Unit-cell size change of the thermotropic copolyester-TPA/PHQ/PEHQ under different annealing conditions

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Wide-angle X-ray diffraction (WAXD) experiments show an anomalous change of the crystal unit-cell parameters in the thermotropic copolyester, poly[phenyl-*p*-phenyleneterephthalate)-co-(1-phenylethyl-*p*-phenyleneterephthalate)], under different annealing conditions, namely, annealing the fibres with free ends, at fixed length, and under tension. The crystallographic volumes of the crystal unit-cells in the annealed copolyester fibres are larger than those in the as-spun fibres. Density measurements reveal a decrease of the overall density in the annealed fibres. This behaviour is attributed to a partial rearrangement of the large pendant side groups in this copolyester during annealing.

INTRODUCTION

The thermotropic copolyester, poly[phenyl-*p*-phenylene-terephthalate)-co-(1-phenylethyl-*p*-phenyleneterephthalate)]] consists of *p*-benzenedicarboxylic acid (TPA), phenyl hydroquinone (PHQ) and 1-phenylethyl hydroquinone (PEHQ) (in a molar ratio of 50/25/25). Wide-angle X-ray diffraction (WAXD) measurements have shown that this copolymer is highly crystalline[1]. Along the fibre direction of this copolyester, periodic *c*-axis order can be clearly observed due to the fact that the copolyester contains comonomers that are of equal length. Additionally, large pendant side groups have been introduced in this copolyester to disturb the regularities of the lateral packing, which is one of two alternatives for lowering the transition temperatures in thermotropic copolyesters. The other alternative, as used in the cases of Vectra and Xydar copolyesters, is the disturbance of crystalline regularities along the chain direction by introducing monomers of different lengths and solid kinks[1].

Recently, it has been reported that two transition processes occur in these copolyesters during the transition from their nematic to solid states: a fast transition process occurred during quenching, and a slow transition process developed gradually during annealing[1-5]. In the case of the Vectra and Xydar copolyesters, WAXS results show that a hexagonal packing with cylindrical symmetry along the chain direction forms in the fast transition process, and an orthorhombic packing grows in the slow transition process[3,6,7]. It appears that for copolyesters in which the regularities along the chain direction are

disturbed, it is a common observation that two transition processes occur which have different crystal packings[1,8,9].

However, in the case of the TPA/PHQ/PEHQ copolyester, in which two transition processes can also be found, different crystal packings do not develop, but the same crystal packing is developed with different crystal unit-cell sizes[1]. It is apparent that due to the existence of the large pendant side groups cylindrical symmetry along the chain direction in the crystals is no longer kept. Furthermore, it is of special interest that the crystallographic density of the quenched form [monoclinic (I)] is higher than that of the annealed form [monoclinic (II)][1].

In this paper, we report our study of the change of the crystal unit-cell sizes in this copolyester under different annealing conditions. Our WAXS results indicate that the copolyester fibres annealed at a temperature of 590 K under tension, at fixed length, and with free ends lead to slight, but detectable differences in their crystal unit-cell sizes. The crystallographic volumes of these annealed fibres are close to each other, but about 5–6% larger than that of the as-spun fibres. Possible explanations are also addressed.

EXPERIMENTAL

Materials and samples

The copolyester, TPA/PHQ/PEHQ (50/25/25), was kindly provided by Granmort Inc. of Granville, Ohio. The statistical molar mass of the repeating units is 165.16 g/mol. Based on the information obtained, the copolyesters were synthesized via direct condensation reaction of the three monomers in their solution states. To increase molecular mass, solid state polymerization

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was carried out after the precipitation and drying of the copolyester at 573 K for 24 h.

In order to study the crystal unit-cells of the copolyester, the preparation of melt-spun fibres from its nematic phase (635 K) was carried out in our laboratory. The diameter of a single fibre is about one denier. The drawn ratio of the fibres is about 50 ×. The fibres were examined in the as-spun state and after different annealing processes at $T_a = 590$ K for 7 h (under tension, at fixed length, and with free ends). The following detailed annealing processes were carried out via a VWR high temperature vacuum oven (1410D). The fibres at fixed length were prepared by whirling on a glass tube and mechanically fixing the fibre ends at room temperature. The fibres were then heated to 590 K under vacuum. The fibres under tension were prepared by hanging a heavy load on the fibres which were fixed on a specially designed steel frame. Again, the fibres were heated to 590 K in the vacuum oven. During heating, a 10–20% elongation of the fibre lengths were observed, after which the fibre lengths were fixed.

Specimens for X-ray analyses were prepared as parallel bundles of about 50 fibres. In order to perform differential scanning calorimetry, the fibre samples were put into d.s.c. pans and sample weights were controlled within a range of 12–15 mg. All pan weights were within a deviation of ±0.002 mg.

Wide angle X-ray diffraction (WAXD)

X-ray experiments were carried out on a Rigaku X-ray generator with a 12 kW rotating anode as the source of the incident X-ray beam. The point-focused beam is monochromatized with a graphite crystal and a pulse-height analyser sensitive to CuK_α radiation. X-ray fibre diagrams were recorded on a vacuum camera. The d-spacings were calibrated with silicon powder (325 mesh size).

Differential scanning calorimetry (d.s.c.)

A Dupont 9900 Thermal Analyser was used to determine the transition temperatures and heats of the transition. The d.s.c. was carefully calibrated in temperature and heat flow following the standard procedures applied in our laboratory. The fibre samples were heated from room temperature to 640 K at 10 K/min heating rate. The heating traces were recorded. In this paper, peak temperatures were used as T_d.

Density measurements

A density gradient column was set up using a mixing device that generates a linear density gradient in between 1.3 to 1.5 g/cm³. The copolyester fibre samples were dropped into the column and their flotation levels were measured. The gradient was determined with calibrated floats with an accuracy of ±0.0005 g/cm³ at room temperature.

RESULTS AND DISCUSSION

Figure 1 shows a fibre diagram of the crystal diffraction photograph for the annealed TPA/PHQ/PEHQ (50/25/25) copolyester fibres at fixed length at 590 K for 7 h. Along the equator, there are four diffraction spots which can be identified. Along the meridian, periodic diffraction spots can be observed up to four layers. The spots
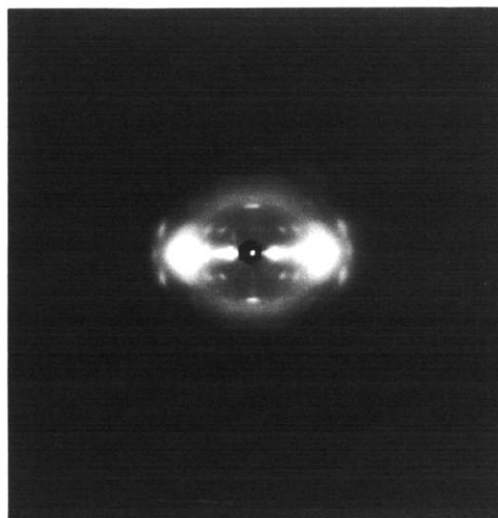

Figure 1 Wide angle X-ray fibre diagram of the TPA/PHQ/PEHQ copolyester fibres annealed at 590 K for 7 h at fixed fibre lengths

diffracted by the odd-number layers are missing or very difficult to find, and those attributed to the even-number layers show strong diffraction intensities, indicating that the crystal has a space group close to $P2_1$. In the quadrants, four diffraction spots along the first layer, four along the second, two along the third, and one along the fourth can be precisely distinguished. Thus, a total of fifteen diffraction spots were considered in the determination of the crystal unit-cell.

Following the standard procedure as described in reference 1, the size and shape of the crystal unit-cell was determined by the calculation of an $hk0$ reciprocal lattice net as well as an l index (the layer line-spacing). After the least-square refinements via our computer program, it was found that the crystal unit-cell of the annealed copolyester fibre is monoclinic with $a = 13.30$ (±0.005) Å, $b = 9.719$ (±0.004) Å, $c = 12.35$ (±0.005) Å, and $\gamma = 78.03°$ (±0.02°). Therefore, the unit-cell volume is 1561.7 Å³. In each unit-cell four chains are contained. The calculated crystallographic density is 1.405 g/cm³. In *Table 1* the sixteen hkl crystal plane assignments are listed, as well as their corresponding 2θ angles and d-spacings both experimentally observed and calculated.

Figures 2–4 show the WAXD fibre diagrams of the as-spun copolyester, annealed with free ends, and under tension, respectively. The sizes and shapes of the unit-cells of these samples can also be determined, and their crystallographic parameters are listed in *Table 2*.

Of special interest is that the crystallographic volumes of the three annealed fibres are close to each other, which is about 50–60 Å³ different from that of the as-spun fibres, indicating an approximate 5–6% volume difference. This illustrates that the annealed samples basically have the monoclinic II crystal packing regardless of the annealing conditions. Nevertheless, if one investigates the detailed crystal unit-cell parameters (a, b, c and γ) of the crystals under different annealing conditions, as listed in *Table 2*, it is found that these parameters are not the same and are dependent upon the annealing conditions. The a-axis of the monoclinic II packing in the fibres annealed under tension is 13.30 Å, and that of the fibre annealed at fixed length is also 13.30 Å. When the fibres were annealed with free ends, it is slightly increased to 13.31 Å. A similar situation can be observed in the case of b-axes. They are

Table 1 Experimental and calculated crystallographic parameters of monoclinic crystal unit-cell for the annealed TPA/PHQ/PEHQ copolyester fibres at fixed lengths[a]

(hkl)	2θ(°)		d-spacing (Å)		Intensity[b]
	Experimental	Calculated	Experimental	Calculated	
(100)	6.796	6.794	13.01	13.01	vs
(200)	13.60	13.61	6.510	6.506	s
(210)	18.17	18.05	4.882	4.914	s
(300)	20.50	20.48	4.332	4.336	s
(011)	11.68	11.74	7.576	7.538	m
(111)	14.56	14.52	6.084	6.100	m
(121)	19.80	19.85	4.483	4.472	w
(221)	26.27	26.41	3.392	3.375	m
(002)	14.30	14.34	6.193	6.176	s
(102)	16.04	15.89	5.525	5.577	vw
(212)	23.13	23.13	3.845	3.845	w
(222)	25.36	25.30	3.512	3.520	w
(312)	25.36	25.25	3.512	3.527	w
(003)	21.85	21.59	4.067	4.116	vw
(103)	22.85	22.65	3.891	3.925	w
(004)	28.96	28.92	3.083	3.087	m

[a] The calculated data listed are based on a monoclinic unit-cell with $a = 13.30$ Å, $b = 9.719$ Å, $c = 12.35$ Å, and $\gamma = 78.03°$
[b] The intensities are semi-quantitatively estimated via a microdensitometer. The intensities are classified as very strong (vs), strong (s), medium (m), weak (w), and very weak (vw)
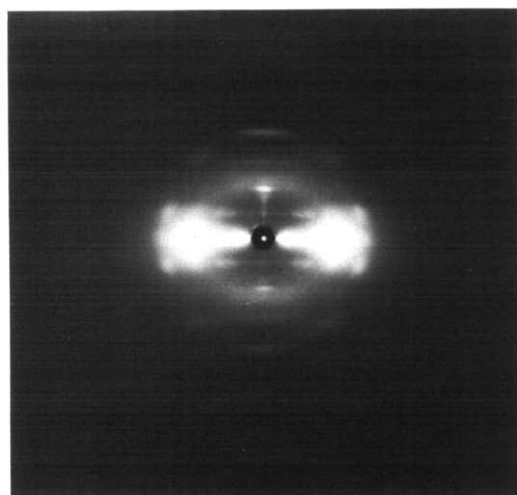

Figure 2 Wide angle X-ray fibre diagram of the TPA/PHQ/PEHQ copolyester as-spun fibres
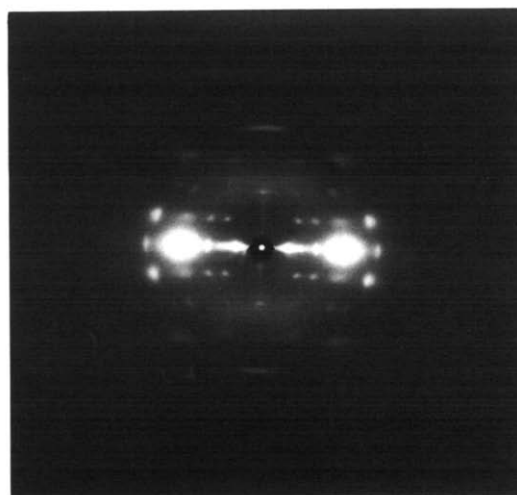
Figure 4 Wide angle X-ray fibre diagram of the TPA/PHQ/PEHQ copolyester fibres annealed at 590 K for 7 h under tension
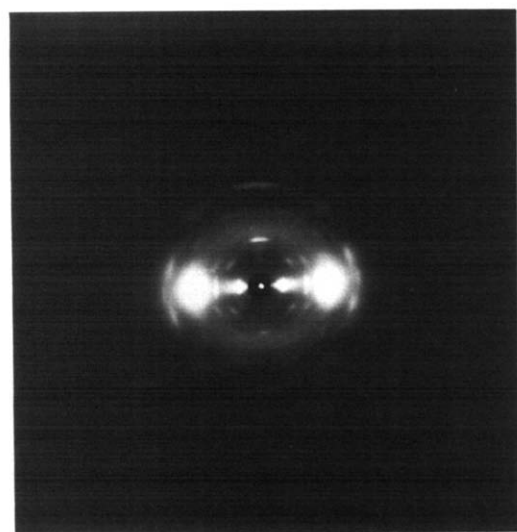
Figure 3 Wide angle X-ray fibre diagram of the TPA/PHQ/PEHQ copolyester fibres annealed at 590 K for 7 h with free fibre ends

9.693 Å for the fibres annealed under tension, 9.719 Å for those annealed at fixed length, and 9.732 Å for those annealed with free ends, respectively. On the other hand, the c-axis of the fibres annealed with free ends is only 12.15 Å, which is even shorter than that of the as-spun fibres (12.24 Å). It increases to 12.35 Å for the fibres annealed at fixed length, and further reaches to 12.51 Å for the fibres annealed under tension. It is also interesting to note that the angle (γ) in the crystal unit-cell of the annealed fibres with free ends ($\gamma = 81.01°$) is larger than that of the as-spun fibres ($\gamma = 80.87°$). On the other hand, the angle (γ) in the crystal unit-cell of the annealed fibres at fixed length ($\gamma = 78.03°$) is in between the angles of the unit-cells of the as-spun fibres and the annealed fibres under tension ($\gamma = 76.11°$).

The d.s.c. measurements, as shown in *Figure 5*, indicate that the transition temperature of the as-spun fibres appears at 605 K with a heat of transition of 2.47 kJ/mol. For the annealed fibres with free ends, two transition peaks can be observed, and they are similar to the case

Table 2 Crystallographic parameters of the monoclinic unit-cell sizes and shapes of the TPA/PHQ/PEHQ copolyester fibres under different annealing conditions

Crystallographic parameters	As-spun	Free ends	Annealed fixed lengths	Under tension
a (Å)	13.04	13.31	13.30	13.30
b (Å)	9.514	9.732	9.719	9.693
c (Å)	12.24	12.15	12.35	12.51
γ (°)	80.87	81.01	78.03	76.11
V (Å^3)	1499.3	1554.4	1561.7	1565.6
ρ_c (g/cm^3)	1.464	1.412	1.405	1.402
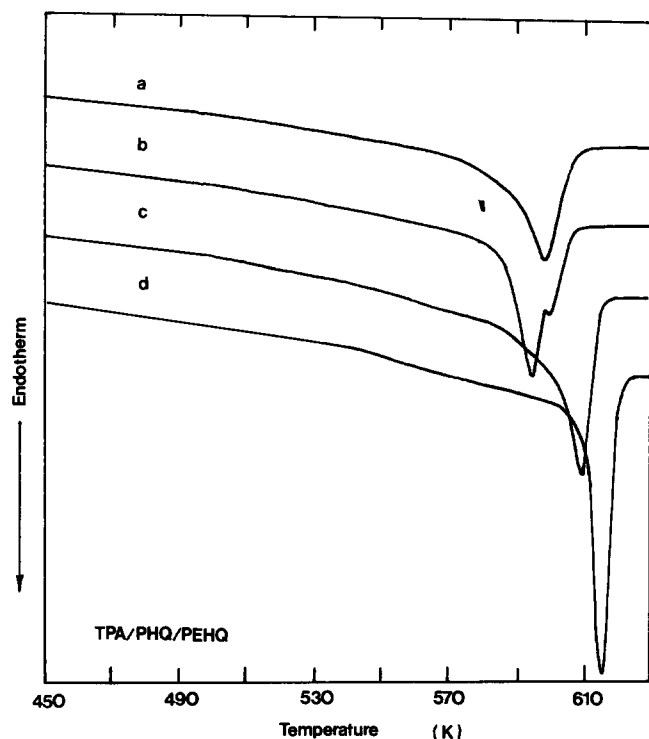
Figure 5 D.s.c. heating curves of the TPA/PHQ/PEHQ copolyester fibres in the cases of curve a, as-spun fibres; curve b, annealed fibres with free ends; curve c, annealed fibres at fixed lengths; curve d, annealed fibres under tension at 590 K for 7 h

of bulk copolyester samples reported in reference 1. One is located at 605 K with a heat of transition of 1.10 kJ/mol, which has been characterized as the fast transition process, and another is at 595 K with a heat of transition of 2.01 kJ/mol, which has been identified as the slow transition process[1]. The WAXD results of these annealed fibres with free ends are thus possible averages of the two monoclinic packings. The annealed fibres at fixed length and under tension both show only one peak at 610 K and 619 K with 3.20 kJ/mol and 3.31 kJ/mol, respectively.

In order to determine whether the observations of the changes in the crystal unit-cell via WAXD measurements was significant, an independent experimental method was carried out, namely, density measurements via a density gradient column. However, special care had to be taken for the measurements because these experimental data only provide information about overall densities, which include the density contributed by both the crystalline and amorphous portions of the materials[10]. As shown in our d.s.c. measurements, the heats of transitions of the annealed fibres with free ends and at fixed length are close because the annealing temperature and time are essentially the same. The annealed fibres under tension

show a higher heat of transition due perhaps to crystallization induced by deformation. Three fibre samples were measured to have 1.359 g/cm^3, 1.358 g/cm^3, and 1.359 g/cm^3 for those annealed with free ends, at fixed length, and under tension, respectively. Comparing with the density of the as-spun fibres, 1.371 g/cm^3, it is clearly found that all the densities of the annealed fibres are lower than the density of the as-spun fibre, revealing that the WAXD results are reliable.

The next step is to give an explanation of the change of crystal unit-cell for this copolyester under different annealing conditions. Comparing the crystal unit-cell of the annealed fibres with free ends to that of the as-spun fibre, one can clearly observe a slight shrinkage of c-axis, and expansions of the a- and b-axes, indicating a relaxing of internal stress along the chain direction which may have been introduced during the fibre spinning. On the other hand, the crystal unit-cell of the annealed fibres at fixed length shows an elongation of the c-axis, revealing that in the fibres, the relaxation can only occur in the 'amorphous' (less ordered) region in this case, and therefore, the internal stress in the crystalline region is enhanced. It also results in relatively smaller a- and b-axes compared to the case of annealed fibres with free ends. Finally, annealing under tension leads to an introduction of strong internal stress to both crystalline and 'amorphous' regions, and the c-axis of crystal unit-cell in this case shows a significant increase, while both a- and b-axes show a decrease. However, all the annealed fibres appear to have very similar crystallographic volumes (densities), which are different from that of the crystallographic volume (density) in the as-spun fibres. This reveals two different sizes of the monoclinic packings, namely, monoclinic I crystal packing, which corresponds to the as-spun fibres, and monoclinic II crystal packing, which corresponds to the annealed fibres. We have clearly found that the annealed form which develops gradually as the slow transition process shows a relatively low transition temperature. It is due to the 5–6% larger crystallographic volume in the monoclinic II packing compared to the monoclinic I, and therefore, a relatively lower enthalpy change, ΔH_d. On the other hand, the entropy changes during the transition, ΔS_d, are essentially close to each other since both packings are monoclinic. The transition temperature of the annealed form (monoclinic II), which is defined as $\Delta H_d/\Delta S_d$, is thus lower than that of quenched form (monoclinic I)[1]. Furthermore, the kinetic effect may also influence the transition temperatures due to the change of crystal size and perfection.

The remaining unanswered question is why this copolyester demonstrates such anomalous behaviour during the annealing. It is well known that most oriented polymeric materials show a decrease of their crystal unit-cell volumes after annealing under tension. Typical

examples are polyethylene[11], isotactic polypropylene[12], and poly(ethylene terephthalate)[13]. After annealing these materials, it is generally observed that the c-axis increases accompanied by shrinkages of both the a- and b-axes. This results in the overall crystal unit-cell volume decreasing. However, in the case of the TPA/PHQ/PEHQ copolyester, not only the c-axis, but also the a- and b-axes are expanded after annealing, indicating a change of chain conformation in the crystals. It must be noted that for the three comonomers in this copolyester, each has a length of about 6.4 Å. Thus, full extension of a chain would yield a unit-cell dimension along the c-axis of about 12.8 Å. Comparing this value with the length of c-axis which ranged between 12.15 Å to 12.51 Å as determined by WAXD measurements, it may be understood that in the crystalline state the chain conformation of this copolyester is slightly twisted, and is even more twisted in the as-spun fibres. In this copolyester, large pendant side groups are included. In order to keep these side groups in the crystal unit-cell, they have to pack into three-dimensional space as close as they can with their neighbours. We speculate that such packing requires slight twists along the chain direction. During the annealing, the extension of the chain conformation along its c-axis largely eliminates such twists, and therefore, disturbs the original packing of the side groups. As a result, a partial rearrangement of this packing has to occur, and expansions of the a- and b-axes are thus achieved due to steric hindrance of these side groups. A similar rearrangement of the crystal lateral packing can also be seen in poly(p-phenylene terephthalamide) (PPTA) during high temperature annealing even though in this case there is a different driving force (H-bonding)[14–17].

To prove our speculation, a precise determination of the atomic positions in the crystal packing is required.

Computer modelling for such a determination is presently being undertaken in our laboratory. An experimental determination of the internal stress via thermal shrinking stress and strain measurements may also lead to obtaining a crystal unit-cell size of this copolyester at zero internal stress.

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