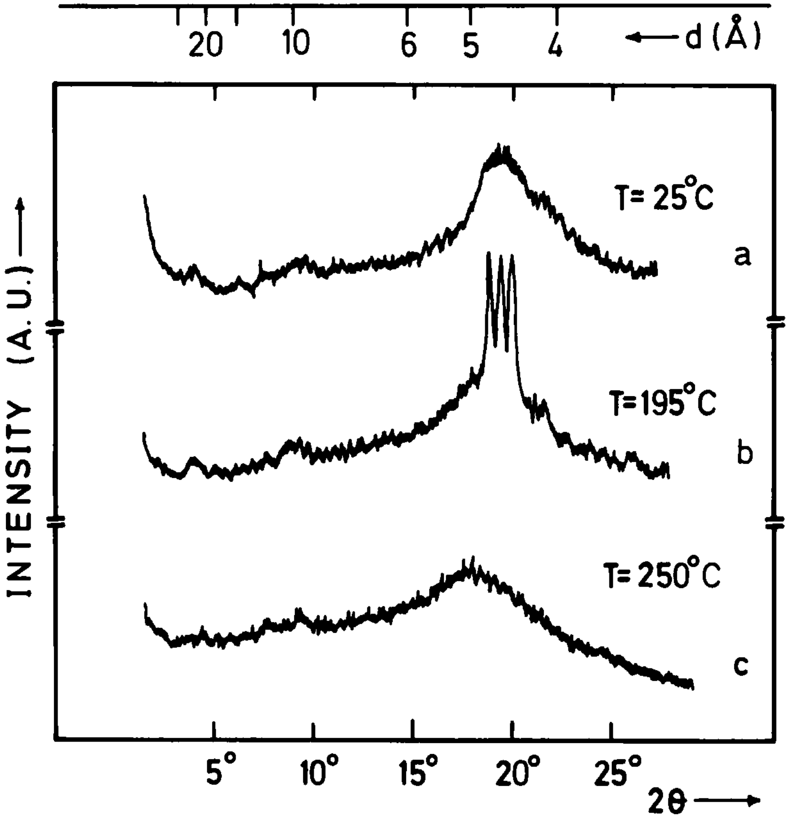


FIGURE 2 X-ray diffraction patterns for co-bipolyester containing 10% of non-linear HIH units, obtained at (a) T = 25°C, (b) T = 195°C and (c) T = 250°C.

tially attributed to the lower crystallinity of the co-bipolyester sample, which indeed appears to be amorphous in character. At about 120°C the position of the small angle peak suddenly shifts toward wider angles, levelling off to $2\theta = 4.22°$ ($d = 20.9 \pm 0.4$ Å) in the range 130–200°C (Figure 3). In the same interval of temperatures, the DSC curves show an intense exotherm of crystallization, which can occur due to the increased segmental motion of the polymer above its glass transition temperature ($T_g \simeq 100°C$). Correspondingly, a continuous modification in the shape of the diffuse peak at about $2\theta = 19.3°$ is observed (Figure 4) which eventually leads, at temperatures higher than 170°C, to a pattern well resolved into three peaks superimposed on a diffuse halo. This fact is consistent with the occurrence of a phase transition leading to a crystal structure with a lateral inter-

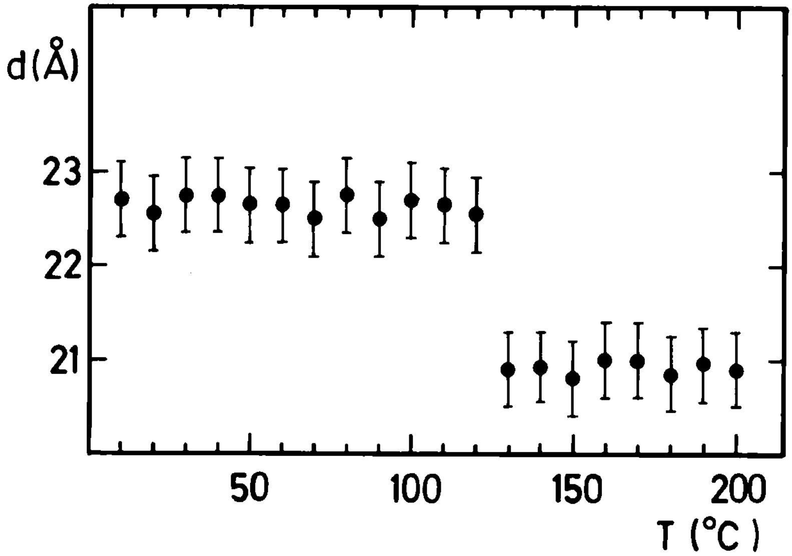


FIGURE 3 Temperature dependence of the *d* values calculated from Bragg's law from the angular position of the low angle peak of co-bipolyester containing 10% of HIH units.

molecular order. This is characterized by a progressive increase of the coherence length of the crystalline regions, that reaches the maximum extension at about 195°C (Figure 2b). The persistence of a residual diffuse peak is indicative of the coexistence, in the sample, of crystalline and amorphous domains. Consequently, the degree of crystallinity at the temperature indicated appears to be lower than that of the HTH/PG homobipolyester. It must be emphasized that the change in lattice spacing takes place in a relatively abrupt way (Figure 3), whereas the crystalline organization occurs by a progressive evolution. The crystalline structure is stable up to about 215°C. At higher temperatures, the intensity of the wide angle peaks progressively decreases, and eventually at T $\simeq$ 240°C the diffraction patterns are typical[6,7] of a short range ordered phase (Figure 2c). This finding confirms the transition to a cholesteric mesophase, in agreement with optical microscopy and DSC observation.[2] In particular, the latter technique revealed a broad melting endotherm between 165 and 235°C with a maximum located at 222°C.

On cooling the sample starting from temperatures lower than about 220°C, i.e. before the transition to the cholesteric phase has occurred, the shape of the diffraction pattern remains unchanged down to room temperature. However, if the sample is cooled from the cholesteric

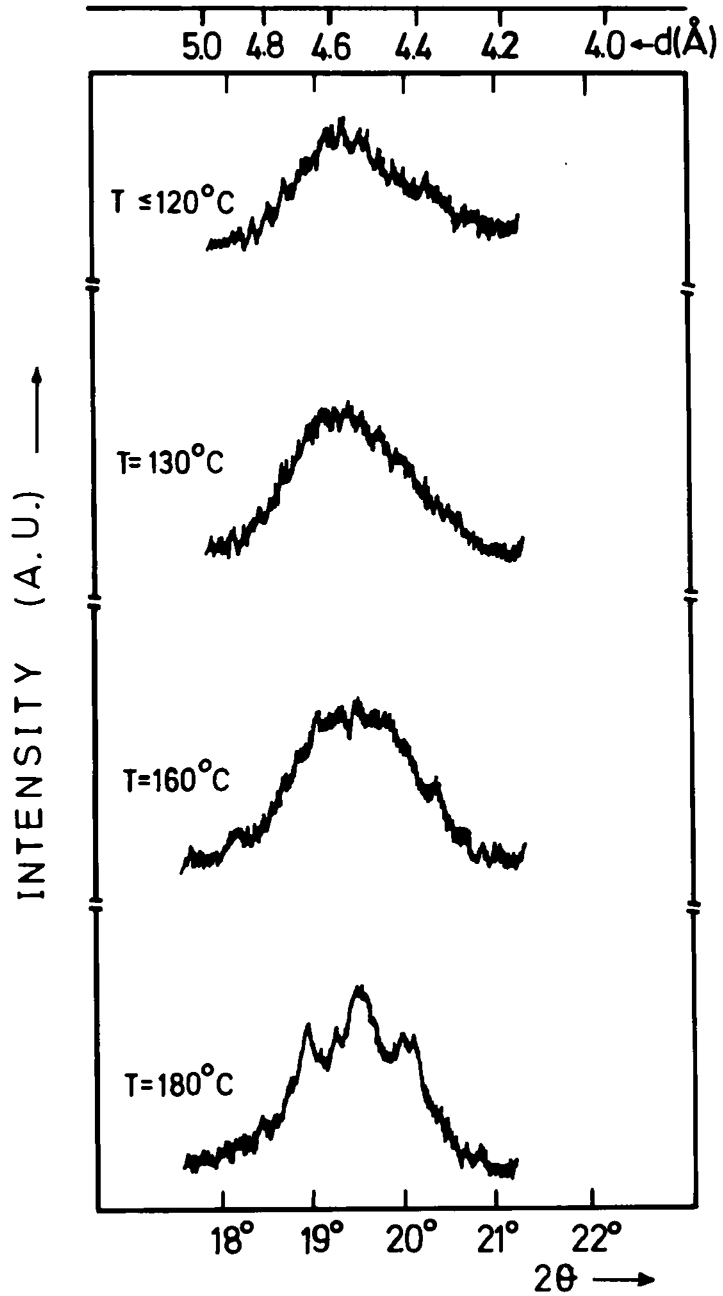


FIGURE 4 Temperature shape modification of the diffuse wide angle peak for co-bipolyester containing 10% of HIH units.

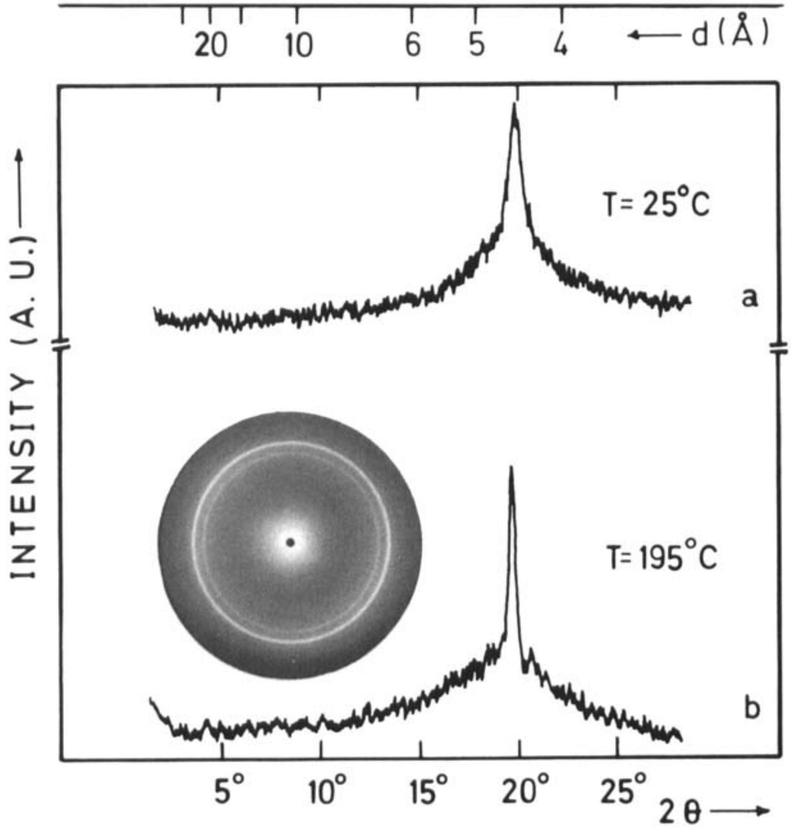


FIGURE 5 X-ray diffraction pattern for co-bipolyester containing 10% of non-linear HIH units obtained after the second thermal cycle at (a) T = 25°C and (b) T = 195°C. The photograph was taken at T = 195°C.

phase one obtains a structure similar to, but more ordered than that of the virgin, untreated sample. The small angle peak maintains the same position assumed at high temperatures. In successive thermal cycles the behaviour of the investigated compounds is rather different. In particular, the room temperature structure becomes more and more ordered as the number of the thermal cycles increases. Figure 5a shows the diffraction pattern at T = 25°C recorded after the second cycle. Moreover, the ordered high-temperature structure is different to that shown by the virgin sample. In fact, at T ⩾ 190°C, only an increase of the wide angle peak intensity can be observed in the goniometer diffractogram (Figure 5b), while the photographs reveal the presence of several very weak rings, as can be seen in the inset of Figure 5. The DSC curves of successive heating cycles are quite similar to each other, the maximum of the melting peak being shifted to 240°C, although, in principle, some degradation process cannot be excluded. A further reduction of crystallinity occurs in the co-bipolyester containing 30% of HIH units (run TI2). Typical diffraction spectra recorded for this sample are reported in Figure 6. Starting from the untreated, virgin sample (Figure 6a), an amorphous-like diffraction pattern is observed up to a temperature of about 100°C. At higher temperatures, some very weak diffraction rings are visible (Figure 6b), whose angular position suggests the existence of a structure similar to that of the ordered phase of co-bipolyester sample TI1. At temperatures above T $\simeq$ 200°C, the diffraction patterns assume the shape typical of a cholesteric phase. Accordingly, the DSC thermograms show a very weak and shallow endotherm in the range 100–210°C with two relative maxima at 145 and 201°C. The melting temperature was taken in correspondence of the first, more intense peak. The second enthalpic maximum may be due to the melting of the crystalline form generated by annealing during the scan. Such a polymorphism in the solid state appears to be rather general in thermotropic liquid crystal polymers,[8,9,10,11] but could not be anticipated in the present copolyester system containing non-linear HIH units and short, relatively flexible 1,2-propanediyl spacers in connection with the linear, mesogenic HTH residues. The diffractograms recorded at T = 230°C and the photograph taken at the same temperature are shown in Figure 6c. On cooling to room temperature, a diffraction pattern indicative of a slightly higher degree of crystallinity, as compared to the virgin sample, can be observed (Figure 6d).

In compounds containing more than 30% of HIH residues, only an amorphous solid and a cholesteric mesophase are observed. Figures 7a and 7b show two typical diffraction patterns of co-bipolyester TI4 containing 70% of non-linear units, obtained in the solid phase and in the cholesteric phase, respectively. For this sample the DSC heating curves are characterized only by the glass transition centered at 97°C. It is worth noting the unusually high value of the glass transition temperature, compared to the softening temperature at 105–112°C. Similar results have been reported recently for other thermotropic polymers[10,12,13] and are interpreted on the assumption that the mesophase can be frozen to some extent in the glassy state. The retention of such molecular ordering in the amorphous phase would result in an enhanced activation energy of polymer motions and, consequently, in an increased glass transition temperature.

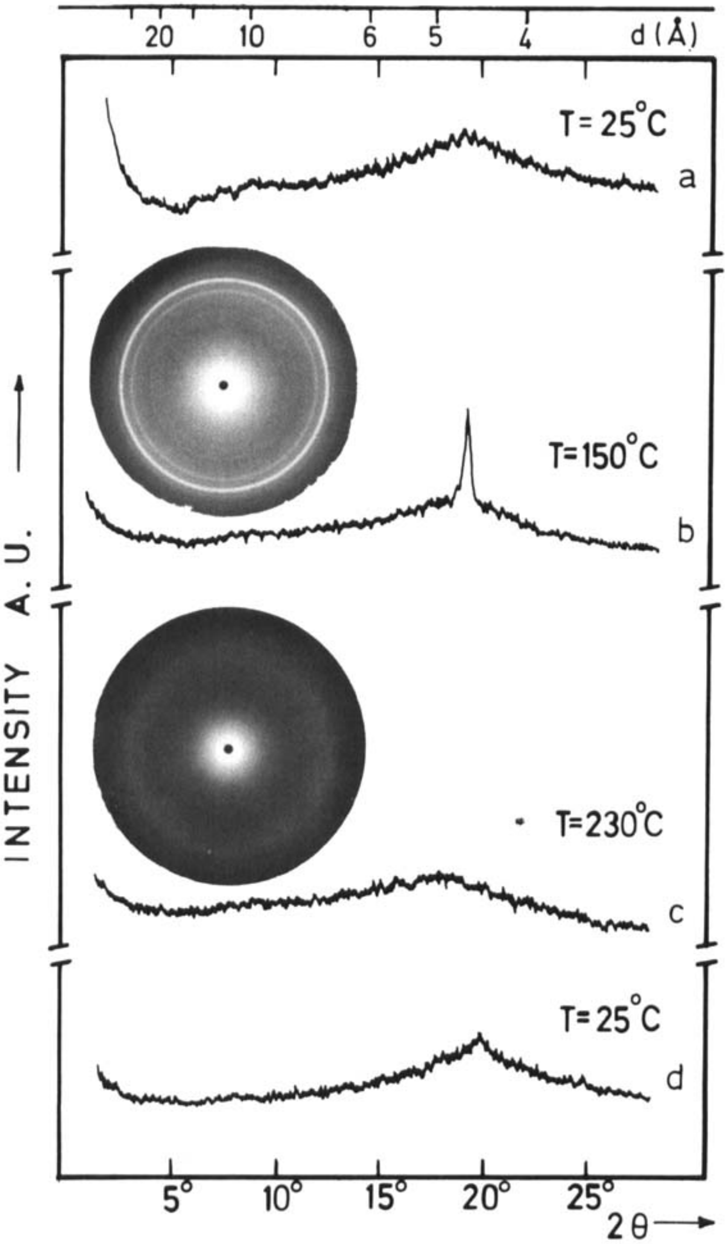


FIGURE 6 Typical X-ray diffraction spectra recorded at different temperatures for the co-bipolyester containing 30% of HIH units. Figures 6a, 6b, 6c were obtained during the first heating, Figure 6d just after cooling to room temperature. Photographs were taken at T = 150°C and T = 230°C.

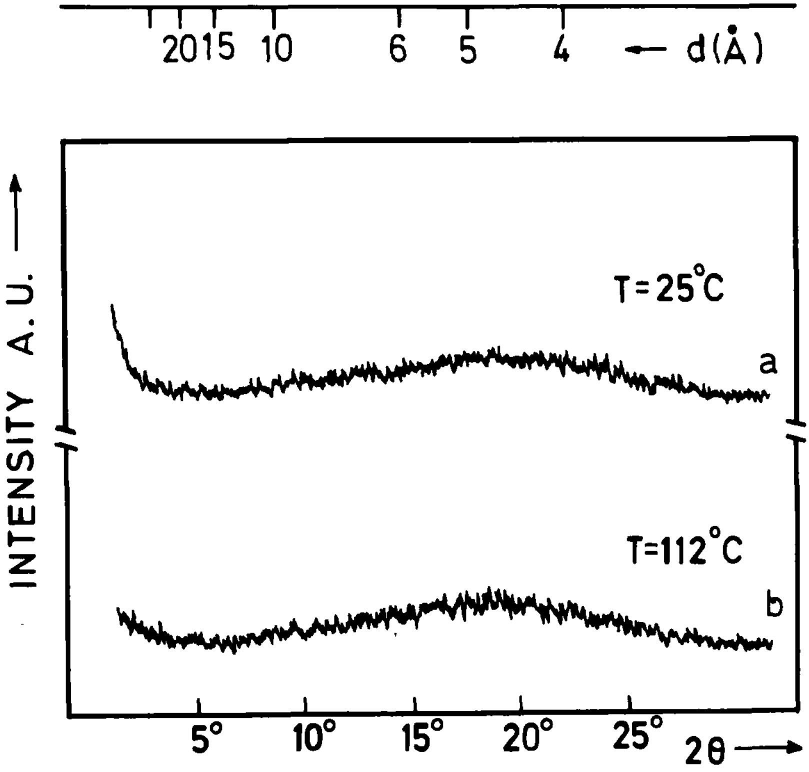


FIGURE 7 Two typical diffraction patterns of co-bipolyester containing 70% of non-linear HIH units.

Conclusions

The copolysters investigated are semicrystalline materials which possess a degree of crystallinity progressively decreasing with increasing content of non-linear HIH units, the maximum being observed in HTH homopolymer. Several polymorphs can exist in the crystalline phase and are characterized by a relatively high long-range intermolecular order. Samples containing more than 30% of HIH units are essentially amorphous in nature, but appear to retain some molecular order frozen in the glassy state. A cholesteric mesophase is exhibited by samples incorporating up to 70% of HIH residues, i.e. in copolymer structures consisting of a statistical distribution of up to two non-linear units per linear, mesogenic HTH unit. Such behaviour is rather rare even in low molar mass mesogens.[14,15]

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