Liquid–Liquid Phase Separation and Oriented Growth of Poly(aryl ether ether ketone) on Friction-Transferred Poly(tetrafluoroethylene) Substrates

P. Damman,[*,†] **C. Fougnies, and M. Dosière**

Université de Mons-Hainaut, Laboratoire de Physico-Chimie des Polymères 20, place du parc, B-7000 Mons, Belgium

J. C. Wittmann

CNRS, Institut Charles Sadron, 6, rue Boussingault, F-67083 Strasbourg, France

Received February 28, 1995; Revised Manuscript Received September 5, 1995[⊗]

ABSTRACT: The morphology and orientation of poly(aryl ether ether ketone) (PEEK) crystallized in the presence of friction-tranferred PTFE layers have been studied by optical and electron microscopy, electron diffraction, and FTIR. Deposition and orientation of PEEK is successfully achieved by a two-stage procedure involving (i) liquid–liquid phase separation by slow absorption of water in a dilute methanesulfonic acid solution and (ii) aggregation–crystallization of the polymer-enriched droplets. PTFE substrates are shown to induce the crystallization of PEEK at a very early stage of the phase separation process. Electron diffraction and FTIR investigations demonstrate that the as-deposited PEEK films have a single crystal-like structure, with the chain axes of both polymers oriented parallel to each other and the PEEK zigzag plane oriented parallel to the (100) PTFE substrate surface. This well-defined polymer/polymer epitaxial relationship rests on a very good matching between (a) the chain axis periodicities and, (b) more importantly, the deposit and substrate interchain distances.

Introduction

The chemical structure of poly(aryl ether ether ketone) (PEEK) confers to this linear semi-crystalline polymer outstanding physical properties, e.g. high mechanical performances, exceptional chemical resistance, and high thermal stability. It is therefore not surprising that PEEK has been the subject of many structural as well as morphological studies in recent years.

Since the preliminary description of Dawson and Blundell[1] in 1980, the structure of PEEK has been reexamined by various authors. The most recent structural refinement was done by Iannelli[2] who applied the fiber whole pattern refinement procedure to the two-ring and six-ring models proposed earlier by Hay et al.[3] and Fratini et al.,[4] respectively. According to Iannelli,[2] the six-ring model is not significantly better than the two-ring model. Furthermore, the results obtained for the two-ring model are very close to those reported by Hay and co-workers.[3] The unit cell of PEEK is orthorhombic (space group *Pbcn*) with $a = 0.777$ nm, $b = 0.590$ nm, and $c = 0.999$ nm (for the two-ring model). The polymer chain adopts a planar zigzag conformation. The zigzag plane, which is parallel to the (100) plane, is defined by the crystallographically equivalent ether and carbonyl groups; adjacent phenyl rings adopt symmetric out-of-zigzag plane positions.

Various studies have been devoted to the thermodynamic properties of PEEK,[5] the morphology of solution-crystallized samples[6,7] as well as of thin films recrystallized from the melt or glassy state.[8,9] Recent morphological investigations,[9,10] aimed at explaining the origin of the double melting behavior of PEEK have in particular focused on the structure of films crystallized at high temperatures ($T_c > 300$ °C). An interesting observation, relevant to the present investigation, was reported earlier by Lovinger and Davis[8] who succeeded in discovering suitable organic solvents and were thus able to study in detail the spherulitic texture obtained after recrystallization of PEEK from the molten or glassy state. They showed in particular that the spherulites are made of very narrow lamellae elongated along the *b* axis direction and oriented preferentially with the (100) plane, i.e. the zigzag plane, parallel to the mica surface on which they grow. However, this specific orientation is not the result of an epitaxial growth of the polymer crystals on the substrate. To the best of our knowledge, oriented growth of PEEK by epitaxy has never been reported so far. One possible reason is the lack of suitable interactive substrates able either to resist highly corrosive solvents or to withstand the high temperatures (200–300 °C) needed to process the polymer in organic solvents (except for inorganic substrates). As reported in the present paper, successful orientation of PEEK can be achieved from solution in methanesulfonic acid, by using friction-transferred PTFE layers which offer the required chemical as well as thermal resistance. Morphological investigations performed using optical and electron microscopy, electron diffraction, and FTIR demonstrate that the growth procedure involves a liquid–liquid phase separation followed by the substrate-directed crystallization. The latter leads to large thin films of PEEK with a single crystal structure.

Experimental Section

Materials. Commercial rods of PTFE were used to prepare the polymer substrates. PEEK (150G, ICI) and methanesulfonic acid (MSA) (Aldrich; nominal concentration, 99%) were used without further purification.

Preparation of Oriented PEEK Thin Films. The monocrystalline PTFE substrates are deposited on freshly cleaned glass slides using the friction-transfer method described in detail elsewhere.[11,12] The PTFE chains are perfectly aligned on the glass slide in the friction direction. The exposed PTFE surface corresponds to a (100) plane with a characteristic interchain spacing of 0.56 nm.

Known as a nonsulfonating solvent, MSA was preferred to other strong acids to prepare dilute (0.1% wt/wt) solutions of

---

[*] To whom correspondence should be addressed.

[†] Research Associate of the Belgian National Fund for Scientific Research.

[⊗] Abstract published in *Advance ACS Abstracts*, October 15, 1995.

0024-9297/95/2228-8272$09.00/0

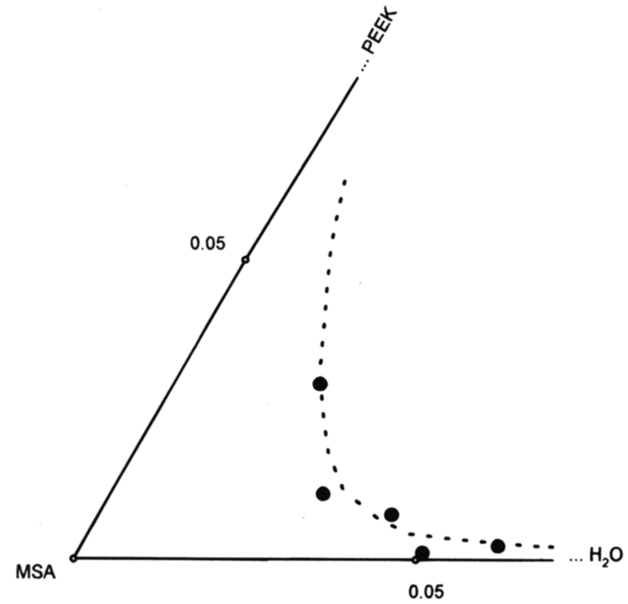

Figure 1. Ternary phase diagram of PEEK in MSA/water solutions measured by the cloud point method (concentrations are given in weight ratios).

PEEK stable at room temperature. After complete dissolution of the polymer, a few drops of the solution are spread between a PTFE-covered glass slide and a coverslip. Following a procedure already used to orient polyaniline,[11] precipitation and crystallization of PEEK are achieved by slow absorption of moisture from the air. Once crystallized, the thin PEEK films are thoroughly rinsed in distilled water, dried in a vacuum oven at 100 °C overnight, and when desired, annealed at 300 °C for 10 h. The samples are then coated with a carbon film, floated on hydrofluoric acid solution, together with the PTFE substrate, and finally picked up on copper grids.

Morphological Characterization of the Oriented PEEK Films. Optical microscopy observations were performed in phase contrast and polarized light using a ZEISS Photomicroscope II. The samples were also examined by bright field electron microscopy (EM) and electron diffraction (ED) in a Philips STEM CM12 microscope operating at 120 kV. The FTIR spectra of oriented PEEK films were recorded using a Bruker IFS113V spectrophotometer equiped with a microscope operating in transmission mode. The observed area is 100 × 100 μm^2. A minimum of 128 interferograms were added at a resolution of 2 cm^{-1}. The notation proposed by Wilson for the normal modes of the aromatic ring was used.[19]

Molecular Modeling. Molecular modeling of the crystalline structure and the polymer/substrate interface was performed on a Silicon Graphics computer system using the Cerius molecular modeling software package for materials research (Molecular Simulations, Inc. of Burlington, MA, and Cambridge, U.K.).

Results and Discussion

Thin Film Morphology. When absorbed in dilute methanesulfonic acid solutions of PEEK, water acts as a nonsolvent and induces a liquid–liquid phase separation before crystallization. The phase behavior of ternary PEEK/MSA/water systems measured by the optical cloud point method (Figure 1) clearly shows that demixing and/or crystallization occurs in a 0.1% (weight ratio) solution already at water concentrations as low as 5% (weight ratio). The typical morphology of a precipitated PEEK film is seen in the optical micrographs shown in Figures 2 and 3. On the amorphous glass surface (Figure 2), the phase separation/ crystallization process yields small and poorly crystalline particles. Their size is rather small (in the range 0.1–0.3 μm) compared to the size ($\Phi \gg 1$ μm) commonly observed for example for polyethylene droplets obtained by liquid–liquid phase separation and crystallization in rapidly quenched solutions, i.e. in the absence of a solid substrate.[13] Since for PEEK, the process involves slow water absorption, it can be assumed that phase separation proceeds via a nucleation and growth mechanism. However, interaction of the PEEK-enriched droplets with the glass surface may well lead to their rapid solidification, i.e. to a noticeable shortening of the growth step.

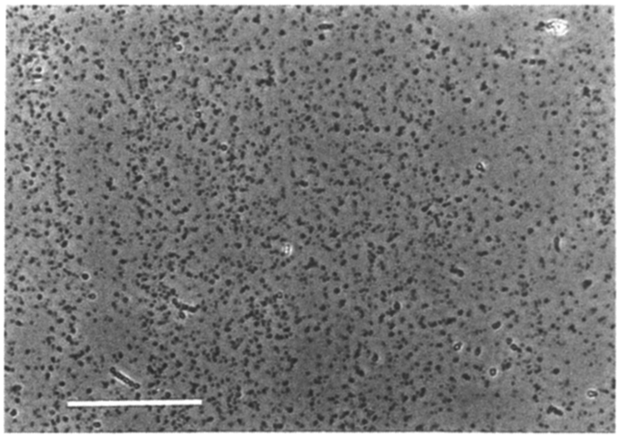

Figure 2. Phase contrast optical micrograph of precipitated particles obtained after liquid–liquid phase separation in a PEEK solution in MSA deposited on a glass slide (scale bar 10 μm).

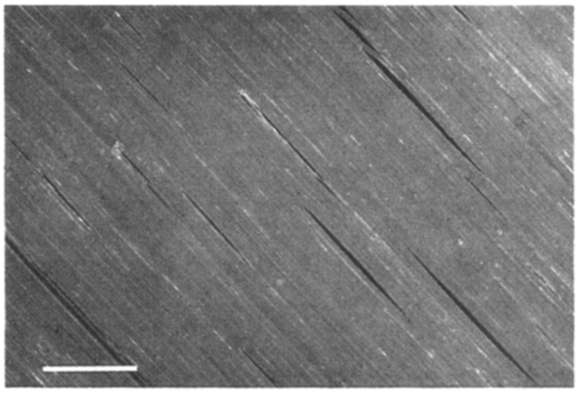

Figure 3. Polarized light optical micrograph of an oriented PEEK film obtained by liquid–liquid phase separation and crystallization of the MSA solution deposited on a PTFE substrate (scale bar 50 μm).

This effect is even more marked for PEEK films precipitated in the presence of a friction-transferred PTFE layer. When examined in polarized light (Figure 3), the as-precipitated films are highly birefringent, and rather uniform and featureless. Careful examination by electron microscopy at much higher magnifications (Figure 4) reveals however that these films are not at all smooth, but are apparently made again of very small, densely aggregated particles of a diameter in the range 10–15 nm, i.e. ~10 times smaller than the particles observed on the glass surface. It is clear therefore that the PTFE layer acts as a strong interactive substrate and induces the crystallization of PEEK at a very early step of the liquid–liquid phase separation process.

Annealing of the as-deposited films well below the melting temperature of PEEK (10 h at 300 °C), results in a dramatic morphological change. As apparent from Figure 5, edge-on PEEK lamellae oriented perpendicular to the PTFE chain axis are formed on annealing, at the expense of the solid particles which have totally

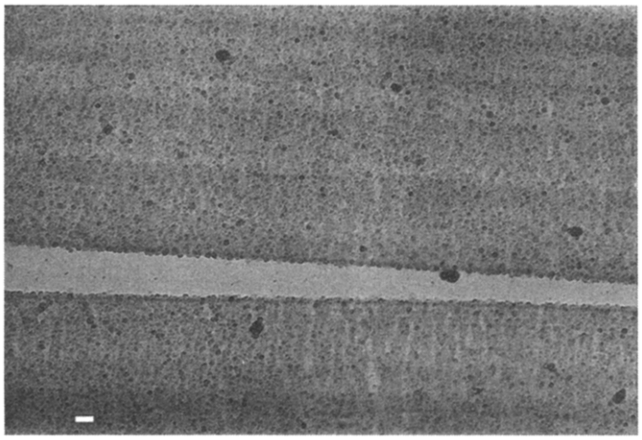

Figure 4. TEM micrograph of the microstructure of a PEEK film epitaxially crystallized on PTFE (scale bar 50 nm).

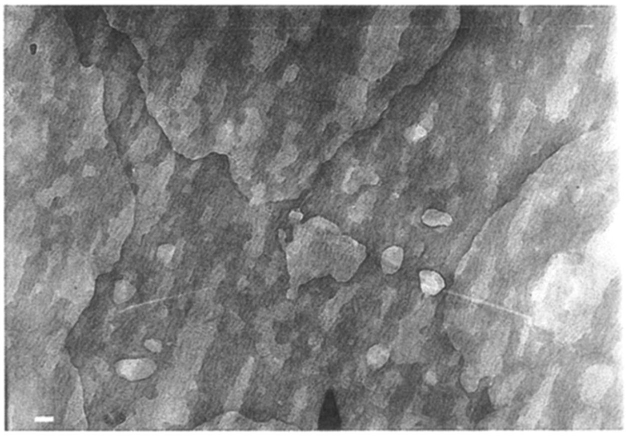

Figure 5. TEM micrograph of a PEEK film epitaxially crystallized on PTFE and subsequently annealed 10 h at 300 °C (scale bar 50 nm).

disappeared from the film surface. The lamellae grown under these conditions have a thickness of about 11 nm, comparable to the diameter of the particles and the thickness of PEEK single crystals grown from solution or from the melt (10–15 nm).[6,7]

Epitaxial Orientation of PEEK. A composite diffraction pattern taken on an as-precipitated PEEK deposit/PTFE substrate bilayer, is shown in Figure 6 together with its indexation based on the orthorhombic unit cell of PEEK and the room temperature hexagonal unit cell of PTFE ($a = 0.56$ nm and $c = 1.95$ nm, $\gamma = 60°$).[14] Despite its complex morphology, the PEEK film is highly oriented. As revealed by the $(002)_{\text{PEEK}}$, $(008)_{\text{PEEK}}$, and $(0015)_{\text{PTFE}}$ reflection pairs, located on the meridian, the PEEK and PTFE chain axes are parallel to each other. Moreover, the set of PEEK reflections on the equator reveals that a near single crystal-like orientation is achieved. Indeed, for a uniaxial fiber orientation the (200) and (110) reflections would be by far the most intense. The fact that in Figure 6, it is the (020) reflection which is more intense strongly suggests that a unique orientation of the PEEK crystals, with the (100) plane contacting the PTFE substrate, is largely predominant in these films.

A similar diffraction pattern is obtained for PEEK thin films annealed at 300 °C. Although the bright field observations of the film surface indicate morphological changes, the overall crystal orientation and the degree of orientation are not significantly changed or improved by this thermal treatment.

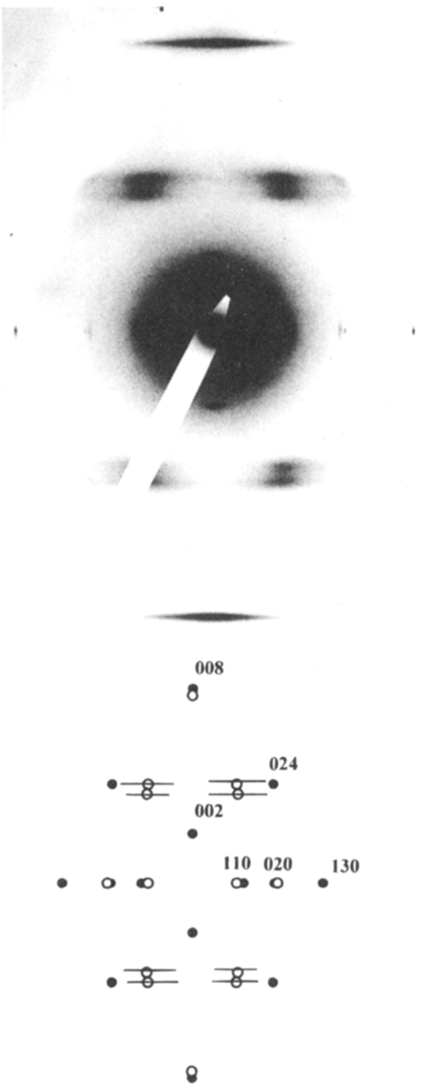

Figure 6. (a, top) Electron diffraction pattern recorded at normal incidence of an oriented PEEK film. (b, bottom) Indexation of the composite electron diffraction pattern: (●) PEEK reflections; (○) PTFE reflections.

In order to confirm this outstanding orientation of PEEK, ED patterns were recorded for thin films tilted at different angles around the PEEK or PTFE chain axes (ED meridian). As shown in Figure 7, a tilt angle of 35° is needed in order to bring the (110) and (111) planes to their best reflecting position. This value is in very good agreement with the 37° tilt angle calculated if one assumes the above PEEK single crystal orientation.

Obviously, friction-transferred PTFE layers are highly efficient substrates able to induce the epitaxial growth of PEEK crystals. The polymer/polymer epitaxial relationship rests on a fairly good matching between the 0.56 and 0.59 nm interchain distances of PTFE and PEEK, respectively, in their (100) contact planes.

The corresponding lattice mismatch defined as $\Delta = 100\,(d_{\text{deposit}} - d_{\text{substrate}})/d_{\text{substrate}}$ is only slightly larger than 5%. A second, probably less important matching also exists between the PTFE repeat distance of 1.95 nm and 2 times the repeat distance ($2c = 1.98$ nm) along the PEEK chain axis.

The PEEK/PTFE epitaxial relationship can thus be summarized as follows:

$$(100)_{\text{PEEK}}//(100)_{\text{PTFE}}$$

$$c_{\text{PEEK}}//c_{\text{PTFE}}$$

Figure 7. (a, top) Electron diffraction pattern recorded with a tilt angle of 35° (the tilt axis corresponds to the PTFE chain axis) of an oriented PEEK film. (b, bottom) Indexation of the composite electron diffraction pattern: (●) PEEK reflections; (○) PTFE reflections.

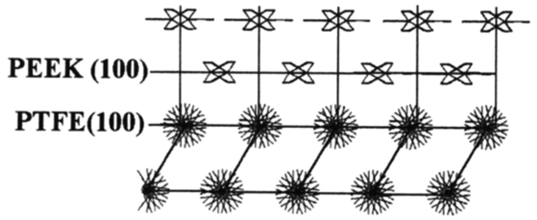

Figure 8. Molecular model of the PEEK/PTFE crystallographic relationship at the interface.

Figure 8 presents a molecular model of the PEEK/PTFE interface seen in projection along the polymer chain axes. As reported by Lovinger et al. for flow-induced crystallization of PEEK on mica,[7] the zigzag plane of PEEK is parallel to the (100) PTFE substrate surface, while successive phenyl rings in the chain are symmetrically inclined to it. Despite the difference in chain conformation, this arrangement of the phenyl rings bears some resemblance to the molecular arrangement observed for thin layers of sexithiophene epitaxially grown on PTFE.[15]

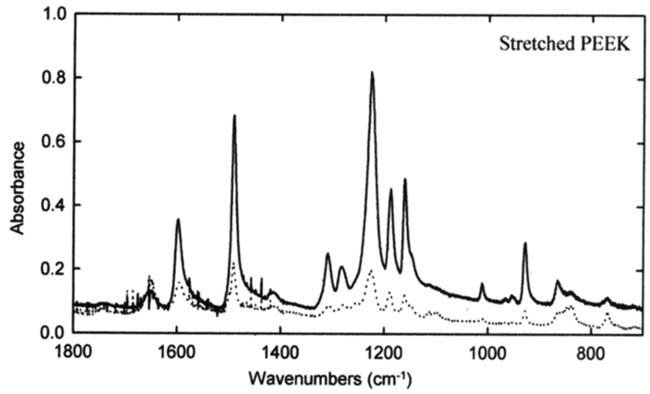

Figure 9. Polarized FTIR spectra of a drawn PEEK film. Solid or broken lines correspond to polarization parallel or perpendicular to the stretching direction.

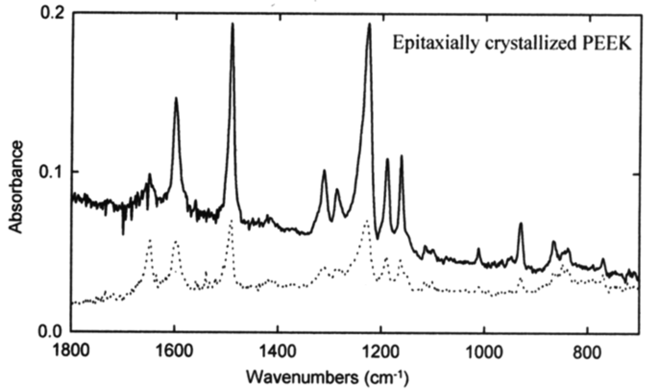

Figure 10. Polarized FTIR spectra of a PEEK film prepared by epitaxial growth on a PTFE substrate. Solid or broken lines correspond to polarization parallel or perpendicular to the PTFE chain axis.

Table 1. Wavenumbers, Assignment, and Dichroic Behavior of PEEK Vibrations in Epitaxially Crystallized PEEK Film

wavenumber (cm^{-1})[a]	dichroic ratio *R*	attribution, symmetry (from benzophenone)	α (deg)
w 771	⊥	11, A	
w 838	∥	11, B	
w 849	⊥	10b, A	
m 865	∥	10b, B	
m 930	3.2	d2, 12, B	27
w 1012	4.0	18a, A,B	20
vw 1114			
sh 1151	⊥	e1, 1, A	
s 1162	3.7	9b, A,B	23
s 1188	3.3	9a, A,B	26
s 1227	4.1	$C_{ar}-O-C_{ar}$	19
m 1284	3.2	e2, 1, B	27
m 1309	4.3	14, A,B	18
s 1490	2.5	19a, A,B	33
s 1598	2.9	8a, A,B	30
m 1645	0.3	$\nu_{C=O}$	90[b]

[a] vw, w, m, and s correspond to very weak, weak, medium, and strong intensity, respectively. [b] Value of α deduced from the crystal structure of PEEK.

IR Vibrational Spectroscopy. These single crystal type PEEK layers are particularly well suited for FTIR investigations. For the sake of comparison, the polarized IR spectra of highly drawn and epitaxially crystallized PEEK films are shown in Figures 9 and 10, respectively. The strong dichroism observed for the epitaxially grown films confirms the parallel orientation of the PEEK and PTFE chain axes (i.e. PTFE sliding direction) described above.

In an attempt to assign the various IR absorption bands observed to particular vibrational modes, crystalline benzophenone has been taken as a model, since (i) it belongs to the same symmetry point group as PEEK

(C_2 point group with the C_2 symmetry axis laying along the C=O bond of the molecule) and (ii) the IR spectra–structure correlations are well established for this aromatic compound.[16] For the C_2 symmetry point group, normal modes belong to either A or B irreducible representations, corresponding to in phase and out of phase displacements of both aromatic rings, respectively. Their transition moments are along the C_2 axis and in the plane normal to the C=O bond, respectively.

Table 1 lists the wavenumbers, dichroic ratios, and proposed assignments of the different PEEK IR bands. It can be noticed that the 18a, 9a, 9b, 19a, 8a, and 14 ring modes[19] which are only slightly affected by coupling or substitution effects, appear always at nearly constant frequencies.[17] On the contrary, the 1, 12, 6a, 10b, and 11 ring modes are strongly affected by such effects and appear thus as doublets with A and B components. Their attributions as reported in Table 1 were performed on the basis of the observed dichroism in drawn and epitaxially oriented PEEK films and by comparison to the aforementioned benzophenone crystals.[16]

Regarding the molecular orientation introduced by epitaxy, the value of the orientation function f has been estimated from the measured dichroic ratio of the stretching C=O vibration for which, according to the known structure of PEEK, the orientation of the transition moment is well-defined ($\alpha_{\nu_{CO}} = 90°$).

f is given by

$$f = \frac{(R-1)}{(R+2)}\frac{(R_0+2)}{(R_0-1)}$$

where R is the measured dichroic ratio and $R^0 = 2\,\mathrm{cotg}(\alpha)^2$ is the theoretical dichroic ratio, α being the angle between the transition moment associated with a given IR band and the orientation (molecular) axis.

The dichroic ratio R observed for the stretching C=O vibration is equal to 0.3 (Table 1) and leads to an f value of 0.61, which is close to that determined for highly drawn PEEK films.

By using the estimated value of f and the experimental dichroic ratios reported in Table 1, the α angles between the transition moments of the various aromatic ring modes and the chain axis can in turn be calculated. Perusal of the last column in Table 1 reveals that for most of the IR bands polarized parallel to the chain axis, angles around 30° are found. This result is in good agreement with the PEEK molecular structure since, as pointed out by Bassigny et al.,[18] the C1–C4 axes of the aromatic rings make an angle of 30° with the chain axis. However, for some of the observed IR bands (e.g. 14, 18a) the estimated values of α are significantly different from 30°. Such a difference may be due to a splitting in two components as a consequence of ring coupling or else the corresponding vibrations rather involve the C_{ar}–CO–C_{ar} or C_{ar}–O–C_{ar} parts of the polymer chain.

A detailed normal mode analysis of the PEEK vibrations based on polarized FTIR spectra of drawn and spherulitic samples is under way.

Conclusion

Friction-transferred PTFE layers were found to induce epitaxial crystallization of PEEK. During the liquid–liquid phase separation involved in the orientation process, the PTFE films act as a strong interactive substrate which induces the crystallization at a very early stage. On the basis of electron diffraction and FTIR investigations, the PEEK films were found to have a single crystalline texture with a (100) contact plane, the chain axes of both polymers being parallel. The lattice matching between the interchain distances in the (100) contact planes of both polymers appears to be at the root of this remarkable orientation. Finally, these epitaxially crystallized polymer films are highly suitable for performing a detailed study by FTIR spectroscopy of the PEEK molecular and crystal vibrations.

Acknowledgment. This work was supported by the "Centre National de la Recherche Scientifique" (France) and the Belgian National Fund for Scientific Research. The authors acknowledge ICI for supplying the polymer.

References and Notes

(1) Dawson, P. C.; Blundell, D. J. *Polymer* **1980**, *21*, 577.
(2) Iannelli, P. *Macromolecules* **1993**, *26*, 2309.
(3) Hay, J. N.; Kemmish, D. J.; Langford, J. I.; Roe, I. M. *Polym. Commun.* **1984**, *25*, 175.
(4) Fratini, A. V.; Cross, E. M.; Whitaker, R. B.; Adams, W. W. *Polymer* **1986**, *27*, 861.
(5) Cheng, S. Z. D.; Cao, M. Y.; Wunderlich, B. *Macromolecules* **1986**, *19*, 1868.
(6) Tsuji, M.; Kawamura, H.; Kawaguchi,A.; Katayama, K. *Bull. Inst. Chem. Res., Kyoto Univ.* **1989**, *67*, 77.
(7) Lovinger, A. J.; Davis, D. D. *Macromolecules* **1986**, *19*, 1861.
(8) Lovinger, A. J.; Davis, D. D. *J. Appl. Phys.* **1985**, *58*, 2843.
(9) Lovinger, A. J.; Hudson, S. D.; Davis, D. D. *Macromolecules* **1992**, *25*, 1752.
(10) Marand, H.; Prasad, A. *Macromolecules* **1992**, *25*, 1731.
(11) Wittmann, J. C.; Smith, P. *Nature* **1991**, *352*, 414.
(12) Motamedi, F.; Ihn, K. J.; Fenwick, D.; Wittmann, J. C.; Smith, P. *J. Polym. Sci., Polym. Phys. Ed.* **1994**, *32*, 453.
(13) Schaaf, P.; Lotz, B.; Wittmann, J. C. *Polymer* **1987**, *28*, 193.
(14) Bunn, C. W.; Howell, E. R. *Nature* **1954**, *18*, 549.
(15) J. C. Wittmann, manuscript in preparation.
(16) Menard, C.; Mellier, A. *Spectrochim. Acta* **1973**, *29A*, 1273.
(17) Garrigou-Lagrange, C.; Lebas, J. M.; Josien, M. L. *Spectrochim. Acta* **1958**, *12*, 305.
(18) Bassigny, V.; Seguela, R.; Rietsch, F.; Jasse, B. *Polymer* **1993**, *34*, 4052.
(19) Wilson, E. B.; Decius, J. C.; Cross, P. C. *Molecular vibrations*; McGraw-Hill: New York, 1955.

MA950267W