

**A NEW APPROACH TO SYNTHESIS METHACRYLIC MONOMERS  
N-ALKYLMETHACRYLAMIDE USING AN ECOLOGIC AND FRIENDLY  
CATALYST MAGHNITE H<sup>+</sup>**

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**ABSTRACT**

In this paper, we have developed a novel procedure to synthesize four monomers formulated as 1,4-bis(Methacryloyl)Piperazine, N-Methacryloylmorpholine, N-Phenylmethacrylamide and N-Formyldimethacrylamide. N-Alkylmethacrylamide monomers are synthesized by the condensation of primary amine aniline and formamide or heterocyclic secondary amines such as piperazine and morpholine with methacrylic anhydride using an ecologic and friendly catalyst “Maghnite H<sup>+</sup>”, a proton exchanged montmorillonite clay by replacing a toxic reactant acryloyl chloride and triethylamine which are using in previously published studies. This new approach is even more interesting since this synthesis is carried out in bulk (without solvent) and at 0 °C for 2 hours, obtaining a better yield around 70% and selectivity to the product 100%. These monomers are characterized and confirmed by Infrared Spectroscopy (FTIR), <sup>1</sup>H and <sup>13</sup>C nuclear magnetic resonance (NMR) spectroscopy.

**Keywords:** Green chemistry; Montmorillonite clay; N-Alkylmethacrylamide; One-pot synthesis; Methacrylic anhydride.

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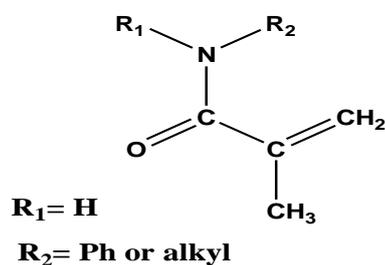


## 1. INTRODUCTION

Whether it is "clean" or "green", today's chemistry intend to limit the production of pollutants and wastes, to save the amount of raw materials and energy, while reducing the risks to health[1].The use of "magnite H<sup>+</sup>" as a green heterogeneous catalyst in organic synthesis has been previously proven by Belbachir and collaborator [2-4]; Navjeet and Dharma Kishore [5].The reactions catalyzed by montmorillonite are usually carried out under mild conditions in environmentally friendly processes with high yields and high selectivity.

The amides are pervasive in nature and technology as structural materials. The amide linkage is easily formed, confers structural rigidity, and resists hydrolysis. Amide linkages in a biochemical context are called peptide bonds when they occur in the main chain of a protein and isopeptide bonds when they occur to a side-chain of the protein. Proteins can have structural roles, such as in hair or spider silk, but also nearly all enzymes are proteins [6].

The N-alkylmethacrylamide has of general formula:



Acrylic/ methacrylic monomers are an important class of functional polymers for their wide range of applications. They can be used to prepare polymers with rigid, flexible, ionic, non ionic, hydrophobic, or hydrophilic properties [7,8]. The synthesis of similar monomers could be realized according to different approaches in various solvents and reactants using acryloyl or methacryloyl chloride with triethylamine in chloroform; synthesis of 1,4-bis(acryloyl)piperazine by Ima K Shundrina et al [9]; Julie L. N. Dubois et al [10] and N-acryloylmorpholine is synthesized by T. Boursier et al [11]; Mark Gorman et al [12]; and N-Phenylmethacrylamide by Brooks A. Abel and Charles L. McCormick [13]; G. Jayasimha Reddy et al [14].

This paper is focused on the developed of a new procedure to synthesis these four monomers in the conditions that respect the principles of green chemistry; using an eco-catalysts

“Maghnite H<sup>+</sup>” by the condensation of primary or heterocyclic secondary amines such as aniline, formamide, piperazine and morpholine with methacrylic anhydride replacing a toxic reactant acryloyl chloride and triethylamine, which have been used previously in other works [9-15].

The reaction occurs in one-pot in bulk using an ice bath for 2 hours. The advantage of this method is that the proton exchanged montmorillonite clay is inexpensive, stable and non corrosive solid acid and can be separated from the reaction mixture by simple filtration.

These monomers are characterized and confirmed by Infrared Spectroscopy (FTIR), <sup>1</sup>H and <sup>13</sup>C nuclear magnetic resonance (NMR) spectroscopy and Electronic Spectroscopy (UV).

## 2. RESULTS AND DISCUSSION

### Catalyst Structure

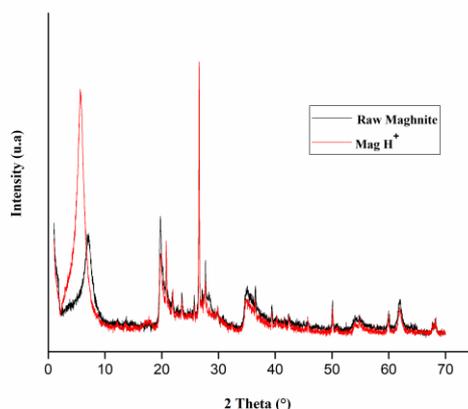
Montmorillonites have both brönsted and Lewis acid sites and when exchanged with cations having a high charges density, as protons, produce highly-active catalysts for acid-catalysed reactions [16]. Inercalated organic molecules are mobile and can be highly polarized when situated in the space between the charged clay layers [17]. These exchanged montmorillonites have been successfully used as catalysts for the reactions of organic syntheses.

**Table 1.** Elementary compositions of “Maghnite” (Compositions wt%)

Sample	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	Na <sub>2</sub> O	K <sub>2</sub> O	TiO <sub>2</sub>	SO <sub>3</sub>
Raw Mag	69,36	14,67	1,16	0,30	1,07	0,50	0,79	0,16	0,91
Mag H <sup>+</sup>	71,7	14,03	0,71	0,28	0,8	0,21	0,77	0,15	0,34

The X-ray powder diffraction profile shown in Figure.1 exhibited the presence of other crystalline phases such as quartz, Felds path and calcite in (raw-Maghnite).

The acid treatment of the Maghnite leads to the substitution of the interlamellar cations by H<sup>+</sup>. This phenomena on results in an increase of the interfoliaire distance of 12 Å° corresponding to a single layer of interfoliaire water in untreated maghnite, around 15 Å°, which is attributed to two interfoliaire water layers in Maghnite H<sup>+</sup> [18].



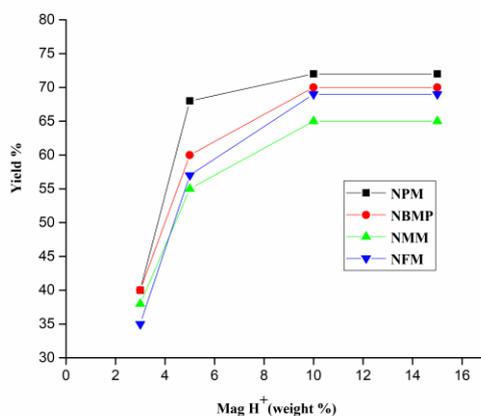
**Fig.1.** X-ray powder Diffraction of Raw-Maghnite and Maghnite-  $H^+$  (0.25M)

### Synthesis and characterization

We have carried out a series of experiments by maintaining the time and temperature constant and varying the quantities of the catalyst  $Mag H^+$  (Table 2). The choice of reaction with catalyst (10 %) was made after obtaining better yields around 72 % (Figure 2).

**Table 2.** Effect of Catalyst Amount ( $Mag H^+$ ) on yield of Monomers, time of reaction 2 hours; temperature 0-5 °C

Monomers	$MagH^+$ (weight %)	3	5	10	15
NPM	YIELD %	40	68	72	72
NBMP		40	60	70	70
NMM		38	55	65	65
NFM		35	57	69	69



**Fig.2.** Effect of Catalyst ( $Mag H^+$ ) on yield of Monomers, time of reaction 4 hours;  $T= 0-5\text{ }^{\circ}C$

We can see from Table 2 and Figure 2 that, the conversion of monomer increases with increasing quantities of the catalyst “Maghnite H<sup>+</sup>0.25M” and becomes steady at 15%.

The yields obtained with different amines (aniline, piperazine, morpholine and formamide) show that the reaction yield depends on the reactivity of the amine molecules, which is connected with its basicity. The effect of the substitution of amines on the catalysed reaction involved electron-donating forces of the substituting group. Aniline in contrast to piperazine, morpholine and formamide groups has more reactivity because of a molecule basicity effect. Therefore, the expected order of reactivity for substituted amines was: aniline > piperazine > morpholine > formamide.

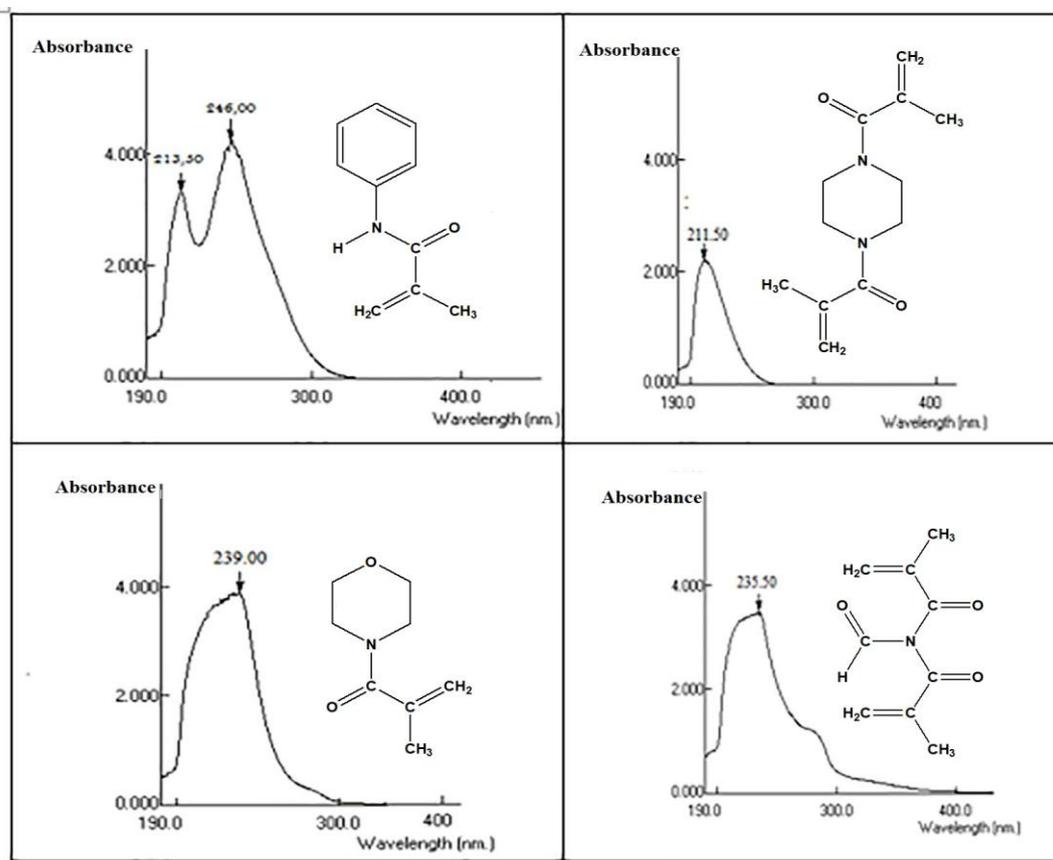
The synthesis of the monomers were obtained with a better yield around 65-72 % of pure product with a 100% of selectivity to confirm the efficiency of catalyst “Mag H<sup>+</sup>” in the synthesis of the N-alkylmethacrylamide monomers. The structures of these four monomers are characterized and confirmed by Infrared Spectroscopy (FTIR), <sup>1</sup>H and <sup>13</sup>C nuclear magnetic resonance (NMR) spectroscopy and Electronic Spectroscopy (UV).

The FTIR analysis confirms the synthesis of methacrylic monomers. All of them present bands corresponding to C-H symmetrical and asymmetrical stretching on CH<sub>2</sub> and CH<sub>3</sub> groups between 2856 and 2982 cm<sup>-1</sup>, respectively, the strong band at 1721 cm<sup>-1</sup> was attributed to amide carbonyl C=O stretching vibration, another strongest band at 1632 cm<sup>-1</sup> corresponded to the C=C stretching vibration and the second strongest and sharp band at 1454 cm<sup>-1</sup> was attributed to the C-N stretch vibration.

The <sup>1</sup>H and <sup>13</sup>C nuclear magnetic resonance (NMR) spectra for NBMP, NMM, NFM and NPM are approximately identical; all spectra confirm the presence of the strongest and sharp peak corresponds to Methyl protons (-CH<sub>3</sub>) and the two medium broad peaks are attributed to Methylene protons (=CH<sub>2</sub>).

The electronic absorption spectrum has confirmed the presence of vinyl functional group in these monomers. The electronic spectrum of the monomer NPM shows two bands at 246 and 213.50 nm assigned to  $\pi \rightarrow \pi^*$  (aromatic) and  $\pi \rightarrow \pi^*$  (vinyl) respectively. The NBMP monomer exhibited absorption bands at 211.50 nm assigned to transition  $\pi \rightarrow \pi^*$ , and the NMM monomer displayed an electronic spectrum with transition at 239 nm assigned to  $\pi \rightarrow$

$\pi^*$ . Finally, the electronic spectrum of NFM shows bands at 235.50 nm assigned to  $\pi \rightarrow \pi^*$  transition.



**Fig.3.** The UV spectrum of the monomers

### Solubility

The monomers NBMP, NMM and NFM are soluble in dichloromethane, chloroform, methanol, ethanol and acetone and insoluble in water and diethylether for NBMP monomers only. The NPM is soluble in chloroform, dimethylsulfoxide, tetrahydrofurane, methanol and insoluble in water and ethanol.

## 3. EXPERIMENTAL

### 3.1 Materials and Methods

The chemicals and reagents used for the synthesis were obtained from commercial sources and were used as received. Methacrylic anhydride and dichloromethane were purchased from (Sigma-Aldrich), piperazine (ACOROS-ORGANICS), morpholine (PROLABO) formamide

from (FLUKA). The aniline (PRONALYS) was vacuum distilled immediately prior to use, MgSO<sub>4</sub> (Biochem, France). Raw-Maghnite clay was obtained from ENOF Maghnia (Algeria). The Maghnite-H<sup>+</sup> (MagH<sup>+</sup>) was prepared as described by Belbachir and collaborator [19, 20]. X-ray diffraction (XRD) for MagH<sup>+</sup> was performed on a D8 Advanced Bruker AXSX-ray diffractometer. Fourier transforms Infrared Spectroscopy (FTIR) spectra were obtained between 400 and 4000 cm<sup>-1</sup> on an Alpha-PATR Bruker No 9501165. <sup>1</sup>H and <sup>13</sup>C Nuclear Magnetic Resonance (NMR) measurements were carried out on a 300 MHz Bruker NMR Spectrometer equipped with a probe BB05 mm, in CDCl<sub>3</sub> Tetramethylsilane (TMS) was used as the internal standard in these cases. UV-Visible spectra was measured in MeOH solution at 10<sup>-3</sup> molar concentration using a Shimadzu UV-Visible 2401 recorder spectrophotometer with 1 cm matched quartz cells. The melting points of solid monomers were determined by a Kofler bench.

## 3.2. Syntheses

### 3.2.1. Preparation of catalyst Maghnite H<sup>+</sup>

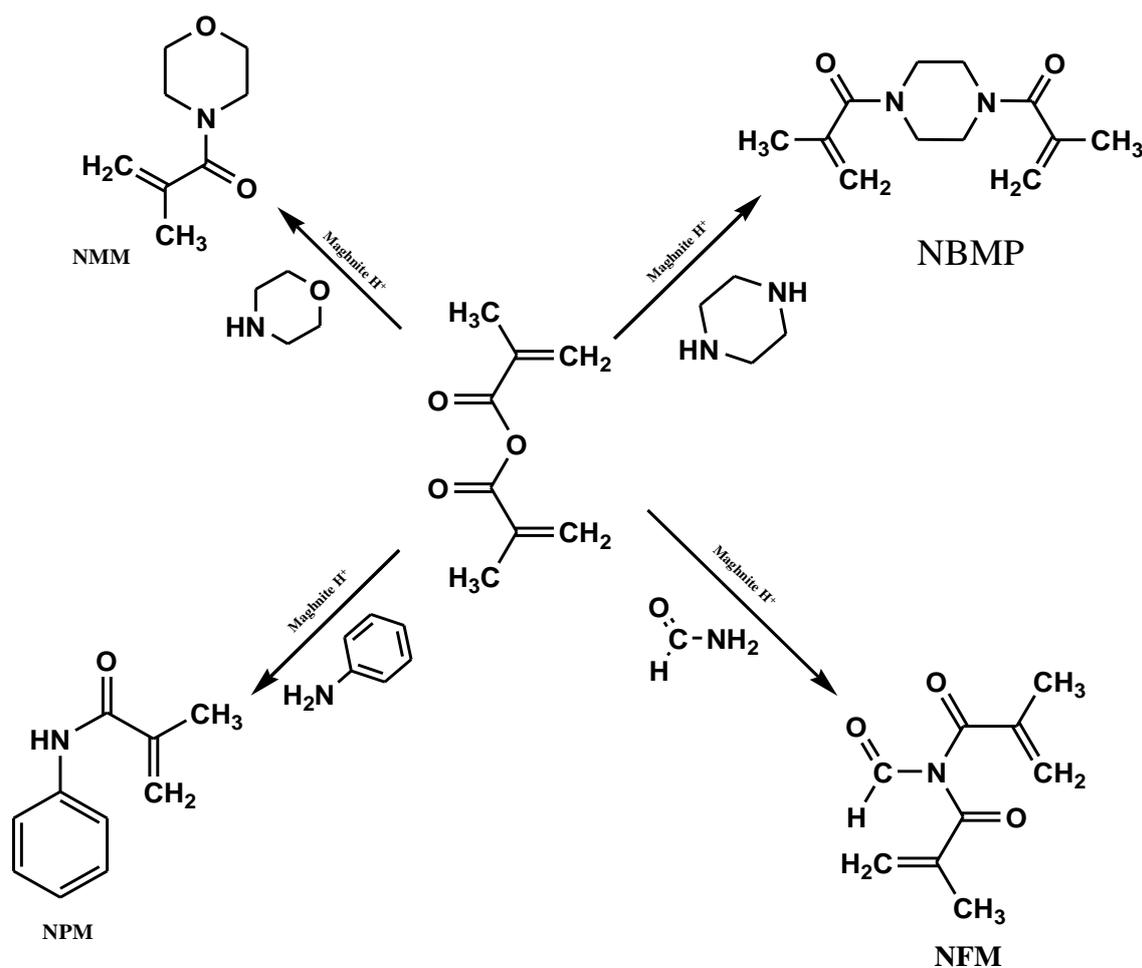
Maghnite H<sup>+</sup> was prepared according to the process reported in our previous study [19, 20]. Raw-Maghnite (20 g) was crushed for 20 mn using a prolabo ceramic balls grinder. It was then dried for 2 h at 105 °C. The Maghnite was placed in an Erlenmeyer flask together with 500 ml of distilled water. The Maghnite/water mixture was stirred using a magnetic stirrer and combined with 0.25 M sulfuric 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 resulting activated bentonite catalyst was then stored in a hermetically sealed container.

### 3.2.2. General procedure for synthesis of the monomers

Synthesis of monomers was carried out by mixing 0.1 mole of amine (10 mL of morpholine or 5 mL of formamide or 10 mL of aniline) with 1g of clay catalyst Maghnite H<sup>+</sup> 0.25 M (10 %) for 30 min in bulk (without solvent); after that, we added 0.1 mole (15 mL) of methacrylic anhydride. Except that for the synthesis of NBMP 0.86 g of piperazine was dissolved in 30 ml

of dichloromethane and mixed with 1 g of clay catalyst Maghnite H<sup>+</sup> 0.25 M (10 %) for 30 min. Following that we added 0.2 moles (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 0-5 °C during 2 h.

After 2 hours, we filtered the solution recover the clay catalyst, which was transferred to a separating funnel washed thoroughly with a 5 % sodium hydroxide solution and water and; extracted with dichloromethane (3×30 mL). The organic layers were combined; dried over anhydrous magnesium sulphate MgSO<sub>4</sub> and filtered. After the evaporation of dichloromethane in vacuum, the products were purified by precipitation and recrystallization in diethyl ether (NBMP) or in an ethanol-water mixture (NPM) or by column chromatography (NMM and NFM).



**Scheme 1.** Schematic representation of the synthesis of N-alkylmethacrylamide Monomers catalyzed by Maghnite H<sup>+</sup>

**1,4-bis(Methacryloyl) Piperazine (NBMP):**

The product was a colorless liquid which was recrystallized in cold diethyl ether; a white crystal solid was obtained. Yield: 70 %;  $C_{12}H_{18}N_2O_2$ ; M.P. 112 °. IR ( $cm^{-1}$ ):  $\nu_{CH_2, CH_3}$  2864, 2974,  $\nu_{C=Oamide}$  1716,  $\nu_{C=C}$  1614, 522,  $\nu_{CN}$  1430;  $^1H$  NMR ( $\delta$  ppm in  $CDCl_3$ ) 1.97 (s, 3H of  $CH_3$ ), 5.06-5.25 (d, 2H of  $=CH_2$ ), 3.60 (m, 8H of  $NCH_2CH_2N$ );  $^{13}C$  NMR ( $\delta$  ppm in  $CDCl_3$ ) 20.53 ( $-CH_3$ ); 31.25-38.15 ( $N-(CH_2)_2-N$ ); 116.17 ( $=CH_2$ ), 139.92 ( $C=C$ ), 171.43 ( $C=O$ )<sub>amide</sub>.

**N-Methacryloylmorpholine (NMM):**

The product obtained was a colorless liquid; was purified by column chromatography using  $CH_2Cl_2/CH_3OH$  (3/2) as the eluent  $R_f = 0.65$  Yield = 65 %;  $C_8H_{13}NO_2$ . IR ( $cm^{-1}$ ):  $\nu_{CH_2, CH_3}$  2856, 2961,  $\nu_{C=Oamide}$  1721,  $\nu_{C=C}$  1609, 558,  $\nu_{C-N}$  1433,  $\nu_{C-O-C}$  heterocyclic 3492.59,  $\nu_{C-O-C}$  oxide 1112;  $^1H$  NMR ( $\delta$  ppm in  $CDCl_3$ ) 1.89 (s, 3H of  $CH_3$ ), 4.97-5.15 (d, 2H of  $=CH_2$ ), 3.54-3.60 (m, 8H of  $NCH_2CH_2O$ );  $^{13}C$  NMR ( $\delta$  ppm in  $CDCl_3$ ) 20.33 ( $-CH_3$ ); 66.82 ( $O-(CH_2)_2-N$ ); 115.86 ( $=CH_2$ ), 139.83 ( $C=C$ ), 171.27( $C=O$ )<sub>amide</sub>.

**N-FormylDimethacrylamide (NFM):**

The product obtained was a yellowish liquid; was purified by column chromatography using  $CH_2Cl_2/CH_3OH$  (3/2) as the eluent  $R_f = 0.75$  Yield = 69 %;  $C_9H_{11}NO_3$ . IR ( $cm^{-1}$ ):  $\nu_{CH_2, CH_3}$  2930, 2979,  $\nu_{CH}$  aldehyde 2612.39,  $\nu_{C=Oamide}$  1691.60,  $\nu_{C=C}$  1632, 597,  $\nu_{C-N}$  1454;  $^1H$  NMR ( $\delta$  ppm in  $CDCl_3$ ) 1.96 (s, 3H of  $CH_3$ ), 5.69 - 6.25 (d, 2H of  $=CH_2$ ), 9.29 (s, 1H of  $CHO$ )<sub>aldehyde</sub>;  $^{13}C$  NMR ( $\delta$  ppm in  $CDCl_3$ ) 17.82 ( $-CH_3$ ), 127.86 ( $=CH_2$ ), 135.72( $C=C$ ), 172.98( $C=O$ )<sub>amide</sub>, 182.74( $C=O$ )<sub>aldehyde</sub>.

**N-Phenylmethacrylamide (NPM):**

The product obtained was a yellow liquid which when recrystallized in an ethanol-water mixture turns into a white solid Yield = 72 %;  $C_{10}H_{11}NO$ ; M.P. 85-86 °C IR ( $cm^{-1}$ ):  $\nu_{NH}$  primary amine 3291, 935, 758,  $\nu_{CH_2, CH_3}$  2927, 2982,  $\nu_{C=Oamide}$  1721.50,  $\nu_{C=C}$  1620, 511,  $\nu_{C-N}$  1437,  $\nu_{C-C}$  phenyl ring 757.61, 694.16;  $^1H$  NMR ( $\delta$  ppm in  $CDCl_3$ ) 2.054 (s, 3H of  $-CH_3$ ), 4.45-5.80 (d, 2H of  $=CH_2$ ), 7.12-7.60 (m, 1H of  $-CH$ )<sub>phenyl ring</sub>, 7.875(s, 1H of  $-NH$ );  $^{13}C$  NMR ( $\delta$  ppm in  $CDCl_3$ ) 18.78( $-CH_3$ ); 124.44 ( $=CH_2$ ), 140.88( $C=C$ ), 166.90( $C=O$ )<sub>amide</sub>, 120.26, 128.97, 137.85( $-CH$ )<sub>phenyl ring</sub>.

#### 4. CONCLUSION

The aim of this work is to develop a green procedure to synthesize N-alkylmethacrylamide monomers: N-Phenylmethacrylamide, N-Formyldimethacrylamide, N-Methacryloylmorpholine and 1,4-bis(Methacryloyl) Piperazine by reaction of derived amine (heterocyclic, aryl and bi functional amine) with a single reactant methacrylic anhydride catalyzed by Maghnite H<sup>+</sup> a Green catalyst, recyclable in one-step and with a 100 % of product selectivity when compared to previously published studies whose used a toxic reactant acryloyl chloride and triethylamine in different solvents. This procedure is an interesting alternative that follows the principles of green chemistry in bulk (without solvent) and at 0 °C under mild conditions.

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