Journal of Organometallic Chemistry 893 (2019) 52–60

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Homopolymerization of methacrylamide by anionic process under effect of Maghnite-Na$^+$ (Algerian MMT)

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ARTICLE INFO

Article history:
Received 16 February 2019
Received in revised form
9 April 2019
Accepted 23 April 2019
Available online 4 May 2019

Keywords:
Green catalyst
Methacrylamide
Montmorillonite
Anionic polymerization
Maghnite-Na$^+$

ABSTRACT

The present study describes a new way for synthesis of methacrylamide (MAM) and it's homologue polymethacrylamide (PMAM) under effect of montmorillonite clay (Algerian MMT). The interlayer cation of montmorillonite clay was exchanged with Na + protons (anionic process). Monomer was successfully synthesized by the condensation of ammonia with methacrylic anhydride in bulk (without solvent) and the polymer with increasing anionic catalyst (Mag-Na+) in Tetrahydrofuran THF. Furthermore, the obtained monomer (MAM) and polymer (PMAM) were characterized and confirmed by Infrared Spectroscopy (FT-IR), 1H nuclear magnetic resonance (NMR) spectroscopy and Thermal properties by thermogravimetric analysis (TGA). The conversion and yield of monomer-polymer increased with the increase of the amount of catalyst "Maghnite-Na$^+$", the reactivity of the ammonia related to its basicity and the effect of amine substitution with methacrylic anhydride involved electron donor forces of the substitution group.

1. Introduction

Recently, Nanocomposites have a dramatic improvement in mechanical and physical properties that can be formed by adding very small amount of clay to neat polymer. Unique and improved properties are often observed when the dispersed clay layers were less than 100 nm thick [1]. Thus, many techniques have been evaluated to achieve homogeneous dispersions of ultrafine silicate clay layers inside polymer matrices [2]. Layered silicates such as sodium-montmorillonite (MMT), which is an aluminosilicates mineral with sodium counter-ions between its layers, are one of the types of materials most commonly used for making polymer-based nanocomposites inorganic materials because of their high aspect ratios, large specific surface areas, high cation exchange capacities and excellent swelling capacities [3].

The existence of acrylamide in foods was discovered in April 2002 by Eritrean scientist Eden Tareke, and considered as carcinogenic in humans [4]. It was detected in starchy foods such as potato chips and cereal products. Probably, acrylamide is a by-product of the Maillard reaction was produced by the reaction between asparagines and a reactive carbonyl at higher temperature than 120 °C [5,6]. For that reason scientists have replacing acrylamide with methacrylamide which is environmentally friendly, biodegradable and estimated to have a quite low bioaccumulation potential because of its low log POW (−0.15) [7]. Methacrylamide is used as a raw material in the production of polymers and co-polymers which are used in industrials applications: textile and paper finishing agents, coating agents and flocculants [8]. The wide range of industrial applications of PMAM is due to their high water solubility and their reactivity. Methacrylamide is very stable and more reactive than acrylamide due to the presence of methyl group CH3 because it's repulsive inductive effect electron donor (+I) [9]. The effect + I of the methyl group is entirely transferred to the unsubstituted carbon"Sp2″ and tends to move the doublet binding of nitrogen and make the NH bond less polarized (Fig. 1).

Methacrylamide is produced by the reaction of acetone cyanohydrin with concentrated sulphuric acid [10] and by reacting methacrylonitrile with water and/or a water donor in the presence of Raney copper catalyst [11]. It's polymerized by both radical and anionic route [12]. The radical polymerization of methacrylamide is

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https://doi.org/10.1016/j.jorganchem.2019.04.024
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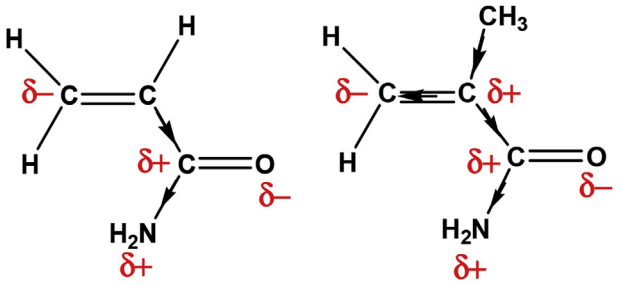


Fig. 1. The schematic representation of reactivity of Acrylamide and Methacrylamide.

described in previous works in various solvents and initiators [13]. In water at 75 °C using potassium persulfate as initiator [14] and in water at 85 °C using benzoyle peroxide as initiator rand their copolymerization was studied [15] onto pectin in water at 70 °C using ammonium persulfate as initiator, and with methylmethacrylate in absolute ethanol using Azobisisobutyronitrile (AIBN) as initiator [16]. The novelty of this work is to study the anionic polymerization of methacrylamide initiated directly by a montmorillonite clay, "Maghnite-Na^+" a new green and recyclable catalyst. Initially, we have synthesized the monomer methacrylamide by the condensation of ammonia with methacrylic anhydride in bulk; and subsequently the polymerization of monomer was carried out under suitable conditions in THF initiated by anionic catalyst "Maghnite-Na^+". This new non-toxic initiator has been used successfully to prepare and study several kinds of polymers [17,18].

2. Experimental section

2.1. Materials and methods

The chemicals and reagents used for the synthesis were obtained from commercial sources and were used as received. Methacrylic anhydride and Methanol were purchased from Sigma-Aldrich; ammonia was obtained from Riedel-de-Haen. Raw-Maghnite clay was obtained from ENOF Maghnia (Algeria). The Maghnite-H^+ (Mag-H^+) was prepared as described by Belbachir et al. [19]. X-ray diffraction (XRD) for MagH^+ was performed on a D8 Advanced Bruker AXSX-ray diffractometer. Fourier transforms Infrared Spectroscopy (FT-IR) spectra were obtained between 400 and 4000 cm^{-1} on an Alpha-PATR Bruker No 9501165.^{1}H and ^{13}C Nuclear Magnetic Resonance (NMR) measurements were carried out on a 300 MHz Bruker NMR Spectrometer equipped with a probe BB05 mm, in $CDCl_3$ Tetramethylsilane (TMS) was used as the internal standard in these cases. TGA analysis was performed on a PerkinElmer instrument STA 6000.

2.2. Preparation of the catalysts

Maghnite-H^+ and maghnite-Na^+ were prepared according to the process described by Belbachir et al. [20]. Raw-Maghnite (20 g) was crushed for 20min using a prolabo ceramic balls grinder. It was then dried for 2 h at 105 °C. The raw Maghnite was 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 0.25 M sulphuric acid solution, until saturation was achieved over 2 days at room temperature. The mineral was then washed with distilled water to become sulfate free and then dried at 105 °C. A barium nitrate test of the rinsing water residue is needed to ensure that the sulfate is eliminated. The "Maghnite-Na^+" was prepared according to the following process:The raw-Maghnite was placed in an Erlenmeyer flask together with 500 ml of 1 M NaCl solution. The Maghnite/water mixture was stirred using a magnetic stirrer until saturation was achieved over 24 h at room temperature, the mineral was then washed with distilled water to become chlorure free and then filtered and dried at 105 °C. The resulting activated bentonite catalyst was then stored in a hermetically sealed container [21].

2.3. Synthesis and polymerization of methacrylamide monomer (MAM)

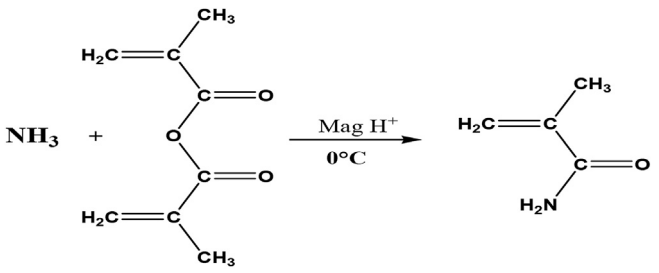
Synthesis of monomer was carried out by mixing 0.1 mol (10 ml) of ammonia with 1 g of clay catalyst Maghnite-H^+ 0.25 M (10%), after that, we added 0.1 mol (15 ml) of methacrylic anhydride (with a molar ratio of 1:1 of methacrylic anhydride to ammonia) in bulk; the reaction mixture was cooled to 0–5 °C using an ice bath during 1 h. After that, we filtered the solution recover the product (Scheme 1). The product obtained was a white powder which when recrystallized in a methanol-diethyl ether mixture. Yield: 85%.The anionic polymerization of MAM was carried out in sealed tubes. Each tube contains a mixture of 1 g of MAM, 10 ml of tetrahydrofuran THF and (0.15 g) 15% of Maghnite-Na^+. The mixtures were kept in an ice bath at 0 °C and stirred with a magnetic stirrer under dry nitrogen for 2 h 30 min. The resulting polymer was precipitated in methanol, washed for several times, dried at 40 °C in vacuum and weighed (yield = 55%). (Scheme 2).

3. Results and discussion

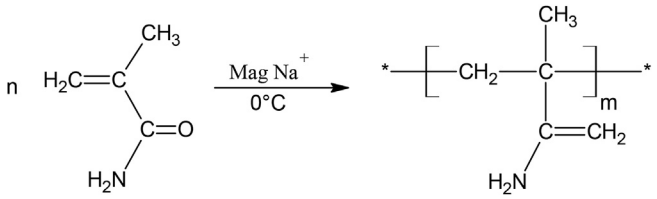
We have developed a novel procedure to synthesize Methacrylamide by using a heterogeneous silica catalyst that can effectively catalyzed amide synthesis and anionic polymerization, without production of toxic by-products. Montmorillonite have both Brønsted and Lewis acid sites and when exchanged with cations having a high charge density, as protons, produce highly active catalysts for acid-catalyzed reactions. These exchanged montmorillonite have been successfully used as catalysts for the reactions of synthesis and polymerization of methacrylamide. The chemical composition of montmorillonite clay "Maghnite" is reported in Table 1. SiO_2 and Al_2O_3 are main components of the different catalysts with a low amount of Fe_2O_3, MgO and others. The bulk structures of the catalysts were analyzed by XRD.

The X-ray diffractogram of acidic and sodium montmorillonite shows an offset of the angle 2θ from 7.0° to 6.8°and 5.8°, respectively. Thus indicating the increase in the interlayer distance from 12.52 Å to 15.56 Å for acidic clay and to 12.68 Å for sodium clay, confirming the intercalation of Na^+ ions in the space initially occupied by H^+ ions [22] (Fig. 2).

In (Fig. 3) FT-IR analysis results show the formation of the Methacrylamide, The FT-IR spectrum of MAM exhibits two bands around 3376.12 and 3180.88 cm^{-1} (broad), 607 and 550 cm^{-1} which



Scheme 1. Schematic representation of the synthesis of methacrylamide (MAM) catalyzed by Maghnite-H^+.



Scheme 2. Schematic representation of the synthesis of polymethacrylamide (PMAM) catalyzed by Maghnite-Na^+.

Table 1
Elementary compositions of "Maghnite" (Compositions wt%).

Sample	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	TiO_2	SO_3
RawMag	69,36	14,67	1,16	0,30	1,07	0,50	0,79	0,16	0,91
Mag-H^+	71,7	14,03	0,71	0,28	0,8	0,21	0,77	0,15	0,34
Mag-Na^+	65,09	14,17	3,15	0,15	6,50	5,54	1,38	0,12	0,074

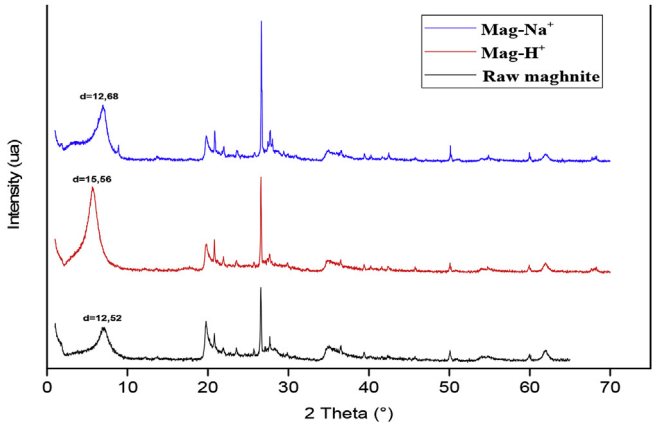


Fig. 2. XRD spectra of Raw-Maghnite, Maghnite- H^+ and Maghnite- Na^+.

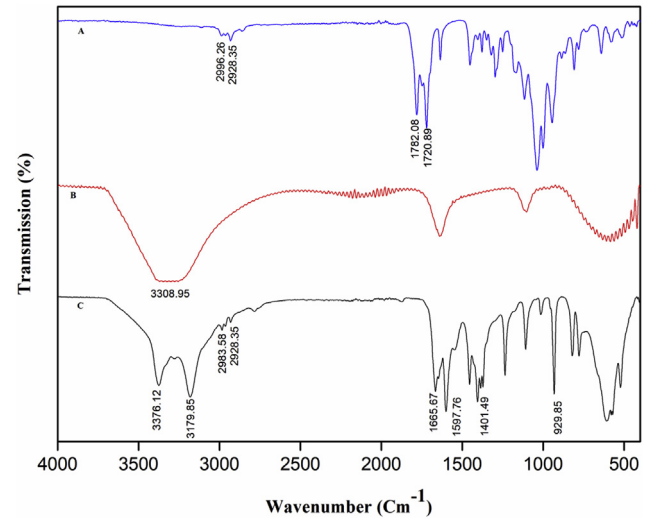


Fig. 3. FT-IR spectra for the starting products (A) Methacrylic anhydride; (B) Ammonia and (C) methacrylamide (MAM) synthesis.

are due to N–H stretching, N–H wagging and out of plane N–H bending, respectively [23]. Three weak peaks between 2922.38 and 2984 cm^{-1}were attributed to C–H symmetrical and asymmetrical stretching on CH_2 and CH_3 groups, respectively [24]. The strong band at 1671.64 $cm^{-1}$was attributed to amide carbonyl C=O stretching vibration. The strongest bands at 1600.15 cm^{-1} corresponded to the C=C stretching vibration. The second strongest and sharp band at 1401.49 $cm^{-1}$was attributed to the C–N stretch vibration [25].

Fig. 4 shows the FT-IR spectrum of poly (MAM); it is identical for the monomer excepting that we observe the increase of the intensity of the bands [26]. Two large and intense bands at 3314.98 cm^{-1} corresponding to N–H stretching and large bands between 2836 and 2990 cm^{-1} were attributed to C–H symmetrical and asymmetrical stretching on CH_2 and CH_3 groups, respectively [27]. The absorptions at 1653 cm^{-1} are assignable to amide carbonyl (C=O) stretching. The decrease in intensity of the band at 1600 cm^{-1} which corresponds to the stretching vibration C=C due the opening of double bond allowing the connection between the monomer units [28].

The ^{1}H NMR and ^{13}CNMR spectrums of MAM are shown in (Figs. 5 and 6) respectively. According to the (Fig. 5) the ^{1}HNMR spectrum of MAM shows the strongest and sharp peak centered at 1.951 ppm corresponding to methyl protons (a) (-CH_3) [29]. A doublet at 5.39–5.76 ppm are assigned to the vinylic hydrogen (b) (=CH_2). Two weak peak between 6.027 and 6.488 ppm were attributed to the amine protons groups (–NH_2) (c) and the signal at 7.28 ppm corresponds to the deuterated solvent ($CDCl_3$) [30].

The ^{13}C NMR spectrum of MAM shows 4 signals the sharp peak centered at 18.63 ppm corresponding to methyl carbon (a) (-CH_3) Sp3; two peaks at 120.88 and 139.12 ppm corresponding to the vinylic carbon (b,c) (C = C) Sp2 [31]. The last peak at 170.95 ppm is attributed to the (C= O) of the amide function (d) [32].

The ^{1}H NMR spectrum in (Fig. 7) confirms the structure of the polymer obtained in this study. Two broad peaks observed between 1.058 and 1.68 ppm are assigned to methylene and methyl protons of the polymer repeating unit and second broad peak between 6.80 and 7.55 ppm corresponding to the protons of amine group (–NH_2) [33]. The small peak at 1.82 ppm and at 3.23 ppm are attributed to the methyl protons groups (-CH_3) at the end of the polymer chain as well as a doublet at 5.39–5.76 ppm are assigned to the vinylic hydrogen (b) (=CH) [34]. The strongest and sharp peak centered at 4.70 ppm corresponds to water deuterated solvent (D_2O) respectively [35] (see Fig. 8).

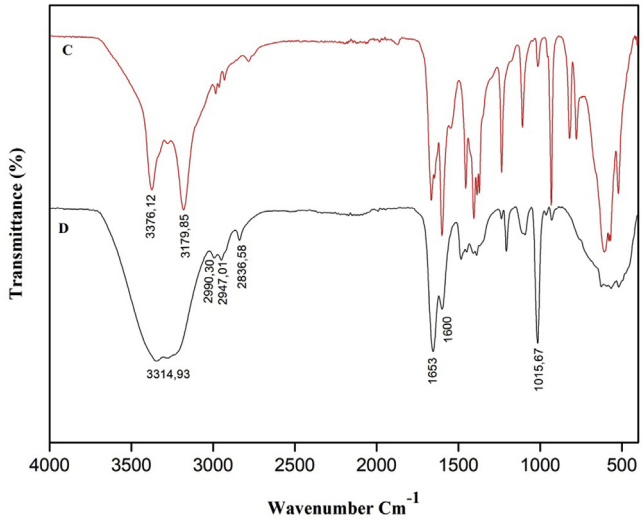


Fig. 4. FT-IR spectra for the methacrylamide (MAM) (C) and poly (methacrylamide) (PMAM) (D).

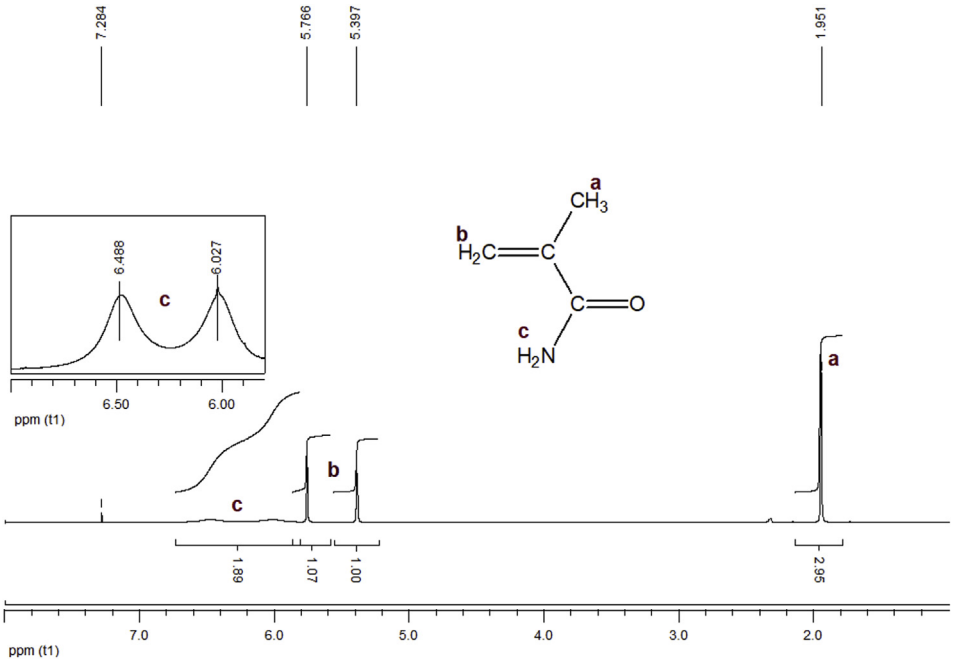


Fig. 5. ^{1}H NMR spectrum of Methacrylamide (MAM) in ($CDCl_3$).

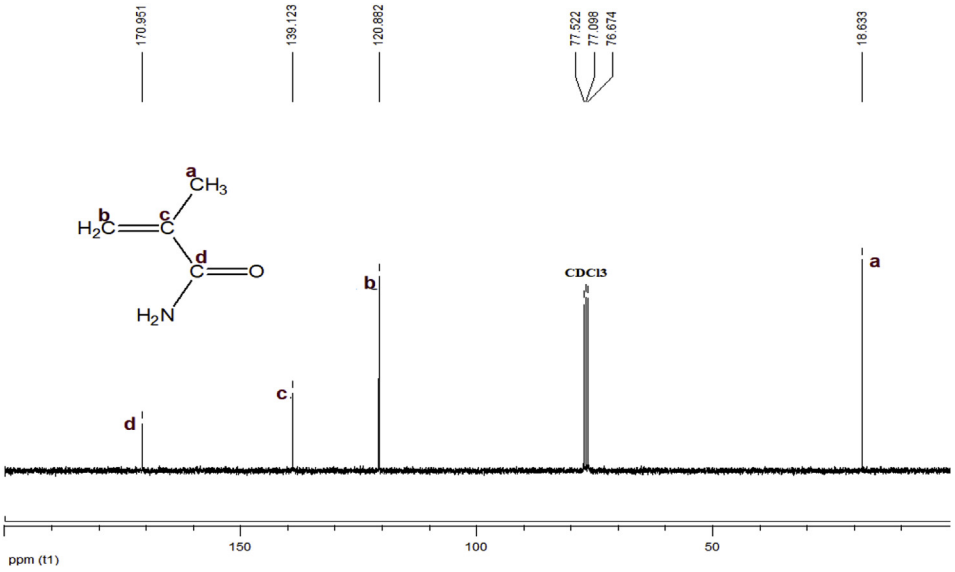


Fig. 6. ^{13}C NMR spectrum of Methacrylamide (MAM) in ($CDCl_3$).

Once the ratio of protons on the end-groups to protons on the polymer chain is determined using the NMR, simple math can be applied to determine the molecular weight Mn value, which has been obtained at around Mn = 3000 g/mole [36].

The ^{13}C NMR spectrum of poly (MAM) shows 9 signals, the multiple signals between 44.75 and 54.29 ppm are assigned to the methylene and methyl carbons of the polymer repeating unit [37]. The signal observed at 16.63 ppm and at 17.43 ppm are attributed to the methyl carbon groups (-CH_3) Sp3 at the end of the polymer chain, two peaks at 122.21 and 138.25 ppm corresponding to the vinylic carbon (C═C) Sp2 [38]. The last peak at 182.81 ppm is attributed to the (C= O) of the amide function [39].

The thermal stability of the polymer was studied by thermogravimetric analysis in air from room temperature. The TGA curve of Poly (MAM) is shown in the (Fig. 9) which clearly indicates that the polymers undergo one stages of degradation. The degradation is varying from 196 °C to 300 °C, which depends on the PMAM decomposition due to the sensitive and the weakest the methyl group from the PMAM chain correspond to 99.38% weight loss indicating that polymer exhibits low thermostability [40]. The PMAM have flexible aliphatic main chains exhibit much lower thermal stability and degrade rapidly at low temperature [41].

To determine the shape, size, and morphology of the particles, SEM was used. In Figure (10, 11, 12) micrographs of powder of raw MMT, Na^{+}-MMT and PMAM/Na^{+}-MMT, samples are presented. It is clear that particles of all samples are irregularly shaped and contain many edges with different sizes. It is known that these factors play an important role in the interaction between filler, matrix, and

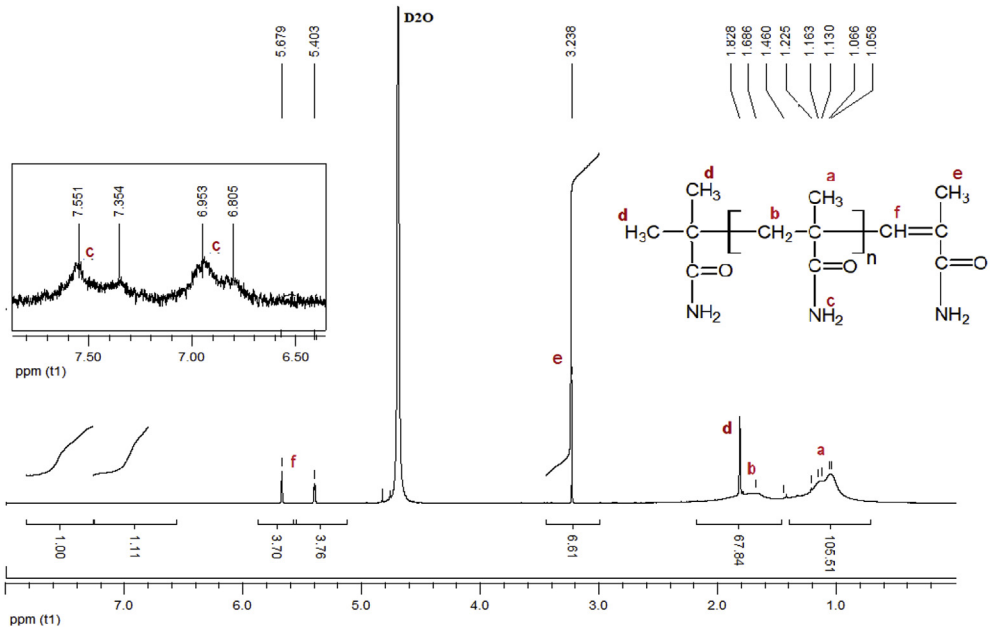


Fig. 7. ^{1}H NMR spectrum of Poly (methacrylamide) (PMAM) in (D_2O).

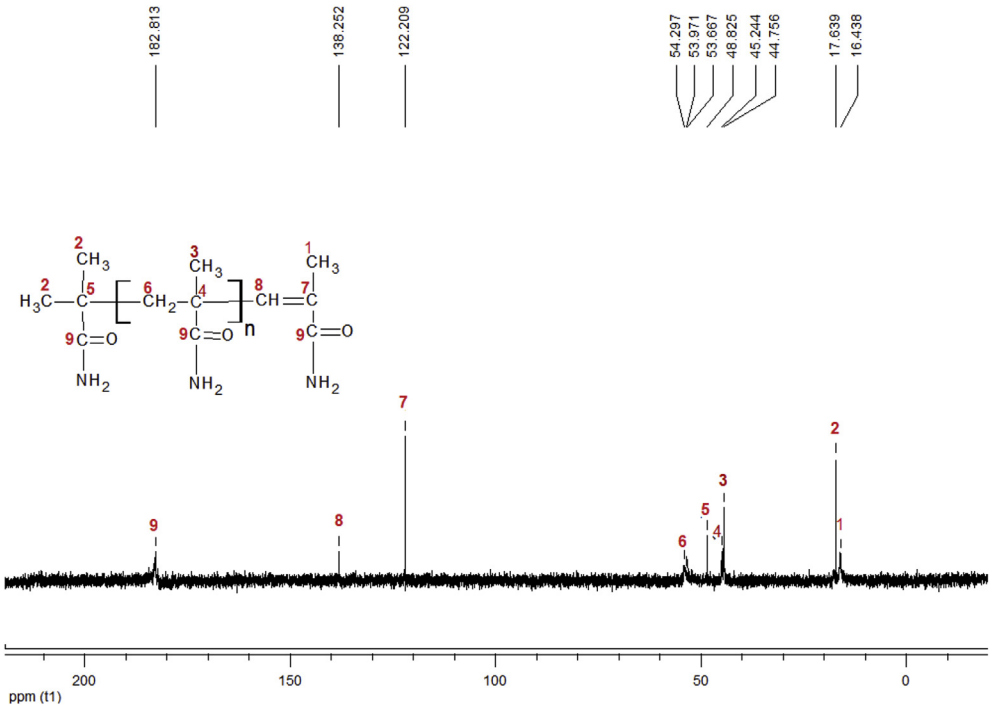


Fig. 8. ^{13}C NMR spectrum (D_2O) of Poly (methacrylamide) (PMAM).

interfacial adhesions. For the morphology of the samples, the images showed that the original raw MMT had massive and curved plates [42]. Compared to the morphology of Na^{+}-MMT, the montmorillonite clay, which was traited with NaOH (1 M), showed significant changes in morphology, and there were a lot of aggregated particles, and the plates became flat. To observe the dispersion of the particles, the nanocomposites after 2 h of sonication were examined using SEM, and the images are presented in (Fig. 12). Incorporation of 15% Na^{+}- MMT with Poly (methacrylamide) matrix resulted in a region with spherical texture (lamella structure). This texture could be related to the crystallinity of the polymer [43]. Spherical-looking crystals with beautiful impinged boundaries were observed in PMAM/Na^{+}-MMT after 2 h of sonication time. Good dispersion of this percentage of MMT throughout the PMAM matrix under sonication could be led to a nucleation effect and increase the percentage of crystallinity. This result strongly agrees with the XRD results [44].

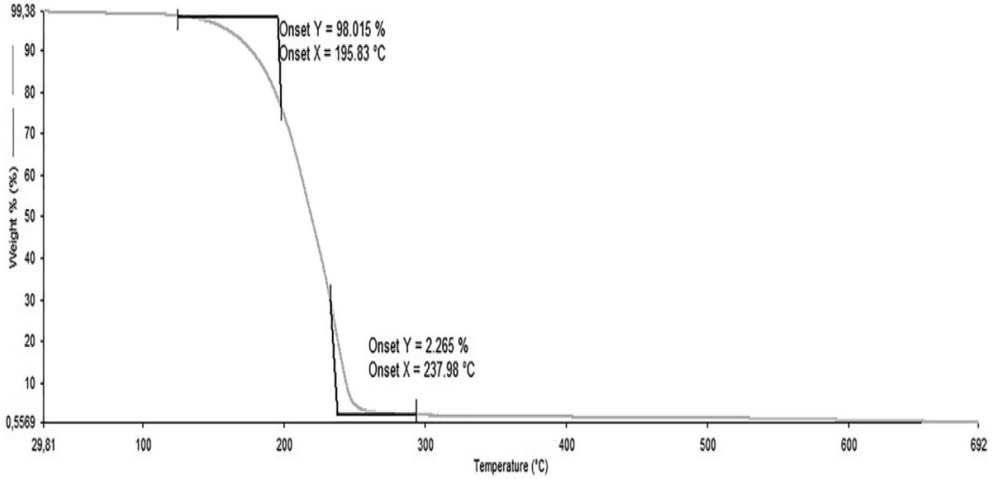


Fig. 9. TGA curve of the Poly (methacrylamide) PMAM in air.

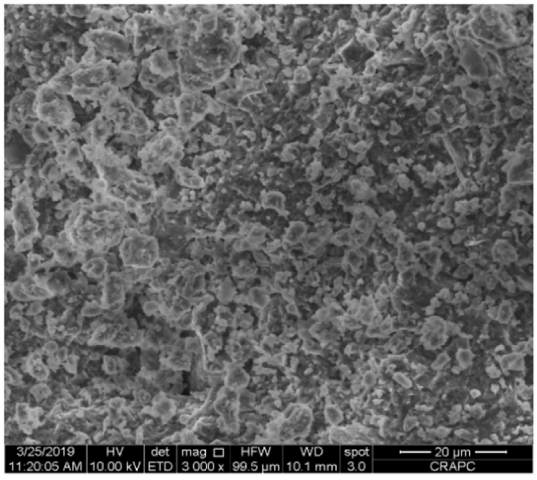


Fig. 10. SEM images of raw MMT.

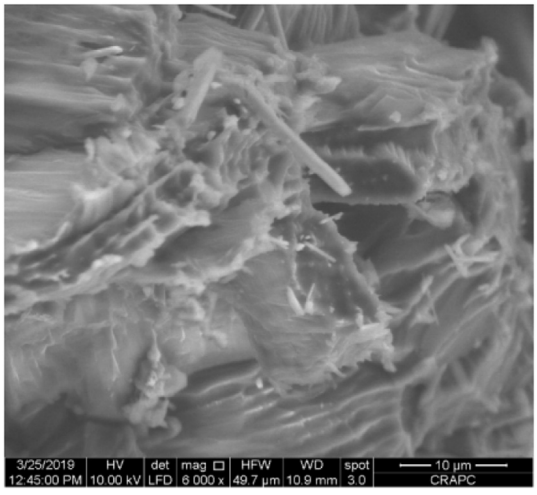


Fig 11. SEM images of Na^{+} -MMT.

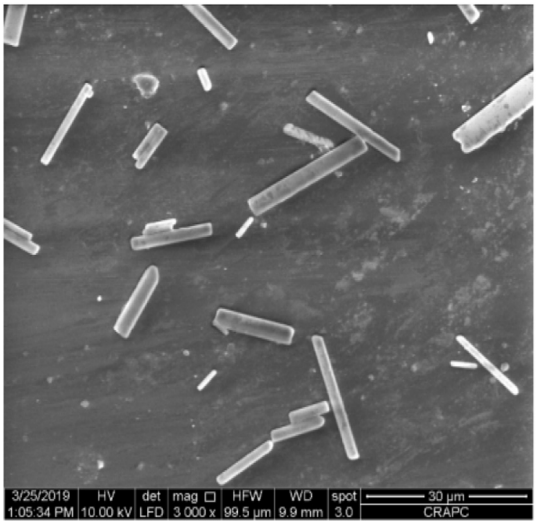


Fig. 12. SEM images of Polymer (PMAM)/Na^{+} -MMT.

3.1. Kinetics studies

A series of experiments were performed by keeping the time and temperature constant and varying the amounts of the catalyst Mag-Na+ (3, 5, 10, 15 and 20%) (Table 2). The choice of the reaction with catalyst (10%) and (15%) by weight for the monomer and the polymer respectively were made after obtaining better yields around 85% for monomer MAM and 60% for the polymer (Fig. 13).

We can see from (Table 2) and Fig. 10 that, the conversion of monomer and polymer increased with the increase of the amount of catalyst "Maghnite-Na^{+}" and becomes stable at 15% [42]. The synthesis of the monomers were obtained with a better yield around 85% of pure product with a selectivity of 100% to confirm the efficiency of catalyst "Mag-Na^{+}" in the synthesis of the monomer methacrylamide that depends on the reactivity of the ammonia related to its basicity and the effect of amine substitution with methacrylic anhydride involved electron donor forces of the substitution group [43].

Viscosity measurements were carried out with an Ubbelohde capillary Viscosimeter (viscologicTI1, version 3-1Semantec). Intrinsic viscosity, [η] (mL/g), was measured at 30 °C in water.

Table 2
Effect of Catalyst Amount of (Mag-H^+) and (Mag-Na^+) on conversion of Monomer and Polymer; temperature 0–5 °C.

Monomer/Polymer	Catalyst (weight %)	Yield (%)
MAM	3	40
	5	45
	10	80
	15	85
	20	85
PMAM	3	10
	5	35
	10	45
	15	60
	20	60

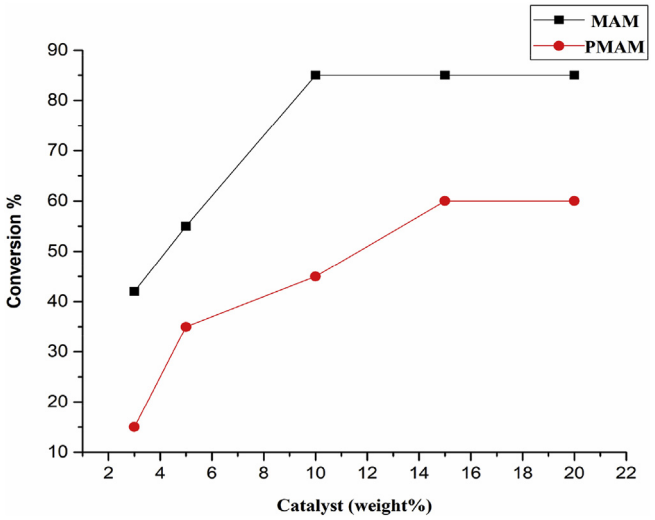


Fig. 13. Effect of Catalyst (Mag-H^+/Mag-Na^+) on yield of Monomer and Polymer, T = 0–5 °C.

Viscosity-average molecular weight Mv, was calculated according to the following equation [44].

$$[\eta] = 6{,}31 \times 10^{-3} x\ Mv^{0,8}$$

The results depicted on Fig. 14 and 15 and (Table 3) shows that at

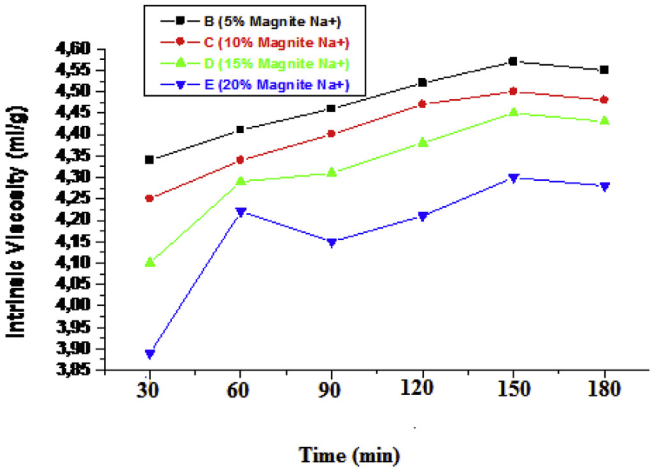


Fig. 14. Evolution of the intrinsic viscosity according to time on the polymerization of methacrylamide[c]Maghnite-Na^+, (5, 10 15% and 20%); T = 0 °C.

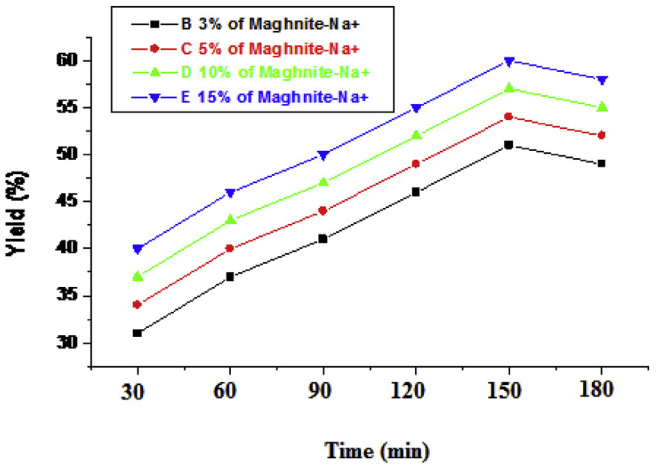


Fig. 15. Evolution of the yield according to time on the polymerization of methacrylamide [d]Maghnite-Na^+, (3, 5, 10 and 15%); T = 0 °C.

Table 3
Evolution of the yield and the intrinsic viscosity with time for different amount of Maghnite-Na^+1 M[c,d]: B)5%; C)10%; D) 15%; E) 20% by weight.

Time (min)	30	60	90	120	150	180
Yield % (B)	31	37	41	46	51	49
Yield % (C)	34	40	44	49	54	52
Yield % (D)	37	43	47	52	57	55
Yield % (E)	40	46	50	55	60	57
η (ml/g) (B)	4.34	4.41	4.46	4.52	4.57	4.55
η (ml/g) (C)	4.25	4.34	4.40	4.47	4.50	4.48
η (ml/g) (D)	4.10	4.29	4.31	4.38	4.45	4.43
η (ml/g) (E)	3.89	4.22	4.15	4.21	4.30	4.28

the end of 150 min the polymerization evolves/moves quickly and reaches a best performance of 60% at the end of 180 min, after this time it slows down gradually and the yield becomes almost constant. Similar results were obtained by Ayat et al. and Rahmouni et al. [45,46].

3.2. Reaction mechanism

According to the results of polymer analysis obtained, a reaction mechanism has been proposed in (Scheme 3).

Initiation: Creation of the active center by fixing Na^+ ions on the methylene groups which open the double bond and leave the carbenium ion at the same time [47].

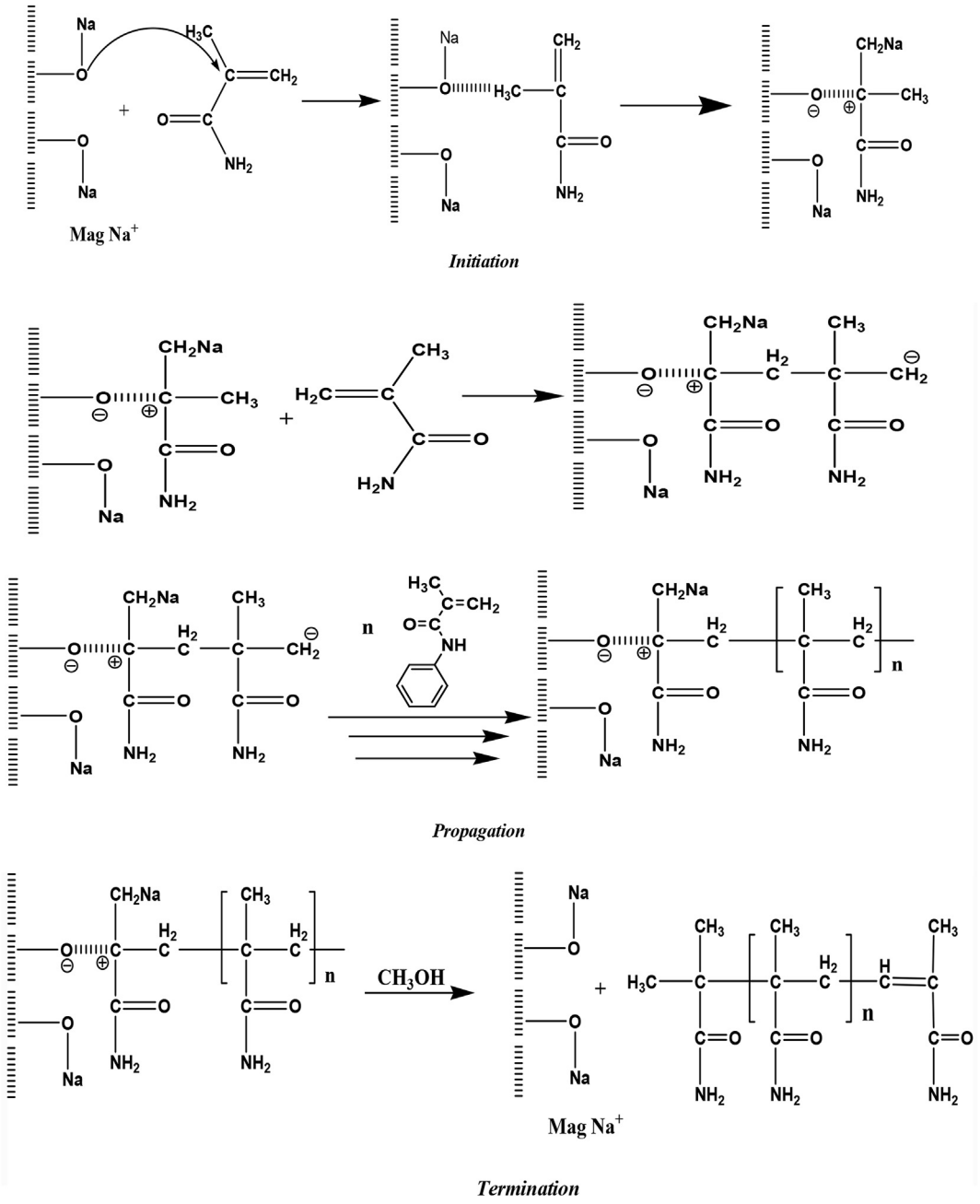
Propagation: The carbenium ion binds to a methylene group of another monomer unit and the process continues one after the other [48].

Termination: Elementary step in which the active particle loses its activity by recombination of two free radicals and Na^+ ions return to the leaves of clay, recover the clay catalyst by filtration; which allows to reuse them [49].

From the mechanism studies, it was showed that monomer was inserted into the growing chains.

4. Conclusion

This paper has described a novel method to synthesis of methacrylamide and it's homologue polymethacrylamide catalyzed by solid and non-toxic Maghnite-Na+ (Algerian MMT) at room temperature and in the conditions that respect the principles of green chemistry compared to previously published studies which using commercial methacrylamide. The synthesis of the



Scheme 3. Proposed mechanism of Methacrylamide homopolymerization.

monomer is carried out by the reaction of ammonia with methacrylic anhydride in bulk at 0 °C for 1 h obtaining a better yield around 85% and selectivity 100%. The conversion of the polymer increased with the increases of the amount of catalyst which gives a molecular weight Mn = 3000 g/mol. The simplicity of the method, good properties catalytic of the catalyst (Maghnite-Na+) are less expensive and environmentally friendly make it attractive method for the green synthesis of polymethacrylamide and it's homologue polymethacrylamide or their derivates.

Acknowledgements

We thank all laboratory staff of polymer chemistry from the University of Oran for their kind cooperation and we wish the best of luck to Pr Mohammed Belbachir.

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