Synthesis and Characterization of Water Soluble Poly(*N*-acetyl)iminoethylene and Poly(ethyleneimine) by Ion-Exchanged Clay Montmorillonite

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ABSTRACT: The cationic polymerization of 2-méthyl-2-oxazoline was carried out at 0°C in acetonitrile using an acid-exchanged montmorillonite as acid solid ecocatalyst (Maghnite-H$^+$). The effect of the amount of catalyst, solvent, and times of polymerization on yield and viscosity of polymer was studied. A typical reaction product (PMOX) was analyzed by infrared and nuclear magnetic resonance spectroscopy as well as by gel-permeation chromatography and MALDI-TOF MS. The polymers presented similar spectrometric results and narrow molecular weight distribution. The poly(*N*-acetyl)iminoethylene was hydrolyzed in acid medium obtaining a linear poly(ethyleneimine). © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 3741–3750, 2006

Key words: montmorillonite; ecocatalyst; 2-méthyl-2-oxazoline; poly(ethyleneimine); ring-opening polymerization; living polymerization

INTRODUCTION

It is well known that poly(ethyleneimine) produced by ring-opening cationic polymerization of ethyleneimine has highly branched structure[1–3] and normally it is accompanied by side reactions such as a reaction between the growing species and the amino group of the produced polymer chain. In some cases cyclic oligomers are also produced. Therefore, the cationic polymerization of 2-alkyl-2-oxazolines has been studied for many years.[4–7] The 2-methyl- and 2-ethyl-substituted oxazolines are particularly interesting because of their solubility in water and their low toxicity demonstrated by pharmacological tests.[8] Their polymers can be incorporated in grafted or block copolymers imparting amphiphilic properties.[9,10] The polymerization of 2-MeOXZ in acetonitrile in the presence of cationic initiators, such as alkyl halogenides, has been studied in detail by Kagiya et al.[7,11] and by Saegusa et al.[12,13] Subsequently, the linear poly(ethyleneimine), which is a very useful polymer support,[14–16] is obtained by basic or acid hydrolysis of poly(*N*-acyl) iminoethylene.

Various initiating systems able to promote the polymerization of cyclic iminoethers have been reported: Lewis acids, stable cationic salts, strong protonic acids and their salts, esters of sulfuric, sulfonic and picric acids and acid anhydrides, as well as alkyl halides.[4] However, the search for new initiators remains a subject of topical interest. There is, to date, no information on the ring-opening polymerization of substituted oxazolines with clay catalyst. In this article, and in continuation of our program to develop environmentally benign methods using solid supports,[17–24] we report that acid-exchanged montmorillonite [Maghnite-H$^+$ (Mag-H$^+$)] is a novel, efficient solid catalyst for the ring-opening polymerization of 2-méthyl-2-oxazoline (MOX) to produce PMOX (Scheme 1). In contrast to the more usually used catalysts, Mag-H$^+$ can be easily separated from the polymer and regenerated by heating to a temperature above 100°C. The effects of the relative amounts of Mag-H$^+$, temperature, and solvent were discussed.

EXPERIMENTAL

Materials

2-Méthyl-2-oxazoline [MOX, (Aldrich, France)] was purified by distillation and stored over molecular sieves. Toluene, dichloromethane, acetonitrile, and diethyl ether were purified following standard techniques and used after distillation over their respective drying agents.

The clay, which has been used as catalyst, is supplied by a local company known as ENOF Maghnia
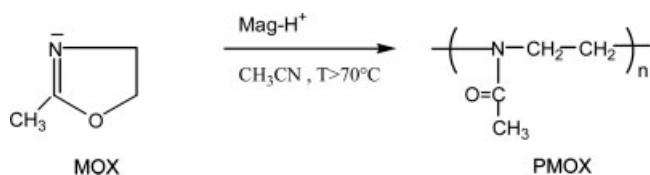
Scheme 1 Cationic polymerization of 2-méthyl-2-oxazo-line (MOX) by Mag-H$^+$ catalyst.

(Western of Algeria). Its chemical composition is given in Table I. The greatest proton saturation of the < 2 mm fractions of clay were obtained by first saturating with Na$^+$ ions using 1M NaCl solution, then the protonated forms of montmorillonite (Mag-H$^+$) were prepared by shaking the clay in a solution of 0.25M sulfuric acid 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 present in the filtrate using BaCl$_2$. The Mag-H$^+$ was then isolated by filtration, dried at 105°C, and then finely ground.

Experimental procedure

Polymerization

Polymerizations were performed in acetonitrile at 70°C. The procedure was identical in both cases, involving addition of catalyst to the stirred solution containing MOX in acetonitrile. Prior to use, Mag-H$^+$
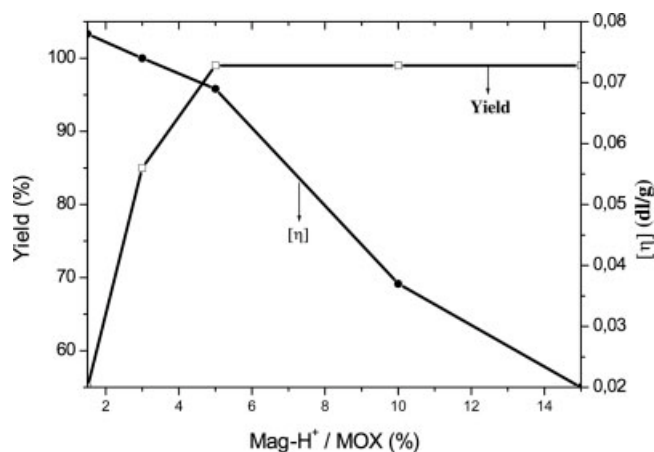
TABLE I
Chemical Composition of the Catalyst

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

L.O.I., loss on ignition (wt %) at 900°C.

TABLE II
The Effect of Solvent Sort on the Polymerization of MOX (2M) by Mag-H$^+$ (5%) Catalytic System at 70°C

| Solvent	Yield (%)	[η] (dL/g)
Toluene	28	0.015
Dichloromethane	69	0.042
Acetonitrile	99	0.057

Figure 1 Effect of the amount of catalyst on the yield and the intrinsic viscosity of formed polymer.
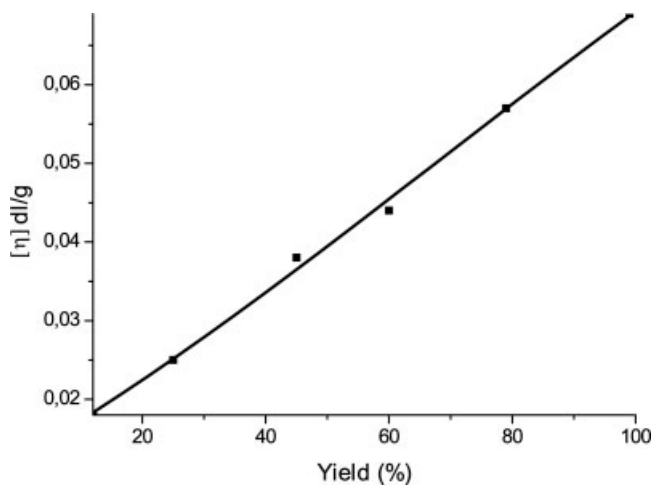
was dried at 120°C overnight and then transferred to a vacuum desiccator containing P$_2$O$_5$ to cool to room temperature overnight. An example reaction is detailed here. After charging the reaction vessel with MOX solution in acetonitrile (2M), the catalyst (5% w/w to monomer) was added at a polymerization temperature, e.g. 70°C. At the end of the reaction, water was added to stop the polymerization. The resulting mixture was filtered to remove the clay and then poured into ether to precipitate the polymeric product. The latter was dried in a vacuum oven prior to submission for GPC, MALDI-TOF MS, ^{1}H NMR, and ^{13}C NMR analysis (yield of this example was 99%).

Hydrolysis of poly(N-acetyl)ethyleneimine

An aqueous solution of PMOX (1 g) was refluxed with 5N H$_2$SO$_4$ in 48 h under a continuous stream of nitrogen. PEI · H$_2$SO$_4$ was dissolved in water, reprecipitated in a large amount of ether.
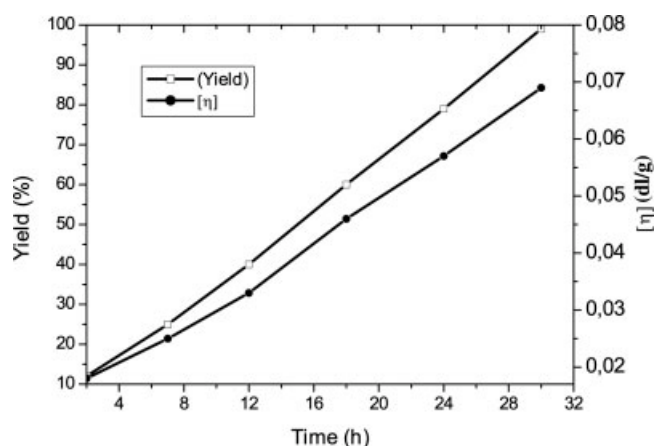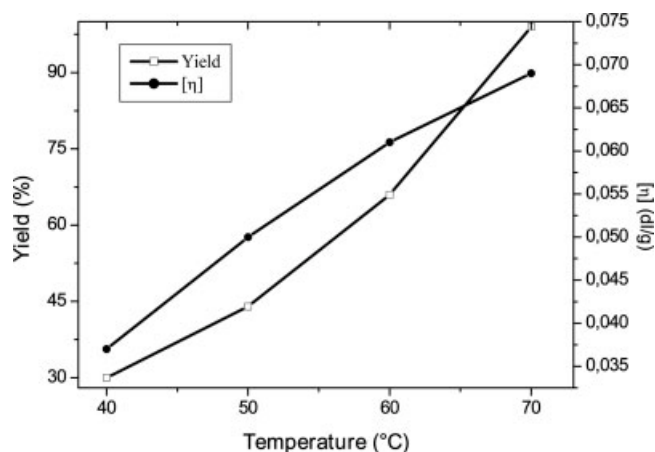

Figure 2 Effect of polymerization duration on yield and [η] of PMOX ([MOX] = 2M in CH$_3$CN at 70°C and 5% of Mag-H$^+$.

Figure 3 Effect of yield on [η] of PMOX ([MOX] = 2M in CH$_3$CN at 70°C and 5% of Mag-H$^+$).

Figure 5 Temperature effect on the poly MOX yield and [η] "5% of Mag-H$^+$ for 30 h."

Characterization of the products

^{1}H NMR and ^{13}C NMR measurements were carried out on a 200 MHz Bruker NMR spectrometer equipped with a probe BB05 mm, in CDCl$_3$. Tetramethylsilane (TMS) was used as the internal standard in these cases. IR spectra of the monomer and the polymers as thin films or KBr pellets were recorded with a ATI Matson FTIR No. 9501165 spectrometer. Intrinsic viscosity [η] measurements were performed at 30°C in toluene using a capillary viscometer SEMATECH (VISCOLOGIC TL1). The sample concentration was 1 mg/mL. 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

Cyclic iminoethers are highly nucleophilic monomers, second only to cyclic amines. It is also established that the polymerization occurs by ionic or covalent species. Therefore, the nature of propagation is influenced by several factors e.g., the substituent of monomers,
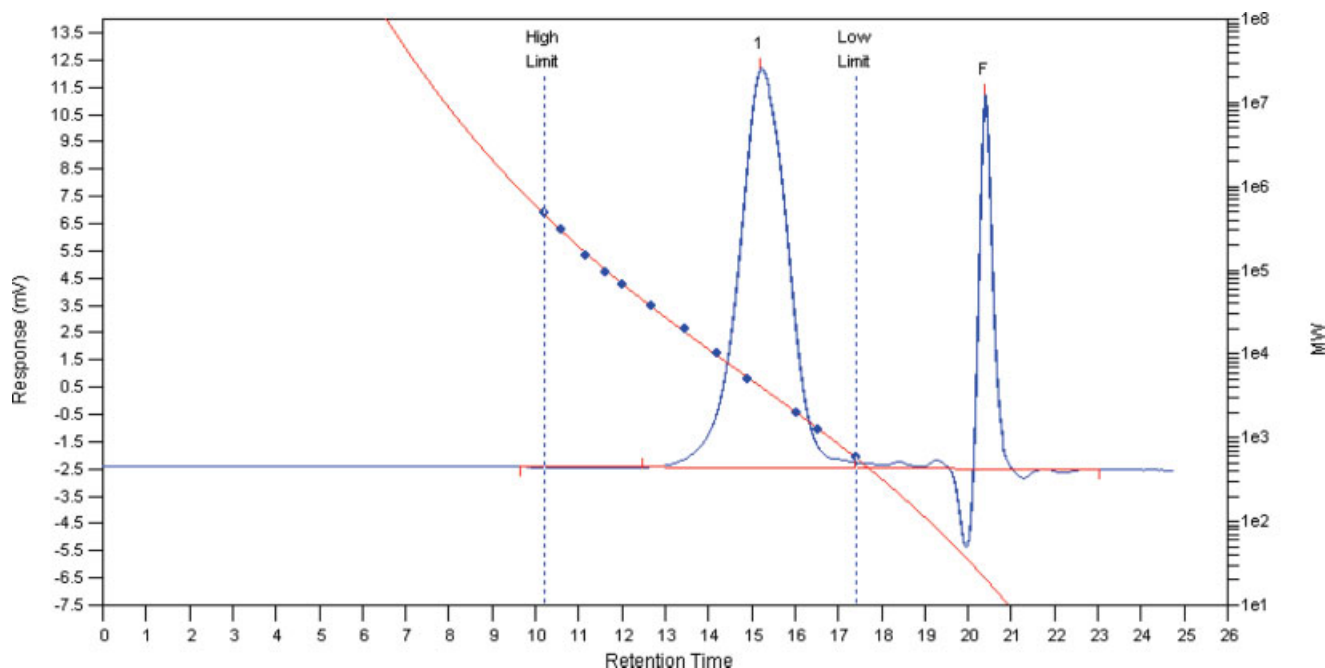
Figure 4 GPC chromatogram of PMOX obtained by Mag-H$^+$ catalytic system at: 5% of Mag-H$^+$, 70°C, 24 h (M_w = 3100 g/mol M_n = 2400 g/mol I = 1.29). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
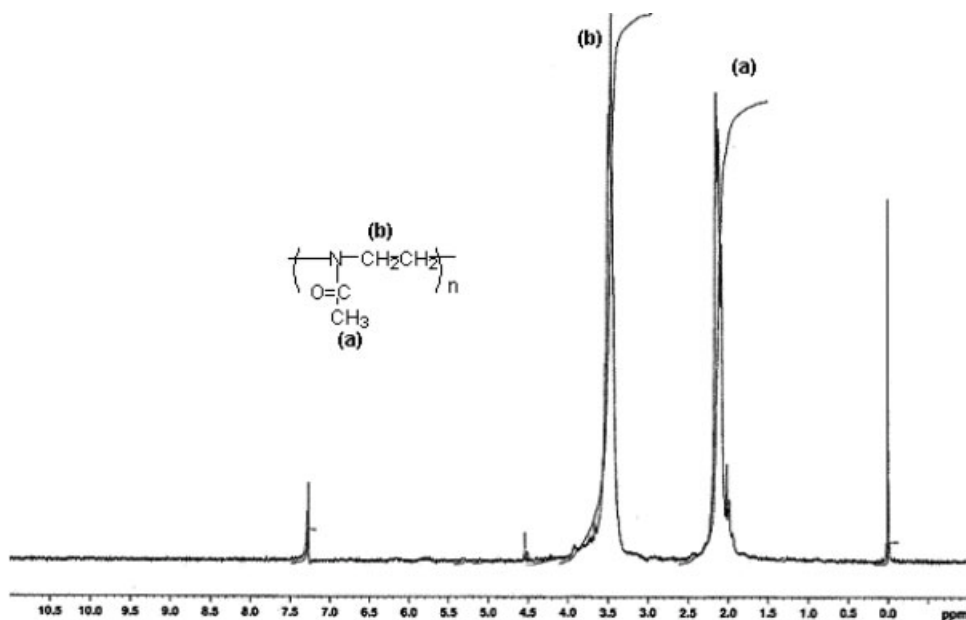
Figure 6 ^{1}H NMR (200 MHz) spectrum of poly MOX in CDCl$_3$.

nucleophilicity of monomer, and the counter-ion, polarity of solvent.

The influence of solvent on the polymerization was presented on Table II. The data showed that the polymerization reaction proceeded better in acetonitrile and dichlorométhane. The rate of polymerization in acetonitrile was found to be much higher than that of dichloromethane and toluene. There is an effect of the dielectric constant of solvent (acetonitrile, dichloro-

methane, and toluene) on the yield and polymer viscosity. The most polar solvent produces a polymer with the highest yield and viscosity.

Amount of catalyst (Mag-H$^+$/MOX) was an important factor of polymerization. Figure 1 showed 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 poly-
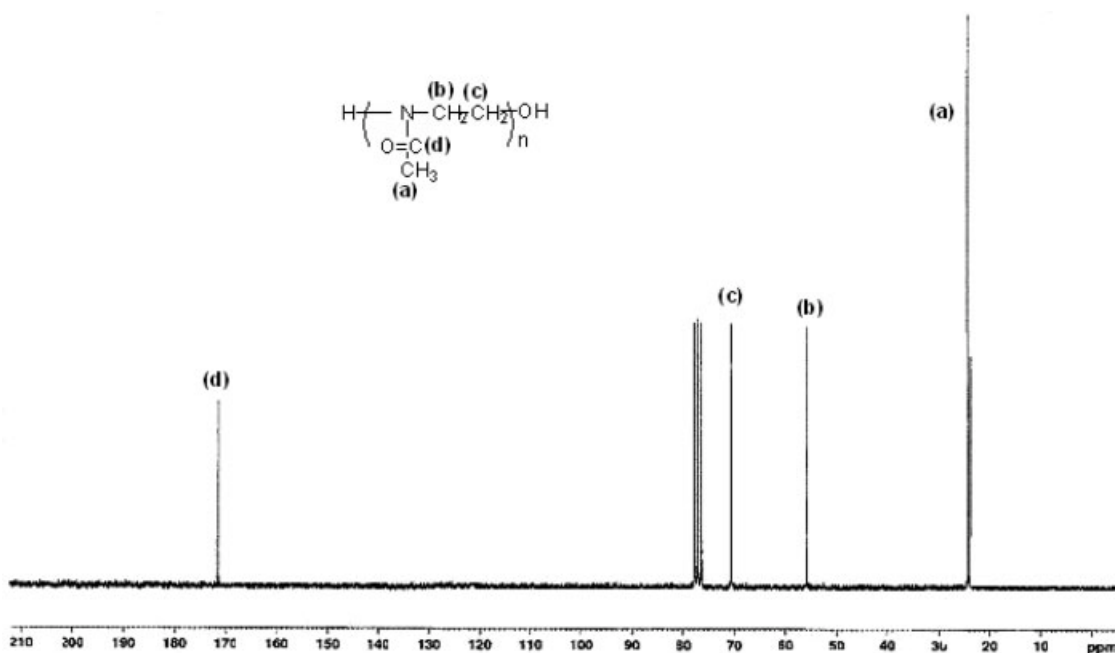

**Figure 7** ^{13}C NMR (200 MHz) spectrum of poly MOX in CDCl$_3$.

merization, this number is prorating to the catalyst amount used in reaction. Similar results are obtained by Yahiaoui et al.[17–20] and Njopwouo et al.[25] in the polymerization of epichlorhydrin, propylene oxide, and cyclohexene oxide by Mag-H^{+} and the polymerization of styrene by montmorillonite, respectively.

As depicted in Figure 1, the viscosity was found to decrease, depending on the amount of Mag-H^{+} (i.e., [η] ↘ when amount of Mag-H^{+} ↗) in the following order: 15 < 10 < 5 < 3 < 1.5%. This finding is in good agreement with the proposal that Mag-H^{+} is present as the active initiator species, since the number of those species should be related to their surface area. Similar results are obtained by Kadakowa et al.[26] and Crivello and Fan,[27] in the polymerization of lactones by Sn-montmorillonite and cyclohexene oxide by Cobalt, respectively.

Figure 2 shows the yield of polymer versus time for the acetonitrile solution polymerization of MOX using Mag-H^{+} as catalyst. As the figure shows, polymerization takes place slowly and smoothly, reaching a yield of 99% after 30 h at 70°C. The polymerization yield became constant at a time; this is probably the result of an increase in the medium viscosity.

The effect of polymerization duration on the intrinsic viscosity, as shown in Figure 2, has the same trend as that of yield, i.e., both the viscosity of PMOX increased with the increasing polymerization time from 2 to 30 h. It is clear from Figure 3 showing the linear variation of the intrinsic viscosity with
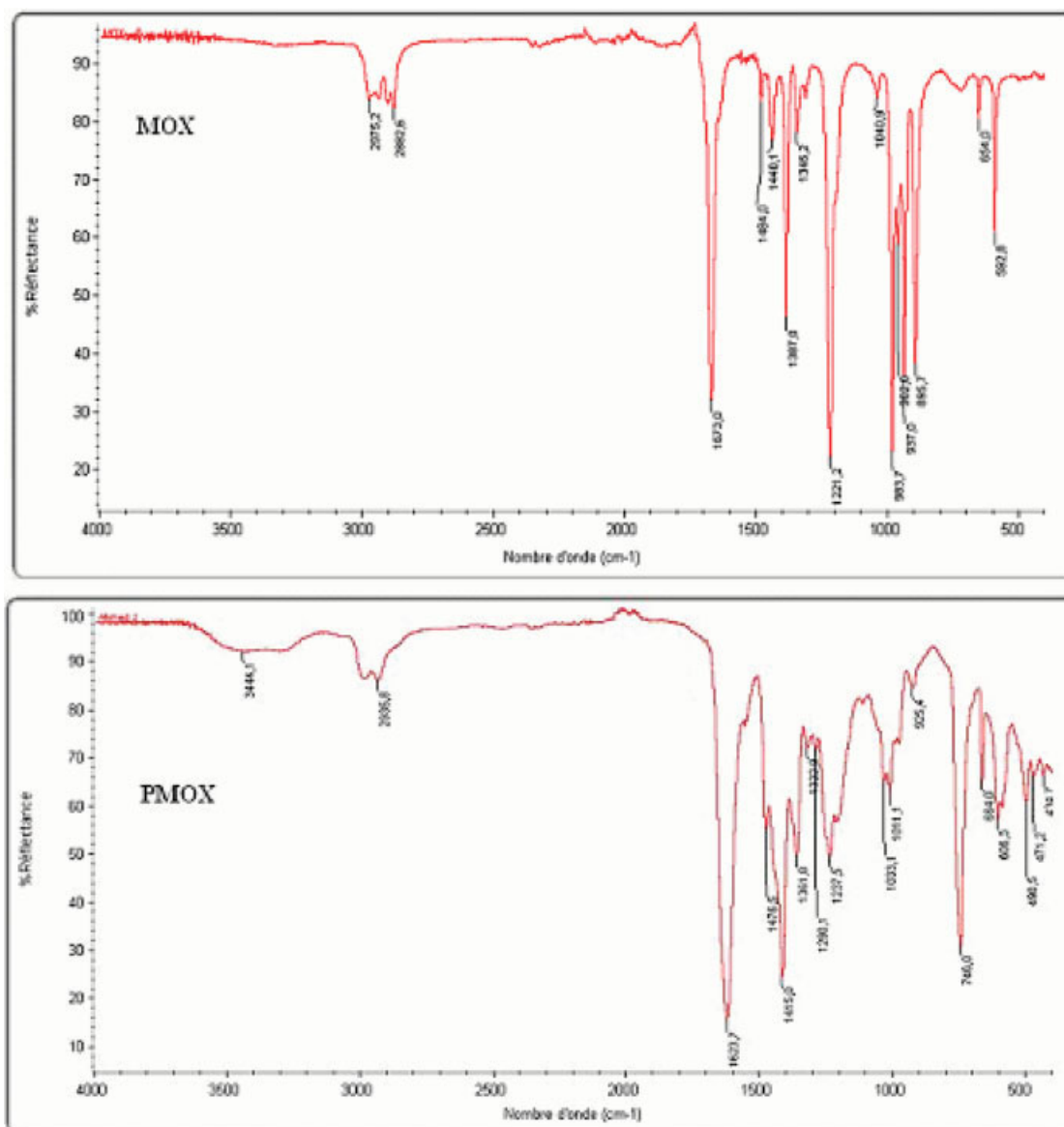

Figure 8 IR spectra of MOX and poly MOX recorded from thin films and KBr pellets, respectively. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

the yield of polymer (at constant initial MOX concentration) that the polymerization was living. The results of the analysis of the polymer by gel permeation chromatography (GPC) are shown in Figure 4. As shown, the macromolecular weight distribution of the obtained polymer is narrow, which confirms the living character of the polymerization.

Temperature effect

The temperature is an important factor in the initiation process and its influence is studied. Using MOX solution in acetonitrile (2M) and 5% [Mag-H$^+$/MOX] (w/w), the polymerization was carried out at 40, 50, 60, and 70°C. In the absence of Mag-H$^+$ no polymerization could be detected. In the presence of Mag-H$^+$, however, the polymerization was initiated. Figure 5 shows that polymerization temperature has much influence on the yield of PMOX. The yield increased with the temperature rising from 40 to 70°C and reached a high yield of 99% at 70°C.

The effect of temperature on the degree of polymerization is more complex. In most polymerization reactions, an increase in temperature causes a decrease in the molecular polymer weight. In the case of the poly (epichlorohydrin),[17] we have found that the intrinsic polymer viscosity decrease, depending on the polymerization temperature, in the following order: 20 > 30 > 50 > 70°C. Namely, the result indicates that the decrease in the intrinsic viscosity is enhanced by increasing the polymerization temperature. This is because increasing the temperature causes an increase in the rate of chain transfer reaction of the growing polymer cation (inter and intramolecular).[28,29] The notable exception was for MOX. As depicted in Figure 5, an increase in polymerization temperature increases the intrinsic viscosity. In the products of reaction of this oxazoline compound with Mag-H$^+$, no macrocyclics groups were observed in the GPC curves of the final products (Fig. 4). The unique behavior of MOX may be explained by the living character of the polymerization.
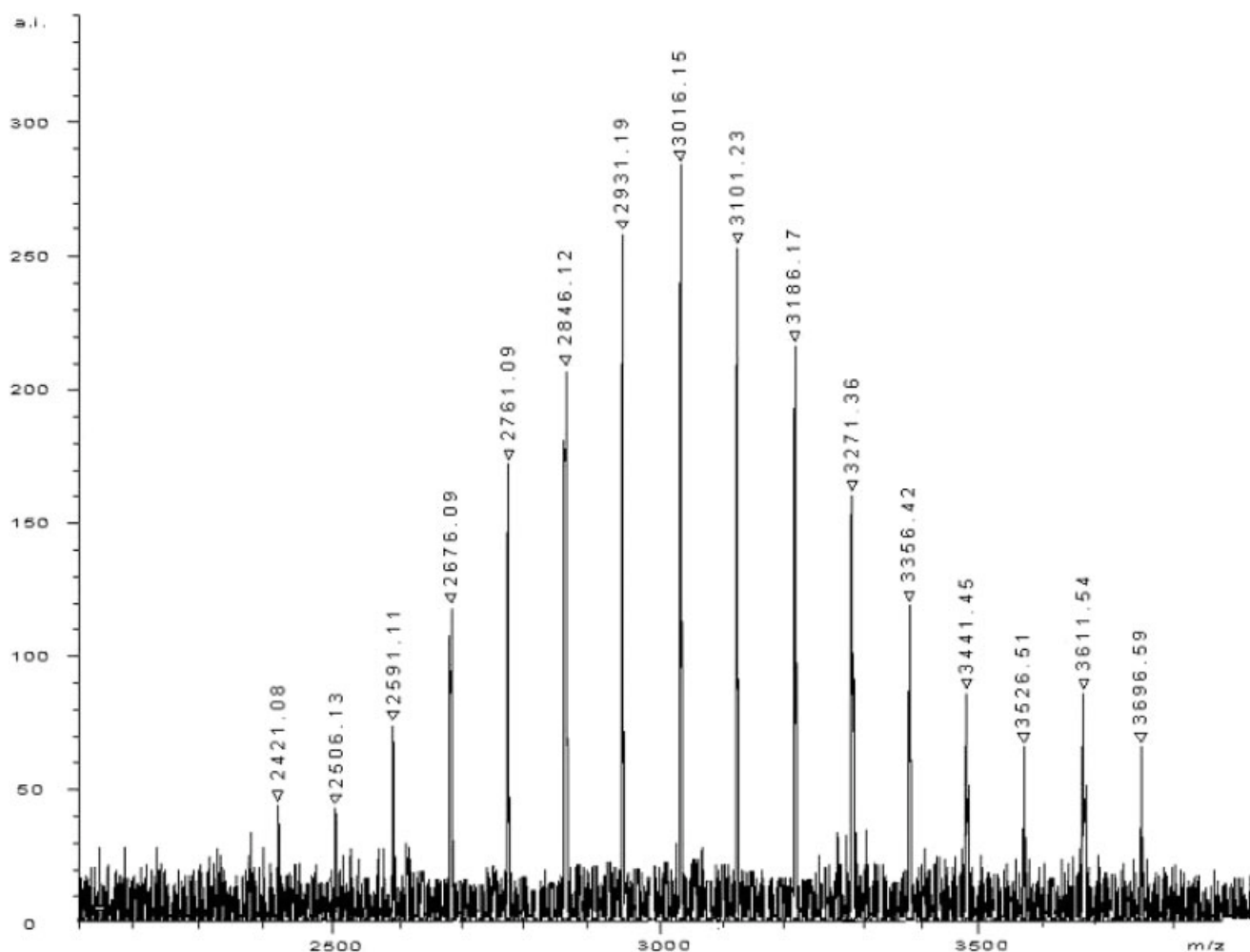
Figure 9 MALDI-TOF MS spectrum of poly MOX obtained by the solution polymerization of MOX (2M) using 5% of Mag-H$^+$ at 70°C and for 30 h.

Characterization of polymer

The structure of the MOX polymer was determined by ^{1}H NMR, ^{13}C NMR, IR spectra, and MALDI-TOF MS. Figure 6 shows the ^{1}H NMR spectrum of the isolated product (CDCl$_3$). Signal at 2.05 ppm (a) is due to methyl protons of the acetamido group (3H) and the signal at 3.4–3.8 ppm (b) is attributed to methylene protons of the main chain (4H).

The ^{13}C NMR spectrum (Fig. 7) presents four signals. The signals at 55.95 and 70.64 ppm are due to carbons of CH_2—N and CH_2—O, respectively. Signals at 171.53–23.83 ppm are assigned to carbonyl and methyl carbons of acetamido group, respectively. The IR spectrum (Fig. 8) of the product showed the disappearance of the absorption at 1673 cm^{-1} due to C=N of monomer, the appearance of the new absorption at 1623 cm^{-1} due to C=O of the acetamido and a large band at 3444 cm^{-1}, characteristic of OH and NH groups.

To further investigate the polymer, MALDI-TOF MS (Fig. 9) was performed on the poly MOX synthesized by Mag-H$^+$. To improve the ionization/desorption process, the polymer was mixed with both dithranol and NaI before spotting. The difference between the peaks was found to be 85 mass units, which corresponds to the mass of a 2-methyl-2-oxazoline mono-

mer unit. End-group analysis confirmed that the polymer was initiated with Mag-H$^+$ and terminated with hydroxyl. Successful termination of the living polymer chains with hydroxyl group also demonstrated the living character of the polymerization performed Mag-H$^+$ catalytic system.

The subsequent acid hydrolysis of poly(N-acetyl) iminoethylene (PMOX) produced a linear poly(ethyleneimine) almost quantitatively.

The ^{1}H NMR spectrum (Fig. 10) of the hydrolyzed product showed the disappearance of the signal at 2.05 ppm, due to methyl protons of the acetamido group and the appearance of the new signal at 2.7 ppm due to amine proton of the main chain (HN—CH$_2$—CH$_2$—) groups.

Figure 11 shows the MALDI-TOF MS spectra (in linear mode) of poly(ethyleneimine) (PEI) obtained by the acid hydrolysis of poly(N-acetyl)iminoethylene. In the case, it was confirmed that the repeating units have a mass of m/z 43, which corresponds to the molecular weight of ethyleneimine monomer. Also, each peak of the MALDI-TOF MS correspond to the PEI having hydroxyled terminal structure with one Na$^+$ ion (H—(HN—CH$_2$—CH$_2$)$_n$—OH, Na$^+$), which once again, shows that PEI is linear.
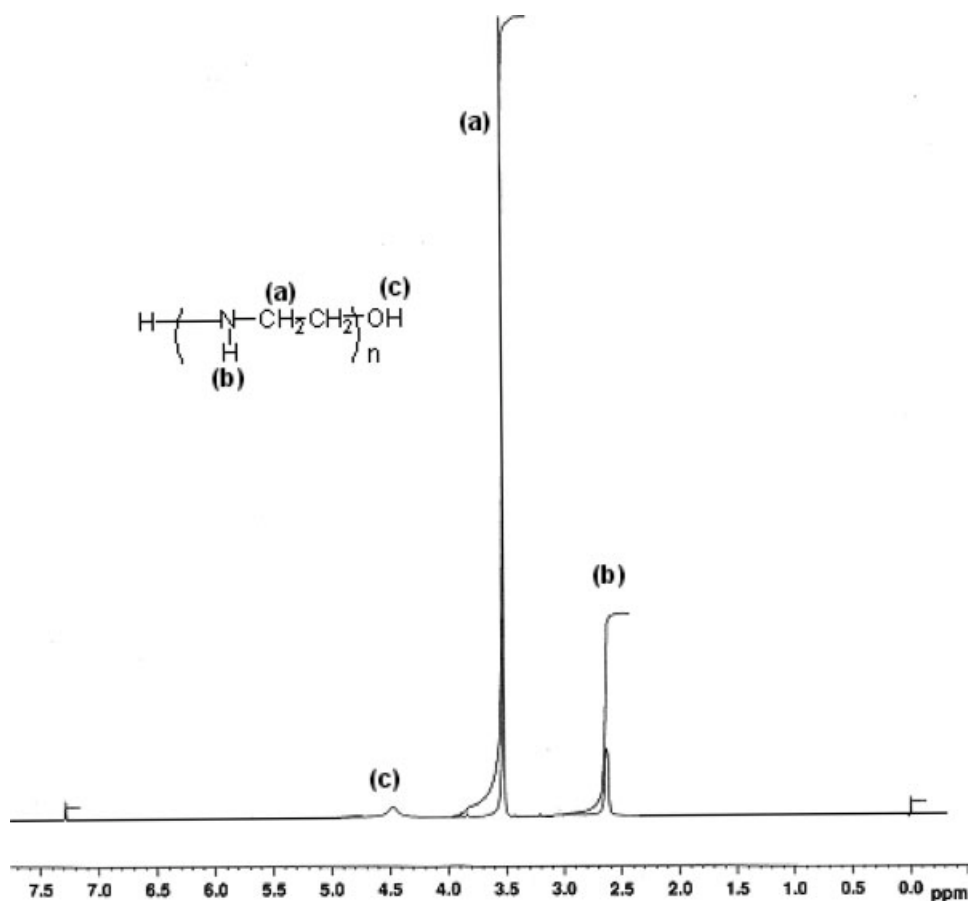

Figure 10 ^{1}H NMR (200 MHz) CDCl$_3$ of PEI obtained by the hydrolysis of PMOX.
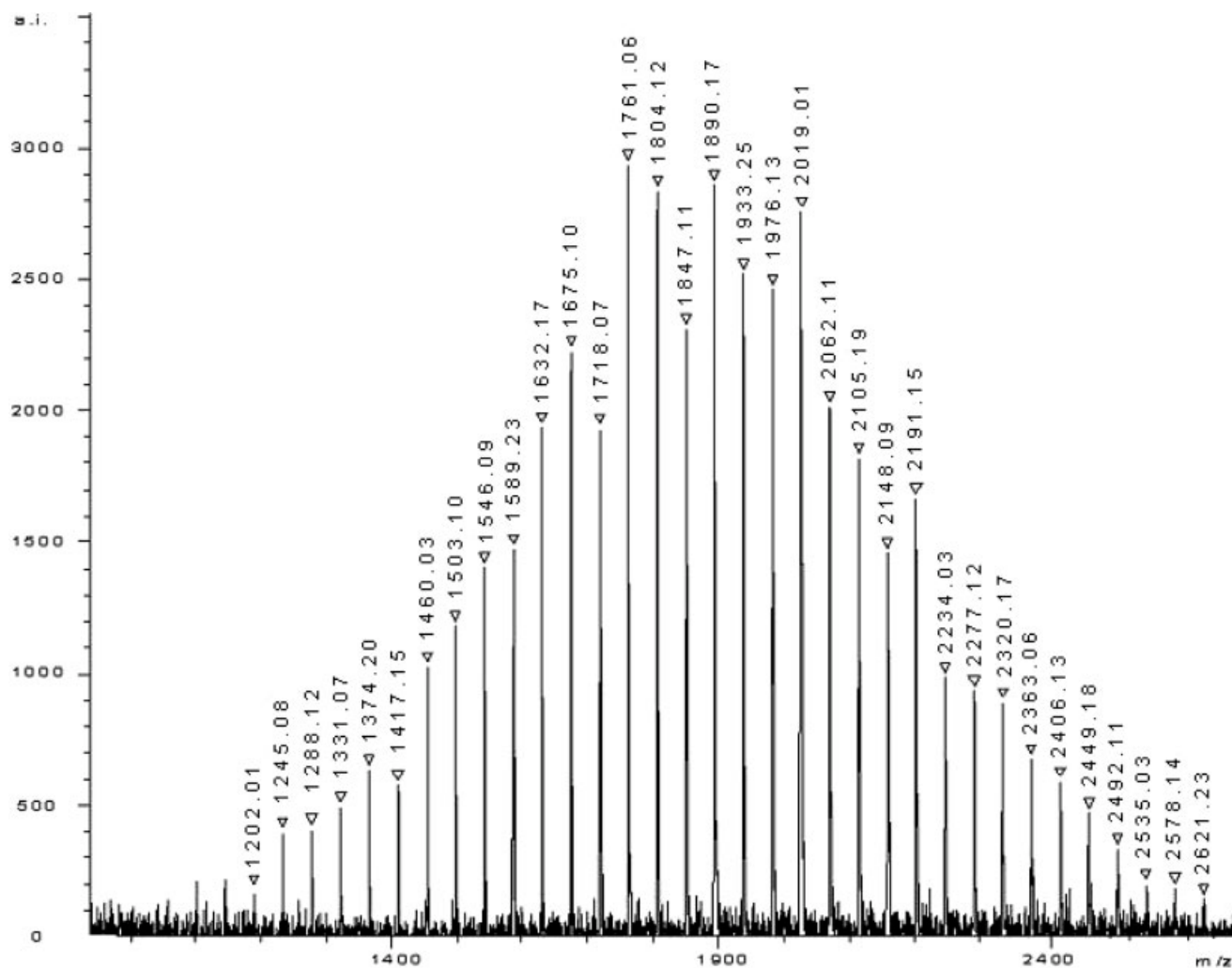
Figure 11 MALDI-TOF MS spectrum of PEI obtained by the hydrolysis of PMOX.

Polymerization mechanism

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.[30] 2-Methyl-2-oxazoline polymerizes cationically by opening of the O-alkyl bond in the immonium cation, which is attacked by the most nucleophilic N-atom of the monomer involving ionic species. 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-H$^+$ (Scheme 2) induce the cationic polymerization. Propagation then takes place by a conventional cationic mechanism.

Initiation. Initiation involves the reaction between MOX and Mag-H$^+$ and yields intermediate of oxazolinum; the formation of this species is the rate determining step. These montmorillonite sheets take place as counter-anions.

Propagation. The propagation step is the successive reaction of MOX with the intermediate of oxazolinum.
Termination. The termination occurs through the addition of water in the end of reaction to the reactional medium.

CONCLUSIONS

The present work shows that the preparation of poly MOX can be induced in heterogeneous phase by proton-exchanged montmorillonite clay ''Mag-H$^+$''.

The catalytic activity of this catalyst (measured by the conversion) and the molecular weight of the formed polymer depend on the proportion of catalyst in the reaction medium, the solvent, and the temperature of reaction. Mag-H$^+$-initiated polymerizations of MOX yield powdery and linear polymers. Poly MOX was produced by a very simple procedure: just by filtering, the clay can be separated from the reaction mixtures, and acidic clay is inexpensive, stable, and noncorrosive.
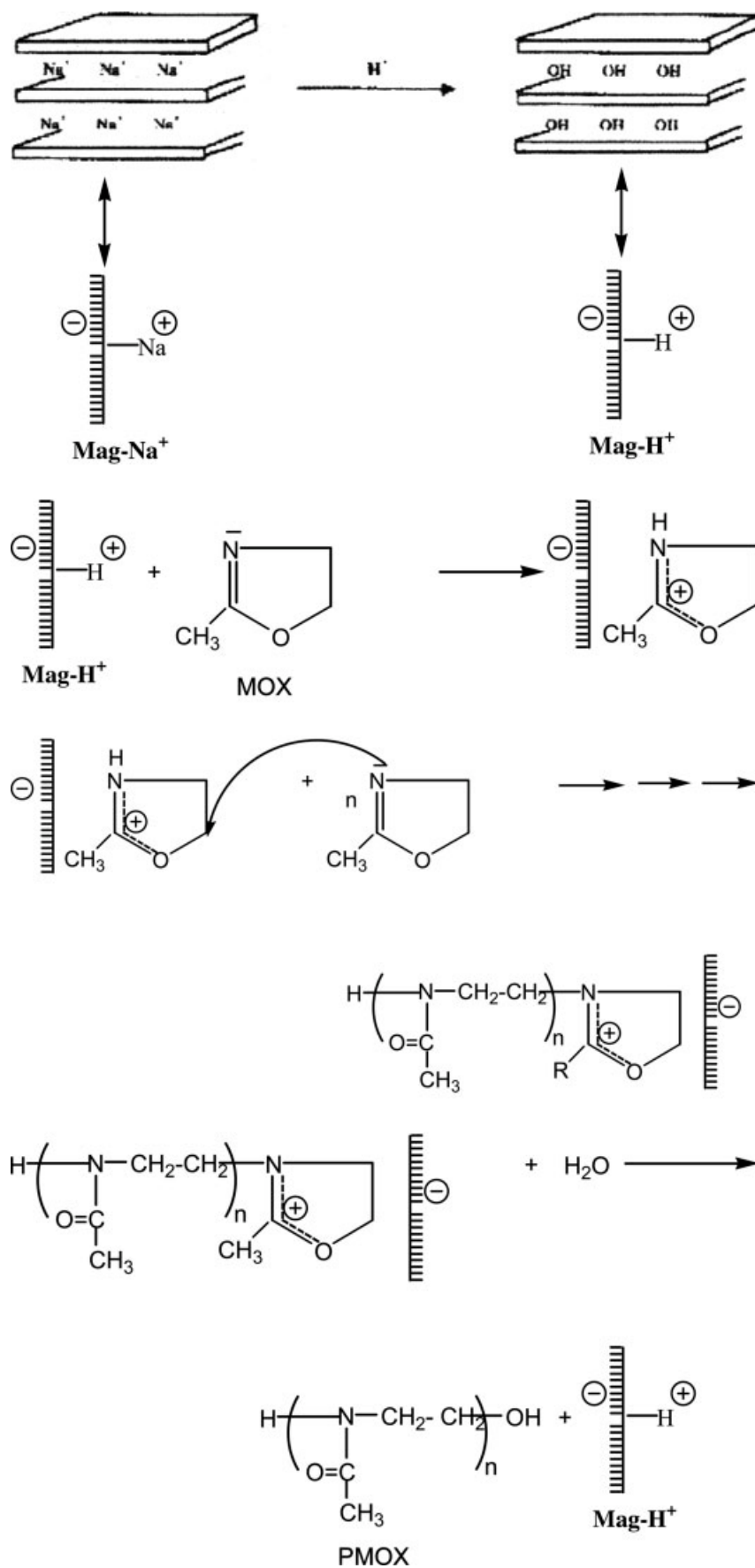
Scheme 2 Schematic representation of Mag-Na$^+$ and Mag-H$^+$.

Finally, we have synthesized the poly(ethylene-imine) linear in two steps by the acid hydrolysis of the poly(*N*-acetyl-ethyleneimine). The structure was confirmed by ^{1}H NMR and MALDI-TOF MS.

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