

SYNTHESIS AND CHARACTERIZATION OF DIMETHACRYLATE MACROMONOMER USING MAGHNITE-H⁺ AS AN ECO-FRIENDLY CATALYST

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Received: 29 September 2018 / Accepted: 27 April 2020 / Published online: 01 May 2020

ABSTRACT

The dimethacrylate macromonomer named bis (2-hydroxy-3-(méthacryloyloxy) propyl) fumarate (HMPF), was synthesized by ring opening reaction of epoxide function of glycidyl methacrylate (GMA) with maleic anhydride (MA) in presence of Maghnite-H⁺ as a catalyst at room temperature and at free solvent. The Maghnite-H⁺ is a proton exchanged montmorillonite clay it is an Algerian clay activated by sulfuric acid 0,23M. The HMPF was characterized by FT-IR, ¹H NMR and ¹³C NMR spectroscopic techniques. A kinetic study was carried out to determine the amount of the catalyst (5, 10, 20 and 30%) which will give a better yield of the synthesis reaction. The yield of the reaction was 62.23% for a quantity of Maghnite-H⁺ (20% relative to the monomer) and for a reaction time of 72h.

Keywords: Maghnite-H⁺; glycidyl methacrylate; maleic anhydride; bis-methacrylate macromonomer.

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doi: <http://dx.doi.org/10.4314/jfas.v12i2.19>



1. INTRODUCTION

Multifunctional methacrylate monomers are most used in the synthesis of polymers, especially in the synthesis of the cross-linked materials and in the synthesis of polymers by photopolymerisation [1,2]. Indeed, the poly(ethylene glycol)-dimethacrylate was cross-linked with poly(propylene fumarate) for synthesis of biodegradable polymer composites [3], also the poly(propylene glycol) and urethane dimethacrylates was used in the improve conversion of dental composites [4]. In addition, the 2,2-Bis-4-(2-hydroxy-3-methacryloyloxypropoxy)-phenyl] propane (Bis-GMA) and triethylene glycol dimethacrylate (TEGDMA) were used in the synthesis of dental composites [5] and the ethylene glycol dimethacrylate was used on the preparation of new ion-selective cross-linked poly(vinylimidazole-co-ethylene glycol dimethacrylate) [6]. In other, the Hydrogels are prepared from poly (ethylene glycol) diacrylate (PEGDA), poly (ethylene glycol) dimethacrylate (PEGDMA) and from tetra (ethylene glycol) dimethacrylate (TEGDM) [7]. The glycidyl methacrylate (GMA) is interested monomer, it can be used in synthesis of several macromonomers [8, 9], in synthesis of polymers and copolymers [10-13]. The maleic anhydride (MA) was also used in many chemical reactions, the poly (styrene sulfonic acid–maleic anhydride) nanofibers was prepared using maleic anhydride and styrene sulfonic acid [14], and the poly (methyl methacrylate-co-maleic anhydride) copolymers was synthesized by copolymerization of methyl methacrylate with maleic anhydride [15].

The reactions of synthesis of macromonomers and polymers are catalyzed by different initiators, the Maghnite- H^+ is one of this catalyst, it was used in several studies of polymerization and copolymerization of different monomers [16-20].

In this present work, we were interested in the synthesis of bis (2-hydroxy-3-(methacryloyloxy)propyl)fumarate (HMPF). The dimethacrylate macromonomer (HMPF) is a very interesting compound which can be used in different additions reactions on its double bonds, it can be used in the synthesis of different polymers and copolymers, and also, it can be used as a corrosion inhibitor because it have hydroxyl functions, carbonyl groups and carbon-carbon double bonds. The synthesis of HMPF is easy with simple operating conditions, by ring opening reaction of epoxide of glycidyl methacrylate and maleic anhydride at room

temperature, using an eco-friendly catalyst, named Maghnite-H⁺ [21]. Thereafter, Techniques of analysis, IR, ¹H NMR, ¹³C NMR, are used for the characterization and the determination of the structure of HMPF.

2. RESULTS AND DISCUSSION

2. 1. Characterization of HMPF

The FT-IR absorption spectrum was recorded by Shimadzu IRAffinity-1 spectrometer technique. Measurements of ¹H NMR and ¹³C NMR spectrums were conducted in DMSO at ambient temperature in an AM 300 FT Bruker.

FT-IR spectral analysis

The FT-IR spectrum (Fig.1) of the obtained compound is in good agreement with HMPF chemical structure. The carbonyl group (C=O) and (C-O) bands, are observed respectively at 1725 and 1152cm⁻¹. The peak associated to C=C double bond was observed at 1650cm⁻¹. The C-H symmetric and asymmetric stretching due to the (-CH₃ and -CH₂-) groups were observed between 2960 and 2900cm⁻¹. A wide band is observed at 3450cm⁻¹ due to the hydroxide group (OH). The H-C= stretching due to the (H₂C=C) was observed at 3100cm⁻¹.

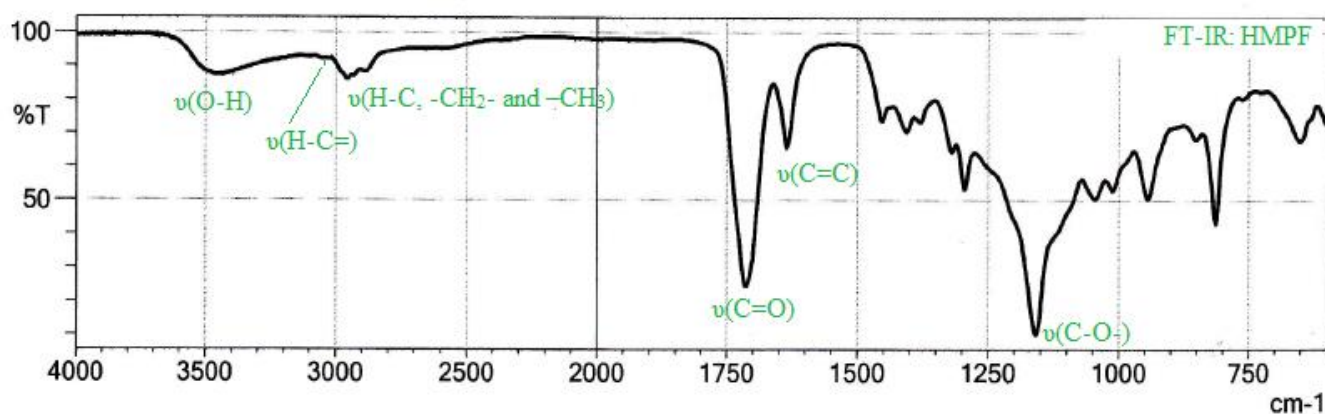


Fig.1. FT-IR spectrum of HMPF

¹H NMR spectroscopic analysis

The ¹H NMR (DMSO-d₆, 300MHz) spectrum of HMPF (Fig. 2 (a) and (b)), given the following resonance signals (δ: ppm): 6,2-5,7 (d, CH₂=C); 1,8 (s, -CH₃); 3,8-3,4 (s, OH); 4,2-3,2 (d,-CH₂-O; quintuplet, -CH-OH).

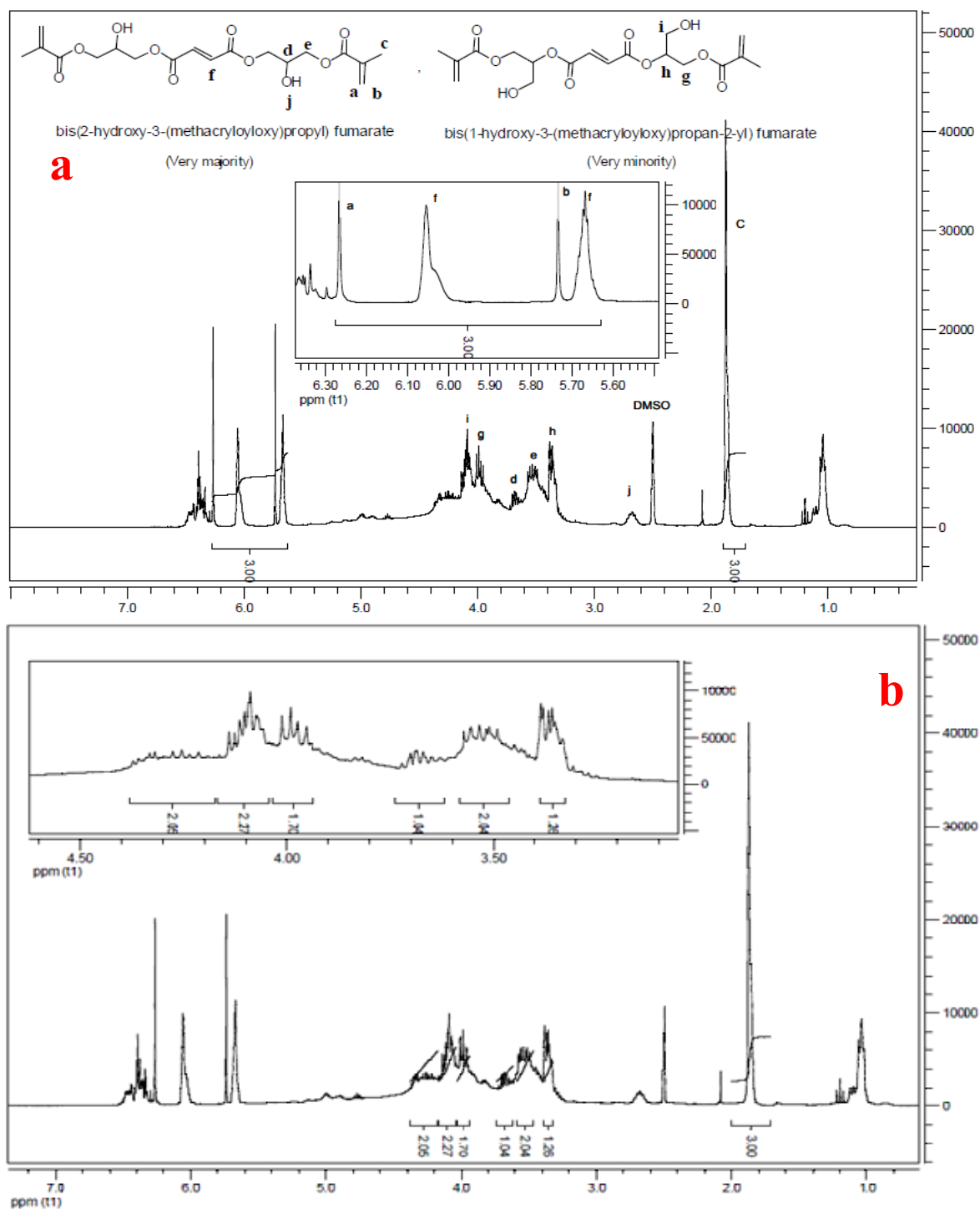


Fig. 2. (a and b) ^1H NMR spectrum of HMPF in DMSO-d_6

The peaks observed at 1 ppm are impurities and the peak at 6.4 ppm represents the proton of the unreacted maleic anhydride.

^{13}C NMR spectroscopic analysis

The ^{13}C NMR (DMSO- d_6 , 75 MHz) spectrum of HMPF (Fig. 3), given the following resonance signals (δ : ppm): 18 (C_b , CH_3), 125 (C_a , $\text{CH}_2=\text{C}$), 130 ($\text{C}_h = \text{CH}$), 167, 165 (C_d , C_g , $\text{C}=\text{O}$), 60-72 (C_c , C_e , C_f , C_i , C_j , $-\text{CH}_2\text{-O}$, $-\text{CH-OH}$).

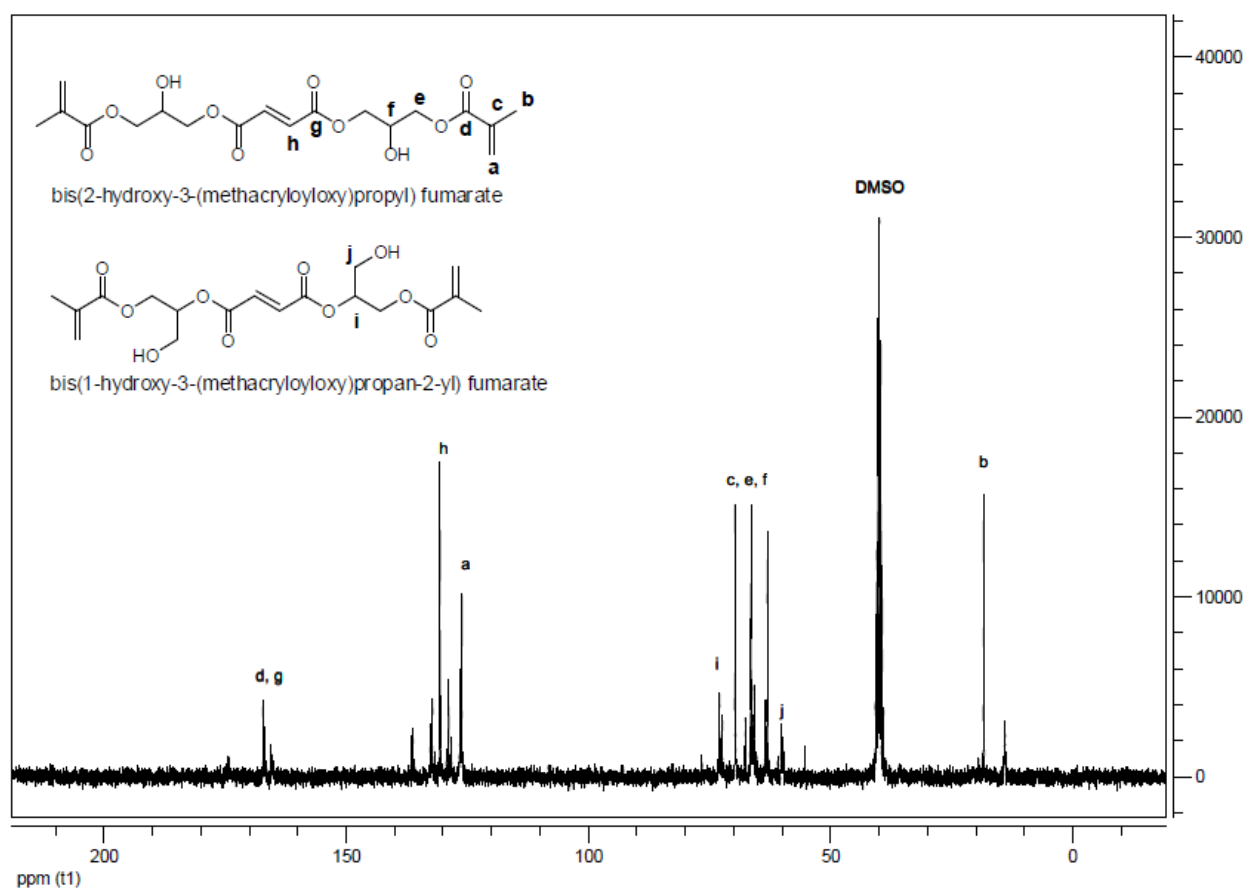


Fig. 3. ^{13}C NMR spectrum of HMPF in DMSO- d_6

2. 2. Effect of the amount of the catalyst on the reaction yield

The (table 1 and Fig.4) represents the yields obtained with various percentages of the amount of catalyst (5%, 10%, 20%, 30%) were used for a reaction time of 72h at $T = 20^\circ\text{C}$. m (GMA)= 4g, m (AM) = 1,36g.

Table 1. Yields obtained with (5%, 10%, 20%, 30%) of Maghnite- H^+

Amount of Mag-H+ (%) / GMA	5	10	20	30
Yield (%)	33,4	48,2	62 ,23	62,6

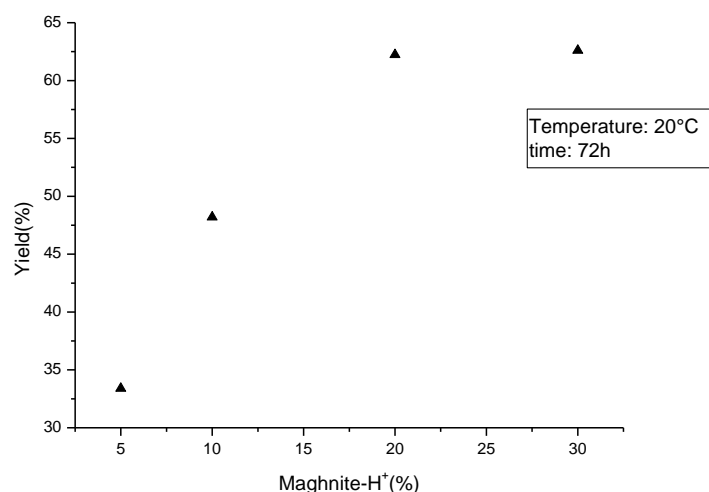


Fig. 4. Yield of the HMPF synthesis reaction as a function of the amount of Maghnite-H⁺

The yields obtained with 5% and 10% of the Maghnite-H⁺ are yields a little low since the amount of Maghnite-H⁺ used is an insufficient which can not initiate all molecules of glycidyl methacrylate. At 20% and 30% the yield of the reaction obtained almost the same, the protons linked to the surface of the Maghnite-H⁺ are sufficient to initiate a large number of glycidyl methacrylate.

2. 3. Reaction Mechanism

The reaction mechanism is based on the nucleophilic attack of epoxide function of the glycidyl methacrylate by the maleic anhydride (fig. 5).

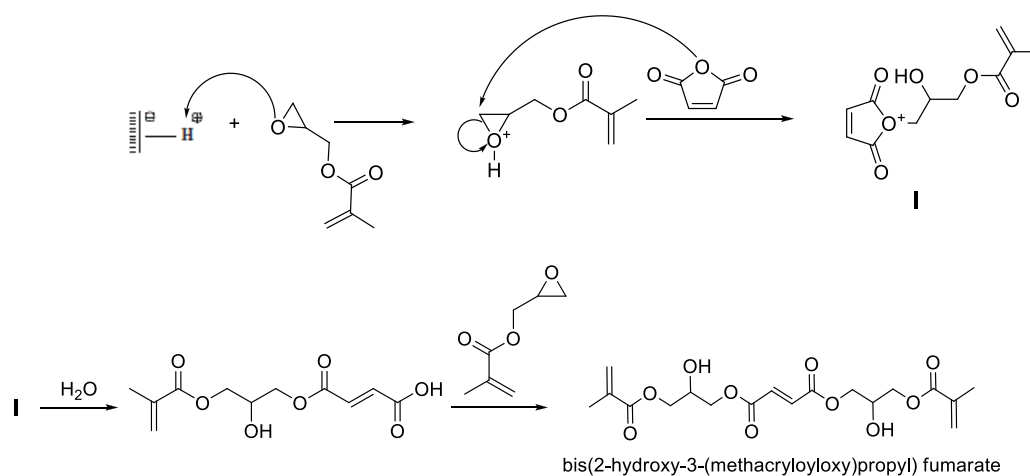


Fig. 5. Scheme of mechanism of reaction of glycidyl methacrylate with maleic anhydride catalyzed by Maghnite-H⁺

3. EXPERIMENTAL

3. 1. Materials

Glycidyl methacrylate (GMA) (Sigma-Aser) was purified by a column chromatography to remove the inhibitor. Maleic anhydride (MA) (Chemopharma), Sulfuric acid (Sigma-Aldrich), acetone (Sigma Aldrich) was used as received. Raw-maghnite, Algerian montmorillonite clay was product from “BENTAL” (Algerian Society of Bentonite).

3. 2. Preparation of Maghnite-H⁺

The Maghnite-H⁺ is an activated clay, it was prepared according to the method described by Belbachir et al [21]. 20g of raw-Maghnite was crushed for 20minutes using a ceramic ball grinder to obtain a fine powder. The latter, it was dried at 105°C to remove any trace of humidity for about two hours. After drying, the 20g of Maghnite was put in 250ml of distilled water with stirrer; the 250ml of sulfuric acid solution 0.46M was added to the mixture Magnite/water and agited for about 48hours at room temperature. After that, the mineral part of the whole mixture was wached by distilled water until it become a free sulfate and finally dried at 105°C for about 2hours.

3. 3. Synthesis of dimethacrylate macromonomer (HMPF)

The HMPF was synthesized by reacting of 4g (0.0246 mol) of GMA with 1,36g (0.00614 mol) of MA in presence of 0.8g of Maghnite-H⁺ catalyst in a reactor with continues agitation at room temperature for 72h. When the reaction time is finished, the mixture was dissolved in 40ml of acetone and filtered to remove the catalyst and the acetone was retrieved by rotary evaporator. The obtained product was then purified by column chromatography filled with silica gel to remove unreacted monomers. The final HMPF was colorless viscous liquid at a yield of 62.23%. The schematic representation of the HMBC synthesis is shown in fig. 6.

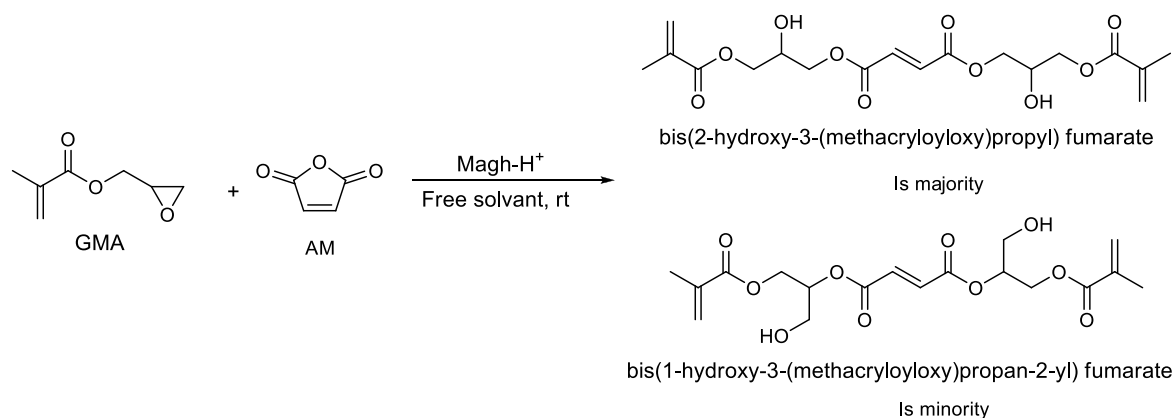


Fig. 6. Scheme of synthesis of HMPF

3. 4. Kinetic studies

The ring opening reaction of GMA with maleic anhydride was carried out in round bottom flask. The latter contained a mixture of 4g of GMA and 1,36g of maleic anhydride with amount of Maghnite-H⁺ (5, 10, 20 and 30%) weight percentage. The mixtures were kept in thermostat at desired temperature (20°C) and stirred with a magnetic stirrer. The yield of reaction was determined gravimetrically by weighing of unreacted glycidyle methacrylate.

4. CONCLUSION

Bis (2-hydroxy-3- (methacryloyloxy) propyl) fumarate (HMPF), was successfully synthesized using simple operating conditions (room temperature and without the use of solvents which are often expensive and toxic). Analysis by infrared spectroscopy clearly shows the disappearance of the glycidyl methacrylate epoxide function and the appearance of the (OH) function in the synthesized macromonomer and the ¹H NMR, ¹³C NMR, confirmed the structure of HMPF.

The catalyst (Maghnite-H⁺) used in this synthesis is activated clay, non toxic, cheaper and recyclable, a small amount of it can initiate the reaction by giving a very high yield.

The reagents used in the synthesis of the macromonomer (glycidyl methacrylate and maleic anhydride) are cheaper, but the HMPF obtained is very interesting compound which will be used in the synthesis of the several polymers or copolymers.

5. ACKNOWLEDGEMENTS

The authors acknowledge the Ziane Achour University of Djelfa, the Oran University, Ahmed Benbella 1 and the Algeria Ministry of Higher Education and Scientific Research for their financial support.

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How to cite this article:

Souli L, Meghabar R, Lahrech MB. Synthesis and characterization of dimethacrylate macromonomer using Maghnit-H⁺ as an eco-friendly catalyst. J. Fundam. Appl. Sci., 2020, 12(2), 814-824.