Epitaxial Polymerization of Poly(*p*-oxybenzoate) on Friction-Transfer Poly(tetrafluoroethylene) Substrates

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Received July 14, 1997; Revised Manuscript Received September 23, 1997⊗

ABSTRACT: Epitaxial polymerization/crystallization of poly(*p*-oxybenzoate) (POBA) from *p*-acetoxybenzoic acid vapors on friction-transferred PTFE substrates is demonstrated. Depending on the reaction conditions, two different morphologies are observed. At low temperatures (180 °C $< T <$ 210 °C) and short reaction times, highly oriented and uniform thin films are formed, while at higher temperatures and/or longer reaction times, small crystallites grow and orient on top of the POBA films formed initially. Both morphologies correspond to phase II of POBA. The composite electron diffraction patterns of the PTFE/low temperature deposit clearly show that the POBA thin films grow epitaxially, the $(100)_{\mathrm{POBA}}$ plane contacting the $(010)_{\mathrm{PTFE}}$ substrate surface. This epitaxy is achieved with a very good lattice mismatch of 0.4%, corresponding to the difference between the b_{POBA} and a_{PTFE} cell parameters. The POBA crystallites/POBA film mutual orientation with $(001)_{\mathrm{crystallite}}//(100)_{\mathrm{film}}$ and $[010]_{\mathrm{crystallite}}//[010]_{\mathrm{film}}$, is analyzed in terms of POBA homoepitaxial interactions.

Introduction

Poly-*p*-oxybenzoate (POBA) is a rigid-rod, fully aromatic polymer which has attractive high-temperature properties but which, owing to its chemical structure, is highly insoluble and nonmeltable. Therefore, most of the structural and morphological investigations performed up to now are on as-polymerized POBA powders or single crystals. According to G. Lieser[1] and P. Iannelli and D. Yoon,[2] two crystal modifications called phase I and phase II coexist at room temperature, the relative proportion depending on the polymerization or preparation conditions. In both modifications the polymer chains adopt a 2_1 helical conformation and pack in orthorhombic unit cells with the following cell parameters:

$$\text{phase I: } a = 0.742 \text{ nm};\ b = 0.570 \text{ nm};\ c = 1.245 \text{ nm}$$

$$\text{phase II: } a = 0.383 \text{ nm};\ b = 1.116 \text{ nm};\ c = 1.256 \text{ nm}$$

Additionally, POBA exhibits on heating at high temperatures first a crystal/liquid-crystal transition at $T \sim 340$ °C, followed by a liquid-crystal/liquid-crystal phase transition near $T = 440$ °C.

As recently shown by Geil and co-workers,[3,4] POBA single crystals can be grown using *p*-acetoxybenzoic acid monomer (ABA) thin films confined between two glass slides and polymerized/crystallized at various temperatures (130−400 °C). Polymerization below the monomer melting temperature seems to occur via a sublimation/recrystallization/melting process. Electron diffraction data indicate that lamellar crystals approximatively 10 nm thick grow in either phase I or phase II with the chain axis oriented normal to the lamellar surface, i.e., the glass surface. Polymerization above the melting temperature of the monomer leads to lamellae displaying holes which increase in size with increasing polymerization temperature. The authors propose that these lamellae grow and nearly simultaneously undergo rearrangements similar to those observed for annealed single crystals.

The same preparation techniques have later been used by Rybnikar[5] and Wang et al.[6,7] in order to produce oriented POBA thin films by epitaxial growth on various substrates including mica, KBr, and oriented PTFE layers. On mica, the polymer chain axis is, as expected, parallel to the substrate surface and oriented in three different directions rotated by 60°,[5,6] while on highly oriented PTFE layers deposited on various supports (CaF_2 and quartz) the as-polymerized POBA thin films are uniaxially oriented with the deposit and substrate chain axes lying parallel to each other.[7]

Friction-transferred PTFE layers are known to be highly efficient substrates for a wide range of crystalline materials.[8,9] They have recently been used with success to induce the epitaxial growth of organic compounds such as *p*-nitrophenol,[10] hydroquinone, *p*-nitroaniline[11] and sesquithiophene[12] and of monomers or polymers e.g. poly(diacetylene)[13] and poly(aryl−ether−ether−ketone).[14] In this paper, we report a detailed study of the polymerization/crystallization of POBA on PTFE substrates deposited on glass slides or silicon wafers using transmission electron microscopy, electron diffraction, and FTIR spectroscopy.

Experimental Section

Materials and Preparation of the POBA Layers. *p*-Acetoxybenzoic acid was purchased from Aldrich and used without further purification ($T_m = 196$ °C). Commercial rods of PTFE were used to prepare the polymer substrates by the friction-transfer method described in detail elsewhere.[8] The exposed substrate surface corresponds to the $(010)_{\mathrm{PTFE}}$ crystallographic plane of the high-temperature form ($a = b = 0.56$ nm, $c = 1.95$ nm, and $\gamma = 60°$). As shown by AFM and electron microscopy (EM) investigations, the PTFE interchain distance in this plane is 0.56 nm.[9] The POBA films were prepared by using a “constrained polymerization” method similar to the method devised by Geil et al.[3,4] The monomer thin films were cast on bare glass slides from acetone solutions. After complete evaporation of the solvent, the monomer crystals were covered with the slide supporting the PTFE layers. The glass/monomer/PTFE/glass sandwich was then annealed at various temperatures (180 °C $< T <$ 250 °C). Once polymerized, the thin POBA films were carbon coated, floated off on

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[⊗] Abstract published in *Advance ACS Abstracts,* December 1, 1997.

S0024-9297(97)01034-6 CCC: $14.00

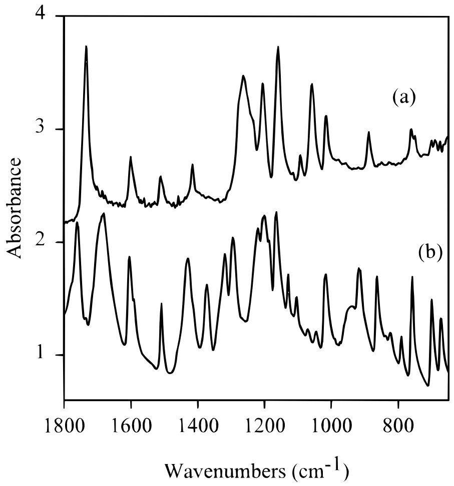

Figure 1. FTIR spectra of POBA polymerized on (a) PTFE and (b) *p*-acetoxybenzoic acid.

diluted hydrofluoric acid/H_2O solutions, and picked up on copper EM grids. Note that both the deposited POBA film and PTFE substrate are removed from the glass substrate, thus allowing the recording of the substrate/deposit composite diffraction patterns.

Characterization of the Polymerized Thin Films. Optical microscopy observations were performed with a Leica DMR microscope using polarized light or Nomarski interferential contrast. The same samples were also examined by bright field electron microscopy and electron diffraction using a Philips STEM CM12 operating at 120 kV. The FTIR spectra of the ABA monomer and oriented POBA films were recorded (resolution 2 cm^{-1}) with a Bruker IFS113v spectrophotometer fitted with a microscope operating in transmission mode. The observed area is about 100 × 100 μm^2. Polymerization is evidenced by the disappearence of the characteristic C=O stretching IR bands of the monomer at 1760 and 1690 cm^{-1} and the appearance of C=O stretching bands at 1740 and 1698 cm^{-1} typical of the polymer (Figures 1 and 8).

Results and Discussion

Polymerization/Crystallization of POBA on PTFE Substrates. Polymerization of POBA on glass or PTFE substrates was performed at temperatures ranging from 180 to 250 °C, i.e., close to or well above the melting temperature of the ABA monomer.

On *bare glass slides*, growth of thin lamellar crystals similar to those described by Lieser[1] and Geil[3,4] was observed (Figure 2a). These authors have demonstrated that both crystal modifications I and II of POBA are obtained at relative concentrations which depend on the experimental conditions used. Electron diffraction investigations have shown that the POBA crystals contact the glass substrate with their $(001)_{\mathrm{POBA}}$ crystallographic plane. As a consequence, the POBA chain axes are oriented perpendicular to the glass substrate.

The polymerization and crystallization of POBA on *oriented PTFE substrates* give rise to two different types of morphologies. At low substrate temperatures and short reaction times (e.g. $T = 190$ °C, $t = 60$ min), very thin and fairly uniform films of POBA are obtained (Figure 2b). For higher reaction temperatures and/or longer polymerization times, an overgrowth of small POBA rodlike crystallites, predominantly aligned along the PTFE ridges or steps, is observed in addition to the uniform film formed initially (Figure 2c). For both morphologies, the strong birefringence observed when the PTFE chain axis is oriented at 45° to the polarizers points to a very high degree of orientation.

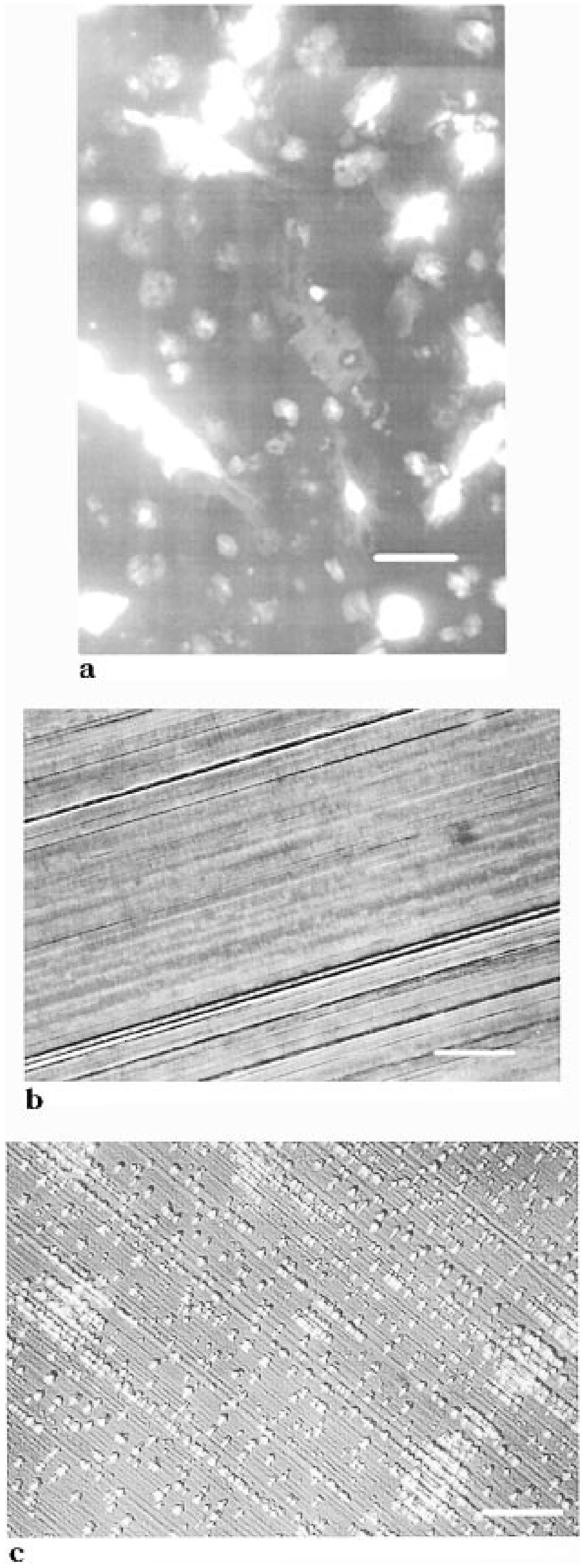

Figure 2. Optical photomicrographs of POBA thin films polymerized/crystallized on (a) a bare glass slide (crossed polarizers; scale bar: 20 μm), (b) a highly oriented PTFE substrate held at 190 °C (crossed polarizers; scale bar: 20 μm), and (c) a PTFE substrate held at 250 °C, Nomarski interference contrast (scale bar: 20 μm).

Closer examination of the as-polymerized POBA thin films by bright field electron microscopy reveals the presence of lamellae about 10 nm thick which are

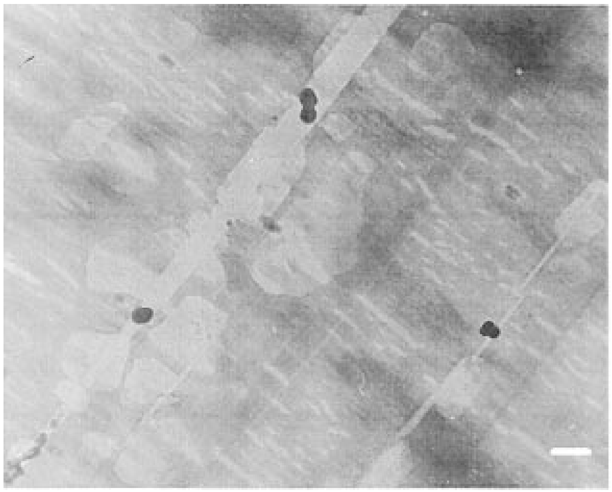

Figure 3. Bright field electron micrograph of a thin film of POBA epitaxially oriented on PTFE ($T_{\text{polymerization}} = 210$ °C; scale bar = 50 nm).

stacked edge-on and oriented normal to the PTFE chain axis (Figure 3). Assuming that the POBA chains are fully extended, the measured lamellar thickness corresponds to a degree of polymerization of about 15 (see below).

POBA/PTFE Crystallographic Relationship. The crystalline structure of the as-polymerized thin film and its crystallographic relationship with the PTFE oriented layer can easily be derived from the composite substrate/deposit electron diffraction patterns.

Parts a and b of Figure 4 show the selected area electron diffraction patterns recorded for POBA thin films polymerized on PTFE at 180 and 210 °C, respectively. As indicated by the position of the strong $(0015)_{\text{PTFE}}$ reflection on the meridian (Figure 4a), the PTFE chain axis is vertical. The low angular dispersion of the POBA reflections confirms the high degree of orientation achieved with the deposition method used. Both diffraction patterns can be indexed on the basis of the phase II orthorhombic unit cell (Figure 4c). Since only ($0kl$) reflections are observed, such diffraction patterns correspond to a [100] zone axis single crystal pattern. It can thus be deduced that the POBA lamellae grow epitaxially on the PTFE substrate surface with a $(100)_{\text{POBA}}$ contact plane.

The exact deposit/substrate epitaxial relationships can be summarized as follows

$$(100)_{\text{POBA}}//(010)_{\text{PTFE}}$$

$$[001]_{\text{POBA}}//[001]_{\text{PTFE}} \text{ and } [010]_{\text{POBA}}//[100]_{\text{PTFE}}$$

The lattice mismatch in a direction perpendicular to the chain axes defined by

$$\Delta = (b_{\text{POBA}} - 2a_{\text{PTFE}})/2a_{\text{PTFE}}$$

is equal to 0.4%. This very low value of Δ underlines the near perfect polymer chain stacking at the POBA/PTFE interface. A molecular model of this interface, projected along the polymer chain axes, is shown in Figure 5.

Furthermore, closer examination of the diffraction patterns shown in parts a and b of Figure 4 reveals that the meridional POBA (00l) reflections are split. This superstructure arises from the near perfect stacking of POBA lamellae oriented edge-on and perpendicular to the PTFE chain axis. A similar effect has been described by Dorset et al. for epitaxially crystallized paraffins.[15] It is noteworthy that the spacing between two adjacent meridional reflections varies with the polymerization conditions, i.e., with the thickness of the POBA lamellae. Lamellar thicknesses of 8 and 12 nm were measured for thin films polymerized at 180 and

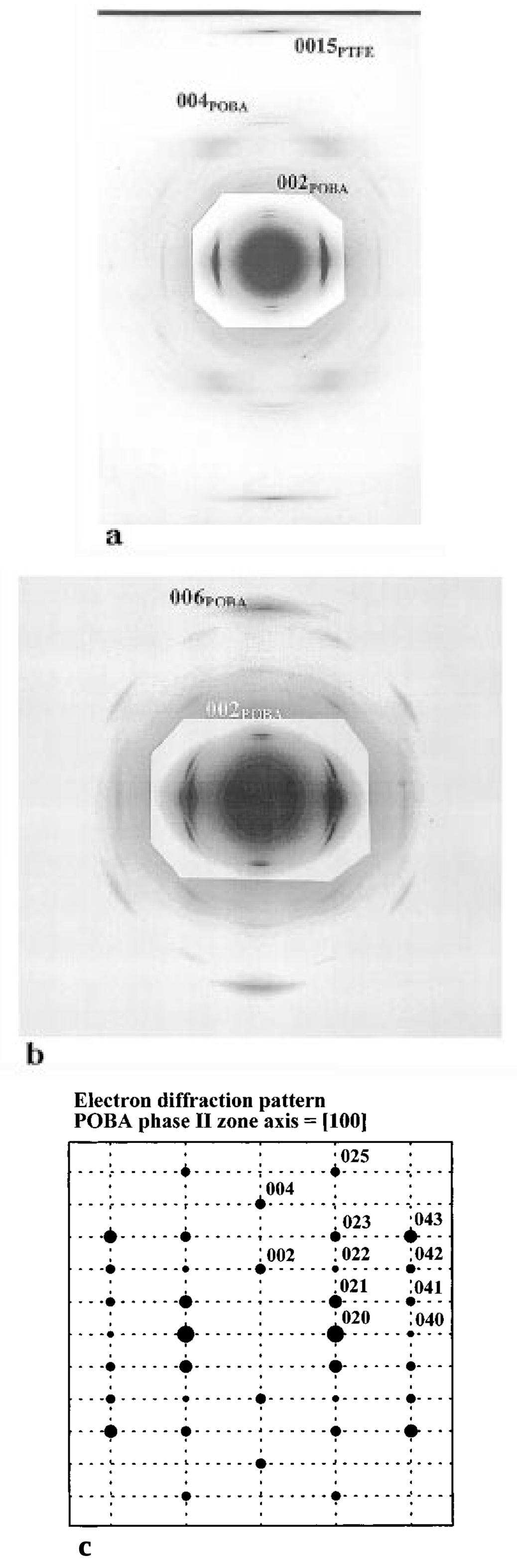

Figure 4. Selected area electron diffraction patterns of POBA thin films grown epitaxially on PTFE (PTFE chain axis vertical, see text) (a) polymerized at 180 °C, (b) polymerized at 210 °C, (c) computer generated electron diffraction pattern corresponding to a (100) contact plane of phase II POBA crystals.

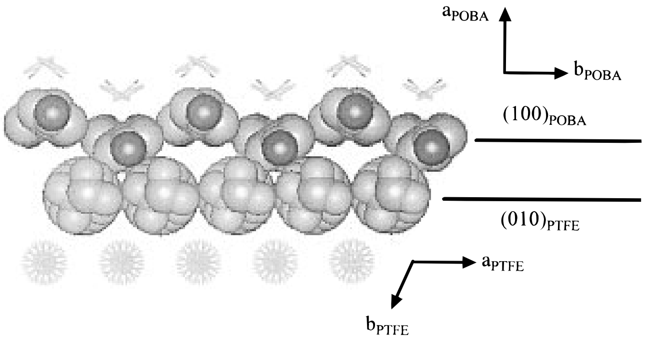

Figure 5. Molecular model of the POBA/PTFE interface projected along the polymer chain axes. The orientation of the crystallographic axes of both phases are as indicated.

210 °C, respectively. Assuming that the chains are fully extended and considering a rise per residue of 1.265 nm/2, these thicknesses correspond to degrees of polymerization Dp of 12 and 19, respectively. Such an increase of Dp with temperature or reaction time has been previously reported by Kricheldorf et al. for polymerization in solution.[16] In fact, chain growth in the crystal was related to the condensation and transesterification reactions occurring in the solid state even in the absence of monomer.

These electron diffraction data demonstrate that the epitaxial polymerization on PTFE substrate yields highly ordered thin films made of regularly stacked lamellae of well-defined thickness, oriented edge-on. As a consequence of the quasi simultaneous nucleation of POBA crystals over the whole substrate, the polydispersity or polymolecularity of the epitaxially polymerized POBA samples is probably very low.

POBA/POBA Homoepitaxy. As already mentioned, when the epitaxial polymerization is performed at high temperatures and/or long reaction times, the uniform $(100)_{POBA}$ thin films are covered with small POBA crystallites with an apparently well defined orientation relative to the underlying film and substrate (Figure 2c). Figure 6 shows an electron diffraction pattern of such a sample which displays significant differences from the patterns presented in Figure 4. This composite diffraction pattern contains indeed reflections arising from (i) the PTFE substrate and (ii) the (100) epitaxially polymerized POBA thin film described previously but also from (iii) the POBA small crystallites (noted hereafter as POBA*) crystallographically related either to the $(100)_{POBA}$ thin film and/or to the PTFE substrate. The presence of the POBA overgrowth is revealed by a set of strong (hk0) reflections again of phase II. A computer simulated (001) zone axis diffraction pattern is shown in Figure 6b. It can be deduced that these "flat-on" crystallites contact the thin oriented film or the substrate with the $(001)_{POBA^*}$ crystallographic plane. Note that the azimuthal orientation of the crystallites is such that the b axis is perpendicular to the PTFE chain axis as is the case for the thin film.

The corresponding crystallographic relationships can thus be summarized as follows

$$(001)_{POBA^*}//(100)_{POBA} \text{ or } (010)_{PTFE}$$

$$[010]_{POBA^*}//[010]_{POBA} \text{ or } [100]_{PTFE}$$

In other words, the b axes of the two POBA crystalline deposits are parallel, while the chain axes are normal to each other. It is believed that at high polymerization temperatures, the "flat-on" crystallites grow epitaxially on top of the uniform and highly oriented thin POBA film itself oriented epitaxially on the PTFE substrate in a first step.

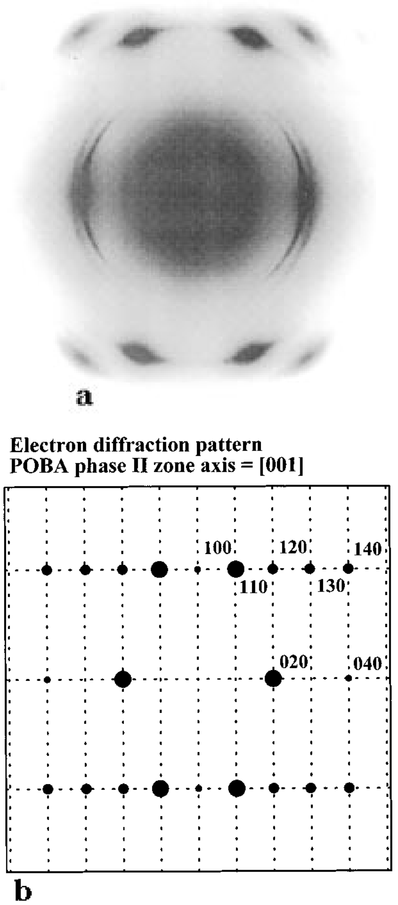

Figure 6. (a) Selected area electron diffraction pattern of a POBA overlayer polymerized/crystallized on PTFE at 220 °C (PTFE chain axis vertical). (b) Computer simulated electron diffraction pattern of phase II (001)POBA crystals.

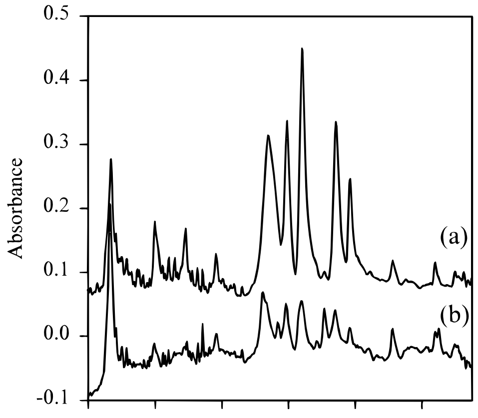

Figure 7. Polarized FTIR spectra of a (100) POBA thin film polymerized on PTFE at 210 °C with polarization (a) parallel and (b) perpendicular to the PTFE chain axis direction, respectively.

FTIR Spectroscopy of POBA. Polarized FTIR investigations were performed on the $(100)_{POBA}$ thin films epitaxially polymerized at low temperatures. The spectra recorded with an incident beam polarized parallel or perpendicular to the PTFE chain axis are shown in Figure 7. The wavenumbers and dichroism of the different IR bands observed are reported in Table 1.

Table 1. Wavenumbers, Dichroism, Dichroic Ratio (*R*) and Proposed Attribution of POBA Polymerized on PTFE Substrates (∥ and ⊥ Refer to Polarization Parallel or Perpendicular to the PTFE Chain Axis, with R Defined by the Ratio $A_{//}/A_{\perp}$)

wavenumbers (cm^{-1})[a]	dichroism, R	assgnt
w 750	⊥ 0.2	A′
w 760	∥ 2.3	A″
m 887	⊥ 0.7	A′
m 1015	∥ 6	A″
s 1057	∥ 6	A″
w 1092	⊥ 0.2	A′
s 1159	∥ 5	
ms 1205	∥ 4	A″
s 1261	∥ 6	ν_{C-O}
sh 1279		A′
w 1416	∥ 2	A″
w 1510	∥ 4	A″
m 1601	∥ 3	A″
s 1734	⊥ 0.7	$\nu_{C=O}$

[a] w, m, and s refer to weak, medium, and strong, respectively.

Given the thinness of the PTFE substrate, only POBA vibrations are observed. The polymer chain in the crystalline conformation has the symmetry elements of the C_s point group, the glide plane (σ_g) being parallel to the chain axis. The transition moments associated with the normal modes are thus either in the glide plane or normal to it. For A′ and A″ irreducible representations, the vibrations are thus polarized along the *a* axis or in the (*bc*) plane, respectively. As previously reported for epitaxially grown PEEK thin films,[14] the IR bands of POBA may be attributed to either the ring or the −COO− group vibrational modes. It should be underlined however that for simplicity the interactions between −COO− and the aromatic ring are neglected. The POBA monomeric unit can be assimilated to para-disubstituted aromatic molecules for which the ring vibrations are associated with the *X*, *Y*, and *Z* orientations of the transition moments,[17] corresponding to the out of plane axis, the in plane axis normal to the C1−C4 direction, and the C1−C4 axis, respectively. Due to the presence of a glide plane, each *X*, *Y*, or *Z* ring modes are splitted into two POBA normal modes, corresponding to the symmetric (A′) and antisymmetric (A″) vibrations. However, since the aromatic rings are inclined by only 5° with respect to the chain axis, the *Z* vibrations only give one A″ component polarized along the c axis. Taking into account the results obtained for para-disubstituted aromatic molecules, the 760, 1015, 1057, 1159, 1205, 1416, 1510, and 1601 cm^{-1} bands can be assigned to the *Z* modes (A″) which are observed only when the IR beam is polarized parallel to the PTFE chain axis (Figure 7). The out of plane modes at 750, and 887 cm^{-1} (*X* modes), and the in plane *Y* modes at 1092 and 1279 cm^{-1} are polarized perpendicular to the PTFE sliding direction. In addition, the carbonyl C=O stretching vibration (1740 cm^{-1}) and the ester C−O stretching vibrations (1261 cm^{-1}) are observed when the incident IR beam is polarized perpendicular and parallel to the PTFE chain axis, respectively. These results clearly confirm that POBA and PTFE chain axes are parallel. They are thus in total agreement with the orientation deduced from the EM diffraction experiments.

Finally, as shown in Figure 8, the carbonyl stretching IR bands observed for POBA polymerized in bulk and for POBA epitaxially polymerized on PTFE differ significantly. For the bulk polymerized sample, two C=O stretching modes are observed at 1740 and 1698 cm^{-1}. In contrast, for the highly oriented POBA film deposited on PTFE only the mode at 1740 cm^{-1} polarized along the *b* axis is present. Two explanations can be proposed to account for this observation. First, as proposed by Geil and co-workers,[4] the 1698 cm^{-1} mode would correspond to residual carboxyl groups, this mode being unseen for the high molecular weight POBA polymerized on PTFE. Second, these IR bands would be the result of a crystal splitting, the unit cell containing two polymer chains related by a $C_{2v}{}^{5}$ symmetry space group.[18] They would then be attributed to the in phase and out of phase vibrations of both chains in the unit cell. This observation provides an additional proof of the single-crystal nature and the high degree of orientation of the epitaxially polymerized POBA thin films.

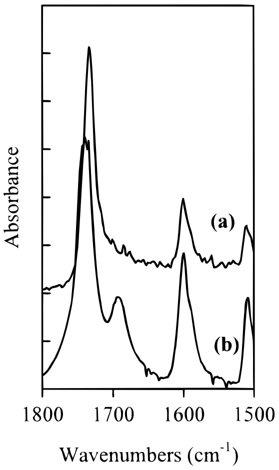

Figure 8. Carbonyl stretching vibrations of POBA polymerized (a) on the PTFE substrate or (b) in the bulk.

Conclusions

Polymerization/crystallization of POBA performed in the presence of friction-transfer PTFE substrates using the constrained polymerization method of Geil and coworkers yield highly oriented epitaxial thin films exclusively made of phase II crystals. At low substrate temperatures, the growth of uniform thin films with a single crystal-like orientation is observed. The (100) planes of POBA crystals contact the (010) PTFE substrate surface, both polymer chain axes being parallel. At high substrate temperatures and/or long times of reaction, the additional growth of small crystallites oriented with respect to the substrate is additionnally observed. It is believed that this additional growth is due to a homoepitaxy of POBA, the crystallites contacting the already formed POBA thin films with their (001) planes.

Finally, careful analysis of the electron diffraction patterns highlights the very low polydispersity or polymolecularity of POBA in the epitaxially grown films.

Acknowledgment. The authors gratefully acknowledge Dr. B. Lotz (Institut Charles Sadron) for fruitful discussions. P.D. is a Research Associate of the Belgian National Funds for Scientific Research (FNRS). This work was supported by the FNRS (Belgium) and the CNRS (France).

References and Notes

(1) Lieser, G. *J. Polym. Sci, Polym. Phys. Ed.* **1983**, *21*, 1611.
(2) Iannelli, P.; Yoon, D. Y. *J. Polym. Sci., Part B: Polym. Phys.* **1995**, *33*, 977.

(3) (a) Liu, J.; Geil, P. H. *J. Macromol. Sci.—Phys.* **1992**, *B31*, 163. (b) Liu, J.; Rybnikar, F.; Geil, P. H. *J. Macromol. Sci.—Phys.* **1993**, *B32*, 395.

(4) Rybnikar, F.; Yuan, B. L.; Geil, P. H. *Polymer* **1994**, *35*, 1863.

(5) Rybnikar, F. *J. Polym. Sci., Part B: Polym. Phys.* **1996**, *34*, 1935.

(6) Wang, J.; Kaito, A.; Yase, K.; Tanigaki, N. *Polymer* **1996**, *37*, 3247.

(7) Wang, J.; Kaito, A.; Ohnishi, S.; Tanigaki, N.; Yase, K. *Macromolecules* **1996**, *29*, 8271.

(8) Wittmann, J. C.; Smith, P. *Nature* **1990**, *352*, 414.

(9) (a) Hansma, H.; Motamedi, F.; Smith, P.; Hansma, P. K.; Wittmann, J. C. *Polymer* **1992**, *33*, 647. (b) Dietz, P.; Hansma, P. K.; Ihn, K. J.; Motamedi, F.; Smith, P. *J. Mater. Sci.* **1993**, *28*, 1372.

(10) Damman, P.; Dosière, M.; Smith, P.; Wittmann, J. C. *J. Am. Chem. Soc.* **1995**, *117*, 1117.

(11) Damman, P.; Dosiere, M.; Brunel, M.; Wittmann, J. C. *J. Am. Chem. Soc.* **1997**, *119*, 4633.

(12) Lang, P.; Valat, P.; Horowitz, G.; Garnier, F.; Yassar, A.; Wittmann, J. C.; Lotz, B.; Meyer, S.; *J. Chim. Phys.* **1995**, *92*, 963.

(13) Meyer, S.; Smith, P.; Wittmann, J. C. *J. Appl. Phys.* **1995**, *77*, 5655.

(14) Damman, P.; Fougnies, C.; Dosiere, M.; Wittmann, J. C. *Macromolecules* **1995**, *28*, 8272.

(15) Dorset, D. L. *J. Electron Microsc. Tech.*, **1985**, *2*, 89.

(16) Kricheldorf, H. R.; Schwarz, G. *Makromol. Chem.* **1983**, *184*, 475.

(17) (a) Garrigou-Lagrange, C.; Lebas, J. M.; Josien, M. L. *Spectrochim. Acta* **1958**, *12*, 305. (b) Green, J. H. S. *Spectrochim. Acta* **1970**, *26A*, 1503. (c) Stojiljkovic, A.; Whiffen, D. H. *Spectrochim. Acta* **1958**, *12*, 57.

(18) Tadokoro, H. *Structure of crystalline polymers*; John Wiley: New York, 1981.

MA9710343