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Phase transitions and Structure Changes in Poly[bis(phenoxy)Phosphazene]-PBPP

by

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ABSTRACT

Phase transition behavior in PBPP has been studied by electron microscopy, x-ray diffraction techniques and differential scanning calorimetry. Thermal analysis has provided the relative enthalpy change associated with the thermotropic transition, T(1), as a function of heat treatment. The structural and morphological changes corresponding to the enthalpy change have been established.

INTRODUCTION

Some semicrystalline linear phosphazene homopolymers exhibit a thermotropic T(1) transition above which temperature they exist as disordered material. Their attractive properties depend upon some physical characteristics that are associated with the type and size of substitutents (4). Much interest has been focussed on the T(1) transition behavior recently, in so far as it relates to morphology, crystal structure and chemical constitution. Thermal (1,2), structural and morphological investigations (3) - (7) of poly-[bis(phenoxy)phosphazene]-PBPP have been carried out in order to understand the thermotropic transition which is strongly affected by sample history (heat treatment conditions (2)). Crystalline modifications of solution grown PBPP crystals prepared using xylene as a solvent, have been elucidated (3) - (6). Monoclinic (α-form) of PBPP crystals heated up through the T(1) and then cooled to room temperature again, undergo a change to 3D orthorhombic (γ-form) from the 2D pseudohexagonal δ-form which exists above T(1) (4). The influence of sample history on enthalpy and crystal modifications of PBPP are reported here.

EXPERIMENTAL

Materials;

Poly[bis(phenoxy)phosphazene]-PBPP ($\bar{M}w/\bar{M}n$=5.7) was kindly provided by Dr. T. Masuko of Yamagata University, Yonezawa, Japan.

Film Preparations;

PBPP films were cast from using 10% w/w THF solutions.

Solution Grown Crystals;

Crystals were prepared from PBPP in xylene using 0.03% w/w concentration.

Differential Scanning Calorimetry;

A Perkin-Elmer DSC 2 calorimeter was used with an IBM PC computer for data analysis. The DSC output was digitized and stored. Measurements were made at selected heating/cooling rates as a function of temperature through Tg and T(1).

X-Ray Diffraction Measurements;

X-ray diffraction measurements on PBPP films were made using Statton type vacuum camera with heater and temperature control accessories. Ni filtered Cu Kα radiation was used, at 35Kv.

Specimen Heat Treatment and Fracture Surface Morphology Preparation;

Sample history conditions for film and crystals of PBPP are indicated in the figure captions. All experiments were conducted in nitrogen. Following heat treatment the polymer films were fractured mechanically in liquid nitrogen and examined by scanning electron microscopy.

Scanning Electron Microscopy;

A JEOL JSM-T300 scanning electron microscope was used to study specimens after they were coated with Pd/Au alloy.

Transmission Electron Microscopy;

Single crystals were examined using a JEOL, JEM-200 CX electron microscope at 200 Kv.

Results and Discussion

Solution Cast Films

DSC curves of PBPP exhibit single or double peaks depending upon the sample history (2). For instance, upon heating and cooling the original solution cast sample at 10°C/min Figures 1(a) and 1(b) show that exothermic and endothermic peaks occur at 133° and 92°C respectively. The endothermic peak is to be associated with the transformation of an α-monoclinic form* to a pseudohexagonal 2D δ-form. The latter transforms to a highly crystalline 3D structure upon cooling. Figure 2(a) and (b) illustrates X-ray diffraction patterns obtained at 25° and 130°C respectively. Figure 2(c) depicts the δ-structure formed at 159°C. From other kinetic measurements it has been established (9) that formation of the 3D from the 2D phase occurs with an Avrami exponent of n =2. This has been interpreted as meaning that the ordering behavior occurs by a 2D growth perpendicular to the molecular chain direction. A small displacement of no more than one monomer unit is all that is required to create the 3D γ-form from the δ phase. This pattern appears to be common to many semicrystalline polyphosphazenes. Rapid cooling of PBPP from 180° (ie. above T(1)) to room temperture invariably produces the γ-modification.

A more complicated behavioral pattern is found upon slow heating or cooling. For example, multiple peaks are found whenever PBPP (from Figure 1(b)) is reheated at 2.5°C/min to 180° approximately. They are observed at 111°C, 126°C and 143°C respectively, the foremost being relatively small. Corresponding X-ray diffraction measurements made at (a) room temperature, (b) 115°C, (c) 130°C and (d) 152° respectively are shown in Figure 3. The stable phases that exist at these temperatures are labelled in this figure. The DSC curve, Figure 1(c) illustrates

*Comprised of lamellar crystals of relatively low crystallinity <50%.

transitions found using the dynamic technique. In line with the enthalpy measurements, only the pattern in Figure 3(d) shows that the PBPP specimen is disordered. Clearly, the first and second DSC peaks in Figure 1(c) correpsond to the transitions $\gamma \rightarrow \alpha$ and $\alpha \rightarrow \delta$ respectively. Elsewhere, with poly[bis(4-isopropylphenoxy)phosphazene] (PBiPP) (10) exhibits two similar crystal modifications that have been reported as occuring in an almost analogous fashion. Of note is an exothermic peak in PBiPP which is not measurable in PBPP in between the 126°C and 143°C transitions. Either, it is too weak to be detected or it does not exist at all whenever shorter side group substituents are present in the polymer. The generality of this statement requires further testing. However, on the next heating cycle only a single peak (corresponding to the $\alpha \rightarrow \delta$ transition) is noted. In these circumstances the peak temperature now moves higher as reported already (2). While it is established that only the 3D γ-form obtains from the 2D δ-form as long as the specimen is not heated above 180°C and is cooled rapidly to room temperature. Other work (12) has shown that whenever PBPP is held at 250°C for 2 hrs. and cooled slowly crystallization occurs in the α -form only. In our work this same transformation is verified by X-ray diffraction as illustrated in Figure 4. This pattern is obtained after the specimen is heated for 1 hr. 250°C and cooled at 2°/min to room temperature. Whenever it is heated subsequently in the DSC, only a single peak corresponding to the $\alpha \rightarrow \delta$ transition is found. These observations prove the co-existence of two distinct phases in the T(1) transition region.

Scanning electron microscopy proved to be a useful morphological probe to examine some of these samples of PBPP of known history. The fracture surface morphology of several specimens are depicted in Figure 5 where

(a) shows the original unheated specimen,

(b) the sample heated to 180°C after one,

(c) specimen heated at 250°C,* 1 hr. followed by cooling at 2°C/min, and lastly

(d) specimen heated for one hour a 250°C followed by quenching into liquid nitrogen before warming to room temperature where measurements were made.

Figure 6 nicely illustrates the spherulitic texture in thin films cast from THF. The structure is the α-form, comprised of intertwinning fibrils merge and overlap but the boundaries between spherulites are visible. Compared to Figure 5(d), heated treated in the thermotropic phase below Tm, there is a striking difference in morphology and physical properties (4). For example, solution crystallized PBPP is readily oriented up to X10 its original length whereas the heat treatment specimen, although strong is brittle because of its much higher crystallinity and extended chain morphology (13). A comparison amongst these different textures, with PBPP crystallized from dilute solution, is in order.

Figure 5(a) is devoid of spherulitic details until the sample is heated above T(1), say to 180°C, when a coarse texture develops, containing globular (rounded) particles that resemble small spherulites (see Figure 5(b)). The features after fracture, shown in Figures 5(c) and 5(d) for the higher heat treatment (250°C) appear to be more rod-like (in line with PBFP specimen that underwent similar heat treatment including fusion above 245°C (the Tm of PBFP)[4],[13]. The PBFP specimens slowly cooled from 250° feature rod-like textures 1000 nm (long) X 200 nm (wide), were of high crystallinity. It is conjectured that the long direction of these crystals corresponds to the chain extended direction.

*Still below Tm of PBPP which is 390° approximately.

Solution grown crystals:

Well-defined lathe-shaped PBPP crystals have been reported from dilute xylene solution (3), (4). Figure 7 shows the typical morphology of these crystals. The electron diffraction pattern is that of the monoclinic α-form already established (3), (4). The striations across the lateral surface direction seem to be associated with an array of chain-folded crystal lamellae wherein the polymer chains are extended in the longitudinal direction in the original PBPP crystals (6). The surface corrugations on the crystals seem to have been formed during crystallization. After specimens are heated above T(1) and subsequently cooled slowly to room temperature, the striations in Figure 7 become obscured through roughening of the lamellar surface(s), but Figure 8 indicates that many features still remain. Whenever solution grown PBPP crystals are heated above on the carbon supported grids T(1) and then cooled down to room temperature again, the transformation is $\alpha \rightarrow \delta \rightarrow \gamma$ forms whenever they have been heated to high temperatures (250°C for example) and slowly cooled to room temperature. This transitional behavior differs from that encountered with thicker cast films of PBPP. It seems that there may be some interaction is suspected between the crystals and the carbon film supported on the microscope grids. The crystals in Figure 8 are of the γ-form modification. The relationships amongst the crystalline forms have been summarized in Figure 9 for different heat treatments. Transformations occur only in the direction of the arrows according to the conditions specified in this figure (which is monoclinic)(7). The ε-form described elsewhere in detail,is only produced when the δ-form is quenched rapidly into liquid nitrogen followed by heating to just below T(1). The ε- and α-forms are equivalent crystallographically although they are not morphologically similar.

CONCLUSIONS

(1) PBPP crystallizes from solution, only in moderate 3D crystallinity as the monoclinic (α-form) structure, however it undergoes chain extension upon being heated above t(1) transition, where it exists as a 2D phase (δ-form), until it is cooled below T(1) again.

(2) The original solution grown α-form crystals convert to the orthorhombic γ-form or even remain in the α-form depending upon temperature and/or cooling rates.

(3) After PBPP is heated up to 250°C and cooled very slowly it exhibits rod-like aggregates of the α-form below the T(1) temperature. The shape and distribution of these rod-like structures are almost randomly disturbed by rapid quenching into liquid nitrogen .

(4) The DSC heating curve of γ-form PBPP exhibits two endothermic peaks in the transition region.

(5) X-ray diffraction pattern obtained at temperatures between the two DSC peaks are of the α-form and the δ-form respectively. These two enthalpy changes correspond after higher temperature peak to the γ→α and the α→δ transitions, respectively.

(6) Depending upon heating cooling conditions, the α-form of PBPP exhibits a different morphology from that of the unheated (original) α-form PBPP.

(7) When solution grown single crystals are heat treated on carbon coated microscope grids the crystal transformation to the γ-form form the α-form via the δ-form occurs irreversibly. Some interaction between the polymer crystals and carbon substrate may be responsible for this behavior.

Acknowledgements

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FIGURE LEGENDS

Figure 1 DSC (a) initial heating and, (b) first cooling curves for solution cast PBPP films, (c) second heating DSC curve for PBPP films following Figure 1 (b).

Figure 2 X-ray diffraction patterns of PBPP films recorded (a) at room temperature, (b) at 130°C, and (c) at 150°C.

Figure 3 X-ray diffraction patterns obtained at elevated temperature corresponding to the enthalpy changes in Figure 3. These are (a) at room temperature (γ-form), (b) at 115°C (lower crystallinity, γ-form), (c) at 130°C (α-form), and (d) at 152°C (δ-form).

Figure 4 Room temperature x-ray diffraction pattern of PBPP films after fusion at 250°C for 1 hour and then cooling to room temperature at a rate of 2°C/minute.

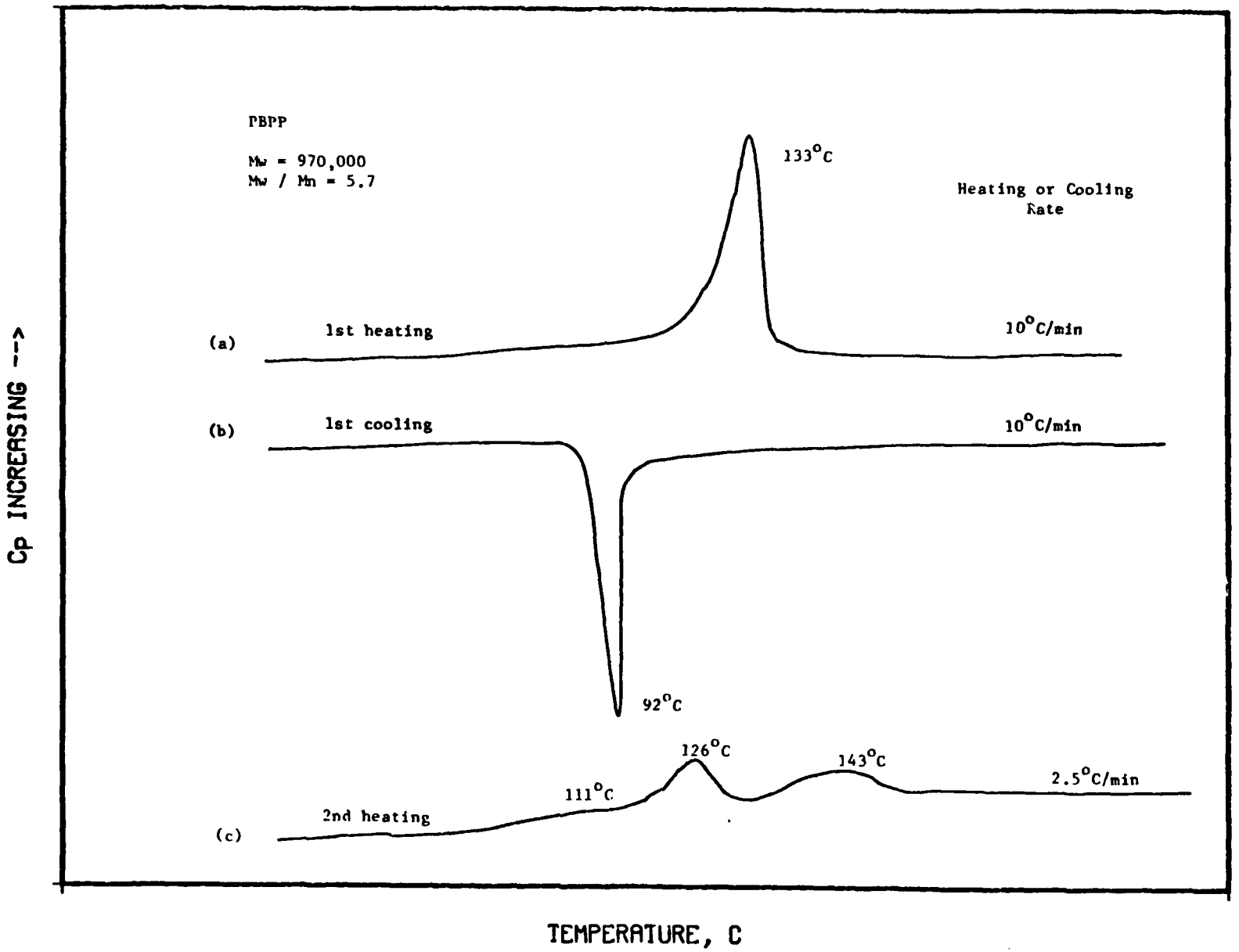
Figure 5 Scanning electron micrographs of PBPP fracture surface (a) original, unheated, (b) heated at 180°C for 1 hour, then cooled to room temperature, (c) heated at 250 °C for 1 hour, then cooled to room temperature at 2°C/minute, and (d) heated at 250°C for 1 hour, followed by quenching into liquid nitrogen and warming up to room temperature.

Figure 6 Scanning electron micrograph of PBPP spherulite cast from THF solution as a film.

Figure 7 Electron micrograph of solution grown PBPP crystals with its electron diffraction pattern insert.

Figure 8 Electron micrograph of solution grown PBPP crystals after fusion at 250°C for 1 hour and then cooling slowly to room temperature.

Figure 9 Transition map for PBPP showing the inter-relationships that exist amongst various crystal modifications.



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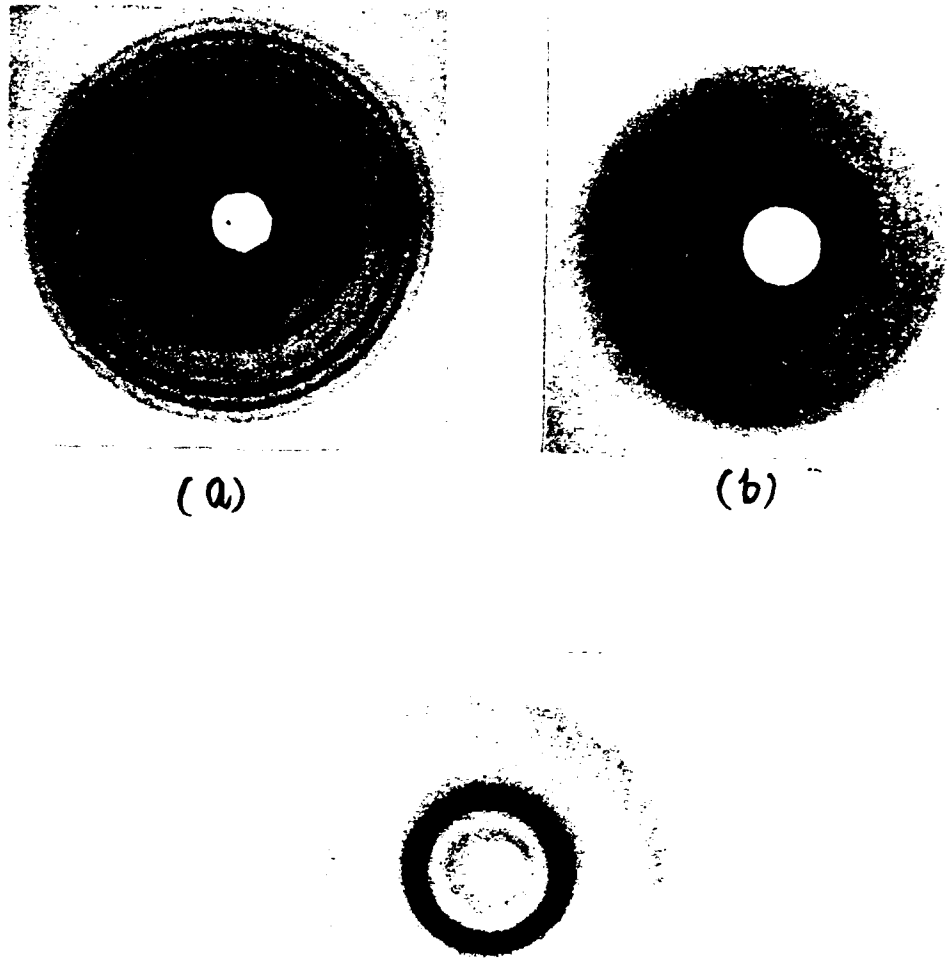

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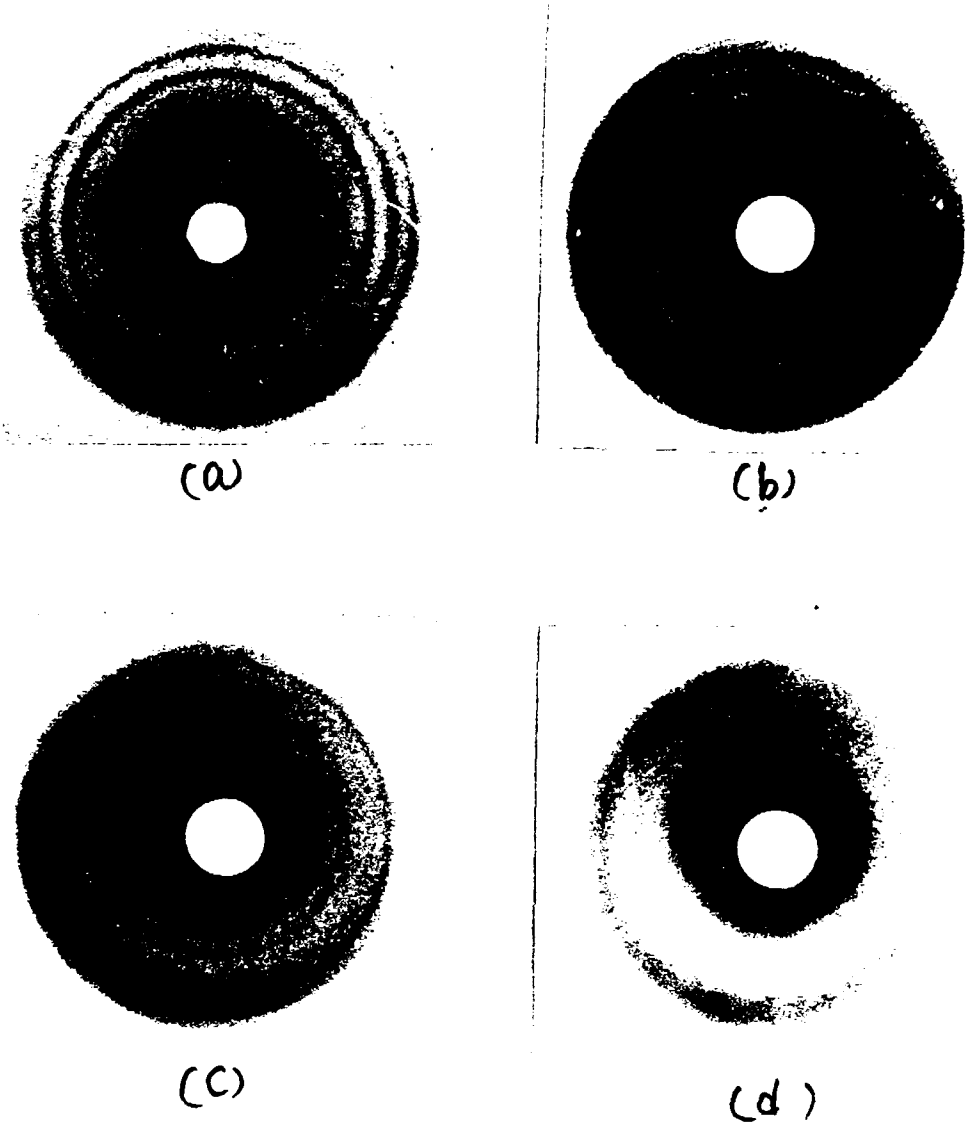

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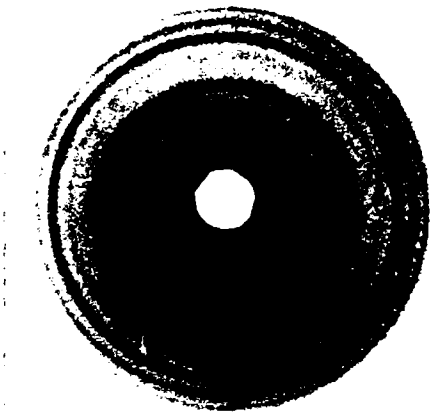
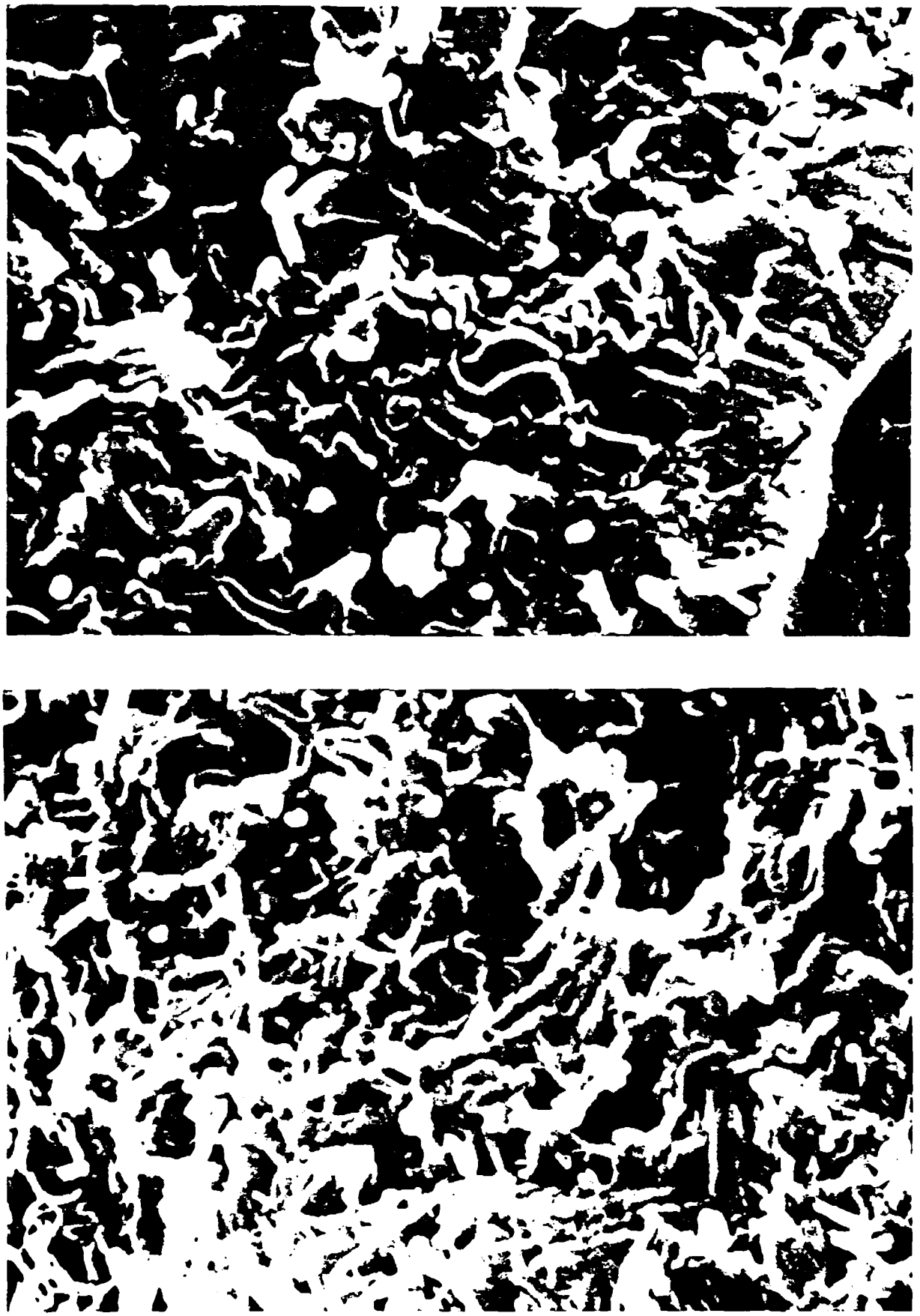


Figure 4 Room temperature x-ray diffraction pattern of PBPP films after fusion at 250°C for 1 hour and the cooling to room temperature at a rate of 2°C/minute.

(a)

(b)

Figure 5 Scanning electron micrographs of PBPP fracture surface (a) original, unheated, (b) heated at 180°C for 1 hour, then cooled to room temperature, (c) heated at 250 °C for 1 hour, then cooled to room temperature at 2°C/minute, and (d) heated at 250°C for 1 hour, followed by quenching into liquid nitrogen and warming up to room temperature.



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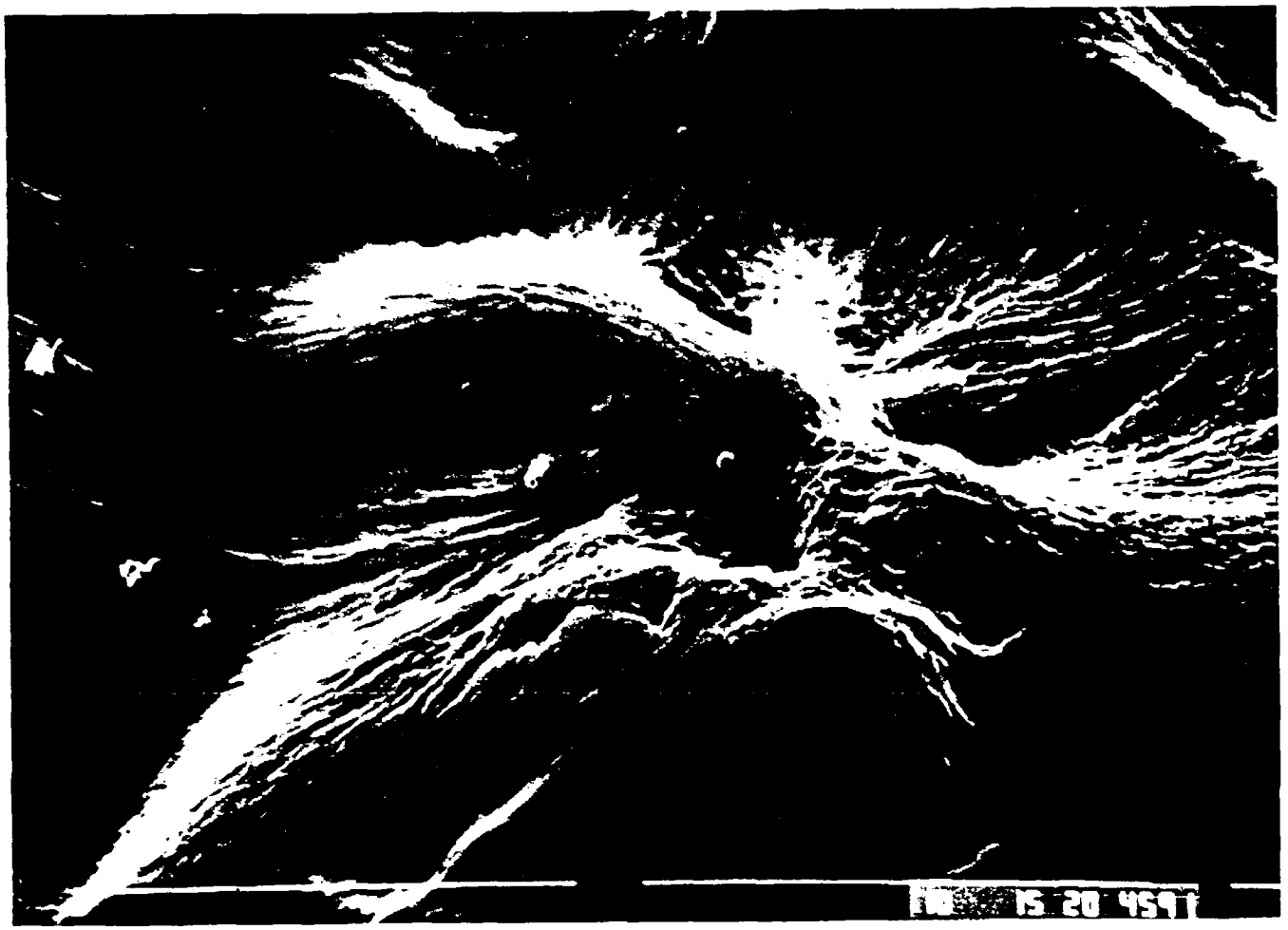

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Figure 7 Electron micrograph of solution grown PBPP crystals with its electron diffraction pattern insert.

FIGURE 7.

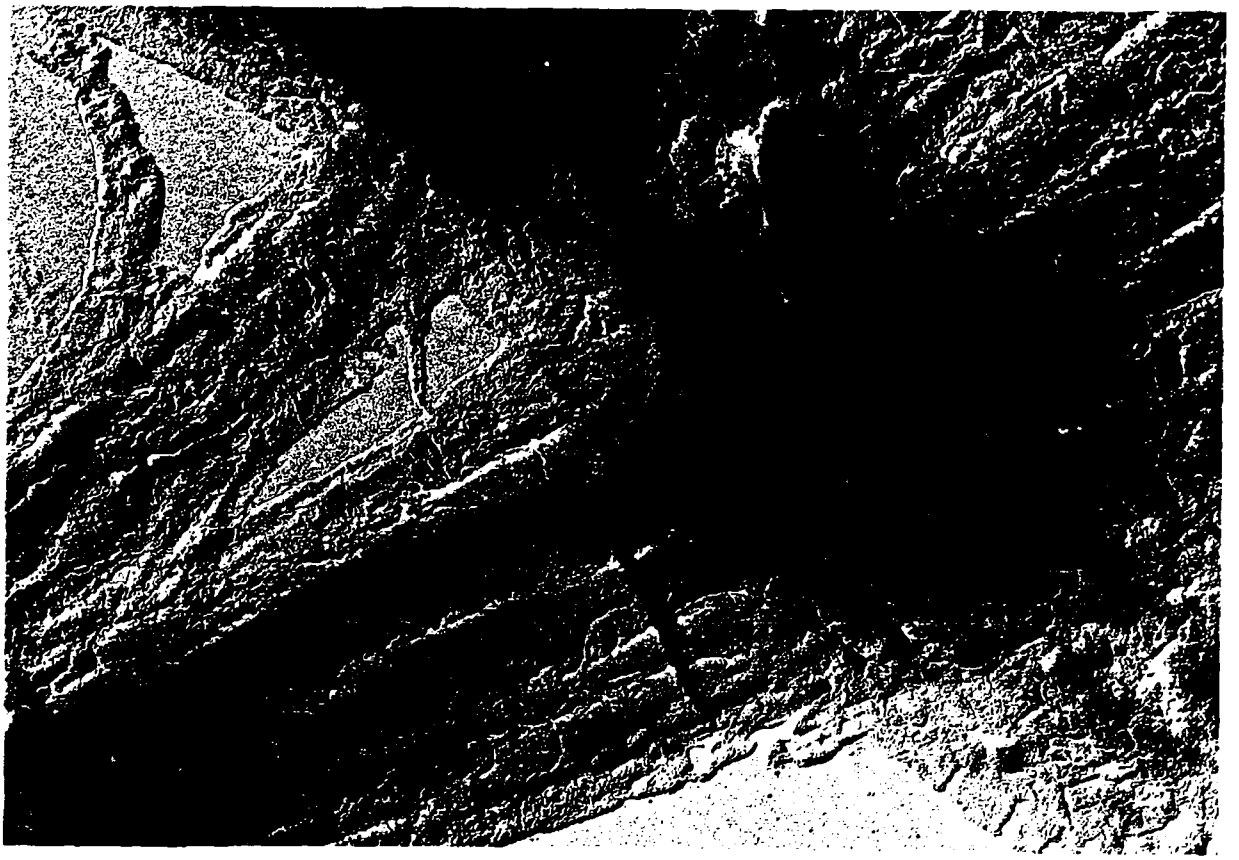

Figure 8 Electron micrograph of solution grown PBPP crystals after fusion at 250°C for 1 hour and then cooling slowly to room temperature.

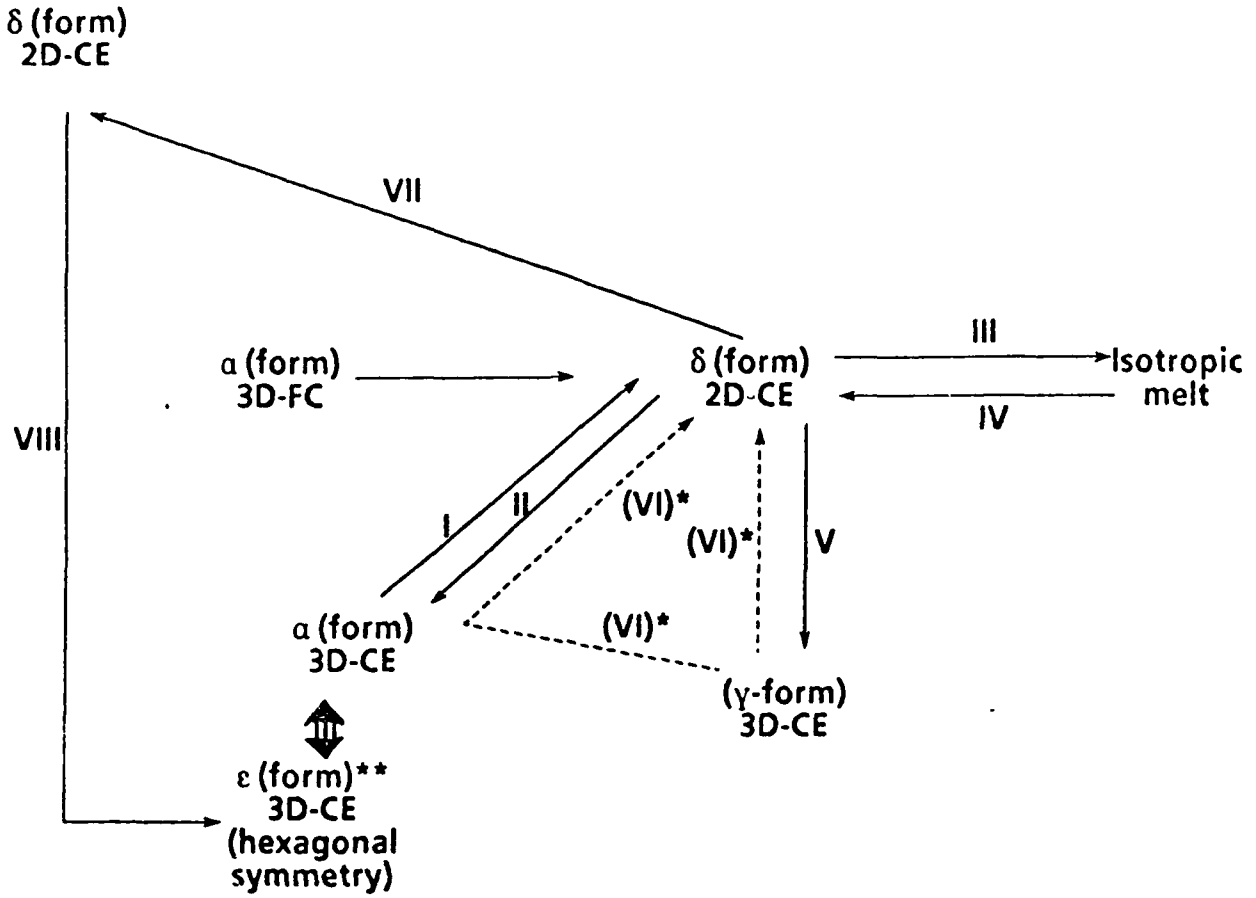

Figure 9. Transition map showing interrelationships amongst PBPP crystal modifications. The conditions are:

I. Heating through T(1)
II. Show cooling from above T(1)
III. Heating to or above T_m where melting takes place
IV. Cooling from condition III
V. Rapid cooling from T(1) to ambient temperature
VI. Heating to above T(1)
VII. Rapid quenching to liquid N_2 temperature
VIII. Heating to just below T(1)

} ref(7).

Greek letters denote crystal modifications; the terms FC and CE are basically used to describe folded chain and chain extended lamellae. The * indicates that the note is not completely defined yet, and ** designates observation for solution grown crystals only.

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