A GREEN CATALYST FOR SYNTHESIS OF *BIS*-MACROMONOMERS OF POLY (STYRENE OXIDE)

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The synthesis of macromonomers is made by anhydrides to prevent the reducing average molecular weight of synthesized polymers in order to obtain poly α, w unsaturated (styrene oxide) more stable, using a proton exchanged montmorillonite clay called Maghnite-H$^+$. For cationic polymerization of the styrene oxide, we have used the Maghnite-H$^+$ as a heterogeneous polymerization catalyst to synthesis poly (styrene oxide), which is performed in solution of dichloromethane with methacrylic anhydride at temperature 20 ºC. We have investigated the effect of the amount of catalyst and methacrylic anhydride on yield of polymer, and analysed the structures of modified montmorillonite by X-Ray Diffraction (XRD). Also, we have characterized the polymers by infrared spectroscopy (IR) and nuclear magnetic resonance (NMR), gel permeation chromatography (GPC) and differential scanning calorimetry (DSC).
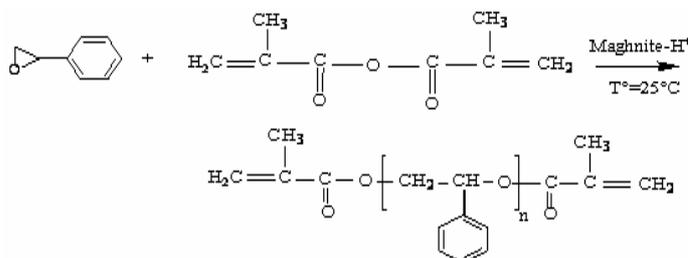
INTRODUCTION

Green chemistry is mainly concerned with the prevention of pollution through the minimization of waste and the toxic avoidance and hazardous substances in the production and application of chemicals products.[1] The 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] which forms environmental disposal problems for the chemists. Green chemistry principles have the power to refocus pharmaceutical operations on integration of development and production.[3] However, the

heterogeneous catalysts are green catalysts and are topical subjects for the green chemistry. Among of these the Maghnite-H$^+$ is non-toxic available eco-catalyst, it has great efficiency as catalyst system for cationic polymerization of a number of vinylic and heterocyclic monomers.[2,4-6]

Styrene oxide is an important organic intermediate in the synthesis of the fine chemicals and the pharmaceuticals, it has been synthesized by the epoxidation of styrene which is considered as a commercially important reaction.[7] It has also been used to make a polymer with linoleic acid dimer, ethylene diamine and 2-éthoxyethylacetate.[8] The boron trifluoride is able to catalyze the

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phenyloxiranne (epoxystyrene), which is polymerized by cationic or anionic catalysts.[9] The polymerization of styrene oxide has been performed under some polymerization conditions such as higher temperature, longer polymerization time and vacuum environment.[10,11] A several works have studied the applications of poly(styrene oxide) in versatile fields such as hydrophobic nanocarriers for drug delivery, block copolymer micelle formation in water,[12] coating materials, surface modifiers[13] and in the production of polystyrene carbonate.[14] The preparation of graft copolymers by the usage of macromonomers has been extensively studied. However macromonomers method provides an excellent means of designing graft copolymers of controlled structure.[15,16]

The Maghnite-H^{+} is used as a heterogeneous polymerization catalyst for cationic polymerization of styrene oxide to synthesize poly (styrene oxide) with the presence of methacrylic anhydride methacrylic anhydride in solution (dichloromethane) at 20 °C (scheme 1). In our study, we have performed a new approach to synthesize poly (styrene oxide) bis-macromonomers in one stage with new initiator. Our contribution is to present a new experimental method to prevent the phtotodegradation of synthesized polymer and to have a more stable poly (styrene oxide).

EXPERIMENTAL

1. Reagents

Styrene oxide, methacrylic anhydride, dichloromethane, and methanol are purchased from Aldrich and used as received. Also, we have prepared the montmorillonite-H^{+} (Mag-H^{+}).

2. Preparation of Mag-H^{+}

Most of the polymerizations were carried out in solutions, initiated either by: Lewis acids[17] or by radiation.[18] These synthesis processes have several inconveniences such as the acids are not recoverable, their elimination is difficult and costly and they are toxic. These disadvantages cause serious problems for human health and the environment. However, the new Maghnite-X (X: ions, H, Na) catalyst responds positively to these criteria.

The Maghnite-H^{+} is based on montmorillonite, it was obtained with a cation exchange by using a green natural clay. Belbachir *et al.*[4] have developed Maghnite-H^{+}, which was used for the polymerization reactions of several vinyl and heterocyclic monomers, replacing the toxic solvents used in industrial chemistry. The Maghnite-H^{+} is recyclable, reusable and easy to wash with water. It is safe for human health and the environment, so Maghnite- H^{+} is a green catalyst.

We have prepared the Maghnite-H^{+} according to the similar process reported in the previous study of Belbachir *et al.*[4] The Maghnite is activated with a sulfuric acid solution to give 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 a magnetic stirrer during two hours at room temperature. Then, we added the solution of sulfuric acid of 0.23 M (100 mL). The obtained solution is maintained two days 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 hours at temperature of 105 °C and then it is crushed.

3. Experimental procedure

The exothermicity of the reaction of synthesis of poly (styrene oxide) in bulk is processed in solution of dichloromethane, and thus we have studied the effect of solvent on polymerization of styrene oxide.

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

We have prepared four mixtures by using various amount of methacrylic anhydride of $0.05 \ 10^{-3}$, $2.5 \ 10^{-3}$, $5 \ 10^{-3}$ and $10 \ 10^{-3}$ mol as shown in Table 2. Each mixture is composed by 6 g (0.05 mol) of styrene oxide and 0.3 g of Mag-H^{+} (5 % by weight). For each mixture, we have added 40 mL of CH_2Cl_2. The reaction mixtures are stirred for 24 hours at room temperature, and hence we have investigated the effect of the amount of catalyst and the methacrylic anhydride on yield of polymer.
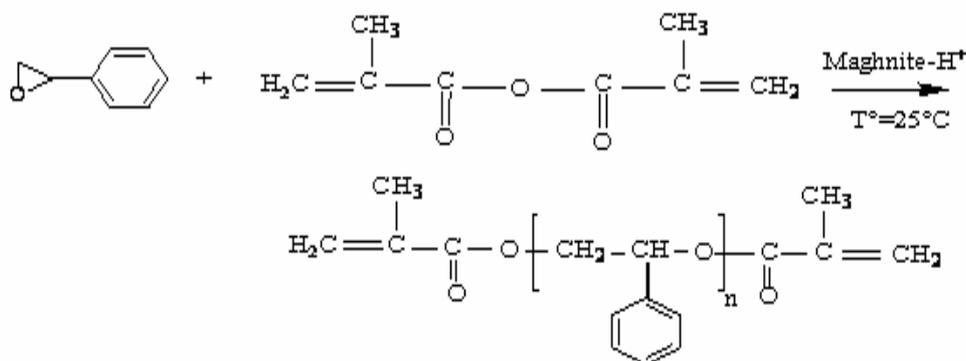
Scheme 1 – Ring-opening polymerization of styrene oxide by Maghnite-H^{+} catalyst with the presence of methacrylic anhydride in dichloromethane.

RESULTS AND DISCUSSION

1. Structural characterization

Natural clay can not be the effective catalyst; its modification with acid activation gives activated clay. One of the better known chemical modifications of the clay is its activation by the acids. Usually, the clay is processed with a solution of HCl or H2SO4 to obtain a dissolved material having an increased surface area, porosity and surface acidity.[19]

The XRD shows that the Maghnite belongs to the montmorillonite clays group.[20-22] The structure of Maghnite-H+ has been characterized by different methods such as infrared spectroscopy (IR), nuclear magnetic resonance (NMR) and X-Ray Diffraction (XRD).[2,4,6,11] In our study, the experimental analysis by XRD shows that the Maghnite-H+ is characterized by a lamellar structure formed by silicate. The Maghnite is a montmorillonite sheet silicate clay, which is exchanged with protons to produce Maghnite-H+.[2,11] However, the XRD determines the interlayer spacing after the activation of clay. The XRD diffractograms of Maghnite-H+ (0.23 M) are displayed by Fig. 1. From this plot, the intense stripes are observed around the angle of $2\theta = 6.05$ and the interlayer distance (d = 14.23 Å) corresponding to the treated Maghnite is larger than the raw Maghnite (11.45 Å). The basal spacing (d001) is calculated from XRD patterns, using the Bragg equation.[23]

The typical reaction product of poly (styrene oxide) has end groups of methyl methacrylate. It is characterized by infrared spectroscopy (IR), nuclear magnetic resonance (^{1}H-NMR and ^{13}C-NMR), gel permeation chromatography (GPC) and differential scanning calorimetry (DSC).
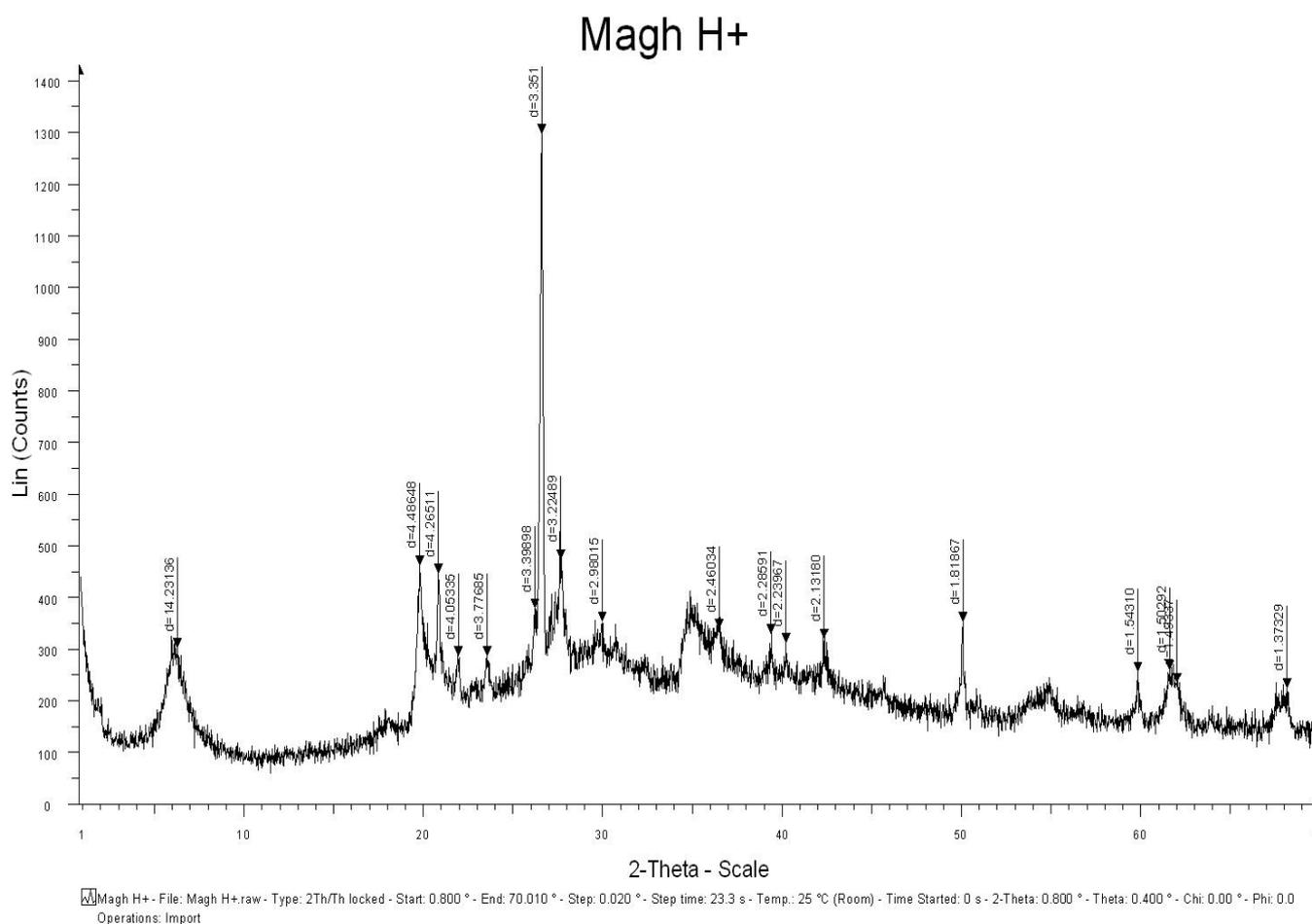

Fig. 1 – XRD diffractograms of Mag-H$^+$ (0.23 M).

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 is linked to the polymer chain–end. The IR spectra of our polymer and polystyrene oxide (PSO) characterized by ^{1}H and ^{13}C NMR are similar to the PSO synthesized by other catalysts.[24] A. Kayan [24] has found that all poly(styrene oxide) catalyzed by different methods have similar IR spectra and they exhibit strong characteristic absorption bands of benzene and C–O group. The methacrylate end groups are clearly visible in the ^{1}H-NMR spectrum (1.97 ppm, 5.67 ppm, 6.22 ppm) signals and IR spectrum (1602.68, 1721.79 cm^{-1}) of telechelic poly (styrene oxide) as shown in Figs. 2 and 3. The ^{1}H-NMR spectroscopy confirms the structure of our polymer under study.

The ^{13}C-NMR spectrum of poly (styrene oxide) was previously studied by S. Kobayashi *et al.*[25] For our poly(styrene oxide), the Fig. 4 depicts the existence of carbons of 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 in both region and stereo, which is consistent to the results of PSO found by H. Misaka *et al.*[26] and A.L. Brocas *et al.*[27] The styrene oxide is considered to be less reactive than aliphatic and other alicyclic epoxides, but it undergoes a ring-opening via acids and bases.[28]

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).[29] In our experimental work, we have synthesized the α-ω methacryloyloxy poly (styrene oxide) macromonomer in a single stage. The Table 1 shows that the increase of maghnite-H^{+} proportion leads to an increase in the polymerization yield as shown in Fig. 5. However, the Fig. 6 depicts that the yield increases when the proportion of methacrylic anhydride is reduced due to a multiplication of active centers.[30] This leads to the increase in the number of methyl groups at the chains ends, which block the growth of the polymer chains.
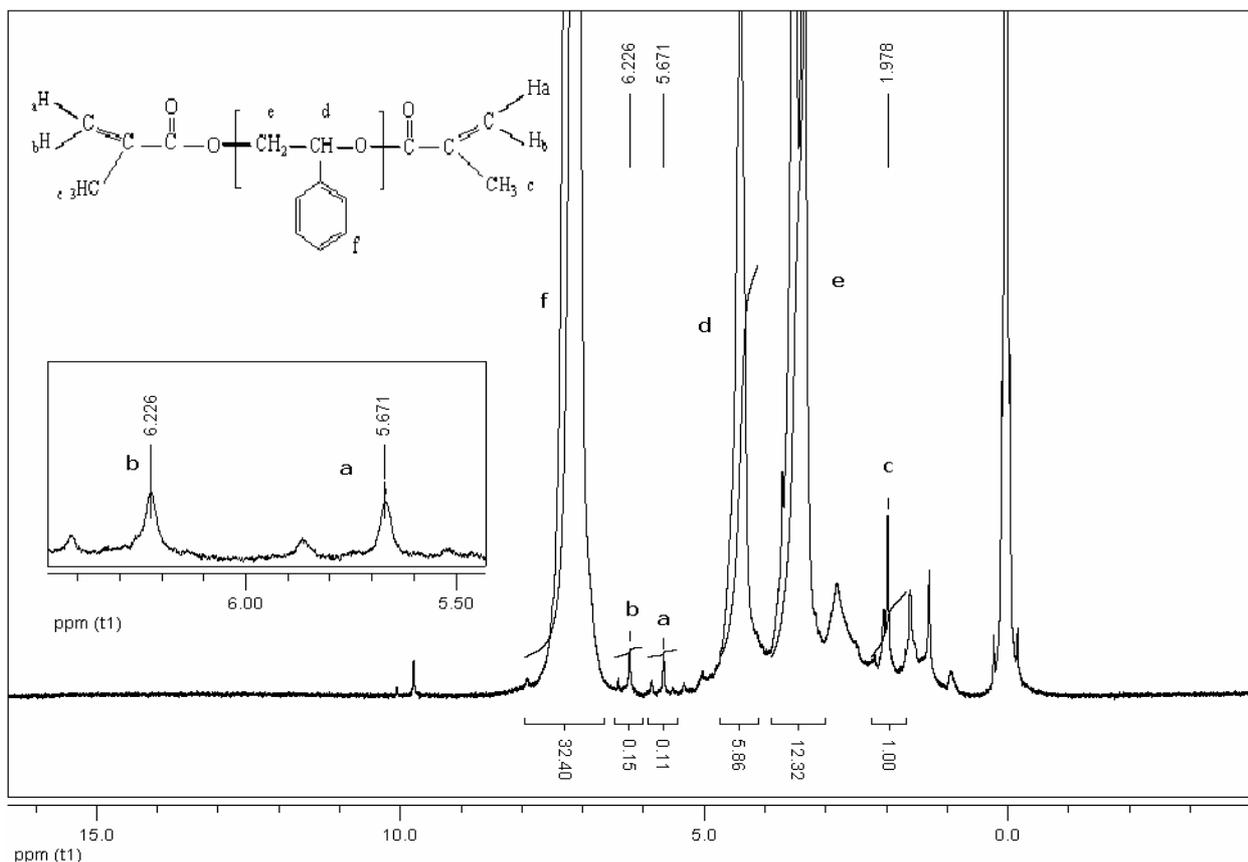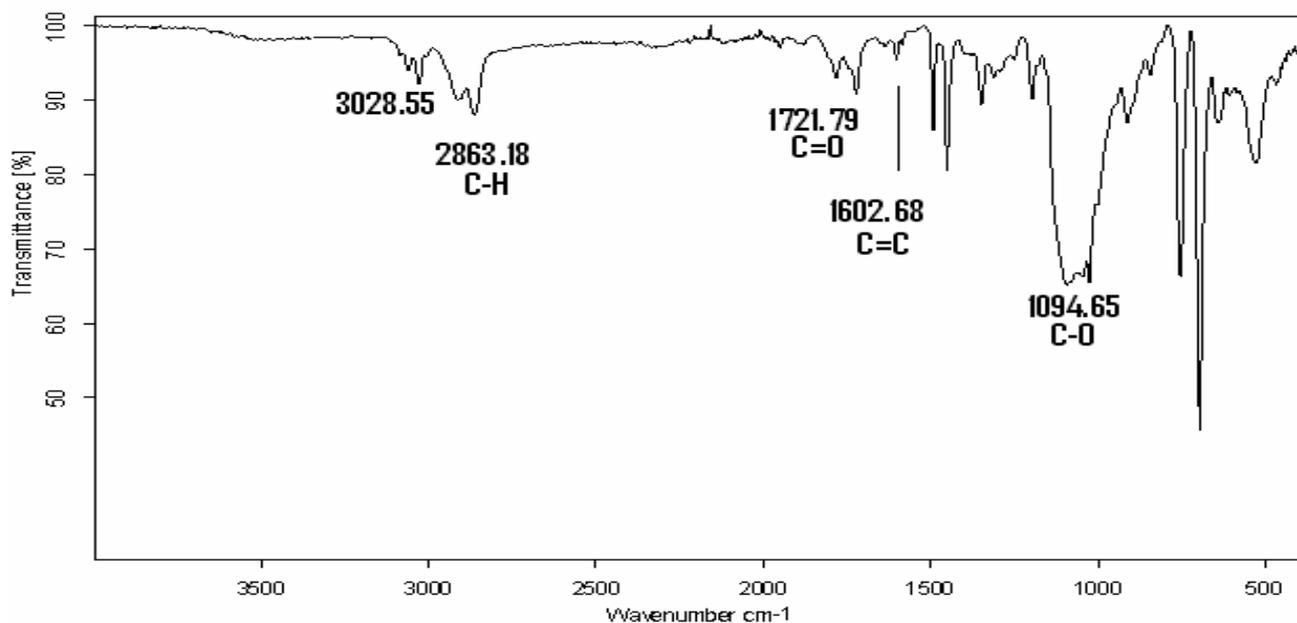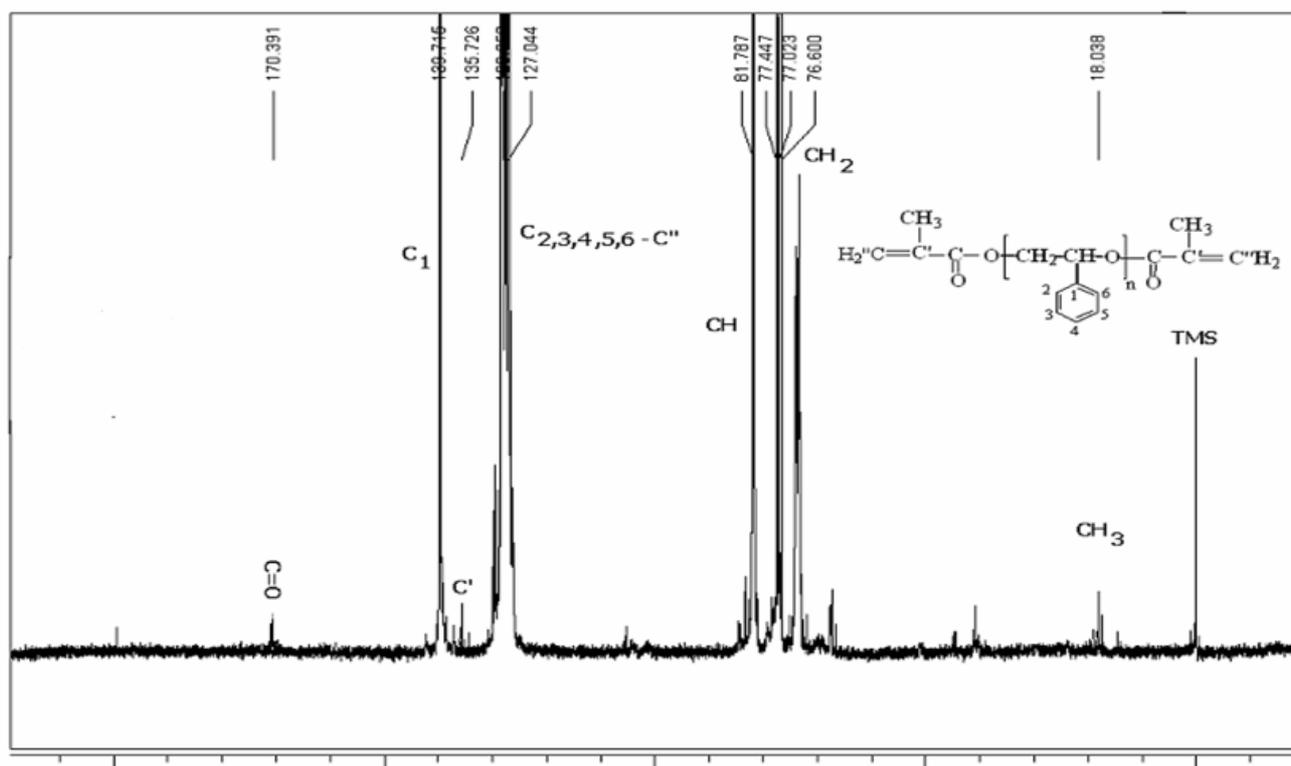
Fig. 2 – ^{1}H-NMR spectrum (300 MHz) of α-ω methacryloyloxy poly(styrene oxide) in CDCl$_3$.

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

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

The differential scanning calorimetry (DSC) analysis of poly(styrene oxide) (Fig. 7) shows that the glass transition temperature (T_g) equal to 72.6 ºC and the melting point (T_m) is situated between the range temperatures of 250 to 300 ºC. Therefore, the existence of both the glass transition temperature and the melting point indicates that the poly (styrene oxide) is a semi-crystalline polymer.

The nature of irregularities and end-groups in poly(styrene oxide) were studied by A. Hachemaoui et al.[31] They detected the head-to-head (H-H) and tail-to-tail (T-T) irregularities, and

identified the secondary hydroxyl terminal groups in polymers. It is found that the poly(styrene oxide) undergoes a chain scission by aging at temperature of 25 °C. However, the oxidation of this type of polymer results from the important sensitivity of the polyether soft segment to oxidative degradation. Consequently, the scissions due to the oxidation of the material, lead to the considerable quantities of low-molecular-weight photoproducts.

Table 1

Effect of the amount of Mag-H$^+$ on the yield of poly (epoxystyrene) with 1% of methacrylic anhydride and 0.02 mol of epoxystyrene

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

Table 2

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

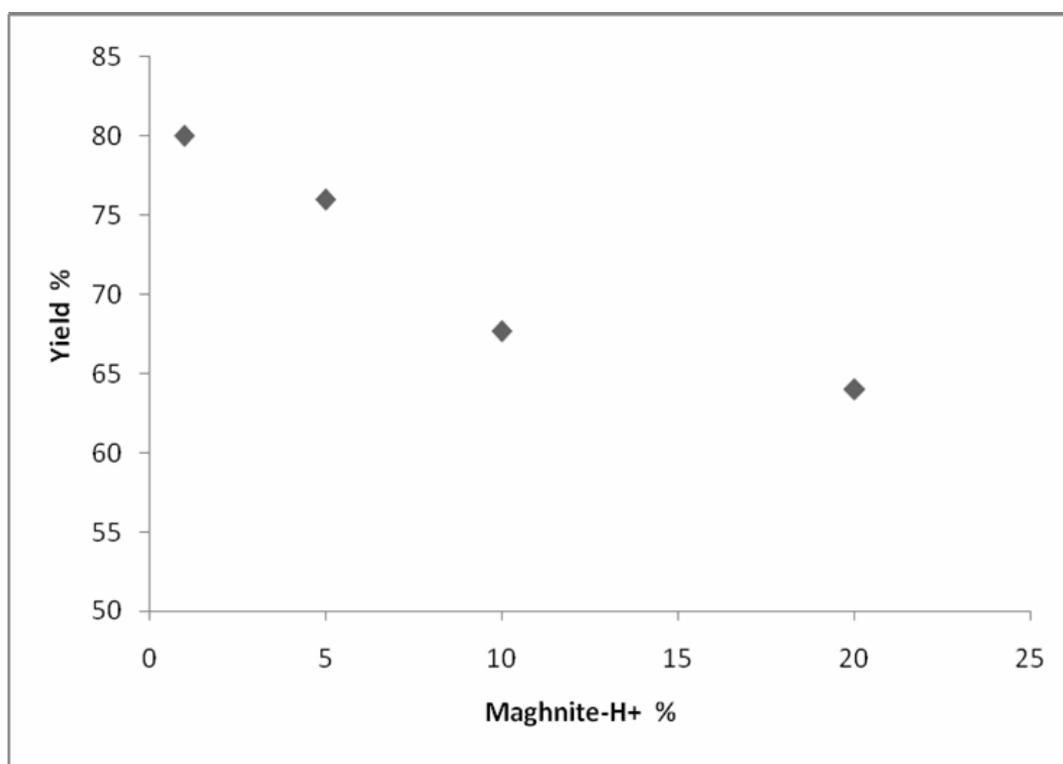| Experiment	Epoxystyrene (mol)	Methacrylic anhydride (mol)	Mag-H$^+$ (g)	Yield (%)
1	0.05	0.05 10^{-3}	0.15	80
2	0.05	2.5 10^{-3}	0.15	76
3	0.05	5 10^{-3}	0.15	67.77
4	0.05	10 10^{-3}	0.15	64

Fig. 5 – Effect of amount of the catalyst on polymerization of styrene oxide with the presence of methacrylic anhydride.
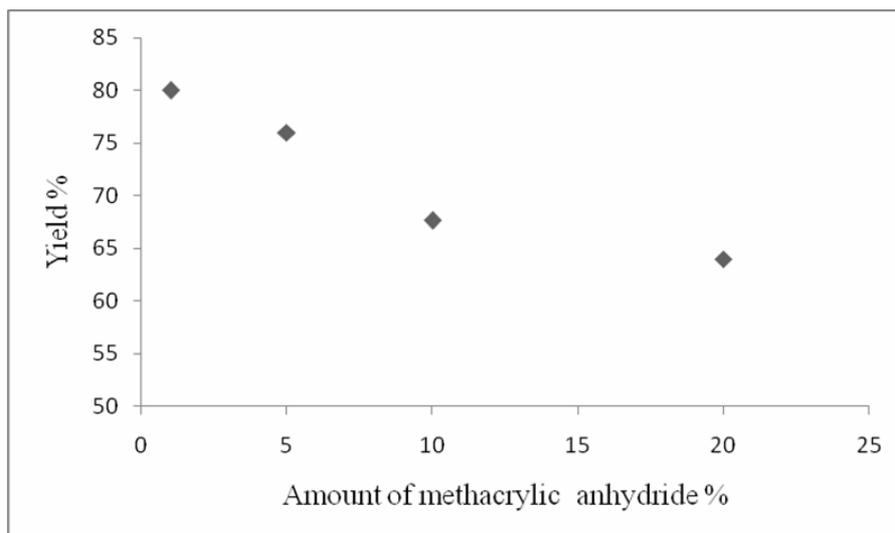
Fig. 6 – Effect of the amount of methacrylic anhydride on the yield of poly(styrene oxide) telechelic.
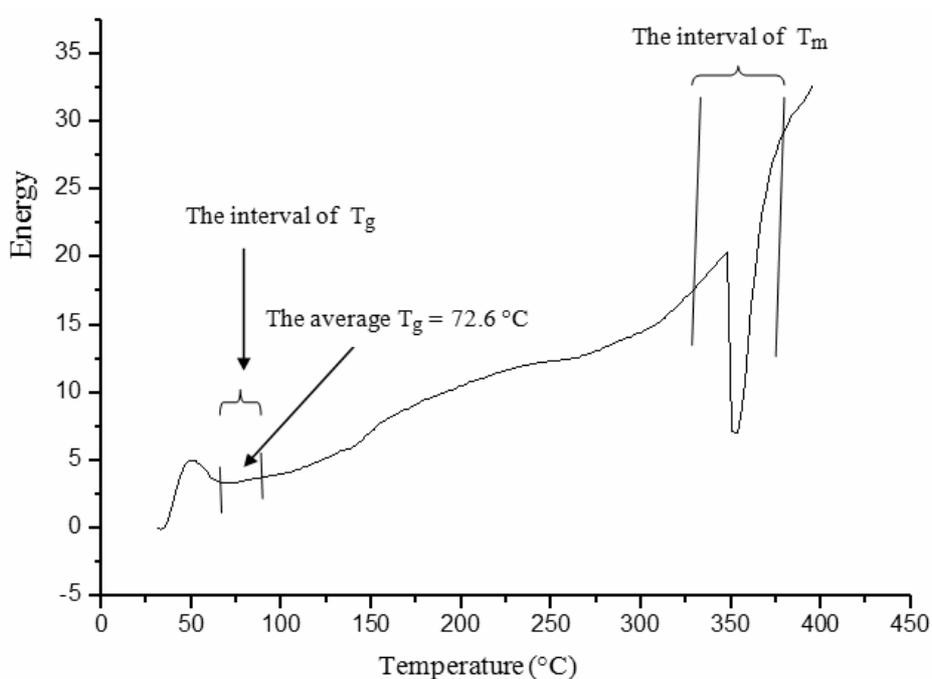

Fig. 7 – DSC thermogram of poly(styrene oxide) macromonomer TA Instrument: DSC Q2000 (speed of heating : 10 °C min^{-1}).

For each polymer, we have achieved high molecular weights. This behavior has confirmed by the gel permeation chromatography (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 of molecular weight (M_n) calculated by ^{1}H-NMR equals to 6154 g.mol^{-1}. Also, the GPC chromatogram of methacryloyloxy poly(styrene oxide) shows, after four months, that the number average of molecular weight (M_n) decreases to 4441 g.mol^{-1}. From Fig. 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.

2. Mechanism of polymerization

The polymerization of styrene oxide is initiated only through a cationic path (see scheme 2). The protons carried by Mag-H$^+$ initiate the polymerization of styrene oxide and Mag-H$^+$ acts as counterion propagation (scheme 3) and the termination (scheme 5) then take place by the mechanism of conventional cationic.

The methacrylic anhydride acts as a transfer agent,[22] and then the step of chain transfer (scheme 4) proceeds to give α, w bis unsaturated poly (styrene oxide).
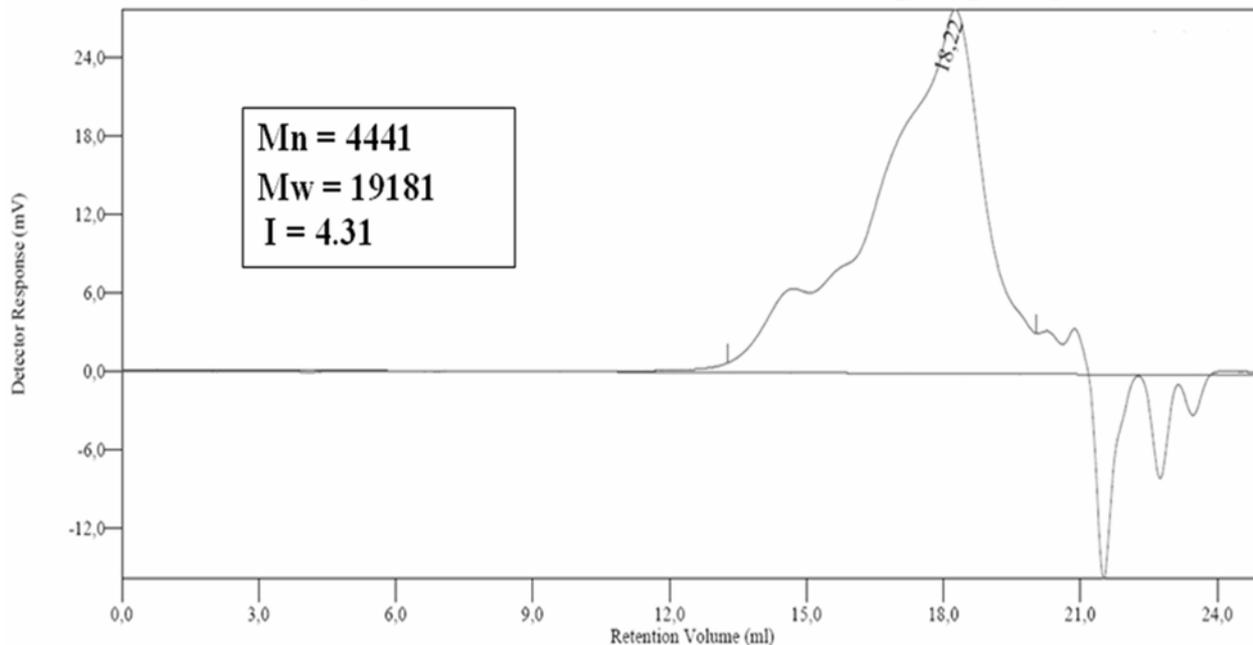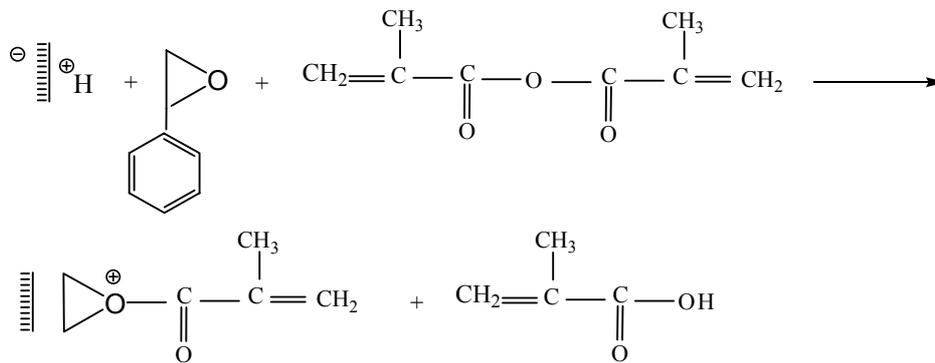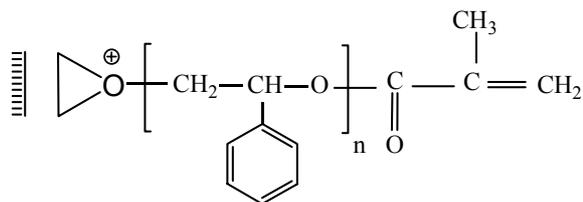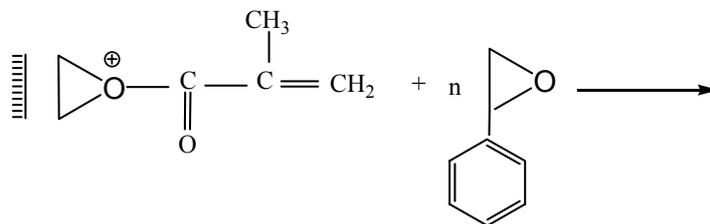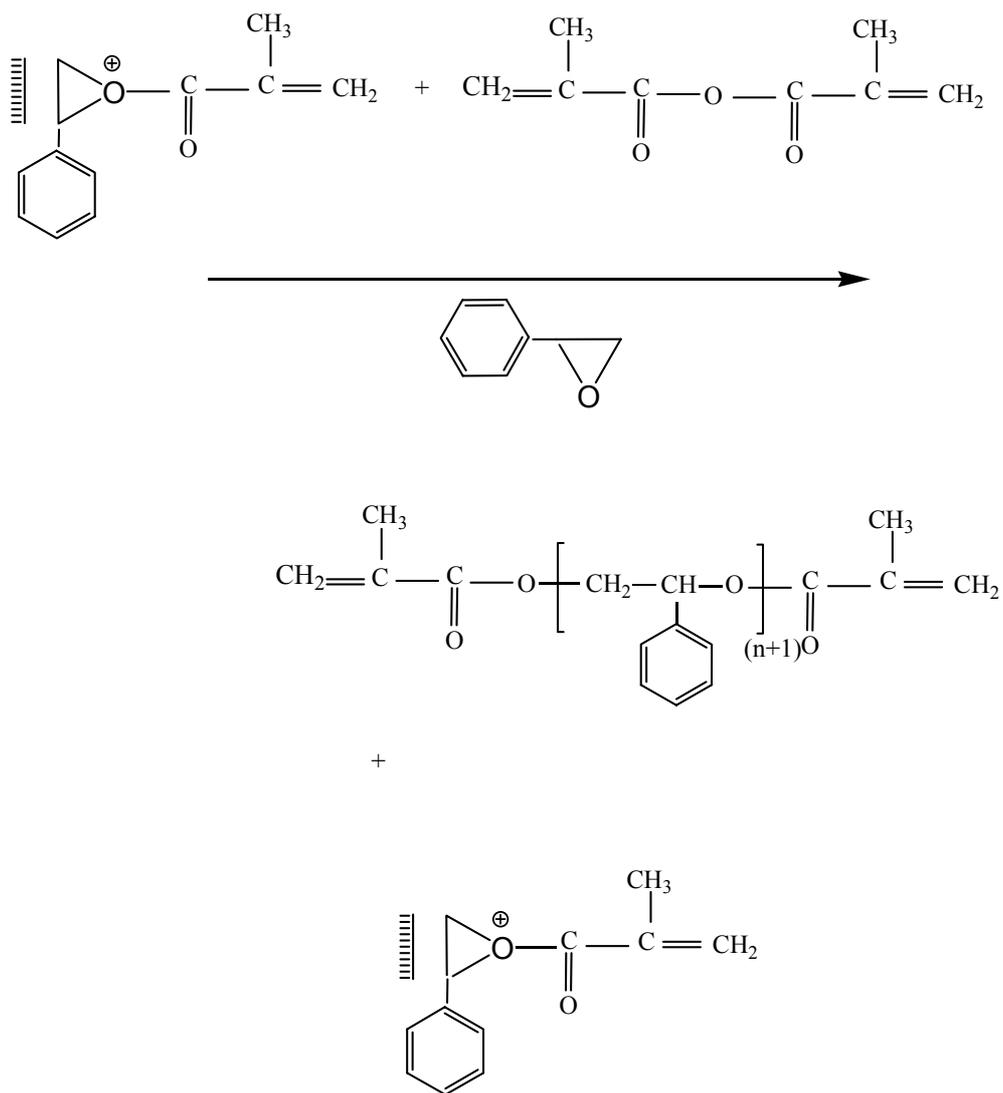

Fig. 8 – GPC chromatogram of α, ω methacryloyloxy poly (styrene oxide) after 4 months (THF mobile phase, etalon: polystyrene) spectra physics RI SP 8430.
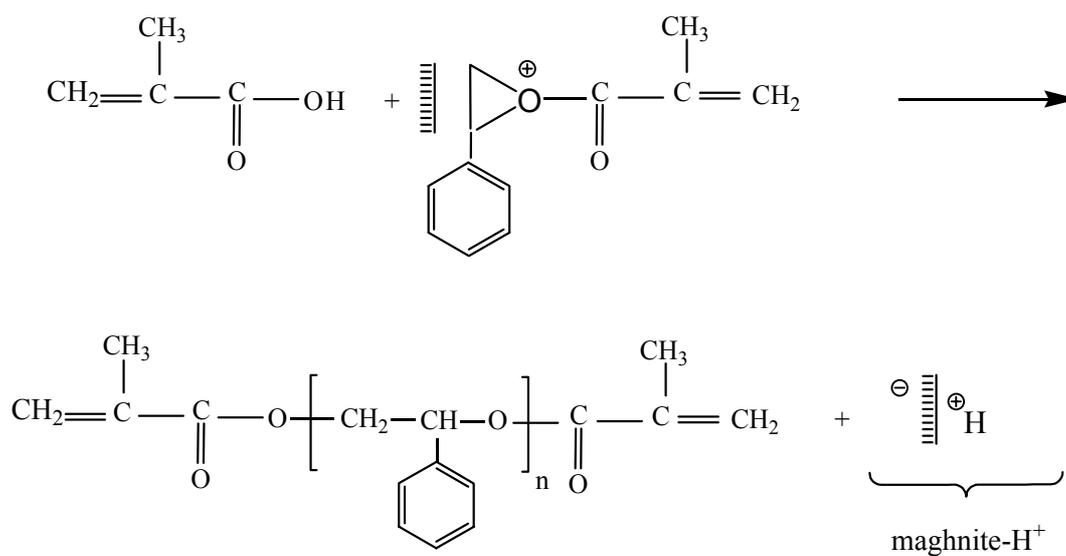

Scheme 2 – Initiation.

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 synthesize telechelic poly (styrene oxide) in one stage, where the methacrylate end groups are clearly visible.

The XRD spectrum shows that the Maghnite is a montmorillonite sheet silicate clay. 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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