Fluorinated Poly(butylene terephthalate): Preparation and Properties

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SYNOPSIS

Fluorinated poly(butylene terephthalate) (PBT) can be easily prepared using a telechelic perfluoropolyether (PFPE) as a comonomer. The functional groups of the PFPE react completely with other monomers, but the distribution of the PFPE blocks is not homogeneous and in the final polymeric material there is a significant fraction of PFPE bonded to very short segments of polyester. Due to the very poor miscibility of PFPE and PBT, the PFPE is present as a separate phase dispersed in an almost pure PBT matrix. Accordingly, both thermal and mechanical properties of PBT are little affected by the PFPE. The presence of PFPE induces a slight improvement on the fracture resistance and on surface properties such as wear resistance and coefficient of friction. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Fluorination, i.e., the introduction of fluorine into polymeric chains, is a widely recognized route for the modification of the surface properties of polymers; properties such as coefficient of friction, wear resistance, wettability, biocompatibility, adhesion, solvent resistance, etc., are expected to be strongly modified by this treatment. Fluorination can be accomplished in several different ways; in the case of polycondensates, a very easy method of introducing fluorine into the polymer chains is to use suitable fluorinated comonomers. Particularly interesting is the use of telechelic perfluoropolyethers (PFPE), available with different types of terminal groups and molecular weight and characterized by very low T_g ($\approx$ −120°C).

In previous papers[1-3] we discussed the results of fluorination of poly(ethylene terephthalate) (PET) when different types of PFPEs and catalysts were used. We found that PFPE blocks can be easily introduced into PET chains; that because of segregation phenomena, the surface composition of the fluorinated PET samples is much richer in PFPE than the bulk composition[4,5]; and that the crystallization rate of PET is significantly affected by the presence of PFPE.[6]

Poly(1,4-butylene terephthalate) (PBT) is another polyester that has found industrial application, mainly for injection molding, due to generally good mechanical properties and to a high crystallization rate. We thought it interesting to investigate the possibility of introducing PFPE blocks into PBT and to study the ways in which thermal and mechanical properties are changed by the presence of PFPE. For this purpose we prepared PBT samples containing different amounts of PFPE using Fomblin ZDOLTX, a PFPE with —O—CH₂CH₂—OH terminal groups (hereinafter indicated as HO—PFPE—OH) as a comonomer; in the present paper we report the results of the preparation, of the chemical and thermal characterization, and of the measurements of some mechanical properties of these samples.

EXPERIMENTAL

Reagents

Dimethyl terephthalate (DMT), 1,4-butanediol (BD), and titanium tetrabutylate [Ti(OBu)₄] were reagent-grade products and were used as supplied.

The Fomblin ZDOLTX (HO — PFPE — OH), kindly supplied by Ausimont, Italy, is an oil with formula (1) with an average value of y ≈ 1.5, a number-average molecular weight of about 2200, a comonomer m/n ratio of 0.7, and a mean functionality of about 1.95 (the other types of terminal groups are CF_3 groups).

$$H(OCH_2CH_2)_yOCH_2 — CF_2O[(C_2F_4O)_m$$

$$— (CF_2O)_n]CF_2CH_2O(CH_2CH_2O)_yH \quad (1)$$
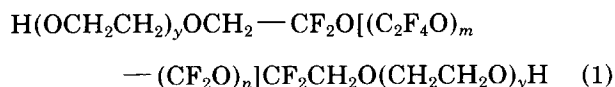
The solvents, 1,1,2,2-tetrachloroethane (TCE) and 1,1,2-trichloro-1,2,2-trifluoro ethane (TCTFE), were distilled before use.

Synthesis

The polymerizations were performed by the usual two-stage process, using $Ti(OBu)_4$ as catalyst. Multiblock — (A — B)$_n$ — copolymers were synthesized by melt polycondensation of DMT, BD, and HO — PFPE — OH in a 1.8 L stainless-steel batch reactor equipped with a paddle agitator (driven at 30 rpm) with a strain-gauge bridge mounted on the drive shaft to indicate the extent of polymerization. A typical procedure of polymerization is as follows: on starting the first stage, DMT, BD and HO — PFPE — OH were stirred at atmospheric pressure while the temperature was raised from 160° to 200°C and maintained at this value until more than 95% of the theoretical amount of methanol was distilled off. Then, during the second stage, the pressure was reduced to 0.3 mbar and the temperature was raised to, and maintained at, 250°C until the end of the run.

During polymerization, a fraction of PFPE evaporated from the reactor together with other volatile products (mainly BD, and small amounts of low molecular weight oligomers), so that its percentage in the final product is less than expected. Data relative to the loss of PFPE by volatilization were obtained by evaluating the PFPE content in the resulting polymeric material by degradation of the ester sequences with methanol, at high temperature under pressure, and by recovering the HO — PFPE — OH by extraction with water/ TCTFE. The initial amount of HO — PFPE — OH added to the reactor and the residual amount of PFPE in the final products are reported in Table I.

Selective Solubility

To separate unreacted PFPE from the crude sample, we exploited the different solubility of PFPE and polyesters. The procedure for the extraction of unreacted PFPE was carried out by weighing about 2 or 3 g of the sample, which was then refluxed with 30 ml of TCE. The resulting liquid was added to about 150 ml of TCTFE. The precipitate was separated by filtration and was again refluxed as above. The two TCTFE solutions were combined and after the solvent was evaporated, the residue, consisting of a fraction of PFPE (unreacted or bonded to short blocks of PBT) and PBT cyclic oligomers, was washed with CH_2Cl_2 to remove the latter. By this procedure pure HO — PFPE — OH was quantitatively separated from a mixture with PBT prepared by dissolving the polymers in a common solvent and evaporating the solvent.

Characterization

Samples were characterized by FTIR (Brucker IFS 48) and ¹H-NMR (Varian 200 MHz); ¹H-NMR

Table I Composition and Characterization Data

| | Wt % of PFPE | | Wt % of PFPE Not Extractable[c] | $[\eta]^{[d]}$ dl/g | Crystallization Temperature (°C) | |
| | | | | | On Crude Samples | On Samples After Extraction |
Sample	Initial[a]	After Pol.[b]				
PBT	—	—	—	0.91	182	—
PBT–S1	4.4	3	57	0.94	173	189
PBT–S2	8.9	6	41	0.98	175	188
PBT–S3	18.1	11	36	n.d.	176	186
PBT–S4	27.4	16	22	n.d.	176	185

[a] Wt % with respect to DMT; [b] wt %, estimated by separation of PFPE after alcoholysis of PBT segments; [c] by the dissolution-precipitation method described in Experimental section; [d] in Phenol/TCE, 40/60, wt/wt, at 30°C

spectra were obtained using a mixture of TCTFE/ CDCl$_3$/CF$_3$COOD (50/40/10 v/v) as the solvent. Intrinsic viscosity measurements were obtained from phenol/TCE (60/40) solutions at 30°C.

Degradation of Polyester Moieties

In order to evaluate the total amount of PFPE in the final samples, a complete degradation of the polyester sequences was also carried out. About 2 g of the sample was added to 1 ml of CH$_3$ONa 5M and 10 ml of BD, and refluxed under stirring for about 1 h. The resulting mixture was washed with water and TCTFE. The organic phase was separated and the solvent was evaporated to recover the HO —PFPE—OH.

Thermal Characterization

The thermal properties of both the crude samples and the samples obtained after selective extraction of non-bonded PFPE were investigated by non-isothermal tests in a DSC at 10 K/min. Crystallization and melting temperature were taken as the maxima of the relative peaks.

Mechanical Properties

The tests reported in Table II were performed on specimens derived from discs (100 mm of diameter, 3 mm thick) obtained from the crude samples by injection molding.

RESULTS AND DISCUSSION

Synthesis and Chemical Characterization

PBT samples containing various amounts of PFPE were prepared by the usual two-stage melt polycondensation from DMT, BD, and HO—PFPE—OH using Ti(OBu)$_4$ as the catalyst. As previously observed for PET,[3] HO—PFPE—OH does not inhibit the catalytic activity of Ti(OBu)$_4$ in the first stage of transesterification; therefore it could be added to the reactor with the other monomers on starting the first stage of polymerization. In both the first and second stages of polymerization we observed no significant difference in comparison with the synthesis of pure PBT; the samples obtained were white, very glossy, and with relatively high molecular weights, as it appears from the data of intrinsic viscosity reported in Table I. No exudation was observed, and all samples could be stretched into fibers and gave tough films by casting from solution.

As previously reported for PET,[1-3] it was found that the PFPE content in the final polymer is lower than the initial amount introduced in the reactor (see Table I) due to the distillation of part of the PFPE during polymerization.

Because of the low miscibility of PBT and PFPE, the polymerization reaction occurs in a non-homogeneous medium and it is possible that a part of the overall amount of PFPE contained in the samples is simply blended with PBT (non-bonded form) rather than reacted with it to form block copolymers

Table II   Mechanical Properties of PBT and Perfluoropolyether–Modified PBT

Property	Method	Units	Sample		
			PBT	PBT–S1	PBT–S2
Flexural Modulus[a]	ASTM D 790	MPa	2691	2519	2345
Tensile strength[b]	ASTM D 638	MPa	58.1	53.3	48.6
Elongation at br.[b]	ASTM D 638	%	37	22	21
Impact resistance[c]					
K_{IC}		MPa m	2.64	2.64	3.0*
G_{IC}		kJ m^{-2}	2.80	2.84	5.2*
Rockwell Hardness	ASTM D 785		M78	M71	M68
Taber Abraser Test[d]	FTM STD 406/1091[e]	mg/Kg cycle	25	25	20
Coefficient of friction[f]	ASTM D 1894				
Static			0.17	0.18	0.14
Dynamic			0.15	0.13	0.11

* Semifragile fracture; [a]V_0 = 2 mm/min, span = 50 mm, thickness = 3 mm; [b]V_0 = 5 mm/min, L$_0$ = 40 mm; [c]Fracture mechanics, V$_0$ = 1 m/s, span = 70 mm, S/W = 7, a/w 0.35–0.55; [d] CS wheel, weight = 1 kg; [e]Federal Test Method STD 406, method 1091; [f]Specimen 40 × 40 mm, V$_0$ = 100 mm/min, weights 6 and 21 N, on steel surface Ra = 0.03 μm.

(bonded form). This is an important point to check because the final properties may differ depending on whether PFPE is present in a bonded or non-bonded form.

^{1}H-NMR spectroscopy is a valuable analytical technique for investigating what fraction of PFPE is bonded to PBT; in particular it can be used to determine whether the aliphatic terminal portion of PFPE is bonded or non-bonded to PBT segments. However, in the crude samples the concentration of junctions between segments of PFPE and PBT is too low to reveal any information.

In order to achieve data about the fraction of un-reacted PFPE, we exploited the different solubility of PBT and pure PFPE. In fact, PBT is almost completely insoluble in TCTFE (only a small fraction of cyclic oligomers is extracted) whereas, on the contrary, unreacted PFPE is readily soluble and therefore, in principle, it is possible to separate un-reacted PFPE by selective extractions (see the Ex-

perimental section). By the application of such a procedure to the crude samples, we obtained in every case two fractions: one insoluble in TCTFE, rich in polyester segments; and another one, soluble in TCTFE, which is rich in PFPE and, most important, contains all the unreacted PFPE when present. However, block copolymers can also be present in the soluble fraction because their solubility depends on their chemical composition (type, length, and number of blocks) and block copolymers with a rel-atively high weight fraction of PFPE blocks can be soluble in TCTFE.

Although a complete separation of unreacted PFPE from block copolymers was impossible by the selective-extraction procedure described in the Ex-perimental section, ^{1}H-NMR spectroscopy analysis of the fractions soluble in TCTFE gave information about the relative amount of bonded and non-bonded PFPE. A typical ^{1}H-NMR spectrum of an extracted fraction is reported in Figure 1(a). In

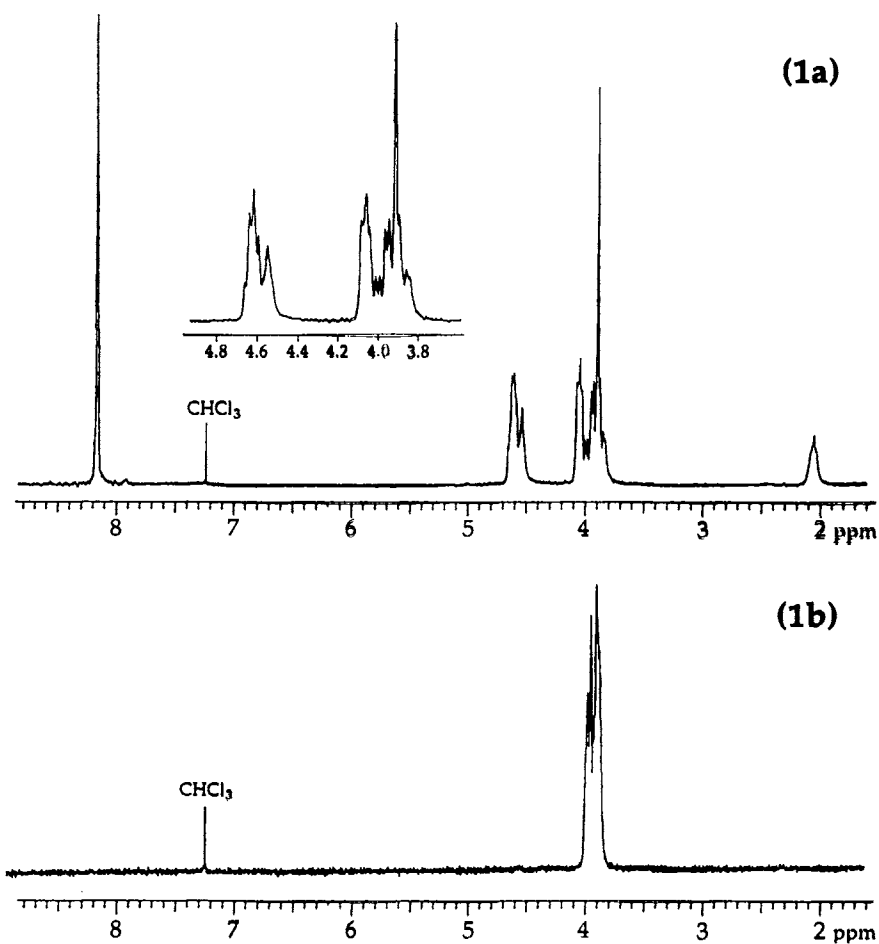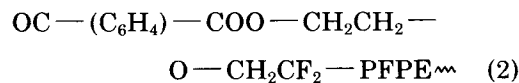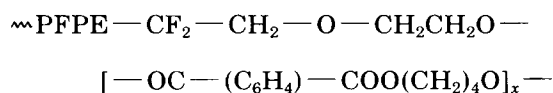**Figure 1** ^{1}H-NMR spectra of: (a) the fraction extracted from sample PBT-S4; (b) pure HO — PFPE — OH.

comparison with the spectrum of the initial
HO — PFPE — OH [see Fig. 1(b)], it shows: changes
in the 3.8–4.0 ppm region, typical of the signals of
the protons of unreacted HO–PFPE–OH; and the
appearance of peaks at about 2.05, 4.1, 4.5, and 4.7
ppm (typical of aliphatic protons), and at 8.15 ppm,
in the region of the aromatic protons.

The signals at 8.15, 4.5, and 2.05 ppm, characteristic
of PBT, means that segments of PBT are bonded to
PFPE. The signal at 4.6–4.7 ppm is attributable to
— PFPE — CF$_2$ — CH$_2$ — O — CH$_2$CH$_2$ — OOC —
PBT — protons, derived from the reaction of terminal
groups of HO — PFPE — OH with terephthalate
units. The ratio of the area of this signal to the overall
area of the signals in the 3.8–4.1 region gives a "mea-
sure" of the fraction of the terminal groups of
HO — PFPE — OH which have reacted with tere-
phthalate moieties: it can range from 0 (for completely
unreacted PFPE) to 0.33 for the complete reaction of
terminal hydroxyl groups; in every case we found a
value close to 0.33 that means an almost complete
reaction of the terminal groups of HO — PFPE — OH.

On the other hand, if we consider that the in-
tensity of the peak at 8.15 ppm (divided by 4)
is a "measure" of the terephthalate units and
that the intensity of the 2.05 ppm peak of
— COO — CH$_2$CH$_2$CH$_2$CH$_2$ — OOC — protons
(divided by 4) is a "measure" of the BD moieties,
we can estimate the ratio between the terephthalate
and the BD units in the soluble fractions. This ratio
ranges from 0.87 to 0.32, increasing from PBT–S4
to PBT–S1 samples; because in the soluble fractions
there are more terephthalate units than BD units,
it is evident that the blocks which connect two PFPE
blocks frequently consist of a single terephthalate
unit. In fact, in the presence of PBT blocks, even
though relatively short, the ratio would be close
to 1.

This conclusion is further supported by the com-
parison of the area of the peak at 4.6–4.7 ppm
(which, divided by 2, is a "measure" of the number
of junctions between PFPE segments and tere-
phthalate blocks) to that of the peak at 8.15 ppm.
From the ratio of these areas we can estimate the
average length [x in formula (2)] of the PBT blocks
joined to PFPE blocks in the fraction soluble in
TCTFE: for all samples the average value of x ranges
from about 1.6 to 0.3, decreasing from sample PBT–
S1 to PBT–S4.

PFPE — CF$_2$ — CH$_2$ — O — CH$_2$CH$_2$O —

[— OC — (C$_6$H$_4$) — COO(CH$_2$)$_4$O]$_x$ —

OC — (C$_6$H$_4$) — COO — CH$_2$CH$_2$ —

O — CH$_2$CF$_2$ — PFPE   (2)

Results show that the fraction soluble in TFTCE
consists of PFPE blocks joined together by very
short PBT segments or even by a simple terephthal-
ate unit.

In addition, the relative amount of the soluble
fraction (i.e., the amount of PFPE blocks bonded to
very short segments of PBT) increases when the
initial amount of HO — PFPE — OH increases, as
it appears from the data in Table I.

PFPE is also present in the fraction insoluble in
TCTFE, and it is reasonable to assume that this
PFPE is bonded to relatively long polyester seg-
ments which make it insoluble in TCTFE. Its pres-
ence was clearly indicated by a decrease of the
transmittance in the 1100–1200 cm^{-1} region of the
FTIR spectrum, but its quantitative evaluation is
quite difficult by direct analytical methods because
of the low levels of residual PFPE. However, the
difference between the overall amount of PFPE and
the amount of PFPE in the soluble fraction gives
the quantity of PFPE bonded to long chains of PBT
(see Table I).

In conclusion, from selective solubility tests and
^{1}H-NMR investigation it can be argued that the
polymeric material resulting from polymerization of
PBT in the presence of HO — PFPE — OH contains
all the PFPE in a bonded form, but that a significant
part of PFPE is bonded to very short blocks of PBT.

Thermal Characterization

One of the most important properties of PBT is its
high crystallization rate at relatively high temper-
atures. The presence of PFPE in PBT could modify
its thermal properties with important consequences
on the crystallization rate and crystallinity degree;
DSC curves were recorded from −20° to +270°C in
order to check these points. No significant changes
were found in T_g, T_m, and ΔH_m in comparison with
the values recorded for pure PBT. These results
confirm, as expected, that PFPE is present as a sep-
arate phase in the PBT matrix, as previously found
for PET containing PFPE.[1]

On the other hand, we observed some changes in
the crystallization rate measured as the temperature
of the crystallization peak in non-isothermal crys-
tallization from the melt (see Table I). The crude
samples showed crystallization temperatures a few
degrees lower than those observed for pure PBT (T_c
$\approx$ 182°C), whereas we observed crystallization tem-

peratures a few degrees higher for samples containing PFPE in the bonded form only, i.e., for samples obtained after extraction of the PFPE-rich fraction.

Mechanical Properties

Several measurements of mechanical properties were carried out on samples PBT–S1, PBT–S2, and pure PBT, usually according to ASTM tests; the main results are reported in Table II.

As expected from the biphasic nature of the samples, there is a small decrease of the flexural modulus and a decrease of the tensile strength and the elongation at break. An improvement of fracture properties was observed for sample PBT–S2, as it appears from the values of K_{IC} and G_{IC} reported in Table II. A slight decrease of the hardness and a slight improvement of the wear resistance were also observed.

Measurements of coefficient of friction were performed on a stainless-steel surface by both static and dynamic methods according to ASTM D 1894; we found a slight decrease when the PFPE content in the samples increased.

CONCLUSIONS

PBT samples containing PFPE can be easily prepared by the conventional polymerization used for pure PBT by using HO — PFPE — OH as a comonomer. During polymerization the telechelic PFPE blocks are bonded to PBT blocks and the final material contains both PBT homopolymer and PBT–PFPE multiblock copolymers, even though a large fraction of PFPE is bonded to very short segments of PBT. Due to the poor miscibility of PFPE and PBT segments, the PFPE is present as a separate phase dispersed in a PBT matrix. Accordingly, only very slight changes are induced in the thermal properties of PBT by the presence of PFPE.

A preliminary survey of some mechanical properties has shown that the presence of low amounts of PFPE induces a small decrease of the tensile properties and a little improvement of the fracture resistance. Surface properties such as wear resistance and coefficient of friction are also slightly increased and decreased, respectively.

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