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Chemical modification of maleic anhydride polymers with carbazole

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Abstract

Maleic anhydride (MAN) copolymers with methyl methacrylate (MMA), ethyl methacrylate (EMA), methyl acrylate (MA), ethyl acrylate (EA) and buthyl acrylate (BA) (in a 1:1 mole ratio) were synthesized by free radical polymerizations method under vacuum condition using α, α' -azobis(isobutyronitrile) (AIBN) as an initiator of reaction at $70 \pm 1^\circ\text{C}$. The copolymer compositions were determined using related ^1H NMR spectra technique and the polydispersity indices of the copolymers determined using gel permeation chromatography (GPC) method. Then Carbazole (Cz) groups were attached to the obtained copolymers by ring opening reaction between carbazole and anhydride groups of MAN units to give the copolymers $\text{I}_{\text{Cz}}\text{-V}_{\text{Cz}}$ in high yields. The anhydride group possesses a higher reactivity with the carbazole group. The ring opening reaction between the anhydride group and the carbazole is simple and fast. All the prepared polymers, were characterized by FT-IR and ^1H NMR, spectroscopic techniques. The glass transition temperature (T_g) of all copolymers was determined by dynamic mechanical thermal analysis (DMTA). All the polymers containing carbazole groups presented a high glass transition temperature in comparison to unmodified copolymers (I-V). It was found that these polymers with carbazole moieties have high thermal stability and the presence of bulky carbazole groups in polymer side chains leads to an increase in the rigidity of polymers.

Keywords: Chemical modification; Maleic anhydride; Carbazole; Dynamic mechanical thermal analysis; Glass transition temperature.

1. Introduction

The interest for maleic anhydride (MAN) copolymers is continuously growing, due to their successful application in various industrial medicine and pharmacy processes [1]. Maleic anhydride has an extremely low tendency, to homopolymerize in a radical polymerization condition and copolymerizes with a variety of donor monomers [2]. Copolymers of maleic anhydride are commercially available; bearing reactive anhydride groups, the anhydride groups of polymer chain can easily undergo an opening reaction with nucleophilic reagents which contain hydroxyl or amine groups [3, 4]. Anhydride moieties in polymers are chemically reactive toward oxidized surfaces and form strong bonds of the carboxylate type [5]. The presence of anhydride moieties results in low backbone flexibility and consequently a high glass transition temperature (T_g) [6]. Chemical modification of polymer structures is an important method for

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modification of polymer properties such as mechanical, thermal and surface properties [7-11]. The T_g is an important intrinsic characteristic that influences the properties of polymer and its chemical usage. Furthermore, polymers with high glass transition temperatures are important for polymer industrial science for strong economic rewards that may arise from their potential applications [12]. Carbazole (Cz), as a heterocyclic aromatic compound containing a dibenzopyrrol system, obtained during coal gasification and in cigarette smoke coal tar produced at high temperature contains an average of 1.5 % carbazole. Several thousand tons of carbazole are produced from coal tar and crude oil each year [13]. It is widely used in the synthesis of dyes, pharmaceuticals, and plastics and is a suspected carcinogen [14]. Carbazole-substituted polymers are well known as precursors for electrophotographical materials with valuable optical, photoconductive, photo refractive, and other useful applications such as organic light emitting diodes [15-17]. A few numbers of polymers with pendant carbazolyl groups have been prepared [18]. As we know, there is no information about incorporation of the carbazole group to maleic anhydride polymer. Thus, the present research describes the incorporation of carbazole group to maleic anhydride polymers. Study of thermal properties of the obtained polymers by DMTA curves revealed that the incorporation of bulky carbazolyl groups as side chains, lead to stiffness of the polymer chains and increase of glass transition temperature.

2. Experimental

All experiments were carried out under nitrogen atmosphere to exclude oxygen moisture from the reaction systems.

2.1. Materials

Carbazole (Acros) was purified by crystallization from ethyl alcohol solution before use. Methyl methacrylate (Merck), ethyl methacrylate (Merck), methyl acrylate (Merck), ethyl acrylate (Merck), and buthyl acrylate (Merck) were distilled under reduced pressure to remove inhibitors before use. Maleic anhydride (Aldrich) recrystallized from chloroform. Ethyl acetate was stirred over calcium hydride for 24 h and distilled in argon atmosphere. The radical initiator of α,α' -azobis(isobutyronitrile) (Merck) was purified by crystallization from methanol. N,N-dimethylformamide (DMF) was distilled under reduced pressure.

2.2. Measurements

Infrared spectra were recorded by a Bruker-IR spectrophotometer as KBr pellets. ¹H NMR spectra were run on a Bruker 250 MHz spectrometer at room temperature using DMSO-d₆ as solvent. The T_g was determined by a Tritec 2000 DMA at a heating rate of 5 °C/min in air.

2.3. Copolymerization of maleic anhydride with methacrylate and acrylate monomers

Poly(MAN-co-MMA) (I) or poly(MAN-co-EMA) (II) or poly(MAN-co-MA) (III) or poly(MAN-co-EA) (IV) or poly(MAN-co-BA) (V) were synthesized based on the following general method. In five pyrex glass ampoules, a mixture of 1.96 g (20 mmol) of MAN, 0.065 g (0.4 mmol) of AIBN, 2.00 g (20 mmol) of MMA or 2.28 g (20 mmol) of EMA or 1.73 g (20 mmol) of MA or 2.00 g (20 mmol) of EA or 2.56 g (20 mmol) of BA was dissolved in 15 ml of ethyl acetate, respectively. Then the ampoules were degassed, sealed under vacuum condition and maintained at 70±1 °C in a water bath and shaken by a shaker machine for about 24 h. Then the viscous solutions were poured separately 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 condition at room temperature to give 2.80 g of copolymer I, 2.52 g of copolymer

II, 2.85 g of copolymer III, 2.77 g of copolymer (IV) and 3.12 g of copolymer V. The yields of copolymers are presented in Table 1.

For I: ^1H NMR (DMSO- d_6 , 250 MHz) ppm: 0.76-1.29 (3 H, in $\text{CH}_3\text{-C}$), 1.89-2.28 (2 H, in $\text{-CH}_2\text{-C}$), 3.70 (2H, in -CH-CH-), 3.50 (3H, in -OCH_3); FT-IR (KBr, cm^{-1}): 2999, 2959 (aliphatic C-H), 1854, 1781 (C=O stretching of anhydride unit), 1726 (C=O ester), 1240, 1148 (C-O ester), 1061, 1022 (C-O-C).

For II: ^1H NMR (DMSO- d_6 , 250 MHz) ppm: 0.80-1.20 (3 H, in $\text{CH}_3\text{-C}$) 1.70-2.80 (2 H, in $\text{-CH}_2\text{-C}$), 4.05 (2H, in -CH-CH-), 3.66 (2H, in -OCH_2); FT-IR (KBr, cm^{-1}): 2988, 2956 (aliphatic C-H), 1857, 1784 (C=O of anhydride unit), 1726 (C=O ester), 1240, 1148 (C-O ester), 1020 (C-O-C).

For III: ^1H NMR (DMSO- d_6 , 250 MHz) ppm: 1.58-2.85 (3 H, in $\text{-CH}_2\text{-CH-}$), 3.84 (2H, in -CH-CH-), 3.63 (3H, in -OCH_3); FT-IR (KBr, cm^{-1}): 3005, 2957 (aliphatic C-H), 1849, 1781 (C=O of anhydride unit), 1733 (C=O ester), 1169, 1223 (C-O ester), 1101, 1059 (C-O-C).

For IV: ^1H NMR (DMSO- d_6 , 250 MHz) ppm: 1.70-2.84 (3 H, in $\text{-CH}_2\text{-C}$), 4.20 (2H, in -CH-CH-), 4.00 (2H, in -OCH_2); FT-IR (KBr, cm^{-1}): 2965, 2876 (aliphatic C-H), 1843, 1770 (C=O of anhydride unit), 1732 (C=O ester), 1148, 1223 (C-O ester), 1097, 1022 (C-O-C).

For V: ^1H NMR (DMSO- d_6 , 250 MHz) ppm: 1.29-1.50, 1.5-1.80 (4 H, in $\text{-CH}_2\text{-CH}_2\text{-}$), 2.21-2.86 (3 H, in $\text{-CH}_2\text{-C}$), 3.94 (2H, in -CH-CH-), 3.64 (2H, in -OCH_2); FT-IR (KBr, cm^{-1}): 2957, 2989 (aliphatic C-H), 1854, 1781 (C=O of anhydride unit), 1728 (C=O ester), 1148, 1240 (C-O ester), 1087, 1020 (C-O-C).

Table 1

The conditions of preparation of polymers (I-V) at 70 °C.

Sample	Monomer 1	Monomer 2	Amount of 1 in mmol	Amount of 2 in mmol	Time (h)	Weight (g)	Yield (%)
I	MAN	MMA	20	20	24	3.1	76
II	MAN	EMA	20	20	24	2.67	80
III	MAN	MA	20	20	24	3.07	83
IV	MAN	EA	20	20	24	3.1	78
V	MAN	BA	20	20	24	3.38	75

2.4. Preparation of sodium carbazole salt

To prepare sodium carbazole, sodium hydride (4mmol, 0.096 g) was slowly added to carbazole (4mmol, 0.670g) dissolved in 15ml of DMF at room temperature. Then mixture was stirred under nitrogen atmosphere for 30 min.

2.5. Synthesis of the modified copolymers (I_{Cz} - V_{Cz}) by the coupling reaction between the anhydride groups of (I-V) with carbazole

Polymers containing carbazole groups, poly(MAN-co-EMA) containing carbazole groups (I_{Cz} - V_{Cz}) were prepared as follows. In a 100 ml two-necked round bottom flask equipped with a dropping funnel, a solution of sodium carbazole in DMF (15 ml) was prepared. Then, while vigorous stirring mixture was cooled to -5 °C in ice-salt mixture. A solution of copolymer I (0.198 g, 2 mmol) or copolymer II (0.230 g, 2 mmol) or copolymer III (0.200 g, 2 mmol) or copolymer IV (0.230 g, 2 mmol) or copolymer V (0.226 g, 2mmol) in DMF (15 ml)

was prepared and transferred into dropping funnel under nitrogen atmosphere. Then, a solution of copolymer (I-V) was stirred by adding drops of sodium carbazole into flask at -5°C , within 1 h. The reaction mixture was kept at -5°C temperature for another 3h while stirring. Then, the solution was poured into excess cold distilled water and the white precipitate filtered and washed with distilled water. The resulted polymer washed sequentially by diethylether and water (50 ml). Finally, the white obtained polymers containing carbazole substituents in the side chains were collected and dried under vacuum condition at room temperature.

For I_{Cz}: ^1H NMR (DMSO- d_6 , 250 MHz) ppm: 0.77-1.163 (3H, in $\text{CH}_3\text{-C-}$), 2.49-2.86 (2H, in $\text{CH}_2\text{-CH}$), 7.09-8.08 (8 H, in Ar-H of carbazole) ;11.25(1H, in O-H); FT-IR (KBr, cm^{-1}): 3049 (Ar-H of carbazole), 1492, 1601 (C= C aromatic), 1327 (C-N), 2400-3400 (OH acid).

For II_{Cz}: ^1H NMR (DMSO- d_6 , 250MHz): 0.76-1.15(3H, in $\text{CH}_3\text{-C-}$), 2.03-2.85 ($\text{CH}_2\text{-C-}$), 7.11-8.11 (8H, in Ar-H of carbazole), 11.22 (1H, in O-H); FT-IR (KBr, cm^{-1}): 3048 (Ar-H of carbazole), 1603 (C= C aromatic) , 1328 (C-N), 2400-3400 (OH acid).

For III_{Cz}: ^1H NMR (DMSO- d_6 , 250MHz) ppm: 0.74-2.83 (3H, in $\text{CH}_2\text{-CH}$), 7.10-8.08 (8H, in Ar-H of carbazole), 11.25 (1H, in O-H); FT-IR (KBr, cm^{-1}): 3050 (Ar-H of carbazole) , 1491, 1602 (C=C aromatic), 1329 (C-N), 2400-3400 (OH acid).

For IV_{Cz}: ^1H NMR (DMSO- d_6 , 250MHz) ppm: 0.84-1.49 (3H, in $\text{CH}_2\text{-CH}$), 7.10-8.10 (8H, in Ar-H of carbazole), 11.30 (1H, in O-H); FT-IR (KBr, cm^{-1}): 3060(Ar-H of carbazole), 1489, 1600 (C=C aromatic), 1329 (C-N), 2400-3400 (OH acid).

For V_{Cz}: ^1H NMR (DMSO- d_6 , 250MHz) ppm: 7.45-8.11 (8H, in Ar-H of carbazole), 11.31 (1H, in O-H); FT-IR (KBr, cm^{-1}): 3060 (Ar-H of carbazole), 1492, 1600 (C=C aromatic), 1328 (C-N), 2400-3400 (OH acid).

3. Results and discussion

3.1. Synthesis of MAN copolymers

The MAN monomer was, copolymerized with Carbazole, respectively, EMA, MA, EA and BA monomers in ethyl acetate at $70\pm 1^{\circ}\text{C}$ using AIBN as the radical polymerization initiator. The reaction conditions are shown in Table 1. The obtained polymer is a white solid and is soluble in benzene, ethyl acetate, N,N-dimethyl formamide and dimethylsulfoxide, and insoluble in n-hexane, tetrahydrofuran, methanol, ethanol, chloroform and ether.

3.2. The modification of maleic anhydride copolymers with carbazole

The sufficient number of Carbazole groups attached onto the copolymer chains causes strong interfacial interaction, probably due to the formation of chemical bonds between MAN groups and sodium carbazole as a result of nucleophilic substitution reaction. The maleic anhydride functional group which grafts on the copolymers backbone acts as the chemical link between the anhydride group and the carbazole salt. Carbazole, as a heterocyclic aromatic compound, contains a weaker acidic proton at the N-H position, which is deprotonated easily by strong bases such as sodium hydride. Copolymers of MAN attract a great attention due to the presence of reactive anhydride ring, which offers an opportunity to enter into a wide range of chemical reactions. The anhydride group possesses a higher reactivity for the carbazole, even though this coupling reaction is very rapid at -5°C . A solution of carbazole as a nucleophilic reagent reacted by anhydride groups in copolymers I-V with ring opening of all anhydride groups to give new modified copolymers. These new modified copolymers I_{Cz}-V_{Cz} were isolated in high yields at

distilled water as a non-solvent. Copolymers I_{Cz}-V_{Cz} were soluble in the same solvents in which copolymers I-V are dissolved.

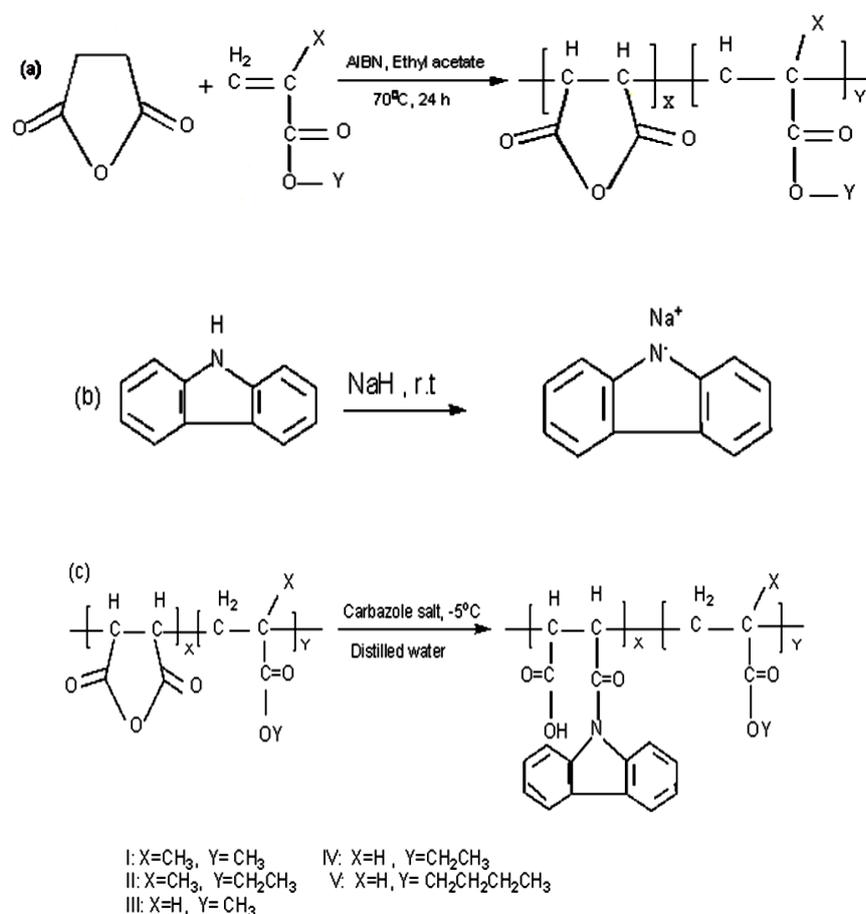


Fig. 1. (a) Copolymerization of MAN with acrylate and methacrylate monomers (b) Synthesis of sodium carbazole salt (c) Reaction of MAN copolymer with carbazole salt

3.3. Molecular weights

The number and weight average molecular weights (M_n, M_w) and poly dispersity index of copolymer samples were determined by gel permeating chromatography (GPC) and are presented in Table 2.

Table 2
Molecular weights and Tg of MAN copolymers.

Polymer	$M_w/10^3$	$M_n/10^3$	M_w/M_n	Tg(°C)
I	37.4	19.35	1.94	77.3
II	39.2	19.8	1.97	94
III	28	15.5	1.8	36
IV	32.1	16.05	2.0	39
V	47	24.73	1.9	52

3.4. Infrared spectra

The IR spectra of the copolymers (I-V) shows bands at 1857 and 1784 cm^{-1} corresponding to the antisymmetric and symmetric C=O stretch and the asymmetrical and symmetrical

stretchings due to the methyl and methylene groups (I-V) are observed at 2933 and 2957 cm^{-1} , respectively. The band at 1733 cm^{-1} is attributed to the ester carbonyl stretching of methacrylate and acrylate monomer units. The two bands at 1059 and 1101 cm^{-1} are attributed to the asymmetrical stretching C–O–C anhydride ring. The bands at 1223 and 1169 cm^{-1} were due to C–O stretching (Fig. 2a).

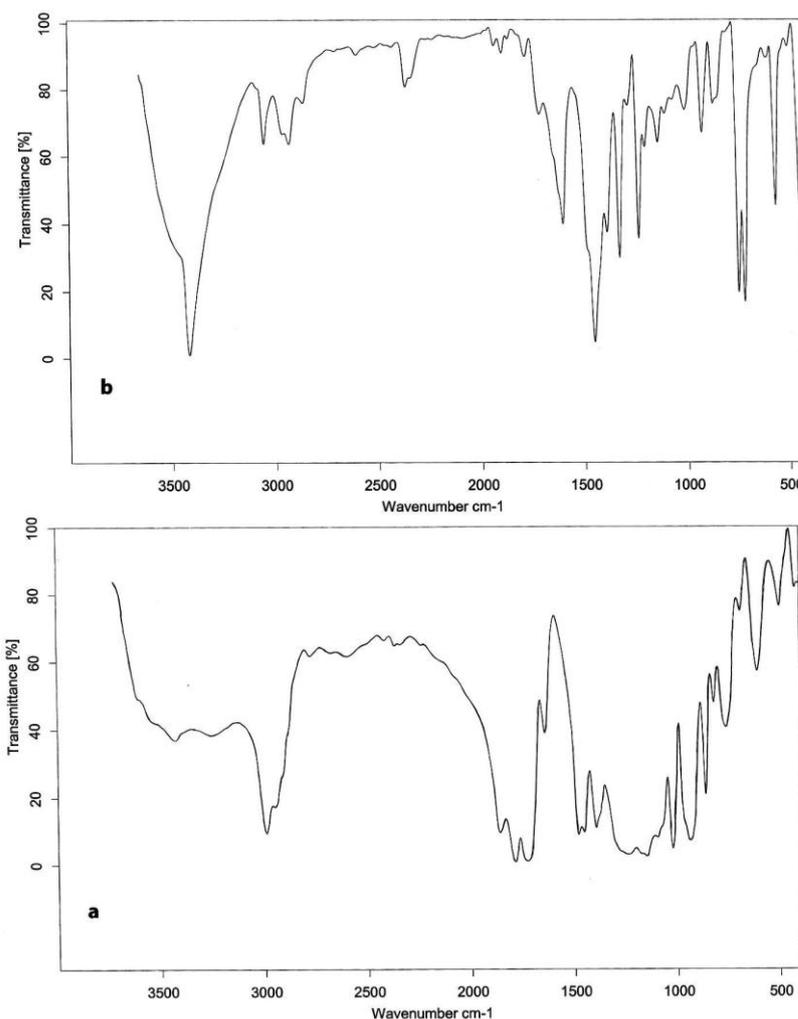


Fig. 2. Infrared spectra of: (a) II and (b) II_{ez}.

Modification of the poly(MAN-co-EMA) is confirmed by the infrared spectrum (Fig. 2b). The absorbance intensity is substantially diminished at 1849 and 1781 cm^{-1} , whereas a broad band arises between 2400–3400 cm^{-1} of O–H acid, indicating that the ring-opening reaction of the maleic anhydride unit with carbazole was completed. The band at 3050 cm^{-1} is due to C–H stretching of the aromatic ring. The ring stretching vibrations of the aromatic nuclei were observed at 1600, and 1491 cm^{-1} . The vibration of N–C group is seen at 1329 cm^{-1} .

3.5. ^1H NMR spectra

In the ^1H NMR spectra of the copolymers I-V, the H resonances of the C–H in anhydride groups in copolymers I, II, III, IV and V are located at 3.70, 4.05, 3.84, 4.20 and 3.94 ppm. The chemical shifts for the methyl groups are ranged within (0.8–1.20) and the protons of CH_2 bands exhibits a chemical shift at (1.70–2.85) ppm, respectively and aliphatic protons of CH and CH_2 in copolymers of (III–V) are located at 1.53–2.85 ppm, respectively. The resonance signal at 3.66 ppm was attributed to two methylene protons of COOCH_2 in copolymer II, IV, V and three

protons methoxy of COOCH₃ in copolymer I and III appeared at 3.60 ppm. At first Modification of copolymer II and III is confirmed in the ¹H NMR spectrum by the presence of peaks between 7.10- 8.11 ppm are due to 8 protons of the carbazol group. The peaks at 11.25 ppm are due to the hydrogen of acidic group. It should be noted that the anhydride groups, which are well defined in the unmodified copolymer disappear almost completely after modification. A typically ¹H NMR spectrum of the copolymer V before and after modification is shown in (Fig.3).

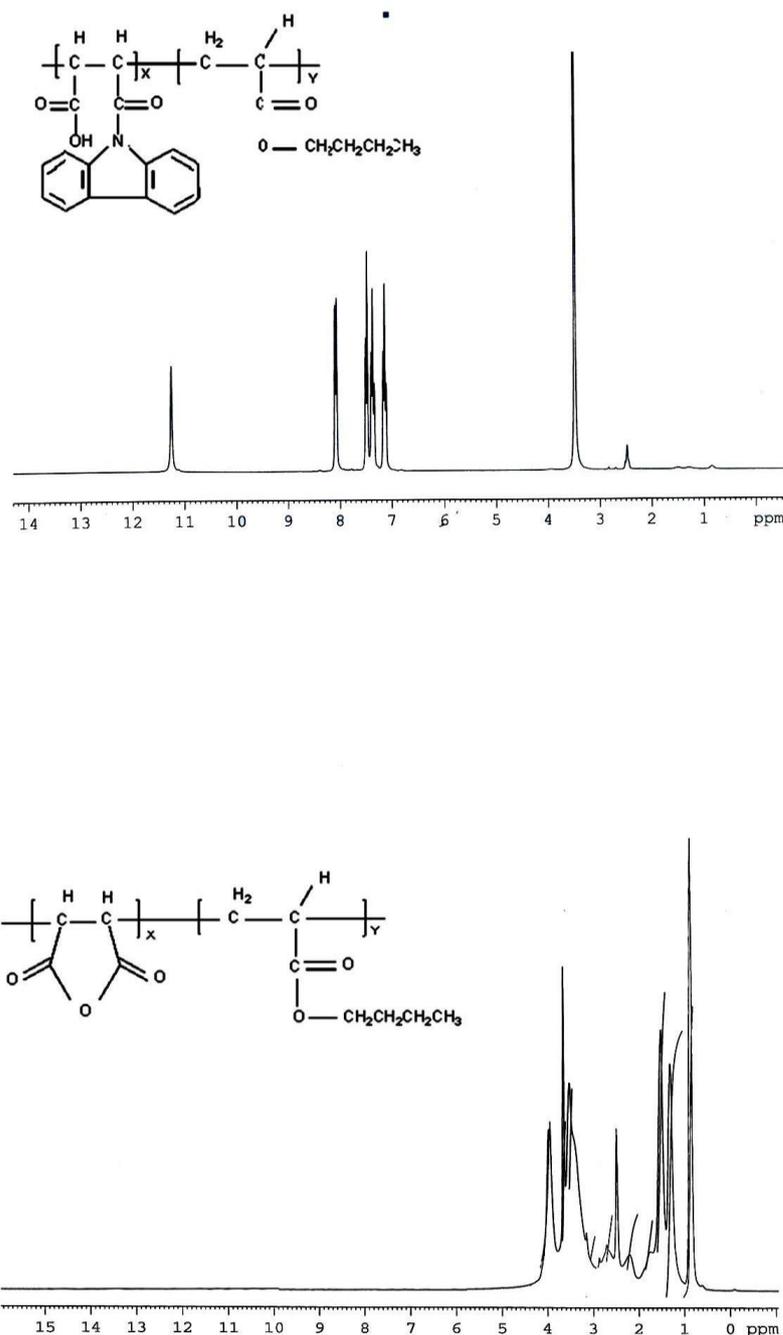


Fig. 3. ¹H NMR spectra: (a) V and V_{cz} in DMSO.

3.6. Copolymer composition

The average composition of the copolymer samples was determined from the corresponding ¹H NMR spectra. ¹H NMR spectroscopic analysis has been established as a powerful tool for the determination of copolymer compositions because of its simplicity, rapidity and sensitivity [19-

20]. The copolymer compositions were calculated by the ^1H NMR spectra data (Table 3). So the compositions of copolymers synthesized using various monomer feed ratios were determined by ^1H NMR method were achieved by comparing the integrals of the maleic anhydride, methyne and methoxy groups regions in the spectra of the comonomer units (m_1 and m_2) in copolymers using ^1H NMR analysis data which were calculated according to the following equations:

$$\frac{Am_1(\text{CH})}{A_{\text{total}}} = \frac{n_1 m_1}{a_1 m_1 + b_2 m_2} \quad (1)$$

$$\frac{Am_2(\text{OCH}_3 \text{ or } \text{OCH}_2)}{A_{\text{total}}} = \frac{n_2 m_2}{a_1 m_1 + b_2 m_2} \quad (2)$$

$$m_1 + m_2 = 1 \quad (3)$$

where Am_1 and Am_2 are the normalized areas per H from the corresponding functional groups of the monomer unit regions in ^1H NMR spectra; A_{total} is the total area of protons in the copolymer; n_1 and n_2 are the integers of proton(s) in the functional group of the monomers a and b are integers of protons in the monomer units (m_1 and m_2), monomer unit ratios can be calculated from Eqs. (1) and (2) using the following simplified from:

$$\frac{m_1}{m_2} = f = \frac{n_2 Am_1(\text{CH})}{n_1 Am_2(\text{OCH}_3 \text{ or } \text{OCH}_2)} \quad (4)$$

Table 3

The molar composition of copolymer (I-V).

Polymer	MAN(mol%)	MMA(mol%)	EMA(mol%)	MA(mol%)	EA(mol%)	BA(mol%)
I	56	44	-	-	-	-
II	55.25	-	44.75	-	-	-
III	61.77	-	-	38.27	-	-
IV	45	-	-	-	55	-
V	61.34	-	-	-	-	38.65

3.7. Thermal behavior of the copolymers

The thermal behavior of the copolymers was investigated by DMTA analysis. The DMTA analysis showed that the presence of carbazole groups lead to an increase in the T_g from 77.3 °C for copolymer I to 190 °C for copolymer I_{Cz} and from 94 °C for copolymer II to 195 °C for copolymer II_{Cz} and from 36 °C for copolymer III to 163 °C for copolymer III_{Cz} and from 39 °C for copolymer IV to 145 °C for copolymer IV_{Cz} and from 52 °C for copolymer V to 125 °C for copolymer V_{Cz} . The study of DMTA curves presented that incorporation of carbazole groups into the copolymer backbone should significantly increase T_g of the copolymers. Consequently the incorporation of high sterically hindered carbazole substituents in side chains of synthesized copolymers, a series of novel modified polymers exhibiting new properties is obtained and these can find some applications in the polymer industry. The T_g s of these polymers are shown in Tables of 2 and 4. A typically DMTA curve of the copolymer II before and after modification is shown in (Fig.4).

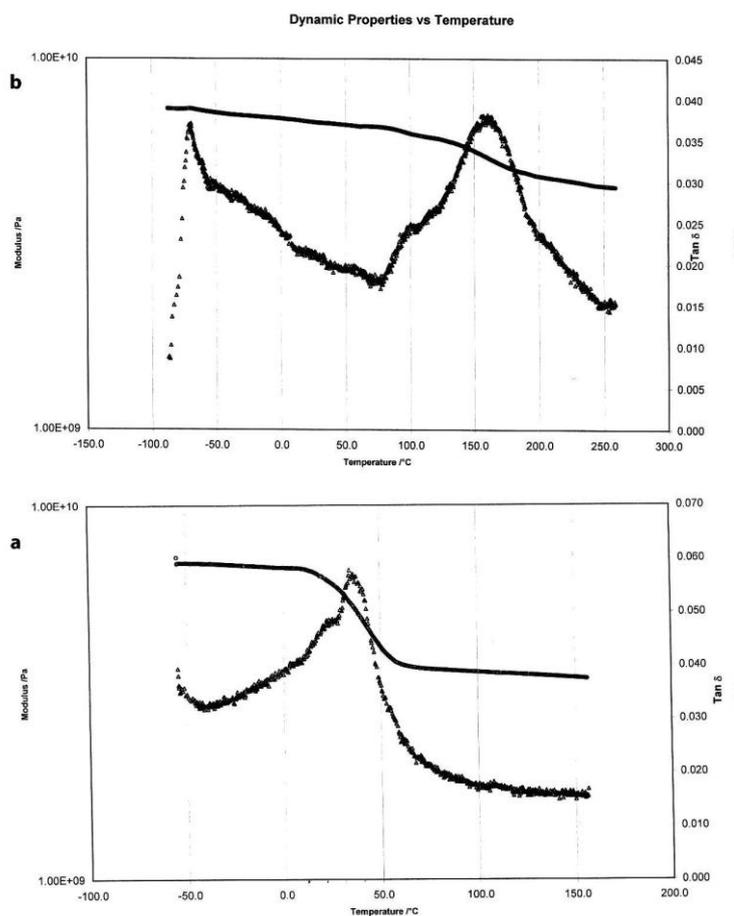


Fig. 4. DMTA Curves of copolymers: (a) III and (b) III_{ez} 5 °C/min in air.

Table 4

The result of reaction between 2 mmol of each polymers (I-V) with Cz.

Modified copolymer	Weight(g)	Yield(%)	Tg(°C)
I _{Cz}	0.68	89	190
II _{Cz}	0.72	91	195
III _{Cz}	0.65	85	163
IV _{Cz}	0.66	87	145
V _{Cz}	0.60	76	125

4. Conclusions

We have detailed the preparation and characterization of novel MAN copolymers bearing carbazole groups of side chain substituents. The procedure described in this paper deals with the nucleophilic ring-opening of anhydrides by the salt of carbazole. The copolymers of MAN with different methacrylate and acrylate monomers were synthesized by free radical solution polymerization. The molar compositions of the obtained copolymers were calculated by the corresponding ¹H NMR analysis compared to the previous coupling methods for the preparation of modified copolymers of maleic anhydride, this is simple, the coupling reaction is fast it produced and pure copolymers. The anhydride group possesses a higher reactivity for the carbazole than modification process. Comparison of the ¹H NMR and IR spectra of copolymers before and after modification revealed disappearance of the peaks assigned to the anhydride ring and appearance of a new peaks characteristic of carbazole moieties, thus proving the modification of MAN copolymers. Study of the DMTA curves of all copolymer indicated that

the Tg value of copolymer increase by incorporation of carbazole groups as side chains. The presence of bulky carbazolyl group in polymer structure increases the polymer's rigidity with increasing glass transition temperature and creates new modified polymers with novel properties and applications.

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