Crystal structure, morphology and phase transitions in aromatic polyimide oligomers: 2. Poly(1,4-phenylene-oxy-1,4-phenylene-oxy-1,4-phenylene pyromellitimide)

Jiang Liu, Doyun Kim, Frank W. Harris and Stephen Z. D. Cheng*
Maurice Morton Institute and Department of Polymer Science, The University of Akron,
Akron, OH 44325-3909, USA

(Received 28 January 1994; revised 28 March 1994)

Crystal structure, morphology and thermal effects of poly(1,4-phenylene-oxy-1,4-phenylene-oxy-1,4-phenylene pyromellitimide) (PMDA-TPE-Q), synthesized from *N*,*N*′-dimethyl pyromellitic bisimide and 1,4-bis(4-aminophenoxy) benzene in the melt, have been studied by transmission electron microscopy (TEM), electron diffraction (ED) and wide angle X-ray diffraction (WAXD) measurements. The unit cell of PMDA-TPE-Q is determined by ED and WAXD to be a two-chain orthorhombic lattice with dimensions of $a = 0.823$ nm, $b = 0.558$ nm and $c = 2.209$ nm. The observed crystal morphology from TEM is primarily lamellar with extended chain conformations. The thickness of the lamellar crystals varies with the polymerization conditions. Possible thermal effects on PMDA-TPE-Q have been studied by annealing the crystals at different temperatures. The results indicate that with increasing annealing temperature, the lateral dimensions of the lattice expand, primarily along the *a*-axis. The *c*-axis shrinks slightly with increasing the reflection intensities of (0 0 *l*) planes when *l* = odd. This is confirmed by using order correlation changes along these directions measured by WAXD experiments. Crystal defects are found in dark field TEM observations.

(Keywords: polyimide; crystal unit cell; morphology)

INTRODUCTION

Aromatic polyimides such as poly(4,4′-oxydiphenylene pyromellitimide) (PMDA-ODA) are playing an increasingly important role in modern industrial applications[1,2]. The excellent performance at high temperatures, outstanding chemical resistance, high dimensional stability and low dielectric constants of these materials have received increasing interest both academically and industrially. Most attention has focused on the structure and property relationships of these polyimides, in particular, in the form of thin films. It is well known that anisotropic structures in thin polyimide films lead to anisotropic thermal, mechanical, dielectric and optical properties[3–9].

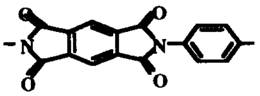
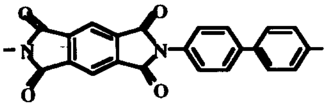
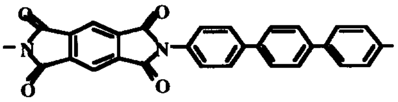
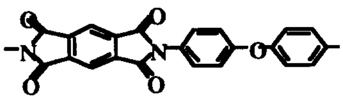
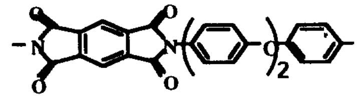
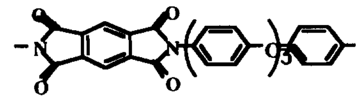
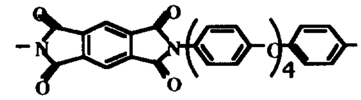
In a previous report[10] we investigated the crystal structure, morphology and phase transitions of PMDA-ODA by an unusual melt-polymerization method. Crystallization during melt-polymerization led to PMDA-ODA oligomers with better defined, large, single lamellar crystals. Using transmission electron microscopy (TEM), electron diffraction (ED) and wide angle X-ray diffraction (WAXD) methods, a new two-chain orthorhombic crystal structure was found in PMDA-ODA with dimensions of $a = 0.836$ nm, $b = 0.563$ nm and $c = 3.303$ nm (unit cell I). This structure is less stable compared to that commonly observed in PMDA-ODA annealed at elevated temperatures (one-chain orthorhombic unit cell II), and a phase transition between these two cells was observed[10] when the crystals were annealed between 300 and 360°C. As a result, PMDA-ODA exhibits polymorphous behaviour. The discovery of unit cell I provides a logical explanation of the crystal structural similarity of *ab* lateral packing in some simple PMDA-based polyimides, as listed in *Table 1*. Most of the other PMDA-based polyimides possess two-chain orthorhombic crystal lattices, and their lateral dimensions show only minor variations[11–17], with $a = 0.83$–0.85 nm and $b = 0.55$–0.57 nm. Nevertheless, the crystal structure of poly(1,4-phenylene-oxy-1,4-phenylene-oxy-1,4-phenylene pyromellitimide) (PMDA-TPE-Q), which was synthesized from pyromellitic dianhydride (PMDA) and 1,4-bis(4-aminophenoxy) benzene (TPE-Q), was reported[11] to be a two-chain monoclinic lattice with $a = 0.830$ nm, $b = 0.564$ nm, $c = 2.18$ nm and $\alpha = 98.44°$. This indicates that the angle between *b*- and *c*-axes deviates by 8.44° from 90°. If the direction of chain molecules is parallel to the *c*-axis of the crystal lattice in PMDA-TPE-Q lamellar crystals, the *b*-axis is thus 8.44° apart from the end lamellar surface (and the substrate). On the other hand, if the *ab* plane is parallel to the end surface of the lamellar crystal, the *c*-axis of the crystal lattice, and therefore the chain direction, must be 8.44° apart from the end lamellar surface. Another report focused on the *c*-dimension changes of the PMDA-TPE-Q

---

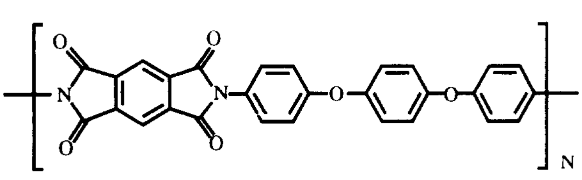
* To whom correspondence should be addressed

0032-3861/94/19/4048-09

Table 1 Comparison of lattice parameters of PMDA-based aromatic polyimides

Repeat unit of polyimide	*a* (Å)	*b* (Å)	*c* (Å)	α, β, γ (deg)	No. of chains per cell
	8.5	5.6	12.3	90	2
	8.4	5.6	16.6	90	2
	8.4	5.5	20.9	90	2
	Cell I 8.36	5.63	33.03	90	2
	Cell II 5.93	4.7	33.0	90	1
	8.3	5.64	21.8	98.4, 90, 90	2
	8.4	5.65	53.3	90	2
	8.35	5.6	30.1	90	2

crystals in fibres[16]. Sidorovich *et al.*[12] concluded that the dianhydride (PMDA) portion is the element determining the crystal lattice of polyimides after an investigation of 14 PMDA-based polyimides, including PMDA-TPE-Q crystals. No morphological observations for this polyimide have been reported in the literature. The chemical structure of PMDA-TPE-Q is



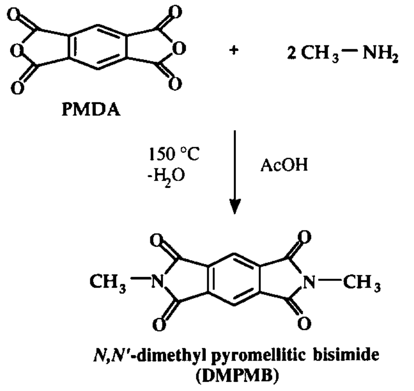
In this publication, we attempt to re-examine the crystal structure of PMDA-TPE-Q via TEM, ED and WAXD by using the melt-polymerization method. Based on our experimental results, PMDA-TPE-Q possesses a two-chain orthorhombic crystal lattice, which is consistent with other PMDA-based polyimides along both *a*- and *b*-directions. Crystal defects and the morphology of this polymer are also investigated.

EXPERIMENTAL

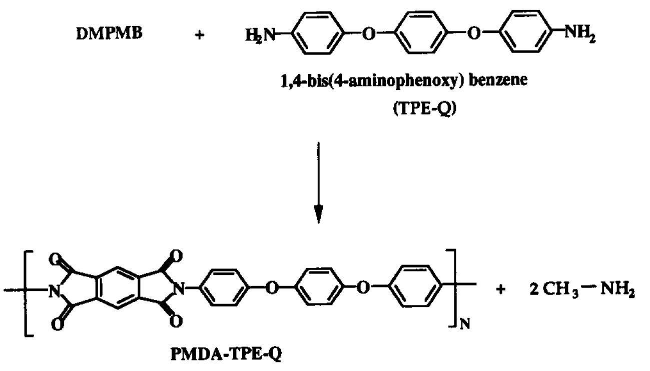
Materials and melt-polymerization

PMDA and TPE-Q monomers were purchased from Chriskev Inc. The melting peaks of these monomers were detected by d.s.c. (Seiko DSC-200) at a heating rate of 10°C min^{-1}, and were found to be 289 and 177°C, respectively. When equimolar quantities of the two monomers were dissolved in acetone, a condensation polymerization occurred instantly. To prevent this reaction from occurring in the dissolved state at room temperature, a *N*,*N*′-dimethyl pyromellitic bisimide (DMPMB) was prepared[18]. In brief, the preparation of DMPMB was carried out in a 1 l, three-necked flask equipped with a stirrer. PMDA (10 g), $MeNH_2$ HCl (7.8 g, 0.115 mol) and anhydride NaOAc (9.4 g, 0.115 mol) were mixed with 200 ml of AcOH as a catalyst, and then heated to reflux with stirring for 6 h. After cooling to room temperature, the product was filtered and dried under vacuum. The final DMPMB was recrystallized from dimethylacetamide with a yield of 8.8 g (87%).

The DMPMB monomer does not react with TPE-Q diamine at room temperature, but the reaction does occur at elevated temperatures in the melt state. First, the DMPMB powder and TPE-Q monomer solution were mixed in an equimolar ratio. Thin films were cast on a microscope glass slide and allowed to dry. A clean glass slide was used to cover the film after drying. The sandwiched slides obtained were wrapped in aluminium foil and heated to various predetermined temperatures and times under dry nitrogen in an oven (Isotemp Vacuum Oven, model 282 A). After polymerization, the recovered materials were heated to even higher temperatures under vacuum to complete the imidization by



Scheme 1 The preparation of DMPMB



Scheme 2 The polymerization of DMPMB with TPE-Q

elimination of the CH_3NH_2 by-product and residual monomers. The high temperature treated polyimide specimens were then separated, and washed three times in boiling acetone or tetrahydrofuran. This procedure is similar to the method used by Liu *et al.* to study polyesters and copolyesters[19,20]. The intrinsic viscosity of the PMDA-TPE-Q is 0.20 in the mixed solvent of trichlorobenzene and phenol (50:50) at 115°C, indicating an oligomeric nature of the melt-polymerized samples. A minor increase of the viscosity was determined after the samples were annealed. Based on the molecular weight information obtained from PMDA-ODA, it can be estimated that the molecular weight of the oligomer PMDA-TPE-Q is several thousand[10]. Bulk samples of PMDA-TPE-Q were also prepared directly from PMDA and TPE-Q monomer powders by melt-polymerization at elevated temperature followed by high temperature annealing. The chemical reactions in the preparation of DMPMB and the polymerization of DMPMB with TPE-Q are shown in *Schemes 1* and *2*, respectively.

It is also important to note some special features of the polymerization carried out in the melt. First, the poly(amic acid) precursors in this reaction are not isolated. When the reaction temperature is above the melting temperatures of both DMPMB and TPE-Q, the reaction is carried out in the melt state; when the temperature is in between the melting temperatures of these two monomers, the reaction takes place on the surface of bisimides or dianhydrides as an interfacial polymerization. Second, this kind of polymerization usually results in low molecular weight oligomers due to the limited melt flow. This leads to the growth of relatively large single lamellar crystals, which is necessary for the study of PMDA-TPE-Q crystal structure and morphology by TEM and ED experiments. It has also been proven, in the case of PMDA-ODA crystals, that the crystal lattice is independent of the preparation methods of the polyimide[10], such as the two-step polymerization where the poly(amic acid)s were isolated *versus* the melt-polymerization[21].

Instrumentation and experiments

The polyimide films (thickness ~0.1 μm) from the glass slides were examined by TEM (Jeol 1200EX II) at 120 kV, and by ED. The thin films were first shadowed with Pt-C and coated with carbon, retrieved from the glass slides by using poly(acrylic acid) films, and then floated on water and picked up on TEM grids. Calibration of the electron diffraction spacings was carried out using Au and TlCl (the largest spacing of TlCl is 0.384 nm). Spacing values larger than 0.384 nm were calibrated by doubling the *d*-spacings of those reflections of the polymer based on the spacing of its first order reflections. Low beam dosage techniques were used and the ED patterns obtained from the polyimide films were considerably more stable in electron radiation than other polymer single crystals[22]. In order to determine the three-dimensional crystal lattice, a tilting angle stage in TEM was used to examine ED patterns.

PMDA-TPE-Q samples were also sheared at its softening temperature on a hot stage by using a razor blade. The obtained thin films were then coated by carbon and prepared as TEM specimen for ED and TEM observations.

WAXD experiments were conducted using a Rigaku 12 kW rotating anode generator coupled with a diffractometer. A monochromatized X-ray beam consisting of CuKα with a wavelength of 0.154 nm was used for this measurement. The melt-polymerized bulk PMDA-TPE-Q oligomer samples were annealed at different temperatures, ranging between 200 and 520°C, for 1 h under nitrogen, and then quenched to room temperature. The angular range in WAXD experiments was $2\theta = 1.8$–$35°$.

The density measurements of the samples were carried out in a density gradient column using the hexane–carbon tetrachloride system at 25°C.

RESULTS AND DISCUSSION

Crystal structure of PMDA-TPE-Q

Figure 1 is a typical TEM micrograph of PMDA-TPE-Q crystals melt-polymerized at 175°C for 9 h and annealed at 220°C for 0.5 h. The crystals are lamellar with different thicknesses. The side-edge of the lamellae is curved and rough, and in general the lamellae show leaf-shaped morphology. Stacks of lamellae are an indication of the screw dislocation defects formed during the crystal growth[23]. The lamellar end surfaces are, however, smooth. *Figure 2* is an $hk0$ ED pattern taken from the crystals shown in *Figure 1*. This pattern indicates that the chain molecules are perpendicular to the lamellar end surface. Along the a^*-axis the intensity of the ED pattern is even- odd alternated, with stronger reflections of $h00$ when h = even. The $h10$ and $h\bar{1}0$ reflections also show slightly alternating intensities of the reflections, with stronger reflections of $h10$ when $h+1$ = even. This reciprocal lattice suggests that the unit cell of PMDA-TPE-Q crystals is a two-chain lattice, with $a = 0.823$ nm, $b = 0.558$ nm and $\gamma = 90°$. Based on the alternating

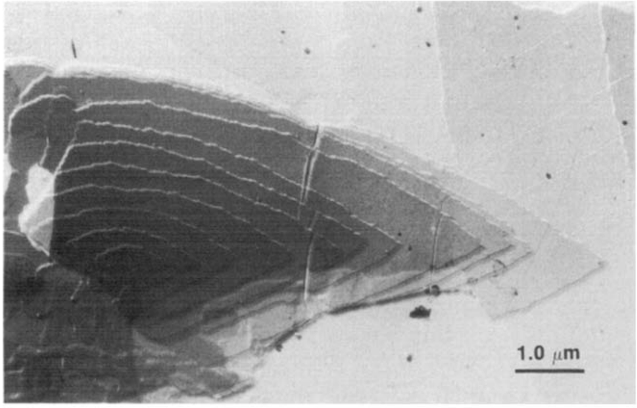


Figure 1 Lamellar crystals of PMDA-TPE-Q polymerized at 175°C for 9 h and annealed at 220°C for 0.5 h

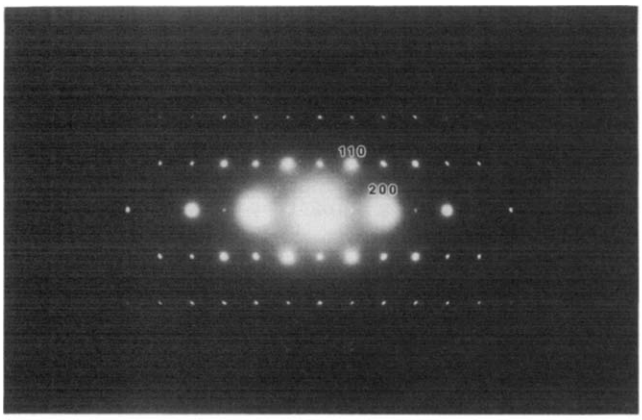


Figure 2 ED pattern of PMDA-TPE-Q crystals from *Figure 1*

intensities, it is suggested that one chain molecule is at the centre of the *ab* plane of the cell, and other $4 \times \frac{1}{4}$ chain molecules are at the corners. Furthermore, there is no experimental evidence from *Figure 2* to suggest that the angles between either *a*- and *c*-axes or *b*- and *c*-axes are not 90°. This is because, as indicated in the Introduction, if the chain direction is parallel to the *c*-axis, the *ab* plane should not be perpendicular to the electron beam, and thus a symmetric *ab* reciprocal lattice pattern may not be obtained. On the other hand, if the *ab* plane is perpendicular to the electron beam, the *c*-axis is no longer parallel to the beam. As a result, a clear ED pattern, like that in *Figure 2*, should not be observed.

In order to determine the dimension and direction along the *c*-axis, we sheared the sample at elevated temperature. *Figure 3* shows an ED fibre pattern taken on the sheared sample. A TEM micrograph of this sheared sample is also shown as an insert in *Figure 3*. Although the chain molecules are not perfectly oriented, as indicated by the arced reflections, the pattern does give quite high orders of the reflections along the chain direction. It is evident that the intensities of the even-numbered $00l$ reflections are weaker than those of the odd-numbered reflections, and the 004 reflection is completely absent. On the original negatives, the 002 reflection is weak but clear, and the layer lines of c^* are measured to be as high as 20. The alternating intensities along the meridian direction were also reported before[16]. It is known that the lowest rotational potential chain conformation of PMDA-TPE-Q is not exactly a zigzag conformation[11]. The even–odd alternation of the reflection intensity in PMDA-TPE-Q crystals may suggest that the chain packing along the *c*-axis follows a pattern in which the dianhydride portions are packed together, as are the diamine portions. In this packing scheme, $00l$, when l = even, have more or less equivalent electron densities which therefore results in a decrease of their reflection intensities. Detailed analysis requires computer modelling of the crystal structure, and will be reported in the future. The dimension of the *c*-axis can be determined as 2.209 nm. Other reflections are either on the equatorial or quadrant, and assigned as shown in *Figure 3*. Again, no evidence of the non-90° angle of α or β is found.

Figure 4 shows a WAXD pattern for the bulk sample polymerized at 195°C for 8 h and annealed at 280°C for

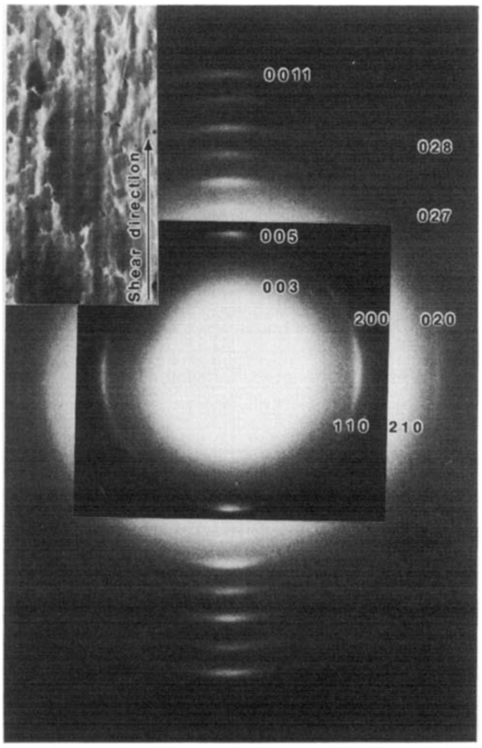


Figure 3 ED fibre pattern of sheared PMDA-TPE-Q crystals

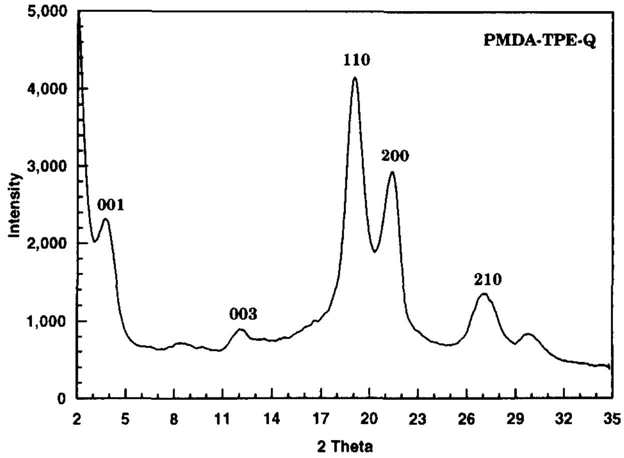


Figure 4 WAXD pattern for PMDA-TPE-Q bulk sample. The indices are based on the crystal structure determined in this work

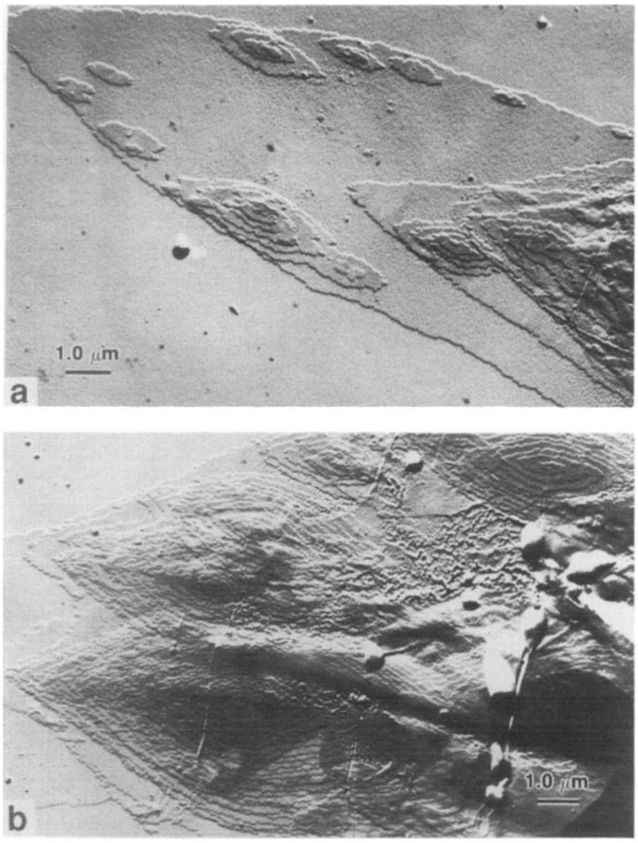


Figure 5 PMDA-TPE-Q lamellar crystals polymerized at 180°C for 4 h and annealed at 220°C for 0.5 h: (a) large plate, leaf-shaped lamellae; (b) many layers of the leaf-shaped lamellae

1 h. Six reflection peaks can be identified, and their *hkl* planes are assigned as indicated in the figure. From both WAXD and ED experiments, therefore, the crystal unit cell of PMDA-TPE-Q can be determined as a two-chain orthorhombic lattice with $a = 0.823$ nm, $b = 0.558$ nm and $c = 2.209$ nm. The calculated crystallographic density is 1.55 g cm^{-3}, which can be compared to the measured density of ~1.48 g cm^{-3}. This agreement between the observed and calculated (assuming two-chain) densities strongly supports a two-chain orthorhombic unit cell.

In order to examine the possibility that the unit cell is monoclinic, as reported by Kazaryan *et al.*[11], a careful least-regression analysis with repeated refinements was conducted by using the same set of reflections obtained from the WAXD experiments. The results show that a monoclinic unit cell with dimensions of $a = 0.830$ nm, $b = 0.560$ nm, $c = 2.227$ nm and $\alpha = 97.4°$ is obtained. However, both the mean square-root deviation and the standard deviation are almost one order of magnitude smaller for the orthorhombic lattice compared to the monoclinic lattice. Furthermore, we have not found any sign of a non-90° angle between the *b*- and the *c*-axes in the reciprocal lattice based on our ED experiments (over 50 independent measurements). As a result, we conclude that the crystal unit cell of PMDA-TPE-Q possesses a two-chain orthorhombic unit cell. This apparent discrepancy may result from the fact that when the PMDA-TPE-Q crystal lattice determination was conducted, its fibres were spun from the poly(amic acid)s, and then the poly(amic acid) fibres were thermally imidized at elevated temperature[11]. The monoclinic lattice was determined because a slight off-line of some of the quadrant reflections from 00*l* lines was found. We speculate that these small deviations may be introduced due to incomplete imidization in poly(amic acid) forms. When a poly(amic acid) precursor is imidized, the length of the repeat unit is decreased slightly because of the ring closure. In poly(amic acid) fibres under tension or fixed length, the ring closure may not be completed. This process thus leads to a relatively high percentage of residual poly(amic acid)s, which remains after the annealing process and causes a slight deviation of the dimension for some reflections along the *c*-axis in the WAXD fibre pattern.

Morphological observations

The spiral growth of lamellar crystals, as shown in *Figure 1*, is frequently found in our TEM observations. *Figures 5a* and *b* show the lamellar crystals of PMDA-TPE-Q polymerized at 180°C for 4 h and annealed at 220°C for 0.5 h. In *Figure 5a*, large, flat lamellae are seen, with a curved leaf shape. The lamellar thickness is about 15 nm, which should correspond to seven chemical repeat units. However, a careful examination indicates that these apparently non-faceting lamellar edges consist of, in some cases, very small (less than 0.2 μm) zigzag-type edges which seem to be very small leaf-shaped crystals. In *Figure 5b*, the spiral growth of the lamellar crystals is found, with as many as 30 layers of uniform thickness. From a number of lamellar crystals observed by TEM, both single and double spiral growths can be found. For single-spiral crystals, both left- and right-handed spiral growths are clearly seen. The random appearance of the handedness in spiral growths is an indication that the direction of screw dislocations formed during the crystal growth is isotropic; this provides further experimental evidence that chain molecules are perpendicular to the lamellar end surfaces.

Figure 6 illustrates an area of large diamond-shaped lamellar crystals with rough but defined 110 growth planes. This type of faceted lamella is also observed in other samples, but less frequently. The thickness of the lamellae shown in *Figure 6* is about 19 nm, which is close to the length of nine PMDA-TPE-Q repeat units. More interestingly, the lamellae seem to be able to fold to form corrugations. This is reminiscent of the hollow, pyramidal, non-planar lamellar crystals of polyethylene[24–26]. We speculate that the corrugations may have formed when the crystal was in the poly(amic acid) precursor stage, where the chain molecules were less rigid compared to

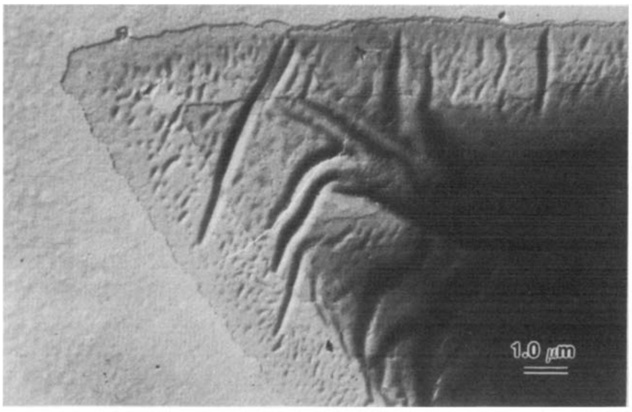


Figure 6 Large hollow, pyramidal, non-planar lamellar crystals

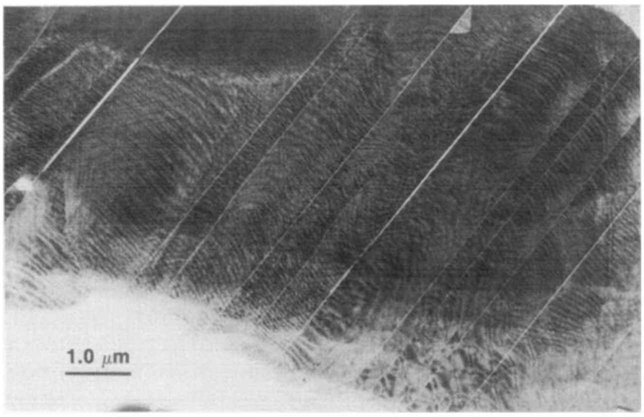


Figure 7 Bright diffraction contrast images of PMDA-TPE-Q lamellar crystals polymerized under the same conditions as those in *Figure 5*

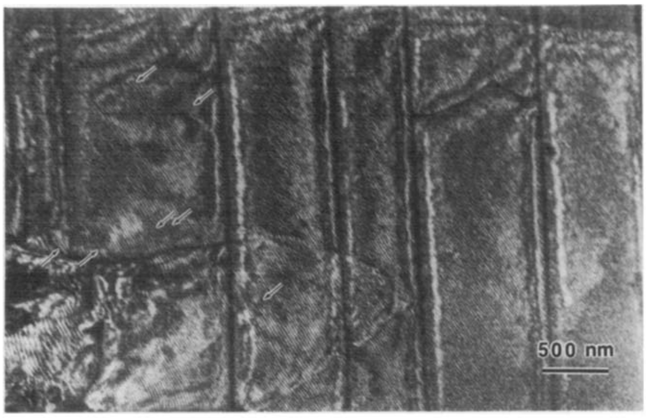


Figure 8 The 1 1 0 dark field image of PMDA-TPE-Q lamellar crystals polymerized at 175°C for 9 h and annealed at 220°C for 0.5 h

the polyimide. However, the formation mechanism of this observation in PMDA-TPE-Q lamellar crystals is not yet understood.

Figure 7 shows a bright diffraction contrast micrograph of PMDA-TPE-Q crystals polymerized under the same conditions as those shown in *Figures 5a* and *b*. The bright-field Moiré lines essentially cover all of the images of the crystals. The orientation of the Moiré lines suggests that they are overlying lamellae which are slightly rotated from one to another.

Figure 8 shows a 110 dark field image of the PMDA-TPE-Q crystals polymerized at 175°C for 9 h and annealed at 220°C for 0.5 h. The parallel Moiré lines in a large area indicate that the lamellar crystals are quite perfect and superimposed on each other with a constant rotating angle. The micrograph also provides an observation of lattice dislocations, as indicated by the arrows, where Moiré lines are terminated.

Figure 9 shows a set of micrographs taken from the same area of the PMDA-TPE-Q crystals polymerized at 250°C for 8 h. The bright field image (*Figure 9a*) shows the lamellar crystals with quite well defined ⟨110⟩ planes. The lamellae have very smooth end surfaces with a uniform thickness of about 25 nm, except for the difference in lateral size of the crystals. The 110 dark field (*Figure 9b*) clearly shows the Moiré lines along the 1 1 0 direction, while the 200 dark field image (*Figure 9c*) exhibits the Moiré lines primarily along the *a*-axis. It is unusual to obtain two dark field images from the same polymeric crystal location; this is evidence of the excellent resistance to electron beam damage for PMDA-TPE-Q crystals. In fact, the ED patterns can last as long as 20 min under an electron beam intensity which is suitable for exposure recording.

In *Figures 7–9*, many cracks along the *b*-axis are observed. This is most likely caused by different coefficients of thermal expansion along the *a*- and *b*-axes during cooling from the crystallization, polymerization and/or annealing temperatures (see *Figure 12* below).

Dimensional changes in the crystal structure at high temperatures

The PMDA-TPE-Q crystals were annealed at different temperatures to examine dimensional changes in the crystal structure via WAXD. *Figure 10* shows a set of WAXD patterns of the bulk powder samples of PMDA-TPE-Q crystals after annealing at temperatures between

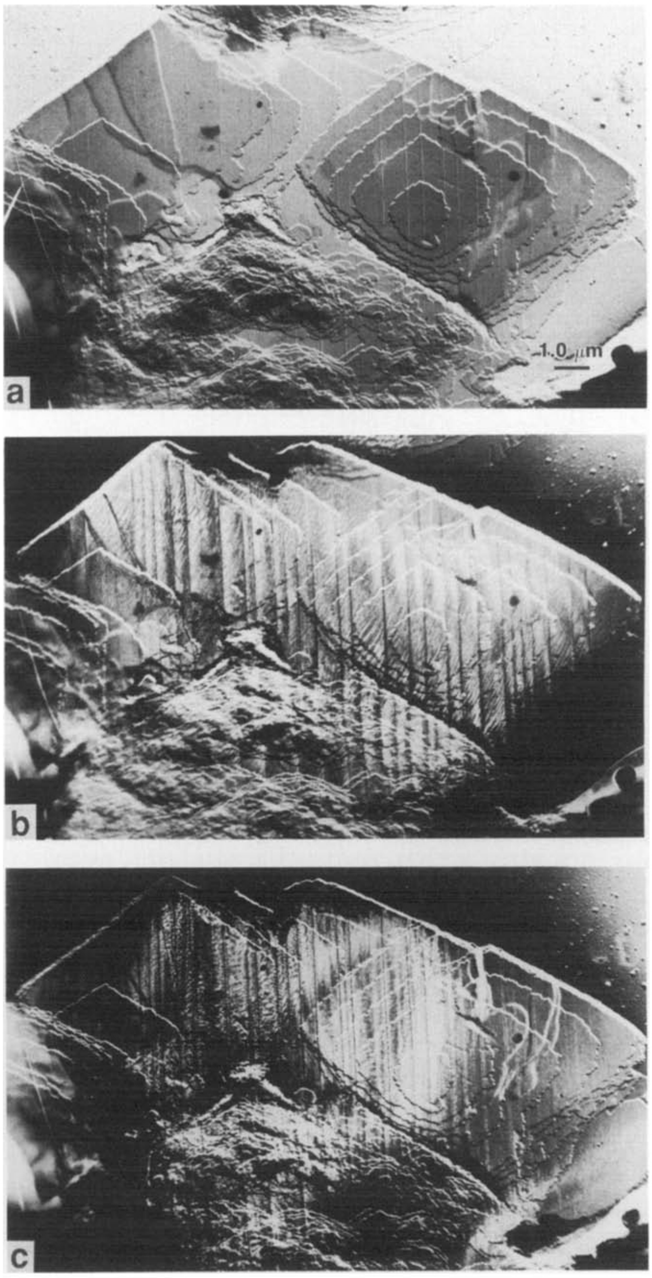


Figure 9 PMDA-TPE-Q lamellar crystals under (a) bright field; (b) 1 1 0 dark field; (c) 2 0 0 dark field

250 and 510°C for 1 h. The 001 reflection intensity for the as-polymerized sample is relatively low compared to 110 and 200 reflection intensities, while it gradually increases with annealing temperatures. The 003 reflection also appears and its intensity increases as a function of temperature. In order to illustrate the intensity increase of the 001 reflection, two intensity ratios, *I*(001)/I(110) and *I*(001)/*I*(200), from the WAXD patterns are shown in *Figure 11*. Both ratios exhibit significant increases.

Accompanying the intensity changes, the *a*-axis dimension of the crystals has also significantly increased with annealing temperature (*Figure 12*). The lattice spacing of 010 plane is calculated based on the experimental observations of the dimensional changes of 110 and 200 planes, and it remains almost constant. This must be associated with chain packing and interaction changes in the crystals since no chain folding is expected in the oligomer crystals. On the other hand, the *c*-axis shrinks continuously with increasing the annealing temperature, as shown in *Figure 13*. Combining both dimensional changes, the crystallographic volume still decreases close to 10% with increasing the annealing temperature from 230 to 530°C. This observation, together with the increased intensities of 001 and 003 reflections (*Figures 10* and *11*) with increasing annealing temperature, indicates that PMDA-TPE-Q crystals possess an increasingly ordered structure along the *c*-axis; however,

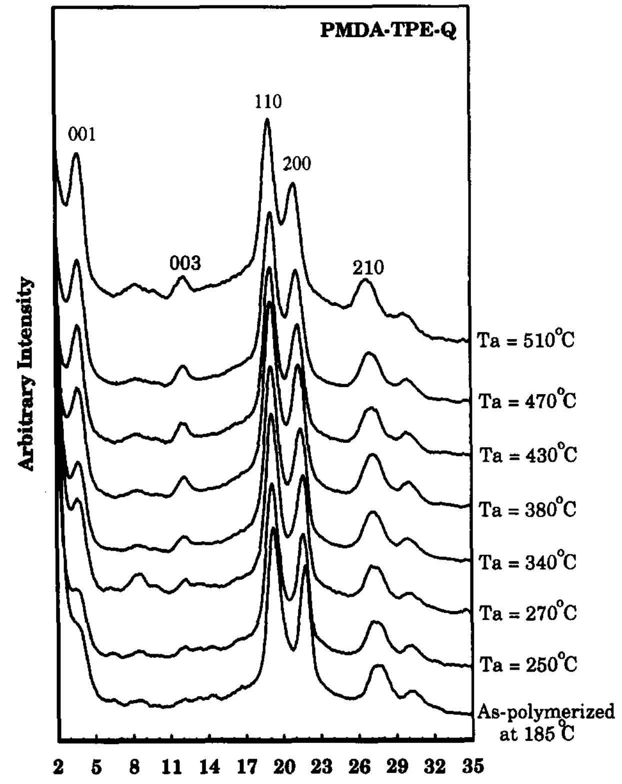


Figure 10 Set of WAXD patterns for PMDA-TPE-Q crystals after annealing at different temperatures (Ta)

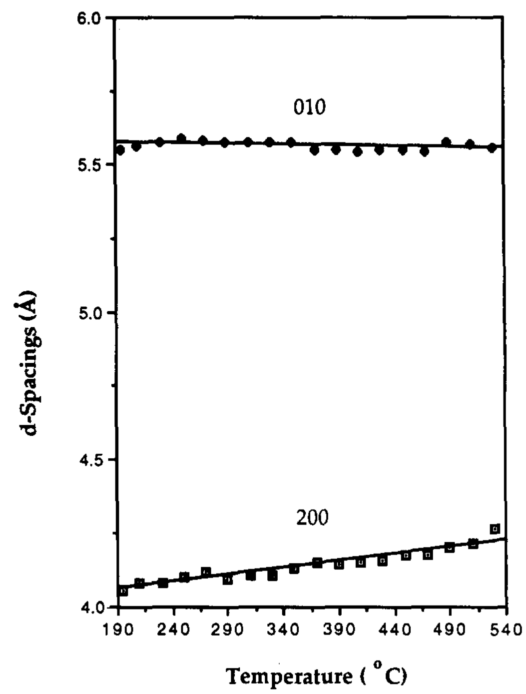


Figure 12 Lateral lattice expansions of 200 and 010 planes with annealing temperature

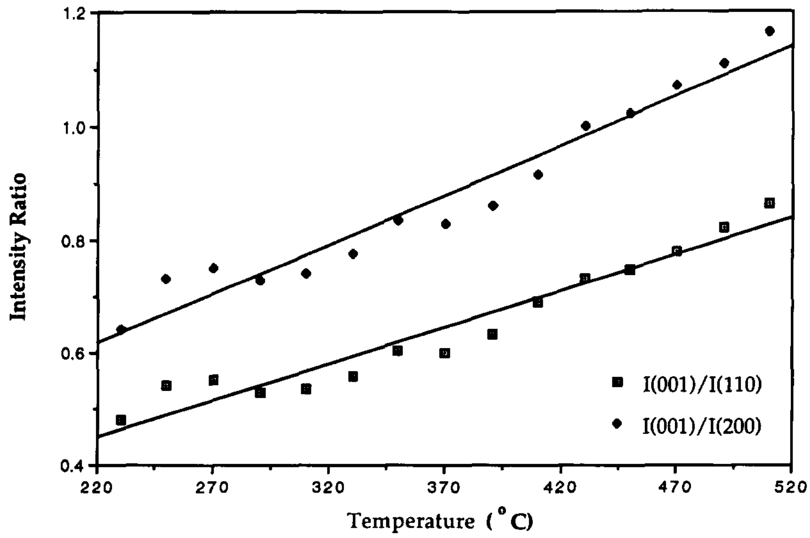


Figure 11 Change of intensity ratios, *I*(001)/*I*(200) and *I*(001)/*I*(110), with annealing temperatures

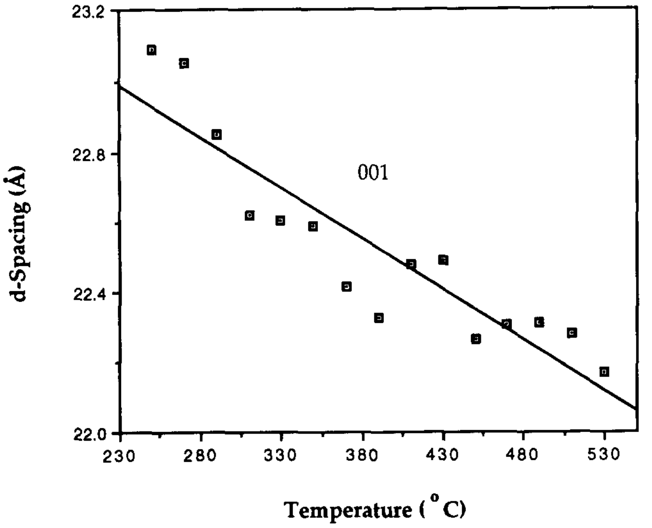


Figure 13 Lattice shrinkage along the *c*-axis with annealing temperature

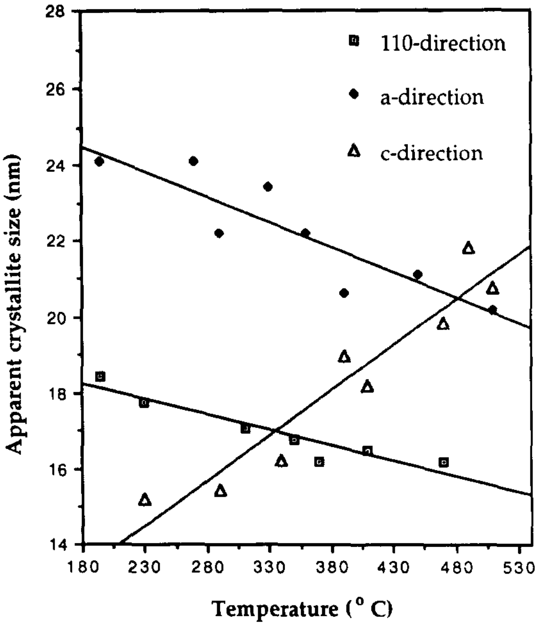


Figure 14 Order correlation changes of the crystals along different crystallographic axes with annealing temperature

the lateral packing becomes loosened, as evidenced by the lateral dimensional expansions.

This observation can be further confirmed by the order correlation changes with annealing temperature, which is calculated based on WAXD experiments. The Scherrer equation was used as a first approximation. As shown in *Figure 14*, the apparent crystallite sizes along both 110 and 200 decrease with increasing annealing temperature. On the other hand, the apparent crystallite size along the 001 increases with annealing temperature. This reveals that a continuous disordering process is occurring along the lateral packing directions, while an ordering process appears along the *c*-axis. Nevertheless, annealing at elevated temperatures does not lead to a discontinuous change of volume (or enthalpy and entropy), and therefore no first-order thermodynamic phase transition is observed. The case differs from that of the PMDA-ODA crystals, in which the phase transition is accompanied by a crystal lattice change[10].

CONCLUSION

A new monomer, *N*,*N'*-dimethyl pyromellitic bisimide, has been prepared to prevent the condensation reaction in the monomer solution to form poly(amic acid) precursors and ensure the interfacial melt-polymerization. The structure of PMDA-TPE-Q crystals is determined to be a two-chain orthorhombic unit cell with $a = 0.823$ nm, $b = 0.558$ nm and $c = 2.209$ nm, which is different from the previously reported monoclinic lattice[11]. The crystals formed during melt-polymerization are primarily lamellar crystals with molecular chains perpendicular to the lamellar end surface. Lamellar thickness varies with polymerization conditions. Crystal morphology is dominated by leaf-shaped lamellae with spiral growth. Some 110 faceted lamellar crystals are also observed. When the crystals are annealed at elevated temperatures, lateral expansion along the *a*-axis has been found. However, the *c*-axis shrinks with enhanced $00l$ reflection intensities. This indicates an increased order along the chain direction; this is also supported by WAXD experiments in which the apparent crystallite size changes along the different crystallographic axes with annealing temperature.

ACKNOWLEDGEMENT

This research was supported by the President Young Investigator Award (S.Z.D.C.) provided by the National Science Foundation (DMR-9157738).

REFERENCES

1 Lee, H., Stoffey, D. and Neville, K. 'New Linear Polymers', McGraw-Hill, New York, 1967, pp. 183, 224
2 Sroog, C. E. *J. Polym. Sci. Macromol. Rev.* 1976, **11**, 161
3 Ikeda, R. M. *J. Polym. Sci., Polym. Lett. Edn* 1966, **4**, 353
4 Russell, T. P., Gugger, H. and Swalen, J. D. *J. Polym. Sci., Polym. Phys. Edn* 1983, **21**, 1745
5 Yoon, D. Y., Parrish, W., Depero, L. E. and Ree, M. 'Material Science of High Temperature Polymers for Microelectronics', MRS Symposium Proceedings, Vol 227, Pittsburgh, 1991
6 Cheng, S. Z. D., Arnold, F. E. Jr, Zhang, A., Hsu, S. L. C. and Harris, F. W. *Macromolecules* 1991, **24**, 5856
7 Arnold, F. E. Jr, Cheng, S. Z. D., Hsu, S. L. C., Lee, C. J. and Harris, F. W. *Polymer* 1992, **33**, 5179
8 Arnold, F. E. Jr, Shen, D., Lee, C. J., Harris, F. W., Cheng, S. Z. D. and Starkweather, H. W. Jr *J. Mater. Chem.* 1993, **3**, 189
9 Arnold, F. E. Jr, Shen, D., Lee, C. J., Harris, F. W., Cheng, S. Z. D. and Lau, S.-F. *J. Mater. Chem.* 1993, **3**, 353
10 Liu, J., Cheng, S. Z. D., Harris, F. W., Hsiao, B. S. and Gardner, K. H. *Macromolecules* 1994, **27**, 989
11 Kazaryan, L. G., Tsvankin, D. Ya., Ginsburg, B. M., Tuichiev, Sh., Korzhavin, L. N. and Frenkel, S. Ya. *Vysokomol. Soedin., Ser. A* 1972, **14**, 1199
12 Sidorovich, A. V., Baklagina, Yu., G., Kenarov, A. V., Nadezhin, Yu. S., Adrova, N. A. and Florinskii, F. S. *J. Polym. Sci., Polym. Symp.* 1977, **58**, 359
13 Conte, G., Iliaro, L., Patel, N. V. and Giglio, E. *J. Polym. Sci., Polym. Phys. Edn* 1976, **14**, 1553
14 Freilich, S. C. and Gardner, K. H. in 'Polyimides: Materials, Chemistry and Characterization' (Eds C. Feger, M. M. Khojasteh and J. E. McGrath), Elsevier, Amsterdam, 1989, p. 520
15 Bessonov, M. I., Koton, M. M. and Kudryavtsev, V. V. in 'Polyimides, Thermally Stable Polymers', 2nd edn, Plenum, New York, 1987, p. 250
16 Tuichiev, Sh., Lorzhavin, L. N., Prokhorov, O. Ye., Ginzburg, B. M. and Frenkel, S. Ya. *Vysokomol. Soyed. Ser. A* 1971, **13**, 1463
17 Korzhavin, L. N., Prokopchuk, N. R., Baklagina, Ya. G., Florinskii, F. S., Yefanova, N. V., Dubnova, A. M., Frenkel, S. Ya. and Koton, M. M. *Vysokomol. Soyed. Ser. A* 1976, **18**, 707
18 Kim, D. PhD dissertation, Department of Polymer Science, The University of Akron, 1994

19 Liu, J., Rybnikar, F. and Geil, P. H. *J. Polym. Sci., Polym. Phys.* 1992, **13**, 1467

20 Liu, J., Rybnikar, F. and Geil, P. H. *J. Macromol. Sci. B. Polym. Phys.* 1993, **32**(4), 395

21 Harris, F. W. in 'Polyimides' (Eds D. Wilson, H. D. Stenzenberger and P. M. Hergenrother), Chapman and Hall, New York, 1989, pp. 1–37

22 Tsuji, M., Roy, S. K. and Manley, R. St. J. *J. Polym. Sci., Polym. Phys. Edn* 1985, **23**, 1127

23 Geil, P. H. and Reneker, D. H. *J. Polym. Sci.* 1961, **51**, 569

24 Reneker, D. H. and Geil, P. H. *J. Appl. Phys.* 1960, **31**, 1916

25 Bassett, D. C., Frank, F. C. and Keller, A. *Phil. Mag.* 1963, **8**, 1739, 1753

26 Keller, A. *Kolloid Z. Z. Polym.* 1964, **197**, 98