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Synthesis and Characterization of 3,5-Dimethoxyphenyl Methacrylate and Methyl Methyacrylate Copolymers: Determination of Monomer Reactivity Ratios

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A new monomer, 3,5-dimethoxyphenyl methacrylate (DMOPM) has been synthesized from the precursor viz.,3,5-dimethoxy phenol. Copolymerization of DMOPM with methyl methacrylate (MMA) has been carried out in ethyl methyl ketone (EMK) by free radical solution polymerization at 70 ± 1°C utilizing benzoyl peroxide (BPO) as initiator. Poly(DMOPM-co-MMA) copolymers were characterized by ^{1}H-NMR,^{13}C-NMR, and the copolymer compositions were evaluated by ^{1}H-NMR spectroscopy. The monomer reactivity ratios were estimated using Fineman-Ross, Kelen-Tudos and extended Kelen-Tudos methods. The solubility was tested in various polar and non polar solvents. The molecular weight and polydispersity indices of the copolymers were determined by using gel permeation chromatography. By TGA and DSC analyses, the thermal properties of the polymers have been studied.

Keywords: 3,5-dimethoxyphenyl methacrylate; copolymerization; reactivity ratios; ^{1}H-NMR and ^{13}C-NMR spectra; methyl methacrylate; thermal studies

1 Introduction

At the present time, a strong demand prevails for functional polymers with specific properties. In recent years, some comprehensive work has been published on functional monomers and their polymers (1–6). Functional polymers can be prepared by a simple route of copolymerization reaction of functional monomers. 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) generally possess high tensile strength, high thermal stability, and their glass transition temperature is higher than their corresponding acrylate polymers due to the presence of a alpha methyl group on their main chain. Therefore, they find a wide range of applications for the preparation of materials (7–17). Methyl methacrylate copolymers are mainly used in the production of primers for automotive finishes, lacquers for polishing metals, enamels for household appliances and formulations of base and top coats for leather and binders in protective coatings because of their durability and transparency (18, 19).

NMR spectroscopy played a dominant role in the understanding of polymer stereochemistry. In the past few decades, ^{1}H-NMR spectroscopy analysis has been established as a powerful tool for the determination of tacticity, sequence distribution and estimation of copolymer composition as well, because of its simplicity, rapidity and high sensitivity (20–24). The accurate estimation of copolymer composition and determination of monomer reactivity ratios are significant to synthesize tailor-made copolymers with the required physical and chemical properties. The main aim in commercial copolymerization is to achieve a narrow composition as much as possible. Knowledge about the monomer reactivity ratios of the comonomer would be helpful in achieving this. In chemical abstracts neither the synthesis of 3,5-dimethoxyphenyl methacrylate (DMOPM) monomer, nor its copolymer systems for the determination of monomer reactivity ratios, has been reported to date. The present research paper mainly describes synthesis and characterization of copolymers of 3,5-dimethoxyphenyl methacrylate (DMOPM) with methyl methacrylate (MMA). The monomer reactivity ratios and thermal properties were also discussed.

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2 Experimental

2.1 *Materials*

3,5-Dimethoxy phenol (Wako Chemical Industries, for synthesis) was used as received. Methyl methacrylate (MMA) (Wako Chemicals) was purified by distillation under reduced pressure. Benzoyl peroxide (BPO) (Acros) was recrystallized from chloroform-methanol (1:1) mixture. Triethylamine (Wako), methacrylic acid (Wako) and benzoyl chloride (Wako) were used as such. All the solvents were purified by distillation prior to their use.

2.2 *Synthesis of 3,5-Dimethoxyphenyl Methacrylate (DMOPM)*

Methacryloyl chloride was prepared from methacrylic acid and benzoyl chloride using the procedure of Stampel et al. (25). For the synthesis of 3,5-Dimethoxy phenyl methacrylate, 3,5-Dimethoxy phenol (10 g, 0.065 mol) and triethylamine (9.1 ml, 0.065 mol) were dissolved in 250 ml of ethyl methyl ketone (EMK) and the reaction mixture was stirred in an ice bath at 0–5°C. Methacryloyl chloride (6.4 ml, 0.065 mol) is dissolved in 25 ml of EMK and added dropwise through a dropping funnel over a period of 30 min. After the addition, the reaction mixture was stirred for 1 h. The cooling bath was then removed and the reaction mixture was allowed to be stirred at room temperature for a period of 1 h. The precipitated triethylammonium chloride was then filtered off and solvent in the filtrate was removed by using a rotary evaporator. The residue obtained was dissolved in ether and washed twice with a 0.1% solution of NaOH and then with distilled water. Finally, the ether solution was dehydrated using anhydrous Na_2SO_4. The ether solution was evaporated to get a residue which was distilled under reduced pressure to give pure DMOPM. The yield of the monomer was 70%. The monomer was examined by FT-IR and ^{1}H-NMR spectra as follows:IR cm-^{1}; 3112 and 3102 (=C-H), 2935 and 2839 (C-H stretching), 1735 (C=O), 1677 (CH_2=C), 1586 and 1402 (aromatic C=C), 1396 (CH_3 symmetrical bending), 1112 (C-0), 822 and 682 (C-H out-of-plane bending).

^{1}H-NMR; 6.50 and 6.34 (aromatic protons), 6.26 and 5.76 (CH_2=C), 3.46 (aromatic-OCH_3), 2.04 (α-CH_3).

2.3 *Copolymerization*

Predetermined quantities of DMOPM, MMA 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 40°C for 24 h. The copolymer conversions were restricted to less than 10%.

2.4 *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 2 ml of the solvent in a test tube and kept overnight with the tube tightly closed. The solubility of the polymers was noted after 24 h.

2.5 *Measurements*

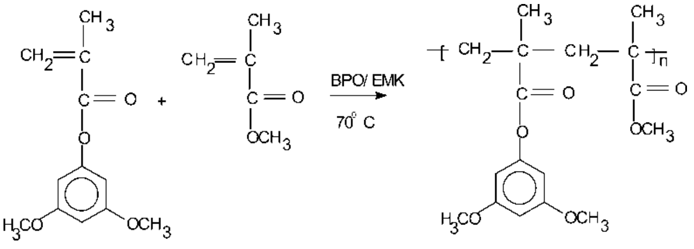
Infrared spectra were recorded with a Jasco 460 FT-IR spectrophotometer as KBr pellets. ^{1}H-NMR spectra of the monomer and all the polymer samples were run on a JEOL–JNM-LA 400 FT-NMR spectrophotometer at room temperature using CDCl3 solvent and TMS as an internal standard, respectively. The proton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

3 Results and Discussion

3.1 *Synthesis of Polymers*

Poly(DMOPM) was obtained by the free radical solution polymerization of the monomer at 70 ± 1°C in a EMK solvent using BPO as an initiator. The copolymerization of DMOPM with MMA in the EMK solution was studied in a wide composition interval with mole fractions of DMOPM 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 the Scheme 1. The data on the composition of feed and copolymers are presented in Table 1.

The homopolymer and the copolymers were soluble in chloroform, acetone, dimethyl acetamide, dimethyl



Sch. 1. Synthesis of poly(DMOPM-co-MMA).

Table 1. Composition data for free radical polymerization of DMOPM 1 with MMA 2 in EMK solution at 70 ± 1°C

			Integral peak height			
Copolymer	$M_1{}^a$	Conversion (%)	I_{Ar}	I_{Al}	C	$m_1{}^b$
1	0.1488	8.76	3.000	269.292	0.0111	0.0299
2	0.2755	9.54	3.000	75.911	0.0395	0.1096
3	0.5015	9.03	3.785	37.829	0.1001	0.2966
4	0.6466	8.87	3.000	20.7325	0.1447	0.4511
5	0.7842	9.25	3.000	15.8450	0.1893	0.6227
6	0.8956	8.69	3.000	13.0832	0.2293	0.7934

[a] M_1 is the molefraction of DMOPM in the feed.
[b] m_1 is the molefraction of DMOPM in the copolymer.

formamide, dimethyl sulfoxide, tetrahydrofuran, benzene, toluene, xylene and insoluble in n-hexane and hydroxyl-group containing solvents such as methanol and ethanol.

3.2 Characterization of Polymers

The FT-IR spectrum of the copolymer poly(DMOPM-co-MMA) (0.2966:0.7034) is shown in Figure 1. It shows a peak at 2998 cm^{-1} corresponding to the C-H stretching of aromatic system. The symmetrical and asymmetrical stretching peaks due to the methyl and methylene groups are observed at 2951 and 2840 cm^{-1}. The peak at 1734 cm^{-1} is attributed to the ester carbonyl stretching of DMOPM and MMA units. The aromatic C=C stretching vibrations are observed at 1615, 1596, and 1477 cm^{-1}. The symmetrical bending vibrations of methyl groups are seen at 1389 cm^{-1}. The C-O stretching due to the ester groups of DMOPM units and MMA units showed signals at 1155, 1242 and 1326 cm^{-1}, respectively. The C-H out-of-plane bending vibrations of aromatic nuclei are observed at 840 and 754 cm^{-1}. The out-of-plane bending vibration of aromatic C=C is seen at 682 cm^{-1}.

The ^{1}H-NMR spectrum of the copolymer of poly(DMOPM-co-MMA) (0.2966:0.7034) is shown in Figure 2. The aromatic protons show signals between 6.31 and 6.24 ppm. The methoxy protons of the DMOPM group show a signal at 3.86 ppm. Signals at 3.69 ppm were due to the methoxy protons of the MMA unit. The broad resonance signals shown at 2.12–0.82 ppm are due to the existence of tacticity of backbone methylene groups and the α-methyl group.

The proton decoupled of ^{13}C-NMR spectrum of poly (DMOPM-co-MMA) (0.2966:0.7034) is shown in Figure 3. It shows resonance signals at 175.06 ppm due to the ester carbonyl carbon of DMOPM and MMA units. The aromatic carbon attached to the oxygen atom shows a signal at 152.15 ppm. The other aromatic carbon signals are observed

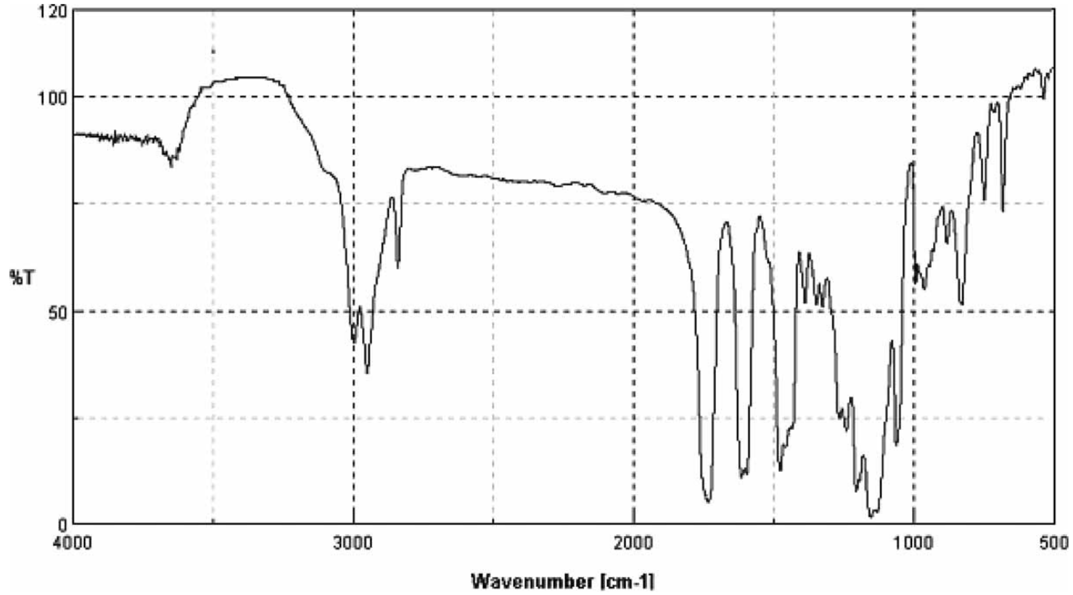


Fig. 1. FT-IR spectrum of poly(DMOPM-co-MMA) system (0.2966:0.7034).

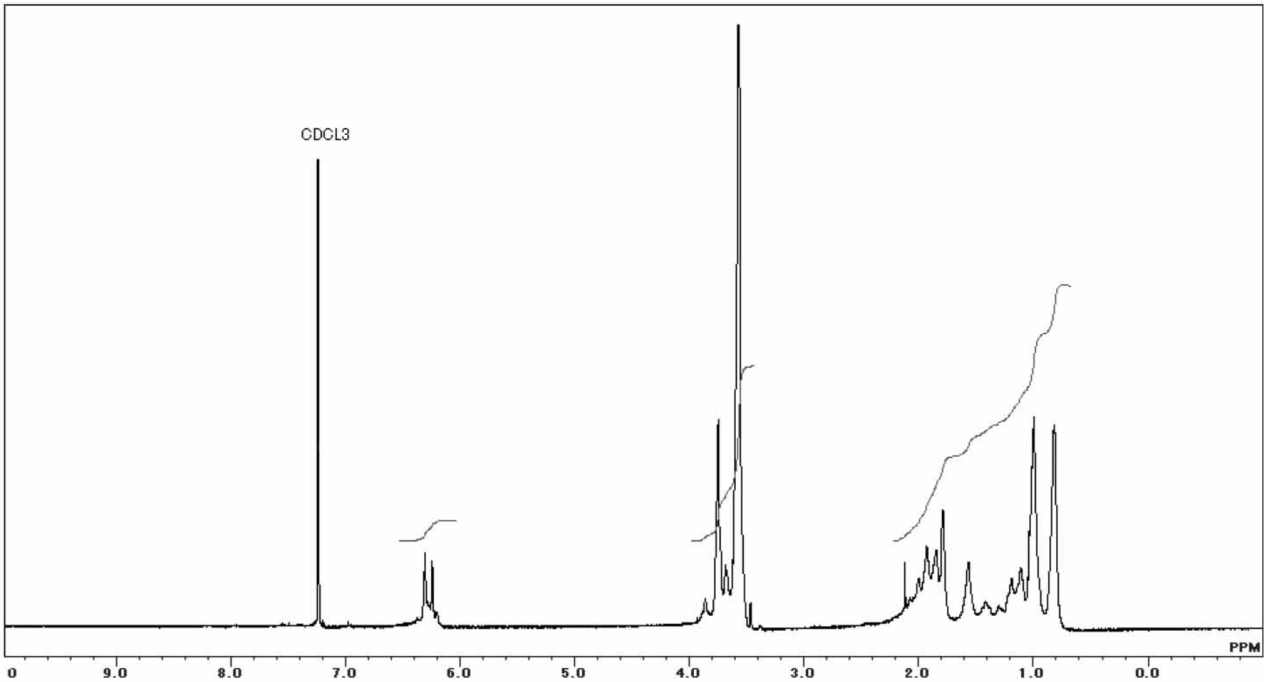


Fig. 2. ^{1}H-NMR spectrum of poly(DMOPM-co-MMA) system (0.2966:0.7034).

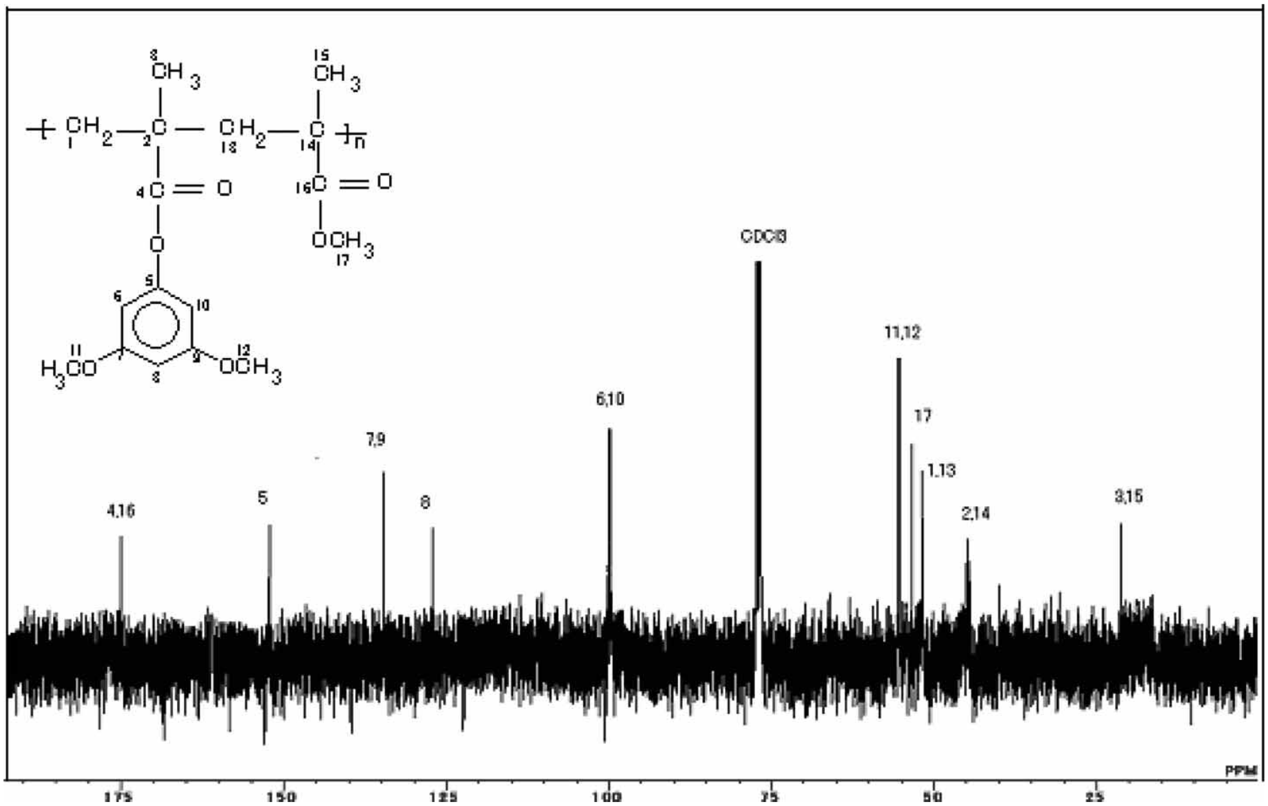


Fig. 3. ^{13}C-NMR spectrum of poly(DMOPM-co-MMA) system (0.2966:0.7034).

Table 2. Molecular weight data for homo and copolymers of DMOPM-MMA

Polymer	$m_1{}^a$	$M_w \times 10^{-4}$	$M_n \times 10^{-4}$	M_W/M_n
Poly(DMOPM)	1.0000	3.20	1.93	1.66
Poly(DMOPM-MMA)	0.0299	3.54	1.95	1.82
	0.1096	3.57	2.03	1.76
	0.2966	3.72	2.07	1.80
	0.4511	3.63	2.03	1.79
	0.6227	3.85	2.13	1.81
	0.7934	3.46	2.01	1.72
Poly(MMA)	0.0000	3.35	2.01	1.84

[a] m_1 is the mole fraction of DMOPM in the copolymer.

at 139.56 (C_7 and C_9), 127.90 (C_8) and 100.18 ppm (C_6 and C_{10}). The methoxy carbon of MMA unit observed at 58.51 ppm. The signal due to the backbone methylene and tertiary carbon atoms are observed at 51.81 and 44.91 ppm. The methoxy group attached to the aromatic nuclei shows a signal at 55.46 ppm. The α-methyl group of both the monomer units shows resonance signal at 18.92 ppm.

3.3 Molecular Weights

The number and weight average molecular weight of poly(DMOPM), poly(MMA) and six copolymer samples were determined by gel permeation chromatography. The data are presented in Table 2. The polydispersity indices of poly(DMOPM) and poly(MMA) are 1.66 and 1.84, respectively. The theoretical value of Mw and Mn for polymers produced via radical recombination and disproportionation are 1.5 and 2.0, respectively (26). In the homopolymerization of MMA the growing chains undergo termination by disproportionation (27). The polydispersity values of poly(MMA) and poly(DMOPM) suggest that the tendency for chain termination by disproportionation is greater for MMA than for DMOPM. The values of Mw/Mn in the copolymerization are also known to depend on chain termination in the same way as in homopolymerization. The polydispersity indices of the copolymers suggest that when the mole fraction of MMA is higher than that of DMOPM in the feed, there exist a strong tendency for chain termination by disproportionation.

3.4 Glass Transition Temperature

The glass transition temperatures (T_g) of the copolymers were determined using differential scanning calorimetry and T_g data are given in Table 3. All the copolymers show single T_g, indicating the absence of formation of mixture of homopolymers or the formation of a block copolymer. The T_g of poly(DMOPM) is 84°C and that of poly MMA is 105°C. The result clearly indicates that the T_g values of copolymers depend on the composition of comonomers, and the value increases with increases in the mole fraction of MMA in copolymer. The variation of T_g of copolymers with mole fraction of the DMOPM unit in the copolymer is shown in Figure 4.

3.5 Thermogravimetric Analysis

The TGA data for the homopolymers and copolymers of DMOPM and MMA are given in Table 3. TGA curves for poly(DMOPM), poly(MMA), and a sample of poly (DMOPM-co-GMA) (0.2966:0.7034) are shown in Figure 5. The thermograms clearly indicate that poly(DMOPM) and poly(DMOPM-co-MMA) undergo two-stage decomposition while poly(MMA) undergoes single-stage decomposition. The initial decomposition temperature of poly(DMOPM), poly (DMOPM-co-MMA), and poly(MMA) are 224, 201, and 244°C. TGA results indicate that the thermal stability of the copolymer increases with increases of DMOPM content in the copolymer. The first decomposition may be due to the rupture of weak linkages and volatilization of low molecular weight species. The decomposition of polymers at higher temperature may be due to the breakage of main chain accompanied by volatilization of the cleaved products.

3.6 Copolymer Composition

The chemical structure of copolymers may be represented as in Scheme 1. The average compositions of the copolymer samples were determined from the corresponding ^{1}H-NMR spectra. The assignment of the resonance peaks in the

Table 3. DSC and TGA data for DMOPM-MMA copolymer system

				Temp (°C)	Weight	Loss (%)		
Polymers	m_1	$T_g{}^a$ (°C)	IDT^b (°C)	10%	30%	50%	70%	90%
Poly(MMA)	0.0000	105	244	270	284	300	334	384
	0.1096	94	215	245	274	312	348	390
Poly(DMOPM-MMA)	0.2966	91	201	220	263	323	362	398
	0.4511	86	212	232	272	335	375	404
Poly(DMOPM)	1.0000	84	224	272	287	346	387	414

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

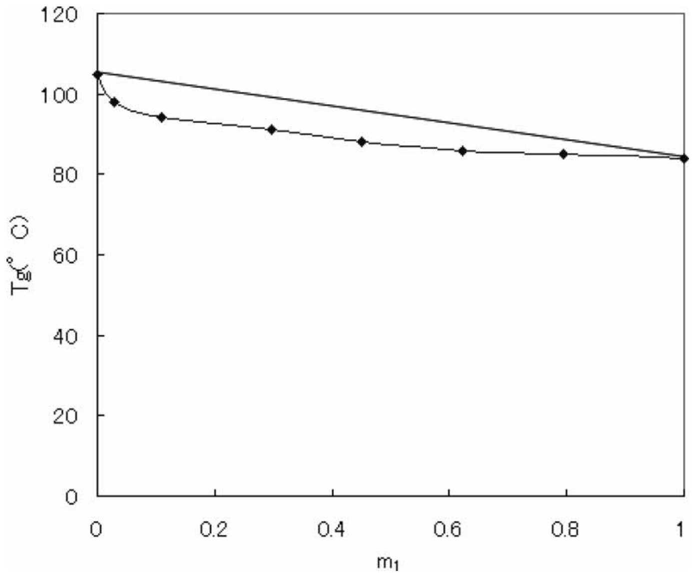


Fig. 4. Variation of Tg(°C) with composition of poly(DMOPM-co-MMA) system.

^{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 DMOPM in the copolymer was calculated by measuring the intergrated peak heights of aromatic protons of DMOPM to that of total aliphatic protons in the copolymer.

The following expression is used to determine the composition of the copolymers. When m_1 is the mole fraction of DMOPM and 1-m_1 is that of MMA, DMOPM contains three aromatic protons and eight aliphatic protons, and MMA contains eight aliphatic protons.

$$C = \frac{\text{Integral peak height of aromatic protons}}{\text{Integral peak height of total aliphatic protons}} = \frac{3m_1}{11m_1 + 8(1 - m_1)} \tag{1}$$

which on simplification gives:

$$m_1 = \frac{8C}{3(1 - C)} \tag{2}$$

From Equation (2), the mole fractions of DMOPM in the copolymers were determined by measuring the integral peak height of aromatic proton and aliphatic proton signals. Table 1 gives the values of C and the corresponding mole fraction of DMOPM in the copolymers. The plot of mole fractions of DMOPM (M_1) in the feed vs. that in the copolymer (m_1) is shown in Figure 6. It clearly indicates that the composition of DMOPM in the copolymer is always lower than that in the feed.

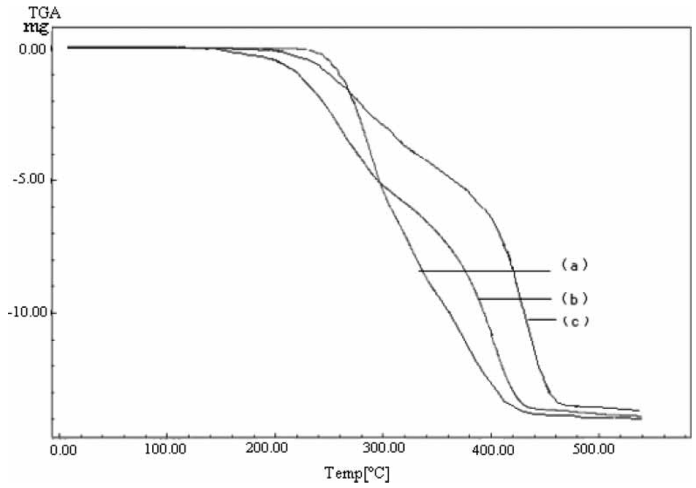


Fig. 5. TGA curves for (a) poly(MMA), (b) poly(DMOPM-co-MMA), (c) poly (DMOPM).

3.7 *Reactivity Ratios*

From the monomer feed ratios and the copolymer composition, the reactivity ratio of DMOPM and MMA were determined by the application of conventional linearization methods, such as Fineman-Ross (F-R) (28), Kelen-Tudos (K-T) (29) and extended Kelen-Tudos (Ext. K-T) (30). The monomer reactivity ratios values are given in Table 4. Since the value of r_1 is less than 1 and the value of r_2 is greater than 1, this indicates the presence of a lower amount of DMOPM units in the copolymer than in the feed. However, the product of r_1 and r_2 is greater than 1, which indicates that the system leads to random distribution of monomer units with a longer sequence of MMA units in the copolymer chain. Generally, neutral olefin molecules and those olefin molecules containing moderately electron-donating or electron-withdrawing groups favor free radical polymerization. MMA consists of an electron-withdrawing ester group and an electron-donating methyl group and attached to an olefin

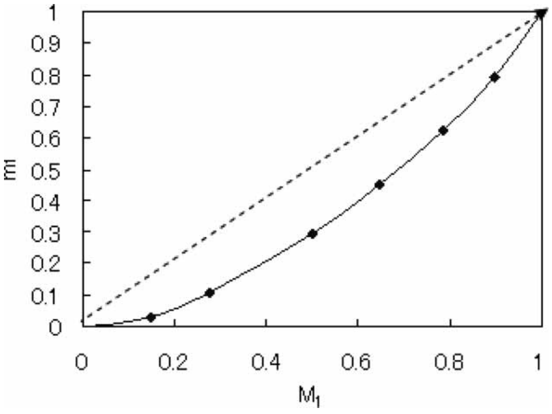


Fig. 6. Copolymer composition diagram of poly(DMOPM-co-MMA) system.

Table 4. Copolymerization parameters for the free radical copolymerization of DMOPM with MMA

Methods	r_1^a	r_2^b	$r_1 \times r_2$
Fineman-Ross	0.622	3.356	2.087
Kelen-Tudos	0.637	3.235	2.061
Ext.Kelen-Tudos	0.645	3.237	2.088
Average	0.635	3.276	2.080

$^a r_1$ and $^b r_2$ are the reactivity ratios of DMOPM and MMA, respectively.

molecule, while DMOPM consists of electron withdrawing phenyl ester group and an electron-donating methyl group attached to an olefin molecule. But the net charge on the MMA molecule is less when compared to DMOPM, and therefore, the reactivity of MMA is more than that of DMOPM. Moreover, 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.

4 Conclusions

Poly(DMOPM) and the copolymers of DMOPM with MMA were synthesized by free radical solution polymerization techniques. Characterization of poly(DMOPM) and poly (DMOPM-co-MMA) were performed by FT-IR, ^{1}H-NMR and ^{13}C-NMR techniques. The homopolymer and copolymers are 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 DMOPM units in the copolymer. The glass transition temperature increases with MMA content. The polydispersity index values for poly(DMOPM), poly (DMOPM-co-MMA) and poly(MMA) suggests a strong tendency for chain termination by disproportionation in all cases and the tendency increases with increasing MMA content in the feed. The reactivity ratios were determined by conventional linearization methods such F-R, K-T and Ext K-T methods. The r_1 values from these methods are less than 1, and r_2 values are greater than 1. This indicates that DMOPM is less reactive than MMA. The value of the product of r_1 r_2 is greater than 1, which indicates that the system forms a random copolymer with a longer sequence of MMA units in the copolymer chain.

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