Synthesis and Characterization of New Polymer Systems Containing Indole

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A R T I C L E   I N F O

K E Y W O R D S

A B S T R A C T

Synthesis of some novel indole derivatives has been undertaken by the reaction of poly(maleic anhydride-*co*-styrene), P(MA-*co*-St), poly(maleic anhydride-*co*-chloromethyl styrene), P(MA-*co*-CMS), poly(maleic anhydride-*co*-methyl methacrylate), P(MA-*co*-MMAc) and poly(maleic anhydride-*co*-methacrylate) P(MA–*co*–MAc), copolymers with indole in the presence of NaH at -5°C. Compositions of the copolymers were obtained using related ^{1}H NMR spectra and the polydispersity indices of the copolymers determined using gel permeation chromatography (GPC). The anhydride group possesses a higher reactivity with the indole group. The ring opening reaction between the anhydride group and the indole is simple and fast. All the resulted polymers were characterized by FT-IR and ^{1}H NMR spectroscopic techniques. The glass transition temperature (T_g) of all the copolymers was determined by dynamic mechanical thermal analysis (DMTA). All the polymers containing indole groups showed a high glass transition temperature in comparison with the unmodified copolymers (I-IV). It was found that these polymers with indole moieties have high thermal stability and the presence of bulky indole groups in polymer side chains leads to an increase in the rigidity of polymers.

G R A P H I C A L   A B S T R A C T

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Introduction

The interest for maleic anhydride (MA) copolymers is continuously growing, due to their successful application in various industrial processes or in medicine and pharmacy [1]. Maleic anhydride has an extremely low tendency, to homopolymerize in a radical polymerization and copolymerizes with a variety of donor monomers [2]. Copolymers of maleic anhydride are commercially available; bearing reactive anhydride groups, these anhydride groups present in the polymer chain can easily undergo an opening reaction with nucleophilic reagents which contain hydroxyl or amine groups [3-5]. Anhydride moieties in polymers are chemically reactive toward oxidized surfaces and form strong bonds of the carboxylate type [6]. The presence of anhydride moieties results in low backbone flexibility and consequently a high T_g [7].

Chemical modification of polymer structures is an important route for modification of polymer properties such as mechanical, thermal and surface properties [8-12]. The glass transition temperature is an important intrinsic characteristic that influences the properties of a polymer and its potential applications. Furthermore, polymers with high glass transition temperatures are attractive for polymer industrial science because of strong economic rewards that may arise from their potential applications [13].

Indole derivatives have been a topic of substantial research interest and continue to be one of the most active areas of heterocyclic chemistry, particularly due to their natural occurrence and pharmacological activities. In recent years, considerable attention has been paid on the synthetic methods leading to indole derivatives. Various indole derivatives, such as 3 substituted indole [14] and indolocarbazole [15] are common components of drugs. Indole derivatives also occur widely in many natural products such as those from plants, fungi and marine organisms [16].

From our knowledge, there is no information about the incorporation of indole group to maleic anhydride polymer. Thus, this present research work describes the incorporation of indole group to maleic anhydride polymers. Study of thermal properties of the obtained polymers by DMTA curves showed that the supporting of bulky indole groups as side chains leads to stiffness of the polymer chains and an increase in glass transition temperature.

Experimental

All reactions were carried out under nitrogen atmosphere to exclude oxygen moisture form the reaction systems.

Materials

Solvents such as chloroform, DMF and diethyl ether and chemical material such as indole, CMS MA, MMA, St were obtained from Merck and distilled under reduced pressure to remove inhibitors before use. The radical initiator of azobis (isobutyronitrile) (AIBN) was purchased from Merck and purified by recrystallization from absolute ethanol. Sodium hydride (60%) obtained from Aldrich chemical company.

Measurements

The infrared spectra were recorded on Bruker spectrometer scientific 500 IR in KBr discs. ^{1}H NMR spectra were run on a Bruker 300 MHz spectrometer at room temperature using chloroform-d and dimethyl sulfoxide-d$_6$ as solvent and TMS as internal standard. Dynamic mechanical thermal analyses (DMTA) were characterized by Triton (Tritec 2000 DMN) with heating rate of 5 °C/min in air.

Copolymerization of maleic anhydride with (MAc), (MMAc), (CMS) and (St) General procedure

Poly (MA-*co*-MAc) (I), poly (MA-*co*-MMAc) (II), poly (MA-*co*-CMS) (III) or poly (MA-*co*-St) (IV) were synthesized as follows. In a Pyrex polymerization tube, mixture of 1.96 g (20 mmol) of MA, 0.065 g (0.4 mmol) of AIBN and 1.72 g (20 mmol) of MAc, or 0.5 g (20 mmol) of MMA or 2.08 g (20 mmol) of St or 3.04 g (20 mmol) of CMS were dissolved in 15 ml related solvent. Polymers **I** and **II** were dissolved in ethyl acetate, that of **III** and **IV** were dissolved in toluene and acetone respectively. Then the ampoules were degassed, sealed under vacuum and maintained at 70 ±1 °C in a water bath and shaken by a shaker machine for about 24 h. The viscous solutions were poured from the ampoules into 150 mL of cooled methanol (I), ethanol (II), toluene (III) and petroleum ether (IV) separately. The precipitates were collected and washed with the mentioned solvents for several times and dried under vacuum at room temperature. The yields of copolymers are presented in Table 1.

For **I**: ^{1}H NMR (DMSO-d$_6$, 250 MH$_Z$) ppm: 1.6-2.7 (3H, –CH$_2$–CH), 3.9 (2H, –CH–CH), 3.55 (3H, –OCH$_3$); FT-IR (KBr, cm^{-1}): 3005, 2957 (aliphatic C–H), 1733 (C=O ester), 1849, 1781 (C=O stretching of anhydride unit), 1223, 1169 (C–O ester), 1101, 1059 (C–O–C)

For **II**: ^{1}H NMR (DMSO-d$_6$, 250 MH$_Z$) ppm: 0.76-1.20 (3H, –CH$_3$–C), 1089-2.47 (2H, –CH$_2$–C–), 3.53 (3H, –OCH$_3$–C), 4.07 (2H, –CH–CH–); FT-IR (KBr, cm^{-1}): 1857, 1785 (C=O stretching of anhydride unit), 1730 (C–O ester), 2999, 2956 (aliphatic C–H), 1240, 1150 (C–O ester).

For **III**: ^{1}H NMR (DMSO–d$_6$, 250 MH$_Z$) ppm: 4-4.5 (CH$_2$Cl), 7-7.5 (Ar–H of styrene), 3.5 (2H, –CH–CH); FT-IR (KBr, cm^{-1}): 1880, 1770

(C=O stretching of anhydride unit), 3060, 2887 (aliphatic CH), 1220 (CH₂Cl).

For **IV**: ¹H NMR (DMSO–d₆, 250 MH$_Z$) ppm: 70.1 (Ar–H of styrene), 4.32 (2H, –CH–CH), 1.6-2.8 (2H, –CH₂–C–); FT-IR (KBr, cm⁻¹): 1860, 1780 (C=O stretching of anhydride unit), 1602, (C=C aromatic 3002 (C–H of aliphatic).

Attachment of indole group to the side chain of copolymer (I-IV)

Poly (MA-*co*-MAc), poly (MA-*co*-MMAc), poly (MA-*co*-CMS) and poly (MA-*co*-St) containing indole groups were prepared as follows. In a 100 mL two-necked flask equipped with a dropping funnel, argon atmosphere and magnetic stirring, sodium hydride (4 mmol, 0.96 g) was slowly added to indole (5 mmol, 0.58 g) dissolved in 15 mL of DMF at room temperature for 30 min. After this time, the mixture were cooled to -5 °C in ice-salt mixture while vigorous stirring. Then solution of polymers (I-IV) (2.5 mmol) in 15 mL of DMF was added drop wise within 1 h. The contents were kept at ambient temperature for another 3 h while stirring the mixture of (I, II, IV) where then poured drop wise into a large excess of cold water then 5 mL HCl 37% added drop wise within the contents and keep in 0°C for 15 h. But the mixture of **III** 15 mL HCl 37% added drop wise within the contents and keep in 0
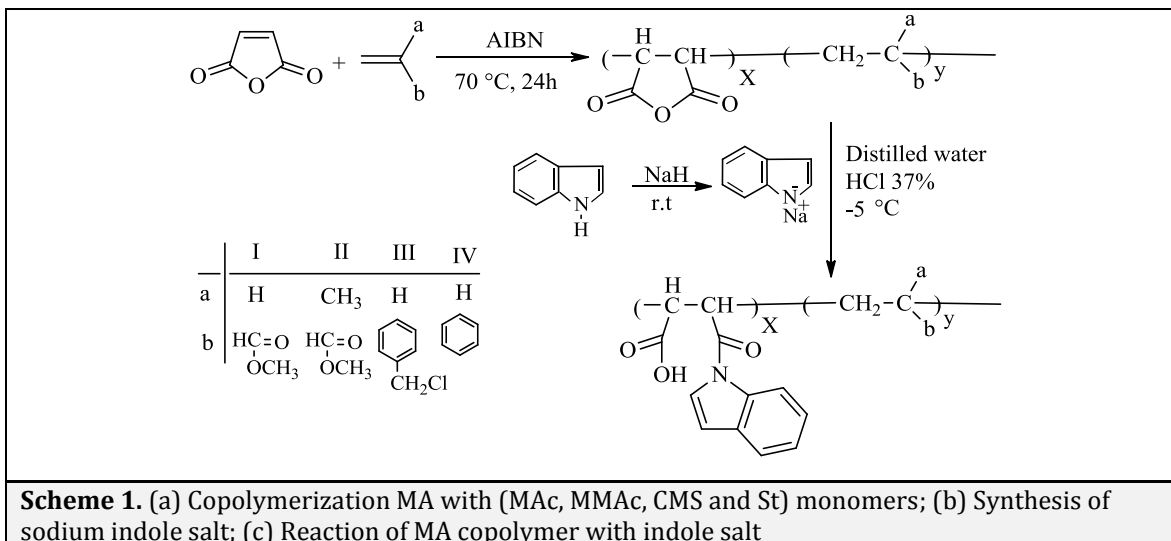
°C for 80 h. The precipitated solid was recovered by filtration washed successively with water. The resulted polymers were dissolved in 50 mL diethyl ether for removing surplus indole. Finally the polymers containing indole substituents in the side chains were collected and dried under vacuum at room temperature.

For **I$_{In}$**: ¹H NMR (DMSO-d₆, 250 MH$_Z$) ppm: 2.27-1.85 (2H, –CH₂–CH), 6.3-7.9 (Ar–H of indole), 11.04 (1H, O–H); FT-IR (KBr, cm⁻¹): 3060 (Ar–H of indole), 2400-3400 (OH acid), 1637 (C=O amide), 1770 (C=O acid).

For **II$_{In}$**: ¹H NMR (DMSO-d₆, 250 MH$_Z$) ppm: 0.92-1.78 (3H, –CH₃–C–), 2.48-2.85 (2H, –CH₂–CH), 6.3-8.6 (Ar–H of indole), 11.08 (1H, –OH); FT-IR (KBr, cm⁻¹): 3393 (Ar–H of indole), 1651 (C=O amid), 1734 (C=O acid), 2400-3400 (–OH acid).

For **III$_{In}$**: ¹H NMR (DMSO-d₆ 250 MH$_Z$) ppm: 2.49-2.85 (2H, in –CH₂–CH), 608-7.9 (Ar–H of indole and styrene), 10.85 (1H, O–H); FT-IR (KBr, cm⁻¹): 3445 (Ar–H of indole and styrene), 1620 (C=O amid), 2400-3400 (–OH acid).

For **IV$_{In}$**: ¹H NMR (DMSO-d₆ 250 MH$_Z$) ppm: 2.41-2.85 (2H, –CH₂–CH), 6.3-7.9 (Ar– H of indole and styrene), 11.07 (1H, O–H); FT-IR (KBr, cm⁻¹): 3399 (Ar–H of indole and styrene), 1720 (C=O acid), 1638 (C=O amide), 2400-3400 (1H, –OH).

Scheme 1. (a) Copolymerization MA with (MAc, MMAc, CMS and St) monomers; (b) Synthesis of sodium indole salt; (c) Reaction of MA copolymer with indole salt

Table 1. The conditions of preparation of polymers (I-IV) at 70 °C

Sample	Manomer 1	Manomer 2	Amount of 1 in mmol	Amount of 2 in mmol	Time (h)	Weight	Yield%
I	MA	MAc	20	20	24	3.3	%89
II	MA	MMAc	20	20	24	2.9	%73
III	MA	CMS	20	20	24	3.2	%64
IV	MA	St	20	20	24	4.2	%74

Macromolecular grafting is a synthetic approach that involves the functionalization of a reformed polymer backbone containing reactive groups with an appropriate reagent. Since polymer properties are often heavily influenced by the identity of their pendant groups, a variety of different materials with a wide range of properties can be synthesized from only one antecedent. The use of maleic anhydride copolymers is attractive because of the variability in their properties achieved through the introduction of different comonomers. Furthermore, these copolymers contain the reactive anhydride unit, which offers possibilities for subsequent chemical modification of the polymer in order to tune the electrical and optical properties. Maleic anhydride copolymers can be modified by low-molecular-weight compounds containing active hydrogen (water, alcohols or amines) because of the reactivity of the anhydride functions. In the recent study, functionalization of maleic anhydride copolymers by grafting indole were achieved in the presence NaH at -5 °C.
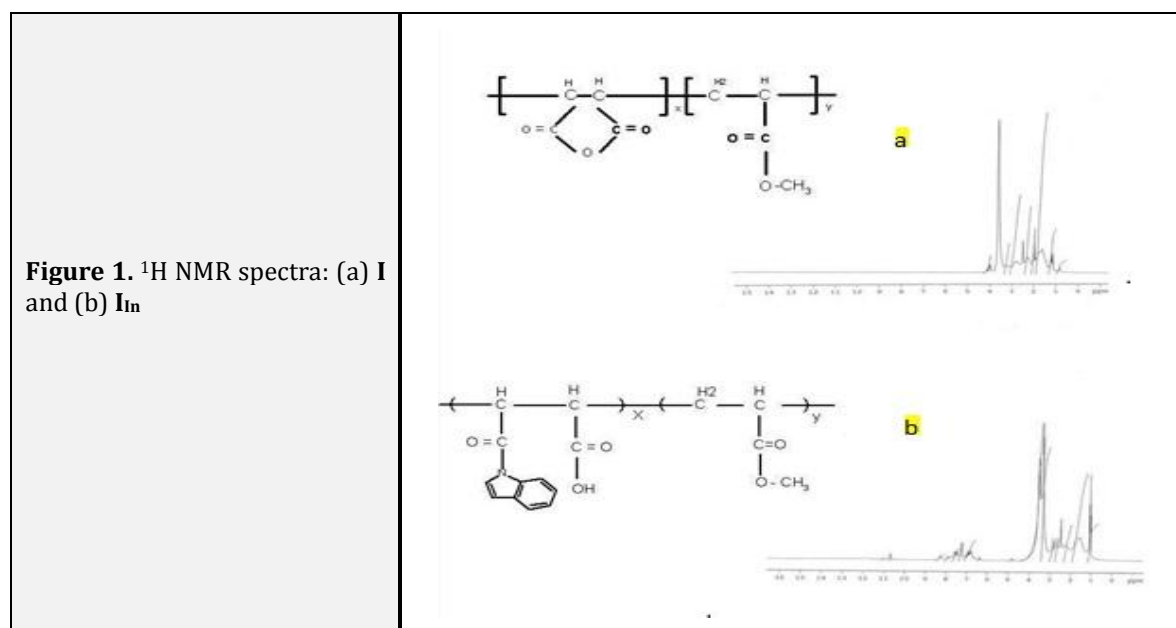
The maleic anhydride (MA) monomer was copolymerized with methacrylate (MAc), methyl methacrylate (MMAc) in ethyl acetate, chloromethyl styrene (CMS) in toluene and styrene (St) in acetone at
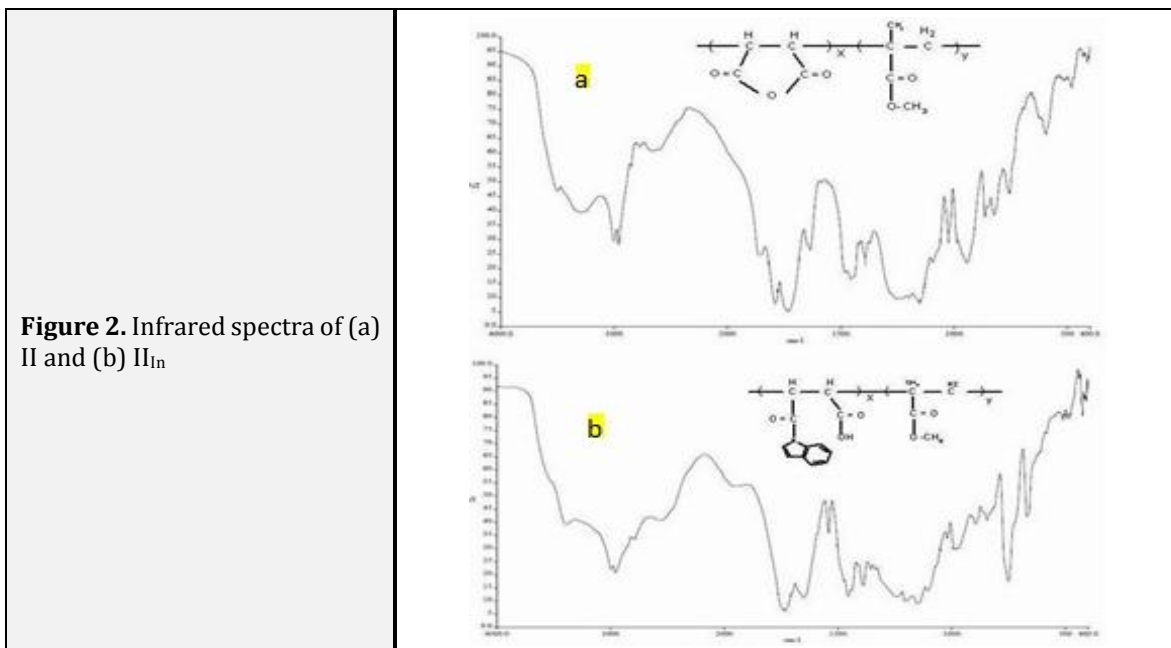
70±1°C using AIBN as the radical polymerization initiator to obtain P(MA–*co*–MAc) (I), P(MA-*co*-MMAc) (II), P(MA-*co*-CMS) (III) and P(MA-*co*-St) (IV) copolymers respectively (Scheme 1). The reaction conditions are shown in Table 1. The resulted copolymers are color solid and soluble in chloroform, N, N-dimethyl form amide and dimethyl sulphoxide.

Indole was reacted with the copolymers **I-IV** in the presence of sodium hydride at -5 °C to yield **I$_{In}$-IV$_{In}$** with an isolation yield of 65-85%. The ring-opening reaction resulted in the formation of carboxyl and amide groups (Scheme 1).

The principal evidence for construction of functional groups onto polymers is appearance and loss of IR and ^{1}H NMR peaks that correspond to the introduction or transformation of distinct functional groups

in each stage. The obtained ^{1}H NMR spectra for the modified copolymers (I-IV) show that indole is in corporate with some of the anhydride groups. It also shows that within the corporation of anhydride groups by indole group the peak around 6–7 ppm corresponding to two methylene protons of anhydride in MA disappeared and new acidic proton peaks appeared around 10–11 ppm owing to ring opening reaction of anhydride group (Figure 1). The infrared spectra of the modified products show the broad characteristic of (O-H) group at wave number of 2600-3000 cm^{-1} and new peak appeared 1630 cm^{-1} corresponding to carbonyl of the amide group and corresponding to two carbonyl groups of the MA copolymers revealed that the other group remained during the reaction (Figure 2).

Figure 1. ^{1}H NMR spectra: (a) **I** and (b) **I$_{In}$**

Figure 2. Infrared spectra of (a) II and (b) II_{In}

Molecular Weights

The number and weight average molecular weights ($M_{n2}M_w$) and polydispersity index of copolymer samples were determined by gel permeating chromatography (GPC) and are presented in Table 2.

Copolymers Compositions

^{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 [17, 18]. So the compositions of copolymers synthesized using various monomer feed ratios were determined by known NMR method and were achieved by comparing the integrals of the maleic anhydride, methylen and methoxy groups regions in the spectra of the comonomer units (m_1 and m_2) in copolymers using [1]H

NMR analysis data were calculated according to the following equations:

$$\frac{Am1(CH)}{Atotal} = \frac{n1m1}{a1m1 + b2m2} \tag{1}$$

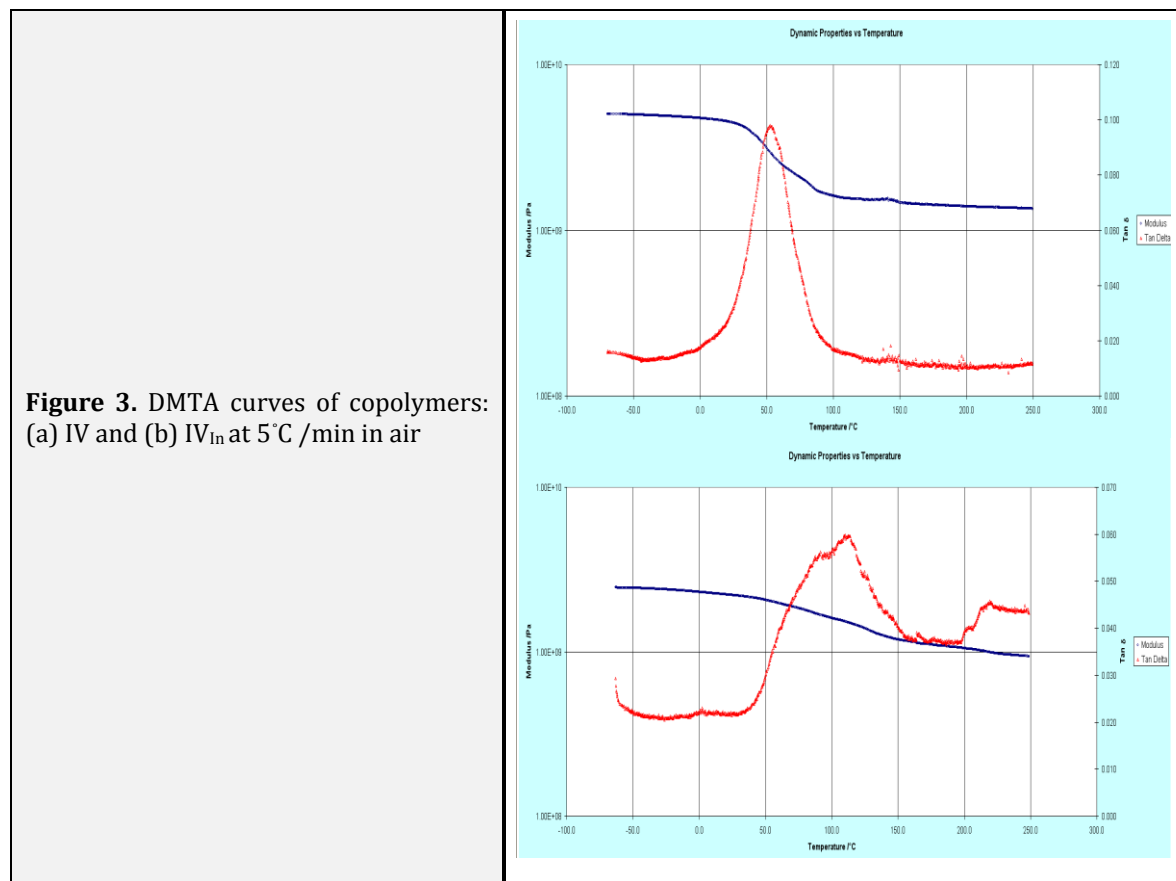$$\frac{Am2(OCH3\ or\ OCH2)}{Atotal} = \frac{n2m2}{a1m1 + b2m2} \tag{2}$$

$$m1 + m2 = 1 \tag{3}$$

Where Am_1 and Am_2 are the normalized areas per H from the corresponding functional groups of the monomer unit regions in ^{1}H 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:

$$\frac{m1}{m2} = f = \frac{n2Am1(CH)}{n1Am2(OCH3\ or\ OCH2)} \tag{4}$$

Table 2. Molecular weight and T_g of MA copolymers

Polymer	$M_W/10^3$	$M_n/10^3$	M_W/M_N	T_g (°C)
I	37.4	19.35	1.94	56
II	39.2	19.8	1.97	85
III	28	15.5	1.8	139
IV	32.1	16.05	2.0	55

Figure 3. DMTA curves of copolymers: (a) IV and (b) IV_{In} at 5°C /min in air

Table 3. The molar composition of copolymer (I-IV) with indole

Polymer	MA (mol %)	MAC (mol %)	MMA (mol %)	CMS (mol %)	St (mol %)
I	55	45	-	-	-
II	53.5	-	46.5	-	-
III	45	-	-	55	-
IV	52	-	-	-	48

Table 4. The result of reaction between 2 mmol of each polymer (I-IV) with indole

Modified Copolymer	Weight (g)	Yeild (%)	T_g (°C)
I_{In}	0.35	70	111
II_{In}	0.36	72	80
III_{In}	0.28	56	182
IV_{In}	0.35	10	127

Conclusions

The copolymers of MA with MMAc, MAc, CMS, and St (I-IV) were synthesized by free radical solution polymerization and the copolymer compositions calculated by corresponding ^{1}H NMR analysis. The resulted copolymers are soluble in chloroform, THF, N, N– dimethyl form amide and dimethyl sulpoxide and insoluble in diethyl ether and water. Characterization of all the obtained polymers were performed with FT-IR, and ^{1}H NMR spectroscopic techniques. The study of DMTA curves for the modified copolymers indicated that glass transition temperature values of the copolymer increase with incorporation of indole groups as side chains. The presence of the indole groups in polymer structures increases the rigidity of macromolecules and creates the modified polymers with novel properties and applications.

Acknowledgement

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