Synthesis, Characterization, and Thermal Behavior Study of Methyl Methacrylate Polymers Containing 4-Carbazole Substitutes

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ABSTRACT: A new polymerizable monomer, [4-(9-ethyl)-carbazolyl]methyl methacrylate (**2**), was synthesized by reacting of methacrylic acid and 4-hydroxymethyl-9-ethyl carbazole (**1**) by esterification procedure in the presence of N,N'-dicyclohexylcarbodiimide. The resulting monomer was then polymerized free-radically to form the poly (methyl methacrylate) containing 4-(9-ethyl)carbazolyl pendent groups. Also, copolymerization of monomer **2** with various acrylic monomers such as methyl methacrylate, ethyl methacrylate, methyl acrylate, ethyl acrylate, and *n*-butyl acrylate by azobisisobutyronitrile as a free radical polymerization initiator gave the related copolymers in high yields. The structure of all the resulted compounds was characterized and confirmed by FTIR and ^{1}H NMR spectroscopic techniques. The average molecular weight of the obtained polymers was determined by gel permeation chromatography using tetrahydrofurane as the solvent. The thermal gravimetric analysis and differential scanning calorimeter instruments were used for studying of thermal properties of polymers. It was found that, with the incorporation of bulky 4-(9-ethyl)carbazolyl substitutes in side chains of methyl methacrylate polymers, thermal stability and glass transition temperature of polymers are increased. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 4989–4995, 2006

Key words: 4-substituted carbazole; poly(methyl methacrylate); chemical modification; thermal stability; glass transition temperature

INTRODUCTION

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. For example, poly (methyl methacrylate) (PMMA) is a transparent polymeric material possessing many desirable properties, such as light weight, high light transmittance, chemical resistance, colorlessness, resistance to weathering corrosion, and good insulating properties.[1] The glass transition temperature of PMMA, however, is relatively low at about 100°C, which limits its applications in the optical-electronic industry, for materials such as compact discs (CDs), optical glasses, and optical fibers, because it undergoes distortion when used in an inner glazing material.[2,3] To raise T_g, the incorporation of rigid or bulky substituents in structure of PMMA has been widely reported.[4–6]

Carbazole-derived monomers and polymers have been extensively studied for their good photoconductive properties.[7,8] Properties of these materials such as good optical photoreactive and charge transporting combined with ease of processing have simulated a tremendous amount of new researches in different areas of material science.[9] The synthesis of some carbazole-containing methacrylate polymers, except the 4-substitued carbazole methacrylate, and studying of their properties have been reported in some articles.[10–12]

Previous articles about synthesis and study of the modified properties of various polymers containing highly sterically hindered tris(trimethylsilyl)methyl substituent showed that, incorporation of very bulky organosilyl groups into polymer structures leads to an increase in T_g and creates macromolecules with novel architecture that could be used as membranes for gas or fluid separation.[13–16]

This present research work firstly describes the synthesis of [4-(9-ethyl)-carbazolyl)]methyl methacrylate (**2**) as a new methyl methacrylate derivative monomer. Then, monomer **2** was homopolymerized and copolymerized with some methacrylic and acrylic monomers by the free radical polymerization method. Study of thermal properties of the obtained polymers showed that the incorporation of bulky 4-sustituted carbazole groups as side chains leads to stiffness of the polymer chains with increasing of thermal stability and glass transition temperature.

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EXPERIMENTAL

Instruments

The infrared spectra were recorded on a Bruker Spectrometer Tensor 27 FTIR. ^{1}H NMR spectra were run on a Bruker 400 MHz spectrometer at room temperature using $CDCl_3$ as a solvent. Elemental analysis was carried out with a Heareus CHN-ORAPID instrument. The molecular weights (M_w and M_n) were determined using a Waters 501 gel permeation chromatograph fitted with 10^2 and 10^3 Waters Styragel columns. THF was used as elution solvent and polystyrene standards employed for calibration. Thermal properties were characterized by thermal gravimetric analyses (TGA, TA2050) and differential scanning calorimeter (DSC, TA2010) instruments at a heating rate of 10°C/min. The T_gs were taken at the midpoints of the heat flow changes.

Materials

The radical initiator of azobisisobutyronitrile (AIBN) was purchased from Merck (Darmstadt, Germany) and purified by recrystallization from absolute ethanol. Methacrylic acid (MAA), methyl methacrylate (MMA), ethyl methacrylate (EMA), ethyl acrylate (EA), and *n*-butyl acrylate (BA) were obtained from Merck and distilled under reduced pressure to remove inhibitors before use. Methyl acrylate (MA) was obtained from Merck, distilled at atmospheric pressure, and freshly used in polymerization. *N,N*-dimethylformamide (DMF, Merck) was dried over anhydrous $MgSO_4$ for 2 days and later with phosphoric anhydride overnight. After drying, DMF was distilled under reduced pressure. *N,N'*-dicyclohexylcarbodiimide (DCC) was purchased from Merck and used as received. All other chemicals were of reagent grade or purer.

Synthesis of 4-hydroxymethyl-9-ethyl carbazole (1)

This compound was prepared according to the described method by Keyanpour-Rad[17–19] via microwave-assisted synthesis of 1-chloro-4-carboxy-5,6,7,8-tetrahydrocarbazole followed by further steps, such as reduction of the 4-substituted methyl carboxylate and dechlorination of the ring. The preparation route of compound **1** is shown in Figure 1.

Synthesis of monomer [4-(9-ethyl)carbazolyl]methyl methacrylate (2)

A solution of 6.20 g (30 mmol) of DCC in 40 mL of DMF was added dropwise at −20°C to a solution of 2.60 g (30 mmol) of MAA dissolved in 50 mL of DMF. Then, a solution of 6.75 g (30 mmol) of compound **1** in 20 mL of DMF was added dropwise to the mixture at −20°C. The reaction mixture was slowly returned to room temperature and stirred for 12 h. The white precipitation of dicyclohexylurea was filtered and the solvent evaporated in vacuum. The oily residue was purified by T.L.C. chromatography (silica gel, chloroform as eluent) to yield 61% of monomer **2**. FTIR (neat film, cm^{-1}): 3060 (C—H aromatic), 2960 (C—H aliphatic), 1725 (C=O), 1630 (C=C vinyl), 1600, 1470 (C=C aromatic), 1320 (C—N); ^{1}H NMR (CDCl$_3$ with tetramethylsilane, ppm): 1.5 (t, 3H, N—C—CH$_3$), 2.1 (s, 3H, C=C(CH$_3$)), 4.6 (q, 2H, N—CH$_2$), 5.7 (s,1H, C=CH$_2$), 6.0 (s, 2H, CH$_2$—O), 6.2 (s, 1H, C=CH$_2$), 7.5–8.5 (m, 7H, Ar-H). Elemental analysis for C$_{19}$H$_{19}$NO$_2$ (293) (%): calcd. C 77.79, H 6.53, N 4.77; found: C 77.68, H 6.48, N 4.82.

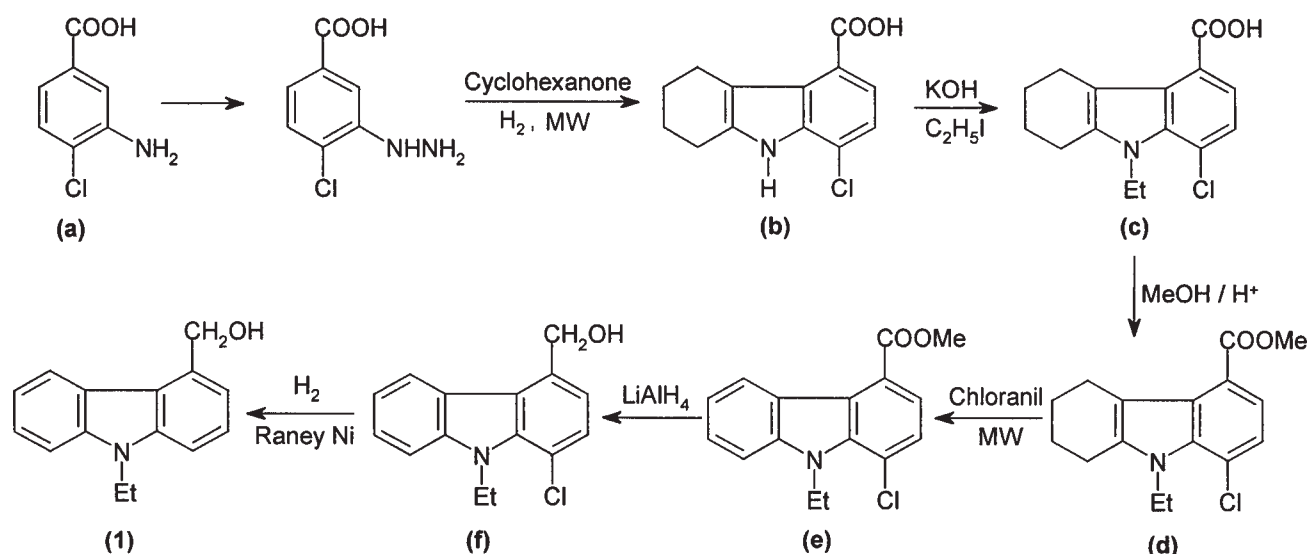**Figure 1** The preparation route of 4-hydroxymethyl-9-ethyl carbazole.[19]

Copolymer	Monomer	[Monomer] (mmol)	Comonomer	[Comonomer] (mmol)	Time (h)	Yield (%)
I	2	10	MMA	30	20	83
II	2	10	EMA	30	20	82
III	2	10	MA	30	20	86
IV	2	10	EA	30	20	72
V	2	10	BA	30	20	81

Polymerization of monomer 2 to obtain P2

In a Pyrex glass ampoule, a mixture of 2.90 g (10 mmol) of monomer **2** and 0.033 g (0.2 mmol) of AIBN was dissolved in 10 mL of DMF. The ampoule was then degassed, sealed under vacuum, and shaken in a thermostatic water bath at (70 ± 1)°C by a shaker machine for 12 h. After this time, the viscous solution was poured into 150 mL of cooled methanol as nonsolvent. The white precipitated poly(4-(9-ethyl)carbazolyl)-methyl methacrylate (**P2**) was collected, washed with methanol several times, and dried in vacuum at room temperature to give 2.2 g (76%) of **P2**. FTIR (KBr, cm^{-1}): 3060 (C—H aromatic), 2960 (C—H aliphatic), 1730 (C=O), 1600, 1470 (C=C aromatic), 1330 (C—N); ^{1}H NMR (CDCl$_3$ with tetramethylsilane, ppm): 0.8–2.0 (8H, CH$_3$ of ethyl group and CH$_2$—C(CH$_3$)), 4.2 (2H, CH$_2$—N), 5.5 (2H, CH$_2$—O), 7.1–8.2 (7H, aryl-H).

Copolymerization of monomer 2 with different monomers: General procedure

Poly(2-*co*-MMA) (**I**), poly(2-*co*-EMA) (**II**), poly(2-*co*-MA) (**III**), poly(2-*co*-EA) (**IV**), and poly(2-*co*-BA) (**V**) were separately synthesized as follows. In a Pyrex polymerization tube, 2.9 g (10 mmol) of monomer **2** and 0.065 g (0.4 mmol) of AIBN were dissolved in 15 mL of DMF. Then 3 g (30 mmol) of MMA or 3.42 g (30 mmol) of EMA or 2.58 g (30 mmol) of MA or 3 g (30 mmol) of EA or 3.84 g (30 mmol) of BA was added to the tube and the mixture was flushed with argon for 20 min. Each tube was sealed under vacuum, immersed in a thermostated water bath maintained at (70 ± 1)°C, and shaken vigorously by a shaker for 20 h. Pouring of the solution into excess cooled methanol precipitated the polymer. The precipitated polymer was filtered off and purified by reprecipitation. Finally, the obtained copolymers were dried under vacuum in room temperature for 24 h. The yields of the obtained copolymers are presented in Table I.

RESULTS AND DISCUSSION

Synthesis of compound 1

As reported in the literature[19] and shown in Figure 1, the commercial *p*-chloro-*m*-aminobenzoic acid was treated with sodium nitrile to form the related diazonium salt, which reduced by sulfur dioxide *in situ* to form compound **a**. The compound **c** was synthesized by treatment of **b** with KOH and followed by the addition of ethyl iodide. This compound was esterified by methanol to obtain compound **d**, which was aromatized by microwave irradiation in dry condition, using chloranil as the oxidizing agent. Reduction of compound **e** by LiAlH$_4$ gave compound **f**, which in turn was dechlorinized with Raney nickel to give compound **1**. The aromatization of **d** to **e** was performed according to the microwave method.[18]
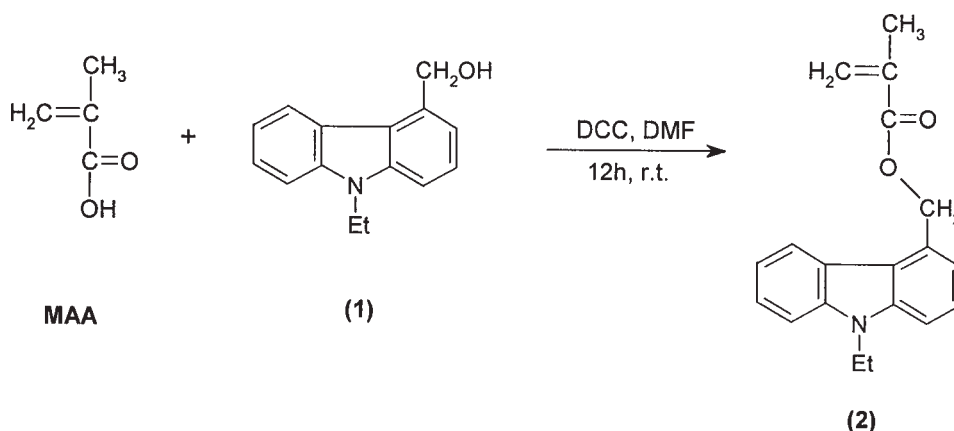

Figure 2 The preparation route of [4-(9-ethyl)carbazolyl]methyl methacrylate.

Synthesis of monomer 2

Compound **1** was attached to MAA by esterification procedure. Esterification reaction was carried out in the presence of DCC as a water absorber. The hydroxyl group from compound **1** reacted with carboxylic acid group from MAA to give a new derivative of MMA containing 4-substituted carbazole (Fig. 2). In this reaction, obtained water was absorbed by DCC and produced N,N'-dicyclohexylurea as a white precipitate. After completing of reaction, the white precipitate was isolated and solvent evaporated to give stable monomer **2**. Finally, the monomer **2** was oily in nature and showed one spot on T.L.C. The elemental analysis, ^{1}H NMR, and FTIR data confirmed the structure of monomer **2** and its purity. ^{1}H NMR spectrum of monomer **2** is shown in Figure 3.

Polymerization of monomer 2

The monomer **2** was polymerized using AIBN as a free radical initiator at $(70 \pm 1)^\circ$C for about 12 h to obtain **P2** with 76% yield. This polymer was purificated by dissolving the polymer into THF and its reprecipitation into methanol for several times. The resulted homopolymer is soluble in DMF, DMSO, THF, CHCl$_3$, and CH$_2$Cl$_2$ but insoluble in n-hexane, water, and alcohols. Gel permeation chromatography (GPC) was used for determination of weight- and number-average molecular weights of **P2**. The weight-average molecular weight of **P2** and its polydispersity indices were 2.4×10^5 and 2.1, respectively.

Study of thermal properties of P2

The decomposition temperature (T_d) of **P2** was determined using TGA. Figure 4 shows TGA thermodiagrams of **P2** and PMMA. The initial T_d value of **P2** with about 5% loss is about 360°C. Comparison of this
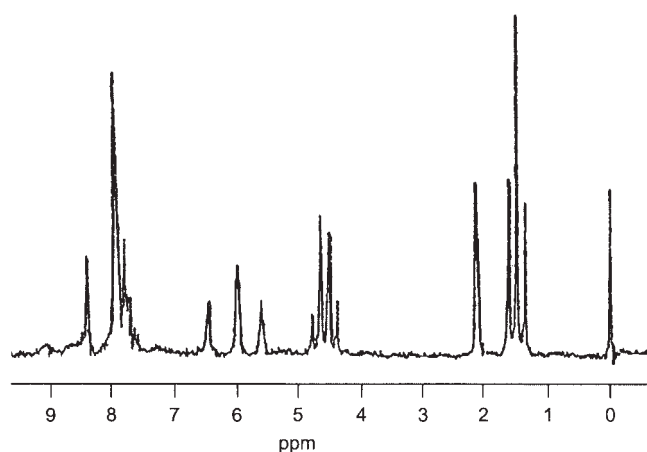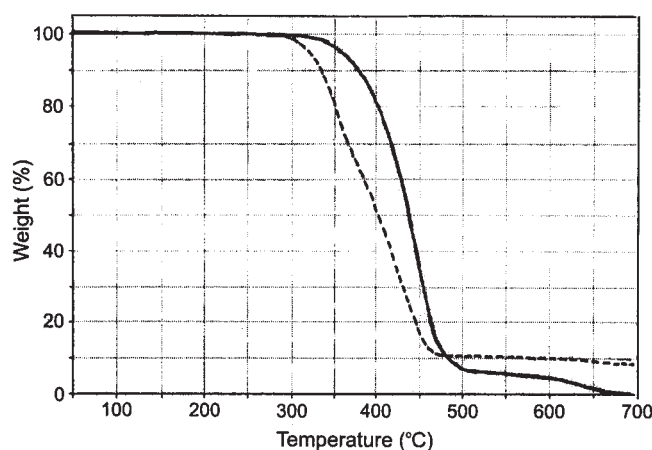

Figure 4 TGA thermodiagrams of **P2** (———) and PMMA (-------) at a heating rate of 10°C/min in air.

temperature with T_d value of PMMA with about 5% loss (320°C) shows that the introducing of bulky 4-sustituted carbazole groups in PMMA structure increases the thermal stability of polymer.

The glass transition temperature (T_g) of the resulting **P2** was determined by differential scanning calorimeter (DSC) and is shown in Figure 5. The T_g value of **P2** is 260°C. This result shows that with the introducing of 4-substituted carbazole group into PMMA structure as a side chain, the T_g value of PMMA increases from 103°C until 260°C (Fig. 5). The high glass transition temperature of **P2** can be attributed to the stiffness of the polymer chain due to the presence of bulky 4-substituted carbazole groups. This effect causes increasing of the chain rigidity and increasing of polymer T_g value.

Synthesis of copolymers I–V

The monomer **2** was respectively, copolymerized with MMA, EMA, MA, EA, and BA at $(70 \pm 1)^\circ$C in DMF

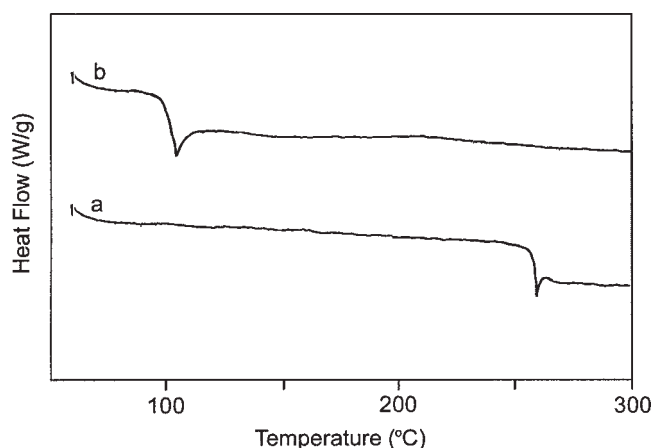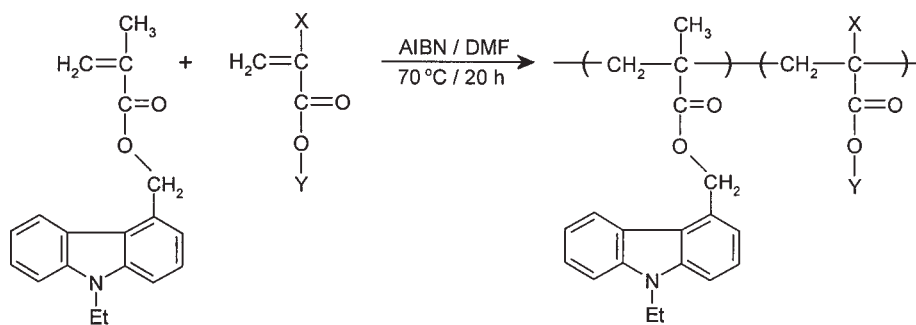**Figure 3** ^{1}H NMR spectrum of monomer **2** in CDCl$_3$.

Figure 5 DSC thermodiagrams of **P2** (a) and PMMA (b) at a heating rate of 10°C/min.

Copolymer	I	II	III	IV	V
X	CH_3	CH_3	H	H	H
Y	CH_3	C_2H_5	CH_3	C_2H_5	C_4H_9
Co-monomer	MMA	EMA	MA	EA	BA

Figure 6 Copolymerization of monomer **2** with various methacrylic and acrylic monomers.

solvent using AIBN to obtain copolymers **I–V** in good yields (Fig. 6). The reaction conditions are shown in Table I. These copolymers are soluble in DMF, DMSO, THF, and CHCl$_3$ but insoluble in *n*-hexane, water, and alcohols.

Characterization of copolymers I–V

The FTIR spectra of copolymers **I–V** showed a peak at 3035 cm^{-1} due to C—H stretching of the aromatic ring. The peaks at 2996 and 2950 cm^{-1} were attributed to the asymmetrical and symmetrical C—H stretching of methylene and methyl groups. The ester carbonyl stretching was observed at 1735 and 1725 cm^{-1}. The ring stretching vibrations of the aromatic nuclei were observed at 1600 and 1485 cm^{-1}. The stretching vibration of N—C group is seen at 1330 cm^{-1}. The peaks at 1270 and 1160 cm^{-1} were due to C—O stretching.

A typical FTIR spectrum of copolymer **I** is shown in Figure 7.

In the ^{1}H NMR spectra of the copolymers **I–V**, two protons of CH$_2$—N appeared at 4.2 ppm. The signal at 5.5 ppm was due to the methylene protons of CH$_2$-Ar. The proton signals of the aryl group were seen between 7.0 and 8.3 ppm. The resonance signal at 4 ppm was attributed to two methylene protons of —COOC*H*$_2$ due to EMA, EA, BA units in copolymers **II**, **IV**, and **V**, respectively. Also three methyl protons of —COOC*H*$_3$ due to MMA and MA units in copolymers **I** and **III**, respectively, appeared at 3.7 ppm. The broad signal at 0.9–2.6 ppm was due to the methylene groups of backbone and other alkyl groups.

The number- and weight-average molecular weights of synthesized copolymers **I–V** were determined by gel permeation chromatography (GPC) and are presented in Table II. The average composition of the
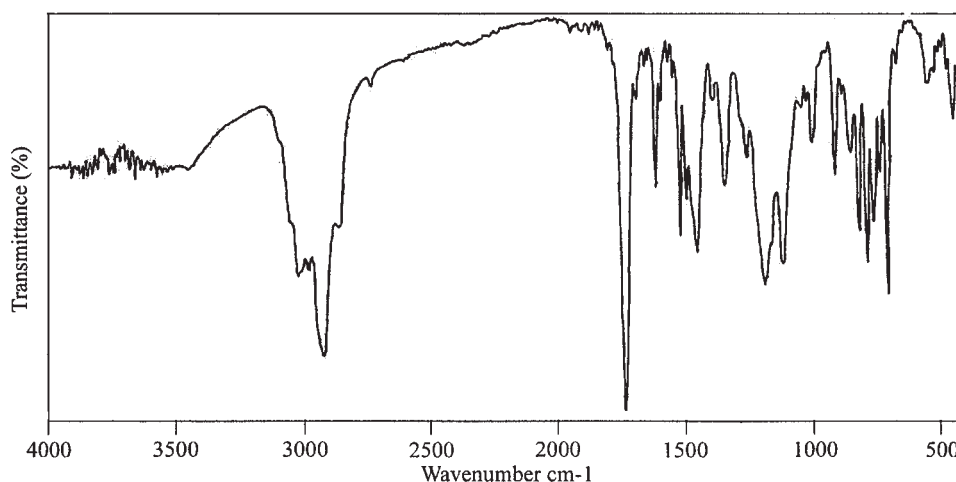

Figure 7 FTIR spectrum of copolymer **I** in KBr pellet.

TABLE II
Mole Compositions and Molecular Weights of the Copolymers I–V

Copolymer	Monomer 2 (%)	Comonomer (%)	M_w ($\times 10^5$)	M_n ($\times 10^5$)	M_w/M_n
I	22	78	2.6	1.6	1.6
II	33	67	2.2	1.1	2.0
III	33	67	2.9	1.3	2.2
IV	25	75	2.6	1.4	1.9
V	30	70	2.4	1.3	1.7

copolymer samples was determined from the corresponding ^{1}H NMR spectra. In the past few decades, ^{1}H NMR spectroscopic analysis has been established as a powerful tool for the determination of copolymer compositions because of its simplicity, rapidity, and sensitivity.[14,16,20–22] Table II gives the values of the mole fractions of **2** and related comonomer in the copolymers. For example the following expression is used to determine the composition of copolymer **I**. Let m_1 be the mole fraction of **2** and $1 - m_1$ be the mole fraction of MMA monomer. Unit of **2** contains seven aromatic protons and seven aliphatic protons. Also, MMA unit contains ten aliphatic protons. Therefore, the mole fraction of **2** in the copolymer **I** is determined from the below equations:

$$B = \frac{\text{integrated peak area of aromatic protons } (I_{\text{Ar}})}{\text{integrated peak area of aliphatic protons } (I_{\text{Ali}})}$$

$$= \frac{7m_1}{7m_1 + 10(1 - m_1)} \quad (1)$$

This on simplification gives:

$$m_1 = \frac{10B}{3B + 7} \quad (2)$$

A similar method was used to calculate of the mole compositions of the other copolymers.

Study of thermal properties of copolymers I–V

DSC curves of the copolymers **I–V** are shown in Figure 8 and the related T_g values are presented in Table III. All the synthesized copolymers show a single T_g, showing the absence of formation of a mixture of homopolymer or the formation of a block copolymer. The higher T_g value of the copolymers **I** and **II** than T_g value of the copolymers **III** and **IV** is due to the α-methyl groups, which facilitate chain entanglement. The observed T_g value for all the copolymers is approximately according to Fox and Pochan equations, where T_{g1} and T_{g2} are the glass transition temperatures (°K) of homopolymer of **2** and homopolymer of comonomer.[23] Also, w_1 and w_2 are weight fractions of **2** and comonomer, respectively.
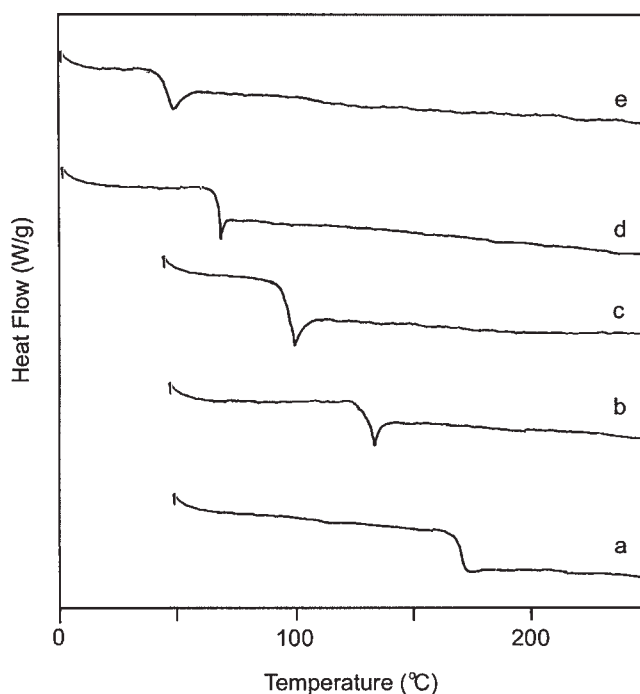
Figure 8 DSC thermodiagrams of copolymers **I** (a), **II** (b), **III** (c), **IV** (d), and **V** (e) at a heating rate of 10°C/min.

Fox's equation is:

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}}$$

and Pochan's equation is:

$$\text{Ln}T_g = w_1 \text{ Ln}T_{g1} + w_2 \text{ Ln}T_{g2}$$

Comparison of the obtained T_g values from Fox and Pochan equations with observed T_g value from DSC curves showed that 4-substituted carbazole group is a

TABLE III
Comparison of Observed T_g Value of the Copolymers I–V with Calculated T_g Value from Fox and Pochan Equations

Copolymer	w_1[a]	w_2[b]	T_{g1}[c] (°C)	T_{g2}[d] (°C)	T_g[e] (°C)	T_g[f] (°C)	T_g[h] (°C)
I	0.49	0.51	260	103	166	173	170
II	0.46	0.54	260	65	133	143	137
III	0.53	0.47	260	−9	87	110	100
IV	0.49	0.51	260	−22	56	90	82
V	0.45	0.55	260	−54	25	53	50

[a] Weight fraction of monomer 2 in the feed.
[b] Weight fraction of comonomer in the feed.
[c] T_g of homopolymer of monomer 2 (**P2**).
[d] T_g of homopolymer of comonomer.
[e] Calculated by Fox equation.
[f] Calculated by Pochan equation.
[h] Observed in relating DSC curve (Fig. 8).

bulky substitution and with introducing of 4-substituted carbazole moieties in polymer structures, the rigidity and the T_g value are increased. Consequently, chemical modification of MMA polymers by bulky 4-substituted carbazole groups creates a series of novel modified MMA polymers with new properties. These modified polymers will be suitable for some applications in polymer industries.

CONCLUSIONS

[4-(9-Ethyl)carbazolyl]methyl ligand was attached to methacrylic acid by esterification reaction between 4-hydroxymethyl-9-ethyl carbazole and methacrylic acid to obtain [4-(9-ethyl)carbazolyl]methyl methacrylate as a new functionalized methyl methacrylate monomer. The obtained monomer was homopolymerized and copolymerized with some acrylic monomers by free radical solution polymerization method to obtain homopolymer **P2** and copolymers **I–V**. Characterization of all the synthesized polymers was performed by spectroscopic techniques and the copolymer compositions calculated by corresponding ^{1}H NMR analysis. Study of TGA and DSC thermodiagrams of polymers indicated that thermal stability and glass transition temperature of polymers are higher due to the presence of bulky 4-substituted carbazole ligand in polymer structures. Optical properties of the synthesized polymers are under investigation and will be reported.

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