

## Copolymers of 4-Methoxybenzyl Methacrylate and Isobornyl Methacrylate: Synthesis, Characterization and Determination of Monomer Reactivity Ratios

ESİN KAYA

*Department of Science Education, Faculty of Education,  
University of Mus Alparslan, 49100, Muş/Turkey.  
esin\_kaya\_@hotmail.com\**

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**Summary:** Homopolymerization of 4-methoxybenzyl methacrylate (MBMA) and copolymerization with isobornyl methacrylate (IBMA) by the atom transfer radical polymerization method (ATRP) were performed at 90 °C. The homopolymer [poly(MBMA)] and copolymer [poly(MBMA-co-IBMA)] were characterized by Fourier transform infrared (FTIR), <sup>1</sup>H and <sup>13</sup>C NMR and gel permeation chromatography (GPC) techniques. The compositions of the copolymers were calculated from <sup>1</sup>H NMR spectra. For the atom transfer radical copolymerization system, their monomer reactivity ratios were obtained by using the Kelen–Tüdös and Fineman–Ross equation, as  $r_1: 0.88, r_2: 0.63$  ( $r_1$  is the monomer reactivity ratio of IBMA) and  $r_1: 0.90, r_2: 0.65$ . The initial decomposition temperatures of the resultant copolymers decreased with an increasing mol fraction of IBMA, which indicates that the heat resistance of the copolymer has been improved by decreasing the MBMA units.

### Introduction

Recently, the controlled “living” radical polymerizations have been used for synthesis of well defined, narrow dispersity polymers [1, 2]. One of the most successful methods is atom transfer radical polymerization (ATRP), based on a copper halide nitrogen based ligand catalyst [3, 4]. Since ATRP is a controlled/living radical polymerization well defined polymers with molecular weights determined by the ratio consumed monomer to introduced initiator are obtained  $\Delta P_n = \Delta[M]/[I_0]$ , polydispersities are generally low ( $M_w/M_n \leq 1.3$ ). Because of its mechanism, ATRP allows for the preparation of more precisely controlled polymer and many new materials have been synthesized [5]. This process generates oxidized metal complexes, as persistent radicals to reduce the stationary concentration of growing radicals and thereby minimize the contribution of termination. A successful ATRP will have not only a small contribution terminated chains, but also a uniform growth of all the chains, which is accomplished through fast initiation and rapid reversible deactivation [6].

On the other hand ATRP to synthesize well-defined copolymers is controlled radical polymerization. Kinetic considerations indicate that the composition of statistical copolymers prepared by ATRP should be identical to copolymers prepared under conventional radical polymerization conditions [7]. (Meth)acrylic copolymers have achieved prime importance in various avenues of industrial applications [8-12]. Copolymers formed from substituted phenyl methacrylate are used in the

production of printing plates [13, 14] and electrical circuits [15, 16]. Phenyl(meth)acrylates have been used as weather-resistant high gloss top coats for automobile finishes [17].

Moreover, copolymerization is an important and useful way to develop new materials [18-22]. Copolymerization modulates both the intramolecular and intermolecular forces exercised between like and unlike polymer segments. Therefore, properties such as the glass transition temperature, melt point, solubility, crystallinity, permeability, adhesion, elasticity, and chemical reactivity may be varied within wide limits. [23, 24].

This article reports on the homo- and copolymerization of MBMA and IBMA by ATRP initiated with ethyl 2-bromoacetate, the characterization of the polymers by <sup>1</sup>H, <sup>13</sup>C NMR, Fourier transform infrared (FTIR), gel permeation chromatography (GPC), and thermal analysis techniques. This article also reports on determining of monomer reactivity ratios with the Kelen–Tüdös and Fineman–Ross equation method.

### Results and Discussion

#### *Characterization of Polymers*

The FTIR spectra of poly(MBMA) obtained via free radical polymerization and ATRP are shown in Fig. 1, respectively. The strong band at 1725 cm<sup>-1</sup> is the stretching vibration of the carbonyl group in

\*To whom all correspondence should be addressed.

ester. The FTIR spectrum of the poly(MBMA) shows a peak at  $2900\text{ cm}^{-1}$  due to the C-H stretching of the aromatic ring. The ring stretching vibrations of the aromatic nuclei were observed at  $1612$ ,  $1585$  and  $1463\text{ cm}^{-1}$ . The bands at  $1173\text{ cm}^{-1}$  and  $1248\text{ cm}^{-1}$  are symmetric stretching and asymmetric stretching of the  $-\text{C}(=\text{O})-\text{O}-\text{C}$  group, respectively. Appearing as a doublet of the last group of bands is probably due to the helix conformation of the syndiotactic structure [25]. The small bands of increasing intensity at  $1775\text{ cm}^{-1}$  observed when ATRP conditions is characteristic for in a lactone ring with five members. It may be suggested that a lactone ring forms by means of removing benzyl bromide at the chain end, as suggested in Scheme 2. This band was not observed of poly(BMA) is synthesized under free-radical polymerization conditions [26]. Also, the presence of benzyl bromide with a sharp smell was sensed as soon as the polymerization tube was opened.

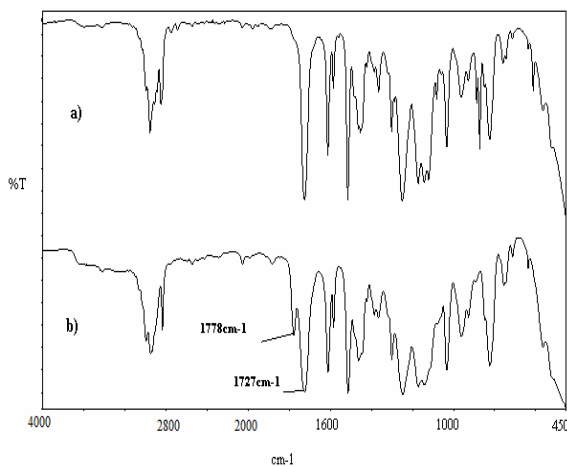
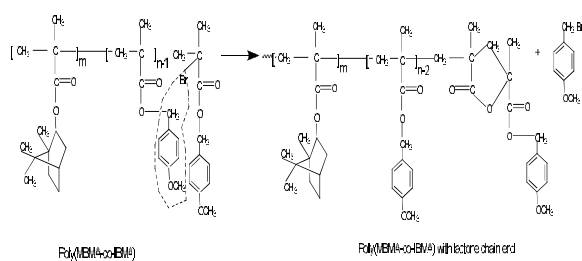


Fig. 1: FTIR spectra of poly(MBMA) prepared via (a) free-radical polymerization; (b) ATRP method at  $100\text{ }^{\circ}\text{C}$ ;



Scheme 2: Poly(MBMA-co-IBMA) with lactone chain end.

The FTIR spectra of the copolymers prepared by ATRP in various feed ratios of MBMA

to IBMA also showed carbonyl bands corresponding to a lactone ring at  $1780\text{ cm}^{-1}$  and the intensity of this band increased when the MBMA unit increased in the copolymer. The  $^1\text{H NMR}$  spectra of six copolymers prepared via ATRP are illustrated in Fig. 2. The peaks at  $7.25\text{--}6.87\text{ ppm}$  reveal the phenyl ring protons, and the signal at  $4.85\text{ ppm}$  is assigned to methylene protons adjacent to ester oxygen in the MBMA unit while the signal at  $4.02\text{ ppm}$  is assigned to methyn proton in the IBMA unit. As the MBMA units in the copolymer increase from  $14\%$  to  $91\%$ , the intensity of the aryl protons in the MBMA units gradually increases. The other signals are due to the methyl and methylene protons of the comonomeric units. The initiator residue at one end of the copolymer molecules, and the bromine atom at the other end may be attached to both kinds of monomeric units.

The monomer feed ratio and the  $M_n$  and  $M_w/M_n$  for copolymers are listed in Table-1 (where  $M_w$  is the weight-average molecular weight and  $M_n$  is the number-average molecular weight). The decrease in  $M_n$  values with an increasing molar fraction of MBMA in the copolymer is probably because of an increase in lactone ring formation. Although it is unknown whether lactone formation is preceded by a radical or an ionic mechanism, the stability of a benzylic radical or carbocation as an intermediate will be important. Because both the benzylic radical and benzylic carbocation are more stable than those corresponding to alkyl, it is thought that lactone formation increases with an increase in MBMA units of poly(MBMA-co-IBMA)s. This, therefore indicates that the decreasing average molecular weight of the copolymer can be manipulated by the controlled polymerization conversion of IBMA units. The resulting copolymers possess relatively polydispersities ( $1.1 < M_w/M_n < 2.2$ ). The single GPC profiles of several resulting copolymers are presented in Fig. 3, after purification.

Table-1: Copolymerization of IBMA and MBMA at Various Monomer Feeds and Copolymer Characteristics

Sample <sup>a</sup>	$M_1$ <sup>b</sup>	Intensity of aliphatic protons in MBMA and IBMA unit (IAl)	Intensity of OCH3 protons in MBMA unit	$m$ , $M_n$ ( $M_w/M_n$ ) (GPC)
1	0.08	45	19	0.91 7421 (1.1)
2	0.19	57	17	0.80
3	0.38	80	15	0.66 12511 (1.6)
4	0.58	70	8	0.49 20308 (1.9)
5	0.80	95	4	0.24
6	0.90	95	2	0.14 11990 (2.2)

<sup>a</sup> Conditions of polymerization; [IBMA]:[MBMA]:[CuBr]:[bpy] = 10:90:1:1:2, at  $100\text{ }^{\circ}\text{C}$ .

<sup>b</sup> Mole fraction of IBMA in feed.

<sup>c</sup> Mole fraction of MBMA in copolymer.

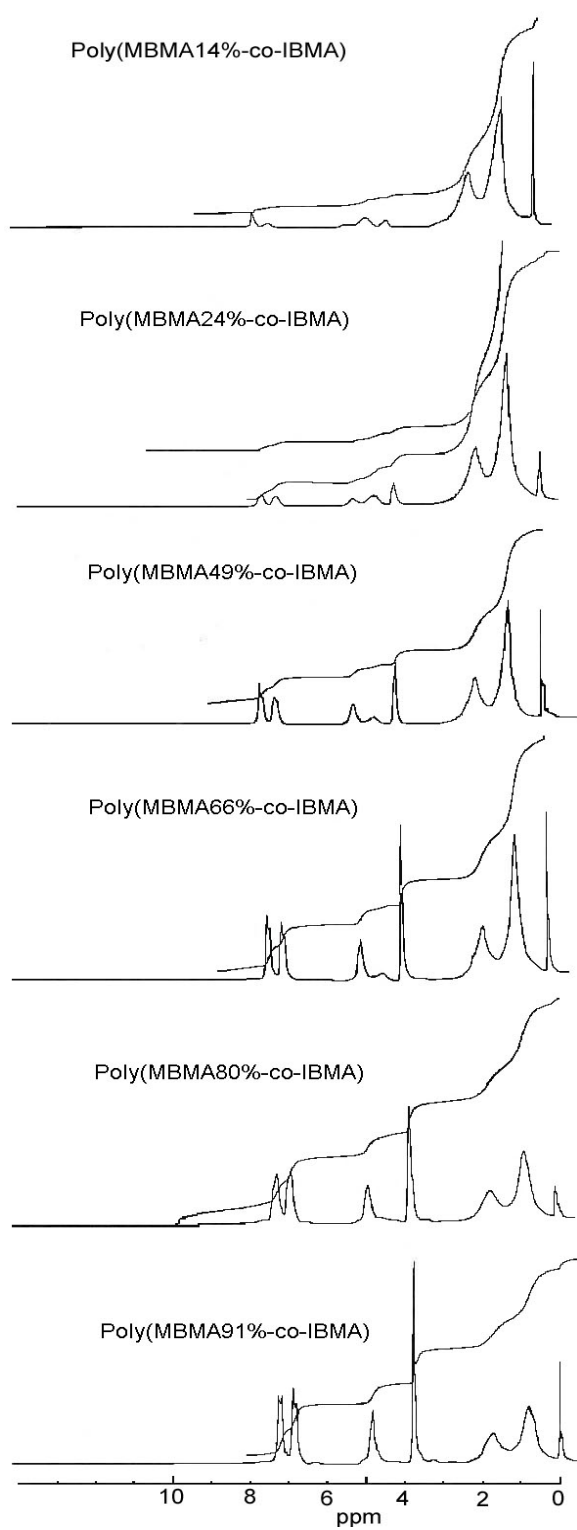


Fig. 2:  $^1\text{H}$  NMR spectra of random copolymers prepared by ATRP with compositions of MBMA and IBMA.

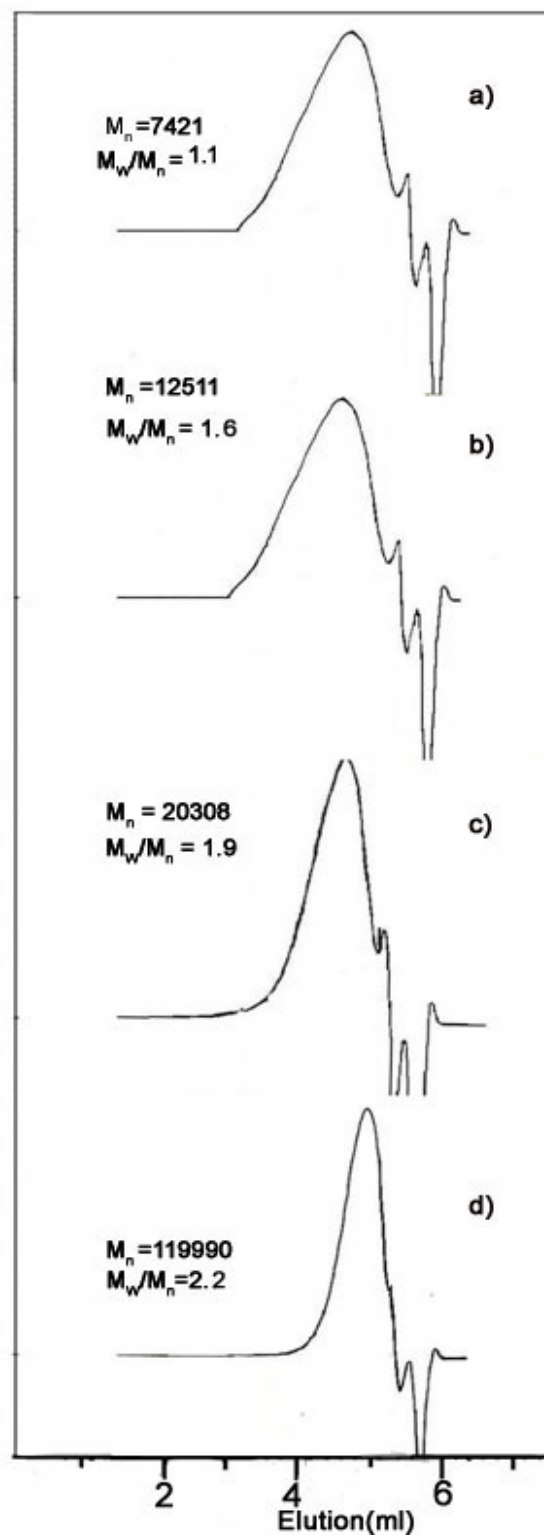


Fig. 3: GPC traces of poly(MBMA-co-IBMA) obtained via ATRP [(a) poly(MBMA91%-co-IBMA), (b) poly(MBMA66%-co-IBMA), (c) poly(MBMA49%-co-IBMA), (d) poly(MBMA14%-co-IBMA)].

### Monomer Reactivity Ratios

The atom transfer radical random copolymerization of IBMA and MBMA initiated by ethyl bromoacetate for various ratios of IBMA to MBMA had been carried out. The copolymer compositions were determined with  $^1\text{H}$  NMR spectra. Fig. 2 shows  $^1\text{H}$ -NMR spectra of the six copolymers prepared by ATRP. While the signal centered at 3.75 is assigned to OCH<sub>3</sub> protons in MBMA units, the signals centered at 0.88-1.80 are assigned to aliphatic protons in IBMA and MBMA units. Thus, the mole fraction of IBMA in the copolymer chain was calculated from measuring the integrated intensities of OCH<sub>3</sub> protons in MBMA and aliphatic protons of IBMA and MBMA. Copolymer compositions have been calculated from the following equation:

$$C = \frac{\int \text{heights of aliphatic protons (MBMA unit and IBMA unit)}}{\int \text{heights of OCH}_3 \text{ protons in MBMA unit}}$$

$$= \frac{3(m_1 - 1)}{21m_1 + 5(m_1 - 1)}$$

On simplification;

$$m_1 = \frac{3C - 5}{3C - 26}$$

where  $m_1$  and  $m_2$  are the mol fraction of IBMA and MBMA in the copolymer, respectively. Table-1 shows the data obtained on the copolymerization.

It is well known that monomer reactivity ratios can offer the message of the relative reactivity of comonomers [27-29]. To estimate the relative reactivity of IBMA and MBMA in the atom transfer radical copolymerization, the Kelen Tüdös [30] and Fineman-Ross [31] equation was used, which is  $\eta = (r_1 + r_2/\alpha)\xi - r_2/\alpha$  (the notation descriptions and the calculation results are summarized in Table-2). The plots of versus are shown in Fig. 4 and Fig. 5. From the slope and intercept of the straight line, the monomer reactivity ratios of IBMA and MBMA were determined as  $r_1$  (Monomer reactivity ratio of IBMA) = 0,88 and  $r_2 = 0,63$  and given in Table-3. The monomer reactivity ratio of IBMA is higher than that of MBMA. These values suggest that IBMA is more reactive than MBMA and the copolymer will be richer in IBMA units. The product  $r_1 r_2$  is very much less than 1 suggesting that the system shows strong alternating tendency.

Table-2: Kelen- Tüdös and Fineman-Ross Parameter for the Copolymerization of IBMA and MBMA.

Sample No	F=M <sub>1</sub> /M <sub>2</sub>	f=m <sub>1</sub> /m <sub>2</sub>	G = F(f-1)/f	H = F <sup>2</sup> /f	$\eta = G/\alpha + H$	$\xi = H/\alpha + H$
1	0,087	0,099	-0,792	0,076	-0,736	0,071
2	0,230	0,250	-0,705	0,221	-0,577	0,181
3	0,613	0,515	-0,577	0,729	-0,334	0,422
4	1,381	1,041	0,054	1,832	0,029	0,647
5	4,000	3,166	2,737	5,053	0,452	0,835
6	9,000	6,142	7,535	13,187	0,531	0,929

<sup>a</sup>M<sub>1</sub> = Mole fraction of IBMA in feed; M<sub>2</sub> = mole fraction of MBMA in feed, m<sub>1</sub> = mole fraction of IBMA in copolymer, m<sub>2</sub> = mole fraction of MBMA in copolymer. (Hmin Hmax)<sup>1/2</sup> = 1.0, Hmin: lowest value of H, Hmax: highest value of H.

Table-3: Monomer Reactivity Ratios obtained by Kelen- Tüdös and Fineman-Ross methods.

System	Method	r <sub>1</sub>	r <sub>2</sub>	r <sub>1</sub> .r <sub>2</sub>
ATRP	K-T	0,88	0,63	0,55
	F-R	0,90	0,65	0,58

r<sub>1</sub>: IBMA

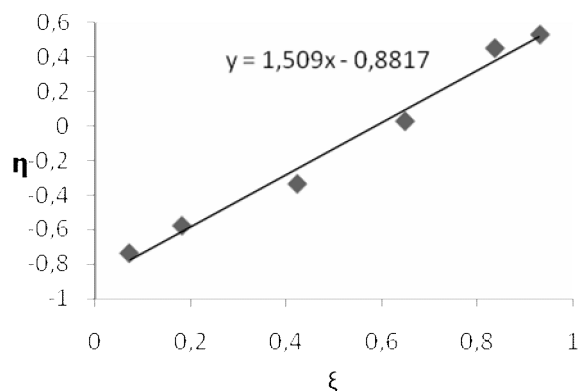


Fig. 4: Kelen-Tüdös plots for the ATRP of MBMA and IBMA.

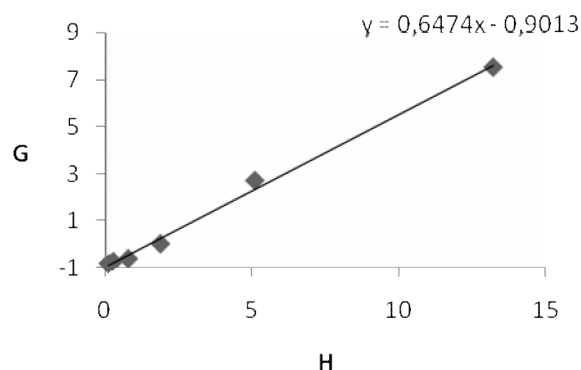


Fig. 5: Fineman-Ross plots for the ATRP of MBMA and IBMA

### Thermogravimetric Study

The thermogravimetric curves for poly(IBMA), poly(MBMA) and their copolymers prepared by ATRP, obtained at room temperature to 500°C at a heating rate of 10°C/min under nitrogen

flow. TGA curves for poly(IBMA), poly(MBMA) and an sample of poly(IBMA-co-MBMA) are shown in Fig. 6. The technique of thermogravimetric analysis (TGA) has been widely used in polymer characterization in thermal stability studies [32]. The results of the differential thermogravimetric analysis are presented in Table-4. The thermograms clearly indicate that poly(MBMA) and poly(IBMA-co-MBMA) undergo two stage decomposition while poly(IBMA) undergoes single stage decomposition. The initial decomposition temperatures of poly(MBMA), poly(IBMA-co-MBMA), and poly(IBMA) are 230, 247, 250 and 260°C respectively. TGA results indicate that the thermal stability of the copolymer increases with rising IBMA content.

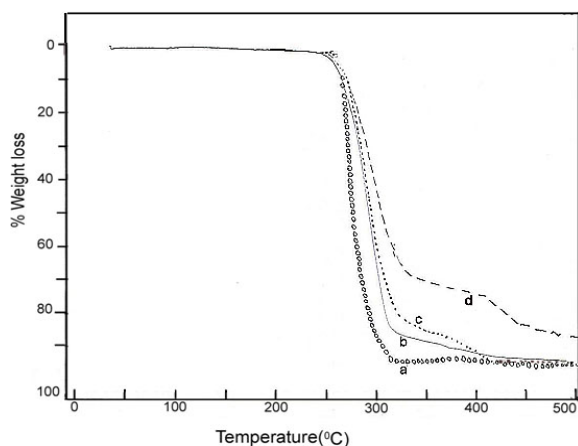


Fig. 6: TGA curves of polymers heated under nitrogen at 10°C/min heating rate from room temperature to 500°C: a) PolyMBMA(%66)-co-IBMA, b) PolyIBMA, c) PolyMBMA(%91)-co-IBMA d) PolyMBMA.

#### Glass Transition Temperature

The glass transition temperature ( $T_g$ ) of homopolymers and copolymers were determined by Differential Scanning Calorimetry. All the prepared copolymers show a single  $T_g$ , showing the absence of formation of a mixture of homopolymers or the formation of a block copolymer. The  $T_g$  of

poly(MBMA) is 50 °C and that of poly(IBMA) is 198 °C. The glass transition temperature of the copolymer increases with increase in IBMA content. This results in increasing of free volume in polymers, and decreasing of their  $T_g$  values with respect to linearity. The stereoeffects strongly depend on the monomer structures [33]. Therefore, enhancing the stereoeffect may be effective in view of syndiotactic for methacrylates with the relatively bulky side group such as phenyl group [34]. The variation of  $T_g$  of copolymers with the mole fraction of MBMA unit in the copolymer is shown Table-5 and plots of the  $T_g$  values versus mole fractions of MBMA in the copolymers are shown in Fig. 7.

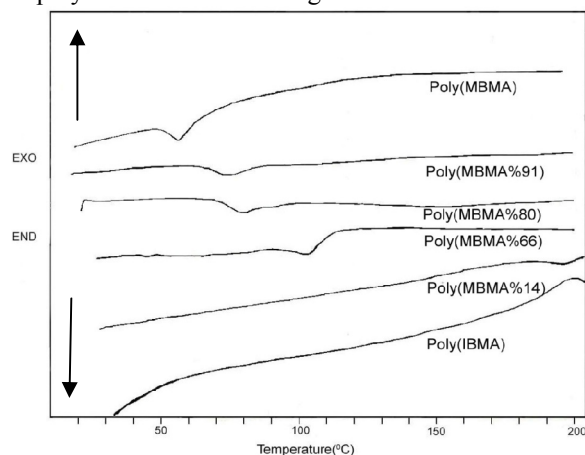


Fig. 7: DSC traces of poly(MBMA) and poly(IBMA).

#### Molecular Weight

$M_n$  and  $M_w$  of four samples of copolymers determined by gel permeation chromatography are presented in Fig. 3. The polydispersity index copolymers of are 1.1 and 2.2. The theoretical values of  $M_w/M_n$  for polymers produced via radical recombination and disproportionation are 1.5 and 2.2, respectively. The polydispersity index values of the copolymers suggest that chain termination takes place by disproportionation when the mole fraction of IBMA in the feed is high and radical recombination is predominant when the mole fraction of MBMA is high in the feed.

Table-4: TGA Data of the Polymers.

Polymer	<sup>a</sup> T <sub>i</sub> (°C)	<sup>b</sup> T <sub>%50</sub> (°C)	%Weight Loss at 300 °C	%Weight Loss at 350 °C	%Weight Loss at 400 °C
PolyMBMA	230	328	35	65	80
PolyMBMA(%91)-co-IBMA	247	305	43	70	75
PolyMBMA(%66)-co-IBMA	250	270	58	84	90
PolyIBMA	260	275	87	92	93

a Initial decomposition temperature.

b Decomposition temperature at 50% weight loss.

c By mole.

T<sub>i</sub>: initial decomposition temperature; T<sub>%50</sub>: Decomposition temperature at 50% weight loss

Poly(MBMA) and the copolymers of MBMA with IBMA were synthesised by atom transfer radical polymerization. Characterization of poly(MBMA) and poly(MBMA-co-IBMA) was performed by FTIR and  $^1\text{H-NMR}$  techniques. Thermogravimetric analysis indicated that the thermal stability of the copolymers increases with the increase of IBMA content. Values of the polydispersity index for poly(MBMA-co-IBMA) and poly(IBMA), suggest a strong tendency for chain termination by disproportionation in all cases and that the tendency increases with increasing MBMA content in the feed. The copolymer compositions were found by  $^1\text{H-NMR}$  analysis of the polymers. The reactivity ratios were determined by F–R and K–T methods giving values in good agreement. The values of  $r_1$  and  $r_2$  are less than unity indicating that the system gives rise to an azeotropic polymerization. The value of the product  $r_1r_2$  indicates a strong tendency to alternation.

## Experimental

### Materials

IBMA was vacuum-distilled after washing with a 15% NaOH aqueous solution just before homopolymerization and copolymerization. MBMA was prepared by a reaction of 4-methoxybenzyl bromide with sodium methacrylate. Cuprous(I) bromide, 2,2'-bipyridyne (bpy), and ethyl 2-bromoacetate (analytical reagent) were used as received.

### Synthesis of MBMA

MBMA was synthesized by the reaction of 4-methoxybenzylbromür and sodiummethacrylate at 0–5°C with potassium carbonate. It was distilled under vacuum (bp: 114°C at 20mmHg). The monomer was examined by FTIR and  $^1\text{H NMR}$  spectra.

$^1\text{H NMR}$ : 7.24–6.89 (4H) (Ar-H), 6.01 and 5.52 (2H)(CH<sub>2</sub>=C), 5.01 (-OCH<sub>2</sub>)( 2H), 3.74(CH<sub>3</sub>O-Ar) (3H), 1.93 (3H) ( $\alpha$ -methyl).

FTIR (cm<sup>-1</sup>, the most characteristic bands): 1715 (C–O stretching), 1638 (C=C in the vinyl group), 1611 (C=C stretch in aromatic ring).

$^{13}\text{C NMR}$ (CDCl<sub>3</sub>,  $\delta_{\text{ppm}}$ ): 18.0 (CH<sub>3</sub>), 55.0(OCH<sub>3</sub>),66.05 (-OCH<sub>2</sub>-), 124.9–128.2 (CH on aromatic ring), 136.18 (=C), 159.59 (ipso carbon on aromatic ring), 166.86(C=O).

### ATRP Procedures

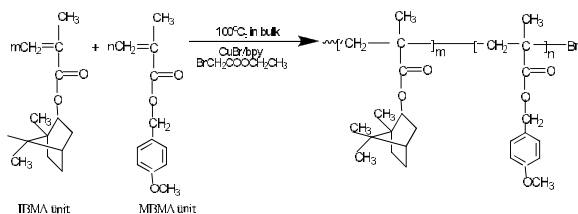
All ATRP reactions were carried out following the same experimental procedure. The copolymers of MBMA and IBMA was synthesized with ethyl 2-bromoacetate as the initiator and CuBr/bpy as the catalytic system. The molar ratio of the compounds in the ATRP system was 1 : 1 : 2 : 100 [initiator/Cu(I)Br/ bpy/monomers]. First, CuBr was introduced into a glass tube. The glass tube was cycled between a vacuum and argon twice and was sealed with a rubber septum. The mixture containing monomer or monomers, initiator (ethyl 2-bromo acetate), and ligand (bpy) were degassed by argon purging for 10 min before adding it to the glass tube. The sealed tube was immersed in a preheated oil bath at a desired temperature. The tube was then removed from the oil bath and the reaction mixture was dissolved in dichloromethane (or chloroform), filtered, and then poly(MBMA) and the copolymers were precipitated in excess petroleum ether, *n*-hexane, and ethanol, respectively. They were filtered off and dried *in vacuo* at 70 °C. Conversions were determined gravimetrically or with  $^1\text{H NMR}$ .

### Free-Radical Polymerization of MBMA

The monomer was polymerized at 60 °C in 1,4-dioxane in the presence of AIBN as an initiator. The poly(MBMA) was purified by precipitation in petroleum ether. This process was repeated twice. The polymer was then dried.

### ATRP Copolymerization of IBMA with MBMA

The general procedure for the copolymerization of MBMA with IBMA with six compositions was as follows: In all cases, predetermined amounts of monomers, initiator (ethyl 2-bromoacetate), ligand (2,2'-bipyridyne), and calculated amount of CuBr as catalyst were added into a flask. The mixture was degassed three times by freeze–pump–thaw cycles and sealed *in vacuo*. The flask was shaken until the mixture dissolved, immersed in an oil bath, and heated to the required temperature (100°C). After particular time duration, the flasks were opened and dichloromethane was added to the sample to dissolve the copolymer. The heterogeneous solution was filtered. The copolymers were isolated by precipitation in *n*-hexane and dried at 40 °C for 24 h. The conversion of the copolymerization was determined gravimetrically and was found to be under 15%. Scheme 1 shows the reaction for the synthesis of copolymers.



Scheme 1: Synthesis of poly(MBMA-co-IBMA).

#### Characterization Techniques

Infrared spectra were obtained by a Mattson 1000 FTIR spectrometer. NMR spectra were recorded on a Jeol FX 90Q NMR spectrometer at room temperature in CDCl<sub>3</sub>. Thermogravimetric analysis (TGA) measurements were carried out under a nitrogen flow with a TGA-50 thermobalance at a heating rate of 10°C/min. Gel permeation chromatography (GPC) analyses were carried out using Agilent 1100 system equipped with a high-pressure liquid chromatography pump, a vacuum degasser, and a refractive index detector. The eluting solvent was tetrahydrofuran (THF) and the flow rate was 1 mL/min. Calibration was achieved with polystyrene.

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