

Epitaxial growth of poly(*p*-oxybenzoate) crystals on crystalline substrates

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We report the epitaxial polymerization and characterization of poly(*p*-oxybenzoate) (POBA) on various crystalline substrates. Acetoxybenzoic acid was polymerized onto solid crystalline substrates immersed in the paraffin solution. The resulting POBA films were characterized by polarized Fourier transform infra-red spectroscopy, transmission electron microscopy, scanning electron microscopy, wide-angle X-ray diffraction, and electron diffraction. The morphology of the POBA films was found to depend on the polymerization conditions and crystal structures of substrate. On single-crystal mica and KBr substrates, POBA films formed layer-like structures with their crystal *c*-axes (chain axis) parallel to the substrate surface with azimuthal orientations. On polycrystalline gold, the POBA film consisted of lamellae standing with the *c*-axis parallel to the gold surface. For all of the above substrates, a small disturbance (light shaking of the reaction flask) at the beginning of the reaction results in POBA lamellar morphology with the *c*-axis vertical to the surface, showing that early-stage nucleation determines morphology and orientation of the POBA crystal growth. Copyright © 1996 Elsevier Science Ltd.

(Keywords: poly(*p*-oxybenzoate); epitaxial crystal growth; *in situ* polymerization)

INTRODUCTION

Epitaxy is a nucleation and growth relationship between two crystalline phases, in which one crystalline phase (the guest phase) intergrows in a structure-dependent manner onto an already existing crystalline phase (the host phase). Between the two crystalline phases is a heterogeneous interfacial region^{1–3}. Epitaxial polymerization is a phenomenon in which macromolecules crystallize onto a solid crystalline substrate during the polymerization process⁴. Many polymerization processes have been used for epitaxial growth, including free radical, anionic, cationic, and polycondensation reactions^{4–6}. One caution in choosing a polymerization process is that the components or by-products in the system beside the monomer and solvent may contaminate the substrate crystal lattice. So far, most of the polymers that have successfully formed epitaxial films possess flexible chain structures.

We present here an attempt to grow epitaxial films of poly(*p*-oxybenzoate) (POBA), a polymer with totally rigid rod-like-chain structure, onto various crystalline substrates. Because many polymers that possess potential non-linear optical and non-linear electronic applications have rigid π -conjugated chain structure, the processibility is always a great concern. Often rigid chain structure has to be chemically modified to obtain processable polymers. Epitaxial polymerization may offer an alternative solution for the problem.

POBA is one of very few rigid chain polymers which are able to form needle-like whisker crystals during *in situ*

polymerizations^{7–10}. Two crystalline phases are known to exist in the POBA crystals at room temperature. The crystal lattice of phase I is orthorhombic with lattice dimensions of $a_1 = 7.5 \text{ \AA}$, $b_1 = 5.6 \text{ \AA}$, and $c_1 = 12.6 \text{ \AA}$. The lattice constants of another crystal modification (phase II) are $a_2 = 11.2 \text{ \AA}$, $b_2 = 3.8 \text{ \AA}$, and $c_2 = 12.6 \text{ \AA}$. The proposed molecular packings in the two phases have been further corrected by a total energy calculation⁹. The crystal–liquid crystal and liquid crystal–liquid transitions (T_{c-1c1} and $T_{1c1-1c2}$) are normally at 340°C and 430°C, respectively, although T_{c-1c1} drifts to lower values and is molecular-weight-dependent when the average degree of polymerization (DP) is below 100¹¹.

POBA is neither soluble in most of the organic solvents nor dissolvable before decomposition starts. For the purpose of making a thin film sample for electron microscopy observation, the Lin and Geil group described a technique using *in situ* polymerization⁷. A thin layer of 4-acetoxybenzoic acid solution was sandwiched between two glass plates, which were clipped together and then immersed in the reaction solution before proceeding with the polymerization. The resulting POBA crystals grown on the amorphous glass plates arranged themselves with the *c*-axis (chain axis) vertical to the glass surface ('standing up').

In this work, it was found that when solid crystalline substrates were placed in the reaction solution, under certain conditions POBA crystals grew with the *c*-axis parallel to the substrate surface. The focus of this work is on the interfacial orientation profiles of the POBA crystals. The characterization was done by polarized Fourier transform infra-red (FTi.r.) spectroscopy, transmission

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electron microscopy (TEM), scanning electron microscopy (SEM), and wide-angle X-ray diffraction (WAXD).

EXPERIMENTAL

4-Acetoxybenzoic acid was recrystallized from butyl acetate. Paraffin oil was vacuum-distilled before use. Mica and potassium bromide (KBr) were freshly cleaved under a nitrogen atmosphere before each reaction. The gold substrate was prepared by vacuum deposition of a thin layer of gold on a glass plate.

Polymerizations of 4-acetoxybenzoic acid were conducted in a paraffin oil solution. The reaction flask was equipped with an argon inlet and an argon outlet, which was then connected to a condenser. In a typical reaction, 4-acetoxybenzoic acid (1.5 g/160 ml ratio to the solvent) and substrates were added to the paraffin solvent. The suspension was diluted with diethyl ether, filtered, extracted with diethyl ether and finally dried in a vacuum oven at 100°C for 4 h.

Table 1 shows the reaction condition and relative thickness of each sample. Samples 1 and 3–7 were prepared at 320°C. In the case of samples 8–10, the solution flask was lightly shaken until the monomer melted and then the temperature was raised to 320°C and held at 320°C for about 7 h without such disturbance. A slow flow of argon gas was passing over the system before the temperature reached 320°C and was flushed over the solution surface throughout the reaction.

Thermal transitions of POBA were observed by differential scanning calorimeter (d.s.c.) measurement.

The thickness of one POBA film on a mica substrate was measured mechanically using a Tencor Alpha-step 300.

The polarized FTi.r. spectra were obtained with a Bio-rad FTS-60A/896 FTi.r. spectrometer equipped with a wire-grid polarizer. Samples on smaller substrates such as KBr were characterized by FTi.r. microspectroscopy. Samples on gold were measured by the specular reflection method.

The morphology of the POBA crystals on the substrates was observed with a TOPCON DS-720 SEM. The sample surface was coated with Pd–Pt

before observation. The morphology of the thin samples was also observed, with a Zeiss CEU-902 TEM, equipped with a Casting–Henry electron energy filter. The accelerating voltage was 80 kV.

Wide-angle X-ray diffraction (WAXD) was performed with a Rotaflex RU-300 X-ray diffractometer (Rigaku Co. Ltd). The WAXD profile was obtained by the reflection method. The WAXD intensity was measured as a function of the scattering angle 2θ (θ : Bragg angle), at the fixed incident angle, $\theta = 1^\circ$.

RESULTS

With crystalline substrates immersed in the reaction solution, POBA crystals grew epitaxially onto the single-crystalline substrates forming layer-like structure with azimuthal orientations. In comparison, POBA crystals had a lamellar morphology on the polycrystalline substrate. The crystal structure of POBA belonged to phase I, which is favoured by high-temperature reaction.

From the d.s.c. diagram, T_{c-jc1} occurred at 350°C, which indicates that DP was above 90 or 100 repeat units¹¹. However according to the well-established polymerization mechanism of POBA¹², POBA oligomers with DP of 6–8 precipitate out of the solution and their molecular weights continue to increase in the solid state by transesterification. Therefore, the morphology of epitaxially grown crystals could influence the actual DP in each case.

Mica

Mica ($KAl_2(AlSi_3O_{10})$) has a layered structure. A freshly cleaved mica surface typically consists of a sheet of oxygen atoms in pseudo-hexagonal symmetry which is bonded to an underlying layer of silicon atoms¹³. The distance between two adjoining oxygen atoms is roughly from 2.6 to 2.8 Å^{14,15}. A schematic structural configuration of the mica surface is shown in Figure 1. A crystal lattice of mica is monoclinic with a rectangular ab plane parallel to the surface where the [100], [110], and $[1\bar{1}0]$ axes are parallel to the three edges of the pseudo-hexagonal symmetry. The $[hkl]$ axis points to the coordinate hkl from the origin in the unit cell. The directions of the mica crystal-axes a and b in each sample were determined by WAXD with azimuthal angle scanning at a fixed Bragg angle, $2\theta = 19.8^\circ$.

Table 1 Reaction condition and film thickness

Sample no.	Substrate	Reaction condition	Film thickness (nm)
1	mica	320°C, 7 h	thin ^a
2	mica	270°C, 10 h	150–200
3	mica	320°C, 7 h	300–400 ^b
4	KBr	320°C, 7 h	thin ^a
5	KBr	320°C, 7 h	110–150
6	KBr	320°C, 7 h	470–640
7	gold	320°C, 7 h	1000–1370
8	mica	230°C, 1 h, shaking	190–250
9	KBr	230°C, 1 h, shaking	170–230
10	gold	230°C, 1 h, shaking	940–1200
		320°C, 7 h	

^a The film is so thin that the thickness cannot be determined

^b The film thickness of sample 3 was measured mechanically, while the rest of the samples were related to sample 3 by absorption peak ratio of FTi.r. spectra

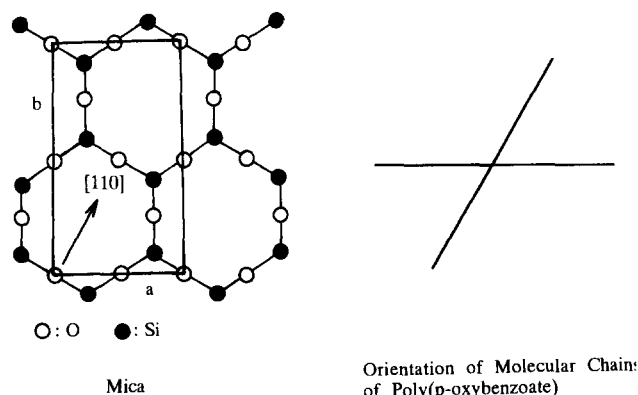


Figure 1 Oxygen ion network structure on the mica (001) plane¹⁵, and orientation of the c -axis of POBA crystals relative to the mica crystal lattice: (○) oxygen; (●) silicon; (a), (b) crystal axes of mica

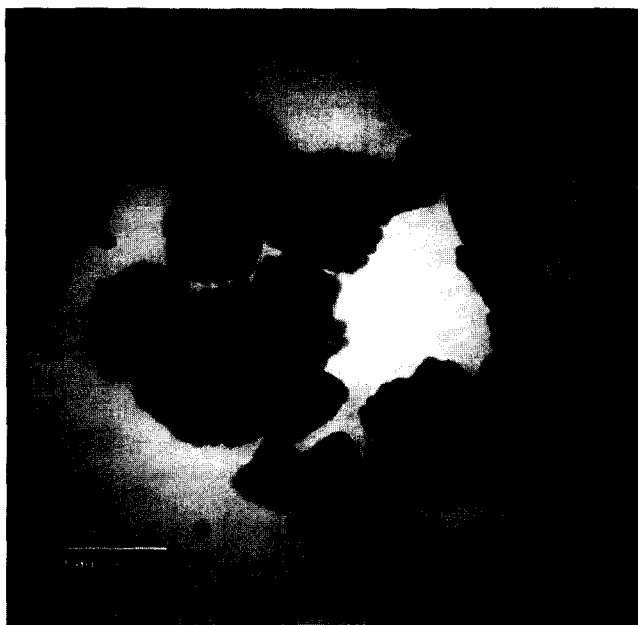


Figure 2 TEM photograph of sample 1 (mica)

Sample 1 was very thin due to the low initial monomer concentration (0.11 g/116 ml, monomer to solvent ratio). A TEM photograph of sample 1 in Figure 2 shows that many triangular single-crystal nuclei grew epitaxially on mica. Some of the outskirts of the triangles were outgrown with rugged crystal growth.

Samples 2 and 3 were prepared at 270°C and 320°C, respectively, with a film thickness ratio of about 2 according to the FTi.r. peak ratio estimation (Table 1). The polarized FTi.r. spectra of sample 3 are shown in Figure 3. The FTi.r. spectra of sample 2 are similar to those of sample 3. Some absorption bands, which are dependent on chain orientation, are categorized into groups of parallel bands and perpendicular bands, respectively, depending upon whether absorption happens when polarization of the i.r. beam is parallel to the polymer chain or is perpendicular to the chain. The absorption bands at 1599 cm⁻¹, 1510 cm⁻¹, 1414 cm⁻¹ and at 1258 cm⁻¹ are parallel bands, whereas the absorption bands at 1272 cm⁻¹, 1227 cm⁻¹ and 1089 cm⁻¹ are perpendicular bands. As seen in Figure 3,

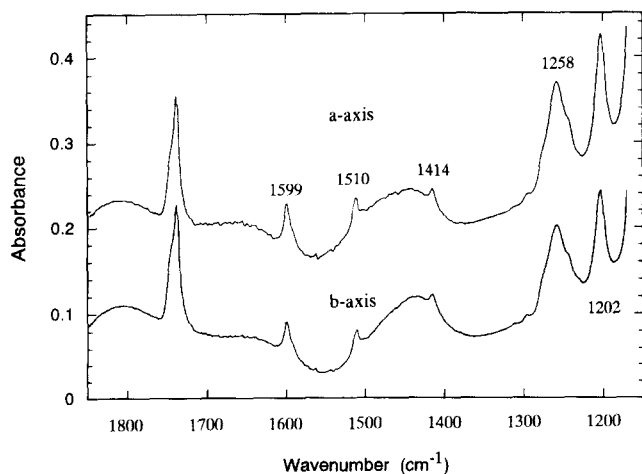


Figure 3 Polarized FTi.r. spectra of sample 3 (mica). The polarization is parallel to the *a*-axis (upper) and the *b*-axis (lower) of mica

the perpendicular bands at 1272 cm⁻¹ and 1227 cm⁻¹ are weak compared to the parallel bands at 1258 cm⁻¹, 1599 cm⁻¹, and 1414 cm⁻¹. Thus POBA crystals grew with the *c*-axis (chain axis) parallel to the substrate surface.

SEM photographs of samples 2 and 3 are shown in Figure 4. Crystals align mostly along the [100] and [110] axes of mica. The relation between the crystal structure of mica and POBA molecular chains is shown in Figure 1. However a TEM micrograph of sample 3 in Figure 5 shows clearly a weak third orientation of the crystals along the [1 $\bar{1}$ 0] axis of mica in addition to the strong orientations along the [100] and [110] axes. The morphological difference between the two samples is obvious: the domains of sample 2 are like small chip flakes networked together mostly in the directions of the [100] and [110] axes of mica, while the domains of sample 3 are like relatively large and long ribbons. Probably, transesterification in the solid state near the surface in sample 2 was not totally completed and therefore some low-molecular-weight portions in sample 2 had been washed away by ether extraction after polymerization. In general, it was found that the average size of POBA domains increased with the film thickness.

An electron diffraction (ED) pattern of sample 2 in Figure 6 shows 110 and 200 reflections in addition to the 002, 004 and 006 reflections of the POBA crystal. The intensity of the 200 reflection is much stronger than that of the 110 reflection in sample 2, but the intensity difference is not distinguishable in sample 3. WAXD 2 θ scans of the two samples are presented in Figure 7, which

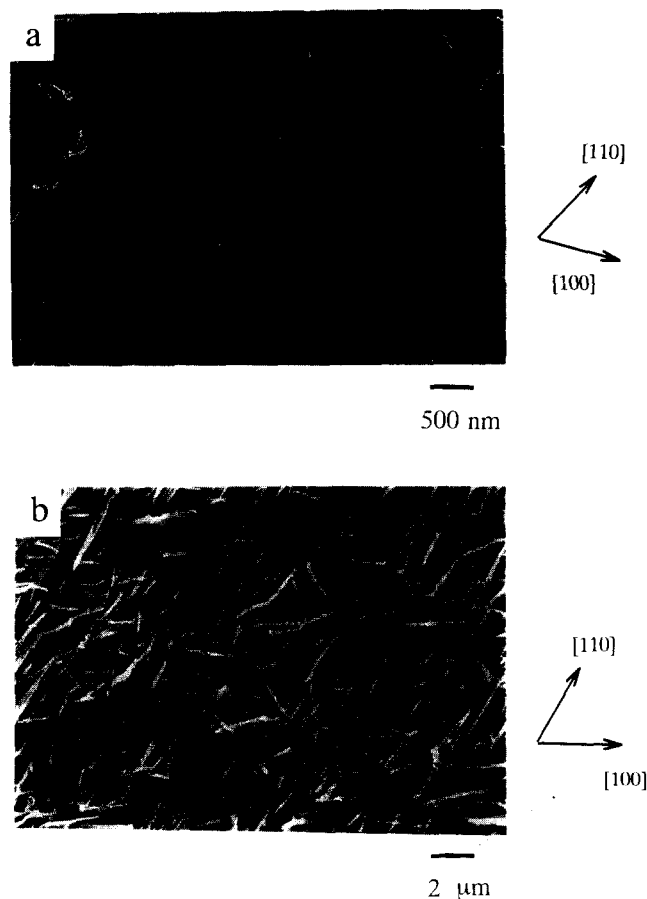


Figure 4 SEM photographs of POBA crystals on mica: (a) sample 2; (b) sample 3

are consistent with previously reported X-ray 2θ scans of POBA whisker crystals¹⁶. In the WAXD profiles, the 110 reflection in sample 2 is stronger than the 200 reflection, contrary to the results of ED, suggesting that the (100) plane tends to be perpendicular to the substrate surface in sample 2.

Potassium bromide (KBr)

A KBr single crystal has an fcc structure with the lattice dimension of 6.57 Å (see Figure 8). Structurally, K and Br atoms arrange in alternating positions in the lattice. Cleaving a KBr single crystal often leads to a stepped crystal-surface structure. The crystal axis of KBr

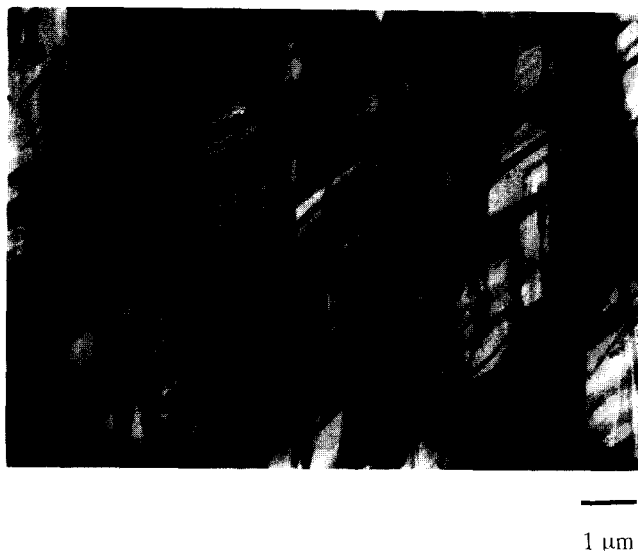


Figure 5 TEM photograph of sample 3 (mica)

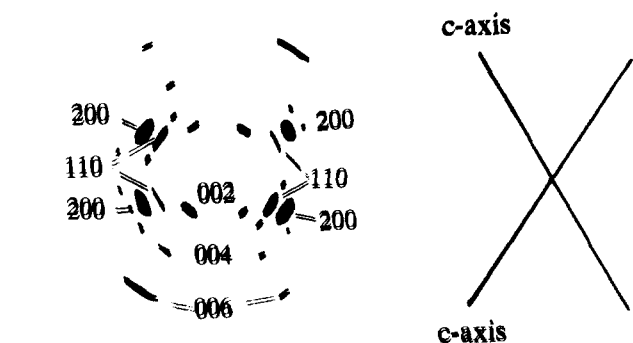
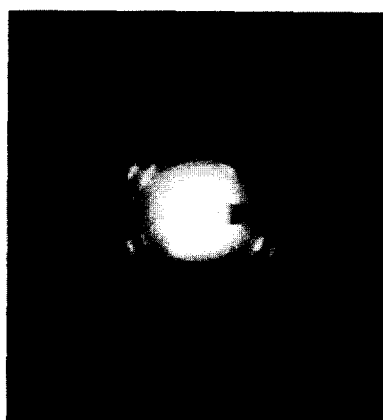


Figure 6 ED pattern of sample 2 (mica)

in each sample was determined by WAXD with azimuthal angle scanning at a fixed angle, $2\theta = 27.15^\circ$.

Three samples of POBA films on KBr single crystals, prepared under the same reaction conditions but with different initial monomer concentrations, are presented.

An SEM photograph of sample 4 (KBr) is shown in Figure 9a. As seen in the photograph, POBA crystal-clusters with dimensions of about 500 nm are scattered on the KBr substrate, leaving much KBr bare space uncovered. Each POBA cluster, often in a shape similar to an upside-down rowing-boat with one or two junction lines perpendicular to the long axis of the domain, aligns in one in-plane direction. Apparently, the junction lines mark slight change of orientation in the vertical direction. Some two or three clusters overlap each other, growing independently without much orientation correlation. From thermodynamic considerations, it does not seem here that epitaxial crystal-growth of POBA on KBr is much favoured as a process to minimize the total free surface-energy¹.

An SEM photograph of sample 5 (KBr) is shown in Figure 9b. This photograph shows long crystals with a

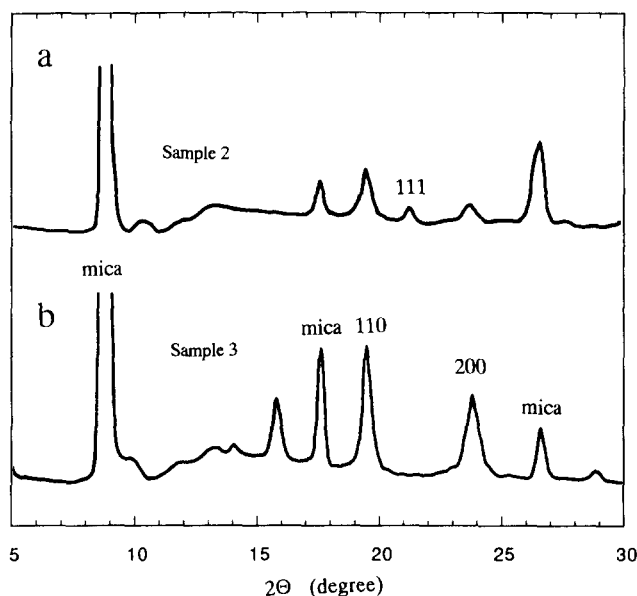


Figure 7 WAXD 2θ scans of POBA crystals on mica: (a) sample 2; (b) sample 3

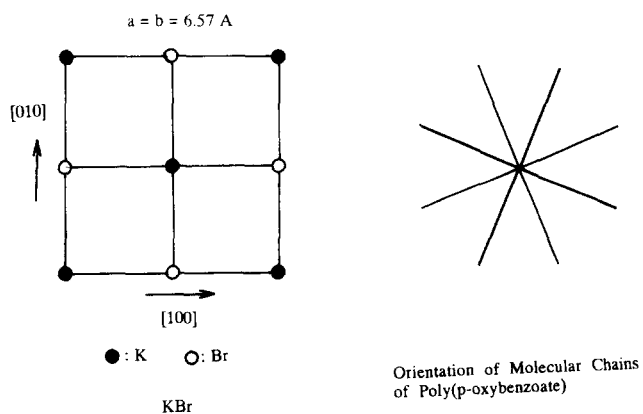


Figure 8 KBr crystal lattice and the orientation of the POBA *c*-axis relative to the KBr crystal lattice

consistent width of 150 or 160 nm formed on top of small domains. The long axis of the crystals is distributed in four directions, each at 22.5° angle with one of the crystal axes of KBr (see Figure 8). The thickness of the long crystals is rather small and uniform as seen in the photograph. Obviously, POBA crystals achieved three-dimensional epitaxial growth on KBr single crystals. The FTi.r. spectrum of this sample is shown in Figure 10, indicating an in-plane orientation of the molecular chain of POBA crystals.

The SEM photograph of the rather thick sample 6 (KBr) shown in Figure 9c indicates a relatively uniform coverage. Consistent with the crystal orientation of sample 5, POBA crystal-ribbons remain oriented in four directions each at 22.5° from one of the KBr crystal axes coplanar with the surface. The crystal *c*-axis is expected to be either parallel or normal to the long axis of ribbons. Yamashita *et al.* studied the morphology of POBA whiskers and reported that the molecular-chain-axis coincided with the long axis of POBA whiskers¹⁷. The ribbon-like morphology of POBA crystals on KBr resembles the reported morphology of POBA whiskers and thereby the parallel orientation of the crystal *c*-axis

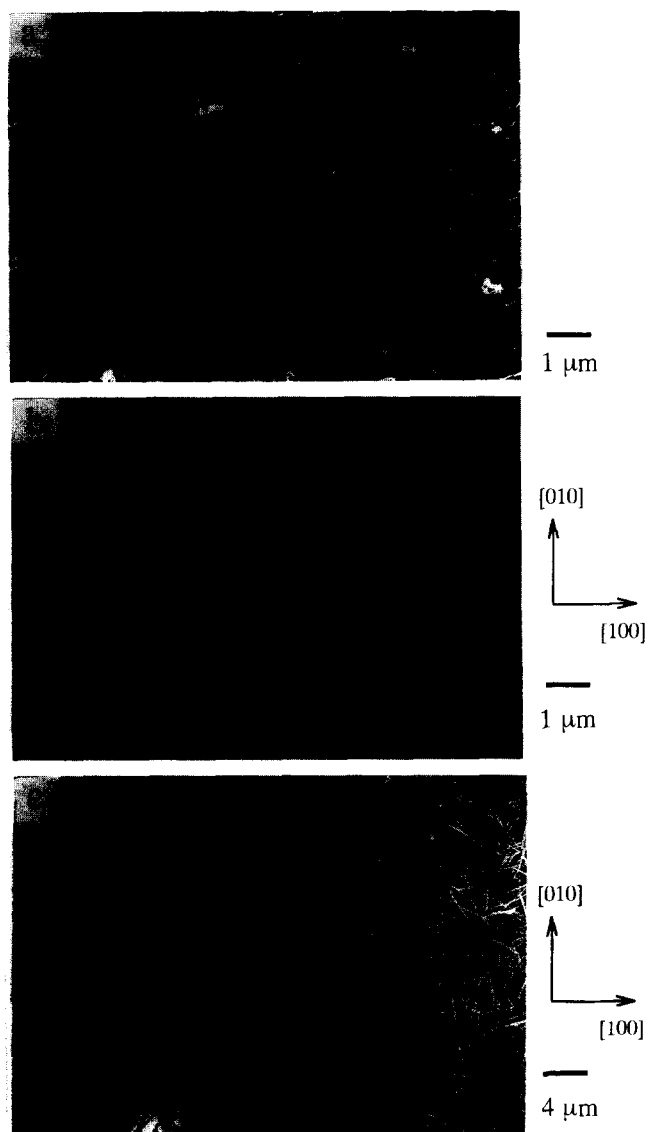


Figure 9 SEM photographs of POBA films on KBr: (a) sample 4; (b) sample 5; (c) sample 6

in the ribbons is considered to be more probable than the normal orientation.

An ED pattern of sample 6 in Figure 11 shows relatively strong 110 reflections, which are in contrast to the very weak or missing 200 reflections, in addition to the 002 and 006 reflections. Each reflection exhibits eight spots along the azimuthal direction, suggesting that the crystal *c*-axis is distributed in the four directions forming 45° angles from each other. Figure 12 shows a WAXD 2θ scan of sample 6, which is measured by the reflection method. The 200 reflection is observed more strongly than the 110 reflection in the WAXD profile. The results of ED and WAXD suggest that the (100) plane orients parallel to the substrate surface.

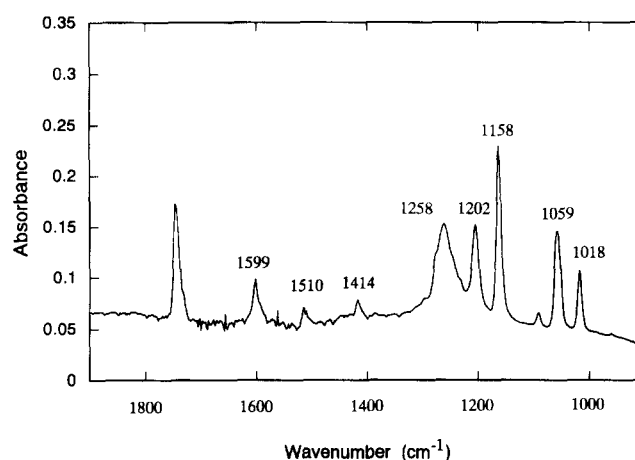


Figure 10 FTi.r. spectra of sample 5 (KBr)

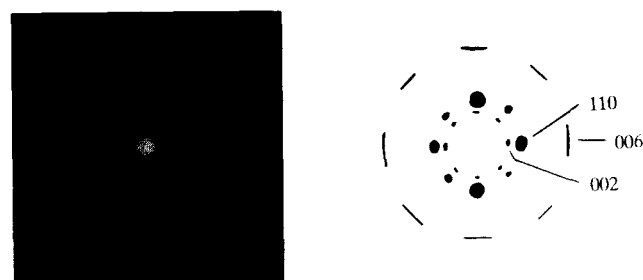


Figure 11 ED pattern of sample 6 (KBr)

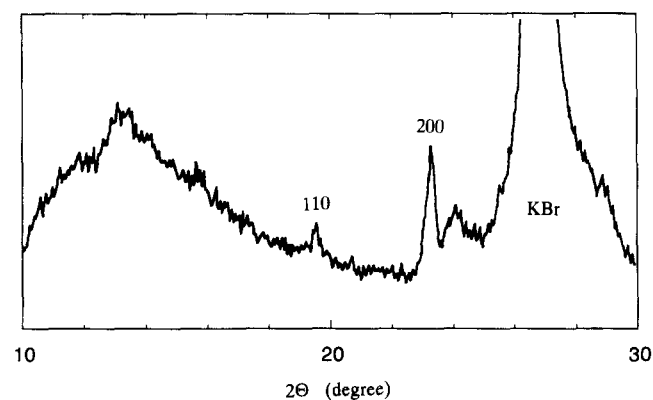


Figure 12 WAXD 2θ scans of sample 6 on KBr

Gold

The crystal structure of gold is an fcc with the lattice dimension of 4.0786 Å. Because the gold substrate used in this work was prepared by vapour deposition on amorphous glass, the gold substrate is polycrystalline. The surface of the substrate is smooth optically, but granular microscopically.

An SEM photograph of sample 7 (gold) is shown in Figure 13. As seen, the morphology of the POBA crystals is lamellar with rough or bumpy surfaces in contrast to the smooth surfaces of the POBA films in the above cases. It is believed that the POBA chain axis is vertical to the lamellar surface. Some lamellae are bilayered: sample 7 is similar to the sample of the Geil group which was prepared at 300°C for 1.5 h with a monomer solution sandwiched between two amorphous glass plates⁷. The FTi.r. spectrum analysis in Figure 14 indicates that some of the crystals aligned with the polymer chain axis (*c*-axis) parallel to the surface with random azimuthal orientation. Thus a lot of the lamellae was standing up on the gold surface. The in-plane orientation of the POBA *c*-axis is probably influenced by the crystal lattice of the gold substrate.

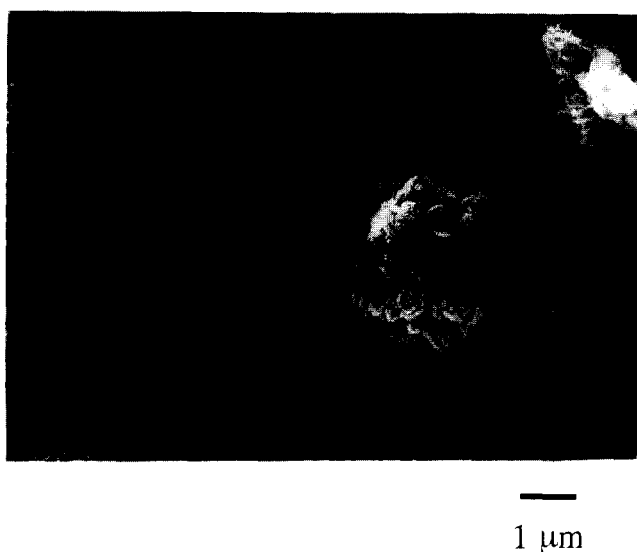


Figure 13 SEM photograph of sample 7 (gold)

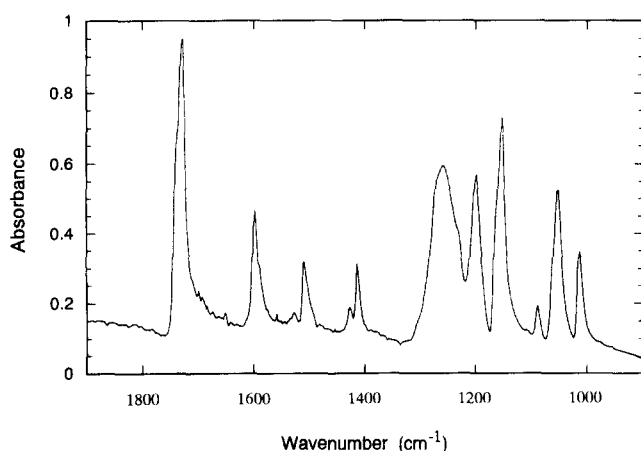


Figure 14 FTi.r. spectrum of sample 7 (gold)

Effects of shaking on the morphology of POBA crystals

A series of reactions were carried out at 230°C for 1 h with constant gentle hand-shaking of the flask before raising the temperature to 320°C (samples 8–10). The FTi.r. spectra of samples 8–10 are shown in Figure 15. The perpendicular bands (1272 cm⁻¹, 1227 cm⁻¹, 1089 cm⁻¹) are observed strongly in the spectra. Thus the POBA crystals aligned with the chain axis vertical to the surfaces for all of the above substrates. The SEM photographs of samples 8–10 (shown in Figure 16) show the lamellar morphology, which is not observed for samples 1–6. It is of interest to compare the two SEM photographs (Figure 13 and Figure 16c) of POBA on gold substrates. Their lamellar morphologies are similar,

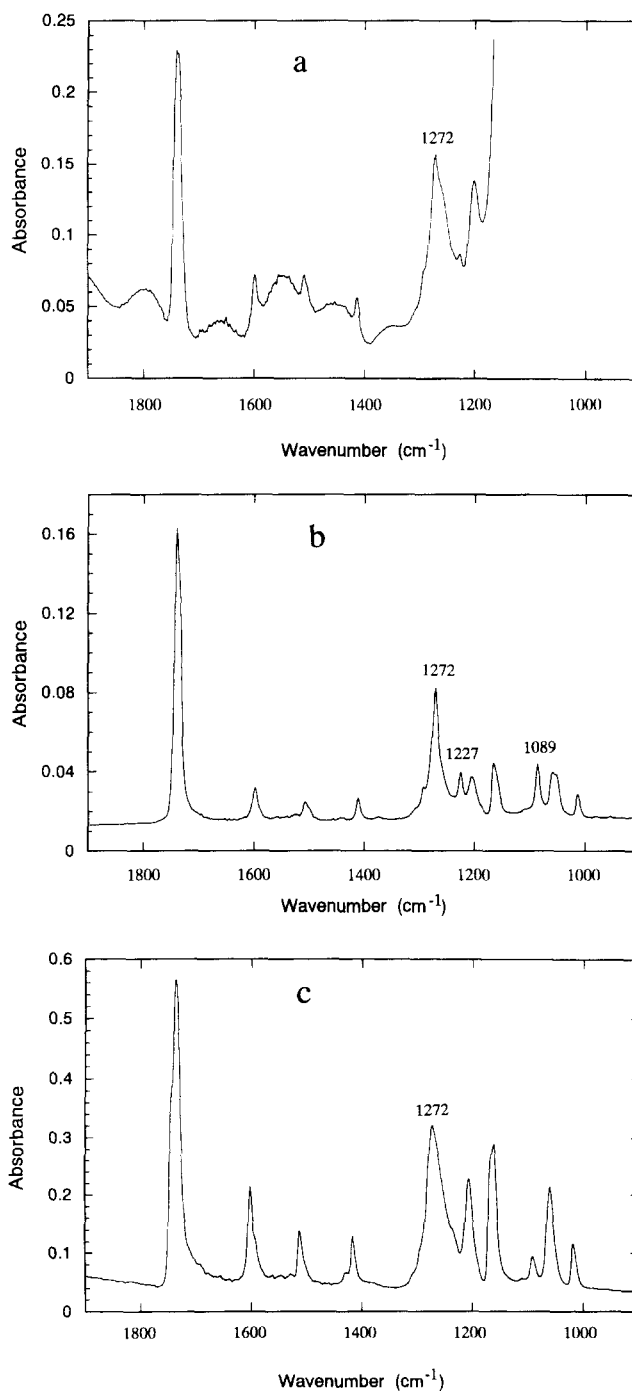


Figure 15 FTi.r. spectra of POBA films prepared under shaking at 230°C: (a) sample 8 (mica); (b) sample 9 (KBr); (c) sample 10 (gold)

but the average orientation of lamellar surface is different from each other. Sample 7 prepared without hand-shaking exhibits flower-like morphologies in which lamellar surfaces tend to stand up on the gold substrate (Figure 13). On the other hand, we observe some lamellar surfaces oriented parallel to the substrate surface (Figure 16c), besides the flower-like structure, for sample 10 prepared with hand-shaking. As the *c*-axis of POBA is reported to be normal to the lamellar surface⁸, molecular chains in sample 10 are expected to be perpendicular to the substrate, as compared with those in sample 7. The result of SEM observation is consistent with the result of FTi.r. spectra that the absorption intensity of the perpendicular bands is stronger in the spectrum of sample 10 than in the spectrum of sample 7.

In order to examine whether or not the crystal growth could have been influenced by the reaction temperature, another reaction was carried out at 230°C without hand-shaking for comparison. The result shows that these POBA crystals formed layer-like structures with their chain axis aligning parallel to the surfaces of the above

substrates, as found in samples 1–7. Therefore the difference in morphology and orientation of POBA crystal is totally due to the disturbance by the hand-shaking at the beginning of the reaction.

DISCUSSION

The polymerization conditions for this set of experiments were identical to those in which POBA crystal whiskers grew in a pattern that resembled the pseudo-hexagonal spiral growth¹⁷. In the work reported here, the crystal lattices of the substrates in the reaction system strongly influenced the morphology of the POBA crystals. On the single-crystalline substrates of mica and KBr, POBA grew epitaxially with azimuthal orientations. The orientations retained even beyond the first few layers of the coverage where POBA crystals could not 'feel' the substrate, a phenomenon usually observed for epitaxial growth of small molecules¹. On the polycrystalline gold substrate, some of the POBA crystals still grew with the *c*-axis parallel to the substrate surface as characterized by FTi.r. In comparison, shaking of the reaction flask at an early stage of the reaction totally eliminates the epitaxy-induced orientations of the POBA crystals and consequently results in a lamellar crystal morphology. These observations lead to the conclusion that the early-stage nucleation determines the morphology and orientation in the following POBA crystal-growth.

Nucleation in epitaxial growth may generally be described as either two-dimensional (2D) mode or three-dimensional (3D) mode, depending on whether the substrate is covered with a monolayer of epitaxially grown crystals before proceeding to homogeneous crystal-growth, or has 3D epitaxial nuclei formed directly on the substrate. A high adhesion-energy between the two phases is critical for 2D-epitaxial growth. An atomic force microscopy (AFM) study of sample 1 (a POBA thin film on the mica substrate) to be discussed in our following paper, suggests a strong possibility of 2D-epitaxy-monolayer formation of POBA on mica. The 3D-nucleation domains further grew on the top of the uniformly formed 2D-epitaxy-monolayer (see Figure 2), so-called Stranski–Krastanov growth mode¹⁸. As shown in Figure 9a, POBA on a KBr single-crystal substrate unequivocally formed 3D clusters in the initial crystallization stage. The epitaxy growth is revealed in relative thick films (see sample 5 in Figure 9b), where the *c*-axis of POBA crystals formed angles of 22.5° with the axis of the KBr crystal. Considering that the KBr substrate had a stepped surface with edges along the crystal axis as a result of cleaving, the apparent phobic feature in the case of the KBr substrate could be attributed partially to the stepped surface. Generally, on both mica and KBr single-crystal substrates, 3D-epitaxial nucleation domains grew, coalesced, and were followed by overlayer growth of relatively large crystal domains. On SEM photographs of less thick samples on mica and KBr substrates, bumps or 'germs' are often noted underneath the crystal films.

It was found that the domain size of POBA crystals on both mica and KBr substrates increased with the average film thickness. It is common knowledge that elevated temperature and dilution of solution normally lead to large-crystal growth. In our case, POBA oligomers precipitate out of solution before crystallizing. Thus

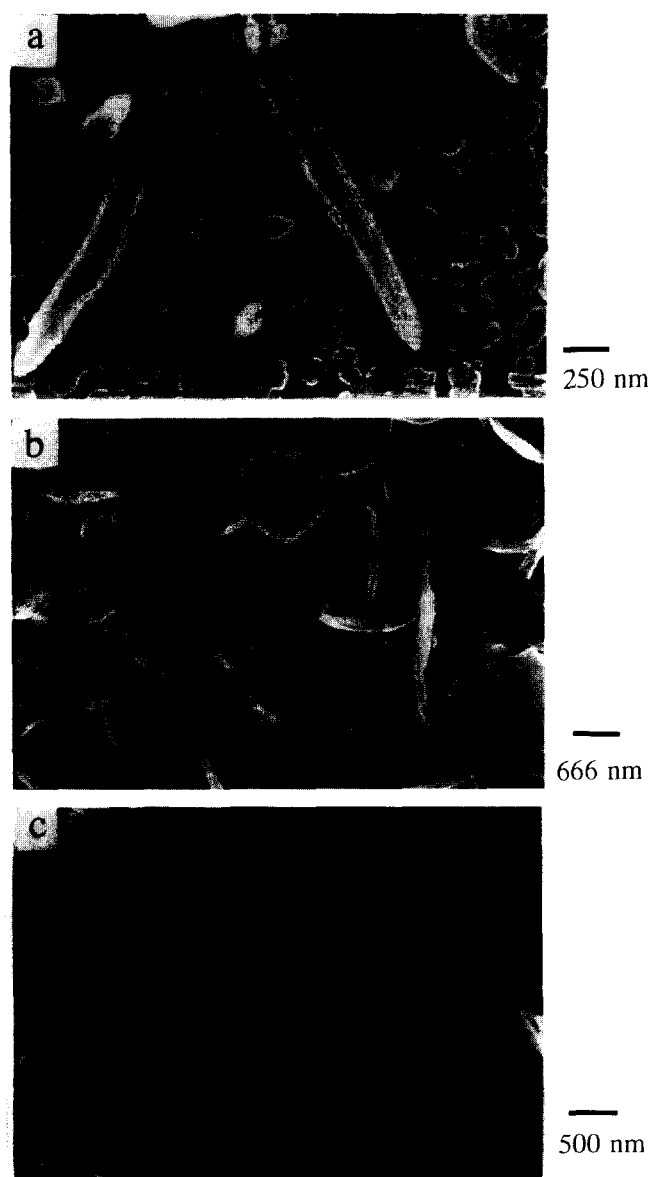


Figure 16 SEM photographs of POBA films prepared under shaking at 230°C: (a) sample 8 (mica); (b) sample 9 (KBr); (c) sample 10 (gold)

the degree of saturation of the POBA oligomer solution is practically a function of the reaction rate. As the reaction proceeds, the monomer is gradually consumed and the reaction slows down, which is equivalent to a decrease of the oligomer concentration. As a result, the average domain size increases with the reaction time. There is another possibility that the actual reaction temperature has played a role in influencing the POBA domain size, as we recall that the reaction had already started at 230°C, 40 min before the temperature reached the final 320°C. Therefore the change of the temperature as well as the accompanied reaction-rate change may have affected the domain size. Normally for polycondensation of acetoxybenzoic acid at 320°C, a complete conversion only takes about 10 min, although the reaction-rate decreases exponentially with the temperature¹⁹.

One aspect of studying epitaxial crystal growth is to identify the interfacial crystal-contact-plane. So far we have found the relative orientation of the *c*-axis of the POBA crystals to the crystal lattice of the substrates. In the case of a mica substrate, the *c*-axis of POBA orients along the edges of the pseudo-hexagonal oxygen arrays. The periodicity of one unit of the POBA *c*-axis measures two and a half times the length of the *a*-axis of mica crystal (the relative mismatch = 3.4%). Unfortunately, the ED patterns of samples 2 and 3 (mica) cannot provide information about which POBA crystallographic plane to be the interfacial contact plane for the mica substrate. In the case of a KBr substrate, the *c*-axis of POBA crystals forms an angle of 22.5° with the crystal axes of KBr. One unit of the POBA *c*-axis spans 89% of two units of the KBr unit cell. The large mismatch suggests that the lattice matching is not always critical in the epitaxial growth. The ED pattern of sample 6 (KBr) as well as X-ray data indicates that the (100) crystal plane of POBA crystal is predominantly parallel to the KBr surface. Thus there is a strong possibility that the POBA (100) plane is the interfacial contact plane, presuming that most of the crystal planes retain their azimuthal orientations during the crystal growth and that the crystal orientation is uniform in the direction of the film thickness.

CONCLUSION

By *in situ* polymerization, POBA crystals intergrow on the crystal lattice of the substrates with azimuthal orientations. The nucleation or the early-stage crystallization determines the overall crystal morphology and orientation. Thus the polymerization condition and crystal morphology of the substrate are critical in determining the existence and morphology of epitaxial crystals.

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