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Research Article

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Water-soluble poly (HMBC-co-AM) prepared using tetrafunctional methacrylate macromonomer

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ABSTRACT

A water-soluble poly (tetra(2-hydroxy-3-(methacryloyloxy)propyl)benzene-1,2,4,5-tétracarboxylate-co-acrylamide) (poly (HMBC-co-AM)) has been synthesized by free radical polymerization of tetrafunctional methacrylate macromonomer named tetra(2-hydroxy-3-(methacryloyloxy)benzene-1,2,4,5-tetracarboxylate (HMBC) and acrylamide (AM) in THF solution at 80°C employed AIBN as an initiator. The HMBC was synthesized by direct addition reaction between the glycidyl methacrylate (GMA) and pyromellitic dianhydride (PMDA) in acetone in the presence of Maghnite-H^+ as a catalyst at room temperature (20°C). The Maghnite-H^+ is a proton exchanged montmorillonite clay. The HMBC and poly (HMBC-co-AM) were characterized by FT-IR, ^1H NMR and ^{13}C NMR spectroscopic techniques. The molecular weights and polydispersity index of the HMBC were determined employed gel permeation chromatography GPC. The thermal analysis of the poly (HMBC-co-MA) was performed by thermogravimetric analysis (TGA) and DSC.

Key words: Maghnite-H^+, Glycidyl methacrylate, Tetrafunctional methacrylate macromonomer, Water-soluble copolymer.

INTRODUCTION

Dimethacryaltes, trimethacrylates and tetramethacrylates monomers are very interesting compounds for synthesis of polymer materials. Indeed, the dimethacryltes monomers such as the Bis-GMA, triethylene glycol dimethacrylate (TEGDMA) and urethane dimethacrylate (UDMA) are used in the synthesis of polymers by photopolymerization [1, 2], as well as the trimethacrylates monomers are used in the synthesis of copolymers [3, 4].

The glycidyl methacrylate (GMA) was used in synthesis of several polymers and copolymers [5-11]. In this context, a material, used for thermal energy storage, was synthesized through the ring-opening crosslinking reaction of poly (glycidyle methacrylate) (PGMA) in the presence of polyethylene glycol (CPEG) [12]. A Dendritic GMA-HPAM macromonomers was synthesized by ring opening reaction of glycidyle methacrylate and the dendron 3,3'-dimethyl-(4-hydroxyphenylazanediyl) bis(N-(2-aminoethyl)-2- methylpropanamide) (HPAM) [13]. The bis (glycidyl methacrylate) was synthesized by reaction of glycidyl methacrylate with bisphenol A [14].

Pyromellitic dianhydride (PMDA) was used in many chemical reactions. Indeed, the direct addition reaction between palygorskite and pyromellitic dianhydride can be used for the synthesis of the ahydride-cured epoxy resin/ palygorskite nanocomposites [15]. A various dianhydrides was polymerized with 2-trifluoromethyl-4,4'-diaminodiphenyl ether [16]. The pyromellitic dianhydride was used in synthesis of the N-(4-trimethylsiloxyphenyl) pyromellitimide-N'-phenylacrylate[17] and in synthesis of the soluble polyimides [18].

Acrylamide (AM) is a monomer widely used in the copolymerization reaction with several monomers. It is used for synthesized a new copolymer of N-[(tert-butylperoxy) methyl] acrylamide (tBPMAAm) [19], and for synthesis a novel alkaline anion-exchange membrane from poly (vinyl alcohol)/poly (acrylamideco-diallyldimethylammonium chloride) [20].

The Poly (dimethyldiallylammoniumchloride-co-acrylamide)-graft-triethylenetetramine–dithiocarbamate (PDCATD) was synthesized using dimethyldiallylammonium chloride, acrylamide, triethylenetetramine, formaldehyde, carbon bisulfide and sodiumhydroxide [21]. Also, a novel water-soluble copolymers based on acrylamide were successfully prepared initiated by redox initiation system in an aqueous medium [22].

In this present work, we were interested in the synthesis of tetrafunctional methacrylate macromonomer (HMBC) by grafting reaction of glycidyle methacrylate (GMA) with pyromellitic dianhydride (PMDA) at room temperature, using a catalyst, non toxic, which can be recycled and not polluting based on clay of the montmorillonitic type called Maghnite-H^+ [23]. Thereafter, this HMBC has been copolymerized with acrylamide for synthesis of the poly (HMCB-co-AM). Techniques of analysis, IR, ^{1}H NMR, ^{13}C NMR, TGA, DSC and the GPC are used for the characterization and the determination of the structure of HMBC) and of poly (HMBC-co-AM).

EXPERIMENTAL SECTION

Materials

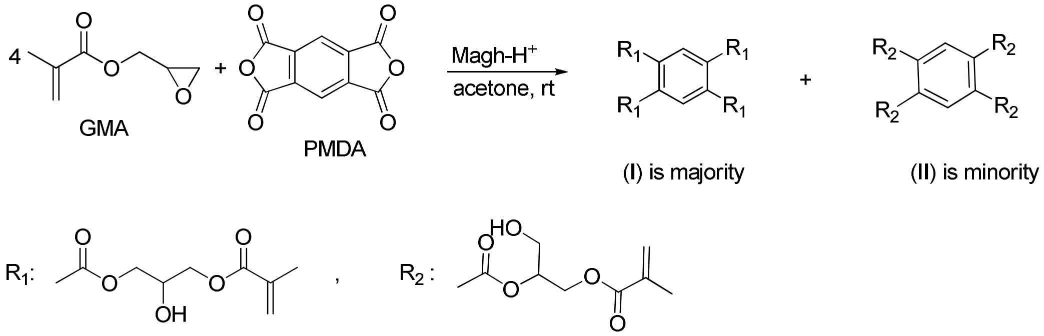
Glycidyl methacrylate (GMA) (Sigma-Aser) was purified by a column chromatography to remove the inhibitor. Pyromellitic dianhydride (PMDA) (Sigma-Aser) was purified by recrystallisation from the mixture of acetic anhydride and acetic acid at a volume ratio of 1/5. Acrylamide (AM), Tetrahydrofuran (THF) and acetone were used as received. Raw-Maghnite, Algerian montmorillonite clay was procured from “BENTAL” (Algerian Society of Bentonite). Azobisisobutyronitrile (AIBN) was used as a free radical initiator.

Preparation of Maghnite-H^+

Maghnite-H^+ was used as a catalyst in several studies in the polymerization and copolymerization of different monomers [24-27]. It was prepared following to the method described by Belbachir et al [28]. An amount of 20g raw-Maghnite was crushed for about 20 minutes using a ceramic ball grinder. It was dried for two hours at a temperature of 105°C to remove any traces of humidity. After drying, the Maghnite was put in an Erlenmeyer containing 500ml distilled water, then 0.23M sulfuric acid solution was added at once to the mixture Maghnite / water and agitated by a mechanical stirrer for about two days at room temperature. After that, the mineral part of the whole mixture was washed by distilled water until it become a free from sulfate and finally dried at 105°C for about 2hours.

Synthesis of tetrafunctional methacrylate macromonomer (HMBC)

The HMBC was synthesized by reacting a 3.5g (0.0246 mol) of GMA with 1.34g (0.00614 mol) of PMDA and the presence of 0.7g of Maghnite-H^+ catalyst in a reactor containing 40 ml of acetone with continues agitation at room temperature for about 72h. When the reaction is finished, the mixture was 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 HMBC was yellow oily product at a yield of 62.14%. The schematic representation of the HMBC synthesis is shown in Fig 1.



(I) : Tétra(2-hydroxy-3-(methacryloyloxy)propyl) benzene-1,2,4,5-tetracarboxylate

(II) : Tétra(1-hydroxy-3-(methacryloyloxy)propan-2-yl) benzene-1,2,4,5-tetracarboxylate

Fig. 1 Scheme of synthesis of HMBC

Synthesis of poly (HMBC-co-MA)

The poly (HMBC-co-AM) was synthesized by a free radical copolymerization of HMBC and acrylamide (AM). 3g (3.646mmol) of HMBC, 1.036g (14.57mmol) of AM and 11.9mg ($7.24.10^{-2}$mmol) of AIBN were added to a reactor containing 50 ml THF. The reactor equipped with reflux condenser was put in oil bath. The reaction mixture was allowed to react at 80°C for about 6hours under continuous magnetic stirring. After cooling, the product was filtered and washed by 3x50 ml of THF. Finally, the copolymer was dissolved in distilled water and recrystallized by adding THF. The Poly (HMBC-co-AM) was white powder at a yield of 68.37%. The schematic representation of poly (HMBC-co-AM) is shown in Fig 2.

Fig. 2 Scheme of synthesis of poly(HMBC-co-AM))

Characterization

The FTIR absorption spectra were recorded by an ATI Matson FTIR N° 9501165 spectrometer using the KBr pressed disc technique. Measurements of ^{1}H NMR and ^{13}C NMR spectra were conducted in DMSO (dimethylesulfoxyde) solution for HMBC and in D_2O solution for poly (HMBC-co-AM), at ambient temperature in an AM 300 FT Bruker spectrometer using tetramethylsilane (TMS) as an internal standard. Gel permeation chromatography (GPC) of HMBC was performed with a Spectra-Physics chromatograph, equipped with four columns connected in series and packed with Ultrastyragel 10^3, 10^4, 10^5, 10^6Å and tetrahydrofuran (THF) was used as a solvent with flow rate of 1.5 ml/min. The instrument was calibrated by polystyrene samples of known molecular weights. The thermogram of Differential Scanning Calorimetry (DSC) was taken in an appliance model Calorimeter DSC SETARME 92, from ambient temperature to 200°C at a heating rate of 10°C/min under helium atmosphere with flow rate 20mL/min. Thermogravimetric analysis TGA of poly (HMBC-co-AM) have been studied as a function of percentage weight loss at a heating rate of 10°C/min under nitrogen atmosphere with flow rate 20ml/min.

RESULTS AND DISCUSSION

Characterization of HMBC

FT-IR spectral analysis

The FT-IR spectrum of HMBC is presented in Fig. 3.

The FT-IR spectrum of the obtained product is in good agreement with HMBC chemical structure. The carbonyl groups (C=O) and (C-O) bands, are observed respectively at 1700 and 1161cm^{-1}. The peak associated to C=C double bonds was observed at 1635cm^{-1}. The C–H symmetric and asymmetric stretching due to the (-CH_3 and –CH_2-) groups were observed around 2957cm^{-1}. A large band at 3414 cm^{-1} appeared in the spectra of HMBC due to the hydroxyl group.

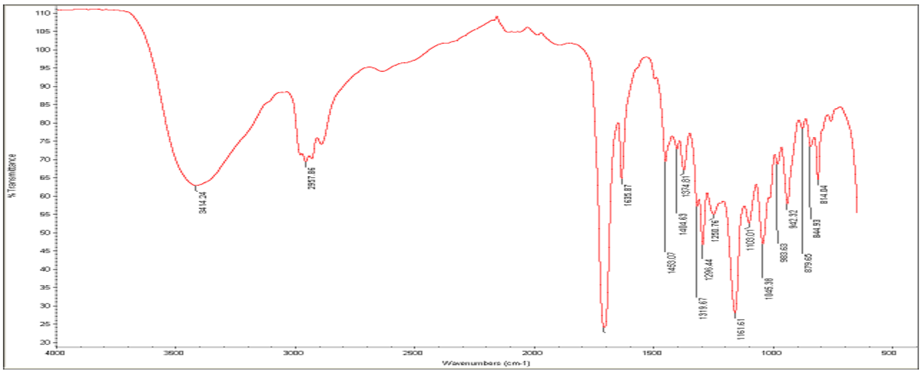


Fig. 3 FT-IR spectra of HMBC

NMR spectroscopic analysis

The ^1H NMR (DMSO-d_6, 300 MHz) spectrum of HMBC (Fig. 4), shows the following resonance signals (δ: ppm): 7.8-8.2 (m, Ar-H), 6.0-5.6 (d, CH_2=C), 1.95(s, -CH_3), 3.8- 3.4 (s, OH), 4.2- 3.9 (d,-CH_2-O, q, -CH-O).

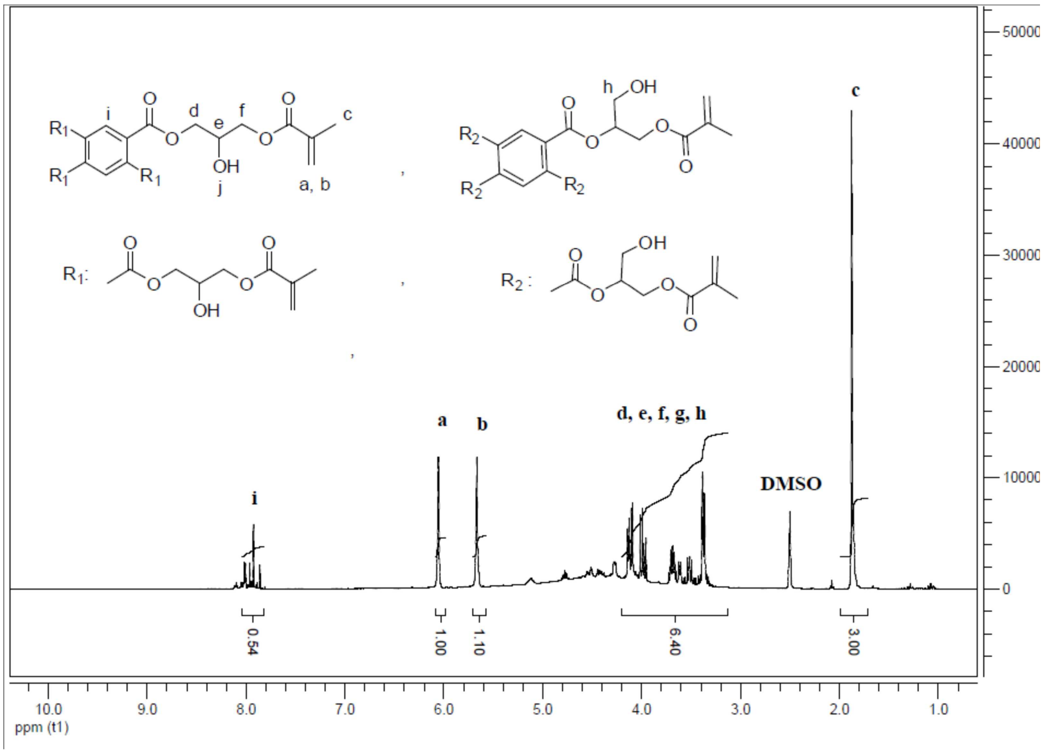


Fig. 4 ^1H NMR spectra of HMBC in DMSO-d_6

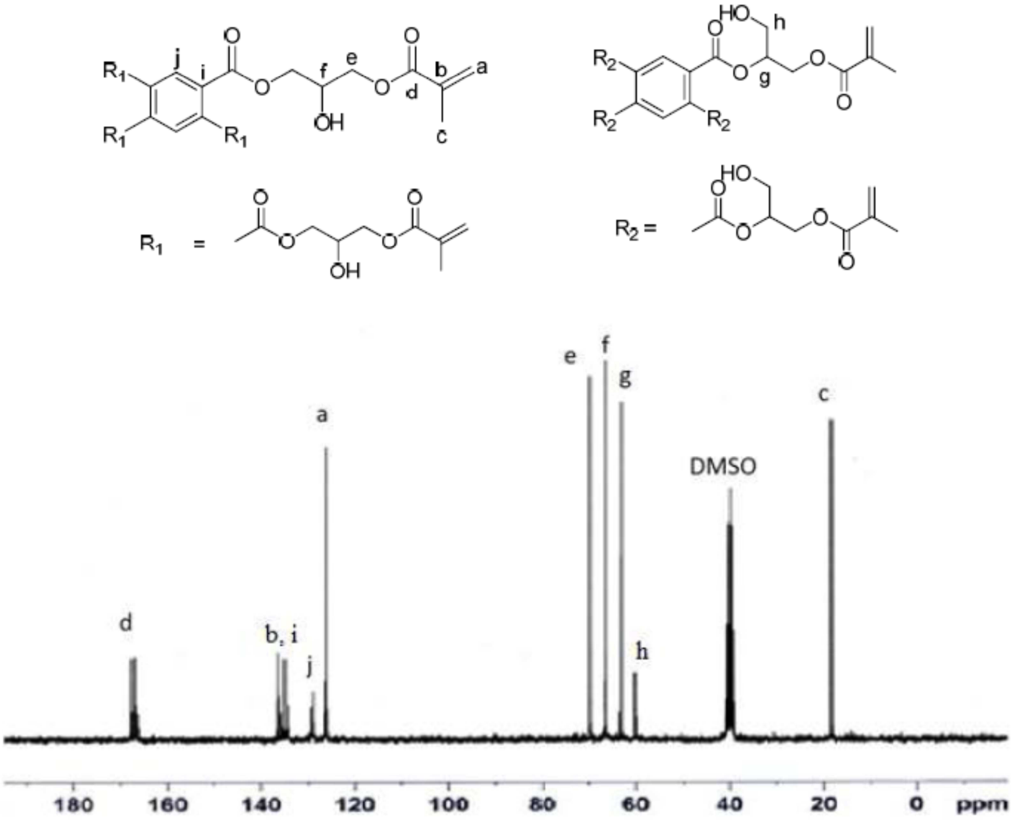


Fig. 5 ^{13}C NMR spectrum of HMBC in DMSO-d_6

The ^{13}C NMR (DMSO-d$_6$, 300 MHz) spectrum of HMBC (Fig. 5), shows the following resonance signals (δ: ppm): 167.8 (C_d, -C=O), 135.8 (C_b, =CH), 134.36 and 129.41 (C_i and C_j, C-Ar) respectively. 126.5 (C_a, CH_2=), 70(C_e, CH_2-O), 60 and 61.8 (C_h , C_g) (-CH_2-, CH-O) respectively. 18.28 (C_c, -CH_3).

Molecular weight determination

The $\overline{M_n}$ and $\overline{M_w}$ of HMBC was determined by gel permeation chromatography (GPC) and it is shown in Fig. 6. The polydispersity index $\frac{\overline{M_w}}{\overline{M_n}}$ of the HMBC is 1.08.

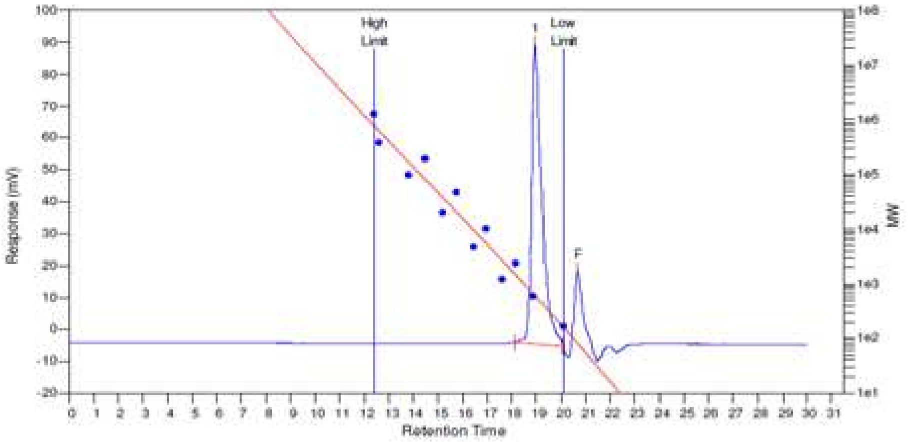


Fig. 6 GPC Spectrum of HMBC

Characterization of poly (HMBC-co-AM)

FT-IR analysis

The FT-IR spectrum of the poly (HMBC-co-AM) is illustrated in Fig. 7.

The characteristic bands are: A large band was observed in the range of 3200-3400 cm^{-1} due to (O-H and N-H stretching). The carbonyl groups (C=O) band and (C=C) bands, are observed at 1700 cm^{-1} and 1600cm^{-1} respectively. The C–N stretching was observed at 1650cm^{-1}. The C–H symmetric and asymmetric stretching due to the (-CH_3 and –CH_2-) groups were observed around 2945cm^{-1}. The peaks associated to (C-N and C–O, stretching) ware observed around 1388 and 1159 cm^{-1} respectively.

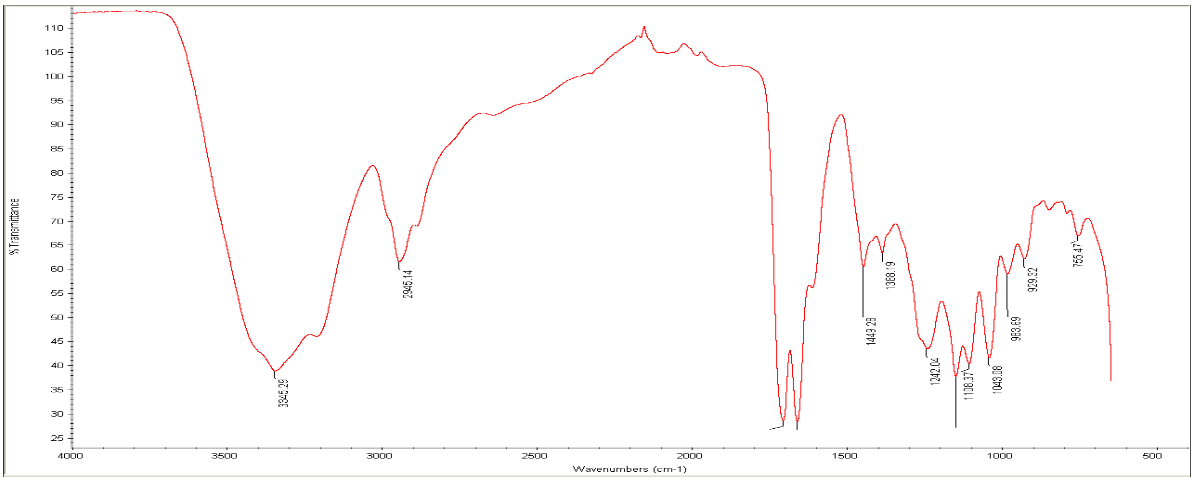


Fig. 7 FT-IR spectra of poly (HMBC-co-AM)

NMR spectroscopic analysis

The ^{1}H NMR (D_2O, 300 MHz) spectrum of poly (HMBC-co-MA) is shown in Fig. 8. It shows a following resonance signals: (δ: ppm): 8 (m, H-Ar); 4-3.4 (ester-CH_2O, -CH-OH), 2.2 -1.6 (-CH- , -CH_2) and at 0.94 (-CH_3).

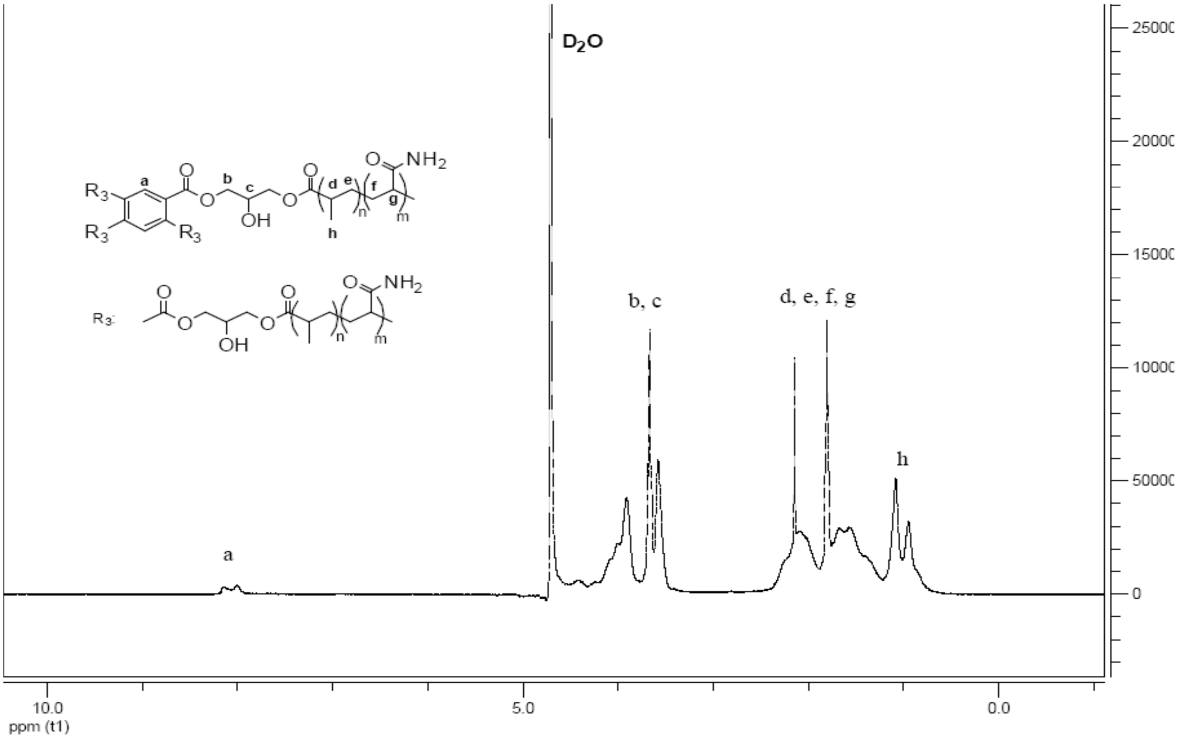


Fig. 8 ^{1}H NMR Spectra of poly (HMBC-co-AM) in D_2O

The proton decoupled of ^{13}C NMR (D_2O, 300 MHz) spectrum of poly (HMBC-co-AM) is shown in Fig. 9. The observed peak values are as follows: (δ: ppm): 179.44 (C_a, $C_{a'}$, $C_{a''}$), 128.49 et 129.46 (C_h , C_i), 69.25 and 65.89 (C_b, C_c), 62.368 (C_d, C_f and C_j) 41.57(C_g), 30.24 (C_e).

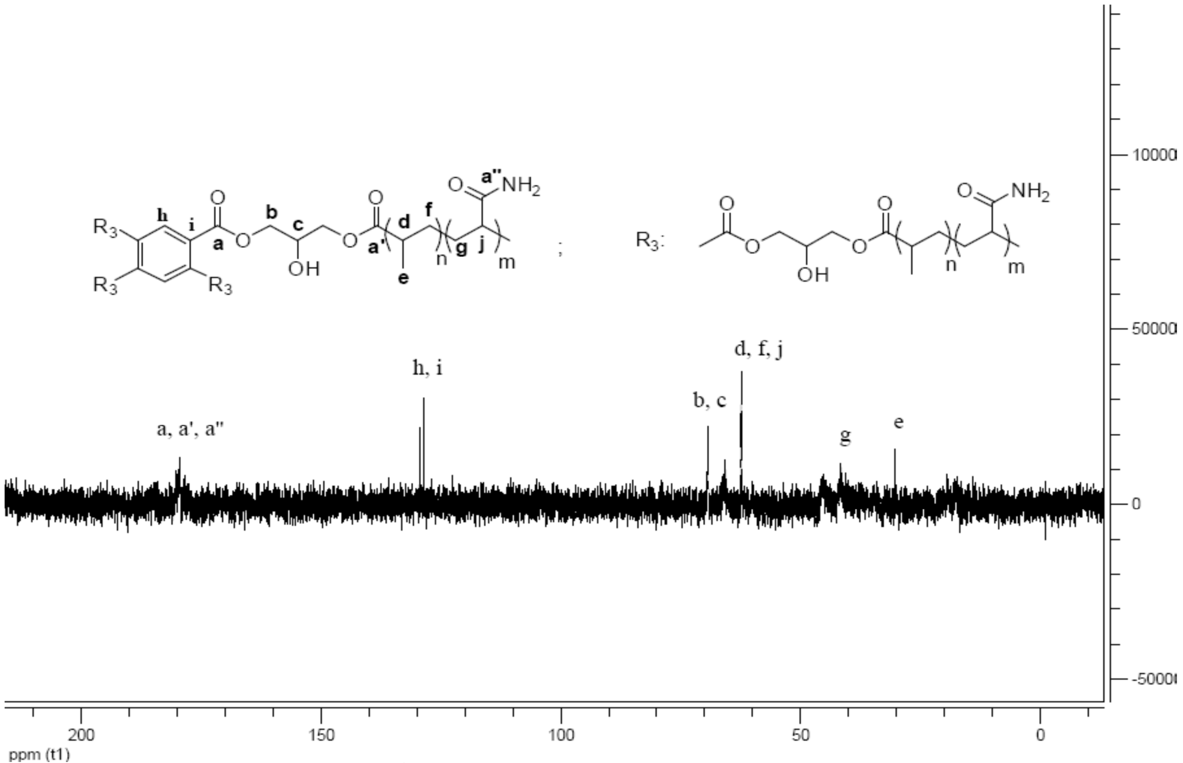


Fig. 9 ^{13}C NMR Spectra of poly (HMBC-co-AM) in D_2O

Thermal analysis

The thermogravimetric curve of poly (HMBC-co-MA) is shown in Fig. 10. TGA thermogram of poly (HMBC-co-AM), is found to be similar to that of poly (AM-DMDAAC-BA) copolymer [29]. Three regions of weight loss were observed. The weight loss was around 2.829% follow in the range of 20 to 150°C, corresponding to the evaporation of moisture [30-32]. The weight loss was about 21.64%, occurred in the range of 200 to 320°C, corresponding to the imine reaction of the amide group and the thermal decomposition of hydrophobic side chain [33, 30]. The weight loss was around 55.85% occurred from 325°C and up. At about 490°C, the poly (HBC-co-AM) completely decomposed.

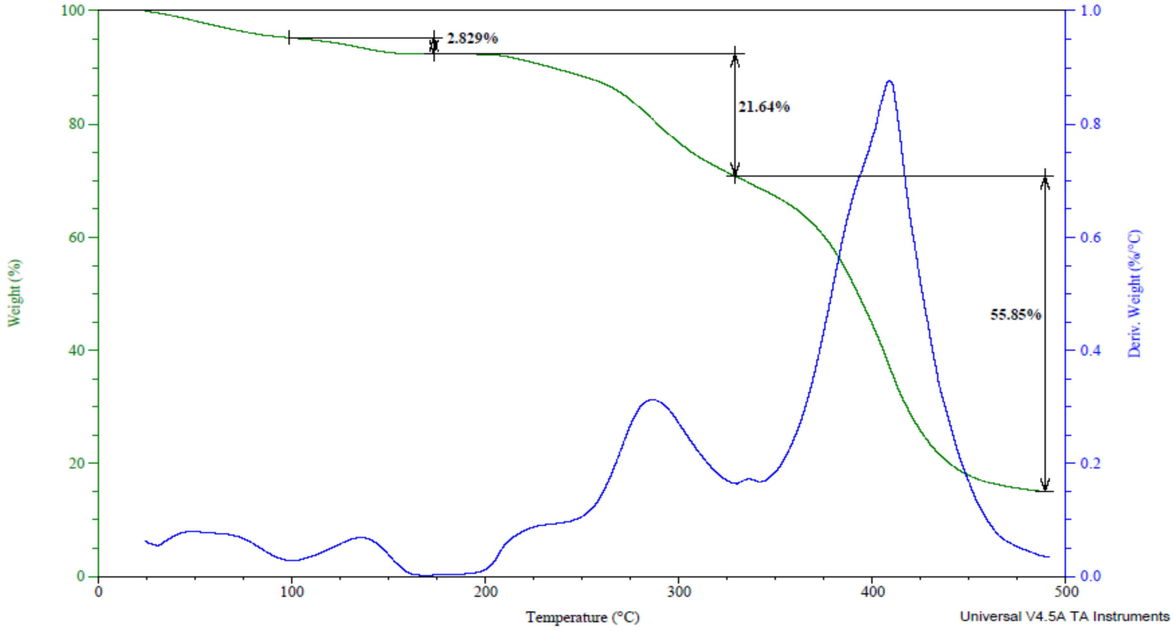


Fig. 10 Thermal gravimetric curve of poly (HMBC-co-AM)

DSC measurements

The DSC thermogram (Fig. 11) has three peaks. The first peak corresponds to the glass transition temperature of the copolymer. The T_g of copolymer is observed around 17°C. The second peak is observed about 65°c can be attributed to the loss of THF and the melting temperature (Third peak) is observed around 139°C.

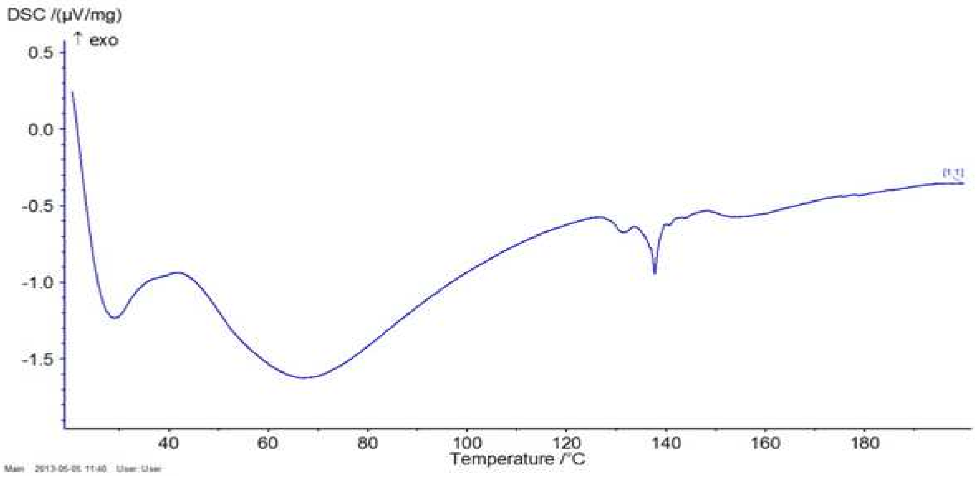


Fig. 11 DSC curve of poly (HMBC-co-AM)

CONCLUSION

The tetrafunctional methacrylate macromonomer HMBC synthesized is a very interesting product, it is considered as an intermediate in different synthesis. It can be employed in the production of several types of copolymers and dental composites. The HMBC was successfully prepared by the grafting reaction of pyromellitic dianhydride (PMDA) on glycidyl methacrylate (GMA) at room temperature using Maghnite-H^+ as a catalyst. Its purity was confirmed by FTIR, ^{1}H NMR and ^{13}C NMR spectroscopies. Polydispersity index of macromonomer were found by GPC technique.

Poly (HMBC-co-AM) is a water-soluble copolymer, easily synthesized by free radical solution polymerization. It can be used in several applications as an antioxidant or as an inhibitor of corrosion of metals. Its purity was confirmed by IR, ^{1}H NMR, ^{13}C NMR spectroscopy, and good thermal stability of the copolymer was found by TGA.

Acknowledgments

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