Synthesis of Perfluorohexyl-Terminated Poly(ethylene oxide) Using Maghnite-H as Clay Catalyst

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ABSTRACT: Activated monomer cationic ring-opening polymerization of ethylene oxide initiated with 1H,1H,2H,2H-perfluorooctan-1-ol, using acid exchanged montmorillonite clay called Maghnite-H$^+$ (Mag-H$^+$) as an effective catalyst, was carried out to obtain the corresponding homopolymers with narrow polydispersity ratios. The molecular weights of the obtained polymers could be controlled with the feed ratio of the monomer and initiator. The effect of amount of catalyst and time on the polymerization yield and viscosity of the polymers were studied. The structure was confirmed by ^{1}H-NMR and MALDI-TOF-MS. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 118: 3445–3452, 2010

Key words: cationic polymerization; ecocatalyst; ethylene oxide; montmorillonite; ring opening polymerization; 1H,1H,2H,2H-perfluorooctan-1-ol; maghnite-H

INTRODUCTION

Polymers that contain atoms of fluorine in or along the backbone exhibit many desirable physical properties, such as strong surface activity, enhanced chemical resistance, and high thermal stability.[1,2] Their interfacial properties in liquid systems play an important role in their practical application to food, paint, cosmetic and medical emulsions, as well as in polymerization, solvent extraction and other processes. Polymeric surfactants are often more surface active and form more stable emulsions compared with smaller molecular weight compounds.[3]

Hydrophobically modified PEO can be obtained by different methods including various linkers used to connect the PEO chain with the hydrophobic segment. The syntheses of modified PEO with linkers such as ethers,[4] esters,[5,6] urethanes[7,8] or diurethanes[9,10] were reported.

Recently, it was shown that PEO end-functionalized with semifluorinated groups [C_nF_{2n+1}—$(CH_2)_m$] called F-HEUR presents stronger hydrophobic association and a higher viscosifying effect than the corresponding hydrocarbon derivatives.[11] Small changes in the perfluorinated segment or hydrocarbon spacer $(CH_2)m$ have a considerable influence on the viscoelasticity.[12,13]

However, the cationic initiators used to make perfluoroalkyl end-capped poly(ethylene oxide) are expensive and often give rise to impurities, such as chromium, mercury or antimony, in the end product which often render the material unsuitable for medical or veterinary applications and make its disposal in the environment problematic. In addition, such initiators require the use of very high or very low temperatures during the polymerization reaction, and lead to relatively poor yields.

The search for new initiators remains a subject of topical interest. There is still a great demand for heterogeneous catalysis under mild conditions and in environmentally friendly processes. Montmorillonites, a class of inexpensive and noncorrosive solid acids have been used as efficient catalysts for a variety of organic reactions. The reactions catalyzed by montmorillonites are usually carried out under mild conditions with high yields and high selectivities and the workup of these reactions is very simple; only filtration to remove the catalyst and evaporation of the solvent are required. Montmorillonite catalysts are easily recovered and reused.[14,15]

There is, to date, no information on the ring-opening polymerization of ethylene oxide (EO) with clay catalyst. In continuation of our studies on environmentally benign methods using solid supports,[16–19] we report for the first time the synthesis of perfluoroalkyl end-capped poly(ethylene oxide)s via cationic

$$\text{EO} + C_6F_{13\text{-}f}CH_2CH_2OH \xrightarrow[\text{CH}_3\text{CN, 0 °C}]{\text{Mag-H}^+} R_fCH_2CH_2O(CH_2CH_2O)_nH$$
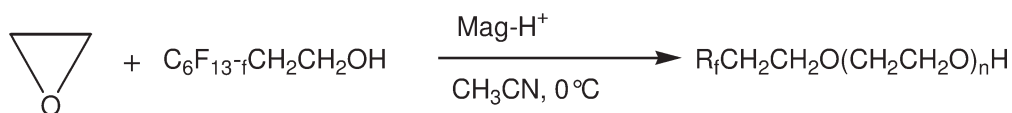
Scheme 1 Polymerization of EO by Mag-H$^+$ system in the presence of 1H,1H,2H,2H-perfluorooctan-1-ol.

ring-opening polymerization by an acid exchanged montmorillonite called Maghnite-H$^+$ (Mag-H$^+$). Poly(ethylene oxide)s are successfully synthesized by the polymerization of EO in conjunction with saturated alcohols as modifiers.

1H,1H,2H,2H-perfluorooctan-1-ol (R_f-OH) is chosen as modifiers for the synthesis of perfluoroalkyl-terminated poly(ethylene oxide), in the presence of an acid exchanged montmorillonite (Mag-H$^+$), which is an efficient solid catalyst for the ring opening polymerization of epoxides (Scheme 1).

EXPERIMENTAL

1H,1H,2H,2H-perfluorooctan-1-ol was obtained from commercial source (PECK) and used without further purification. EO, (Aldrich) was used as received. Dichloromethane, acetonitrile and methanol were purified following standard techniques and used after distillation over their respective drying agents.

Preparation of the maghnite-h

The clay, which has been used as catalyst, is supplied by a local company known as ENOF Maghnia (Western of Algeria). Maghnite-H was prepared according to the process reported in our previous study20. Raw-Maghnite (montmorillonite clay) (20 g) was crushed for 20 min using a Prolabo ceramic balls grinder. It was then dried by baking at 105°C for 2 h. The Maghnite was then weighted and placed in an Erlenmeyer flask together with 500 mL of distilled water. The Maghnite/water mixture was stirred using a magnetic stirrer and combined with different concentrations of sulphuric acid solution to obtain various forms of "Maghnite-H$^+$ × M" catalyst. Until saturation was achieved over 2 days at room temperature, the mineral was washed with distilled water until became sulfate free and then dried at 105°C. The chemical composition of Maghnite-H is given in Table I.

Polymerization

Polymerizations were performed with dichloromethane at 0°C. The procedure is identical in all manipulations, involving slow addition of EO to the stirred acetonitrile (50 mL) solution containing 1H,1H,2H,2H-perfluorooctan-1-ol (R_f-OH) and the catalyst. Before use, Mag-H$^+$ was dried at 120°C overnight and then transferred to a vacuum desiccator containing P_2O_5 to cool at room temperature overnight. An example reaction is detailed as follows: After charging the reaction vessel with the mineral (0.33 g; 3% in weight to EO) and Rf-OH (0.01 mol), the EO (0.25 mol) was slowly added. At the required time, an aliquot of the reaction mixture was taken in such manner to exclude any clay mineral. At the end of the reaction, the resulting mixture was filtered to remove the clay and dried under vacuum to yield the polymer. The later was dried in a vacuum oven before submission for MALDI-TOF MS and ^{1}H-NMR, ^{13}C-NMR, and ^{19}F-NMR analysis (the yield of this example was 59%).

Characterization of the products

^{1}H, ^{13}C nuclear magnetic resonance (NMR) measurements were carried out on a 200 MHz Bruker NMR Spectrometer. ^{19}F nuclear magnetic resonance (NMR) measurements were carried out on a 400 MHz Bruker spectrometer. Average molecular weights and molecular weight distributions of the different polymers were measured using size exclusion chromatography (SEC) on a system equipped with a SpectraSYSTEM AS1000 autosampler, with a guard column (Polymer Laboratories, PL gel 5 μm Guard, 50 × 7.5 mm) followed by 2 columns (Polymer Laboratories, 2 PL gel 5 μm MIXED-D columns, 2 × 300 × 7.5 mm), with a SpectraSYSTEM RI-150 and a SpectraSYSTEM UV2000 detectors. The eluent used is THF at a flow rate of 1 mL min^{-1} at 35°C. Poly(ethylene oxide) standards (483–580 × 10^3 g mol^{-1}) were used to calibrate the SEC. Intrinsic viscosity [η] measurements were performed at 30°C in

TABLE I
Chemical Composition of the Catalyst

Species	SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	MgO	CaO	Na$_2$O	K$_2$O	TiO$_2$	As	L.O.I
% (w/w)	69.4	14.7	1.2	1.1	0.3	0.5	0.8	0.2	0.05	11

TABLE II
Synthesis Conditions of the R_f-POE at: $T = 0°C$, Time = 12 h and 3% of Mag-H$^+$

[EO]/[R$_f$OH]	Yield (%)	$\overline{M}_{nGPC}$	$\overline{M}_{nRMN}$	$\overline{M}_{nTheo}$	$\overline{DP}_n$	$\overline{M}_w/\overline{M}_n$
05	40	570	460	600	4	1.23
10	47	600	590	804	5	1.21
15	50	700	695	1024	7	1.25
20	54	820	831	1244	10	1.24
25	59	900	920	1464	12	1.27

toluene using a capillary viscometer SEMATECH (VISCOLOGIC TL1). "The MALDI-TOF mass spectra (m.s.) were recorded on a Bruker Biflex III equipped with a nitrogen laser ($l = 337$ nm). All m.s. were recorded in the linear mode with an acceleration voltage of 19 kV. The irradiation targets were prepared from THF or CH$_2$Cl$_2$ solutions with dithranol as matrix and NaI as dopant.

RESULTS AND DISCUSSION

The ring-opening polymerization of 1,2-propylene oxide (PO) by primary alcohol in the presence of Mag-H$^+$ satisfactorily proceeds to give linear polyPO with the controlled $\overline{M}_n < 3200$.[20] The key feature of this polymerization may be the acidity of the added Mag-H$^+$, which is not as large to polymerize the monomer by itself but is sufficient to activate the monomer. To extend this facile method to others epoxies, we performed the ring-opening polymerization of EO to examine the $\overline{M}_n$ and $\overline{DP}_n$ of the polymer. Table II summarize the results of the polymerization of EO with 1H,1H,2H,2H-perfluorooctan-1-ol (Rf-OH) in the presence of Mag-H$^+$ as catalyst. The polymerization did not proceed with Rf-OH alone, the addition of Mag-H$^+$ was quite effective to give perfluoroalkyl end-capped poly(ethylene oxide) quantitatively. The bulk ring opening polymerization of EO proceeds by an exothermic and spontaneous reaction at room temperature using 0.5% of Mag-H$^+$. Such bulk reactions are difficult to control and gave irreproducible molecular weight results due to the uncontrollable rise in temperature observed during these polymerizations, for this reason we have studied the polymerization of EO in the presence of solvent (in solution). This lead was followed up by a series of experiments, in which the yield of poly(ethylene oxide) with time was observed at various amounts of catalyst.

Amount of catalyst (Mag-H$^+$/EO) is an important factor of polymerization. Figure 1 shows the effect of amount of catalyst on polymerization. The higher the amount of catalyst, the higher the yield. This phenomenon is probably the result of number of "initiating active sites" responsible of inducing polymerization, this number is proportional to the catalyst amount used in reaction. Similar results are obtained by Yahiaoui et al.,[16] and Njopwouo et al.,[21] in the polymerization of

styrene oxide by Mag-H$^+$ and the polymerization of styrene by montmorillonite, respectively.

As shown in Figure 1, the viscosity was found to decrease, depending on the amount of Mag-H$^+$ (i.e, [η] decreases when amount of Mag-H$^+$ increases) in the following order: 3% < 2.5% < 2% < 1.5% < 1%. The concentration of initiator or growing macromolecules should be constant and only active monomer increase with the increase of catalyst, and as result we have a competition between the two mechanisms (ACEM and AMM). The AMM give linear polymers and the ACEM gives cyclic dimers which decrease the molecular weight. Similar results are obtained by Kadakowa et al.,[22] and Crivello and Fan,[23] in the polymerization of lactones by Sn-montmorillonite and cyclohexene oxide by Cobalt respectively.

Polymerization conditions for the synthesis of EO polymers are shown in Tables II. A perfluoroalcohol modifier, R_f-OH, is employed to replace a conventional modifier, such as ethylene glycol or water.[24,25] Table II shows the effect of [EO]/[R$_f$OH] molar ratio on the yield of polymerization and on the molecular weight respectively. When the [EO]/[R$_f$OH] molar ratio was increased, the yield of polymerization was increased, and the resulting polymers exhibited increasing in molecular weight. The results of the analysis of the polymer by gel permeation chromatography
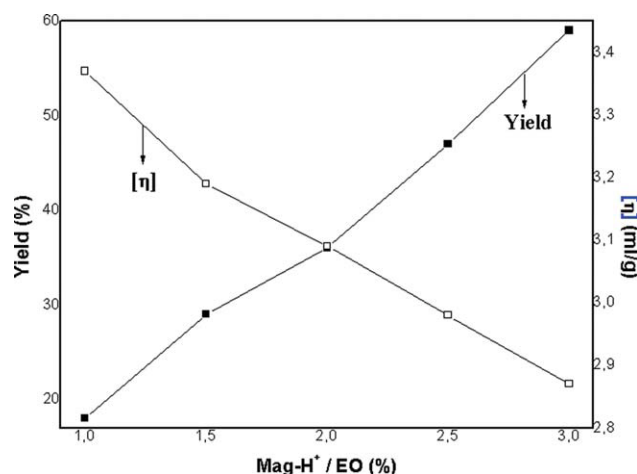

Figure 1 Effect of the Amount of catalyst on the yield and the intrinsic viscosity of formed polymer: [EO] = 5 M in acetonitrile at 0°C and for 12 h. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
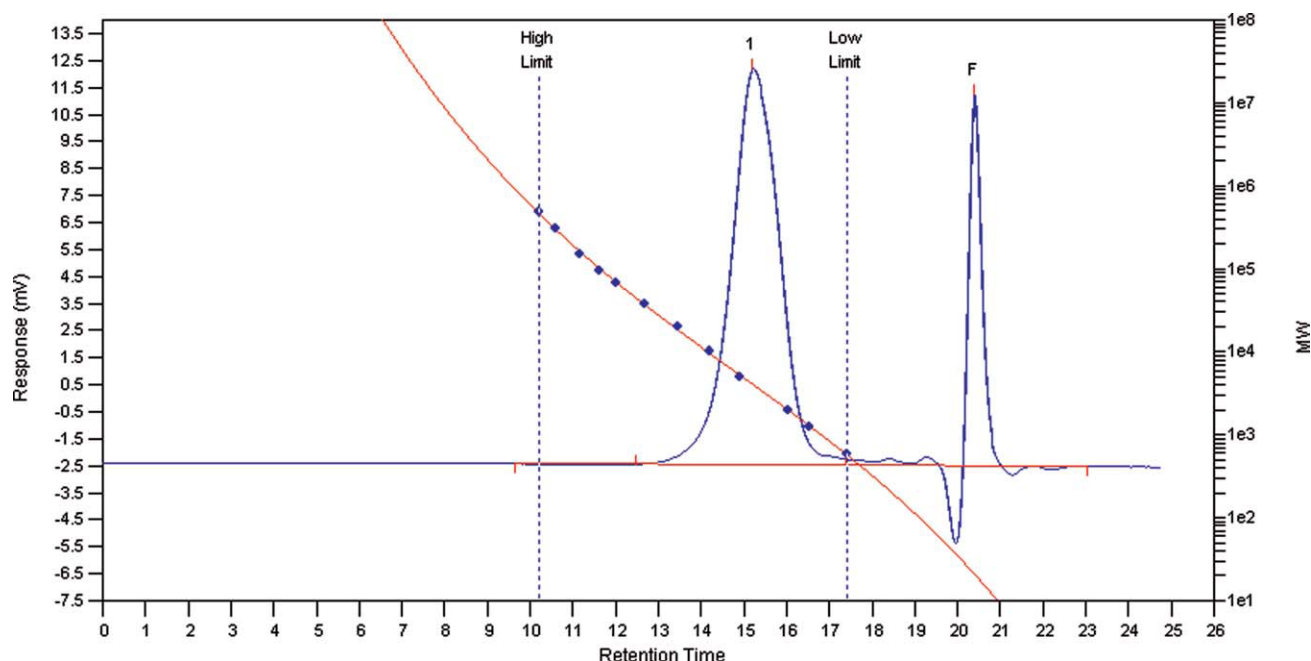
Figure 2 GPC chromatogram of R_f-PEO at: $T = 0°C$, Time = 12 h and 3% of Mag-$H^+ 0.2$ [EO]/[RfOH] = 25. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

(GPC) are shown in Figure 2. As shown, the macromolecular weight distributions of the obtained polymers are narrow.

As shown Table II, when the ratios of monomers to initiator are equal to 5, the $\overline{DP}_n$ values of the product polymers are in good agreement with the calculated values (entries 1 in s II). The $\overline{DP}_n$ values become smaller than the calculated values, when the ratios of monomers to initiator are >5 (entries 2 to 5). These observations are probably due to the presence of moisture in the polymerization system at the larger monomer/initiator ratios. Kadakowa et al.[22] obtain similar results in the polymerization of lactones by Sn-montmorillonite in the presence of ethanol as initiator. Also the decrease in polymer molecular weight in this polymerization is due primarily to an increase in intramolecular chain transfer to polymer as indicated by the corresponding increase in the yield of cyclic tetramer with increasing monomer to initiator ratios.

The structure of the fluoropolymer was determined by ^{1}H-NMR, ^{13}C-NMR, ^{19}F-NMR, and MALDI-TOF MS. The ^{1}H-NMR spectrum (Fig. 3) shows the absence of epoxy protons (in the 2.4–3.1 ppm range) and the presence of a complex system (doubled AB system) centered at 2.4 ppm assigned to the methylene group adjacent to the perfluorinated chain **(C)**. The signal at $\delta = 4$ ppm is assigned to Rf—CH_2—CH_2—O **(b)**. The relative intensity of these signals was 2 : 2, indicating that the polymerization was initiated by perfluoroalcohol with incorporation of the perfluorinated end group at the initiating site of the polymer chain. The degree of polymerization (DP_n), therefore, was calculated by the integrated ratio of the signal due to the methylene end group to the signals due to the polymer main chain. The molecular weights of the polymers calculated based on NMR spectra were in agreement with the molecular weights obtained by GPC (Table II). These results support the presence of one perfluorinated group per molecule.

The signal centered at 3.7 ppm gives the evidence of the CH_2—O **(a)** group while the broad singlet at 2.1 ppm shifting with dilution is attributed to the hydroxyl function **(d)**.

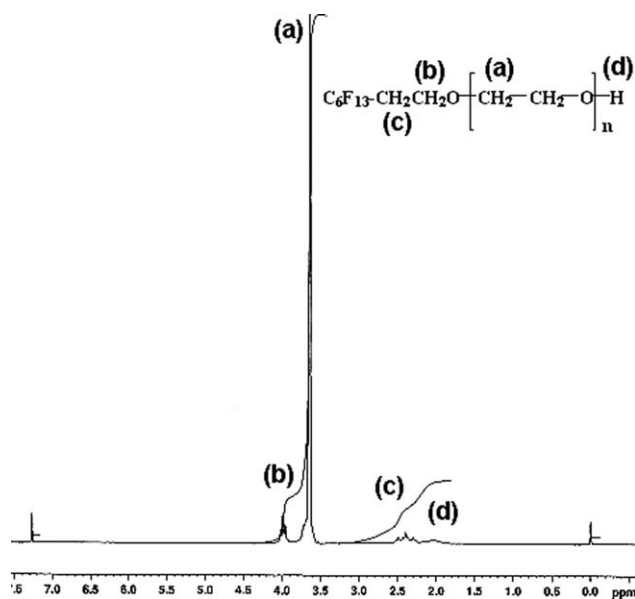**Figure 3** ^{1}H-RMN (200 MHz) of HO-POE-$CH_2CH_2C_6F_{13}$ in $CDCl_3$.
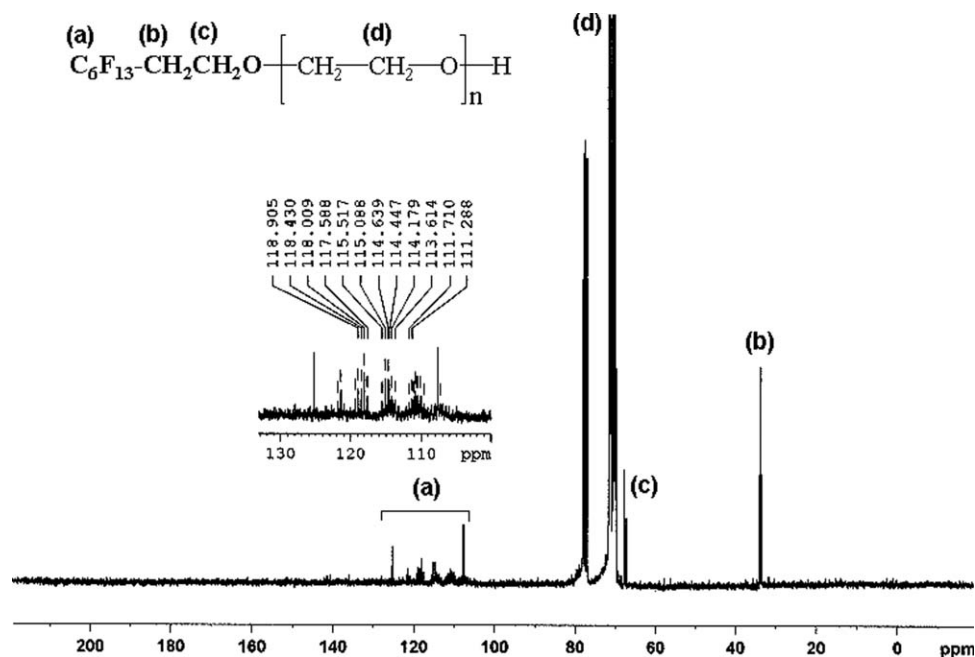
Figure 4 ^{13}C-RMN (200 MHz) of HO-POE-CH$_2$CH$_2$C$_6$F$_{13}$ in CDCl$_3$.

The most interesting feature in the ^{13}C-NMR spectrum concerns the presence of perfluorinated group signal. The ^{13}C-NMR spectrum (Fig. 4) exhibits the characteristic triplets or quartet in the 108 to 125 ppm range assigned to the perfluorinated group. The adjacent methylene group gave an expected triplet centered at 35 ppm while that adjacent to the OH function **(d)** is represented by a singlet at 70 ppm.

Finally, ^{19}F-NMR (Fig. 5) shows: δ: −127 ppm (s.2F); −124.2 ppm (t.2F); −123.7 ppm (s.2F); −122.5 ppm (s, 2F); −116 ppm (s, 2F); −82 ppm (t, 3F).

Interestingly, for PEO end capped by 1H,1H, 2H,2H-perfluorooctan-1-ol one series of peaks is observed as shown in Figure 6. As expected, the signals of every series are separated by 44 m/z. The series corresponds to the fluoropolymer HO—PEO—CH$_2$—CH$_2$—C$_6$F$_{13}$ with Na$^+$ as the counter ion. The molar masses involved are: repeat unit, —CH$_2$—CH$_2$—O—, 44 g/mol, counter ion Na$^+$, 23 g/mol, end group, —H, 1.01 g/mol, and initiator group, —O—CH$_2$—CH$_2$—C$_6$F$_{13}$, 363 g/mol. Subtracting the initiator group, end group and the counter ion masses from each of the signals and dividing the result by the repeat unit mass an integral number for the degree of polymerization was obtained, e.g.:

$$(1179.79 \text{ g/mol} - 363 \text{ g/mol} - 1 \text{ g/mol} - 23 \text{ g/mol})/ 44 \text{ g/mol} = 18.$$

This finding is in good agreement with the proposal that 1H,1H,2H,2H-perfluorooctan-1-ol is present as the active initiator species and the result would confirm that the polymerization of EO proceeds through the opening of the epoxide ring by the activated monomer mechanism (AMM).

Calvet et al.[26] have prepared a series of perfluoroalkyl end-capped poly(ethylene oxide) (PEO), with a well-defined structure were synthesized in two reaction steps. The reaction of PEO with a large excess of isophorone diisocyanate (IPDI) leads to an isocyanate-terminated prepolymer which is then reacted with the semifluorinated alcohol [C$_8$F$_{17}$(CH$_2$)$_{11}$—OH]. Our method occurs in one simple reaction step, and so on under mild conditions; only filtration to remove the catalyst and evaporation of the solvent are required. This makes this work an attractive method for its simplicity.

Polymerization mechanism

Maghnite-H$^+$ (Mag-H$^+$) is a proton-exchanged montmorillonite sheet silicate clay. The montmorillonite lattice is composed of layers made up of two silica tetrahedral sheets with a central alumina octahedral sheet.[19] EO polymerizes cationically by opening of the O—C bond in the oxonium cation, which is attacked by the most nucleophilic O-atom of the C$_6$F$_{13}$—CH$_2$—CH$_2$—OH (R_f-OH) initiator involving non ionic species (hydroxyl). According to the foregoing discussion and the results of product analysis, we may suggest a cationic mechanism for the resulting reaction of polymerization induced by Mag-H$^+$. Protons carried by montmorillonite sheets of Mag-
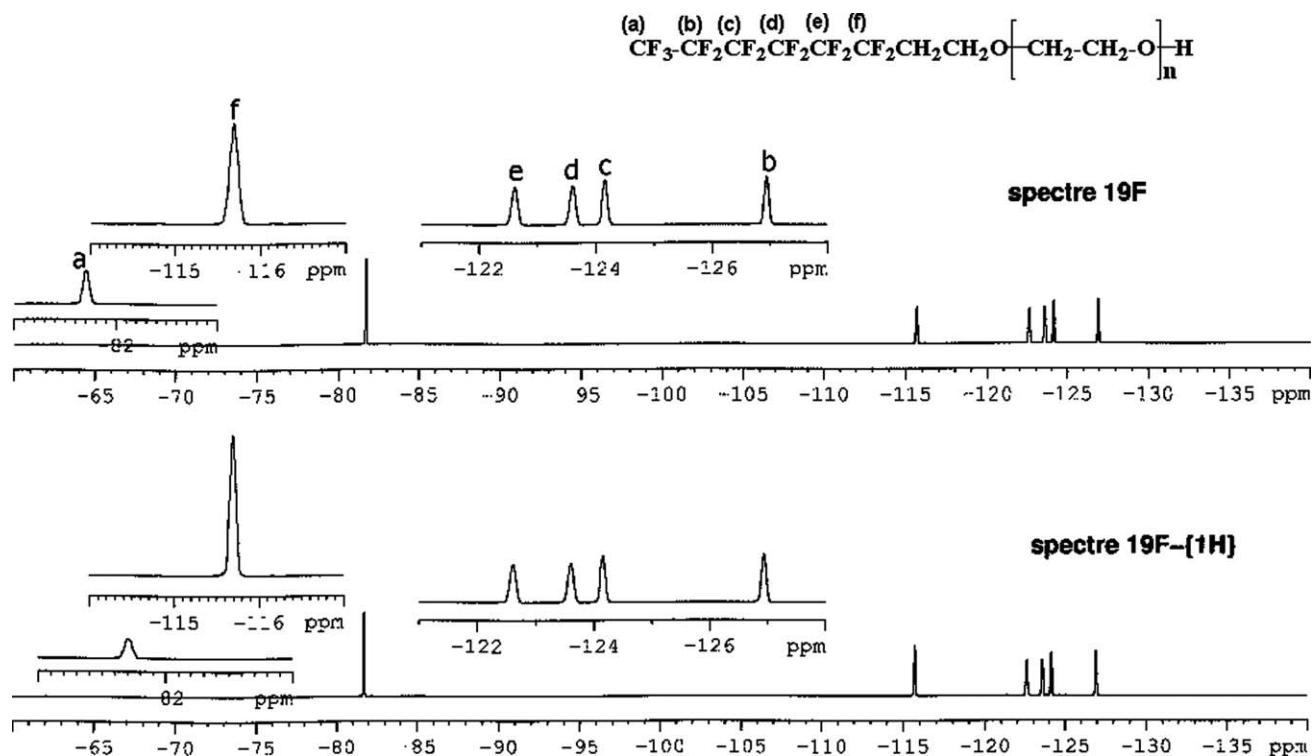
$$\underset{(a)\ (b)\ (c)\ (d)\ (e)\ (f)}{CF_3\text{-}CF_2CF_2CF_2CF_2CF_2CH_2CH_2O}\left[CH_2\text{-}CH_2\text{-}O\right]_n H$$

**Figure 5** ^{19}F-RMN of HO-POE-CH$_2$CH$_2$C$_6$F$_{13}$ in CDCl$_3$.

H$^+$ (Scheme 2) induce the cationic polymerization. Propagation then takes place by a cationic actived monomer mechanism.

Initiation

Initiation involves the reaction between EO and Mag-H and yields intermediate of oxonium (actived monomer); the formation of this species is the rate determining step. These montmorillonite sheets take place as counter-anions.
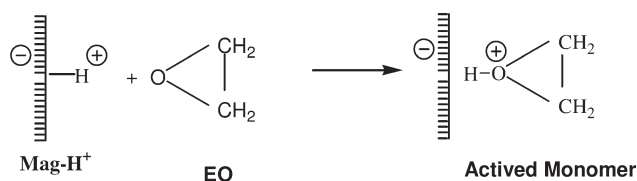
There is competition between conventional (ACE) and AM Ring-opening polymerization (ROP) mechanism.
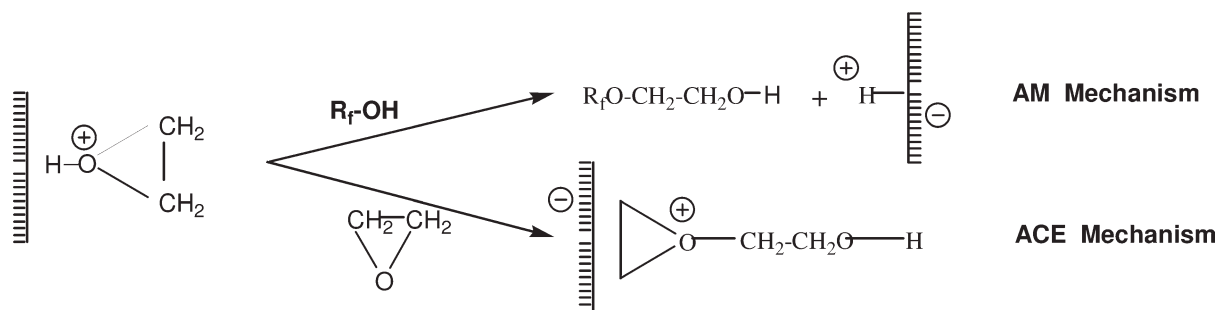
Initiation in conventional ROP is first-order each in protonated monomer and unprotonated monomer. AM ROP is first-order each in protonated monomer and alcohol. The ratio of the rates of AM-to-conventional ROP depends on [R$_f$OH]/[EO] and the ratio of the rate constants for the two reactions. Assuming that the two

rate constants are comparable, AM ROP becomes the dominant process at high [R$_f$OH] and low [EO]. Thus, AM ROP is carried out under monomer-starved conditions. The instantaneous monomer concentration is very low, but monomer is continuously added to the reactor at a rate equal to its rate of consumption.

Propagation

The propagation step is the successive reaction, a molecule of R_f-OH attacks in a nucleophilic way the protonated monomer of EO.

AM propagation continues in a similar manner with nucleophilic attack by hydroxyl end groups of polymer on protonated monomer

perfluorohexyl-terminated poly(ethylene oxide)

At low [R_fOH] and high [EO], we have a competition between the AMM mechanisms and the ACEM one.

Propagation:

Termination:

The relative nucleophilicity of a cyclic ether compared to a polymer chain ether is lowest for the 3-membered ring. Propagation for an oxirane involves an increase in bond angle strain on conversion of the sp3-hydridized oxygen in monomer to the *sp2*-hybridized oxygen in the oxonium ion. The cyclic dimer 1,4-dioxane is the major cyclic oligomer formed in the polymerization of EO.[27]

Termination

Termination may occur by chain transfer with the moisture present in the polymerization system.

In conclusion, it was proved that Mag-H$^+$ can be used to induce the polymerization of EO, thus offering new possibilities for the selective study of

Figure 6 MALDI-TOF MS spectrum of HO-POE-CH$_2$CH$_2$C$_6$F$_{13}$ at: [EO]/[Rf-OH] = 25, 3% of Mag-H$^+$ at 0°C and 12 h.

Scheme 2 Schematic representation of Mag-Na$^+$ and Mag-H$^+$.

montmorillonites catalysts and for the synthesis of new polymeric materials. The cationic ring-opening polymerization of EO in conjunction with a per-fluorinated alcohol as a modifier in the presence of an acid-exchanged montmorillonite clay (Mag-H$^+$) as a catalyst provides a convenient synthesis of tele-chelic polymers. Characterizations show that the polymers synthesized are terminated with a per-fluorinated group of the modifier at one end of the polymer chain and a hydroxyl group at the other end. The structure of poly(ethylene oxide) with per-fuorinated pendant groups was confirmed by ^{1}H-NMR, ^{13}C-NMR, ^{19}F-NMR, and MALDI-TOF-MS.

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