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Macromonomers of epichlorohydrin and propylene oxide liquid polymers: synthesis and characterization

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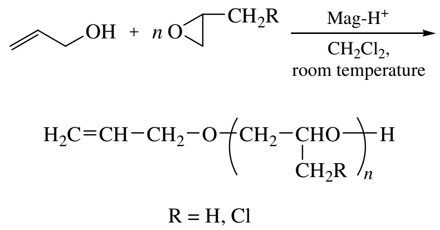
A mild and efficient catalytic method for the synthesis of allyl-terminated macromonomers from epichlorohydrin and propylene oxide derivatives in the presence of an acid-exchanged montmorillonite as a catalyst is described.

Macromonomers (defined as polymers with polymerisable entities at one or both chain ends and generally low molar masses) were shown to copolymerise with low molar mass monomers more than 40 years ago.[1] They were used for some applications.[2,3] Macromonomers have been employed for macromolecular engineering.[4,5] Macromonomers with various chemical structures are now accessible.[6] They can either be homopolymerised to yield comb polymers or copolymerised with a large number of comonomers to yield graft copolymers.

Graft copolymers are of interest as coatings, adhesives, emulsifiers, moisture retention agents, biomaterials, *etc*.[7,8]

Montmorillonites, a class of inexpensive and non-corrosive solid acids, have been used as efficient catalysts for organic reactions. Montmorillonite catalysts are easily recovered and reused.[9,10]

In continuation of our studies on environmentally benign methods using solid supports,[11–13] we report the synthesis of macromonomers *via* cationic ring-opening polymerization. Macromonomers are successfully synthesised by the polymerization of epichlorohydrin (ECH) and propylene oxide (PO) in conjunction with ethylenically unsaturated alcohols as modifiers. Allyl alcohol (AA) is chosen as a modifier for the synthesis of allyl-terminated macromonomers 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).[†]



Scheme 1 Ring opening polymerization of epoxides.

The ring-opening polymerization of 1,2-propylene oxide by a primary alcohol in the presence of Mag-H$^+$ satisfactorily proceeds to give linear polyPO with the controlled $\overline{Mn} < 3200$. The key feature of this polymerization may be the acidity of the added Mag-H$^+$, which is not as large to polymerise the monomer by itself but is sufficient to activate the monomer. To extend this facile method, we performed the ring-opening polymerization of PO and ECH to examine the $\overline{Mn}$ and $\overline{DPn}$ of the polymer. Tables 1 and 2 summarise the results of the polymerization of PO and ECH with allyl alcohol in the presence of Mag-H$^+$ as a catalyst. The polymerization did not proceed with allyl alcohol alone (Table 1, run 1), the addition of Mag-H$^+$ was quite effective to give polyECH macromonomers (EA) quantitatively (runs 2–5).

Polymerization conditions for the synthesis of macromonomers of ECH and PO polymers are shown in Tables 1 and 2. An ethylenically unsaturated modifier, AA, is employed to replace a conventional modifier, such as ethylene glycol or water.[14,15] Lower $\overline{Mw}$ macromonomers are free from cyclic oligomers.

As shown in Tables 1 and 2, when the ratios between monomers and an initiator are < 10, the $\overline{DPn}$ values of the product polymers are in good agreement with the calculated values (entries EA2, EA3 in Table 1 and PA1, PA2 in Table 2). With increasing monomer-to-initiator ratios above 10, the $\overline{DPn}$ values become smaller than the calculated values (entries EA4, EA5 in Table 1 and PA3, PA4 in Table 2). These observations are probably due to the presence of moisture in the polymerization system at larger monomer/initiator ratios. Kadakowa *et al.*[16] obtained similar results in the polymerization of lactones by Sn-montmorillonite in the presence of ethanol as an initiator.

The structures of macromonomers were determined by ^{1}H NMR and FT IR spectroscopy, GPC and MALDI-TOF mass spectrometry. The NMR and IR spectra of macromonomers show characteristic chemical shifts and absorption bands, respectively, corresponding to polyECH glycol,[11] polyPO[12] and the incorporation of the ethylenically unsaturated group of the modifier. The FT IR spectra of allyl-terminated macromonomers show weak absorption bands at 1650 and 3080 cm^{-1} for the C=C stretching vibrations of the allyl group. Chemical shifts in the ^{1}H NMR spectra of macromonomers corresponding to the terminal unsaturated groups are given below.

Table 1 Synthesis conditions of the polyECH macromonomers (EA); $T = 20$ °C, $t = 24$ h.

Entry	[ECH]$_0$/[AA]$_0$	Conversion (%)	$\overline{Mn}^a$	$\overline{Mn}_{\mathrm{NMR}}$	$\overline{Mn}_{\mathrm{Theo}}$	$\overline{DPn}$	$\overline{Mw}/\overline{Mn}$
EA1	5	0	—^{b}	—^{b}		—^{b}	—^{b}
EA2	5	97	506	510	520	4.84	1.17
EA3	10	94	927	900	983	9.4	1.24
EA4	15	96	1120	1100	1445	11.48	1.27
EA5	20	98	1460	1420	1908	15.15	1.20

^{a}Determined by GPC. ^{b}Not determined.

Table 2 Synthesis conditions of the polyPO macromonomers (PA); $T = 20$ °C, $t = 24$ h.

Entry	[PO]$_0$/[AA]$_0$	Conversion (%)	$\overline{Mn}^a$	$\overline{Mn}_{\mathrm{NMR}}$	$\overline{Mn}_{\mathrm{Theo}}$	$\overline{DPn}$	$\overline{Mw}/\overline{Mn}$
PA1	5	96	336	305	348	4.8	1.24
PA2	10	98	626	612	638	9.8	1.21
PA3	14	95	660	620	870	10.37	1.25
PA4	29	92	1430	1390	1740	23.65	1.29

^{a}Determined by GPC.

For macromonomer EA2, the signals *a* and *b*, at δ 5.3–6.0 ppm (ABX) are assigned to the vinyl group. The relative intensity of these signals was 2:1, indicating that the polymerization was initiated by allyl alcohol with incorporation of the allyl end group at the initiating site of the polymer chain. The degree of polymerization ($\overline{DPn}$), therefore, was calculated by the integrated ratio of the signal due to the methine end group to the signals due to the polymer main chain. Signal *c* at 2.7 ppm is assigned to methylene protons adjacent to the vinyl group. Signals *d*, *e*, *f*, *g* and *h* at 3–4.2 ppm are assigned to methylene and methine protons linked to the oxygen atom (Figure 1).

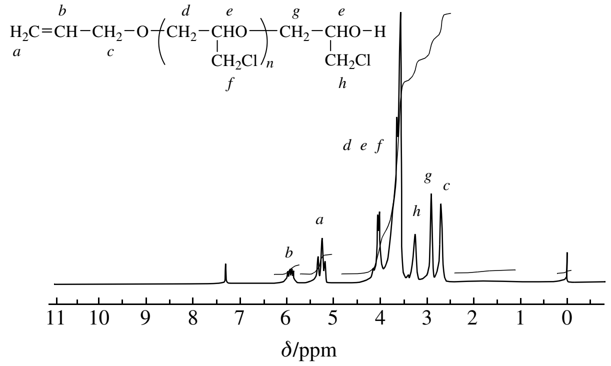


Figure 1 ^{1}H NMR (300 MHz) spectrum of macromonomer EA2 in CDCl$_3$.

For macromonomer PA1, the signals *a* and *b* at δ 5.3–6.0 ppm (ABX) are assigned to the vinyl group. Signal *c* at 3.8 ppm is assigned to methylene protons adjacent to the vinyl group. Signals *d* and *e* at 3.0–3.7 ppm are assigned to methylene and methine protons linked to the oxygen atom. Signal *f* at δ 1 ppm is assigned to methyl protons adjacent to the methine group (Figure 2).

The molecular weights of the macromonomers calculated based on NMR spectra were in agreement with the molecular weights obtained by GPC (Tables 1 and 2). These results support the presence of one vinyl group per molecule. The polydispersities (PD = $\overline{Mw}/\overline{Mn}$), as determined by GPC, were relatively narrow (PD ≤ 1.29), which is in agreement with a living polymerization process with fast initiation.

Mass-spectrometric analysis was carried out using a MALDI-TOF technique. Sodium iodide was added so that the molecular ions [MNa]$^+$ were produced. The MS spectra provide qualitative distributions of various species in macromonomers. Most

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[†] *Materials.* 1,2-Propylene oxide (PO) (Aldrich), 1,2-epoxy-3-chloropropane (epichlorohydrin, ECH) and allylic alcohol (AA) (Merck) were dried over calcium hydride and distilled under reduced pressure before use. Montmorillonite clay was obtained from ENOF Maghnia (Algeria). The Montmorillonite-H$^+$ (Mag-H$^+$) was prepared as described by Yahiaoui *et al.*[11–13]

^{1}H and ^{13}C NMR measurements were carried out on a 300 MHz Bruker NMR spectrometer equipped with a probe BB05 mm in CDCl$_3$. TMS was used as an internal standard. Average molecular weights and molecular weight distributions of different polymers were measured using gel permeation chromatography (GPC) on a system equipped with a Spectra SYSTEM AS1000 auto sampler. The MALDI-TOF mass spectra were recorded on a Bruker Biflex III instrument equipped with a nitrogen laser (λ = 337 nm) at an acceleration voltage of 19 kV. The irradiation targets were prepared from THF or CH$_2$Cl$_2$ solutions with dithranol as a matrix.

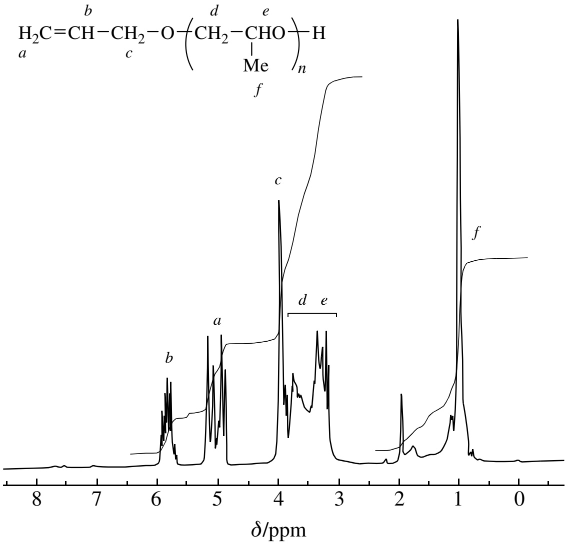
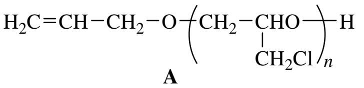


Figure 2 ^{1}H NMR (300 MHz) spectrum of macromonomer PA1 in $CDCl_3$.

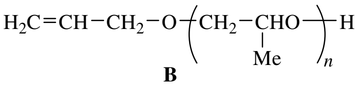
importantly, the spectra provide positive structural information for the incorporation of one unit of the ethylenically unsaturated modifier allylic alcohol per polymer chain.

Figures 3 and 4 show the MALDI-TOF mass spectra (in linear mode) of polyECH allyl-terminated and polyPO allyl-terminated obtained by the solution polymerization of ECH and PO (2 M) using 2% Mag-H$^+$ at 20 °C for 24 h in the presence of allylic alcohol, respectively. In the two cases, it was confirmed that the repeating units have *m/z* 92.5 and 58, which correspond to the molecular weights of ECH and PO monomers, respectively. Each peak of the MALDI-TOF MS corresponds to polyECH and polyPO having one hydroxyl terminal structure with one Na$^+$ ion [CH_2=CH–CH_2–$(ECH)_n$–OH, Na$^+$], respectively.

For polyECH allyl-terminated macromonomers, a major series of species **A** with $\overline{M}w$ of [58 + 92.5*n*] is identified. It corresponds to macromonomer species of [AA + *n*(ECH)] (Figures 5 and 6). For polyPO allyl-terminated macromonomers, a major series species **B** with $\overline{M}w$ of [58 + 58.08*n*] is identified. It corresponds to a second macromonomer species of [AA + *n*(PO)] (Figure 4).


$\mathrm{H_2C{=}CH{-}CH_2{-}O{-}(CH_2{-}\underset{CH_2Cl}{CHO})_n{-}H}$

A


$\mathrm{H_2C{=}CH{-}CH_2{-}O{-}(CH_2{-}\underset{Me}{CHO})_n{-}H}$

B

The molecular structure of macromonomers determined by MALDI-TOF agreed with that determined by ^{1}H NMR spectroscopy.

In conclusion, the cationic ring-opening polymerization of ECH and PO in conjunction with an ethylenically unsaturated alcohol as a modifier in the presence of an acid-exchanged montmorillonite clay (Mag-H$^+$) as a catalyst provides a convenient synthesis of macromonomers. Characterizations show that the macromonomers synthesised are terminated with an ethylenically unsaturated group of the modifier at one end of the polymer chain and a hydroxyl group at the other end. The structures of macromonomers are consistent with the non-conventional mechanism discussed here. The polymer chains propagate from the hydroxyl group of a modifier through polyaddition of monomers. This approach to the synthesis of macromonomers is not limited to ECH and PO. We successfully used this method for the synthesis of macromonomers of polyethers based on other heterocyclic monomers and copolymers of THF.

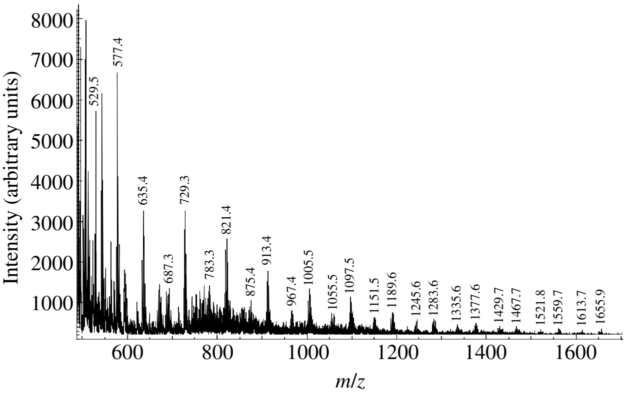


Figure 3 MALDI-TOF mass spectrum of polyECH macromonomer EA5.

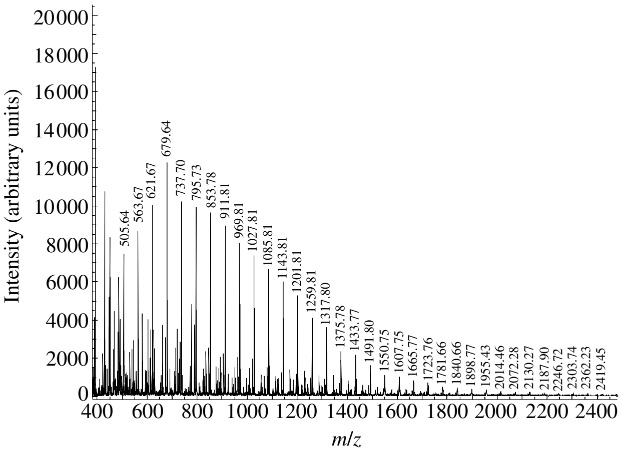


Figure 4 MALDI-TOF mass spectrum of macromonomer PA4.

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