Cationic Polymerization of Ethylene Oxide with Maghnite-H as a Clay Catalyst in the Presence of Ethylene Glycol

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ABSTRACT: The activated-monomer cationic ring-opening polymerization of ethylene oxide, initiated with ethylene glycol and using an acid-exchanged montmorillonite clay called Maghnite-H$^+$ as an effective catalyst, was carried out to obtain the corresponding homopolymers with narrow polydispersity ratios. The molecular weights of the obtained polymers were controlled with the feed ratio of the monomer to the initiator. The effects of the amount of the catalyst and time on the polymerization yield and viscosity of the polymers were studied. The structure was confirmed with proton nuclear magnetic resonance and matrix-assisted laser desorption/ionization time-of-flight mass spectrometry. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 113: 535–540, 2009

Key words: clay; gel permeation chromatography (GPC); heteroatom-containing polymers; polyethers; synthesis

INTRODUCTION

Poly(ethylene glycol) (PEG) is a nontoxic, water-soluble polymer that resists recognition by the immune system. The term PEG is often used to refer to polymer chains with molecular weights below 20,000, whereas poly(ethylene oxide) (PEO) refers to higher molecular weight polymers.[1] It exhibits rapid clearance from the body and has been approved for a wide range of biomedical applications. Because of these properties, hydrogels prepared from PEG are excellent candidates as biomaterials. PEG may transfer its properties to another molecule when it is covalently bound to that molecule. This could result in toxic molecules becoming nontoxic or hydrophobic molecules becoming soluble when coupled to PEG.[1–10]

However, the cationic initiators used to make PEO are expensive and often give rise to impurities such as chromium, mercury, and 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.

Montmorillonites, a class of inexpensive and noncorrosive solid acids, have been used as efficient catalysts for organic reactions. Montmorillonite catalysts are easily recovered and reused.[11,12]

There is, to date, no information on the ring-opening polymerization of ethylene oxide (EO) with a clay catalyst. In a continuation of our studies on environmentally benign methods using solid supports,[13–16] we report for the first time the synthesis of PEOs via cationic ring-opening polymerization with an acid-exchanged montmorillonite called Maghnite-H$^+$ (Mag-H$^+$). PEOs were successfully synthesized by the polymerization of EO in conjunction with saturated alcohols as cocatalysts.

Ethylene glycol (EG) was chosen as the cocatalyst for the synthesis of hydroxyl-terminated PEO in the presence of Mag-H$^+$, which is an efficient solid catalyst for the ring-opening polymerization of epoxides (Scheme 1).
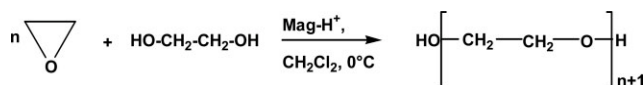
EXPERIMENTAL

Materials

Pure EG was obtained from a commercial source (Peck, France) and used without further purification. EO (Aldrich, France) was used as received. Dichloromethane and methanol were purified according to

Scheme 1 Ring-opening polymerization of epoxides with the Mag-H$^+$ system.

standard techniques and used after distillation over their respective drying agents.

The clay, which was used as a catalyst, was supplied by a local company known as ENOF Maghnia (Western Algeria). Its chemical composition is given in Table I. The greatest proton saturation of the <2-μm fractions of clay was obtained as follows. First, it was saturated with Na$^+$ ions with a 1M NaCl solution, and then the protonated forms of montmorillonite (Mag-H$^+$) were prepared through the shaking of the clay in a solution of sulfuric acid (0.25M) until saturation was achieved (normally after 2 days at room temperature). The cation-exchanged clay was then recovered by filtration and again suspended in deionized water. This process was repeated until no sulfate ions were indicated in the filtrate with BaCl$_2$. Mag-H$^+$ was isolated by filtration, dried at 105°C, and then finely ground.

Experimental procedure

Polymerization

Polymerizations were performed with dichloromethane at 0°C. The procedure was identical in both cases, involving the slow addition of EO to a stirred dichloromethane (50 mL) solution containing EG and the catalyst. Before use, Mag-H+ was dried at 120°C overnight and then transferred to a vacuum desiccator containing P$_2$O$_5$ to cool at room temperature overnight. A sample reaction occurred as follows. After the reaction vessel was charged with the mineral (0.05 g) and EG (0.005 mol), EO (0.3 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 *in vacuo* to yield the polymer. The latter was dried in a vacuum oven before submission for matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) and proton nuclear magnetic resonance (^{1}H-NMR) analysis (the yield of this example was 54%).

Characterization of the products

^{1}H-NMR measurements were carried out on a Bruker (France) 200-MHz NMR spectrometer equipped with a BB05 mm probe in CDCl$_3$. Tetramethylsilane was used as the internal standard. Average molecular weights and molecular weight distributions of the different polymers were measured with size exclusion chromatography on a system equipped with a Spectra System AS1000 autosampler with a guard column (Polymer Laboratories, France; PL gel 5-μm guard column, 50 × 7.5 mm) followed by 2 columns (Polymer Laboratories; 2 PL gel 5-μm mixed-D columns, 2 × 300 × 7.5 mm) and Spectra System RI-150 and Spectra System UV2000 detectors. The eluent was tetrahydrofuran at a flow rate of 1 mL/min at 35°C. Polystyrene standards (580–483.10^3 g/mol) were used to calibrate the size exclusion chromatography. Intrinsic viscosity ([η]) measurements were performed at 30°C in toluene with a Sematech Viscologic TL1 (France) capillary viscometer. The sample concentration was 1 mg/mL (the unit for [η] was mL/g). The MALDI-TOF mass spectra were recorded on a Bruker Biflex III equipped with a nitrogen laser (l = 337 nm). All mass spectra were recorded in the linear mode with an acceleration voltage of 19 kV. The irradiation targets were prepared from tetrahydrofuran or CH$_2$Cl$_2$ solutions with dithranol as the matrix and NaI as the dopant.

RESULTS AND DISCUSSION

The cationic polymerization of epoxides, in the presence of hydroxyl-containing compounds, proceeds via two competitive mechanisms:[17–20]

1. The active chain end mechanism (ACEM), in which three-membered cyclic tertiary oxonium ions constitute the growing species, as detailed in Scheme 2(a). Propagation is accompanied in this case by end-biting and back-biting reactions, giving rise to cyclics[13] (dimer, trimer, or tetramer, depending on the epoxide used).
2. The activated-monomer mechanism (AMM), in which propagation involves the addition of an activated (e.g., protonated) monomer to the hydroxyl end group of the initiator or the growing macromolecule, as shown in Scheme 2(b).

TABLE I
Chemical Composition of the Catalyst

Species [% (w/w)]									
SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	MgO	CaO	Na$_2$O	K$_2$O	TiO$_2$	As	LOI (wt %)[a]
69.4	14.7	1.2	1.1	0.3	0.5	0.8	0.2	0.05	11

[a] Loss on ignition at 900°C.
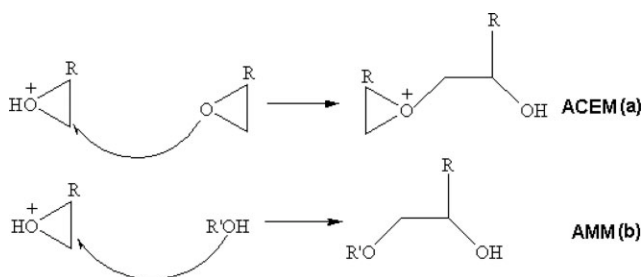
Scheme 2 Ring-opening polymerization by the ACE and AM mechanisms (R′OH = initiator or growing macromolecules).

To limit the formation of cyclic oligomers in these reactions and therefore reduce the possibility of the reaction following the pathway shown in Scheme 2(a), it is necessary to add the monomer slowly to the reaction medium so as to increase the probability that the monomer will be protonated and then go on to react with these nucleophiles. If, as here, the chain end of the epoxide polymer is an alcohol, the addition of the protonated monomer effectively leads to the re-formation of the alcohol chain end. If this is the dominant process, the formation of cyclic oligomers may be suppressed.

In this work, we have chosen the polymerization of EO with the AMM mechanism because in the case of the polymerization of EO by the ACEM mechanism, propagation is accompanied by end-biting and back-biting reactions, giving rise to an 80% concentration of the cyclic dimer (1,4-dioxane),[21] but with the AMM mechanism, the polymerization produces linear polymers free from cyclic oligomers.

Mag-H$^+$ is an efficient catalyst for the polymerization of epoxides. The bulk ring-opening polymerization of EO proceeds by an exothermic and spontaneous reaction at 0°C with 0.5% Mag-H$^+$.

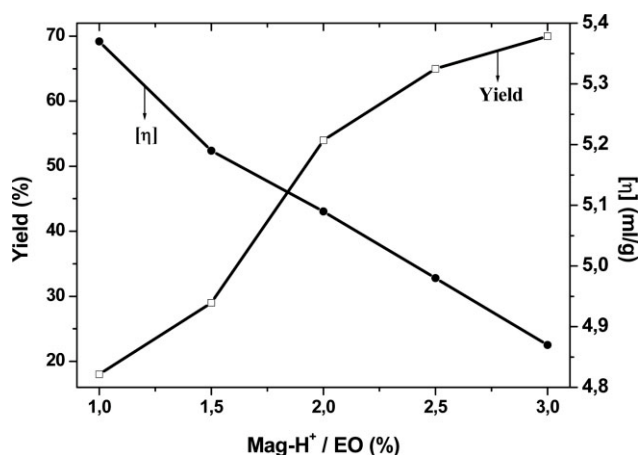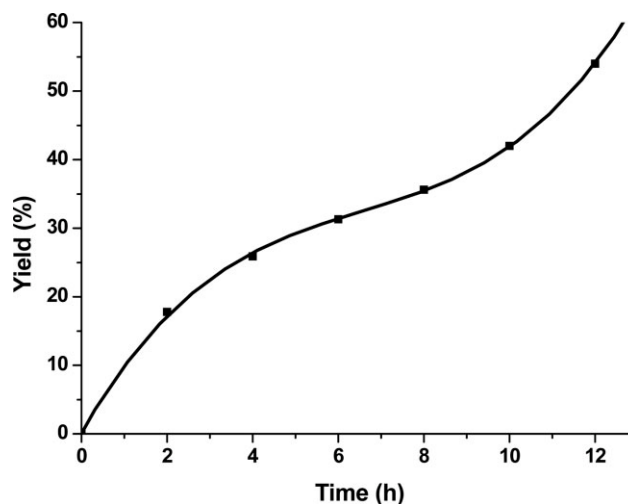**Figure 2** Effect of the polymerization duration on the yield of PEO (with an [EO]/[EG] ratio of 60 and 2% Mag-H$^+$ in CH$_2$Cl$_2$ at 0°C).

Such bulk reactions are difficult to control and yield irreproducible molecular weight results because of the uncontrollable rise in temperature observed during these polymerizations; for this reason, we have studied the polymerization of EO in the presence of dichloromethane as a solvent.

The amount of the catalyst (Mag-H$^+$/EO) is an important factor of polymerization. Figure 1 shows the effect of the amount of the catalyst on polymerization. The higher the amount is of the catalyst, the higher the yield is. This phenomenon is probably the result of a number of initiating active sites responsible of inducing polymerization, and this number is proportional to the amount of the catalyst used in the reaction. Similar results were obtained by Yahiaoui and Belbachir[13] and Njopwouo et al.[22] in the polymerization of styrene oxide by Mag-H$^+$
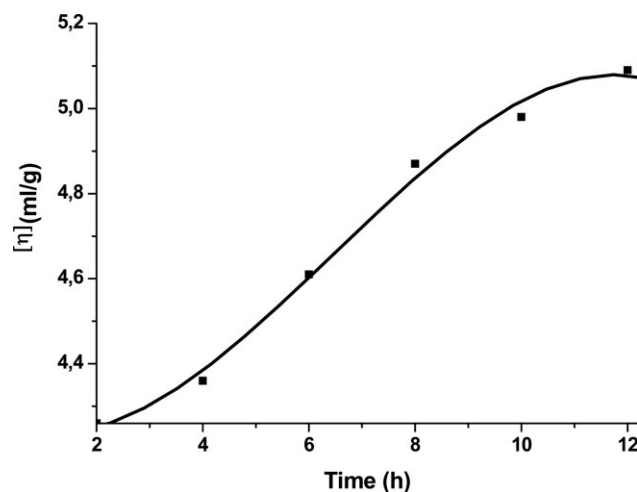

Figure 1 Effect of the amount of the catalyst on the yield and [η] of the formed polymer (with 6M EO in CH$_2$Cl$_2$ at 0°C for 12 h).

Figure 3 Effect of the polymerization duration on [η] of PEO (with an [EO]/[EG] ratio of 60 and 2% Mag-H$^+$ in CH$_2$Cl$_2$ at 0°C).
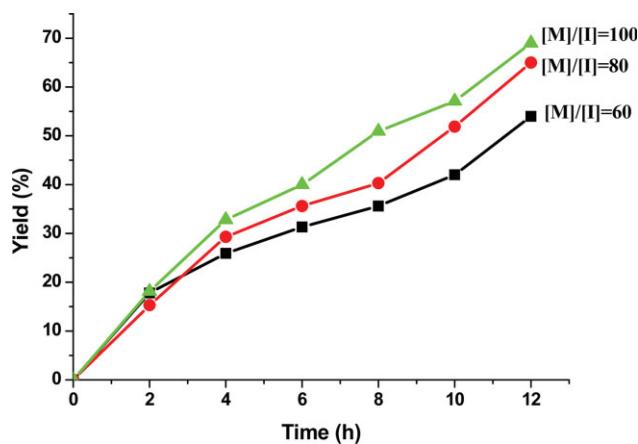
Figure 4 Effect of [EO]/[EG] on the yield of PEO (at 0°C with 2% Mag-H$^+$). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE II
Synthesis Conditions of PEO at 0°C for 12 h with 0.005 mol of EG, 2% Mag-H$^+$, and 50 mL of CH$_2$Cl$_2$

Experiment	[EO]/ [EG]	Amount of EO (mol)	Yield (%)	M_n (GPC)	M_w/ M_n
EO1	60	0.3	54	1200	1.20
EO2	80	0.4	65	2000	1.15
EO3	100	0.5	69	2900	1.19

M_n = number-average molecular weight; M_w = weight-average molecular weight.

and the polymerization of styrene by montmorillonite, respectively.

As shown in Figure 1, the viscosity decreases, depending on the amount of Mag-H$^+$ (i.e., [η] decreases when the amount of Mag-H$^+$ increases), in the following order: 3% < 2.5% < 2% < 1.5% < 1%. The concentration of the initiator or growing macromolecules should be constant, and only the active monomer increases with the increase in the amount of the catalyst; as a result, we have a competition between the two mechanisms (ACEM and AMM). AMM produces linear polymers, and ACEM produces cyclic dimers, which decrease the molecular weight. This finding is in good agreement with the proposal that Mag-H$^+$ is present as the active initiator species because the number of those species should be related to their surface area. Similar results were obtained by Kadakowa et al.[23] and

Crivello and Fan[24] in the polymerization of lactones by tin montmorillonite and cyclohexene oxide by cobalt, respectively.

Figure 2 shows the yield of the polymer versus time for the dichloromethane solution polymerization of EO with Mag-H$^+$ as the catalyst, with the [EO]/[EG] ratio kept constant, and with the reaction time varied. As the figure shows, polymerization takes place slowly and smoothly, reaching a yield of 54% after 12 h at 0°C.

The effect of the polymerization duration on [η], as shown in Figure 3, shows the same trend as that of the yield; that is, the viscosity of PEO increases with the polymerization time increasing from 2 to 12 h.

The results obtained with Mag-H$^+$ as the catalyst are in a good agreement with those of Biedron et al.[20] for the preparation of telechelic oligomers of epichlorohydrin with a diol as the initiator and HBF$_4$ as the catalyst. They also agree with those of Xu et al.[25] for 1,2-epoxy-3-nitropropane with 1,3-butanediol as the initiator. The authors indicated the formation of oligomers with a number-average molecular weight of 1100 g/mol; however, the end groups of these systems were not presented. The advantage of our method is that acidic clay is inexpensive, stable, and noncorrosive; moreover, the work-up procedures are
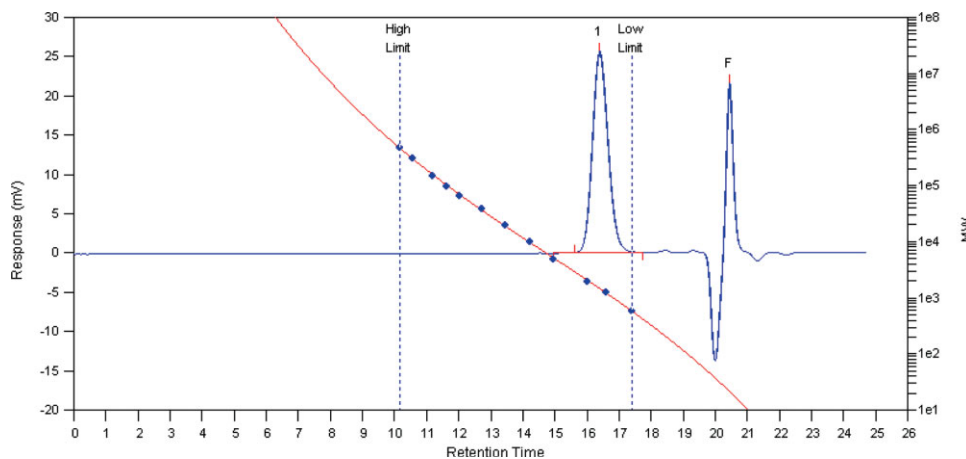

Figure 5 GPC chromatogram of PEO (with 2% Mag-H$^+$ and an [EO]/[EG] ratio of 80 at 0°C for 12 h; number-average molecular weight = 2000 g/mol, weight-average molecular weight = 2300 g/mol, and weight-average molecular weight/number-average molecular weight = 1.15). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
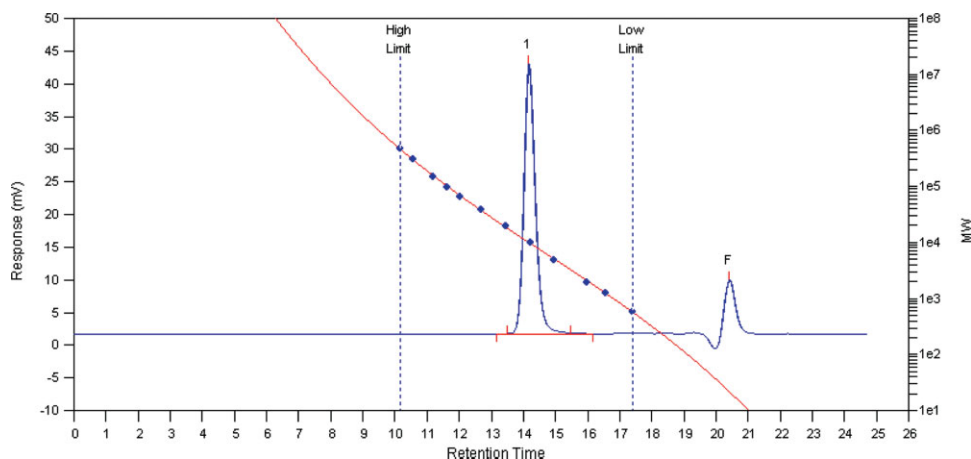
Figure 6 GPC chromatogram of PEO (with 2% Mag-H$^+$ and an [EO]/[EG] ratio of 100 at 0°C for 12 h; number-average molecular weight = 2900 g/mol, weight-average molecular weight = 3450 g/mol, and weight-average molecular weight/number-average molecular weight = 1.19). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

very simple: just by filtration, the clay can be separated from the reaction mixtures. Thus, we became interested in exploring the use of clays in the synthesis of polymers compounds.

In the presence of Mag-H$^+$ and with different [EO]/[EG] molar ratios, the polymerization was carried out for 12 h at 0°C. Figure 4 and Table II show the effect of the [EO]/[EG] molar ratio on the rate of polymerization and on the molecular weight, respectively. When the [EO]/[EG] molar ratio was increased, the rate of polymerization increased, and the resulting polymers exhibited increases in the molecular weight. The results of the analysis of the polymer by gel permeation chromatography (GPC) are shown in Figures 5 and 6. The macromolecular

weight distributions of the obtained polymers are narrow. These results suggest that no termination or chain-transfer reaction occurs; that is, this polymerization proceeds via an active monomer mechanism.

Characterization of the polymer

The structure of the EO polymer was determined with ^{1}H-NMR and MALDI-TOF MS. Figure 7 shows the ^{1}H-NMR spectrum of the isolated product (CDCl$_3$). The signal at 3.2 ppm (a) is due to the end groups' hydroxyls protons, and the signal at 3.7 ppm (b) is attributable to methylene protons of the main chain (4H).

To further investigate the polymer, MALDI-TOF MS (Fig. 8) was performed on the PEO synthesized with Mag-H$^+$. To improve the ionization/desorption process, the polymer was mixed with both dithranol
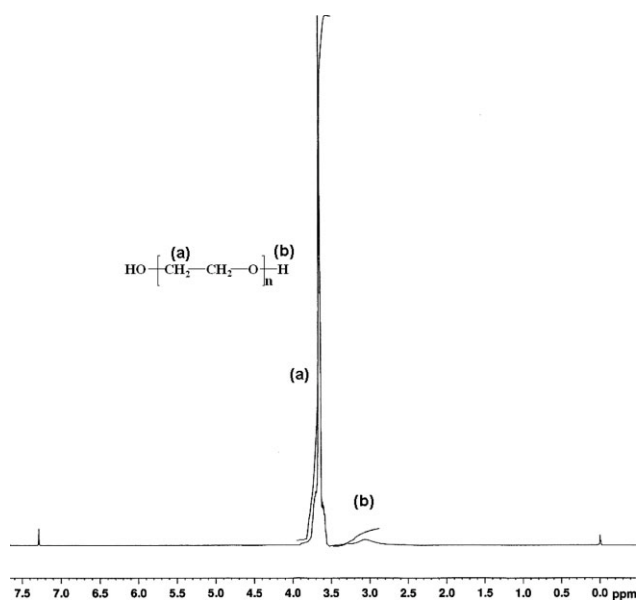

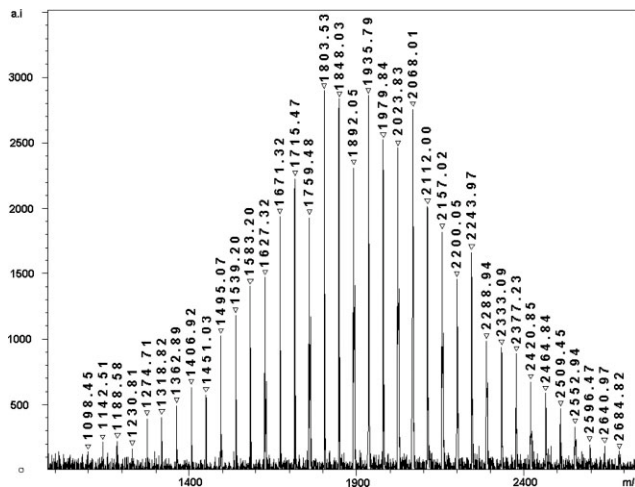**Figure 7** ^{1}H-NMR (200-MHz) spectrum of PEO in CDCl$_3$.

Figure 8 MALDI-TOF MS spectrum of PEO (with an [EO]/[EG] ratio of 100 and 2% Mag-H$^+$ at 0°C for 12 h).

and NaI before spotting. The difference between the peaks was found to be 44 mass units, which corresponds to the mass of the EO monomer unit. End-group analysis confirmed that the polymer was initiated with EG and terminated with hydroxyl. Also, each MALDI-TOF MS peak corresponded to the PEO having a dihydroxylated terminal structure with one Na^+ ion [HO—$(EO)_n$—OH, Na^+]. No peak due to the macrocyclic structure was observed; this once again shows that PEO is linear and demonstrates the living character of the polymerization performed with the Mag-H^+ catalytic system in the presence of EG.

CONCLUSIONS

It has been proved that Mag-H^+ can be used to induce the polymerization of EO, and this offers new possibilities for the selective study of montmorillonites as catalysts and for the synthesis of new polymeric materials. The cationic ring-opening polymerization of EO in conjunction with an aliphatic alcohol as a cocatalyst in the presence of an acid-exchanged montmorillonite clay (Mag-H^+) as a catalyst provides a convenient method of synthesizing telechelic polymers. Characterizations show that the synthesized polymers correspond to PEO with a dihydroxylated terminal structure. The structures of the polymers are consistent with the nonconventional mechanism (AMM). The macromolecular weight distribution of the obtained polymers is narrow, and this confirms the living character of the polymerization. The structure of PEO has been confirmed with ^{1}H-NMR and MALDI-TOF MS.

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