

Synthesis of Hydrosoluble Polymers of Oxazoline Using Maghnite-H as Catalyst

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ABSTRACT: 2,4,4-Triméthyl-2-oxazoline was polymerized, using an acid exchanged montmorillonite clay as catalyst, with the aim to study the influence of the methyl group size in the initiation and propagation processes. The effect of amount of catalyst temperature, time, and solvent on the polymerization yield and viscosity of the polymers were studied. The polymers obtained were characterized by spectrometric methods and their average molecular weights were determined by viscosimetry and GPC data. The polymers presented similar spectrometric results and narrow molecular weight distributions. The kinetics indicated that the

polymerization rate is first order with respect to monomer concentration. The polymerization results showed that the methyl groups present in the monomer affected the initiation process. Mechanism studies showed that polymerization of TMOX involves nucleophilic ring opening by attack of nitrogen to cleave the CH₂—O bond of the oxazoline ring. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 1792–1800, 2007

Key words: montmorillonite; ecocatalyst; 2,4,4-triméthyl-2-oxazoline; ring opening polymerization; living polymerization

INTRODUCTION

Cyclic iminoethers are interesting materials from both theoretical and practical points of view. The living nature of their cationic polymerization allows the engineering of macromolecular compounds with controlled dimensions, shapes, and functionality rise to a wide range of properties and possible applications.^{1–3}

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

Various initiating systems able to promote the polymerization of cyclic iminoethers have been reported: Lewis acids, stable cationic salts,¹³ strong protonic acids and their salts,¹⁴ esters of sulfuric, sulfonic, and picric acids, and acid anhydrides, alkyl

halides,¹⁵ as well as photocationic initiators.¹⁶ 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 (Mag-H⁺) is a novel, efficient solid catalyst for the ring opening polymerization of 2,4,4-triméthyl-2-oxazoline (TMOX) to produce PTMOX (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

2,4,4-triméthyl-2-oxazoline (TMOX) (Aldrich, France), was purified by distillation and stored over molecular sieves. DMF, dichloroethane, acetonitrile, and diethyl ether were purified following standard techniques and used after distillation over their respective drying agents.

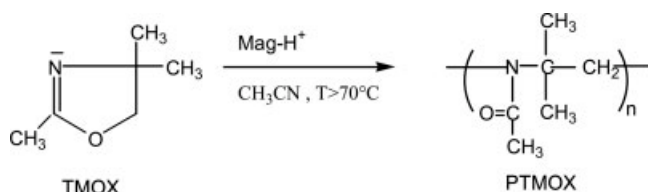
Preparation of “Maghnite-H+ × M”

Maghnite-H⁺ was prepared according to the process reported in our previous study.^{17,25}

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Scheme 1 Cationic polymerization of 2,4,4-trimethyl-2-oxazoline (TMOX) by Mag-H⁺ catalyst.

The clay, which has been used as catalyst, is supplied by a local company known as ENOF Maghnia (Western of Algeria). Its chemical composition is given in Table I (Run 1). 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 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 present in the filtrate using BaCl₂. The Mag-H⁺ was then isolated by filtration, dried at 105°C, and then finely ground. Sulfuric acid of concentrations 0.05M, 0.10M, 0.15M, 0.20M, 0.25M, 0.30M, and 0.35M were used to prepare the samples, respectively, denoted Mag-H⁺ 0.05M, Mag-H⁺ 0.10M, Mag-H⁺ 0.15M, Mag-H⁺ 0.20M, Mag-H⁺ 0.25M, Mag-H⁺ 0.30M, and Mag-H⁺ 0.35M.

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 TMOX in acetonitrile. Prior to use, Mag-H⁺ was dried at 120°C overnight and then transferred to a vacuum desiccator containing P₂O₅ to

cool to room temperature overnight. An example reaction is detailed here. After charging the reaction vessel with TMOX solution in acetonitrile (2M), the catalyst (10% w/w to monomer) was added at a polymerization temperature, e.g., 70°C. At the end of the reaction (72 h), 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 later was dried in a vacuum oven prior to submission for gel permeation chromatography (GPC), ¹H and ¹³C nuclear magnetic resonance (NMR) analysis (yield of this example was 92%).

Characterization of the products

¹H and ¹³C NMR measurements were carried out on a 200 MHz Bruker NMR Spectrometer equipped with a probe BB05 mm, in CDCl₃. Tetramethylsilane 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 an ATI Matson FTIR N°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. Average molecular weights and molecular weight distributions of the different polymers were measured, using GPC on a system equipped with a Spectra SYSTEM AS1000 auto sampler, with a guard column (Polymer Laboratories, PL gel 5-μm Guard, 50 × 7.5 mm²) followed by 2 columns (Polymer Laboratories, 2 PL gel 5-μm MIXED-D columns, 2 × 300 × 7.5 mm³), with a Spectra SYSTEM RI-150 and a Spectra SYSTEM UV2000 detectors. The eluent used is THF at a flow rate of 1 mL min⁻¹ at 35°C. Polystyrenes standards (580–483 × 10³ g mol⁻¹) were used to calibrate the GPC. The samples were prepared through the dissolution of 10 mg of the polymer in 10 mL of THF, and toluene was added as a flow time retention marker. The MALDI-TOF

TABLE I
Elementary Compositions of Proton Exchanged Samples Maghnite-H⁺ × M

Sample	Composition wt %											Polymers yield ^b (%)
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	TiO ₂	SO ₃	As	FL ^a	
Raw-Maghnite	69.39	14.67	1.16	0.30	1.07	0.50	0.79	0.16	0.91	0.05	11	00
H-Mag 0.05M	70.75	14.67	1.05	0.30	1.01	0.49	0.78	0.16	0.75	0.04	10	15
H-Mag 0.10M	71.00	14.60	1.00	0.30	0.98	0.39	0.78	0.16	0.55	0.04	10.2	26
H-Mag 0.15M	71.58	14.45	0.95	0.29	0.91	0.35	0.77	0.15	0.42	0.03	10.1	30
H-Mag 0.20M	71.65	14.20	0.80	0.28	0.85	0.30	0.77	0.15	0.39	0.01	10.6	44
H-Mag 0.25M	71.70	14.03	0.71	0.28	0.80	0.21	0.77	0.15	0.34	0.01	11	56
H-Mag 0.30M	73.20	13.85	0.70	0.27	0.78	0.20	0.76	0.13	0.31	0.02	9.78	25
H-Mag 0.35M	75.31	13.52	0.71	0.26	0.78	0.18	0.75	0.13	0.32	0.01	8.03	20

^a Pert in fire.

^b Maghnite-H⁺/TMOX weight ratio = 10%, T = 70°C, and reaction time = 48 h.

mass spectra (m.s.) were recorded on a Bruker Biflex III equipped with a nitrogen laser ($\lambda = 337$ 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_2Cl_2 solutions with dithranol as matrix and NaI as dopant.

Maghnite- H^+ samples were characterized by XRF (a Philips PW 2400XRF spectrometer at the Laboratory of Inorganic Chemistry, Granada University, Spain), using the LiB_4O_7 fusion method. XRD profiles for pressed powder samples were recorded on a Philips PW 1710 diffractometer, using $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418$ Å).

RESULTS AND DISCUSSION

The use of acid treated clays as a solid source of protons in many industrial significant reactions continues because they constitute a widely available, inexpensive solid source of protons, e.g., they were employed as cracking catalysts until the 1960s,²⁶ and are still used actually in industrial processes, such as the alkylation of phenols and the dimerization and polymerization of unsaturated hydrocarbons.²⁷

Montmorillonites have both Brönsted and Lewis acid sites and when exchanged with cations having a high charges density, as protons, produce highly-active catalysts for acid catalyzed reactions.²⁸ Intercalated organic molecules are mobile and can be highly polarized when situated in the space between the charged clay layers. These exchanged montmorillonites have been successfully used as catalysts for the reactions of polymerization.^{17–24,26}

The present study is also concerned with polymerization and examines the catalytic activity of an Algerian proton exchanged montmorillonite clay via oxazoline cationic ring opening polymerization. The structure and the composition of the catalyst were reported in previous works.^{17,25} The elementary analysis of the selected samples obtained, using XRF spectroscopy and monomer conversions are as settled in Table I.

It can be seen that there is an excellent correlation between the acid treatment and the catalytic activity of Maghnite. Acid treatment of "Raw-Maghnite" causes reduction in octahedral content (Al_2O_3) resulted

TABLE II
The Effect of Solvent Sort on the Polymerization of TMOX (2M) by Mag- H^+ (10%) Catalytic System at 70°C, 72 h

Entry	1	2	3
Solvent	Dichloroethane	DMF	Acetonitrile
Yield (%)	31	35	46
$[\eta]$ (dL/g)	0.035	0.058	0.064

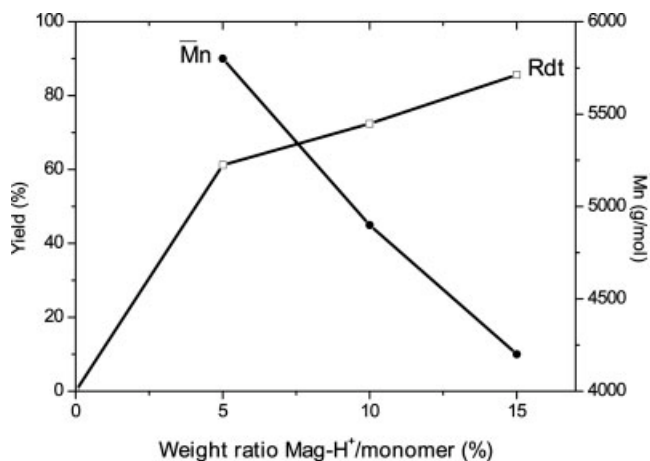


Figure 1 Effect of Maghnite- H^+ /monomer weight ratio on the yield and the molecular weight of the formed polymer; $T = 70^\circ\text{C}$.

in an increase in the proportion of silica (SiO_2) (Table I). It is necessary to report that the best value of monomer conversion was obtained with "Maghnite- H^+ 0.25M," in which there is a complete saturation of montmorillonite with protons without destruction of catalyst structure.^{29,30} For this reason we have used this sample for all kinetic studies.

Cationic polymerization of TMOX

Cyclic iminoethers are well known to undergo cationic ring-opening polymerization with various initiating systems.^{13–15} 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, the

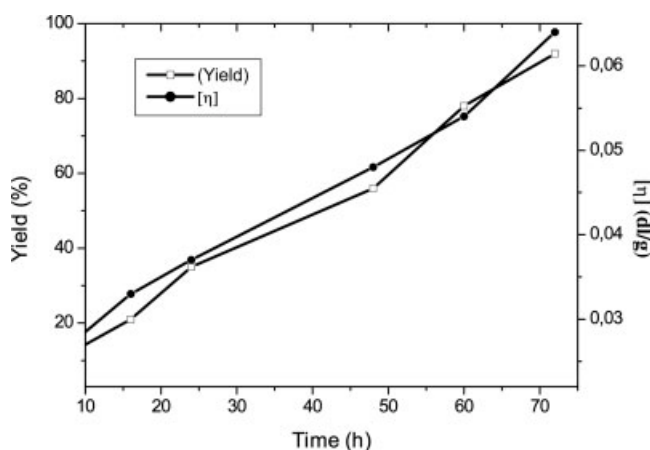


Figure 2 Effect of polymerization duration on yield and $[\eta]$ of PTMOX ($[\text{TMOX}] = 2\text{M}$ in CH_3CN at 70°C and 10% of Mag- H^+).

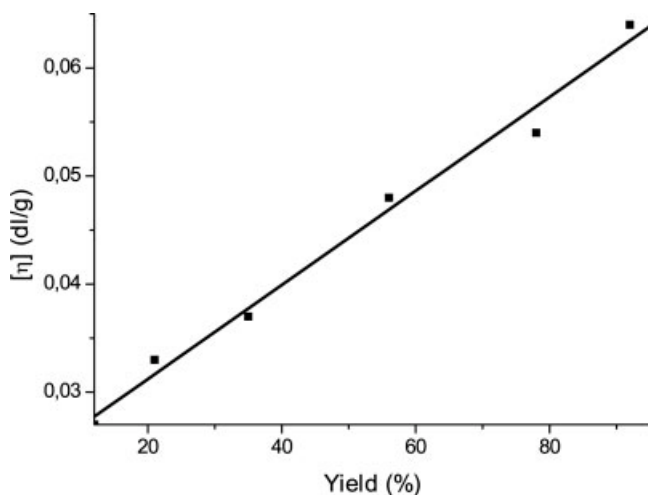


Figure 3 Effect of yield on $[\eta]$ of PTMOX ($[TMOX] = 2M$ in CH_3CN at $70^\circ C$ and 10% of $Mag-H^+$).

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 DMF. The rate of polymerization in acetonitrile was found to be much higher than that of dichloroethane and DMF. There is an effect of the dielectric constant of solvent (acetonitrile, DMF, and dichloroethane) on the yield and polymer viscosity.

The most polar solvent produces a polymer with the highest yield and viscosity.

Figure 1 shows the effect of the amount of $Mag-H^+$, expressed by using various weight ratios $Mag-H^+$ /monomer, on the polymerization rate of TMOX. The polymerization of TMOX was carried out in CH_3CN solution at $70^\circ C$. The yield of PTMOX increased with the amount of $Mag-H^+$, in which the effect of $Mag-H^+$ as a cationic catalyst for TMOX polymerization is clearly shown. Similar results are obtained by Yahiaoui et al.,¹⁷⁻²⁰ and Njopwou et al.,³¹ in the polymerization of epichlorhydrin, propylene oxide, and cyclohexene oxide by $Mag-H^+$ and the polymerization of styrene by montmorillonite, respectively. This phenomenon is probably the result of number of "initiating active sites" responsible of inducing polymerization, this number is proportionate to the catalyst amount used in reaction.

The effect of $Mag-H^+$ proportion on average molecular weight was studied. Figure 1 shows the effect of weight ratio $Mag-H^+$ /monomer on M_n , increasing the $Mag-H^+$ amounts yielded lower poly-(TMOX) M_n s in the following order: 15% < 10% < 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.,³² and Crivello and Fan,³³ in the polymerization of lactones by Sn-montmorillonite and cyclohexene oxide by Cobalt, respectively.

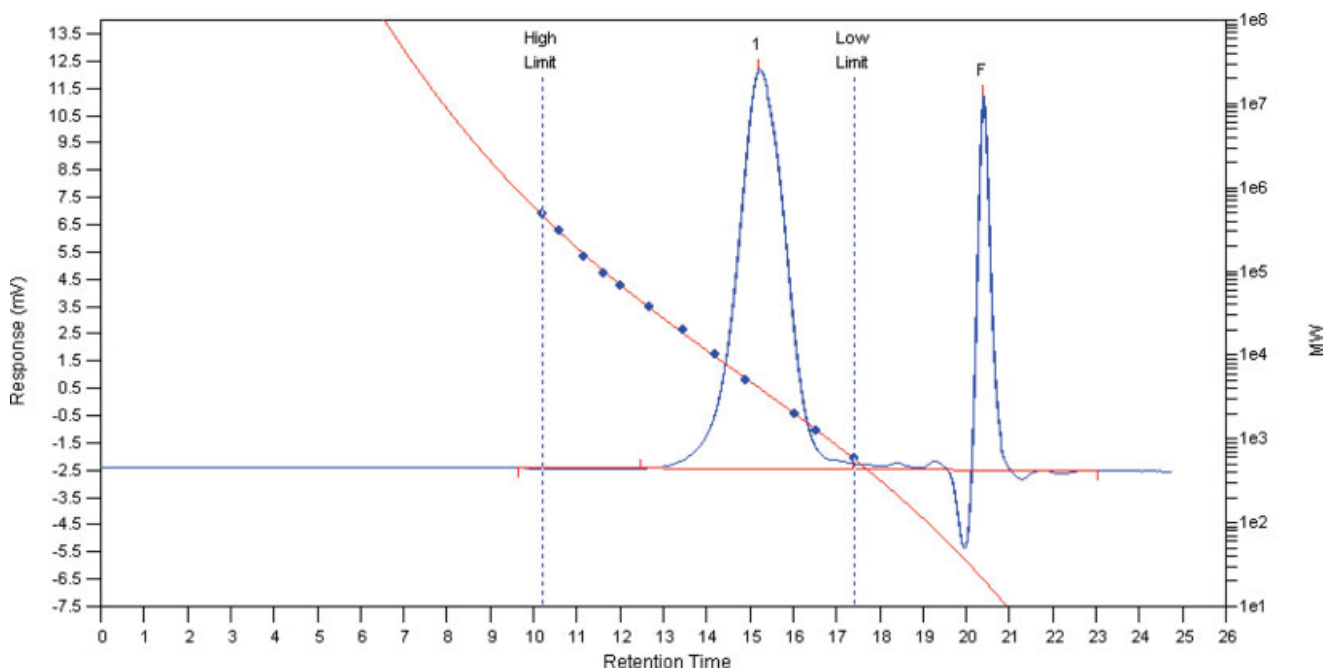


Figure 4 GPC chromatogram of PTMOX obtained by $Mag-H^+$ catalytic system at: 10% of $Mag-H^+$, $70^\circ C$, 36 h ($M_w = 5000$ g/mol, $M_n = 4000$ g/mol, and $I = 1.25$). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com]

TABLE III
Living Nature of the Recycled Catalysts (10%) Catalytic System at 70°C, 72 h in CH₃CN

	Mag-H	1st recovered Mag-H	2nd recovered Mag-H
Yield (%)	46	45.4	45.8
[η] (dL/g)	0.064	0.065	0.064

Figure 2 shows the yield of polymer versus time for the acetonitrile solution polymerization of TMOX, using Mag-H⁺ as catalyst. As the figure shows, polymerization takes place slowly and smoothly, reaching a yield of 92% after 72 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 PTMOX increased with the increasing polymerization time from 8 to 72 h. It is clear from Figure 3 showing the linear variation of the intrinsic viscosity with the yield of polymer (at constant initial TMOX concentration) that the polymerization proceeds without transfer reactions. The results of the analysis of the polymer by GPC are shown in Figure 4. As shown, the macromolecular weight distribution of

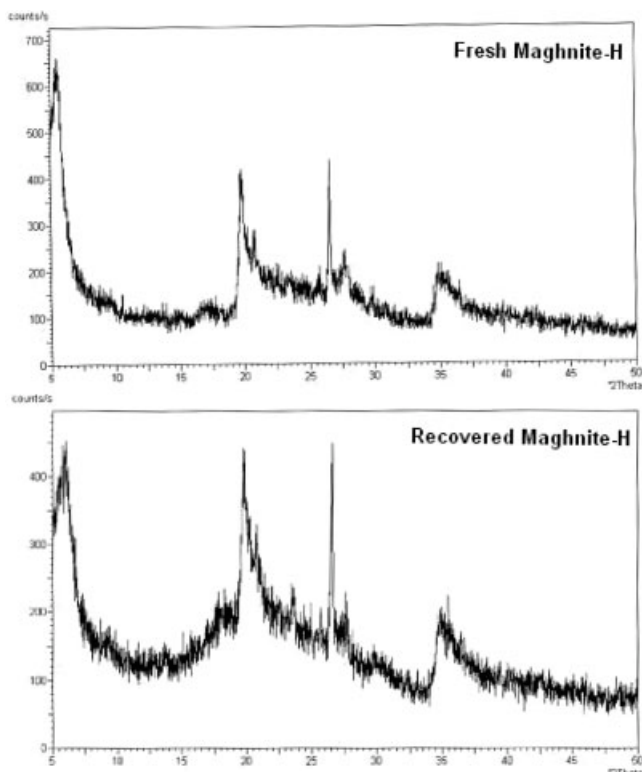


Figure 5 X-ray diffraction patterns of fresh and recovered Maghnite-H⁺.

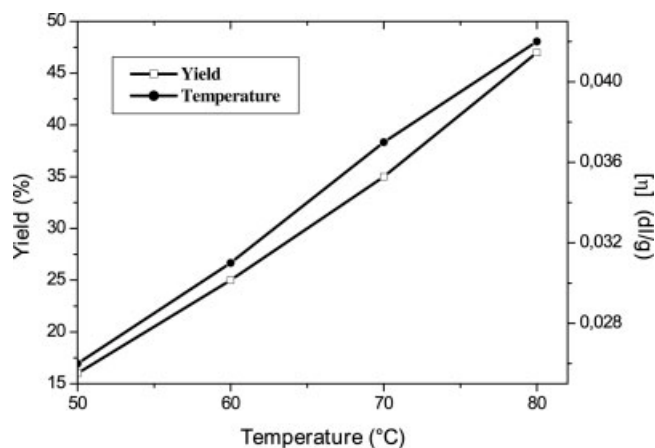


Figure 6 Temperature effect on the poly(TMOX) yield and [η] "10% of Mag-H⁺ for 24 h".

the obtained polymer is narrow. This suggests that chain transfer does not occur.

After the polymerization, the Mag-H catalyst was removed from the reaction mixture by filtration. The recovered Mag-H was dried at 120°C for 3 h under reduced pressure, and used as the catalyst again for the polymerization of TMOX under the same conditions as above. The yield and [η] values were comparable to those shown in Table II. For example, when the polymerization was carried out, using the removed Mag-H under the conditions as in Entry 3, poly(TMOX) was obtained in 45.4% yield. The [η] value was 0.065 dL/g. When the catalyst after the 2nd run was recovered further and used once more for the polymerization under the same conditions, poly(TMOX) with [η] = 0.064 dL/g was obtained in 45.8% yield (Table III). These experimental results indicate that the catalytic activity did not decrease

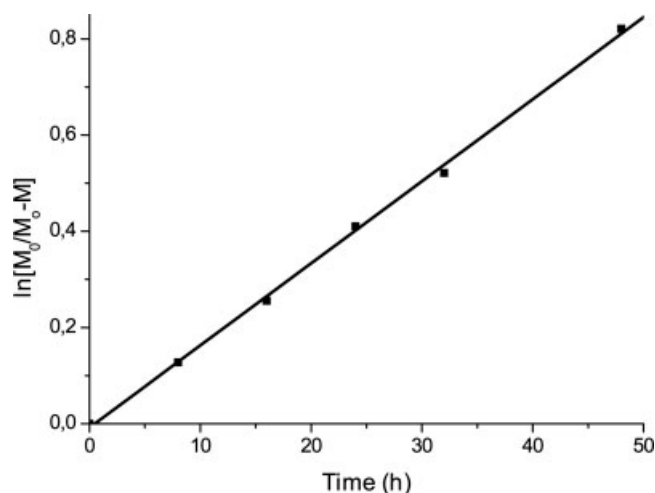
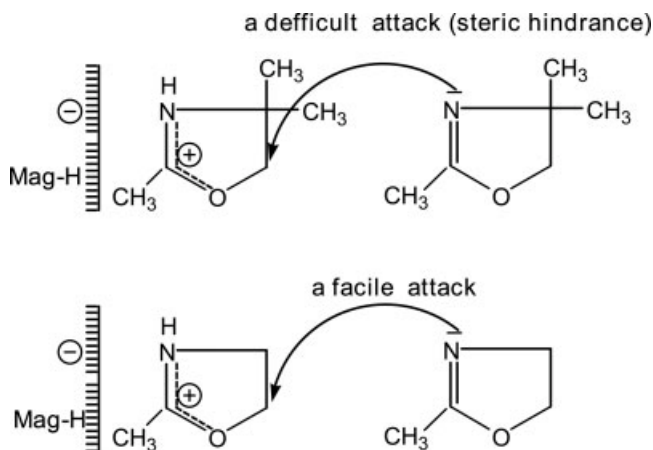


Figure 7 Kinetic curves of 2,4,4-trimethyl-oxazoline in CH₃CN ([M₀] = 2M) polymerization by Mag-H⁺ (10%) at 70°C.



Scheme 2 Steric hindrance in the cationic polymerization of 2,4,4-trimethyl-2-oxazoline (TMOX) by Mag-H⁺ catalyst.

for the 2nd and 3rd runs. Although the X-ray peak of the fresh and the recovered Maghnite-H⁺ did not change. This implies that the original structure was well preserves after polymerization and no delamination of the clay was observed (Fig. 5).

Temperature effect

The temperature is an important factor in the initiation process and its influence was studied. Using TMOX solution in acetonitrile (2M) and 10% [Mag-H⁺/TMOX] (w/w), the polymerization was

carried out at 50, 60, 70, and 80°C for 24 h of reaction. In the absence of Mag-H⁺ no polymerization could be detected. In the presence of Mag-H⁺, however, the polymerization was initiated. Figure 6 shows that polymerization temperature has much influence on the yield of PTMOX. The yield increased with the temperature rising from 50 to 80°C and reached a high yield of 47% at 80°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°C > 30°C > 50°C > 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).^{34,35} The notable exception was for MOX. As depicted in Figure 6, 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).

To get more insight into the TMOX polymerization by Mag-H⁺, the kinetics of TMOX polymerization

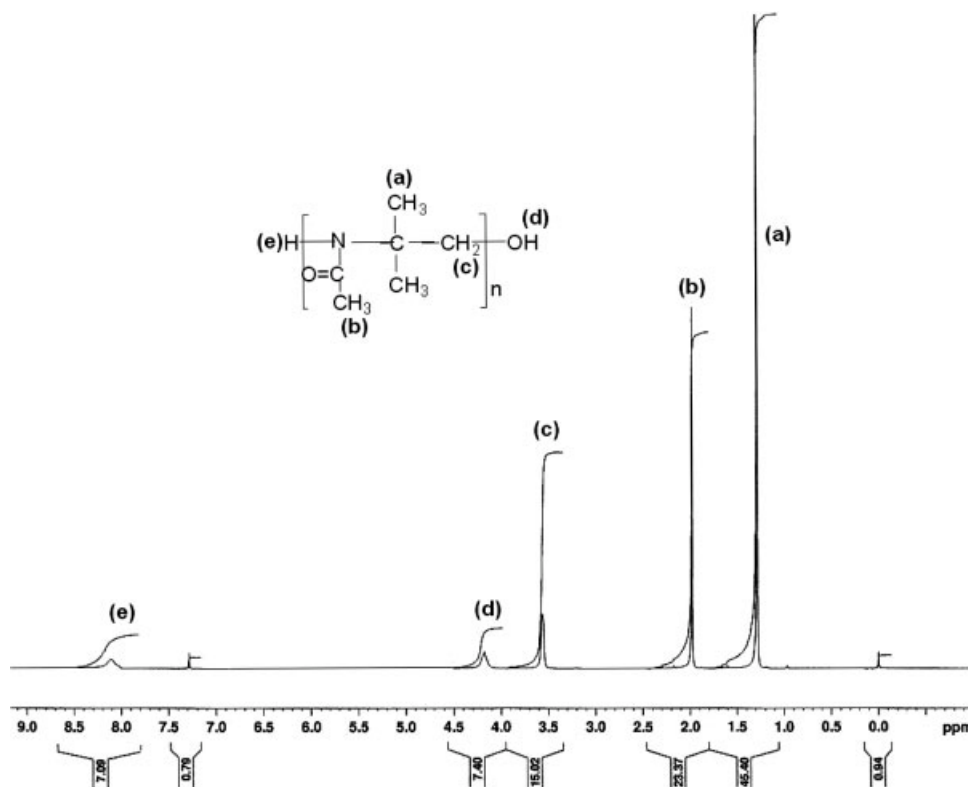


Figure 8 ¹H NMR (200 MHz) spectrum of poly(TMOX) in CDCl₃.

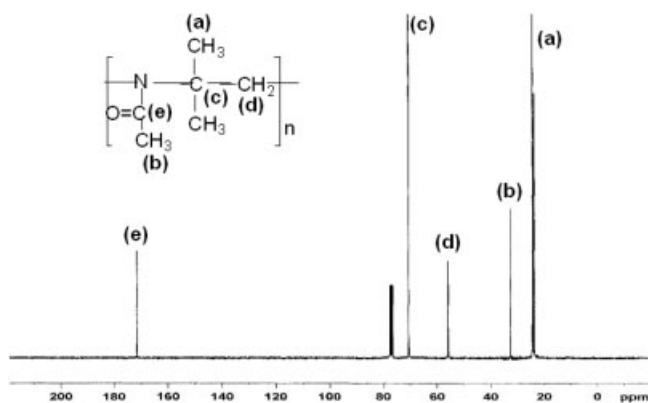


Figure 9 ^{13}C NMR (200 MHz) spectrum of poly(TMOX) in CDCl_3 .

with Mg-H^+ in CH_3CN has been studied. Figure 7 show that the polymerization is accurately first-order with respect to monomer.

TMOX polymerization is slow and produces polymers with lower rates than other oxazolines, e.g., MOX, because of the steric hindrance (presence of two methyl) (Scheme 2).^{36,37}

Characterization of polymer

The structure of the TMOX polymer was determined by ^1H NMR, ^{13}C NMR, IR, and MALDI-TOF-MS. Figure 8 shows the ^1H NMR spectrum of the isolated product (CDCl_3). Signal at 1.2 ppm (a) is due to methyl the protons (6H), signal at 2.05 ppm (b) is

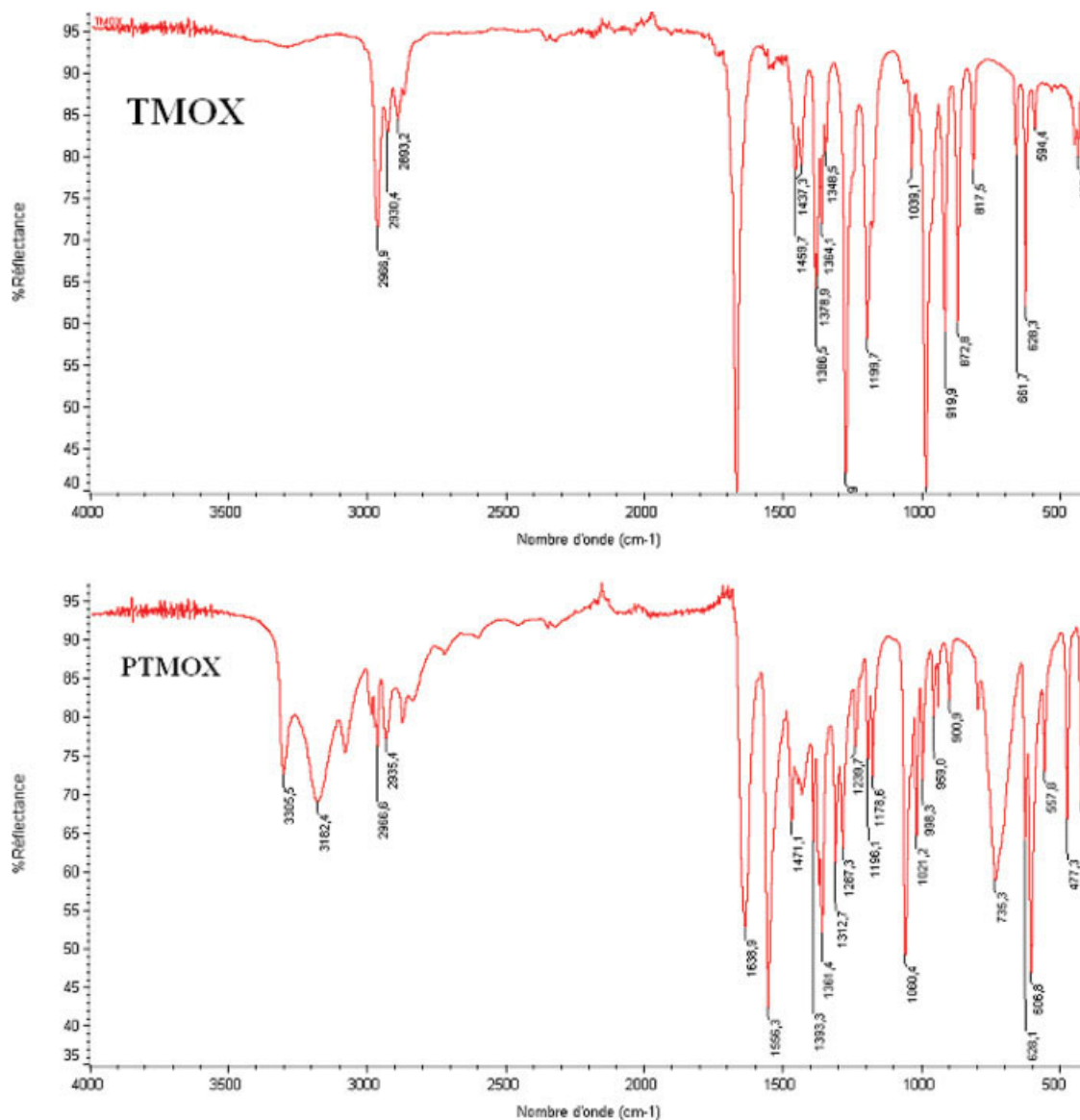


Figure 10 IR spectra of TMOX and poly(TMOX) recorded from thin films and KBr pellets, respectively. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com]

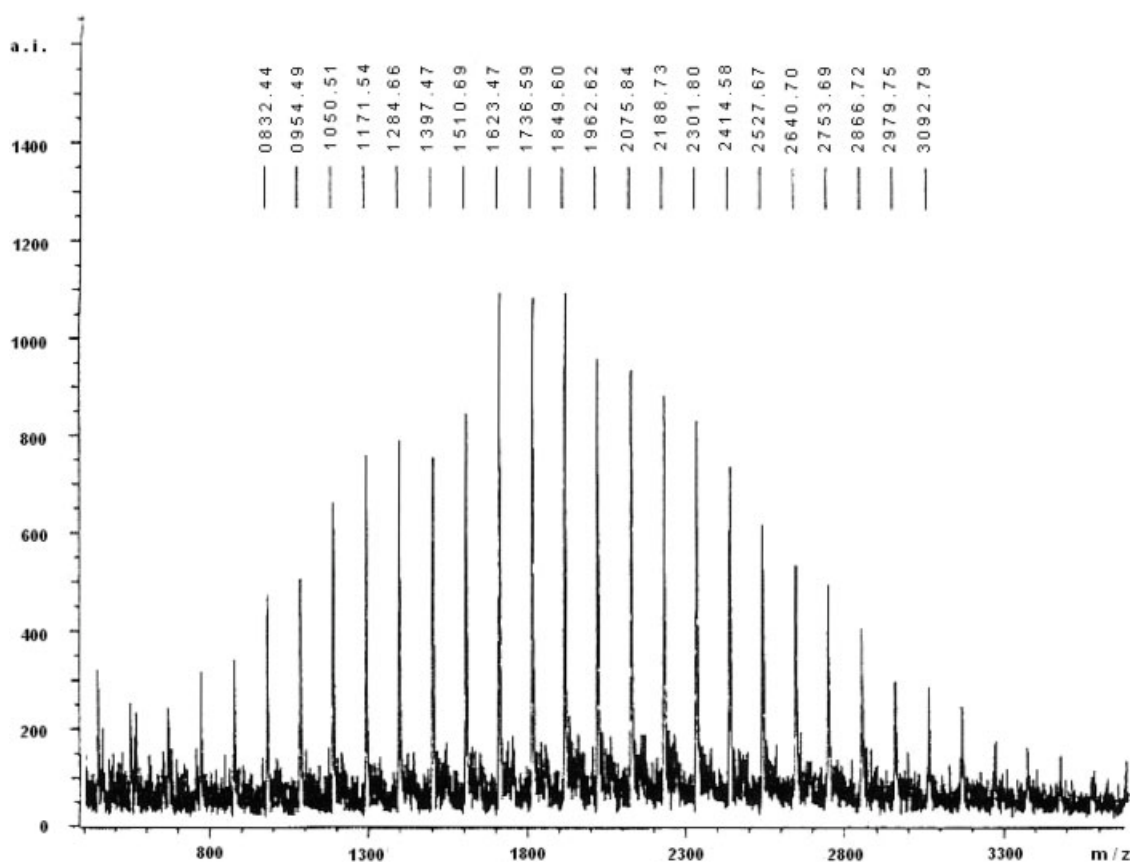


Figure 11 MALDI-TOF MS spectrum of poly(TMOX) obtained by the solution polymerization of TMOX (2M), using 10% of Mag-H⁺ at 70°C and for 24 h.

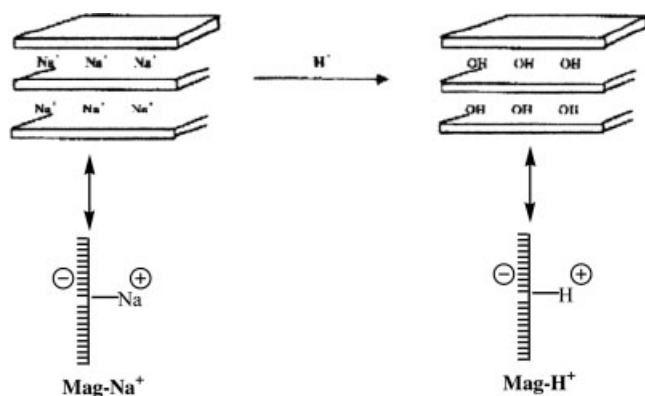
assigned to the methyl protons (3H) attached to carbonyl group (acetamido group), and the signal at 3.6 ppm (c) is attributed to methylene protons of the main chain attached to nitrogen (4H). In addition to these peaks due to the polymer chain, a set of small signals assignable to —OH at 4.2 ppm (d) and —C(O)NH at 8.1 ppm (e) is observed. The relative intensity of these signals was 1 : 1, indicating that the polymerization was terminated by water with incorporation of the hydroxyl end group at the terminal site of the polymer chain.

The ¹³C NMR spectrum (Fig. 9) presents five signals. The signal at 23.81 ppm corresponds to methyl carbons attached to carbon of the main chain; signal at 36.97 ppm was assigned to methyl carbon attached to carbonyl group; signal at 55.91 ppm was attributed to the methylene carbon of the main chain; the signal at 70.85 ppm was assigned to quaternary carbon attached to nitrogen and the signal at 171.51 ppm was ascribed to the carbonyl carbon. The IR spectrum (Fig. 10) 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 1639.9 cm⁻¹ due to C=O of the acetamido and two bands at 3305.5 and 3182.4 cm⁻¹ characteristic of OH and NH groups, respectively.

To further investigate the polymer, MALDI-TOF-MS (Fig. 11) was performed on the poly(TMOX) 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 113 mass units, which corresponds to the mass of a TMOX monomer unit. End-group analysis confirmed that the polymer was initiated with Mag-H and terminated with hydroxyl. Also, each peak of the MALDI-TOF MS correspond to the PTMOX having hydroxylated terminal structure with one Na⁺ ion (H—(N(OCCH₃)—C(CH₃)₂—CH₂)_n—OH, Na⁺).

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.²⁵ 2,4,4-trimethyl-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



Scheme 3 Schematic representation of Mag-Na⁺ and Mag-H⁺.

cationic mechanism for the resulting reaction of polymerization induced by Mag-H⁺. Protons carried by montmorillonite sheets of Mag-H⁺ (Scheme 3) induce the cationic polymerization. Propagation then takes place by a conventional cationic mechanism.

Initiation

Initiation involves the reaction between TMOX and Mag-H and yields intermediate of oxazolinium; 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 TMOX with the intermediate of oxazolinium.

Termination

The termination occurs through the addition of water in the end of the reaction to the reactional medium.

In conclusion, it was proved that Mag-H⁺ can be used to induce the polymerization of 2-substituted 2-oxazoline, thus offering new possibilities for the selective study of montmorillonites catalysts and for the synthesis of new polymeric materials. On the basis of the observations done in this work it seems reasonable to assume that the two methyl groups have a direct influence on the polymerization. The kinetics of polymerization demonstrates that the polymerization rate has the first-order in monomer concentration. The macromolecular weight distribution of the obtained polymers is narrow, which confirms the living character of the polymerization.

Mechanism studies showed that polymerization of TMOX involves nucleophilic ring opening by attack

of nitrogen to cleave the CH₂—O bond of the oxazoline ring.

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