

# Synthesis and characterization of macromonomers of poly (2-methyl-2-oxazoline)-allyl by an acid exchanged clay as eco-catalyst

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**Abstract** Macromonomers from oxazoline derivatives were synthesized by using in conjunction with ethylenically unsaturated modifier. allyl chloride (AC) is chosen as representative modifier for the synthesis of allyl-terminated macromonomers in the presence of an acid exchanged montmorillonite as catalyst. The macromonomers were characterized by FT-IR,  $^1\text{H}$ -NMR,  $^{13}\text{C}$ -NMR and MALDI-TOF mass spectroscopy. The effects of amount of catalyst, amount of initiator, solvent and temperature on yields and intrinsic viscosity were studied. NMR and IR spectra of macromonomers show characteristic chemical shifts absorptions of the ethylenically unsaturated group of the modifier. The MALDI-TOF spectrum shows that the macromonomers synthesized accordingly are terminated with ethylenically unsaturated group of modifier at one end of the polymer chain and a hydroxyl group at the other end.

**Keywords** Maghnite- $\text{H}^+$  · Macromonomer ·  
2-Méthyl-2-oxazoline · Cationic polymerisation

## Introduction

The cationic polymerization of 2-alkyl-2-oxazolines has been studied for many years [1–3]. 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 [4]. Their polymers can be incorporated in grafted or block copolymers imparting amphiphilic properties [5,6]. The polymerization of 2-MOX in acetonitrile in the presence of cationic initiators, such as alkyl halogenides has been studied in detail by Kagiya et al. [3,7] and by Saegusa et al. [8].

Furthermore, some of the cationic initiators used to make polymers are expensive. Frequently, these initiators require the use of very high or very low temperature during the polymerization reaction, thus the yield is often poor. The separation of the initiators from the polymer is not always possible. Therefore, the presence of toxic initiators presents problems in the manufacture of polymers used especially in medical and veterinary procedures.

In this presentation and in continuation of our program to develop environmentally benign methods using solid supports [9,10], we report a novel synthesis of macromonomers via cationic ring-opening polymerization. Macromonomers are successfully synthesized by polymerization of 2-methyl-2-oxazoline (MOX) in the presence of allyl chloride (CA) as initiator and an acid-exchanged montmorillonite ( $\text{Mag-H}^+$ ) as solid catalyst (Scheme 1).

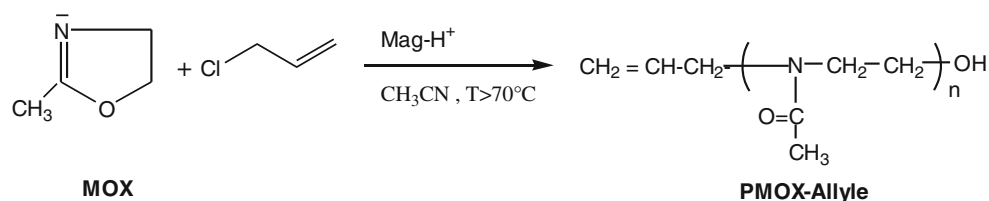
## Experimental

The 2-méthyl-2-oxazoline (Aldrich) monomer and Allyl chloride (*MERCK, France*) were distilled before use. The clay, which has been used as catalyst, is supplied by a local company known as ENOF Maghnia (Western of Algeria).  $^1\text{H}$  and  $^{13}\text{C}$  nuclear magnetic resonance (NMR) measurements were carried out on a 300 MHz Bruker (France) NMR Spectrometer. The molecular

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**Scheme 1** Synthesis of macromonomers PMOX-Allyle in CH<sub>3</sub>CN by Mag-H<sup>+</sup> catalyst



structure of the polymer was characterized by ALPHA-P FTIR spectrometer with Diamond ATR (Bruker, France). Intrinsic viscosity  $[\eta]$  measurements were performed at 30 °C in toluene using a capillary viscometer SEMATECH (VISCOLOGIC TL1, France). The sample concentration was 1 mg/ml. Average molecular weights and molecular weight distributions of the different polymers were measured using gel permeation chromatography (GPC, France) on a system equipped with a Spectra SYSTEM AS1000 auto sampler, with a guard column (Polymer Laboratories, PL gel 5  $\mu\text{m}$  Guard, 50  $\times$  7.5 mm) followed by 2 columns (Polymer Laboratories, 2 PL gel 5  $\mu\text{m}$  MIXED-D columns, 2x300x7.5 mm), 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<sup>-1</sup> at 35 °C. Polystyrenes standards (580–483.10<sup>3</sup> g.mol<sup>-1</sup>) 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 mass spectra (m.s.) were recorded on a Bruker Biflex III (France) 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<sub>2</sub>Cl<sub>2</sub> solutions with dithranol as matrix.

Maghnite-H<sup>+</sup> samples were characterised by XRF (a Philips PW 2400XRF spectrometer at the Laboratory of Inorganic Chemistry, Granada University, Spain) using the LiB<sub>4</sub>O<sub>7</sub> fusion method. XRD profiles for pressed powder samples were recorded on a Philips PW 1,710 diffractometer using Cu-K  $\alpha$  radiation ( $\lambda=1.5418$  Å).

**Polymerization** After charging the reaction vessel with MOX (0.01 mol) and Allyle chloride (0.0005 mol) solution in acetonitrile (100 ml), the catalyst (20 % w/w to monomer) was added at a polymerization temperature, e.g. 80 °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 (yield of this example was 35 %). The later was dried in a vacuum oven prior to submission for GPC, <sup>1</sup>H- and <sup>13</sup>C-NMR and IR analysis. The MALDI-TOF 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

**Table 1** Elementary compositions of proton exchanged samples Maghnite-H<sup>+</sup> × M

Sample	Composition wt%											Polymers yield % <sup>a</sup>
	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	Na <sub>2</sub> O	K <sub>2</sub> O	TiO <sub>2</sub>	SO <sub>3</sub>	As	FL*	
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-Mag0.05M	70.75	14.67	1.05	0.30	1.01	0.49	0.78	0.16	0.75	0.04	10	05
H-Mag0.10M	71.00	14.60	1.00	0.30	0.98	0.39	0.78	0.16	0.55	0.04	10.2	16
H-Mag0.15M	71.58	14.45	0.95	0.29	0.91	0.35	0.77	0.15	0.42	0.03	10.1	20
H-Mag0.20M	71.65	14.20	0.80	0.28	0.85	0.30	0.77	0.15	0.39	0.01	10.6	29
H-Mag0.25M	71.70	14.03	0.71	0.28	0.80	0.21	0.77	0.15	0.34	0.01	11	34.8
H-Mag0.30M	73.20	13.85	0.70	0.27	0.78	0.20	0.76	0.13	0.31	0.02	9.78	25
H-Mag0.35M	75.31	13.52	0.71	0.26	0.78	0.18	0.75	0.13	0.32	0.01	8.03	20

\*Pert in fire

<sup>a</sup> Maghnite-H<sup>+</sup> /MOX weight ratio=20 %, T=70 °C, reaction time 8 h

$\text{CH}_2\text{Cl}_2$  solutions with Alpha-cyano-4-hydroxycinnamic Acid (HCCA) as matrix.

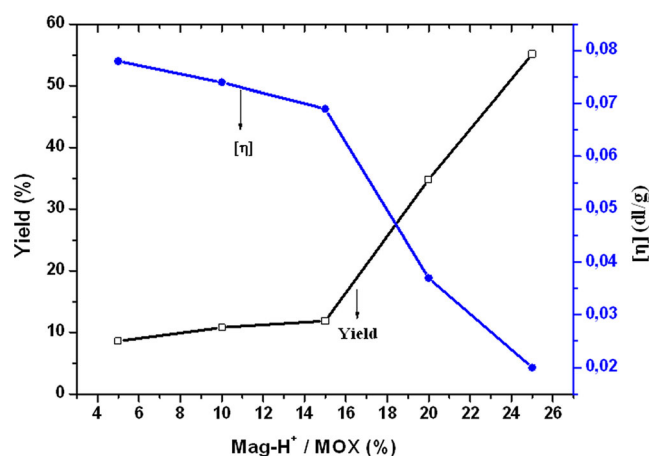
## Results and discussion

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 [11], and are still used actually in industrial processes such as the alkylation of phenols and the dimerization and polymerization of unsaturated hydrocarbons [12]. Recently, monomers were found to intercalate into lattice layers of montmorillonite clay, permitting in situ polymerizations yielding polymer/clay nano-composites. Several polymers, for example, carrageenan-based hydrogel [13], and acrylonitrile-butadiene-styrene/polyvinyl chloride [14], have been prepared via this route.

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 [15]. 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 [9,10,16–20].

The present study is also concerned with polymerization and examines the catalytic activity of an Algerian proton exchanged montmorillonite clay via oxazoline macromonomer synthesis by cationic ring opening polymerization. The structure and the composition of the catalyst were reported in previous works [9,20]. The elementary analysis of the selected samples obtained using XRF spectroscopy and monomer conversions are as settled in Table 1.

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 ( $\text{Al}_2\text{O}_3$ ) resulted in an increase in the proportion of silica ( $\text{SiO}_2$ ) (Table 1). It is necessary to report that the best value of monomer conversion was obtained with “Maghnite- $\text{H}^+$ 0.25 M”, in which there is a complete saturation of montmorillonite with protons without destruction of catalyst structure [21,22]. For this reason we have used this sample for all kinetic studies.

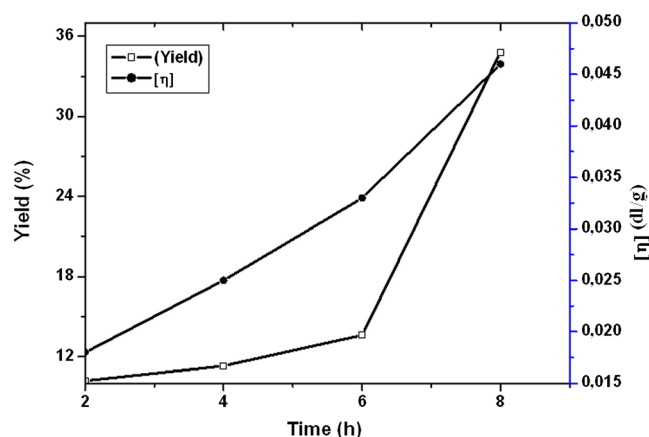


**Fig. 1** Effect of Maghnite- $\text{H}^+$ /monomer weight ratio on the yield and  $[\eta]$  of the formed polymer;  $T=80^\circ\text{C}$

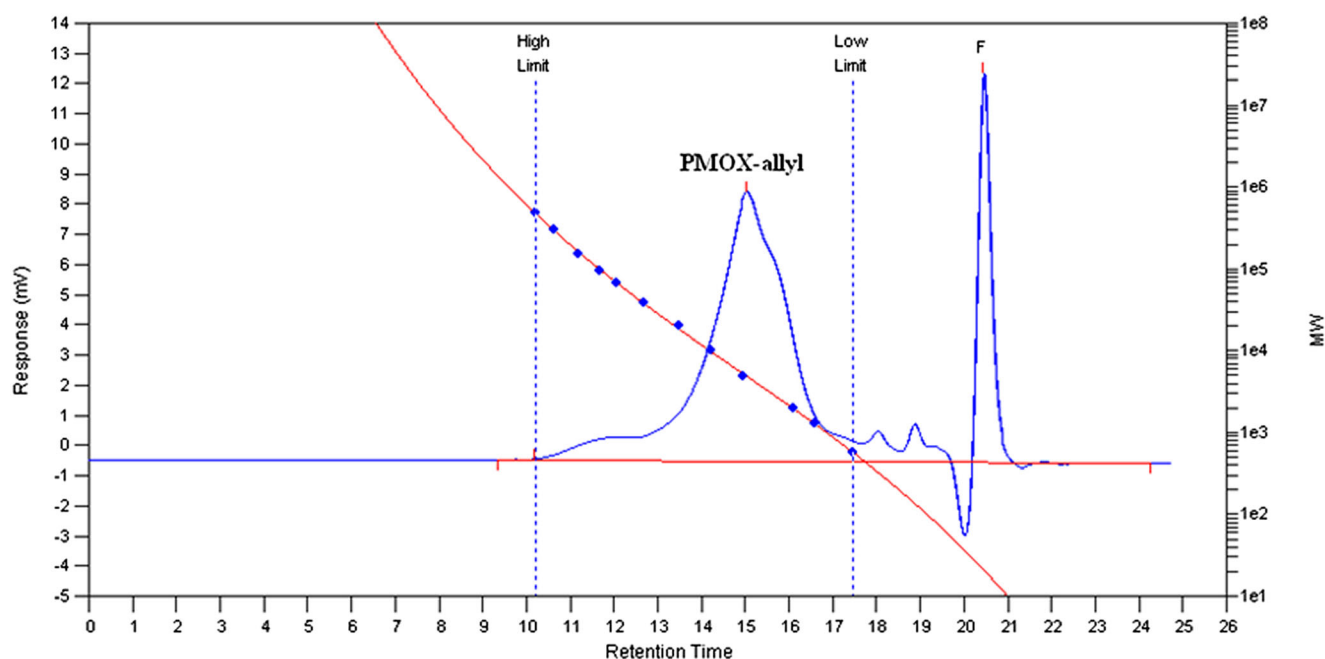
## Macromonomers synthesis

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

Amount of catalyst (Mag- $\text{H}^+$ /MOX) was an important factor of polymerization. Figure 1 shows the effect of the amount of Mag- $\text{H}^+$ , expressed by using various weight ratios Mag- $\text{H}^+$ /monomer, on the polymerization rate of MOX. The polymerization of MOX was carried out in  $\text{CH}_3\text{CN}$  solution at  $80^\circ\text{C}$ . The yield of PMOX increased with the amount of Mag- $\text{H}^+$ , in which the



**Fig. 2** Effect of polymerization duration on yield and  $[\eta]$  of PMOX  $\text{CH}_3\text{CN}$  at  $70^\circ\text{C}$  and 20 % of Mag- $\text{H}^+$



**Fig. 3** GPC chromatogram of PMOX obtained by Mag- $H^+$  catalytic system at: 20 % of Mag- $H^+$ , 80 °C, 8 h ( $\overline{M}_w$  = 3000 g/mol,  $\overline{M}_n$  = 2300 g/mol and  $I=1.3$ )

effect of Mag- $H^+$  as a cationic catalyst for MOX polymerization is clearly shown. Similar results are obtained by Yahiaoui et al. [9,10], and Njopwouo et al. [23], 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 prorating to the catalyst amount used in reaction.

As depicted in Fig. 1, the viscosity was found to decrease, depending on the amount of Mag- $H^+$  (i.e.,  $[\eta]$   $\searrow$  when amount of Mag- $H^+$   $\nearrow$ ) in the following order:

25 % < 20 % < 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. [24], and Crivello and Fan [25], in the polymerisation 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 13 % after 6 h at 80 °C. After this time the polymerization yield increase to reach a maximum of 35 % in 8 h. Isolation of the polymer after

8 h followed by GPC determination of molecular weight gave a  $M_n=2300$  g/mol $^{-1}$ , and  $M_w=3000$  g/mol $^{-1}$  (Fig. 3).

The effect of polymerization duration on the intrinsic viscosity, as shown in Fig. 2, has the same trend as that of yield, i.e., both the viscosity of PMOX increased with the increasing polymerization time from 2 h to 8 h.

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 MOX under the same conditions as above.

When the polymerization was carried out using the removed Mag-H under the conditions, poly (MOX) was obtained in 33.2 % yield. The  $[\eta]$  value was 0.042 dl/g. When the catalyst after the 2nd run was recovered further and used once more for the polymerization under the same conditions, poly (MOX) with  $[\eta]=0.039$  dl/g was obtained in 32.8 % yield (Table 2). These experimental results indicate that the catalytic

**Table 2** Living nature of the recycled catalysts (20 %) catalytic system at 70 °C, 8 h in  $CH_3CN$

	Mag-H	1 <sup>st</sup> recovered Mag-H	2 <sup>nd</sup> recovered Mag-H
Yield (%)	34.8	33.2	32.8
$[\eta]$ (dl/g)	0.046	0.042	0.039

activity did not decrease for the 2nd and 3rd runs. Although the X-ray peak of the fresh and the recovered Maghnite-H<sup>+</sup> did not show important changes, the signal at  $2\theta=5.9^\circ$ , which corresponds to the d-spacing ( $15.0^\circ$ ) of fresh Maghnite-H<sup>+</sup>, is shifted to  $2\theta=5.4^\circ$ , corresponding to an average interlayer distance of 16.4 Å. The increase of 1.4 Å in the distance between the platelets could be attributed to the intercalation of polymer chains into the clay galleries (Fig. 4) without destruction of catalyst structure.

#### Temperature effect

The temperature is an important factor in the initiation process and its influence was studied. Using MOX solution in acetonitrile and 20 % [Mag-H<sup>+</sup>/MOX] (w/w), the polymerization was carried out at 40, 50, 60, 70 and 80 °C. In the absence of Mag-H<sup>+</sup> no polymerization could be detected. In the presence of Mag-H<sup>+</sup>, 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 °C to 80 °C and reached a high yield of 34.8 % 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) [9], 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

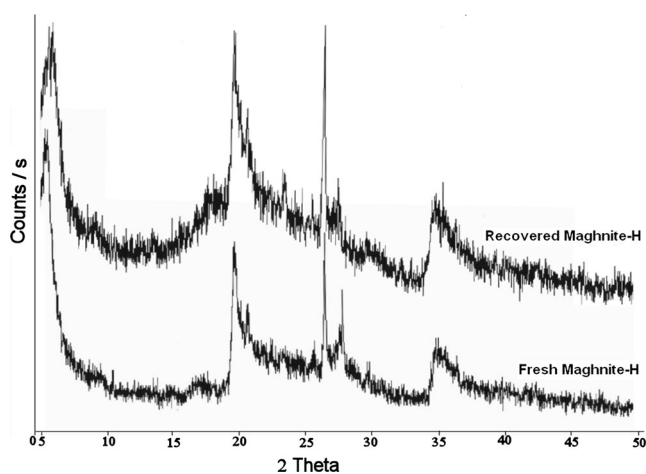


Fig. 4 X-ray diffraction patterns of fresh and recovered Maghnite-H<sup>+</sup>

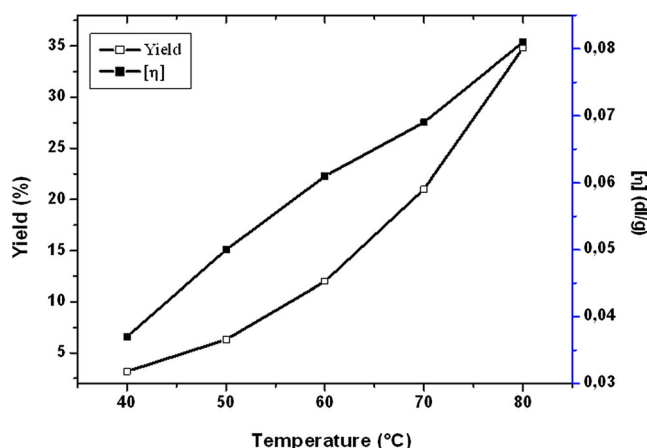


Fig. 5 Temperature effect on the poly MOX yield and  $[\eta]$  "20 % of Mag-H<sup>+</sup> for 8 h"

increasing the temperature causes an increase in the rate of chain transfer reaction of the growing polymer cation (inter and intramolecular) [26, 27]. The notable exception was for MOX. As depicted in Fig. 5, an increase in polymerization temperature increases the intrinsic viscosity. In the products of reaction of this oxazoline compound with Mag-H<sup>+</sup>, no macrocyclic groups were observed in the GPC curves of the final products (Fig. 3). The unique behaviour of MOX may be explained by the living character of the polymerization.

The Fig. 6 shows that the yield increases as the proportion of allyl chloride increases. This result is due to a multiplication of the active centers. This result is due to an increase in the number of allyl groups at the extremities of the chains that block the growth of polymer chains. As depicted in Fig. 6, the viscosity was found to decrease, depending on the amount of allyl chloride.

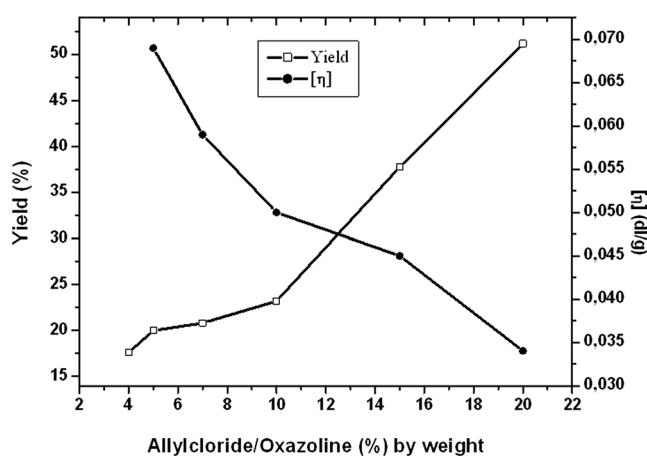
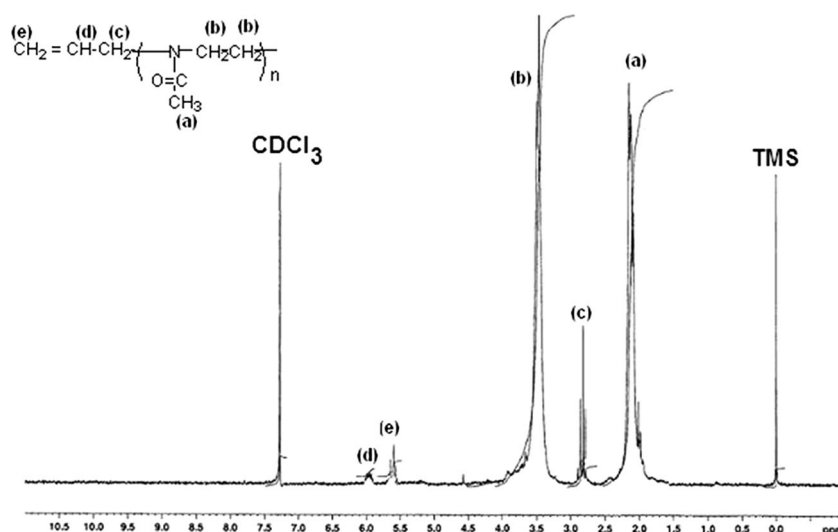


Fig. 6 Effect of Allyl chloride/monomer weight ratio on the yield and  $[\eta]$  of the formed polymer; T=80 °C

**Fig. 7**  $^1\text{H}$ -NMR (200 MHz) spectrum of macromonomer PMOX-Allyle in  $\text{CDCl}_3$



**Characterization of polymer** The structure of the MOX polymer was determined by  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and IR. Fig. 7 shows the  $^1\text{H}$  NMR spectrum of the isolated product ( $\text{CDCl}_3$ ). The signals a and b, at  $\delta=5.3$ -6.0 ppm (ABX) are assigned to vinyl group. Signal c at 2.7 ppm is assigned to methylene protons adjacent to vinyl group. Signal at 2.2 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).

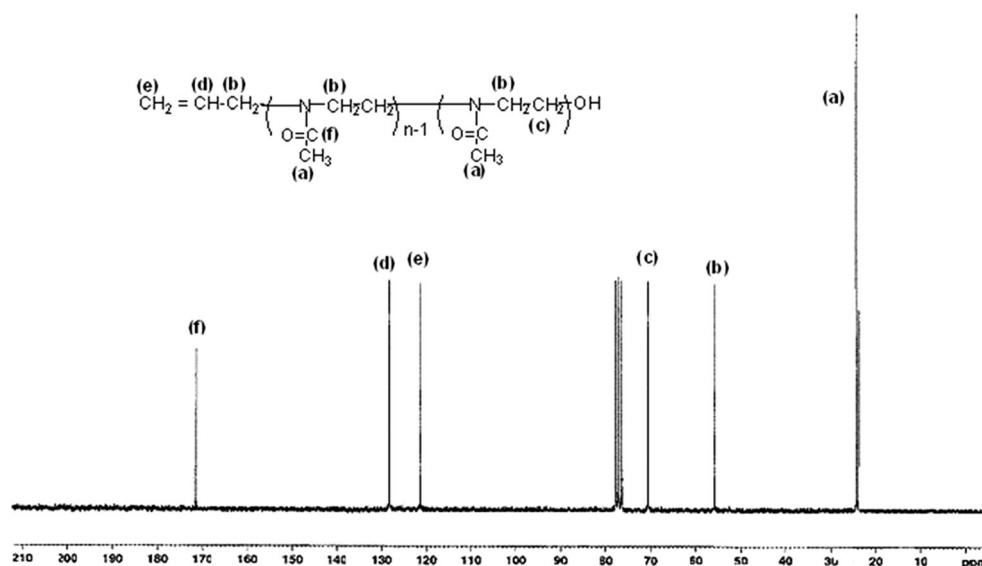
The  $^{13}\text{C}$  NMR spectrum (Fig. 8) presents six signals. The signals at 55.95 ppm and 70.64 ppm are due to carbons of  $\text{CH}_2\text{-N}$  and  $\text{CH}_2\text{-O}$ , respectively. Signals at 171.53 ppm and

23.83 ppm are assigned to carbonyl and methyl carbons of acetamido group, respectively. The signals e and d, at  $\delta=121$  and 128 ppm are assigned to carbons of vinyl group.

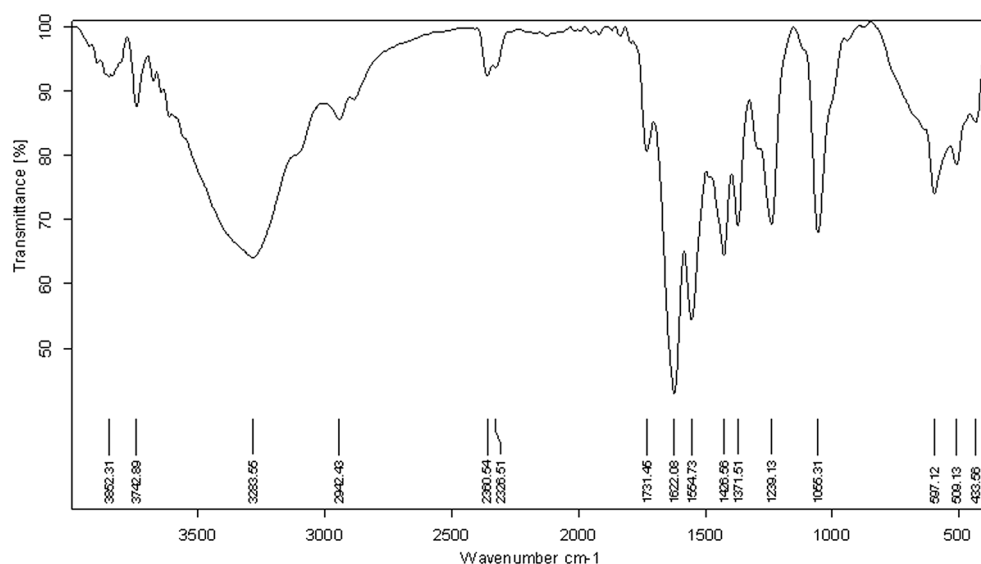
The IR spectrum (Fig. 9) of the product showed the disappearance of the absorption at  $1673\text{ cm}^{-1}$  due to  $\text{C}=\text{N}$  of monomer, the appearance of the new absorptions at  $1622\text{ cm}^{-1}$  and  $1731\text{ cm}^{-1}$  due to  $\text{C}=\text{O}$  of the acetamido and vinyl end group ( $\text{C}=\text{C}$ ). The large band between  $3100\text{ cm}^{-1}$  and  $3600\text{ cm}^{-1}$  is assigned to OH groups.

Mass spectroscopic analysis was carried out with MALDI-TOF (MS). Alpha-cyano-4-hydroxycinnamic Acid (HCCA) was added so that ionized molecular ions  $[\text{MH}]^+$  were pro-

**Fig. 8**  $^{13}\text{C}$ -NMR (200 MHz) spectrum of macromonomer PMOX-Allyle in  $\text{CDCl}_3$





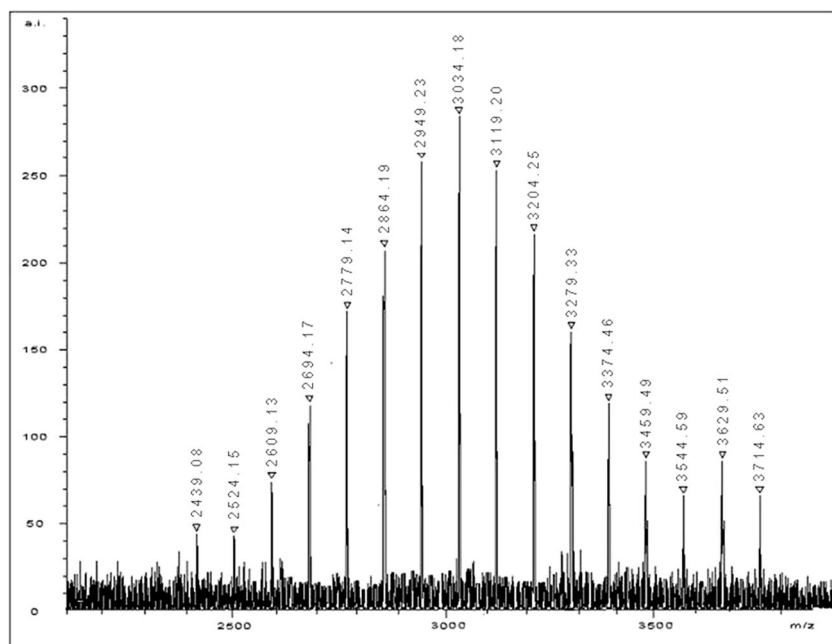
**Fig. 9** IR Spectra (4000–400  $\text{cm}^{-1}$ ) of PMOX-Allyle

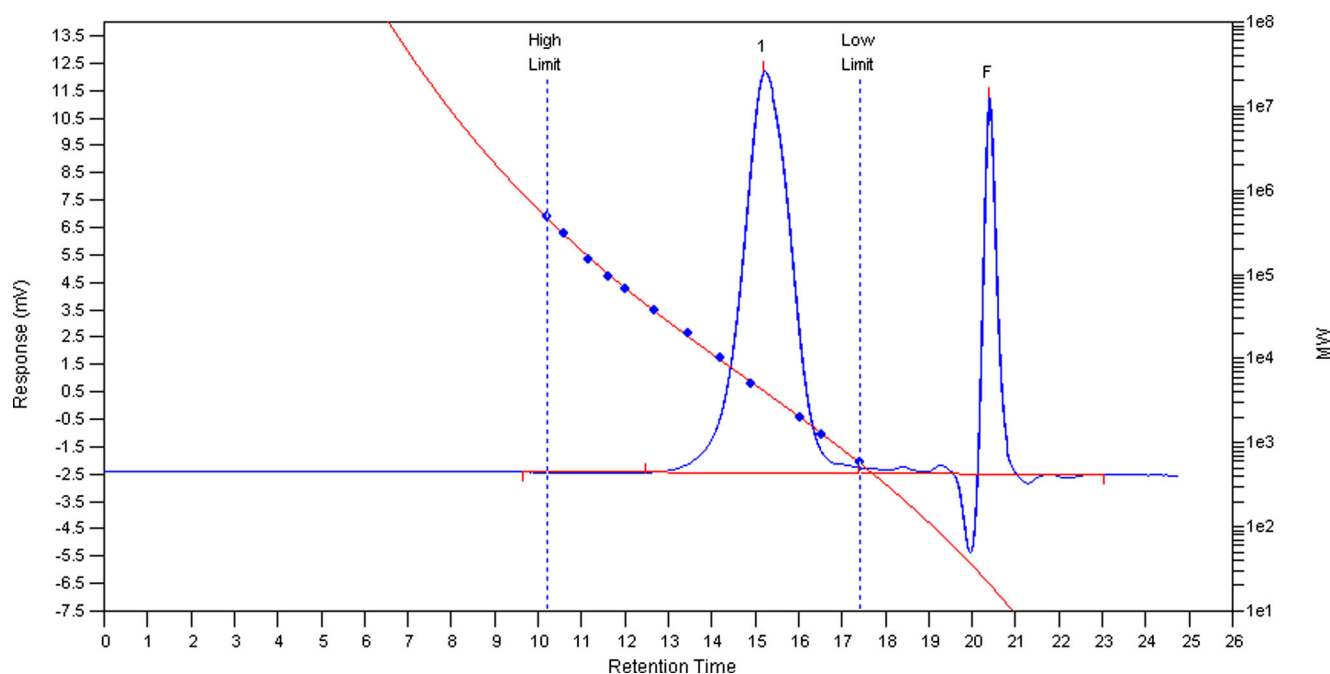
duced. The MS spectra provide qualitative distributions of various species in macromonomers. Most importantly, the spectra provide the positive structural information for the incorporation of one unit of the allylic group (AA), per polymer chain.

Figure 10 shows the MALDI-TOF MS spectrum (in linear mode) of polyMOX allyl-terminated obtained by the solution polymerization of MOX using Mag- $\text{H}^+$  in the presence of allyl chloride. It was confirmed that the repeating units have a mass of  $m/z$  85 mass units, which

corresponds to the mass of a 2-methyl-2-oxazoline monomer unit. Also, each peak of the MALDI-TOF MS correspond to the PolyMOX having one hydroxyl terminal structure with one  $\text{H}^+$  ion ( $\text{CH}_2=\text{CH}-\text{CH}_2-(\text{MOX})_n-\text{OH}$ ,  $\text{H}^+$ ) respectively.

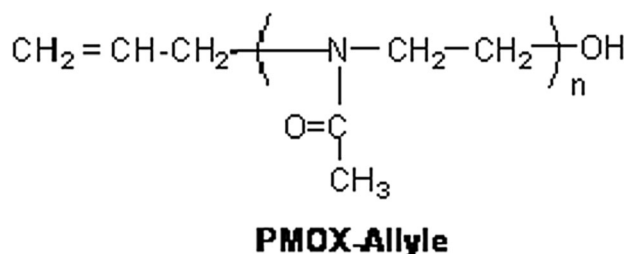
For PolyMOX allyl-terminated macromonomers, a major series of species A with  $\overline{M}_w$  of  $[58+85n]$  is identified. It corresponds to macromonomer species of  $[\text{AA}+n(\text{MOX})]$  (Fig. 10). This is confirmed by the GPC curve of the same sample (Fig. 11), where no peaks were observed at raised

**Fig. 10** MALDI-TOF MS spectrum of poly MOX-allyl obtained by the polymerization of MOX using 20 % of Mag- $\text{H}^+$  at 70 °C and for 8 h after precipitation into ether ( $\overline{M}_w = 3150$  g/mol,  $\overline{M}_n = 3050$  g/mol and  $I=1.03$ )



**Fig. 11** GPC chromatogram of poly MOX-allyl obtained by the polymerization of MOX using 20 % of Mag-H<sup>+</sup> at 80 °C and for 8 h ( $\overline{M}_w$  = 3900 g/mol,  $\overline{M}_n$  = 3220 g/mol and I=1.21)

elution volumes indicating the absence of macrocyclic groups, which, once again, shows that PolyMOX is linear.



From this data, we can calculate the values of  $M_w$ ,  $M_n$  and  $M_w/M_n$ , giving 3150, 3050 and 1.03 respectively. Results obtained from MALDI-TOF MS don't agree with those obtained from GPC, because the  $M_w$ ,  $M_n$  and  $M_w/M_n$  values, as obtained by SEC, are relative to the calibration standard polymer (polystyrene in our case) and those obtained by MALDI-MS are absolute molecular weights without a standard polymer [28].

## Conclusion

Cationic ring-opening polymerization of MOX in conjunction with an ethylenically unsaturated initiator as a modifier in the presence of an acid exchanged montmorillonite clay as catalyst provides a convenient synthesis of macromonomers. Characterizations show that macromonomers synthesized accordingly are terminated with ethylenically unsaturated group of modifier at one end of the polymer chain and a hydroxyl

group at the other end. macromonomer (PMOX-Allyl) were completely soluble in water and were produced by a very simple procedure. Through simple filtering the clay can be separated from the reaction mixtures. Moreover this acidic clay is inexpensive, stable and non corrosive.

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