may be a manifestation of either an extended molecular array or short-range configurational interactions. A highly structured, extended array of molecules such as that found in a β-structure (pleated sheet), a liquid crystal, or Langmuir–Blodgett type molecular orientation[9] at the AgCl surface may account for the anomalous peaks. Alternatively, the simple repetition of a head–tail arrangement of the carbonyl units should lead to highly ordered materials. In the absence of a known crystal structure, the exact assignment of the observed bands would be impossible. However, by analogy to dimethyl carbonate crystallized at low temperature, the site symmetry around the carbonate moiety would be anticipated to have lower than C_{2v} symmetry.[5e,g]

Summary

The use of solution VT-IR methodology indicates the occurrence of polycrystalline films from both polymeric and monomeric organic carbonates at low temperature. BPA polycarbonate solutions are found to behave analogously to those of the simple, monomeric carbonates. As suggested by earlier researchers,[5] simple crystallinity within these materials is insufficient to explain the observed results. The low-temperature solution preparation of these oriented polycrystalline films is demonstrated to be both general and quite facile.

Acknowledgment. We thank Drs. M. F. Grabauskas and J. T. Bendler for access to the crystal structure data of DPC and Professor K. Karlin for the use of the VT-IR cell.

Registry No. LEXAN, 24936-68-3; DMC, 616-38-6; DEC, 105-58-8; DPC, 102-09-0.

References and Notes

(1) Henrichs, P. M.; Luss, H. R. *Macromomolecules* **1988**, *21*, 860. (b) Perez, S.; Scaringe, R. P. *Macromolecules* **1987**, *20*, 68. (c) Bicerano, J.; Clark, H. A. *Macromolecules* **1988**, *21*, 585. (d) Bicerano, J.; Clark, H. A. *Macromolecules* **1988**, *21*, 597. (e) O'Reilly, J. M.; Karasz, F. E.; Bair, H. E. *J. Polym. Sci., Part C* **1963**, *6*, 109. (f) Schaefer, J.; Stejskal, E. O.; Perchak, D.; Skolnick, J.; Yaris, R. *Macromolecules* **1985**, *18*, 368. (g) Li, K. L.; Inglefield, P. T.; Jones, A. A.; Bendler, J. T.; English, A. D. *Macromolecules* **1988**, *21*, 2940. (h) Schaefer, J.; Stejskal, E. O.; McKay, R. A.; Dixon, W. T. *Macromolecules* **1984**, *17*, 1479. (i) Bendler, J. T. *Am. Inst. Phys. Conf. Proc.* **1985**, *137*, 227. (j) Jones, A. A. *Macromolecules* **1985**, *18*, 902. (k) Jones, A. A.; O'Gara, J. F.; Inglefield, P. T.; Bendler, J. T.; Yee, A. F.; Ngai, K. L. *Macromolecules* **1983**, *16*, 658 and references therein.

(2) The nomenclature for these conformational isomers has varied historically. Equivalent names (those used previously) to the IUPAC *E*/*Z* nomenclature used here are the following: *trans,trans* (1), *trans,cis* (2); *cis* (1), *trans* (2); *trans* (1), *cis* (2); *s-trans-s-trans* (1), *s-trans-s-cis* (2).

(3) Perrin, D. D.; Armarego, W. L. F. In *Purification Of Laboratory Chemicals*, 3rd ed.; Pergamon Press: plc, Oxford, 1988.

(4) The polycarbonate M_w was determined relative to a polystyrene standard corrected to universal calibration with Mark–Houwink constants ($\alpha = 0.82$, $K = 1.2 \times 10^{-4}$).

(5) (a) Katon, J. E.; Cohen, M. D. *Can. J. Chem.* **1974**, *52*, 1994. (b) Katon, J. E.; Lang, P. L. *J. Mol. Struct.* **1988**, *172*, 113. (c) Jones, G. I. L.; Owen, N. L. *J. Mol. Struct.* **1973**, *18*, 1. (d) Garahi, M.; Badelle, F.; Noe, E. A. *J. Org. Chem.* **1987**, *52*, 3942. (e) Katon, J. E.; Cohen, M. D. *Can. J. Chem.* **1975**, *53*, 1378. (f) Oki, M.; Nakanishi, H. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 3419. (g) Collingwood, B.; Lee, H.; Wilmhurst, J. K. *Aust. J. Chem.* **1966**, *19*, 1637. (h) Nyquist, R. A.; Potts, W. J. *Spectrochim. Acta* **1961**, *17*, 679. (i) Thiebaut, J.-M.; Rivail, J.-L.; Greffe, J.-L. *J. Chem. Soc., Faraday Trans. 2* **1976**, *72*, 2024. (j) Angell, C. L. *Trans. Faraday Soc.* **1956**, *52*, 1178.

(6) Neither solvent produces any new bands in this region upon cooling. Condensation of atmospheric moisture on the cell windows was not observed during our experiments. Due to the necessity of subtracting the methylene chloride (solvent) spectrum from the data, only the infrared region from ~2000 to 1550 cm^{-1} could be analyzed reliably.

(7) (a) Nyquist, R. A. *Spectrochim. Acta* **1972**, *28*, 285. (b) Katon, J. E.; Sinha, D.; Griffin, M. G.; Condit, D. A. *Can. J. Chem.* **1972**, *50*, 3255. (c) Krimm, S. In *Infra-red Spectroscopy and Molecular Structure*; Davies, M., Ed.; Elsevier: New York, 1963; Chapter 8. (d) Katon, J. E.; Sinha, D. *Spectrochim. Acta* **1977**, *33*, 45. (d) Oki, M.; Nakanishi, H. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 1552.

(8) The diphenyl carbonate used for solid analysis was recrystallized from anhydrous ethanol.[3] The DPC crystallizes to form an orthorhombic lattice with four molecules in the unit cell. The space group is $P2_12_12_1$ with the following lattice constants: a, 6.077 (2) Å, b, 7.297 (1) Å, c, 23.4297 (7) Å; $\alpha = 90°$, $\beta = 90°$, $\gamma = 90°$. The calculated density was 1.37 g cm^{-3}, and the data were reduced to an R value = 0.0543 with an R_w = 0.0687. The solid-state conformation of DPC and its extended intermolecular relationships have been published previously.[1i]

(9) Crystal field splitting in the infrared spectra of oriented molecules has been observed previously in Langmuir–Blodgett films: (a) Kamata, T.; Umemura, J.; Takenaka, T. *Chem. Lett.* **1988**, 1231. (b) Snyder, R. G. *J. Mol. Spectrosc.* **1961**, *7*, 116.

Surface Investigation by ESCA of Poly(ethylene terephthalate)–Perfluoro Polyether Block Copolymers

F. PILATI AND M. TOSELLI

Dipartimento di Chimica Applicata e Scienza dei Materiali,
Facoltà di Ingegneria, Università di Bologna, Viale
Risorgimento 2, 40136 Bologna, Italy

A. RE

Montefluos crs, Via S. Pietro 50, 20021 Bollate, Milano,
Italy

F. A. BOTTINO, A. POLLICINO, AND A. RECCA*

Istituto Chimico, Facoltà di Ingegneria, Università di
Catania, Viale A. Doria 6, 95125 Catania, Italy.

Received February 1, 1989;
Revised Manuscript Received April 27, 1989

Introduction

In the last few years there has been increasing interest in the synthesis of polymeric structures containing fluorine atoms in the chain in order to increase the thermoxidative and chemical resistance and to have low surface energy and a low coefficient of friction. Fluorine atoms can be introduced into polymers by different ways, which in turn can influence the properties of the resulting materials. The recent availability of telechelic perfluoro polyethers (PFPEs) having the general formula $XCF_2(OC_2F_4)_m(OCF_2)_nOCF_2X$ with $m/n = 0.7$ and X = CF_3 (Fomblin Z) and $COOCH_3$ (Fomblin ZDEAL) allows the preparation of polymeric materials containing PFPE, with the possibility of obtaining PFPE blocks bonded to other polymer chains. The presence of a fraction of PFPE as a block copolymer may improve the properties of the resulting heterophase material and could also influence the concentration of PFPE on the surface. Recently, samples consisting of poly(ethylene terephthalate) (PET) and PFPE homopolymers and containing a fraction of PET–PFPE block copolymers have been prepared by the addition of Fomblin ZDEAL (a PFPE with X = $COOCH_3$) during the polymerization of PET via transesterification reactions. Fluorine elemental analysis and selective extractions were employed to characterize the composition of these samples.[1,2] The results showed that at least a part of ZDEAL reacts with the PET chains lead-

0024-9297/90/2223-0348$02.50/0 © 1990 American Chemical Society

Table I

sample	compositn	wt % of fluorine	F_{1s}/C_{1s} bulk (calc)	F_{1s}/C_{1s} exptl[a]	F_{1s}/C_{1s} exptl[b]	C_2F_4/CF_2 bulk (calc)	C_2F_4/CF_2 exptl[c]
1	PET + ZDEAL[e]	4.8[d]	0.051	1.16	1.24	1.40	1.31
2	PET + Fomblin Z/15[e]	9.2[d]	0.103	1.13	1.34	1.40	1.52
3	PET-*b*-PFPE + Fomblin Z/15[e]	11.0[d]	0.126	1.31	1.91	1.40	1.98
4	PET-*b*-PFPE + PFPE[f]	4.8[i]	0.051	1.36	1.41	1.40	1.47
5	PET-*b*-PFPE + PFPE[f]	10.6[i]	0.121	1.23	1.29	1.40	1.92
6	PET + ZDEAL[g]	4.8[i]	0.051	0.47	1.13	1.40	1.60
7	PET-*b*-PFPE + PFPE[f]	4.8[i]	0.051	1.00	1.32	1.40	1.87
8	PET-*b*-PFPE[h]	1.9[i]	0.022	0.20	0.46	1.40	1.20
9	PET-*b*-PFPE[h]	2.1[i]	0.020	0.25	0.52	1.40	1.46

[a] These values have been calculated considering the area ratio between the −C(O)O and −CF functionalities of the C_{1s} region centered at 289.3 and 293.7 eV, respectively. [b] In order to calculate the experimental area ratios, the corrected C_{1s} area (obtained by detracting the hydrocarbon contamination area from the C_{1s} area of CH region) has been used. In addition, the instrument sensitivity factors have been taken into account (0.52). [c] Obtained by taking into account the area ratios between the peak at 293.7 and 295.2 eV, respectively. [d] The ratio has been calculated from the initial amounts; however, owing to the incompatibility of PFPE with PET, some PFPE was lost, and therefore these values are probably lower. [e] From melt mixing in a minimixer of PET and PFPE homopolymers. [f] From polymerization of PET in the presence of Fomblin ZDEAL. [g] From melt mixing in a minimixer of a PET/ZDEAL blend previously prepared from a homogeneous solution in hexafluoro-2-propanol. [h] From samples 4 and 5 after selective extraction of nonbonded PFPE. [i] Evaluated by elemental analysis of fluorine.

ing to PET–PFPE block copolymers and that the overall samples are heterophase in nature. Only a slight effect of PFPE on T_g, T_m, and ΔH_m of the PET-rich phase was observed. In addition, the wetting of PFPE-modified PET decreases for both water and hydrocarbons compared with PET itself. Samples containing PFPE only in a nonbonded form were prepared by melt mixing PFPEs with PET, while samples containing PFPE only in a bonded form (as PET–PFPE block copolymer) were obtained by extraction of the nonbonded PFPE from the products prepared by polymerization of PET in the presence of Fomblin ZDEAL. Data relative to the composition of the samples are collected in Table I. Electron spectroscopy for chemical analysis (ESCA) has been shown to be a technique of prime importance in the characterization of polymer surfaces and has been successfully applied to the study of a wide range of fluorinated materials.[3-6] Consequently, we have employed ESCA to investigate the surface aspects of PFPE–PET block copolymers. The technique was used to characterize the surface of samples containing different percentages of PFPE either completely nonbonded to PET (samples 1, 2, and 6), bonded in part to PET (samples 3–5 and 7), or completely bonded to PET (samples 8 and 9).

The samples were generally used as extruded wires, but also powders were utilized without significant changes in the spectra. The C_{1s} envelope for all the samples shows three prominent photoionization peaks. The first is attributable to the −CH plus C−O functionalities and a variable amount of hydrocarbon contamination, the second peak arises from the carboxylate functionality of the PET, and the third peak is indicative of the $-CF_2$ and $-C_2F_4$ functionalities (Figure 1a).

A standard line-shape analysis (Figure 1b) of the total C_{1s} envelope reveals components at 285, 285.7, 286.9, 289.3, 292.2, 293.7, and 295.2 eV, arising from $-\mathit{C}H$, $-\mathit{C}C(O)O$, $-\mathit{C}H_2O$, $-\mathit{C}(O)O$, $-\mathit{C}F_2CO$, $-O\mathit{C}_2F_4O$, and $-O\mathit{C}F_2O$, respectively. The O_{1s} envelopes (Figure 1a) for all the samples show two photoionization peaks, which are consistent with those expected from the structural formula (oxygens bonded to −CF functionalities or not). Line-shape analysis reveals three components at 531.8, 533.6, and 535.7 eV corresponding to $-\mathit{O}{=}CO$, $-O{=}C\mathit{O}$, and $\mathit{O}CF$, respectively. The region centered at 689 eV (Figure 1a) encompasses the F_{1s} contribution for all the samples.

In all cases a variable amount of hydrocarbon contamination is present as is evident in comparing the area of the −C(O)O peak with that of the large C_{1s} contribution centered at 286 eV. The effect of this contamination will be to attenuate the signals arising from the core levels of the pure samples.

The main objective of this work has been the determination of the relative F_{1s}/C_{1s} area ratios after the inclusion of the appropriate instrument sensitivity factors for the stoichiometries. Taking into account the −C(O)O (centered at 289.3 eV) and the three C−F functionalities of the C_{1s} region (centered at 292.2, 293.7, and 295.2, respectively), it is possible to calculate the F_{1s}/C_{1s} area ratios corrected from hydrocarbon contamination. These values are representative of the average F_{1s}/C_{1s} area ratios in the C_{1s} sampling depth (~50 Å). In addition, when the −C(O)O and C−H functionalities of the C_{1s} region are compared, it is possible to calculate the hydrocarbon contamination and subtract it from the total C_{1s} area ratio. This yields the area of the C_{1s} envelope due only to the original samples. The new F_{1s}/C_{1s} area ratios considering these corrected C_{1s} areas and the F_{1s} envelope area can then be calculated. These values will be more sensitive to the outer 20 Å considering that the F_{1s} has a shorter mean free path with respect to the C_{1s}. The relevant data are collected in Table I.

It is evident from the results for the F_{1s}/C_{1s} ratios that there is more fluorine in the surface with respect to the amount predicted from the composition reported in Table I. In particular, the samples containing PFPE nonbonded to PET (completely or in part) show nearly the same F_{1s}/C_{1s} ratio, which decreases when all the PFPE is bonded to PET. The different values of the F_{1s}/C_{1s} area ratios (see Table I) indicate that the outer 50 Å are not homogeneus, indicating a greater concentration of the PFPE block in the very surface region (~20 Å). The data for samples 1, 3–5, and 7 are quite similar, and the small differences are probably due to the uncertainty of the instrument sensitivity. They mean that the fluorinated polymer is by far the most abundant on the surface even when its percentage in the bulk is less than 10%.

Sample 6 shows a lower value of the *C*(O)O/*C*F ratio, probably because it was prepared from an hexafluoro-2-propanol (HFIP) solution. As is well-known, this sol-

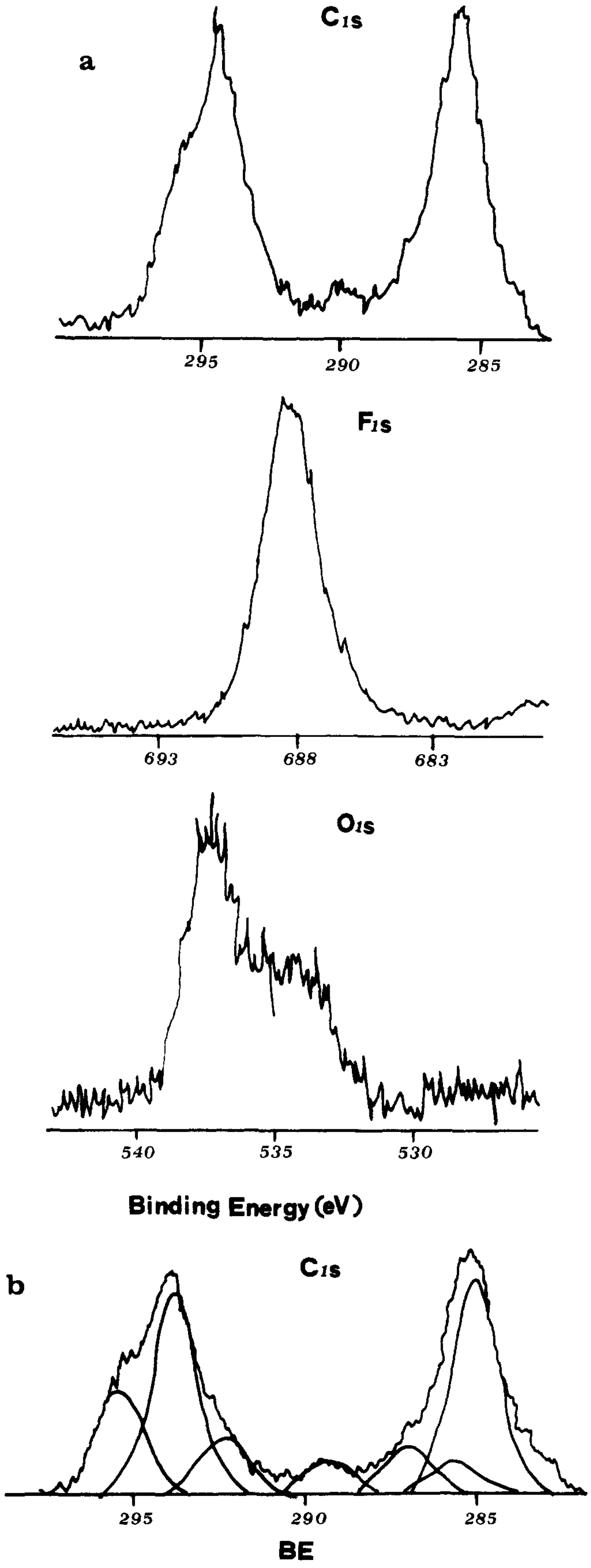

Figure 1. (a) Typical C_{1s}, F_{1s}, and O_{1s} envelopes. (b) Typical standard line-shape analysis of the C_{1s} envelope.

vent is removed with great difficulty from PET even at high temperature under vacuum, and the low value of the $C(O)O/CF$ ratio could be ascribed to residual traces of HFIP, which contribute to the CF signal without contributing to the $C(O)O$ signal.

For samples 8 and 9 the data of both columns a and b are significantly lower. The low data of column b mean that for these samples there is a lower fraction of PFPE on the surface. This result is not surprising if we consider that only in these samples are all the fluorinated chains bonded to PET chains. However, on the basis of this result, a higher fraction of PET is expected on the surface, and it is difficult at present to explain the low values of column a. It is also interesting to compare the calculated C_2F_4/CF_2 atomic ratios predicted from the ZDEAL repeat units with the experimental values (see Table I), because it is possible to have some idea on the nature of the perfluorocarbon chains present in the surface. In some cases, it seems that in the last 50 Å of the samples there is a greater concentration of C_2F_4 with respect to the CF_2 groups.

Experimental Section

Samples 1–9 were prepared using Fomblin ZDEAL (M_n = 2000) and Fomblin Z15 (M_n = 9500) by the procedures already described in the literature.[1,2] In particular, sample 6 was prepared as follows: 1.844 g of PET and 0.156 g of ZDEAL were dissolved in 8 mL of HFIP to form a homogeneous solution. The solvent was then evaporated in a rotoevaporator and further in a vacuum oven for 16 h at 90 °C. The blend was then stirred in the molten state for 1 min at 275 °C before extrusion.

The ESCA spectra were run on AEI ES300 electron spectrometer using a Mg $K\alpha_{1,2}$ X-ray source operated in a fixed retardation ratio mode. Spectra were analyzed using a Du Pont 310 curve resolver. Binding energies were referenced to the C–H level at 285 eV. The instrument sensitivity factors were obtained experimentally at fixed flux (12 kV, 15 mA to anode) in the fixed retardation mode.

The samples were studied mainly in extruded form, but also powders were utilized without significant changes in the spectra.

Acknowledgment. We gratefully acknowledge the Italian Public Instruction Minister and Italian CNR (Target Project "Special Materials") for financial support. Prof. F. A. Bottino is also indebted to NATO for a senior fellowship.

Registry No. PET, 25038-59-9; Fomblin ZDEAL, 107852-49-3; Fomblin Z15, 99752-21-3; (ethylene glycol)(Fomblin ZDEAL)(terephthalic acid) (block copolymer), 123700-50-5; (ethylene glycol)(Fomblin Z15)(terephthalic acid) (block copolymer), 123700-51-6.

References and Notes

(1) Pilati, F.; Bonora, V.; Manaresi, P.; Munari, A.; Toselli, M.; Re, A.; De Giorgi, M. *J. Polym. Sci., Polym. Chem. Ed.*, in press.

(2) Pilati, F.; Manaresi, P.; Toselli, M.; Re, A. *J. Polym. Chem., Polym. Chem. Ed.*, in press.

(3) Clark, D. T. In *Electron Emission Spectroscopy*; Dekeyser, W., Reidel, D., Eds.; D. Reidel Publishing Co.: Dordrecht, Holland, 1973; p 373.

(4) Clark, D. T. In *Electronic Structure of Polymers and Molecular Crystals*; Ladik, J., Andre, J. M., Eds.; Plenum Press: New York, 1975.

(5) Clark, D. T. In *Advances in Polymer Science*; Springer-Verlag: Berlin, 1977.

(6) Clark, D. T. *Pure Appl. Chem.* **1982**, *54*, 415.