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### Synthesis and Characterization of Novel Methacrylic Copolymers: Determination of Monomer Reactivity Ratios

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# Synthesis and Characterization of Novel Methacrylic Copolymers: Determination of Monomer Reactivity Ratios

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A new methacrylic monomer, 4-nitro-3-methylphenyl methacrylate (NMPM) was prepared by reacting 4-nitro-3-methyl phenol dissolved in methyl ethyl ketone (MEK) in the presence of triethylamine as a catalyst. Copolymerization of NMPM with methyl methacrylate (MMA) has been carried out in methyl ethyl ketone (MEK) by free radical solution polymerization at  $70 \pm 1^\circ\text{C}$  utilizing benzoyl peroxide (BPO) as initiator. Poly (NMPM-co-MMA) copolymers were characterized by FT-IR,  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  spectroscopy. The molecular weights ( $M_w$  and  $M_n$ ) and polydispersity indices ( $M_w/M_n$ ) of the polymers were determined using a gel permeation chromatograph. The glass transition temperatures ( $T_g$ ) of the copolymers were determined by a differential scanning calorimeter, showing that  $T_g$  increases with MMA content in the copolymer. Thermogravimetric analysis of the polymers, performed under nitrogen, shows that the stability of the copolymer increases with an increase in NMPM content. The solubility of the polymers was tested in various polar and non-polar solvents. Copolymer compositions were determined by  $^1\text{H-NMR}$  spectroscopy by comparing the integral peak heights of well separated aromatic and aliphatic proton peaks. The monomer reactivity ratios were determined by the Fineman-Ross ( $r_1 = 7.090$ ;  $r_2 = 0.854$ ), Kelen-Tudos ( $r_1 = 7.693$ ;  $r_2 = 0.852$ ) and extended Kelen-Tudos methods ( $r_1 = 7.550$ ;  $r_2 = 0.856$ ).

**Keywords:** 4-nitro-3-methylphenyl methacrylate; copolymerization; reactivity ratios;  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  spectra; methyl methacrylate; thermal studies

## 1 Introduction

Today, there exists a strong demand for functional polymers for industrial applications in commercial markets. The use of special designed homopolymers and copolymers, having pendant functional groups or substituents on the main chain, is a topic of continued research. Incorporation of different chemical groups in macromolecular chains can be achieved by copolymerization of two or more monomers. Copolymerization is the most successful method adopted in order to obtain systematic changes in the polymer properties (1–6). Macromolecules of this type possess significant importance from both a fundamental and an applied point of view. Aromatic acrylates and methacrylates are highly reactive monomers due to the presence of an aromatic ring, forming an interesting class of polymers. Poly(phenyl methacrylates) generally possesses high tensile strength and high thermal stability, along with higher glass transition temperature than the parent methacrylate homopolymers, due to the

presence of the  $\alpha$ -methyl group on the main chain. Therefore, they find a wide range of application in the preparation of materials such as photo luminescent (7), photo resist (8), adhesives for leather (9–11), photosensitive (12), biomaterials (13, 14), optical telecommunication materials (15), polymer catalyst (16), etc. Methyl methacrylate (MMA) copolymers are mainly used in the production of primers for automotive finishes, lacquers for polishing metals, enamels for household appliances, formulations of base and top coats for leather and a binder in protective coatings, due to their durability and transparency (17, 18).

Reactivity ratios are one among the most important parameters for the copolymer equation, which gives very good information regarding relative reactivity of the monomer pairs and copolymer composition determination. The calculation of monomer reactivity ratios requires the mathematical treatment of experimental data based on the composition of the copolymers related to the initial feed.  $^1\text{H-NMR}$  spectroscopy analysis has been established as a powerful tool for the determination of tacticity, sequence distribution and estimation of copolymer composition, due to its simplicity, rapidity and sensitivity (19–23). The presence of aromatic side substituents, instead of aliphatic residues in polyacrylic chains, gives rise to noticeable effects on the splitting of the NMR signals of several acrylic systems. The accurate

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estimation of copolymer composition and determination of monomer reactivity ratios are significant for synthesizing tailor-made copolymers with required physical and chemical properties. In commercial copolymerization, the main aim is to achieve as narrow composition distribution as far as possible. The knowledge about the monomer reactivity ratios of the comonomer would be very helpful in achieving this aim.

The synthesis of 4-nitro-3-methylphenyl methacrylate (NMPM) monomer nor its copolymer systems for the determination of reactivity ratios has not been reported by Chemical Abstracts. In continuation of our efforts, we synthesized this novel polymeric material for industrial applications. This research work mainly focuses on the synthesis of novel substituted phenyl methacrylate copolymers and their characterization. The present article describes the synthesis, characterization and thermal properties of copolymers prepared from 4-nitro-3-methylphenyl methacrylate with methyl methacrylate. The monomer reactivity ratios and its corresponding copolymerization parameters, describing the distribution of monomer units along the copolymer chains in the whole range of compositions, are reported in this paper.

## 2 Experimental

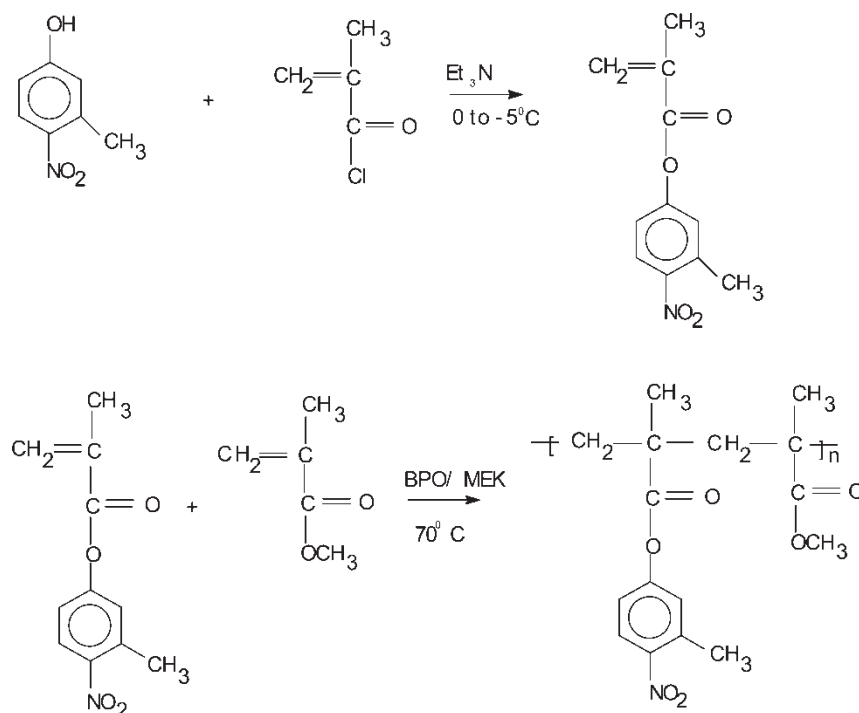
### 2.1 Materials

4-Nitro-3-methyl phenol (Wako Chemical Industries) was used as received. MMA (Wako Chemicals) was purified by distillation under reduced pressure. Benzoyl peroxide (BPO, Aldrich) was recrystallised from a chloroform-methanol

(1:1) mixture. Triethylamine, methacrylic acid and benzoyl chloride were used as received from Wako. All the solvents were purified by distillation prior to their use.

### 2.2 Synthesis of 4-Nitro-3-methylphenyl Methacrylate (NMPM)

Methacryloyl chloride was prepared from methacrylic acid and benzoyl chloride using the procedure of Stampel et al. (24). For the synthesis of NMPM, 4-Nitro-3-methyl phenol (10 g, 0.065 mol), MEK (250 ml) and triethylamine (9.1 ml, 0.065 mol) were combined in a three-necked, RB flask. A mechanical stirrer and dropping funnel, with a pressure equalizing arrangement, along with a guard tube were attached to the reaction flask. The RB flask was placed in an ice bath and the contents were stirred well at 0–5°C. Methacryloyl chloride (6.4 ml, 0.065 mol), dissolved in 20 ml of MEK, contained in the dropping funnel was added dropwise with constant stirring. After the addition, the reaction mixture was allowed to be stirred under the 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, washed twice with 0.1% solution of NaOH and then with distilled water. The ether solution was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The ether solution was evaporated to obtain a residue which was distilled under reduced pressure, providing a 72% yield of crude NMPM. The reaction scheme for the synthesis of NMPM is shown in Scheme 1.



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

NMPM monomer was examined by FT-IR and  $^1\text{H-NMR}$  spectra, with IR ( $\text{cm}^{-1}$ ) exhibiting absorptions at 3112 and 3084 ( $=\text{C-H}$ ), 2983 and 2937 ( $\text{C-H}$  stretching), 1732 ( $\text{C=O}$ ), 1621 ( $\text{CH}_2=\text{C}$ ), 1591 and 1470 (aromatic  $\text{C=C}$ ), 1538 and 1362 ( $\text{N-O}$  asymmetrical and symmetrical stretching), 1368 ( $\text{CH}_3$  symmetrical bending), 1329 ( $\text{C-N}$ ), 1130 ( $\text{C-O}$ ), 841 ( $\text{C-H}$  out-of-plane bending), confirming chemical structure. The  $^1\text{H-NMR}$  (ppm) with 8.03 and 7.31 (aromatic protons), 6.36 and 5.81 ( $\text{CH}_2=\text{C}$ ), 2.31 (Aromatic- $\text{CH}_3$ ), 2.12 ( $\alpha\text{-CH}_3$ ) also confirmed structure.

### 2.3 Copolymerization

Predetermined quantities of NMPM, MMA, MEK and BPO were placed 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 a oil bath at  $70 \pm 1^\circ\text{C}$ . The copolymer conversions were restricted to less than 10% in order to follow the copolymer equation. After the required time, the polymer was precipitated in methanol. The precipitated polymer was filtered off and purified by repeated reprecipitation from chloroform solution using methanol and finally dried in vacuum at  $40^\circ\text{C}$  for 24 h.

### 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. The tube was closed tightly and kept overnight. The solubility of the polymers was observed after 24 h.

### 2.5 Measurements

Infrared spectra were recorded with Jasco 460 FT-IR spectrophotometer as KBr pellets.  $^1\text{H-NMR}$  spectra of the monomer and all polymer samples were run on a JEOL 400 MHz FT-NMR spectrophotometer at room temperature using  $\text{CDCl}_3$  solvent and TMS as an internal standard, respectively. The proton decoupled  $^{13}\text{C-NMR}$  spectrum was run on the same instrument operating at 100 MHz at room temperature, and the corresponding chemical shifts were recorded under similar conditions. The molecular weights ( $M_w$  and  $M_n$ )

were estimated using a Shimadzu Gel Permeation Chromatography, where tetrahydrofuran was used as the eluent and polystyrene standard for calibration. Thermogravimetric analysis of the samples was performed with a Shimadzu Thermal Analyzer under a nitrogen atmosphere at a heating rate of  $10^\circ\text{C}/\text{min}$ . The glass transition temperature was determined with a Shimadzu Differential Scanning Calorimeter at a heating rate of  $10^\circ\text{C}/\text{min}$  under nitrogen atmosphere.

## 3 Results and Discussion

### 3.1 Synthesis of Polymers

Poly(NMPM) was obtained by free radical solution polymerization of the monomer at  $70 \pm 1^\circ\text{C}$  in MEK solvent, using BPO as the initiator. Copolymerization of NMPM with MMA in MEK solution was studied in a wide composition interval with the mole fractions of NMPM ranging from 0.15 to 0.9 in the feed. The reaction time was selected between 1 and 2 h to give conversions less than 10%, in order to satisfy the differential copolymerization equation. The monomeric units of the copolymer are shown in Scheme 1. The data on composition of feed and copolymers are presented in Table 1.

### 3.2 Characterization of Polymers

The homopolymer and the copolymers were soluble in chloroform, acetone, dimethyl acetamide, dimethyl formamide, dimethyl sulfoxide, tetrahydrofuran, benzene, toluene and xylene. It is insoluble in n-hexane and hydroxyl-group containing solvents, such as methanol and ethanol.

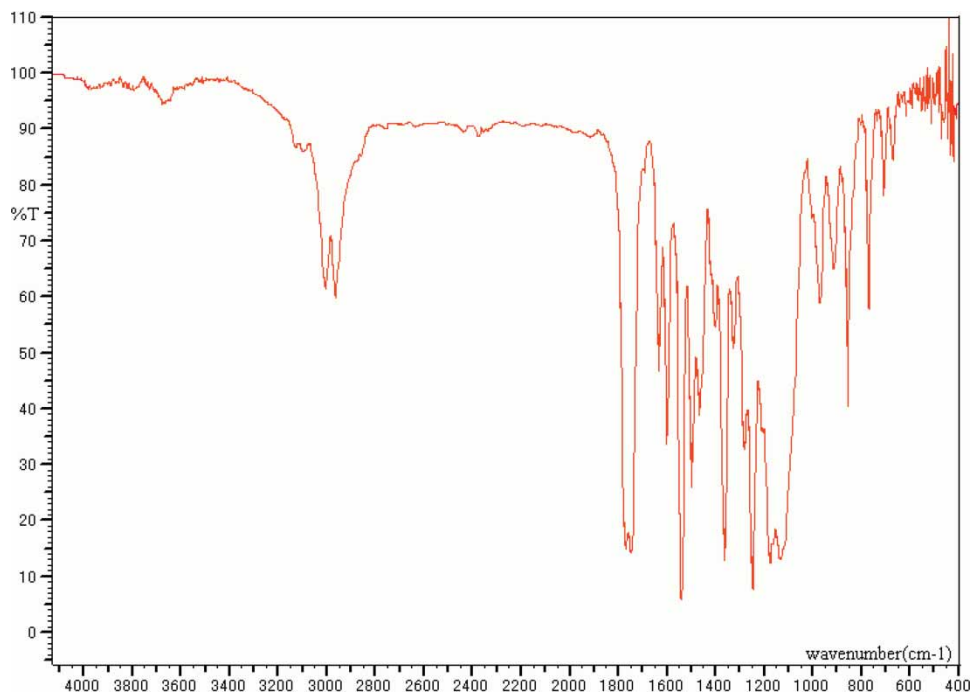
The FT-IR spectrum of the copolymer poly (NMPM-co-MMA) (0.7565:0.2435) is shown in Figure 1. It shows peaks at 3115 and  $3080\text{ cm}^{-1}$  corresponding to the C-H stretching of the aromatic system. The symmetrical and asymmetrical stretching due to the methyl and methylene groups are observed at 2996 and  $2950\text{ cm}^{-1}$ . The peaks at 1750 and  $1735\text{ cm}^{-1}$  are attributed to the ester carbonyl stretching of NMPM and MMA units. The aromatic  $\text{C=C}$  stretching is observed at 1620, 1585 and  $1483\text{ cm}^{-1}$ . The symmetrical bending vibrations of methyl groups is seen at  $1380\text{ cm}^{-1}$ . The intense band at  $1347\text{ cm}^{-1}$  is due to C-N

**Table 1.** Composition data for free radical polymerization of NMPM(1) with MMA(2) in EMK solution at  $70 \pm 1^\circ\text{C}$

Copolymer	$M_1^a$	Conversion (%)	Integral $I_{Ar}$	Peak heights $I_{Al}$	C	$m_1^b$
1	0.1497	8.52	7.102	69.402	0.1023	0.2728
2	0.3566	7.56	7.815	34.933	0.2237	0.5965
3	0.5010	9.12	4.816	16.975	0.2837	0.7565
4	0.6469	8.79	4.242	12.491	0.3396	0.9056
5	0.8055	7.86	3.648	10.109	0.3609	0.9624
6	0.9005	8.21	3.521	9.536	0.3692	0.9845

<sup>a</sup> $M_1$  is the mole fraction of NMPM in the feed.

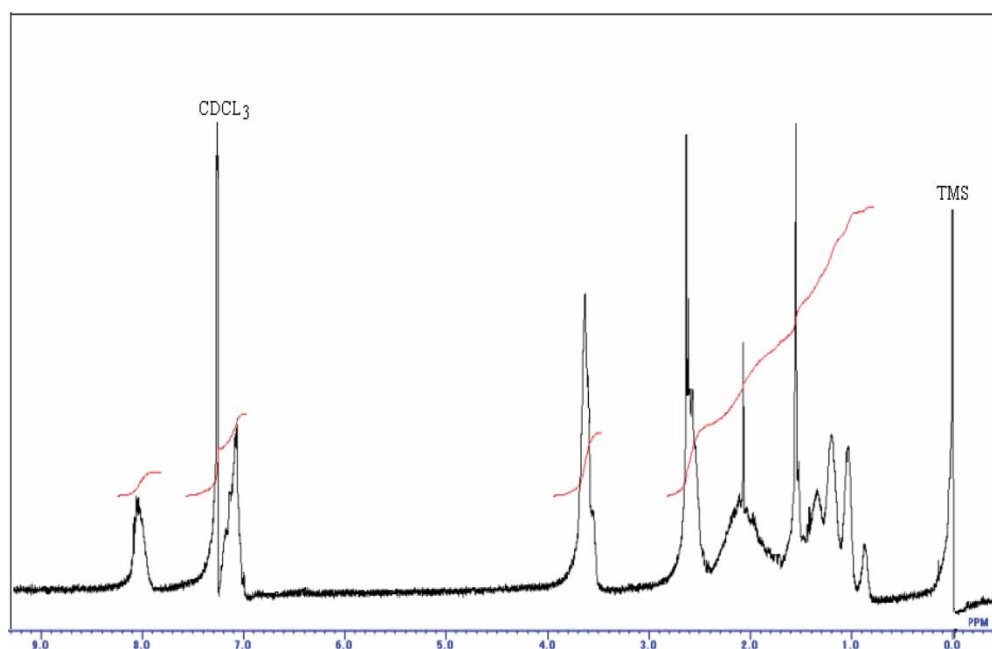
<sup>b</sup> $m_1$  is the mole fraction of NMPM in the copolymer.



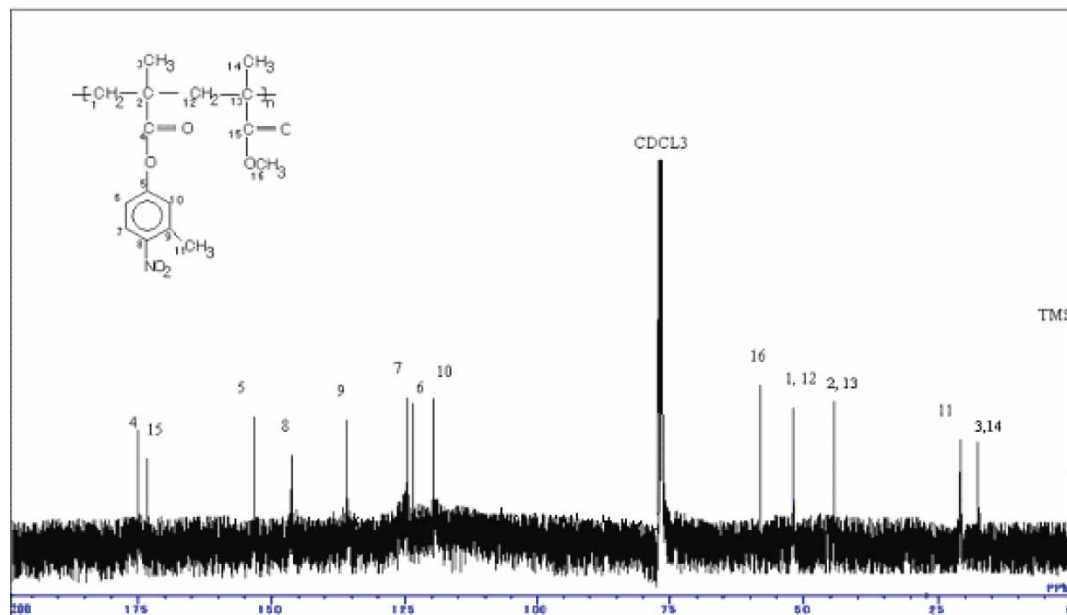
**Fig. 1.** FT-IR spectrum of poly(NMPM-co-MMA) system (0.7565:0.2435).

vibration, while the absorptions at  $1519$  and  $1347\text{ cm}^{-1}$  are due to the asymmetric and symmetric vibrations of N-O stretching. The C-O link in the ester of NMPM and MMA unit shows signals at  $1231$  and  $1347\text{ cm}^{-1}$ , respectively. The C-H out of plane bending vibrations of the aromatic nuclei is observed at  $839$  and  $753\text{ cm}^{-1}$ . The out-of-plane bending vibration of aromatic C=C is seen at  $689\text{ cm}^{-1}$ .

The  $^1\text{H-NMR}$  spectrum of the copolymer of poly (NMPM-co-MMA) (0.7565:0.2435) is shown in Figure 2. The chemical shifts assignments for the copolymers were based on the chemical shifts observed for the respective homopolymers. The aromatic protons show signals between  $8.03$  and  $7.07$  ppm. The resonance signal at  $3.63$  ppm is due to the methoxy protons of the MMA unit. The broad resonance signals



**Fig. 2.**  $^1\text{H-NMR}$  spectrum of poly(NMPM-co-MMA) system (0.7565:0.2435).



**Fig. 3.**  $^{13}\text{C}$ -NMR spectrum of poly(NMPM-co-MMA) system (0.7565:0.2435).

observed at 2.63–0.87 ppm are due to the existence of tacticity of backbone methylene groups and the  $\alpha$ -methyl groups.

The proton decoupled  $^{13}\text{C}$ -NMR spectrum of poly (NMPM-co-MMA) (0.7565:0.2435) is shown in Figure 3. It shows resonance signals at 175.11 ppm and 173.21 ppm are due to the ester carbonyl carbon of NMPM and MMA units. The aromatic carbon attached to the oxygen atom shows a signal at 153.32 ppm. The aromatic carbons attached to nitro and methyl group gave signals at 146.39 and 136.05 ppm, respectively. The other aromatic carbons gave signals at 126.42 ( $\text{C}_7$ ), 124.92 ( $\text{C}_6$ ) and 119.81 ppm ( $\text{C}_{10}$ ). The methoxy carbon signal of MMA unit was observed at 58.45 ppm. The signal due to the backbone methylene and tertiary carbon atoms are observed at 54.45 and 44.60 ppm. The methyl group attached to the aromatic nuclei shows a signal at 20.85 ppm. The  $\alpha$ -methyl group of both the monomer units shows resonance at 18.41 ppm.

### 3.3 Molecular Weights

The weight average molecular weights ( $M_w$ ) and number average molecular weights ( $M_n$ ) of poly (NMPM), poly(MMA) and six copolymer samples were determined by gel permeation chromatography. The values are presented in Table 2. The polydispersity indices of poly (NMPM) and poly (MMA) are 1.79 and 1.84, respectively. The theoretical value of  $M_w$  and  $M_n$  for polymers produced via radical recombination and disproportionation are 1.5 and 2.0, respectively (25). In the homopolymerization of MMA the growing chains undergo termination by disproportionation (26). The poly dispersity values of poly (MMA) and poly(NMPM) suggests that the tendency for chain termination by disproportionation predominates over coupling. The values of  $M_w/M_n$  in the copolymerization range between 1.81 and 1.85, also suggests that in the copolymerization the chain also terminates mainly by disproportionation which is predominate over coupling.

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

Polymer	$m_1^a$	$M_w \times 10^{-4}$	$M_n \times 10^{-4}$	$M_w/M_n$
Poly(NMPM)	1.0000	3.10	1.73	1.79
Poly(NMPM-MMA)	0.2728	4.10	2.18	1.88
	0.5965	3.82	2.06	1.85
	0.7565	3.98	2.19	1.82
	0.9056	3.85	2.13	1.81
	0.9624	3.86	2.13	1.81
	0.9845	3.92	2.14	1.83
Poly(MMA)	0.0000	3.35	2.01	1.84

<sup>a</sup> $m_1$  mole fraction of monomer NMPM in the copolymer.

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

Polymers	$m_1$	$T_g^a$ (°C)	IDT <sup>b</sup> (°C)	Temp (°C) 10%	Wt 30%	Loss 50%	70%	90%
Poly(MMA)	0.0000	105	244	270	284	300	334	384
	0.5965	103	252	283	296	315	360	415
Poly(NMPM-MMA)	0.7565	102	260	292	308	325	378	435
	0.9056	101	265	304	318	336	394	450
Poly(NMPM)	1.0000	101	272	309	326	343	408	466

<sup>a</sup> $T_g$ (°C) is the glass transition temperature.

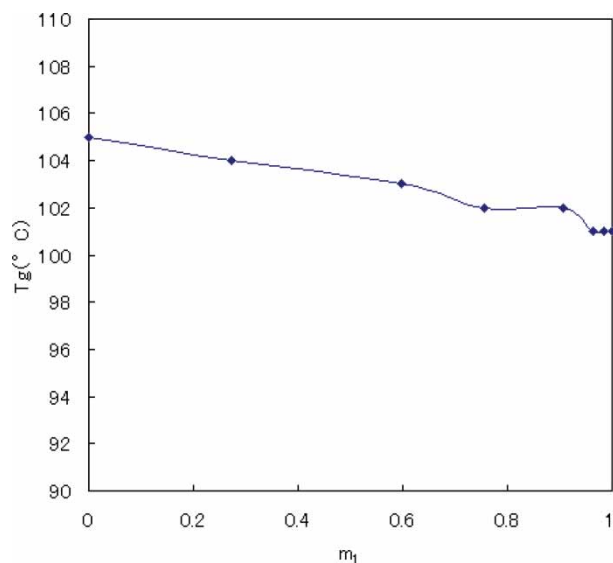
<sup>b</sup>IDT is the initial decomposition temperature.

### 3.4 Glass Transition Temperature

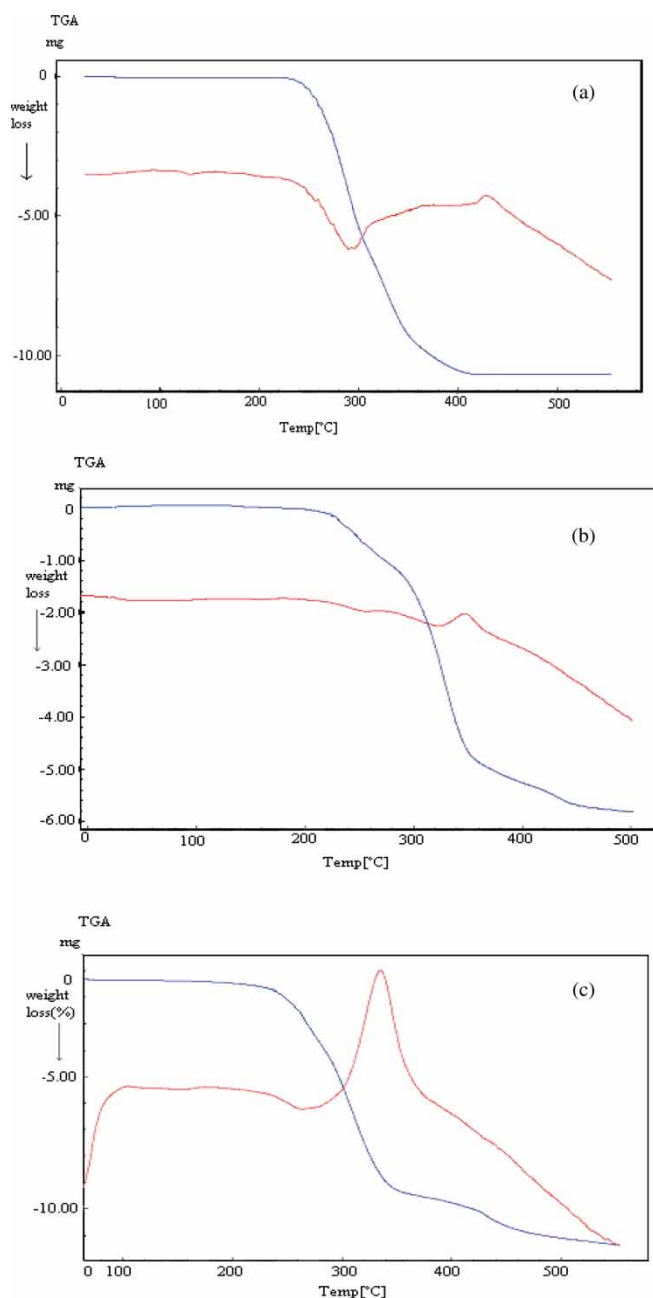
The glass transition temperatures ( $T_g$ ) of the copolymers were determined using differential scanning calorimetry and the data are given in Table 3. The variation of  $T_g$  of copolymers with mole fraction of the NMPM unit in the copolymer is shown in Figure 4. All the copolymers show a single  $T_g$ , indicating the absence of a mixture of homopolymers or the formation of a block copolymer. The  $T_g$  of poly (NMPM) is 101°C and that of poly MMA is 105°C. The results clearly indicate that the  $T_g$  values of the copolymers mainly depend on the composition of comonomers and the value decreases with an increase in the mole fraction of NMPM in the copolymer.

### 3.5 Thermogravimetric Analysis

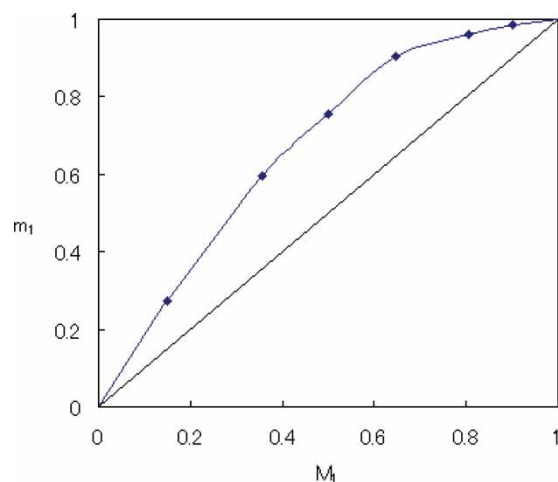
The TGA data for the homopolymers and copolymers of NMPM and MMA are given in Table 3. TGA curves for poly (NMPM), poly(MMA) and a sample of poly(NMPM-co-GMA) (0.7565:0.2435) are shown in Figure 5. The initial decomposition temperature of poly(NMPM), poly(NMPM-co-MMA), and poly(MMA) are 272, 232,



**Fig. 4.** Variation of  $T_g$  (°C) with composition of poly(NMPM-co-MMA) system.



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



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

and 244°C. The thermograms clearly indicate that poly (NMPM) and poly (NMPM-co-MMA) undergoes two-stage decomposition. This behavior can be explained by assuming the following mechanism for the decomposition. The first step of decomposition is due to the rupture of weak linkages and volatilization of low molecular weight species with loss of CO<sub>2</sub>. This process is followed by the loss of the benzene ring by the breakage of main chains and thereby volatilization of the cleaved products. Thus, TGA results clearly indicate that the thermal stability of the copolymer increases with rising NMPM content in the copolymer.

### 3.6 Copolymer Composition

The chemical structure of the copolymers may be represented as in Scheme 1. The average compositions of the copolymer samples were determined from the corresponding <sup>1</sup>H-NMR spectra. The assignment of the resonance peaks in the <sup>1</sup>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 NMPM in the copolymer was calculated by measuring the integrated peak heights of aromatic protons of NMPM to that of total aliphatic protons in the copolymer. Let  $m_1$  be the mole

fraction of NMPM and  $1-m_1$  be that of MMA. NMPM contains three aromatic protons and eight aliphatic protons, and MMA contains eight aliphatic protons. Then the following expression (Equation 1) is used to determine the composition of copolymers:

$$C = \frac{\text{Integral peak height of aromatic protons (I}_{Ar})}{\text{Integral peak height of total aliphatic protons (I}_{Ali})}$$

$$= \frac{3m_1}{8m_1 + 8(1 - m_1)} \quad (1)$$

This, on further simplification gives:

$$m_1 = \frac{8C}{3} \quad (2)$$

Based on (Equation 2), the mole fractions of NMPM in the copolymers were determined by measuring the integral peak heights of aromatic protons and aliphatic protons from the spectra of all copolymers. Table 1 gives the values of C and corresponding mole fraction of NMPM in the copolymers. The plot of mole fraction of NMPM ( $M_1$ ) in the feed vs. that in the copolymer ( $m_1$ ) is shown in Figure 6. The copolymer composition curve clearly indicates that the composition of NMPM in the copolymer is always higher than that in the feed.

### 3.7 Reactivity Ratios

From the monomer feed ratios and the copolymer composition, the reactivity ratio of NMPM and MMA were determined by the application of conventional linearization methods, such as Fineman-Ross (F-R) (27), Kelen-Tudos (K-T) (28), and the extended Kelen-Tudos (Ext.K-T) (29). The F-R and K-T parameters for the copolymers are presented in Table 4 and those for Ext K-T are shown in Table 5. The  $r_1$  and  $r_2$  values obtained from F-R plot (Figure7), K-T and Ext K-T plots (Figure 8) are presented as follows:

Methods	$r_1$	$r_2$	
Fineman-Ross	7.090	0.854	
Kelen-Tudos	7.693	0.852	
Ext.Kelen-Tudos	7.550	0.856	
Average	7.444	0.854	$r_1 \times r_2 = 6.357$

**Table 4.** F-R parameters for NMPM-MMA copolymer system

$F = M_1/M_2$	$f = m_1/m_2$	$H = F^2/f$	$G = F(f - 1)/f$	$\eta = G/(\alpha + H)^a$	$\xi = H/(\alpha + H)^a$
0.1761	0.3751	0.0827	- 0.2934	- 0.7168	0.2021
0.5542	1.4783	0.2078	0.1793	0.3355	0.3888
1.0040	3.1068	0.3245	0.6808	1.0456	0.4984
1.8321	9.5932	0.3499	1.6411	2.4259	0.5172
4.1414	25.5957	0.6701	3.9800	3.9932	0.6723
9.0503	63.5161	1.2896	8.9078	5.5116	0.7979

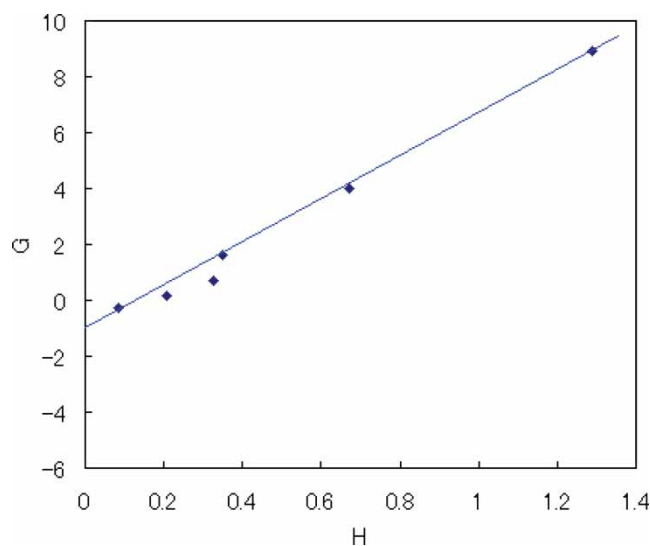
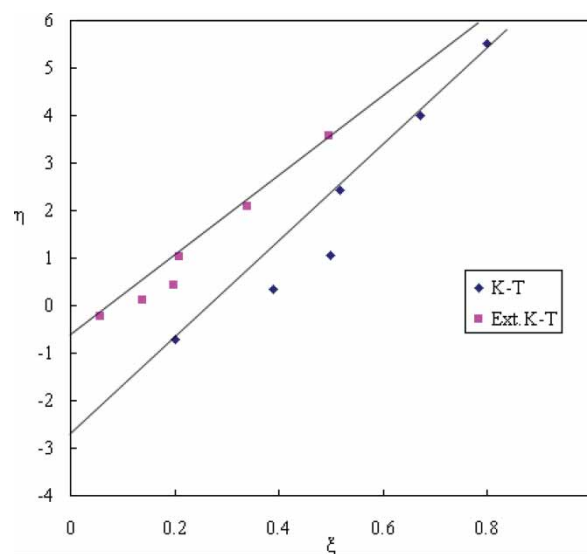
<sup>a</sup> $\alpha = (H_{\max} \times H_{\min}^{1/2}) = 0.3266$ .



**Table 5.** Extended K-T parameters for NMPM-MMA copolymer system

Parameters	Copolymer system					
	1	2	3	4	5	6
$\zeta_2$	0.06471	0.0394	0.0373	0.0200	0.0139	0.0122
$\zeta_1$	0.1378	0.1051	0.1154	0.1047	0.0859	0.0856
Z	2.2381	2.7625	3.2257	5.4743	6.4165	7.2902
F	0.1676	0.5351	0.9631	1.7524	3.9890	8.7125
H	0.0749	0.1937	0.2986	0.3201	0.6217	1.1951
G	-0.2792	0.1731	0.6531	1.5697	3.8332	8.5754
$\eta$	-0.2176	0.1235	0.4334	1.0270	2.0945	3.5679
$\xi$	0.0584	0.1381	0.1981	0.2094	0.3397	0.4972

$$\alpha = (F_{\max} \times F_{\min})^{1/2} = 1.2084.$$

**Fig. 7.** F-R plot for poly(NMPM-co-MMA) system.**Fig. 8.** K-T and Ext. K-T plot for poly(NMPM-co-MMA) system.

Since the value of  $r_1$  is greater than 1 and the value of  $r_2$  is lesser than 1 suggests the presence of a higher amount of NMPM units in the copolymer than in the feed, since NMPM is more reactive compared to MMA. However, the product of  $r_1$  and  $r_2$  is greater than 1 (i.e., 6.357), which clearly indicates that the system forms a random copolymer with longer sequences of NMPM units in the copolymer chain.

#### 4 Conclusions

The novel methacrylic monomer, NMPM was synthesized and characterized. Copolymers of NMPM with MMA having different composition were synthesized by free radical solution polymerization techniques and characterized by FT-IR,  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  spectroscopic techniques. The homopolymer and 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 an increase of NMPM units in the copolymer. The  $T_g$  of the copolymer increases with MMA content. The polydispersity index values of poly(NMPM), poly(NMPM-co-MMA) and poly(MMA) suggest 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 three known linearization methods, i.e., the F-R, K-T, and Ext K-T methods. The  $r_1$  values from these methods are all greater than 1, and  $r_2$  values are less than 1, indicating that NMPM is more reactive than MMA. The product value of  $r_1$  and  $r_2$  is greater than 1, which clearly indicates that the system forms a random copolymer with longer sequence distribution of NMPM units in the copolymer chain.

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