Cumhuriyet Üniversitesi Fen Fakültesi
Fen Bilimleri Dergisi (CFD), Cilt:36, No: 3 Özel Sayı (2015)
ISSN: 1300-1949

Cumhuriyet University Faculty of Science
Science Journal (CSJ), Vol. 36, No: 3 Special Issue (2015)
ISSN: 1300-1949

Chemical Modification of Glycidyl Methacrylate Copolymers with Alcoholes Containing Pyridine Groups

Zahra JAVADİ[1,*], Mohammad Hossein NASİRTABRİZİ[1]

[1]*Department of Applied Chemistry, Ardabil Branch, Islamic Azad University, Ardabil, Iran*

Received: 01.02.2015; Accepted: 05.05.2015

Abstract. In this work the homopolymer and copolymers of glycidyl methacrylate (GMA) with ethylmethacrylate (EMA), methylacrylate(MA) and ethylacrylate (EA) were synthesized by free radical polymerization using azobis(isobutyronitrile) (AIBN) as initiator at 70 ±10C. Then, copolymers of glycidyl methacrylate have been modified by incorporation of 2-(2-pyridile)ethanol by the ring opening reaction of the epoxy groups. The polymers were characterized by 1H-NMR and FT-IR. Presence of bulk the 2-(2-pyridile)ethanol groups in polymer side chains leads to an increase in the rigidity and glass transition temperature of polymer as shown by DMTA analysis. The research demonstrated that the synthesized modified polymer could successfully remove heavy metals from solution. With the incorporation of the 2-(2-pyridile)ethanol 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.

Keywords: Glycidyl methacrylate (GMA), 2-(2-pyridile)ethanol, Chemical Modification, Ring opening, Glass transition temperature(DMTA)

1. INTRODUCTION

Glycidyl methacrylate (GMA) contains functional groups of epoxy and methacrylic that their acrylic factor (vinyl) makes to – polymerize with other vinyl monomers in aqueous and non – aqueous systems [1]. Epoxy groups provided attacks of various nucleophiles to glycidyl meth acrylate polymerize monomers [2]. The content of nucleophiles to homopolymer (GMA) remain in some of epoxy rings without reactions, but in copolymers of GMA all of epoxide opens neoclophils like phenols that because of monomers separation by Acrobatic monomers in copolymer prevent low space of homopolymer, and revised monomers polymerization with phenol polymerization achieved [3]. Poly glycidyl meth carbonate synthesized and then this polymer revised by amido di acetonitrile (IDAN) and thus revised rings factored by (IDAN). These changes continued by FT–IR. And then level morphology and revised PGM. Surveyed by scanning electron microscopy technique and thermal weighting technique have been surveyed [4]. The reaction of different nucleophiles with epoxy of GMA achieved by reuse of chemical structure and by creation of polymers with new characteristics of different factor groups. The character and new manners of revised polymers by SEM and TGA technique have been surveyed [5]. For example, other reactions of GMA polymer have with done types of Amins, that in fifth reaction, amino tetrazole along with glycidyl meta carbonate and Amin groups contacts with epoxy rings and cause ring opening epoxide ring [6]. Benzophenon oximino carbonyl ethyl methacrylate amino (BCM) as monomer that content urtan oxime group prepared with Benzophenon oxime, isocyanate and ethyl methacrylate and after determining its chemical structure with spectroscopic methods and elemental analysis, copolymer with urtan oxime prepared with BCM and MMA polymerization with azobisisobutyronitrile (AIBN) as initiator, then the characteristics of improved copolymers with urtan oxime groups is investigated [7]. Using the improved GMA polymers with di-ethylene tri-amine tetra acetic acid for using in efficient removal such metals as Ca (II) and Mg (II) has investigated and reported [8]. Using the

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[*] Corresponding author. *Email address: Zahra8668@ymail.com*

Special Issue: The Second National Conference on Applied Research in Science and Technology

improved GMA polymers by linkage with low polypropylene, for synthesis the exchange of metal sorbents has investigated and reported [9]. Improved polymers with oximes as toxic metals absorbents by various metals coordination such as Mn, Ni, Cd, Ru, Os have been investigated [10]. Eliminate the mentioned metals from waters, wastewaters and contaminated environments through formation the stable complex of improved polymers containing oxime groups with metals have been investigated [11].

According this results, have been expected that the factored polymers with the ability to absorb heavy metals achieve with preparing the GMA polymers and copolymers by vinyl monomers and this polymers chemical reactions with alcohols containing pyridine.

Table 1. The condition of preparation of copolymers I–III.

Sample	Monomer 1	Monomer 2	Amount of Monomer 1(mmol)	Amount of Monomer 2(mmol)	Time (h)
I	GMA	EMA	20	20	24
II	GMA	EA	20	20	24
III	GMA	MA	20	20	24

2. EXPERIMENTAL

2.1. Instrument

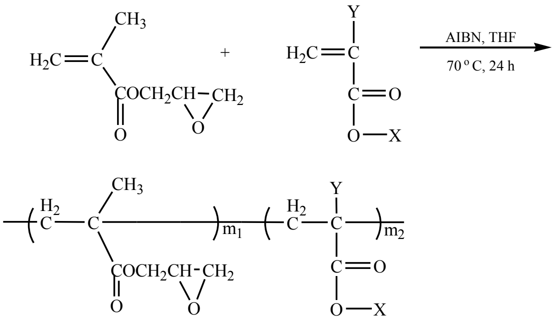
The infrared spectra were recorded on Bruker spectrometer scientific 400 IR. 1H-NMR spectra were run on a Bruker 250 MHz spectrometer at room temperature using CDCl3 and DMSO-d6 as solvents and TMS as internal standard. Dynamic mechanical thermal analysis (DMTA) was characterizedby Triton (Tritec 2000 DMN) with the rate of 10_C/min.

2.2. Materials

2-(2-pyridile)ethanol was obtained from Merck Chemical Company. The radical initiator of azobis (isobutyronitrile) (AIBN) was purchased from Fluka and purified by recrystallization from absolute ethanol. Ethylmethacrylate (EMA), Ethylacrylate (EA), methyl acrylate (MA) and glycidyl methacrylate (GMA) were obtained from Merck and distilled under reduced pressure to remove inhibitors before use. Benzyltriethyl ammonium chloride (BTAC) was obtained from Merck Chemical Company. N,N-di-methyl formamide (DMF. Merck) and tetrahydrofuran (THF) were dried over anhydrous MgSO4 for 2 days and distilled under reduced pressure.

2.3. Synthesis of the acrylic copolymers and methacrylic copolymers (I–III)

Poly(GMA-co-EMA) (I), poly(GMA-co-EA) (II) and poly(GMA-co-MA) (III) were synthesized by a general method using 2 g (20 mmol) of Ethyl methacrylate, 2 g (20 mmol) of ethyl acrylate or 2 g (20 mmol) of methyl acrylate and also a mixture of 2.84 g (20 mmol) of GMA and 0.065 g (0.4 mmol) of AIBN in 15 mL of tetrahydrofuran (THF). The reaction mixture was heated to 70 ± 1 _C with constant stirring under a nitrogen atmosphere. The reaction conditions were maintaind for 24 h.



Copolymer	I	II	III
X	CH_2CH_3	CH_2CH_3	CH_3
Y	CH_3	H	H
	EMA	EA	MA

Scheme 1. Synthesis of copolymers I–III

Polymer solutions were poured dropwise into a large excess of methanol. The obtained polymer was purified by precipitating twice into methanol. The polymer was filtered and dried under vacuum at room temperature. The reaction condition is shown in Table 1 and Scheme 1.

FT-IR spectra of polymers I–III

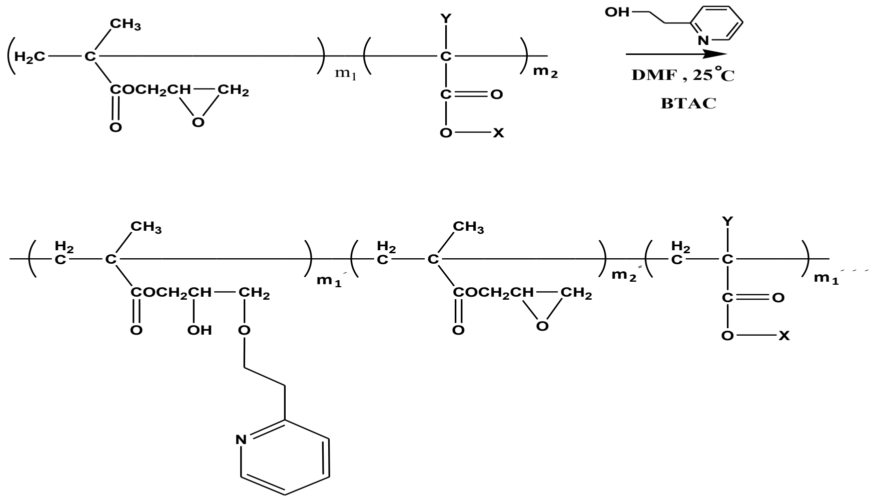
I FT-IR (KBr) ν cm^{-1} : 2995.61, 3001.01(C-H aliphatic), 1737.86(C=O), 1149.57 , 1271.09 (C-O stretch in ester), 908.47(C-O epoxide ring).

II FT-IR (KBr) ν cm^{-1} : 2980.02-3043.3 (C-H aliphatic), 1732.06 (C=O), 1174.65-1261.45 (C-O stretch in ester), 908.47(C-O epoxide ring).

III FT-IR (KBr) ν cm^{-1} : 2980.02-3043.3 (C-H aliphatic), 1732.06 (C=O), 1174.65-1261.45 (C-O stretch in ester), 908.47(C-O epoxide ring).

2.4. Attachment of 2-(2-pyridile)ethanol group to the side chain of copolymers

Benzyltriethyl ammonium chloride (BTAC) (5.2 mmol, 1.2 g) was slowly added to 2-(2-pyridile)ethanol (5.2 mmol, 1.1 g) dissolved in 15 mL of DMF at room temperature while stirring the mixture under a nitrogen atmosphere for 30 min. Then, 3.5 mmol of epoxide-containing monomer unit of polymers I EMA–II EA and III MA (0.5, 0.5, 0.5, g) of polymers, respectively, in 15 mL of DMF was added dropwise within 1 h. The contents were kept at ambient temperature for another 24 h while stirring. The mixture was then poured dropwise into a large excess of cold acidic water (5 %). The precipitated solid was recovered by filtration, washed successively with diethyl ether and then dried in vacuum at room temperature for 48 h (Scheme 2).



Copolymer	I	II	III
X	CH_2CH_3	CH_2CH_3	CH_3
Y	CH_3	H	H
	EMA	EA	MA

Scheme 2. Reaction of copolymers I–III with 2-(2-pyridile)ethanol

FT-IR spectra of Reaction of copolymers I–III with 2-(2-pyridile)ethanol of copolymers I-III

I FT-IR (KBr) ν cm^{-1}: 3447.57 (stretch of O-H), 1678 (C=O ester),1718.58 (C=O aromatic), 1570.06 (C=C stretching of aromatic ring), 1251.08- 1151.50(C-O ester).

II FT-IR (KBr) ν cm^{-1}: 3446.79 (stretch of O-H), 1734.01 (C=O), 1568.20-1585.49 (C=C stretching of aromatic ring), 1159.22-1261.45(C-O ester).

III FT-IR (KBr) ν cm^{-1}: 3446.79 (stretch of O-H), 1734.01 (C=O), 1541.12(C=C stretching of aromatic ring), 1163.08-1244.09 (C-O ester).

3. RESULTS AND DISCUSSION

Radical polymerization reaction, glycidyl methacrylate monomer with various monomers of methacrylate and acrylate such as ethyl methacrylate (EMA), methyl methacrylate (MA) and ethyl acrylate (EA), with readical initiator of azobisisobutyronitrile (AIBN) and solvent of dry tetrahydrophoran (THF) had been carried in fixed temperature conditions. Preparation state of copolymers has shown in Table 1. The prepared polymer solubility before bonding 2-(2-pyrdil) ethanol in various solvents in room temperature has been studied. These polymers within polar aprotic solvents such as $CDCL_3$ and DMSO and DMF are soluble and they are insoluble in non-polar protic and aprotic solvents. Alcoholic pyridine polymer sovents in room temperature also have been studied. ^{1}HNMR spectrum of copolymers before bonding 2-(2-prydil) ethanol had studied that attraction of two methylene proton connected to ester group $-COOCH_2$ related to EMA units in 3.67.3.77 ppm region in EA in 3.72 ppm region and MA in 3.58-3.8 ppm have appeared. For calculation of participated monomer molar percent in acrylate and methacrylate structure based on glycidyl methacrylate from related ^{1}HNMR has been used. If m_l is GMA monomer molar part and m_2 is molar part of each auxiliary monomer, according to equation in two unknowns, it can be determined amounts of m_l and m_2 related to each copolymer from ^{1}HNMR.

By using following equation, GMA molar percent and BA monomer in poly (GMA-Co-MA) copolymer are determined. By using this, also it can be determined monomer molar percent in other copolymers. The results have shown in Table 2.

$$\frac{\text{Integrared peak area of } 2.5 - 3.5 \text{ ppm}}{\text{Integrared peak area of } 4 - 3.58 \text{ ppm}} = \frac{3m1}{3m2} = A$$

$$m_1 + m_2 = 1$$

Table 2. Molar percentage of copolymer making monomers.

Copolymer	(%) m_2	(%) m_l
Poly(GMA-co-MA)	53	47
Poly(GMA-co-EMA)	39	61
Poly(GMA-co-EA)	51	49

3.1. Characterization of copolymers I–III before and after modification with 2-(2-pyridile)ethanol

3.1.1. Infrared spectra

The asymmetrical and symmetrical stretching due to the methyl and methylene groups in copolymers I–III are observed at 2,953 and 3,001 cm-1. The band at 1,731 cm-1 is attributed to the ester carbonyl stretching of GMA and comonomers EMA, EA and MA units. Another band seen at 907 cm-1 is due to the asymmetric stretching of the epoxy group. The bands of 1,149 and 1,271 cm-1 are attributed tothe ester C–O stretching of GMA and comonomers EMA, EA and MA and units; for example, IR spectra of copolymer (GMA-co-EMA) are shown in Fig. 1. The infrared spectra of the modified products show the broadbands characteristic of the hydroxyl groups at wave number 3,446 cm-1 which is indicative of the ring opening reaction. Aromatic = C–H bands appeared at 3,000 cm-1. The bands at 1,718 cm-1 are attributed, respectively, to the ester carbonyl stretching of GMA, comonomers EMA, EA and MA and aromatic ring. The IR spectrumof poly(GMA-co- EMA) with 2-(2-pyridile)ethanol has been shown in Fig. 2.

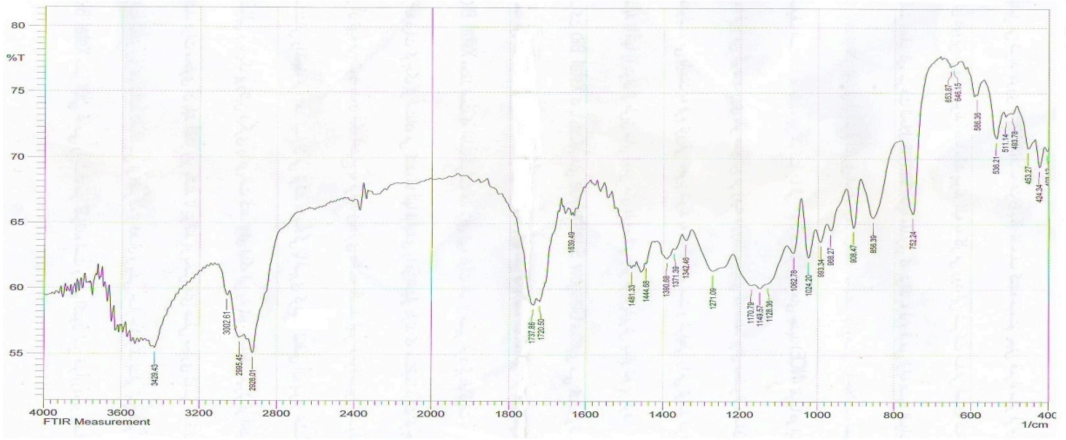


Figure 1. Infrared spectra of poly(GMA-co-EMA).

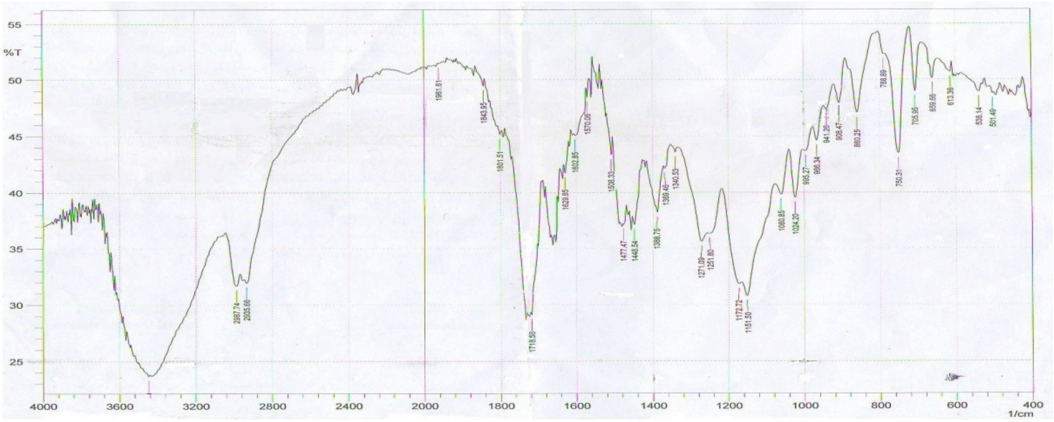


Figure 2. Infrared spectra of poly(GMA-co-MMA) after reaction with 2-(2-pyridile)ethanol.

3.1.2. H NMR spectra

H NMR spectra of copolymers I–III showed two signals at 3.77 and 3.67 ppm due to the splitting of methylene protons in the CH2O– group attached to the carbonyl group of the GMA group. The peak at 3.22 ppm is due to the methyne proton of the epoxy group. The methylene protons of the epoxy group show signals at 2.63 and 2.84 ppm .The resonance signal at 4.02 and 4.3 ppm was attributed to two methylene protons of –COOCH2 in copolymer EMA. The broad signal at 0.92–1.85 ppm was due to the methylene groups of backbones and other alkyl groups. For example, the 1H-NMRspectra of copolymer (GMA-co-EMA)are shown in Fig. 3. The 1H NMR spectra of the pure and modified polymers show epoxy groups 2.5–2.7 ppm, which are well defined in the unmodified polymers but decrease after modification. According to these results, part of the epoxy groups were modified and created random polymers .The peaks at 4.01–4.47 ppm is due to the methyne proton attached to the alcohol group, methylene protons in the – CH2O – group attached to the carbonyl group of the GMA and protons in the – CH2– group attached to the 2-(2 pyridile)ethanol group of GMA. The peaks at 7.71–7.94 ppm are due to the 2-(2-pyridile)ethanol protons. The H-NMR spectrum of poly(GMA-co-EMA) with 2-(2-pyridile)ethanol has been shown in Fig. 4.

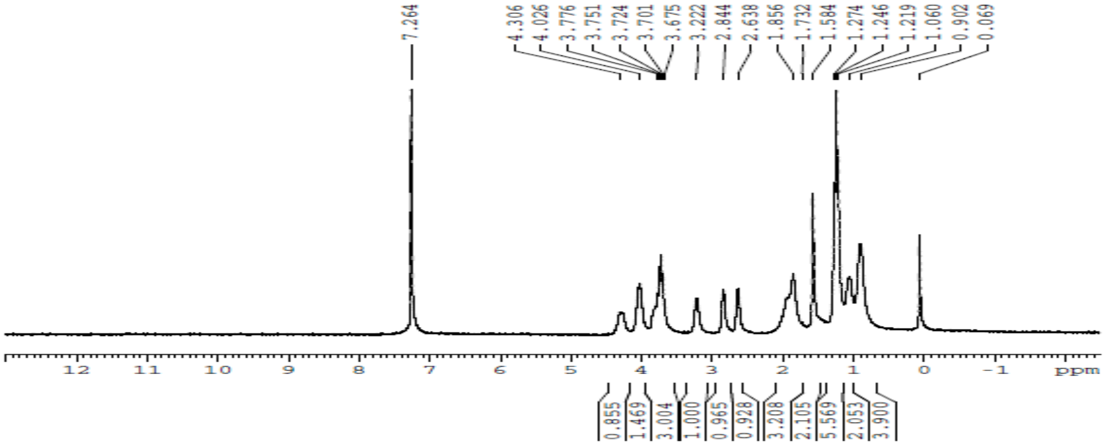


Figure 3. 1H NMR spectra of poly(GMA-co-EMA).

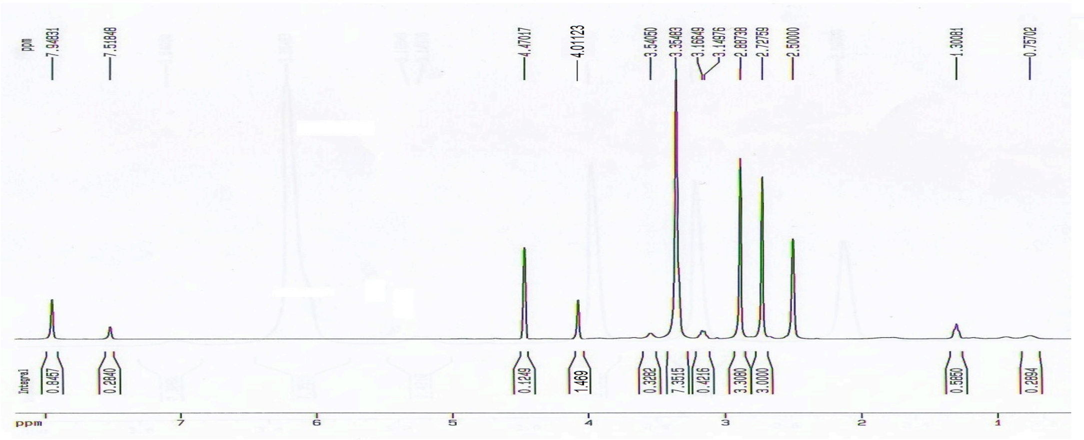


Figure 4. 1H NMR spectra of poly (GMA-co-EMA) after reaction with 2-(2-pyridile)ethanol.

3.1.3. DMTA curve

In the curve of DMTA, glycidyl methacrylate copolymers only a Tg temperature is obseerverd that indicates the formation of a random polymer. Due to existing the metil groups on main chain, methacrylate copolymers causes the decreasing of reflex ability in polymer chain, and at the end, the temperature of Tg is increased. This reason can be due to the decreasing free density among polymeric chains and also the possibility of connecting hydro genic among chains. In agent polymers, the existing of epoxide ring and pyridine ring causes the increasing of the separation and also the increasing of Tg. For example, according to these curves (the figures 5 and 6), the temperature of glossy transfer of EMA copolymer has been changed from the temperature 93, after connecting pyridine alcohols, to the temperatures 120 centigrade degree.

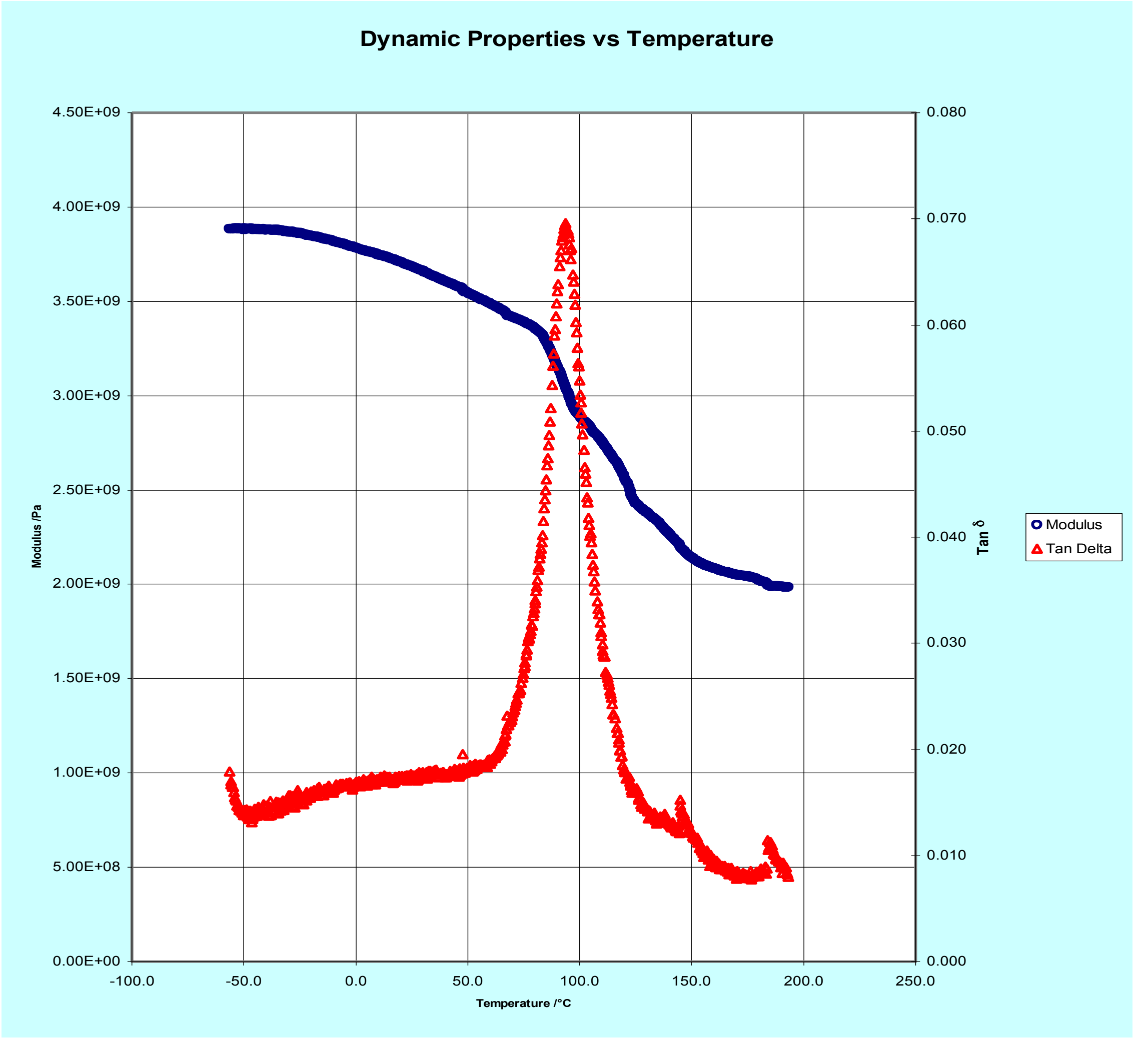


Figure 5. DMTA curves of poly(GMA-co-EMA) before reaction with 2-(2-pyridile)ethanol.

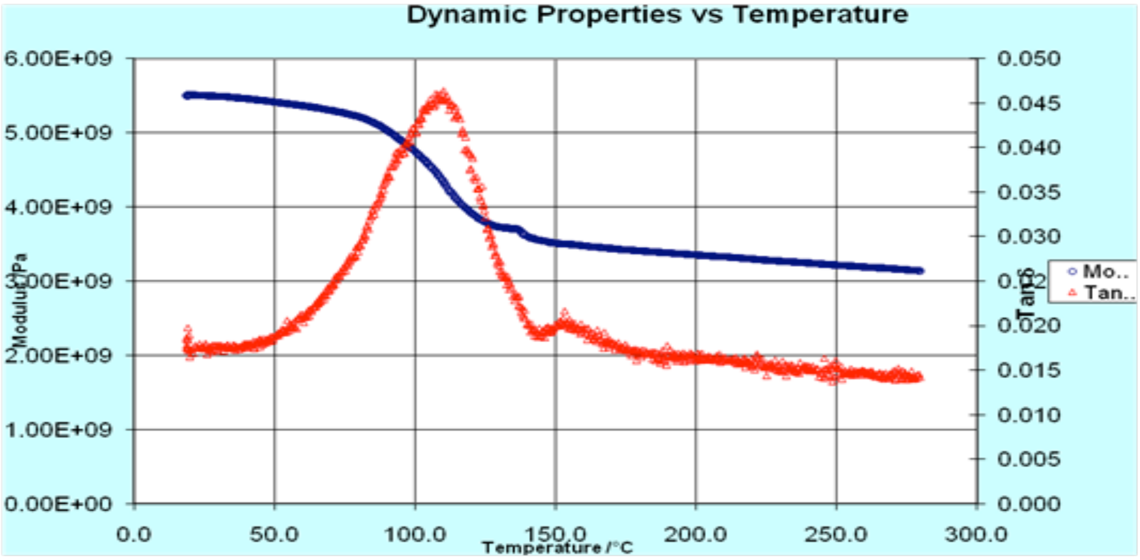


Figure 6. DMTA curves of poly(GMA-co-EMA) after reaction with 2-(2-pyridile)ethanol.

4. CONCLUSION

Our aims of this work are modification of chemical characteristics in homopolymer and glycidyl methacrylate copolymers with glycidyl methacrylate monomers, ethyl acrylate, methyl methacrylate and ethyl methacrylate with 2-(2-pyridile) ethanol for changing temperature of glass transition. It can be determined from DTME analyses that with ethanol 2-(2-pyridile) group in copolymer structure lead to increasing polymers, thus Tg temperature is increased and flexibility of the resulted copolymers is decreased. As a result of connection the elastic properties of the copolymer is limited. Chemical reaction of reaction of these polymers has been carried by reopening of epoxide glycidyl methacrylate ring with voluminous group 2-(2-pyridile) ethanol and its bonding to primary polymers as impendent group from polymer. It can be said that with approach voluminous group 2-(2-pyridile) ethanol towards polymer structure, it can be prepared and analyzed new macro molecules with newest characteristics.

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