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Investigations on the texture and structure of crystalline and liquid-crystalline phases of a side group polyacrylate with a biphenyl mesogenic moiety

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Polyacrylates and polymethacrylates with mesogenic side groups have been synthesized for a structural investigation by observations of textures and by X-ray diagrams of smectic and crystalline phases. With the preparation of well developed textures, characteristic features of the various phases were recognized and related to different structures. Changes of textures within one phase and at the phase transition were studied. Various crystalline modifications, dependent on sample treatment and transformations, were identified by different textures. X-ray diffraction experiments on analogously treated samples confirmed and completed the results of the optical investigations. The results for one polymeric compound are represented and discussed in detail.

1. Introduction

Polarization microscopic observations represent one of the oldest methods for investigating liquid crystals. Therefore, textures in the polarization microscope of low mass liquid crystals have been widely studied and many appearances can be explained [1]. Polarization microscopic investigation is thus a helpful tool for the structural characterization of samples at relatively low experimental expenditures. The resemblance of textures of low mass liquid crystals of various samples is recognized as a criterion of isomorphism, and the structural features of the observed phases are alike [2].

In contrast, the textures of liquid crystal polymers with mesogenic side groups, which have been under investigation for the past decade, are rarely described in detail. It is argued that well developed textures of these polymers cannot be prepared because of the high viscosity of polymeric liquid crystal phases [3]. A recent polarization microscopic study of a side group polymer at the isotropic-smectic phase transition resulted in a domain-like structure of a smectic phase and illustrated by the observation of characteristic textures [4].

In this paper typical textures of smectic and partially crystalline states of a side group polymer are discussed extensively and compared with X-ray investigations in order to obtain some insights into supermolecular structures and molecular arrangements.

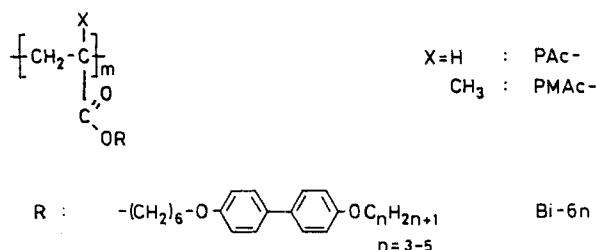
2. Experimental

The synthesis of the monomers, followed by a radical polymerization, is documented in the literature [5]. The compounds were characterized by infrared and ¹H-N.M.R. spectroscopy as well as by elementary analysis.

Thermal analysis was performed with D.S.C.-2 and D.S.C.-7 Perkin-Elmer equipment. The optical observations were carried out with an Olympus polarization

microscope with a hot stage of Mettler (FP 5/52). The samples were prepared as a thin film between two glass plates. They were cooled very slowly at the isotropic–smectic phase transition in order to allow the smectic domains to grow to a sufficient size and to form characteristic textures.

The X-ray diagrams were taken with a temperature controlled Kratky compact camera with position-sensitive counter (Braun) and a flat film camera. Nickel-filtered Cu- K_α radiation was used, and CaF₂ powder served for calibration purposes for the flat film exposures.



Scheme 1. Synthesized side group polymers and abbreviations used.

3. Results and discussion

The phase behaviour of a series of synthesized polymers was determined by D.S.C. measurements, polarization microscopic observations and X-ray experiments. The phase transition temperatures (onset) are collected in the table and correspond to differential calorimetric measurements.

Phase transition temperatures (in K) of the polymers investigated at heating († at cooling); heating and cooling rate: 10 K min⁻¹. PC, Partially crystalline; S, smectic; I, isotropic.

PAC-Bi-63	PC	414	S	437.5	I		
	PC†	410	PC or S	412	S	436.5	I
PMAc-Bi-63	PC	408	S	428.5	I		
PAC-Bi-64	PC	407	PC or S	412	S	441	I
PMAc-Bi-64	PC	399.5	S	430	I		
PAC-Bi-65	PC	413	S	438	I		
PMAc-Bi-65	PC	428	I				

The results of the investigation on the side group polyacrylate with the abbreviation PAC-Bi-63 is presented now in detail. The polymer PAC-Bi-63 only shows focal-conic texture or focal-conic (f.c.) fan textures in the smectic phase. The typical discontinuity lines of this kind of texture are clearly visible in the form of ellipse-hyperbola pairs (figure 1). A fan-like arrangement of the f.c. domains is preferred at small sample thickness so that f.c. fan textures arise (figure 2(a)). The back of the fans appear relatively smooth in the proximity of the clearing temperature. Increasing numbers of additional discontinuities are visible as the temperature is lowered in the smectic phase (figure 2(b)). These can be interpreted as parabolic f.c. defects as described at low mass liquid crystal phases [6]. These defects gradually disappear on heating and the backs of the fans look increasingly smoother. These appearances are typical for S_A phases of low molar mass liquid crystals.

A monotropic phase, denoted P-0, is formed at slowly cooling of the polymer within a small temperature range (412–410 K). The texture at the smectic–P-0 phase transition shows smooth fan backs which are furnished with bars (figure 2(c)).

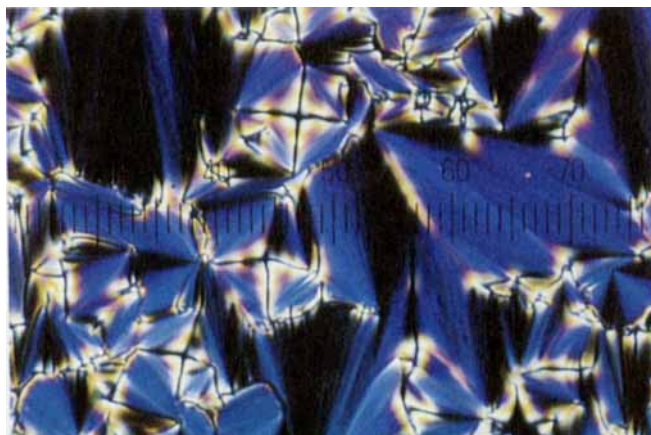


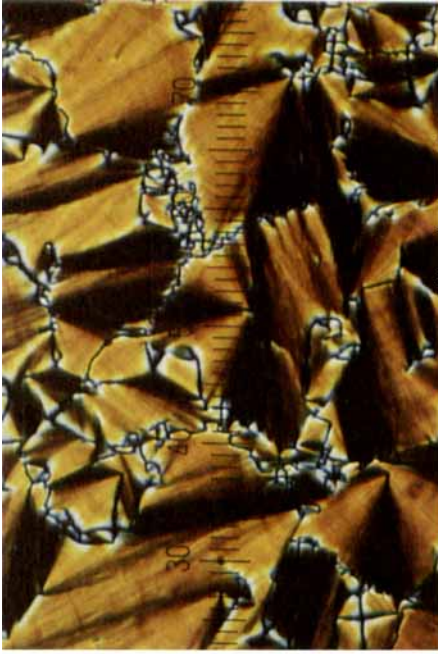
Figure 1. Polarization microscopic exposure of the smectic phase of the polymer PAc-Bi-63. Focal-conic texture with fan-like arrangements (10 bars \approx 0.057 mm).

The appearance of the paramorphic fan texture of the partially crystalline state depends on the sample treatment, since different modifications (P-I and P-II) are formed. The texture of the slowly cooled sample, resulting in the modification P-I, is characterized by a number of small, parabolic defects, coloured lines on the fan backs as well as a different colour of the preceding phase (figures 2(d) and 2(e)). It is interesting to note further changes in colour of the texture at cooling until about 373 K. Below this limiting temperature a change in colour will no longer occur. A reversal of behaviour is found on heating. A change in colour is only observed above the limiting temperature. The colour originates from interference and is dependent on the thickness and birefringence of the samples. Therefore, changes in colour are caused by structural changes of the sample.

Characteristic features of textures and changes of interference colours are best observed on thin samples. A thin sample of the modification P-I shows small, regularly concentric running lines as typical distinguishing marks of this texture (figure 3(a)). Thicker samples instead show only a non-uniform striation (figure 3(b)), and the texture is characterized by the appearance of additional cracks.

The texture of a quenched sample of the modification P-II do not show the typical lines as P-I (figure 2(f)). A few thin cracks are observed. Some of the fan backs are covered with many parabolic f.c. defects (figure 2(g)). The texture appears in the same colour at room temperature as in the smectic phase. A change in colour takes place from brown-yellow to gray-yellow at heating above 373 K (figure 2(h)). This changes points towards a transition P-II \rightarrow P-I and is confirmed by X-ray diffraction exposures. The transition at heating does not cause the typical formation of lines in the textures. Additional annealing at 393–398 K does not lead to further prominent changes in textures. It seems that the most stable form, P-I, is already present.

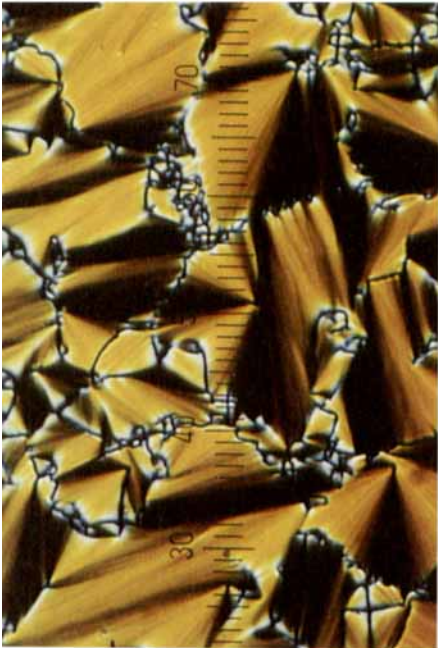
The characteristic features of the observed f.c. texture can be summarized as follows: the appearance of parabolic f.c. defects, a typical formation of lines, the formation of cracks and a change in colour with a variation of temperature. It should be noted that the appearance of the texture is greatly influenced by the thickness of the sample. The partially crystalline state always forms a paramorphic f.c. texture, the elements of which are as easily recognized as in the smectic phase. The texture of the



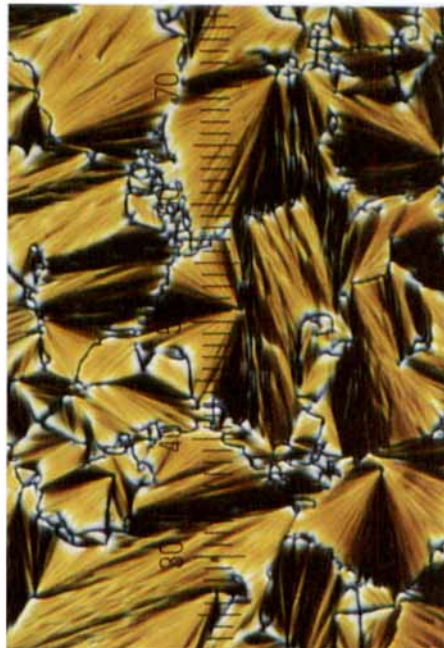
(c)



(d)



(a)



(b)

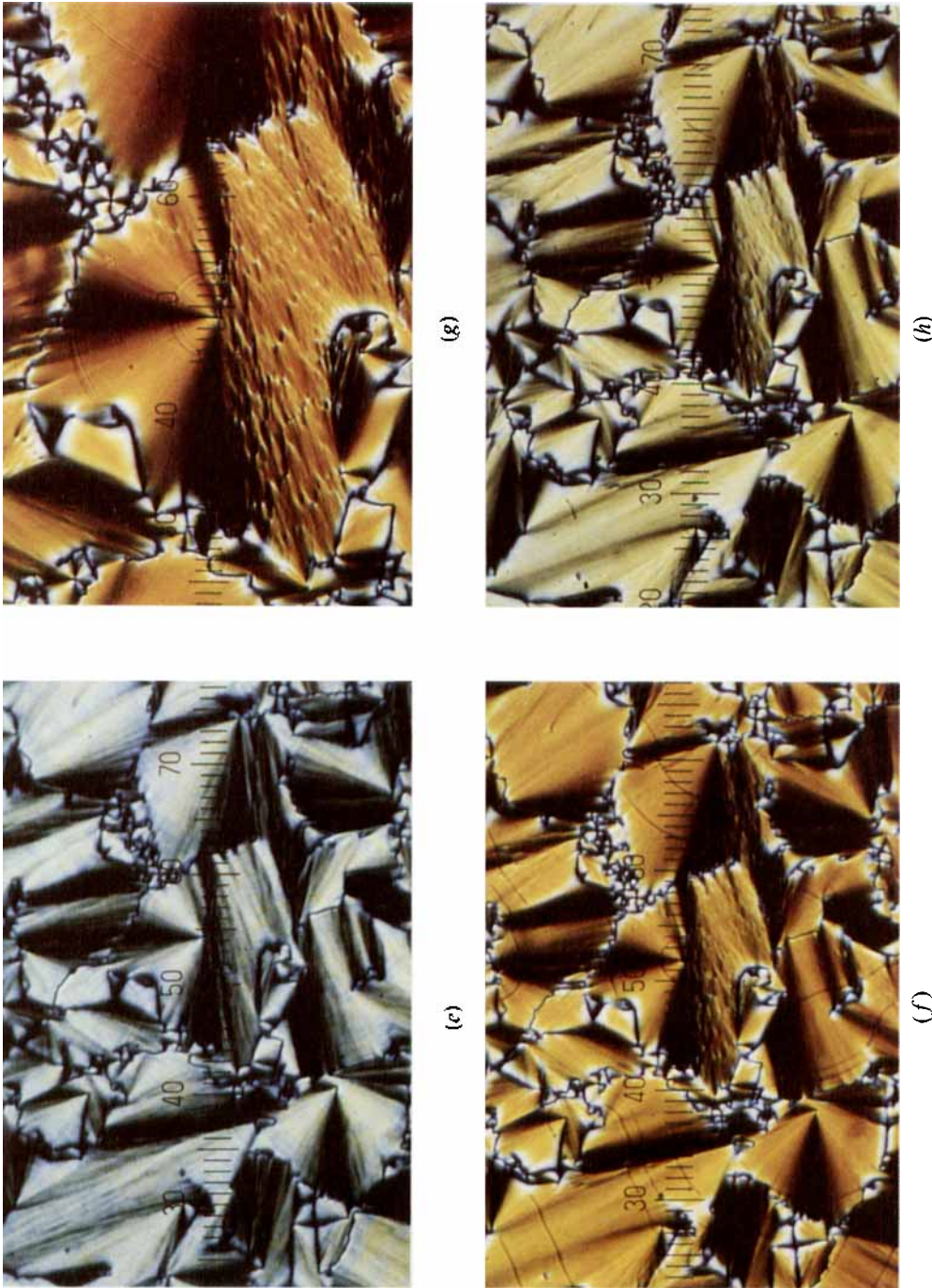
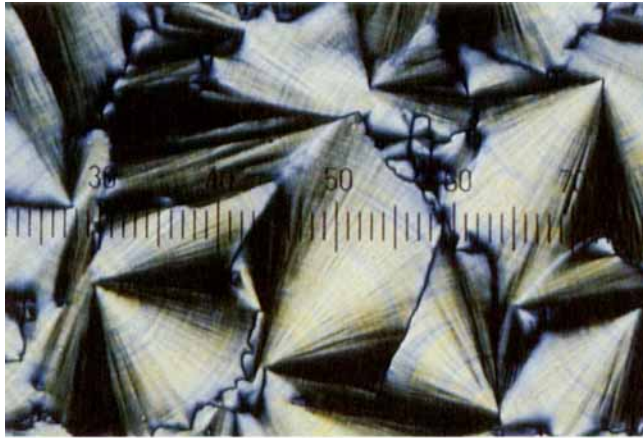
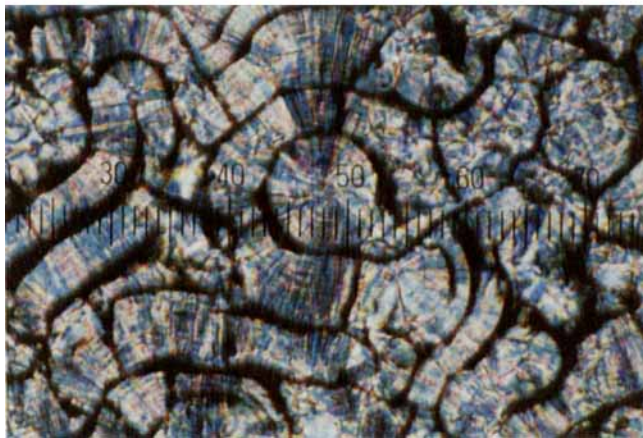


Figure 2. Polarization microscopic exposures of the differently heated or cooled polymer PAc-Bt-63. Focal-conic fan textures of (a-e) the slowly cooled sample, (f) and (g) the quenched sample, and (h) the quenched sample heated. (g), 10 bars ≈ 0.029 mm; all other exposures, 10 bars ≈ 0.057 mm. (a) Smectic phase at 435 K, (b) smectic phase at 408 K, (c) phase transition smectic-P-0 at 412 K, (d) partially crystalline state (modification P-I) at 408 K, (e) partially crystalline state (modification P-I) at room temperature, (f) partially crystalline state (modification P-II) at room temperature, (g) the same as (f) but different magnification, and (h) partially crystalline state (modification P-I upon heating) at 403 K.



(a)



(b)

Figure 3. Polarization microscopic exposures of the polymer PAC-Bi-63: paramorphic f.c. textures of the partially crystalline modification P-I for different thickness of the samples. (a) Small sample thickness (10 bars \approx 0.029 mm), (b) larger sample thickness (10 bars \approx 0.057 mm).

smectic phase of the polymer investigated shows many common features of an S_A phase of low molar mass compounds. A comparison of the texture of the partially crystalline state does not provide complete agreement with any known texture. The formation of stripes in the texture of the modification P-I resembles S_E phases of low mass liquid crystals.

X-ray diffraction diagrams of magnetic field-oriented samples of PAC-Bi-63 in the smectic phase point towards a low order of the side group packing within the smectic layers (figure 4(a)), as does the corresponding f.c. texture. A diffuse wide angle reflection is observed on the equator. The X-ray reflections in the small angle region are placed on the meridian and represent a measure of the thickness of the smectic layers. It can thus be concluded that the side groups are placed perpendicular to the layers on an average scale.

In the partially crystalline state the appearance of several wide angle reflections points to a regular packing of the side group within the layers (figures 4(b) and 4(c)).

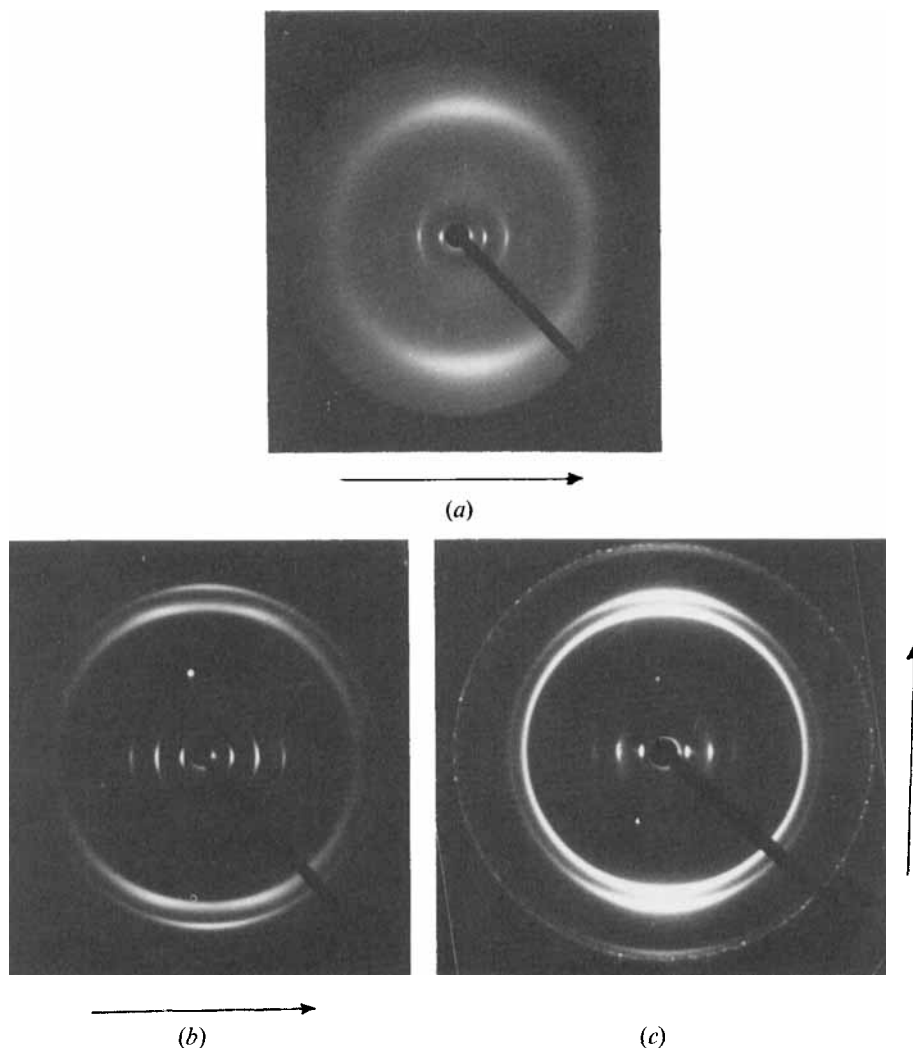


Figure 4. X-ray diffraction exposures of oriented samples of the polymer PAc-Bi-63. The arrows show the direction of the magnetic field and of stretching, respectively, and coincide with the direction of the fibre axes. (a) Smectic phase (approximately 432 K) aligned in a magnetic field; (b) partially crystalline state (room temperature) modification P-I, aligned in a magnetic field; and (c) partially crystalline state (room temperature), modification P-II, drawn fiber.

The X-ray diagram of a magnetic field-aligned sample also shows a perpendicular placement of side groups within the layers.

The two crystalline modifications (P-I and P-II) can be easily distinguished if X-ray diagrams of oriented samples are available. Figures 4(b) and 4(c) show the X-ray exposures of a sample oriented slowly to a magnetic field (P-I) and a stretched fibre (P-II). It should be stressed that the orientation procedure does not influence the structure, e.g. packing within the crystallites; rather, only a different orientation of the crystallites occurs. This was clearly demonstrated for polymethacrylate PMAc-Bi-63 [4]. The d -spacings of the wide angle reflections of both modifications P-I and P-II are nearly identical. The two patterns essentially differ in the intensity distribution of the

reflections with $d = 4.5 \text{ \AA}$, which is placed on a meridional position of the drawn fibre (P-II) and appears as a four point distribution for the sample P-I. This latter reflection originates through a regular packing of the side groups in one direction in space. The packing within the layers are uniformly directed with respect to the fibre axis only for modification P-I. Modification P-II shows this packing somewhat differently directed in space. The reflection is no longer in the meridional direction, resulting in a four point diagram. The evaluation of exact models needs more information than is available in the X-ray diagram for the single compound considered here. In particular, an explanation has to be provided for the transition P-II \rightarrow P-I, which will be obtained for a quenched sample upon heating above 373 K.

The investigation of the X-ray reflections in the small angle region were carried out on non-aligned samples with a Kratky camera. The d -spacing of the first order reflection from the layered structure is shown as a function of temperature in figure 5. The layer thickness of the polymeric material changes uniformly upon cooling and upon heating. This thickness is slightly larger for the crystalline modification of the quenched sample P-II than for the modification P-I at room temperature. The X-ray diagrams of these two modification can be distinguished by the number and intensity of the reflections in the small angle region and the transition P-II \rightarrow P-I detected by a change of intensity and d -spacing upon heating P-II. The layer thickness above 373 K is in accord with the values of P-I (see figure 5). Annealing the sample at 393–398 K only increases the crystallinity. Further structural changes cannot be observed in the X-ray diagram.

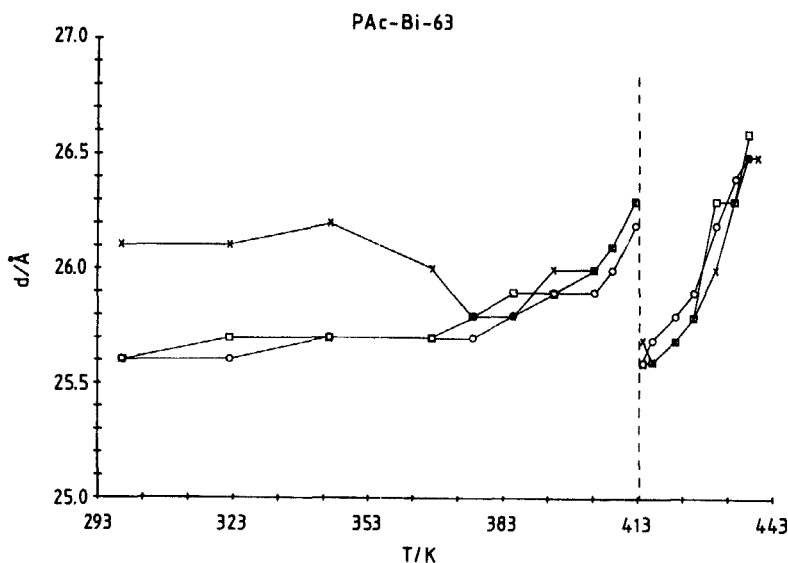


Figure 5. d -Spacing of the first order X-ray reflection at small angle of the polymer PAc-Bi-63 upon cooling and heating. (□) Slow cooling, (○) successive heating and (x) heating of a quenched sample. The transition temperature for partially crystalline-smectic lies at approximately 414 K.

4. Conclusion

In conclusion it can be stated that the X-ray exposures of the polymeric samples clearly show a layered structure in which the side groups are packed quite irregular, yet

aligned along their axes, in the smectic phase and regular with parallel axes in the crystalline modifications. An evaluation of the X-ray diagrams will be published elsewhere, together with an investigation on the other polymers listed in the table [7]. The results of the X-ray investigation confirm the polarization microscopic observations. A careful observation of the texture of polymeric liquid crystal side group polymers represents a useful tool in the structure and phase determination of these polymers.

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