*J. Am. Chem. Soc.* **1995,** *117,* 1117–1120

# Orientation of *p*-Nitrophenol Molecules Induced by Epitaxial Crystallization on Friction-Transferred Poly(tetrafluoroethylene) Substrates

**P. Damman,*,† M. Dosière,† P. Smith,‡ and J. C. Wittmann§**

*Contribution from the Université de Mons-Hainaut, 20 Place du Parc,*
*B-7000 Mons, Belgium, Materials Department, University of California at Santa Barbara,*
*Santa Barbara, California 93106, and Institut Charles Sadron (CRM-EAHP),*
*6 rue de Boussingault, F-67083, Strasbourg, France*

*Received September 26, 1994*®

**Abstract:** The crystallization of *p*-nitrophenol molecules (PNP) onto monooriented poly(tetrafluoroethylene) (PTFE) films prepared by friction transfer on glass slides was found to yield highly oriented thin layers of the former species. Polarized Fourier-transform infrared spectroscopy and X-ray diffraction studies clearly show that the thin PNP layers adopt the $\beta$ crystal form and have a single-crystal-like orientation with a (001) contact crystal plane, the crystallographic *a* axis being aligned with the PTFE chain axis. Materials of this outstanding orientation are very suitable for analysis by FTIR spectroscopy of the crystal field effect on molecular vibrations.

Macroscopic orientation of small molecular and polymeric materials is an important step in both the study of their structure and improvement of their physical properties which may be enhanced by several orders of magnitude with respect to their isotropic counterparts. Recently, the ability was reported of highly oriented poly(tetrafluoroethylene) (PTFE) films to induce the oriented growth of many types of molecules, small organics (adipic acid, ...), inorganics (thallium chloride, ...), liquid crystals (4-cyano-4′-*n*-alkylbiphenyls, ...), and polymers (PET, nylon, PE, polyaniline, ...), by crystallization from solution, the melt,- and the vapor phase, and during epipolymerization directly on the substrate.[1] In this paper, we report a study of crystallization of *p*-nitrophenol (PNP) onto oriented PTFE substrates. The type of orientation texture (uniaxial or single crystalline) and the crystallographic orientation of the small aromatic molecules in the deposited films were characterized by X-ray diffraction and polarized FTIR spectroscopy. The particular substance PNP was selected because its normal mode assignment was already investigated for its molecular complexes with poly(ethylene oxide).[2]

## Experimental Section

**Preparation of the Samples.** Monooriented PTFE thin films were prepared by sliding a PTFE rod at constant pressure, and temperature, on freshly cleaned glass slides according to the process that has been fully described in previous publications.[1,3] Atomic force microscopy, used to characterize the exposed PTFE surfaces, revealed a periodicity of 0.56 nm between adjacent PTFE chains, as is expected for the (100) crystal plane.[4] These friction-transferred films were used as substrates for the crystallization of the PNP molecules deposited from the vapor phase. The PTFE-covered glass slides were held above a PNP melt kept at atmospheric pressure and at 130 °C. The thickness of the PNP layers studied by FTIR spectroscopy was estimated from their absorbance and found to be a few tenths of a micrometer. For X-ray diffraction experiments, however, much thicker samples (around 1 $\mu$m) were produced and used. As shown below, increasing the thickness did not lead to a significant loss of orientation of the PNP crystals.

**Characterization.** Polarized optical microscopic observations of the PNP layers were carried out with a Zeiss photomicroscope II. FTIR spectra were recorded on a Bruker IFS 113v FTIR spectrometer fitted with a microscope working either in reflection or in transmission mode. Generally, 128 interferograms with a resolution of 2 cm$^{-1}$ in transmission and 4 cm$^{-1}$ in reflection were added. The FTIR spectrum of isotropic PNP was recorded on Al substrates by reflection. The polarized FTIR spectra of the epitaxial layers, which were picked up on KRS-5 windows, were recorded with the microscope in transmission mode with an Al wire grid polarizer. To record the spectra below 650 cm$^{-1}$ (the microscope being limited to the wavenumbers above 650 cm$^{-1}$), we deposited the epitaxial PNP layer on polypropylene foils as the mechanical support. The diffraction patterns of thick PNP oriented samples were recorded on phosphorimager plates (Molecular Dynamics) at LURE (DCI beamline D43) with a flat plate camera. The values of the wavelength, and the diameter of the collimator were 0.126 nm and 150 $\mu$m, respectively.

## Results and Discussion

**Optical Microscopy.** Crystallization of PNP from the vapor phase onto PTFE substrates yields very well oriented macroscopic layers. The optical photomicrograph shown in Figure 1 clearly demonstrates the effect of the PTFE substrate on the nucleation and crystallization processes. On uncovered glass, small disordered crystals without any preferential orientation are observed. By contradistinction, on PTFE, the nucleation density is largely enhanced and we observe the crystallization of elongated small crystals preferrentially oriented in the PTFE friction direction, i.e., the PTFE chain axis (near diagonal). The presence of needle-like crystals is indicative of the growth of PNP in the $\beta$ form (monoclinic unit cell with $a$ = 1.540 nm, $b$ = 1.111 nm, $c$ = 0.379 nm, and $\alpha$ = 107.4°). The latter is known to be stable at room temperature[5] while the $\alpha$ form is

---

† Université de Mons-Hainaut.
‡ University of California at Santa Barbara.
§ Institut Charles Sadron (CRM-EAHP).
® Abstract published in *Advance ACS Abstracts,* December 15, 1994.

(1) Wittmann, J. C.; Smith, P. *Nature* **1990**, *352*, 414.
(2) (a) Point, J. J.; Damman, P. *Macromolecules* **1992**, *25*, 1184. (b) Damman, P.; Point, J. J. *Macromolecules* **1994**, *27*, 3919.
(3) Motamedi, F.; Ihn, K. J.; Fenwick, D.; Wittmann, J. C.; Smith, P. *J. Polym. Sci., Polym. Phys. Ed.* **1994**, *32*, 453.
(4) (a) Hansma, H.; Motamedi, F.; Smith, P.; Hansma, P.; 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.
(5) Coppens, P.; Schmidt, G. M. J. *Acta Crystallogr.* **1965**, *18*, 654.

0002-7863/95/1517-1117$09.00/0

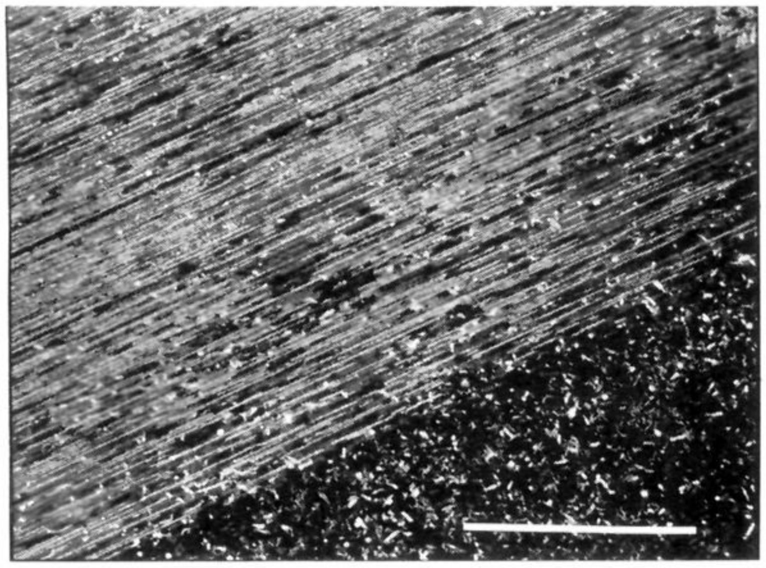


**Figure 1.** Optical photomicrograph of a PNP layer crystallized on a friction-transferred PTFE substrate (upper part, PTFE covered glass; lower part, uncovered glass). The scale bar corresponds to 50 μm.

only stable below 90 K.[6] The presence of crystals in the β form is further confirmed by X-ray diffraction analysis on thick films.

**X-ray Diffraction Analysis.** The X-ray diffraction pattern recorded in transmission for a thick PNP layer deposited on PTFE is shown in Figure 2a. As can be noticed, the degree of orientation is fairly high, despite the larger thickness of the PNP layer, and all the diffraction spots can be indexed on the basis of the β unit cell, as (*hk*0) reflections. A computer-simulated diffraction pattern of a PNP single crystal with a [001] zone axis (Figure 2b) is in very good agreement with the observed pattern. From these observations, it can be deduced that (i) the PNP needles contact the exposed PTFE surface with their (001) crystallographic plane; (ii) the PNP crystallographic *a* axis is parallel to the PTFE chain axis (*c* axis). This unique orientation is highly suitable for further detailed analysis of the molecular orientation by polarized FTIR spectroscopy.

**PNP Normal Mode Assignments.** Since to our knowledge no work on the assignement of the specific normal modes of PNP has been performed, we based our attributions of the observed vibrations on several IR studies on different substituted aromatic molecules.[7,8,10] According to the crystal structure of the β form,[5] the PNP molecule belongs to the $C_1$ point group, since the angle between the aromatic ring and the $NO_2$ plane is equal to 10°. However, the small number of vibrations observed in Figure 3 for a randomly oriented PNP sample, and the dichroism measured for oriented poly(ethylene oxide)−PNP molecular complexes described elsewhere,[2] indicate that a $C_{2v}$ point group has to be taken into consideration for the ring vibrations. The latter correspond to three different irreducible representations, $a_1$, $b_1$, and $b_2$. The transition moments of $a_1$, $b_1$, and $b_2$ modes are along the 1−4 axis of the molecule, in the plane of the ring but normal to the 1−4 axis, and normal to the ring (out of plane modes), respectively. As observed in the FTIR study of poly(ethylene oxide)−*p*-dihalobenzenes complexes, the vibrations of the aromatic ring are only slightly affected by substitution (18a, 19a, 19b, 8a, ...).[8] By contradistinction, some normal modes are well known to shift depending upon the substituent.[7,8] Normal mode calculations on differently substituted aromatic molecules led Le Calvé et al. to propose that vibrations 6a and 6b (around 600 cm$^{-1}$, c and d modes) and 1 and 12 (around 1000 cm$^{-1}$, e and e′ modes)[9] are strongly coupled with CN and CO stretching. Finally, we also take into account the combination modes which are generally attributed to 400 (a2) + 800 (a2) = 1200 cm$^{-1}$ (a1), 2 × 800 (a2) = 1600 cm$^{-1}$ (a1), and 2 × 755 (b2) = 1510 cm$^{-1}$ (a1) for *para*-

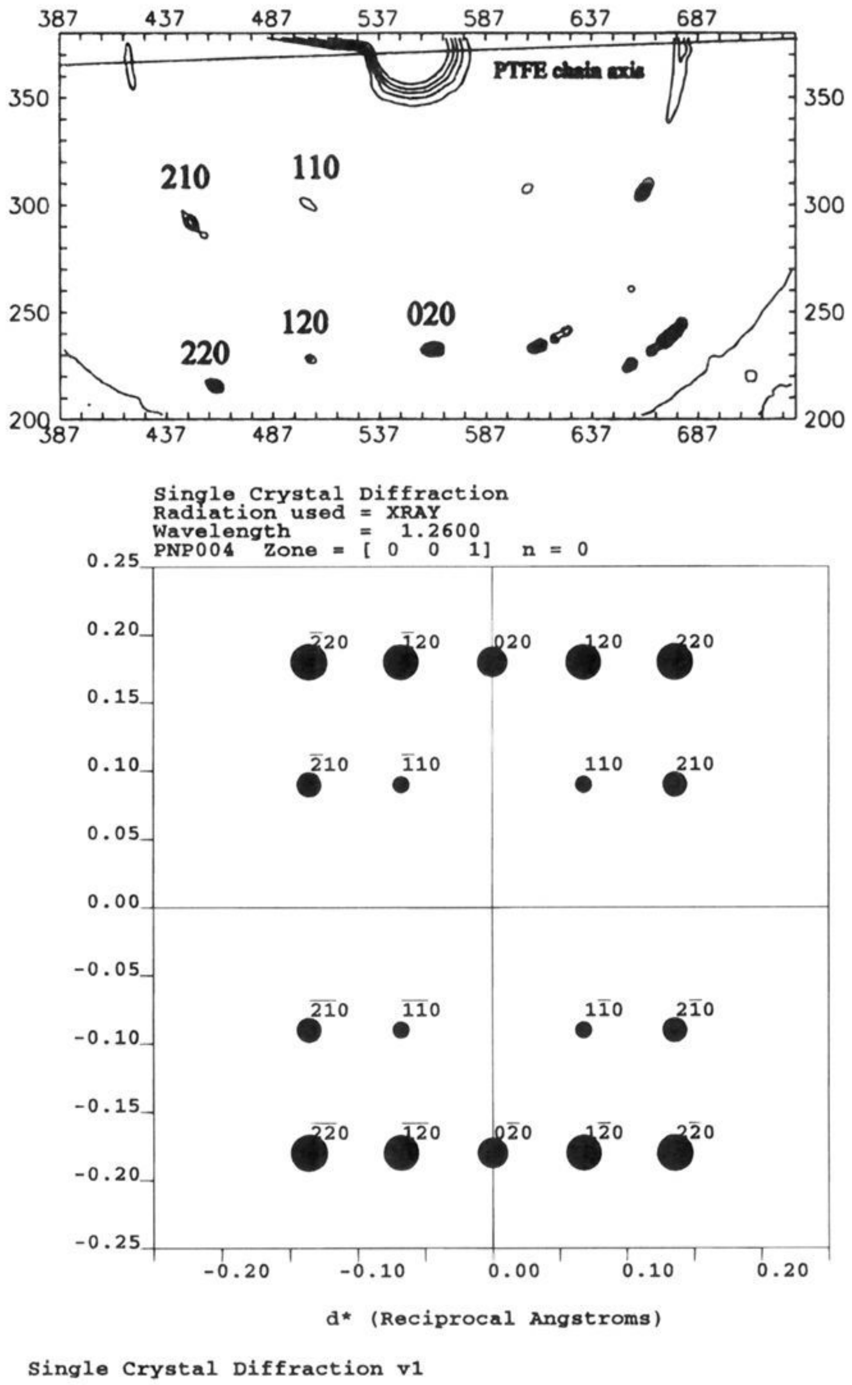


**Figure 2.** (a, top) X-ray diffraction pattern of a thick layer of PNP crystallized onto a PTFE substrate. (b, bottom) Computer-simulated X-ray diffraction pattern of a [001] zone axis single crystal of PNP (CERIUS2 software).

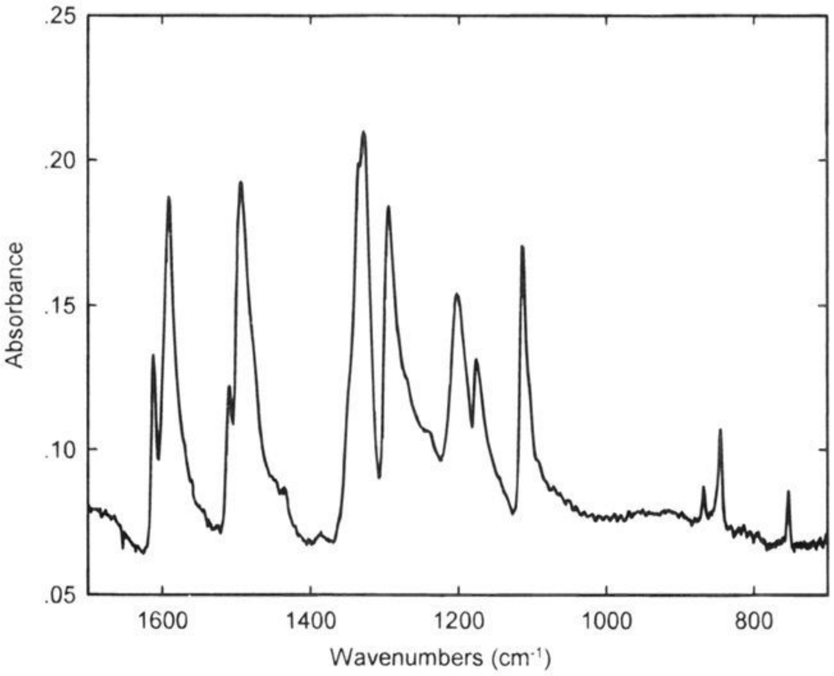
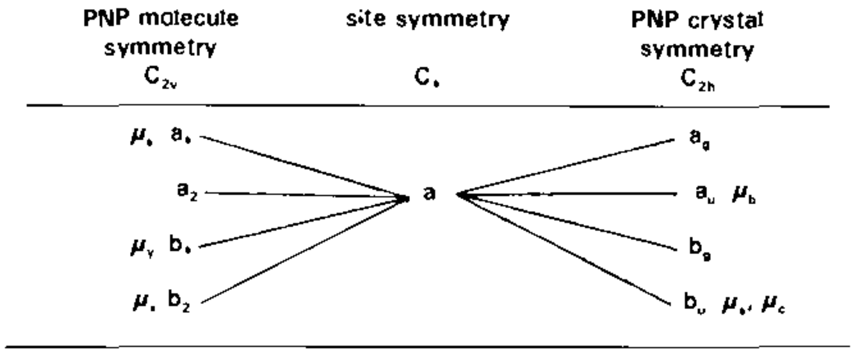


**Figure 3.** Reflection FTIR spectra of a randomly oriented PNP sample crystallized on Al.

---

(6) Coppens, P.; Schmidt, G. M. J. *Acta Crystallogr.* **1965**, *18*, 62.
(7) Green, J. H. S. *Spectrochim. Acta* **1970**, *26A*, 1503.
(8) Point, J. J.; Jasse, B.; Dosière, M. *J. Phys. Chem.* **1986**, *90*, 3273.
(9) Le Calvé, N.; Labarbe, P. *Spectrochim. Acta* **1970**, *26A*, 77.

Table 1. PNP Crystal Vibrations, Correlation Diagram[a]



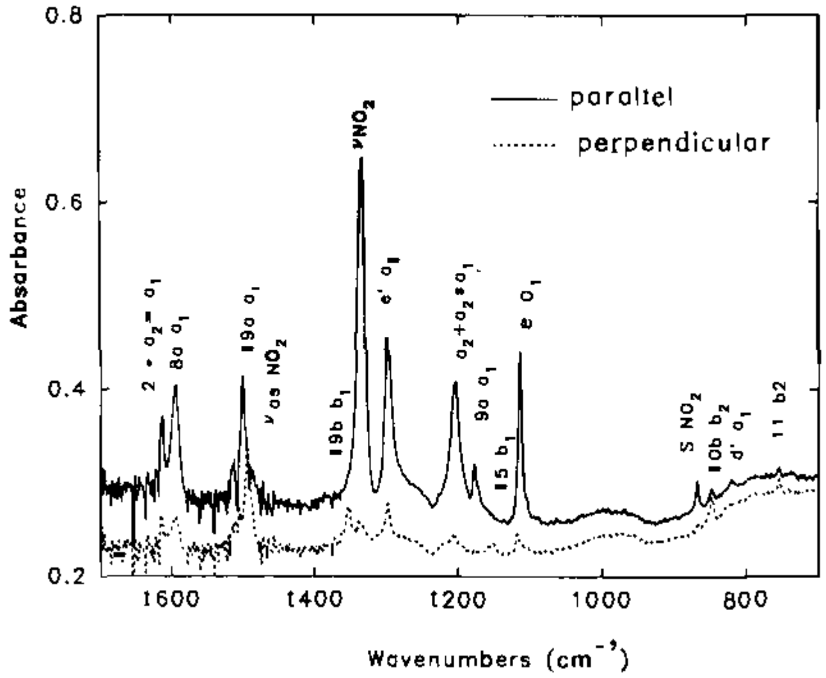


Figure 4. Transmission polarized FTIR spectra of PNP crystallized onto PTFE, and picked up on a KRS-5 window. Solid and broken lines correspond to polarization parallel and perpendicular to the chain axis, respectively.

disubstituted molecules.[10] Regarding the vibrations of the PNP crystals, the site symmetry corresponds to the $C_i$ point group as no symmetry elements belong to both the PNP molecule and crystal ($C_{2h}$ space group). Thus, from the correlation diagram (Table 1), we can deduce that the vibrations of the molecule may be split into two crystal modes depending upon the crystal field: the $a_u$ transition moments in the *ac* crystal plane, and the $b_u$ transition moments along the *b* axis.

**Molecular Orientation from FTIR Spectra.** Figure 4 gives the FTIR spectra obtained with the electric vector parallel and perpendicular to the PTFE chain axis. The observed dichroic ratios are given in Table 2. The comparison of figure 3 recorded for isotropic PNP layers deposited on Al substrate and Figure 4 recorded for PNP molecules epitaxially crystallized on a PTFE film shows that the out of plane vibrations (16b, 4, 11, 10b; see Table 2) have their intensity significantly reduced in the oriented layer. Table 2 also indicates that $a_1$ modes which possess their transition moments along the 1–4 axis are polarized parallel to the PTFE chain axis, the $b_1$ modes being polarized perpendiculary. These observations can only be interpreted on the basis of a (001) monocrystalline texture (Figure 5). The aromatic rings are nearly parallel to the *ab* plane (angle of 15°), and the 1–4 axis is preferrentially oriented along the *a* axis. The observed orientation of PNP crystals explains, firstly, the decrease in intensity of the out of plane modes and, secondly, the parallel polarization of the $a_1$ vibrations, if the *a* axis is assumed to be parallel to the PTFE chain axis.

Finally, because of their monocrystalline texture, the PNP layers are suitable for the investigation of crystal field effects on the FTIR spectra of PNP. On the basis of the simplified oriented gas model and taking into account the orientation of the molecules in the (001) crystal plane (Figure 5), we calculate theoretical dichroic ratios of 6 and 0.2 for the $a_1$ and $b_1$ vibrations, respectively. They are generally in good agreement with the observed dichroic ratios (cf. Table 2). The dichroic ratios measured for $NO_2$ symmetric stretching and the 6a ring mode are equal to 16 and above 30, respectively (Figure 6). The large departure from the theoretical values (the expected dichroic ratio was equal to 6) suggests that these vibrations are strongly affected by the crystal field as is expected for hydrogen-bonded molecular crystals. A splitting of these modes (628–638 $cm^{-1}$ for 6a and 1334–1354 $cm^{-1}$ for the $NO_2$ symmetric stretching) is induced, with both components being polarized parallel either to the *a* or *b* axis.

Table 2. Summary of the FTIR Observations on PNP Layers Epitaxially Crystallized onto the PTFE Substrate[a]

| wavenumbers[b] ($cm^{-1}$) | dichroism | dichroic ratio | mode attribution[d] |
|---|---|---|---|
| m 497 | $\perp^c$ | | 16b, b2 |
| m 536 | $\perp^c$ | | $W_{NO_2}$ |
| s 628 | $\parallel$ | 30 | 6a, d, a1[e] |
| w 638 | $\perp$ | | 6a (splitting) |
| m 693 | $\perp^c$ | | 4, b2 |
| m 755 | $\perp^c$ | | 11, b2 |
| w 820 | $\parallel$ | | d', a1[e] |
| s 849 | $\perp^c$ | | 10b, b2 |
| m 868 | $\parallel$ | 6 | $S_{NO_2}$ |
| vs 1115 | $\parallel$ | 8 | 1, e, a1[e] |
| w 1150 | $\perp$ | | 15, b1 |
| m 1177 | $\parallel$ | 6 | 9a, a1 |
| s 1203 | $\parallel$ | 8 | comb. a1 |
| vs 1298 | $\parallel$ | 4 | 12, e', a1[e] |
| vs 1334 | $\parallel$ | 16 | $\nu_{s\,NO_2}$ |
| w 1354 | $\perp$ | | $\nu_{s\,NO_2}$ (splitting) |
| m 1493 | $\perp$ | | $\nu_{as\,NO_2}$ |
| m 1500 | $\parallel$ | | 19a, a1 |
| w 1512 | $\parallel$ | | comb. a1 |
| m 1595 | $\parallel$ | 5 | 8a, a1 |
| w 1611 | $\parallel$ | 4 | comb. a1 |

[a] Dichroic ratios are defined by the ratio of the peak absorbance measured with an electric vector parallel and perpendicular to the PTFE axis. [b] w, m, s, and vs correspond to weak, medium, strong, and very strong intensity. [c] Vibrations which have their intensity reduced for the oriented layers. [d] $W_{NO_2}$, $S_{NO_2}$, $\nu_{s\,NO_2}$, and $\nu_{as\,NO_2}$ correspond to wagging, scissoring, symmetric stretching, and asymmetric stretching of $NO_2$. [e] Coupled modes (see text).

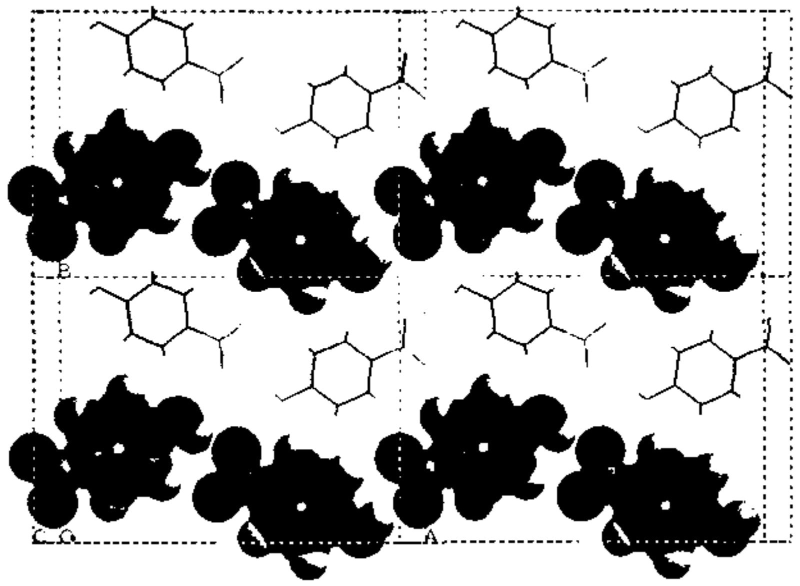


Figure 5. Crystal structure of the b form of PNP projected on the (001) contact plane. Stick and ball drawn molecules correspond to fractional coordinates along the *c* axis of 0.25 and 0.75, respectively (CERIUS2 software).

**Epitaxial Relationship.** As apparent from Figure 4, the crystal structure of the *β* form of PNP can be broadly described

---

(10) Stojiljkovic, A.; Whiffen, D. H. *Spectrochim. Acta* **1958**, *12*, 57.

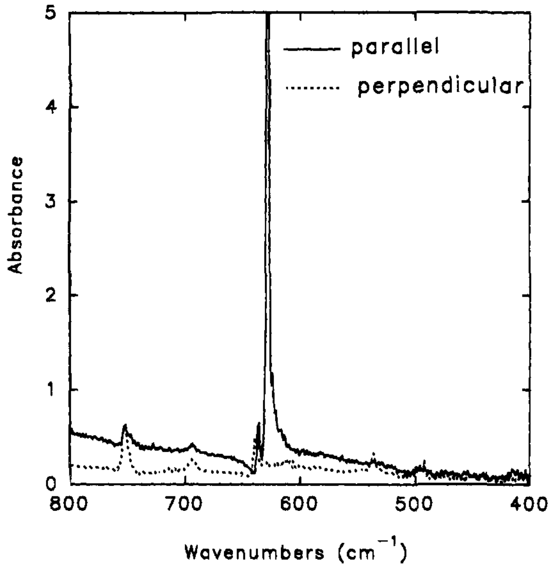


**Figure 6.** Low wavenumber transmission polarized FTIR spectra of a PNP layer picked up on a polypropylene foil. Solid and broken lines correspond to polarization parallel and perpendicular to the chain axis, respectively.

as resulting from the stacking of planar chains or ribbons of hydrogen-bonded PNP molecules, lying flat in the (001) contact plane. Furthermore, the chains are oriented parallel to the crystallographic *a* axis, and the spacing between two neighboring chains is therefore equal to the *b* parameter (1.11 nm). This peculiar crystal geometry fully accounts for the orientation and epitaxial relationship between this aromatic compound and the polymeric substrate. The crystallographic epitaxial relationship described above can be summarized as follows:

$$(001)_{\mathrm{PNP}}//(100)_{\mathrm{PTFE}}$$

$$a_{\mathrm{PNP}}//c_{\mathrm{PTFE}}$$

Accordingly, the PNP molecular chains are oriented with their plane and axis parallel to the PTFE surface and chain axis, respectively. As a consequence, a perfect matching is established between the PNP "interchain" distance (1.11 nm) and twice the PTFE interchain distance (0.56 nm × 2 = 1.12 nm). Obviously, this excellent geometrical fit between PNP crystals and the highly oriented PTFE substrate is the origin of the outstanding orientation revealed by the present FTIR, X-ray, and optical microscopy investigations for the present specimen.

## Conclusion

In line with previous results,[1] friction-transferred PTFE layers were found to successfully induce the oriented growth of crystals of aromatic compounds and *p*-nitrophenol in particular. From the results of the present X-ray and FTIR investigations, it can be concluded that the structure of the vapor-deposited aromatic thin films is monocrystalline with a well-defined (001) contact plane and a unique orientation of the *a* axis parallel to the PTFE chain axis. This orientation is apparently the result of a nearly perfect lattice matching between the *b* periodicity of PNP and twice the PTFE interchain distance. The epitaxial grown layers are very suitable for a detailed analysis by FTIR of the molecular orientation and crystal field effects.

**Acknowledgment.** P.D. is a Research Assistant of the Belgian National Fund for Scientific Research. The authors are indebted to Professor J. J. Point for the fruitful discussions about the interpretation of the FTIR observations. This work was supported by the Belgian National Fund for Scientific Research and by the European Community (Science Program).

JA943181B