A New Type of Poly(GMA) with Carbazole: Synthesis and Characterization

Yeni Tip Karbazollü Poli(GMA): Sentezi ve Karakterizasyonu

Research Article

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ABSTRACT

The synthesis, characterization and thermal behaviour of styrenic copolymers of glycidyl methacrylate without and with carbazole groups are reported. The copolymers based on glycidyl methacrylates belong to the potential class of functional polymers. Epoxide ring opening reaction is a route that explains the chemical modification of glycidyl methacrylate (GMA) polymers with nucleophilic reagent containing hydroxyl, carboxyl or amine groups. In this work, copolymers of GMA have been modified by incorporation of bulky carbazole groups.The homopolymer of glycidyl methacrylate (GMA) and its random copolymers with styrene , methyl styrene, methoxy styrene were synthesized by free radical polymerization using azobis(isobutyronitrile) (AIBN) as initiator at 70±1°C. The polymers were characterized by ^{1}H-NMR and IR spectroscopic techniques. This modification increases the rigidity of polymers and, subsequently, their glass transition temperature of polymer as shown by DMTA analysis. The results show that, with the incorporation of the carbazole 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.

Key Words
Glycidyl methacrylate, Carbazole, Styrene, Ring opening, Modified polymer.

ÖZ

Karbazol grupları varlığında ve yokluğunda glisidil metakrilatın stirenik kopolimerlerinin sentezi, karakterizasyonu ve ısıl davranışları rapor edilmiştir. Glisidil metakrilat temelli kopolimerler fonksiyonel polimerler sınıfına aittir. Epoksit halka açma tepkimesi, hidroksil, karboksil veya amin grupları içeren nükleofilik reaktif ile glisidil metakrilat (GMA) polimerlerinin kimyasal modifikasyonunu açıklayan bir yoldur. Bu çalışmada, GMA kopolimerleri büyük karbazol gruplarının birleşmesiyle modifiye edilmiştir. Glisidil metakrilat (GMA) homopolimeri ve stiren, metil stiren, metoksi stirenli rasgele kopolimerler 70±1°C'da başlatıcı olarak azobis(izobütironitril) (AIBN) kullanılarak serbest radikal polimerizasyonu ile sentezlendi. Polimerler, ^{1}H-NMR ve IR spektroskopik teknikleriyle karakterize edildi. Bu modifikasyon, polimerlerin sertliğini ve ardından DMTA analizi ile gösterilen polimerlerin camsı geçiş sıcaklığını arttırır. Sonuçlar, karbazol gruplarının polimer yan zincirlerine dahil edilmesi ile, polimer endüstrisinde bazı uygulamalar bulabilen yeni özelliklere sahip bir dizi yeni modifiye edilmiş polimer elde edildiğini göstermektedir.

Anahtar Kelimeler
Glisidil metakrilat, Karbazol, Stiren, Halka açılması, Modifiye polimer.

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INTRODUCTION

2,3-Epoxypropyl methacrylate or glycidyl methacrylate (GMA) is a fascinating monomer exhibiting polymarizable methacrylic unsaturation and an oxiran function of potential reactivity [1]. Copolymers based on glycidyl methacrylate (GMA) have applications in biological drugs and biomolecules and in electronics as negative electron-beam resists materials [2]. Due to the reactive nature of the epoxy group, copolymers containing GMA have led to an interesting class of new materials.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 [3]. This monomer has been homopolymerized and copolymerized by means of free radical initiators known to selectively attack methacrylic double bonds.There already exist examples of some interesting polymers that are modified by carbazole groups [4-6]. Carbazole is well-known hole– transporting and electroluminescence (EL) unit. Polymers containing carbazole moieties in the main chain or side chain have attracted much attention because of their unique properties, which allow various optoelectronic applications such as photoconductive, EL and photoreactive material [7-10] . Present research work describes the novel synthesis and properties of poly (GMA) and copolymers of GMA modified with carbazole. The glass transition temperature (T_g) is an important intrinsic characteristic that influences the material properties of a polymer and its potential applications. Furthermore, polymers with high glass-transition temperatures are attractive for industrial polymer science because of strong economic rewards that may arise from their potential applications [11]. Study of thermal properties of the obtained polymers show that incorporation of bulky carbazole groups as side chains leads to stiffness of the polymer chains with increasing of thermal stability and glass transition temperature [12]. Chemical modification of polymer structures is an important method formodification of polymer properties such as mechanical, thermal and surface properties. A few numbers of polymers with pendant carbazolyl groups have been prepared [13].

As we know, there is no information about incorporation of the carbazole group to glycidyl methacrylate polymer.

EXPERIMENTAL

Instrument

The infrared spectra were recorded on Bruker spectrometer scientific 500 IR. ^{1}H-NMR spectra were run on a Bruker 300 MHz spectrometer at room temperature using chloroform-d as solvent and TMS as internal standard. Dynamic mechanical thermal analysis (DMTA) were characterized by Triton (Tritec 2000 DMN) with rate 5°C/min.

Materials

Carbazole obtained from Aldrich chemical company. Azobis(isobutyronitrile) (AIBN)was purchased from Merck and purified by recrystallization from absolute ethanol. Styrene, methyl styrene, methoxy styrene and glycidyl methacrylate (GMA) were obtained from Merck and distilled under reduced pressure to remove inhibitors before use. Sodium hydride (60%) obtained from Aldrich chemical company. Tetrahydrofuran (THF) was distilled over sodium/ benzophenone.

Polymerization of Glycidyl Methacrylate

To a solution of glycidyl methacrylate (5.6 g , 40 mmol) in 15 mL chloroform was added (0.065 g, 0.4 mmol) AIBN. Polymerization studies were carried out for 24h at 70°C whilestirring under a nitrogen atmosphere. Polymer solution were poured drop wise into a large excess of methanol. The obtained polymer were purified by precipitating twice from chloroform into methanol. Polymer were filtered and dried under vacuum at room temperature (Figure 1).

Synthesis of Copolymers(I-III)

Poly(GMA-co-St) (I), Poly(GMA-co-Metyl St) (II) and Poly(GMA-co-Metoxy St) (III) have been synthesized as a general method using1.04 g (10 mmol) of styrene(I) or (1.19 g, 10 mmol) of methyl styrene(II) or 1.35 g (10 mmol) of 4-methoxystyrene. Also, a mixture of 4.26 g (30 mmol) of GMA and 0.065 g (0.4 mmol) of AIBN in 20 mL of tetrahydrofouran (THF). The reaction mixture was heated to 70±1°C with constant stiring under a nitrogen atmosphere. The reaction conditions were maintaind for 24h.

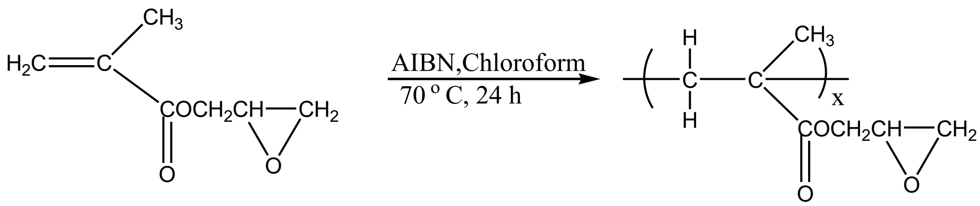


Figure 1. Polymerisation reaction of glycidyl methacrylate.

Polymer solutions were poured dropwise into a large excess of methanol. The obtained polymer was purified by precipitating twice into methanol. Polymer were filtered and dried under vacuum at room temperature. The reaction conditions are shown in Table 1 and Figure 2.

^{1}H- NMR and FT-IR Spectra of Polymers I-III.

I. FT- IR (KBr) ν cm^{-1}: 3438, 3060, 2943, 1727, 1633, 1602,1452, 1388, 1341, 1261, 1127, 994.1087, 906. ^{1}H-NMR ($CDCl_3$, TMS, 250 MHz) ppm: 1.08-1.94 (3H), 1.90-1.97 (2H), 2.64 (m, 1H), 2.83 (m, 1H), 3.23 (m, 1H), 3.85 (m, 1H), 4.25 (m, 1H).

II. FT-IR (KBr) ν cm^{-1}: 3046 (w), 2944 (s), 2986 (w), 1720(s), 1478 (s), 1327 (w), 1255(m), 1153 (s), 905 (w).

^{1}H-NMR ($CDCl_3$, TMS, 250 MHz) δ ppm: 0.92-1.10 (9H), 1.25-1.60 , 1.60-1.72 (m, 4H), 1.85-1.94 (4H), 2.63 (m, 1H), 2.83 (m, 1H), 3.21 (m, 1H), 3.75 (m, 1H), 4.30 (m, 1H), 4.00 (s, 2H).

III. FT-IR (KBr) ν cm^{-1}: 3046(w), 2986 (s), 2938 (s), 1720 (s), 1478 (m), 1327 (w), 1255 (m), 1153 (s), 905 (w).

^{1}H-NMR ($CDCl_3$, TMS, 250 MHz) δ ppm: 0.88-1.05 (6H), 1.46-1.90 (s, 4H), 2.64 (m, 1H), 2.84 (m, 1H), 3.22 (m, 1H), 3.79 (m, 1H), 4.31 (m, 1H), 3.60 (s, 3H).

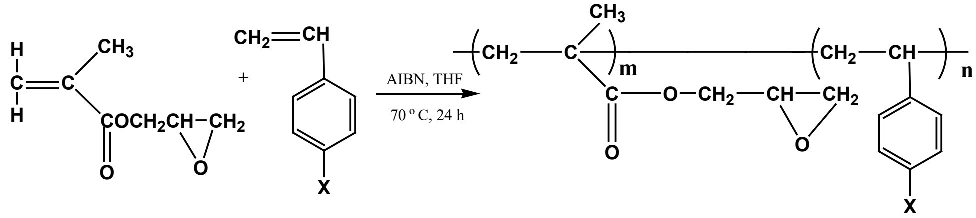
Attachment of Carbazolyl Group to the Side Chain of Homopolymer and Copolymers

Sodium hydride (60 mmol, 1.44 g) was slowly added to carbazole (60 mmol, 10.14 g) dissolved in 10mL of THF at room temperature mixture stirring under nitrogen atmosphere for 30 min. After this time, mixture was cooled to -5°C in ice-salt mixture while vigorous stirring. Then a solution of polymer I (7.8 g, with 30 mmol of epoxide containing monomer unit) or II (7.6 g, with 30 mmol of epoxide containing monomer unit) or III (8.2 g, with 30 mmol of epoxide containing monomer unit) in 20 ml of dry THF was added drop wise within 1 h. The contents were kept at ambient temperature for another 3 h while stirring. The

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

Sample	Monomer1	Monomer2	Amount of Monomer1 (mmol)	Amount of Monomer2 (mmol)	Time (h)
I	GMA	St	30	10	24
II	GMA	Metyl-St	30	10	24
III	GMA	Metoxy-St	30	10	24

[AIBN]= 100 , [1]+[2]/ [AIBN]= 0.04 /[1]+[2]



Copolymer	I	II	III
X	H	CH_3	CH_3O

Figure 2. Polymerisation reaction of Glycidyl methacrylate and styrene.

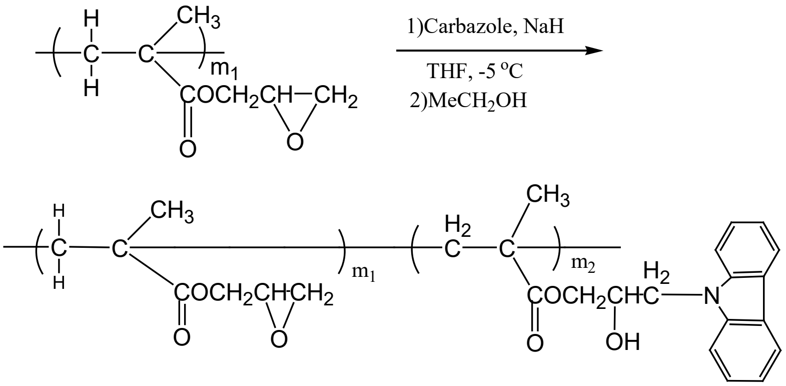
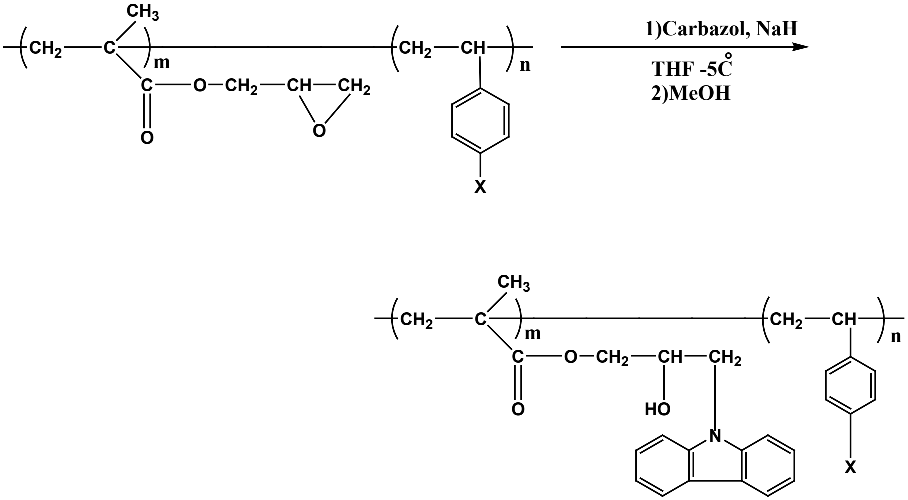


Figure 3. Carbazolyl attachment to the poly(glycidyl methacrylate).



Copolymer	I	II	III
X	H	CH_3	CH_3O

Figure 4. Carbazolyl attachment to the poly(glycidyl methacrylate-styrene).

mixture were then poured drop wise into a large excess of cold ethanol. The precipitated solid was recovered by filtration, washed successively with water, ethanol, and then dried in vacuum at room temperature for 28 h. The reaction conditions are shown in Figures 3 and 4.

^{1}H- NMR and FT-IR Spectra of Polymers I with Carbazole-III with Carbazole.

I. FT-IR (KBr) ν cm^{-1}: 3160-3620 (br), 3040 (w), 2986 (m), 2938 (m), 1720 (s), 1478 (s), 1327 (m), 1255 (m), 1153 (s), 905 (w). ^{1}H-NMR ($CDCl_3$, TMS, 250 MHz) ppm: 1.08-1.94 (3H), 1.90-1.97 (2H), 2.64 (m, 1H), 2.83 (m, 1H), 3.50-4.25 (5H), 6.92-8.03 (8H).

II. FT-IR (KBr) ν cm^{-1}: 3250-3610 (br), 3040 (w), 2943 (s), 2858 (w), 1721 (s), 1326 (m), 1253 (m), 1156 (s). ^{1}H-NMR ($CDCl_3$, TMS, 250 MHz) δ ppm: 0.92-1.10 (9H), 1.25-1.60, 1.60-1.72 (m, 4H), 1.85-1.94 (4H), 2.63 (m, 1H), 2.83 (m, 1H), 3.21 (m, 1H), 3.75- 4.30 (5H), 4.00 (s, 2H), 6.62-8.03 (8H).

III. FT-IR (KBr) ν cm^{-1}: 3150-3640 (br), 3040 (w), 2986 (m), 2938 (s), 1720 (s), 1327 (m), 1255 (s), 1153 (s). ^{1}H-NMR ($CDCl_3$, TMS, 250 MHz) δ ppm: 0.88-1.05 (6H), 1.46-1.90(s, 4H), 2.64 (m, 1H), 2.84 (m, 1H), 3.22 (m, 1H), 3.60 (s, 3H), 3.75-4.30 (5H), 6.62-8.03 (8H).

RESULTS and DISCUSSION

The presence of oxirane group in GMA polymers and copolymers favours futher chemical modification for various application [12]. Monomer of GMA was homopolymerized and copolymerized with styrene , methyl styrene, methoxy styrene by free radical polymerization in solution. The chemical structure of the related polymers are represented in Figures 5 and 6. The resulting polymers are soluble in polar aporotic solvents (e.g. dimethyl formamide, dimethyl sulphoxide, tetrahydrofuran) and chlorinated solvents (e.g. chloroform, and methylene chloride) but insoluble in hydrocarbons (e,g. benzene, toluene, xylenes) an solvents containing hydroxyl groups such as methanol, ethanol and 2-propanol. The presence of the epoxy group in GMA leads to modification of poly (GMA) and copolymers for various applications. But here, we have succeeded in preparing polymers having side chains containing carbazole groups the strongly affect the properties of the polymers. The assignment of the resonance peaks in the ^{1}H NMR spectrum leads to the accurate evaluation of the content of each kind of monomeric unit incorporated into the copolymer chains.

Characterization of homopolymer and copolymers I-III before and after of modification with carbazole

Infrared spectra

The asymmetrical and symmetrical stretching due to the methyl and methylene groups (I-III) are observed at 2986 and 2938 cm^{-1} . The band at 1720 cm^{-1} is attributed to the ester carbonyl stretching of GMA. Another band seen at 905 cm^{-1} is due to the asymmetric stretching of the epoxy group. The bands at 1153.1 and 1255.6 cm^{-1} is attributed to the ester C-O stretching of GMA units. To study the modification of GMA polymers by infrared spectroscopy, the peak at 905 cm^{-1} corresponding to the C-O bond of the epoxy ring was selected as the most suitable wave number (Figure 5a).

Partial modification of the copolymers is confirmed by the infrared spectrum (Figure 5b). The absorbance intensity is substantially diminished at 905 cm^{-1}, whereas a broad band appears between 3200 and 3700 cm^{-1}, indicating alcohol formation. Band in 1327 cm^{-1} corresponding to C-N band in carbazole, C-H aromatic appears in 3040.7 cm^{-1}. The infrared spectra of the modified products show the broad bands characteristic of the hydroxyl groups at wavenumber 3200 and 3700 cm^{-1}, which is indicative of the ring opening reaction. A decrease in the epoxide absorbance at 905 cm^{-1} is clearly observed (Figure 5b).

^{1}H NMR spectra

^{1}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_2O- group attached to the carbonyl group of the GMA group. The

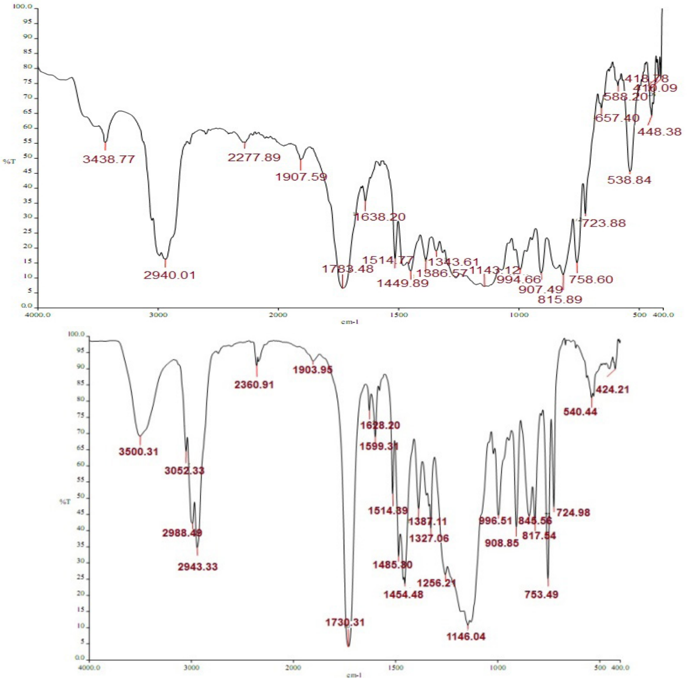


Figure 5. FTIR spectra of polymers.

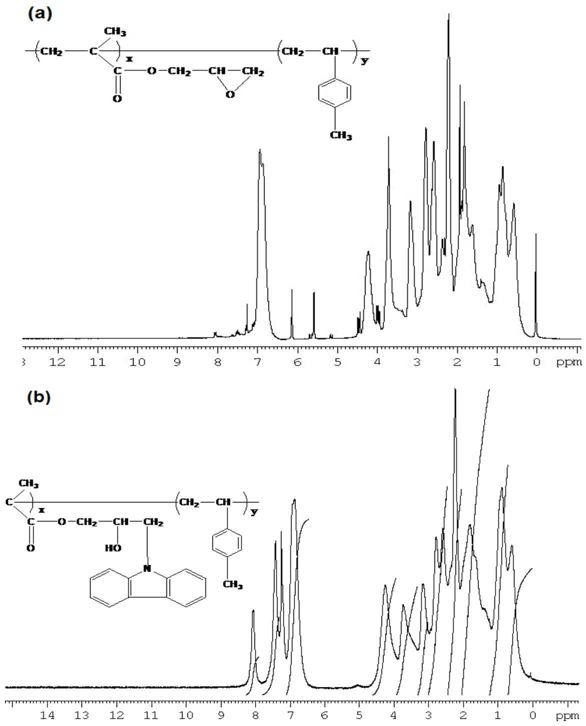


Figure 6. NMR spectra of polymers.

peack 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 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 δ =2.64 and δ =3.22 ppm were used as references to follow the GMA polymer modification (Figure 6a). The ^{1}H NMR spectra of the pure and modified polymers show the epoxy groups (δ =2.64-3.22 ppm), which are well defined in the unmodified polymers decrease after modification (Figure 6b).

DMTA curve

The Tg of polymers were determined by dynamic mechanical thermal analysis (DMTA). All the synthesized polymers show a single Tg showing the absence of formation of a mixture of homopolymer or the formation of a block copolymer.

DMTA scans show that the presence of bulky carbazole groups lead to an increase in the glass transition temperature from I-III copolymers. Study of thermal properties of the obtained polymers by DMTA curves showed that the incorporation of bulky carbazolyl groups as side chains leads to stiffness of the polymer chains and increase in glass transition temperature (Figure 7).

CONCLUSION

In recent years, polymers based on glycidyl methacrylate have received increasing attention owing to their versatile applications. The present paper reports the synthesis, spectroscopic and thermal characterization of glycidyl methacrylate polymers and copolymers containing very bulky carbazole substituents as side chains. The GMA homopolymer and its copolymers with styrene , methyl styrene, methoxy styrene were prepared by radical polymerization. GMA homopolymer and its copolymers containing epoxy side groups have been modified with the carbazole groups. In these cases, part of the epoxy groups are reacted. Such a dramatic reactivity decrease is likely due to the close proximity of the epoxy groups, which leads to a close packing of moieties. DMTA analyses have shown that, attachment of carbazole groups into the polymer structures causes dramatic increase in their Tg.

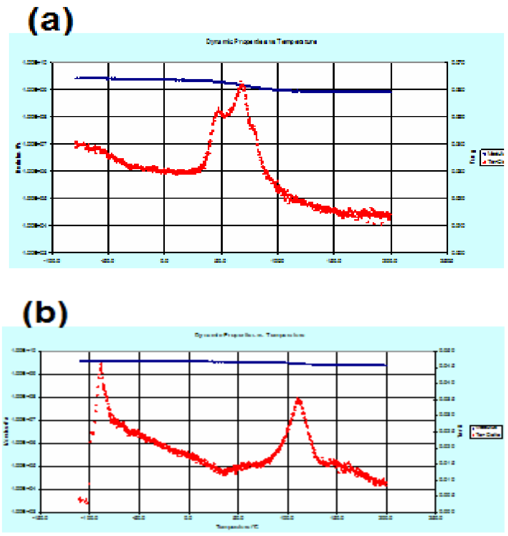


Figure 7. DMTA curves of polymers.

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