



Synthesis and Characterization of Poly(α -Methylstyrene) by Cationic Polymerization Using a New Solid Ecological Catalyst

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ABSTRACT

The cationic polymerization of α -methylstyrene (AMS) is examined at 0°C in bulk and in solution in heterogenous phase using Maghnite-Na as a new solid ecological and efficient catalyst. Maghnite-Na is Algerian Montmorillonite sheet silicate clay, exchanged with sodium. Poly (α -methylstyrene) (PAMS) have been successfully prepared and characterized by differents techniques, such as, ^1H NMR, ^{13}C NMR, IR and DSC. The structural characteristics and thermal properties of the resulting polymers are elucidated. The influences of reaction temperature, initiator/monomer weight ratio and reaction time on the yields and the molecular weights are investigated. A mechanism for the reaction was proposed.

Key words: Solid catalysts; Montmorillonite; α -methylstyrene; Poly(α -methylstyrene); Cationic polymerization; Mechanism.

INTRODUCTION

Cationic polymerization is a widely used method for preparing hydrocarbon polymers¹. Numerous examples of the polymerization of vinyl monomers by a cationic pathway using various Lewis acids such as AlCl_3 ² and BF_3 ³ catalyst systems can be found in the literature. These homogenous polymerization reactions are fast and efficient, using cheap catalysts, but molecular

weight control is generally poor. Moreover, these homogeneous Lewis acid catalysts present some major drawbacks: their corrosive nature makes them difficult to handle and they are difficult to separate from the reaction products. Indeed the catalyst has to be removed from the polymer by a water-quenching step that not only destroys the Lewis acid, but also leads to a large volume of acidic aluminum waste^{4,5}.

Recently, Hee-Jung and Dong-Ryul⁶ have prepared new nanocomposites from montmorillonite and some vinyl polymers such as PAMS. Another group developed the cationic polymerization of AMS initiated by different catalysts^{7,8}. In others researches, Belbachir et al use a montmorillonite clay that exhibits good catalytic activity named "Maghnite" to induce the cationic polymerization of many heterocyclic and vinyl monomers⁹⁻¹³.

In continuation of studies on environmentally benign methods using solid supports, we use a new solid catalyst named Maghnite-Na in the cationic polymerization of AMS, which is the purpose of this article. Maghnite-Na is a new ecological solid catalyst; it does not imply the disposal of solvents or metal catalysts. This catalyst can be easily separated from the polymer product and regenerated by heating to a temperature above 100°C⁹. The effect of some factors such as the amount of the Maghnite-Na, the effect of the time on the polymerization and the mechanism of initiation are discussed.

MATERIALS AND METHODS

Reagents

The monomer AMS (99%; Aldrich, Paris, France) was purified by fractional distillation under reduced pressure. Methanol was dried over magnesium sulfate. Dichloromethane was used as received. Raw-Maghnite is Algerian Montmorillonite clay, was procured from 3 BENTAL3 (Algerian Society of Bentonite).

Preparation of Maghnite-Na

The Clay is purified by separation of the argillaceous phase and the coarse phases. Rough clay is put in suspension in distilled water. In the suspension, the solide/liquide report/ratio is approximately 1/10. The suspension is then filtered on a sieve 0.02 mm in diameter of pores to eliminate the coarse matter and stones. It then versed in test-tubes and is left at rest during 2 hours. The separation of the argillaceous phase of the coarse fraction which remains at the bottom makes by siphonage. The recovered suspension is then centrifuged with 4500 tr/min during 20 min. Recovered clay is treated with a solution 1M of

sodium Hexametaphosphate (NaPO_3)₆ (clay 20g in 100ml), by maintaining agitation, during 3h. The suspension is versed then in the test-tubes of separation and Na-Montmorillonite separate while exploiting its falling speed, MMT crosses with 20°C, a distance of 10 cm each 8h. Therefore Na-MMT is recovered by siphonage at a distance of 20 cm after 16h of decantation. One adds water distilled to the test-tubes after each siphonage, one agitates during 15min and one lets the suspension be elutriated before proceeding to new a siphonage. Na-MMT is then recovered by centrifugation with 4500 tr/min during 1h. With the end, it is washed with distilled water (on several occasions), filtered using one sintered of porosity 3 (maximum diameter of pores from 16 to 40 μm), dried in the drying oven with 105 °C, crushed using a mortar and kept in a desiccator^{14,15}. In further work, we use the word *Maghnite-Na* in place of *Na-MMT* because it is original Maghnia.

Polymerization procedures

The polymerization of AMS was carried out in a heterogeneous system. Each mixture was prepared with 16.9 mmol of AMS and 0.3g of Maghnite-Na and was introduced in several sealed tubes. The mixture was stirred with a magnetic stirrer. After a definite period of time, the resulting polymer was extracted with dichloromethane, precipitated in methanol, washed for several times, dried at 40°C in vacuum, and weighed. The monomer yield was determined gravimetrically by weighing the precipitated PAMS chains. The polymers were re-dissolved in dichloromethane and precipitated into methanol before characterization.

Polymer characterization

Fourier Transform Infrared (FT-IR) spectroscopy (ATI Matson FTT Næ% 9501165) was used to confirm the structure of PAMS.

¹H and ¹³C nuclear magnetic resonance (NMR) measurements were carried out on a 300 MHz Bruker spectrometer equipped with a probe BB05 mm, in CDCl₃ solution under ambient temperature using Tetramethylsilane (TMS) as internal standard in these cases.

Gel-permeation chromatography was performed with a Spectra-Physics chromatograph,

equipped with four columns connected in series, and packed with Ultrastyrigel 10³, 10⁴, 10⁵, 10⁶ Å THF was used as Solvent and the instrument was calibrated to a first approximation with polystyrene of known molecular weights.

Differential scanning calorimetry (DSC) studies were conducted with a SETARAM-DSC92 in a nitrogen atmosphere at a heating rate of 10 °C/min.

Catalyst characterization

X-ray diffraction (XRD) analysis of Maghnite-Na were obtained by using a Philips PW 1880 powder diffractometer using Cu-K α radiation ($\lambda = 1.541 \text{ \AA}$).

RESULTS AND DISCUSSION

Catalyst

Belbachir et al show that the Maghnite is a montmorillonite sheet silicate clay²¹, and it has 11.9 % more SiO₂ than that from Wyoming 19.35 than from Montmorillon (Vienne, French). When treated with sulfuric acid, this difference is even greater; 14.21 % and 21.66 % as compared to Wyoming and Vienne Bentonite, respectively. Maghnite contains 5.60 % and 5.49 % less Al₂O₃, than the Wyoming and Vienne Bentonites, respectively^{16,17}.

The x-ray powder diffraction profiles shown in Figures 1 & 2 exhibited the presence of

Table 1: ¹H NMR Chemical shift for various protons of PAMS

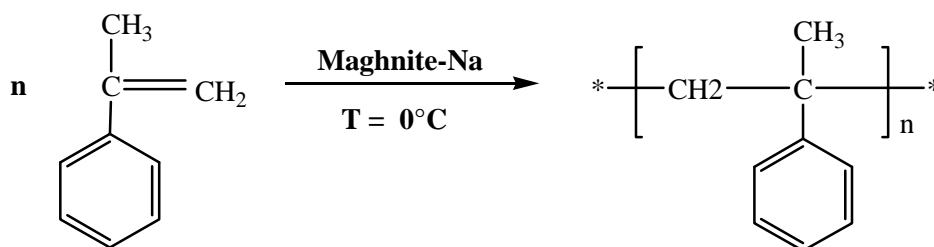
Chemical shift δ (ppm)	6,720-7,193	5,100	1,838-1,879	1,671-1,725	1,564-1,621	1,033-1,053
Attribution	2H ₂₊ 2H ₃ +1H ₄	1H ₇	2H ₆	3H ₅	3H ₈	3H ₁

Table 2: ¹³C-NMR Chemical shift for various carbons of PAMS

Chemical shift δ (ppm)	23,86	28,15	34,17	38,44	43,07	61,08	123,09 – 128,08	150,08
Attribution	C-(8)	C-(1)	C-(6)	C (1')	C (10)	C-(5)	C-(2,3,4,7,9)	C (4')

Table 3: Polymerization of AMS induced by the Maghnite-Na

Amount of Maghnite-Na (g)	0.1	0.15	0.20	0.30	0.40
Mn (g/mol)	1440	1271	1222	1212	1015
M _w (g/mol)	2084	2151	1722	1510	1732
I = M _w /M _n	1.45	1.69	1.41	1.25	1.70
Yield (%)	49	55	65	69	75



Scheme 1: Polymerization of α -methylstyrene

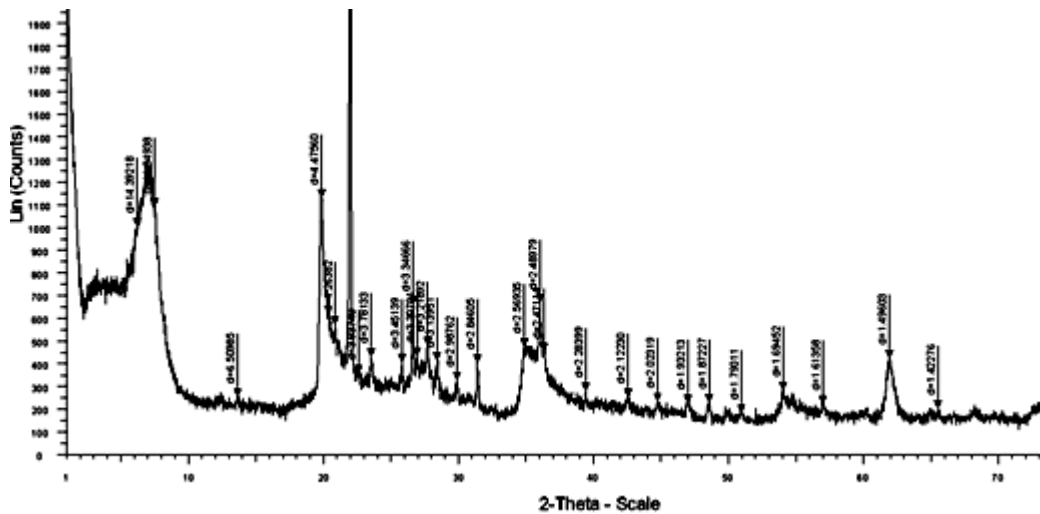


Fig. 1: XRD profiles of Maghnite-Na

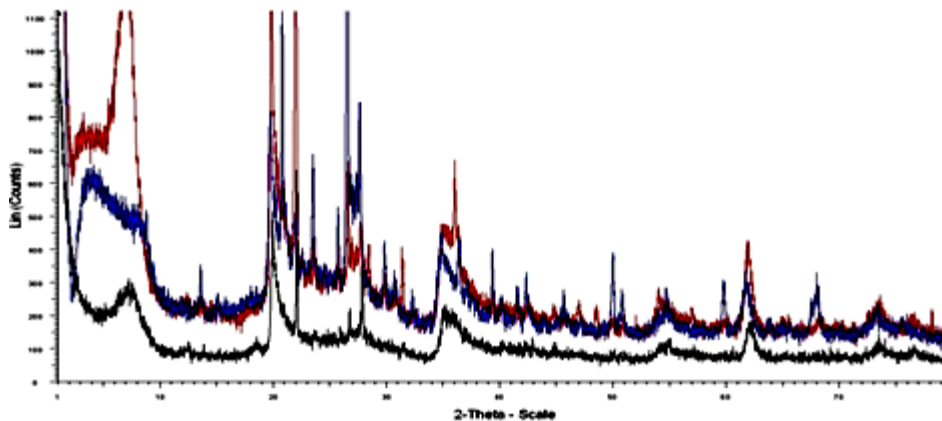


Fig. 2: XRD profiles of Raw-Magh; Maghnite- H⁺ and Maghnite-Na

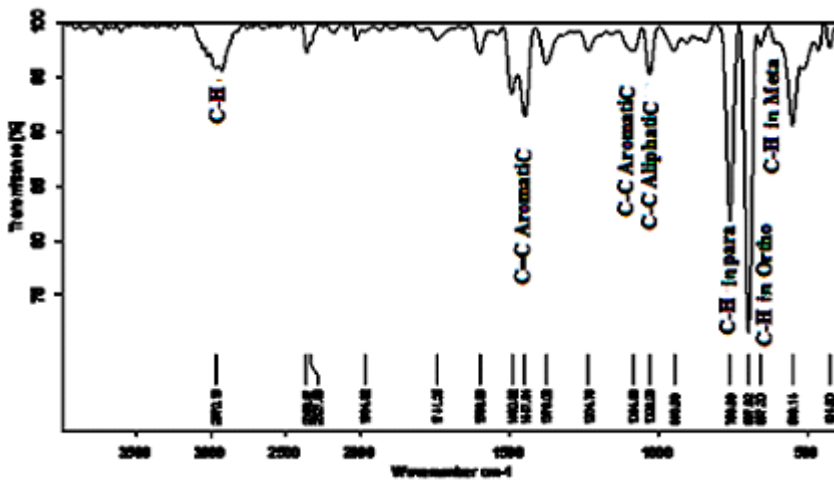


Fig. 3: IR spectrum of PAMS

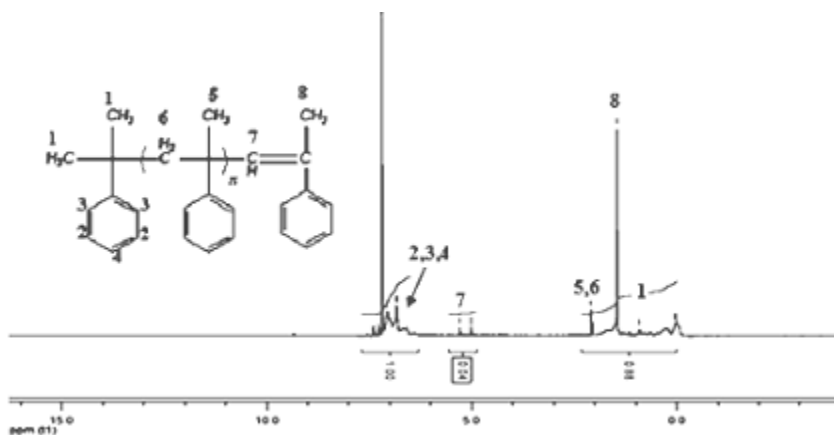


Fig. 4: ¹H NMR spectrum (CDCl₃) of PAMS catalyzed by 15% Maghnite-Na, T = 0°C

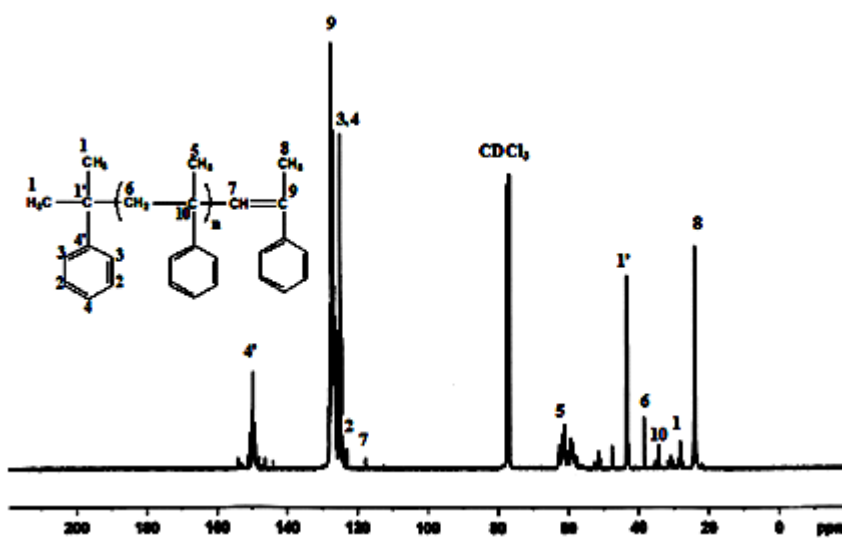


Fig. 5: ¹³C NMR spectrum (CDCl₃) of PAMS catalyzed by Maghnite-Na, T = 0°C

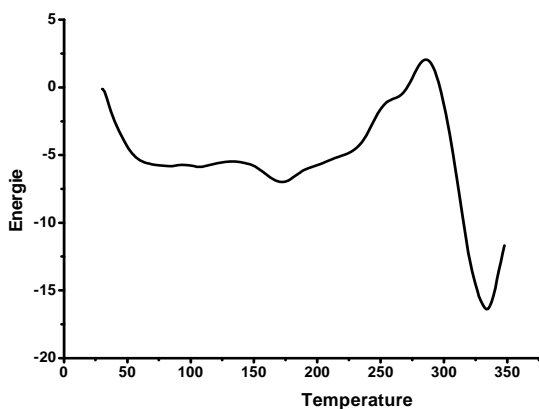


Fig. 6: DSC measurements of PAMS

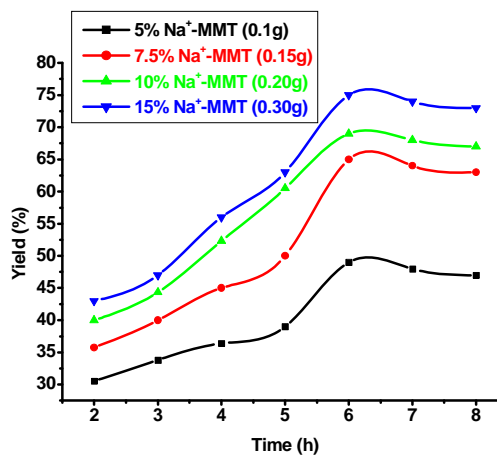


Fig. 7: Effect of the time on polymer yield; for 2g of AMS, at 0°C in bulk

other crystalline phases such as quartz, feldspath and calcite in raw-Maghnite. Under acid treatment, all trace of calcite was removed in "Maghnite-H". The increase in basal spacing from 12.5 Å in "raw-Maghnite", characteristic of a single water layer between the sheets, to a 15.02 Å value in "Maghnite" for two interlamellar water layers reflects the changes in interlayer cation and its associated hydration state as a result of the acid treatment.

Others researchers reported that the decrease in the basal spacing indicates a loss of the interlayer water upon the replacement of Na⁺ for H⁺^{18,19}.

Sodium hexametaphosphate treatment of "raw-maghnite" causes reduction in octahedral content (Al₂O₃) which resulted in an increase in the proportion of silica⁹. Maghnite-Na has a complete saturation of montmorillonite with sodium cations without destruction of catalyst structure. Similar results were obtained in previous works²⁰⁻²².

Polymer

The structure of the PAMS was confirmed by IR, ¹H NMR, ¹³C NMR and GPC measurements.

IR measurements

The IR spectrum of the polymer (Figure 3) showed principal bands characteristic of poly AMS: Peaks at 657,30 and 697,92 and 758,88cm⁻¹ (out of plane C-H bending vibration), at 1029,23 and 1084,59cm⁻¹ (C-C aromatic and aliphatic), at 3000cm⁻¹ (C-H aromatic stretching).

¹H and ¹³C NMR measurements

The ¹H-NMR and ¹³C-NMR spectrum of the PAMS are shown in figures 4 & 5. The results are presented in Table 1 & 2, respectively. The cationic polymerization of AMS was examined in the presence of Maghnite-Na as a catalyst at 0°C for 6h.

The spectrum (Figure 4) showed different peaks, the methylene groups of the main chain as large signal in the range of 1.5–2 ppm, the terminal methyl groups at 1.2 ppm. Besides these well-known resonances, analysis shows at 5 ppm the characteristic resonance of the protons borne by the terminal double bond. Similar results are obtained using a Maghnite -H⁺ as catalyst¹⁴.

DSC measurements

Figure 6 shows the results of the DSC measurements. Glass transition temperature T_g of the resulting polymer was observed in the temperature range of 150-175°C. This analysis shows also closely neighbouring melting endotherms at temperatures between 225-250°C, This analysis indicates the semi-crystalline state of the resulted polymer.

Effect of the amount of Maghnite-Na on the polymerization

The results of experiments of AMS polymerization induced by Maghnite-Na are reported in Table 3 which shows the effect of the amount of Maghnite-Na on the polymerization rate of AMS. Indeed, using various amounts of Maghnite-Na: 5; 7.5; 10; 15 and 20% by weight, the polymerization of AMS was carried in bulk at 0°C. For all these experiments the temperature was kept constant at 0°C for 6 hours. The amount of catalyst (Maghnite-Na /AMS) was an important factor of polymerization. We can see from Table 3 that the polymerization rate increased with the amount of Maghnite-Na, in which the effect of Maghnite-Na as a cationic catalyst for AMS polymerization is clearly shown. This phenomenon is probably the result of the number of 3 initiating active sites³ responsible of inducing polymerization; this number is prorating to the catalyst amount used in reaction. Similar results were obtained in the polymerization of AMS¹⁴ by Maghnite-H⁺ and in the polymerization of styrene with Maghnite-Na²².

In contrast, as depicted in Table 3, the molecular weight is inversely proportional to the amount of Maghnite-Na. This finding is in good agreement with the proposal that Maghnite-Na 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 Chabani *et al*²².

Effect of the time on the polymerization

Figure 7 shows the yield of polymer versus time for the polymerization of AMS using Maghnite-Na as catalyst. As the figure shows that at the end of 4h, polymerization takes place quickly and reaching a best yield of 75% at the end of 6h in the presence of 15% of Maghnite-Na at 0°C, after this time the

polymerization slows down gradually and the yield becomes almost constant.

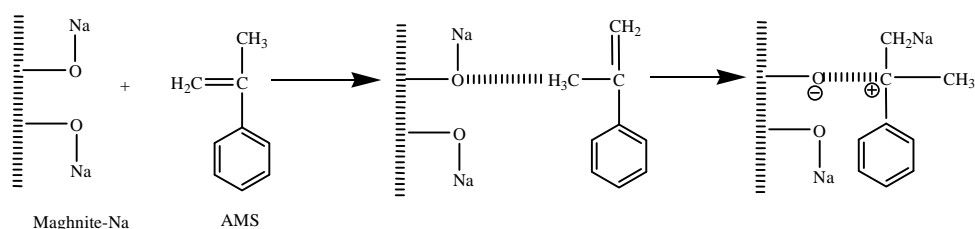
Mechanism of polymerization

Maghnite-Na is a cation-exchanged montmorillonite sheet silicate clay. The Montmorillonite lattice is composed of layers made up of two silica tetrahedral sheets with a central alumina octahedral sheet. AMS polymerizes cationically by opening of the double bond in the monomer. According to the foregoing discussion and the results of product analysis, we may suggest a cationic mechanism for the resulting reaction of

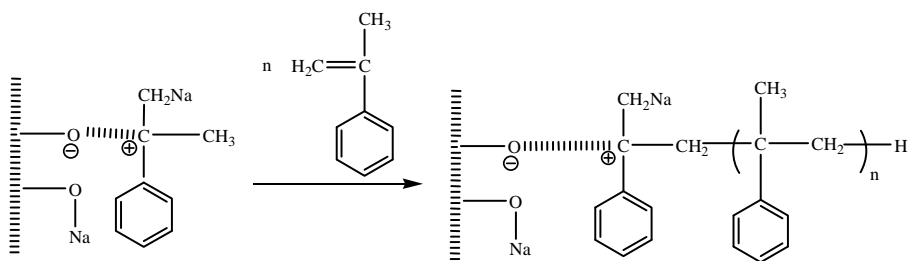
polymerization induced by Maghnite-Na. Cations carried by Montmorillonite sheets of Maghnite-Na (Scheme 2) induced the cationic polymerization. Propagation and termination then take place by conventional cationic mechanism (Scheme 3). Termination occurs by proton transfer to monomer and/or to initiator produced by unsaturation as shown in the reaction (Schemes 4).

Initiation

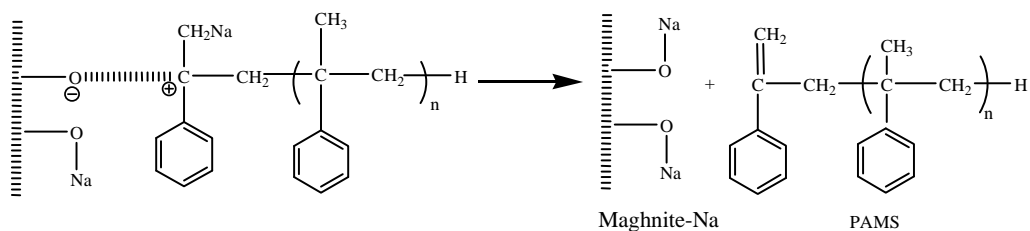
Initiation is done between the initiator and a first molecule of the monomer to form the active species (Scheme2).



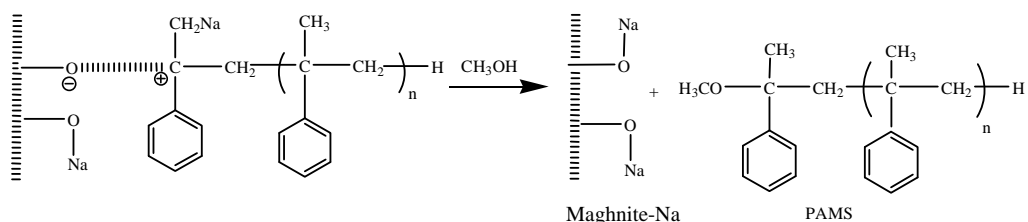
Scheme 2: Initiation



Scheme 3: Propagation



Scheme 4-1: Spontaneous Transfert



Scheme 4 -2: Termination

Propagation

The propagation step is the successive reaction of AMS with the carbocation intermediate (Scheme 3).

Termination

We suppose that there was formation of a double bond at the end of the chain of the AMS by spontaneous transfer (Scheme 4-1) or by methanol added as quenching agent to the PAMS growing chains (Scheme 4-2) and regeneration of catalyst.

CONCLUSIONS

The present work shows that AMS

polymerization can be induced in heterogeneous phase by sodium exchanged montmorillonite clay called Maghnite-Na. PAMS was successfully obtained by direct method by the use of a cheap non-toxic catalyst and by an easy-to-handle procedure and just by filtering, the catalyst can be separated from the reaction mixtures. The polymerization was found to be initiated by Maghnite-Na powder. The structure of the polymer is confirmed with ^1H and ^{13}C NMR spectra. The mechanism of this reaction involves both, Brønsted and Lewis acidic sites on the clay interface, to initiate the polymerization. This chemistry may be a potential direct method to produce PAMS/Montmorillonite nanocomposites.

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