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ORIGINAL CONTRIBUTION

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The effect of molecular weight on the structure and temperature behavior of a thermotropic main-chain liquid crystalline copolyester

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Abstract The structure of a fully aromatic thermotropic liquid crystalline (LC) copolyester poly-[(phenyl-*p*-phenylene)-co-(terephthalate)-co-(*p*-hydroxybenzoate)] (PES) prepared from terephthalic acid, phenylhydroquinone, and *p*-hydroxybenzoic acid at a molar ratio of 45/45/10, respectively, was studied at ambient and elevated temperatures by means of x-ray diffraction and differential scanning calorimetry as a function of molecular weight. On heating of PES fibers with fixed ends an irreversible phase separation process takes place above the glass transition point and two different crystalline phases are formed. A model is proposed where the phases are assumed to contain the constituents of the statistical copolymer in different amounts. The relative volume fraction of the two crystalline modifications depends on the molecular weight of the investigated fibers. At higher temperatures the melting of the two crystalline phases and their transition to a LC nematic mesophase is observed.

Key words Structure – phase transitions – x-ray scattering

Introduction

Thermotropic fully aromatic copolyesters are of commercial interest due to their ease of processing, thermal stability, and their ability to form fibers, films and coatings [1, 2]. They are also of interest academically since they provide the opportunity to study the effect of chain rigidity and chemical structure on macromolecular order and motion in polymeric materials. Fully aromatic copolyesters are believed to be very rigid due to the low flexibility of the chain backbone and may thus form quite interesting mesomorphic phases. To achieve a better processability and molding behavior for commercial applications of these materials, quite often statistical copolymers are used where the ideal sequence distribution is disturbed resulting in a lower melting point or better solution behavior [3, 4].

In another approach, processable systems are obtained when flexible side chains are attached to the aromatic backbone [5, 6]. Chains are still relatively stiff and rigid as can be judged from viscosity and light scattering experiments, while the flexible side chains act similar to a chemically attached "solvent" and cause a significant reduction of the melting point [7, 8]. Both approaches lead to interesting materials with different crystalline and liquid–crystalline phases as well as high-modulus mechanical properties when spun in the form of fibers. Here, we will discuss the structure and properties of a particular fully aromatic copolyester where the formation of a perfect crystal structure is inhibited by the statistical incorporation of a "mismatched" component. Different materials of this sort have been described in the literature.

Polymers from hydroxybenzoic acid and *p*-phenylene terephthalate for example have high melting points and cannot be mold processed by standard techniques. A commercial material like Vectra (a Celanese polymer), on the other hand, is a copolymer which contains *p*-hydroxybenzoic acid (HBA) and 2-hydroxy-6-naphthoic acid (HNA) in a largely random manner. The melting point is considerably lowered and melt processing becomes feasible. The used monomeric groups are generally quite different in length and may contain side groups, which disturb the formation of the ideal crystal structure. The example of a copolymer of HBA and HNA of different compositions has been extensively studied by x-ray scattering [9–12]. While a considerable amount of disorder is present, a crystalline order can still be observed. Several models are discussed which explain the formation of crystalline structure in such a random copolymer system. While most of the studies are performed at room temperature with previously annealed samples [9, 11], recent experiments also report on the temperature behavior of the structure of this copolymer at elevated temperatures [13]. Depending on composition mostly a transformation from an orthorhombic to a quasi-hexagonal phase is observed.

A much more complex phase behavior is reported for random fully aromatic copolyesters (PES) composed of 90 mol% phenylhydroquinone terephthalate and 10 mol% poly(oxy-1,4-phenylenecarbonyl) at ambient [14–16] and elevated [17] temperatures. This copolymer is crystalline in spite of the random monomer sequence and forms two crystalline phases (crystal 1 and crystal 2) as revealed from x-ray diffraction patterns at different temperatures. Both polymorphs are orthorhombic with slightly different unit cell dimensions and coexist within a wide temperature range. The material transforms into a LC nematic state above 330 °C. It was also proposed [14–17] that both crystalline modifications are thermodynamically equilibrium phases. In such a case the question arises as to why two different stable phases with similar lattices are coexisting for one polymeric substance. To answer this question it will be helpful to find conditions under which either crystal 1, or crystal 2 will exist alone, or where either a crystal 1 or a crystal 2-rich phase will be observed.

The purpose of this paper is to concentrate on the study of the same PES copolyester, but with different values of relative viscosities indicative of different molecular weights of the copolymers. The molecular weights of fully aromatic copolyesters are difficult to determine due to their low solubility and rigid rod nature. We thus will use the viscosities obtained from solutions in mixed solvents as a relative measure of molecular weights. It will be shown that the change of molecular weight quite significantly affects the crystalline structure and thermal behavior of this random copolyester.

Experimental section

Materials and samples

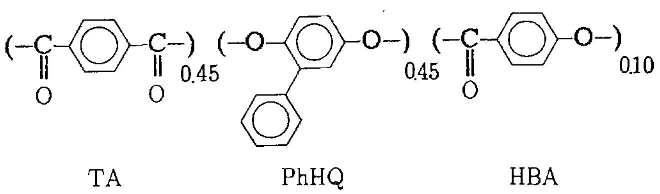
The copolyesters are composed of three monomeric units: terephthalic acid (TA), phenylhydroquinone (PhHQ), and 4-hydroxybenzoic acid (HBA) (see Fig. 1). They were kindly provided by Prof. A.V. Volokhina (NPO "Khimvolokno", Russia). The material composition consisted of TA/PhHQ/HBA in relative mole percentages of 45/45/10. According to preparation conditions described elsewhere [18] the received copolymers are expected to be random. The PES copolyesters were synthesized via a direct condensation reaction of the three monomers in solution. To increase the molecular weight after precipitation and drying of the copolymer, solid-state polymerization was carried out by annealing at 260 °C for different times in vacuum (e.g., for a medium molecular weight for 10 h). Viscosities were measured in a mixture of trifluoroacetic acid and chloroform (weight ratio 60/40) at a concentration of 0.5 g per 100 ml. For samples with different time of chemical reaction relative viscosities (η) with respect to the polymers prior and after the chemical reaction were equal to 2.7, 3.4, 4.4, 4.7, and 6.4, respectively.

The preparation of melt-spun fibers was carried out by melt drawing from the nematic phase (320 °C). Fibers were examined in the as-spun state with fixed ends by x-ray analysis at different temperatures. The diameter of single fibers is about 1 μm. So, the specimens for x-ray analysis were prepared as parallel bundles with about 300 single fibers. In order to perform differential scanning calorimetry (DSC), the fiber samples were put into DSC pans which were then sealed. To avoid the effect of previous thermal history, each sample was used only once. Sample weights were typically in the range 10–20 mg.

Wide-angle x-ray diffraction (WAXS) at elevated temperatures

X-ray experiments were carried out using a standard Siemens x-ray Θ–Θ diffractometer D500T equipped with

Fig. 1 Chemical composition of poly[(phenyl-*p*-phenylene)-co-(terephthalate)-co-(*p*-hydroxybenzoate)] (PES)



a scintillation counter. Equatorial and meridional x-ray diagrams were recorded in reflection and transmission geometries, respectively. The slit-focussed beam (CuKα) was monochromatized with a graphite crystal ($\lambda = 0.154$ nm). In addition, a pulse-height analysis sensitive to CuKα radiation was used with the scintillation counter. Temperature measurements were carried out under vacuum in a heatable sample-holder with fibers at fixed ends.

Differential scanning calorimetry (DSC)

A Mettler TA 4000 was used to determine the transition temperatures and temperature behavior of PES fibers. Samples were heated from room temperature to 380 °C, usually at a heating rate of 20 K/min. Different heating rates were used only where indicated and for calibration of the instrument. After holding the temperature for 10 min the samples were subsequently cooled at the previous rate to room temperature. All DSC measurements were performed with the fibers kept with free ends. The glass transition point was taken as the temperature at 50% vitrification as determined by the heat capacity change during the transition.

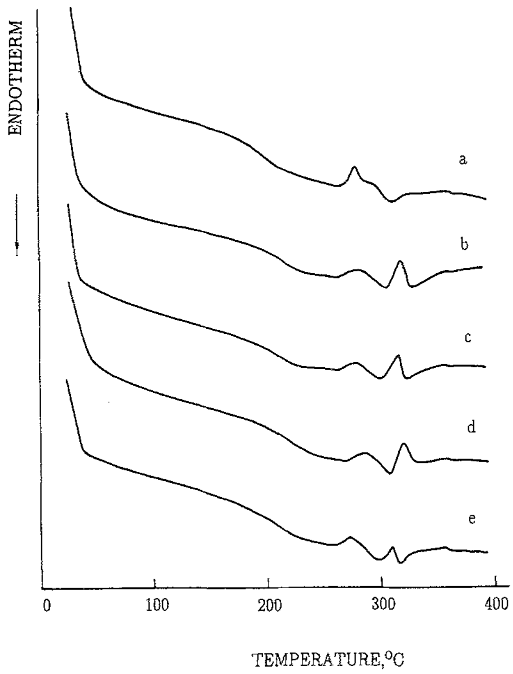


Fig. 2 DSC traces of PES as-spun fibers with relative viscosities 2.7 (a), 3.4 (b), 4.4 (c), 4.7 (d) and 6.4 (e) on first heating with a rate of 20 K/min

Results

Calorimetric measurements

DSC traces obtained with PES copolymers of different molecular weights heated at a rate of 20 K/min are shown in Fig. 2. Heating curves show a single glass transition in the range 130–240 °C. A broad endothermic region follows covering the temperature range of about 200–250 °C. Next, an exothermic process is observed having its peak temperature at 275–286 °C depending on the copolymer viscosity and showing an apparent heat of transition between 0.63 and 1.14 kJ/mol. Details are difficult to determine due to the overlap with the previous endothermic peak.

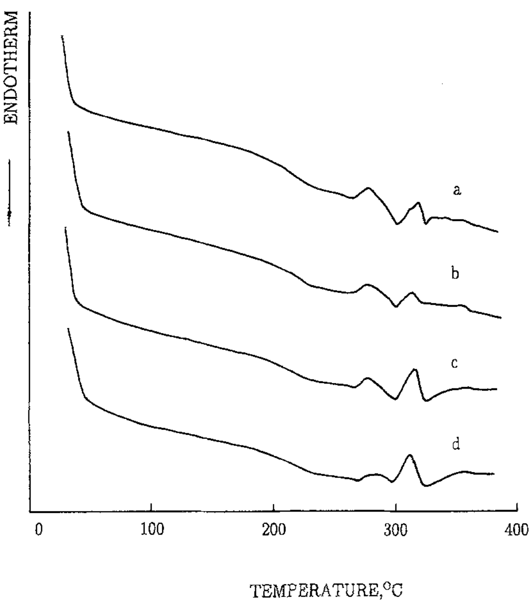


Fig. 3 DSC traces of PES as-spun fibers with relative viscosity of 4.4 during the first heating with different heating rates: 10 K/min (a), 20 K/min (b), 30 K/min (c) and 40 K/min (d), respectively

The other endothermic process is attributed to the melting of crystal 2 (see below). It has a peak temperature between 300–310 °C which also depends on the copolymer viscosity and a heat of transition of 0.57–1.14 kJ/mol. With the exception of the copolyester with relative viscosity 2.7, all other samples have one more exothermic and one more endothermic peak (see Fig. 2) corresponding to the recrystallization and subsequent melting of crystal 1 phase (see below). Subsequently, a nematic LC phase is reached (see below), and no further transitions are observed up to the decomposition temperature. When the PES copolymer is heated at rates varying from 10 to 40 K/min (see for example DSC traces for the sample with $\eta = 4.4$ in Fig. 3) the general shape of the curves is un-

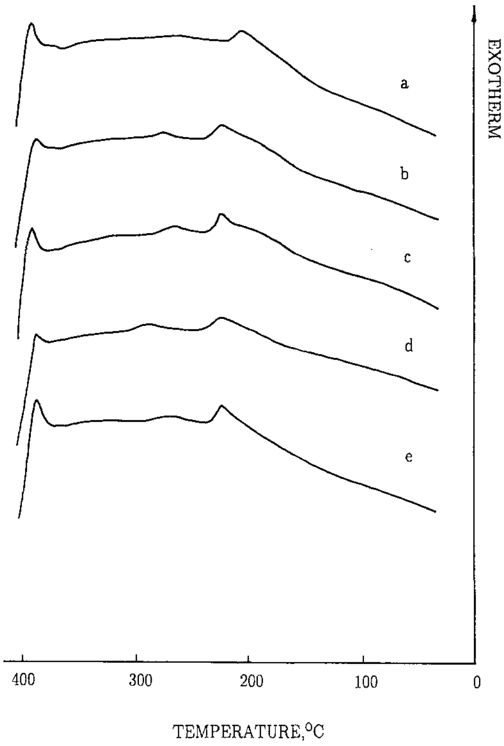


Fig. 4 DSC traces for PES as-spun fibers with relative viscosities 2.7 (a), 3.4 (b), 4.4 (c), 4.7 (d) and 6.4 (e) during the first cooling with a rate of 20 K/min

changed from the ones shown in Fig. 2. When samples are cooled at 20 K/min (Fig. 4), two exothermic processes are observed. The first process has a peak temperature between 255° and 288 °C depending on copolymer viscosity and a heat of transition of 0.12–0.57 kJ/mol. The second transition has a peak temperature of 205°–226 °C and a heat of transition between 0.75–1.32 kJ/mol.

In order to understand the nature of endo- and exothermal phenomena a series of WAXS measurements was carried out at elevated temperatures. DSC traces of PES copolymers with different molecular weights (or different values of viscosity) shown in Figs. 2 and 4 have a quite similar character for all samples under investigation with the exception of the fiber with $\eta = 2.7$. Therefore, only two samples with lowest ($\eta = 2.7$) and highest ($\eta = 6.4$) viscosities were chosen for comparative WAXS studies at elevated temperatures. Analogous data for the PES copolyester with medium molecular mass ($\eta = 4.4$) will be taken for the discussion from ref. [17].

WAXS measurements at elevated temperatures: EQUATOR

Equatorial diffraction scans for the as-spun PES fibers with two different molecular weights obtained on the Θ–Θ goniometer in the temperature region 25°–270 °C are shown in Fig. 5. The x-ray patterns for both copolymers in the as-spun original state at 25 °C exhibit strong diffuse scattering in the equator over an angular range of approximately 10–35 degrees in addition to two reflections at a relatively low angle ($2\Theta = 12$–15 and 5–9 degrees) which are broad and have a weak intensity. According to our previous experiments [14, 16], such an equatorial pattern can be explained to arise from a polycrystalline structure with a very small crystallite size of 5–7 nm, which coexists with another phase of "frozen-in" oriented LC nematic material.

Upon heating to 180 °C which corresponds approximately to the glass transition point [17] nothing significant happens in the equator of the x-ray patterns for both samples besides the usual shift of the peak positions due to thermal expansion. A small increase of the intensity due to annealing effects is observed in the vicinity of the glass transition temperature. At higher temperatures starting approximately from 200 °C one can see the beginning of the development of Bragg spots indicating the development of long-range order within the plane perpendicular to the macromolecular axis or the fiber direction. For example, at 250 °C well-pronounced crystalline reflections are observed in the x-ray patterns of both samples. Simultaneously, the intensity of the main diffuse maximum strongly decreases. This corresponds to a transformation of the initial crystalline structure into a new crystalline phase (a first-order phase transition) with lateral crystallite sizes of 20 nm, which is a typical value for semi-crystalline polymers.

PES fibers with viscosity 2.7 (see Fig. 5A) reveal at least five Bragg spots in the equator of the x-ray pattern. The data analysis shows that positions and intensities of equatorial reflections correspond to crystal 1 modification identified in our previous papers [14, 16]. It is an orthorhombic crystalline lattice with four chains per unit cell. The crystal 1 phase exists within a relatively wide temperature range up to 320 °C (see Fig. 6A). It is followed by a melting peak in DSC traces and a transition to a LC nematic mesophase (the system is strongly birefringent). It should be noted that the development of long-range ordered structure in PES fibers with $\eta = 2.7$ begins approximately at 200 °C. This is significantly earlier than in the sample with $\eta = 4.4$ [14], where this process starts to be detectable at 240 °C.

Figures 5B and 6B show the temperature evolution of the equatorial x-ray pattern of PES fibers with $\eta = 6.4$. Again, starting approximately from 210 °C, one can see the beginning of the development of a well-ordered crystalline structure in the system. But in contrast to the sample with $\eta = 2.7$, in this a case of *splitting* of almost all Bragg reflections is observed. An analysis shows that the set of

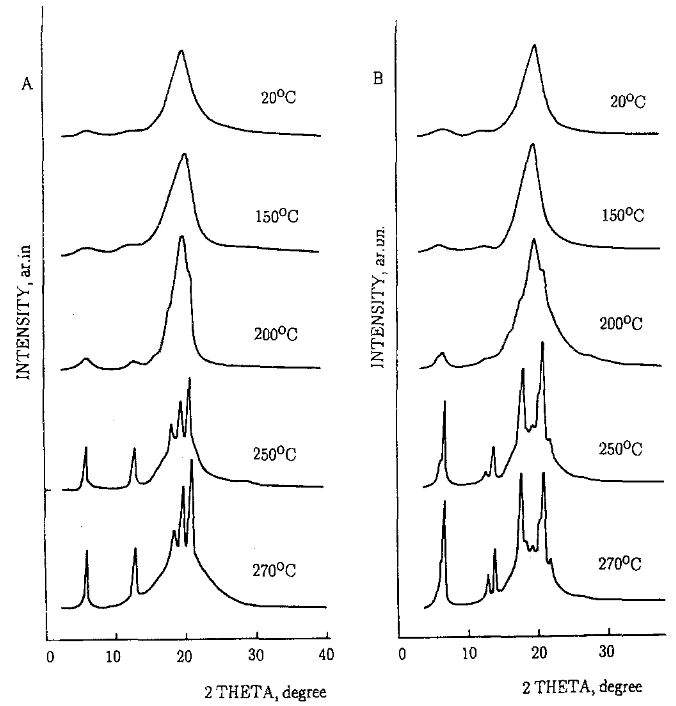
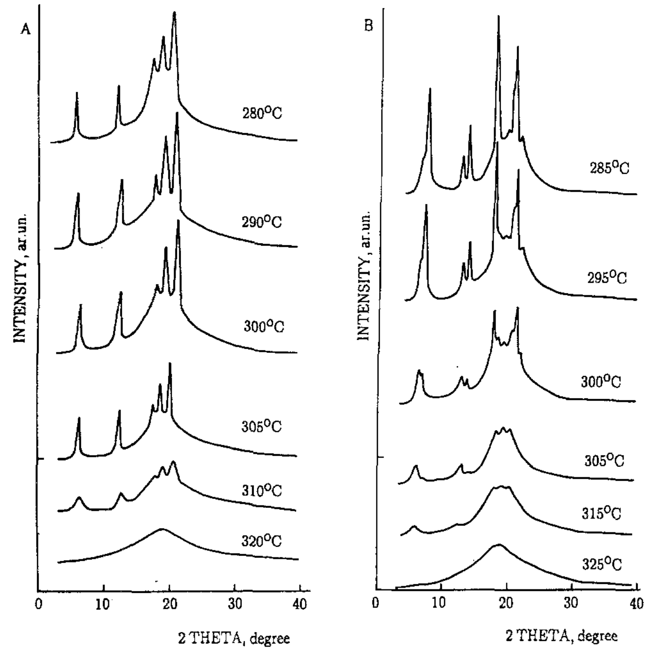


Fig. 5 Equatorial x-ray diffraction scans of as-spun and quenched PES fibers with relative viscosities 2.7 (A) and 6.4 (B) measured up to 270 °C

Fig. 6 Equatorial x-ray diffraction scans of as-spun and quenched PES fibers with relative viscosities 2.7 (A) and 6.4 (B) measured between 270°–330 °C



low-angle reflections again corresponds to crystal 1 modification, which is also observed for the sample with $\eta = 2.7$. In the case of the PES copolymer with $\eta = 6.4$, peak intensities of crystal 1 phase are relatively small. Intensities of high-angle reflections are substantially higher. An analysis shows that the second set of Bragg spots corresponds to crystal 2 modification identified in our previous papers [16, 17]. It is also an orthorhombic crystalline lattice with slightly different unit cell dimensions as compared to crystal 1. So it is possible to conclude that both "new" crystalline phases are developed simultaneously from the initial phase during heating of the sample with $\eta = 6.4$. The analogous behavior was observed for the sample with $\eta = 4.4$ [17]. At temperatures higher than 200 °C crystal 1 and 2 phases are coexisting at least up to 300 °C. Then crystal 2 melts and between 300° and 320 °C one can see only reflections of crystal 1 modification in the equator of the x-ray pattern. Above 320 °C the transformation to the LC nematic state, which is strongly birefringent, takes place. One can estimate that the volume ratio of crystal 1 to crystal 2 phases for the sample with $\eta = 6.4$ is approximately 1:3. This is obtained from a powder pattern of finely grained PES fibers. A further analysis of the powder x-ray pattern allows us to determine the total degree of crystallinity to about 50%. Following the same procedure, one can determine a crystallinity of the other PES sample with $\eta = 2.7$ to be about 45% while the volume ratio of crystal 1 to crystal 2 turns out to be about 10:1 (see below). We note here that the analogous estimate for the PES copolymer with $\eta = 4.4$ [17] gives concentrations of crystal 1 and 2 phases at 15 and 20%, respectively.

Thus, from analysis of the data, one can conclude that the highest content of the crystal 1 modification is observed for the relatively low molecular weight PES copolymer with $\eta = 2.7$. This indicates that the higher the molecular weight of PES copolyester, the larger the content of crystal 2 phase and, respectively, the less the content of crystal 1 phase in the system.

WAXS measurements at elevated temperatures: MERIDIAN

The temperature evolution of meridional x-ray patterns for both PES samples under investigation is shown in Figs. 7 and 8. Three narrow and very strong Bragg reflections are observed in the meridian of the x-ray patterns of both as-spun samples, which correspond to different orders of a reflection in the 2nd, 4th, and 6th layers' lines, indicating a $P2_1$ space group. On heating of as-spun PES fibers below the glass transition point, as it was observed in the equator, there are no significant changes of the

Fig. 7 Meridional x-ray diffraction scans of as-spun and quenched PES fibers with relative viscosities 2.7 (A) and 6.4 (B) measured up to 270 °C

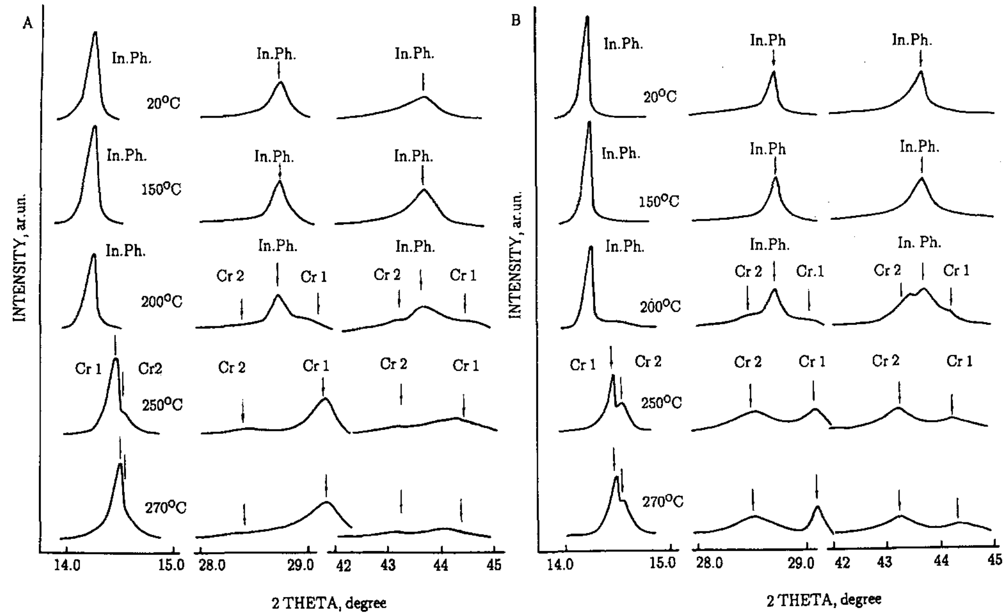
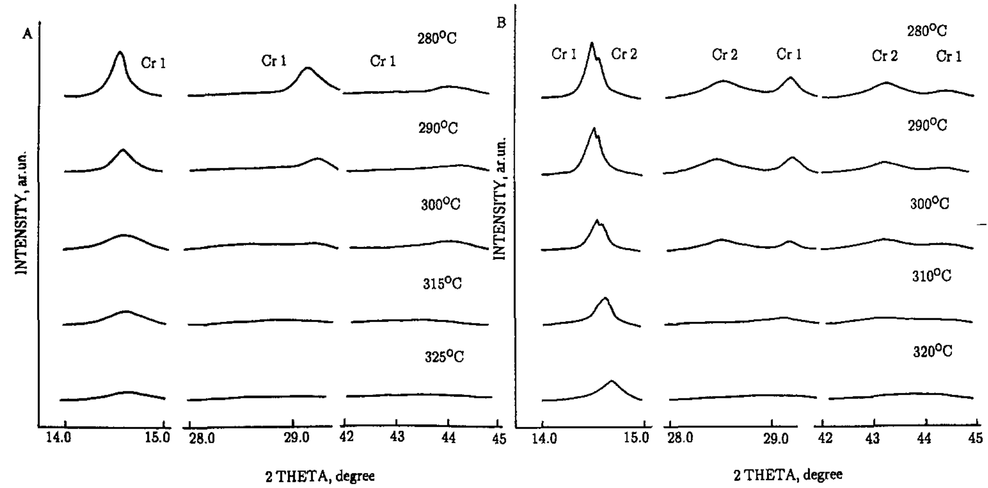


Fig. 8 Meridional x-ray diffraction scans of as-spun and quenched PES fibers with relative viscosities 2.7 (A) and 6.4 (B) measured at temperatures between 270°–330 °C



character of scattering in the meridian of the x-ray patterns of both samples.

At higher temperatures (starting from approximately 200 °C) it is possible to clearly see the rise of two sets of new reflections in the meridian of the sample with $\eta = 6.4$ (see Fig. 7B). The initial phase melts and its reflections disappear completely at 250 °C. Instead of three original maxima, one can see at this temperature the coexistence of double-peaks on each even layer line. In support of the equatorial data, this means that two "new" conformations instead of the "old" one are developing in the system during heating. One of them, in our opinion, corresponds to crystal 1 phase, while the other one, respectively, corresponds to crystal 2 modification. Again, both phases coexist within a wide temperature range (see Fig. 8B), i.e., at least up to 300 °C, where crystal 2 melts. The melting point of crystal 1 modification is about 320 °C. Thus, the analysis of meridional data shows a good correlation with the equatorial ones.

It is not surprising to find also for the PES copolymer with low molecular mass ($\eta = 2.7$) two crystal structures indicated through the double-reflections in the even layers of the x-ray pattern (see Figs. 7A and 8A). Again, one can see, besides the three Bragg spots of the initial phase, the appearance of additional maxima starting approximately from 200°–220 °C and their development in a wide temperature range up to 300 °C. Thus, besides crystal 1 modification, this copolyester also contains a small amount of crystal 2 phase, however, with a concentration which is not larger than 5%. Maybe because of this low value of volume content of the second modification it is impossible to observe this phase in the equator of the x-ray pattern.

One can thus conclude that all PES fibers under investigation with different molecular weights exhibit two crystalline phases at elevated temperatures. Varying the molecular mass (or corresponding values of viscosities from 2.7 to 4.4 and 6.4) the content of crystal 1 phase will be changed from 40 to 15 and 12%, respectively, while the content of crystal 2 modification is increasing from 5 to 20 and 38%, respectively.

Discussion

First, our discussion will focus on the transition behavior exhibited by PES copolymers with different molecular weights. Thus, one may ask about the nature of the endotherms observed in DSC traces on heating (see. Fig. 2) of PES fibers with different viscosities. The WAXS measurements and data obtained in ref. [17] indicate that the broad endothermic region in the range of 200°–270 °C corresponds to a melting of the initial polycrystalline phase developed in the as-spun fiber due to rapid cooling of the LC nematic phase from 320 °C to room temperature. This phase contains the three different monomeric units of the random copolyester in the crystal lattice and is thermodynamically unstable.

The range of long-range order in a particular crystallographic direction, which we will identify with the size of the crystallites in this direction, is estimated from the widths of the crystalline reflections. The crystallites of the initial phase are of strongly anisotropic shape with longitudinal sizes of 100 nm and lateral dimensions less than 10 nm. This phase is metastable below the glass transition point and coexists with the "frozen-in" LC nematic phase at room temperature.

Two other endotherms are present (see Fig. 2) at 300°–310 °C and 320°–330 °C (with an exception of the sample with $\eta = 2.7$, which has only one endotherm at 307 °C). They correspond to the melting of crystal 2 and 1 modifications, respectively. At higher temperatures the LC nematic phase is observed which exists up to the decomposition temperature. If the cooling rate of the sample is relatively low (for example 20 K/min) there are two exotherms at 200°–225 °C and 250°–270 °C (Fig. 4) for all samples, without an exception. They correspond to two crystallization processes of the different crystalline modifications. Thus, there is always a chance that the initial sample (as-spun fiber) will contain small parts of crystal 1 and 2 phases, which, however, are not detectable in x-ray diffraction scans.

As was mentioned above, PES copolymer with $\eta = 2.7$ contains preferentially the crystal 1 phase (40%) while the content of the second phase does not exceed 5%. This is the reason why there is only one well-pronounced endotherm in the DSC trace of this sample (Fig. 2). Still, it is interesting to note that remains of the crystallization process of crystal 2 form on cooling of this fiber and are seen in the DSC trace (see Fig. 4). Thus, all samples under investigation contain more or less both crystal 1 and crystal 2 modifications.

The temperature dependencies of intensities and spacings of meridional maxima of PES copolymers with $\eta = 2.7$ and 6.4 are shown in Figs. 9 and 10, respectively. The intensities are approximately proportional to the phase content in the system. Analyzing the data displayed in Fig. 9, one again can conclude that the PES sample with $\eta = 2.7$ consists preferentially of crystal 1 phase, while the sample with $\eta = 6.4$ contains more of crystal 2 modification.

According to our previous data analysis [17] an existence of two different crystalline modifications reflects the fact that phase separation on heating of the PES copolymer takes place. The thermodynamically non-equilibrium initial phase breaks up into two new phases above the glass transition point (see Figs. 9 and 10). It has been proposed [17] that crystal 1 phase mainly consists of crystallites, where the orthorhombic unit-cell preferentially contains two strictly alternating monomeric units (TA/PhHQ) in the macromolecular chain. Crystal 2 phase is the HBA rich orthorhombic modification with slightly different unit-cell dimensions. The lower the molecular weight of the PES copolymer, the easier segments will "find" each other to become crystalline. "Inconvenient" units for the crystallization process are the HBA units which can be forced out by the crystallization front into noncrystalline regions. From our viewpoint, this may be the main reason why the phase composition is reciprocally affected by the molecular weight of the PES copolymer. We can presently, however, not exclude the possibility of a tendency to block formation during the synthesis of the copolymer, which of course might be different for the different materials. The sequence distribution will of course also affect the crystallization of the materials.

The presence of two PES samples which are rich either in crystal 1 or crystal 2 modification allows us to make a refinement of unit-cell dimensions for different phases. In ref. [15] for the copolyester of exactly the same composition, but provided by Du Pont, the proposition was made that the structure of the as-spun fibers is close to a pseudohexagonal modification. In our opinion, it is difficult to make the detailed determination of the unit-cell symmetry of the as-spun fiber due to the significant disorder of the structure perpendicular to the fiber direction.

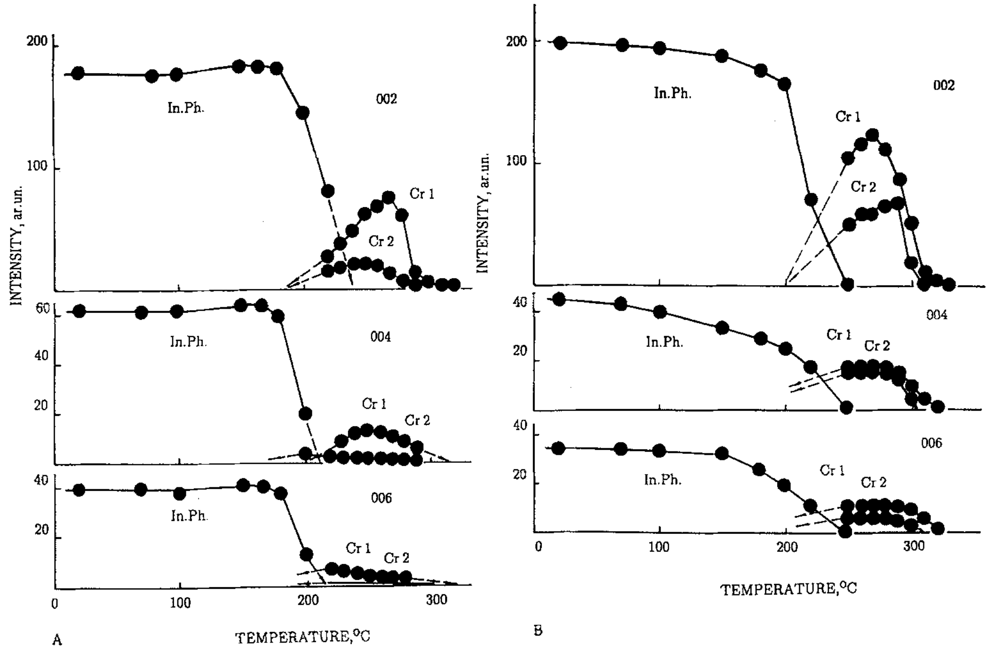


Fig. 9 Temperature dependencies of the intensity of meridional maxima for the as-spun copolyester fibers with relative viscosities 2.7 (A) and 6.4 (B) during heating (samples are kept at fixed ends)

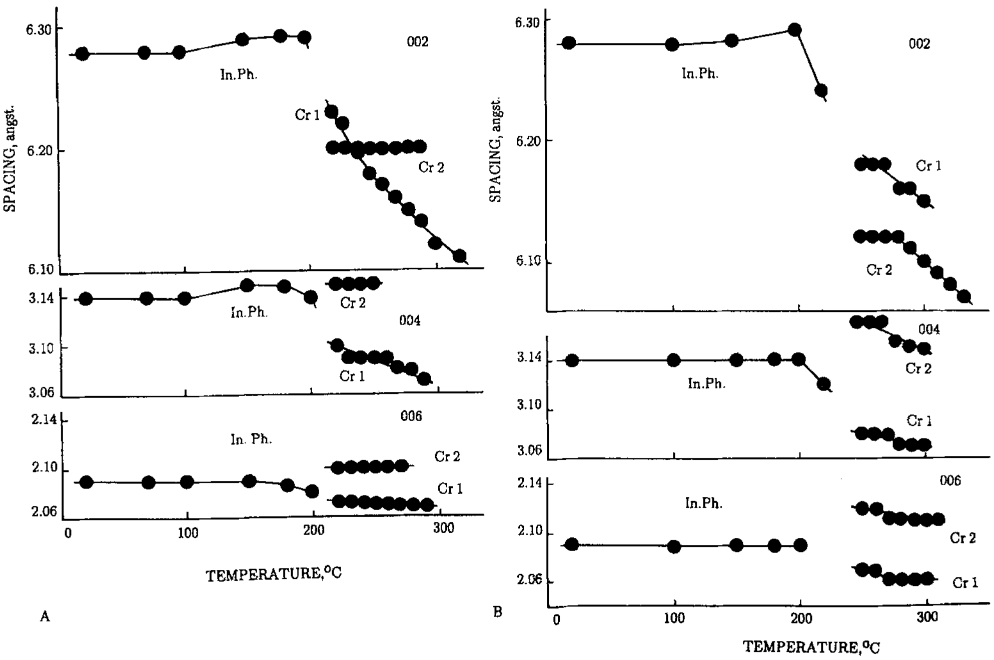


Fig. 10 Temperature dependencies of meridional spacings for the as-spun copolyester fibers with relative viscosities 2.7 (A) and 6.4 (B) during heating (samples are kept at fixed ends)

Assuming, however, a pseudohexagonal structure in our case would lead to a lattice with unit-cell parameters of $a = 1.320$ nm and $c = 1.254$ nm.

The x-ray pattern of the fiber with $\eta = 2.7$ shows five spots in the equator, three spots in the meridian and eight spots in the quadrants for crystal 1 modification. Thus, a total of 16 Bragg spots was identified in this fiber pattern. The strongest peaks are found in equatorial and meridional directions. The diffraction spots in the quadrants are generally weak. The crystal 1 unit-cell parameters are determined at 270 °C to be $a = 1.365$ nm, $b = 1.072$ nm, $c = 1.240$ nm and $V_c = 1.814$ nm^3. The lattice has orthorhombic symmetry. Four chains are assumed to occupy one unit-cell.

The pattern for the fiber with $\eta = 6.4$ shows six spots in the equator, three spots in the meridian and 11 spots in the quadrants for the crystal 2 modification. Thus, 20 Bragg spots are identified. The most intense reflections are again along the equatorial and meridional directions. This unit-cell is also orthorhombic, but unit-cell parameters at

270 °C are significantly different: $a = 1.314$ nm, $b = 0.991$ nm, $c = 1.250$ nm and $V_c = 1.628$ nm^3. Four chains are again contained in each unit-cell.

Another experimental result can be explained on the basis of data shown in Fig. 10. It was observed during WAXS measurements at different temperatures that during heating PES fibers with fixed ends can be described by straight strings. During cooling such a sample with fixed ends undergoes a self-elongation, and fibers become wavy and appear to be suspended. This thermal behavior is a result of the significant shrinkage of PES fibers due to conformational transformations taking place in the system.

The change of diffraction behavior during structural transitions above T_g, in particular in the equatorial x-ray pattern, can be assumed to be accompanied by a rearrangement of local chain conformations. Instead of the rigid-rod conformation of the as-spun fiber, a more conformationally disordered phase is developed at elevated temperatures indicating some flexibility and mobility of the PES copolymer chains. This can be concluded from the development of the diffuse maxima in equator and meridian as already mentioned earlier [17]. This increased mobility above T_g enables the development of the two new crystal phases which seem to be thermodynamically stable crystal structures.

Conclusions

Detailed x-ray analysis at elevated temperatures as well as DSC measurements of fibers of the thermotropic main-chain LC PES copolyester with different molecular weights reveal a complicated phase behavior of this copolymer.

The initial phase of the as-spun PES fibers has a structure, which may be considered to be pseudohexagonal and where the three different monomeric units of the statistical copolymer, TA/PhHQ/HBA, are incorporated into the lattice. Equilibrium crystallization of all PES copolymers under investigation can be achieved by heating above the glass transition temperature, which is in the range between 170° and 190 °C. During WAXS measurements at elevated temperatures (each diffraction scan takes about 1.5 h) two kinds of crystal structures slowly emerge, one with a relatively low and one with a relatively high melting point. This unusual behavior is indicative of a phase separation process due to the random nature of the PES copolymer. The unit cells of the two crystal structures are both orthorhombic but have slightly different sizes. A rearrangement of the local chain conformations is necessary for this transformation indicating some mobility and flexibility of PES copolyesters.

By a variation of the molecular weight of PES fibers, one can alter the relative content of crystal 1 and crystal 2 phases in the system. The copolymer with the low molecular weight ($\eta = 2.7$) contains about 40% of crystal 1 phase and less than 5% of crystal 2 phase. The copolymer with medium viscosity $\eta = 4.4$ has a content of crystal 1 and 2 phases of 15 and 20%, respectively. Finally, the copolymer with the high molecular weight ($\eta = 6.4$) contains 12 and 38% of the first and second crystalline modification. This relatively strong dependence of structure on molecular weight might be due to different chain mobilities, but could be also explained on the basis of a different (and possibly non-statistical) sequence distributions of the individual samples. Details of the sequence distribution are, however, difficult to determine. By a combination of different techniques structural features of the investigated aromatic copolyesters could be largely resolved and are quite similar to other already commercially available materials of this sort.

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