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A Green Catalyst for Synthesis of Bis-macromonomers of Poly (Styrene Oxide)

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ABSTRACT

The synthesis of macromonomers is made by anhydrides to prevent the reducing average molecular weight of synthesized polymers and obtain poly α, ω unsaturated (styrene oxide) more stable, using a proton exchanged montmorillonite clay called Maghnite-H^+, which is an effective green catalyst useful for the pollution prevention and the protection of environmental. The Maghnite-H^+ is used as a heterogeneous polymerization catalyst for the styrene oxide cationic polymerization to synthesis poly(styrene oxide) in solution (dichloromethane) at temperature 20°C in the presence of methacrylic anhydride. We have examined the structures of modified montmorillonite using X-ray Diffraction (XRD), and the effect of the amount of catalyst and methacrylic anhydride on yield of polymer was investigated. We have characterized the polymers by Infrared Spectroscopy (IR) and Nuclear Magnetic Resonance (NMR), gel permeation chromatography (GPC) and Differential Scanning Calorimetry (DSC).

Keywords: Green chemistry, Maghnite-H^+, Cationic polymerization, Poly(styrene oxide), Macromonomers

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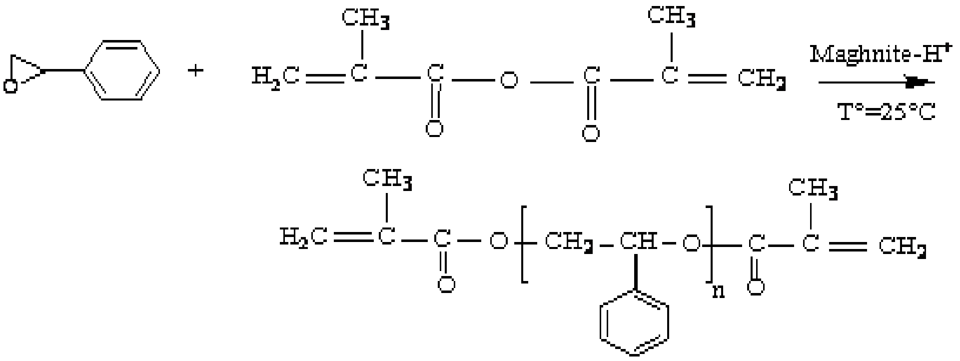
INTRODUCTION

Green chemistry is mainly concerned to the pollution prevention through the minimization of waste and the toxic avoidance and hazardous substances in the production and application of chemicals products [1]. The heterogeneous catalyst is a green catalyst and a topical subject; most of the initiators used in the synthesis of polymers are expensive. They may be poisoned by products of the reaction or impurities present in the monomer feed [2], this forms environmental disposal problems for the user. The Maghnite-H^+ is non-toxic available eco-catalyst and has great efficiency as catalyst system for cationic polymerization of a number of vinylic and heterocyclic monomers [2-5].

Styrene oxide has been synthesized by the epoxidation of styrene reaction; it is considered a main organic intermediate in the synthesis of the fine chemicals and the pharmaceuticals [6]. It has also been used to make a polymer with linoleic acid dimer, ethylene diamine and 2-éthoxyethylacetate [7]. The boron trifluoride is able to catalyzing catalyze the polymerization of alkyleneoxide such as phenyloxiranne (epoxystyrene) who has been polymerized either by cationic or anionic catalysts [8]. The polymerization of styrene oxide has been conducted under severe polymerization conditions, such as higher temperature, longer polymerization time, and vacuum conditions [9,10]. A various works studied the applications of poly(styrene oxide) in versatile areas such as hydrophobic nanocarriers for drug delivery, block copolymer micelle formation in water [11]; coating materials, surface modifiers [12] and in the production of polystyrene carbonate [13]. The preparation of graft copolymers by the usage of macromonomers has been extensively studied, where the use of macromonomers method provides an excellent means of designing graft copolymers of controlled structure [14,15].

In the present experimental study, we carry out an approach to synthesize poly(styrene oxide) bis-macromonomers in one stage. The Maghnite-H^+ is used as a heterogeneous polymerization catalyst for the styrene oxide cationic polymerization to synthesize poly(styrene oxide) in solution (dichloromethane) at 20ºC in the presence of methacrylic anhydride (Scheme 1).



Scheme 1: Ring-opening polymerization of styrene oxide by Maghnite-H$^+$ catalyst in presence of methacrylic anhydride in dichloromethane

EXPERIMENTAL

Reagents

Styrene oxide, methacrylic anhydride, dichloromethane, and methanol are purchased from Aldrich and used as received. The montmorillonite-H$^+$ (Mag-H$^+$) is prepared.

Preparation of Mag-H$^+$

Maghnite-H$^+$ is prepared according to the process described in the experimental study of Belbachir and Bensaoula [3]. It is activated with a sulfuric acid solution to give rise a Maghnite exchanged with protons, called Mag-H$^+$ (0.23 M). In an Erlenmeyer flask, crushed raw Maghnite (30 g) is dispersed in a volume of distilled water (120 mL). The mixture is stirred by using a magnetic stirrer for 2 h at room temperature. Then, the solution of sulfuric acid 0.23 M (100 ml) is added. Thus, the obtained solution is maintained 2 d under stirring and then the mineral is filtered off and washed several times with distilled water up to pH 7. After filtration, the Mag-H$^+$ is dried in an oven for 24 h at 105°C and is then crushed.

Experimental procedure

Considering the exothermicity of the reaction of synthesis of poly(styrene oxide) in bulk, we preferred to work in solution (dichloromethane), for that bearing on the effect of solvent on polymerization is carried out.

Synthesis of α-ω methacryloyloxy poly(styrene oxide) in solution

We have prepared four mixtures given in Table 1. Each mixture is composed by 6 g (0.05 mol) of styrene oxide and 0.3 g of Mag-H$^+$ (5% by weight), using various quantities of methacrylic anhydride of 0.05 10^{-3}, 2.5 10^{-3}, 5 10^{-3} and 10 10^{-3} mol. For each mixture, 40 ml of CH_2Cl_2 are added. The reaction mixtures are stirred for 24 h at room temperature. The effect of the amount of catalyst and the methacrylic anhydride on yield of polymer is investigated.

Table 1: Yields of poly(epoxystyrene) synthesized in dichloromethane with methacrylic anhydride for 5% of maghnite-H$^+$ and 0.05 mol of epoxystyrene with time=24 h at temperature of 20°C

Experiment	Epoxystyrene (mol)	Methacrylic anhydride (mol)	Mag-H$^+$ (g)	Yield (%)
1	0.05	0.05 10^{-3}	0.15	80
2	0.05	2.5 10^{-3}	0.15	76
3	0.05	5 10^{-3}	0.15	67.77
4	0.05	10 10^{-3}	0.15	64

RESULTS AND DISCUSSIONS

Structural characterization

Natural clay cannot be the effective catalyst, its modification with acid activation results activated clay. It is proven effective according to the literature. One of the most common chemical modifications of the clays is activation by the acids. This consists of treatment of clay usually with acids HCl or H_2SO_4 solution to get dissolved material of increased surface area, porosity and surface acidity [16].

The XRD shows that the Maghnite belongs to the montmorillonite clays group [17-19]. The XRD determines the interlayer spacing after activation of clay. The diffractograms of Maghnite-H$^+$ (XRD of Mag-H$^+$ 0.23 M) are given in Figure 1. From this plot, the intense stripes are observed around the angle θ=6.05, and the interlayer distance (d=14.23 Å) corresponding to the treated Maghnite is larger than the raw Maghnite (11.45 Å). A typical reaction product poly(styrene oxide) bearing methyl methacrylate end groups is characterized by Infrared Spectroscopy (IR), nuclear magnetic resonance (^{1}H-NMR,^{13}C-NMR), Gel Permeation Chromatography (GPC) and Differential Scanning Calorimetry (DSC). The α-ω methacryloyloxy-poly(styrene oxide) is obtained by ring opening polymerization of styrene oxide in the presence of methacrylic anhydride catalyzed by Mag-H$^+$. Each methacrylate group being linked to the polymer chain–end. Therefore, we have found that the IR spectra of our polymer and the characterized poly(styrene oxide) by ^{1}H, ^{13}C NMR appear identically to whose synthesized with other catalysts [20]. The methacrylate end groups are clearly visible in the ^{1}H-NMR spectrum in (1.97 ppm, 5.67 ppm, 6.22 ppm) signals and IR spectrum in (1602.68, 1721.79 cm^{-1}) of telechelic poly(styrene oxide) as shown in Figures 2 and 3. The ^{1}H-NMR spectroscopy confirms the structure of our polymer under study.

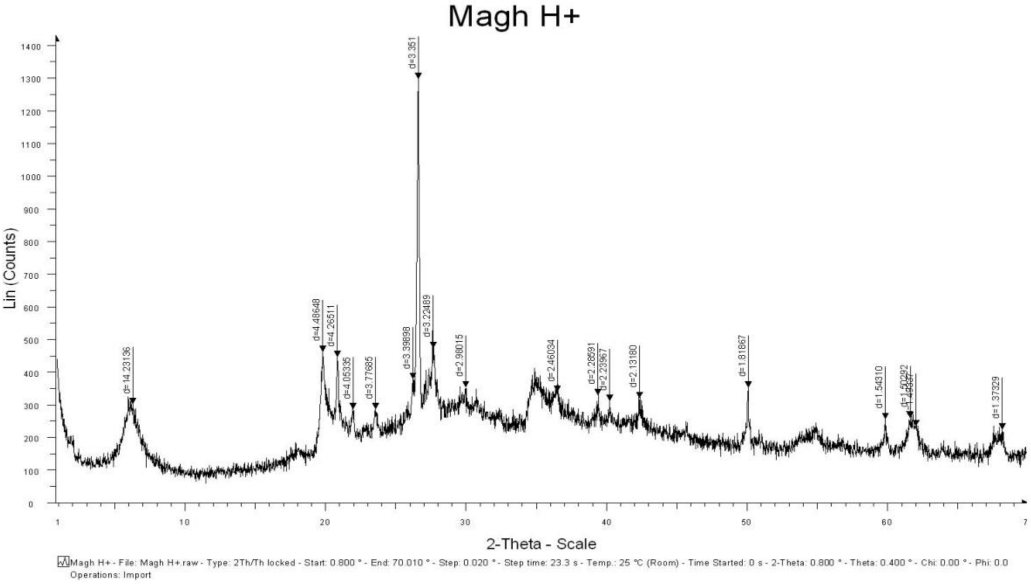


Figure 1: XRD diffractograms of Mag-H^+ (0.23 M)

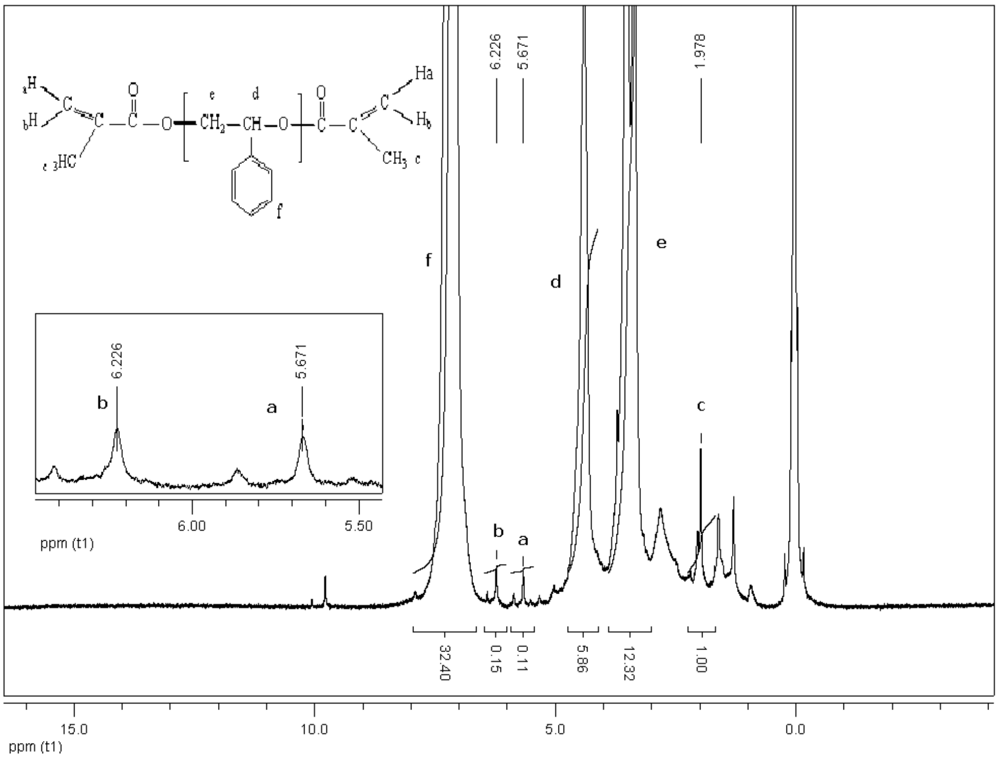


Figure 2: ^{1}H-NMR spectrum (300 MHz) of α-ω methacryloyloxy poly(styrene oxide) in $CDCl_3$

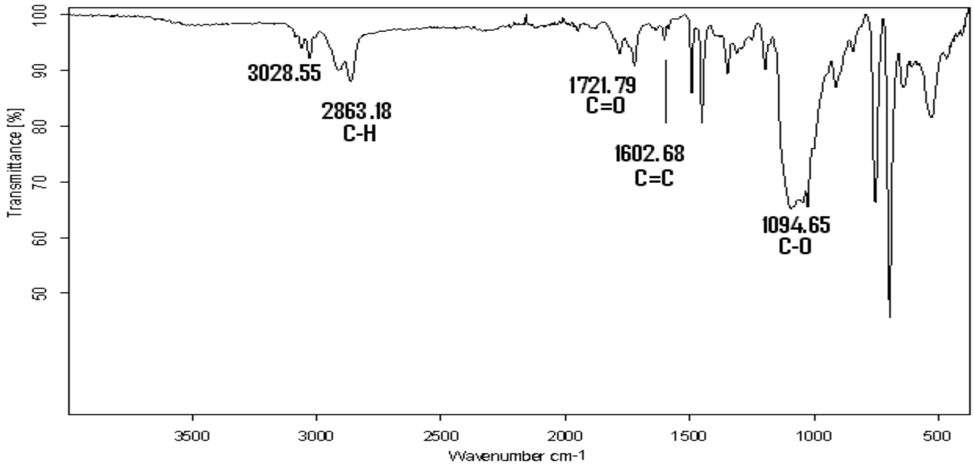


Figure 3: IR spectrum of α-ω methacryloyloxy poly(styrene oxide) (Alpha. Bruker ATR Diamant)

The ^{13}C-NMR spectrum of poly(styrene oxide) was previously studied by Kobayashi et al. [21]. For our poly(styrene oxide), the Figures 3 and 4 depicts the presence of carbons of the methacrylate, the carbon of methyl resounds in 18 ppm, the methylen in 127 and 135.7 ppm, and the carbonyl resounds in 170.3 ppm. According to the ^{13}C NMR measures, we have found that our polymer has a regular structure as both region and stereo, which is consistent to the result of poly(styrene oxide) found by Misaka et al. [22] and Brocas et al. [23]. The styrene oxide is notably less reactive than aliphatic and other alicyclic epoxides, but it undergo ring-opening with acids and bases [13].

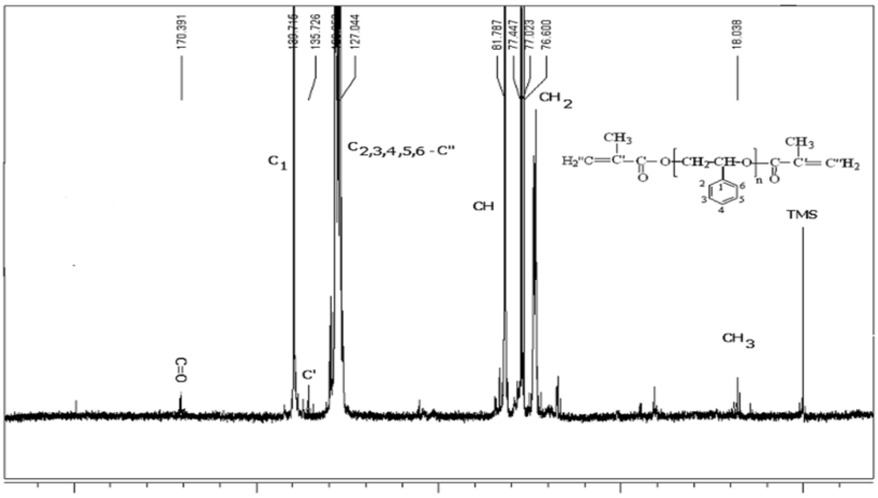


Figure 4: ^{13}C-NMR spectrum (300 MHz) of α-ω methacryloyloxy poly(styrene oxide) in CDCl$_3$

In the presence of methacrylic anhydride catalyzed by Mag-H$^+$, the design telechelic poly(1,3-dioxolane) (PDXL) was prepared in two stages by cationic ring-opening polymerization of 1,3-dioxolane (DXL) [24]. In our experimental work, we have synthesized the α-ω methacryloyloxy poly(styrene oxide) macromonomer in a single stage. The Table 2 shows that the increase of maghnite-H$^+$ proportion leads to an increase in the polymerization yield as shown in Figure 5. However, the Figure 6 depicts that the yield increases when the proportion of methacrylic anhydride is reduced due to a multiplication of the active centers [25], leading to the increase in the number of methyl groups at the ends of chains that block the growth of the polymer chains.

Table 2: Effect of the amount of Mag-H$^+$ on the yield of poly (epoxy styrene) with 1% of methacrylic anhydride and 0.02 mol of epoxy styrene

Maghnite H$^+$/monomere (%)	Yield (%)
1	54
2	70.5
3	73.8
4	75
5	78.3

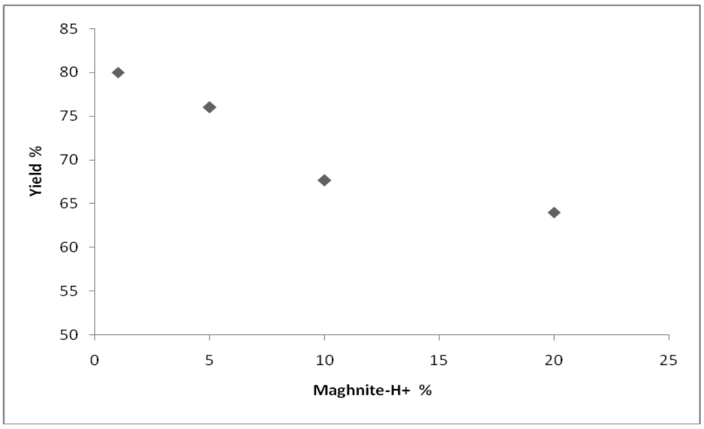


Figure 5: Effect of amount of the catalyst on polymerization of styrene oxide in presence of methacrylic anhydride

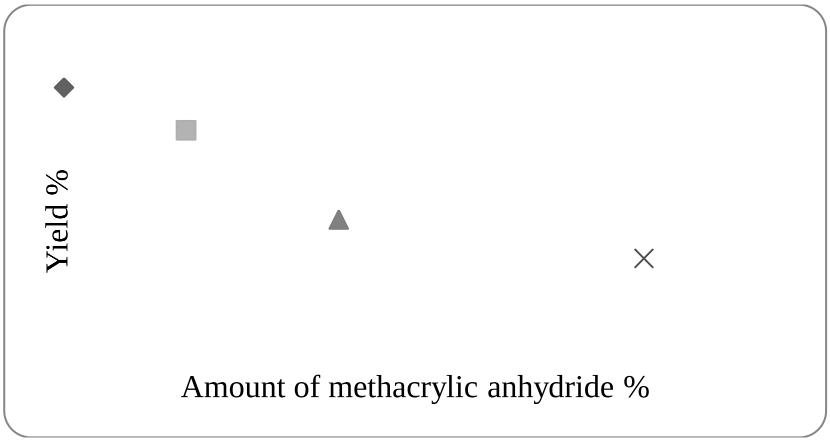


Figure 6: Effect of the amount of methacrylic anhydride on the yield of poly(styrene oxide) telechelic

The Differential Scanning Calorimetry (DSC) analysis of the poly(styrene oxide) (Figure 7) shows that the glass transition temperature (T_g) equal to 72.6°C and the melting point (T_m) is situated between the range temperatures of 250 to 300°C. Therefore, the existence of both the glass transition temperature and the melting point indicates that the poly(styrene oxide) is a semi-crystalline polymer.

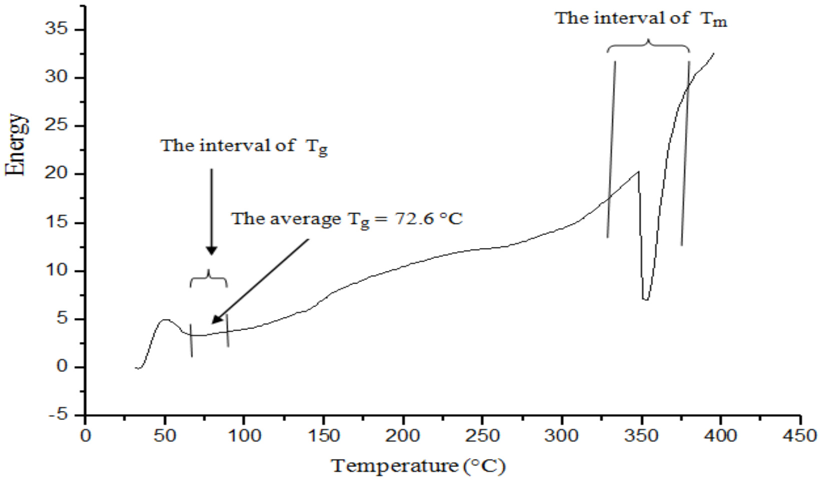


Figure 7: DSC thermogram of poly(styrene oxide) macromonomer TA Instrument: DSC Q2000 (speed of heating: 10°C min^{-1})

The objective of our work is to prevent the photodegradation of synthesized polymer and to have a more stable poly(styrene oxide). For each polymer, we have achieved high molecular weights. This result has confirmed by the GPC. The GPC method gives the measure of the molecular weight distribution that confirms the stability of the synthesized polymer. We notice that the number average molecular weight (M_n) calculated by ^{1}H-NMR equals 6154 g/mol^{-1}. Also, the GPC chromatogram of methacryloyloxy poly(styrene oxide) shows, after four months, that the number average molecular weight (M_n) decreases to 4441 g/mol^{-1}. From Figure 8, the NMR tends to towards higher value compared to the GPC, and thus the functionalized poly(styrene oxide) is more stable by the usage of methacrylic anhydride.

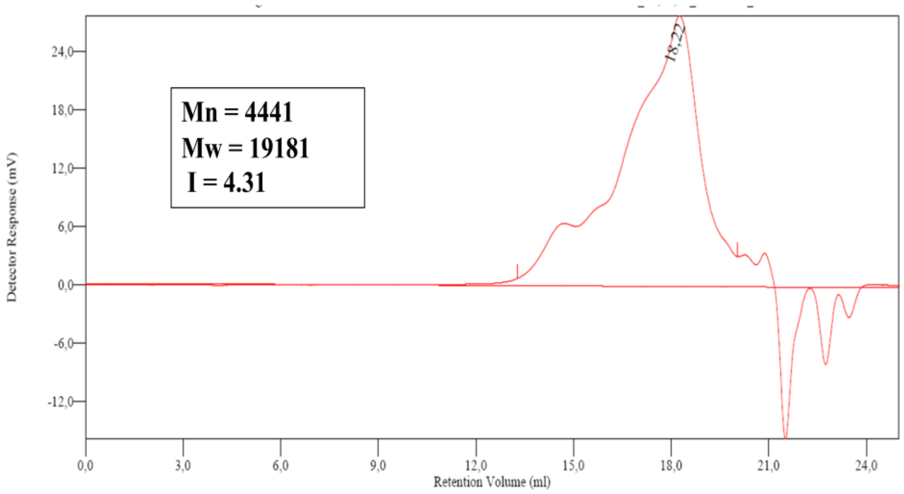
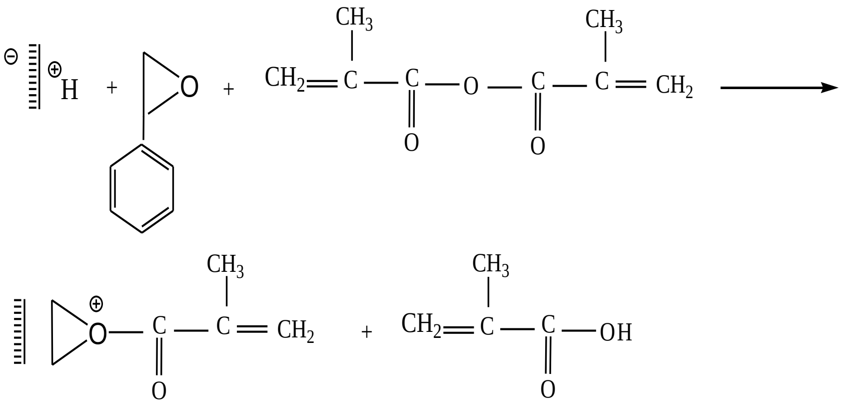


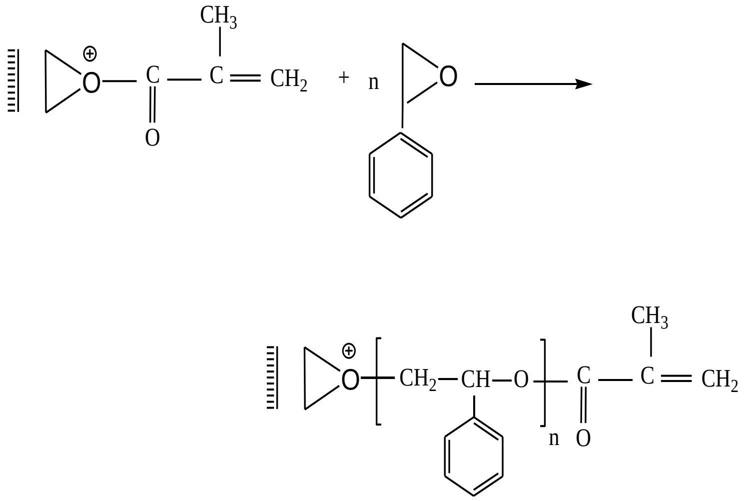
Figure 8: GPC chromatogram of α, ω methacryloyloxy poly(styrene oxide) after 4 mon (THF mobile phase, etalon: polystyrene) spectra physics RI SP 8430

Mechanism of polymerization

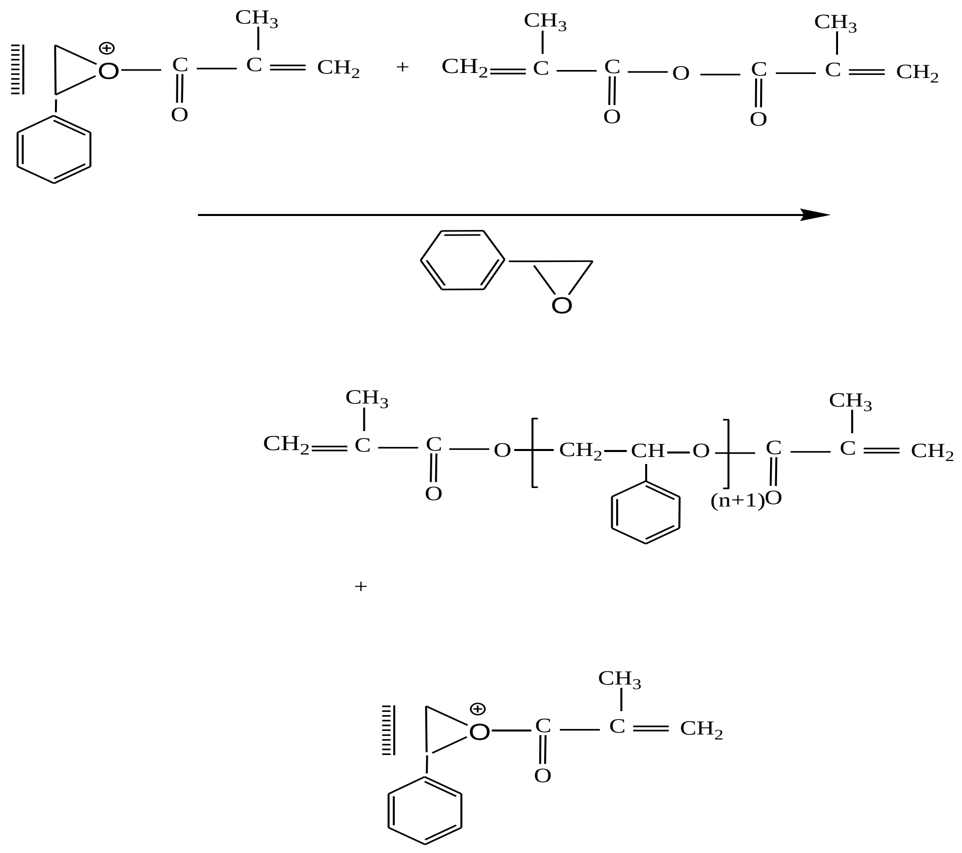
The polymerization of styrene oxide is initiated only through a cationic path (Scheme 2). The protons carried by Mag-H$^+$ initiate the polymerization of styrene oxide and Mag-H$^+$ acts as counter ion propagation (Scheme 3) and termination then take place by the conventional cationic mechanism. The methacrylic anhydride acts as a transfer agent [26] and then the chain transfer (Schemes 4 and 5) step proceeds to give α, w bis unsaturated poly(styrene oxide).



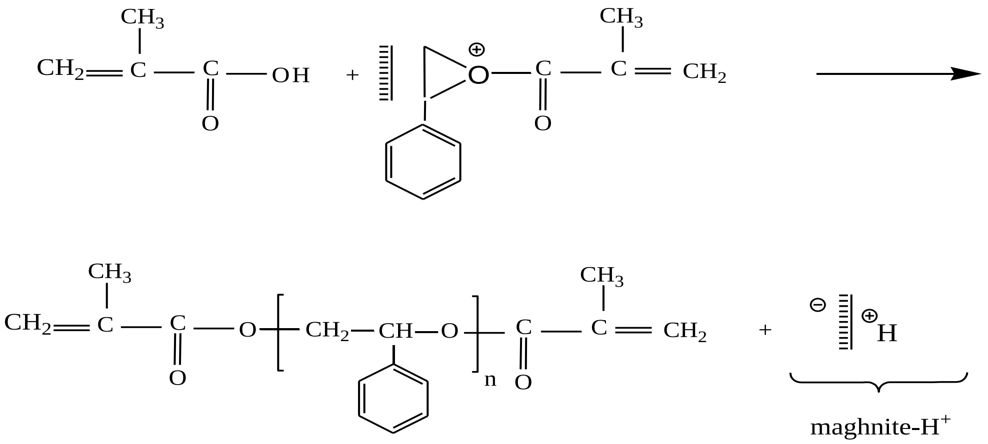
Scheme 2: Initiation



Scheme 3: Propagation



Scheme 4: Transfer of chain



Scheme 5: Termination

CONCLUSION

The green catalyst Maghnite-H$^+$ is effective for the polymerization of styrene oxide in the presence of methacrylic anhydride at room temperature. In this study, a new approach to design telechelic poly(styrene oxide) in one stage, where the methacrylate end groups are clearly visible.

The XRD spectrum shows a crystalline structure and lamellar trained by silicate. The clay can be easily separated from the reaction mixture and regenerated by simple filtration. The yield of synthesized α, ω Methacryloyloxy poly(styrene oxide) depends on the amount of catalyst and methacrylic anhydride. The grafting of the groupings methacrylate is not able to limit the photodegradation but it is better to stabilize the poly(styrene oxide). The polymers liquid crystals and the photochemical properties present the perspectives of this work.

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