Poly(ϵ-caprolactone)−Poly(fluoroalkylene oxide)−Poly(ϵ-caprolactone) Block Copolymers. 1. Synthesis and Molecular Characterization

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ABSTRACT: Hydroxyl-terminated telechelic poly(fluoroalkylene oxide)s, (PFPE)s, with molecular weights ranging from 1100 to 3400 were employed as transfer agents for the ring-opening polymerization of ϵ-caprolactone (CL) in the presence of various catalysts/initiators. The highest conversion rate of CL was observed using $Ti(OBu)_4$ and Bu_2SnO as catalysts/initiators. The polymerization of CL started only from the hydroxyl groups of PFPE, leading to the formation of ABA triblock copolymers without formation of homopolymer poly(ϵ-caprolactone) (PCL). The rate of insertion of the first unit of CL is much faster than the insertion of the other CL units, and the average molecular weight of the ABA copolymers was that expected by the CL/PFPE ratio. The polymerization rate of CL in the presence of PFPE using aluminum alkoxides as initiator was very slow, contrary to what is known about the homopolymerization of CL.

Introduction

Fluorinated products are attractive for their unusual properties involving mainly chemical inertia, solvent and high-temperature resistance, barrier properties, low coefficient of friction, and low surface tension. For this reason, the possibility of modifying some characteristics of polymeric materials, and in particular the surface properties, by the addition of fluorine-containing monomers or by surface fluorination has been studied and industrially exploited.[1−3]

Usually the copolymerization of fluorinated monomers with other comonomers leads to random copolymers which provide new polymeric materials with properties intermediate between those of the parent homopolymers. As a consequence, a significant modification of the surface properties requires a high molar ratio of fluorinated comonomers which is frequently accompanied by a strong modification also of the bulk properties. The high cost of fluorinated monomers leads in addition to very expensive polymeric materials.

Alternatively, surface properties can be modified by surface fluorination of previously molded items;[4] however, this is also a highly expensive technology.

In a different approach, fluorination can be achieved by blending fluorinated polymers with other polymers; by this approach, the ability of fluorinated polymers to segregate preferably on the surface can allow to reduce the overall amount of fluorinated polymer requested to have a high fluorine concentration on the surface. However, due to thermodynamic reasons, fluorinated polymers are usually immiscible with nonfluorinated polymers and segregate in a separate phase with poor adhesion to the nonfluorinated matrix, leading to very poor mechanical properties.

The availability of telechelic poly(fluoroalkylene oxide)s, (PFPE)s, with reactive terminal groups[5] makes possible the preparation of multiblock copolymers containing fluorinated blocks by using PFPEs as macromers during polymerization.[6−9] It was shown that the PFPE segments contained in polyester−PFPE multiblock copolymers still maintained the ability to migrate onto the surface, leading to a fluorine-rich surface even when the amount of PFPE in the bulk was very low.[10−12] The main drawback of this last approach is that the chemical modification has to be done during polymerization and that a fraction of PFPE remains unreacted at the end of the polymerization;[13] this may not be economically convenient, and it can be exploited for a limited number of polymers, as it requires that the terminal groups of the telechelic macromers are able to react with the monomers.

A different and more versatile approach to fluorination of different polymer matrices is to prepare separately block copolymers containing fluorinated segments and then to add them to other polymers. In this case the compatibility with the host polymer and the potential capability of fluorinated segments to migrate onto the surface may be controlled by an appropriate choice of the type and length of the nonfluorinated blocks. In this respect, block copolymers with a limited and well-defined number of blocks should provide better results than multiblock copolymers.

Of course, the chemical nature of the nonfluorinated block is of primary importance to obtain compatibilization with the host polymer. In this respect, poly(ϵ-caprolactone) (PCL) is a polymer which presents some interesting features because it is miscible with PVC, ABS, SAN, PC, and several other polymers.[14−16] A further interesting characteristic of PCL blocks is the possibility that ester linkages undergo exchange reactions with other polyesters, polyamides, and polycarbonates, etc.[17−21] Also, the biodegradability of PCL[21] may be interesting in some applications. A telechelic CL

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chain extension of PFPE was recently reported[22] for the preparation of PFPE−silica hybrids.

Hydroxyl-terminated compounds have been widely used as transfer agents in the ring-opening polymerization of ϵ-caprolactone (CL) catalyzed by various metal alkoxides, such for the preparation of PCL-based block copolymers with AB, ABA, and hyperbranched structures.[23−29] Therefore, also PFPEs with hydroxyl terminal groups can in principle be employed to prepare block copolymers, containing PCL segments along with PFPE blocks, which appear interesting because of the possible compatibility with several polymer matrices, the ability to react in reactive processing with some suitable polymers, and the biodegradability.

For this reason, we decided to study the possibility of preparing ABA block copolymers containing PCL blocks (A) together with PFPE blocks (B), and in this paper we describe the synthesis and the molecular characterization of the copolymers prepared using various catalysts/initiators. Copolymers with different lengths of PFPE and PCL blocks were prepared by using PFPEs of different molecular weights (1100−3400) and various CL/PFPE molar ratios (4−110).

Experimental Section

Reagents. The fluorinated macromers HO−R$_H$−PFPE−R$_H$−OH were supplied by Ausimont (registered name Fomblin Z-DOL TX); they are liquids with the following formula:

$$H-(OCH_2CH_2)_n-OCH_2CF_2O-(CF_2CF_2O)_p-(CF_2O)_q-CF_2CH_2O-(CH_2CH_2O)_n-H$$

in which the constitutional units $-CF_2CF_2O-$ and $-CF_2O-$, randomly distributed along the macromolecular chains, constitute the internal body where $p/q \approx 0.9$. The poly(ethylene oxide) chain (schematically R$_H$) is the end-capping segment containing the functional hydroxyl group, with an average n value close to 1.5. The molar mass of the three studied fluorinated macromers is 1100, 2250, and 3400 g mol^{-1}. (In the following they are named Z-DOL TX 1100, Z-DOL TX 2250, and Z-DOL TX 3400, respectively.) The average hydroxyl functionality of these macromers is very close to 2 (>1.98). The commercial products also contain carboxylic terminal groups (about 1% with respect to hydroxyl terminal groups); taking into account that they are very acidic and can catalyze the polymerization of CL, all three Z-DOL TXs have been purified before use by reaction with activated basic alumina (10 wt %, purchased from Aldrich Chemicals) for 4 h followed by filtration.

ϵ-Caprolactone (CL), purchased from Aldrich Chemicals, was distilled under reduced pressure in the presence of CaH_2. Poly(ϵ-caprolactone) diol (PCL, with molecular weight of 2000), titanium tetrabutoxide ($Ti(OBu)_4$), dibutyltin oxide (Bu_2SnO), samarium acetate ($Sm(OAc)_3$), calcium acetate ($Ca(OAc)_2$), and antimonium trioxide (Sb_2O_3) (all purchased from Aldrich Chemicals) were used as received without further purification. Aluminum isopropoxide ($Al(i\text{-}OPr)_3$) (purchased from Aldrich Chemicals) was distilled under reduced pressure and treated according to Duda[30] in order to obtain a trimer- or tetramer-rich initiator.

Block Copolymer Synthesis. The liquid nature of both PFPE and CL and the difficulty of finding a common solvent for both PFPE and PCL lead us to react preferably PFPE and CL in bulk, at a temperature of 110−120 °C, higher than the melting temperature of PCL (≈60 °C).

Typically the fluorinated macromer HO−R$_H$−PFPE−R$_H$−OH and the initiator (in different amounts ranging from 0.1 to 3.6 wt % with respect to the total quantity of reagents and with a molar ratio of hydroxyl terminal groups to the metal ranging from 200 to 2) were premixed for about 1 h at the temperature of 110−120 °C, under mechanical stirring. Then, CL was added to the system (in different CL/HO−R$_H$−PFPE−R$_H$−OH molar ratios ranging from 4:1 to 200:1), and the reaction was carried out for different times. In a few cases PFPE and CL were premixed before the addition of the initiator.

Crude products with long PCL segments were usually completely insoluble in methanol and were purified twice by dissolution in chloroform and reprecipitation in methanol. After filtration samples were dried at the temperature of 50 °C under reduced pressure overnight. The copolymers are indicated with the code TXmCL(n) in which m (1, 2, or 3 for Z-DOL TX 1100, Z-DOL TX 2250, or Z-DOL TX 3400, respectively) identifies the fluorinated macromer and n corresponds to the average number of repeating units contained in PCL blocks.

Control polymerizations of CL (without PFPE) were also carried out under the same conditions.

Selective Solubility Tests. Selective solubility tests have been carried out by dissolution of about 1.0 g of product in 10 mL of chloroform and reprecipitation in about 100 mL of 1,1,2-trichloro-1,2,2-trifluoroethane (TCTFE), a typical solvent for fluorinated macromers. After filtration, the soluble fraction was recovered by elimination of solvent in a rotary evaporator.

Molecular Characterization. ^{1}H NMR analysis was performed on a Varian Gemini System 300 MHz instrument by using $CDCl_3$ as solvent for the reaction products, CL and PCL homopolymer. A $CDCl_3$/TCTFE mixture (50:50 vol:vol) was used as solvent in the case of pure HO−R$_H$−PFPE−R$_H$−OH.

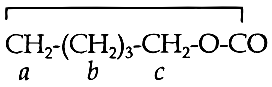
Size-exclusion chromatography (SEC) analysis was performed by using tetrahydrofuran or chloroform as eluents (elution rate of 0.8 mL/min) on a Knauer apparatus equipped with two columns PL-Gel (10^3 and 500 Å) and with a refractive index detector. A calibration for molecular weight (MW) and molecular weight distribution (MWD) was not possible for these systems because PCL and PFPE moieties modify in an opposite way the signal of the RI detector and the intensity and shape of peaks depend on the relative PCL/PFPE content. A further reason that does not allow a quantitative evaluation of MW and MWD derives from the observation that the log $\bar{M}_n$−log [η] relationship is not linear in the range of PFPE/PCL content investigated,[31] probably due to the formation of micelles at high PCL content.

Number-average molecular weight, $\bar{M}_n$, was evaluated by vapor pressure osmometry (VPO) measurements, performed at 37.0 °C, using chloroform as solvent on a Wescan 233 apparatus. The instrument calibration constant was obtained from monodispersed polystyrene samples having known molecular weights.

Results and Discussion

Ring-opening polymerization of cyclic esters using an as low as possible initiator concentration in the presence of a suitable transfer agent represents a well-established method for the preparation of telechelic polymers. In this approach the molecular weight of the final polymer is determined by the initial monomer/transfer agent molar ratio, if the concentration of initiator is low and the transfer reaction is fast and quantitative. Hydroxyl-terminated polyesters have been synthesized by ring-opening polymerization of cyclic monomers (lactones, lactide, and glycolide) with various mono-alcohols[32−36] as transfer agents and several initiators, mainly metal alkoxides. The use of diols as transfer agents represents an attractive way to produce α,ω-dihydroxyl-terminated polymers. This concept has been employed for example for the preparation of α,ω-dihydroxyl-terminated PCL and ABA block copolymers using low molecular weight diols and α,ω-dihydroxy polyethers, respectively, as transfer agents and aluminum isopropoxide as initiator.[37,38] From a kinetic point of view, it has to be stressed that polymerization carried out in the presence of low

Table 1. ^{1}H NMR Assignments (m = Multiplet; t = Triplet; s = Singlet)

1	 $\underset{a}{CH_2}\text{-}\underset{b}{(CH_2)_3}\text{-}\underset{c}{CH_2}\text{-O-CO}$	a: 2.65 ppm, m, 2H; b: 1.80-1.85 ppm, m, 6H; c: 4.25, m, 2H
2	$\text{-}\underset{a}{CH_2}\text{-}\underset{b}{(CH_2)_3}\text{-}\underset{c}{CH_2}\text{-O-CO-}$	a: 2.30 ppm, t, 2H; b: 1.40-1.65 ppm, m, 6H; c: 4.05, t, 2H
3	$\text{-PFPE-CF}_2\text{-}\underbrace{CH_2\text{-O}(CH_2\text{-}CH_2}_{a}\text{-O})_{1.5}\underset{b}{H}$	a: 3.50-4.00 ppm, m, 8H; b: 2.20 ppm, s, 1H
4	$\text{-PFPE-CF}_2\text{-}\underbrace{CH_2\text{-O}(CH_2\text{-}CH_2\text{-O})_{0.5}\text{-}CH_2}_{a}\text{-}\underset{b}{CH_2}\text{-O-(CO-}\underset{c}{CH_2}\text{-}\underset{d}{(CH_2)_3}\text{-}\underset{e}{CH_2}\text{-O)}_n\text{-CO-}\underset{c}{CH_2}\text{-}\underset{d}{(CH_2)_3}\text{-}\underset{f}{CH_2}\text{-OH}$	a: 3.70-3.95 ppm, m, 6H; b: 4.25 ppm, m, 2H; c: 2.30, t, 2H; d: 1.40-1.65, m, 6H; e: 4.05, t, 2H; f: 3.65, t, 2H

molecular weight diols was inhibited in its early stages, probably due to a coordination of the initiator by alcohols and diols, and the polymerization rate increased after an induction period. On the other hand, no induction period has been observed by using α,ω-dihydroxy polyethers as transfer agents.

Taking into account that several glycols and hydroxyl-terminated macromers have been successfully used as transfer agents, also telechelic PFPEs, which contain primary hydroxyl terminal groups, can be considered potential transfer agents for the ring-opening polymerization of CL in the presence of suitable initiators for the preparation of ABA block copolymers. However, contrary to the common transfer agents, PFPEs are initially immiscible with CL (the miscibility changes during reaction and depends on the molecular weight of PFPE, decreasing when the molecular weight of PFPE increases), and the capability of HO−R_H−PFPE−R_H−OH to start CL polymerization can be affected by some factors such as the preferential segregation of the catalyst/initiator in one of the phases, a different activity of the initiator in the fluorinated phase, and a low concentration of CL close to the active catalytic sites in the fluorinated phase. Therefore, the reaction products deriving from the use of PFPEs as transfer agents in the polymerization of CL are not easily predictable; for instance, a preferential segregation of the initiator in the CL-rich phase would give PCL plus unreacted PFPE rather than ABA block copolymers. Similarly, the conversion rate of CL into PCL, observed for common hydrogenated transfer agents, may be different in the presence of a PFPE-rich phase.

The conversion of CL into PCL segments and the extent of reaction of hydroxyl terminal groups of PFPE with CL can be easily estimated by ^{1}H NMR spectroscopy. Spectra of pure HO−R_H−PFPE−R_H−OH, of CL + PCL, and of a typical crude product with total conversion of CL monomer are respectively shown in Figure 1a−c, and the relative assignments are reported in Table 1. In Figure 1b, the spectrum of PCL + CL shows that the signals of PCL (at 2.30 ppm, protons 2a in Table 1) and of CL (at 2.65 ppm, protons 1a in Table 1) are sufficiently separated from each other and from those of PFPE to be used to calculate the conversion of CL into PCL. Figure 1c shows the spectrum of a typical reaction product; the signals of PCL and of the hydrogenated moieties of the HO−R_H−PFPE−R_H−OH are clearly evident and sufficiently separated to estimate the extent of reaction of the hydroxyl groups of HO−R_H−PFPE−R_H−OH. In fact, the ratio of the peak at 4.25 ppm (protons 4b in Table 1) over the overall complex signal at 3.65−3.95 ppm (protons 4a and 4f in Table 1) allows to estimate the fraction of the terminal groups of PFPE reacted with CL, with the assumption that no PCL homopolymer formation occurs.

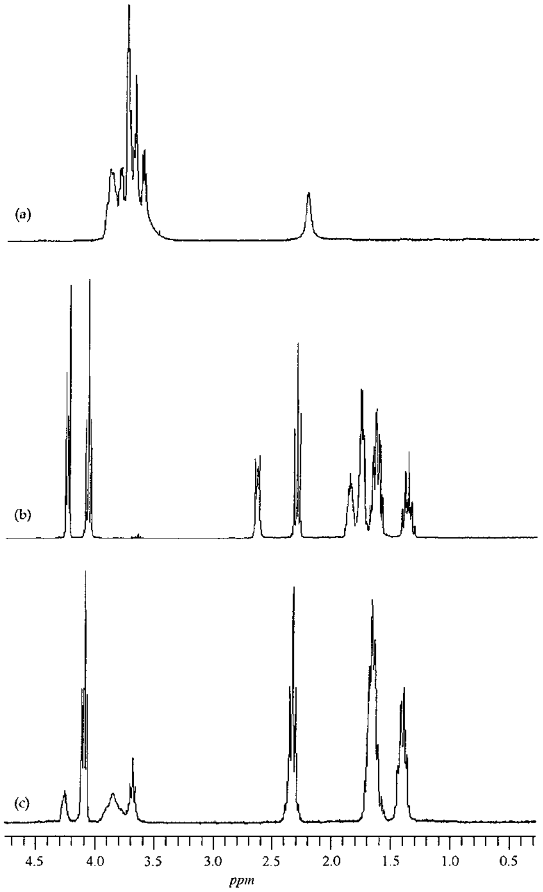


Figure 1. ^{1}H NMR spectra of (a) Z-DOL TX 2250, (b) CL and PCL mixture (1:1 by weight), and (c) typical reaction product obtained from Z-DOL TX 2250 and CL (1:10 molar ratio) and $Ti(OBu)_4$ as initiator (0.1 wt % with respect to the total quantity of reagents) reacted for 24 h [spectrum a recorded in $CDCl_3$/TCTFE mixture (50:50 vol:vol), spectra b and c recorded in $CDCl_3$].

Table 2. Data of CL Conversion after 4 and 18 h of Reaction at 110 °C Using Various Initiators and Z-DOLTX 2250 as Transfer Agent (Z-DOL TX/CL Molar Ratio = 1:20, Initiator Concentration = 0.25 wt % with Respect to the Total Quantity of Reagents)

	CL conversion (%)	
initiator	rxn time = 4 h	rxn time = 18 h
none	0	0
Bu_2SnO	36	100
$Ti(OBu)_4$	18	100
$Ca(OAc)_2$	0	23
$Al(i\text{-}OPr)_3$[a]	0	15
$Sm(OAc)_3$	0	8
Sb_2O_3	0	0

[a] Mainly in the tetramer form.

Various metal-based catalysts/initiators were tested, chosen among the most efficient catalysts/initiators cited in the literature for the polymerization of CL[39] (aluminum, tin, and titanium alkoxides) and among the catalysts efficient toward transesterification reactions.[40]

Data of CL conversion after 4 and 18 h of reaction at 110 °C using various initiators and Z-DOLTX 2250 as transfer agent (Z-DOL TX/CL molar ratio = 1:20, initiator concentration = 0.25 wt % with respect to the total quantity of reagents) are reported in Table 2.

From these data we can conclude that under these conditions the catalytic activity decreases in the order

$$Bu_2SnO > Ti(OBu)_4 \gg Ca(OAc)_2 > Al(i\text{-}OPr)_3 > Sm(OAc)_3 \gg Sb_2O_3 \approx \text{no initiator} \approx 0$$

in agreement with the data reported for the homopolymerization of CL.[35]

It is interesting to note that $HO-R_H-PFPE-R_H-OH$ when not purified from the presence of traces of very acidic carboxylic groups was able to start the ring-opening polymerization of CL also in absence of initiator (50% of conversion has been achieved after 18 h of reaction at 110 °C).

Except for $Ti(OBu)_4$, the above initiators are solids not miscible in $HO-R_H-PFPE-R_H-OH$ (the reaction medium appeared not homogeneous for the presence of undissolved solid initiator), and the low solubility can explain the slow polymerization rate of CL observed in some cases.

However, the low conversion rate observed with $Al(i\text{-}OPr)_3$, observed in the form of either trimer and tetramer, is quite surprising because it is known to be one of the most active initiators for the polymerization of CL, and it appears miscible with PFPE. The results of further experiments carried out with Al initiators to understand the reason for the low catalytic activity will be discussed separately below.

On the basis of the data of Table 2, about 10 copolymers for each type of PFPE were prepared using $Ti(OBu)_4$ or Bu_2SnO as initiators in concentrations ranging from 0.1 to 3.6 wt % (corresponding to a HO−/metal molar ratio ranging from 200 to 2) and with CL/PFPE molar ratio ranging from 4 to 110. A complete conversion of CL was achieved in most cases, and the living character of the polymerization was confirmed by further additions of CL, which lead to a molecular weight increase of the PCL blocks.

The main effect of the molecular weight of PFPE on the reaction seems related to its solubility with CL. In fact, initially CL was immiscible with all PFPEs and the reaction medium appeared milky, but as the reaction proceeded, it became transparent. The time necessary to achieve the this point was found to depend mainly on the molecular weight of $HO-R_H-PFPE-R_H-OH$ and only slightly on the initial CL/PFPE ratio. At 110 °C it ranged from few minutes for Z-DOL TX 1100 to about few hours for Z-DOL TX 3400. A significant increase of melt viscosity of the reaction medium was noted when the PCL segments became particularly long (degree of polymerization of PCL segments higher than 30).

The ^1H NMR spectra of all copolymers obtained with $Ti(OBu)_4$ or Bu_2SnO showed that the ratio between the signal at 4.25 ppm and the complex signal ranging from 3.65 to 3.95 ppm remained constant for different CL conversions and independent by the initial CL/PFPE ratio, as expected for a fast and complete reaction of the hydroxyl terminal groups of PFPE and for a PCL chain growth onto hydroxyl terminal groups of PFPE only. This ratio was always close to 1:4, as expected from a complete reaction of the −OH groups of PFPE, and was observed even at a very high PFPE/Ti molar ratio (≈50). On the basis of these evidences, we can also conclude that during the polymerization of CL a continuous fast exchange of the Ti ligands with −OH-terminated species ($HO-R_H-PFPE-R_H-OH$ and terminal groups of block copolymers) occurs and, as a consequence, that PCL blocks can grow on all the PFPE terminal groups.

The evidence that all −OH groups of $HO-R_H-PFPE-R_H-OH$ reacted (as derived from ^1H NMR spectra) suggests that triblock copolymers (PCL−PFPE−PCL) are formed during the reaction. Further evidences confirmed the formation of ABA block copolymer and excluded the parallel formation of PCL homopolymer.

Selective solubility in various solvents is frequently exploited to confirm the formation of block copolymers and to separate them from homopolymers. However, in the case of block copolymers with blocks of low molecular weight, solubility can change dramatically depending on the relative length of the blocks. In the present case, $HO-R_H-PFPE-R_H-OH$ has average molecular weights ranging from 1100 to 3400 and is soluble only in fluorinated solvents when the molecular weight is ≥2250, but when the molecular weight is 1100, a significant fraction becomes soluble in other solvents such as chloroform.

On the other hand, PCL of relatively high molecular weight is soluble in a large number of common solvents (chloroform, methylene chloride, toluene, THF, etc.) and is insoluble in methanol and TCTFE; however, again, a significant fraction of PCL becomes soluble also in methanol for very low molecular weights (≤2000).

Therefore, in the present study selective solubility tests, performed by dissolving samples in chloroform or THF and reprecipitating in TCTFE, are significant only for samples obtained from $HO-R_H-PFPE-R_H-OH$ with molecular weight higher than 2000 and for relatively long PCL blocks. In these cases a quantitative recovering of the starting products was observed; because unreacted $HO-R_H-PFPE-R_H-OH$ or copolymers with very short PCL segments would be soluble in TCTFE, we can conclude that, after reaction with CL, all PFPE blocks are bonded to long PCL segments, although this result do not exclude the presence of PCL homopolymer of high molecular weight.

A support to the conclusion that only ABA copolymer was formed was obtained from a quantitative analysis

Table 3. $\bar{M}_n$ Measurements by Vapor Pressure Osmometry

code	measd $\bar{M}_n$ (g mol^{-1})	theor $\bar{M}_n$ (g mol^{-1})
PCL	1850	2000[a]
TX2CL(5)	3660	3390
TX2CL(10)	4000	4530
TX2CL(40)[b]	11860	11370
TX1CL(10)	3460	3380

[a] Determined by NMR. [b] After purification by dissolution/reprecipitation.

of the terminal groups performed by ^{1}H NMR; in fact, if all the hydroxyl terminal groups of HO−R$_H$−PFPE−R$_H$−OH react with CL and if PCL homopolymer is not formed, the number of PCL hydroxyl terminal groups is expected to be equal to that of the initial HO−R$_H$−PFPE−R$_H$−OH.

The ^{1}H NMR spectrum of Figure 1c shows that the signal of methylene groups adjacent to the hydroxyl terminal groups of PCL is clearly evident (triplet at 3.65 ppm, protons 4f in Table 1), and it is easy to compare its relative intensity with that of a signal at 4.25 ppm attributable to the methylene groups adjacent to the hydroxyl terminal groups of HO−R$_H$−PFPE−R$_H$−OH reacted with CL (protons 4b in Table 1). In every case, within the experimental error, we found that the intensities of these two signals are nearly the same as expected for the formation of PCL blocks growing only from the hydroxyl terminal groups of HO−R$_H$−PFPE−R$_H$−OH. Therefore, we can conclude that linear PCL homopolymer was never present in a significant amount in the crude products obtained from reaction of HO−R$_H$−PFPE−R$_H$−OH with CL.

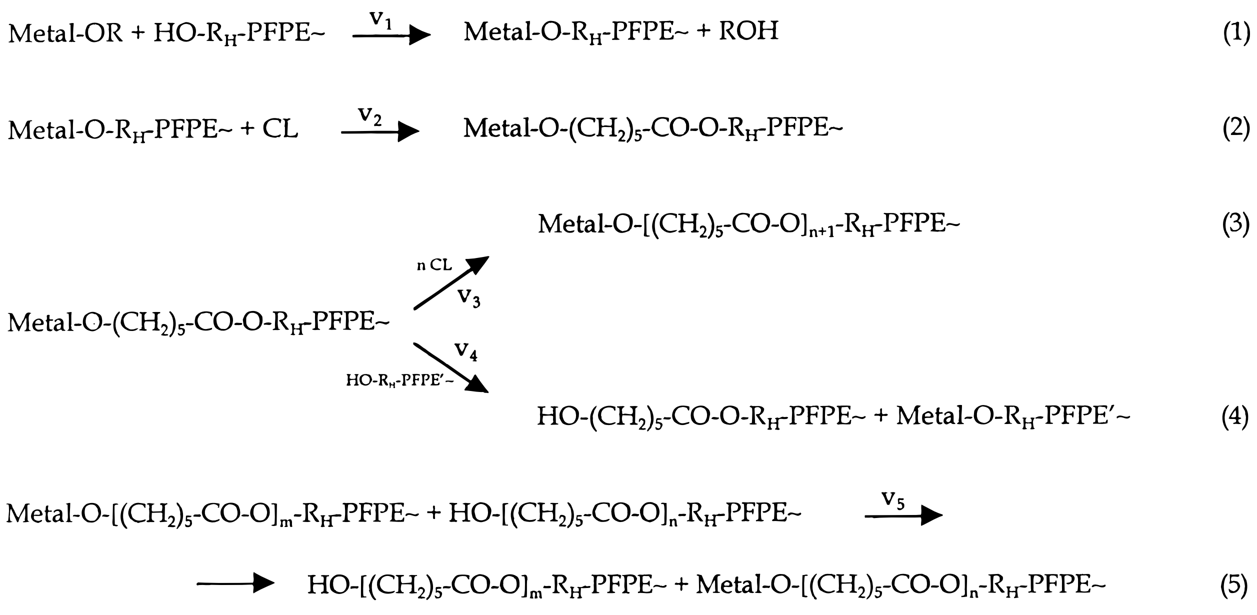
This conclusions was also confirmed by SEC and VPO measurements. Experimental data of VPO measurements are reported in Table 3 along with the theoretical number-average molecular weight (calculated from the initial CL/PFPE ratio and assuming that all the hydroxyl terminal groups of PFPE have reacted). As it appears, the correspondence between theoretical and measured $\bar{M}_n$ values is quite good.

Furthermore, if a significant fraction of PFPE would be bonded to very short PCL segments and/or PCL homopolymers would be present in the crude product, we should find peaks attributable to these products in SEC curves. These peaks should appear at higher retention volumes (lower molecular weights) with respect to the peak expected for PCL−PFPE−PCL block copolymers. Actually, we never observed the presence of a second peak at low molecular weight except a signal attributable to CL monomer, present when the conversion of CL was not complete. As expected, SEC traces of homologous samples (same Z-DOL TX and different CL amount) exhibit a decrease of retention volume by increasing the PCL segment length. Molecular weights calculated via calibration with standard polystyrene samples were not reliable because of the very different hydrodynamic properties of polystyrene with respect to PCL homo- and copolymers.

Mechanism of PCL Segment Growth. A good understanding of the reaction mechanism is a prerequisite for the design and the control of the resulting chemical structure. In the present case, the possible reactions occurring in the formation of PCL−PFPE−PCL copolymers are reported in Scheme 1.

An exchange reaction between hydroxyl terminal groups of the transfer agent with the ligands of the catalyst/initiator is commonly assumed (reaction 1). Taking into account that the concentration of the catalyst/initiator is usually much lower than that of the hydroxyl terminal groups of the transfer agents and that the resulting low molecular weight alcohol is probably removed from the reaction medium because of its high volatility, we can assume that all the original ligands of the catalyst/initiator (−OR groups) are replaced by transfer agents. As a consequence, when initiators with more than two ligands are used (such as Ti(OBu)$_4$ and Al(i-OPr)$_3$, etc.) along with bi- or multifunctional transfer agents, a gel should be formed if all ligands are able to undergo reaction 1 and when the concentration of the ligands is close to that of the reactive groups of the transfer agents. Indeed, in the present case, when the concentration of Ti(OBu)$_4$ was increased up to a molar ratio HO−/Ti = 4 (PFPE/Ti = 2), a gel was quickly formed, making difficult the mechanical stirring. This confirms a fast exchange of the original BuO− ligands with hydroxyl terminal groups of PFPE and that the Ti initiator is preferably contained in the fluorinated

Scheme 1. Mechanism of Block Copolymer Formation



phase. On the basis of these results, we can conclude that reaction 1 is much faster than the growth of PCL (reactions 2 and 3). As the reaction with CL proceeded, the initial gel disappeared progressively, leading to a clear liquid.

From the above-discussed results, and in particular by considering that all hydroxyl terminal groups of HO−R_H−PFPE−R_H−OH react, we have to assume that an exchange reaction between hydroxyl terminal groups and Ti−OR bonds occurs continuously, according to reaction 4. A further transfer reaction between metal-coordinated copolymer and noncoordinated copolymer (reaction 5) is also possible.

It is commonly accepted that when metals having free p- and d-orbitals with suitable energy (Sn, Ti, Zn, Al, etc.) are used as initiators in ring-opening polymerization of CL, a two-step “coordination−insertion” mechanism, consisting of lactone complexation to the catalyst/initiator followed by monomer insertion into the metal−oxygen bond, is operating.[39,41]

From Scheme 1 it appears that the first CL unit enters into the block copolymer by reaction 2 and, when it is bonded to the metal of the catalyst, can undergo further reaction with CL, leading to a growth of the PCL segment length (reaction 3) or with an hydroxyl terminal group, leading to an exchange of the segments bonded to the metal (reaction 4). The relative rates of reactions 3 and 4 and of reactions 2 and 3 can lead to different mechanism of growth.

By analyzing the ^{1}H NMR spectra, we derived interesting information about the mechanism of growth.

When a terminal hydroxyl group of PFPE reacts with a molecule of CL, a peak at 4.25 ppm (protons 4b in Table 1) should appear. However, this peak is masked by the presence of the signals from proton of CL monomer (protons 1c in Table 1). In principle, the separation of unreacted CL monomer should allow the peak to appear; however, the dissolution−reprecipitation method necessary for this scope could lead to a partial fractionation of PFPE and could lead to unreliable results.

The same information can be derived also by considering the other peaks present in the ^{1}H NMR spectra. For this purpose, spectra have been collected for a typical reaction product obtained from Z-DOL TX 2250 and CL (1:20 molar ratio) and Bu_2SnO as initiator (0.25 wt % with respect to the total quantity of reagents) reacted for various reaction times. ^{1}H NMR spectra of reaction products recorded after 2, 4, and 15 h are presented in Figure 2 together with some useful signal assignments. The ratio $a/(a + a' + a'' + c)$ represents the fraction of the first unit of CL bonded to the PFPE chain with respect to the total amount of CL units (as both monomer and polymer). The numeric value of this ratio can be determined according to the following equation

$$\frac{a}{(a + a' + a'' + c)} = \frac{(a + a' + a'')}{(a + a' + a'' + c)} - \frac{(b + b')}{(a + a' + a'' + c)}$$

taking into account that $a' = b'$ (signals from the same CL unit) and $a'' = b$ (signals from the last and first CL units, respectively) and that all terms in brackets are directly accessible from the spectrum.

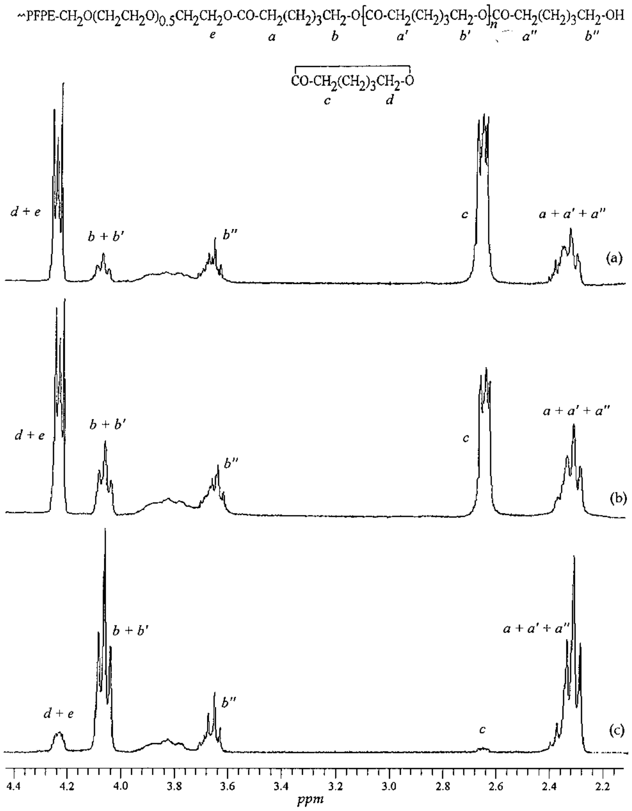


Figure 2. ^{1}H NMR spectra of a typical reaction product obtained from Z-DOL TX 2250 and CL (1:20 molar ratio) and Bu_2SnO as initiator (0.25 wt % with respect to the total quantity of reagents) reacted for (a) 2, (b) 4, and (c) 15 h [spectra recorded in $CDCl_3$].

In the case of the three spectra reported, the $a/(a + a' + a'' + c)$ ratio is always close to 0.10, indicating that about 10% of the total amount of CL (which also corresponds to the amount of PFPE terminal groups) is bonded to PFPE chain as first unit in the early stage of reaction and that this amount remains constant until complete conversion of CL. Taking into account the low concentration of initiator, this indicates that all hydroxyl groups of HO−R_H−PFPE−R_H−OH react with at least one unit of CL before the growth of PCL segments, and therefore the rate of the first unit addition (v_2) is faster than further propagation reactions (v_3). This means also that the exchange reaction to hydroxyl groups of HO−R_H−PFPE−R_H−OH with the metal−CL bond (v_4) is much faster than the addition of further CL units to the growing chain (v_3), according to the simplified mechanism proposed in Scheme 1. This demonstrates also that HO−R_H−PFPE−R_H−OH is a very efficient transfer agent.

Furthermore, 10% corresponds to the maximum value that can be reached without PCL homopolymerization, and this is a further indication of the absence of homopolymerization.

It is also interesting to consider the results obtained when Al alkoxides were used as initiators, taking into account that $Al(O\textit{i}Pr)_3$, in its trimer form (A3), has been recognized as one of the most interesting initiators for the ring-opening polymerization of CL.[42] In the absence of transfer agents, the polymerization is very fast, even at low temperature, and leads to a very narrow MWD of PCL at temperature <150 °C.[43] In the presence of low molecular weight glycols the rate of polymerization was found to be strongly reduced, while in the presence

Table 4. Data of CL Conversion after 3 and 18 h of Reaction at 110 °C Using Al(OiPr)$_3$ (Trimer Form, A3) as Initiators and Z-DOLTX 2250 as Transfer Agent

amount (g)			CL conversion (%) after	
Z-DOLTX 2250	CL	Al(OiPr)$_3$	1 h	17 h
	4.00	0.01	100[a]	100
4.00	2.00	0.01[b]	2	19
4.00	2.00	0.01[c]	25	61

[a] CL total conversion was achieved in less than 10 min. [b] CL added to a Z-DOL TX/Al(OiPr)$_3$ mixture prereacted for about 1 h at 110 °C. [c] Al(OiPr)$_3$ added to the Z−DOL TX/CL mixture.

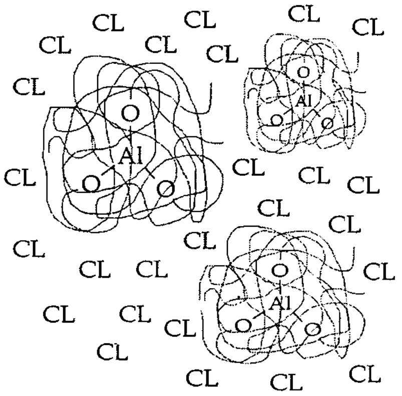


Figure 3. Schematic representation of envelope formation around catalytic site.

of α,ω-dihydroxypoly(oxyethylene) (HO−POE−OH) the polymerization rate was nearly the same as for pure CL.[37]

When we used A3 as initiator (see Table 4), different results were found when the initiator was added to the PFPE/CL mixture or to PFPE followed by the slow addition of CL. In the first case the reaction was slower than for the polymerization of CL with A3 in the absence of transfer agents, but a conversion of about 60% was achieved in 17 h. On the contrary, CL was polymerized to a very low extent after 17 h (less than 20% of conversion), when added to the PFPE/A3 mixture. In this last case a small volume of gel was found on the stirrer.

To explain the above results, we can assume that the hydroxyl groups of PFPE exchange rapidly with −*i*OPr ligands of A3 and that the exchange involves just the fraction of PFPE around to the initiator. This leads to the formation of a gel, forming a tight envelope around the catalytic sites (see Figure 3), which can be considered responsible of the reduced polymerization rate either by changing the catalytic activity of A3 (for instance, by hindering the coordination of CL onto Al, according to the well-known mechanism for ring-opening polymerization of lactones) or by reducing the concentration of CL close to the catalytic sites for polymerization. The rapid exchange of the hydroxyl groups of PFPE with the ligands of A3 was confirmed by the fast formation of a complete gel when A3 was added to PFPE at a molar concentration equal to $^2/_3$ of the PFPE molar concentration (ratio of ligand concentration over −OH groups = 1).

One can also be tempted to explain the above results by assuming that the preferential segregation of A3 in the fluorine-rich phase is due to the interaction of the fluorinated−alkoxide moieties of PFPE with aluminum. However, the polymerization of CL carried out by adding A3 to Fomblin Z, a PFPE without hydroxyl terminal groups, and then by slowly adding CL to this mixture showed a polymerization rate for CL just a little slower than for CL alone. The exchange of the hydroxyl groups of HO−R$_H$−PFPE−R$_H$−OH with the Al ligands of A3 has therefore to be assumed as the primary cause of the retarded polymerization. The effect of low molecular weight alcohols and diols, as inhibitors in polymerization initiated with A3 and as accelerators in polymerization initiated with A4, has been explained by Duda in terms of their capability to facilitate the transformation of the otherwise low-active A4 into A3 or other more active species.[34] In the present case, we can assume that, after the exchange of ligands, a medium with a composition different from the average composition surrounds the catalytic sites, modifying the catalytic activity of A3 and/or the rate of access of CL to the catalytic sites and retarding the polymerization of CL.

Conclusions

Telechelic PFPEs containing primary hydroxyl groups are efficient transfer agents for the polymerization in bulk of CL in the presence of a suitable catalyst/initiator. Ti(OBu)$_4$ and Bu$_2$SnO are the most active catalysts/initiators. All the characterization techniques indicate that the ring-opening polymerization of CL occurs only onto the hydroxyl groups of PFPE with formation of a triblock copolymer ABA and without detectable formation of PCL homopolymer. The average molecular weight is that expected on the basis of the initial CL/HO−R$_H$−PFPE−R$_H$−OH ratio. The formation of ABA block copolymers starts on the terminal groups of PFPEs after an exchange with the −OR ligands of the initiators. After this fast exchange reaction, the growth of PCL segments occurs by a relatively fast addition of one single CL units to all PFPE terminal groups followed by a slow insertion of the other CL units.

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