

Synthesis and thermogravimetric analysis of modified glycidyl methacrylate copolymers with oxime groups

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Abstract: In this work the homopolymer and copolymers of glycidyl methacrylate (GMA) with methyl methacrylate (MMA), ethyl methacrylate (EMA), methyl acrylate (MA) and ethyl acrylate (EA) were synthesized by free radical polymerization using azobis(isobutyronitrile) (AIBN) as initiator at 70 ± 1 °C. Then, copolymers of glycidyl methacrylate have been modified by incorporation of highly sterically hindered demanding benzophenone oxime through the ring opening reaction of the epoxy groups. The polymers were characterized by $^1\text{H-NMR}$ and FT-IR. Presence of bulk the benzophenone oxime groups in polymer side chains leads to an increase in the rigidity and glass transition temperature of polymer as shown by DMTA analysis. The thermal stability of all copolymers was determined by thermogravimetric analysis (TGA). This modification increases the thermal stability of polymers. With the incorporation of the benzophenone oxime groups in the polymer side chains, a series of novel modified polymer containing new properties are obtained, that can find some applications in polymer industry.

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Key words: chemical modification, thermogravimetric analysis, benzophenone oxime, glycidyl methacrylate

INTRODUCTION

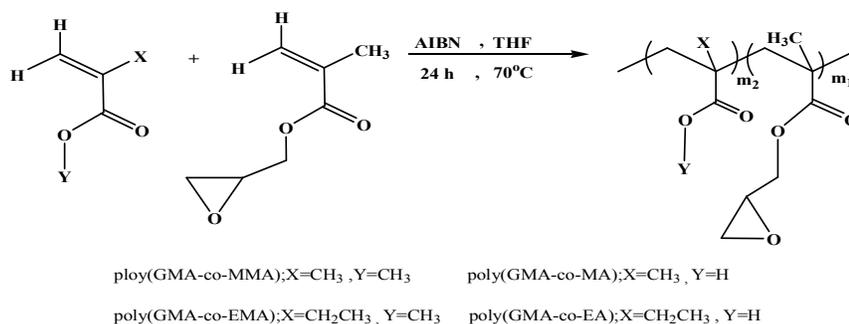
2,3-Epoxypropyl methacrylate (or glycidyl methacrylate = GMA) is a fascinating monomer exhibiting polymerizable Methacrylic unsaturation and an oxirane function of potential reactivity [1]. Due to the reactive nature of the epoxy group, copolymers containing GMA have led to an interesting class of new materials. This monomer has been homopolymerized and copolymerized by means of free-radical initiators (organic peroxides or azo-catalysts) known to selectively attack methacrylic double bonds [2, 3, 4]. The copolymers based on the potential class of functional polymers. Free-radical random copolymerizations of GMA with conventional monomers have been widely investigated for their potential applications [5, 6]. The interest in these copolymers is largely due to the ability of the pendant epoxy group to enter into a large number of chemical reactions [7]. Copolymers based on glycidyl methacrylate (GMA) have applications in biological drugs and biomolecules and in electronics as negative electron-beam resists materials [8, 9]. The epoxide opening reaction with nucleophiles is generally performed with acidic or basic catalysis and in the absence of such catalysts, the reaction is moderately slow [10, 11]. Oxime and oxime ethers are important intermediates in organic synthesis. O- and N-Alkylated products were obtained by reaction of pyridine-2-, -3-, and -4-carbaldehyde oximes with epoxy compounds (1-chloro-2,3-

epoxypropane, and 1-bromo-2,3-epoxypropane) in the presence of a base and under condition of phase-transfer catalysis [12, 13, 14]. Present research work describes the novel synthesis and properties of copolymers of GMA modified with benzophenone oxime. The thermal stability of the modified polymer was determined by TGA analysis. This scans show that the presence of bulky benzophenone oxime groups leads to higher thermal stability for modified polymers.

MATERIALS AND METHODS

Synthesis of (glycidyl methacrylate-co-ethyl acrylate) copolymer; poly(GMA-co- EA)

In a flask 100 mL, initiator (0.4 mmol, 6.500×10^{-2} g) and glycidyl methacrylate (20 mmol, 2.840 g) and ethyl acrylate (20 mmol, 2.560 g) are dissolved in tetrahydrofuran (THF) solvent 20 mL. The solution is de-oxygenated by nitrogen gas flow. Then, it is stirred in 70 ± 1 °C temperature for 24 hours. The resulted sticky solution is poured into a beaker containing cold ethanol 125 mL. While it is stirred by a magnetic stirrer. Gradually, polymeric precipitations are formed, the polymeric precipitations are separated by decantation of methanol and are washed by methanol and are dried under vacuum in room temperature. The resulted polymer weight is 3.9 g and reaction yield is %72. The reaction condition is shown in Scheme 1.

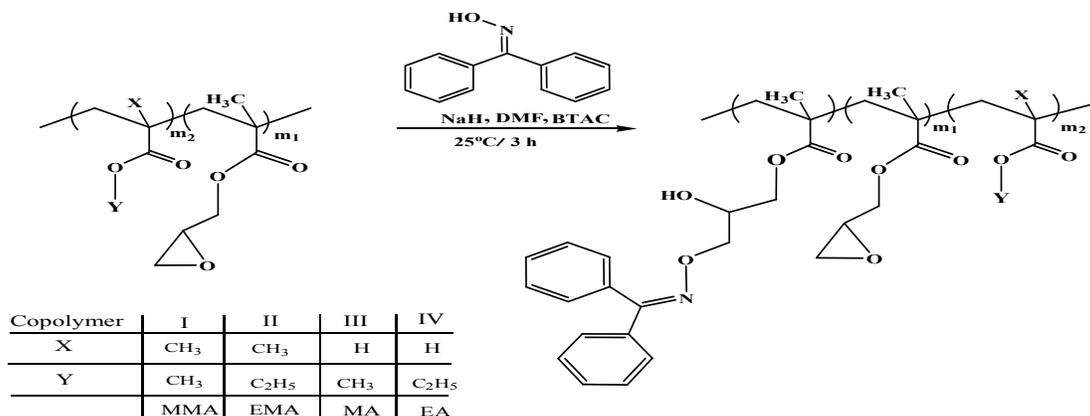


Scheme 1. Synthesis of glycidyl methacrylate copolymers

Synthesis of (glycidyl methacrylate-co-ethyl acrylate) copolymer containing benzophenone oxime:

In a 100 mL tow-necked flask equipped a dropping funnel and a reflux condenser, benzophenone oxime (3.92 g, 20 mmol) was dissolved in dry DMF solvent (20 mL) under nitrogen gas and guard tube of chloride calcium. After one hour, BTAC (20 mmol, 4.46 g) is added into the flask containing oxime. Then Sodium hydride (20 mmol, 0.48 g) was slowly added to benzophenone oxime. Then, in a 100 mL flask (10 mmol, 2.56 g) of copolymer (GMA-co-EA) was dissolve in 15 mL of DMF, next, flask contents that containing solved copolymer are added dropwise into tow-necked flask(containing oxime group) during one hour. There action solution is stirred in 25 °C for 3 hours. For

precipitation of flask contents, cold ethanol 150mL is added in to a beaker. Then, polymeric precipitation is formed in the bottom of beaker, next it is preserved in a refrigerator for one night to formed alkoxide is converted to hydroxide. Polymer is filtered by helping a funnel and filter paper. For washing of unreacted oxime, the resulted precipitation is continued with ethanol 50mL twice and with water 50mL twice. Also, for washing of potassium carbonate, we continue washing with water and the resulted white precipitation was dried under vacuum for one hour and in room temperature for 48 hours. The resulted weight is 4.1 g and the reaction yield is %63. Reaction condition is shown in Scheme 2.



Scheme 2. Synthesis of glycidyl methacrylate copolymers containing benzophenone oxime groups

RESULTS AND DISCUSSION

Study of FT- IR spectra: Poly (GMA -co- EA)

Symmetric and asymmetric stretch vibrations of aliphatic C-H bonds have seen in 3043 and 2980 cm⁻¹. The stretch vibration of

carbonyl ester has seen in 1732 cm⁻¹.The peak in 908 cm⁻¹ is related to asymmetric stretch vibration of epoxy ring C-O bonds. The peaks in 1261 cm⁻¹ and 1147 cm⁻¹ are related to stretch vibration of ester C-O bonds. Figure 1.

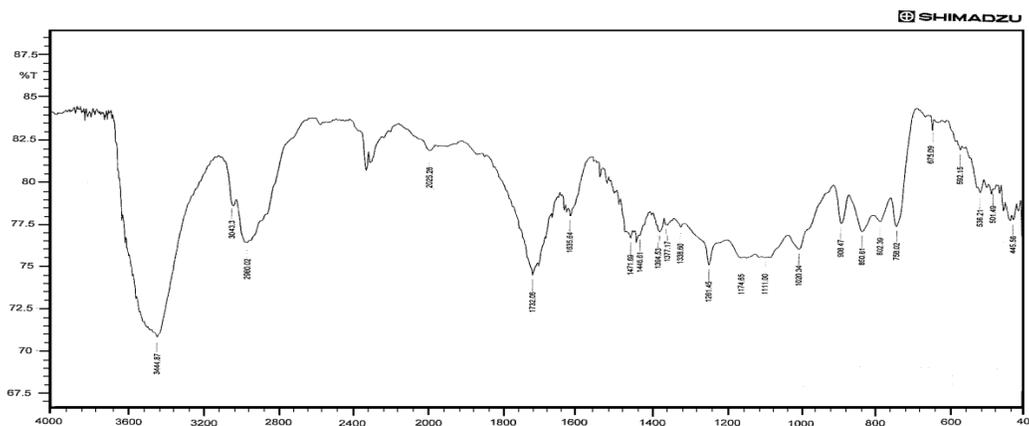


Figure 1. FT-IR Spectra of poly(GMA-co-EA) before reaction with benzophenone oxime.

Study of ¹H-NMR spectra: Poly(GMA-co- EA) in CDCl₃

In ¹H-NMR Spectra, glycidyl methacrylate-co-ethyl acrylate copolymer, CH₃ protons of the main polymer chain and CH₂ protons of the main chain and CH ethyl acrylate have seen in 0.87-2.19 ppm. Methylen protons of epoxy rings have seen in 2.56 ppm and 2.76 ppm. 3.14ppm peak is caused by methyn

protons of epoxy rings. Two methylen protons through COOCH₂ ester group in polymer GMA unit have seen in 4.00 ppm and 4.23 ppm. The absorption of two methylen protons through COOCH₂ ester group related to EA units have seen in 3.72 ppm. Figure 2.

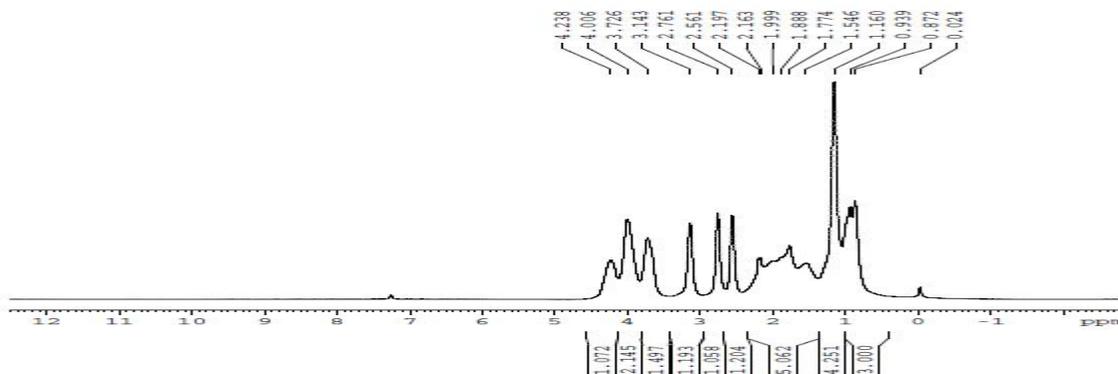


Figure 2. $^1\text{H-NMR}$ Spectra of poly(GMA-co-EA) before reaction with benzophenone oxime.

Study of FT- IR spectra: Poly (GMA -co- EA) containing benzophenone oxime group

In FT- IR spectrum, modified polymer of related peak to epoxide ring C-O in 912 cm^{-1} has destroyed peak to epoxide ring C-O in 908 cm^{-1} has destroyed to secondary alcohol functional group in polymeric chain that it is indicative of opening ring reactions in fundamental polymer. The related peak to ester group has stretched from 1732 cm^{-1} , probably it is

formed with generated OH of hydrogen bonding peak to alcohol in 3434 cm^{-1} . The peaks with average intensity that have seen in 1514 and 1465 cm^{-1} are related to aromatic ring C=C after through oxime. The related peak to oxime N-O bond has seen after through in 945 cm^{-1} . The remain peaks of IR spectrum similar with polymer peaks have not reacted. Figure 3.

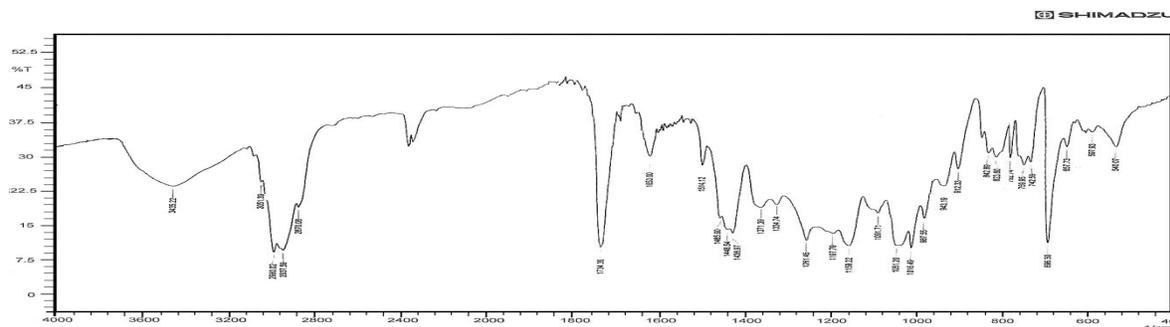


Figure 3. FT-IR Spectra of poly(GMA-co-EA) after reaction with benzophenone oxime.

Study of $^1\text{H-NMR}$ spectra: Poly(GMA-co-EA) containing benzophenone oxime in CDCl_3 .

In $^1\text{H-NMR}$ spectra, glycidyl methacrylate-ethyl acrylate modified copolymer hadn't destroyed perfectly due to spatial inhibition of benzophenone oxime groups, CH_2 two protons of epoxide ring in 2.6 ppm . The peak in 3.8 ppm is related to two protons methylen through COOCH_2 ester group in EA unit. Related protons to CH_2 , CH of epoxide ring overlapped after

opening the amount of epoxides in $4.27\text{-}4.34\text{ ppm}$ with related protons to COOCH_2 two protons in GMA unit and the peak of OH groups that caused by opening epoxide ring. The peaks in $6.8\text{-}7.33\text{ ppm}$ are indicative of benzophenone oxime protons. Other protons in copolymer structure have remained in $0.998\text{-}1.96\text{ ppm}$ range. Figure 4.

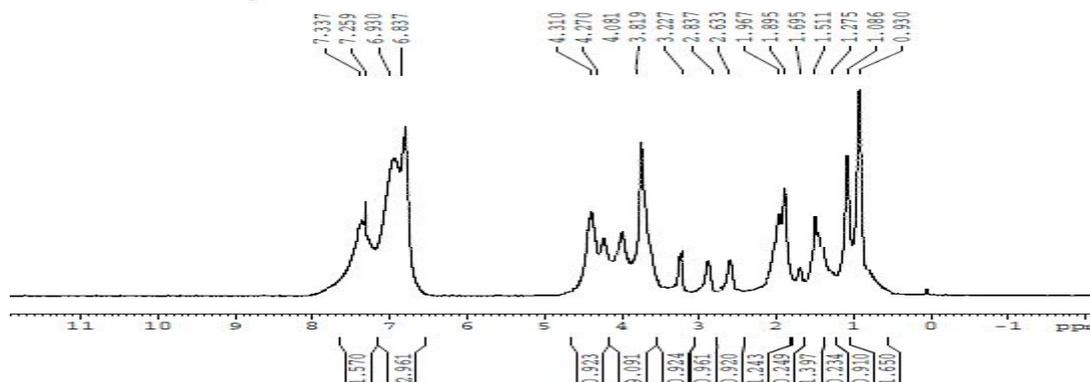


Figure 4. $^1\text{H-NMR}$ Spectra of poly(GMA-co-EA) after reaction with benzophenone oxime.

TGA Analysis

The thermal stability of polymers were determined by thermogravimetric analysis (TGA) as it is shown in Figure 5. Thermal gravimetric analysis (TGA) reveals that the framework of polymer before reaction with benzophenone oxime is stable up to 280 °C, and an abrupt well-defined weight loss follows from 300 to 435 °C. Poly(GMA-co-EA) after reaction with benzophenone oxime exhibits three relatively well-defined steps for its weight loss. The first weight loss at 25–90 °C corresponds to the loss of excess water remaining in polymer. Then it's stable up to 280 °C. Above which, the second weight loss occurs at 290–345 °C,

corresponding to the loss of oxime-polymer bounds (-N-O-CH₂). Above this temperature range, the framework breaks down gradually. The third weight loss occurs at 350–450 °C. According to the TGA data, the frameworks of polymers have practically the same thermal stability, but their decomposition modes appear to depend on breaking of the new connections after modification. Study of thermal properties of the obtained polymers by TGA curves showed that, thermal stability of acrylate and methacrylate copolymers containing oxime groups was found to be increased (about 25%) with incorporation of oxime groups in polymer structures. Figure 5.

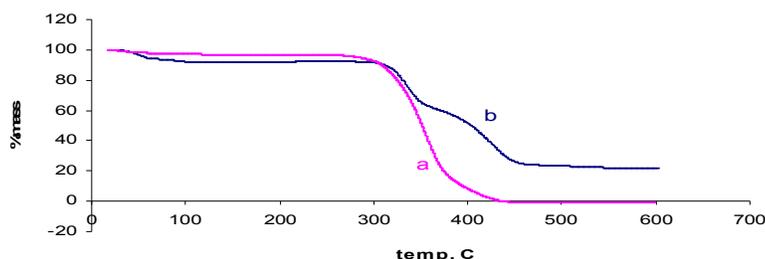


Figure 5. TGA Curves of poly (GMA-co-EA): (a) before reaction and (b) after reaction with benzophenone oxime

The presence of oxime groups in the polymer side chains created new polymers with novel modified properties that may find some applications in polymer industry. For example, the polymer systems with very bulky oxime side chain substituents can be used as fluid separation membranes.

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