

A Green Catalyst “Maghnite Na⁺” For Synthesis and Anionic Polymerization of Methacrylamide

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Abstract—The novelty of this work is to study the anionic polymerization of methacrylamide using an environmentally friendly catalyst Maghnite Na⁺, a proton exchanged montmorillonite clay, in an ice bath. We have synthesized the monomer methacrylamide (MAM) by the condensation of Ammonia with methacrylic anhydride in bulk (without solvent) at 0°C for 1 hour and its polymer was synthesized using a green catalyst “maghnite Na⁺” in tetrahydrofurane THF at 0°C. The Poly methacrylamide structure is characterized and confirmed by Infrared Spectroscopy (FTIR), ¹H nuclear magnetic resonance (NMR) spectroscopy and Thermal properties of the polymers were determined using thermogravimetric analysis (TGA).

Keywords— Anionic polymerization; Maghnite-Na⁺; Methacrylamide; Montmorillonite; Green catalyst.

I. INTRODUCTION

Heterogeneous catalysis is of vital importance to the world's economy, allowing us to convert raw materials into valuable chemicals and fuels in an economical, efficient, and environmentally benign manner. For example, heterogeneous catalysts have numerous industrial applications in the chemical, food, pharmaceutical, automobile and petrochemical industries [1]. They are preferred due to their robustness and lower operational cost, in particular through easier recovery/separation from the products. [2].

The wide range of industrial applications of PMAM is due to their high water solubility. The most important uses for the polymers are as flocculating agents for minerals, coal, industrial waste, and additives in paper manufacturing [3].

The methacrylamide monomer is polymerized by both radical and anionic route [4]. The radical polymerization of methacrylamide is described in previous works; in various solvents and initiators by R. Anbarasan et al in water at 75°C using potassium persulfate as initiator [5] and by Muserref Onal and Meltem Celik in water at 85°C using benzoyl peroxide as initiator [6] and their copolymerization was studied by M. Sadeghi et al onto pectin in water at 70°C using ammonium persulfate as initiator [7], and with methylmethacrylate in absolute ethanol using

Azobisisobutyronitrile (AIBN) as initiator by N. Grassie et al [8].

The novelty of this work is to study the anionic polymerization of methacrylamide initiated directly by a montmorillonite clay, —Maghnite-Na⁺ a new nontoxic and recyclable catalyst. initially, we have synthesized the monomer methacrylamide by the condensation of ammonia with methacrylic anhydride in bulk (without solvent) at 0°C for 1 hour; and subsequently the polymerization of monomer was carried out under suitable conditions in THF at (0°C) for 24 hours initiated by anionic catalyst —maghnite Na⁺.

The monomer and polymer are characterized and confirmed by Infrared Spectroscopy (FTIR), ¹H nuclear magnetic resonance (NMR) spectroscopy and Thermal properties of the polymers are determined using thermogravimetric analysis (TGA).

II. EXPERIMENTAL

1. Preparation of Catalyst “Maghnite-Na⁺”

—Maghnite-Na⁺ was prepared as described by Belbachir and collaborators [9, 10]. Raw-Maghnite (20 g) was crushed for 20 min using a prolabo ceramic balls grinder. It was then dried for 2 h at 105 °C. The 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 chloride free and then filtered and dried at 105 °C.

• XRD analysis of Catalyst

The X-ray diffractogram of sodic montmorillonite shows an offset of the angle 2θ from 6.8 to 12°, thus indicating the increase in the interlayer distance of 12.52 Å for raw maghnite and 12.34 Å for sodic clay, confirming the intercalation of Na⁺ ions in the space initially occupied by H⁺ ions.

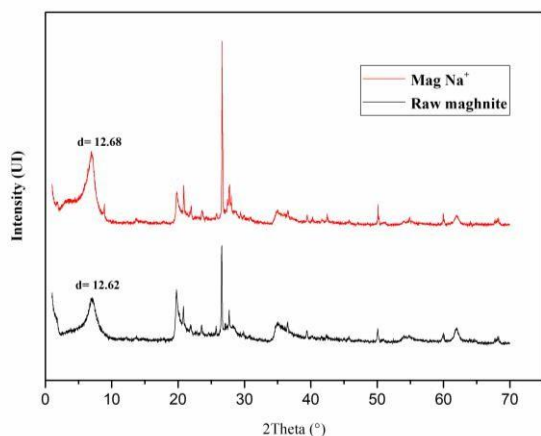


Fig 1. XRD spectra of Raw-Maghnite and Maghnite- Na⁺.

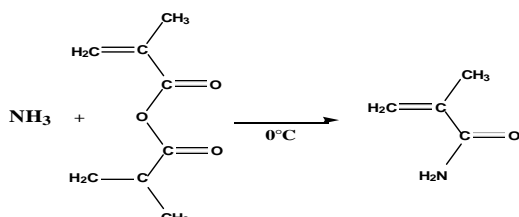
2. Syntheses

2.1. Synthesis of methacrylamide monomer (MAM)

Synthesis of monomer was carried out by mixing 0.1mole (10ml) of ammonia with 0.1mole (15ml) of Methacrylic anhydride in bulk (without solvent); the reaction mixture was cooled to 0-5°C using an ice bath during 1h.

After that, we filtered the solution recover the product. The product obtained was a white powder which when recrystallized in a methanol-diethylether mixture.

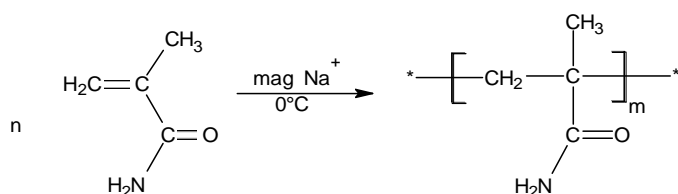
➤ Yield=85%



Scheme1. Schematic representation of the synthesis of methacrylamide (MAM)

2.2. polymerization of MAM

The anionic polymerization of MAM was carried out in sealed tubes. Each tube contains a mixture of 1 g of MAM, 10ml of tetrahydrofuran THF and (0.15g) 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 24 hours. The resulting polymer was precipitated in methanol, washed for several times, dried at 40°C in vacuum and weighed.



Scheme 2. Schematic representation of the synthesis of Poly (methacrylamide) (PMAM) catalyzed by Maghnite Na⁺.

3. RESULTS AND DISCUSSION

3.1 Characterization of the monomer (MAM)

The structures of monomer are characterized and confirmed by Infrared Spectroscopy (FTIR), ¹H and ¹³C nuclear magnetic resonance (NMR) spectroscopy.

The IR (cm⁻¹) spectrum of (MAM): ν_{NH} primary amine 3374.45, 3179.85, 607, ν_{CH₂,CH₃} 2930.75, 2984, ν_{C=Oamide} 1671.64, ν_{C=C} 1600, ν_{C-N} 1401.49.

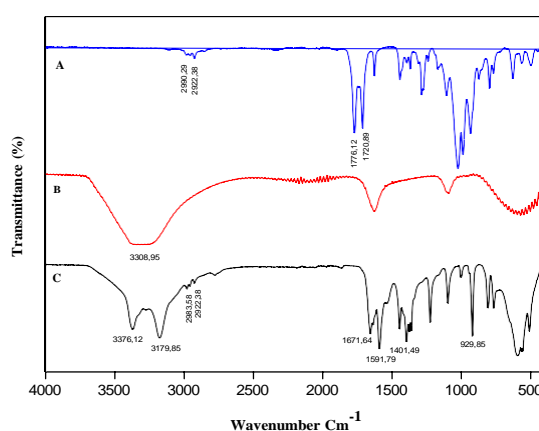


Fig 2. FTIR spectra for the starting products (A) Methacrylic anhydride; (B) Ammonia and product synthesis (C) methacrylamide (MAM)

The ¹H NMR in (CDCl₃) shows: (δ ppm) 1.951(s, 3H of -CH₃), 5.39-5.76 (d, 2H of =CH₂), 6.027- 6.488 (2s, 2H of -NH₂).

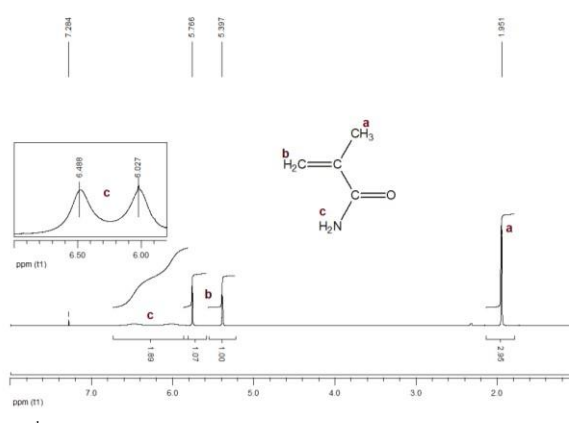


Fig 3. ¹H NMR spectrum (CDCl₃) of Methacrylamide (MAM) obtained.

The ¹³C NMR in (CDCl₃) shows: (δ ppm) 18.63(-CH₃); 120.88 (=CH₂), 139.123(C=C), 170.95(C=O)_{amide}.

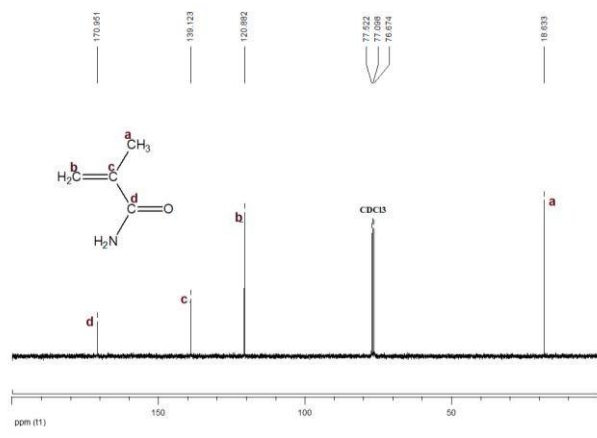


Fig 4. ^{13}C NMR spectrum (CDCl_3) of Methacrylamide (MAM).

3.2. Characterization of Poly (methacrylamide)

The IR spectrum of poly (MAM) is identical for the monomer excepting that we observe the increase of the intensity of the bands. Two large and intense bands at 3314.93cm^{-1} corresponding to N-H stretching and large bands between 2836 and 2990cm^{-1} were attributed to C-H symmetrical and asymmetrical stretching on CH_2 and CH_3 groups, respectively. The absorptions at 1653cm^{-1} are assignable to amide carbonyl ($\text{C}=\text{O}$) stretching.

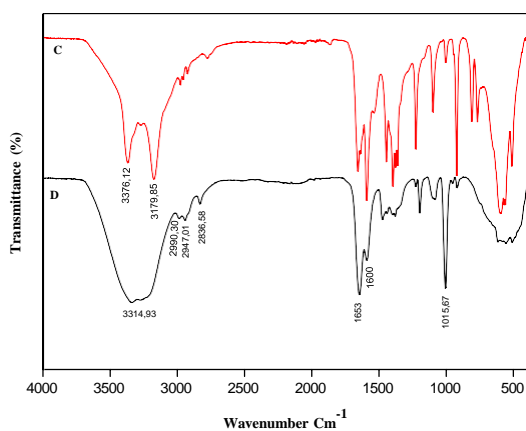


Fig 5. FTIR spectra for the methacrylamide (MAM) monomer (A) and polymer methacrylamide (PMAM) (B)

The ^1H NMR spectrum in figure 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 ($-\text{NH}_2$). The small peak at 1.82ppm

and at 3.23ppm are attributed to the methyl protons groups ($-\text{CH}_3$) at the end of the polymer chain; as well as a doublet at $5.39\text{-}5.76$ ppm are assigned to the vinylic hydrogens (b) ($=\text{CH}$). The strongest and sharp peak centered at 4.70 ppm corresponds to water deuterated solvent (D_2O) respectively.

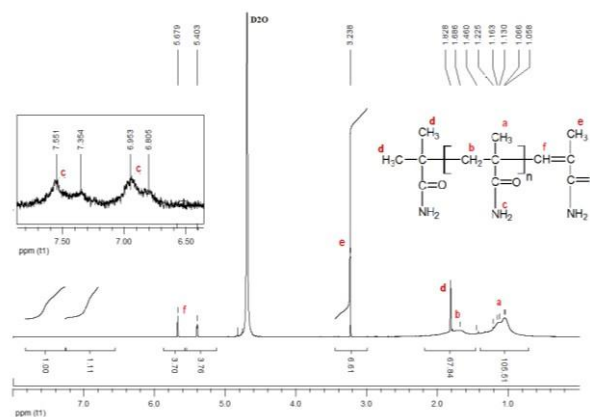


Fig 6. ^1H NMR spectrum (D_2O) of Poly(methacrylamide) (PMAM) obtained.

3.3. Thermal studies

The thermal stability of the polymer is studied by thermogravimetric analysis in air from room temperature. The TGA a curve of PMA is shown in the Figure 7 clearly indicates that the polymers undergo one stages of degradation. The degradation is varying from 196°C to 238°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 the polymer exhibits low thermostability. The PMAM have flexible aliphatic main chains exhibit much lower thermal stability and degrade rapidly at low temperature.

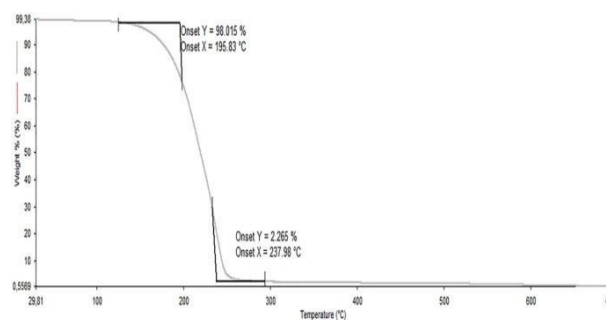
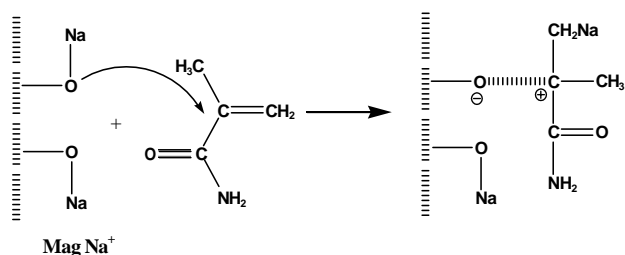
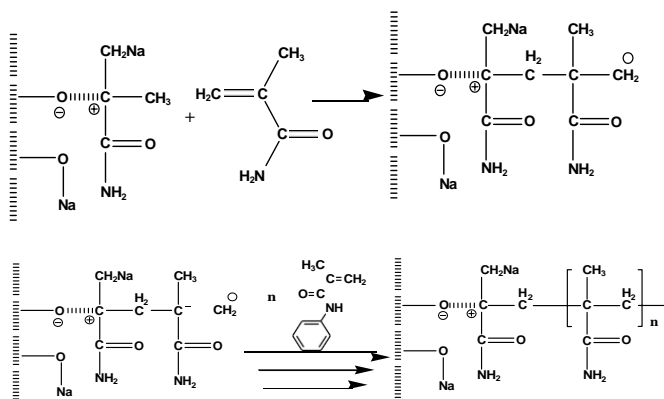


Fig 7. TGA a curve of the Poly(methacrylamide) PMAM in air.

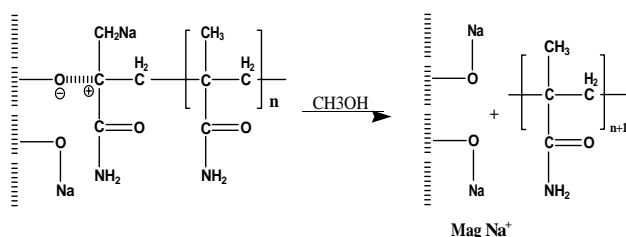
An anionic mechanism for the reaction was proposed. From the mechanism studies, it was showed that monomer was inserted into the growing chains.



Scheme 1. Initiation



Scheme 2. Propagation



Scheme 3. Termination

III. CONCLUSION

This paper has described a novel method to synthesis and polymerization of methacrylamide initiated by solid and non-toxic Maghnite-Na⁺ clay at room temperature in the conditions that respect the principles of green chemistry. The synthesis of the monomer is carried out by reaction of ammonia with a single reactant methacrylic anhydride in bulk (without solvent)

and at 0 °C for 1 hour, obtaining a better yield and selectivity to the product 100% and the structure of monomer and polymer are confirmed by Infrared Spectroscopy (FTIR), ¹H and ¹³C nuclear magnetic resonance (NMR) spectroscopy. The result of thermogravimetry indicated that the polymer exhibits low thermostability.

Finally, The simplicity of the method, good properties catalytic of the support catalyst solid (Maghnite-Na⁺) make it an attractive method for the synthesis and polymerization of methacrylamide.

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