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Copolymerization of Benzyl Methacrylate and a Methacrylate Bearing Benzophenoxy and Hydroxyl Side Groups: Monomer Reactivity Ratios, Thermal Studies and Dielectric Measurements

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Abstract: Statistical copolymers of 2-hydroxy-3-benzophenoxy propyl methacrylate (HBPPMA) and benzyl methacrylate (BzMA) in different feed ratios were synthesized by free radical copolymerization method at 60 °C in presence of AIBN initiator. The compositions of copolymer were estimated from ^{1}H-NMR technique. The monomer reactivity ratios of HBPPMA and BzMA were calculated as r_1 (r_{HBPPMA})=0.51±0.076 and r_2 (r_{BzMA})=1.07±0.140 for Kelen-Tüdos method, and was estimated as r_1=0.37±0.0006 and r_2=0.64±0.0485 according to Fineman Ross equation. The average values estimated from the two methods showed that monomer reactivity ratio of benzyl methacrylate was a slightly high in comparison to HBPPMA. The copolymer system showed an azeotropic point, which is equal to $M_{BzMA}=m_{BzMA}=0.43$. DSC measurements showed that the T_g's of poly(HBPPMA) and poly(BzMA) were 84 °C and 73 °C, respectively. The T_g in the copolymer system decreased with increase in benzyl methacrylate content. The decomposition temperature of poly(BzMA) and poly(HBPPMA) occurs in a single stage at about 207 °C and 260 °C, respectively. Those of HBPPMA-BzMA copolymer systems are between decomposition temperatures of two homopolymers. The dielectric constant, dielectric loss factor and electrical conductivity were investigated depend on the frequency of the copolymers. The highest dielectric constants depending on all the studied frequencies were recorded for the poly(HBPPMA) and the copolymer containing the highest HBPPMA unit. The dielectric constant for P(HBPPMA) and P(BzMA) at 1 kHz are 6.56 and 3.22, respectively. Also, those of copolymer systems were estimated between these two values. Similarly, poly(HBPPMA) and copolymers, which are prepared under the same conditions show the dissipation factor and conductivity as well.

Keywords: Copolymerization, Monomer reactivity ratios, Thermal studies, Dielectric behaviors, Poly(benzyl methacrylate)

Introduction

In a polymer production, estimation of monomer reactivity ratios in copolymer synthesis is known as one of the important copolymerization studies. Estimation of monomer reactivity ratios is considerably important in view of polymer productivity and copolymer sequence distribution. On the other hand, to control the polymer property parameters, such as copolymer composition, sequence distribution in copolymer system and average molecular weights is of particular importance for copolymerization system [1]. Having an important information as to the relative reactivities of two different monomers serves as an important clue about the calculation of copolymer composition. Also, the precise estimation of monomer reactivity ratios is to serve as a useful tool towards the accurate determination of copolymer composition, understanding their properties and utility for tailoring copolymers bearing desired physical and chemical properties [2,3]. Although the monomer reactivity ratios are assumed as regardless of the conversion, they are generally estimated for synthesis with low conversion [4]. There are a number of methods such as Kelen-Tüdos and Extended Kelen-Tüdos (EKT) [5], Finemann-Ross (FR)-Inverted Finemann-Ross (IFR) [6,7], Yezrielev-Brokhina-Roskin (Y-B-R) [8] and Tidwell-Mortimer (TM) [9], which have been used for estimating monomer reactivity ratios at copolymerizations with low conversion. The uses of copolymerization processes to develop new materials are an important and useful way. Copolymerization simplifies both intramolecular and intermolecular forces exercised among moieties on the polymer chain. Therefore, specific properties of a polymer such as the melting point for crystallinity, T_g for amorphous morphology, permeability, solubility, adhesion, and chemical reactivity may be changed within a wide range [10]. The copolymerization of olefinic monomers bearing a substituent group with bulky that also carries a benzophenone structure having two aryl groups is not discussed yet. To observe reactivity behavior of such side group with respect to reactivity is important [11]. The dielectric behavior of materials importantly depends on the polar groups on the monomer units, their percentage of composition and distribution on the main chain. The frequency and medium temperature strongly affect the dielectric properties of a polymer or materials. Both effects depend on the number of the polar groups per unit volume and equilibrium of temperature. Besides, the external field frequency affects the amount of oriented dipole moment [12,13]. The dielectric property of copolymers is a fact that will vary depending on the copolymer composition.

The poly(HBPPMA) is a polymer containing hydroxyl, ketone and ester side groups. The same polymers with OH

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*Corresponding author: kdemirelli@firat.edu.tr group possess hydrogels properties. The polymers such as poly(2-hydroxy ethyl methacrylate) and poly(2-hydroxy propyl methacrylate) a major component in materials for contact lenses, drug delivery, and hydrogels used for a variety of applications. As the swollen hydrogels have shown extensive properties such as high water content, good biocompatibility, soft consistency similar to natural tissue, and elasticity, structural integrity. In this context, it may be interesting expectations being an important polymer in view of materials for contact lenses, drug delivery, and hydrogels of poly(HBPPMA), which is similar to hydroxylated homologs. In both poly(HBPPMA) and copolymer systems, polar groups such as C-O and O-H in HBPPMA moieties have an important effect on the dielectric constant. Thus, there is the potential to be a good dielectric material of the poly (HBPPMA) and its copolymers with BzMA. So, in our present study, we have demonstrated that the reason for choosing the above-mentioned monomers is mainly due to their variation in glass transition temperatures, the difference in monomer reactivities and electrical behaviors between both moieties. Also, according to our research literature, there was no any report recorded on the monomer reactivity ratios of HBPPMA-BzMA from estimated copolymers composition of HBPPMA-co-BzMA by ^{1}H-NMR spectroscopy.

This paper reports the homopolymerization of 2-hydroxy-3-benzophenoxy propyl methacrylate (HBPPMA) and its copolymerization with benzyl methacrylate (BzMA) in different feed ratios, the characterization of the polymers by ^{1}H, ^{13}C-NMR, FT-IR, GPC, thermal analysis techniques, and dielectric measurements. The monomer reactivity ratios of HBPPMA and BzMA were estimated by using Fineman-Ross (FR) and Kelen-Tüdos (K-T) methods.

Experimental

Materials

4-Hydroxybenzophenone, epichlorohydrin and benzyl methacrylate were kindly supplied from Sigma and Aldrich, and they were used as received. The 2,2'-azobisisobutyronitrile (AIBN) was used as an initiator. All other reagents used were of analytical purity and used as received commercial.

Synthesis of 1,2-epoxy-3-benzophenoxy propane (EBFP)

The synthesis of EBFP was carried out according to the method adapted from literature [14]. For this purpose, the EBFP was prepared from the reaction of 4-hydroxybenzophenone (6 g, 0.03 mol) with 35 m*l* epichlorohydrin in presence of extreme natrium hydroxide at 110 °C. Then, the solution was mixed for 6 hours at room temperature. After completion of the reaction, the salt was filtered and product was thoroughly washed with diethyl ether. The solvent in the organic phase was evaporated by a rotary pump and the resulting product was obtained as a white solid.

Synthesis of 2-hydroxy-3-benzophenoxypropyl methacrylate (HBPPMA) Monomer

The HBPPMA was synthesized from the reaction of EBFP (0.015 mol) and methacrylic acid (1.47 g, 0.017 mol) in presence of pyridine (1 m*l*). A solution of 1,2-epoxy-3-benzophenoxy propane (3.32 g, 0.017 mol) in dry dioxane (25 m*l*) was slowly added over 30 min at room temperature and then the solution of the reaction was stirred for 22 h at 85 °C in presence of 1-2 ppm hydroquinone. The monomer to remove inhibitor was washed with an aqueous solution of natrium hydroxide (5 % by weight) for five times and then was washed with distilled water until the pH is 7. After being dried over anhydrous $MgSO_4$ overnight, the solvent was removed by an evaporator, and the product was stored in the refrigerator prior to use. Some important signals characterizing the structure of 2-hydroxy-3-benzophenoxy propyl methacrylate (HBPPMA) synthesized are summarized following as:

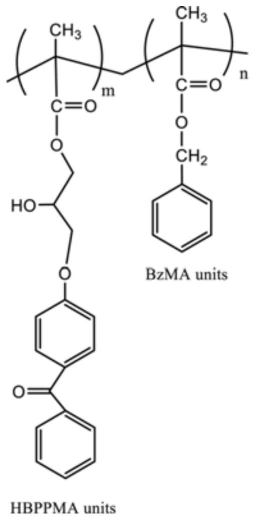
FT-IR (ν_{max}, cm^{-1}): 3445 (O-H stretching), 3078-3010 (=C-H stretching), 1720 (C=O stretching), 1650 (ketone C=O stretching between two aromatic ring), 1598 (C=C stretching), 1459 and 1320 (aliphatic C-H stretching).

^{1}H-NMR ($CDCI_3$, δppm): 7.97-6.9 (9H, protons on the two aromatic ring), 4.6-3.9 ($\underline{CH_2}O$-, -$\underline{CH}$-OH, aryl-O-$\underline{CH_2}$), 6.1 and 5.6 (2H, cis and trans protons on CH_2=C according to C=O group, respectively), 1.97 (3H, -CH_3 protons).

^{13}C-NMR ($CDCI_3$, δppm): 195.7 (C=O in ketone on benzophenone group), 167.5 (ester C=O group), 162 (aromatic ipso carbon next to oxygen), 135.8 (quaternary carbon), 69-65 (Aryl-OCH_2-, -CH-OH, -CH_2O), 18.1 (CH_3).

Free Radical Copolymerization of HBPPMA with BzMA

HBPPMA and BzMA monomers were used to prepare



Scheme 1. Structure of copolymer system prepared with HBPPMA and BzMA.

copolymer system at 60 °C in presence of 1,4-dioxane using AIBN as an initiator. A certain amount of the monomers, AIBN and 1,4-dioxane as a solvent were mixed within a polymerization tube. Argon gas was passed through the mixture of monomers and solvent for about 10 minutes and then incubated in a thermostated oil bath to 60 °C. After a certain time, the mixture of polymerization was cooled to about 25 °C. The synthesized copolymers were isolated by precipitating within excess n-hexane and purified by reprecipitation, and later the copolymer systems were dried under vacuum at 40 °C for a day. The structure of copolymer synthesized from the reaction of 2-hydroxy-3-benzophenoxy propyl methacrylate and benzyl methacrylate (HBPPMA) was illustrated in Scheme 1.

Characterization

The ^{1}H, ^{13}C-NMR and FT-IR spectra were recorded on an AVANCE III 400 MHz Bruker and a Mattson 1000 FT-IR spectrometer, respectively. The measurements of thermogravimetric analysis (Shimadzu TGA-50) of homo and copolymers were recorded using a TGA-50 by the heating rate of 10 °C min^{-1} under a nitrogen flow. DSC-50 technique (Shimadzu DSC-50) was used to measure T_g of copolymers prepared by copolymerization process. The samples were measured at the heating rate of 20 °C min^{-1} under argon gas from room temperature to 200 °C. The T_g values were recorded as a midpoint of transition ring. The GPC measurements were carried out using Agilent 1100 system having a high-pressure liquid chromatography pump equipped with a vacuum degasser and a refractive index detector. The tetrahydrofuran (THF) was used as carrier solvent at a flow rate of 1 m*l* min^{-1} at 20 °C. A linear standard polystyrene was used to calibrate GPC instrument.

Dielectric Measurements of the Homo- and Copolymers

A QuadTech 7600 LRC impedance analyzer was used to investigate the dielectric behaviors of copolymers. The copolymers were put into a thermostated oven at 40 °C for 24 hrs. Therefore, the films with the diameter of 5-6 mm were prepared from every HBPPMA-BzMA copolymer system. The surface of films was coated by Al plate, and electrodes were positioned on each surface. The dielectric measurements were recorded for the frequency range from 100 Hz to 40 kHz by sandwiching under four tons pressure into disk-shaped at room temperature.

Results and Discussion

Spectroscopic and GPC Characterizations

The ^{1}H-NMR enlarged spectra of poly(HBPPMA) and HBPPMA-BzMA copolymer systems prepared by free radical polymerization were showed in Figure 1. The ^{1}H-NMR spectrum of poly(HBPPMA) indicates the characteristic signals at 7.96-6.9 ppm (protons on benzophenone ring), 4.4-3.9 ppm (CH_2 next to ester oxygen and CH adjacent to alcohol oxygen and CH_2 protons next to aryl group). All the HBPPMA-BzMA copolymer systems showed at 7.96-6.9 ppm (protons on benzophenone and aromatic protons in BzMA unit), 4.96 ppm (OCH_2- protons in BzMA unit). As the BzMA units in copolymer system increase, the signal intensity of OCH_2- protons in BzMA unit is increasing.

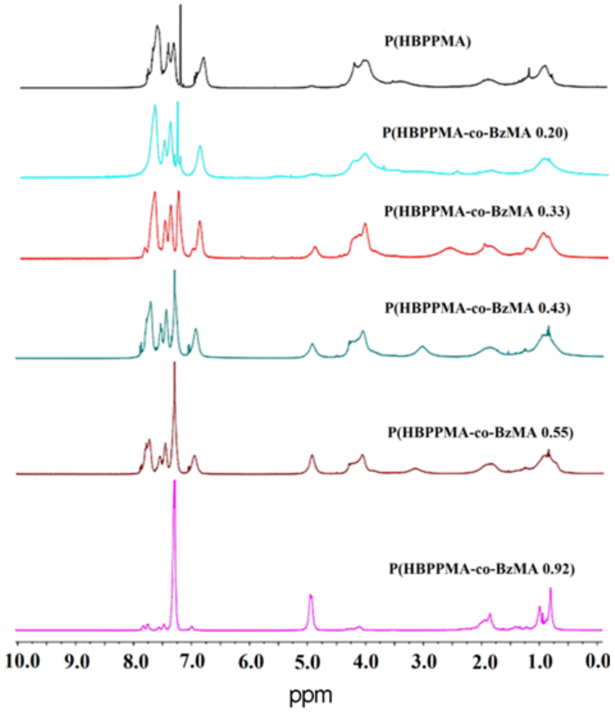


Figure 1. ^{1}H-NMR spectra of P(HBFPMA) and HBFPMA-BzMA copolymer systems (Solvent: d-chloroform).

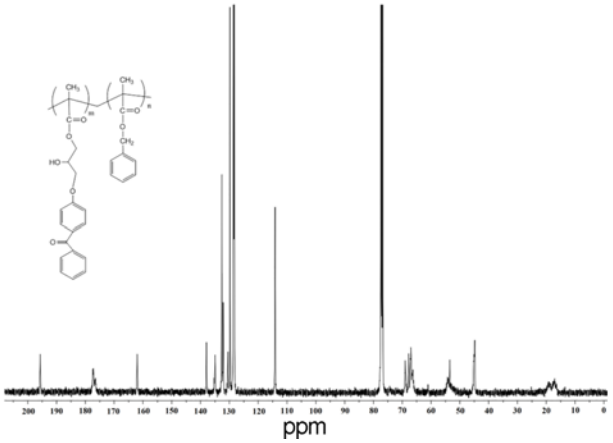


Figure 2. ^{13}C-NMR spectrum of P(HBFPMA-co-BzMA0.33) (d-chloroform).

The high intensive bands at 1650 cm^{-1} and 1720 cm^{-1} in FT-IR spectrum of poly(HBPPMA) characterize the ketone C=O band between two aryl groups and ester C=O bands in both HBPPMA and BzMA units, respectively. The ^{13}C

Table 1. GPC results of homo and copolymers

Polymers	Mn	Mw	HI(=Mw/Mn)
P(HBPPMA)	7750	14900	1.92
P(HBPPMA-co-BzMA 0.92)	33300	124000	3.72
P(HBPPMA-co-BzMA 0.55)	11700	30700	2.62
P(HBPPMA-co-BzMA 0.43)	12800	34700	2.71
P(HBPPMA-co-BzMA 0.33)	11760	32200	2.73
P(HBPPMA-co-BzMA 0.20)	12400	31700	2.41

NMR spectrum of a copolymer, which is shown in Figure 2 (33 % BzMA unit, by mole) has the most characteristic peaks for the two monomer units at 195.7 ppm (ketone C=O band between two aryl groups), 178.2 ppm (C=O in both BzMA and HBPPMA units), 67 ppm (-OCH_2 on BzMA unit), 62 (-OCH_2 on HBPPMA unit), 52-54 ppm (quaternary carbon on the backbone), 45 ppm (CH_2 carbon, which is some broad on the backbone), 17 and 19 ppm (CH_3 carbons on the backbone).

The average molecular weights of the (co)polymers were measured by GPC in presence of PSt as the standard and THF as a solvent. The number average (Mn) and weight average molecular weights (MW), and the polydispersity index (HI=Mw/Mn) for homo and copolymers are presented in Table 1.

The (co)polymers exhibited Mn in the range of 33300 to 12400 g mol^{-1} and Mw between 31700 and 12400 $gmol^{-1}$. The Mw of P(HBPPMA) shows lower values than that of PBzMA. Both Mw and Mn of P(HBPPMA-co-BzMA)s decrease together with increasing content of HBPPMA unit in the copolymer system. This decreasing is probably due to increasing in chain transfer reactions resulting in OH group on HBPPMA units. Thus, this phenomenon indicates that it can be manipulated by the polymerization conversion of BzMA units having more limited chain transfer reactions during copolymerization. The polydispersity (PD) of P(HBPPMA) and P(BzMA) prepared under the same conditions is 1.92 and 1.54, respectively. The resulting copolymers possess slightly relatively higher polydispersities (2.41<HI<3.72). The fact of larger PD suggests that the contribution of chain transfer and breaking as well as termination reactions during copolymerization is important, and can not be ignored up to the higher polymerization conversion. The copolymer compositions can be determined using various spectroscopic techniques. Recently, there were reports on the applicability of some methods such as ^{1}H-NMR, FT-IR and MALDI-TOFF Mass Spectrometry [15,16]. In this study, co-monomer feed compositions were analyzed by ^{1}H-NMR spectroscopy. For this purpose, the co-monomeric composition was quantitatively calculated by comparison of proton signals on the aromatic ring in BzMA units and the CH_2 protons next to ester oxygen in HBPPMA units.

Monomer Reactivity Ratios of Copolymers

The copolymerization of HBPPMA and BzMA in presence of AIBN for different feed ratios of HBPPMA to BzMA was carried out by the free radical polymerization method. Figure 1 shows ^{1}H NMR spectra of the five different copolymers prepared by FRP. The composition of copolymers was estimated from ^{1}H-NMR spectra. The analysis of ^{1}H-NMR spectroscopy proves the quantitative nature of a copolymer. Also, the NMR method can be advantageous in most of the cases. One of them provides compositional information of feed and copolymer prepared during a single polymerization experiment, another one generates many data points automatically [17]. The signals centered at 4.93 ppm are assigned to methylene protons, which is adjacent to oxygen in BzMA unit. Thus, the mole fractions of BzMA and HBPPMA in the copolymer system were estimated from the relative ratio of the signal intensities of CH_2 protons, which is adjacent to ester oxygen at 4.93 ppm for BzMA units and integral heights of aliphatic protons around oxygen in HBPPMA moieties between 3.72 and 4.50 ppm, respectively. The monomeric units in copolymer have been calculated according to the following equation:

$$C=\frac{\text{Integral heights of aliphatic protons around oxygen in HBPPMA units}}{\text{Integral heights of -OCH}_2\text{ protons in BzMA units}}$$

$$=\frac{5_{m1}}{2_{m2}}$$

$$m_1 = 2C/(5+2C)$$

So, monomer compositions in the feed for preparing copolymers and integral heights for HBPPMA and BzMA units were submitted in Table 2. The monomer composition data in the feed and copolymer of HBPPMA and BzMA system were given in Table 3.

The monomer reactivity of a copolymer depends on the time of copolymerization, concentrations of units in the

Table 2. Monomer compositions in feed of copolymers and integral heights for HBPPMA and BzMA units

	M_1^b	Integral highest of aliphatic protons next to oxygen in HBPPMA units	Integral highest of -OCH_2- protons in BzMA units	m_1^c
HBPPMA	0.10	0.43	2.0	0.08
	0.50	4.10	2.0	0.45
	0.65	6.90	2.0	0.58
	0.75	10.15	2.0	0.67
	0.90	38.00	2.0	0.80

Where m_1 and m_2 are mole fraction of HBPPMA and BzMA in copolymer system, respectively.

Table 3. Monomer composition data in feed and copolymer of HBPPMA and BzMA system

Sample code	Mole fraction of monomer in feed		Mole fraction of monomers in copolymer	
	HBPPMA (M_1)	BzMA (M_2)	HBPPMA (m_1)	BzMA (m_2)
BzMA	0.00	1.00	0.00	1.00
HBPPMA-BzMA-1	0.10	0.90	0.08	0.82
HBPPMA-BzMA-2	0.50	0.50	0.45	0.55
HBPPMA-BzMA-3	0.65	0.35	0.58	0.42
HBPPMA-BzMA-4	0.75	0.25	0.67	0.33
HBPPMA-BzMA-5	0.90	0.10	0.80	0.20
HBPPMA	1.00	0.00	1.00	0.00

comonomer and its reactivity such as polarity, steric and resonance effects [18]. The copolymerization of olefinic monomers with a bulky substituent that can carry a big group like a benzophenone is not discussed in the literature yet. The degree of effect of such a benzophenone structure in the side group with respect to reactivity is important. Mayo and Lewis [19] revealed the first kinetic model to be used by the free radical copolymerization system on the terminal kinetic model, the monomer reactivity of a radical depends merely on the monomeric unit in end of the terminated chain structure. According to Mayo and Lewis equation, the relative reduction of the two monomers is given by:

$$\frac{dM_1}{dM_2} = \frac{r_1 M_1^2}{r_2 M_2^2} + \frac{M_1 M_2}{M_1 m_2} \tag{1}$$

M_1 and M_2 are the mole fractions of the each monomer used in the feed, r_1 and r_2 are the monomer reactivity ratios of the species involved.

$$\frac{F(1-f)}{f} = r_2 - \frac{F^2}{f} r_1 \tag{2}$$

From the simplified equation (2) is provided as equation (3), where notations in equation (3) is defined as $H = F^2/f$ and $G = F(f-1)/f$

$$G = r_1 H - r_2 \tag{3}$$

A plot of H as abscissa and G as ordinate is a straight line with an intercept as -r_2 and slope as r_1. The graph plotted for the HBPPMA-BzMA system according to the Fineman Ross method is illustrated in Figure 3.

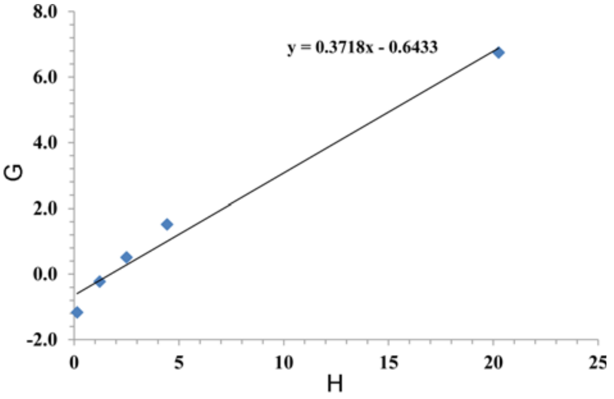


Figure 3. Determination of reactivity ratios using Finemann-Ross method for HBPPMA-BzMA copolymer.

Table 4. Kelen-Tüdos and Fineman-Ross parameter for the copolymerization of BzMA and HBPPMA

Sample no.	F= M_1/M_2	f= m_1/m_2	G= F(f-1)/f	H= F^2/f	η= G/α+H	ξ= H/α+H
1	0.11	0.08	-1.16	0.14	-0.63	0.07
2	1.00	0.81	-0.22	1.22	-0.07	0.42
3	1.85	1.38	0.57	2.50	0.12	0.59
4	3.00	2.03	1.52	4.43	0.24	0.72
5	9.00	4.00	6.75	20.25	0.30	0.92

[a] M_1=Mole fraction of HBPPMA in feed; M_2=mole fraction of BzMA in feed, m_1=mol fraction of BzMA in the copolymer, m_2= mole fraction of HBPPMA in the copolymer. $\alpha = (H_{min}\ H_{max})^{1/2}$= 1.695, H_{min}: lowest value of H, H_{max}: highest value of H.

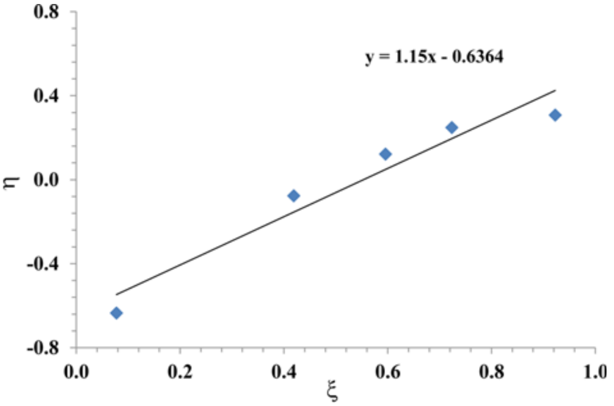


Figure 4. Determination of reactivity ratios using Kelen-Tüdos method for HBPPMA-BzMA copolymer.

The monomer reactivity ratios are assumed not to depend on the conversion; however, the monomer reactivity ratios are generally estimated for low conversions [18]. So, determination of the monomer reactivity ratio in this study was carried out at low conversions for about 30 min. It is good to know that the monomer reactivity ratios can submit an important message about the relative reactivity of comonomers. For this purpose, to estimate the relative reactivity of BzMA and HBPPMA monomers by the free radical copolymerization method, the Kelen-Tüdos, which is $\eta = (r_1 + r_2/\alpha)\xi - r_2/\alpha$, F-R methods which are $G = r_1 H - r_2$ (the descriptions and the calculated results are given in Table 4). The plots of versus x are shown in Figure 4.

Table 5. Comparison of monomer reactivity ratios estimated by two methods

Methods	r_1	r_2	$r_1.r_2$	$1/r_1$	$1/r_2$
F-R	0.37±0.0006	0.64±0.0485	0.23	2.70	1.56
K-T	0.51±0.076	1.07±0.140	0.54	1.75	0.93
Average	0.44±0.038	0.85±0.094	0.38	1.13	0.58

From the intercept of the straight line and slope, the reactivity ratios of BzMA and HBPPMA were calculated as r_1 (r_{HBPPMA})=0.51±0.076 and r_2 (r_{BzMA})=1.07±0.140. The confidence intervals for monomer reactivity ratios of copolymerization estimated by the linear Kelen-Tüdos method were calculated according to the literature [20]. Their monomer reactivity ratios, which were determined by using Fineman Ross equation are r_1=0.34±0.0006 and r_2=0.76±0.0485 [21]. The average values and comparison of monomer reactivity ratios estimated by two methods were summarized in Table 5. According to the two methods, the monomer reactivity ratio of BzMA is slightly higher than that of HBPPMA. The r_1 and r_2 values indicate that BzMA is more reactive than HBPPMA, hence the copolymers contain a higher proportion of BzMA units. Moreover, the product of r_1 and r_2 is less than one or one, which indicates that the system follows a random distribution of monomeric unit.

The monomer reactivity ratios of 4-bromobenzyl methacrylate, which is an analog of benzyl methacrylate and ethyl methacrylate by free radical copolymerization method are r_1=0.44 and r_2=0.63 (for K-T method), respectively [19]. For atom transfer radical copolymerization (ATRP) system of benzyl methacrylate (BzMA) and ethyl methacrylate (EMA), which were performed at 90 °C, their monomer reactivity ratios, r_1 and r_2, were estimated from Kelen-Tüdos equation, as r_1=0.812, r_2=1.162 (r_{BzMA}) [22]. The monomer reactivity ratios calculated for HBPMMA and BzMA system in this study have been compared with those of the values estimated for the BzMA monomers and that of various monomers recorded in the literature. The electron rich HBPPMA copolymerizes with the electron-deficient acrylate monomers in a significantly alternating approach. Apparently, both in this work and the above-mentioned literature studies, the values of r_1 and r_2 indicated that the radicals growing with HBPPMA ends were attached to BzMA monomer in slightly higher tendency, but the radicals having BzMA end were slightly lower in the tendency to be added to HBPPMA. The monomer reactivity ratios of two monomers are less than one. The monomer reactivity of growing radicals with HBPPMA units in their end (terminal model), as measured by 1/r, seems to be higher towards BzMA monomers relative to its own monomer. It is also mentioned in Table 5 that $r_{HBPPMA} \times r_{BzMA} < 1$, meaning that the copolymerization is inclined to produce alternative copolymers [23]. So, the value of the monomer reactivity ratios is less than 1 leaning toward an alternating copolymerization, whereas there is a tendency for BzMA to be selectively incorporated relative to HBPPMA. The azeotropic point for this system was calculated by achieved values, which is equal to $M_{BzMA}=m_{BzMA}=0.43$. Figure 5 details the behavior of the system via a plot of the feed composition versus copolymer composition. It is very clear from the plot that this system shows an azeotropic behavior, which is equal to $M_{BzMA}=m_{BzMA}=0.43$. The points of interception, which is equal to $M_{BzMA}=m_{BzMA}=0.43$ represent the occurrence of azeotropic copolymerization, that is, polymerization proceeds without a change in the composition of either the feed or the copolymer. Also, this azeotropic point means it contains a higher proportion of BzMA units in the copolymer system up to 0.43 and after an azeotropic point, the copolymer will be richer by HBPPMA units.

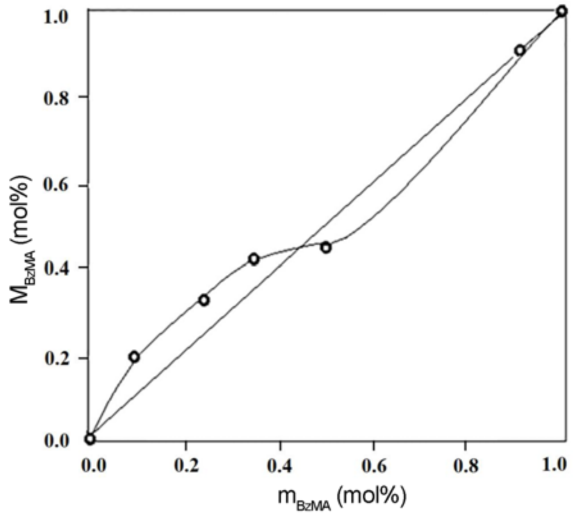


Figure 5. HBPPMA mole fraction in feed versus its mole fraction in copolymer.

DSC Measurements

DSC was used to measure T_g's of HBPPMA-BzMA copolymer systems. To achieve this, measurements were carried out at a heating rate of 20 °C min^{-1} in under nitrogen atmosphere, so the results revealed are submitted in Table 6. In the use of polymer materials and at their various applications, it is important to consider the concept of the glass transition temperature. From DSC measurements, T_g of copolymers was considered as the midpoint of the transition region on the DSC curve. Every copolymer system

Table 6. T_g measurements of homo and copolymer systems

Polymer	T_g (°C)
P(HBPPMA)	84
P(HBPPMA-co-BzMA0.43)	81
P(HBPPMA-co-BzMA0.55)	79
P(HBPPMA-co-BzMA0.92)	77
P(BzMA)	73

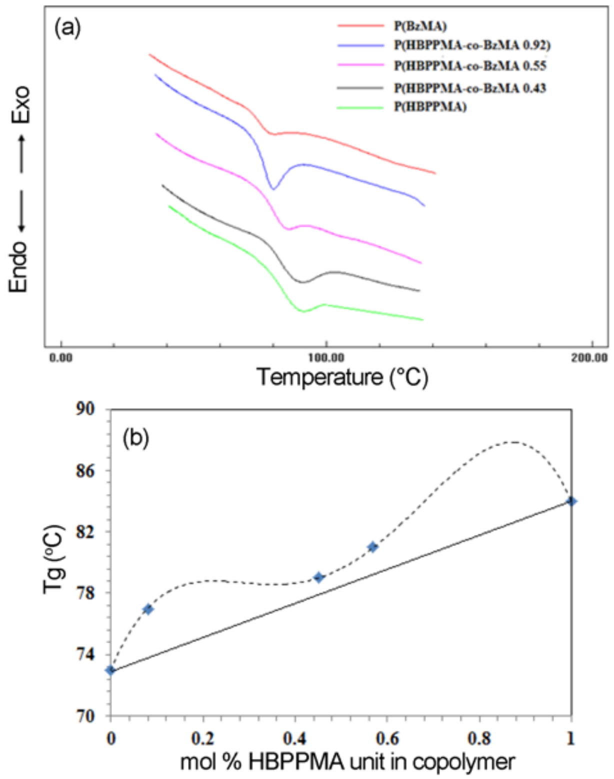


Figure 6. (a) DSC curves of HBPPMA-BzMA copolymer system, poly(HBPPMA) and poly(BzMA) AND (b) Change of T_g's as function of mol % HBPPMA unit in copolymer.

exhibited only one distinct T_g value between 73 and 84 °C, thus indicating the absence of the formation of a compatible copolymer or a mixture of homopolymers. This phenomenon confirms that there is a production of a copolymer with phase separation, which is not ordinary block copolymer. This means that there is a formation of homogeneous phase due to being compatible with each of the two monomeric moieties. Understanding the segmental mobility of polymer is one of the techniques and also a most characteristics properties for T_g measurement of the polymer. The glass transition temperature (T_g) characteristics for amorphous polymers is directly related to chain flexibility [24]. In the HBPPMA-BzMA copolymer systems, it was observed that the BzMA moieties increased the chain mobility and free volume. This means that the glass transition temperature will decrease. As the homopolymer content of HBPPMA in the HBPPMA-BzMA system increased from 100:0 to 0:100, the T_g of the copolymer systems was found to increase toward higher value as HBPPMA content increases. Figure 6(a) shows the measured T_g's of the HBPPMA-BzMA copolymer systems, P(HBPPMA) and P(BzMA). As was observed from Table 2, T_g's of P(HBPPMA) and poly(BzMA) are 84 °C and 73 °C, respectively. Poly(2-hydroxyethyl methacrylate) [PHEMA] and poly(2-hydroxypropyl methacrylate) [PHPMA] have been recorded as 100 °C [25] and 95 °C [26] in the literature. The T_g of poly(HBPPMA) (T_g=84°C) was measured as lower than that of PHEMA and PHPMA. It means that free volume increase of poly(HBPPMA) depend on the chain flexibility increase due to the presence of ketone C=O and two aryl groups as a result of the long side group. Change in T_g's as a function of HBPPMA (mole %) unit in copolymer systems was illustrated in Figure 6(b). For HBPPMA and BzMA copolymer system indicated n Figure 6(b), the composition is necessarily homogeneous (no phase separation) and, as discussed above, the glass transitions are intermediate between those of the two homopolymers. The increased disorder resulting from the random or alternating distribution of monomers enhances the free volume and consequently reduces T_g below. As result, the observed T_g's of the copolymer system indicate a slightly positive deviation with respect to linearity from (the ideal state), which can be associated with a slightly lower free volume than that of a mixture of HBPPMA and BzMA.

TGA Measurements

The thermogravimetric curves of HBPPMA-BzMA copolymer systems, which are recorded from room temperature to 500 °C at a heating rate of 10 °Cmin^{-1} under nitrogen flow are illustrated in Figure 7 as a comparison to that of poly (HBPPMA) and poly(BzMA) prepared by the free radical

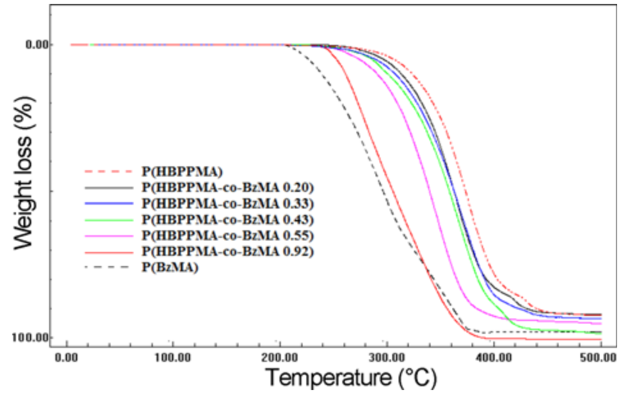


Figure 7. TGA curves of HBPPMA-BzMA copolymer systems, P(HBPPMA) and P(BzMA).

Table 7. TGAresults of HBPPMA-BzMA copolymer systems, P(HBPPMA) and P(BzMA)

Sample	$T_{initial}$ (°C)	T_{finaly} (°C)	%50 weight loss	% Residue
P(HBPPMA)	260	440	371	8
P(HBPPMA-co-BzMA0.20)	258	421	360	8
P(HBPPMA-co-BzMA0.33)	356	419	360	6
P(HBPPMA-co-BzMA0.43)	254	421	346	4
P(HBPPMA-co-BzMA0.55)	250	399	336	5
P(HBPPMA-co-BzMA0.92)	240	385	301	4
P(BzMA)	204	382	292	3

polymerization method.

The decomposition temperatures of both poly(BzMA) and poly(HBPPMA) occurred in a single stage at about 207 °C and 260 °C, respectively. The thermal stabilities of these two homopolymers are considerably different from each other, the residues at 500 °C for two homopolymers are 8 % and 3 %, respectively. Those of HBPPMA-BzMA copolymer systems are between decomposition temperatures of two homopolymers. Some of the thermal degradation characteristics for poly(BzMA) and poly(HBPPMA) and those of copolymer systems are summarized in Table 7.

Dielectrical Measurements

The change in the dielectric constants depending on the frequency of P(HBPPMA), P(BzMA) and HBPPMA-BzMA copolymer systems at room temperature was illustrated in Figure 8. The dielectric behavior of the copolymers varies depending on the copolymer composition. The highest dielectric constant was observed for poly(HBPPMA) for all frequencies at room temperature. The dielectric constant of P(HBPPMA) and P(BzMA) at 1 kHz were 6.56 and 3.22, respectively. Those of copolymers were between 6.56 and 3.22 at 1 kHz. In addition, it was observed that dielectric constant increases as HBPPMA units increase in the copolymer system. The dielectric behavior of a polymer depends on significantly polar or non-polar features. So, the presence of polar groups such as O-H, C=O groups in HBPPMA units bearing high polar group is a reason for the increase in dielectric constant.

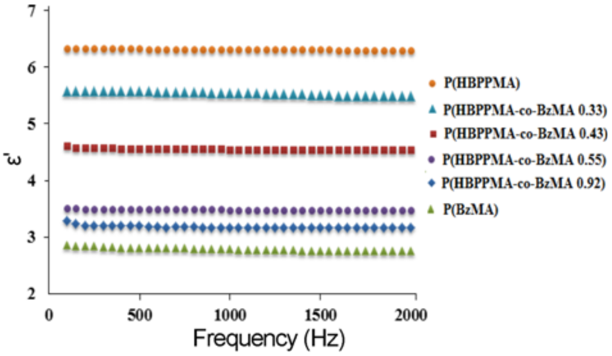


Figure 8. Dielectric constant vs. frequency for P(HBPPMA), P(BzMA) and copolymer systems.

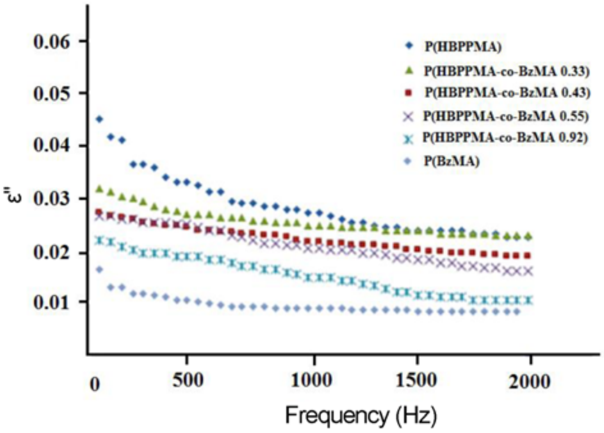


Figure 9. Dielectric loss tangent vs. frequency for P(HBPPMA), P(BzMA) and copolymer system.

According to Figure 8, decreasing in the dielectric constant with increasing frequency can be associated with frequency dependency of orienting dipoles [27,28]. One of the reasons for the decrease in dielectric constant is not having enough time to orient the dipoles at higher frequencies. Under alternating electric field, polymers with polar structure require some time to aligned their dipoles. The dielectric loss factor versus frequency for P(HBPPMA), P(BzMA) and copolymer systems was illustrated in Figure 9.

The higher dissipation factors were attributed to the higher segment quantity of HBPPMA in the copolymers. Thus, the highest dissipation factor was observed for P(HBPPMA-co-BzMA 8 %) copolymer because of the larger HBPPMA segment. The degree of crystallinity of the polymer, molecular weight, and polymer morphology, are known as important factors affecting loss tangent or dissipation factor. The reason of dielectric loss is due to the inability of polarization process of molecules to follow the rate of change of the oscillating when an electrical field is applied. So, this phenomenon reveals from the relaxation time needing for the dipoles to return to its original random orientation [29]. The variation of σ_{ac} conductivity with frequency for four different compositions of HBPPMA-BzMA copolymer systems at room temperature is shown in Figure 10. The conductance value is a phenomenon related to the conduction mechanism occurring within a material during the application of an electromagnetic field. In general, the direct current conductivity and electrode polarization, dielectric relaxation phenomenon can be distinguished at low and high-frequency intermediate, respectively [30,31]. It can be clearly seen from Figure 10 that an increase in HBPPMA content leads to

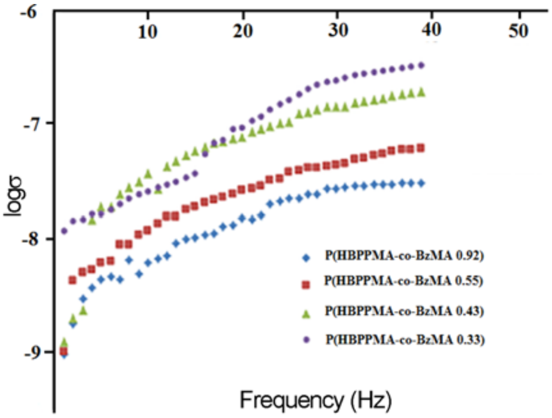


Figure 10. Variation of AC log conductivity with frequency for copolymer systems.

an increase in conductivity. Thus, it is also noted that the higher amount of HBPPMA in the HBPPMA-BzMA copolymer systems reduces the rate decreasing conductivity as the mole percentage of HBPPMA increases.

Conclusion

The present article deals with the homopolymerization of HBPPMA and its copolymerization with BzMA at different feed ratios. The homo and copolymerizations were carried out at ambient temperature. The copolymer compositions were estimated by ^{1}H NMR analysis. Characterizations of HBPPMA-BzMA copolymer systems were performed by ^{1}H and ^{13}C NMR, FT-IR, and GPC instruments. From GPC measurements, average molecular weights and its polydispersity of the copolymers were revealed. The TGA analysis results supported the claims that copolymers have a good thermal stability. The monomer reactivity ratios of HBPPMA and BzMA were estimated by K-T and F-R methods. The value of the monomer reactivity ratios is less than 1 leaning toward an alternating copolymerization, whereas there is a tendency for BzMA to be selectively incorporated relative to HBPPMA. Because all the r_2 values were higher than all the r_1 values, there was a preference for the incorporation of BzMA. The copolymer system shows an azeotropic point, which is equal to $M_{BzMA}=m_{BzMA}=0.43$. The DSC measurements revealed that the synthesized copolymers exhibited a single glass transition temperatures. The T_g's of the copolymers decreased with increasing of BzMA units, by indicating slightly positive deviation from the ideal state. The dielectric behaviors of the copolymers were changed depending on the copolymer composition, the highest values of dissipation factor and dielectric constant measured at room temperature was observed at copolymer system richer by HBPPMA units.

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References

1. A. Habibi, E. Vasheghani-Farahani, M. A. Semsarzadeh, and K. Sadaghiani, *Polym. Int.*, **52**, 1434 (2003).
2. I. Erol, B. Arslantürk, and Z. Gürler, *Polym. Sci.-Ser. B.*, **57**, 228 (2015).
3. G. Stergiou, P. Dousikos, and M. Pitsikalis, *Eur. Polym. J.*, **38**, 1963 (2002).
4. A. D. Azzahari, R. Yahya, A. Hassan, and M. R. K. Sheikh, *Fiber. Polym.*, **13**, 555 (2012).
5. T. Kelen and F. Tüdos, *J. Macromol. Sci. Part A-Pure Appl. Chem.*, **9**, 1 (1975).
6. M. Finemann and S. D. Ross, *J. Polym. Sci.*, **5**, 259 (1950).
7. A. L. Yezrielev, E. L. Brokhina, and Y. S. Roskin, *Vysokomol. Soedin.* **A11**, 1670 (1967).
8. U. Nakan, R. K. Rahmetullaeva, G. A. Mun, E. M. Shaiutdinov, G. Z. H. Yeligbaeva, and M. N. El-Sayed, *Oriental J. Chem.*, **32**, 2347 (2016).
9. P. W. Tidwell and G. A. Mortimer, *J. Polym. Sci. Part A: Gen Papers*, **3**, 369 (1965).
10. S. W. Kuo, H. C. Kao, and F. C. Chang, *Polymer*, **44**, 6873 (2003).
11. D. Thirumoolan, K. Anver Basha, T. Kanai, S. S. Mohammed, K. Vetrivel, K. Abdul Wasi, and B. Ranjithkumar, *J. Saudi Chem. Soc.*, **20**, 195 (2016).
12. K. Koran, F. Özen, F. Biryan, K. Demirelli, and A. O. Görgülü, *Inorganica Chimica Acta*, **450**, 162 (2016).
13. P. Ilangovan, M. Safiullah, S. Anver, and B. Kottur, *Mater. Chem. Phys.*, **193**, 203 (2017).
14. Y. Jinliang, T. Ruifen, S. Suqing, and N. Jun, *Photochem. Photobiol. Sci.*, **12**, 923 (2013).
15. R. R. Patil, S. T. Cohen, J. Srogl, D. J. Kiserow, and J. Genzer, *Langmuir*, **31**, 2372 (2015).
16. D. L. Patton, K. A. Page, E. A. Hoff, M. J. Fasolka,and K. L. Beers, *Polym. Chem.*, **3**, 1174 (2012).
17. I. Hiroshi, D. Charlie, P. Andrew, M. Sherwood, S. Rikiya, R. Sooriyakumaran, G. Kip, and B. Greg, *Macromolecules*, **33**, 5080 (2000).
18. F. R. Mayo and F. M. Lewis, *J. Am. Chem. Soc.*, **66**, 1594 (1994).
19. M. F. Coşkun, İ. Erol, K. Demirelli, and M. Coşkun, *J. Macromol. Sci. Part A-Pure Appl. Chem.*, **A39**, 889 (2002).
20. T. Kelen, F. Tüdos, and B. Turcsanyi, *Polym. Bull.*, **2**, 71 (1980)
21. K. Demirelli, Ph.D Dissertation, University of Firat, 1997.
22. K. Demirelli, M. Coşkun, and E. Kaya, *J. Polym. Sci. Part A: Polym. Chem.*, **42**, 5964 (2004).
23. F. Ziaee and M. Nekoomanesh, *Polymer*, **39**, 203 (1998).
24. Z. Mao and J. Zhang, *J. Appl. Polym. Sci.*, **133**, 43353 (2016).
25. K. Demirelli, M. Coskun, E. Kaya, *Polym. Degrad. Stabil.*, **72**, 75 (2001).
26. K. Demirelli, M.F. Coskun, E. Kaya, and M. Coskun, *Polym. Degrad. Stabil.*, **78**, 333 (2002).
27. E. Lee and Y. G. Jeong, *Fiber. Polym.*, **16**, 2021 (2015).
28. H. H. Park, Y. Choi, D. J. Park, S. Y. Cho, Y. S. Yun, and H. J. Jin, *Fiber. Polym.*,**14**, 1521 (2013).
29. J. G. Drobny, 1st ed., Chap. 3, John Wiley, Hoboken, NJ, *Polymeric Materials*, 2012.
30. D. Bhadra, M. G. Masud, S. Sarkar, J. Sannigrahi, S. K. De, and B. K. Chaudhuri, *J. Polym. Sci. Part B: Polym. Phys.*, **50**, 572 (2012).
31. M. M. Chithra, K. Karuppiah, and R. Somasundaram, *Polym. Int.*, **64**, 750 (2015).