

Synthesis and Chemical Modification of Maleic Anhydride Copolymers with 2-Amino Ethyl Benzoate Groups

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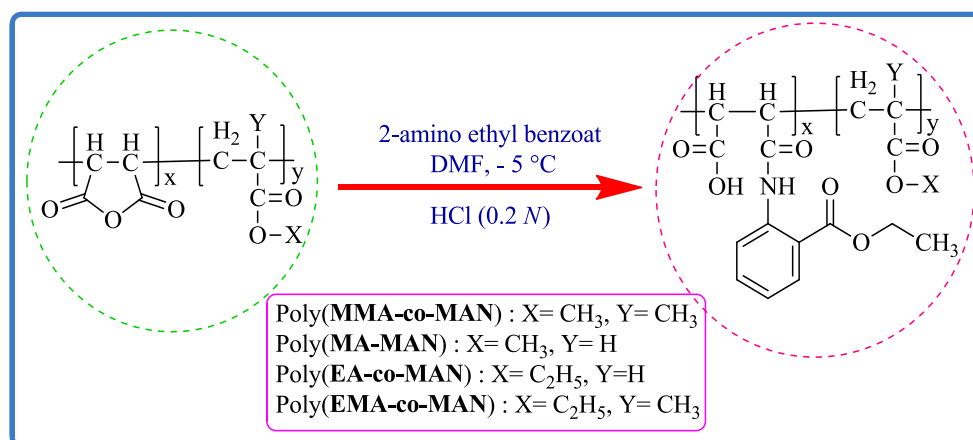
Received: 30 September 2018, Revised: 21 October 2018, Accepted: 15 November 2018

ABSTRACT

Maleic anhydride (MAN) copolymers with methyl methacrylate, ethyl methacrylate, methyl acrylate, ethyl acrylate, and butyl acrylate monomers at 1:3 mole ratios were synthesized by free radical polymerization in the presence of azobis(isobutyronitrile) as initiator and dry ethyl acetate as solvent. Copolymer compositions were obtained using the related proton nuclear magnetic resonance ($^1\text{H NMR}$) spectra, and the polydispersity of the copolymers was determined by gel permeation chromatography. Then, a solution of 2-amino ethyl benzoate salt as a nucleophilic reagent reacted through the ring opening of anhydride groups in copolymers resulting to modified copolymers I_{ab} to V_{ab} . All the prepared polymers were characterized by Fourier transform Infrared and $^1\text{H NMR}$ spectroscopic techniques. The glass transition temperature (T_g) of all copolymers before and after modification was determined by dynamic mechanical thermal analysis (DMTA). It was shown that the chemical modification of MAN copolymers with 2-amino ethyl benzoate substituents as side chains decreased the free volume of the polymers, and therefore, the rigidity and T_g is increased.

Keywords: Chemical modification, Infrared spectra, Dynamic mechanical thermal analysis (DMTA), Thermo-gravimetric analysis (TGA), Maleic anhydride (MAN) copolymers.

GRAPHICAL ABSTRACT



1. Introduction

The mid-nineteenth century saw the first successful attempts to modify polymers in a useful way. The nitration of cellulose was reported in 1833 and Goodyear's vulcanization process was patented in 1844 [1-4]. Celluloid was in common use by the end of the century and could be said to be the first synthetics, or at least partly synthetic plastic. Since then the scope of application of many polymers, both natural and synthetic, has been widened by suitable chemical modification [5]. The prime aim of the chemical modification has been to produce materials with new and improved properties and many such materials are now produced in commercial quantities. The technical importance of many chemically modified polymers has stimulated research at a fundamental level.

The chemistry of heterocyclic compounds has been an interesting field of study for a long time. The synthesis of novel Maleic anhydride (MAN) copolymers modified with any groups and its derivatives and investigation of their chemical and mechanical behavior have gained more importance in recent decades for chemical industries, medicinal and agricultural reasons. The thermal stability of polymers closely relates to molecular structures, and a detailed analysis of thermal transitions provides additional insight in the

molecular arrangement of complex copolymers. In order to get a better insight in the thermal transitions thermogravimetric analysis (TGA) are traditionally used, The copolymerization of maleic anhydride and then its modification with amino ethyl benzoate groups provides good physicochemical properties with high polarity, rigidity, glass transition temperature, and functionality. Maleic anhydride (MAN) is an excellent monomer which can provide interesting copolymers, and that it can homo polymerize by a radical polymerization condition [6-10].

In this work, we explored the polymerization of Maleic anhydride (MAN) copolymers, with some monomers (such as methyl methacrylate (MMA), ethyl methacrylate (EMA), methyl acrylate (MA), ethyl acrylate (EA), and butyl acrylate (BA) and then resulted polymers have been modified by using of 2-amino ethyl benzoate groups. All the prepared polymers were characterized by Fourier transform infrared, dynamic mechanical thermal analysis (DMTA) and ¹HNMR spectroscopic techniques. The glass transition temperature (T_g) of all copolymers before and after modification was determined by dynamic mechanical thermal analysis (DMTA).

2. Experimental

2.1. Materials

2-amino ethyl benzoate, methyl methacrylate (MMA), ethyl meth-acrylate (EMA), methyl acrylate (MA), ethylacrylate (EA), and butyl acrylate (BA) (Merck, Whitehouse Station, NJ, USA) were distilled under reduced pressure to remove inhibitors before use. Maleic anhydride (Aldrich, St. Louis, MO, USA) was recrystallized from chloroform. Ethyl acetate was stirred over calcium hydride for 24 h and distilled in argon atmosphere. The radical initiator of azobis (isobutyronitrile) (AIBN; Merck) was purified by crystallization from methanol. Sodium hydride (60%) was obtained from Aldrich. *N,N*-Dimethyl form amide (DMF) was dried over anhydrous MgSO₄ for 2 days and later with phosphine anhydride overnight. After drying, DMF was distilled under reduced pressure.

2.1.1. General procedure for solubility

The polymer (0.1 g) and solvent (10 ml) were placed in an airtight vial and agitated about 25°C for 1 h. The samples were considered to be soluble if a single-phase, clear, gel free solution was observed. This procedure was carried out again with the same condition as mentioned but for a much longer time (overnight) using a shaker.

The resulting copolymers I to V were

soluble in ethyl acetate, *N,N*-dimethylformamide, and dimethylsulfoxide and insoluble in n-hexane, chloroform, tetrahydrofuran, and hydroxyl group-containing solvents such as methanol, ethanol, or water.

2.1.2. Preparation of MAN copolymers

The MAN monomer was copolymerized with methyl methacrylate, ethyl methacrylate, methyl acrylate, ethyl acrylate, and butyl acrylate monomers in ethyl acetate at 70°C ± 1°C using AIBN as the radical polymerization initiator. For simplicity, we have labeled the obtained copolymers by numbers from one to five (I to V). Copolymerization of maleic anhydride with methacrylate and acrylate monomers poly(MAN-co-MMA) (I), poly(MAN-co-EMA) (II), poly(MAN-co-MA) (III), poly(MAN-co-EA) (IV), and poly(MAN-co-BA) (V) were synthesized based on the following general procedure: In five different Pyrex glass ampoules, a mixture of 1.96 g (20 mmol) of MAN, 0.065 g (0.4mmol) of AIBN, and 2.00 g (20mmol) of methyl meth- acrylate, 2.28 g (20mmol) of ethyl methacrylate, 1.73 g (20mmol) of methyl acrylate, 2.00 g (20mmol) of ethyl acrylate, or 2.56 g (20mmol) of butyl acrylate was dissolved in 15 ml of dry ethyl acetate, respectively. Then, the ampoules were degassed, sealed under vacuum condition, and maintained at 70°C ± 1°C in

a water bath and shaken using a shaker for about 24 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 to give 3.1 g of copolymer I, 3.39 g of copolymer II, 3.07 g of copolymer III, 3.1 g of copolymer IV, and 3.38 g of copolymer V (Table 4, Figure 4a).

2.1.3. Preparation of sodium 2-amino Ethyl benzoate salt

For preparing sodium 2-amino ethyl benzoate, sodium hydride (4 mmol, 0.096 g) was slowly added to 2-amino ethyl benzoate (4 mmol, 1g) dissolved in 15 ml of DMF at room temperature. Then, the mixture was stirred under nitrogen atmosphere for 30 min.

2.1.4. Modification

Attaching 2-amino ethyl benzoate groups to copolymers (I to V) poly(MAN-co-MMA), poly(MAN-co-EMA), poly(MAN-co-MA), poly(MAN-co-EA) and poly(MAN-co-BA) containing 2-amino ethyl benzoate groups were prepared as follows:

In a 100-ml two-necked round-bottom flask equipped with a dropping funnel, a solution of sodium 2-amino ethyl benzoate in DMF (15 ml) was prepared.

After this time, the mixture was cooled to -5°C in an ice-salt mixture under vigorous stirring. A solution of copolymer I (0.198 g, 2 mmol), copolymer II (0.230 g, 2 mmol), copolymer III (0.200 g, 2 mmol), copolymer IV (0.230 g, 2 mmol), or copolymer V (0.226 g, 2 mmol) in DMF (15 ml) was prepared and transferred into the dropping funnel under argon atmosphere.

Then, a solution of copolymers (I to V) was added dropwise with stirring to the solution of sodium 2-amino ethyl benzoate into the flask at -5°C within 1 h. The reaction mixture was kept at -5°C temperature for another 3 h under stirring. Then, the solution was poured into an excess cold HCl (0.2 N), and the white precipitate was filtered and washed with HCl (0.2 N). The resulting polymer was washed sequentially with NaOH (0.2 N) and water (50 ml). Finally, the obtained white polymers containing 2-amino ethyl benzoate substituents in the Side chains were collected and dried under vacuum at room temperature (Figure 4c). The yields of modified copolymers are presented in Table 1.

Note: the resulted copolymers after reaction with azobis (isobutyronitrile) as initiator have been labeled by I_{ab} to V_{ab} and the obtained polymers after modification have been labeled by I_{pht} to V_{pht} .

Table 1. The result of reaction between 2 mmol of each polymers (I to V) with ab

Modified copolymer	Weight (g)	Yield (%)	Tg (°C)
I _{Pht}	0.68	89	120
II _{Pht}	0.72	91	133
III _{Pht}	0.65	85	85
IV _{Pht}	0.66	87	96
V _{Pht}	0.60	76	102

2.2. Instruments

Infrared spectra were recorded using a Bruker-IR Scientific spectrophotometer as KBr pellets (Madison, WI, USA). ¹HNMR spectra were run on a Bruker 250 MHz spectrometer at room temperature using deuterated dimethyl sulfoxide (DMSO-d₆) as solvent. The molecular weights (M_w and M_n) were determined using a Waters 501 gel permeation chromatograph fitted with 103-nm Water-Styren gel columns (Milford, MA, USA). T_g was determined using Tritec 2000 DMA (Triton Technology, Ltd., Keyworth, UK) at a heating rate of 5°C/min in air.

3. Results and discussion

3.1. Molecular weights

The number and weight average molecular weights (M_n and M_w, respectively) and polydispersity index of copolymer samples were determined by gel permeation chromatography and are presented in Table 2.

3.2. Copolymer composition

In the past few decades, ¹HNMR

spectroscopic analysis has been established as a powerful tool for the determination of copolymer compositions because of its simplicity, rapidity, and sensitivity [9-11]. The copolymer compositions were calculated by the ¹HNMR spectral data (Table 3).

The compositions of copolymers synthesized using various monomer feed ratios were determined by the ¹HNMR method and were achieved by comparing the integrals of the maleic anhydride, methyne, and methoxy group regions in the spectra of the comonomer units (m₁ and m₂) in copolymers using ¹HNMR analysis data that were calculated according to the following equations:

$$\frac{Am_1(CH)}{A_{total}} = \frac{n_1 m_1}{a_1 m_1 + a_2 m_2} \quad (\text{Eq. 1})$$

$$\frac{Am_2(OCH_3 \text{ or } OCH_2)}{A_{total}} = \frac{n_2 m_2}{a_1 m_1 + b_2 m_2} \quad (\text{Eq. 2})$$

$$m_1 + m_2 = 1 \quad (\text{Eq. 3})$$

where Am₁ and Am₂ are the normalized are as 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, and a and b are integers of protons in the monomer units (m_1 and m_2). Monomer unit ratios can be calculated from Equations 1 and 2 using the following simplified formula:

$$\frac{m_1}{m_2} = \frac{n_2 A m_1 (CH)}{n_1 A m_2 (OCH_3 \text{ or } OCH_2)} \quad (\text{Eq. 4})$$

3.3. Infrared and ^1H NMR spectra

Infrared and ^1H NMR spectra for copolymers before and after the modification were recorded and investigated. The Figures (1) to (15) are shown in supplementary data and their commentaries are recorded in Table 4. But due to some reasons the spectra of copolymer IV is not available

Table 2. Molecular weights and Tg of MAN copolymers

Polymer	Mw (103)	Mn (103)	Mw/Mn	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

Table 3. The molar composition of copolymers (I to V)

Polymer	MAN (mol%)	MMA (mol%)	EMA (mol%)	MA (mol%)	EA (mol%)	BA (mol%)
I	45	45	-	-	-	-
II	45	-	55	-	-	-
III	38	-	-	62	-	-
IV	45	-	-	-	55	-
V	39	-	-	-	-	61

Table 4. The commentaries of Infrared and ^1H NMR spectra for copolymers before and after the modification.

Compound	FT-IR spectra	^1H NMR spectra (in Chloroform)
Copolymer I (MAN-MMA)	Stretching vibration of C=O ester has appeared in 1729 cm^{-1} and stretching	3H, in CH_3 related to main chain of copolymer has appeared in: (0.75

	<p>vibration of C=O Maleic anhydride has appeared in 1783 and 1856 cm^{-1}. and appeared bands in 1019 and 1090 cm^{-1} was related to asymmetric stretching vibration of C-O for Anhydride ring, and appeared bands in 699 and 764 cm^{-1} was related to Bending vibration of C-H for Anhydride ring, C-O ester: (1150 and 1242 cm^{-1}), Aliphatic C-H: (2955 and 2997 cm^{-1}), Bending vibration of methylene group: (1450 cm^{-1}).</p>	<p>to 1.27 ppm), 2H, in -CH₂-c: (1.87 to 2.47), Methine protons of anhydride groups in: (3.54 ppm), and Three Methyl protons of -COOCH₃ related to methyl methacrylate has appeared in: (3.31 ppm).</p>
<p>Copolymer I (MAN-MMA) after modification with 2-amino ethyl benzoate groups</p>	<p>Stretching vibration of C=O Maleic anhydride in 1783 and 1856 cm^{-1} was disappeared, Aliphatic C-H: (2995 cm^{-1}), C=O ester: (1623 cm^{-1}), C=O Aromatic ring: (1469 cm^{-1}).</p>	<p>Protons of aromatic ring has appeared in: (7 to 8 ppm), 2H, in -CH₂-c ester: (4.36 ppm), 3H, in CH₃: (0 to 1 ppm).</p>
<p>Copolymer II (MAN-EMA)</p>	<p>C=O ester: (1729 cm^{-1}), C=O Maleic anhydride: (1784 and 1855 cm^{-1}), C-O Anhydride ring: (1026 cm^{-1}), C-H Anhydride ring: (593 and 763 cm^{-1}), C-O ester: (1153 and 1244 cm^{-1}), Aliphatic C-H: (2999 and 2953 cm^{-1}).</p>	<p>3H, in CH₃ related to main chain of copolymer has appeared in: (0.7 to 1.17 ppm), 2H, in -CH₂-c: (1.9 to 2.26 ppm), Methine protons of anhydride groups in: (4 ppm), and Three Methyl protons of -COOCH₃ related to Ethyl methacrylate has appeared in: (3.72 ppm).</p>
<p>Copolymer II (MAN-EMA) after modification with 2-amino ethyl benzoate groups</p>	<p>The bands related to C=O Maleic anhydride in (1784 and 1855 cm^{-1}) was disappeared, Aliphatic C-H : (1497 cm^{-1}), C=O Aromatic ring: (1677 cm^{-1}), a broad band that it was related to presence of acidic hydroxyl groups in the polymer chains has appeared in 3457 cm^{-1}, this broad band is represents the ring opening reaction in the base polymers.</p>	<p>H in C-H Anhydride: (4 ppm), 3H, in CH₃ related to Carbonyl group of Ethyl 2-amino-benzoic acid has appeared in: (2.98 ppm), H, in Ar-CH: (7 to 8 ppm).</p>
<p>Copolymer III (MAN-MA)</p>	<p>C=O ester: (1733 cm^{-1}), C=O Maleic anhydride: (1787 and 1847 cm^{-1}), C-O Anhydride ring: (1101 and 1043 cm^{-1}), C-H Anhydride ring: (696 and 760 cm^{-1}), C-O ester: (1165 and 1261), Aliphatic C-H: (2960 and 3007 cm^{-1}).</p>	<p>2H, in -CH₂-c and H in CH has appeared in: (1.58 to 2.85 ppm), Methine protons of anhydride groups in: (3.84 ppm), 3H in -COOCH₃ ester: (3.63 ppm).</p>
<p>Copolymer III (MAN-MA) after modification with 2-amino ethyl benzoate groups</p>	<p>Aliphatic C-H : (2932 cm^{-1}), C=O ester: (1680 cm^{-1}), C=O aromatic ring: (1499 cm^{-1}), a broad band that it was related to presence of acidic hydroxyl groups in the polymer chains has appeared in 3455 cm^{-1}, this broad band is represents the ring opening reaction in the base polymers.</p>	<p>The peaks in (7 to 8 ppm) are related to Aromatic ring that they are Indicated to Poor absorption, The peaks in (7.28 ppm) are related to impurities of chloroform, and the peaks in (8.02 ppm) are related to impurities of DMF.</p>

**Copolymer V
(MAN- BA)**

C=O ester: (1728 cm^{-1}), C=O Maleic anhydride: (1788 and 1855 cm^{-1}), C-H Anhydride ring: (600 and 746 cm^{-1}), C-O ester: (1154 and 1391 cm^{-1}), Aliphatic C-H: (2961 cm^{-1}).

**Copolymer V
(MAN- BA)
after modification
with 2-amino ethyl
benzoate groups**

Aliphatic C-H:(2932 cm^{-1}), C=O related to COOH group: (1679 cm^{-1}), a broad band that it was related to presence of acidic hydroxyl groups in the polymer chains has appeared in 3461 cm^{-1} , this broad band is represents the ring opening reaction in the base polymers.

The peaks in (7 to 8 ppm) are related to Aromatic ring that they are Indicated to Poor absorption, The peaks in (7.36 ppm) are related to impurities of chloroform, and the peaks in (8.42 ppm) are related to impurities of DMF.

H in C-H Anhydride: (4 ppm), that due to the space prohibitions, some of Anhydride rings can't reacted with Ethyl 2-amino-benzoic acid.

3.4. Glass transition temperature analysis

The thermal behavior of all the copolymers was investigated by DMTA. The glass transition temperature of MAN copolymers with methacrylate monomers is higher than that of MAN copolymers with acrylate monomers since the α -methyl group in the main chain of methacrylate copolymers has reduced the flexibility of the polymer chains and so the T_g has increased.

The modification of copolymers with 2-amino ethyl benzoate the maleic anhydride functional group which grafts on the copolymers' backbone acts as the chemical link between the anhydride group and the sodium 2-amino ethyl benzoate in a nucleophilic substitution reaction. Copolymers of MAN are receiving great attention due to the presence of a reactive

anhydride ring, which offers it an opportunity to enter into a wide range of chemical reactions. The anhydride group possesses a higher reactivity for phthalimide even though this coupling reaction is very rapid at -5°C . A solution of 2-amino ethyl benzoate salt as a nucleophilic reagent reacted with anhydride groups in copolymers I to V with a ring opening of all anhydride groups to give new modified copolymers. These new modified copolymers I_{ab} to V_{ab} were isolated in high yields at distilled HCl (0.2 N) as a non-solvent. Compared to the previous coupling methods for the preparation of modified copolymers of maleic anhydride in the literature [11], the present method is simple the coupling reaction is fast.

Although the methods of 2-amino ethyl benzoate connection to initial copolymers

and their modification has been carried out using similar methods that we have worked previously [9], 2-amino ethyl benzoate connection has been done in the present paper for the first time. The ring-opening reaction of maleic anhydride copolymer at low temperature (-5°C) is attempted for the first time in our research group.

The thermal behavior of all the

copolymers was investigated by DMTA. DMTA analysis showed that the presence of 2-amino ethyl benzoate led to an increase in Tg from 92°C for copolymer I to 120°C for copolymer I_{ab}, from 94°C for copolymer II to 133°C for copolymer II_{ab}, to 85°C for copolymer III_{ab}, from 39°C .

Also the conditions of preparation of polymers (I to V) at 70°C are recorded in Table 5.

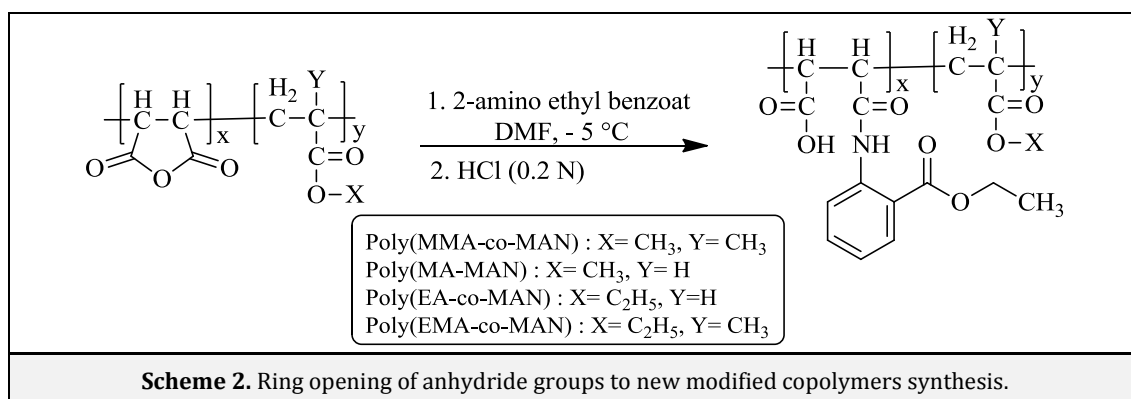
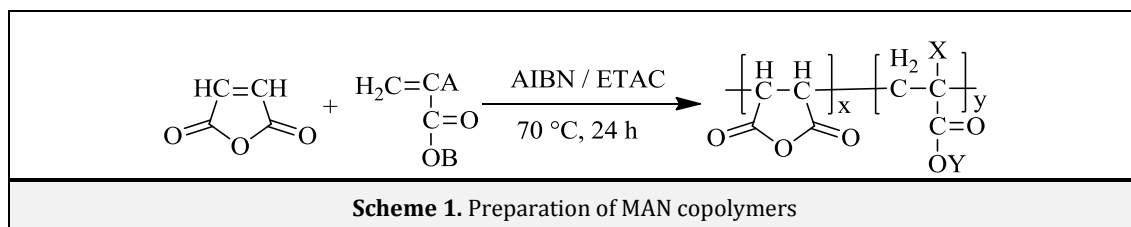


Table 5. The conditions of preparation of polymers (I to V) at 70°C

Sample	Monomer1	Monomer2	Amount of 1(mmol)	Amount of 2(mmol)	Time (h)	Weight (g)	Yield (%)
I	MAN	MMA	20	20	24	3.1	78
II	MAN	EMA	20	20	24	3.39	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

4. Conclusions

We have detailed the preparation and characterization of novel MAN copolymers bearing 2-amino ethyl benzoate groups of side chain substituents. The work described in this paper deals with the nucleophilic ring opening of anhydrides by 2-amino ethyl benzoate groups. 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 ¹HNMR analysis. The anhydride group possessed a higher reactivity for the 2-amino ethyl benzoate in the modification process. Comparison of the ¹HNMR and IR spectra of copolymers before and after modification showed disappearance of the peaks assigned to the anhydride ring and appearance of a new peak characteristic of 2-amino ethyl benzoate moieties, thus proving the modification of MAN copolymers. The MAN copolymers prepared here should be useful for the construction of well-defined functional polymers. DMTA indicated that the T_g of copolymers increases with incorporation of bulky 2-amino ethyl benzoate groups in side chains of MAN

units. The presence of the 2-amino ethyl benzoate groups in the polymer structure reduces the free volume of macromolecules with modification of their properties and applications.

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How to cite this manuscript: Mohammad Hossein Nasirtabrizi*, Seid Jafar Mousavi, Synthesis and Chemical Modification of Maleic Anhydride Copolymers with 2-Amino Ethyl Benzoate Groups, *Adv. J. Chem. A*, **2018**, *1*, 56-65.