Lamellar crystallization during bulk polymerization of poly(*p*-oxybenzoate)*

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Poly(*p*-oxybenzoate) (P*p*OBA) has been polymerized in the bulk at temperatures below the melting point of the monomer. Polymerization involves, isothermally, sublimation–recrystallization–melting (chemical reaction)–polymerization–liquid crystal domain formation–crystallization processes. Lamellae, about 100 Å thick for P*p*OBA, are observed along with particulate material. D.s.c. and *FT*i.r. scans indicate that the sublimate is identical to the monomer, but that the 'melt' has undergone some esterification. The polymer produced is of relatively low molecular weight, but the degree of polymerization can be rapidly increased by heating to elevated temperatures.

(Keywords: poly(*p*-oxybenzoate); crystallization; lamellae)

INTRODUCTION

In previous reports we have described the polymerization of *p*-, *m*- and *o*-acetoxybenzoic acid, (*p*-, *m*-, *o*ABA), 2,6-acetoxynaphthoic acid (ANA) and 4-acetoxy-4′-carboxybiphenyl (ACBP) homopolymers and copolymers as constrained thin films between glass slides at temperatures below the melting point of the monomers as measured by d.s.c.[1–9]. Contrary to the case for polymerization of the monomers in bulk solution in high temperature heat transfer fluids, for which ~0.1–0.5 μm thick lamellae or whiskers of the polymers form[3,10], polymerization in the constrained films yields single crystal lamellae on the order of 100 Å in thickness consisting, presumably, of extended chains. In as much as the commercial polymers based on *p*ABA and ANA are polymerized in the bulk molten state[11], it is of interest to examine the morphology of the homopolymers resulting from such polymerization of these monomers. We know of no reports of the morphology of these materials as polymerized in the molten state, either homo- or copolymer, at temperatures either above or below the melting points of the monomers. In this paper we describe our results for poly(*p*-oxybenzoate) (P*p*OBA); similar research is in progress on poly(2,6-oxynaphthoate) and its copolymers.

EXPERIMENTAL

*p*ABA was obtained from Aldrich and TCI America. The TCI material has a single melting peak at 196°C at a heating rate of 20°C min^{-1} (*Figure 1*). The Aldrich material has two additional small peaks at 172 and 178°C which we attribute to impurities. Samples (5 g) of the monomer were placed in test tubes partially immersed in oil baths at 180°C for various periods from 2 to 96 h. This is the temperature used for most of the prior studies, with lamellar polymerization/crystallization of *p*ABA being observed for temperatures between 130 and 280°C (ref. 1). The test tubes were sealed loosely with corks to permit escape of the acetic acid given off during polymerization.

The resulting samples were prepared for electron microscopy and electron diffraction (e.d.) by breaking up the resulting solid at the bottom of the tube, if present, dispersing the material in and extracting with acetone (which will dissolve any residual monomer), and then dispersing some of the remaining material on a slide. The samples were shadowed with Pt-C and observed in a Jeol-100C electron microscope. D.s.c. scans were obtained using a Perkin–Elmer DSC-4. *FT*i.r. scans were obtained (64 scans) on a Perkin–Elmer 1600 using KBr pellets.

For comparison purposes an electron micrograph of P*p*OBA prepared by polymerization in a constrained thin film is also shown. The monomer was cast on a glass cover slip from acetone solution, dried, covered with another cover slip, the sandwich wrapped in aluminium foil and heated on a thermostatted hot plate for 1 h at 180°C. Following splitting of the slips, they were washed in acetone, shadowed and carbon coated, and then floated on HF before picking up on electron microscope grids.

RESULTS

Figure 2 is representative of the phase I crystals of P*p*OBA grown by the constrained thin film method at 180°C. As previously described[1], they consist of 100 Å thick lamellae. The lateral shape varies from well formed diamonds to rounded or lath-like lamellae. Optical microscopy observations on a hot stage show that part of the *p*ABA monomer sublimes and recrystallizes as large lath-like crystals at temperatures as low as 120°C, melting

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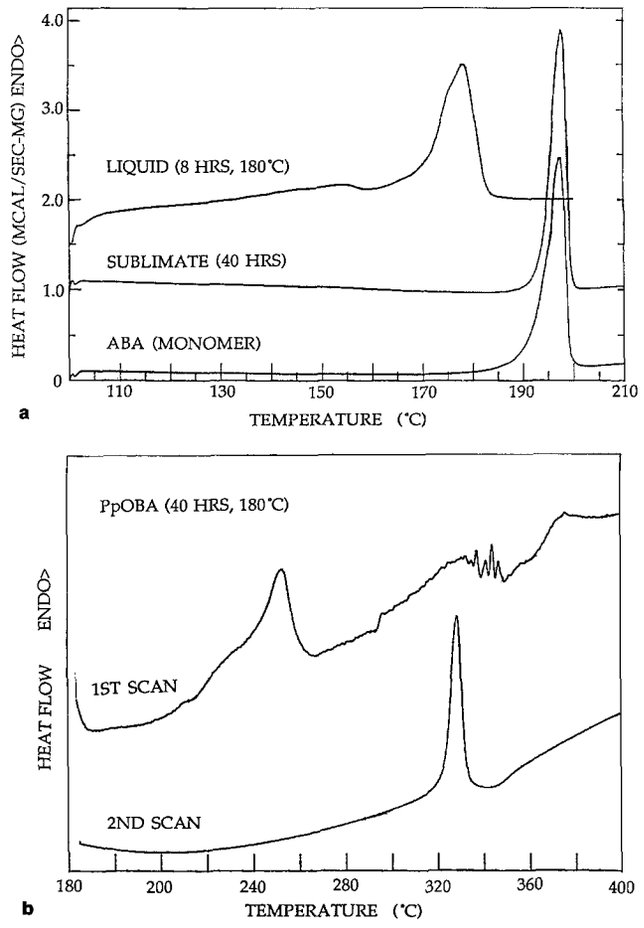

Figure 1 D.s.c. scans of (a) monomer *p*ABA as received (TCI), sublimate (40 h), and the liquid present after 8 h storage at 180°C, and (b) first and second scans of P*p*OBA polymerized for 40 h at 180°C (extracted with acetone). Both the sublimate and liquid, as well as the ABA, are soluble in acetone

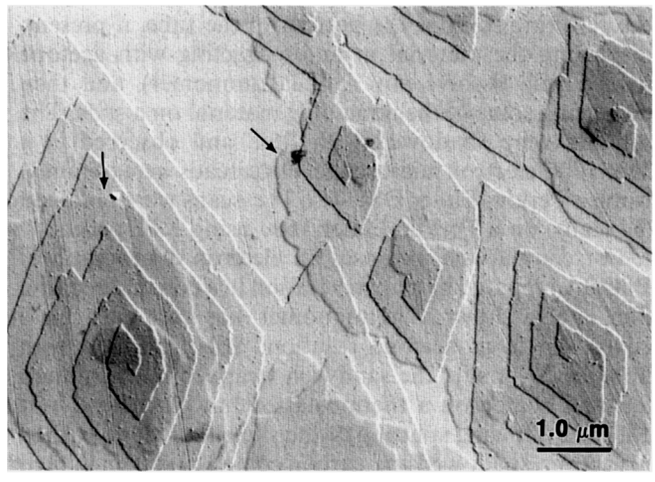

Figure 2 Portions of a phase II P*p*OBA crystal grown by polymerization at 180°C for 1 h between slides. The diamond shaped lamellae (100 Å thickness) overlap rounded edge lamellae, probably from underlying crystals that may have been 'trapped' before completion of growth (arrows)

again with time at temperatures as low as 130°C, or with more rapid heating, at about 150°C (ref. 1). It is in this melt that polymerization occurs. Some of the crystals, at least, grow free of the substrate and overlap each other as they settle. Single disclination domains also form, which crystallize with increasing time (as $T_{k\text{-}m}$ reaches the polymerization temperature, T_p). They also consist of 100 Å thick lamellae when observed after cooling to room temperature[1].

A similar process also occurs in the bulk. When the test tube with ABA is placed in the 180°C oil bath, the originally opaque monomer partially sublimes and recrystallizes on the upper part of the tube, above the oil, as thin lath-like crystals up to 1 cm in length. After several hours the residual monomer melts, becoming transparent. This is followed by turbidity as the ABA polymerizes. D.s.c. scans of material from the sublimate, from the transparent melt (cooled to room temperature) and from the particulate material in the tube, extracted with acetone, are shown in *Figure 1* along with the scan of the as-received monomer. The sublimate, regardless of the time of polymerization, has the same melting temperature, T_m, as the monomer. The liquid in the tube is seen to have both a lower main T_m with a very broad peak and another even lower temperature broad peak or peaks that extend down to 130°C, in agreement with the optical microscope observations of melting at 130°C.

The first scan of the extracted material has a broad, multiple peak with its maximum at 246°C, and additional broad peaks at around 335 and 375°C. The second scan has a single sharp peak at 329°C and is similar to that of bulk solution polymerized material[12]. We interpret the difference as being due to further polymerization during the scan, the peak at 329°C corresponding to the $T_{k\text{-}m}$ transition for P*p*OBA with number average degree of polymerization, $\overline{DP}_n$, of around 100 (ref. 13). Economy *et al.*[13] have reported melting points of 230 and 262°C for the acetoxy-dimer and -tetramer respectively, while Klepl[14] reports 216.5 and 230°C for the acetoxy-dimer and -trimer. The low temperature peaks in the first scan may thus be due to such short chain oligomers. Not stated in either report is whether there is a lower temperature $T_{k\text{-}m}$ transition, or the degree of polymerization, DP, at which mesomorphic behaviour is observed. We see no evidence of mesomorphic behaviour in our 'melts' as a whole; the turbidity, however, could arise from either crystalline or liquid crystalline domains.

Whether the 335°C peak is due, in part, to polymer polymerized at 180°C or to the rapid polymerization during the d.s.c. scan is not clear. In a sample polymerized for 96 h at 180°C, peaks of similar breadth were seen at 228 and 344°C, with the 344°C peak area being 1.5 times that of the 228°C peak. This scan was stopped at 380°C and thus it is not known if the 375°C peak was present. The origin of the latter peak is unknown; it is considerably lower than the $T_{m\text{-}n}$ peak observed in bulk solution polymerized P*p*OBA[12]. If the 335°C peak is due to polymer polymerized in the pan during heating, the extracted material has a much more rapid polymerization rate than ABA. Polymerization of *p*ABA in Therminol 66*, for instance, at 300°C takes more than 5 h to reach a similar DP, i.e. a $T_{k\text{-}m}$ of 340°C.

Polymerization in the bulk is much slower than in the constrained thin films, a feature we attribute to a catalytic effect of the glass surface. In one experiment, a 50/50 mixture of *p*ABA and glass beads (diameter $\leqslant 10^6$ μm) was polymerized at 180°C. 'Melting' occurred within 2 h, with solid polymer forming in 6 h, as compared to 8 and

* Registered trademark of Monsanto Company for a heat transfer fluid composed of bi- and terphenyls

24 h in the absence of the beads. Other catalysts would presumably also accelerate the reactions.

*FT*i.r. scans of the *p*ABA monomer, sublimate, 'melt' (after 8 h at 180°C) and acetone extracted 'polymer' (after 40 h at 180°C) are shown in *Figure 3* along with a scan of P*p*OBA polymerized for 1.8 h in a 1/100 Therminol 66 at 350°C. This material, which consists of whiskers (see ref. 10), had a d.s.c. measured $T_{k\text{-}m}$ of 360°C with a subsidiary peak at 348°C. The scans are shown for two ranges of the spectrum. Clearly the monomer and sublimate are identical, in agreement with our d.s.c. results. The small peak at 1736 cm^{-1} in the Aldrich monomer is not seen in the TCI monomer, consistent with our explanation for the 'extra' d.s.c. peaks. Economy *et al.*[15] have indicated that a sublimate formed when *p*ABA was heated to 280°C in Therminol 66 or heated in the melt to 350°C was the phenyl ester of phenoxybenzoic acid, as first described by Klepl[14]. Although neither paper lists a T_m, this product does not appear to be involved in our much lower temperature process as either the sublimate or 'melt'.

The new bands in the 'melt' are seen to be the same as those in the melt polymerized polymer and whiskers (see *Table 1*) but to have lower intensities. A rough estimate of the $\overline{DP}_n$ can be determined by comparing the relative peak heights of the polymer ester C=O stretch band at ~1740 cm^{-1} and half the sum of the peak heights of the monomer acetoxy and carboxy C=O stretch bands at 1760 and 1690 cm^{-1}. The ratio of these values is zero for the monomer and sublimate, large for the polymers (only a shoulder of the 1760 cm^{-1} band and a considerably reduced, single (double in the monomer) 1690 cm^{-1} band remains), and small but present for the 'melt'. Actual values would require resolution of the individual peaks, use of absorption peak areas and determination of the origin of the splitting of the 1690 cm^{-1} band which is present in the monomer and 'melt', but nearly absent in the polymer. Although, based on the i.r. scan, one might thus suggest our 'melt' is composed of low molecular weight oligomers, this is unlikely to be due to the low melting points. Rather the 'melt' probably consists of such components as the phenyl ester of *para*-hydroxybenzoic acid (T_m = 176°C; Klepl[14] lists a material with this melting point as *para*-oxybenzoic acid phenyl ether, but the formula given appears to be the ester) or its isomer phenyl *para*-oxybenzoic acid (T_m = 159.5°C (ref. 14)) and the acetylated version of the ester. That reaction has occurred in producing the melt is indicated by the release of acetic acid. The *FT*i.r. scans, on the other hand, indicate (band at 1760 cm^{-1}) that a substantial portion of the acetoxy groups are retained in the 'melt'. N.m.r. characterization of the 'melt' is in progress.

The *FT*i.r. scan of the 'polymer' indicates that nearly all of the acetoxy groups have been released, with a

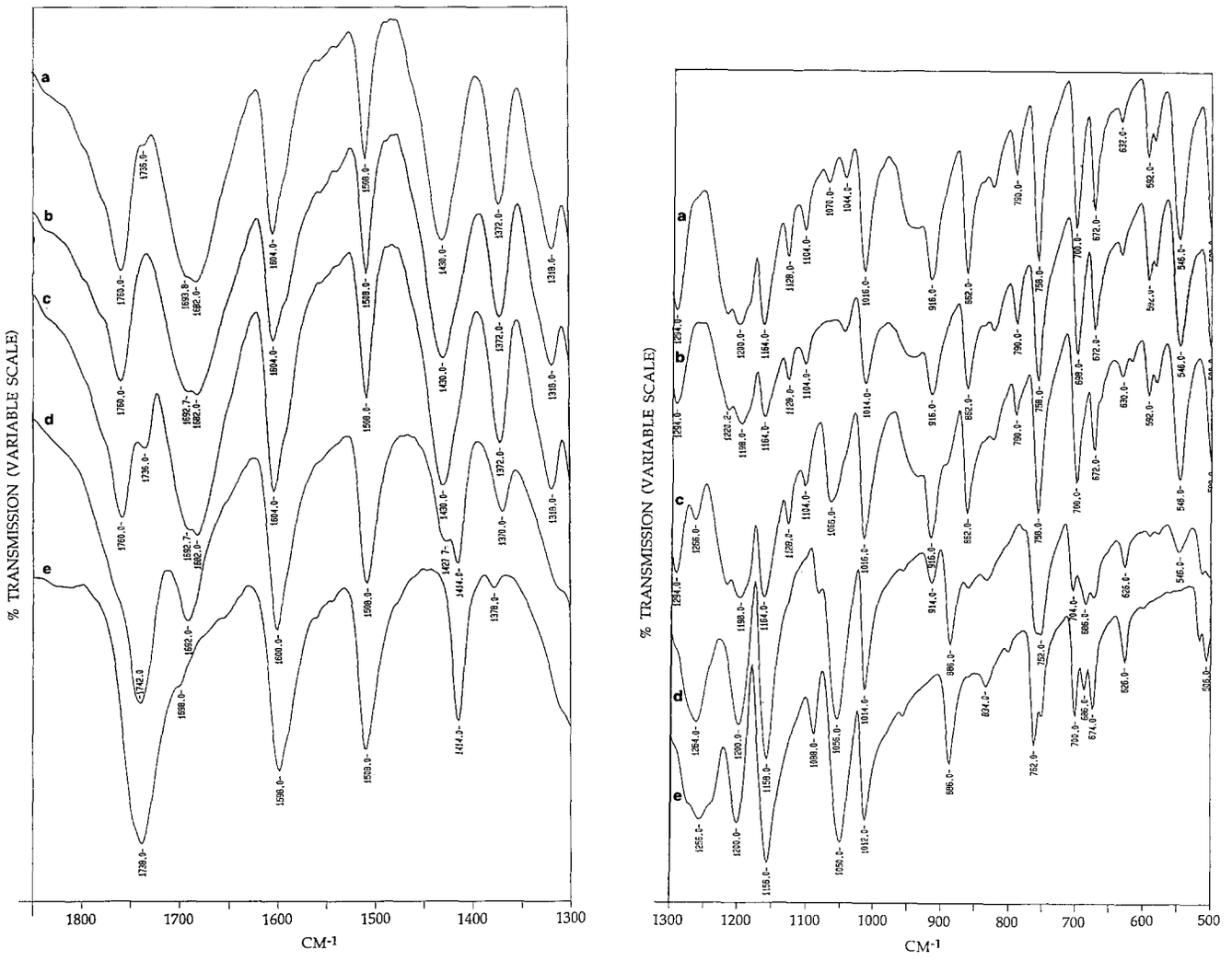

Figure 3 *FT*i.r. scans of similar material to that in *Figure 1* in the ranges 1850–1300 cm^{-1} and 1300–500 cm^{-1}. (a) Monomer similar to *p*ABA as received (Aldrich); (b) sublimate (40 h); (c) liquid (180°C, 8 h); (d) P*p*OBA (180°C, 40 h, acetone extracted; (e) P*p*OBA whiskers (350°C, 110 min, 1/100)

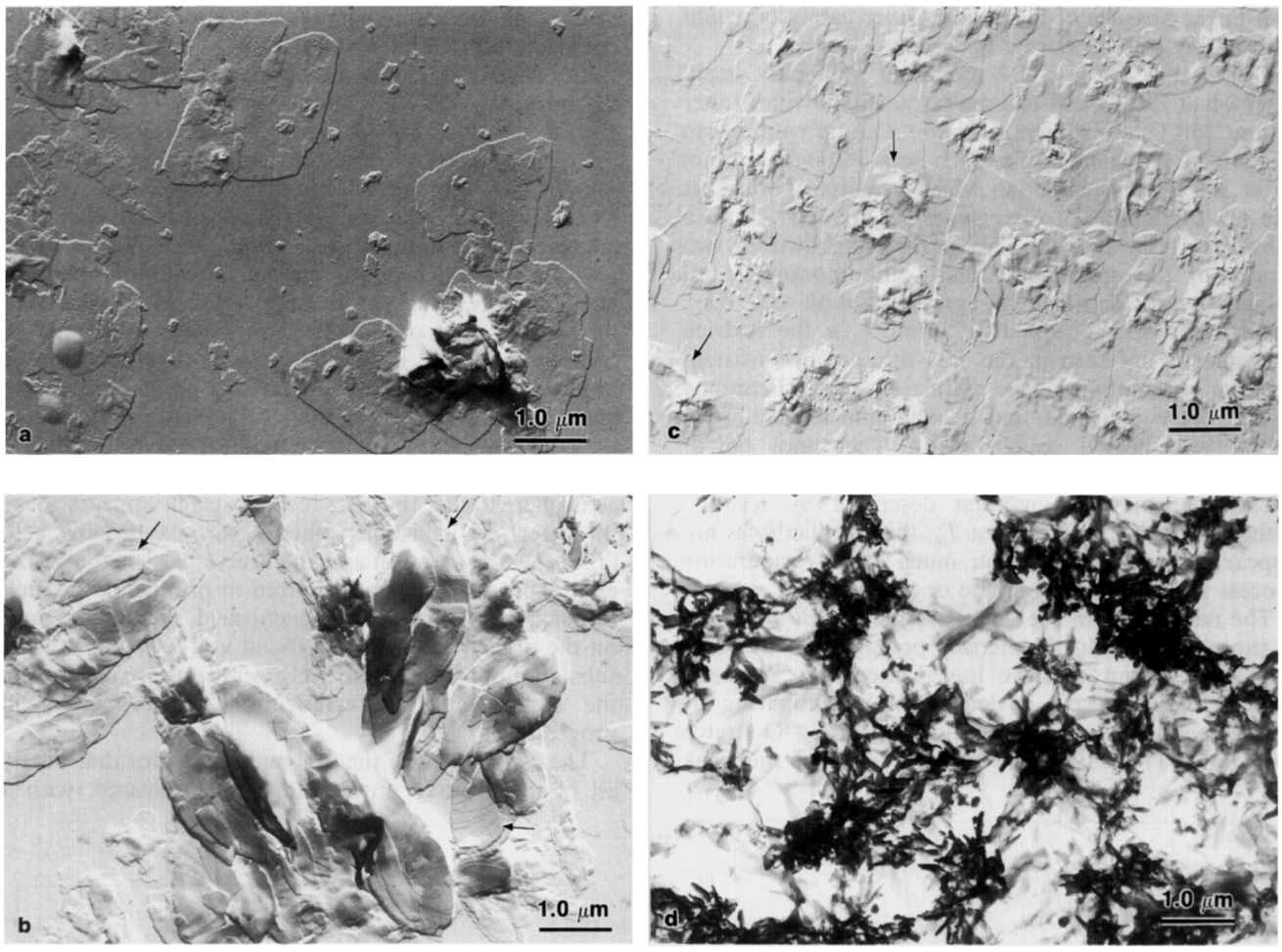

Figure 4 P*p*OBA crystals grown by bulk melt polymerization at 180°C for (a) 8 h, (b) 24 h and (c) 32 h. The crystals are a mixture of phase I and phase II. The arrows in (b) and (c) indicate overgrowths of thinner lamellae. A more aggregated region of the dispersion is shown in (d) (20 h, 180°C)

Table 1 Summary of primary infra-red band changes for ABA and P*p*OBA

Monomer bands	Polymer bands
1760[a]	1740
1682	1698
1693	
1430	1414
1372	–[b]
1318	1260
1294	
1220	–
1164	1156[c]
1128	–
1104	1088
1070	1050
1044	
916	886
862	
790	
–	686
592	–
546	–

[a] Brace indicates bands that have presumably 'merged'
[b] –, Absent in the spectra
[c] The height strongly increases

substantial number of ester groups formed. The original two carboxyl peaks at 1694 and 1682 cm^{-1} have been reduced to a single, smaller peak at 1692 cm^{-1}. Corresponding changes have occurred in the other ranges of the spectrum, suggesting significant *DP*s but the retention of some carboxyl groups.

Figure 4 shows representative areas of P*p*OBA that were polymerized for 8, 24 and 32 h at 180°C before extraction with acetone and dispersion on the slides. In all three samples the crystals are clearly lamellar. These samples all give rise to both phase I and phase II e.d. patterns (*Figure 5*). Only occasionally are full *hk*0 single crystal patterns seen, however; usually there are multiple sets of reflections and tilt. In the constrained thin film samples individual crystals are either phase I or II, the phase apparently being determined during the transition from the mesomorphic state to the crystalline state as the chain length increases[1]; the same effect presumably occurs here.

Whereas the crystals in *Figures 4a* and *c* consist primarily of single lamellae, those in *Figure 4b* are clearly stacks of lamellae. In the sample polymerized for 8 h (*Figure 4a*) there is a tendency for a diamond shape, with some surface texture on the crystals. The latter has the appearance of partially developed (or etched) lamellae on the larger, 170 Å thick lamellae. Clusters of ill-defined material are also seen. The crystals in the 24 h sample appear to be made up of clusters of lamellae, ~70 Å

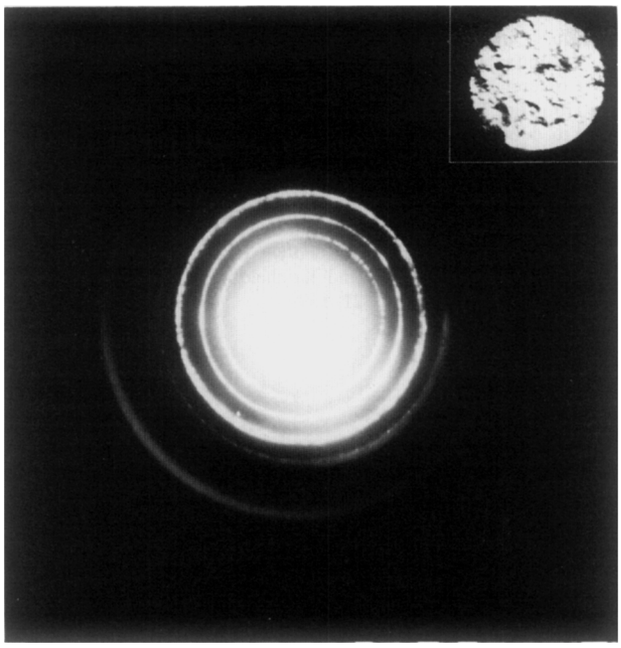

Figure 5 E.d. pattern and selected area of P*p*OBA aggregate material as in *Figure 4d*. The inner ring corresponds to 200 (phase II), the second ring to 110 (phase I), the third (split) to 200 (I), 110 (II). The diffuse outer ring is platinum

thick, with some fragments of single lamellae 100 Å thick. The lamellae in *Figure 4c* (32 h polymerization time) are ~100 Å thick. Thinner lamellae (~70 Å) develop as sheaves at the centres or at re-entrant faces (arrows). Regions of the dispersion containing larger clusters are shown in *Figure 4d*. This material also appears to be lamellar, with a somewhat greater thickness than the well-dispersed material.

In our limited studies to date of the bulk polymerization of ANA (at 200°C), the d.s.c. and *FT*i.r. results are similar to those reported here for ABA; i.e. the sublimate is identical to the monomer, the 'melt' has low intensity i.r. bands representative of the polymer, and the acetone extracted polymer (after 24 and 48 h) shows nearly complete transformation of the acetoxy and carboxy C=O stretch bands to the ester band. The d.s.c. first scan of the polymer has, as for P*p*ABA, a broad low temperature peak, here below 200°C, and a peak in the range 300–350°C. In second scans the low temperature peak is absent. Micrographs indicate a lamellar texture (phase I) with somewhat thinner lamellae than for P*p*OBA.

DISCUSSION AND CONCLUSIONS

Both *p*ABA and ANA can be polymerized in the bulk at temperatures below their nominal melting point as measured by d.s.c. Melting actually occurs, however, as shown both by optical microscopy and visual observation. We suggest that the melting, observed below the d.s.c. T_m, is accompanied by a chemical reaction. If the portion of the tube containing the sublimed material is lowered into the bath, it also will 'melt'; clearly the large, relatively perfect crystals formed during the sublimation/recrystallization process should not melt below the melting point of the (initially) powder in the d.s.c. if they are still *p*ABA, even considering the differences in heating rate. Similar polymerization below the melting points in constrained thin films, also occurs in all of the homo- and copolymers listed in the introduction.

The rate of polymerization in the thin films is significantly faster for a given temperature, than in the bulk. This is attributed to catalysis by the glass surface. The enhancement of the rate by adding glass beads to the bulk is in agreement with this suggestion. It is noted that the process described by Calundann and Jaffe[11] for the typical melt polymerization of a *p*ABA/ANA copolymer involves an initial heating step at 200°C with a clear melt being formed; this is above the T_m of *p*ABA but below that of ANA. Although not discussing the nature of this melt, they indicate acetic acid as being given off and polymerization occurring when this melt is heated to higher temperatures, e.g. 250–280°C for 1–3 h followed by heating at 280–350°C under vacuum for 10–60 min. In our studies, acetic acid is given off even at 180 or 200°C. *FT*i.r. shows that products forming the 'melt' have ester bands, but that significant acetoxy and carboxy groups remain. The material formed in the melt, as it is held isothermally, is at least partially of relatively low molecular weight, but, as pointed out above, it is believed that high molecular weight material is also present.

Morphological examination of the resulting P*p*OBA polymer shows that it is composed of lamellar single crystals on the order of 100 Å in thickness, with the chains normal to the lamellae. As in the case of the lamellar crystals grown in constrained thin films[1–9], the thickness presumably corresponds to the length of the molecules, although end-linking across the lamellar interfaces is possible if the correct end groups are in juxtaposition. Inasmuch as the normal polymerization process for these homopolymers is carried out in heat transfer fluids at temperatures above 300°C, purportedly to permit chain extension in the liquid crystal state by end-linking of oligomer molecules forming the crystals[16], polymerization at these low temperatures is unexpected. Of interest, and still under investigation, are both the effects of longer times and higher temperatures and the origin of the persistent observations of ~100 Å thick lamellae in the as-polymerized extended chain crystals of the various liquid crystal polymers and copolymers[1–9]. As in the case of the constrained thin film studies[1,2,4,5] we conclude that, for the temperatures described above, the polymerization process is occurring by an isothermal sublimation–recrystallization–melting (chemical reaction)–polymerization–liquid crystal domain formation–crystallization process. Although it is possible that polymerization/crystallization occurs until the crystal–liquid crystal transition temperature ($T_{c\text{-}lc}$) rises to the polymerization temperature, a 100 Å thickness for P*p*OBA corresponds to a *DP* of 16, for which $T_{c\text{-}lc}$ is greater than 280°C (ref. 13).

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