

Research Article

Selective Synthesis, Characterization, and Kinetics Studies of poly(α -Methyl styrene) induced by Maghnite- Na^+ Clay (Algerian MMT)

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Abstract

A new and efficient catalyst of Na-Montmorillonite (Na^+ -MMT) was employed in this paper for α -methylstyrene (AMS) cationic polymerization. Maghnite clay, obtained from Tlemcen Algeria, was investigated to remove heavy metal ion from wastewater. "Maghnite- Na^+ " is a Montmorillonite sheet silicate clay, exchanged with sodium as an efficient catalyst for cationic polymerization of many vinylic and heterocyclic monomers. The various techniques, including ^1H -NMR, ^{13}C -NMR, IR, DSC and Ubbelohde viscometer, were used to elucidate structural characteristics and thermal properties of the resulting polymers. The structure compositions of "MMT", " H^+ -MMT" and " Na^+ -MMT" have been developed. It was found that the cationic polymerization of AMS is initiated by Na^+ -MMT at 0 °C in bulk and in solution. The influences of reaction temperature, solvent, weight ratio of initiator/monomer and reaction time on the yield of monomer and the molecular weight are investigated. The kinetics indicated that the polymerization rate is first order with respect to the monomer concentration. A possible mechanism of this cationic polymerization is discussed based on the results of the ^1H -NMR Spectroscopic analysis of these model reactions. A cationic mechanism for the reaction was proposed. From the mechanism studies, it was showed that monomer was inserted into the growing chains. Copyright © 2016 BCREC GROUP. All rights reserved

Keywords: synthesis; cationic polymerization; catalysts; montmorillonite; Na^+ -MMT; poly(α -methylstyrene); mechanism; thermal properties

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1. Introduction

Cationic polymerization is a widely used method for preparing hydrocarbon polymers [1]. Numerous examples of the polymerization of vinyl monomers by a cationic pathway using various Lewis acids, such as AlCl_3 [2,3], BF_3

[4,5], SnCl_4 [6], and TiCl_4 [7,8] 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

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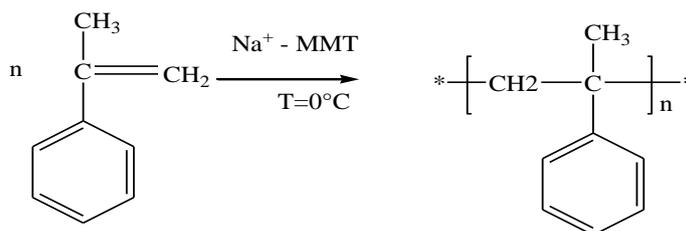
from the polymer by a water-quenching step that not only destroys the Lewis acid making reuse impossible but also leads to a large volume of acidic aluminium waste, unacceptable in these environmentally conscious days [9,10]. Therefore, the conversion of traditional homogeneous Lewis acid-catalyzed polymerization reactions into heterogeneous system represent a prime target in green chemistry and can offer many advantages: ease of separation, possible higher product yields and narrow molecular mass distribution due to pore-size distribution control, mild reaction conditions, less harm to the environment, catalyst reusability and less toxic effluent streams [11]. Recently, Hee-Jung and Dong-Ryul [12] have prepared new nanocomposites from montmorillonite and some vinylic polymers such as poly(AMS). Another group developed the cationic polymerization of AMS and Styrene initiated by different catalysts [13,14].

The purpose of this article is to study the cationic polymerization of AMS initiated directly by a montmorillonitic clay, a new non-toxic cationic catalyst for vinylic and cyclic monomers [15,16]. This catalyst can be easily separated from the polymer product and regenerated by heating to a temperature above 100 °C [17,18]. The interesting aspect of this new nontoxic catalyst is the environmentally friendly nature of the reaction because it does not imply the disposal of solvents or metal catalysts. The effect of some factors such as the amount of the Na⁺-MMT, the temperature or the dielectric constant of solvent, and the mechanism of initiation are discussed. There is, to date, no information on the polymerization of AMS with clay catalyst (Na⁺-MMT). In continuation of our studies on environmentally benign methods using solid supports [19,20], we present a new approach to synthesis a poly(AMS) via cationic polymerization using a Na⁺-MMT. (See Scheme 1)

2. Experimental Section

2.1. Reagents

The monomer (99%; Aldrich, Paris, France)



Scheme 1. Polymerization of AMS

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, Chloroform, 1,4-dioxane, 1,2-dichlorobenzene, and THF (Aldrich Chemical) were used as received. Raw-Maghnite: Algerian Montmorillonite clay, was procured from "BENTAL" (Algerian Society of Bentonite).

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

The Montmorillonite 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 nonferric products and useful substances). The different chemical elements of the native Montmorillonite were transformed into oxides and analysed by FT-IR and X-ray fluorescence (experiment carried out at ENOF). Results are given in Table 1. These results confirm that the maghnite used consists essentially of Montmorillonite (MMT), have been prepared in laboratory chemistry of polymers in ORAN University (LCPO), this 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 rpm during 20 min. Recovered clay is treated with a solution 1 M of sodium Hexametaphosphate (NaPO₃)₆ (clay 20 g in 100 mL), by maintaining agitation, during 3 h. The suspension is versed then in the test-tubes of separation and Montmorillonite-Na is to separate while exploiting its falling speed, MMT crosses with

20 °C, a distance of 10 cm each 8 h. Therefore Na-Montmorillonite is recovered by siphonage at a distance of 20 cm after 16 h of decantation. One adds water distilled to the test-tubes After each siphonage, one agitates during 15 min and one lets the suspension be elutriated before proceeding to new a siphonage. MMT is then recovered by centrifugation with 4500 rpm during 1 h. 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 [21,22].

2.3. Procedure and polymer characterization

The polymerization of AMS was carried out in a heterogeneous system. Each mixture was prepared with 16.9 mmol of AMS and 0.3 g of Na⁺-MMT and were introduced in several (6-8) sealed tubes. The mixture was stirred with a magnetic stirrer under dry 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 yield was determined gravimetrically by weighing the precipitated poly(AMS) chains.

The polymers were re-dissolved in dichloromethane and precipitated into methanol 3 times before characterization. Fourier Transform Infrared (FT-IR) spectroscopy (ATI Matson FTT N° 9501165) was used to confirm the structure of Pα-MS.

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 Ultrastayragel 10³, 10⁴, 10⁵, 10⁶ Å THF was used as a 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, [η] (mL/g), was measured at 25 °C in Toluene. Viscosity-average molecular weight, M_v, was calculated according to the following equation [23, 24]: $[\eta] = 10.1 \times 10^{-3} M_v^{0.71}$

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

2.4. Catalyst characterization

Samples for X-Ray Fluorescence (XRF) analysis were prepared using the LiB₄O₇ fusion method. The resulting beads were analyzed on a Philips PW 2400 XRF spectrometer. Loss on ignition (LOI) was determined by heating the sample at 1000 °C for 60 min and recording the % weight loss. Chemical analysis data of the natural Maghnite and acid treatment of Maghnite are presented in Table 1.

2.5. Catalyst structure

Various methods of analysis, such as: ²⁷Al and ²⁹Si MAS NMR, show that Maghnite is a montmorillonite sheet silicate clay. Table 2 shows the various types of montmorillonites studied, and can see that Maghnite has 11.9 % more SiO₂ than that from Wyoming 19.35 than from Montmorillon (Vienne, French). When treated with sulfuric acid, this difference is

Table 1. Chemical composition of the “Maghnite” (Compositions wt%). PF* : Pert in Fire [20]

Sample	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	TiO ₂	SO ₃	PF*
Raw-Mag(%)	69.39	14.67	1.16	0.30	1.07	0.50	0.79	0.16	0.91	11
Mag-H+(%)	71.70	14.03	0.71	0.28	0.80	0.21	0.77	0.15	0.34	11

Table 2 Comparison in the composition (in %) of American, French and Maghnia Algerian Bentonites

Sample	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	FeO	CaO	MgO	Na ₂ O	K ₂ O	TiO ₂	SO ₃
Wyoming (USA)(%)	50.04	20.16	0.68	00	1.46	0.23	Tr	1.27	00	00
Vienne (France) (%)	57.49	20.27	2.92	0.19	0.23	3.13	1.32	0.28	0.12	00
Raw-Mag (Algeria)(%)	69.39	14.67	1.16	00	0.30	1.07	0.5	0.79	0.16	0.91
Mag-H+ (Algeria)(%)	71.70	14.03	0.71	00	0.28	0.80	0.21	0.77	0.15	0.34

even greater; 14.21 % and 21.66 % as compared to the Wyoming and Vienne Bentonite, respectively. The Maghnite contains 5.60% and 5.49% less Al_2O_3 , than the Wyoming and Vienne Bentonites, respectively [25,26]. In the XRD spectra shown in Figure 1, the first broad peak of Na-MMT centered on a value of 1.29 nm is observed indicating that the layer distance in Na-MMT is 1.29 nm [27,28]. The other weak peaks are related to the structure of aluminum-oxygen octahedron and silicon-oxygen tetrahedron in the MMT. The x-ray powder diffraction profiles shown in Figures 2 and 3 exhibited the presence of other crystalline phases such as quartz, feldspath and calcite in (raw-Maghnite). Kwon *et al.*

[29,30], reported that the decrease in the basal spacing indicates a loss of the interlayer water upon the replacement of Na^+ for H^+ .

3. Results and Discussion

3.1. Spectroscopic characterization of product

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 montmorillonite clay via AMS polymerization. The structure and the

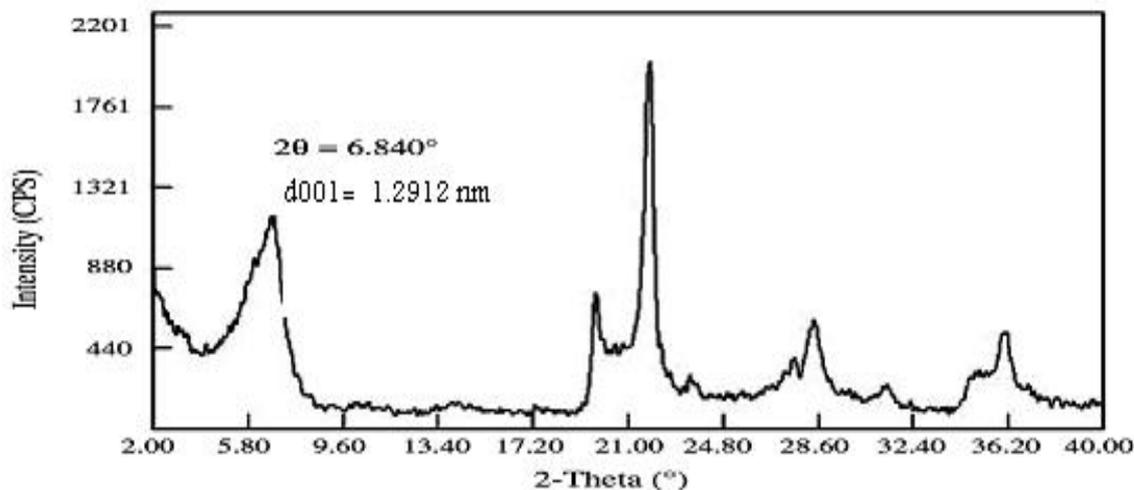


Figure 1. X-ray powder Diffraction of sodium Montmorillonite (Na^+ -MMT) [25]

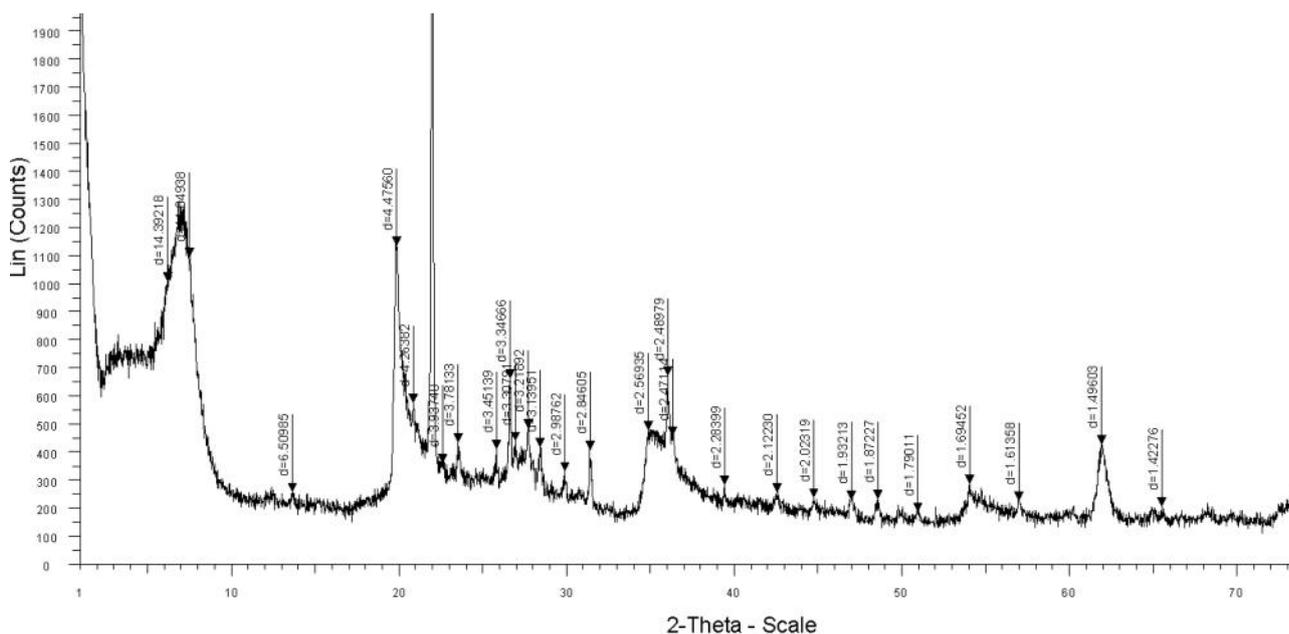


Figure 2. XRD profiles of Na^+ -Maghnite

composition of the catalyst were reported in previous works [31,32]. The elementary analysis of maghnite, obtained using XRF spectroscopy and polymer yields, show that there is an excellent correlation between the $(\text{NaPO}_3)_6$ and the catalytic activity of maghnite. sodium Hexametaphosphate treatment of “raw-maghnite” causes reduction in octahedral content (Al_2O_3) which resulted in an increase in the proportion of silica. It is necessary to report that the best value of polymer yields was obtained with 1 M Na-MMT, in which there is a complete saturation of montmorillonite with sodium cations without destruction of catalyst

structure. Similar results were obtained by Breen *et al.* [33]. The structure of the poly AMS was confirmed by IR, $^1\text{H-NMR}$, $^{13}\text{C-NMR}$ and GPC measurements.

The IR spectrum of the polymer (Figure 4) showed principal bands characteristic of poly AMS: Peaks at 657.30 , 697.92 and 758.88 cm^{-1} (out of plane C–H bending vibration), at 1029.23 and 1084.59 cm^{-1} (C–C aromatic and aliphatic), at 3000 cm^{-1} (C–H aromatic stretching).

The $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectrum of the polyAMS are shown in Figures 5 and 6. The results are presented in Table 3 and 4,

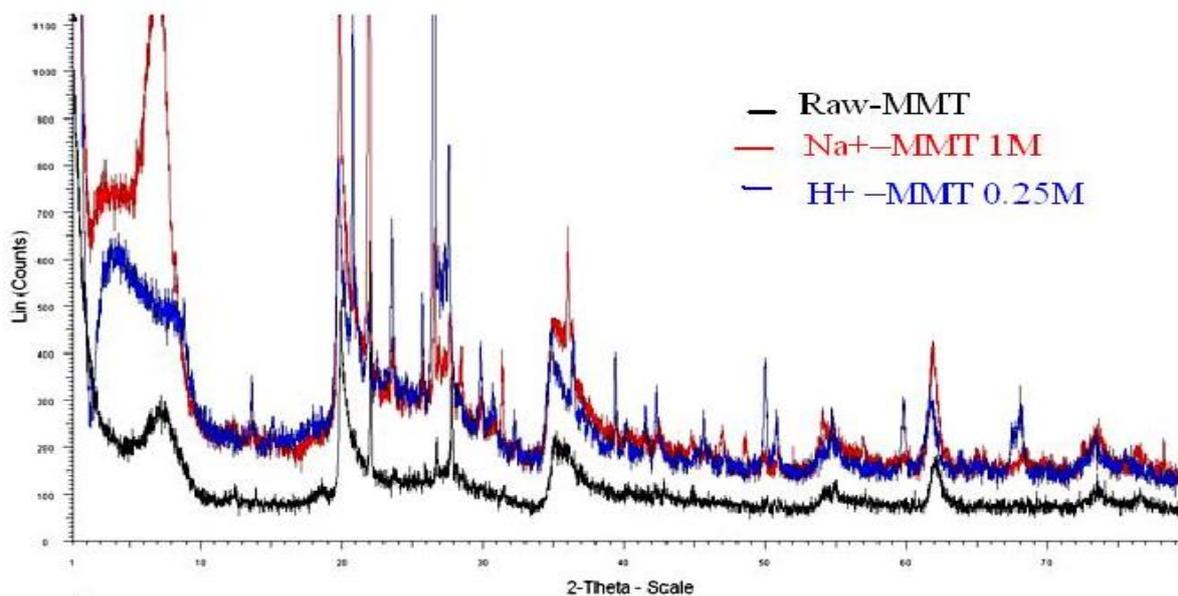


Figure 3. XRD profiles of Raw-Mag , M Mag-H⁺, and Na⁺-Mag

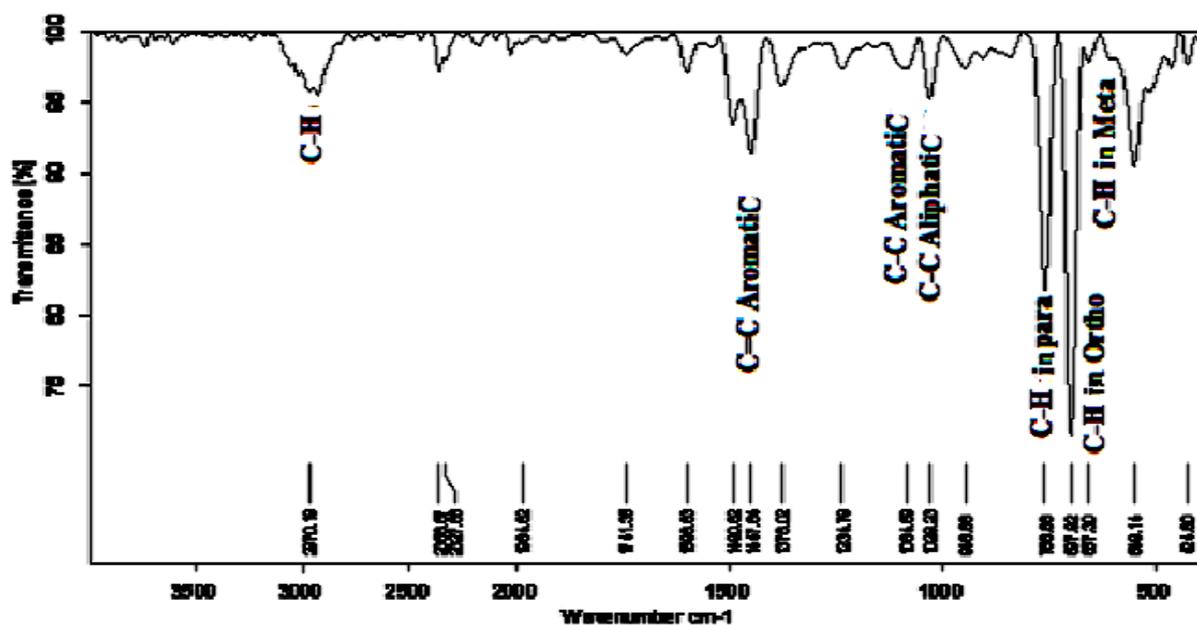


Figure 4. IR spectrum of poly α -Methyl Styrene

respectively. The cationic polymerization of AMS was examined in the presence of Na⁺-MMT as a catalyst at 0 °C for 6 h. The spectrum (Figure 5) showed different peaks [34, 35], 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 by Ayat *et al.* [36] using a Maghnite-H⁺ as catalyst. The proof for this polymerization obtained by ¹H-NMR and ¹³C-NMR spectroscopy are shown in Figures 5 and 6. The results of the analysis of the polymer by GPC are shown in Figure 7. As shown, the macromolecular weight distribution

of the obtained polymer is large. This suggests that chain transfer does occur.

The thermal properties of the polymers were investigated by differential scanning calorimetry (DSC). Figure 8 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. The DSC analysis of polymer, show a closely neighbouring melting endotherms at temperatures between 225-250 °C, This analysis indicates the semi-crystalline state of the resulted polymer [37].

3.2. Effect of the amount of Na⁺-MMT on the polymerization

Figure 9 shows the effect of the amount of

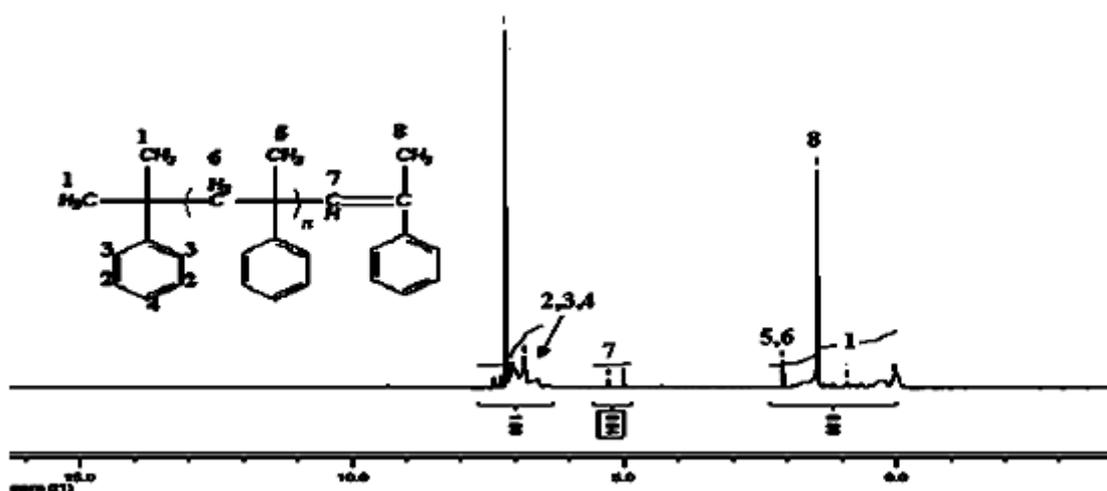


Figure 5. ¹H-NMR spectrum (CDCl₃) of poly(AMS) catalyzed by 15% Na⁺-MMT, T = 0 °C

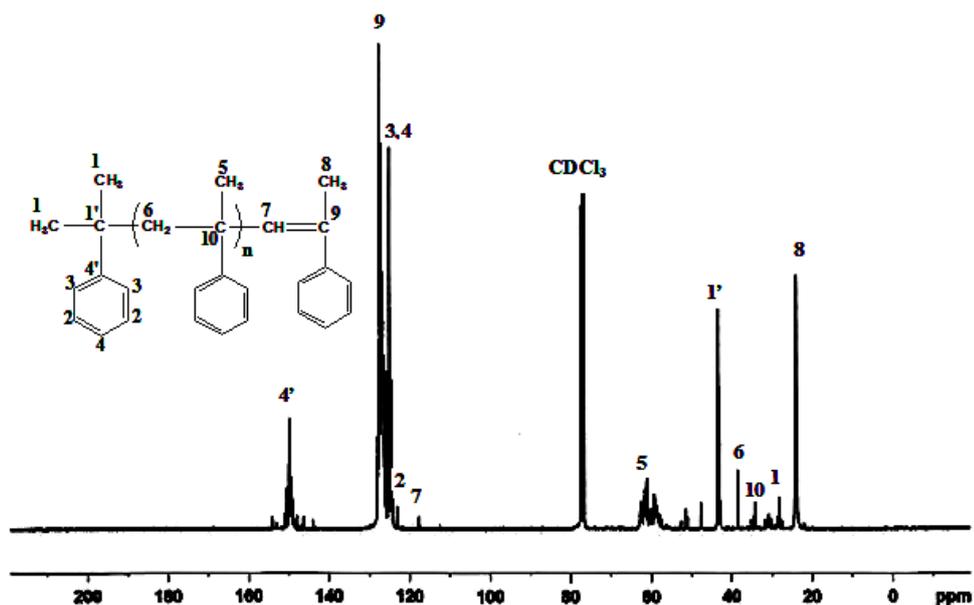


Figure 6. ¹³C-NMR spectrum (CDCl₃) of poly(AMS) catalyzed by Na⁺-MMT, T=0 °C

Na⁺-MMT on the polymerization rate of AMS. Indeed, using various amounts of Na⁺-MMT, 5; 7.5; 10; 15 and 20 % by weight, the polymerization of AMS was carried in bulk at 0 °C. The results of experiments of α -Methyl Styrene polymerization induced by 1 M "Na⁺-MMT" are reported in Table 5. For all these experiments the temperature was kept constant at 0 °C for 6 hours. The amount of catalyst (Na⁺-MMT /AMS) was an important factor of polymerization. We can see from Figure 10 and Table 5, that the polymerization rate increased with the amount of Na⁺-MMT, in which the effect of Na⁺-MMT as a cationic catalyst for AMS 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. Similar results were obtained by Ayat *et al.* [38] and Chabani *et al.* [39], in the polymerization of α -Methyl Styrene and 2-Chloroethyl Vinyl Ether, respectively by Mag-H⁺, which polymerizes only by cationic process.

In contrast, as depicted in Figure 11 and Table 5, the viscosity and the molecular weight are inversely proportional to the amount of Na⁺-MMT. This finding is in good agreement with the proposal that Na⁺-MMT is present as the active initiator species since the number of those species should be related to their surface area. Ferrahi *et al.* and Yahiaoui *et al.* obtain similar results [40,41].

3.3. Effect of the time on the polymerization

Figure 10 shows the yield of polymer versus time for the polymerization of AMS using Na⁺-

Table 3. ¹H NMR Chemical shift for various protons of polyAMS

Attribution	Chemical shift δ (ppm)
2H ₂ +2H ₃ +1H ₄	6.720-7.193
1H ₇	5.100
2H ₆	1.838-1.879
3H ₅	1.671-1.725
3H ₈	1.564-1.621
3H ₁	1.033-1.053

Table 4. ¹³C-NMR chemical shift for various carbons of polyAMS

Chemical shift δ (ppm)	Attribution
23.86	C-(8)
28.15	C-(1)
34.17	C (10)
38.44	C-(6)
43.07	C (1)
61.08	C-(5)
123.09 – 128.08	C-(2,3,4,7,9)
150.08	C (4)

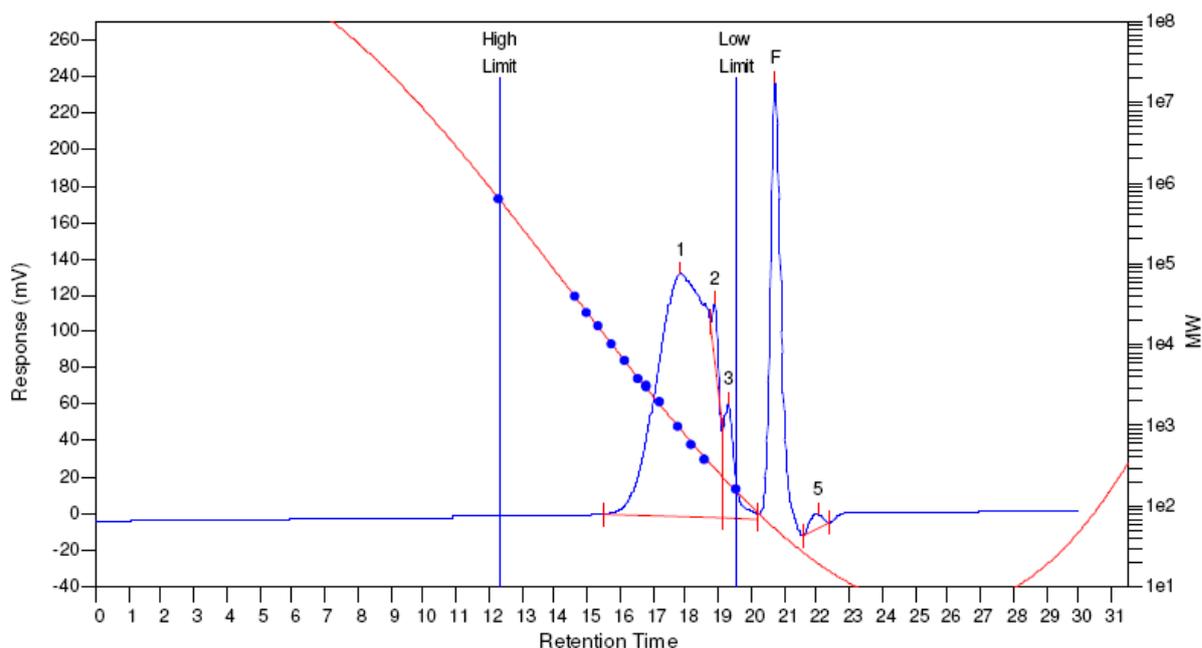


Figure 7. GPC Chromatogram of poly α -MS obtained by 15 % of Na⁺-MMT, catalytic system at 0 °C, $t = 6$ h ($M_w = 1086$ g/mol, $M_n = 639$ g/mol, and $I = 1.69$)

MMT as catalyst. As the figure shows that at the end of 4 h, polymerization takes place quickly and reaching a best yield of 75 % at the end of 6 h in the presence of 15 % of Na⁺-MMT at 0 °C, after this time The polymerization slows down gradually and the yield becomes almost constant; this is probably the result of an increase in the medium viscosity. The effect of polymerization duration on the intrinsic viscosity, as shown in Figure 11, has the same trend as that of yield [42].

3.4. Effect of temperature on the polymerization

Using AMS and 15 % [Na⁺-MMT/AMS] (w/w), the polymerization was carried out at different temperatures 0, 10, 15 and 20 °C and the effect of temperature on polymerization was studied. In the absence of Na⁺-MMT no polymerization could be detected. In the presence of Na⁺-MMT however, the polymerization was initiated. Figure 12 show that polymerization temperature has much influence on the yield of

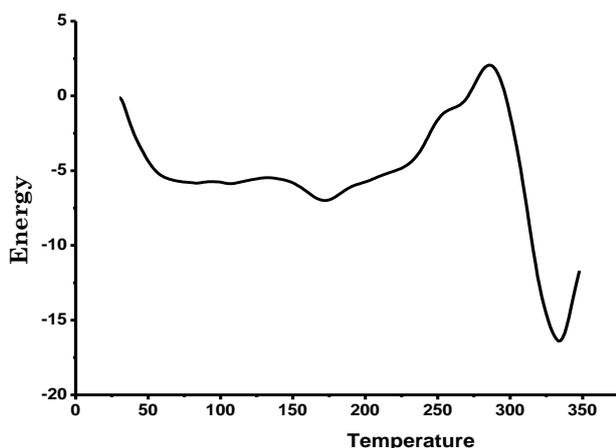


Figure 8. DSC measurements (heating rate 10 °C/min) of poly *a*-MS

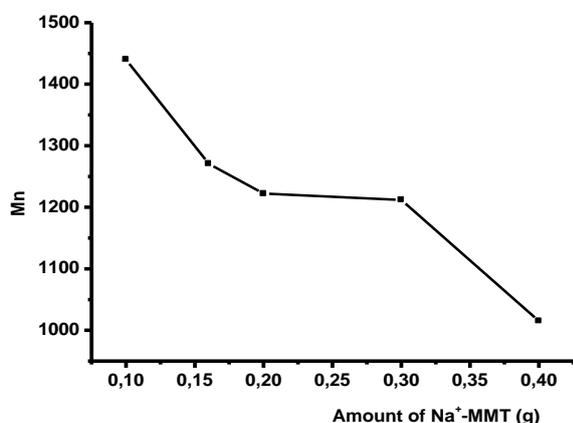


Figure 9. Effect of Na⁺-MMT amount on Mn; AMS: 2 g (time: 6 h, T = 0 °C)

PAMS. The yield decreased with the temperature rising from 0 to 20 °C and reached a high yield of 75 % at 0 °C [43]. As shown in Figure 13, the intrinsic polymer viscosity increases, depending on the polymerization temperature, in the following order: 0 °C > 10 °C > 20 °C. This is because decreasing the temperature causes an increase in the rate of chain transfer reaction of the growing polymer cation (inter and intramolecular).

3.5. Effect of solvent on the polymerization

The effect of different solvents on the polymerization of AMS initiated by Na⁺-MMT is shown in Table 6. It can be seen that the molecular weight and the yield of poly(AMS) achieved in nonpolar solvents are higher than those in polar solvents. The polymer yield 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, Na⁺-MMT shows an affinity for polar particles and, in this case, adsorbed

Table 5. Polymerization of α -Methyl Styrene induced by the “1 M Na-Maghnite”

Amount of Na ⁺ -MMT (g)	0.1	0.15	0.20	0.30	0.40
M _n (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

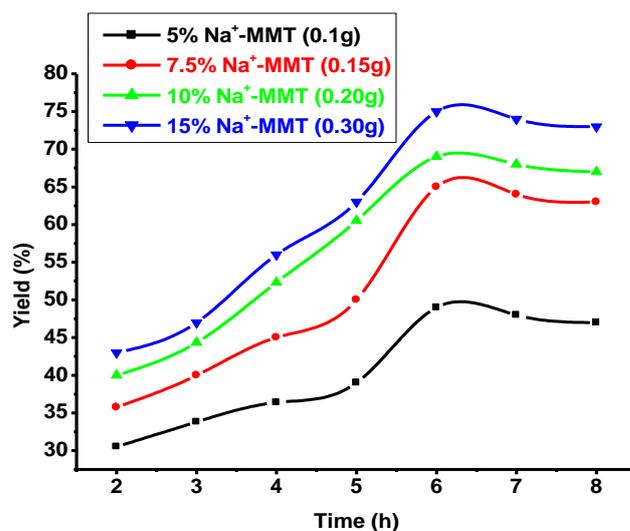


Figure 10 . Effect of the time on polymer yield; for 2 g of AMS, the amounts of Na⁺- MMT 1 M were: a) 0.1 g; b) 0.15 g; c) 0.20 g; d) 0.30 g; at 0 °C in bulk

molecules of polar solvent reduce the contact between the monomer and the "initiating active sites", and lead to low PAMS yields [44].

4. Mechanism of Polymerization

Na⁺-MMT 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 Na⁺-MMT. Cations carried by

Montmorillonite sheets of Na⁺-MMT (Scheme 2) induced the cationic polymerization. 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.

Initiation: Initiation is done between the initiator and a first molecule of the monomer to form the active species without nucleophilic agent (Scheme 1).

Propagation: The propagation step is the successive reaction of AMS with the carbocation intermediate (Scheme 2).

Termination: We suppose that there was formation of a double bond at the end of the chain of the AMS by spontaneous transfer (Scheme 3-I) or by methanol added as quenching agent to the poly (AMS) growing chains (Scheme 3-II) and regeneration of catalyst montmorillonite clay (Na⁺-MMT) and (H⁺-MMT).

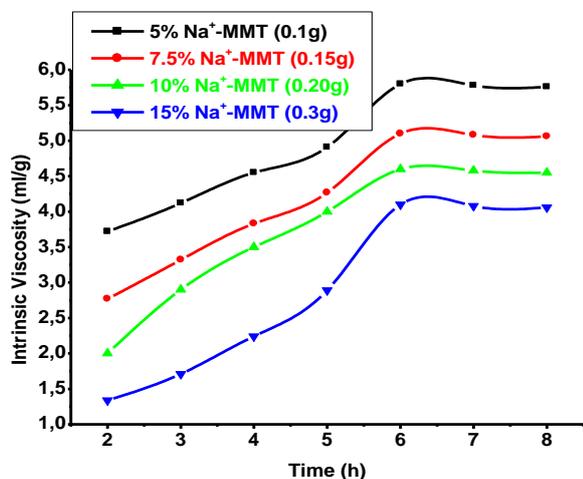


Figure 11. Effect of the time on Intrinsic viscosity; for 2 g of AMS, the amounts of Na⁺-MMT were: a) 0.1 g; b) 0.15 g; c) 0.20 g; d) 0.30 g; at 0 °C in bulk

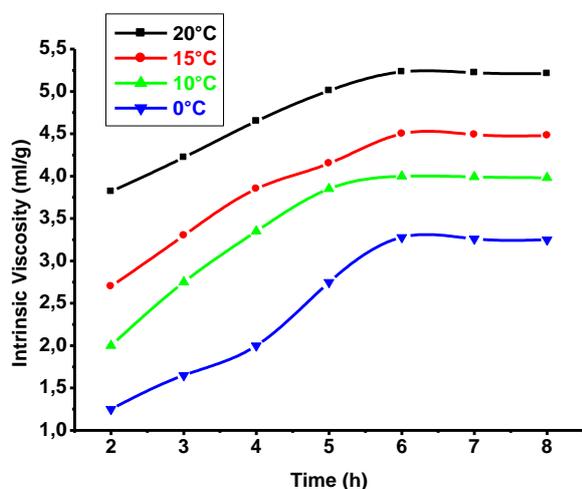


Figure 13. Temperature effect on the intrinsic viscosity of PAMS (AMS: 16.9 mmol, 15 % of Na⁺-MMT in bulk)

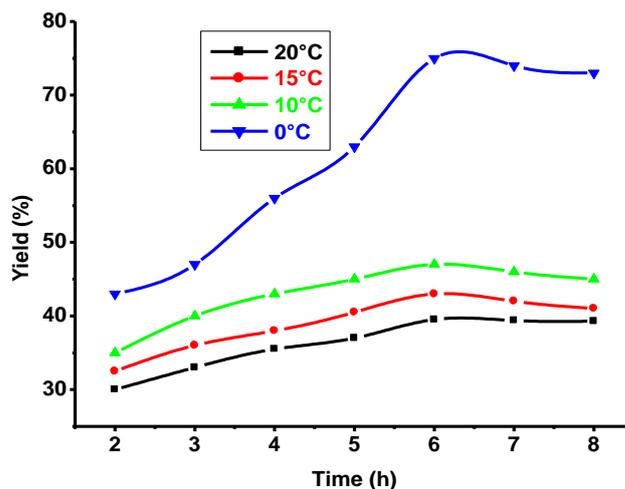
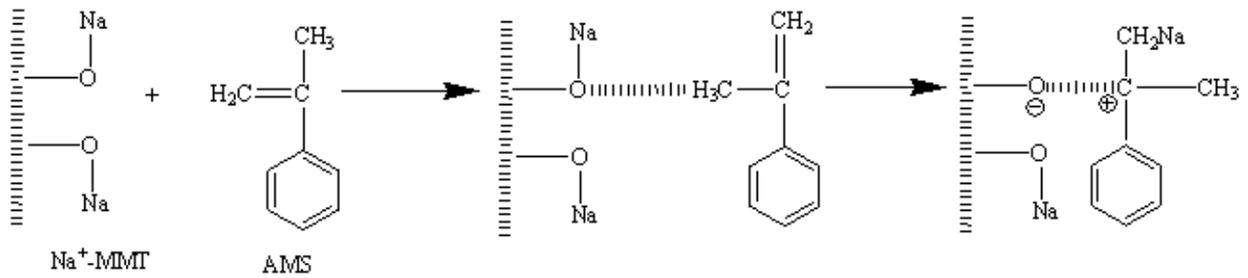


Figure 12. Temperature effect on the polymerization yield (Na⁺-MMT /AMS weight ratio = 15 %)

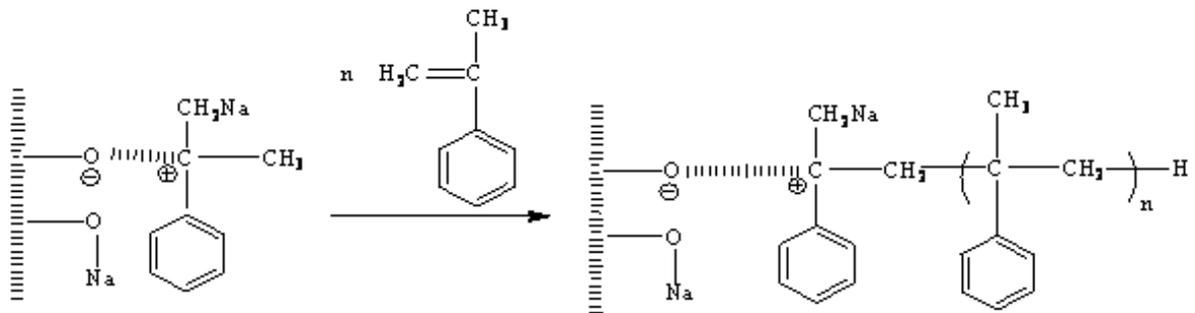
Table 6 . Effect of solvent on the polymerization^a

Solvent	Yield (%)	Dielectric Constant	M _v (g/mol)	I = M _w /M _n
1,4-Dioxane	40.85	2.21	7900	1.23
Toluene	34.55	2.38	7867	1.21
CHCl ₃	30.65	4.81	7670	1.19
CH ₂ Cl ₂	25.75	8.93	7540	1.22
1,2 Dichloro-benzene	22.45	9.93	7420	1.20

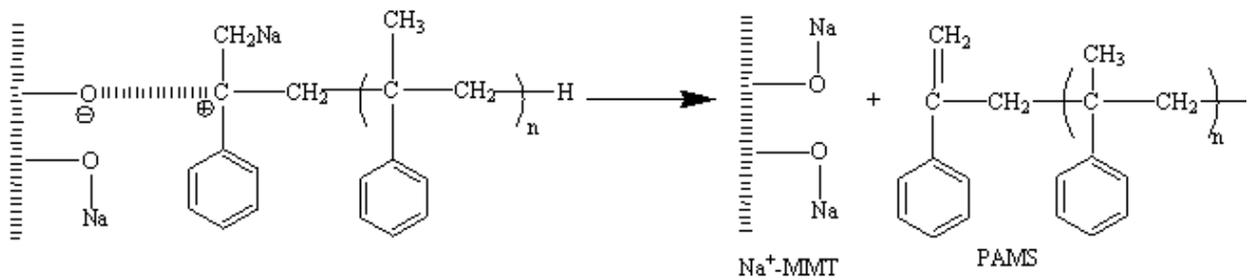
^aNa⁺-Montmorillonite/AMS weight ratio = 15 % reaction time 8 h; T = 0 °C



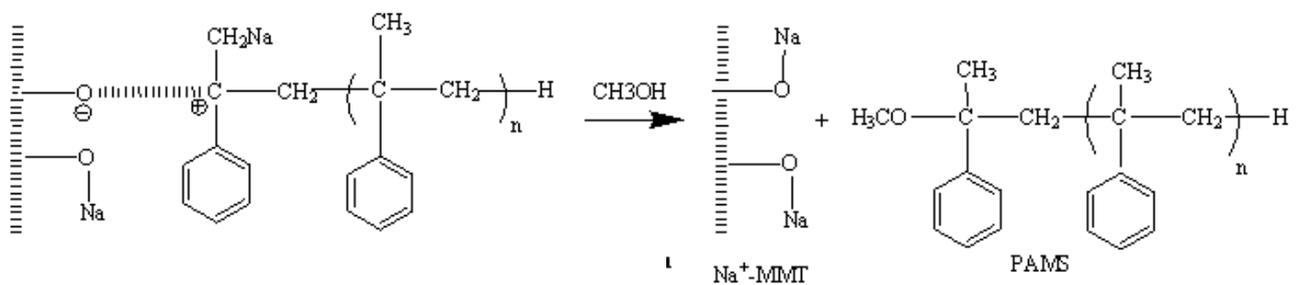
Scheme 1: Initiation



Scheme 2: Propagation



Scheme 3.1: Spontaneous transfer



Scheme 3.2: Termination

4. Conclusions

Free cationic polymerizations of α -methyl styrene (AMS) was induced in heterogeneous phase by montmorillonite clay. This clay has been modified by exchange of the constitutive Na cations called "Na-montmorillonite". PolyAMS were produced accordingly by an easy-to-handle procedure in one batch process. This new chemistry for cationic polymerization will be explored deeply in forthcoming work. In present paper, the catalysis of Na⁺-MMT was used for cationic polymerization of α -Methyl Styrene, the efficiency of this catalyst was studied and the possible mechanism of cationic polymer reaction theory was put forward. The catalytic activity of this catalyst (measured by the yield) and the viscosity of the formed polymer depend on the proportion of catalyst in the reaction medium, the solvent and the temperature of reaction. The relative amount of the low molecular weight fraction increased with increasing the polymerization temperature and amount of catalyst.

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