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Synthesis, Characterization, and Thermal Properties of Poly(isobornyl methacrylate-co-benzyl methacrylate) copolymers

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In this study, novel copolymers of isobornyl methacrylate and benzyl methacrylate in three different compositions were synthesized by free radical polymerization using benzoyl peroxide as an initiator at 70 ◦C. The chemical structures of the poly(isobornyl methacrylate-co-benzyl methacrylate) copolymers were analysed by Fourier transform infrared, ^{1}H-NMR spectroscopy. The percentage compositions of the synthesized copolymers were calculated with the help of H-NMR spectra. Thermogravimetric Analysis (TGA) and Differential Thermal Analysis (DTA) were employed to investigate the thermal properties of these copolymers. Thermal analysis results were demonstrated that the thermal stability of the copolymers increased with the increase of BzMA units in the copolymer chain. DTA measurements were showed that the the glass transition temperatures of the studied copolymers increased with the increase in IBMA content.

Keywords: *Poly(isobornyl methacrylate-co-benzyl methacrylate), Synthesis, Characterization, thermal properties*

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1. Introduction

Polymers, which have different structures, both natural and synthetic, are used in many areas today. In particular, the majority of polymers used for industrial design are synthetic and specially formulated to serve a specific purpose [1-4]. One of the most widely used of these synthetic polymers is poly(methacrylates), which are characterized by ease of processing, biocompatibility, light weight, low cost and excellent transparency. Therefore, these polymers are used in many areas, especially optical devices, medical instruments and optoelectronic applications [5-9]. Among poly(methacrylates), poly(isobornyl methacrylate) P(IBMA) is recently attracted great attention due to its chemical structure. The hard and hydrophobic side group in its structure provides the isobornyl methacrylate polymer with high hardness, high glass transition temperature (Tg_{IBMA} = 110-200 °C) and low water absorption [10-12]. In addition, the isobornyl group can be incorporated into another polymer through copolymerization to give polymers superior optical properties. This makes these copolymers suitable for use in optical coatings, in the development of clear acrylic-based products, and in lenses. In addition, P(IBMA) is often included in production formulations for use in automotive, aerospace, and industrial applications due to its high mechanical strength and thermal resistance. IBMA monomer has already been used more in copolymerization studies [13-17]. Copolymerization is a method for the synthesis of new materials with properties tailor-made according to the demands of industry. The combination of two monomers with different physical or chemical properties in the same polymer can lead to the formation of materials with desired properties. The properties of the synthesized copolymers are related to the structure of the copolymers, so elucidating the copolymer composition is of great importance.

This study focuses on the free radical copolymerization of isobornyl methacrylate (IBMA) and benzyl methacrylate (BzMA). Poly(benzyl methacrylate) P(BzMA) is an amorphous polymer with a low glass transition temperature (Tg_{BzMA}=54 °C). P(BzMA) has many potential applications, such as polymer optical fiber, contact lenses, adhesives and coatings, disinfectant hand gel, lithography [18-21]. The high glass transition temperature of P(IBMA) limits its processability for some applications. Therefore, forming copolymeric structures with a monomer with a lower glass transition temperature makes these polymers softer and easier to process. For this purpose, BzMA monomer was preferred as a comonomer for IBMA monomer in the study. After copolymerization, the resulting poly(isobornyl methacrylate-co-benzyl methacrylate) P(IBMA-co-BzMA) copolymers were transformed into a more processable thermoplastic product depending on the composition. In this case, the synthesized copolymers can be used in fiber optics and contact lenses due to their high optical transparency and processable temperature.

2. Experimental

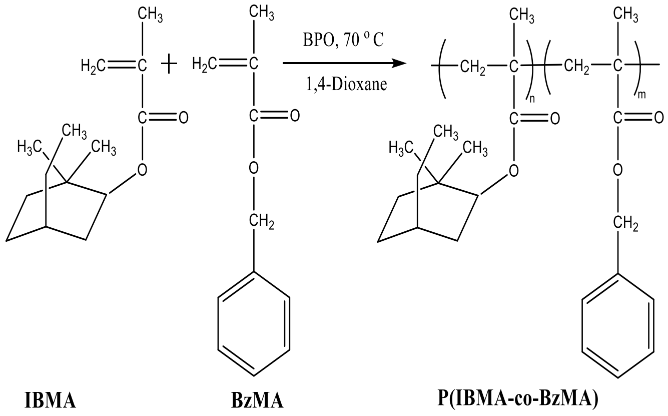
2.1. Materials and instrumental measurements

The isobornyl methacrylate and benzyl methacrylate monomers were supplied from Sigma-Aldrich. The monomers were washed with a 5% NaOH aqueous solution before polymerization and then vacuum distilled.. 1,4-Dioxane, dichloromethane were used as received. Benzoyl peroxide (BPO), used as the initiator, was recrystallized from a chloroform-methanol (1:1) mixture and dried under vacuum.

Infrared spectra were recorded on a PerkinElmer Spectrum One and acquired using the universal ATR sampling accessory at wavelengths of 4000–650 cm^{-1}. ^1H-NMR spectra were performed on an AVANCE III 400 MHz Bruker NMR spectrometer using tetramethylsilane as internal standard. Samples were dissolved in $CDCl_3$ solvent. Thermal stabilities and glass transition temperatures of the polymers were determined using a Perkin-Elmer TGA/DTA 7300 thermal analyzer under N_2 flow with a heating rate of 20 °C/min from room temperature to 500 °C. Polymer samples were taken in the form 4-8 mg weights for thermal analysis.

2.2. Preparation of Poly(isobornyl methacrylate-co-benzyl methacrylate) copolymers

Copolymers of isobornyl methacrylate and benzyl methacrylate monomers with three different compositions were synthesized by free radical polymerization method. For this purpose, required amounts of IBMA and BzMA monomers were taken and added to separate polymerization tubes. Benzoyl peroxide (1% of the monomer amount) and 1.4 dioxane were added to the monomer mixtures as initiator and solvent, respectively. The mixture in the polymer tubes was passed through nitrogen gas for five minutes. The tubes were closed and left to polymerize in an oil bath set at 70 °C for 18 hours. The tubes were then removed from the oil bath and cooled to room temperature. Polymer solutions that were viscous were slightly diluted with dichloromethane solvent. Polymer solutions were precipitated dropwise in ethyl alcohol. The precipitation process was repeated twice to ensure that no monomer remained in the obtained polymers, filtered and dried in a vacuum oven at 40 °C. The schematic representation of the synthesized copolymers was given in Scheme 1. Homopolymerization of both IBMA and BzMA was carried out by the same method.



Scheme 1. Synthesis of P(IBMA-co-BzMA)

3. Results and Discussion

3.1. Characterization of Copolymers

The FTIR spectra of poly(isobornyl methacrylate-co-benzyl methacrylate) are shown in Figure 1. In the FTIR spectra of P(IBMA-co-BzMA) was observed C-H stretching band of aromatic ring at 3085-3030 cm^{-1}. There are symmetrical and asymmetrical stretching bands at 2954 and 2881 cm^{-1} due to the methyl and methylene groups. The band at 1721 cm^{-1} can be attributed to the ester carbonyl stretching vibration of the isobornyl methacrylate and benzyl methacrylate. The three signals around 1477, 1496,and 1595 cm^{-1} are assigned to the stretching vibration of C=C of the benzene skeleton. The signal around 1145 cm^{-1} is assigned to the C-O of the ester group. The peaks at 750 cm^{-1} and 695 cm^{-1} are attributed to the stretching vibration of mono substituted aromatic ring. For the isobornyl methacrylate and benzyl methacrylate monomers, there are a distinct vibrational peak at 1640 cm^{-1} (the stretching vibration peak of the C=C bond of the vinyl structure), which is not present in the FTIR spectra of

P(IBMA-co-BzMA). This confirmed that the double bond of isobornyl methacrylate and benzyl methacrylate monomers reacted.

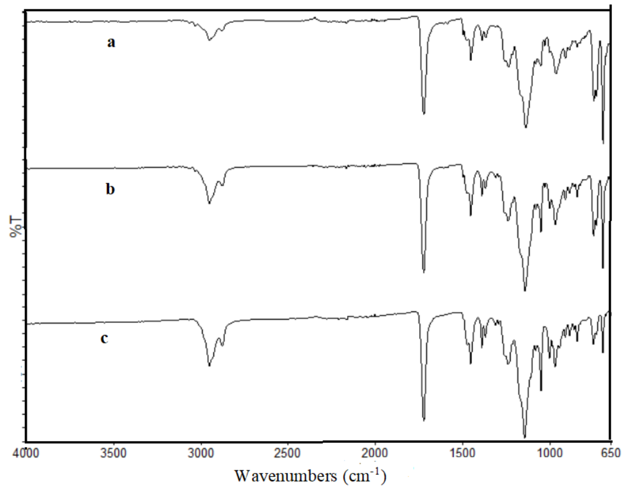


Figure 1. FT-IR Spectrum of a-) P(IBMA0.26-co-BzMA) b-) P(IBMA0.48-co-BzMA) c-) P(IBMA0.78-co-BzMA)

Figure 2 are presented the ^{1}H NMR spectra of three copolymers prepared via free radical polymerization. The chemical shifts between 7.0 and 7.5 ppm are attributed to the protons of phenyl ring of benzyl methacrylate and the signal at 4.93 ppm is assigned to the OCH_2 protons of the BzMA unit, the signal at 4.35 ppm is assigned to the –CH proton in the isobornyl methacrylate. The peaks at 1.9 ppm and 0.7 ppm are due to CH_3 and CH_2 protons in the polymer chain.

3.2 Determining the composition of copolymers

The percentage compositions of P(IBMA-co-BzMA) copolymers were calculated through the ^{1}H-NMR spectra. The OCH_2 protons at 4.93 ppm in the BzMA units and the CH proton at 4.35 ppm in the IBMA units were taken as a basis for the calculation of composition percentages Copolymer compositions were calculated from the following equations.

$$\frac{\text{integral values of CH proton}}{\text{integral values of OCH2 proton}} = \frac{m1}{2m2} \tag{1}$$

where m_1 is mole fraction of IBMA, and m_2 is that of BzMA in copolymer. Since the total mole fraction is always equal to 1, $m_2=1-m_1$ if $m_1+m_2=1$. The calculation method of the copolymer compositions for the P(IBMA0.26-co-BzMA) polymer sample is as follows.

$$\frac{m1}{2m2} = \frac{1}{5.58} \tag{2}$$

It is calculated as % $m_1=0.26$ and % $m_2=1-m_1=0.74$,

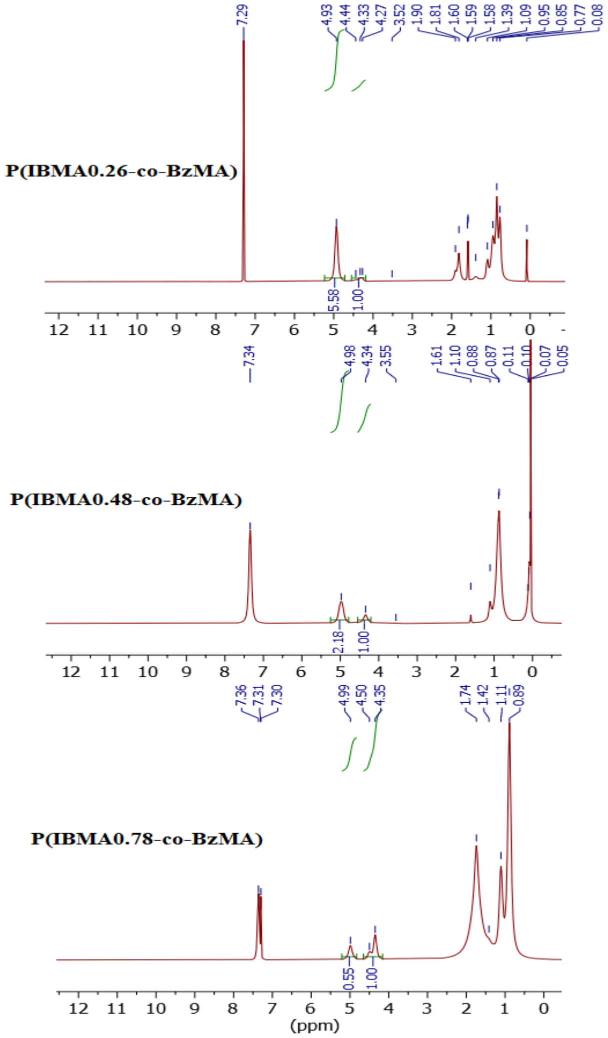


Fig. 2. ^{1}H-NMR spectra of P(IBMA-co-BzMA) copolymers

For the other samples, compositions were determined by similar calculations using the peak heights obtained through the ^{1}H-NMR spectra. The results obtained are given in Table 1.

Table 1. Monomer compositions in feed and in the copolymer

Sample	Feed composition				Copolymer composition	
	IBMA (M_1)	BzMA (M_2)	I_{CH}[a]	I_{OCH2}[a]	IBMA (m_1)	BzMA (m_2)
P(IBMA0.78-co-BzMA)	0.80	0.20	1	0.55	0.78	0.22
P(IBMA0.48-co-BzMA)	0.50	0.50	1	2.18	0.48	0.52
P(IBMA0.26-co-BzMA)	0.20	0.80	1	5.58	0.26	0.74

[a] Integral values of C*H* protons in IBMA units
[b] Integral values of OC*H₂* protons in BzMA units

3.3. Thermal properties of polymers

Differential thermal analysis (DTA) curves can be used to determine the glass transition temperature (Tg) of polymers. This temperature is important and characteristic value for polymers. This temperature measurements were carried out at a heating rate of 20 °C min^{-1} under nitrogen atmosphere from room temperature to 300 °C. The glass transition temperature of the polymers was calculated by taking the midpoint of the sloping region on the DTA curve. The Tg values of P(IBMA) and P(BzMA) were 198 and 54 °C in literature respectively, while the Tg values of P(IBMA0.26-co-BzMA), P(IBMA0.48-co-BzMA) and P(IBMA0.78-co-BzMA) copolymers were determined as 95.8, 127.6 and 173.5 °C, respectively. As seen Figure 3 the glass transition temperatures of P(IBMA-co-BzMA) copolymers were found in the range of Tg of homopolymers. The glass transition temperature of P(IBMA) is higher than P(BzMA). Therefore, as the IBMA units increased in the copolymer, the glass temperatures of the studied polymers increased.

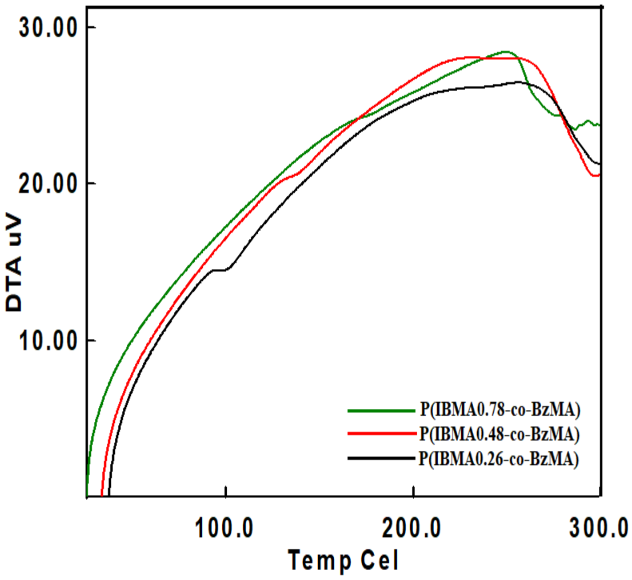


Figure 3. DTA curves of P(IBMA0.78-co-BzMA), P(IBMA0.48-co-BzMA) and P(IBMA0.26-co-BzMA)

3.4. Thermogravimetric Analysis

The effect of benzyl methacrylate units on the thermal stability of poly(isobornyl methacrylate) was investigated by thermogravimetric analysis. The thermograms obtained by plotting the percentage of weight loss versus temperature for poly(IBMA-co-BzMA) copolymers prepared at different compositions are given in Figure 4. The aromatic ring in the side group of P(BzMA) gives this polymer a higher thermal stability. Therefore, the thermal stabilities of the copolymers generally increased with the increase of BzMA units in the polymer chain.

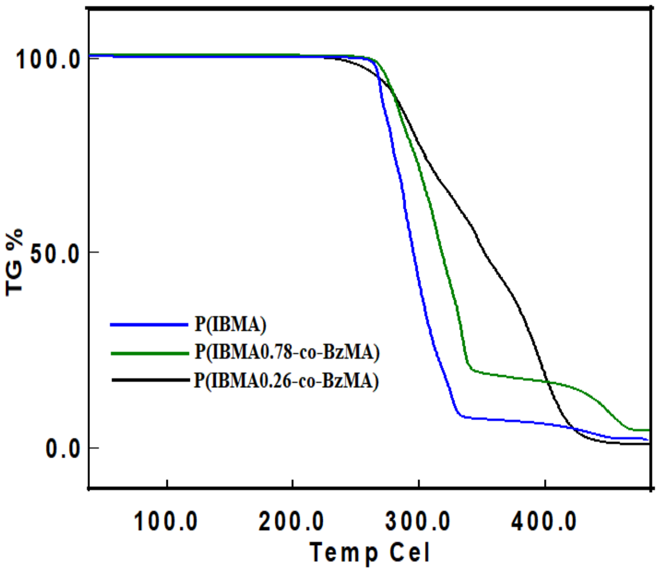


Fig. 4. TGA curves of P(IBMA), P(IBMA0.78-co-BzMA) and P(IBMA0.26-co-BzMA)

4. Conclusions

In this work, the copolymers of IBMA with BzMA and their homopolymers initiated with AIBN were synthesized by free radical polymerization technique at 70 ^{0}C. Basic spectroscopic methods such as FT-IR and ^{1}H-NMR were used for structural analysis of the synthesized polymers. The composition of the copolymers was calculated using the ^{1}H-NMR spectra with the help of integration heights. Thermal analysis of the studied copolymers was performed by TGA/DTA simultaneous system. Differential thermal analysis was indicated that the Tg of the copolymers increased with the increase of IBMA units in the polymer chain. Thermal stability of the copolymers was found to increase with increasing BzMA units in the copolymer.

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