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Research Article

Methyl Methacrylate and Alpha-Methylstyrene: New Strategy for Synthesis of Bloc Copolymers for Use in Potential Biomedical Applications Generated by an Ecologic Catalyst Called Maghnite (Algerian MMT)

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Abstract

A new model for synthesis of the plastics, block copolymers were prepared from methyl methacrylate (MMA) and alpha-methyl styrene (α-MS) by cationic copolymerization in the presence of a new and efficient catalyst of "Maghnite-Na" at 0 °C in bulk. In this paper, the copolymerization of α-MS and MMA was induced in heterogeneous phase catalyzed by Maghnite-Na was investigated under suitable conditions. The "Maghnite-Na" is a montmorillonite sheet silicate clay, with exchanged sodium cations to produce Na-Montmorillonite (Na^+-MMT) obtained from Tlemcen, Algeria, was investigated to remove heavy metal ion from wastewater as an efficient catalyst for cationic polymerization of many vinylic and heterocyclic monomers. The synthesized copolymer were characterized by Nuclear Magnetic Resonance (NMR-^{1}H, NMR-^{13}C), FT-IR spectroscopy, Differential Scanning Calorimetry (DSC), and Gel Permeation Chromatography (GPC) to elucidate structural characteristics and thermal properties of the resulting copolymers. The structure compositions of "MMT", "H^+-MMT" and "Na^+-MMT" have been developed. The effect of the MMA/α-MS molar ratio on the rate of copolymerization, the amount of catalyst, temperature and time of copolymerization on yield of copolymers was studied. The yield of copolymerization depends on the amount of Na^+-MMT used and the reaction time. The kinetic studies indicated that the polymerization rate is first order with respect to monomer concentration. A possible mechanism of this cationic polymerization is discussed based on the results of the ^{1}H-NMR Spectroscopic analysis of these model reactions. A cationic mechanism for the reaction studies showed that monomer was inserted into the growing chains. Copyright © 2016 BCREC GROUP. All rights reserved

Keywords: catalyst; clay; Na-montmorillonite; cationic copolymerization; methyl methacrylate; alpha-methyl styrene; block copolymerization; mechanism

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1. Introduction

A new model has been developed for the preparing plastics polymers. Recently, the aliphatic and aromatic polymers, in particular poly(α-MS), poly(MMA), and their copolymers,

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the variety of binary initiating systems consisting of a protonic acid and a Lewis acid have been reported to induce the living polymerizations of cationically polymerizable vinyl monomers [1-9]. Cationic polymerization was a widely used method for preparing hydrocarbon polymers [10]. Numerous examples of the polymerization of vinyl monomers by a cationic pathway using various Lewis acids, such as: $AlCl_3$ [11], BF_3 [12], $SnCl_4$ [13], and $TiCl_4$ [14] 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 making reuse impossible but also leads to a large volume of acidic aluminum waste, unacceptable in these environmentally conscious days [15,16]. Methyl Methacrylate (MMA) copolymers have a number of excellent characteristics which have placed them in a position of prominence in the plastic industry.

The preparation of poly(methyl methacrylate) (PMMA) plastics and their characteristic structure properties have been thoroughly investigated in recent years [17-20]. This polymer have a several applications such as material chemistry, biological medicine and environmental science [21-25]. Many researchers have reported fabrication of poly Alpha-Methyl Styrene (PAMS) / clay nanocomposites [26-30], polyMethyl Methacrylate (PMMA) / clay nanocomposites and poly styrene-co-methyl methacrylate (PS-co-PMMA) / Na-MMT nanocomposites because of many advantages such as high mechanical property, good gas barrier, flame retardation and, etc. [31,33], polymer/clay nanocomposites have been intensely investigated by researchers at Toyota for light-weight material applications [34-41]. The cationic polymerization of MMA seems unlikely in view of it structure, Lewis acid catalysis explains the difficulties encountered in trying fabricate plastics. Other attempts to induce cationic copolymerization of methyl methacrylate have been unsuccessful [42,43]. There is, to date, no information on the polymerization of MMA with Na^+-MMT catalyst. In continuation of our studies on environmentally benign methods using solid supports, we report for the first time and present a new approach to synthesis of poly(AMS/MMA) via cationic polymerization using a Na^+-MMT [44-46]. In our previous papers, we already reported about polymerization catalyzed by "Na^+-MMT", this new nontoxic cationic catalyst exhibited higher efficiency via the polymerization of vinylic and hetero-cyclic monomers [47-57].

The objectives of this work are the synthesis of block copolymers of poly (MMA-b-AMS) by the use of Na^+-MMT as catalyst. The interesting aspect of this new non-toxic catalyst is the environmentally friendly nature of the reaction because it does not imply the disposal of solvents or metal catalysts. This catalyst can be easily separated from the copolymer product and regenerated by heating at a temperature above 100 °C [44-46]. The effects of different synthesis parameters such as the amount of Na^+-MMT, comonomer AMS, and eventually the mechanism are discussed.

2. Materials and Method

2.1. Materials

Methyl methacrylate (99%) and α-methyl styrene (99%) were purchased from Aldrich (Paris, France) were purified by fractional distillation under reduced pressure. Methanol and 1,4-dioxane were dried over magnesium sulfate $MgSO_4$ and distilled. (Aldrich Chemical) were used as received. Raw-bentonite: Algerian Montmorillonite clay, was procured from "BENTAL" (Algerian Society of Bentonite).

2.2. Preparation of the sodic montmorillonite (Na+-MMT)

The bentonite used in this work came from a quarry located in Maghnia (North West of Algeria) and was supplied by company "ENOF" (an Algerian manufacture specialized in the production of no ferric products and useful substances). Figure 1 and Table 1 show X-ray diffraction patterns of raw-Montmorillonite and Na-Montmorillonite. These results confirm that the bentonite used consists essentially of montmorillonite, prepared in laboratory chemistry of polymers in ORAN University (LCPO). This Clay was purified by separation of the argillaceous phase and the coarse phases. Rough clay was put in suspension in distilled water. In the suspension, the solid/liquid report/ratio was approximately 1/10. The suspension was 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 was left at rest during 2 hours. The separation of the argillaceous phase of the coarse fraction which remains at the bottom was made by siphoning. The recovered suspension was then centrifuged with 4500 rpm during 20 min. Recovered clay was treated with a solution of 1 M of sodium hexametaphosphate $(NaPO_3)_6$ (clay 20 g in 100 mL), by maintaining agitation, during 3 h. The suspension was versed then in the test-tubes of separation and Na-Montmorillonite was separated while exploiting its falling speed, Montmorillonite crosses with 20 °C, a distance of 10 cm each 8 h. Therefore Na-Montmorillonite was recovered by siphoning at a distance of 20 cm after 16 h of decantation. One adds water distilled to the test-tubes. After each siphoning, one agitated during 15 min and one let the suspension to be elutriated before proceeding to new a siphoning. Montmorillonite was then recovered by centrifugation with 4500 rpm during 1 h. With the end, it was washed with distilled water (on several occasions), filtered using one sintered of porosity 3 (maximum di-

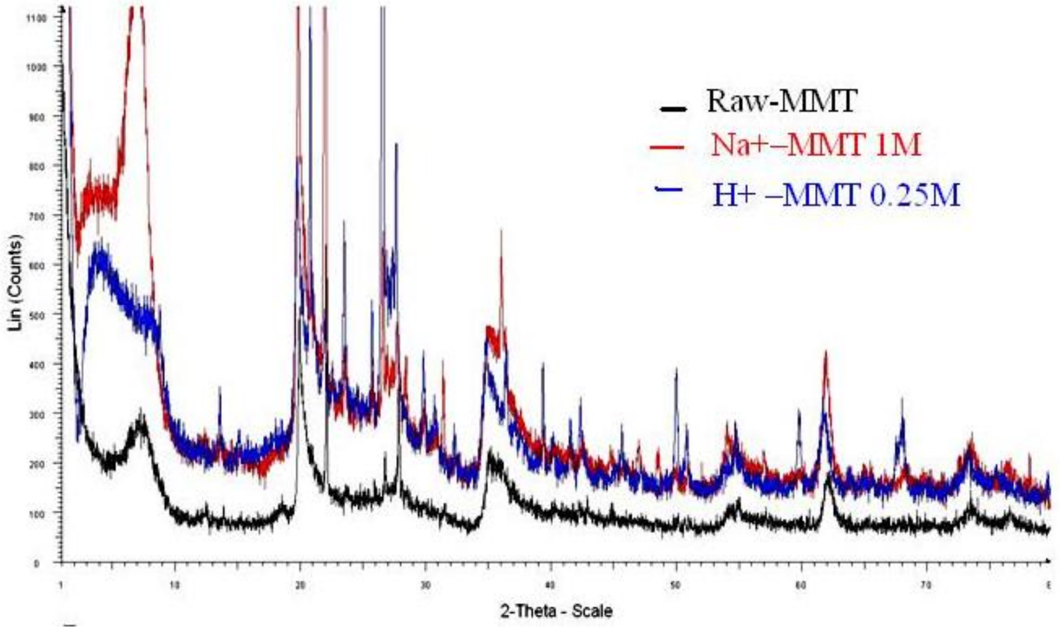


Figure 1. Experimental set-up for glycerol dry reforming

Table 1. Comparison in the RX characteristic of American and Maghnia Algerian Bentonites

	Montmorillonite		Quartz		Dolomite		Calcite		Smectite	
	θ	d	θ	d	θ	d	θ	d	θ	d
Bentonite (Wyoming) [61]	4.50	9.69	13.50	3.35	23.75	1.91	19.5	2.28	31.0	1.50
	10.00	4.48	11.00	4.05	-	-	13.75	3.20	-	-
	17.50	2.56	12.00	3.76	-	-	-	-	-	-
	27.25	1.69	34.50	1.36	-	-	-	-	-	-
MMT Brute [44-46]	4.50	9.692	13.40	3.349	15.75	2.848	14.95	3.001	31.0	1.497
	10.00	4.485	11.00	4.045	-	-	18.25	2.488	-	-
	17.50	2.557	11.75	3.782	-	-	13,90	3.222	-	-
	27.00	1.692	36.25	1.287	-	-	-	-	-	-
Bentonite Na^+ [61]	3.5	12.79	-	-	-	-	14.0	3.13	31.0	1.50
	9.95	4.51	-	-	-	-	-	-	-	-
	17.45	2.58	-	-	-	-	-	-	-	-
	27.25	1.69	-	-	-	-	-	-	-	-
Na^+-MMT [44-46]	3.50	12.766	26.59	3.347	15.75	2.847	14.0	3.221	31.0	1.496
	10.00	4.483	20.76	4.045	-	-	14.25	3.136	-	-
	17.50	2.557	-	3.774	-	-	18,5	2.490	-	-
	27.00	1.696	-	1.286	-	-	-	-	-	-
H^+-MMT [44-46]	8.74	10.097	20.75	4.274	-	-	29.81	2.993	59.82	1.544
	19.71	4.498	26.55	3.353	-	-	27.35	3.256	61.81	1.499
	34.54	2.593	-	-	-	-	27.62	3.225	-	-
	54.77	1.674	-	-	-	-	-	-	-	-

ameter of pores from 16 to 40 µm), dried in the drying oven with 100 °C, crushed using a mortar and kept in a desiccator [58,59].

2.3. Catalyst structure

Various methods of analysis, such as: 27Al and 29Si MAS NMR, show that Maghnia Algerian Bentonite is a montmorillonite sheet silicate clay [47,48]. Figure 1 (a, b, c) and Table 1 show X-ray diffraction patterns of raw-montmorillonite, H^+-MMT and Na^+-MMT, respectively. The basal spacing of the raw- montmorillonite and Na^+-MMT, were exhibited 12.766 Å and 10.097 Å, respectively. The titration of raw-montmorillonite with a solution 1 M $(NaPO_3)_6$ and 0.25 M H_2SO_4 resulted in the exchange of exchangeable cations for H^+ and Na^+ in the interlayer. The X-ray powder diffraction of the dried Na^+-MMT, as shown in Figure 1(c), exhibited 001 reflections corresponding to basal spacing of 9.69 Å. Yun Kwon *et al.* [60] reported that the decrease in the basal spacing indicates a loss of the interlayer H_2O upon the replacement of Na^+ for H^+. In particular, although the X-ray peak of the montmorillonite did not change substantially before or after the sodium hexametaphosphate treatment, there was a decrease in the basal spacing. This implies that the original structure was well preserves after the sodium hexametaphosphate treatment.

2.4. Polymerization procedure

The polymerization of MMA/AMS was carried out in a heterogeneous system, using Na^+-MMT as a catalyst in different molar ratios were copolymerized by bulk polymerization, The bulk Copolymers of various compositions of α-methyl styrene and methyl methacrylate were prepared by a cationic polymerization process at 0 °C with 0.23 g initiator Na^+-MMT under a certain reaction time. The reaction scheme is shown in Figure 2. The resulted polymer was dissolved in 1.4-dioxane, precipitated in cold methanol, and then air-dried at room temperature. The above procedure was repeated several times in order to obtain a highly purified polymer.

2.5. Polymer characterization

The copolymers were re-dissolved in 1.4 dioxane and precipitated into methanol 3 times before characterization. Fourier Transform Infrared (FT-IR) spectroscopy (Alpha-Bruker) was used to confirm the structure of PAMS-PMMA block copolymers. ^1H and ^{13}C nuclear magnetic resonance (NMR) measurements were carried out on a 300 MHz Bruker spectrometer equipped with a probe BB05 mm, in $CDCl_3$ solution under ambient temperature using tetramethyl silane (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 Ultrastyragel 10^3, 10^4, 10^5, 10^6 A° THF was used as solvent and the instrument was calibrated to a first approximation with polystyrene of known molecular weights.

Viscosity measurements were carried out with an Ubbelohde capillary viscosimeter (viscologic TI1, 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 equation (1) [62].

$$[\eta] = 10.1\times10^{-3}\ Mv0.71 \qquad (1)$$

Thermal analysis of poly (MMA-b-AMS) was conducted on a differential calorimetry apparatus (200 PC NETZCH, 204F1 PHOENIX240-12-0110-L DSC) the measurements were carried out with a heating rate of 10 °C/min under 50 cm^3/min nitrogen flow.

3. Results and Discussion

The purpose of this paper is the synthesis of poly (MMA-b-AMS) by bulk polymerization catalyzed by Na^+-MMT [44-46]. Montmorillonites have both Brønsted and Lewis acid sites and when exchanged with cations having a high charge density, as sodiums, produce highly active catalysts for sodium Hexametaphosphate catalyzed reactions. Intercalated organic molecules are mobile and can be highly polarized when situated in the

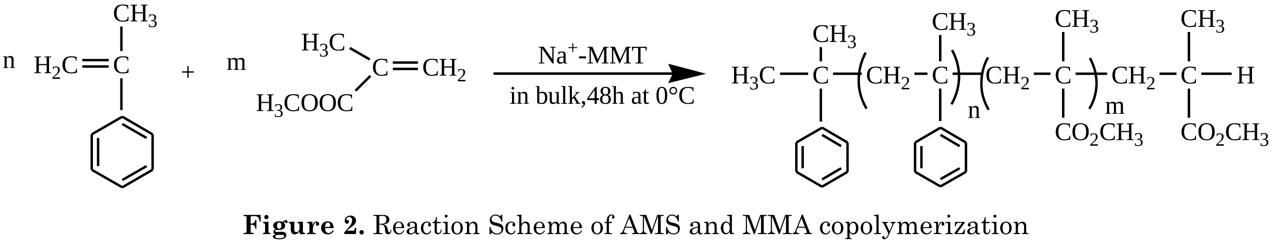


Figure 2. Reaction Scheme of AMS and MMA copolymerization

space between the charged clay layers. These exchanged montmorillonites have been successfully used as catalysts for the reactions of polymerization [61].

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 sodiums-exchanged montmorillonite clay called ″Na^+-MMT″ via cationic copolymerization of methyl methacrylate (MMA) and α-MethylStyrene (AMS). The structure and the composition of the catalyst were reported in previous works [44-46].

3.1. Synthesis of poly(MMA-b-α-MS) by sodic montmorillonite

We intended to prepare poly(MMA-b-α-MS) block copolymers by cationic polymerization with 30% α-MS and 70% MMA in the presence of 15% Na+-MMT as a catalyst for 48 h at 0 °C. The catalyst was dried in an oven at 120 °C overnight and then transferred to a vacuum desiccators containing P_2O_5 to cool to room temperature overnight. The reaction was carried out in tubes sealed and immersed in an glazing bath at 0 °C. Each tube contains an amount of α-MS (0.013 mole, 1.54 g) which contains 0.23 g (15%) of Na^+-MMT, the system is put under mechanical agitation during 10 min; when the mixture becomes viscous and at the end of reaction we added thereafter the second monomer 3 g (0.031 mole) of MMA, the mixture is left under agitation during 48 h. When the reaction time to be over, the polymer was dissolved with 20 mL of 1.4 dioxane to remove the clay and precipitated in cold methanol, after polymerization the samples were filtered and dried in vacuum. The precipitates were characterized by ^{1}H-NMR, ^{13}C-NMR, and infrared spectroscopy (FT-IR) analysis. The results are shown in Table 2, The proof for this copolymerization was obtained by GPC measurements, Chromatogram. The results of the analysis of the polymer by GPC are shown in Figure 3. As shown, the macromolecular weight distribution of the obtained polymer is narrow, this suggests that chain transfer does not occur.

3.2. Effect of the amount of MMT-Na^+ on copolymerization

The results of experiments of *α*-methyl styrene copolymerization induced by ″Na^+-MMT 1 M″ are reported in Table 3, shown the effect of the amount of Na^+-MMT on the copolymerization of AMS and MMA. Indeed, using various amounts of Na^+-MMT, 10, 13, 15, 18 and 20% by weight, the polymerization of AMS with MMA was carried in bulk at 0 °C. The amount of catalyst (Na^+-MMT/AMS) was an important factor of polymerization. We can see from Table 3, that the polymerization rate increased with the amount of Na^+-MMT, in which the effect of Na^+-MMT as a cationic catalyst for AMS/MMA polymerization is clearly shown. This phenomenon is probably the result of the number of ″initiating active sites″ responsible of inducing polymerization, this number is prorating to the catalyst amount used in reaction. also it explained by an increase in the number of chain in propagation in presence of a great quantity of catalyst. We can see also in Table 3, the molecular weight are proportional to the amount of Na^+-MMT. Similar results are obtained by Ayat *et al.* [46] and Harrane *et al.* [63], in the polymerization of α-methyl styrene; diblock copolymers of glycolide and poly(oxyethylene) using a Mag-H^+ as catalyst, respectively.

Table 2. Effect of molar ratio on the copolymerization of AMS (M_1) with MMA (M_2) at 0°C, in bulk[a]

Sample N°	molar ratio [AMS /MMA]	Time in hours	Yield (%)	Mn (g/mol)	Mw/Mn
1	70/30	9	12	2212	1.74
2	60/40	16	20	2341	1.64
3	50/50	20	28	2575	1.97
4	40/60	24	34	2685	1.71
5	30/70	48	54	3994	1.34

[a] Determined by GPC according to polyTHF standards, Na^+-MMT/AMS: 15% (w/w) T=0°C

3.3. Characterization of copolymers

3.3.1. GPC study

The gel permeation chromatogram of the block copolymer shows that the molecular weight are proportional to the polymer yield. The molecular weight distribution is widened with the increase of MMA and decreased with AMS in the monomer ratio. It indicates that the polymer with more MMA content (or less AMS content). The same results are obtained by Guo *et al.* [64].

3.3.2. Infrared spectroscopy

The IR spectrum (Figure 4) and Table 4 of copolymer shows band at 3000 cm^{-1} due to aromatic C–H str vibrations, 2927 and 2850 cm^{-1} due to C–H str vibrations of methyl, methylene and methine groups, 1730 cm^{-1} due to > C=O str vibrations of ester carbonyl, ~ 1600 cm^{-1} due to aromatic C=C str vibrations, 1450-1390 cm^{-1} due to C–H deformation bands, 1160-1120 cm^{-1} due to C–O–C. str vibrations. We quote the bands and their frequencies of poly (MMA-b-AMS) in Table 4. The IR spectrum of Poly (MMA-b-AMS) exhibited all bands belonging to both blocks. The same results are obtained by Mishra *et al.* [65], H–C. Chiu *et al.* [66], and Xu *et al.* [67]. The structure of the resulting copolymer was confirmed by IR, ^{1}H-NMR measurements (Figure 5), which demonstrates PMMA-b-PAMS has essentially been formed.

Table 3. Evolution of the yield and the number - average molecular weight according to amount of MMT-Na$^+$ on the copolymerization ^{b}

Sample N°	Catalyst in %	Yield in %	Mn	Mw/ Mn
1	10	38	2575	1.97
2	13	45	2685	1.71
3	15	54	3994	1.34
4	18	35	2341	1.64
5	20	20	2212	1.74

3.3.3. NMR study

The copolymer poly(MMA-b-α-MS), prepared by the cationic polymerization with Na$^+$-MMT as a catalyst, was characterized by ^{1}H-NMR spectrum. A typical ^{1}H-NMR spectrum of polymer is schown in Figure 5. In comparing with Figure 6 of the homo-polymer (PAMS), various distributions of MMA and AMS units are observed the results are presented in Table 5.

The signals at 1.2-1.3 and 6.8-7.2 ppm belonged to the methyl and the benzyl groups of PAMS units. The signals at 1.8 corresponding, to methylene protons of PAMS units, a new strong peak at 3.7 ppm appears, This signal is attributed to the protons of the methyl of the ester group in the homosequences of PMMA units, it indicated, that the copolymer P (MMA-b-AMS) was synthesized [65,67]. The presence of PAMS [46] chains causes termination step and lead to the

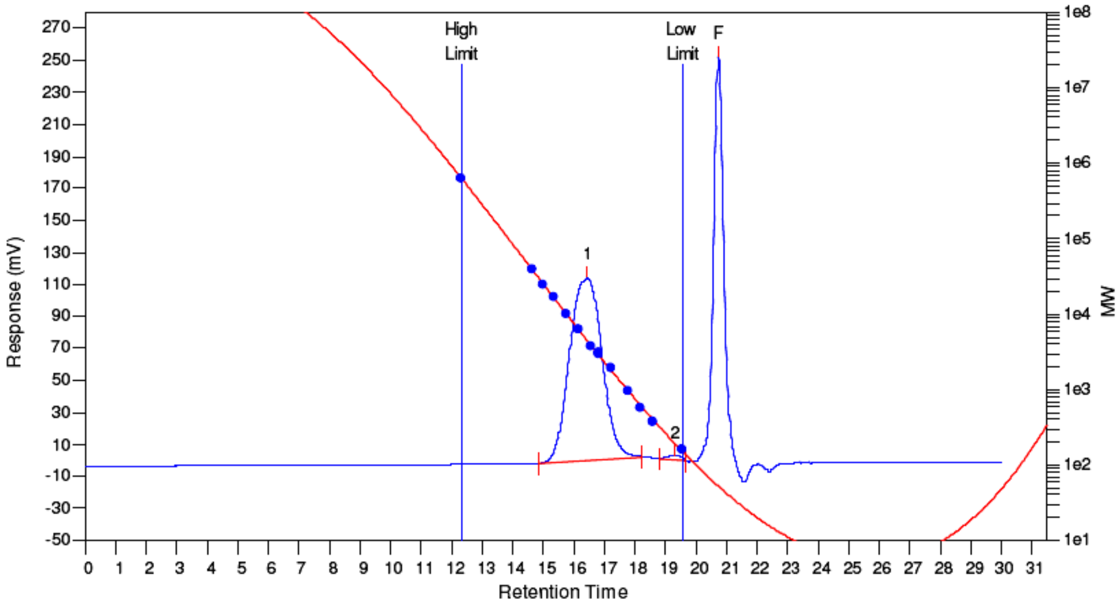


Figure 3. GPC chromatogram of poly (AMS-b-MMA) obtained by Na$^+$-MMT catalytic system at 0 °C: 15% of Na$^+$-MMT, 30% AMS and 70% MMA, 48 h (Mw =5348 g/mol, Mn=3994 g/mol, and I=1.34)

Table 4. The principals bands characteristic of poly(MMA-b-AMS)

Group	υ experimental in cm^{-1}	υ theoretical in cm^{-1} [65, 66]
C–H, CH_2 , CH_3 (str vibrations)	3000-2960.45	3000
C–H aromatic (deformation bands)	757.86-544.66	760-550
C–H methyl, methylene, methyne	2930-2850	2927-2850
C–H (deformation bands)	1489.58-1376.82	1450-1390
C–C aliphatic (deformation vibrations)	1028,23	1000
C–O–C (str vibrations) and C–C aromatic	1242.75-1118.83	1160-1120
C=O str vibrations of ester carbonyl	1750-1730	1730
C=C aromatic (str vibrations)	1597.56	~ 1600

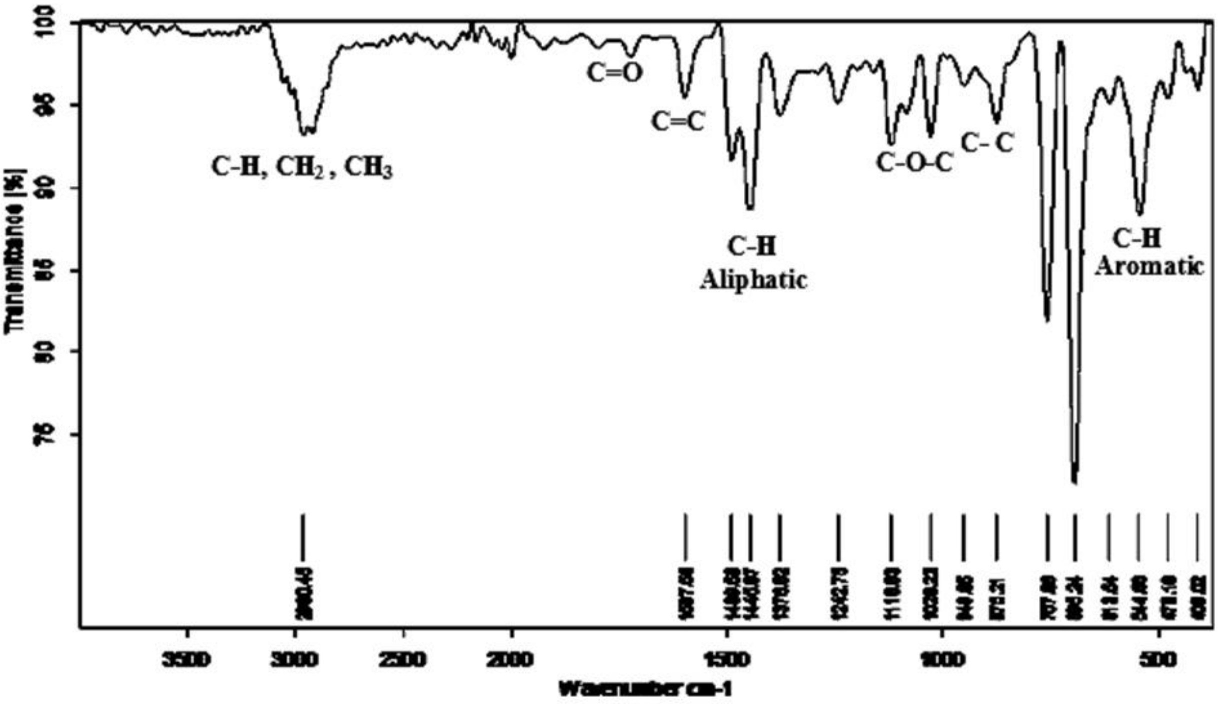


Figure 4. FT-IR spectra of poly(MMA-b-AMS)

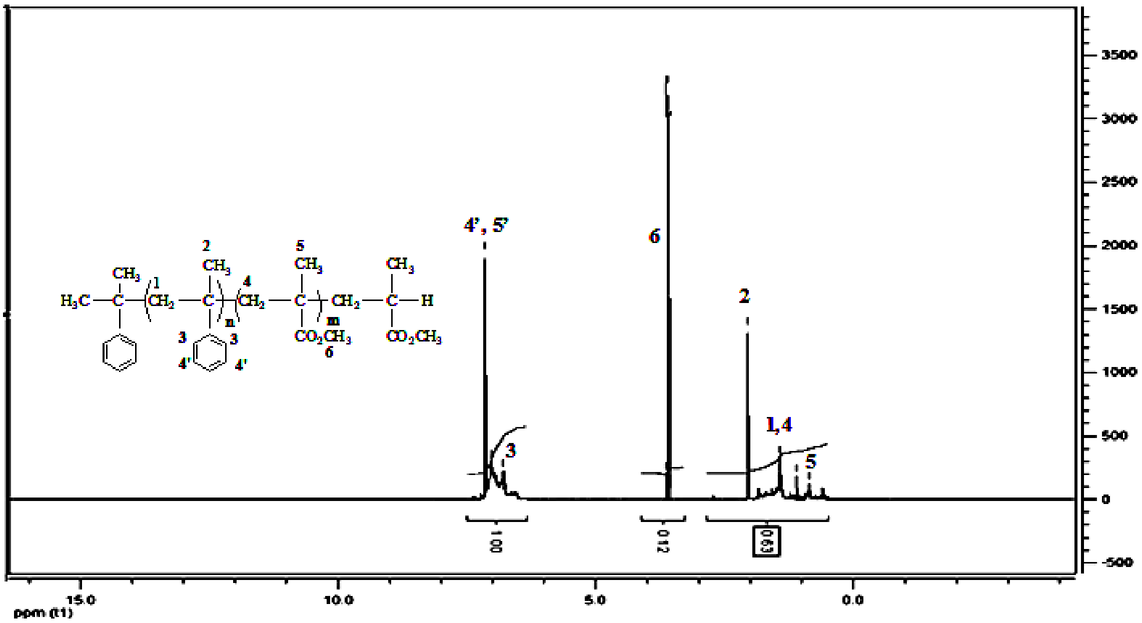


Figure 5. ^{1}H-NMR spectrum of poly(MMA-b-AMS) [MMA=0.03/AMS=0.013], [Na$^+$-MMT =15%]; temperature: 0 °C; reaction time: 48 h.

Table 5. ^{1}H NMR chemical shifts of poly(MMA-b-AMS)

Attribution	δ (ppm) experimental	δ (ppm) theorical [67, 68]
$2H_3$+$2H_{4'}$ +$1H_{5'}$	7.17	7.2-7,15
$2H_3$	6.94	6.8-6,97
$3H_6$	3.50-3.78	3.6-3.56
$2H_2$	2.18-2.86	2.2-2.88
$2H_{1,4}$	1.63	1.5-1.77
$3H_5$	0.73-1.25	1.2-0.5

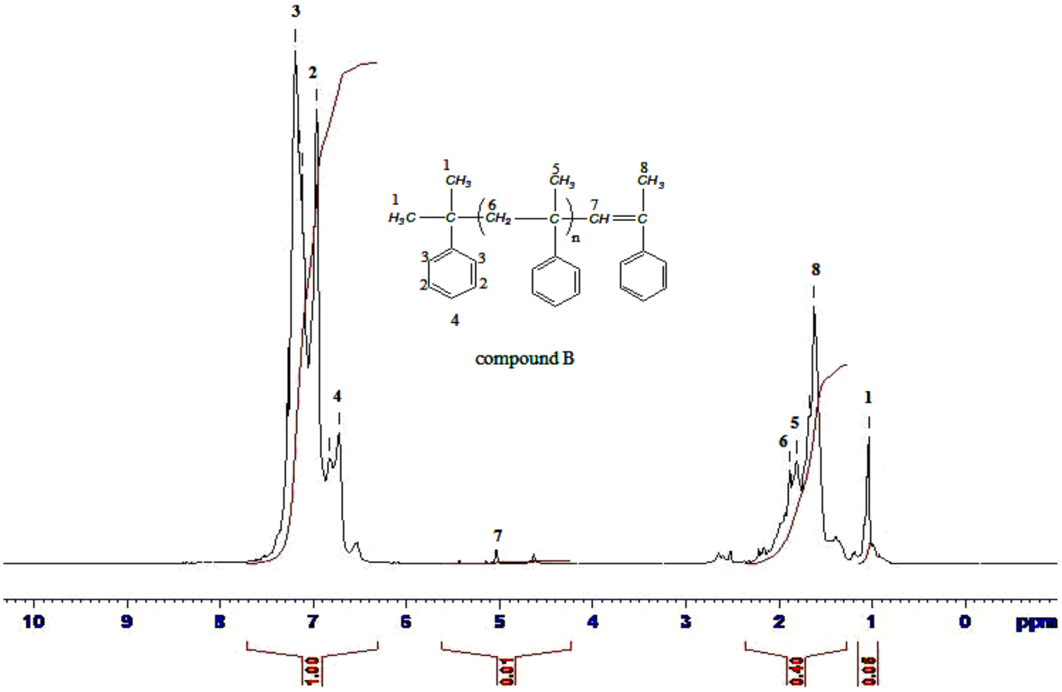


Figure 6. ^{1}H NMR spectrum of PAMS in $CDCl_3$ catalyzed by H^+-MMT [46]

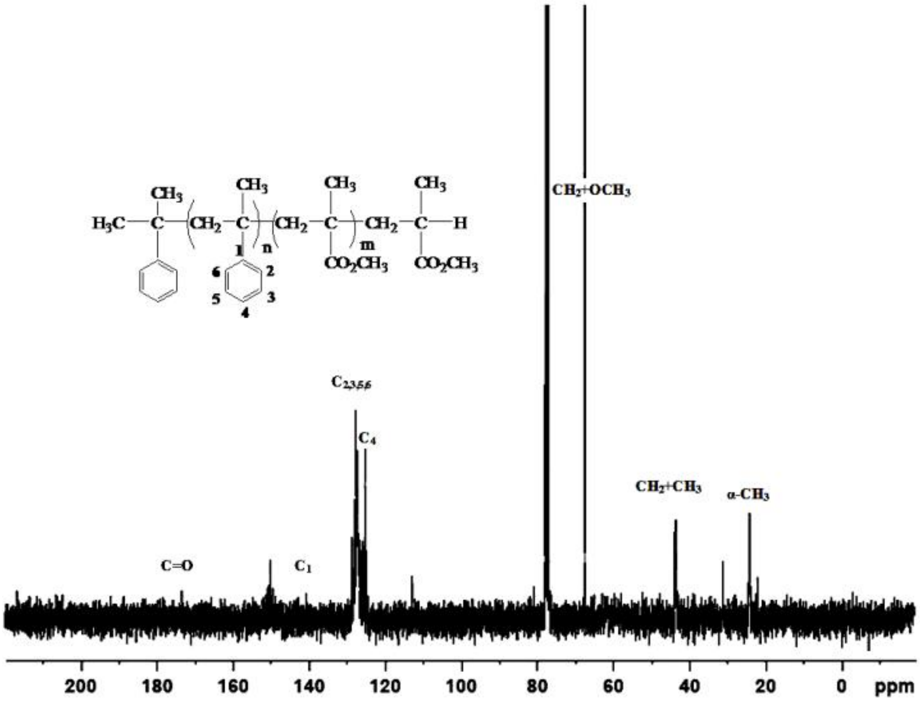
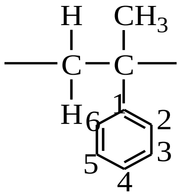
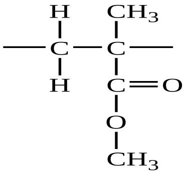
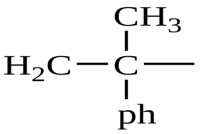


Figure 7. ^{13}C-NMR spectrum of PAMS/PMMA diblock copolymer

Table 6 . ^{13}C-NMR Chemicals shifts and signal assignations of poly(MMA-b-AMS)

Attribution	δ (ppm) experimental	δ (ppm) theoretical [68]
	C_1:149.32-150.152	C_1: 143.5-145.15 C_1:145.15-146.8 C_1:146.8-147.5
$C_{2,3,5,6}$	123.05-128.22	$C_{2,3,5,6}$ 121.7-130
C_4	126.18	C_4 :126
	170-180 43.41-61-15 43.41-61-15	CO: 177 OCH_3: 47-55 + CH_2: 47-55
α-CH_3	21,81-30.75	16.5-23.0
 $H_2C-C(CH_3)(ph)-$	38.45-51.30	44-47

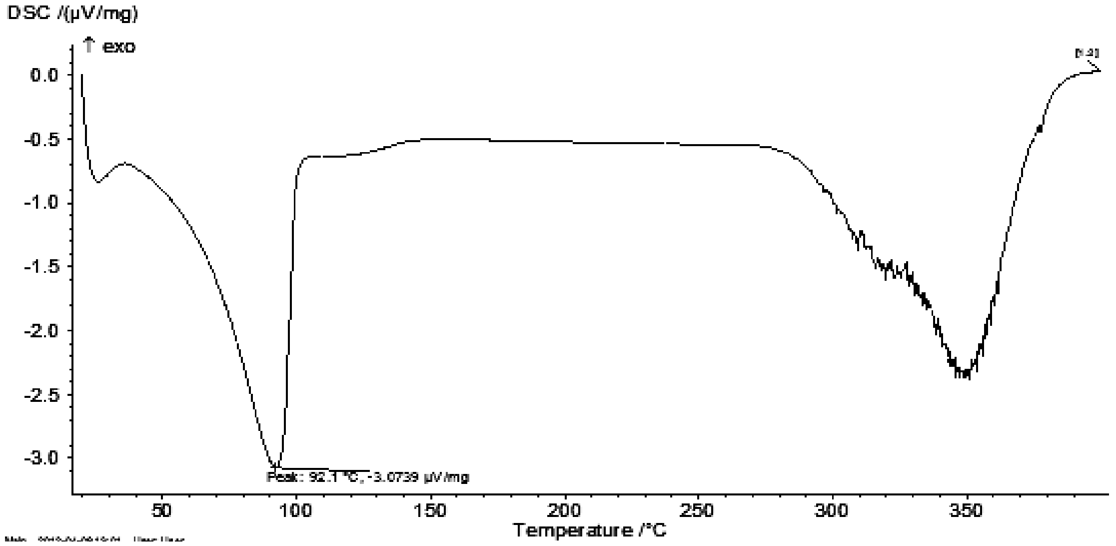


Figure 8. DSC measurements (heating rate 10 °C/min) of Poly (MMA -b-α-MS) copolymers

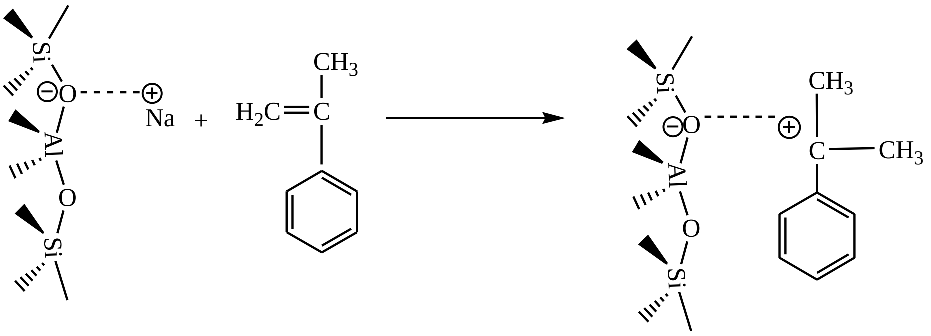


Figure 9. Initiation: fixing of the sodium atom Na+ and formation of the first active center

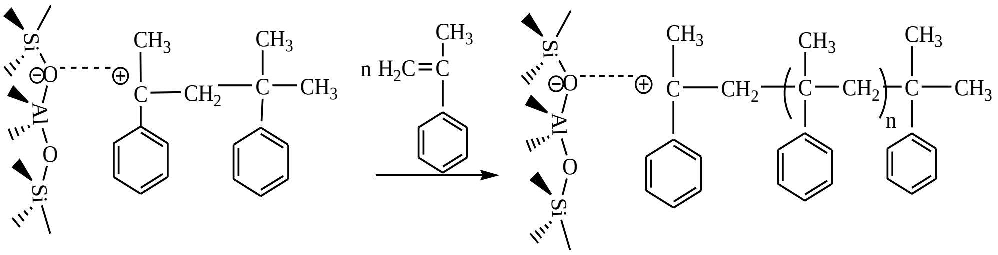


Figure 10. Propagation: the reaction continues with the attack of monomer on the active center formed to lead to the formation of the cation polystyrene. After the formation of cation polystyrene, the attack of the MMA is done of with side or other, and this is due to the possible forms mesomeric of MMA

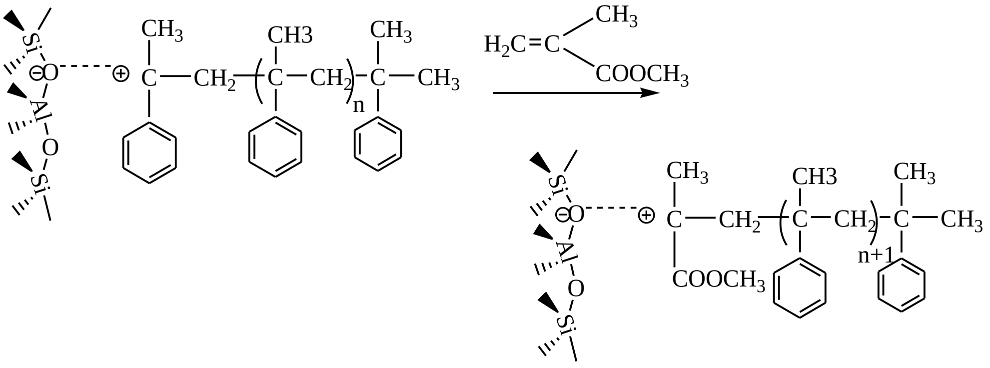


Figure 11. Reinitiating: reaction between the molecule of the MMA and the cation polystyrene

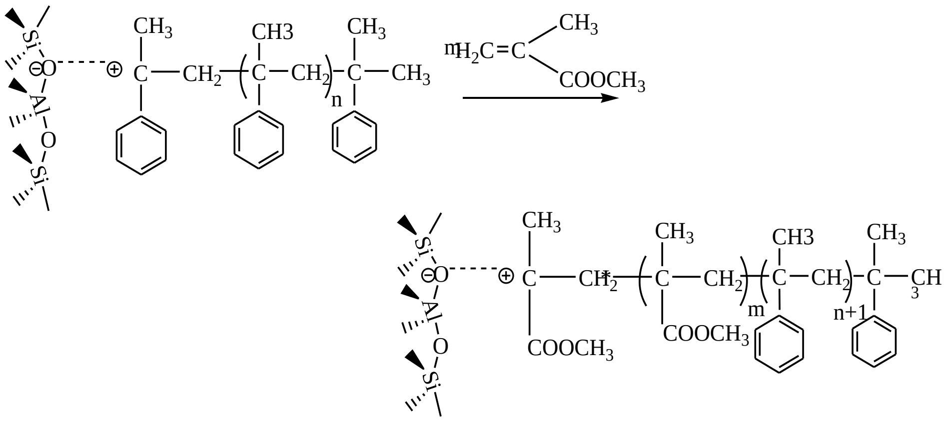


Figure 12. Propagation: after the formation of cation polystyrene, the attack of the MMA is done of with side or other, and this is due to the possible forms mesomeric of MMA

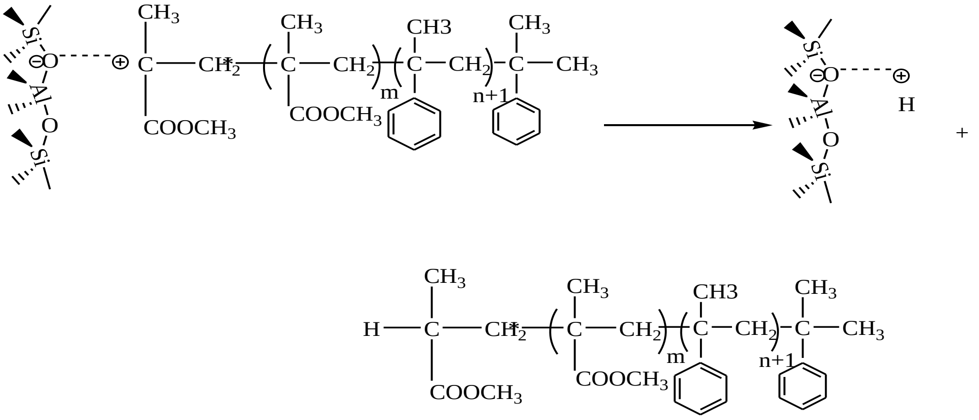


Figure 13. Termination: the reaction ends in a spontaneous transfer of a proton H^+

block copolymers. The CH_3– end group of PAMS [46] reacts with propagating PMMA chain and produces PAMS/PMMA diblock copolymer (Scheme 1). The same results are obtained in the copolymerization of MMA and Styrene, using different catalysts [65,67]. The ^{13}C-NMR spectrum Pα-MS/PMMA diblock copolymer is schown in Figure 7. Some assignment results are given in Table 6. The ^{13}C-NMR spectrum of the product was also confirmed the structure of PAMS / PMMA diblock copolymer. The same results are obtained by Morejòn *et al.* [68].

3.3.4. Thermal analysis

The thermal properties of the copolymers were investigated by differential scanning calorimetry (DSC). Figure 8 shows the results of the DSC measurements. Glass transition temperature T_g of the resulting copolymers was observed in the temperature range of 110-140 °C. The DSC analysis of poly(MMA-b-AMS) copolymers show two closely neighbouring melting endotherms at temperatures between 280-290 °C, they may be interpreted as crystallites. This analysis indicates the semi-crystalline state of the resulted copolymer.

3.3.5. Mechanism of Polymerization

Proposed mechanism of Poly (MMA-b-α-MS) copolymers catalyzed by Mag-H+ was depicted in Figures 9-13. In this mechanism, the initiation is by fixing the sodium atom Na^+ and formation of the first active center (Figure 9), the propagation is the reaction continues with the attack of monomer on the active center formed to lead to the formation of the cation polystyrene (Figure 10), reinitiating is reaction between the molecule of the MMA and the cation polystyrene (Figure 11), after the formation of cation polystérile, propagation is attacking of the MMA is done of with side or other, and this is due to the possible forms mesomeric of MMA (Figure 12), and termination which the reaction ends in a spontaneous transfer of a proton H^+ (Figure 13).

4. Conclusions

In continuation of the studies on environmentally benign methods using solid supports, it is reported the synthesis of block copolymer poly(MMA-b-AMS) via cationic polymerization by a sodium exchanged Montmorillonite, called Na+-MMT, as a new nontoxic cationic catalyst (Algerian MMT) for vinyl monomers. Na+-MMT can be easily separated from the polymer product and regenerated by heating to temperature higher than 100 °C. The synthesized copolymer was characterized by Nuclear Magnetic Resonance (NMR- ^{1}H, NMR- ^{13}C), FT-IR spectroscopy, Differential Scanning Calorimetry (DSC), and Gel Permeation Chromatography (GPC) to elucidate structural characteristics and thermal properties of the resulting copolymer. The kinetic studies indicated that the polymerization rate is first order with respect to monomer concentration. A possible mechanism of this cationic polymerization discussed based on the results of the ^{1}H-NMR Spectroscopic analysis of these model reactions.

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