



## Glycidyl Methacrylate Polymers Containing Indole Groups: Synthesis and Characterization

Mohammad Hossein Nasirtabrizi\*, Samaneh Mohebalizadeh,  
and Aiyoub Parchehbaf Jadid

Department of Applied Chemistry, Ardabil Branch,  
Islamic Azad University, Ardabil-56157/31567, Iran

Received 14 November 2010; accepted 30 May 2011

### ABSTRACT

The synthesis, characterization and thermal behaviour of methacrylic and acrylic copolymers of glycidyl methacrylate without and with indole groups are reported. The copolymers based on glycidyl methacrylates belong to the potential class of functional polymers. Random copolymers of glycidyl methacrylate with methyl methacrylate, ethyl methacrylate and ethyl acrylate were synthesized by free radical polymerization using  $\alpha, \alpha'$ -azobisisobutyronitrile as initiator at  $70 \pm 1^\circ\text{C}$ . The copolymer products of glycidyl methacrylate have been modified by incorporation of indole groups through the ring opening reaction of the epoxy groups. Chemical modification was determined by  $^1\text{H}$  NMR and IR spectroscopic techniques. The modification of polyglycidyl methacrylate was faced with limited conversion which has been attributed to the steric hindering effect of the earlier grafted moieties. The glass transition temperature ( $T_g$ ) of all copolymers was determined by dynamic mechanical thermal analysis. The  $T_g$  value of methacrylate copolymers containing indole groups was found to be decreased with incorporation of indole groups in polymer structures, while it increased in indole-incorporated acrylate copolymer. The presence of indole groups in the polymer side chains created new polymers with novel modified properties that may find some applications in polymer industry.

### Key Words:

glycidyl methacrylate;  
indole;  
ring opening;  
dynamic mechanical thermal analysis;  
chemical modification.

### INTRODUCTION

Copolymers based on glycidyl methacrylate (GMA) have applications in biological drugs and biomolecules and in electronics as negative electron-beam resists materials [1]. Due to the reactive nature of the epoxy group, copolymers containing GMA have led to an interesting class of new materials [2].

Addition reactions of alcohols, phenols, carboxylic acids and amines to pendant epoxide groups

in poly(GMA) and its copolymers are well known [3,4]. 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 [5,6]. Indole is a key structural motif in many biologically and pharmacologically active compounds as well as in many natural products [5]. The N-H centre has a  $pK_a$  of 21 in DMSO and therefore, very strong

(\*) To whom correspondence to be addressed.  
E-mail: [Nasirtabrizi@gmail.com](mailto:Nasirtabrizi@gmail.com)

bases such as sodium hydride or butyl lithium and water-free conditions are required for complete deprotonation.

The more ionic salts such as the sodium or potassium compounds tend to react with electrophiles at nitrogen-1; the same as polar aprotic solvents such as DMF and DMSO which tend to favour attack at the nitrogen, whereas a non-polar solvent such as toluene favours C-3 attack [7].

Polyindoles have received a significant share of attention in the past several years and may be good candidates for application in various domains, e.g., electronics, electro-catalyst anode materials in battery, anti-corrosion coatings and pharmacology [8]. Polyindole family is of much interest due to its several advantages, especially fairly good thermal stability and high redox activity and stability [9]. It is also reported that polyindole films have the advantages of fairly good thermal stability [10].

In recent years, incorporation of carbazole group in polymer structure has been utilized to modify the polymer properties. Carbazole is the best-known chromophore that is often used to construct polymers with photoconduction, photorefractive, and hole transporting properties [11].

However, the size of indole group is smaller than carbazole and it is likely to keep photoconductivity to some extent due to its fused heteroaromatic structure similar to carbazole. Thus, we came to consider the use of the indole moiety as a substitute for carbazole. Present research work describes the novel synthesis and properties of copolymers of GMA modified with indole. DMTA Scans show that the presence of bulky indole groups leads to higher  $T_g$  for (GMA-co-EA) and lower  $T_{gs}$  for (GMA-co-MMA) and (GMA-co-EMA).

## EXPERIMENTAL

### Materials

Indole obtained from Merck, Germany. The radical initiator of azobisisobutyronitrile (AIBN) was purchased from Merck, Germany, and purified by recrystallization from absolute ethanol. Methyl methacrylate (MMA), ethyl acrylate (EA), ethyl methacrylate (EMA) and glycidyl methacrylate

(GMA) were obtained from Merck, Germany and distilled under reduced pressure to remove inhibitors before use. Sodium hydride (60%) obtained from Aldrich, *N,N*-dimethylformamide (DMF) was dried over anhydrous  $MgSO_4$  for 2 days and later with phosphoric anhydride overnight. After drying, DMF was distilled under reduced pressure; tetrahydrofuran (THF) was distilled over sodium/benzophenone.

### Measurements

The infrared spectra were recorded with a Shimadzu Scientific spectrophotometer (Japan), as KBr pellets.  $^1H$  NMR Spectra were run on a Bruker 250 MHz spectrometer (Germany), at room temperature using chloroform-*d* and dimethylsulphoxide-*d*<sub>6</sub> as solvents and TMS as internal standard. The glass transition temperature was determined with a Tritec 2000 DMTA (England), at a heating rate of 5°C/min in air.

### Synthesis of the Acrylic and Methacrylic Copolymers (I-III)

Poly(GMA-co-MMA) (I) or poly(GMA-co-EA) (II) or poly(GMA-co-EMA) (III) were synthesized by the following general method. In three different pyrex glass ampoules, a mixture of 2.84 g (20 mmol) of GMA, 0.065 g (0.4 mmol) of AIBN, 2.28 g (20 mmol) of ethyl methacrylate or 2.00 g (20 mmol) of ethyl acrylate was dissolved in 15 mL of THF. Then the ampoules were degassed, sealed under vacuum, maintained at 70±1°C in a water bath and shaken by a shaker machine for about 48 h. Then, the viscous solutions were poured from the ampoules into 150 mL of cooled methanol, separately. The precipitates were collected and washed with methanol for several times and dried under vacuum at room temperature. The reaction condition is shown in Table 1 and Scheme I.

### $^1H$ NMR and FTIR Spectra of Polymers I-III

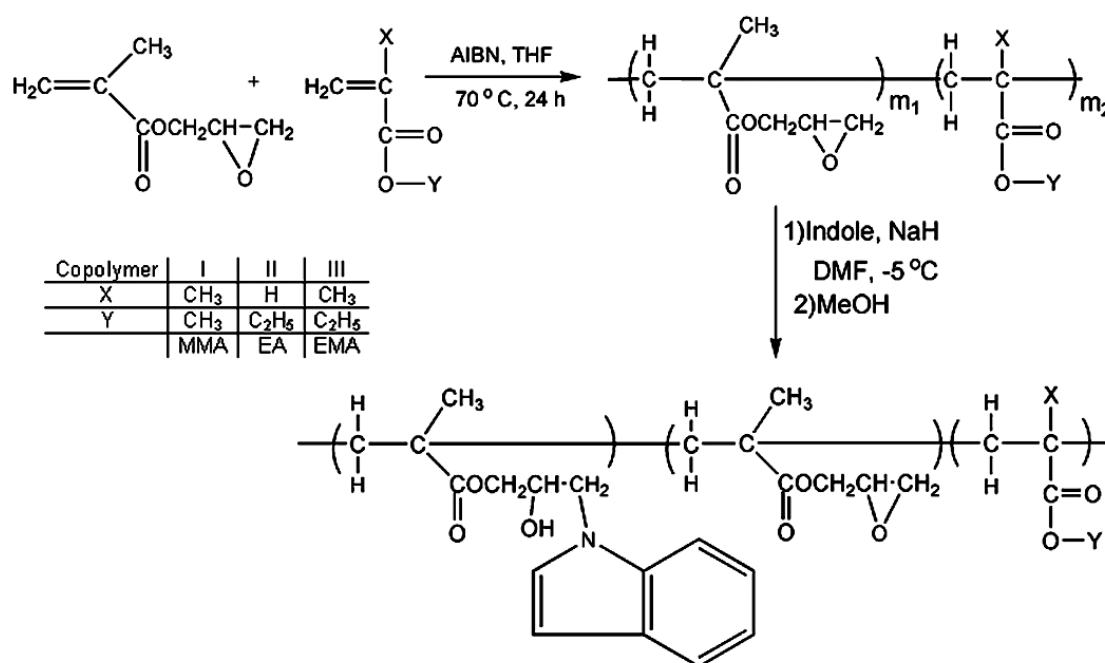
(I) FTIR (KBr)  $\nu$  ( $cm^{-1}$ ): (C-H bending vibration of epoxide ring) 758, (C-H aliphatic) 2999-2952, (C=O) 1738, (C-O) stretch in ester 1267-1149, (symmetric ring stretching) 1244, (O-CH<sub>3</sub> bending vibrations) 1448.

$^1H$  NMR ( $CDCl_3$ , TMS, 300 MHz)  $\delta$  (ppm): 0.86-1.03 (CH<sub>3</sub>), 1.455-1.839 (CH<sub>2</sub>), 2.64-2.84 (CH<sub>2</sub> epoxide), 3.22 (CH epoxide), 3.79-4.30 (COOCH<sub>2</sub>),

**Table 1.** The condition of preparation of poly(GMA) and copolymers I-III.

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

[mmol monomer 1] + [mmol monomer 2]/[mmol AIBN] = 100; [AIBN] = 0.4 mmol; solvent: THF; non-solvent: methanol; temperature: 70±1°C.

**Scheme I.** Synthetic routes for preparation of copolymers I-III and their ring opening reactions with indole.

3.60 (-COOCH<sub>3</sub>).

**(II)** FTIR (KBr)  $\nu$  (cm<sup>-1</sup>): (C-H, bending vibration of epoxide ring) 758, (C-H aliphatic) 2983-2941, (C=O) 1734, (C-O, stretch in ester) 1252-1154, (symmetric ring stretching) 1244.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS, 300 MHz)  $\delta$  (ppm): 0.92-1.20 (CH<sub>3</sub>), 1.67-1.858 (CH<sub>2</sub> and CH), 3.77-4.28 (COOCH<sub>2</sub> of GMA), 3.19 (CH epoxide), 2.60-2.80 (CH<sub>2</sub> epoxide), 4.053 (COOCH<sub>2</sub> of EA).

**(III)** FTIR (KBr)  $\nu$  (cm<sup>-1</sup>): (C-H, bending vibration of epoxide ring) 752, (C-H aliphatic) 2995-2941, (C=O) 1738, (C-O) stretch in ester 1269-1149.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS, 300 MHz)  $\delta$  (ppm): 0.90-

1.25 (CH<sub>3</sub>), 1.37 (CH<sub>2</sub>), 3.47-4.3 (O-CH<sub>2</sub>), 2.6-3.2 (CH and CH<sub>2</sub> epoxide).

#### Attachment of Indole Groups to Side Chains of Copolymers

Sodium hydride (60 mmol, 1.44 g) was slowly added to indole (60 mmol, 7.029 g) dissolved in 20 mL of DMF at room temperature mixture stirring under nitrogen atmosphere for 30 min. Then, mixture was cooled to -5°C in an ice-salt mixture while vigorous stirring. After that, separate solutions of each polymer I (7.8 g, with 30 mmol of epoxide-containing monomer unit), polymer II (8 g, with 30 mmol of

**Table 2.** Composition, molecular weights and  $T_g$  of polymers.

Sample	GMA (mol%)	MMA (mol%)	EA (mol%)	EMA (mol%)	Weight (g)	Yield (%)	$T_g$ ( $^{\circ}\text{C}$ )	Modulus (GPa) $T = 25^{\circ}\text{C}$
I	50	50	-	-	3.62	75	132.0	5.037
II	45	-	55	-	3.44	71	40.3	2.663
III	54	-	-	46	3.62	70	93.0	3.684
I <sub>in</sub>	-	-	-	-	2.00	80	50.9	1.458
II <sub>in</sub>	-	-	-	-	2.10	84	59.8	3.076
III <sub>in</sub>	-	-	-	-	1.86	75	76.3	4.381

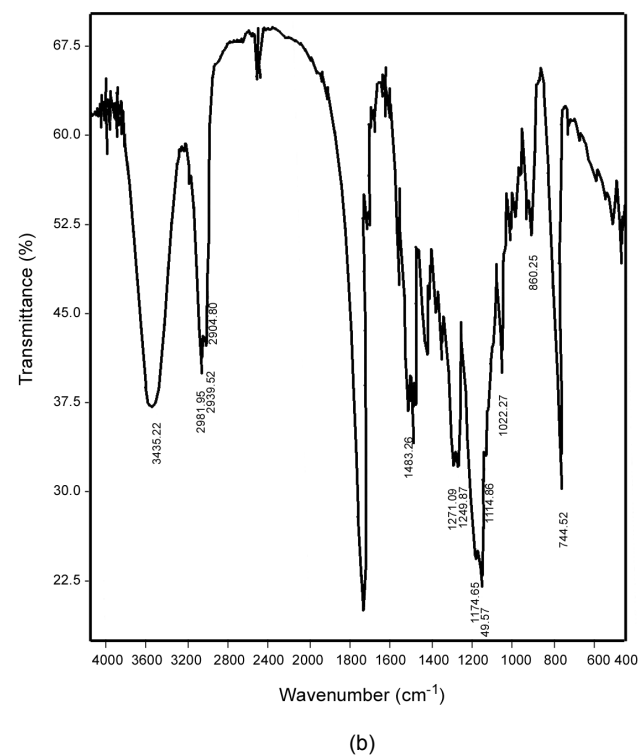
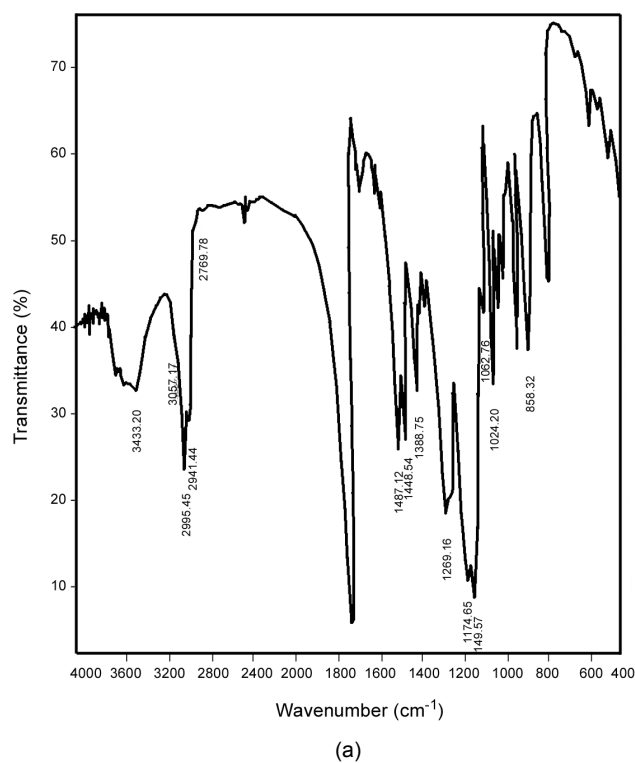
epoxide-containing monomer unit) or polymer III (7.68 g, with 30 mmol of epoxide-containing monomer unit) in 20 mL of dry DMF were added dropwise within 1 h. The contents were kept at ambient temperature for another 3 h while stirring. The mixture, of copolymers I, II and III were then poured dropwise into a large excess of cold acidic methanol and copolymers II and III then poured dropwise into cold water. The precipitated solid was recovered by filtration, washed successively with methanol, and then dried in vacuum at room temper-

ature for 28 h. The yields of modified copolymers are given in Table 2 and Figure 1.

### $^1\text{H}$ NMR and FTIR Spectra of Polymers I<sub>in</sub>III<sub>in</sub>

(I<sub>in</sub>): FTIR (KBr)  $\nu$  ( $\text{cm}^{-1}$ ): (stretch of O-H) 3200-3600, (C-H aliphatic) 2995-2949, (C=O) 1738, (C=C stretching of aromatic ring) 1650-1500, (stretch of C-N) 1330, (C-O stretching of the alcohol group) 1100, (the out of plane C-H bending of benzene) 744.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , TMS, 300 MHz)  $\delta$  (ppm): (aromatic C-H) 6.8-8.01, (O-H) 1.6

**Figure 1.** FTIR Spectra of poly(EMA-co-GMA): (a) before reaction and (b) after reaction with indole.

(II<sub>in</sub>): FTIR (KBr)  $\nu$  (cm<sup>-1</sup>): (stretch of O-H) 3200-3600, (C-H aliphatic) 2983-2941, (C=O) 1734, (C=C stretching of aromatic ring) 1661-1514, (stretch of C-N) 1330, (out-of-plane C-H bending of benzene) 742. <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS, 300 MHz)  $\delta$  (ppm): (aromatic C-H) 6.3-7.93, (O-H) 1.1.

(III<sub>in</sub>): FTIR (KBr)  $\nu$  (cm<sup>-1</sup>): (stretch of O-H) 3435-3600, (C-H aliphatic) 2981-2939, (C=O) 1734, (C=C stretching of aromatic ring) 1671-1520, (stretch of C-N) 1330, (out-of-plane C-H bending of benzene) 744. <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS, 300 MHz)  $\delta$  (ppm): (aromatic C-H) 6.50-8, (O-H) 1.

## RESULTS AND DISCUSSION

### Synthesis of Copolymers I-III

The presence of oxirane group in GMA polymers and copolymers favours further chemical modification for various applications [12]. GMA has higher reactivity ratio relative to other alkyl acrylate monomers [13]. Monomer of GMA was homopolymerized and copolymerized with methyl methacrylate (MMA), ethylacrylate (EA) and ethyl methacrylate (EMA) by free radical polymerization in solution. The resulting polymers are soluble in polar aprotic solvents (e.g., dimethylformamide, dimethylsulphoxide) and chlorinated solvents (e.g., chloroform) but insoluble in solvents containing hydroxyl groups such as methanol and ethanol. We have succeeded in preparing polymers having side chains containing indole groups that affect the properties of the polymers. The IR and NMR spectra of the modified products show the indole reaction from (nitrogen-1) position.

### Copolymer Compositions

The assignment of the resonance peaks in the <sup>1</sup>H NMR spectrum leads to the accurate evaluation of the content of each kind of monomeric unit incorporated into the copolymer chains. The proton resonance of the methylenoxyl group in copolymer EMA, EA 4.00 ppm and the proton resonance of the methyloxyl group in copolymer MMA at 3.6 ppm and those of the epoxide group in GMA at 3.27, 2.88 and 2.7 ppm are clearly resolved. Let  $m_1$  be the mole fraction of GMA and  $m_2$  be that of the other

monomer. GMA containing 3 epoxide protons and EMA, EA contains 2 methylenoxyl protons and MMA contains 3 methyloxyl protons. The following expression is used to determine the composition of copolymer I. Table 2 gives mole fractions of GMA and the related comonomer in the copolymers.

$$\frac{\text{Integrated peak area of } 2.7-3.27 \text{ ppm}}{\text{Integrated peak area of } 3.6 \text{ ppm}} = \frac{3m_1}{3m_2}$$

The following expression is used to determine the composition of copolymers II and III.

$$\frac{\text{Integrated peak area of } 2.7-3.27 \text{ ppm}}{\text{Integrated peak area of } 4.00 \text{ ppm}} = \frac{m_1/3}{m_2/2}$$

### Characterization of Copolymers I-III Before and After Modification With Indole

#### Infrared Spectra

The asymmetrical and symmetrical stretchings due to the methyl and methylene groups (I-III) are observed at 2995 and 2939 cm<sup>-1</sup>. The band at 1750 cm<sup>-1</sup> is attributed to the ester carbonyl stretching of comonomers MMA, EA and EMA units. Another band seen at 905 cm<sup>-1</sup> is due to the asymmetric stretching of the epoxy group. The bands at 1174.65 and 1249.6 cm<sup>-1</sup> are attributed to the ester C-O stretching of GMA and comonomers MMA, EA and EMA units.

In order to study the modification of GMA polymers by infrared spectroscopy, the peak at 905 cm<sup>-1</sup> corresponding to the C-O bond of the epoxy ring was selected as the most suitable wavenumber [14,15] (Figure 1a). Partial modification of the copolymers is confirmed by the infrared spectrum (Figure 1b). The absorbance intensity is substantially diminished at 905 cm<sup>-1</sup>, whereas a broad band appears between 3200 and 3700 cm<sup>-1</sup>, indicating alcohol formation, C-H aromatic appears in 3057 cm<sup>-1</sup> and band in 1330 cm<sup>-1</sup> corresponding to C-N bond. The infrared spectra of the modified products show the broad bands characteristic of the hydroxyl groups at wavenumber 3200 and 3700 cm<sup>-1</sup>, which is the indication of ring opening reaction. A decrease in the epoxide absorbance at 905 cm<sup>-1</sup> is clearly observed.

### <sup>1</sup>H NMR Spectra

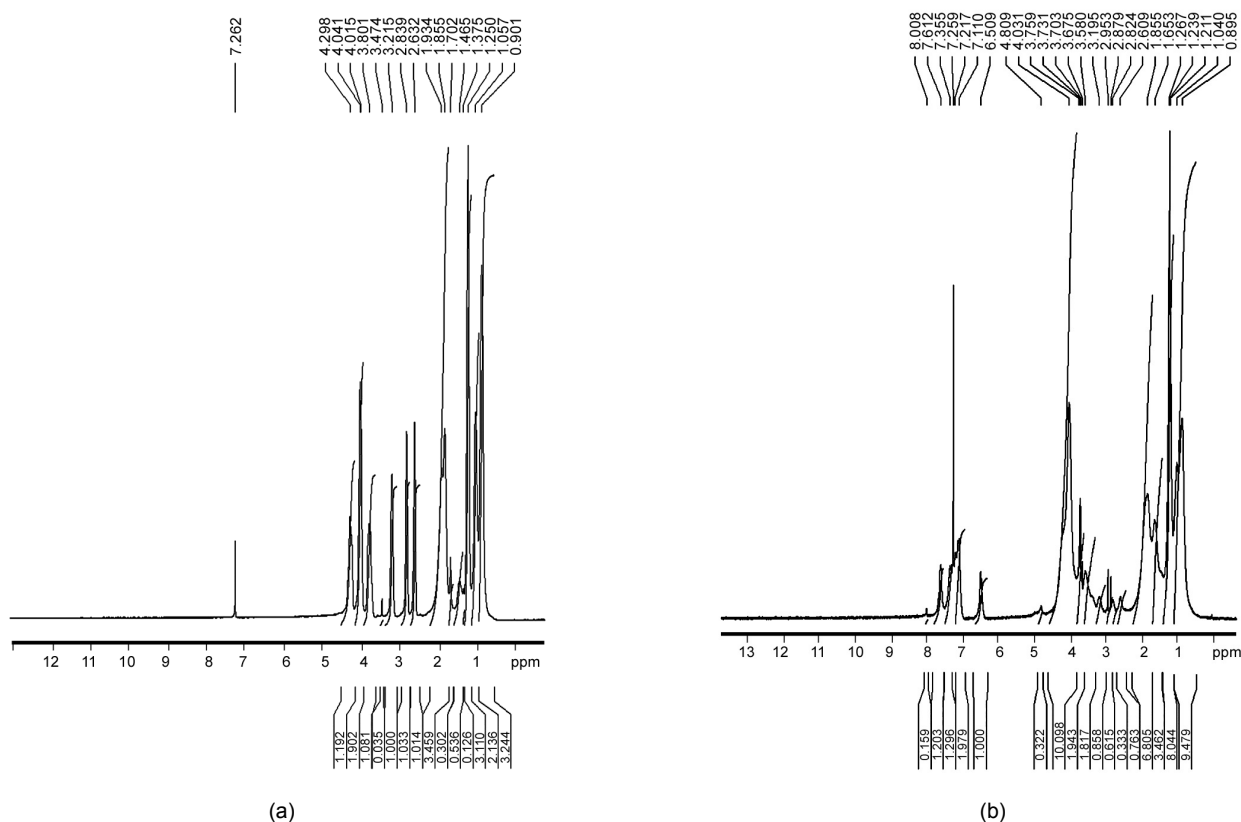
<sup>1</sup>H NMR Spectra of copolymers I-III show two signals at 4.31 and 3.79 ppm due to the splitting of methylene protons in the CH<sub>2</sub>O- group attached to the carbonyl group of the GMA group. The peak at 3.22 ppm is due to the methyne proton of epoxy group. The methylene protons of the epoxy group show signals at 2.64 and 2.85 ppm. The resonance signal at 3.60 ppm was attributed to three methyl protons of COOCH<sub>3</sub> in copolymers MMA.

The broad signal at 0.89-1.89 ppm was due to the methylene groups of backbones and other alkyl groups. Three well-defined peaks, corresponding to the epoxy groups, which appear between 2.64 and 3.22 ppm, were used as references to follow the GMA polymer modification [16-19]. For example <sup>1</sup>H NMR spectra of copolymer (EMA-co-GMA) is shown in Figure 2a. The <sup>1</sup>H NMR Spectra of the pure and modified polymers show the epoxy groups (2.64-3.22 ppm) which are well-defined peaks in the unmodified polymers but decrease after modification.

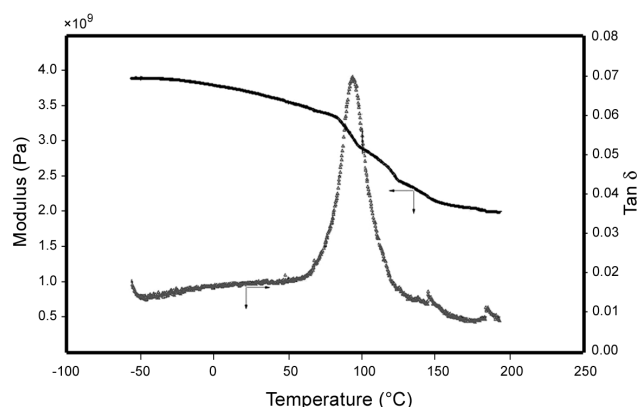
According to these results, part of epoxy groups was modified and created random polymers. The peaks at 3.58-4.27 ppm are due to the methyne proton attached to alcohol group and methylene protons in the CH<sub>2</sub>O- group attached to the carbonyl group of the GMA group and protons in the CH<sub>2</sub>- group attached to the indole group of GMA group. The peak at 6.509-8.1 ppm is due to the indole protons (Figure 2b).

### DMTA Analysis

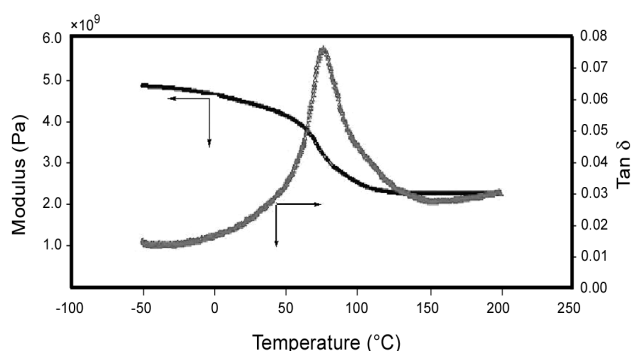
The T<sub>g</sub> of polymers were determined by dynamic mechanical thermal analysis (DMTA) as it is shown in Table 2. All the synthesized polymers that show a single T<sub>g</sub> are due to the absence of block copolymer. Study of thermal properties of the obtained polymers by DMTA curves showed that, T<sub>g</sub> of the acrylate sample (including EA) is increased after the reaction with indole. This may be attributed to the stiff aromatic rings as well as the possibility of hydrogen-bonding formation of OH groups created after the indolization (H-bonding of OH with the adjacent



**Figure 2.** <sup>1</sup>H NMR Spectra of poly(EMA-co-GMA): (a) before reaction and (b) after reaction with indole.



(a)



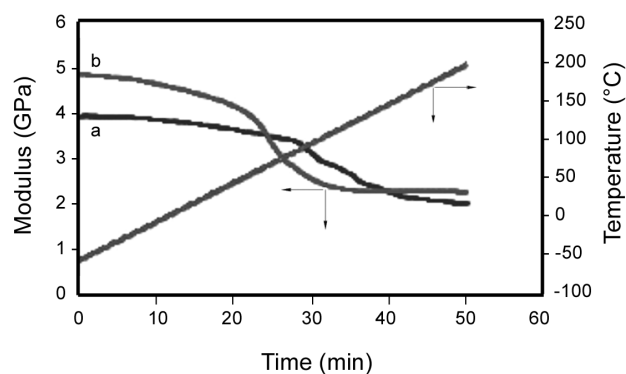
(b)

**Figure 3.** DMTA Curves of poly(EMA-co-GMA): (a) before reaction and (b) after reaction with indole.

chain functional groups of O-H and C=O).

Conversely,  $T_g$  of methacrylate samples (including MMA and EMA) is decreased after the reaction with indole. It can be partially related to the steric hindrance of the methyl groups in samples  $I_{in}$  and  $III_{in}$ . The presence of  $CH_3$  groups on the main chain disfavours the H-bonding formation. In the first stage, the molecular chains start to move freely, and the modulus decreases rapidly to 3 GPa at 50°C.

The modulus of sample III is increased after the reaction with indole, which is due to the presence of macromolecular chains. Its modulus is changed to 4 GPa at 50°C after modification which is due to a high range of stiffness. The sample modulus after its glass temperature is nearly identical before and after the reaction with indole. Because beyond  $T_g$  point, the polymer softens and the identity of polymer before and after modification is the same. Thus, there is not any expectation for reasonable change in the modulus. The modulus curve versus



**Figure 4.** Modulus (GPa) versus time (min) for poly(EMA-co-GMA): (a) before reaction and (b) after reaction with indole.

time (min) for poly(EMA-co-GMA) is shown in Figure 5.

## CONCLUSION

In recent years, polymers based on glycidyl methacrylate have received increasing attention owing to their versatile applications. Indole derivatives are important heterocyclic compounds and have wide applications in medicinal chemistry. Novel polymers containing indole as an electron donor group were synthesized for first time. The present paper reports the synthesis, spectroscopic and thermal characterization of glycidyl methacrylate polymers and copolymers containing very bulky indole substituent as side chains. The GMA copolymers with methyl methacrylate (MMA), ethyl methacrylate (EMA) and ethyl acrylate (EA) were prepared by radical polymerization. GMA Copolymers containing epoxy side groups have been modified with indole groups. In these cases, parts of the epoxy groups are brought into reaction. Such a dramatic reactivity fall is likely due to the close proximity of the epoxy groups, which leads to a close packing of moieties.

## ACKNOWLEDGEMENT

The authors thank the Islamic Azad University of Ardabil Branch for technical supports during this research.

## REFERENCES

1. Kala J, Svec F, Marousek V, Reaction of epoxide groups of glycidyl methacrylate copolymers, *J Polym Sci Polym Symp*, **47**, 155-166, 1974.
2. Navarro-Rodriguez D, Rodriguez-Gonzalez FJ, Romero-Garcia J, Jimenez-Regalado EJ, Guillon D, Chemical modification of glycidyl methacrylate polymers with 4-hydroxy-4'-methoxy biphenyl groups, *Eur Polym J*, **34**, 1039-1045, 1998.
3. Kenawy E-L, Biologically active polymers. IV: Synthesis and antimicrobial activity of polymers containing 8-hydroxyquinoline moiety, *J Appl Polym Sci*, **82**, 1364-1374, 2001.
4. Muscatello MMW, Asher SA, Poly(vinyl alcohol) rehydratable photonic crystal sensor materials, *Adv Funct Mater*, **18**, 1186-1193, 2008.
5. Bandgar BP, Patil AV, Fluoroboric acid adsorbed on silica gel catalyzed regioselective ring opening of epoxides with nitrogen heterocycles, *Tetrahed Lett*, **48**, 173-176, 2007.
6. Kotsuki H, Hayashida K, Shimanouchi T, Nishizawa H, High pressure organic chemistry. 19: High-pressure-promoted, silica gel-catalyzed reaction of epoxides with nitrogen heterocycles, *J Org Chem*, **61**, 984-990, 1996.
7. Heaney H, Ley SV, 1-Benzylindole, *Org Syn*, **54**, 58, 1974. <http://www.orgsyn.org/orgsyn/prep.asp?prep=cv6p0104>.
8. Mokhtar SM, Mostafa TB, Hewedy MA, Chemical induced grafting of indole onto chitin & chitosan -and their antimicrobial activity, *Aust J Basic Appl Sci*, **4**, 3268-3279, 2010.
9. Nie G, Zhou L, Guo Q, Zhang S, A new electrochromic material from an indole derivative and its application in high-quality electrochromic devices, *Electrochem Commun*, **12**, 160-163, 2010.
10. Mispa KJ, Subramaniam P, Murugesan, Synthesis and characterization of polyindole/ZnO nanocomposites, *Int J Nanotechnol Appl*, **4**, 147-152, 2010.
11. Babazadeh M, Thermal stability and high glass transition temperature of 4-chloromethyl styrene polymers bearing carbazolyl moieties, *Polym Degrad Stab*, **91**, 3245-3251, 2006.
12. Safa KD, Hassanpour A, Nasirtabrizi MH, Tofangdarzadeh S, Synthesis and characterization of glycidyl methacrylate polymers containing tris(trimethylsilyl)methyl groups, *Iran Polym J*, **17**, 39-47, 2008.
13. Bakhshi H, Zohuriaan-Mehr MJ, Bouhendi H, Kabiri K, Emulsion copolymerization of butyl acrylate and glycidyl methacrylate: determination of monomer reactivity ratios, *Iran Polym J*, **19**, 781-789, 2010.
14. Horak D, Straka J, Stokr J, Schneider B, Tennikova TB, Svec F, Reactive polymers. 61: Reaction of macroporous poly(glycidyl methacrylate-co-ethylene dimethacrylate) with phenol, *Polymer*, **32**, 1135-1139, 1991.
15. Safa KD, Hassanpour A, Nasirtabrizi MH, Mosaei UO, Synthesis and reactions of [tris(trimethylsilyl)methyl] ethyl dichlorosilane, *J Organomet Chem*, **690**, 1606-1611, 2005.
16. Safa K, Eram H, Nasirtabrizi MH, Chemical modification of some 4-chloromethylstyrene polymers with highly sterically hindered tris(trimethyl silyl)methyl groups, *Iran Polym J*, **15**, 249-257, 2006.
17. Safa KD, Nasirtabrizi MH, One-pot, novel chemical modification of glycidyl methacrylate copolymers with very bulky organosilicon side chain substituents, *Eur Polym J*, **41**, 2310-2319, 2005.
18. Podkościelna B, Synthesis, modification, and porous properties of new glycidyl methacrylate copolymers, *J Appl Polym Sci*, **120**, 3020-3026, 2011.
19. Abdyev O, Radical copolymerization of glycidyl methacrylate and carbonyl-containing phenyl methacrylates, *Polym Sci Ser B*, **53**, 278-282, 2011.