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Ring opening polymerization of glycidyl methacrylate by Maghnite-H^+ a solid catalyst

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ABSTRACT

In the present work the ring-opening polymerization of glycidyl methacrylate (GMA) using Maghnite-H^+, a proton exchanged montmorillonite clay as initiator is reported. The influences of solvent, weight ratio of initiator/monomer and reaction time on the conversion of monomer and on the molecular weight are investigated. Increasing Maghnite-H^+ proportion increases (GMA) conversion and decreases the average molecular weight of resulted polymer. A cationic mechanism for the reaction was proposed.

Keywords: *Maghnite, glycidyl methacrylate, GMA, ring opening polymerization*

1. Introduction

In recent years, polymers based on 2,3-Epoxypropyl methacrylate (glycidyl methacrylate or “GMA”) have received increasing attention[1-7]. GMA seems to be a suitable monomer having cationically polymerizable epoxy group and radically polymerizable methacrylate double bond. Interestingly, polymerization of this monomer via ring opening of the epoxy group has been subjected only in few papers [8]. Yan and coworkers described synthesis of amphiphilic block copolymers by cationic ring opening of the epoxy group of GMA in presence of poly(ethylene glycol) [9]. Bicak et al. have described simultaneous ring opening of the epoxy group of GMA with succinic anhydride, yielding photocurable polyesters [10]. Recently, Karagoz, et al, have synthesized novel fast photocurable copolyethers with methacylate pendant groups [11]. The ring opening polymerization of oxiranes has been usually conducted by the use of cationic species [12–15], and the uses of various solid materials to induce oxiranes polymerization have been also well known [16, 17]. In the solid catalysts, several derivatives based on silica such as aluminium minerals and zeolites are reported. Minerals and zeolites are reported to be effective for the ring opening reaction leading to 1,2-difunctionalized compounds from oxiranes [18–23].

The present work is concerned by a new solid catalyst. The cationic ring opening polymerization of GMA was induced by Maghnite-H^+ [24], a proton exchanged montmorillonite clay, to produce polyethers with methacrylate pendant groups. This new solid non-toxic cationic catalyst has exhibited higher efficiency via the polymerization of vinylic and heterocyclic monomers [25–29]. Techniques such as ^1H NMR, and IR, were used to characterize the products of the

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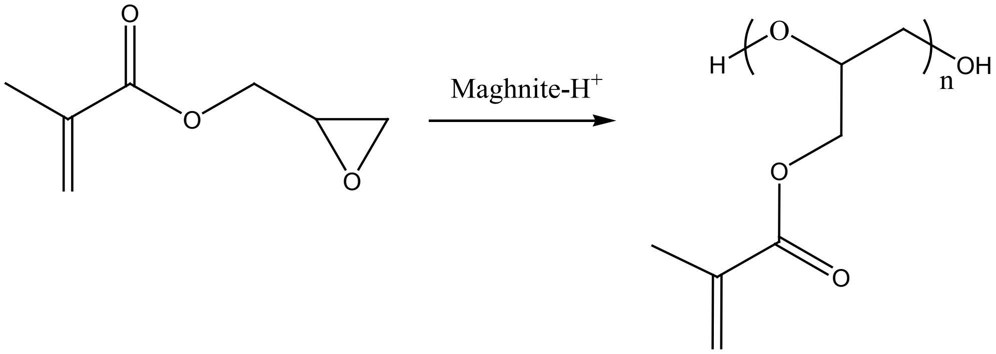
reaction. The effects of catalyst/monomer weight ratio and time on monomer conversion and polymer average molecular weight were also studied.



Scheme1: Ring opening polymerization of glycidyl Methacrylate by Maghnite-H$^+$.

2. Experimental section

2.1. Materials. Glycidyl methacrylate (Sigma-Aldrich): After passing through a column of alumina to remove the inhibitor, GMA, was distilled prior to use. Tetrahydrofuran (THF) was distilled over the blue benzophenone–Na complex. Carbon tetrachloride, dichloromethane and chloroform were dried over CaH_2 and distilled on the day of the experiment. Cyclohexane, acetone and acetonitrile were used as received. Raw-Maghnite: Algerian montmorillonite clay was procured from "BENTAL" (Algerian Society of Bentonite).

2.2. Preparation of Maghnite-H$^+$. Maghnite-H$^+$ was prepared according to the process reported in our previous study [24-26]. Raw-Maghnite (20 g) was crushed for 20 min using a prolabo ceramic balls grinder. It was then dried for 2 h at 105 °C. The Maghnite was placed in an Erlenmeyer flask together with 500 ml of distilled water. The Maghnite/water mixture was stirred using a magnetic stirrer and combined with 0.25 M sulfuric acid solution, until saturation was achieved over 2 days at room temperature. The mineral was then washed with distilled water to became sulfate free and then dried at 105 °C.

2.3. Kinetics procedure. The ring opening bulk polymerization of GMA was carried out in sealed tubes. Each tube contained a mixture of 1 g of GMA and an amount of Maghnite-H$^+$. The mixtures were kept in thermostat at desired temperature and stirred with a magnetic stirrer under dry nitrogen. The reaction was terminated by distilled water. The resulting polymer was extracted with dichloromethane, precipitated into cyclohexane and was dried in a muffle at room temperature and under vacuum all night. The monomer conversion was determined gravimetrically by weighing the precipitated polymer.

2.4. Polymer characterization. Measurements of ^1H NMR spectra were conducted in D_2O solution, under ambient temperature on an AM 300 FT Bruker spectrometer using tetramethylsilane (TMS) as internal standard. IR absorption spectrum was recorded on an ATI Matson FTIR No 9501165 spectrometer using the KBr pressed disc technique. Gel permeation chromatography (GPC) was performed with a Spectra-Physics chromatograph, equipped with four columns connected in series and packed with Ultrastyragel 103, 104, 105, 106 Å. Tetrahydrofuran (THF) was used as solvent and the instrument was calibrated to a first approximation with polystyrene of known molecular weights. Viscosity measurements were carried out with an Ubbelohde capillary viscosimeter (viscologic TI1, version 3-1 Semantec). Intrinsic viscosity, [η] (ml/g), was measured at 25°C in THF.

3. Results section

Montmorillonites have both Brønsted and Lewis acid sites and when exchanged with cations having a high charge density, as protons, produce highly active catalysts for acid-catalysed reactions [27]. It have been demonstrated that intercalated organic molecules on the surface of Montmorillonite are mobile and can be highly polarize when situated in the space between the charged clay layers [19–21,25]. The present study examines the catalytic activity of Algerian proton exchanged montmorillonite clay via GMA cationic ring opening polymerization.

The structure and the composition of the catalyst were previously reported [19, 20]. It was demonstrated that there is an excellent correlation between the acid treatment and the catalytic activity of Maghnite [24]. It was reported that best values of monomer conversions were obtained with Maghnite-H^+ which has been produced by treatment of raw-Maghnite with 0.25 M sulphuric acid solution. This treatment leads to a complete saturation of montmorillonite with protons, without destruction of the catalyst structure [28, 29].

3.1. Ring opening bulk polymerization of GMA. The cationic ring opening bulk polymerization of GMA was examined in the presence of Maghnite-H^+ at 20 °C (Scheme 1). The results are shown in Table 1 and Figure. 1. The proof for this polymerization was obtained by IR, and ^1H NMR spectroscopy (Figures. 2 and 3).

Table 1: Experimental Results of the GMA Polymerization, T=20°C, Time 72h.

m $_{(GMA)}$(g)	m $_{Maghnite\text{-}H+}$ (g)	Conversion%	Mw	Mn	Mw/Mn
10	2	65,5	2700	2150	1.25

The IR measurements of the product are in a good agreement with poly(GMA) structure (figure 2). The characteristic vibrations of linear ester, carbonyl groups (C=O) and (C-O) bands, are observed respectively at 1718 cm^{-1} and 1172 cm^{-1}. The peak associated to C=C double bonds was observed at 1635 Cm^{-1}. A new large band at 3411 cm^{-1} appeared in the spectra of poly (GMA) due to OH hydroxyl groups at the ends of polymer chain. ^1H NMR measurements (Figure 3), confirm the structure of poly(GMA) that resulted from the reaction of polymerization. As shown in ^1H NMR spectrum of the product, signals of untouched double bond were observed as doublet at 6.1 ppm (cis-H) and 5.6 ppm (trans-H). The typical singlet of methyl group of the methacrylate unit appears at 1.9 ppm. The proton signals of COO–CH_2, –CHO and –CH_2O– groups are observed respectively at 4.2, 3.7 and 3.4 ppm.

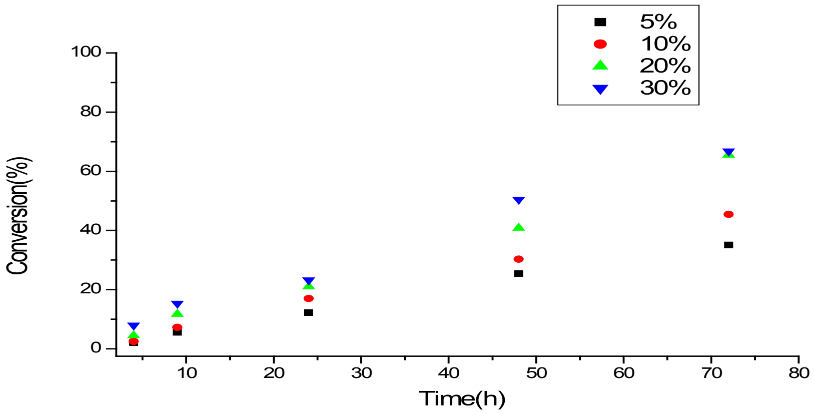


Figure 1: Effect of catalyst proportion upon the conversion of Glycidyl Methacrylate , T=20°C.

3.2. Effect of Maghnite-H$^+$/Monomer weight ratio. Figure 1 and Table 2 show the effect of Maghnite/Monomer weight ratio on the conversion of GMA and on molecular weight of the resulted polymer (expressed by intrinsic viscosity) respectively. Indeed, using various amounts of Maghnite-H$^+$ (5, 10, 20, and 30% by weight) the polymerization of GMA was carried in bulk at 20 °C. It can be noted that increasing the weight ratio Maghnite-H$^+$/GMA increases the conversion of monomer to polymer and decreases the molecular weight of the resulting polymer. These results show the effect of Maghnite-H$^+$ as a cationic catalyst. Similar results were obtained by Belbachir et al. [24, 25] in the polymerization of isobutylene by Maghnite-H$^+$, which polymerizes only by a cationic process [30].

Table 2 : Effect of Catalyst/Monomer weight ratio on the polymerization of Glycidyl Methacrylate, T=20°C, Time 72h.

Catalyst/Monomer weight ratio (%)	5	10	20	30
Conversion (%)	35.12	45.2	65.5	66.8
Intrinsic viscosity [η](ml/g)	5.57	4.37	3.33	3.07

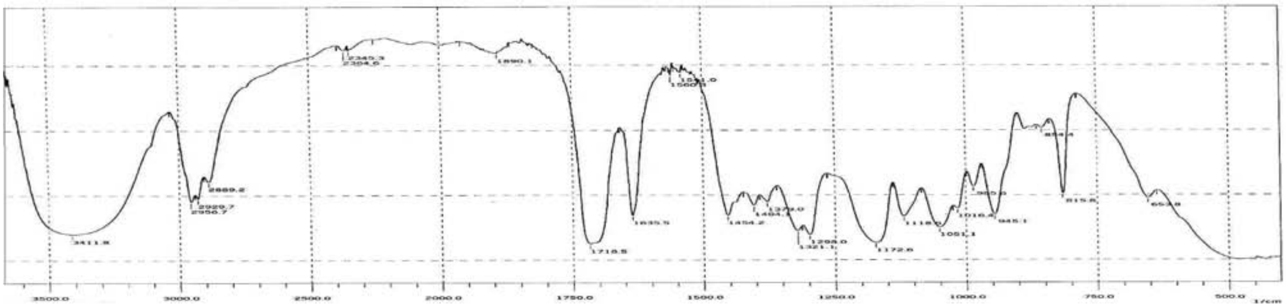


Figure 2: IR spectrum of the resulted Poly(Glycidyl Methacrylate).

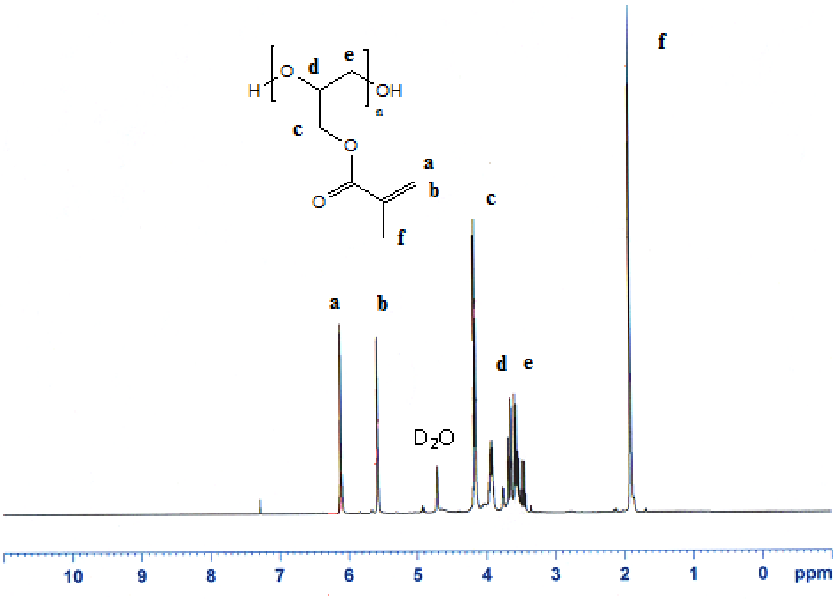


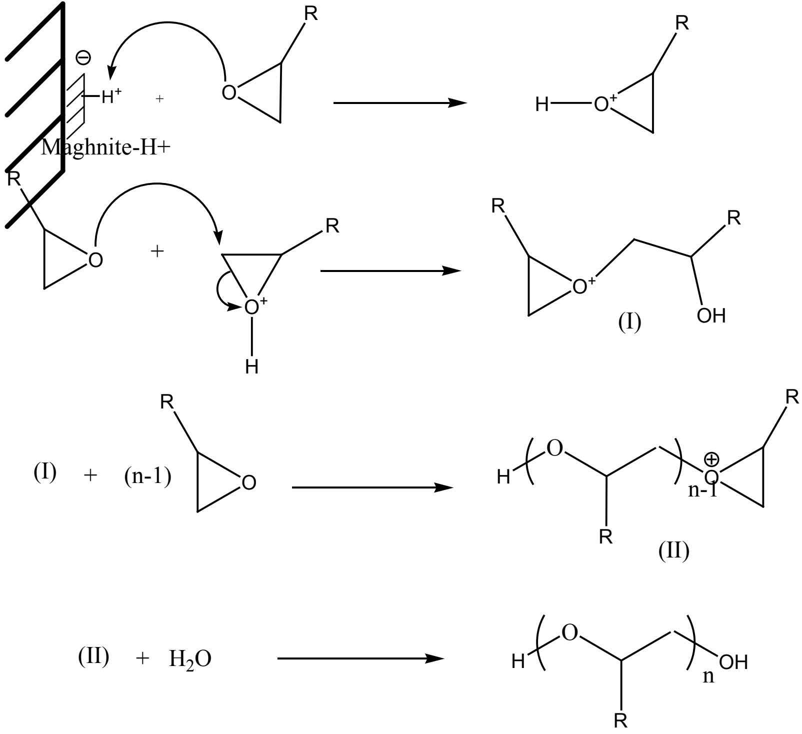
Figure 3: ^{1}H NMR spectrum of the resulted Poly(Glycidyl Methacrylate)

3.3. Effect of solvent on the polymerization. Data in Table 3 show that polymerization carried out in solution lead to higher molecular weights (expressed by higher intrinsic viscosities) However, conversions in solution were smaller than the ones obtained in bulk polymerization. Low conversions in solution polymerization may be explained by ‘‘the initiating active sites’’ of Maghnite-H$^+$ at the surface of Maghnite-H$^+$. Conversions of monomer obtained in non polar solvents were more important than those obtained in polar solvents. This result is due to catalyst structure; as all mineral clays, the Maghnite-H$^+$ shows an affinity over polar particles and in this case, adsorbed molecules of polar solvent reduce the contact between the monomer and the ‘‘initiating active sites’’, and lead to low GMA conversions.

3.4. Mechanism of the reaction. 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 Maghnite-H^+ (Scheme 2). Protons carried by montmorillonite sheets of Maghnite-H^+ induce the cationic polymerization; these montmorillonite sheets take place as counter-anions. Propagation and termination then take place by conventional cationic ring opening mechanism. Termination can be caused by H_2O molecules added at the end of reaction.

Table 3: Effect of solvent on the polymerization of Glycidyl Methacrylate, T=20°C, Time 72h,Catalyst/Monomer weight ratio = 20%.

Solvent	CCl_4 (ε=2.24)	$CHCl_3$ (ε=4.81)	CH_2Cl_2 (ε=8.98)	Acetone (ε=20.7)	Acetonitrile (ε=37.5)
Conversion(%)	33.5	27.3	21.5	11	9
Intrinsic viscosity [η](ml/g)	1.80	1.84	3.50	5.97	13.15



Scheme 2: Mechanism of the ring opening polymerization of Glycidyl Methacrylate catalyzed by Maghnite-H^+

4. Conclusions

Maghnite-H^+, proton exchanged montmorillonite clay, is an effective solid catalyst for the ring opening polymerization of GMA. In this polymerization, the solid catalyst was thought to act as an acid to generate cation species. Two main advantages were shown in the polymerization system using the solid acid Maghnite-H^+: that the catalyst could be removed from the mixture of the products by simple filtration and recycled without a loss of catalytic activity. The resulted polyether with pendent methacrylate groups seems to be a promising material for preparation of block and grafted copolymers based on poly (GMA).

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