

# Copolymers of 4-Nitrophenyl Methacrylate with Styrene: Synthesis, Characterization, and Reactivity Ratios

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**ABSTRACT:** Free-radical copolymerization of 4-nitrophenyl methacrylate (NPMA) with styrene (STY) was carried out at 65°C in 2-butanone by using benzoyl peroxide (BPO) as initiator. NPMA was characterized by spectral and microelemental analysis. Homo- and copolymers were characterized by IR, <sup>1</sup>H-, and <sup>13</sup>C-NMR studies and their copolymer compositions were evaluated by <sup>1</sup>H-NMR spectroscopic technique. The copolymer reactivity ratios were calculated using Fineman–Ross, Kelen–Tüdös, and extended Kelen–Tüdös methods. The *Q*,*e* values for NPMA were determined by Alfrey–Price *Q*,*e* rule. Thermal properties of the homo- and copolymers were studied by thermogravimetric analysis and differential scanning calorimetry methods. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 1186–1193, 1999

**Key words:** 4-nitrophenyl methacrylate (NPMA); styrene; reactivity ratios; thermal properties

## INTRODUCTION

The synthesis and studies on acrylate polymers has attracted the attention of various groups in recent times.<sup>1,2</sup> The extensive applications of both homo- and copolymers of this class of macromolecules have been reported.<sup>3–5</sup> The incorporation of 9-(hydroxy methyl)-10-[naphthyl(methyl)]anthracene into poly(methyl methacrylate) (PMMA) results in a glass polymer film that can be used as an optoelectronic material.<sup>6</sup> The distribution of homopolymers in a symmetric block copolymer like poly(styrene-*b*-methyl methacrylate) was determined from neutron reflectivity studies.<sup>7</sup> The intramolecular structure of styrene–methacrylate (STY–MA) copolymers was evaluated by <sup>1</sup>H- and <sup>13</sup>C-NMR studies and also by 2D–NMR COLOC experiments.<sup>8</sup> The use of phe-

nyl (meth)acrylates as weather-resistant, high-glass top coats for automobile finishes has been reported.<sup>9</sup> Poly(phenyl methacrylates) are harder polymers of higher tensile strength and lower elongation than their acrylate counterparts because substitution of the methyl group for the  $\alpha$ -H on the main chain restricts the freedom of rotation and motion of the polymer backbone. They also find application in pressure-sensitive photoimaging materials<sup>10</sup> and as electrophotographic photoreceptors for offset printing plates.<sup>11</sup>

## EXPERIMENTAL

### Materials

Styrene (STY) was washed with 5% NaOH, then with water, and distilled under reduced pressure before use. Benzoyl peroxide (BPO) was recrystallized from chloroform and methanol mixtures and

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**Table I** Composition of Copolymers

No.	Mole Fraction of NPMA ( $m_1$ )	Mole Fraction of STY ( $m_2$ )
1	0.131	0.869
2	0.250	0.750
3	0.407	0.593
4	0.555	0.445
5	0.711	0.289
6	0.842	0.158
7	0.911	0.089

dried in a vacuum. 2-Butanone, methanol, and chloroform were distilled before use. Methacryloyl chloride was prepared by the reaction of methacrylic acid and benzoyl chloride.<sup>12</sup>

### Synthesis of NPMA

4-Nitrophenyl methacrylate (NPMA) was synthesized by the following procedure. 4-Hydroxy nitrophenol (20 g, 0.15 mol) and 2-butanone (150 mL) were taken in a three-necked round-bottomed flask and freshly distilled methacryloyl chloride (17 mL, 0.16 mol) was slowly added from a 100-mL addition funnel at 0°C in the presence of triethylamine (17.5 mL, 0.15 mol). The reaction mixture was stirred at 0°C for 1 h and then at room temperature for 3 h. The reaction mixture was filtered and the product washed with water, 5% NaOH, and again with water, and the light-yellow-colored product was dried over anhydrous sodium sulphate (Yield = 64%), m.p. = 80–82°C.

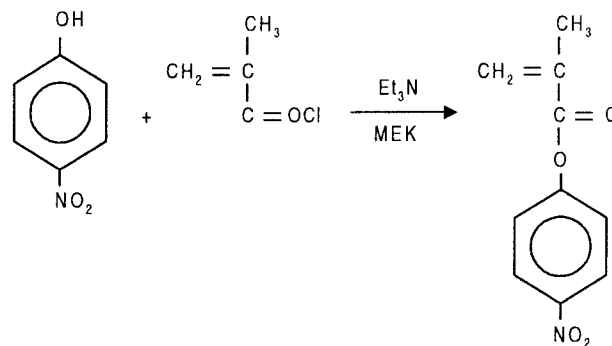
Elemental analysis: Calcd, %C = 57.97; %H = 4.35; %N = 6.76. Experimental, %C = 57.91; %H = 4.39; %N = 6.82.

### Synthesis of Poly(NPMA)

The monomer NPMA (4.14 g/10 mL; 2M), and free-radical initiator BPO (1 wt % of the monomers) in 2-butanone were taken in polymerization tubes, and purified N<sub>2</sub> gas was passed for 10 min and then thermostated at 65°C. The addition of excess methanol to the reaction mixture resulted in the precipitation of the polymer that was redissolved in chloroform and reprecipitated in methanol. This step was repeated twice and the product was dried at ambient temperature (Yield = 52%).

### Synthesis of Copolymers

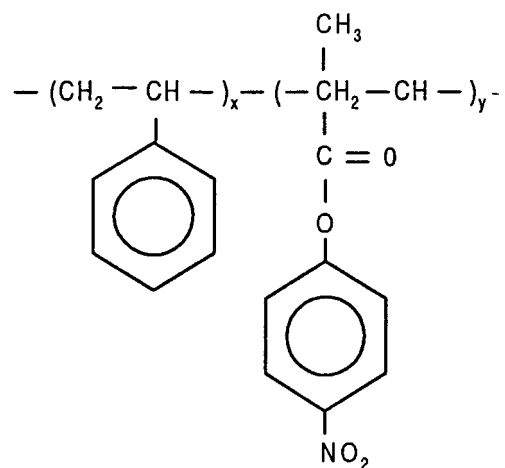
Seven copolymers with different mole fractions of the monomers NPMA (1) and STY (2), 1% of BPO,

**Scheme 1**

and 2-butanone were mixed in a reaction tube that was tightly closed and N<sub>2</sub> gas was bubbled through the reaction mixture for 20 min. After 3 h, the contents were precipitated in excess methanol, filtered, and the samples were dried at 40°C (Table I).

### Physical Measurements

The IR spectra of the polymers were recorded on a Hitachi 270-50 spectrophotometer as KBr pellets. The <sup>1</sup>H-NMR spectra of the polymers were run on a Jeol 400 MHz spectrometer at room temperature using CDCl<sub>3</sub> as solvent and TMS (tetramethyl silane) as internal reference. Thermogravimetric analysis (TA) was performed on a Mettler 3000 TA thermal analyzer in which samples < 10 mg were used and the heating rate was maintained at 20°C/min in the atmosphere of air. The molecular weights ( $\bar{M}_w$  and  $\bar{M}_n$ ) were calculated using a gel permeation chromatograph (Waters 501) equipped with a RI detector and cali-

**Figure 1**

**Table II** Copolymerization of NPMA-STY System

Sample No.	Feed Composition		Conversion (%)	Intensity of Aromatic Protons ( $I_A$ )	Intensity of Total Protons ( $I_a$ )	$C^* = I_A/I_a$	Copolymer Composition in Mole Fraction			$\bar{M}_w$	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$
	$M_1$	$M_2$					$m_1$	$m_2$				
1	0.10	0.90	6.18	0.2	3.1	0.0645	0.131	0.869	—	—	—	
2	0.20	0.80	8.72	0.4	3.3	0.1212	0.250	0.750	4.36	2.95	1.48	
3	0.35	0.65	5.67	0.6	3.1	0.1936	0.407	0.593	—	—	—	
4	0.50	0.50	7.41	0.7	2.7	0.2593	0.555	0.445	4.14	2.62	1.56	
5	0.65	0.35	8.14	0.8	2.45	0.3265	0.711	0.289	—	—	—	
6	0.80	0.20	9.36	0.8	2.1	0.3870	0.842	0.158	3.98	2.46	1.62	
7	0.90	0.10	8.49	0.9	2.2	0.4091	0.911	0.089	—	—	—	

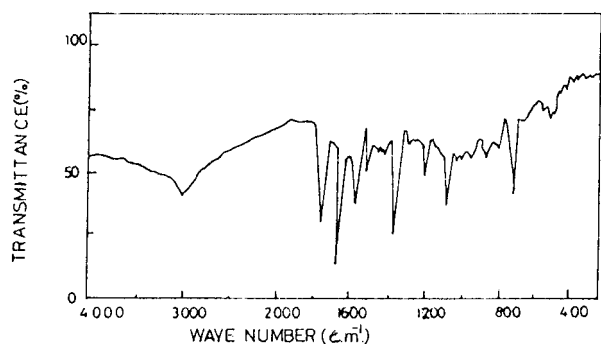
Solvent, 2-butanone; temperature, 65°C. Initiator: BPO (1 wt % of the monomers).  $M_1$ , mole ratio of NPMA in the feed;  $M_2$ , mole ratio of STY in the feed;  $m_1$ , mole ratio of NPMA in the copolymer;  $m_2$ , mole ratio of STY in the copolymer;  $\bar{M}_w$ , weight-average molecular weight;  $\bar{M}_n$ , number-average molecular weight.

brated with polystyrene standard. Tetrahydrofuran (THF) was used as an eluent with a flow rate of 10 mL/min.

## RESULTS AND DISCUSSION

The NPMA monomer was synthesized by transesterification of 4-nitrophenol with methacryloyl chloride, which is a modified Schotten-Bauman method (See Scheme 1).

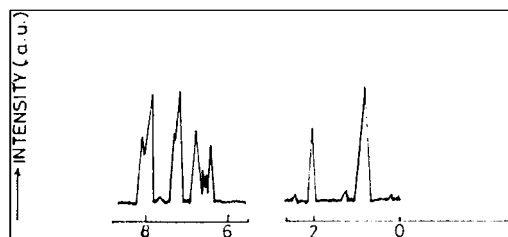
The NPMA monomer was characterized by IR,  $^1\text{H-NMR}$ , and elemental analysis. The monomer was homopolymerized in 2-butanone at 65°C using BPO as the free-radical initiator. The solubility of poly(NPMA) was found to be appreciable in solvents like  $\text{CHCl}_3$ , dimethylformamide (DMF), THF, methyl ethyl ketone (MEK), etc.



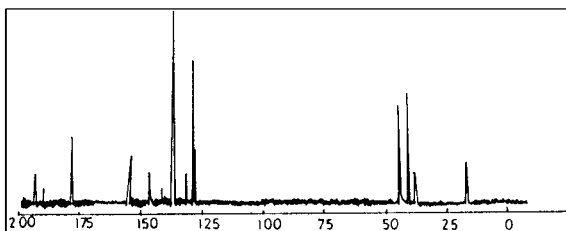
**Figure 2** Infrared spectrum of poly(NPMA-co-STY);  $m_1 : m_2 : 0.56 : 0.44$ .

The IR spectrum of poly(NPMA) shows a broad band at  $3100\text{ cm}^{-1}$  due to the aromatic —OH stretching vibrations. The strong absorption peak at  $1750$  and  $1670\text{ cm}^{-1}$  are due to the ester carbonyl ( $\nu_{\text{CO}}$ ) stretching and keto carbonyl stretching vibrations.<sup>13,14</sup> Aromatic stretching vibrations are observed at  $1610\text{ cm}^{-1}$ . The strong absorption at  $1360\text{ cm}^{-1}$  may be attributed to the nitro group present in the system. The peak at  $785\text{ cm}^{-1}$  is due to the C—H out-of-plane bending. The medium intense band at  $850\text{ cm}^{-1}$  is due to C—N stretch, whereas, at  $1200\text{ cm}^{-1}$ , the medium intense band is due to the ester group of NPMA.

The  $^1\text{H-NMR}$  spectrum of poly(NPMA) shows doublet signals at 8.2 and 7.8 ppm, which are due to two types of aromatic protons. The peaks that appear at 1.58 and 0.95 ppm are attributed to the methylene and  $\alpha$ -methyl protons.<sup>15</sup> The vinylic protons in the monomer appear at 6.52 ppm, and on polymerization this signal is seen at 1.52 ppm.



**Figure 3**  $^1\text{H-NMR}$  spectrum of poly(NPMA-co-STY);  $m_1 : m_2 : 0.56 : 0.44$ .



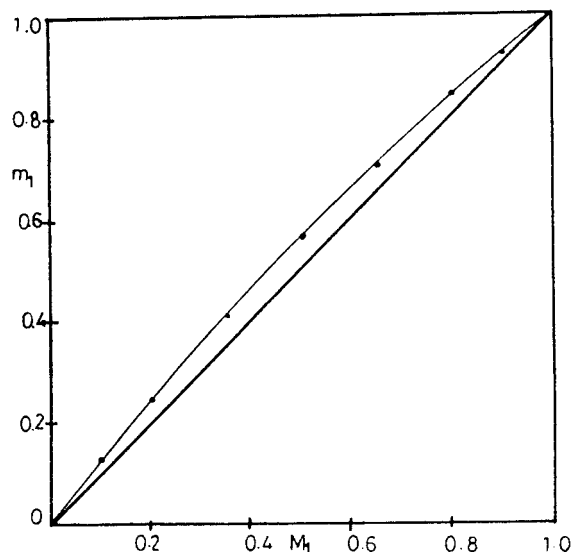
**Figure 4** Proton-decoupled  $^{13}\text{C}$ -NMR spectrum of poly(NPMA-co-STY);  $m_1 : m_2 : 0.56 : 0.44$ .

### Copolymerization

The copolymerization behavior of NPMA and STY in 2-butanone was studied at various compositions wherein the molar fractions of NPMA range from 0.1 to 0.9 in the monomer feed. The reaction time was selected in such a way that the conversion was <10 wt % of the monomer to satisfy the differential copolymerization equation (Table II).

The IR spectrum of poly(NPMA-co-STY) shows absorption bands typical of their monomeric units, and the intensity depends on their composition (Fig. 2). The  $^1\text{H}$ -NMR spectrum of poly(NPMA-co-STY) shows additional signals in the aromatic region at 7.3–7.8 ppm, which are not present in the poly(NPMA), and they are attributed to the aromatic protons of STY, thus confirming the formation of copolymer. A group of multiplets, which are seen at 1.40–2.30, 1.40, and 0.89 ppm, are due to the backbone protons  $-\text{CH}_2-$ ,  $-\text{CH}-$ , and  $\alpha-\text{CH}_3$  respectively (Fig. 3).

The proton-decoupled  $^{13}\text{C}$ -NMR spectrum of the poly(NPMA-co-STY) is shown in Figure 4. The peak at 152.2 ppm is due to the  $^{13}\text{C}$  of the phenyl ring of the NPMA unit. The peaks at 135.4, 129.4, and 120.9 ppm are due to the  $^{4}\text{C}$ ,  $^{3}\text{C}/^{5}\text{C}$ , and  $^{2}\text{C}/^{6}\text{C}$  atoms of the phenyl ring. The ester carbonyl appears at 176.4 ppm and the STY carbon atoms appear at 145.42–146.5 and 129.60 ppm. The



**Figure 5** Composition curves of NPMA-STY copolymer system.

backbone carbons  $-\text{CH}_2-$ ,  $-\text{CH}-$ ,  $-\text{C}-$  show signals at 50.42, 62.1, 38.4 ppm, respectively. The above assignments are in keeping with the earlier observations made for analogous systems.<sup>16,17</sup>

### Copolymer Composition

The composition of monomer mixture in the copolymer was determined by the  $^1\text{H}$ -NMR spectroscopy. The  $^1\text{H}$ -NMR spectrum of the NPMA-STY copolymer (Fig. 3) indicates a monomer ratio of ( $m_1 : m_2$ ; 0.56 : 0.44). The aromatic protons of NPMA show doublet signals at 8.2 and 7.8 ppm, whereas a group of multiplets from 6.9–7.6 ppm are due to the aromatic protons of the STY unit. The mole fraction ( $m_1$ ) of NPMA in the copolymer was determined by the following equation:

$$C = \frac{4m_1}{9m_1 + 8(1 - m_1)} \quad (1)$$

**Table III** *F-R* and *K-T* Parameters of NPMA-STY Copolymer System

Sample No.	$F = M_1/M_2$	$f = m_1/m_2$	$G = F(f - 1)/f$	$H = F^2/f$	$x = G/\alpha + H$	$h = H/\alpha + H$
1	0.1111	0.1508	-0.6259	0.0819	-0.7057	0.0923
2	0.2500	0.3333	-0.5001	0.1875	-0.5039	0.1889
3	0.5385	0.6853	0.2473	0.4231	-0.2014	0.3445
4	1.0000	1.2472	0.1982	0.8018	0.0898	0.4990
5	1.8571	2.4602	1.1023	1.4019	0.4995	0.6352
6	4.0000	5.3291	3.2494	3.0023	0.8535	0.7886
7	9.0000	10.2360	8.1208	7.9133	0.9315	0.9077

$$\alpha = \sqrt{0.0819 \times 7.9133} = 0.8050.$$

**Table IV** Extended *K-T* Parameters for NPMA-STY Copolymer System

Parameter	Sample No.						
	1	2	3	4	5	6	7
$\zeta_2$	0.0504	0.0785	0.0497	0.0636	0.0648	0.0723	0.0751
$\zeta_1$	0.0683	0.1046	0.0632	0.0793	0.0859	0.0963	0.0854
$Z$	1.3698	1.3522	1.2816	1.2576	1.3397	1.3496	1.1436
$F$	0.1101	0.2465	0.5347	0.9917	1.8364	3.9486	8.9504
$H$	0.0804	0.1823	0.4172	0.7886	1.3707	2.9257	7.8262
$G$	-0.6200	-0.4930	-0.2456	0.1966	1.0899	3.2076	8.0760
$\alpha$	0.792967	—	—	—	—	—	—
$\xi$	0.0920	0.1869	0.3448	0.4986	0.6335	0.7878	0.9080
$\eta$	-0.7099	-0.5056	-0.2029	0.1243	0.5037	0.8626	0.9370
$\mu$	0.5	—	—	—	—	—	—

and, on simplifying,

$$m_1 = \frac{8C}{4-C} \quad (2)$$

where  $C$  is the ratio of the integral intensities of aromatic protons to that of the total protons. A plot of mole fraction of NPMA monomer in feed versus copolymer is shown in Figure 5.

### Reactivity Ratios

The reactivity ratio  $r_1$  and  $r_2$  of NPMA and STY, respectively, are computed by graphical methods (viz. Fineman-Ross, Kelen-Tudos, and extended Kelen-Tudos methods<sup>18-20</sup>), and the corresponding parameters are presented in Tables III and IV.

In the Fineman-Ross method, the following equation is employed:

$$G = H r_1 - r_2 \quad (3)$$

where  $G$ ,  $H$  are the functions involving the composition of initial monomer and copolymer composition ( $f = m_1/m_2$  and  $F = M_1/M_2$ ).

$$G = (F - 1)/f, \quad H = F^2/f$$

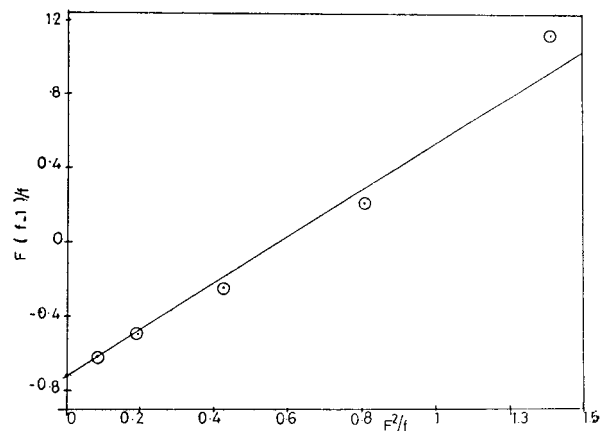
A plot of  $G$  as ordinate and  $H$  as abscissa results in a straight line the slope of which is  $r_1$  and intercept is  $-r_2$  (Fig. 6).

Kelen-Tudos derived a simple graphically evaluable method in which the following equation (eq. 4) is employed:

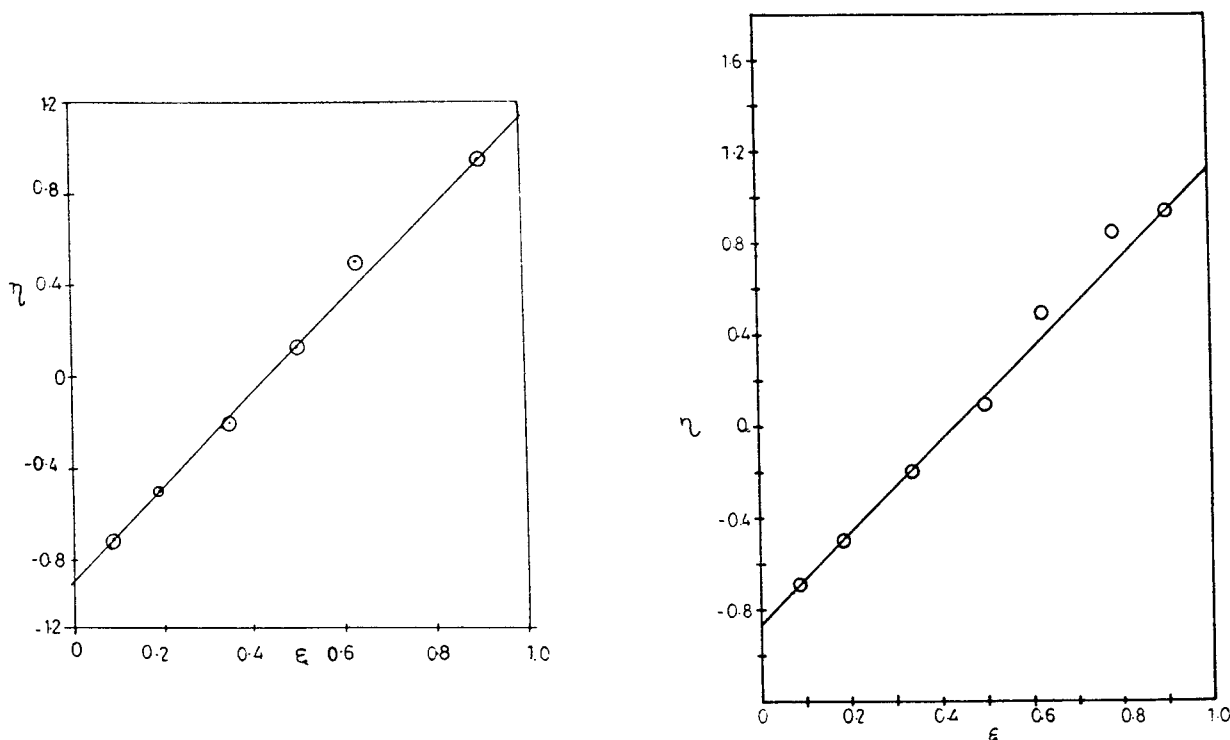
$$\eta = (r_1 + r_2/\alpha)\xi - r_2/\alpha$$

$\eta$ ,  $\xi$ , and  $\alpha$  were determined from  $G$  and  $H$ , which are defined by the mole fraction of monomer concentration in feed and copolymer. A plot of  $\eta$  against  $\xi$  gives a straight line (Fig. 7). The intercept at  $\xi = 0$  and  $\xi = 1$  gives  $-r_2/\alpha$  and  $r_1$ , respectively. The reactivity ratio values with 95% confidence intervals are obtained.

A comparison of reactivity ratios by three methods along with the product of reactivity ratios and the nature of the copolymer sequence are shown in Table V. The copolymer system is within the range  $0 < r_1 r_2 < 1$ . The product of reactivity ratios ( $r_1 r_2$ ) is close to unity and, hence, there is a tendency for the  $M_1$  and  $M_2$  radical to form random distribution in the polymeric chain. From the copolymer composition curve it is found that NPMA is more reactive than STY.



**Figure 6** F-R plot for NPMA-STY copolymer system.



**Figure 7** (a) K-T plot of  $\eta$  versus  $\xi$  for NPMA-STY copolymer system. (b) Extended K-T plot for the NPMA-co-STY copolymer system.

The  $Q$  and  $e$  values for NPMA were determined by the Alfrey-Price method by employing the reactivity ratios determined experimentally by the extended Kelen-Tudos method. The values of  $e_2 = -0.80$  and  $Q_2 = 1.00$  from the literature are used for STY and  $Q_1$  and  $e_1$  are evaluated for NPMA by employing the following equation and are found to be 0.63 and 1.16, respectively.<sup>21</sup>

$$e_1 = e_2 + (|\ln r_1 r_2|)^{1/2}$$

$$Q_1 = Q_2 / r_2 \exp[e_2(e_1 - e_2)]$$

### Molecular Weights

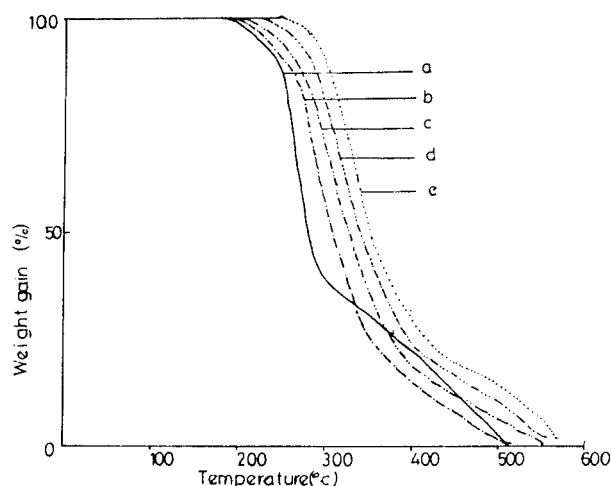
The molecular weight determination of (meth)acrylate polymers have been made by a

variety of techniques, including small-angle X-ray scattering and light-scattering methods.<sup>22,23</sup> The number-average and weight-average molecular weight for poly(NPMA) and poly(NPMA-co-STY) for three different copolymer compositions were determined by gel permeation chromatography (Table II). Liu et al.<sup>24</sup> indicate that emulsion copolymerization of STY with poly(ethyleneoxide) and undecyl- $\alpha$ -methacrylate results in the formation of stable latex, the molecular weight (range  $10^5$ ) of which was determined by GPC. The polydispersity index for these samples are close to 1.50. The theoretical value of  $\bar{M}_w/\bar{M}_n$  for polymers produced in radical disproportionation and radical combination are 2.0 and 1.5, respectively. The polydispersity index of poly(NPMA) is 1.92,

**Table V Comparison of Reactivity Ratios by Various Methods for Poly(NPMA-co-STY)**

Methods	$r_1$	$r_2$	$1/r_1$	$1/r_2$	$r_1 r_2$
F-R	1.17	0.71	0.86	1.41	0.831
K-T	1.10	0.72	0.91	1.39	0.792
Ext(K-T)	1.12	0.70	0.89	1.43	0.784

F-R, Fineman-Ross; K-T, Kelen-Tudos; Ext(K-T), extended Kelen-Tudos;  $r_1$ , reactivity ratio of NPMA;  $r_2$ , reactivity ratio of STY.



**Figure 8** Thermogravimetric analysis (TGA) curves in the air of poly(NPMA-co-STY). Mole fraction of NPMA in copolymer, (a) 0.25, (b) 0.41, (c) 0.56, (d) 0.71, (e) 1.0.

whereas, in the case of the copolymer, it decreases as the concentration of the NPMA unit decreases.

### Thermal Analysis

The glass transition temperature ( $T_g$ ) of poly(phenyl methacrylate) has been reported<sup>25</sup> to be 110°C, which is less than that of the poly(NPMA), indicating the enhanced and thermal stability due to the presence of the nitro group in the polymer, and the  $T_g$  value for poly(STY) is 100°C.<sup>26</sup> The  $T_g$  of the poly(NPMA) is found to be 114°C<sup>27</sup> and of poly(STY) is 100°C, and the copolymer ( $m_1 = 0.56$ ;  $m_2 = 0.44$ ) has an intermediate  $T_g$  value of 107.4°C.

The thermograms of the copolymers poly(NPMA-co-STY) recorded in air (Fig. 8, Table VI) show

that the decomposition of the polymers essentially occur in two stages. However, in the case of poly(STY), the decomposition occurs in a single stage. The decomposition temperature gradually increases with decreasing concentration of NPMA. The decomposition temperature for the first stage commences at 175°C, when the concentration of STY is zero, and it reaches 250°C when NPMA : STY is in the ratio of 0.711 : 0.289. The corresponding temperature for these systems in the second stage are 350 and 425°C, respectively. The maximum temperature, at which the weight loss is 10%, is observed in the case of the fifth system in which  $m_1$  and  $m_2$  are 0.71 and 0.289 and is minimum in the case of the first system in which the  $m_1$ ,  $m_2$  values are 1.0, 0.0, respectively. A similar trend has been observed in these systems when the percentage weight loss are 25, 50, 75, and 90. However, there is a change in this trend in the use of a second system ( $m_1 : m_2$  0.25 : 0.75), in which the temperature slightly decreases when compared to that of the first system. The maximum temperature (535°C) was, however, observed in the case of fifth system when the loss is 90 wt %.

### CONCLUSION

The copolymers obtained from NPMA and STY were characterized by spectral studies. The monomer composition in the copolymers were evaluated by <sup>1</sup>H-NMR spectroscopy. The reactivity ratios of NPMA ( $r_1$ ) and STY ( $r_2$ ), computed by Fineman-Ross, Kelen-Tudos, and extended Kelen-Tudos methods, lie in the range 1.10–1.17 and 0.70–0.72, respectively. The  $Q$  and  $e$  values for NPMA evaluated by Alfrey-Price method are 0.63 and 1.16, respectively. The product of reac-

**Table VI** Thermogravimetric Analysis Data of Poly(NPMA-co-STY) System

Sample No.	Copolymer Composition		Decomposition Temp. (°C) (range)		Temperature (°C) of Weight Loss (%) of Copolymers				
	$m_1$	$m_2$	Stage I	Stage II	10	25	50	75	90
1	1.000	0.000	175–350	350–555	245	285	312	355	440
2	0.250	0.750	190–340	340–520	250	280	307	352	432
3	0.407	0.593	200–318	380–550	263	296	313	376	470
4	0.555	0.445	225–400	400–555	278	307	342	395	507
5	0.711	0.289	250–425	425–565	300	322	351	421	535

$m_1$ , mole fraction of NPMA in the copolymer;  $m_2$ , mole fraction of STY in the copolymer.

tivity ratios is close to unity, and hence, the monomers are arranged in a random fashion in the polymeric chain. The polydispersity index of copolymers is about 1.50. Thermal studies show that the decomposition of the polymers occur in two stages in the temperature range 175–350 and 350–555°C, respectively.

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