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Synthesis and chemical modification of maleic anhydride copolymers with phthalimide groups

Mohammad Hossein Nasirtabrizi*, Zeinab Mohammadpoor Ziaei, Aiyoub Parchehbaf Jadid and Leila Zare Fatin

Abstract

Background: Maleic anhydride (MAN) copolymers with methyl methacrylate, ethyl methacrylate, methyl acrylate, ethyl acrylate, and butyl acrylate monomers at 1:1 mole ratios were synthesized by free radical polymerization in the presence of α,α' -azobis(isobutyronitrile) as initiator and dry ethyl acetate as solvent.

Results: Copolymer compositions were obtained using related proton nuclear magnetic resonance (^1H NMR) spectra, and the polydispersity of the copolymers was determined by gel permeation chromatography. Then, a solution of phthalimide salt as a nucleophilic reagent reacted through the ring opening of anhydride groups in copolymers resulting to modified copolymers I_{PhT} to V_{PhT} . All the prepared polymers were characterized by Fourier transform infrared and ^1H NMR spectroscopic techniques. The glass transition temperature (T_g) of all copolymers before and after modification was determined by dynamic mechanical thermal analysis (DMTA).

Conclusions: It was shown that chemical modification of MAN copolymers with phthalimide substituents as side chains decreased the free volume of the polymers, and therefore, the rigidity and T_g are increased. Solubility of the copolymer products was tested in some organic solvents.

Keywords: Maleic anhydride copolymers, Chemical modification, DMTA, T_g , MAN, Phthalimide

Background

Maleic anhydride (MAN) is an excellent monomer which can provide reactive anhydride or carboxylic groups with nucleophilic molecules, as discussed by Zhou et al. [1]. MAN has an extremely low tendency to homopolymerize in a radical polymerization condition; on the contrary, it copolymerizes with a variety of donor monomers, as discussed by Nieuwhof et al. [2]. The anhydride groups, in the polymer chain, make the MAN polymer very reactive, and therefore, it is commonly used in various fields, as discussed elsewhere [3,4]. The anhydride moiety constitutes a nice handle to modify the polymer [5]. One can modify the polymer via addition of low molecular weight compounds such as water, alcohols, or amines because of the high reactivity of the anhydride group, as discussed by Bruch et al. [6]. The chemical modification of synthetic polymers allows the control of their mechanical and thermal properties [7] and expands their applicabilities, as discussed elsewhere [8-10].

Polymers containing phthalimide groups are found to possess excellent heat resistance and transparency. Copolymers containing phthalimide derivatives have been used as optical brightening agents, as discussed by Jayakumar et al. [11]. The incorporation of the phthalimide group remarkably enhanced the thermal stability of polymers. Polymers bearing the phthalimide group as a pendant group will exhibit relatively high thermal stability and good solubility [12,13]. Recently, we reported the synthesis and properties of MAN polymers modified with carbazole groups [14]. In this research work, we report the synthesis and properties of MAN copolymers modified with highly sterically hindered phthalimide groups. Firstly, copolymers of MAN with different methacrylate and acrylate monomers were synthesized by the free radical polymerization method. Then, phthalimide groups were linked to the resulting copolymers by the ring-opening reaction of the anhydride groups with sodium phthalimide salt. Dynamic mechanical thermal analysis (DMTA) showed that the incorporation of phthalimide groups as side chains decreased the free volume of the polymers, and therefore, the rigidity and the glass transition temperature (T_g) are increased.

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Methods

Materials

Phthalimide, methyl methacrylate (MMA), ethyl methacrylate (EMA), methyl acrylate (MA), ethyl acrylate (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 α, α' -azobis (isobutyronitrile) (AIBN; Merck) was purified by crystallization from methanol. Sodium hydride (60%) was obtained from Aldrich. *N,N*-Dimethylformamide (DMF) was dried over anhydrous $MgSO_4$ for 2 days and later with phosphine anhydride overnight. After drying, DMF was distilled under reduced pressure.

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.

Instruments

Infrared spectra were recorded using a Bruker-IR Scientific spectrophotometer as KBr pellets (Madison, WI, USA). 1H NMR spectra were run on a Bruker 250 MHz spectrometer at room temperature using deuterated dimethyl sulfoxide ($DMSO-d_6$) as solvent. The molecular weights (M_w and M_n) were determined using a Waters 501 gel permeation chromatograph fitted with 10^3 -nm Waters Styragel 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.

For I: 1H NMR ($DMSO-d_6$, 250 MHz) ppm: 0.76 to 1.29 (3H, in CH_3-C), 1.89 to 2.28 (2H, in $-CH_2-C-$), 3.70 (2H, in $-CH-CH-$), 3.50 (3H, in $-OCH_3$); FT-IR (KBr, cm^{-1}): 2,999, 2,959 (aliphatic C-H); 1,854, 1,781 (C=O stretching of anhydride unit); 1,726 (C=O ester); 1,240, 1,148 (C-O ester); 1,061, 1,022 (C-O-C).

For II: 1H NMR ($DMSO-d_6$, 250 MHz) ppm: 0.80 to 1.20 (3H, in CH_3-C), 1.70 to 2.80 (2H, in $-CH_2-C-$), 4.05 (2H, in $-CH-CH-$), 3.66 (2H, in $-OCH_2$); FT-IR (KBr, cm^{-1}): 2,988, 2,956 (aliphatic C-H); 1,857, 1,784 (C=O of anhydride unit); 1,726 (C=O ester); 1,240, 1,148 (C-O ester); 1,020 (C-O-C).

For III: 1H NMR ($DMSO-d_6$, 250 MHz) ppm: 1.58 to 2.85 (3H, in $-CH_2-CH-$), 3.84 (2H, in $-CH-CH-$), 3.63 (3H, in $-OCH_3$); FT-IR (KBr, cm^{-1}): 3,005, 2,957 (aliphatic C-H); 1,849, 1,781 (C=O of anhydride unit); 1,733 (C=O ester); 1,169, 1,223 (C-O ester); 1,101, 1,059 (C-O-C).

For IV: 1H NMR ($DMSO-d_6$, 250 MHz) ppm: 1.70 to 2.84 (3H, in $-CH_2-C-$), 4.20 (2H, in $-CH-CH-$), 4.00 (2H,

in $-OCH_2$); FT-IR (KBr, cm^{-1}): 2,965, 2,876 (aliphatic C-H); 1,843, 1,770 (C=O of anhydride unit); 1,732 (C=O ester); 1,148, 1,223 (C-O ester); 1,097, 1,022 (C-O-C).

For V: 1H NMR ($DMSO-d_6$, 250 MHz) ppm: 1.29 to 1.50, 1.5 to 1.80 (4H, in $-CH_2-CH_2-$), 2.21 to 2.86 (3H, in $-CH_2-C-$), 3.94 (2H, in $-CH-CH-$), 3.64 (2H, in $-OCH_2$); FT-IR (KBr, cm^{-1}): 2,957, 2,989 (aliphatic C-H); 1,854, 1,781 (C=O of anhydride unit), 1,728 (C=O ester); 1,148, 1,240 (C-O ester); 1,087, 1,020 (C-O-C).

For I_{PhI}: 1H NMR ($DMSO-d_6$, 250 MHz) ppm: 0.77 to 1.163 (3H, in CH_3-C-), 2.49 to 2.86 (2H, in CH_2-CH), 7.44 to 8.11 (Ar-H of phthalimide); 11.31 (1H, in O-H); FT-IR (KBr, cm^{-1}): 3,059 (Ar-H of phthalimide); 2,400 to 3,400 (OH acid); 1,774, 1,750 (carbonyls of phthalimide).

For II_{PhI}: 1H NMR ($DMSO-d_6$, 250 MHz) ppm: 0.76 to 1.15 (3H, in CH_3-C-), 2.03 to 2.85 (CH_2-C-), 7.47 to 7.91 (4H, in Ar-H of phthalimide), 11.31 (1H, in O-H); FT-IR (KBr, cm^{-1}): 3,058 (Ar-H of phthalimide); 2,400 to 3,400 (OH acid), 1,771, 1,748 (carbonyls of phthalimide).

For III_{PhI}: 1H NMR ($DMSO-d_6$, 250 MHz) ppm: 0.74 to 2.83 (3H, in CH_2-CH), 7.5 to 7.83 (4H, in Ar-H of phthalimide), 11.28 (1H, in O-H); FT-IR (KBr, cm^{-1}): 3,061 (Ar-H of phthalimide), 2,400 to 3,400 (OH acid); 1,770, 1,733 (carbonyls of phthalimide).

For IV_{PhI}: 1H NMR ($DMSO-d_6$, 250 MHz) ppm: 0.84 to 1.49 (3H, in CH_2-CH), 7.44 to 8.10 (4H, in Ar-H of phthalimide), 11.30 (1H, in O-H); FT-IR (KBr, cm^{-1}): 3,060 (Ar-H of phthalimide); 2,400 to 3,400 (OH acid), 1,770, 1,750 (carbonyls of phthalimide).

For V_{PhI}: 1H NMR ($DMSO-d_6$, 250 MHz) ppm: 7.45 to 8.11 (4H, in Ar-H of phthalimide), 11.31 (1H, in O-H); FT-IR (KBr, cm^{-1}): 3,060 (Ar-H of phthalimide); 2,400 to 3,400 (OH acid); 1,772, 1,720 (carbonyls of phthalimide).

Results and discussion

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 \pm 1°C using AIBN as the radical polymerization initiator.

Solubility

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.

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 1.

Table 1 Molecular weights and T_g of MAN copolymers

Polymer	M_w (10^3)	M_n (10^3)	M_w/M_n	T_g ($^{\circ}\text{C}$)
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

Copolymer composition

In the past few decades, ^1H NMR spectroscopic analysis has been established as a powerful tool for the determination of copolymer compositions because of its simplicity, rapidity, and sensitivity [15-17]. The copolymer compositions were calculated by the ^1H NMR spectral data (Table 2).

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

$$\frac{Am_1(\text{CH})}{A_{\text{total}}} = \frac{n_1m_1}{a_1m_1 + b_2m_2} \quad (1)$$

$$\frac{Am_2(\text{OCH}_3 \text{ or } \text{OCH}_2)}{A_{\text{total}}} = \frac{n_2m_2}{a_1m_1 + b_2m_2} \quad (2)$$

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

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, 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:

$$\frac{m_1}{m_2} = f = \frac{n_2Am_1(\text{CH})}{n_1Am_2(\text{OCH}_3 \text{ or } \text{OCH}_2)} \quad (4)$$

Table 2 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

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 increased T_g .

The modification of copolymers with phthalimide

The maleic anhydride functional group which grafts on the copolymers' backbone acts as the chemical link between the anhydride group and the sodium phthalimide 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 phthalimide 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_{PhT} to V_{PhT} 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 [16], the present method is simple - the coupling reaction is fast.

Although the methods of phthalimide connection to initial copolymers and their modification has been carried out using similar methods that we have worked previously [14], phthalimide 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.

Solubility

Copolymers I_{PhT} to V_{PhT} were soluble in solvents the same as those in which copolymers I to V are dissolved. The solubility of copolymers before and after modification with phthalimide salt was tested with polar and non-polar solvents, and it was observed that the resulting polymers are soluble in polar aprotic solvents and insoluble in polar protic and non-polar solvents. The results showed that the solubility of the modified copolymers with phthalimide has not changed compared to the initial polymers. The results of the solubility test for the longer time (overnight) were similar to those for the short time (1 h).

Infrared spectra

In the IR spectra of the copolymers (I to V), asymmetrical and symmetrical stretching due to the methyl and methylene groups are observed at 3,005 and 2,957 cm^{-1} , respectively. The two bands at 1,849 and 1,781 cm^{-1} are attributed

to symmetric and asymmetric stretching of anhydride carbonyl of copolymers, respectively. The band at $1,733\text{ cm}^{-1}$ is attributed to the ester carbonyl stretching of methacrylate and acrylate monomer units. The two bands at $1,059$ and $1,101\text{ cm}^{-1}$ are attributed to the asymmetrical stretching of the C-O-C anhydride ring. The bands at $1,223$ and $1,169\text{ cm}^{-1}$ are due to C-O stretching. The FT-IR spectra of copolymer II is shown in Figure 1a.

Modification of poly(MAN-co-EMA) is confirmed by the infrared spectrum in Figure 1b. The absorbance intensity is substantially diminished at $1,857$ and $1,784\text{ cm}^{-1}$, whereas a broad band arises between $2,400$ and $3,400\text{ cm}^{-1}$ of O-H acid, indicating that the ring-opening reaction of the maleic anhydride unit with phthalimide was completed. The band at $3,058\text{ cm}^{-1}$ is due to C-H stretching of the aromatic ring. The ring stretching vibration of the aromatic nuclei was observed at $1,600$ and $1,491\text{ cm}^{-1}$.

¹H NMR spectra

¹H NMR spectra of the compounds (I to V) show that the proton resonances of 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, respectively. Aliphatic protons of CH₃ and CH₂ in copolymers I and II are located at 0.80 to 1.20 and 1.70 to 2.85 ppm, respectively, and aliphatic protons of CH and CH₂ in copolymers III to V are located at 1.53 to 2.85 ppm. The resonance signal at 3.66 ppm was attributed to two methylene protons of COOCH₂ in copolymers II, IV, and V, and three methoxy protons of COOCH₃ in copolymers I and III appeared at 3.60 ppm. In the ¹H NMR spectrum of the copolymers (I to V) modified by phthalimide groups, the aromatic resonances between 7.50 and 7.90 ppm are due to the phthalimide protons. The peaks at 11.28 ppm are due to the hydrogen of the acidic group. A typical ¹H NMR spectrum of copolymer III is given in Figure 2.

Glass transition temperature

The thermal behavior of all the copolymers was investigated by DMTA. DMTA analysis showed that the presence of phthalimide groups led to an increase in *T_g* from 92°C for copolymer I to 120°C for copolymer I_{PhI} from 94°C for copolymer II to 133°C for copolymer II_{PhI} from 36°C for copolymer III to 85°C for copolymer III_{PhI} from 39°C

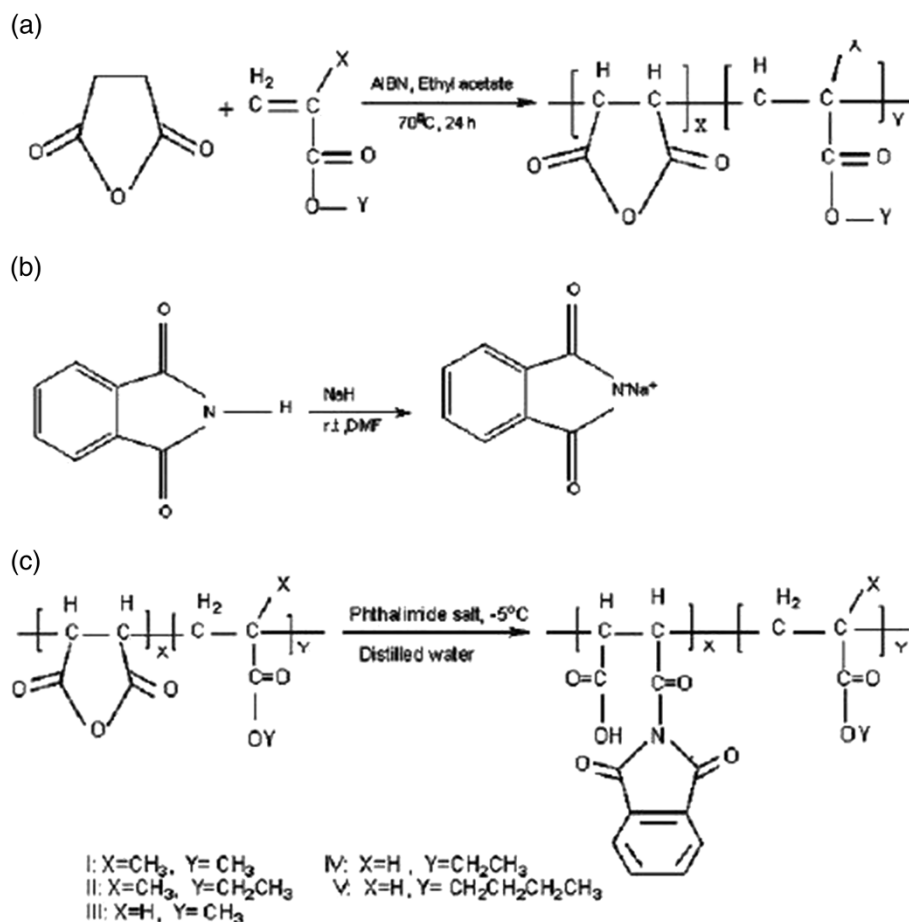


Figure 1 Infrared spectra of copolymers (a) II and (b) II_{PhI}.

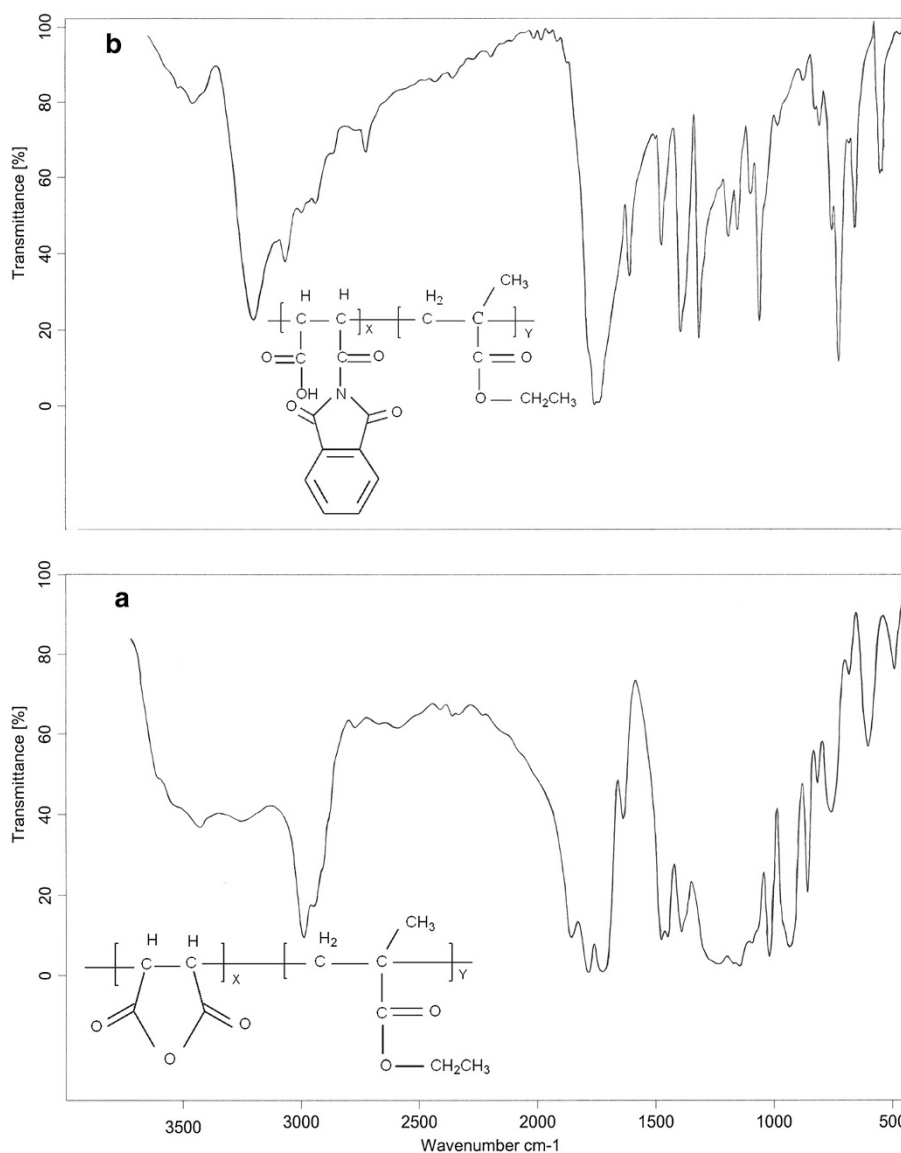


Figure 2 ^1H NMR spectra of copolymers (a) III and (b) III_{Pht} in DMSO-d₆.

for copolymer IV to 96°C for copolymer IV_{Pht} and from 52°C for copolymer V to 102°C for copolymer V_{Pht} (Table 3, Figure 3a,b). Incorporation of phthalimide substituents into the polymer increased T_g as expected because it reduces the free volume of macromolecules; in addition, the π -stacking and ring structure of the aromatic groups increased the rigidity of the polymer. This reduced the flexibility of polymer chains, and hence, more energy has to be induced in order to overcome the interactions. The presence of a number of carbonyl groups also adds to the rigidity of the polymer. Because the bulky group is pendant and not a part of the polymer backbone, the rise in T_g was slight; however, it withstands semiconductor processing [7]. Therefore, novel polymer systems with new physical and chemical properties and new applications can be obtained.

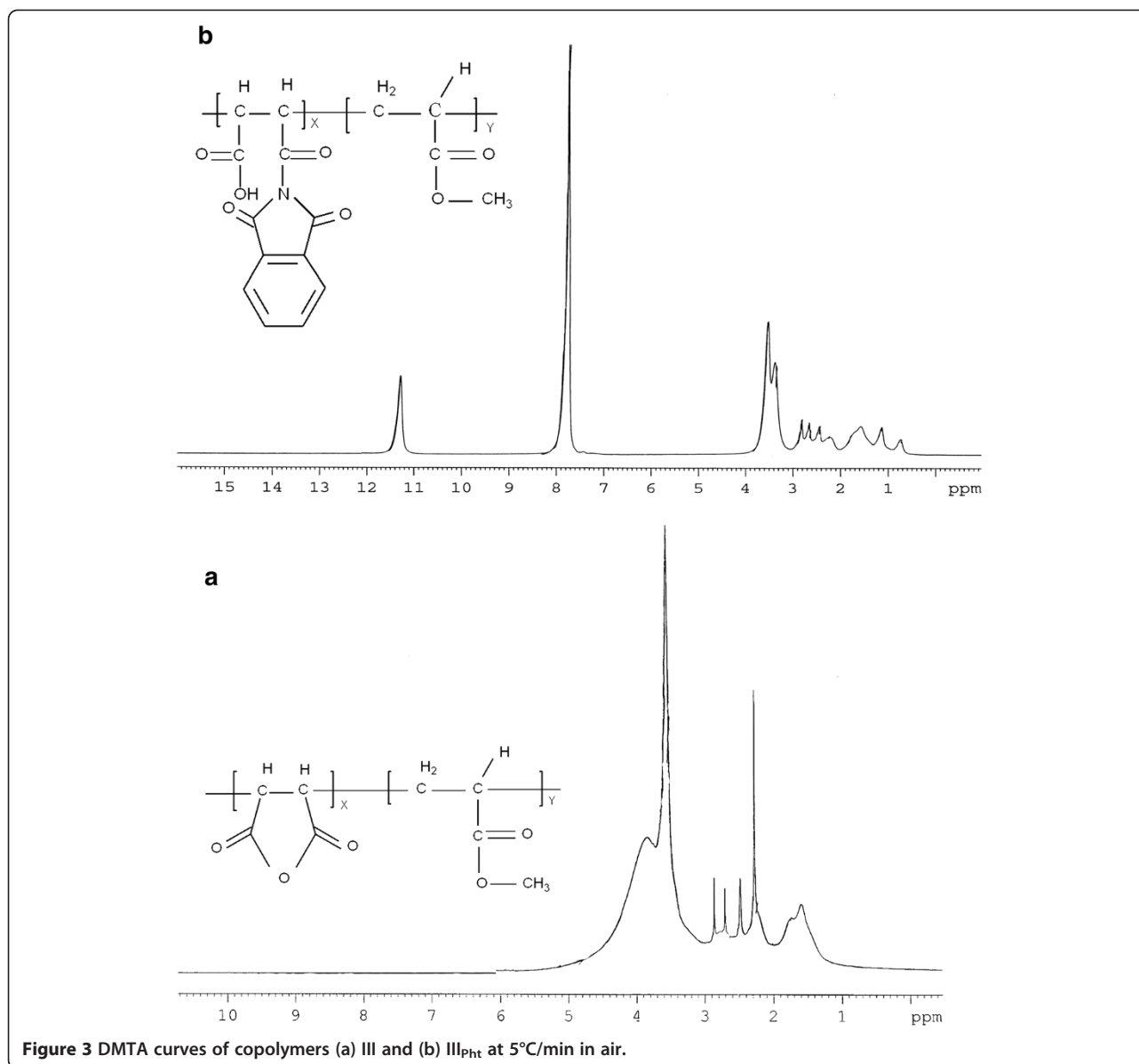
Experimental

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

Table 3 The result of reaction between 2 mmol of each polymers (I to V) with Pht

Modified copolymer	Weight (g)	Yield (%)	T_g (°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



(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 (0.4 mmol) of AIBN, and 2.00 g (20 mmol) of methyl methacrylate, 2.28 g (20 mmol) of ethyl methacrylate, 1.73 g (20 mmol) of methyl acrylate, 2.00 g (20 mmol) of ethyl acrylate, or 2.56 g (20 mmol) 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).

Preparation of sodium phthalimide salt

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

Attaching phthalimide 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 phthalimide groups were prepared as follows: In a

Table 4 The conditions of preparation of polymers (I to V) at 70°C

Sample	Monomer 1	Monomer 2	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

100-ml two-necked round-bottom flask equipped with a dropping funnel, a solution of sodium phthalimide 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, 2mmol) 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 phthalimide 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 phthalimide substituents in the

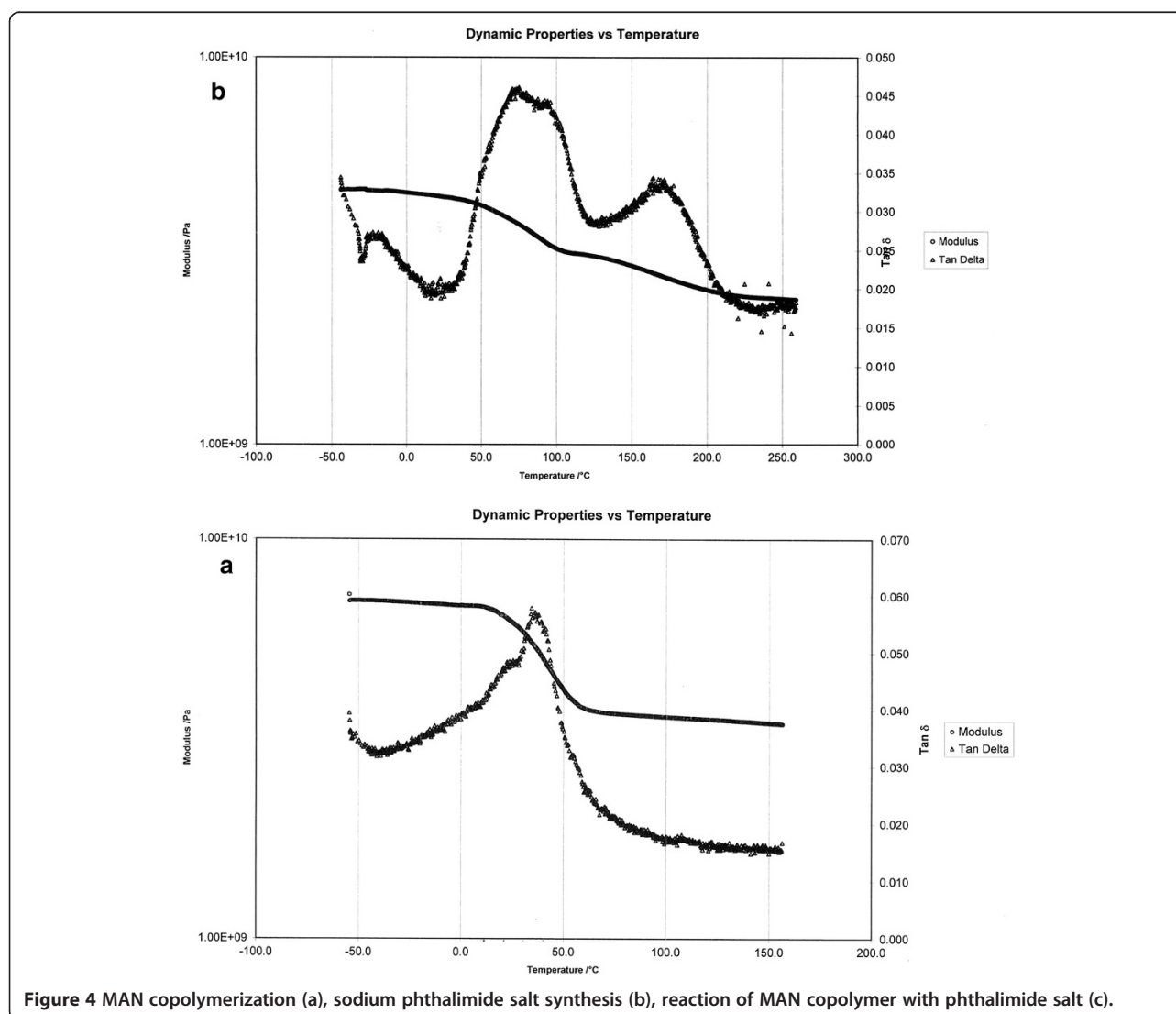


Figure 4 MAN copolymerization (a), sodium phthalimide salt synthesis (b), reaction of MAN copolymer with phthalimide salt (c).

side chains were collected and dried under vacuum at room temperature (Figure 4c). The yields of modified copolymers are presented in Table 3.

Conclusions

We have detailed the preparation and characterization of novel MAN copolymers bearing phthalimide groups of side chain substituents. The work described in this paper deals with the nucleophilic ring opening of anhydrides by $\text{Pht}^- \text{Na}^+$. 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. The anhydride group possessed a higher reactivity for the phthalimide in the modification process. Comparison of the ^1H NMR 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 phthalimide 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 phthalimide groups in side chains of MAN units. The presence of the phthalimide groups in the polymer structure reduces the free volume of macromolecules with modification of their properties and applications.

Competing interests

The authors declare that they have no competing interests.

Authors' contributions

MHN developed the concept. ZMZ drafted the manuscript. APJ advised on the methods of tests. LZP analyzed the data. All authors read and approved the final manuscript.

Acknowledgements

The authors are thankful to Islamic Azad University, Ardabil Branch, for the technical support during this research.

Received: 1 February 2012 Accepted: 9 January 2013

Published: 12 February 2013

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doi:10.1186/2228-5547-4-11

Cite this article as: Nasirtabrizi et al.: Synthesis and chemical modification of maleic anhydride copolymers with phthalimide groups. *International Journal of Industrial Chemistry* 2013 **4**:11.

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