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Synthesis of polyesters-perfluoropolyethers block copolymers

3. Use of various telechelic perfluoropolyethers

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Summary

Multiblock -(A-B)$_n$- copolymers containing polyester segments together with perfluoropolyether (PFPE) segments have been prepared by polymerizing dimethyl terephthalate (DMT), or an equimolar mixture of DMT and dimethyl isophthalate (DMI), with ethylene glycol (EG) in the presence of different telechelic perfluoropolyethers in various amounts (5-30 wt%), using $Ti(OBu)_4$ as the catalyst. Fomblin ZDEAL (a $-COOCH_3$ terminated PFPE), Fomblin ZDOL (a PFPE having $-CH_2OH$ terminal groups), and Fomblin ZDOLTX (a PFPE having $-CH_2O(CH_2CH_2O)_yH$ terminal groups) were used as telechelic PFPEs. Fomblin ZDOLTX gave the best results: the highest yield in block copolymer (less sensitive to hydrolysis with respect to block copolymers prepared from the other PFPEs), a longer average length of polyester segments, and a relatively low fraction of PFPE lost by distillation during polymerization.

Introduction

Perfluoropolymers are characterized primarily for their excellent thermal and chemical stability, inertness, durability, low coefficient of friction, low wettability etc. and are widely used in special applications. These include biomedical applications, lubrication of magnetic media, electrical insulation in the microelectronic industry etc. Perfluoropolyethers (PFPE), in particular, are viscous liquids characterized for their very low glass transition (Tg ≈ -120°C). A series of telechelic perfluoropolyethers having different types of terminal groups has been made available under the trade name of Fomblin by Montefluos; these include the types used in the present paper, namely, Fomblin ZDEAL, Fomblin ZDOL and Fomblin ZDOLTX, having formula 1 with X = $-COOCH_3$, CH_2OH and $-CH_2O(CH_2CH_2O)_yH$, respectively.

$$X\text{-}CF_2O((C_2F_4O)_n\text{-}(CF_2O)_m)CF_2\text{-}X$$

(1)

These terminal groups make them potential comonomers for preparing block copolymers containing perfluoropolyether blocks. In previous papers(1,2) we characterized the polymeric materials obtained by polymerizing dimethyl terephthalate (DMT) and ethylene glycol (EG) in the presence of Fomblin ZDEAL under various experimental conditions. In any case, the polymeric materials consisted of poly(ethylene terephthalate) homopolymer (PET), PET-PFPE multiblock copolymers and unreacted PFPE. The fraction of unreacted PFPE decreased, relatively to the overall PFPE content, by decreasing the initial amounts of ZDEAL, however, even for an initial amount of ZDEAL as low as 5%, there was still a 50% of PFPE unreacted. Therefore, it is practically impossible to obtain a large amount of PET-PFPE multiblock copolymer directly from polymerization when Fomblin ZDEAL is used. Other drawbacks, connected with the use of Fomblin ZDEAL, are a low hydrolytic stability of the ester bonds at the junction between polyester and PFPE segments, and the inhibition of the catalytic activity of the catalysts(1,2) usually employed for the first stage, of transesterification, of polymerization of PET. For this last reason Fomblin ZDEAL has to be added when the first stage is completed, before starting the second stage. It was also interesting to note that the very surface compositon of samples prepared with the polymeric materials obtained from the polymerization of PET in the presence of Fomblin ZDEAL was much richer in fluorine than the bulk composition(3), and that the surface composition profile was dependent on the relative amount of unreacted PFPE(4).

In order to verify the possibility of preparing samples with an high amount of polyester-PFPE multiblock copolymers, we have extended the study to other PFPEs, and in this paper we report the results of polymerizations of polyesters (PET) and copolyesters (from DMT, DMI and EG) carried out in the presence of Fomblin ZDEAL, Fomblin ZDOL and Fomblin ZDOLTX.

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Experimental

Reagents

Dimethyl terephthalate (DMT), dimethyl isophthalate (DMI), ethylene glycol (EG) and titanium tetrabutylate, $Ti(OBu)_4$, were reagent grade products and were used as supplied.

The Fomblins, kindly supplied by Montefluos, (Ausimont), are oils with formula **1** with X = $-COOCH_3$, CH_2OH and $-CH_2O(CH_2CH_2O)_yH$ ($\bar{y} \approx 1.5$) for ZDEAL, ZDOL and ZDOLTX, respectively. Most of the PFPEs used in the present work have a number-average molecular weight, $\bar{M}_n$, of about 2000, a comonomer n/m ratio of 0.7, and a mean functionality of about 1.95. In some cases, Fomblin ZDOLTX with the same chemical compositions, but with $\bar{M}_n$ of about 1200 (sample 9) and 3400 (sample 10) were used.

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 $-(A\text{-}B)_n-$ copolymers were synthesized by melt polycondensation of DMT (or an equimolar mixture of DMI and DMT), EG, and telechelic PFPE in a 1.8 litre 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: during the first stage, DMT (or DMT + DMI) and EG 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. PFPE was then added and allowed to react at 200°C for about 30 minutes. Finally, during the second stage, the pressure was reduced to 0.3 mbar and the temperature was raised to, and maintained at, 260-270°C (≈ 255°C in the case of copolyesters from DMT and DMI) until the end of the run. When Fomblin ZDEAL was used, polymers were obtained only when it was added between the first and the second stage(1,2); however, when Fomblin ZDOL and Fomblin ZDOLTX were used, it made no difference whether they were added before starting the first stage or between the first and second stage. Molar ratios of reactants and polymerization conditions are reported in Table 1.

During polymerization, a fraction of PFPE evaporated from the reactor together with other volatile products (EG mainly, 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 fluorine content in the resulting polymeric material (by elemental analysis and/or degradation of the ester sequences) and by recovering the PFPE from the distilled fraction collected in a cold condenser. They can be derived from Table 1 as the difference between the theoretical amount of PFPE (column 4) and the residual percentage in the final products (column 9).

Table 1: Polymerization data.

Sample	Polyester segment	PFPE		polymerization conditions				PFPE in the final polymer	(η)(d)
				first stage(b)		second stage(c)			
		type	(wt%)(a)	t (min)	T (°C)	t (min)	T (°C)	(wt %)	(dl/g)
1	PET	ZDOL/TX	5.0	88	195	70	265	3.8 *	0.82
2	PET	ZDOL/TX	10.0	130	193	75	265	7.4 *	0.63
3	PET	ZDOL/TX	20.2	112	196	86	262	18.0 *	0.37
4	PET	ZDOL	10.0	100	194	75	268	3.1 *	0.71
5	copol.	ZDOL/TX	5.0	84	196	99	255	3.5 *	0.62
6	copol.	ZDOL/TX	10.0	93	195	103	257	8.3 **	---
7	copol.	ZDOL/TX	20.2	101	198	101	252	18.2 *	---
8	copol.	ZDOL/TX	30.2	134	195	115	254	25.3 **	---
9	copol.	ZDOL/TX	10.0	93	193	128	255	7.9 **	---
10	copol.	ZDOL/TX	10.0	93	197	122	255	7.8 **	---
11	copol.	ZDOL	30.2	93	197	113	254	13.3 *	---
12	copol.	ZDEAL	10.0	93	192	59	254	8.1 **	0.54

a) Theoretical amount ; b) atmospheric pressure; c) 0.3 mbar; d) crude polymer in phenol/TCE or $CHCl_3$ at 30 °C for PET and copolymers, rispectively; * from fluorine elemental analysis; ** from degradation of polyester moieties

Selective solubility

To separate unreacted PFPE from the crude sample, we exploited the different solubility of PFPE and polyesters. In the case of PET samples, the procedure for the extraction of unreacted PFPE was carried out as previously reported(1): about 2 or 3 g of sample was refluxed with 30 ml of TCE and 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 in block copolymer) and PET cyclic oligomers, was washed with CH_2Cl_2 to remove the latter. By this procedure pure PFPEs were completely separated from PET, and more than 97% of each was recovered from a mixture prepared by evaporating the solvent from a hexafluoro-2-propanol solution. Because the copolyesters deriving from the polymerization of equimolar mixtures of DMT and DMI with EG are soluble in chlorinated solvents also at room temperature, the procedure to separate unreacted PFPEs was slightly changed: $CHCl_3$ was used, at room temperature under stirring, instead of TCE.

Characterization

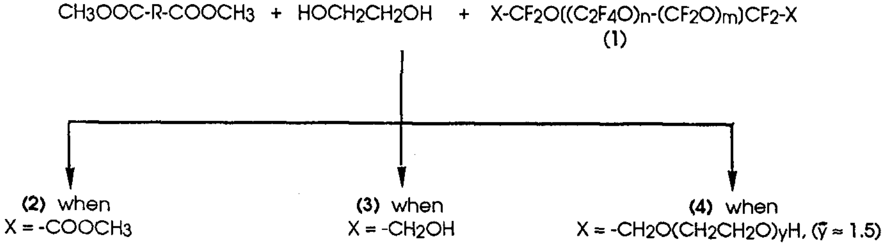
Samples were characterized by FT-IR (Brucker IFS 48) and ^{1}H-NMR (Varian 200MHz). ^{1}H-NMR spectra were usually recorded from TCTFE/$CDCl_3$ solutions, due to the poor solubility of PFPE in the presence of the common deuterated solvents, it was impossible to record ^{1}H-NMR spectra with a high resolution for PFPE rich samples, and in particular for samples derived from ZDOL and ZDEAL. Intrinsic viscosity measurements were obtained, from phenol/TCE (60/40) or $CHCl_3$ solutions. GPC curves were obtained by a set of 4 Ultrastyragel columns (10^5, 10^4, 10^3 and 5×10^2 Å) using an azeotropic mixture (b.p. 47°C) of TCTFE/Acetone at 35°C. Calibration was performed by using almost monodisperse samples ($\bar{M}_w/\bar{M}_n < 1.09$) of Fomblin ZDOL of known molecular weight (1000-5000). Fluorine elemental analysis was performed according to a standardized method involving the transformation of organic fluorine into inorganic fluorine with sodium peroxide, followed by a potentiometric titration.

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 sample was added to 1 ml of CH_3ONa 5M and 10 ml of EG, and refluxed under stirring for about 1 hour. The resulting mixture was washed with water and TCTFE. The organic phase was separated and the solvent was evaporated to recover the PFPE.

Results and discussion

Samples were prepared by melt polycondensation of DMT (or of an equimolar mixture of DMT and DMI) with EG in the presence of various amount of Fomblin ZDEAL, Fomblin ZDOL and Fomblin ZDOLTX, using titanium tetrabutylate as catalyst.



$CH_3OOC\text{-}R\text{-}COOCH_3 + HOCH_2CH_2OH + X\text{-}CF_2O((C_2F_4O)_n\text{-}(CF_2O)_m)CF_2\text{-}X$ (1)

(2) when $X = \text{-}COOCH_3$

(3) when $X = \text{-}CH_2OH$

(4) when $X = \text{-}CH_2O(CH_2CH_2O)_yH$, $(\bar{y} \approx 1.5)$

(2) $\text{-}\{\text{-}(\text{-}OC\text{-}R\text{-}COOCH_2CH_2O\text{-})_r\text{-}(\text{-}OC\text{-}CF_2O((C_2F_4O)_n\text{-}(CF_2O)_m)CF_2\text{-}COOCH_2CH_2O\text{-})_s\text{-}\}_z\text{-}$

(3) $\text{-}\{\text{-}(\text{-}OC\text{-}R\text{-}COOCH_2CH_2O\text{-})_r\text{-}(\text{-}OC\text{-}R\text{-}COO\text{-}CH_2\text{-}CF_2O((C_2F_4O)_n\text{-}(CF_2O)_m)CF_2\text{-}CH_2O\text{-})_s\text{-}\}_z\text{-}$

(4) $\text{-}\{\text{-}(\text{-}OC\text{-}R\text{-}COOCH_2CH_2O\text{-})_r\text{-}(\text{-}OC\text{-}R\text{-}COO(CH_2CH_2O)_yCH_2\text{-}CF_2O((C_2F_4O)_n\text{-}(CF_2O)_m)CF_2\text{-}CH_2(OCH_2CH_2)_yO\text{-})_s\text{-}\}_z$

With R = 1,4-phenylene or an equimolar mixture of 1,3-phenylene and 1,4-phenylene. Polymerizations from DMT and DMI led to random copolyester segments readily soluble in chlorinated solvents; this allowed to overcome some problems of characterization (encountered with PET, due to the low solubility in the usual solvents), and to obtain non-crystallizable samples.

Samples obtained in the presence of PFPE were usually glossier than the equivalent polyesters, and this effect was more and more evident when the percentage of PFPE increased, and in particular when Fomblin ZDOLTX was used. All samples could be stretched into fibres, and gave though films from solution; no exudation was observed. Solution viscosity measurements, carried out either on the overall samples (for samples containing a low amount of PFPE), and on the residue after the fraction soluble in TCTFE has been removed, indicated that the molecular weight was always fairly high (see intrinsic viscosity data in Table 1).

During polymerization a loss of PFPE by volatilization was observed for every type of PFPE; the fraction lost was particularly relevant for Fomblin ZDOL (about 60%, see Table 1). The analysis of the fractions of PFPEs distilled and recovered in a cold condenser showed that they had the same chemical structure of the initial PFPE, and a slightly lower molecular weight ($\bar{M}_n \approx 1500$; $\bar{M}_w/\bar{M}_n \approx 1.2$, from GPC). Data relative to the overall amount of PFPE in the final product, obtained from elemental analysis and selective degradation, are reported in Table 1. The residual amount of PFPE in the final polymer can, in principle, be present either as unreacted PFPE blended with polyester, or as PFPE segments in polyester-PFPE multiblock copolymers; the primary purpose of this work was to estimate to which extent PFPE was bonded to polyester segments.

Only little information can be derived by IR and ^{1}H-NMR spectroscopy on the crude samples, and we exploited the different solubility of polyesters and PFPE in order to achieve data about the fraction of unreacted PFPE. In fact, because PET and the copoly(ethylene isophthalate-co-terephthalate) are almost completely insoluble in TCTFE (only a small fraction of cyclic oligomers is extracted), it is possible to separate unreacted PFPE from pure polyesters by selective extractions (see the experimental part). However, the solubility of multiblock copolymers depends on their chemical composition (type, length and number of blocks), and molecules of block copolymers should be found in both soluble and insoluble fractions, in a variable amount depending on the relative weight of the blocks. In the present case it is expected that the solubility of block copolymers in TCTFE increases when the weight fraction of PFPE in a macromolecule increases, and we indeed observed that, using the same standardized operating conditions, the amount of extractable fraction increased with the initial amount of PFPE.

A complete separation of unreacted PFPE from block copolymers was therefore impossible by the treatment performed as described in the experimental part; however, by such a procedure we obtained in every case two fractions, one insoluble in TCTFE, rich in polyester segments, and another one, soluble in TCTFE, which is reach in PFPE and, most important, contains unreacted PFPE, if present. The PFPE in the fraction insoluble in TCTFE is clearly bonded to relatively long polyester segments, which make the macromolecules containing these PFPE segments insoluble in TCTFE. The presence of PFPE in the fraction insoluble in TCTFE is indicated by a decrease of the transmittance in the 1100-1200 cm^{-1} region of the IR spectra.

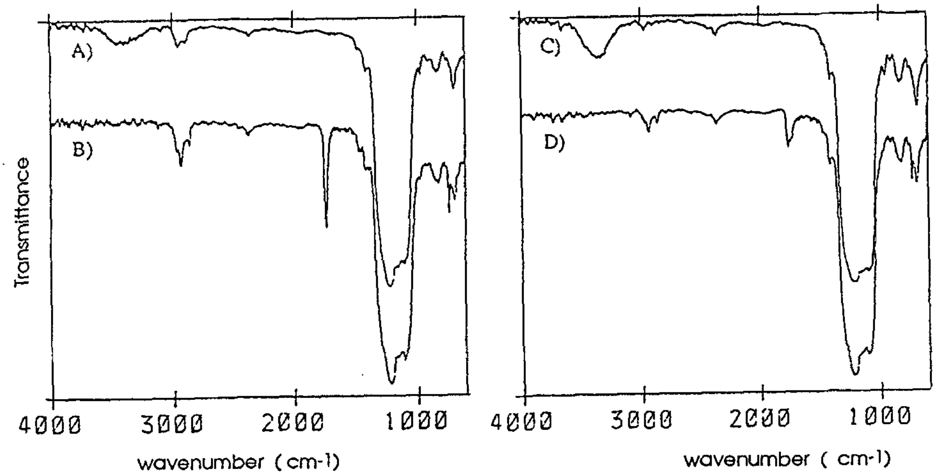


Figure 1:
FT-IR spectra of: Fomblin ZDOLTX (A); Fomblin ZDOL (C); and of typical fractions extracted by selective solubilization of samples prepared from Fomblin ZDOLTX (B) and Fomblin ZDOL (D).

Information about the possible presence of unreacted PFPE can be derived by IR and ^{1}H-NMR spectroscopy analysis of the fractions soluble in TCTFE, where unreacted PFPE, which is readily soluble in TCTFE, is expected to be present, if exhisting.

Typical IR spectra of the fractions soluble in TCTFE of samples obtained from both Fomblin ZDOL and Fomblin ZDOLTX are reported in Figure 1, along with spectra of the initial Fomblin ZDOL and Fomblin ZDOLTX. In both cases, we can observe the complete disappearance of the OH stretching band (at nearly 3430 cm-1), the appearance of a carbonyl stretching band at 1727 cm-1, and the increase of the C-H stretching bands in the 2800-3000 cm-1 region. All this evidence, along with the presence of several other peaks typical of polyesters, means that segments of polyesters are present in the fraction soluble in TCTFE and that there are not free hydroxyl end groups in a detectable amount. Because contamination by homopolyester (from either linear or cyclic oligomers) can be ruled out after the treatment described in the experimental part, these results mean that almost all the terminal groups of the PFPE contained in the soluble fraction are bonded to iso- or terephthalate units.

A more complete characterization of the block copolymer architecture would require also the knowledge of the average length and number of segments. The question of the determination of block copolymer architecture is indeed a difficult feature to elucidate(5), particularly for multiblock

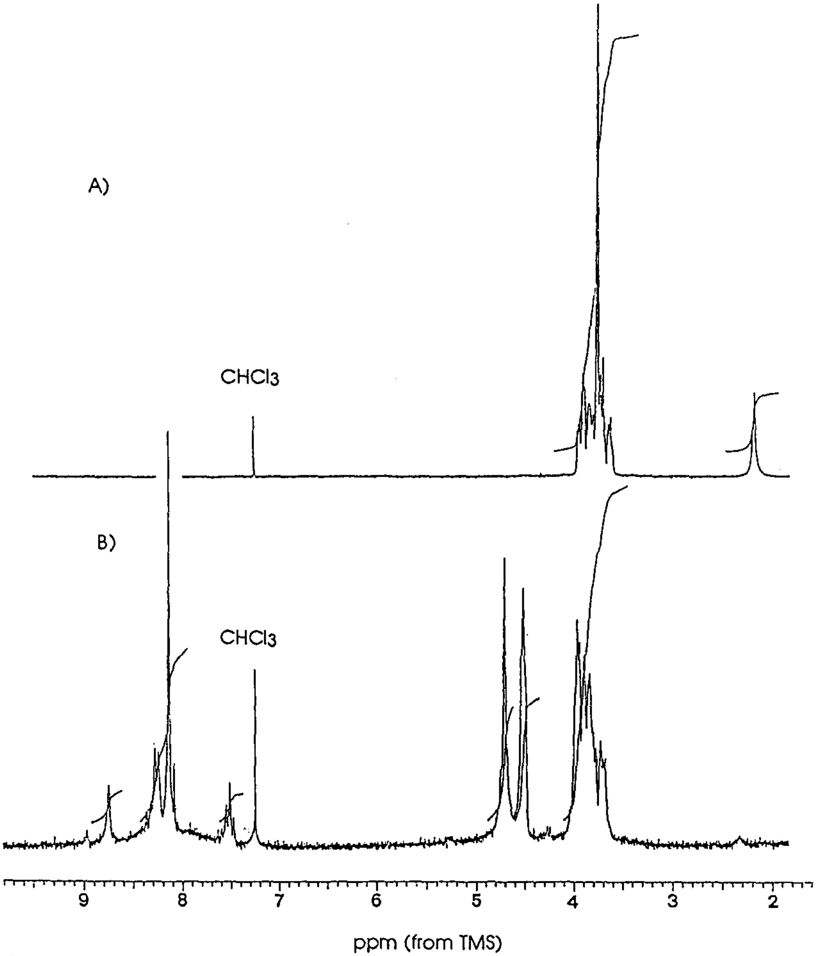


Figure 2:
^{1}H-NMR spectra of: Fomblin ZDOLTX (A), and of a typical fraction extracted by selective solubilization of samples prepared from Fomblin ZDOLTX (B) .

copolymers. Some information about chemical architecture, and further support for the above conclusion, can be obtained by ^{1}H-NMR spectroscopy.

The signals from PFPE protons in the ^{1}H-NMR spectra of crude samples or of the fractions insoluble in TCTFE are too week to allow quantitative information; on the contrary, it was possible to derive some information on the chemical structure of the soluble fractions.

In comparison with the spectrum of the initial Fomblin ZDOLTX (see Figure 2.A), the ^{1}H-NMR spectra of the fractions soluble in TCTFE of samples prepared from Fomblin ZDOLTX show changes in the 3.6-4.0 ppm region, the appearance of peaks at 4.5 and 4.7 ppm, and the presence of peaks in the 7.5-8.8 ppm region typical of the aromatic moieties (a typical spectrum is shown in Figure 2.B). The strong decrease of the relative intensity of the sharp peak at 3.7 ppm, of CH_2-O-$\mathbf{CH_2CH_2}$-O-CH_2 ether protons, and the appearance of a strong peak at 4.5 ppm (attributable to CH_2-O-$CH_2\mathbf{CH_2}$-OOC protons) suggest that the end groups of Fomblin ZDOLTX have almost completely reacted. In fact, the intensity ratio of the peak at 4.5 ppm to that of the 3.6-4.0 region is ≈ 0.32 , when a value of 0.33 would be expected for the complete reaction of hydroxyl end groups. The average length of the polyester blocks joined to PFPE blocks in the fraction soluble in TCTFE seems however very short as it can be inferred from the intensity ratio of the 4.7 ppm peak (of COO-$\mathbf{CH_2CH_2}$-OOC protons), or from the 7.5-8.8 ppm peaks (of aromatic protons) to the 4.5 ppm peak; the estimated average length of the polyester sequences ($(r+1)$ in formula 4) is of 1.5 - 3 repeating units of polyester. Of course, the average length of polyester segments in the insoluble fraction is expected to be higher; unfortunately ^{1}H-NMR sensitivity does not allow to obtain quantitative information on the average length of the polyester sequences in this fraction.

In the ^{1}H-NMR spectra of the fraction extracted from samples prepared using Fomblin ZDOL (see a typical spectrum in Figure 3.B), we can observe the appearance of peaks at 7.5-8.9 ppm (characteristic of aromatic moieties) and at 4.6-4.8 ppm (typical of methylene protons adjacent to ester groups). We can also observe residual traces of protons at 3.8-4.0 ppm, typical of unreacted Fomblin ZDOL (see Figure 3.A). From the relative intensity of these peaks we can conclude that about 10-20 % of the terminal groups of ZDOL did not react, and that there is a significant part of PFPE (about 40%) containing only one aromatic unit every two terminal groups of ZDOL. This last result, along with the

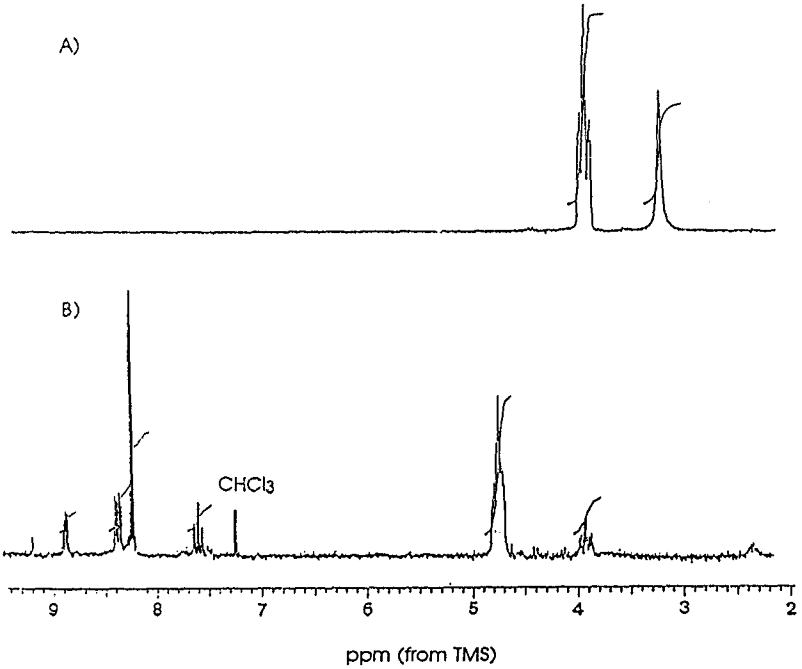


Figure 3:
^{1}H-NMR spectra of: Fomblin ZDOL (A); and of a typical fraction extracted by selective solubilization of samples prepared from Fomblin ZDOL (B).

absence (or the very low concentration) of protons deriving from EG moieties and of OH signal in the IR spectrum (see Figure 1,C,D), suggests that most of the aromatic unit contained in the extracted fraction are bridging two terminal groups, that is r=0 in formula 3.

From the above IR and NMR evidence it can be concluded that the terminal groups of both Fomblin ZDOL and Fomblin ZDOLTX react to a large extent during polymerization, even though a limited part of Fomblin ZDOLTX, and a significant part of Fomblin ZDOL is bonded to very short segments.

In order to confirm the results of our previous works(1,2) (carried out using Fomblin ZDEAL during the polymerization of PET), a sample was prepared using Fomblin ZDEAL during the copolymerization of DMT and DMI (see Table 1). Selective extractions, and IR and ^{1}H-NMR analysis of the fraction soluble in TCTFE confirmed the results we had found previously(1,2). The PFPE extracted from the crude sample (about 70% of the overall amount of PFPE) did not contain iso- or terephthalate units. During this experiment it was also confirmed the inhibiting effect of Fomblin ZDEAL on the catalytic activity during the transesterification stage. Because, we did not observe any inhibiting effect when Fomblin ZDOL and Fomblin ZDOLTX were used, these results confirm that the inhibiting effect is due to the interaction of the ester groups -CF_2COOCH_3 of Fomblin ZDEAL with transesterification catalysts(1,2).

Conclusions

Multiblock copolymers containing polyesters and PFPE segments have been prepared by melt polycondensation of DMT (or DMT+DMI), and EG, in the presence of telechelic PFPEs. The yield in block copolymer was strongly dependent on the nature of the terminal groups of the telechelic PFPE, probably as a consequence of changes in reactivity due to the inductive effect of fluorine atoms, decreasing from Fomblin ZDEAL, to Fomblin ZDOL, to Fomblin ZDOLTX where fluorine atoms are increasingly far from the reactive site.

Accordingly, when Fomblin ZDOLTX was used, most PFPE was bonded to long polyester segments and was insoluble in TCTFE; only a small fraction (about 10%) bonded to short polyester segments (with an average length of 1.5 - 3 units) was extracted with TCTFE.

When Fomblin ZDOL was used, only a fraction (about 40%) of the initial PFPE remained in the final polymer. A significant part (about 40%) of this remaining PFPE was extracted with TCTFE, and about 10-20 % of the terminal groups of the extracted PFPE were found unreacted, while the other ones were bonded with a single iso- terephthalate unit, bridging two terminal groups.

When Fomblin ZDEAL was used, a large fraction (usually 70% or more depending on the initial amount of Fomblin ZDEAL) resulted not bonded to polyester segments.

It should also be remembered that, contrary to what previously found for Fomblin ZDEAL(1,2), Fomblin ZDOLTX and Fomblin ZDOL can be added in the first stage of the process, because they do not inhibit the catalyst during the transesterification stage.

Therefore, we can conclude that the more convenient PFPE for preparing polyester-PFPE multiblock copolymers is Fomblin ZDOLTX, which gives high yields in block copolymer, a limited weight loss by volatilization, and gives block copolymers which show higher stability to hydrolysis(6) than those prepared from the other PFPEs.

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