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Copolymerization of 4-biphenyl methacrylate with glycidyl methacrylate: Synthesis, Characterization, thermal properties and determination of monomer reactivity ratios

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Summary

The methacrylic monomer, 4-biphenylmethacrylate (BPM) was synthesized by reacting 4-biphenyl phenol dissolved in ethyl methyl ketone (EMK) with methacryloyl chloride in presence of triethylamine as a catalyst. The copolymers of BPM with glycidyl methacrylate (GMA) were synthesized by free radical polymerization in EMK solution at 70±1°C using benzoyl peroxide as a free radical initiator. The copolymerization behaviour was studied in a wide composition interval with the mole fractions of BPM ranging from 0.15 to 0.9 in the feed. The copolymers were characterized by FT-IR, ^{1}H-NMR and ^{13}C-NMR spectroscopic techniques. The solubility was tested in various polar and non polar solvents. The molecular weight and polydispersity indices of the polymers were determined using gel permeation chromatography. The glass transition temperature of the copolymers increases with increase in BPM content. The thermogravimetric analysis of the polymers showed that the thermal stability of the copolymer increases with BPM content. The copolymer composition was determined using ^{1}H-NMR spectra. The monomer reactivity ratios were determined by the application of conventional linearization methods such as Fineman-Ross ($r_1 = 0.392 \pm 0.006$, $r_2 = 0.358 \pm 0.007$, Kelen-Tudos ($r_1 = 0.398 \pm 0.004$, $r_2 = 0.365 \pm 0.013$) and extended Kelen-Tudos methods ($r_1 = 0.394 \pm 0.004$, $r_2 = 0.352 \pm 0.006$).

Introduction

Copolymerization is the most successful method adopted for the preparation of materials with tailor made properties [1-6]. Incorporation of different chemical groups in a macromolecular chain can be achieved by the reaction between two distinct monomers. These kinds of macromolecules possess significant importance from fundamental and applied point of views. Glycidyl methacrylate (GMA) enters into a vast number of chemical reactions by opening their oxirane ring, thus offering an excellent opportunity for chemical modification in pendant copolymers. They have acquired prime importance in various avenues of industrial applications such as leather adhesives, pharmaceutical use for drug delivery [7], pressure sensitive adhesives [8], dental composites [9], superabsorbents [10], and non linear optical materials [11] etc. Aromatic acrylates and methacrylates are highly reactive monomers due to the presence of aromatic ring and thus form an interesting class of polymers. Poly(phenyl methacrylates) possesses high tensile strength; high thermal stability and their glass transition temperatures are higher than their corresponding acrylate polymers, due to the presence of alpha methyl group on their main chain. Therefore, they find wide applications in the preparation of materials such as photo luminescent [12], photo resist [13], adhesives for leather [14-16], photosensitive [17], biomaterials [18,19], optical telecommunication materials [20] and polymer supported catalyst [21] etc. Generally, the conventional epoxidized resin adhesives have molecular weight values around 5000 and are mainly based on phenolic intermediates. But they do not have necessary colour stability, possess only a few terminal epoxy groups and require polar solvents for solubilization. Hence, these difficulties were overcomes by taking epoxide containing comonomer (GMA), because of its striking properties.

Monomer reactivity ratio is one of the most important parameters involved in copolymer equation, which can offer detail information regarding relative reactivity of monomer pairs, elucidation of copolymer structure, copolymer composition and monomer sequence distribution. The calculation of the monomer reactivity ratios mainly requires the mathematical treatment of copolymer composition data. The accurate estimation of copolymer composition and determination of monomer reactivity ratios would be very helpful to synthesize tailor-made copolymers possessing desired properties. In past few decades, ^{1}H-NMR spectroscopy analysis has been established as a powerful tool for the determination of tacticity, sequence distribution and as well as for estimation of copolymer composition because of its simplicity, rapidity and sensitivity [22-26]. The presence of aromatic side substituents instead of aliphatic residues in polyacrylic chains gives rise to noticeable effect on the splitting of the NMR signals of several acrylic systems. The main aim in commercial copolymerization is to achieve a product having narrow composition as much as possible. Knowledge about the monomer reactivity ratios of the comonomers would be helpful in achieving this.

In chemical abstracts, synthesis, characterization and monomer reactivity ratios of copolymers of 4-biphenylphenyl methacrylate (BPM) with glycidyl methacrylate (GMA) have not been reported to date. In continuation, we synthesized and characterized this new polymeric material for industrial applications. The present paper describes the synthesis, characterization and determination of monomer reactivity ratios of copolymers of BPM with GMA. The thermal properties of the polymers were also reported.

Experimental

Materials

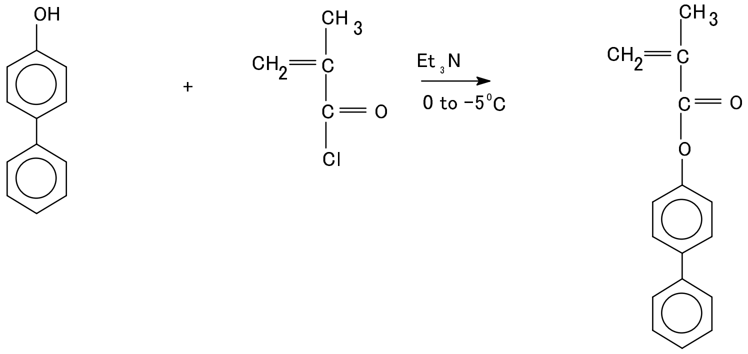
4-Biphenyl phenol (Wako chemical Industries, for synthesis) was used as received. GMA (Wako Chemicals) was purified by distillation under reduced pressure. Benzoyl peroxide (Aldrich) was recrystallised from chloroform-methanol (1:1) mixture. Triethyamine (Wako), methacrylic acid (Wako) and benzoyl chloride(Wako) were used as such. All the other solvents were purified by distillation prior to their use.

Measurements

Infrared spectra were recorded with a Jasco 460 FT-IR spectrophotometer as KBr pellets. ^{1}H-NMR spectra of the monomer and all the polymer samples were run on a JEOL–JNM-LA 400 FT-NMR spectrophotometer at room temperature using CDCl3 solvent and TMS as an internal standard, respectively. The proton decoupled ^{13}C-NMR spectrum was run on the same instrument operating 100 MHZ at room temperature, and the corresponding chemical shifts were recorded under similar conditions. The molecular weights (M_w and M_n) were determined using Shimadzu gel permeation chromatograph, where tetrahydrofuran was used as an eluent with polystyrene standards for calibration. Thermogravimetric analysis was performed with Shimadzu DTG-50 thermal analyzer in air at a heating rate of 10°C per minute. The glass transition temperature was determined with Shimadzu DSC-60 differential scanning calorimeter at a heating rate of 10°C per min in nitrogen atmosphere.

Synthesis of 4-biphenyl methacrylate(BPM)

Methacryloyl chloride was prepared from methacrylic acid and benzoyl chloride using the procedure of Stampel et al [27]. Synthesis of 4-biphenyl methacrylate (BPM) is reported by Alberda et al [28]. Briefly, we modified the procedure for the synthesis of BPM, 4-biphenyl phenol (10g, 0.059 mol), ethyl methyl ketone(250ml) and triethylamine (8.2 ml, 0.059 mol) were taken in 3-necked RB flask. A mechanical strirrer was attached to the centre neck, a dropping funnel with pressure equalizing arrangement was attached to the second neck and a guard tube was attached to the third neck. The RB flask was placed in an ice bath and the contents were stirred well at 0-5°C. Methacryloyl chloride (5.8ml, 0.059 mol) dissolved in 20 ml of EMK was taken in a dropping funnel and added drop wise with constant stirring. After the addition, the reaction mixture was allowed to be stirred in cold condition for 2 h and then at room temperature for 1 h. Then the precipitated triethylammonium chloride was filtered off and the solvent in the filtrate was removed using a rotary evaporator. The residue was dissolved in ether and was washed twice with 0.1% solution of NaOH and then with distilled water. The ether solution was dried using anhydrous Na_2SO_4. The ether solution was evaporated to get a residue which was distilled under reduced pressure to give pure BPM. The yield was 70%. The reaction scheme for the synthesis of BPM is shown in scheme.1.



Scheme 1. Synthesis of BPM

The monomer was examined by FT-IR and ^{1}H-NMR spectra as follows:
IR cm^{-1}; 3110 and 3060(=C-H), 2970 and 2875(C-H stretching), 1728(C=O), 1612(CH_2=C), 1522 and 1489 (aromatic C=C), 1378(CH_3 symmetrical bending), 1115(C-O), 833 and 759 (C-H out of plane bending).
^{1}H-NMR; 7.61-7.31 (aromatic protons), 6.38 and 5.77(CH_2=C), 2.08 (α-CH_3)

Copolymerization

Predetermined quantities of BPM, GMA with EMK and benzoyl peroxide were taken in a standard polymerization tube and the mixture was flushed with oxygen free nitrogen for 20 min. The tube was then tightly sealed and immersed in an oil bath maintained at 70±1°C. After the required time, the polymer was precipitated in excess methanol. The precipitated polymer was filtered off and purified by repeated reprecipitation from chloroform solution using methanol and finally dried in vacuum at 50°C for 24 h. The copolymer conversions were restricted to less than 10%.

Solubility studies

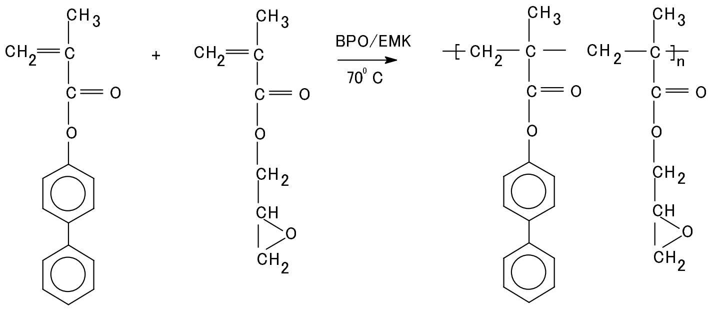
Solubility of the polymers was tested in various polar and non-polar solvents. About 5-10 mg of the polymer was added to about 5 ml of the solvent in a test tube and kept overnight with the tube tightly closed. The solubility of the polymers was noted after 24h.

Results and discussion

Synthesis of polymers

Copolymers were obtained by the free radical solution polymerization of the monomers at 70±1°C in EMK solvent using BPO as the initiator. The copolymerization of BPM with GMA in EMK solution was studied in a wide composition interval with the mole fractions of BPM ranging from 0.15 to 0.9 in the feed. The reaction time was selected in trials to give conversions less than 10% in order to satisfy the differential copolymerization equation. The monomeric units of the copolymer are shown in scheme 2. The data on composition of feed and in copolymers are presented in Table 1.

The copolymers were soluble in chloroform, acetone, dimethyl acetamide, dimethyl formamide, dimethyl sulfoxide, tetrahydrofuran, benzene, toluene and xylene. The



Scheme 2. Synthesis of poly(BPM-co-GMA)

copolymers were insoluble in n-hexane and hydroxyl-group containing solvents such as methanol and ethanol.

Table 1. Copolymer composition data for free radical polymerization of BPM (1) with GMA (2) in EMK solution at 70±1°C.

Copolymer	M_1[a]	Conversion (%)	Integral peak height I_{Ar}	I_{Ali}	m_1[b]	M_w / M_n
1	0.1544	9.02	9.000	44.570	0.2017	1.70
2	0.3393	8.74	9.000	18.724	0.4215	1.79
3	0.4945	8.92	9.000	14.722	0.5070	1.80
4	0.6184	9.04	9.000	12.701	0.5649	1.85
5	0.8022	8.65	9.000	9.034	0.7125	1.88
6	0.8968	9.25	9.000	7.334	0.8108	1.92

[a] M_1 is the mole fraction of BPM in the feed.
[b] m_1 is the mole fraction of BPM in the copolymer.

Characterization of polymers

IR-spectrum
The FT-IR spectrum of the copolymer poly(BPM-co-GMA) (0.5070: 0.4930) is shown in Fig 1. It shows a peak at 3096 and 3010 cm^{-1} corresponding to the C-H stretching of the aromatic system. The symmetrical and asymmetrical stretching due

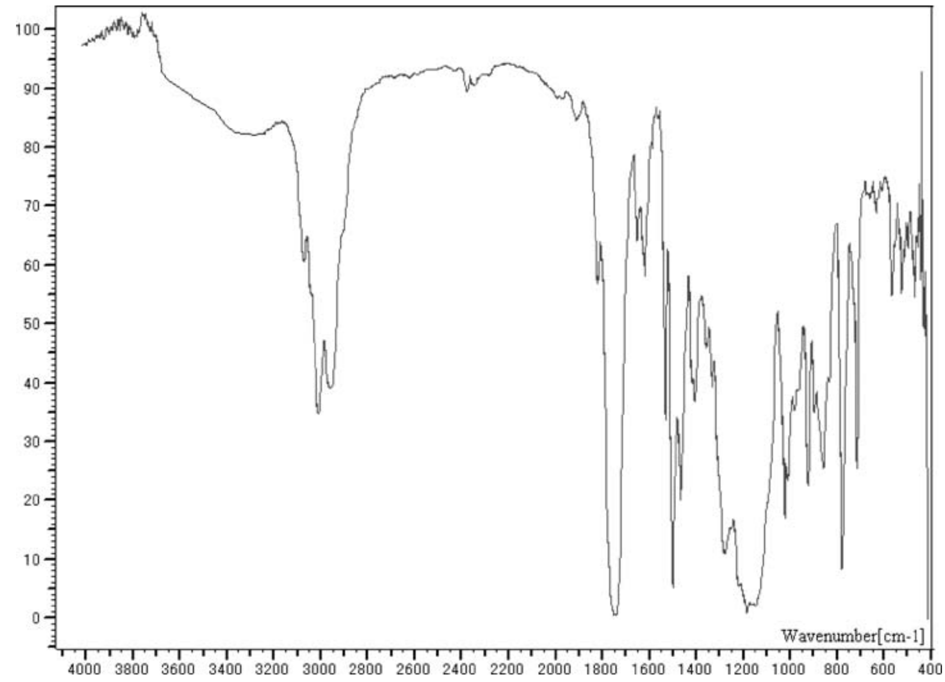


Figure 1. FT-IR spectrum of poly(BPM-co-GMA) (0.5070: 0.4930)

to the methyl and methylene groups is observed at 2992, 2952 and 2850 cm^{-1}. The peaks at 1796 and 1742 cm^{-1} are attributed to the ester carbonyl stretching of BPM and GMA units. The aromatic C=C stretching is observed at 1604, 1518 and 1485 cm^{-1}. The C-O link in the ester of BPM units and in GMA units shows signals at 1167 and 1389 cm^{-1}, respectively. The C-H out of plane bending vibrations of the aromatic nuclei is observed at 881 and 761 cm^{-1}. The out-of-plane bending vibration of aromatic C=C is seen at 680 cm^{-1}.

^{1}H-NMR spectrum

The ^{1}H-NMR spectrum of the copolymer of poly(BPM-co-GMA) (0.5070: 0.4930) is shown in Fig 2. The aromatic protons show signals between 7.62 and 7.19 ppm. The spectrum shows two signals at 4.30 and 3.80 ppm are due to the ester $–CH_2O$ group.

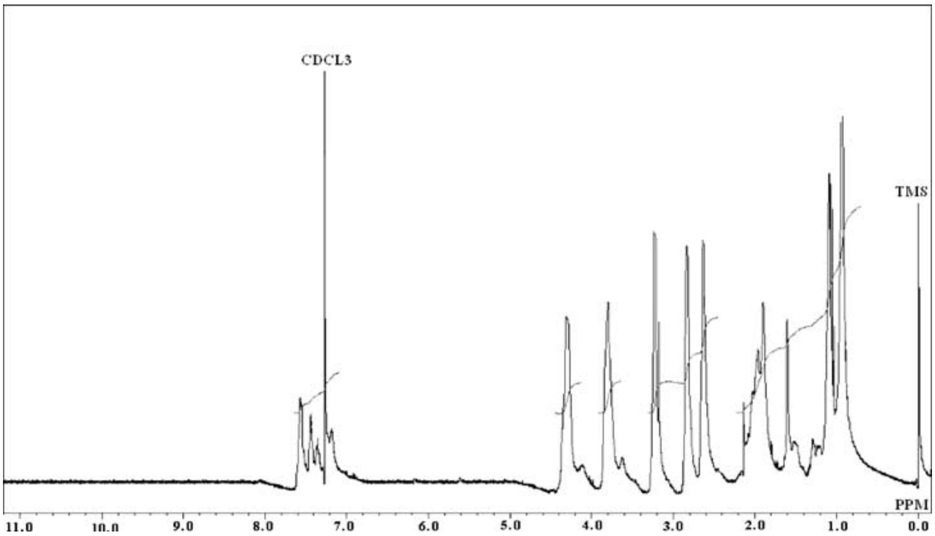


Figure 2. ^{1}H-NMR spectrum of poly (BPM-co-GMA) (0.5070: 0.4930)

The peak at 3.23 ppm corresponds to the methyne proton of the epoxy group. The methylene protons of the epoxy group show signals at 2.83 and 2.63 ppm. Due to the existence of tacticity, the resonance signals corresponding to the methylene group of the polymer backbone are observed between 1.96 and 1.60 ppm. The α-methyl group of the BPM and GMA units shows resonance signal at 1.09 and 0.93 ppm.

^{13}C-NMR Spectrum

The proton decoupled of ^{13}C-NMR spectrum of poly(BPM-co-GMA) (0.5070: 0.4930) is shown in Fig 3. It shows resonance signals at 175.14 ppm and 170.02 ppm are due to the ester carbonyl carbon of BPM and GMA units. The aromatic carbon attached to the oxygen atom shows signal at 153.73 ppm. The other aromatic carbons gave signals at 132.85(C_8), 128.91 (C_9), 127.07 (C_{11} and C_{12}), 126.93 ppm(C_{10}), 118.05 ppm(C_7) and 110.65 ppm(C_7). The methyleneoxy group flanked between the carbonyl group and the epoxy group give signal at 59.54 ppm. The epoxy ring methyne and methylene carbon of GMA unit give signals at 48.95 and 46.17 ppm respectively. The signal due to the backbone methylene and tertiary carbon atoms are observed at 52.45 and 45.07 ppm. The α-methyl group of both the monomer units shows resonance at 18.47 ppm.

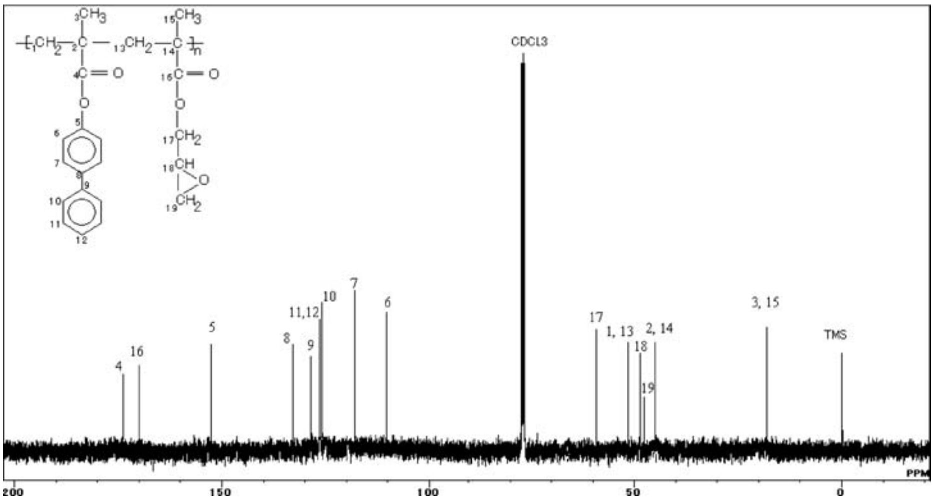


Figure 3. ^{13}C-NMR spectrum of poly(BPM-co-GMA) (0.5070: 0.4930)

Molecular weights

The number and weight average molecular weight of poly(BPM), poly(GMA) and six polymer samples of copolymers were determined by gel permeation chromatography. The polydispersity indices values of the copolymers are presented in Table.1. The polydispersity indices of poly(BPM) and poly(GMA) are 1.62 and 1.97, respectively. The theoretical value of Mw/Mn for polymers produced via radical recombination and disproportionation are 1.5 and 2.0, respectively [29]. In the homopolymerization of GMA the growing chains undergo termination by disproportionation [30]. The polydispersity of poly(GMA) and poly(BPM) suggest that the tendency for chain termination by disproportionation is greater for GMA than BPM. The values of Mw/Mn in copolymerization are also depends on chain termination in the same way as in homopolymerization. The values of Mw/Mn of the copolymers range between 1.70 and 1.92, which suggests that the chain termination takes place predominantly by disproportionation than coupling.

Glass transition temperature

The glass transition temperature (T_g) of the copolymers were determined using differential scanning calorimetry and the data's are presented in Table 2. All the copolymers show a single T_g, showing the absence of formation of mixture of homopolymers or the formation of a block copolymer. The T_g of poly(BPM) is 89°C and that of poly(GMA) is 74°C. The results clearly indicate that the T_g values of the copolymers mainly depend on the composition of comonomers and the value increases with increase of BPM mole fractions in the copolymer. The variation of T_g of copolymers with mole fraction of the BPM unit in the copolymer is shown in Fig 4.

Table 2. DSC and TGA data for BPM-GMA copolymer system.

Polymers	m_1	$T_g{}^a$(°C)	IDT^b(°C)	Temp(°C)	Weight loss(%)			
				10%	30%	50%	70%	90%
Poly(GMA)	0.0000	74	188	263	272	307	322	375
Poly(BPM-co-GMA)	0.4215	80	203	265	276	314	345	390
	0.5070	83	217	266	278	318	360	402
	0.5649	84	222	267	280	320	370	410
Poly(BPM)	1.0000	89	229	270	282	325	384	420

[a] *T_g(°C)* is the glass transition temperature.
[b] *IDT* is the initial decomposition temperature.

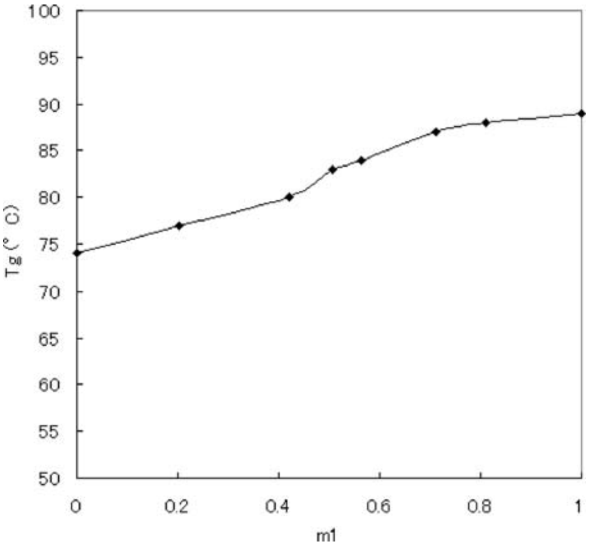


Figure 4. Variation of T_g (°C) with composition of poly(BPM-co-GMA) system

Thermogravimetric analysis

The TGA data for the homopolymers and copolymers of BPM and GMA are given in Table.2. TGA curves for poly(GMA), poly(BPM) and a sample of poly(BPM-co-GMA) (0.5070: 0.4930) are shown in Fig.5. The initial decomposition temperature of poly (BPM), poly(BPM-co-GMA) and poly(GMA) are 229, 217 and 188°C. The thermograms clearly indicate that poly(BPM) and poly(BPM-co-GMA) undergoes two stages decomposition, whereas poly(GMA) undergoes single stage decomposition. This behavior can be explained by assuming the following mechanism. The first step of decomposition is due to the loss of CO_2, rupture of weak linkages in backbone pendant group and thereby volatilization of low molecular weight species. This process is then followed by the loss of benzene ring, by the breakage of main chains and volatilization of the cleaved products. Thus, TGA results clearly indicate that the thermal stability of the copolymer increases with rising BPM content in the copolymer. In case of naphthyl acrylate polymers [31], the initial decomposition temperature is found to be 287 and 302°C, which are higher than that of biphenyl methacrylate polymers. The higher thermal stability is due to the presence bulky hydrophobic group in naphthyl acrylate polymers.

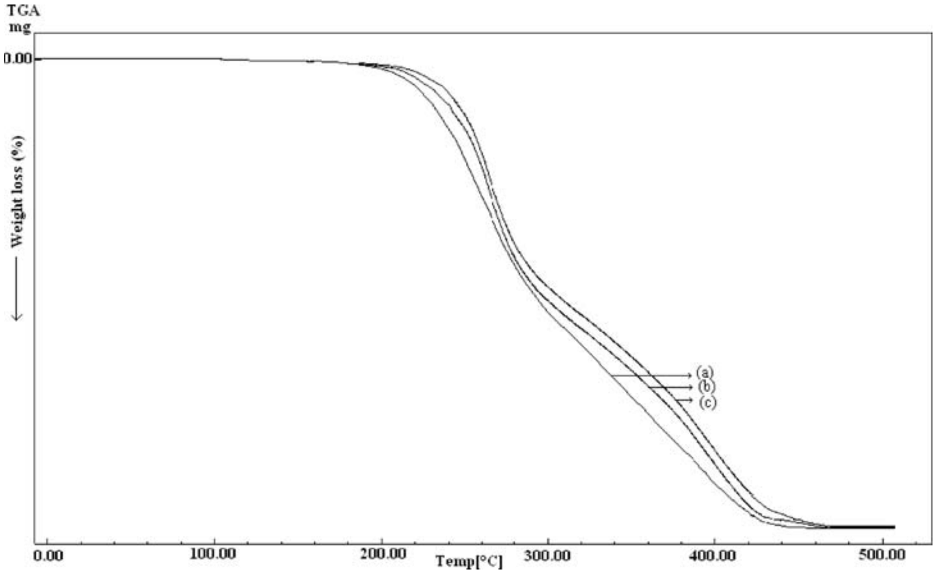


Figure 5. TGA curves (a) poly(GMA), (b) poly(BPM-co-GMA) (0.5070: 0.4930), (c) Poly(BPM)

Copolymer composition

The chemical structure of copolymers is represented in scheme 2. The average compositions of the copolymer samples were determined from the corresponding ^{1}H-NMR spectra. The assignment of the resonance peaks in the ^{1}H-NMR spectrum leads to the accurate evaluation of the content of each kind of monomeric unit incorporated into the copolymer chains. Thus, the mole fraction of BPM in the copolymer was calculated by measuring the integrated peak height of aromatic protons of BPM to that of total aliphatic protons in the copolymer.

The following expression is used to determine the composition of the copolymers. Let m_1 be the mole fraction of BPM and 1- m_1 be that of GMA. BPM contains nine aromatic protons and five aliphatic protons, and GMA contains ten aliphatic protons. The following expression is used to determine the composition of copolymers.

$$C = \frac{\text{Integral peak height of aromatic protons}}{\text{Integral peak height of total aliphatic protons}} = \frac{3m_1}{5m_1 + 10(1 - m_1)} \qquad (\mathbf{1})$$

This on simplification gives,

$$m_1 = \frac{10C}{9 + 5C} \qquad (\mathbf{2})$$

From equation (2), the mole fractions of BPM in the copolymers were determined by measuring the integral peak height of aromatic protons and total aliphatic protons signals. Table 1 gives the values of C and the corresponding mole fractions of BPM in the copolymers. The plot of mole fractions of BPM (M_1) in the feed against that in the copolymer (m_1) is shown in Fig 6. The copolymer composition curve indicates that the system can form an azeotropic polymerization.

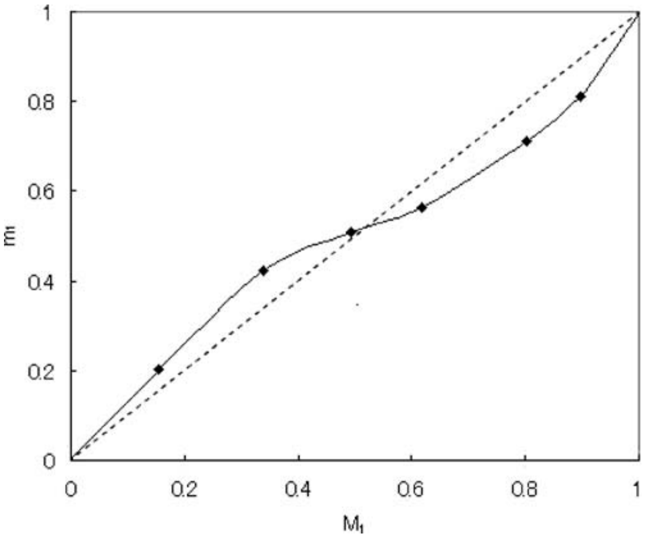


Figure 6. Copolymer composition diagram of poly(BPM-co-GMA)

Monomer reactivity ratios

From the monomer feed ratios and copolymer composition, the monomer reactivity ratios of BPM and GMA were determined by the application of conventional linearization methods, such as Fineman-Ross (F-R) [32], Kelen-Tudos (K-T) [33], and the extended Kelen-Tudos (Ext.K-T) [34]. The reactivity ratio values obtained from F-R, K-T and Ext K-T methods are presented as follows;

Methods	r_1	r_2	
Fineman-Ross	0.392 ± 0.006	0.358 ± 0.007	
Kelen-Tudos	0.398 ± 0.004	0.365 ± 0.013	
Ext. Kelen-Tudos	0.394 ± 0.004	0.352 ± 0.006	
Average	0.394 ± 0.004	0.358 ± 0.007	$r_1 \times r_2 = 0.1410$

Since the value of r_1 and r_2 values are lesser than unity, the system gives rise to an azeotropic polymerization. The azeotropic polymerization at a particular composition, when the mole fraction of the monomer BPM in the feed is 0.5214, the copolymer formed will have the same composition as that of the feed. When the mole fraction of the feed is less than 0.5214 with respect BPM, the formed copolymer is relatively richer in this monomer unit than the feed. When the mole fraction of the monomer BPM in the feed is above 0.5214, the copolymer is relatively richer in GMA unit than in the feed. However, the product value of r_1 and r_2 is lesser than 1, which indicates that the system leads to a strong alternating tendency. In case of phenyl methacrylate (PhMA) copolymerization with glycidyl methacrylate (GMA) comonomer [35], it has been noticed that the reactivity ratios value of PhMA is greater than that of GMA. The reactivity ratio values indicate that the PhMA radical favours its own monomer rather than GMA. Generally the neutral olefin molecules and those olefin molecules containing moderately electron-donating or electron-withdrawing groups favour free radical polymerization. In case of BPM, the electron withdrawing phenyl substituted ester group and electron donating methyl group attached to an olefinic group. Therefore, the net charge of BPM molecule is lesser than the GMA molecule. Hence, the reactivity of the molecule is comparatively high. Further more, the relative reactivity of the comonomers has to be decided not only in terms of the electronic effects but also of the steric effects and the overall polarity of the molecule.

Conclusion

Copolymers of BPM with GMA were synthesized by free radical solution polymerization techniques. Characterization of poly(BPM-co-GMA) were performed by FT-IR, ^{1}H-NMR and ^{13}C-NMR techniques. The copolymers were soluble in chloroform, acetone, dimethyl acetamide, dimethyl formamide, dimethyl sulfoxide, tetrahydrofuran, benzene, toluene, xylene and insoluble in n-hexane and hydroxyl-group containing solvents such as methanol and ethanol. Thermogravimetric analysis indicated that the thermal stability of the copolymer increases with the increase of BPM units in the copolymer. The glass transition temperature of the copolymer increases with BPM content. The values of polydispersity index for poly(BPM), poly(BPM-co-GMA) and poly(GMA) suggest a strong tendency for chain termination by disproportionation in all cases. The monomer reactivity ratios were determined by conventional linearization methods such F-R, K-T, and Ext K-T methods. The r_1 and r_2 values from these methods are lesser than unity indicating that the copolymer system gives rise to an azeotropic polymerization**.** The product value of r_1 and r_2 is lesser than 1, which indicates that the system follows a strong tendency to alternation.

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