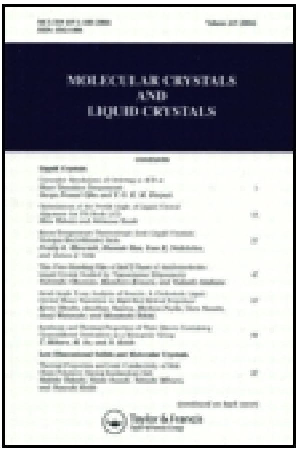

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Calorimetric Study of the Polymorphism of a Novel Polyester Containing Cyanoazobenzene Side Groups

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To cite this article: Eliana L. Tassi, Massimo Paci & Pierluigi Magagnini (1995): Calorimetric Study of the Polymorphism of a Novel Polyester Containing Cyanoazobenzene Side Groups, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 266:1, 135-151

To link to this article: http://dx.doi.org/10.1080/10587259508033638

Mol. Cryst. Liq. Cryst. 1995, Vol. 266, pp. 135–151
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CALORIMETRIC STUDY OF THE POLYMORPHISM OF A NOVEL POLYESTER CONTAINING CYANOAZOBENZENE SIDE GROUPS

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Abstract The phase behavior of a novel comb-shaped polyester (**P8a12**), synthesized from 2-[8-(4-(4-cyanophenylazo)-phenoxy)-octyl]-1,3-propanediol and tetradecanedioic acid, has been studied by differential scanning calorimetry. It has been shown that the phase behavior of this polymer is strongly dependent of the thermal history. Up to four, partially overlapped endothermic effects have been found in the DSC heating scans, whose relative intensities markedly change with the conditions of the previous thermal treatment, as well as with the scanning rate. These effects have been tentatively associated with the transitions of as many different polymer structures. The thermal treatments needed for selectively developing the different structures in **P8a12** specimens have been determined. The structures have been preliminarily studied by X-ray diffraction and optical microscopy.

INTRODUCTION

Among liquid-crystalline polymers (LCPs), those carrying mesogenic side-groups, referred to as side-chain liquid crystalline polymers (SCLCPs), have been studied very intensively during the last years, in view of their potential for optoelectronic applications.[1-9] A mesogen which is particularly useful for photo-induced orientation studies, in view of the development of reversible optical data storage devices, is the cyanoazobenzene group. This mesogen has been mainly employed, in the past, as a pendant for polyacrylate and polymethacrylate backbone chains,[2-9] although different types of SCLCPs with, e.g., polyester main-chains have also been tested.[10-13]

The mesogenic side-groups of most known SCLCPs are commonly linked to the backbone via flexible polymethylene or polyoxyalkylene spacers, according to the principle,[14] that the side-group motions should be preserved, as far as possible, from the restraints imposed by the main-chain on their mobility. Some years ago, we theorized that

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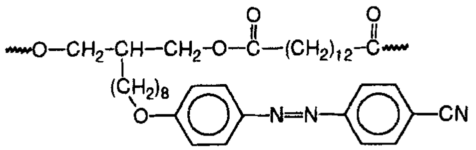
an efficient decoupling of main-chain and side-chain motions could be achieved through the introduction of flexible spacers within the backbone.[15] Actually, even if the rigid mesogens are moved away from the backbone by flexible leashes, their motion may still be hindered if the side-chains are linked on every second main-chain atom, as is the case for the majority of known SCLCPs. This concept was applied to the synthesis of new SCLC polyesters containing aliphatic diacid and substituted ethanediol moyeties,[16] and was subsequently tested in more detail through a study of comb-shaped polyesters containing long paraffinic side-groups linked to the diol units.[17, 18] It was demonstrated that, in fact, a wider spacing between neighbouring side-groups, along an intrinsically flexible main-chain, greatly enhances the side-chain organization ability.[17,18] On the other hand, upon increasing the side-groups distance beyond a certain limit, other possibilities of macromolecular organization, besides that involving the side-groups only, may arise. And, in fact, depending on the thermal and mechanical history of the samples, the main-chains were found to participate in the formation of the organized phases of the comb-like polyesters containing diacid units with an even number ≥4 of methylene groups.[18]

Within the Brite-EuRam II project, a research aimed at the production of new SCLCPs for optical information storage is being performed in our laboratories, in cooperation with the Risø National Laboratory, Roskilde, DK, and the University of Essen, FRG. New SCLC polyesters have been prepared by melt alcoholysis of diphenyl alkanedioates with 2-[ω-(4-(4-cyanophenylazo)-phenoxy-alkyl]-1,3-propanediols, where the diacid units contain 10, 12, and 14 methylenes, and the alkyl spacer is hexa-, octa- and decamethylene in turn. Preliminary results on reversible optical storage and photoinduced anisotropy in thin films of these SCLCPs have recently been reported.[19-21]

In this work, we discuss the phase behavior of one of these polyesters, namely, poly(2-[8-(4-(4-cyanophenylazo)-phenoxy)-octyl]-1,3-propylenetetradecanedioate, referred to as **P8a12** (where **a** indicates the cyanoazobenzene mesogen, and **8** and **12** are the numbers of methylenes in the propanediol and the diacid units, respectively).

EXPERIMENTAL

The chemical structure of **P8a12** is shown below. The synthesis of this polyester has been described elsewhere.[19-21]



The intrinsic viscosity of **P8a12**, measured in THF at 30°C was [η]=0.38 dL/g.

The phase behavior of the polyester was studied by differential scanning calorimetry (DSC), with a Perkin Elmer apparatus mod. DSC-4, equipped with a data station. The calorimeter was calibrated with indium and zinc standards. The polymer specimens (ca. 15 mg) were placed into aluminum pans, and were analyzed under dry nitrogen. The scanning rates were varied in a wide range, in order to monitor the effect of both the heating rate and the rate of the previous cooling cycle. In particular, the polymer specimens were first heated to 110°C, in the calorimeter, and left at this temperature for 10 min, in order to get the complete destruction of the crystalline nuclei. The cooling cycles, down to -40°C, were done with the following rates: -0.1, -0.2, -0.5, -1, -3, -10, and -40 °C/min, although the relevant DSC traces could be recorded with the latter five rates, only. The heating DSC scans were then recorded, for each of the obtained specimens, using the following rates: 0.5, 1, 3, 10, 20 and 40 °C/min. Moreover, prolonged annealing experiments were carried out, as described later, and additional DSC heating scans were run, in order to record the effect of these treatments. The reproducibility of the thermograms was always excellent. A polymer specimen could be rerunned for very many times without appreciable change of the DSC traces, provided that the recent thermal history (after the 110°C conditioning) was carefully reproduced.

Preliminary observations of **P8a12** films were made with a Leitz Ortholux-Pol BK polarizing microscope, equipped with a Mettler FP-52 hot stage and a Mettler FP-5 programmer.

Powder X-ray diffractograms were taken with a Siemens D-500 apparatus, equipped with a DACO-MP interface and Diffrac-AT software, using the Ni-filtered CuKα radiation. Polymer specimens having different thermal history were employed.

RESULTS AND DISCUSSION

The DSC cooling traces recorded for **P8a12** using different cooling rates are shown in Figure 1a. Two sharp exotherms can be readily observed in these traces, whose peak temperatures decrease slightly on increasing the cooling rate. In addition to this, a broad exotherm is clearly visible in all traces, at lower temperatures. A close examination of the

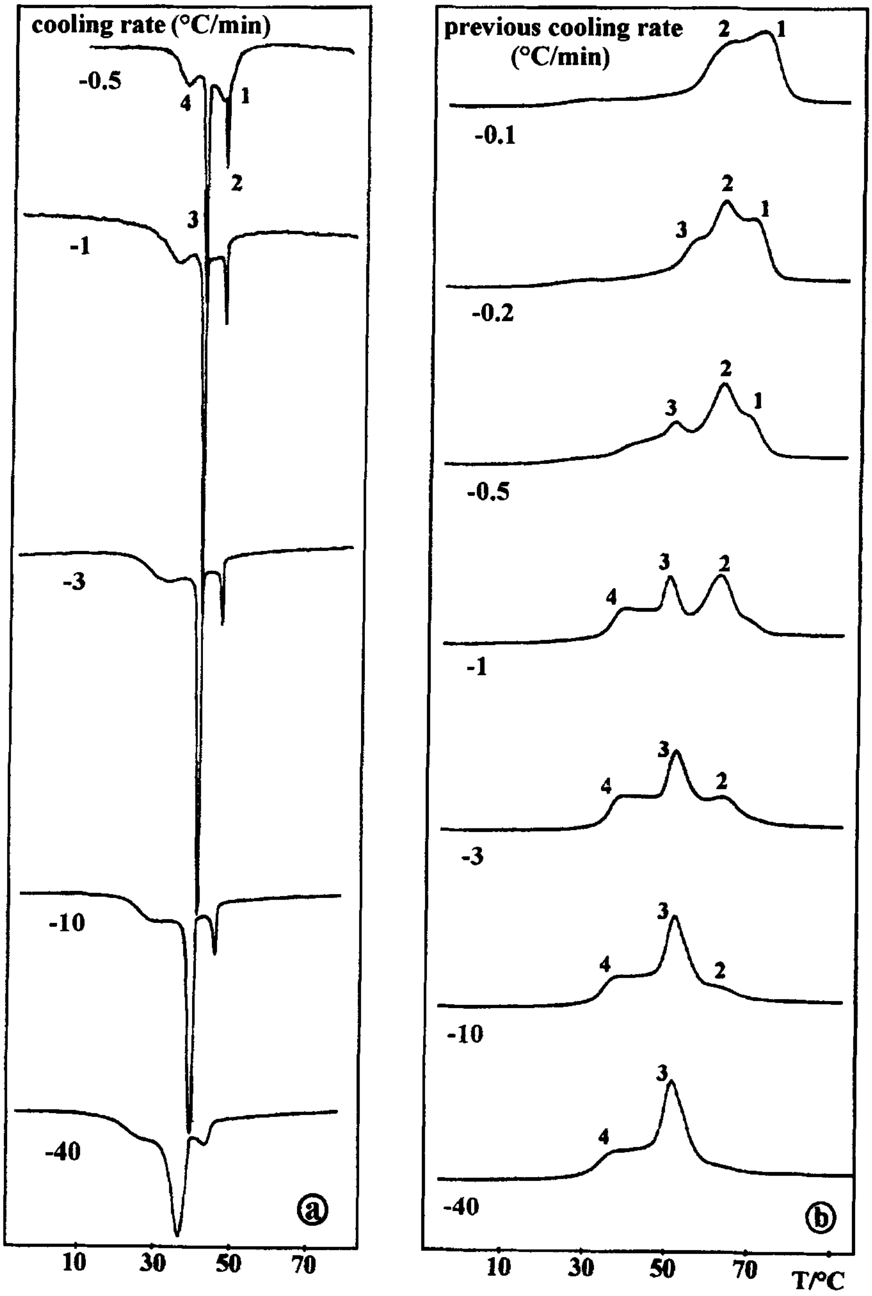


FIGURE 1 DSC traces of **P8a12**. a) cooling traces (scanning rates as indicated); b) heating traces (scanning rate 40 °C/min) of specimens previously cooled with the indicated rates.

traces obtained with the lowest cooling rates (-0.5 and -1 °C/min) reveals a fourth broad exotherm, superimposed upon the higher temperature sharp peak, whose intensity increases on decreasing the cooling rate.

These four exotherms have been tentatively associated with the formation of four different structures, which will be hereinafter referred to as structure 1, 2, 3, and 4, in the order of decreasing transition temperatures (cf. Figure 1a).

Just after the cooling runs illustrated in Figure 1a, the **P8a12** specimens were analyzed with a heating rate of 40 °C/min, and the relevant traces are shown in Figure 1b. Here, the traces recorded for **P8a12** specimens previously cooled with a rate of -0.1, and -0.2 °C/min (the relevant cooling scans could not be recorded with the apparatus used in this work) are also included. The relatively high heating rate of 40 °C/min was used, in this case, in order to limit the structural changes undergone by the polymer during the scans, and to get further information on the structures formed as a result of the previous cooling cycle. Due to the high scanning rate, the endotherms consist of comparatively broad peaks. Despite of this, it may still be noticed that the heating traces also indicate the presence of four, partially superimposed endotherms, whose intensity varies with the rate of the previous cooling cycle. The assignment of these endotherms to the transitions of as many polymer structures was tentatively made as illustrated before, and the endothermic peaks (or shoulders) in Figure 1b are labeled accordingly.

A reliable measurement of the enthalpies associated with the different transitions shown in Figures 1a and 1b is hampered by the partial superimposition of the relevant peaks. Nevertheless, a rough estimation of their magnitude was equally made, in order to obtain a first, qualitative information on the effect of the cooling rate on the extent to which the different structures are developed. The results are shown in Figures 2a and 2b.

Despite of the low quantitative reliability of some of the data, these two figures provide a very useful information on the cooling rate dependence of the molecular organization of **P8a12**. First of all, it may be observed that, as expected, there is fairly good agreement between the heats released upon cooling and absorbed upon subsequent heating, for all four structures. The only noticeable mismatch is observed in the region of intermediate cooling rates (-0.5÷-3 °C/min) for structure 2. Here, the relevant enthalpies appear definitely higher for the heating DSC traces (Figure 2b) than for the corresponding cooling traces (Figure 2a). This finding has been explained assuming that, during heating, the structures of lower order (3 and 4) undergo a rearrangement to structure 2. This point will be discussed in more detail later.

From the plots in Figure 2, it may be concluded that low cooling rates favour the formation of structures 1 and 2 and, among these, the former is further favoured if the cooling rate is very low (-0.1 °C/min). On the contrary, high cooling rates favour the

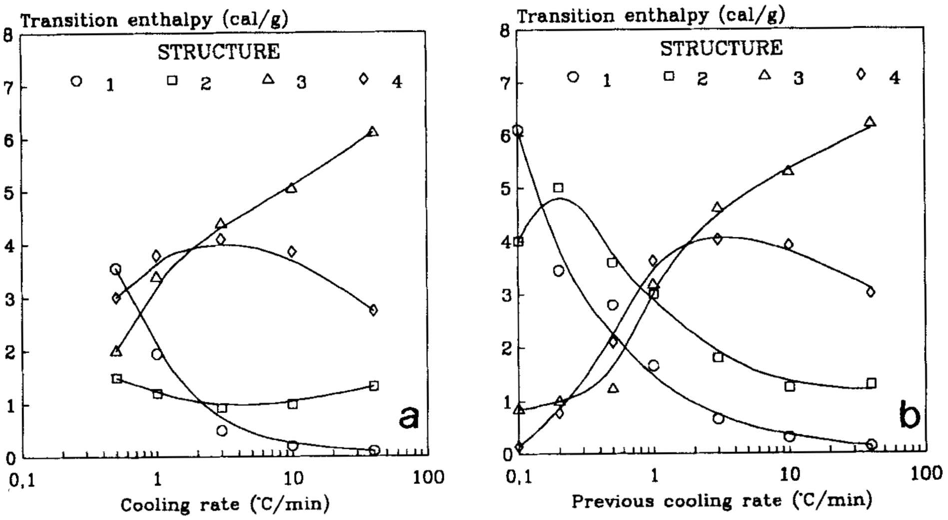


FIGURE 2 Enthalpies of the exotherms (a) and of the endotherms (b) associated to the different structures of P8a12, as estimated from the traces in Figures 1a and 1b.

formation of the lower order structures 3 and 4 and, among these, the former is further favoured by very high cooling rates (-10 and -40 °C/min). Here, obviously, the scanning rates are indicated as low, very low, high and very high, in a relative sense.

In the above discussion, the cooling scans carried out at different rates were compared with the heating ones obtained using a fairly high rate. As already mentioned, the choice of a high heating rate was done in order to limit any eventual phase reorganization during the scan. That structural reorganizations do actually take place during heating scans carried out at low, or moderate heating rates is dramatically demonstrated by Figure 3. In particular, in Figure 3a, the DSC traces measured with a heating rate of 40 °C/min on **P8a12** samples previously cooled at -0.1 and -40 °C/min, are compared with those measured with a heating rate of 0.5 °C/min, on the same specimens. For the slowly cooled sample, the two heating traces, independent of the expectedly higher resolution of that done at -0.5 °C/min, are very similar. Both traces, in fact, show that slowly cooled **P8a12** practically comprises the structures 1 and 2 only, and that the content of the former is ca. 1.5 times that of the latter. On the contrary, the heating traces of the rapidly cooled specimen show very marked differences, even on a qualitative ground, and demonstrate that, during a slow heating cycle, the structures (3 and 4) present in a rapidly cooled polymer undergo extensive rearrangement into structures of higher order (2 and 1).

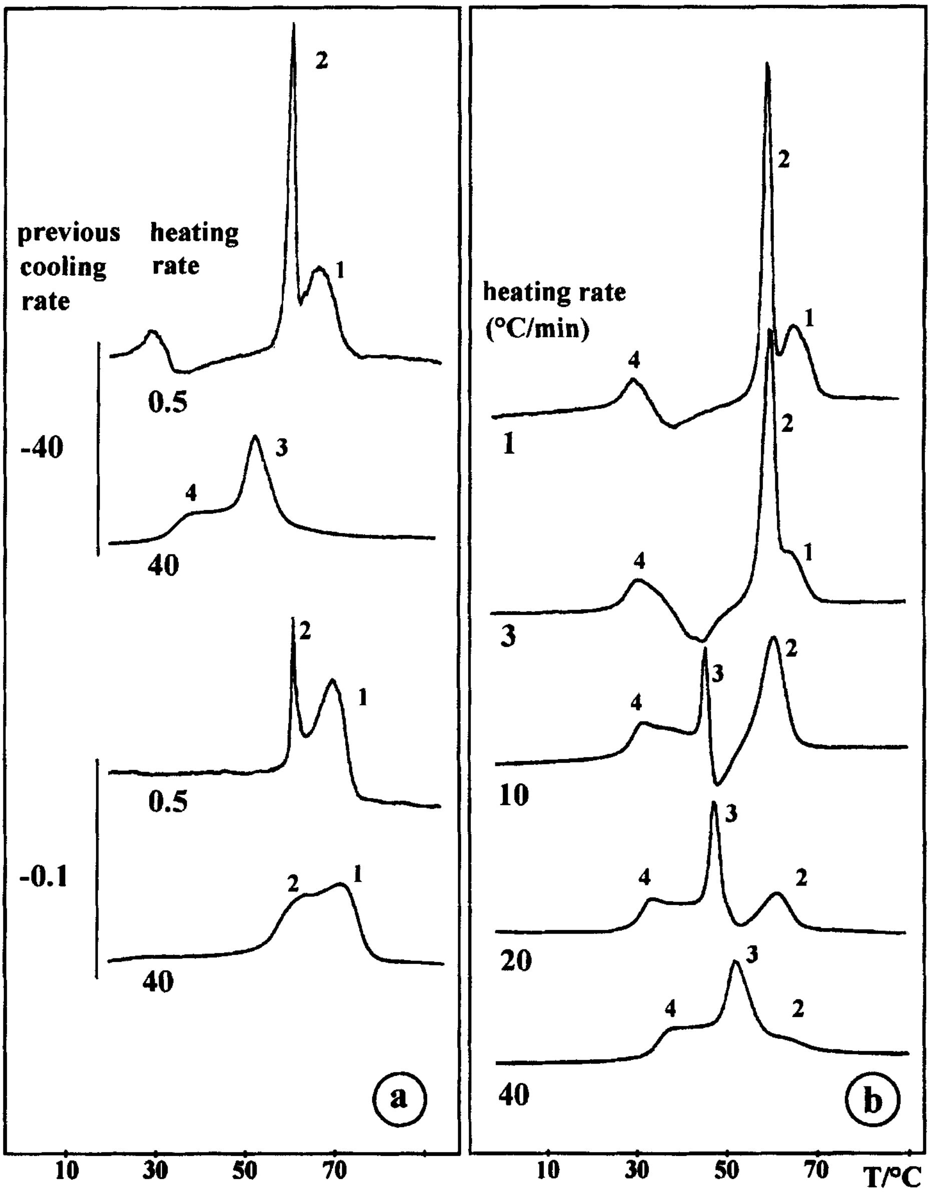


FIGURE 3 DSC heating traces of **P8a12** samples previously cooled from 110 °C with a rate of -40, -0.1 (a), and -10 °C/min (b). Heating rates as indicated.

The structural changes taking place during the heating scans are demonstrated even more clearly in Figure 3b, where the DSC traces measured with different heating rates, on a **P8a12** sample previously cooled at -10 °C/min, are shown. It is evident that the slower the heating the stronger the structure rearrangements taking place during the scanning.

The structure reorganization gives rise to exotherms clearly visible in the DSC traces recorded with low heating rates (1÷10 °C/min).

The above data demonstrate that **P8a12** gives rise to a number of structures, whose transformation temperatures, independent of the expected effect of the scanning rate, are found within well defined temperatures ranges, namely, 30-40°C for structure 4, 46-54 C for structure 3, 59-63°C for structure 2, and 65-71°C, for structure 1. On the other hand, the enthalpies of the transitions associated with these structures vary widely with the history of the samples and with the measurement conditions. This dependence is

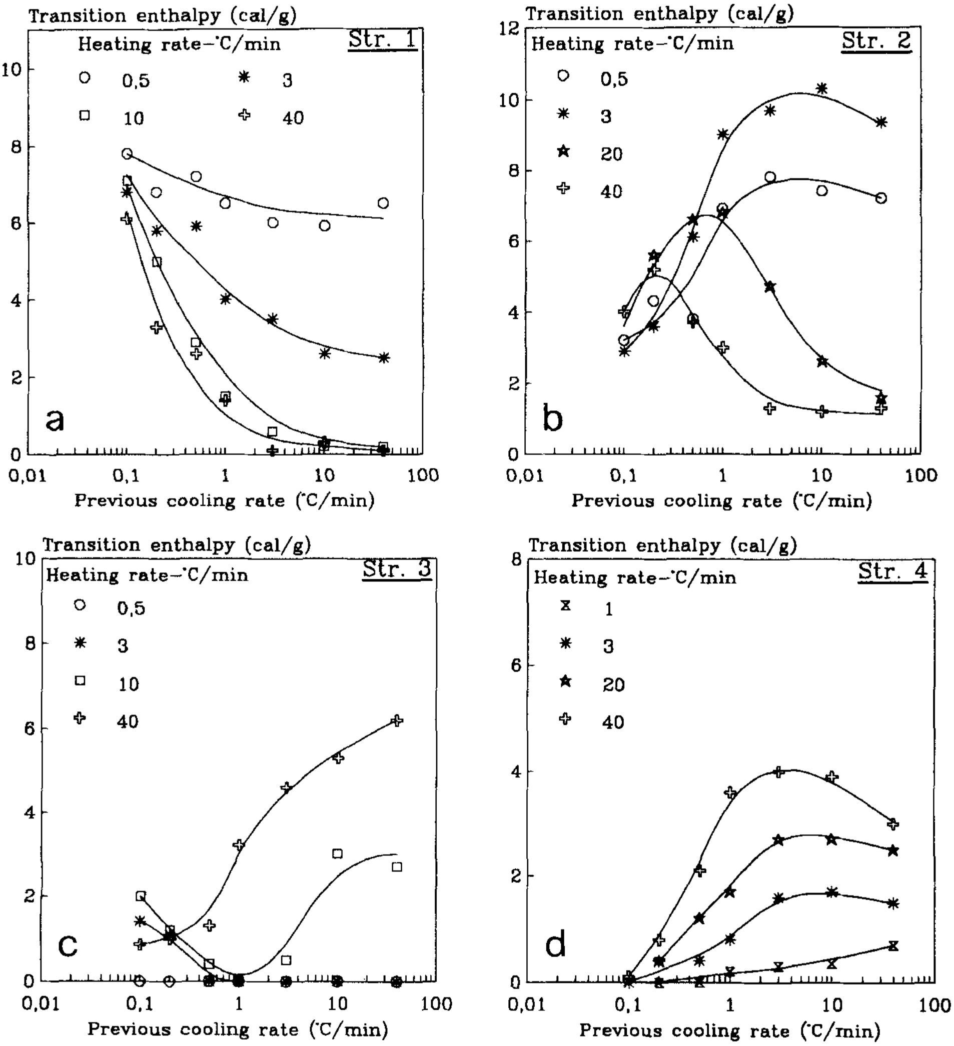


FIGURE 4 Transition enthalpies associated with the different structures of **P8a12**, as measured on samples previously cooled with different rates.

illustrated by the plots shown in Figure 4, obtained from calorimetric measurements carried out over a wide range of cooling and heating rates (cf: Experimental).

It is evident (Figure 4a) that the highest content of structure 1 is found for polyester samples cooled from the isotropic state with a very low rate (-0.1 °C/min), independent of the heating rate used for the measurement. This demonstrates that structure 1 is characterized by the highest stability. On the other hand, a very high content of structure 1 is found, even for rapidly cooled specimens, provided that the heating rate is very low (cf. Figure 4a, heating rate = 0.5 °C/min). This is clearly due to extensive reorganization of the structures of lower order, taking place during the scan. From these considerations, it follows that the content of structure 1 may be further increased by prolonged annealing at appropriate temperatures.

The plots in Figures 4b, 4c, and 4d confirm that structures 2, 3, and 4 can be obtained only under non-equilibrium conditions. In fact, their content is fairly low for slowly cooled specimens, and may be increased by high (structures 3 and 4) or intermediate (structure 2) cooling rates. In particular, the curves in Figure 4b demonstrate that structure 2 is developed at best when a rapidly cooled **P8a12** specimen is heated up with a rate of 3 °C/min: at higher heating rates this process is less favoured, whereas at lower heating rates, structure 1 is formed preferentially.

The above indications, have been used to devise the most appropriate treatments for the development of the different structures of **P8a12**. Thus, one specimen was prepared by quenching the molten polymer in ice-water. The DSC heating trace of this specimen is shown in Figure 5, curve a. The DSC trace is very similar to that of a **P8a12** sample previously cooled with a rate of -40 °C/min (cf. Figure 1b), thus showing that the latter cooling rate is satisfactory in view of the formation of the two structures 3 and 4. We did not succeed in improving the mutual selectivity of development of structures 3 and 4 by room temperature annealing experiments.

Another polymer specimen was annealed 24 h at 38 °C, after quenching. The DSC heating trace of this sample is presented in Figure 5, curve b. It shows that the polymer is fairly rich in structure 2. However, the strong endotherm peaking at 62.8 °C appears asymmetric and is accompanied by weak shoulders in the 30-50 °C region. The asymmetry of the peak suggests that there may be a small contribution of the higher temperature transition associated with structure 1. Nevertheless, this treatment of **P8a12** (quenching, followed by prolonged annealing at 38 °C) is the best we could devise for a selective development of structure 2.

A third specimen was prepared by annealing **P8a12** at 58 °C for 66 h. The previous thermal history did not show any appreciable influence on the shape of the DSC trace recorded for such sample (Figure 5, curve c). This trace demonstrates that the polymer is very rich in structure 1.

These procedures for the selective development of the different structures of **P8a12**, after possible optimization, should be followed for the preparation of polymer samples to be used for a detailed diffractometric analysis. However, it may be anticipated that the exact identification of the organized structures of this polymer will be probably difficult either because, except perhaps for structure 1, the other structures cannot be isolated with sufficient selectivity, and beacause it will be hampered by the need of using powder X-ray diffractometry, only. It has been shown, in fact,[17] that any attempt at the preparation of oriented samples, e.g., by spinning, leads to profound structural changes.

The results of a preliminary diffractometric analysis of the three **P8a12** specimens prepared as described above are shown in Figure 6, in the form of powder X-ray patterns. None of the patterns shows clear reflections in the low angle region (2θ = 2÷5°), and this may be taken as an indication that none of the phases of **P8a12** studied so far is organized into layers, as it would be expected for smectic structures. The X-ray pattern of the quenched sample (curve a) shows a single, very broad reflection in the angular region around 2θ = 22°. This pattern, coupled with the fact that a film of this material shows LC textures on the optical microscope (see below), is indicative of a nematic structure for

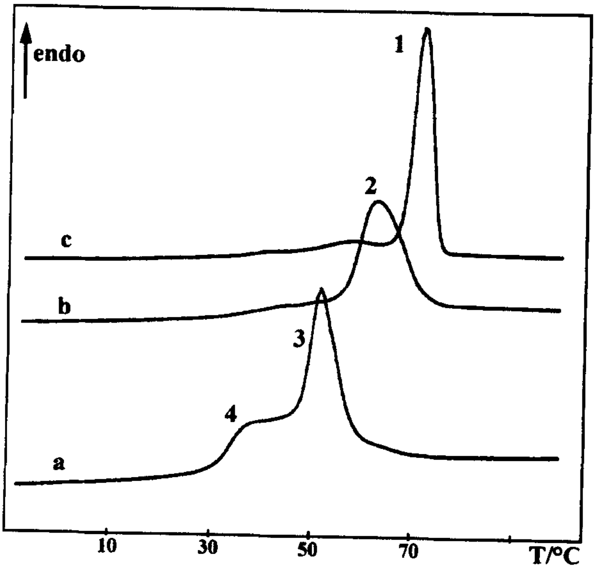


FIGURE 5 DSC heating traces (scanning rate 40 °C/min) of **P8a12** specimens prepared by: a) quenching; b) quenching and annealing at 38 °C for 24 h; c) cooling from 110 °C, with a rate of -3 °C/min, and annealing at 58 °C for 66 h.

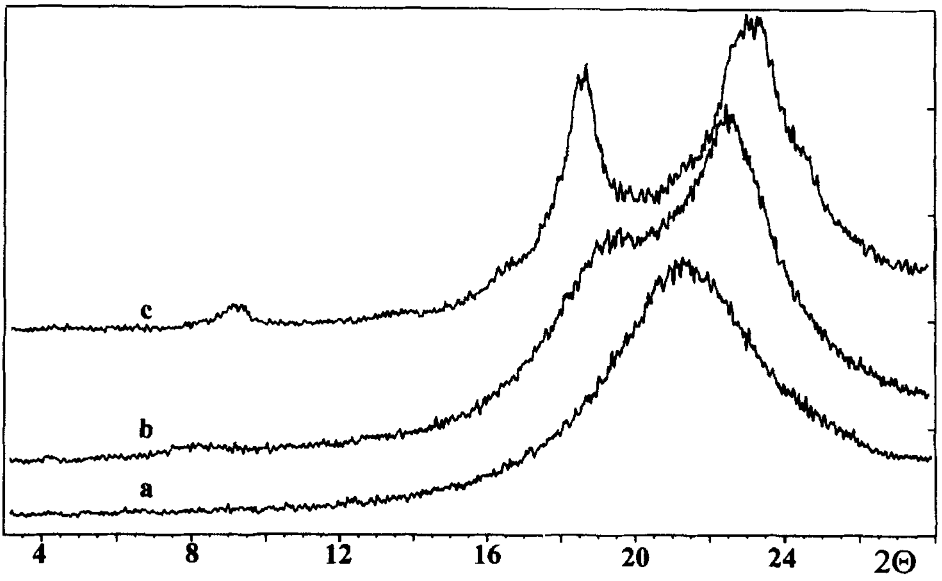


FIGURE 6 Powder X-ray diffraction patterns of the **P8a12** samples described in Figure 5.

quenched **P8a12**. Of course, this X-ray pattern cannot give any information concerning the differences, if any, between the molecular organizations prevailing in the two structures 3 and 4, whose individuality has been suggested by the calorimetric analysis.

The X-ray pattern of the specimen annealed at 58°C (curve c), on the contrary, shows a number of ill-resolved reflections, in the wide angle region, which are indicative of a disordered crystalline structure. It must be kept in mind that **P8a12** is a stereoirregular polyester, and this may be one reason for the poor resolution of the X-ray reflections of this material.

As for structure 2, the X-ray diagram of the sample annealed at 38 °C (curve b) is also indicative of some kind of (even more defective) crystalline organization. The present data are not sufficient for a reliable identification of the crystalline structure of this material. Moreover, it is not possible, with the preliminary information presently at hand, to reach a conclusion even with respect to the possible qualitative differences between structure 2 and structure 1. This, also in view of the fact that, as previously discussed, the **P8a12** specimen at issue probably contains a mixture of the two structures.

The comparison of the X-ray data with those of the calorimetric study leads to the conclusion that **P8a12** shows an interesting polymorphic behavior with two mesomorphic structures (referred to, above, as 4 and 3), and two crystalline structures (2 and 1), whose thermal stability increases in the order. Thus, **P8a12** may be classified as a monotropic LCP, since the upper temperature of mesophase stability is lower than that of the crystalline phase.

A preliminary investigation of the textures shown by films of **P8a12**, after different thermal treatments, was made by polarized optical microscopy. The films were prepared either by spreading with a razor blade a small amount of polymer on a glass slide held at ca. 120°C, or by evaporation of a polymer solution. After conditioning at 110 °C, the films were subjected to appropriate thermal treatments, such as quenching, slow cooling from the isotropic state, and annealing, in order to reproduce the conditions used during the calorimetric study for the selective development of the different polymer structures. The films were then viewed between crossed polarizers on the hot stage of the optical microscope. In most cases, the films showed the so-called "fine grain" or "tight" texture displayed by most comb-shaped polymers,[22] as well as by many main-chain LCPs.[23] This texture is interpreted as the result of a relatively high nucleation density, which leads to ordered domains of very small dimensions, whose morphology can hardly be resolved by optical methods. The tight textures displayed by fairly thick **P8a12** films did not show appreciable changes as a result of the thermal treatments. However, the appropriate treatment of very thin films allowed us to improve the resolution and to obtain clearer textures. Some of the micrographs obtained for quenched **P8a12** films are shown in Figures 7a, b, c. As it is clear from these micrographs, different patterns could be observed, depending on the film thickness, as well as on the time the film was held on the microscope at room temperature (ca. 25 °C). The texture of a film slowly (-0.2 °C/min) cooled from the isotropic state, which, according to the calorimetric analysis should mainly comprise the structures 1 and 2, is shown in Figure 7d. Very small, bright spherulites may be observed within the tight texture. However, if a **P8a12** thin film was slowly cooled from 120 °C down to ca. 60 °C, and left at this temperature for two days, the texture shown in Figure 7e could be observed. On subsequent slow cooling down to room temperature, the tight texture developed troughout the isotropic phase (Figure 7f). A reliable correlation of the textures observed under crossed polarizers with the type of organization prevailing in the different polymer films will be probably far from easy. However, it should be kept in mind that, whereas the strongly anisometric cyanoazobenzene groups give a predominant contribution to the birefringence of the films, the main-chains and the spacers, which represent almost two thirds of the mass of the polymer, do certainly play a role in determining the type of structural organization of the macromolecules.

In this context, a point which deserves some comment is the experimental calorimetric finding that the overall enthalpy change associated with the fusion of **P8a12**

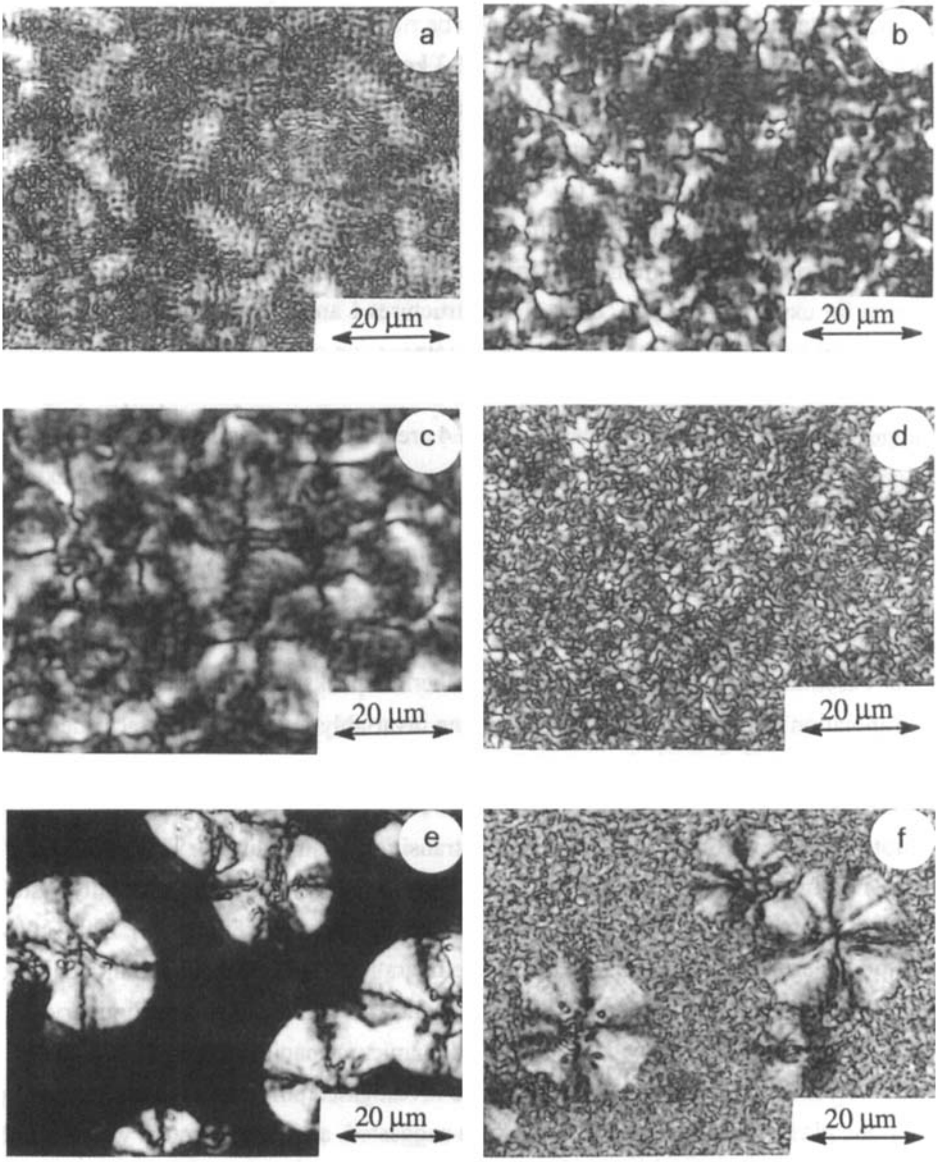


FIGURE 7 Optical textures of **P8a12** films: a), b), c) quenched from 120 °C down to room temperature; d) cooled from 120 to 25 °C with a rate of -0.2 °C/min; e) slowly cooled from 120 to 60 °C, and left at this temperature for 2 days; f) same as e), and slowly cooled down to room temperature. See Color Plate XI.

does not change appreciably with the previous thermal treatment of the specimens and with the measurement conditions. In particular, it may be surprising that, for the quenched samples, that have been shown to be rich of the allegedly nematic structures 3 and 4, the fusion enthalpy (ca. 10 cal/g, or 6.3 kcal/mol) does not differ appreciably from that (ca. 11.5 cal/g, or 7.2 Kcal/mol) measured for the annealed samples, and is, on the contrary, much higher than the enthalpy of isotropization of the mesogenic propanediol used as the precursor of **P8a12** (ca. 1 Kcal/mol)[24]. The stereoirregular microstructure of the polyester, coupled with the presumably high tendency of the cyanoazobenzene groups to become segregated from the predominantly aliphatic main-chains, may be a good reason for expecting the two "crystalline" structures 1 and 2, to be characterized by fairly low fusion enthalpies. On the other hand, a comparison of the enthalpies associated with the fusion of quenched **P8a12** with that of isotropization of the parent propanediol suggests that the organized structures 3 and 4 are not simply originated from the nematic alignment of the mesogenic side-groups, but probably involve, at least to some extent, the main-chains and the spacers.

In the above discussion, which was mainly focused on the polymorfism of **P8a12** and its dependence on the thermal history, no mention was made of the glass transition of this polymer. Actually, in the DSC scans, the glass transition is not visible, in the form of a clear baseline shift, separated from the endothermic peaks. On the other hand, the back extrapolation of the high temperature baseline invariably reveals that, in fact, there must be a baseline shift, but this is masked by the endothermic phenomena. A reasonable assumption may be that the glass transition of **P8a12** coincides with the onset of the first endothermic peak (that associated with the transition of structure 4). This assumption is supported by the observation that a baseline shift of reduced intensity is actually visible, in this temperature region, in some of the DSC heating traces (cf. Figure 1b). If the above assuptions are correct, the glass transition temperature (Tg) of **P8a12** should be in the vicinity of 20 °C. This conclusion is in agreement with the results of a preliminary investigation of this polymer carried out by dynamic mechanical testing (DMTA).[25] However, it cannot be given for sure that the investigated polyester is characterized by only one glass transition. In fact, it has been suggested, and demonstrated with a number of examples,[26] that two glass transitions may be displayed by comb-shaped polymers in which a real decoupling of the side-groups and main-chain motions is granted. On the basis of the chemical structure of **P8a12**, it might be expected that a microphase segregation of the main-chains and the side-groups does actually take place for this polymer, and that the two phases are characterized by two different glass transitions. However, the results of the present study do not provide any direct proof in favour of this hypothesis.

CONCLUSIONS

It has been shown that **P8a12** is a polymorphic material, showing up to four, calorimetrically different, organized structures. Only one of these structures, indicated here as structure 1, is thermodynamically stable, and is transformed directly into the isotropic melt at ca. 70 °C. The others may be developed under non-equilibrium conditions. However, since the formation of structure 1 is kinetically unfavourable, it does take place to only a limited extent under the usual cooling conditions and, therefore, this structure is normally accompanied by one or more of the metastable ones in the solid polymer. The conditions for developing the different structures with the highest possible selectivity have been established. Preliminary X-ray diffraction data indicate that the structures formed as a result of quenching display a diffraction pattern which is typical for nematic mesophases. On the contrary, the two higher melting structures (1 and 2) appear to be characterized by crystalline oder. Thus, since the temperature of fusion of the crystalline phase(s) of **P8a12** is higher than the temperature of transition associated with the mesomorphic structure(s), this polymer might be classified as a monotropic SCLCP. However, the behavior of the present polyester differs from that of common monotropic LCs, either of low molar mass or polymeric, in that the mesophases formed under non-equilibrium conditions cannot give rise to crystallization upon further cooling: once the mesophases are formed, the crystalline structure of higher thermodynamic stability (structure 1) can only be obtained by prolonged annealing at a temperature (ca. 60 °C) which is higher than that of transformation of the mesophases.

ACKNOWLEDGMENTS

This research was started with the financial support of C.N.R., Progetto Finalizzato "Chimica Fine", and is presently financed by the European Communities under the Brite-EuRam Programme.

E.L.T. wishes to thank the Coordenacão de Aperfeiçoamento de Pessoal de Nível Superior (CAPES), Ministério da Educação, Brazil, for a one year fellowship.

The authors want to thank Dr. F. Andruzzi, of the C.N.R., Centro Studi Processi Ionici di Polimerizzazione, Pisa, for providing the polyester sample and for the helpful discussion of the results, and Dr. S. De Petris, of the same institution, for information on the DMA analysis of the polymer.

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