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Green synthesis, anionic polymerization of 1,4-bis(methacryloyl)piperazine using Algerian clay as catalyst

https://doi.org/10.1515/gps-2019-0031
Received December 14, 2018; accepted April 14, 2019.

Abstract: In this work, a chain of reactions has been proposed as a new heterogeneous technique, based on the use of natural treated clays as an environmentally friendly catalysts for the synthesis of poly(1,4-bis(methacryloyl)piperazine). We first synthesized the monomer; 1,4-bis(methacryloyl)piperazine (NBMP) in bulk (without solvent) by the condensation of heterocyclic secondary amines piperazine with methacrylic anhydride catalyzed by maghnite-H$^+$ at room temperature during 2 h. After that, we have polymerized anionically the obtained NBMP in an ice bath using anionic catalyst maghnite-Na$^+$ at 0°C, the reaction took place in 24 h. The poly(1,4-bis(methacryloyl)piperazine) and NBMP structure was characterized and confirmed by infrared spectroscopy, ^{1}H and ^{13}C nuclear magnetic resonance spectroscopies. Thermal properties of the polymer were determined using thermogravimetric analysis. The yield of the reaction was 72% and 59% for the monomer and polymer synthesis respectively. The effect of the weight content of the catalyst on the reaction yield was studied. A polymerization mechanism has been suggested showing the role of maghnite as a catalyst during the reaction courses.

Keywords: catalyst; polymerization; clay; green; monomer

List of abbreviations:
IR – infrared spectroscopy
NBMP – 1,4-bis(methacryloyl)piperazine
NMR – nuclear magnetic resonance
Maghnite – natural Algerian clay
Maghnite-H$^+$ – maghnite treated by acid
Maghnite-Na$^+$ – maghnite treated by NaCl
poly(NBMP) – poly(1,4-bis(methacryloyl)piperazine)
TGA – thermogravimetric analysis
XRD – X-ray diffraction

1 Introduction

Heterogeneous catalysis occupies a very important place in different industrial syntheses, where transformation of the raw reagents into chemicals and commercial fuels can be carried out in an efficient, economical and environmental friendly way. Heterogeneous catalysts are currently used in many industrial sectors such as the oil, pharmaceutical, food and automobile industries [1]. The ease of separating and recovering them from the reaction medium provides the main parameter for them to be preferred to other homogeneous homologs. In addition, they are pretty active (you can run them at higher temperatures as they are more stable) [2]. Nitrogen-containing heterocycles are of considerable importance in the pharmaceutical area; because they are present in many organic compounds with biological activity. Piperazine is one of the most sought heterocyclic compounds for the development of new drug candidates. The piperazine derivatives have pharmacological activity with broad spectrum since they are found as: anticancer [3-5], antibacterial [6], antifungals [7], anti-malarial [8], antipsychotics, antidepressants, HIV protease inhibitors [9].

Poly(1,4-bis(methacryloyl)piperazine) is a distinct class of functional polymers, which has a variety of applications, is very useful for the preparation of cross-linking agent and their use for preparation of polymer suitable for the separation on of amino acid, peptides, protein and viruses [10-13]. The synthesis of 1,4-bis(methacryloyl)piperazine could be realized according to different approaches

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in various solvents and reactants using acryloyl or methacryloyl chloride with triethylamine [11-17].

The novelty of this study is to design a green process to polymerize 1,4-bis(methacryloyl)piperazine, using a heterogeneous clay catalyst (maghnite-Na$^+$) obtained by a chemical modification of the raw maghnite. The advantage of this new catalyst is in its reusability, ease of separation and handling under mild conditions. Maghnite has acid sites of Brönsted and Lewis type. These active sites responsible for priming chemical reactions can be created by binding high charge density cations such as protons on the surface of layers [18-20]. Proton-loaded maghnite has been successfully used as a heterogeneous catalyst for many polymerization reactions [21-23].

2 Experimental

2.1 Materials

All reagents and chemicals were obtained from commercial sources, as they were used without any pre-treatment treatments. Methacrylic anhydride and dichlomethane were purchased from Sigma-Aldrich society in Algeria. The Piperazine and $MgSO_4$ were obtained respectively from ACOROS-ORGANICS and Biochem in France. The raw maghnite was obtained from the ENOF Company located in Maghnia, Algeria. Maghnite-H$^+$ was prepared following the procedure published by Belbachir et al. [18,19]. X-ray diffraction analysis was performed on a D8 Advanced Bruker AXSX diffractometer (Germany). Fourier transform infrared spectroscopy spectra were recorded using a Bruker alpha-PATR No. 9501165 (France) in the range of 400 to 4000 cm^{-1}. The ^{1}H and ^{13}C nuclear magnetic resonance analyzes were performed on a Bruker NMR spectrometer at 300 MHz (Germany), equipped with a probe BB05 mm. Tetramethylsilane (TMS) was used as internal standard and $CDCl_3$ as solvent. TGA analysis was carried out using a Perkin Elmer STA6000 device (USA).

2.2 Preparation of catalysts

Maghnite-H$^+$ and maghnite-Na$^+$ were prepared according to the procedure mentioned in our previous studies [15,16]. 20 g of raw maghnite was milled for 20 min using a ceramic ball mill. It was after dried at 105°C for 2 h. The maghnite was put in an Erlenmeyer flask with 500 mL of distilled water. Then, the mixture was stirred with a magnetic stirrer after adding it to 0.25 M sulfuric acid solution until saturation in 48 h at room temperature. The maghnite-H$^+$ was then washed with water to be free of sulfate ions and then dried at 105°C. The residue of the rinsing water was each time tested by the barium nitrate until the total removal of sulfate ions. The maghnite-Na$^+$ was prepared as follows: The raw maghnite was put in an Erlenmeyer flask with 500 mL of 1 M NaCl solution. The mixture was stirred with a magnetic stirrer until saturation in 24 h at room temperature. The maghnite-Na$^+$ was then washed with water to be free of chloride ions, dried at 105°C and finally stored in a desiccator away from moisture.

2.3 Monomer synthesis

0.86 g of piperazine was mixed with various amounts of maghnite-H$^+$ 0.25 M (3, 5, 10 and 15 %wt) for 30 min. Following that we added 0.2 mol (30 mL) of methacrylic anhydride (with a molar ratio of 2:1 of methacrylic anhydride to piperazine) to the solution. The reaction mixture was cooled to 5°C during 2 h (Figure 1).

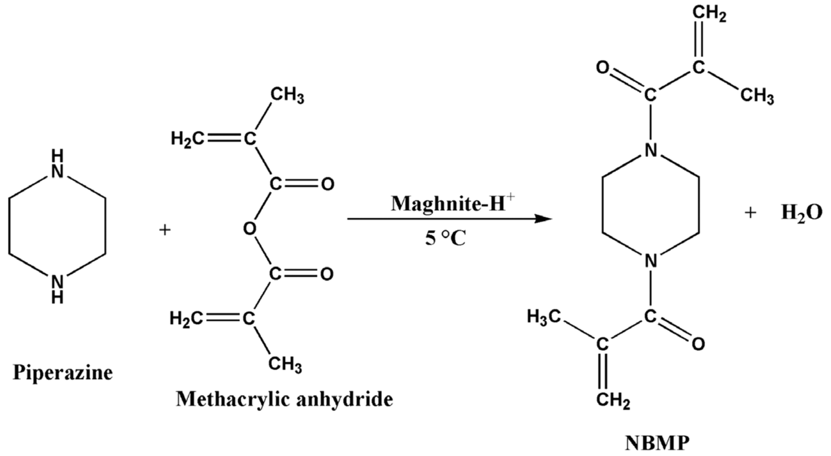

Figure 1: Representative scheme for the synthesis of NBMP catalyzed by maghnite-H$^+$.

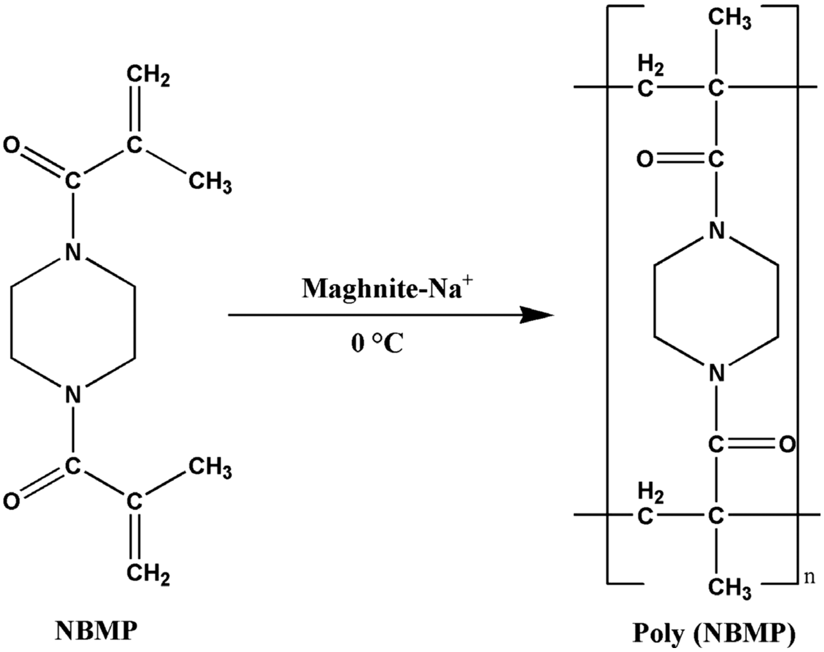

Figure 2: Representative scheme for the polymerization of NBMP catalyzed by maghnite-Na$^+$.

After 2 h, we filtered the solution recover the clay catalyst, which was transferred to a separating funnel washed thoroughly with a 5% sodium hydroxide solution and extracted with dichloromethane (3×30 mL). The organic layers were combined; dried over anhydrous magnesium sulphate $MgSO_4$ and filtered. After the evaporation of dichloromethane in vacuum, the product was recrystallized in cold diethyl ether; a white crystal solid was obtained.

2.4 Polymer synthesis

The anionic polymerization of synthesized NBMP was carried out in sealed tubes. Each tube contains a mixture of 1 g of NBMP 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 24 h. The resulting polymer was precipitated in methanol, washed for several times, dried at 40°C in vacuum and weighed (Figure 2).

3 Results and discussion

3.1 IR and XRD analyses of catalysts

IR and XRD analyses of the raw maghnite and those treated are shown in Figures 3 and 4. The FT-IR spectrum (Figure 3) shows the following bands: The broad bands between 3387 and 3625 cm^{-1} are assigned to AlAlOH coupled by AlMgOH stretching vibrations. The deformation bands at 1641 cm^{-1}, 792 cm^{-1} and 616 cm^{-1} are assigned to AlAlOH, AlFe^{3+}OH and AlMgOH, respectively. The bands between 1004 cm^{-1} and 999 cm^{-1} are assigned to the Si-O elongation bands out of the plane and Si-O-Si (2 bands) in the plane.

The X-ray diffractograms (Figure 4) of the raw, sodium and acidic maghnite show that the montmorillonite peak appears at 2θ angle corresponds to 7.05°, 6.96° and 5.67°, respectively. These were calculated by Bragg's Law, thus indicating the increase in interfoliar distance from 12.52 Å to 12.68 Å for sodium maghnite and to 15.56 Å for acidic maghnite, The intercalation of Na$^+$ and H_3O^+ ions in the space initially occupied by the Ca^{2+} and K$^+$ cations led to the swelling of maghnite.

3.2 Characterization of synthesized monomer and polymer

3.2.1 IR spectroscopy

According to Figure 5, the IR spectrum of NBMP exhibits three weak peaks between 2924 and 3055 cm^{-1} were attributed to C-H symmetrical and asymmetrical stretching on CH_2 and CH_3 groups, respectively. The strong

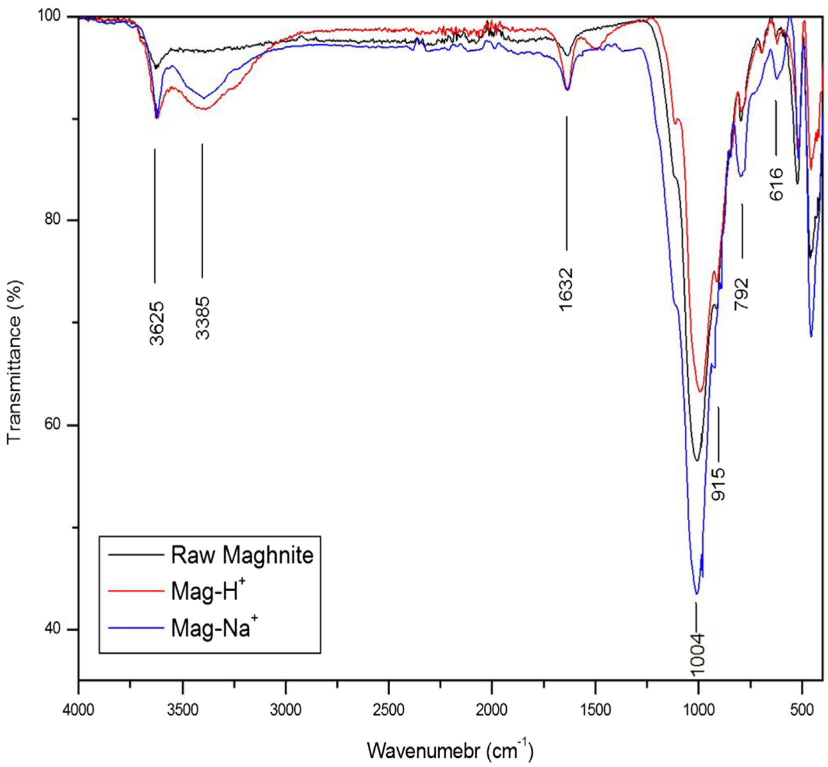

Figure 3: IR spectra of raw maghnite, maghnite sodium and acidic maghnite.

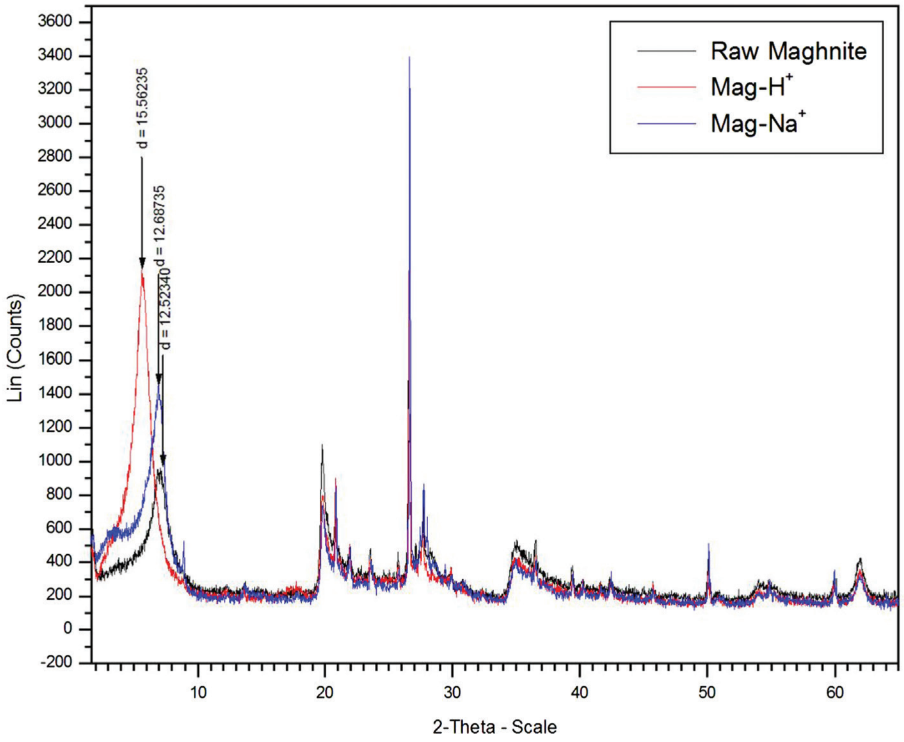

Figure 4: XRD spectra of raw maghnite, maghnite sodium and acidic maghnite.

band at 1716 cm^{-1} was attributed to amide carbonyl C=O stretching vibration. The strongest bands at 1617 cm^{-1} and 522 cm^{-1} corresponded to the C=C stretching vibration. The second strongest and sharp band at 1430 cm^{-1} was attributed to the C-N stretch vibration. Figure 6 shows the IR spectrum of poly(NBMP), it is identical for the

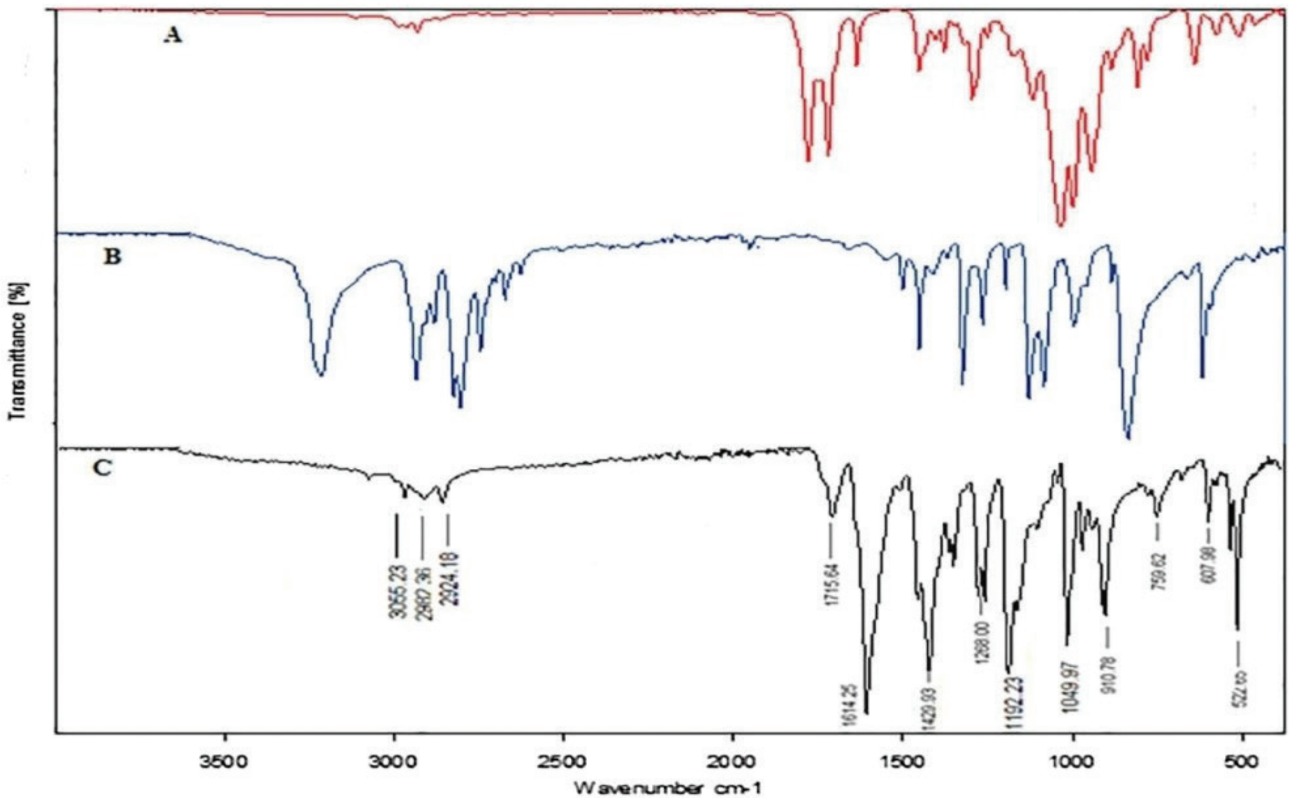

Figure 5: IR spectra of (a) methacrylic anhydride, (b) piperazine and (c) NBMP.

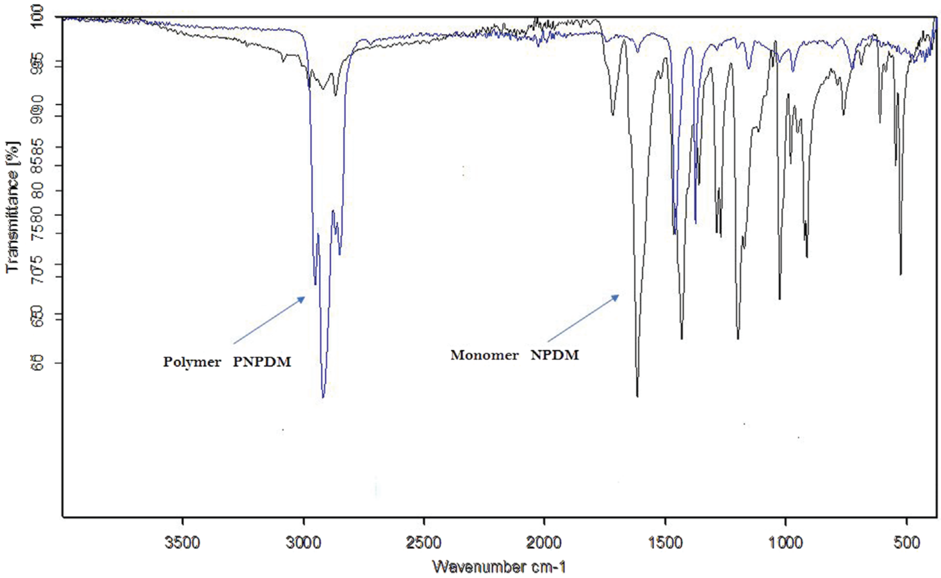

Figure 6: IR spectra of NBMP (black curve) and poly(NBMP) (blue curve).

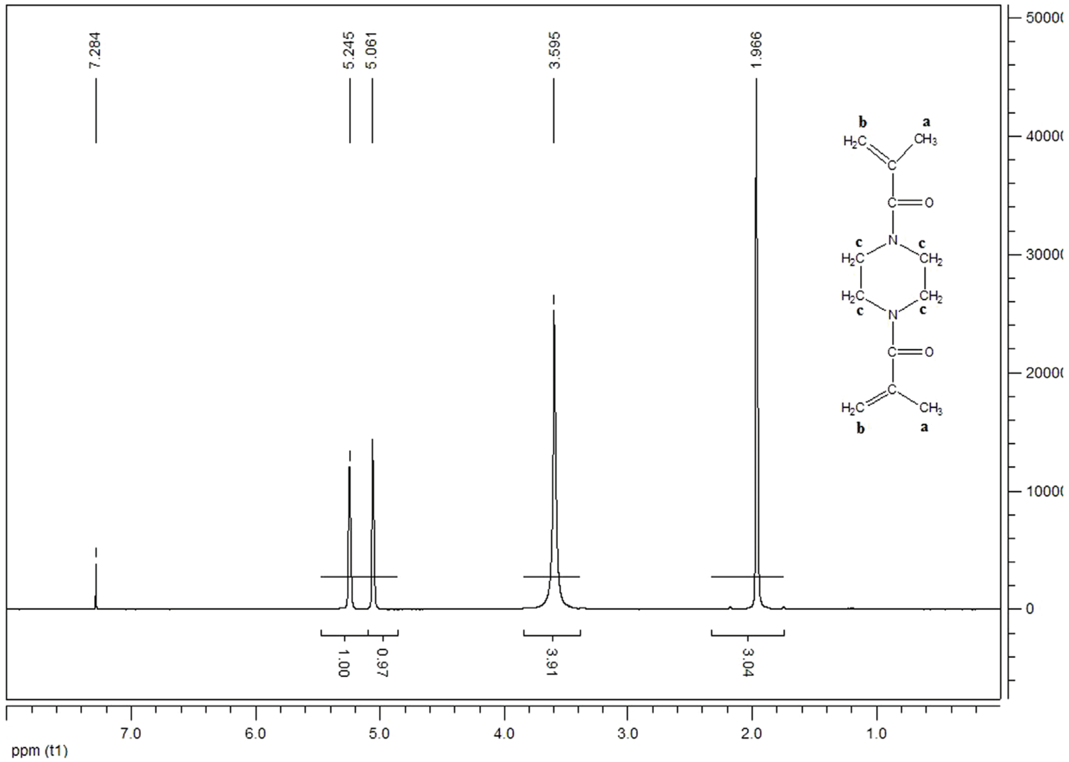

Figure 7: ^{1}H NMR spectrum ($CDCl_3$) of NBMP.

monomer excepting that we observe the increase of the intensity of the bands. Large and intense bands between 2920 and 2952 cm^{-1} were attributed to C-H symmetrical and asymmetrical stretching on CH_2 and CH_3 groups, respectively. The disappearance of the intense band at 1617 cm^{-1} and 522 cm^{-1} which corresponds to the stretching vibration C=C due to the opening of the double bond allowing the connection between the monomer units.

3.2.2 ^{1}H NMR

The ^{1}H NMR spectrum of NBMP and poly(NBMP) and are shown in Figures 7 and 8, respectively. A sharper peak, centered at 1.97 ppm, corresponds to the methyl protons ($-CH_3$), the two peaks of average width between 5.06 and 5.25 ppm are due to methylene protons ($=CH_2$), another broad peak centered at 3.60 ppm corresponds to heterocyclic protons of methylene ($N-CH_2CH_2-N$). In Figure 8 corresponding to the ^{1}H NMR spectrum of the polymer, the stronger peak at 0.76 ppm assigns to the methyl proton groups ($-CH_3$), the broad peak between 0.99-1.35 ppm due to methylene protons ($-CH_2$) and the other broad peak at 1.49 ppm corresponding to heterocyclic protons of methylene ($N-CH_2CH_2-N$). The small peak at 3.53 ppm is attributed to the hydroxide protons at the end of the polymer chain, the comparison between its integration curve with respect to the others makes it possible to calculate the number-average molecular mass which has been obtained at around 18,000 g/mol.

3.2.3 ^{13}C NMR

Figures 9 and 10 show the ^{13}C NMR spectrum of the obtained monomer and polymer, respectively. This characterization technique was carried out in order to complete the information collected by ^{1}H NMR, for identifying and confirming the molecular structure much more in terms of the nature of the existing carbonic groups. Table 1 summarizes the different chemical shifts observed. We clearly see that the two monomer and polymer spectra generally indicate the same functional groups. Except that in the spectrum of the polymer an additional peak shown at 22 ppm and which corresponds to the group. Except that the two peaks at 116.22 and 139.92 ppm in the monomer spectrum are transformed into two new peaks at 41.55 and 30.05 ppm in the polymer spectrum, they correspond to the $-CH_2-$ aliphatic group responsible for the connection between the monomer units, and quaternary carbon resulting from the breaking of the double bond -C=C- existing in the monomer, respectively.

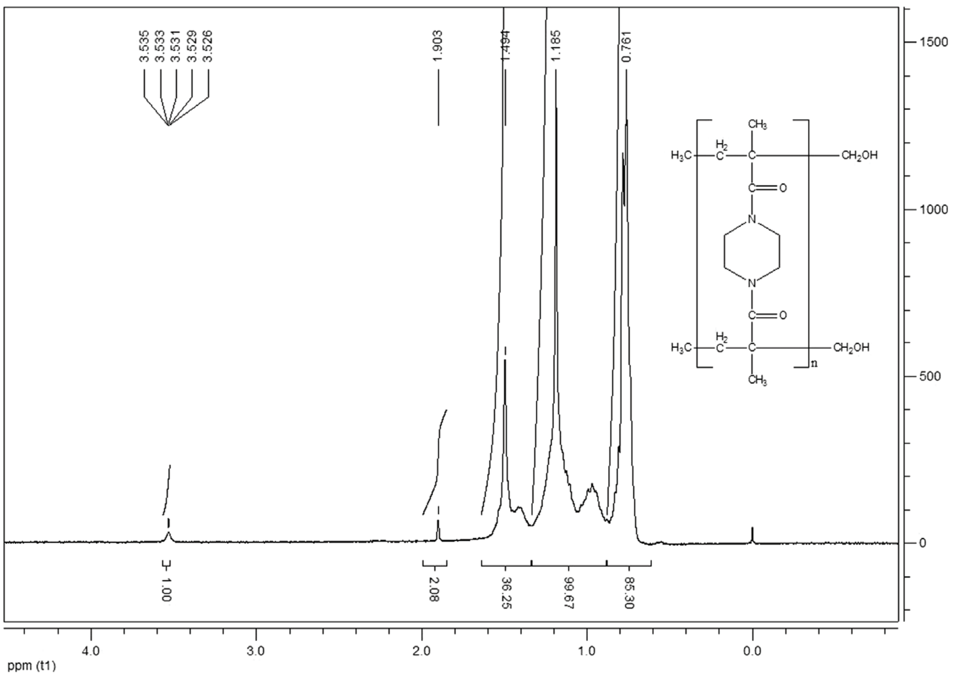

Figure 8: ^{1}H NMR spectrum ($CDCl_3$) of poly(NBMP).

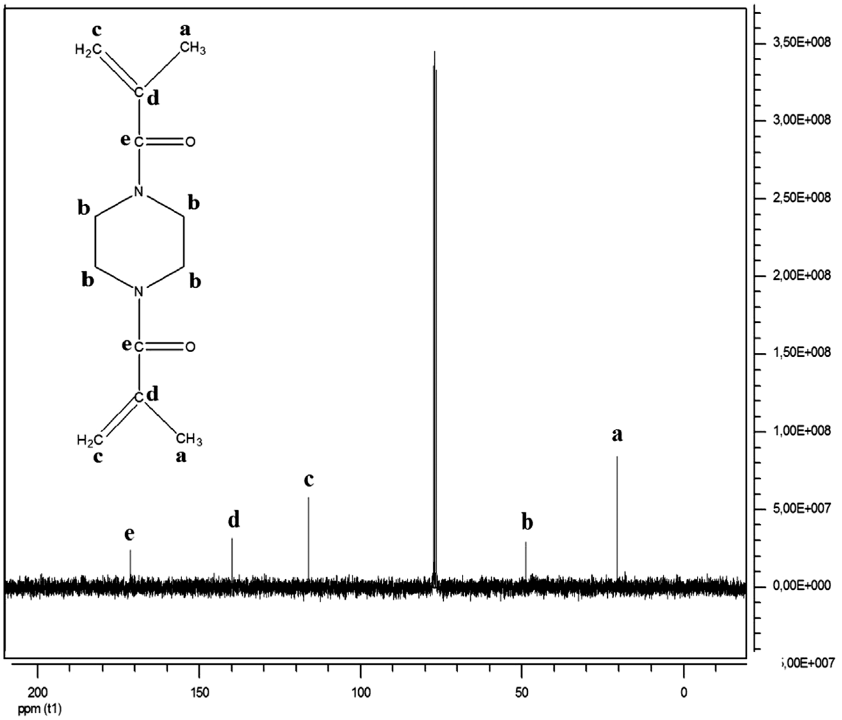

Figure 9: ^{13}C NMR spectrum ($CDCl_3$) of NBMP.

3.2.4 Thermal studies

The thermal behavior of the polymer was evaluated by thermogravimetric analysis in air from room temperature. The TGA curve of poly(NBMP) is shown in Figure 11, which clearly indicates that the polymer has degraded in two successive steps. The initial degradation and at the same time the main one, started from 244.90°C to 350°C, which was

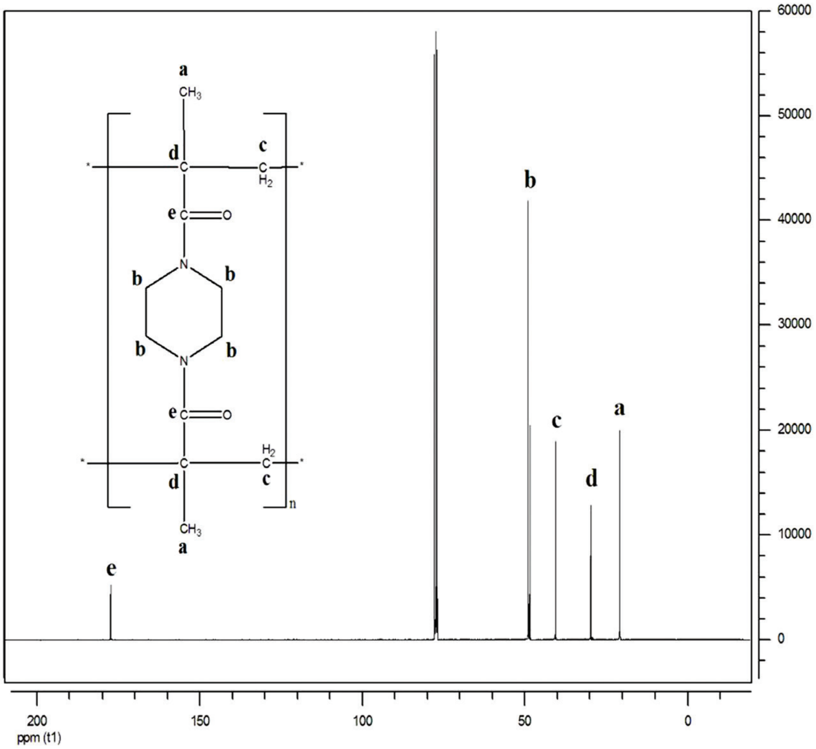

Figure 10: ^{13}C NMR spectrum ($CDCl_3$) of poly(NBMP).

Table 1: ^{13}C NMR chemical shift for various carbons of NBMP and poly(NBMP).

Monomer/Polymer	Attributions	Chemical shift δ (ppm)
NBMP	$-CH_3$ (a)	20.49
	$-CH_2-$ cyclic (b)	47.02
	$=CH_2$ (c)	116.22
	$-C=C$ (d)	139.92
	C=O (e)	171.40
Poly(NBMP)	$-CH_3$ (a)	20.89
	$-CH_2-$ cyclic (b)	48.99
	$-CH_2-$ Aliphatic (c)	41.55
	C quaternary (d)	30.05
	C=O (e)	177.32

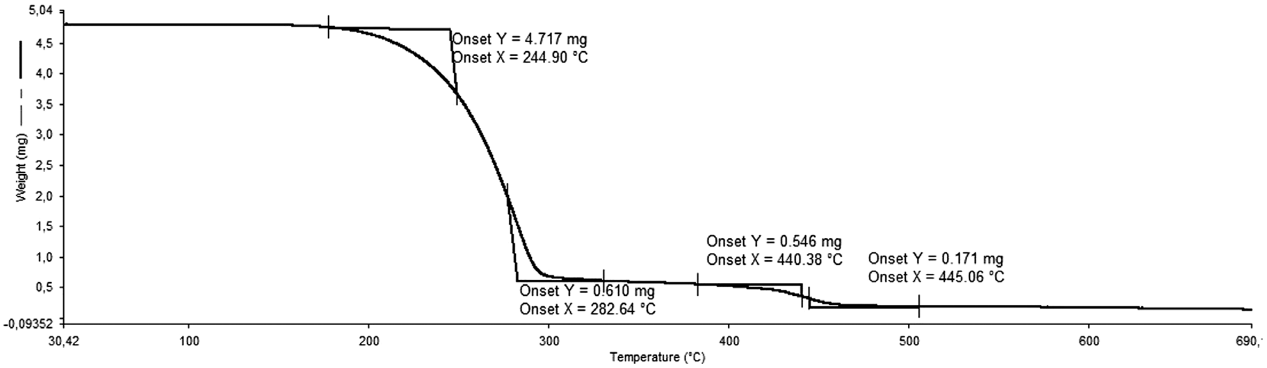

Figure 11: TGA thermogram of poly(NBMP).

due to the decomposition of the poly(NBMP) resulting from the weakness of the methyl groups in the polymer chain, this corresponds to a loss of weight 87.07% (4.11 mg). The second degradation step is from 440.38°C to 445.06°C which was attributed to the complete combustion of the residues. This result concludes that the synthesized poly(NBMP) is thermally stable below the temperature of 244°C.

3.3 Reaction mechanism

According to the results of analysis of the synthesized polymer initiated by maghnite Na^+ as a heterogeneous solid catalyst, a reaction mechanism has been proposed in Figure 12. The initiation step is based on the creation of the active center by the fixation of Na^+ ions on the

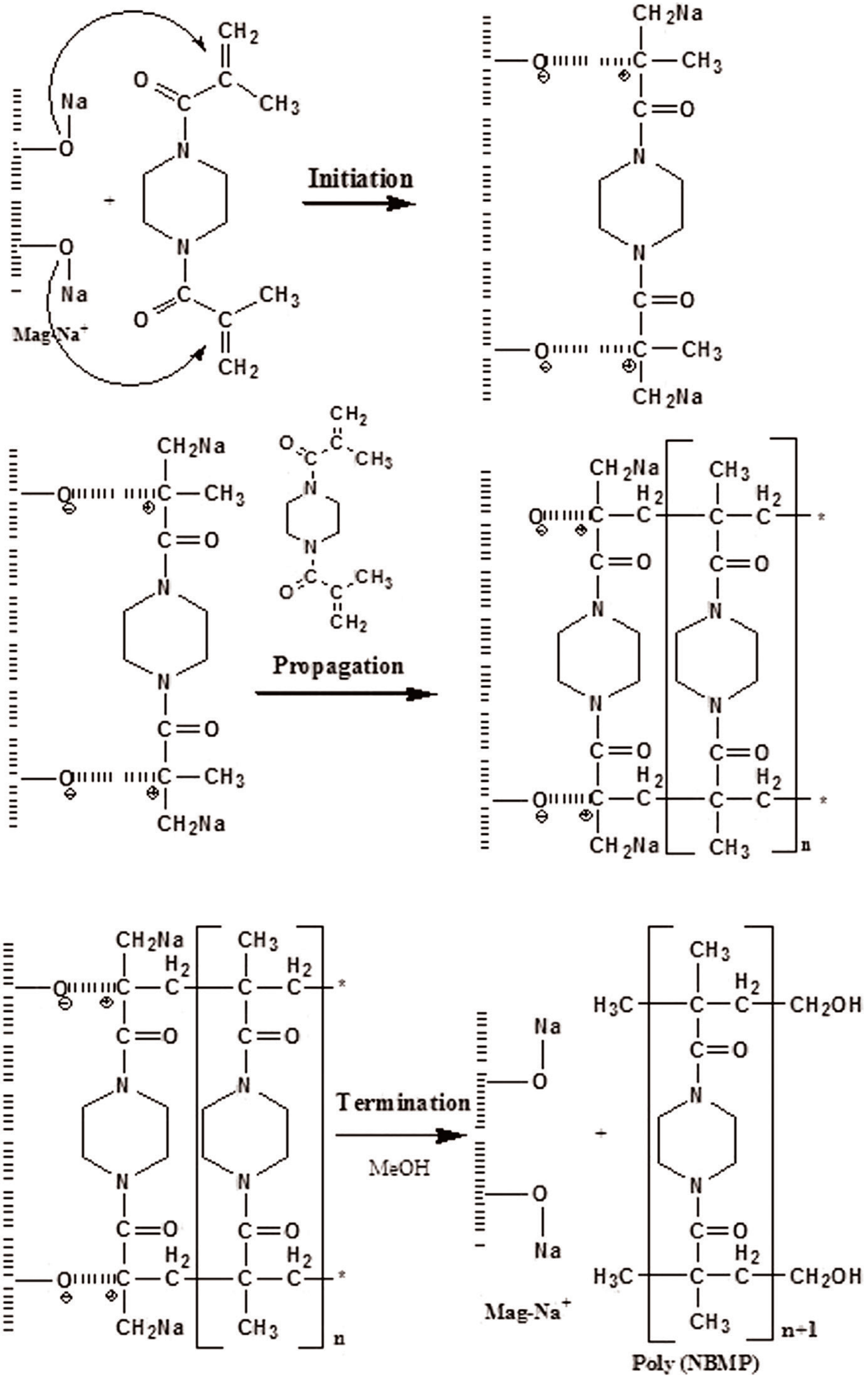

Figure 12: Proposed reaction mechanism of NBMP polymerization.

methylene groups that open the double bond C=C. In the Propagation step the carbonium ion binds to a methylene group of another monomer unit and the process continues one after one. The chains propagate by the chain-growth polymerization method. The termination step is carried out by the addition of methanol, its molecule is subdivided into two; a CH_2OH group binds to the carbonium ions forming one end of the chain, and a proton replaces the Na^+ ions and also forms the other end of the chain. The Na^+ ions return to the leaves of the clay allowing its use again.

3.4 Effect of maghnite-H$^+$ and maghnite-Na$^+$ proportion on the yield of the reaction

We can see in Table 2 that the yield of the monomer and polymer synthesis reaction increased with the increase in the amount of catalyst used, and stabilized at a catalyst proportion of 10% and 15% for the monomer and the polymer synthesis reaction respectively. The synthesis of the monomer was obtained with a better yield around 72% of pure product with a selectivity of 100%. The yield of the polymerization reaction reached a threshold of about 59% using maghnite-Na$^+$ as catalyst.

4 Conclusion

In this work, we have shown that 1,4-bis(methacryloyl) piperazine is polymerizable at room temperature, using a non-toxic and recyclable catalyst prepared from natural clay (maghnite-Na$^+$). The yield of the polymerization reaction was 59% using a weight content of 15% of catalyst. The monomer was synthesized by a new green process under conditions consistent with the principles of green chemistry using maghnite-H$^+$ as catalyst, in which we reacted piperazine and methacrylic anhydride at room temperature for 2 h, the reaction yield was 72%. The molecular structure of the monomer and the polymer was identified by IR, ^{13}C NMR and ^{13}C NMR analyses. The average molecular weight was measured by NMR at 18,000 g/mol. TGA analysis of the polymer obtained showed that it is thermally stable below the temperature of 244°C. In the end, a reaction mechanism has been proposed to show the role of maghnite-Na$^+$ during the various steps of the polymerization reaction.

Table 2: Effect of catalyst amount (maghnite-H$^+$/maghnite-Na$^+$) on conversion of monomer and polymer.

Monomer/Polymer	Catalyst (weight %)	Yield (%)
NBMP (at 5°C)	3	40
	5	60
	10	72
	15	72
	20	72
Poly(NBMP) (at 0°C)	3	5
	5	30
	10	45
	15	59
	20	59

Acknowledgments: We would like to thank Mr. A. Addou (Laboratory of Polymer Chemistry LCP, University of Oran 1) for the IR analysis. We also thank the head of department, Mrs. H. Hidour (Applied Organic Synthesis Laboratory, University of Es-Senia Oran) for the NMR analysis.

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