

# Ring-Opening Polymerization of Styrene Oxide with Maghnite-H<sup>+</sup> as Ecocatalyst

Ahmed Yahiaoui,<sup>1</sup> Mohammed Belbachir<sup>2</sup>

<sup>1</sup>Centre universitaire Mustapha Stambouli, Institut d'hydraulique, BP 763 Mascara 29000, Algérie

<sup>2</sup>Laboratoire de chimie des polymères, Département de Chimie, Faculté des Sciences, Université d'Oran, BP 1524 El'Menouer Oran 31000 Algérie

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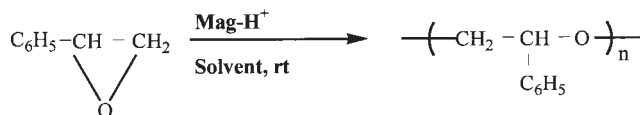
**ABSTRACT:** The polymerization of styrene oxide was carried out at 20°C in chloroform with an acid-exchanged montmorillonite as acid solid ecocatalyst (Mag-H<sup>+</sup>). The effect of the amount of catalyst, solvent, and concentration of monomer on yield and molecular weight of polymer was studied. A typical reaction product (PSTO) was analyzed by infrared and nuclear magnetic resonance spectroscopy, as

well as by gel-permeation chromatography and MALDI-TOFMS. The mechanism of the polymerization appears to be cationic. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 1681–1687, 2006

**Key words:** montmorillonite; ecocatalyst; epoxies; styrene oxide; ring-opening polymerization

## INTRODUCTION

Styrene oxide (SO) has been polymerized either by cationic catalysts<sup>1</sup> or anionic catalysts,<sup>2</sup> but mostly polymerized by zinc dialkyl or zinc dialkyl with an addition of water or alcohol.<sup>3–8</sup> There is, to date, no information on the ring-opening polymerization of SO with clay catalyst. We have found that clay catalysts (Maghnite-H<sup>+</sup>) are highly effective catalysts for the polymerization of propylene oxide (PO), epichlorohydrin (ECH), cyclohexene oxide (CHO), etc.<sup>9–11</sup> It is interesting to see whether the side phenyl group of oxirane will affect the polymerization activity of SO catalyzed by clay catalysts. In this study and in continuation of our program to develop environmentally benign methods using solid supports,<sup>9–11</sup> we report that acid-exchanged montmorillonite (Mag-H<sup>+</sup>) is a novel, efficient solid catalyst for the ring-opening polymerization of SO to produce PSTO (Scheme 1). In contrast to the more usually used catalysts, Mag-H<sup>+</sup> can be easily separated from the polymer and regenerated by heating to a temperature above 100°C. The effects of the relative amounts of Mag-H<sup>+</sup> and solvent were discussed.



**Scheme 1** Ring-opening polymerization of STO by Mag-H<sup>+</sup> catalyst.

## EXPERIMENTAL

### Materials

Styrene oxide (SO, Aldrich) was dried over calcium hydride and distilled under reduced pressure before use. Toluene, dioxane, chloroform, *n*-hexane, and petroleum ether were purified following standard techniques and used after distillation over their respective drying agents.

The clay, which has been used as catalyst, is supplied by a local company (ENOF Maghnia (Western of Algeria)). Its chemical composition is given in Table I. First, the greatest proton saturation of the <2 mm fractions of clay were obtained by saturating with Na<sup>+</sup> ions using 1M NaCl solution, then the protonated forms of montmorillonite (Mag-H<sup>+</sup>) were prepared by shaking the clay in a solution of 0.25M sulfuric acid until saturation was achieved (normally after 2 days at room temperature). The cation-exchanged clay was then recovered by filtration, and again suspended in deionized water. This process was repeated until no sulfate ions were indicated present in the filtrate using BaCl<sub>2</sub>. The Mag-H<sup>+</sup> was then isolated by filtration, dried at 105°C, and then finely ground.

Correspondence to: A. Yahiaoui (yahmeddz@yahoo.fr).

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TABLE I  
Chemical Composition of the Catalyst

Species	% (w/w)
SiO <sub>2</sub>	69.4
Al <sub>2</sub> O <sub>3</sub>	14.7
Fe <sub>2</sub> O <sub>3</sub>	1.2
MgO	1.1
CaO	0.3
Na <sub>2</sub> O	0.5
K <sub>2</sub> O	0.8
TiO <sub>2</sub>	0.2
As	0.05
L.O.I	11

L.O.I: Loss on ignition at 900°C in wt %.

### Experimental procedure

Polymerizations were performed in chloroform at 20°C. The procedure was identical in both cases, involving addition of catalyst to the stirred solution containing STO in chloroform. Prior to use, Mag-H<sup>+</sup> was dried at 120°C overnight and then transferred to a vacuum desiccator containing P<sub>2</sub>O<sub>5</sub>, to cool to room temperature overnight. An example reaction is detailed here. After charging the reaction vessel with STO solution in chloroform (2M), the catalyst (1% w/w to monomer) was added. At the end of the reaction, water was added to stop the polymerization. The resulting mixture was filtered to remove the clay and then dried under vacuum to yield the polymer. The latter was dried in a vacuum oven prior to submission for GPC, MALDI-TOF MS, <sup>1</sup>H-NMR, and <sup>13</sup>C-NMR analysis (yield of this example was 71%).

### Characterization of the products

<sup>1</sup>H and <sup>13</sup>C nuclear magnetic resonance (NMR) measurements were carried out on a 300 MHz Bruker NMR Spectrometer equipped with a probe BB05 mm, in CDCl<sub>3</sub> and C<sub>6</sub>D<sub>6</sub>. Tetramethylsilane (TMS) was used as the internal standard in these cases. Average molecular weights and molecular weight distributions of the different polymers were measured using size-exclusion chromatography (SEC) on a system equipped with a SpectraSYSTEM AS1000 autosampler, with a guard column (Polymer Laboratories, PL gel 5 mm Guard, 50 × 7.5 mm<sup>2</sup>) followed by 2 columns (Polymer Laboratories, 2 PL gel 5 mm MIXED-D columns, 2 × 300 × 7.5 mm<sup>3</sup>), with a SpectraSYSTEM RI-150 and a SpectraSYSTEM UV2000 detectors. The eluent used is THF at a flow rate of 1 mL min<sup>-1</sup> at 35°C. Polystyrene standards (580–483 10<sup>3</sup> g mol<sup>-1</sup>) were used to calibrate the SEC. The MALDI-TOF mass spectra (m.s.) were recorded on a Bruker Biflex III equipped with a nitrogen laser (*l* = 337 nm). All m.s. were recorded in the linear mode with an acceleration voltage of 19 kV. The irradiation targets were pre-

pared from THF or CH<sub>2</sub>Cl<sub>2</sub> solutions with dithranol as matrix and NaI as dopant.

## RESULTS AND DISCUSSION

Mag-H<sup>+</sup> is an efficient catalyst for polymerization of epoxies. The bulk ring-opening polymerization of styrene oxide proceeds by an exothermic and spontaneous reaction at room temperature using 0.5% of Mag-H<sup>+</sup>. Such bulk reactions are difficult to control and gave irreproducible molecular weight results due to the uncontrollable rise in temperature observed during these polymerizations; for this reason, we have studied the polymerization of STO in the presence of solvent.

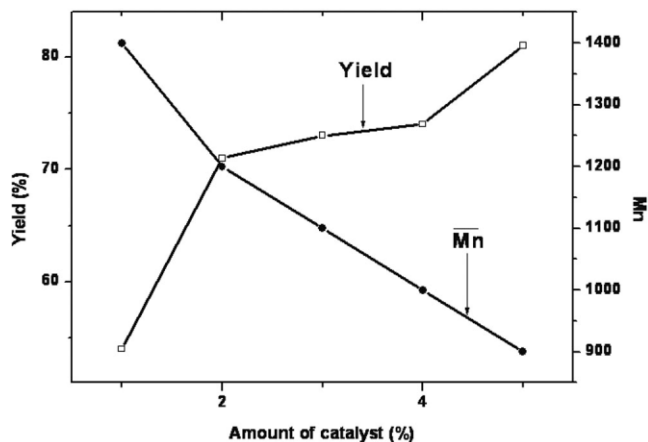
The influence of solvent on the polymerization was summarized in Table II. The data showed that the polymerization reaction proceeded better in chloroform and toluene. The rate of polymerization in chloroform was found to be much higher than that in toluene and *n*-hexane. The chain transfer of growing polymer cation to monomer takes place more easily in chloroform than in toluene and *n*-hexane. Similar results was found, by Tsubokawa et al.,<sup>12</sup> in the cationic polymerization of *N*-vinylcarbazole initiated successively by  $\gamma$ -poly(glutamic acid), carbon fiber, and carbon black.

The effect of monomer concentration [STO], in the range of 0.20–1.00 mol/L, on the polymerization was studied at 2% of Mag-H<sup>+</sup> and shown in Table II. It can be observed that the yield of PSO increased with increasing the [STO] concentrations when the monomer concentration is  $\leq 0.51$  mol/L. Then, the yield of PSO began to drop, which indicates that the growing reaction proceeds faster at lower monomer concentrations.

Amount of catalyst (Mag-H<sup>+</sup>/STO) was an important factor of polymerization. Figure 1 shows the effect of amount of catalyst on polymerization. The higher the amount of catalyst the higher is the yield. 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. Similar results are obtained, by Yahiaoui and coworkers<sup>9–11</sup> and Njopwou et

TABLE II  
The Effect of Solvent Sort on the Polymerization of SO by Mag-H<sup>+</sup> Catalytic System

Solvent	[STO] mol L <sup>-1</sup>	Yield (%)
Toluene	0.51	40
Dioxane	0.51	18
Chloroform	0.20	68
Chloroform	0.51	71
Chloroform	1.00	69
Petroleum ether	0.51	Trace
<i>n</i> -hexane	0.51	28

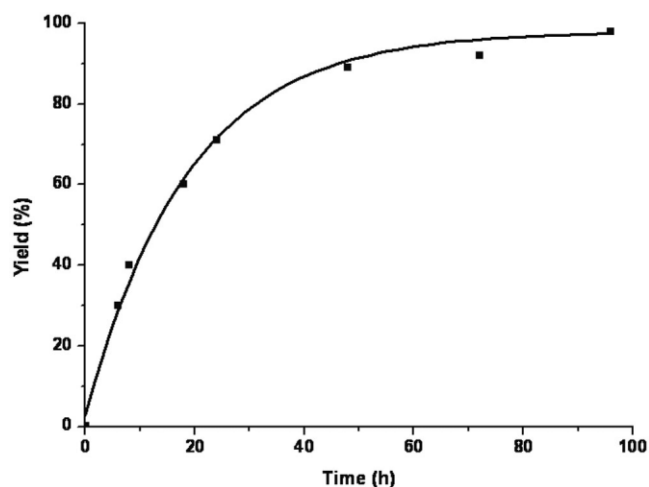


**Figure 1** Effect of the amount of catalyst on the yield and the molecular weight of the formed polymer.

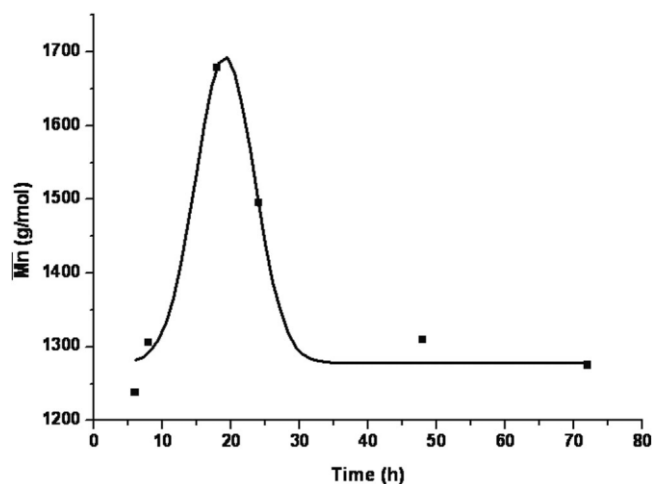
al.,<sup>13</sup> in the polymerization of epichlorhydrin, propylene oxide, and cyclohexene oxide by Mag-H<sup>+</sup> and the polymerization of styrene by montmorillonite, respectively.

As depicted in Figure 1, the molecular weight was found to decrease, depending on the amount of Mag-H<sup>+</sup> (i.e.,  $\bar{M}_n$  decreases when amount of Mag-H<sup>+</sup> increases) in the following order: 5% < 4% < 3 < 2% < 1%. This finding is in good agreement with the proposal that Mag-H<sup>+</sup> 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.<sup>14</sup> and Crivello and Fan,<sup>15</sup> in the polymerization of lactones by Sn-montmorillonite and cyclohexene oxide by cobalt, respectively.

The effect of polymerization duration, as shown in Figure 2, has the same trend as that of catalyst amount, i.e., both the yield of PSO increased with the increasing polymerization time from 6 to 96 h. The polymer-



**Figure 2** Effect of polymerization duration on yield of PSTO [STO] = 0.51M in CHCl<sub>3</sub> at 20°C and 2% of Mag-H<sup>+</sup>.

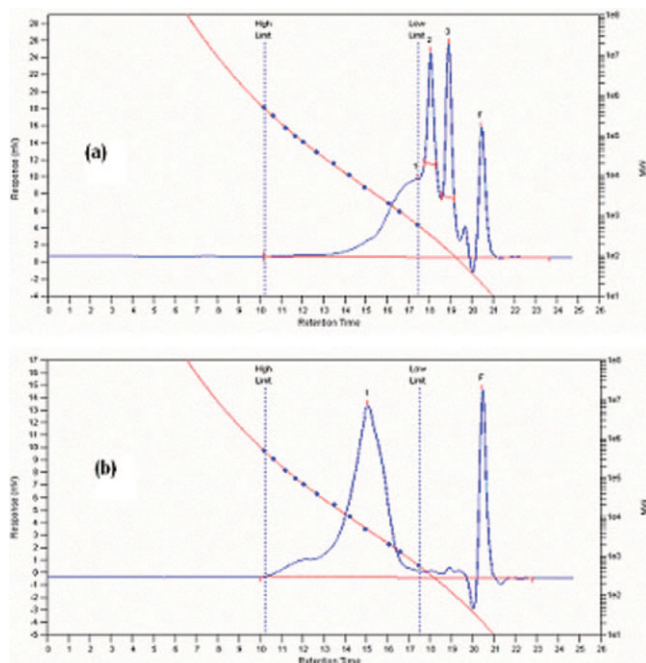


**Figure 3** Effect of polymerization duration on molecular weight of PSTO [STO] = 0.51M in CHCl<sub>3</sub> at 20°C and 2% of Mag-H<sup>+</sup>.

ization yield became constant at a time; this is probably the result of an increase in the medium viscosity.

The results obtained and presented on Figure 3 show that contrary to the yield of polymerization, the molecular weight increase with the polymerization time rising from 6 to 18 h and reached the highest value of 1679 g mol<sup>-1</sup> at 18 h and decreases afterward. This may be caused by a slow depolymerization reaction and the propagation, which takes place through nucleophilic attack of the monomer onto an end-standing cyclic oxonium ion. Nevertheless, a specific character of epoxies lies in its lower nucleophilicity as compared to that of open-chain ether functions. This results in intermolecular chain transfer to polymer (reshuffling reaction), as well as intramolecular chain transfer (back-biting and end-biting) at the origin of macrocyclic formation, consequently resulting in a decrease in the molecular weight.<sup>16,17</sup> This is confirmed by the GPC curve of PSTO (Fig. 4(a)) obtained by Mag-H<sup>+</sup> catalytic system. The peaks at higher elution counts suggested that some oligomers were obtained, which disappears by precipitation (Fig. 4(b)).<sup>18</sup> This result confirms the cationic mechanism of the polymerization of STO by Mag-H<sup>+</sup> catalytic system.

Figure 5 shows the MALDI-TOF MS spectra (in linear mode) of poly(SO) obtained by the solution polymerization of SO (0.51M) using 2% of Mag-H<sup>+</sup> at 20°C and for 24 h. In the case, it was confirmed that the repeating units have a mass of  $m/z$  120, which correspond to the molecular weight of STO monomer (120.15 g mol<sup>-1</sup>). Also, each peak of the MALDI-TOF MS was corresponded to the PSTO having either dihydroxylated terminal structure with one Na<sup>+</sup> ion. Also, in each group, a peak was observed due to the macrocyclic structure, which confirms the existence of transfer reactions.



**Figure 4** GPC chromatograms of poly(SO) obtained by Mag-H<sup>+</sup> catalytic system at following conditions: 2% of Mag-H<sup>+</sup>, 20°C, 24 h, and chloroform as solvent. (a) by evaporation of solvent; (b) by precipitation of PSTO in methanol. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

### Characterization of poly(styrene oxide)

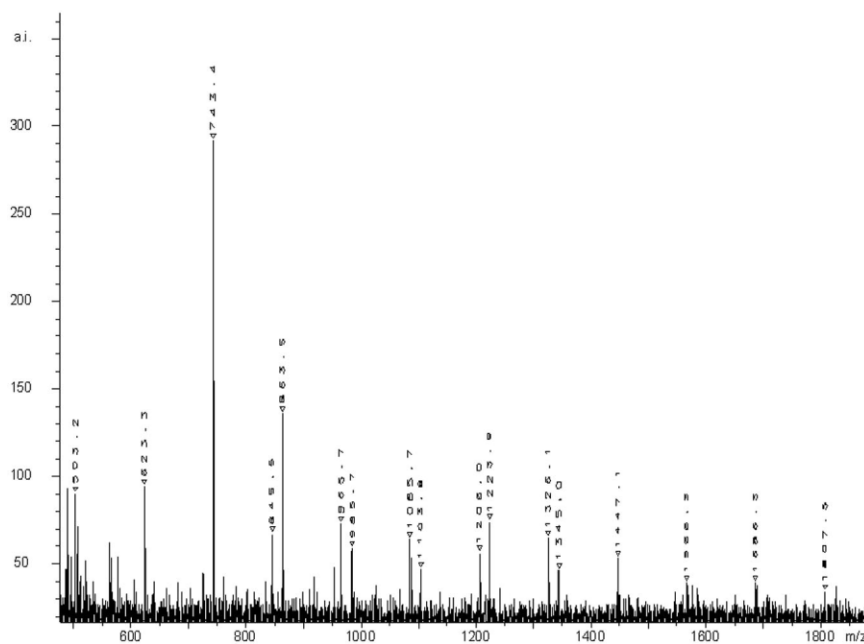
All PSO obtained have similar IR spectra. They all show strong characteristic absorption bands of ben-

zene ring (1607, 1587, and 1493 cm<sup>-1</sup>), —C—O— group (1070 cm<sup>-1</sup>), and of C—H in benzene (700 cm<sup>-1</sup>), which are similar to PSO obtained with other catalysts.<sup>19</sup> The <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra of PSO obtained by Mag-H<sup>+</sup> system are shown in Figures 6 and 7. The PSO obtained by Mag-H<sup>+</sup> system showed similar <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra. By comparing the signals of the spectra with the literature assignments,<sup>2,8,19,20</sup> the signals were assigned as shown in the Figures. In the <sup>1</sup>H-NMR spectrum (Fig. 6), the integration of the aliphatic proton signals and that of the aromatic proton signals gave a ratio of 1:1.61, which corresponded well with that (1:1.67) calculated for a polymer having the ideal formula (SO)<sub>n</sub>. The signal at  $\delta = 1.28$  ppm suggested the presence of methyl protons in the polymer chain, which could have been formed by a chain-transfer reaction.

In the <sup>13</sup>C-NMR spectrum (Fig. 7), there was no peak at  $\delta \approx 76.20$  ppm, which was assigned to methylene carbon and attributed to irregular enchainments of tail-to-tail (T-T) type. Also, there were no peaks at  $\delta \approx 78.30$  ppm and  $\delta \approx 79.40$  ppm assigned to methane carbons and could be attributed to head-to-head (H-H) type. Only peaks of head-to-tail linkage appeared at  $\delta = 82.69$  ppm and  $\delta = 73.59$ – $75.10$  ppm. The signal of the methylene carbon split into two due to m and r dyads.<sup>7</sup>

### Mechanism of polymerization

Maghnite-H<sup>+</sup> (Mag-H<sup>+</sup>) is a proton-exchanged montmorillonite sheet silicate clay. The montmoril-



**Figure 5** MALDI-TOF MS spectrum of poly(SO) obtained by the solution polymerization of SO (0.51M) using 2% of Mag-H<sup>+</sup> at 20°C and for 24 h.

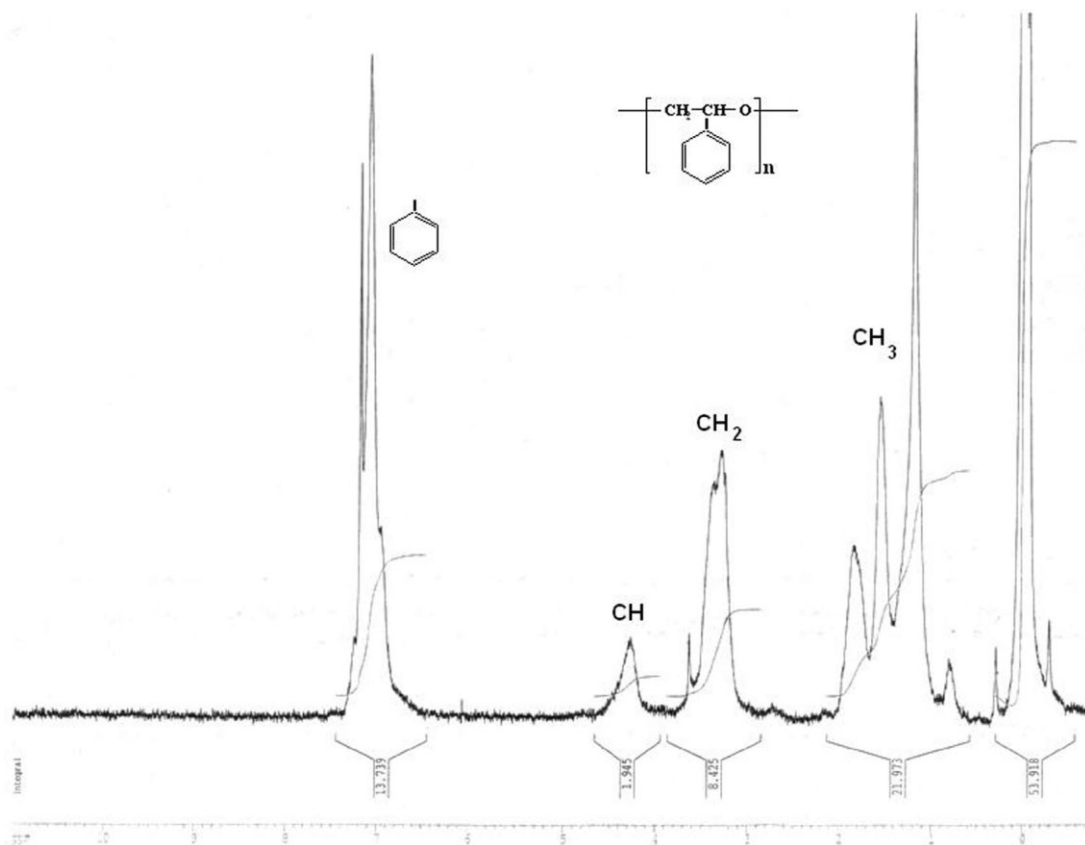


Figure 6 <sup>1</sup>H-NMR spectrum of poly(SO) catalyzed by Mag-H<sup>+</sup> catalytic system in CDCl<sub>3</sub> at 25°C.

lonite lattice is composed of layers made up of two silica tetrahedral sheets with a central alumina octahedral sheet.<sup>21</sup> STO is a monomer, which is polymerizable through a cationic path. 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 Mag-H<sup>+</sup>. Protons carried by montmorillonite sheets of Mag-H<sup>+</sup> induce the cationic polymerization. These montmorillonite sheets take place as counteranions (Scheme 2). Propagation and termination then take place by a conventional cationic mechanism. Termination by proton transfer to an initiator produces cyclization onto PSTO chains.

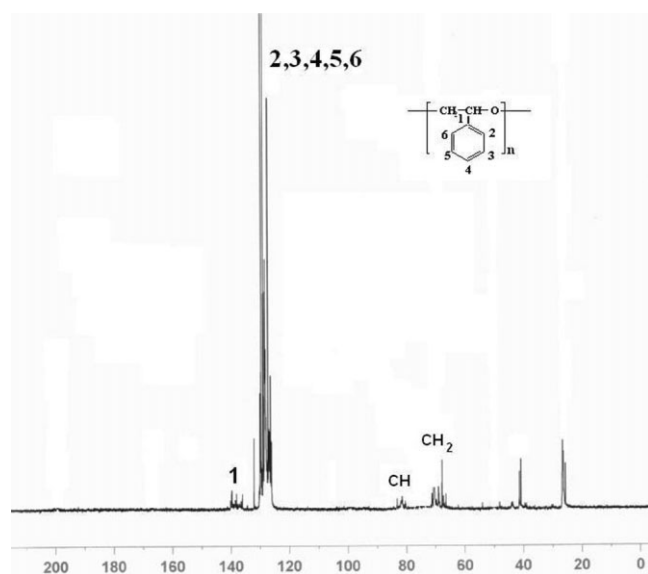
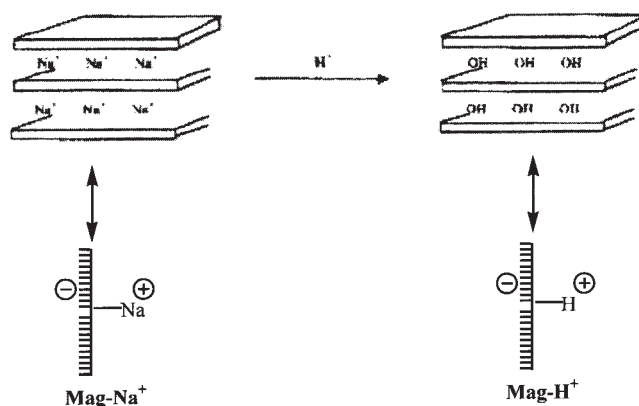


Figure 7 <sup>13</sup>C-NMR spectrum of poly(SO) catalyzed by Mag-H<sup>+</sup> catalytic system in C<sub>6</sub>D<sub>6</sub> at 25°C.

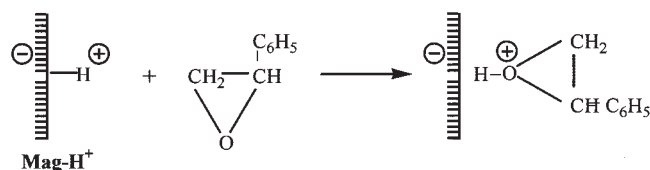


Scheme 2 Schematic representation of Mag-Na<sup>+</sup> and Mag-H<sup>+</sup>.

## Initiation

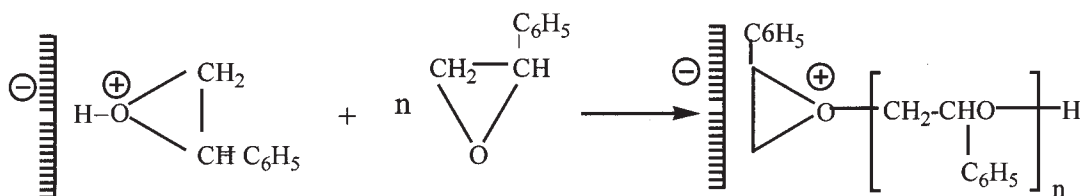
anion carried by montmorillonite sheets, as in

The first stage is the protonation of STO. The formed ions oxonium take place in the vicinity of the counter-

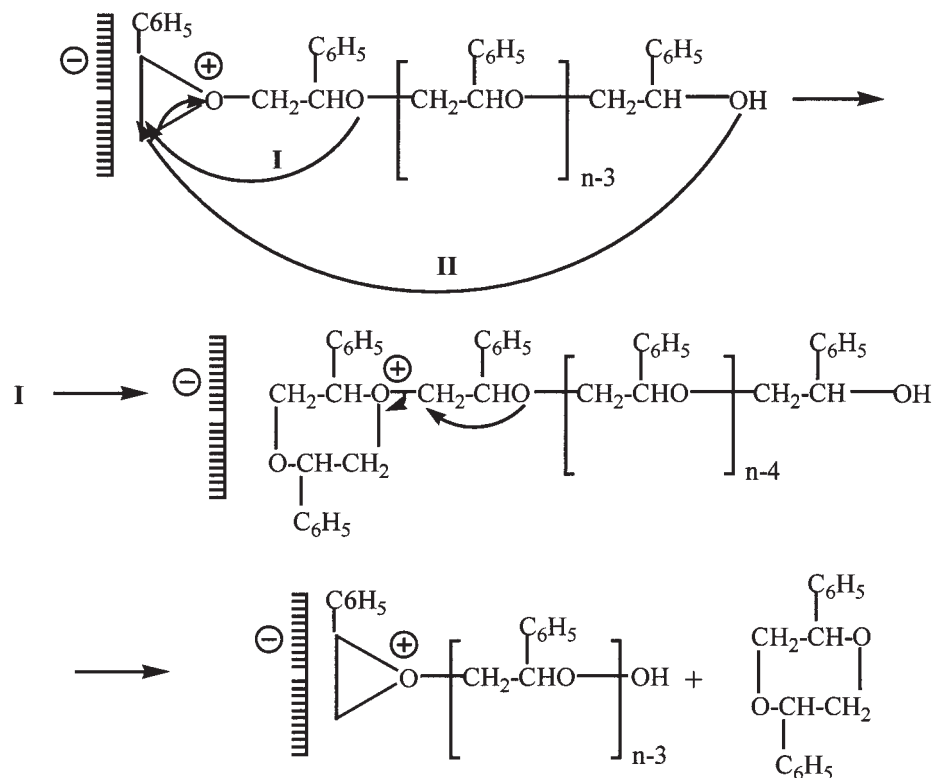
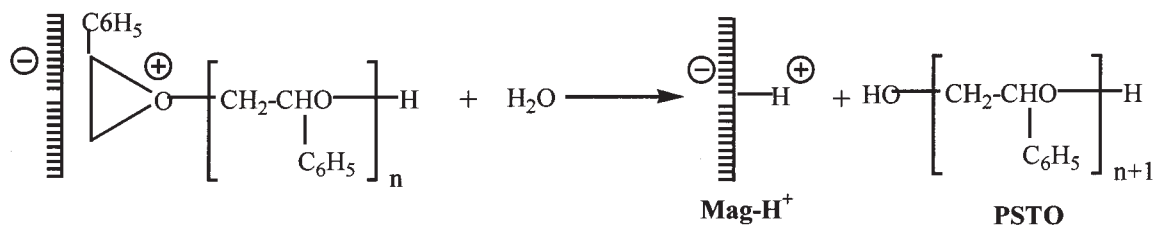


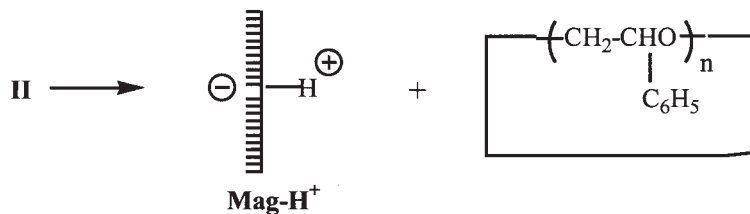
## Propagation

The propagation takes place through a nucleophilic attack of the oxygen of monomer on the carbon atom located in the  $\beta$  position with regard to the  $C_6H_5$  group of the chains in growth.



## Transfer and termination





### CONCLUSIONS

The present work shows that the preparation of poly(SO) can be induced in heterogeneous phase by proton-exchanged montmorillonite clay called Magh-nite-H<sup>+</sup> (Mag-H<sup>+</sup>).

The catalytic activity of this catalyst measured by the yield and the molecular weight of the formed polymer depends on the proportion of catalyst in the reaction medium, solvent, and the concentration of monomer. Poly(SO) was produced by a very simple procedure: just by filtering, the clay can be separated from the reaction mixture, and acidic clay is inexpensive, stable, and noncorrosive.

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