

Maghnite-H⁺, a Solid Catalyst for the Cationic Polymerization of α -Methylstyrene

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ABSTRACT: The polymerization of α -methylstyrene (AMS) catalyzed by Maghnite-H⁺ (Mag-H) was investigated. Mag-H is a montmorillonite sheet silicate clay, exchanged with protons. It was found that the cationic polymerization of AMS is initiated by Mag-H at ambient temperature in bulk and in solution. The effect of the amount of Mag-H, the temperature, and the solvent was studied. The polymerization rate increased with increase in the temperature and the pro-

portion of catalyst, and it was larger in nonpolar solvents. These results indicated the cationic nature of the polymerization. It may be suggested that the polymerization is initiated by proton addition to monomer from Mag-H. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 1476–1479, 2008

Key words: synthesis; cationic polymerization; catalysts; montmorillonite; α -methylstyrene

INTRODUCTION

Traditional processes for the cationic polymerization of α -methylstyrene (AMS) to poly(α -methylstyrene) [poly(AMS)] have made use of Lewis acids such as boron trifluoride or other protic acid catalyst/initiators, such as tetrafluoroboric acid, hexafluorophosphoric acid, and pentafluoroantimonate.^{1–5}

A drawback of most current art methods using cationic and Lewis acid initiators is that they require cold temperatures to control the polymerization and obtain polymers of the desired molecular weight and molecular weight distribution.^{1,6–8}

Recently, Hee-Jang and Dong-Ryul⁹ have prepared new nanocomposites from montmorillonite and some vinylic polymers such as poly(AMS).

The cationic polymerization of AMS was initiated using cationic initiator in the presence of montmorillonite to produce these nanocomposites.

The purpose of this article is to study the cationic polymerization of AMS initiated directly by a montmorillonitic clay called Maghnite-H⁺, a new nontoxic cationic catalyst for vinyl monomers.^{10,11} Mag-H can be easily separated from the polymer product and regenerated by heating to a temperature above 100°C.¹⁰ The effect of some factors such as the amount of the Mag-H, the temperature or the dielectric constant of solvent, and the mechanism of initiation are discussed.

EXPERIMENTAL

Preparation of the maghnite-H⁺

The preparation of the Mag-H was carried out by using a method similar to that described by Belbachir and coworkers.^{10,11} Indeed, the raw-maghnite (20 g) was crushed for 20 min using a Prolabo ceramic balls grinder. It was then dried by baking at 105°C for 2 h. The maghnite was then weighed and 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 0.25M sulfuric acid, until saturation was achieved over 2 days at room temperature, the mineral was washed with water until it became sulfate free, and then dried at 150°C.

Reagents

The monomer (99%; Aldrich, Paris, France) was purified by fractional distillation under reduced pressure. Methanol was dried over magnesium sulfate. Toluene was washed with concentrated sulfuric acid and water, refluxed over sodium, and distilled. Dichloromethane, 1,4-dioxane, 1,2-dichlorobenzene, and THF (Aldrich Chemical) were used as received.

Polymerization procedures

The polymerization of AMS was carried out in a heterogeneous system. Each mixture was prepared with 8.5 mmol of AMS and 0.05 g of Mag-H and were introduced in several (6–8) sealed tubes. The mixture was stirred with a magnetic stirrer under dry

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nitrogen. After a definite period of time, the reaction was terminated by methanol. The resulting polymer was extracted with dichloromethane, precipitated in methanol, washed for several times, dried at 40°C in vacuum, and weighed. The monomer conversion was determined gravimetrically by weighing the precipitated poly(AMS) chains.

Polymer characterization

¹H and ¹³C NMR spectra were recorded in CDCl₃ solution under ambient temperature on an AM 300 FT Bruker spectrometer using tetramethylsilane as internal standard.

Viscosity and molecular weight

Viscosity measurements were carried out with an Ubbelohde capillary viscosimeter (viscologic T11, version 3-1 Semantec). Intrinsic viscosity, $[\eta]$ (mL/g), was measured at 25°C in THF. Viscosity-average molecular weight, M_v , was calculated according to the following equation¹²:

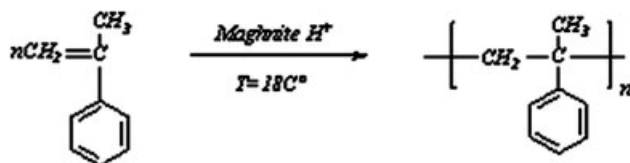
$$[\eta] = 10.1 \times 10^{-3} \times M_v^{0.71}$$

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.

RESULTS AND DISCUSSION

The use of acid-treated clays as a solid source of protons in a number of industrial significant reactions continues because they constitute a widely available, inexpensive solid source of protons, e.g., they have been employed as cracking catalysts until the 1960s,¹³ and are still currently used in industrial processes, such as the alkylation of phenols¹⁴ and the dimerization and polymerization of unsaturated hydrocarbons.^{10,15}

Montmorillonites have both Brønsted and Lewis acid sites and when exchanged with cations having a high charge density, as protons, produce highly



Scheme 1 Polymerization of AMS.

TABLE I
Polymerization^a of AMS Initiated by Mag-H⁺

Time (h)	Conversion %	M_v
0	0	0
2	3.54	560
3	9.81	627
4	37.62	1029
5	43.33	2355
6	61.66	2582
8	69.14	2615

^a AMS, 8.5 mmol; Mag-H, 0.05 g, $T = 18^\circ\text{C}$.

active catalysts for acid-catalyzed reactions.¹⁶ Intercalated organic molecules are mobile and can be highly polarized when situated in the space between the charged clay layers. These exchanged montmorillonites have been successfully used as catalysts for the reactions of polymerization.¹⁵

The aim of this research is to extend the scope of other promising new field of polymer synthesis by the use of another catalyst system that has been shown to exhibit higher efficiency. This study is also concerned with polymerization and examines the catalytic activity of an Algerian proton-exchanged montmorillonite clay called "maghnite" via AMS polymerization. The structure and the composition of the catalyst were reported in previous works.^{10,11} The elementary analysis of maghnite, obtained using XRF spectroscopy and monomer conversions, show that there is an excellent correlation between the acid treatment and the catalytic activity of maghnite. Acid treatment of "raw-maghnite" causes reduction in octahedral content (Al₂O₃) which resulted in an increase in the proportion of silica. It is necessary to

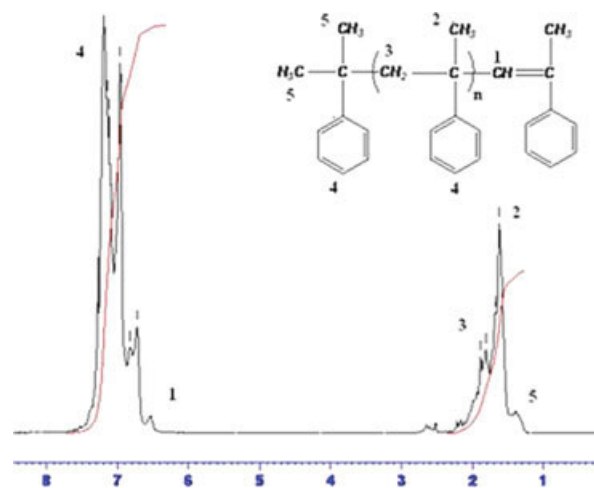


Figure 1 ¹H NMR spectrum (CDCl₃) of poly(AMS) catalyzed by Mag-H, $T = 18^\circ\text{C}$. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

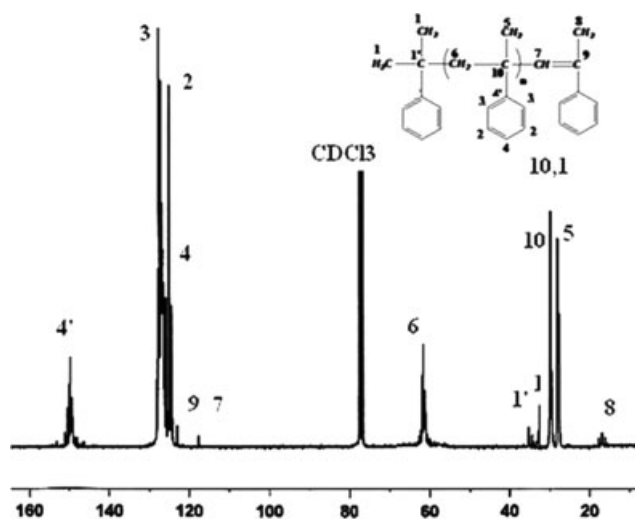


Figure 2 ^{13}C NMR spectrum (CDCl_3) of poly(AMS) catalyzed by Mag-H, $T = 18^\circ\text{C}$.

report that the best value of monomer conversion was obtained with maghnite treated by 0.25M sulfuric acid solution, in which there is a complete saturation of montmorillonite with protons without destruction of catalyst structure.^{17,18}

Polymerization of AMS by Mag-H

The cationic polymerization of AMS was examined in the presence of Mag-H powder in bulk at 18°C (Scheme 1). The results are shown in Table I. The proof for this polymerization obtained by ^1H and ^{13}C NMR spectroscopy (Bruker AM 300, solvent: CDCl_3) is shown in Figures 1 and 2.

Effect of the amount of Mag-H on the polymerization

Figure 3 shows the effect of the amount of Mag-H on the polymerization rate of AMS. Indeed, using

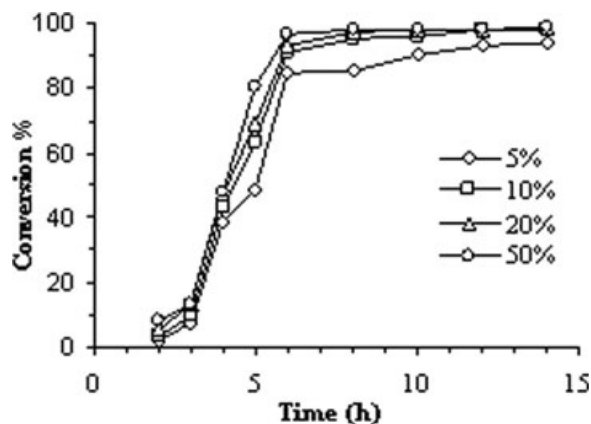


Figure 3 Effect of maghnite- H^+ /monomer weight ratio on the conversion of monomer; $T = 18^\circ\text{C}$.

TABLE II
Effect of Reaction Temperature on the AMS Polymerization^a

T ($^\circ\text{C}$)	Conversion of monomer (wt %)	M_v	M_w/M_n
0	65.44	1.96	1.29
10	88.65	2.15	1.22
20	69.14	2615	1.23
30	70.26	2862	2.32
40	51.33	2015	2.93
45	42.27	1845	2.89

^a Maghnite- H^+ /AMS weight ratio = 10% reaction time 8 h.

various amounts of Mag-H, 5, 10, 20, and 50% by weight, the polymerization of AMS was carried in bulk at 18°C . The polymerization rate increased with the amount of Mag-H, in which the effect of Mag-H as a cationic catalyst of AMS is clearly shown. Similar results are obtained by Belbachir and coworkers¹¹ in the polymerization of isobutylene by Mag-H, which polymerizes only by cationic process.¹⁹

Effect of temperature on polymerization

In the presence of Mag-H, the polymerization of AMS in bulk was carried out at different temperatures and the effect of temperature on polymerization was examined.

The results are shown in Table II. The rate of polymerization was found to increase with the temperature of the polymerization.

The monomer conversion and Molecular weight of polymer reach maximum values around $20\text{--}30^\circ\text{C}$. On the other hand, with the increase in the reaction temperature above 20°C , the molecular weight of the obtained polymer and monomer conversion decrease progressively, suggesting the possible occurrence of thermal degradation. It can be noted that above 20°C , MWD of the resulting polymer was broad, suggesting the occurrence of thermal degradation of the polymers at the reaction temperature over 20°C .

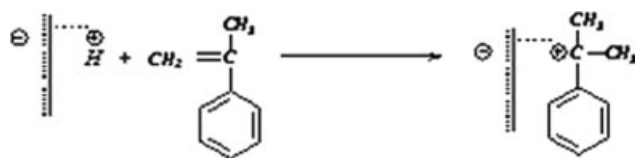
Effect of solvent on the polymerization

The effect of different solvents on the polymerization of AMS initiated by Mag-H is shown in Table III. It

TABLE III
Effect of Solvent on the AMS Polymerization^a

Solvent	Conversion	M_v	M_w/M_n
1,4-Dioxane	45.5	7841	1.19
Toluene	36.15	7669	1.18
CH_2Cl_2	32.8	7602	1.23
1,2-Dichlorobenzene	15.66	7369	1.21

^a Maghnite- H^+ /AMS weight ratio = 10% reaction time 8 h; $T = 18^\circ\text{C}$.



Scheme 2 Initiation.

can be seen that the molecular weight of poly(AMS) and the conversion of AMS achieved in nonpolar solvents are higher than those in polar solvents. The monomer conversion in polar solvents was also found to be slower as compared to that in the nonpolar solvents. This result is due to the catalyst structure: as all mineral clays, Mag-H shows an affinity for 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 AMS conversions.

Mechanism of polymerization

The polymerization of AMS is considered to be initiated by proton addition from Mag-H to AMS and the Maghnite takes place as counterion. Propagation and termination then take place by conventional cationic mechanism. Termination occurs by proton transfer to monomer and/or to initiator produced by unsaturation as shown in the reaction (Schemes 2–4).

Initiation

Initiation is done between the initiator and a first molecule of the monomer to form the active species (Scheme 2).

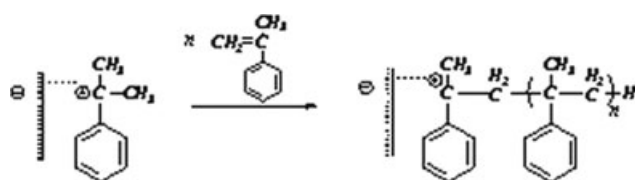
Propagation (Scheme 3)

Termination

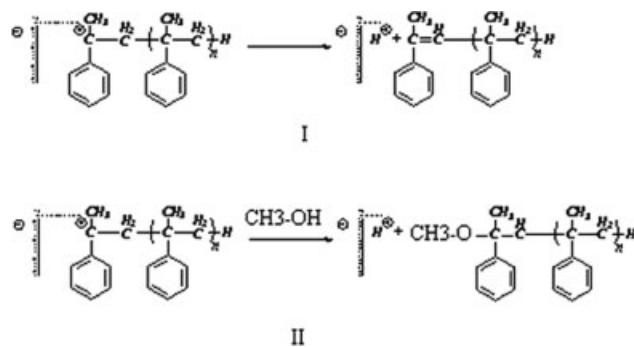
We suppose that termination was caused by spontaneous transfer (Scheme 4, I) or by methanol added as quenching agent to the poly(AMS) growing chains (Scheme 4, II).

CONCLUSIONS

Maghnite-H⁺, a proton exchanged montmorillonite clay, is an effective initiator for the polymerization



Scheme 3 Propagation.



Scheme 4 Termination.

of AMS. This polymerization was found to be initiated by Maghnite-H⁺ powder in heterogeneous phase. The polymerization was considered to be initiated by the proton addition from maghnite-H⁺ to monomer and the propagation proceeds with maghnite as counterion.

In the polymerization, the solid catalyst was thought to act as an acid to generate cation species. Actually, the efficiency of the polymerization reflected the Lewis acidity of maghnite-H⁺. 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.

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