Crystallization relationship between poly[bis(phenoxy)phosphazene] crystals

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Whenever solution grown α-form (3D) crystals of poly[bis(phenoxy)phosphazene] (PBPP) are heated in the thermotropic region between $T(1)$ and T_m (the isotropic temperature) they transform into 2D pseudohexagonal, δ-form crystals. Upon rapid quenching a film into liquid nitrogen, the δ-form is 'frozen-in' and remains in this form when warmed up to room temperature. Further heating close to $T(1)$ produces hexagonal ordering ascertained in the (a^*b^*) plane providing $(hk0)$ reflections which are related to the monoclinic α-form of PBPP; this has been confirmed by electron diffraction measurements.

(Keywords: thermotropic transitions; crystalline modifications; hexagonal symmetry; ε-state)

INTRODUCTION

Structural and morphological investigations of semicrystalline polyphosphazenes have been made in order to examine and to try to clarify the nature of the transformation that occurs through the thermotropic transition[1–9]. Solution grown crystals have been described[1–8] and some crystalline modifications have been identified[1,3,6,7]. Poly[bis(phenoxy)phosphazene] (PBPP) crystals can be grown from xylene solution to form monoclinic (α-form) crystals. When these crystals are heated through $T(1)$ and then cooled again to room temperature, two phases coexist depending upon thermal history of the specimen. These are the 2D pseudohexagonal δ-form and the 3D orthorhombic γ-form[3]. Crystallographic relationships amongst these modifications of PBPP have been established[2]. Our intent in the present work has been to obtain more structural and morphological information relevant to the $T(1)$ phase transition in polyphosphazenes. This paper is concerned with the formation of PBPP crystals from the disordered state, i.e. between temperatures T_m and $T(1)$.

EXPERIMENTAL

Materials

Chemically pure unfractionated poly[bis(phenoxy) phosphazene] (PBPP) of narrow molecular weight distribution ($M_w/M_n<3$) and another sample of broader molecular weight distribution ($M_w/M_n>6$) was used in this study.

Solution grown crystals

Crystals were grown from 0.015 wt% PBPP in xylene solution at 65°C for 20 h. After crystallization, the crystals were washed with fresh xylene at 65°C in order to remove or prevent potentially crystallizable low molecular weight polymer from contaminating the crystals.

Preparations for electron microscopy

PBPP crystals supported on carbon film on microscope grids were heated mostly at 180°C for 1 h, but temperatures as high as 250°C were sometimes used. All heat treatments were conducted in a nitrogen atmosphere to avoid degradation, followed by either quenching into liquid nitrogen or cooling to room temperature at a rate of 2°C min^{-1}.

Alternatively, in other experiments crystals were either heated isothermally at 100 and 120°C, respectively, (i.e. below $T(1)$) or maintained at 150°C (above $T(1)$) for 1 h before being cooled slowly to room temperature again.

Electron microscopy

Samples were examined with a JEOL JEM-200 CX electron microscope at 200 kV. Sometimes samples were shadowed with Pd/Au (40/60) alloy to enhance specimen contrast.

RESULTS AND DISCUSSION

Well defined lath-shaped PBPP crystals have been reported from dilute xylene solution of polymer[1]. Whenever crystals of the α-form are heated above the thermotropic transition temperature, a 2D pseudohexagonal disordered phase results[2]. After cooling this specimen slowly to room temperature, from 180°C for instance, a 3D orthorhombic γ-form results[2,3].

The electron diffraction of the δ-form quenched rapidly into liquid nitrogen from above $T(1)$ is seen as a 'frozen-in' disordered state of the δ-form which is stable at room temperature (see diffraction pattern insert in *Figure 2*). Note that the glass transition temperature of this material is 6°C[10].

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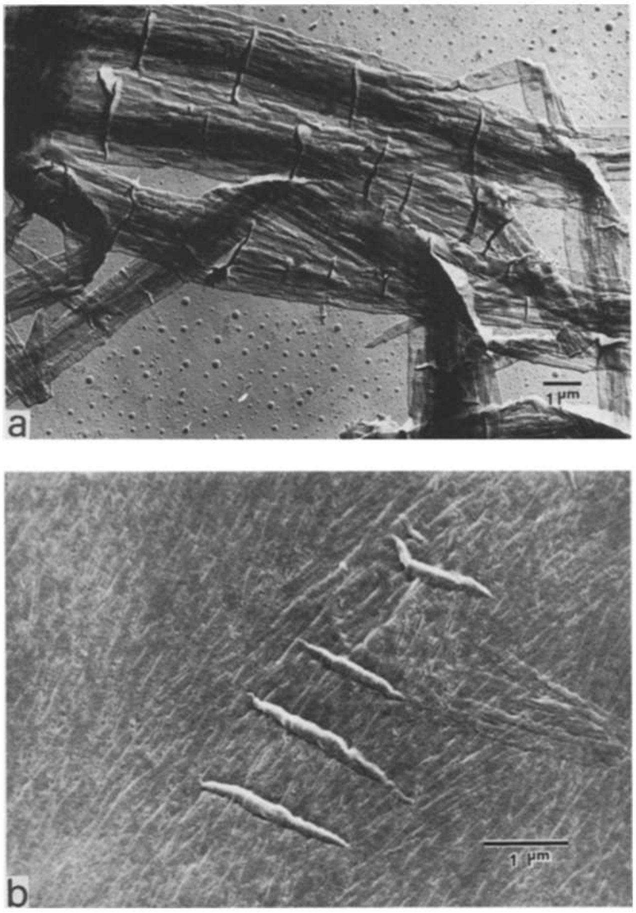

Figure 1 (a) Transmission and (b) scanning electron micrographs of PBPP crystals formed from xylene solution

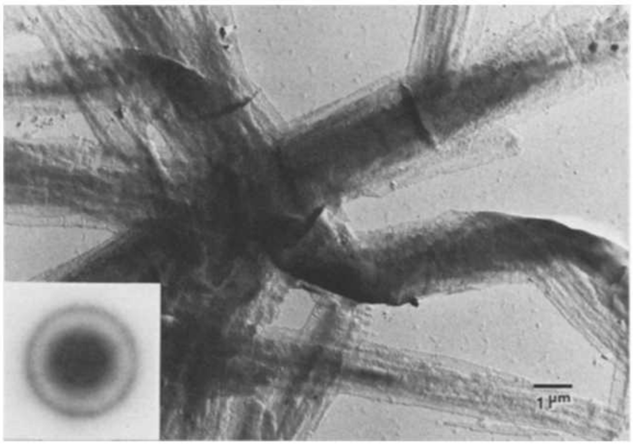

Figure 2 Electron micrograph of PBPP crystals made at room temperature after quenching specimens into liquid nitrogen from 180°C. The electron diffraction insert was obtained at room temperature

Figure 1 is an electron micrograph of PBPP crystals composed of lath-shaped crystals that were obtained from xylene solution by isothermal crystallization at a temperature between 50 and 70°C. The morphology depends somewhat upon the molecular weight of PBPP[1]. Crystals so produced have corrugations across the lateral surface direction. The 'corrugations' which seem to be formed during crystallization are more clearly seen in *Figure 1b*. We can only surmise that this morphology arises to relieve strain within the crystals. Whenever PBPP crystals are heated above $T(1)$, they thicken erratically and this process is seen to be associated with surface roughening of the crystals[3,8]. After quenching into liquid nitrogen from above $T(1)$, the overall crystalline shapes are found to be the same as in the original α-form crystals, but now with only a hint of the surface corrugations remaining (see *Figure 2*).

Both of these textures found for the quenched PBPP and for the unheated α-form PBPP crystals remain unless the specimens are heated above $T(1)$. It is assumed that annealing above $T(1)$ allows rearrangements to occur since both side chain and backbone mobilization is indicated from ^{13}C and ^{31}P nuclear magnetic resonance (n.m.r.)[11]. However, when quenched PBPP is heated above $T(1)$ and cooled subsequently to room temperature, the roughness of surface features is reduced. Some improvement in crystallinity occurs. Whenever the quenched crystal shown in *Figure 2* is heated to 120°C, i.e. not far below $T(1)$, for 1 h and subsequently cooled to room temperature (*Figure 3*), the electron diffraction pattern corresponds to *Figure 4a*. The pattern shows hexagonal symmetry which may be indexed according to the less symmetric α-form of the PBPP crystal. The results so obtained are listed in *Table 1* and are also represented diagrammatically in *Figure 4b*.

Alternatively, whenever PBPP crystallizes upon cooling specimens from above $T(1)$, the γ-form is obtained depending upon thermal history of the specimen[3,12]. In this process the 2D δ-form transforms into the 3D γ-form with the $[100]_\delta$ and the $[100]_\gamma$ directions common to both forms[2]. This relationship which apparently exists between the two forms often gives rise to twinning in the γ-form PBPP crystals[13]. Twinned crystals of poly[bis(trifluoroethoxy)phosphazene] (PBFP) and poly[bis(*p*-fluorophenoxy)phosphazene] (PB(4-F)PP) have been obtained under similar circumstances[14].

A transition map (*Figure 5*) summarizes the conditions for the interrelationships found amongst the various forms of PBPP. The arrows indicate the allowed transformation directions for conditions I–IX explained in the figure caption. Conditions I–V have already been addressed in the literature[2,3] and are included here only for completeness. Route VI covers a transition from γ (3D) to α (3D), which phase is more stable than the γ-form. Its presence has been determined by differential scanning calorimetry (d.s.c.) and X-ray measurements en

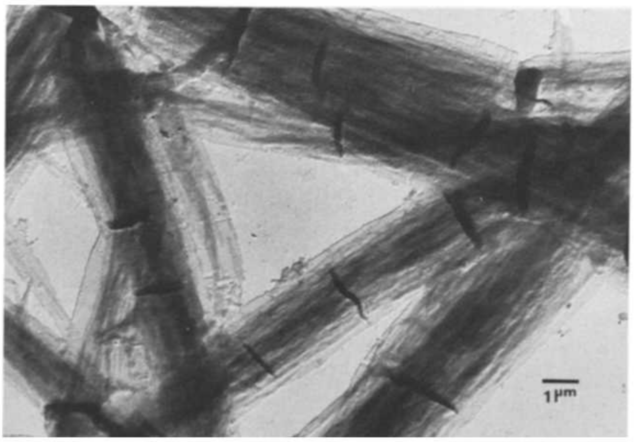

Figure 3 Electron micrograph of PBPP crystals obtained after quenching specimens from 180°C into liquid nitrogen, followed by heating to 120°C for 1 h and afterwards cooling to room temperature

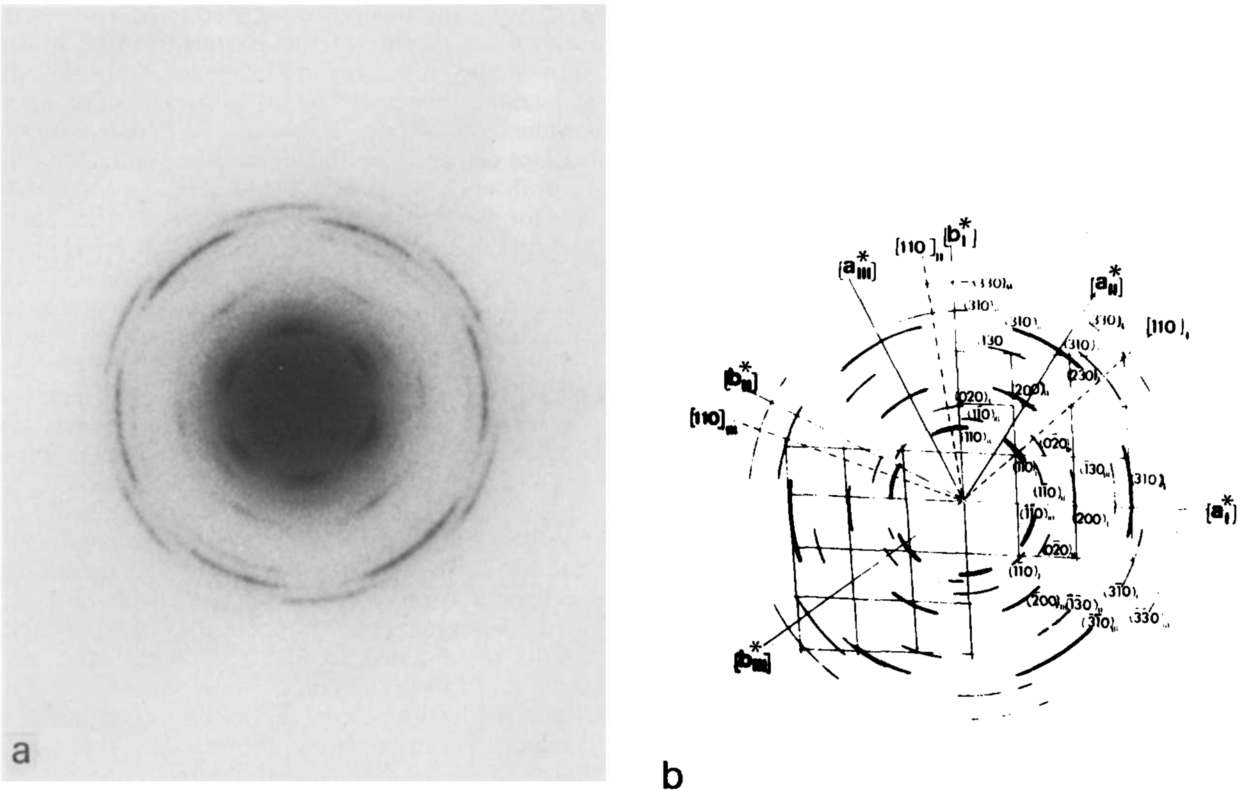

Figure 4 (a) Electron diffraction pattern of PBPP crystals in *Figure 3*. (b) Schematic representation of (a) with indexed reflections

Table 1 Calculated d-spacing with Miller indices for the α-form of PBPP and observed d-spacings for the hexagonally symmetric reflections shown in *Figure 4*

(hkl)	d_{calc}	I^a_{obs}	d_{obs}	I_{obs}
110	1.12	s	1.12	s
110	0.995	s	1.02	s
200	0.823	m	0.826	m
210	0.747	vvw		–
020	0.685	m	0.689	m
120	0.662	vvw		–
300	0.549	vvw		–
$3\bar{1}0$	0.490	m	0.497	m
130	0.454	w	0.456	w
230	0.422	vw	0.426	vw
330	0.374	vw	0.378	vw

$a = 1.65$, $b = 1.37$, $c = 0.97$ nm

[a] Intensity: estimated by electron diffraction of solution grown PBPP crystals

route to the δ-form during *in situ* heating[15]. Conversions VII–VIII are the main concerns in this paper.

Below $T(1)$ the α-form is stable and is only interconvertible to the γ-form via the disordered δ-form. Whenever this transformation occurs from the α-form to the δ-form via $T(1)$, the following crystallographic relationships between these modifications have been deduced: in the α-form the $[\bar{3}20]_\alpha$ and the $[110]_\alpha$ directions remain almost parallel to the $[\bar{1}20]_\delta$ and the $[100]_\delta$ directions, respectively, in the δ-state[2].

PBPP has two molecular chains with eight monomer units per cell, the molecular chains being located at the corners and at the centre of the monoclinic α unit cell. The calculated density of this α-form PBPP is 1.39 g cm^{-3} (Ref. 2), which is in reasonable agreement with the experimentally determined value of 1.37 g cm^{-3} (Ref. 16). During the transformation of the α-form into the δ-form it appears that molecular chains may 'translate' within the $(110)_\alpha$ plane. A plausible axial relationship between the α- and δ-crystalline forms is suggested in *Figure 6*, along with the superposed locations of the molecular chains in both of these crystal forms. The interplanar distance is 1.12 nm in the 2D δ-form[2]. During the α to δ transformation, it appears that the 1.12 nm d-spacing, which is common to both forms, is maintained. These conclusions were established from electron diffraction patterns, obtained from the same portion of PBPP crystals before and after the transformation[2].

It is realized that chain displacement in the lateral direction in the proposed model is unusually large (estimated at ≈0.28 nm). However, it must be realized that the transition from the 2D δ to the 3D α-phase (or vice versa) involves a volume change of more than 6% contraction for poly[bis(trifluoroethoxy)phosphazene] (PBFP)[17]. For PBPP the volume change is estimated to be larger than this amount, in keeping with the larger side groups. Creep[17] and solid state n.m.r.[11] results are supportive of side chain and backbone mobility at and above $T(1)$, but also side chain mobility below this transition.

Molecular chains in the 'disordered' states may 'translate' within the $\{100\}_\delta$ planes and still maintain the interplanar distance of 1.12 nm. On the other hand, whenever PBPP crystallizes from solution in the monoclinic α-form, the molecular chains must grow along the $[\bar{3}20]_\alpha$ direction, which corresponds to the long axis direction of these lath-shaped crystals. Some form of chain folding may occur predominantly within the $(110)_\alpha$ plane[2]. Consequently, whenever molecular chains

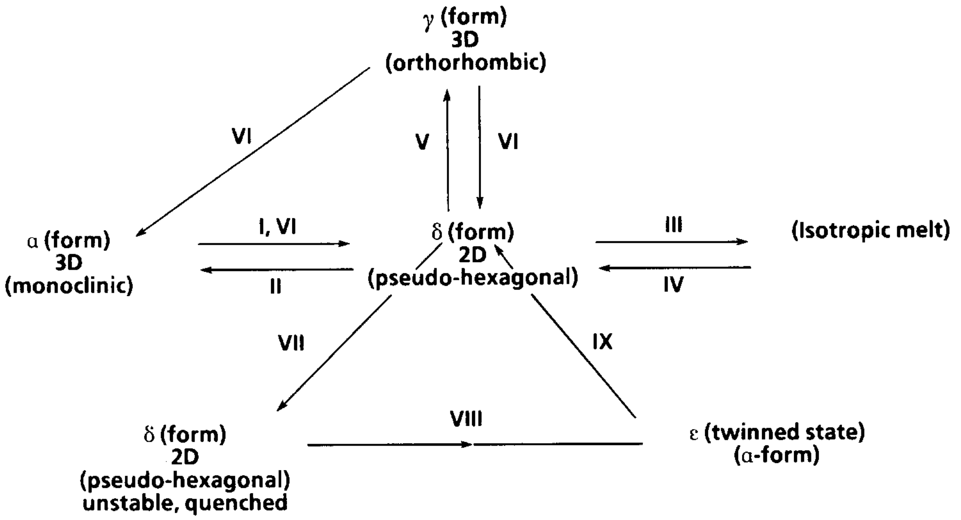

Figure 5 Transition map for PBPP for the following allowed transition (in arrowed directions) conditions: I, Heat above $T(1)$ and but less than T_m. II, Slow cooling. III, Heat to, or above T_m. IV, Cool. V, Fast cool to room temperature. VI, Heat above $T(1)$. VII, Very rapid quench into liquid N_2. VIII, Heat to just below $T(1)$. IX, Heat above $T(1)$ but below T_m

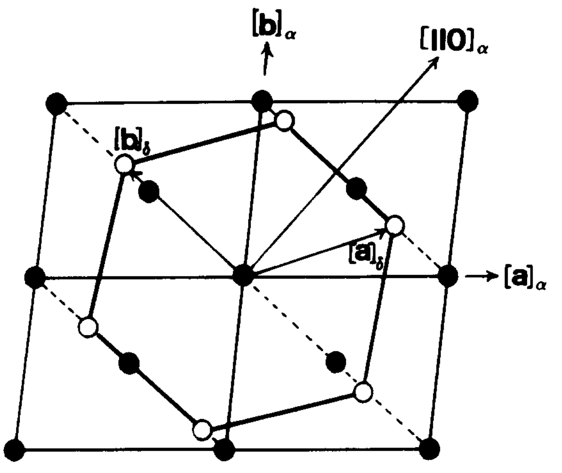

Figure 6 Relationship between α-form (●) and δ-form (○) PBPP, showing crystallographic axes

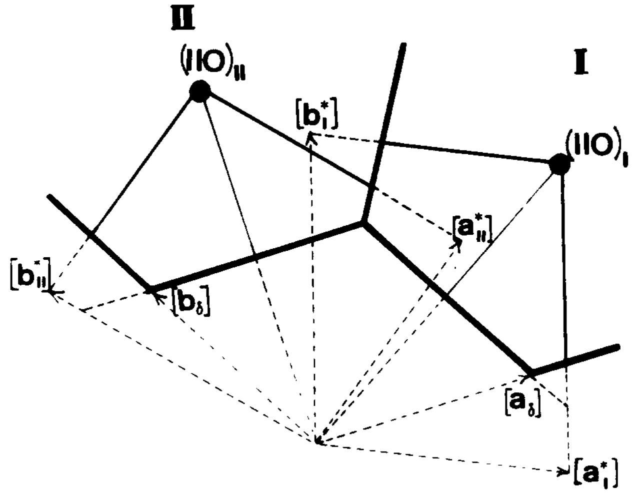

Figure 7 Relationship between the two of the three interrelated orientations of the α-form interpreted as originating from the {100} planes of the δ-form PBPP shown using the reciprocal unit cell. In this figure subscripts I and II refer to two symmetry-related orientations of the α-crystal form

reorganize from the disordered hexagonal state* into the monoclinic α-form, motion may occur along the $\{100\}_\delta$ planes which are parallel to $(110)_\alpha$. The δ-form of PBPP seen in *Figure 2* (insert) has six equivalent (100) planes. Reorganization of the molecular chains in the δ-form occurs simultaneously into the ordered state (condition VIII) along the six $\{100\}_\delta$ planes. These $\{100\}_\delta$ planes, as already stated, are parallel to $\{110\}_\alpha$ planes. *Figure 7* illustrates how two of the three possible axial interrelationships of α-form crystals may originate from two of the three possible $(100)_\delta$ planes. Each $[110]_\alpha$ direction makes an angle of 60°. In fact, all $(hk0)$ and/or $(\bar{h}\bar{k}0)$ reflections, except for the $(1\bar{1}0)$ and $(3\bar{1}0)$ reflections which are located very close to the a^* axis in the a^*b^* reciprocal net, are observed in *Figure 4b*. The d-spacings are given in *Table 1*. From these results it is suggested that the orientational growth occurs in the $\langle 110\rangle_\alpha$ directions for the six $\langle 100\rangle_\delta$ directions of PBPP in the δ-form. Thus the formation of the hexagonally symmetrical pattern of *Figure 4a* can now be explained, since the $[110]_\alpha$ and $[100]_\delta$ directions are related. It therefore seems that this peculiar pattern is a twin-like state of the α-form of the PBPP crystal, specified here as the ε-state. Note that this state can be obtained from the 'quenched-in' δ-form via route VIII only when the latter is warmed to just below $T(1)$, where molecular mobilization occurs. Under these circumstances the system is thermally activated and mobilized, as solid state ^{13}C and ^{31}P n.m.r. confirms[11].

The δ-form does not give rise to the ε-state directly upon normal cooling of the specimen from temperatures anywhere between $T(1)$ and T_m (see *Figure 5*). The cooling rate is a very important parameter in the formation of α- and δ-forms of PBPP, and kinetics also influences the formation of ε-state, which does not exist above $T(1)$. These transformations have been confirmed using d.s.c. measurements[12,15].

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* As a hexagonal rotator phase above $T(1)$.

CONCLUSIONS

The 2D PBPP modification (δ-form) exists at room temperature whenever the sample is quenched from above $T(1)$ to liquid nitrogen temperature and then warmed up to room temperature. The electron diffraction pattern of the material obtained from the quenched δ-form of PBPP by annealing slightly below $T(1)$ shows hexagonal symmetry. All hexagonal reflections have been indexed using the α-form unit cell of the PBPP crystal. This ε-state persists after heating the rapidly quenched δ-form of PBPP to just below $T(1)$ and cooling it down to room temperature. Furthermore, it appears to be a twin-like crystalline modification of the well known α-form of PBPP.

The ε-state can be obtained only after annealing the quenched δ-form of PBPP below, but close to $T(1)$. Normal and relatively fast cooling of the δ-form from above $T(1)$ to room temperature and even below it, only gives rise to the 3D γ-form of PBPP.

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