

Synthesis, Characterization, and Reactivity Ratios of Copolymers Derived from 4-Nitrophenyl Acrylate and *n*-Butyl Methacrylate

S. Thamizharasi,¹ P. Gnanasundaram,¹ and S. Balasubramanian²

¹Department of Chemical Engineering, Anna University, Madras - 600 025, India

²Department of Inorganic Chemistry, A.C. College Campus, University of Madras, Madras - 600 025, India

Received 4 January 2002; accepted 25 June 2002

ABSTRACT: Free-radical copolymerization of 4-nitrophenyl acrylate (NPA) with *n*-butyl methacrylate (BMA) was carried out using benzoyl peroxide as an initiator. Seven different mole ratios of NPA and BMA were chosen for this study. The copolymers were characterized by IR, ¹H-NMR, and ¹³C-NMR spectral studies. The molecular weights of the copolymers were determined by gel permeation chromatography and the weight-average (M_w) and the number-average (M_n) molecular weights of these systems lie in the range of $4.3\text{--}5.3 \times 10^4$ and $2.6\text{--}3.0 \times 10^4$, respectively. The reactivity ratios of the monomers in the copolymer were

evaluated by Fineman–Ross, Kelen–Tudos, and extended Kelen–Tudos methods. The product of r_1, r_2 lies in the range of 0.734–0.800, which suggests a random arrangement of monomers in the copolymer chain. Thermal decomposition of the polymers occurred in two stages in the temperature range of 165–505°C and the glass transition temperature (T_g) of one of the systems was 97.2°C. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 1817–1824, 2003

Key words: acrylates; copolymer; synthesis; reactivity ratio

INTRODUCTION

The copolymers obtained from nitrophenyl acrylates (NPAs) have several interesting applications and a number of studies have been made with these systems in recent years. Self-sensitizable photocrosslinking maleimide-type polymers were synthesized using NPA as a sensitizer monomer.¹ The effect of the polymer backbone structure on the transformation of a crosslinked copoly(styrene-*p*-NPA) with substituted hydrazine indicated a high degree of additional crosslinking.² A pH and sodium chloride-triggered response of anionic microgels was studied using a methacrylic acid methylene bisacrylamide–NPA copolymer hydrogel matrix.³ The graft copolymers obtained from NPA and poly(*N*-vinylcaprolactam) can be chemically attached to fine silica to form bioseparation materials.⁴ The synthesis and application of NPA–methyl methacrylate (MMA)–ethylene glycol diglycidyl ether copolymers as functional material were described.⁵ The covalent immobilization of serum albumin on highly active chemisorbents derived from NPA copolymers was also reported.⁶ Nonlinear optical properties of substituted acrylates and methac-

rylates and the second-order nonlinear coefficient of polymerized films were investigated.⁷

Information-storage devices like laser videodiscs (LVDs) are essentially made from polymeric materials.⁸ Some of the acrylates, like ethylene glycol acrylate, were investigated for LVD applications.^{9,10} Poly(2-hydroxy-ethyl methacrylate) forms hydrogel which can be used as a contact lens because of its biocompatibility.¹¹

In our earlier study, the metal-containing acrylates and the copolymers derived from NPAs and methacrylates were investigated.¹² The synthesis and characterization of copolymers obtained from NPA and *n*-butyl methacrylate (BMA) and their reactivity ratios were evaluated for seven different copolymer compositions by Fineman–Ross, Kelen–Tudos, and extended Kelen–Tudos methods. The thermal properties investigated by thermogravimetry (TG) and differential scanning calorimetry (DSC) for different polymer compositions are discussed.

EXPERIMENTAL

Materials

BMA (Aldrich, USA) was repeatedly washed with 5% NaOH and water and finally distilled under reduced pressure. The free-radical initiator benzoyl peroxide (BPO) (Fluka, Switzerland) was purified by recrystallization from a mixture of chloroform and methanol

Correspondence to: S. Balasubramanian.

TABLE I
Copolymerization Data of NPA-co-BMA System

Sample no.	Feed composition		Conversion (%)	Intensity of aromatic protons (I_a)	$\frac{I_a}{I_m}$ Intensity of methyleneoxy protons (I_m)	$C = \frac{I_a}{I_m}$	Copolymer composition (mole fraction)		Molecular weight data ($\times 10^4$)		
	M_1	M_2					m_1	m_2	\bar{M}_n	\bar{M}_w	\bar{M}_w/\bar{M}_n
1	0.10	0.90	6.94	1.30	6.80	0.1912	0.087	0.913			
2	0.20	0.80	8.63	2.10	5.20	0.4039	0.171	0.829	3.02	5.32	1.76
3	0.35	0.65	9.37	1.75	2.00	0.8750	0.304	0.696			
4	0.50	0.50	9.86	3.30	2.10	1.5714	0.440	0.560	2.78	4.67	1.68
5	0.65	0.35	5.49	5.00	1.75	2.8571	0.588	0.412	2.69	4.36	1.62
6	0.80	0.20	7.19	6.50	1.10	5.9091	0.747	0.253			
7	0.90	0.10	3.64	6.30	1.00	6.3000	0.863	0.137			

Solvent, 2-butanone; temperature, 65°C; initiator, BPO (1.15% wt of the monomer).

and it was finally dried under *vacuo*. The solvents 2-butanone, methanol, and chloroform were purified by simple distillation.¹³ The synthesis of acryloyl chloride was achieved by the reaction of acrylic acid with benzoyl chloride.¹⁴

Synthesis of NPA

4-Nitrophenol (19 g, 0.15 mol), triethylamine (17.5 mL, 0.15 mol), and 2-butanone (150 mL) were taken in a three-necked round-bottom flask and freshly distilled acryloyl chloride (15 mL, 0.16 mol) was added gradually from a 100-mL addition funnel to the reaction mixture which was kept at 0°C by an ice-salt mixture. The reactants were thoroughly stirred for 1 h and the reaction was continued for 3 h more at room temperature. The reaction mixture was filtered and the product was washed with water, 5% NaOH, and once again with water (yield = 76%).

ANAL: Calcd for $C_9H_7NO_4$: C, 55.96%; H, 3.65%; N, 7.25%. Found: C, 55.73%; H, 3.81%; N, 7.12%.

Synthesis of copolymers: poly (NPA-co-BMA)

The copolymerization of NPA (1) and BMA (2) was carried out in 2-butanone. The monomers were taken in seven different mole ratios (*vide*: Table I) along with 1% BPO and 2-butanone in polymerization tubes and deaerated by passing N_2 through the reaction mixture for 30 min. The reaction was allowed to proceed for 6–8 h at 65°C and, finally, the copolymer was precipitated by the addition of excess methanol, filtered, and dried at 40°C *in vacuo*.

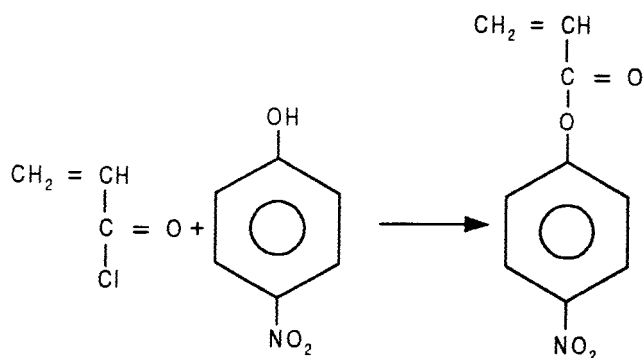
Characterization

The infrared (IR) spectra of polymers were recorded as KBr pellets on a Hitachi 270-50 infrared spectropho-

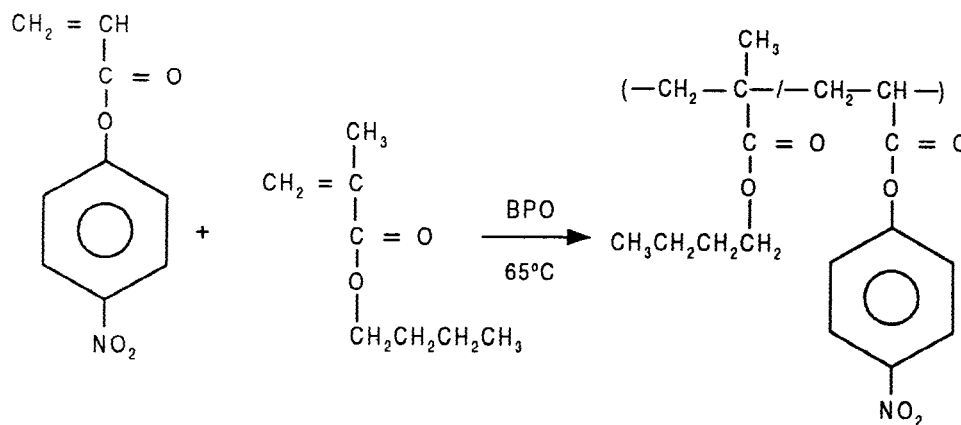
tometer. The 1H -NMR spectra and ^{13}C -NMR spectra of the polymers were run on a JEOL 400-MHz spectrometer. The solvent for the NMR experiments was $CDCl_3$ with TMS as the internal reference. Thermograms were recorded on a Mettler 3000 TA thermal analyzer and DSC experiments were carried out on a DuPont 990 thermal analyzer. Samples of less than 10 mg were used at a heating rate of 20°C/min for the thermal studies. The molecular weights (\bar{M}_w and \bar{M}_n) were determined using a gel permeation chromatograph (Waters 501) equipped with an RI detector. Polystyrene was used as a standard while THF was used as an eluent with a flow rate of 10 mL/min.

RESULTS AND DISCUSSION

The present study deals with the copolymers obtained from an aliphatic acrylate (BMA) and an aromatic acrylate (NPA). The former (BMA) was used after purification from a commercially available product while the latter (NPA) was synthesized according to the Schemes 1 and 2. The copolymers obtained were characterized by spectral and thermal studies and also by molecular weight determination.



Scheme 1



Scheme 2

IR spectra

An IR spectral study was successfully employed in the structural elucidation of the homopolymers,¹⁵ copolymers,¹⁶ and interpenetrating polymers.¹⁷ The IR spectrum of poly(NPA-co-BMA) shows that the strong absorptions due to ester carbonyls from both the acrylates in the copolymer chain overlap each other and they are observed at 1760 cm⁻¹. The methyl and methylene groups of the BMA unit exhibit their absorptions in the region of 2800–3050 cm⁻¹, while the aromatic ring vibrations are observed between 1540 and 1600 cm⁻¹. The medium-intensity bands seen at 1350 and 1520 cm⁻¹ are attributed to the symmetric and asymmetric stretching vibrations of the >C=N group in NPA, respectively. The aliphatic ester carbonyls are generally observed between 1650 and 1720 cm⁻¹. The carbonyl group frequencies have not experienced any

significant change in their position when compared with those of the homopolymers.

NMR spectra

NMR spectral studies of acrylate polymers provide a wealth of information regarding their structure and interactions.¹⁸ The proton NMR spectra of the copolymers recorded in a chloroform solution exhibit signals at 7.2–7.4 δ and 8.0–8.20 δ, which are attributed to the aromatic protons of the NPA unit. The signal observed at 4.10 δ is due to the methyleneoxy protons (C¹⁴) of the BMA unit. The signals due to the methyl (C¹²), methylene (C⁸), and methine protons (C⁹) of the comonomers are observed at 1.03, 2.35, and 1.49 δ, respectively (Table II).

The ¹³C-NMR spectra of the copolymers indicate that the signals due to the ester carbonyls of both

TABLE II
¹H- and ¹³C-NMR Spectral Data for Monomer and Polymer

System	¹ H-NMR resonances (ppm)				¹³ C-NMR resonances (ppm)							
	Aromatic protons	⁹ C	¹⁴ C	⁸ C	¹² C	O—C=O	Aromatic ¹ C, ³ C/ ⁵ C, ² C/ ⁶ C	Aliphatic ¹⁴ C, ¹⁵ C, ¹⁶ C, ¹⁷ C	¹⁰ C	¹² C	⁹ C	¹¹ C
NPA	8.2–8.8 (s, 2H)	5.9 (s, H)	—	6.5 (s, 2H)	—	173.12	150.7, 129.6 120.9	—	132.4	—	132.4	—
	7.0–7.4 (s, 2H)											
Poly (NPA)	8.05–8.2 (s, 2H)	1.58 (s, H)	—	2.3 (s, 2H)	—	173.9	150.3 129.4, 121.2	—	52.32	—	52.36	—
	7.2–7.4 (s, 2H)											
Poly (NPA-co-BMA)	8.0–8.2 (s, 2H)	1.49 (s, H)	4.1 (s, 2H)	2.35 (s, 2H)	1.03	175.3–176.8	151.21 129.94, 120.89	64.31 30.93 19.64	54.73	16.49–18.93	51.42	31.64
	7.2–7.4 (s, 2H)											

^a ¹C–¹⁷C: the numbering scheme for the carbons is provided in Figure 2.

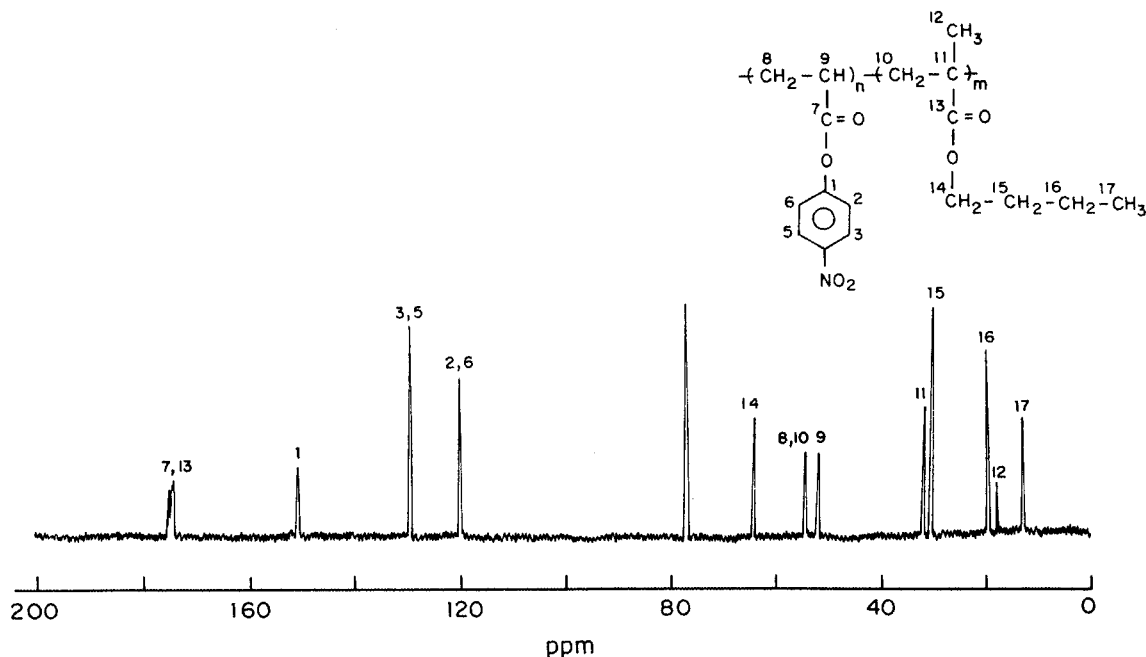


Figure 1 Proton decoupled ^{13}C -NMR spectrum of poly(NPA-co-BMA); $m_1:m_2 = 0.44:0.56$.

acrylates appear in the region of 175.3–176.8 ppm. The signals due to the C^{14} , C^{15} , C^{16} , and C^{17} carbons of the BMA unit are observed at 64.31, 30.93, 19.64, and 13.30 ppm, respectively. The α -methyl carbon, which is observed in the region of 16.49–18.93 ppm, is responsible for the tacticity of the system. The aromatic carbons of NPA, which exhibit their resonances at 151.21, 129.94, and 120.89 ppm, are assigned to C^1 , C^3/C^5 , and C^2/C^7 , respectively (Fig. 1 and Table II).

The composition of the monomeric units incorporated into the copolymer chain can be evaluated from the ^1H -NMR spectral data. The ratio of the intensities of the aromatic protons of NPA to those of the methyleneoxy protons of BMA is employed to arrive at this information. Let m_1 and m_2 be the mole fractions of the NPA and BMA units, respectively. The number of aromatic protons in NPA are four while there are two methyleneoxy protons in BMA. Then, the copolymer compositions can be arrived at by employing the following equation:

$$C = \frac{\text{Integral intensities of aromatic protons } (I_a)}{\text{Integral intensities of methyleneoxy protons } (I_m)}$$

$$C = \frac{4m_1}{2m_2}$$

On simplification of (i),

$$m_1 = \frac{C}{C + 2}$$

Thus, from eq. (ii), the mole fraction of NPA in the copolymer poly(NPA-co-BMA) can be calculated (Table I). A plot of the mole fraction of NPA in the feed versus that in the copolymer (Fig. 2) indicates the way in which the composition in the feed differs from that of the copolymer. The pattern of the curve observed in the present case very closely resembles that of poly(NPA-co-MMA).¹⁹

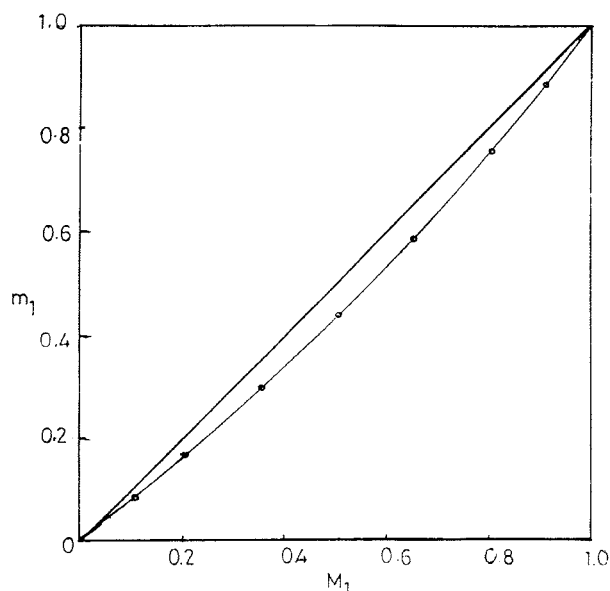


Figure 2 Composition curves of NPA-co-BMA copolymer system.

TABLE III
F-R and K-T Parameters of NPA-co-BMA Copolymer System

Sample no.	$F = M_1/M_2$	$f = m_1/m_2$	$G = F(f - 1)/f$	$H = F^2/f$	$\eta = G/\alpha + H$	$\xi = H/\alpha + H$
1	0.1111	0.0953	-1.0548	0.1295	-0.7428	0.0912
2	0.2500	0.2063	-0.9618	0.3030	-0.6037	0.1904
3	0.5385	0.4368	-0.6943	0.6639	-0.3552	0.3396
4	1.0000	0.7857	-0.2727	1.2727	-0.1064	0.4965
5	1.8571	1.4274	0.5559	2.4170	0.1499	0.6519
6	4.0000	2.9526	2.6453	5.4190	0.3943	0.8077
7	9.0000	6.2993	7.5713	12.8586	0.5351	0.9088

$$\alpha = \sqrt{0.1295 \times 12.8586} = 1.2905.$$

The copolymer composition curve, obtained by plotting the mole fraction of NPA in the feed (M_1) versus the mole fraction of NPA in the copolymer (m_1) (Fig. 2) does not intersect the ideal line. It clearly indicates that the feed composition and copolymer composition do not become equal during the polymerization process and the azeotropic copolymer composition has not been achieved in this case.

Molecular weight

The molecular weights of poly(NPA-co-BMA) with three different compositions were determined from gel permeation chromatography. The molar compositions of NPA (in the feed:in the copolymer) of these systems are 0.20:0.17, 0.50:0.44, and 0.65:0.59 and their corresponding weight-average molecular weights (\bar{M}_w) are 5.32, 4.67, and 4.36×10^4 , respectively. Their respective number-average molecular weights are (\bar{M}_n) 3.02, 2.78, and 2.69×10^4 . The ratio between \bar{M}_w and \bar{M}_n (\bar{M}_w / \bar{M}_n) lies in the range of 1.62–1.76 (Table 1).

Reactivity ratios

The reactivity ratios of the monomers, namely, NPA and BMA, in the copolymer system were evaluated by Fineman–Ross (F–R), Kelen–Tudos (K–T), and extended Kelen–Tudos (ext. K–T) methods. The reactivity ratios are useful in predicting whether the growing chain carrying an active center on a particular monomer unit would prefer to add its own monomer or combine with a different monomer.

The various parameters obtained from the F–R method are tabulated in Table III and the plot of G versus H is provided in Figure 3 for five different polymer compositions. The values for η and ξ determined by the K–T method are also given in the same table and the parameters obtained from the ext. K–T method are provided in Table IV. A plot of ξ versus η is provided in Figure 4. Kelen et al. described^{20–22} methods for determining the reactivity ratios in a copolymer. The r_1, r_2 values obtained from all the three methods closely agree with each other and they are

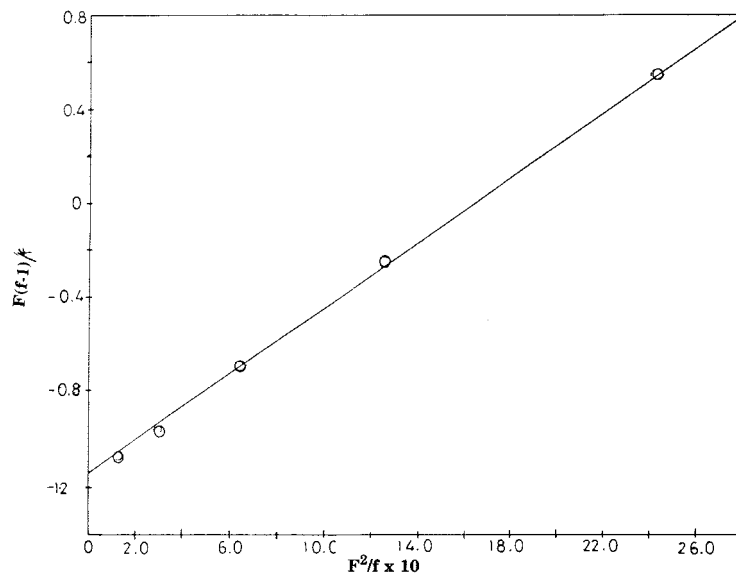


Figure 3 F–R plot for the poly(NPA-co-BMA) system.

TABLE IV
Ext. K-T Parameters of NPA-co-BMA Copolymer System

Parameter	Sample no.						
	1	2	3	4	5	6	7
ζ_2	0.0707	0.0903	0.1018	0.1124	0.0658	0.0922	0.0504
ζ_1	0.0606	0.0745	0.0826	0.0883	0.0505	0.0680	0.0352
Z	0.8532	0.8182	0.8027	0.7754	0.7624	0.7287	0.6945
F	0.1117	0.2521	0.5441	1.0132	1.8720	4.0521	9.0707
H	0.1309	0.3081	0.6778	1.3067	2.4555	5.5610	13.0615
G	-1.0604	-0.9700	-0.7016	-0.2764	0.5603	2.6797	7.6308
α	0.73575						
ξ	0.09101	0.1907	0.3419	0.4998	0.6525	0.8096	0.9090
η	-0.7371	-0.6003	-0.3533	-0.1057	0.1489	0.3901	0.5310
μ	1.30769						

presented in Table V along with their products. Three different situations exist: $r_1 \approx r_2 \approx 1$, $r_1 < 1$, and $r_1 \times r_2 \geq r_1$ and $r_2 \geq 1$. In the first case, there is no preference for either monomer and the copolymerization is entirely random. However, in the second case, the closer to zero the product of r_1 and r_2 becomes, the greater is the tendency for the monomers A and B to alternate in the chain. Long sequences of monomers A and B or blocks of each monomer in the copolymer occur in the last case. Sometimes, this may lead to the formation of a homopolymer.

The product of the r_1 and r_2 values evaluated by the F-R, K-T, and ext. K-T methods are 0.800, 0.752, and 0.734, respectively. These values suggest a situation similar to what has been described in the second case.

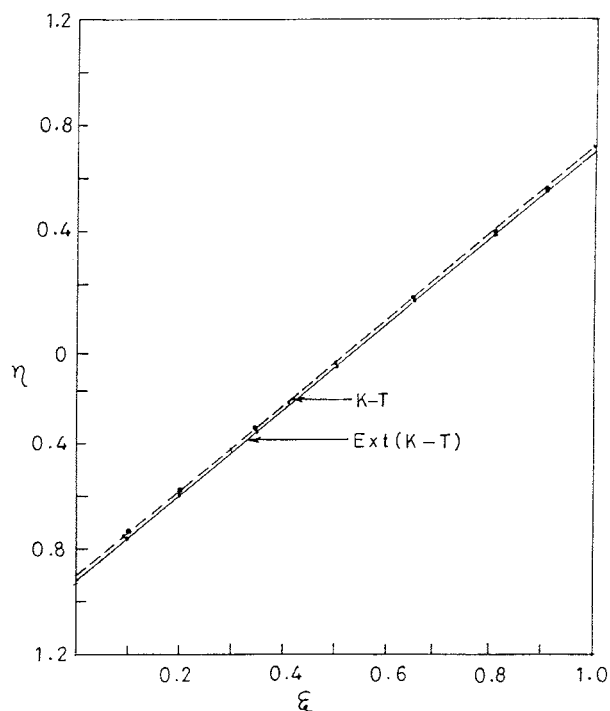


Figure 4 K-T and Ext. K-T plots of poly(NPA-co-BMA).

Since the product of $r_1 \times r_2$ is close to unity, the tendency of NPA and BMA to alternate in the copolymer is minimum. Hence, the comonomer sequences such as NPA-BMA-NPA and BMA-BMA-NPA may be present in these systems.

Thermal studies

The present series of polymers consist of essentially five different compositions and their thermal behavior was investigated by TG and DSC techniques. For the TG studies, thermograms were recorded in air. The data obtained from this study are given in Table VI and the thermograms are reproduced in Figure 5. The decomposition of the copolymers occur in two stages except in the case of the fifth system, where the entire process is complete in a single stage because BMA is the only component in this system. The temperature range in which the first stage occurs lies between 165 and 455°C, while the second stage is complete in the range of 300–505°C. The initial decomposition temperature (IDT) is minimum (165°C) when the system has a zero concentration of BMA and it is 225°C in the case of the last member of the series. The IDT of the copolymers with intermediate compositions are 185, 205, and 240°C when the BMA mole ratios are 0.829, 0.560, and 0.253, respectively. Even though the maximum decomposition temperature range (225–455°C) is observed in the case of the last system in stage one, this is still much less than those of other systems in the second stage. The decomposition is complete at 505°C

TABLE V
Comparison of Reactivity Ratios by Various Methods for Poly(NPA-co-BMA)

Methods	r_1	r_2	$1/r_1$	$1/r_2$	$r_1 r_2$
F-R	0.423	1.930	2.364	0.870	0.800
K-T	0.445	1.951	2.247	0.891	0.752
Ext. K-T	0.420	2.006	2.381	0.899	0.734

TABLE VI
Thermogravimetric Analysis Data of Poly(NPA-co-BMA) System

Sample no.	Copolymer composition		Decomposition temperature range (°C)		Temperature (°C) versus weight loss (%) of copolymers				
	m_1	m_2	Stage I	Stage II	10	25	50	75	90
1	1.000	0.000	165–300	300–505	217	260	290	386	485
2	0.171	0.829	185–335	335–460	237	267	305	348	392
3	0.440	0.560	205–420	420–485	252	280	325	376	427
4	0.747	0.253	240–380	380–505	275	305	348	410	480
5	0.000	1.000	225–455	—	265	290	325	355	395

in the case of the first and fourth members of the series, while for the remaining members, the process is over in the temperature range of 455–485°C.

The temperature versus weight loss data (Table VI) indicate some interesting results. The temperature gradually increases down the series from the first member to the fourth member when the percentage weight loss values are 10, 25, and 50. The copolymer systems containing BMA was investigated by TG and DSC and the thermal stability of the polymer blends containing cellulose and PMMA have also been reported in the literature.^{23,24}

The glass transition temperature (T_g) of poly(NPA-co-BMA) with a composition of 0.44:0.56 was found to be 97.2°C. The T_g of poly(BMA) with atactic and isotactic configurations are reported to be 20 and –24°C, respectively.²⁵ The T_g of the system is low when compared with that of the corresponding NPA polymer ($T_g = 104^\circ\text{C}$).

CONCLUSIONS

The copolymers poly(NPA-co-BMA) with seven different mole ratios of the monomers were synthesized by free-radical copolymerization of NPA and BMA. The IR and NMR spectral data unequivocally confirm the formation of the copolymers. The copolymer compositions in these systems were determined by ¹H-NMR spectral studies. The molecular weight measurements by gel permeation chromatography indicate that the M_w 's of these polymers lie in the range of $4.3\text{--}5.3 \times 10^4$, while their M_n 's are found to be $2.6\text{--}3.0 \times 10^4$. The reactivity ratios of the monomers calculated by F-R, K-T, and ext. K-T methods indicate a random arrangement of monomers in the copolymer chain as their products ($r_1 \cdot r_2$) are close to unity.

Thermal studies showed that the polymers underwent complete decomposition at 505°C and the decomposition occurred in two stages. The relative ther-

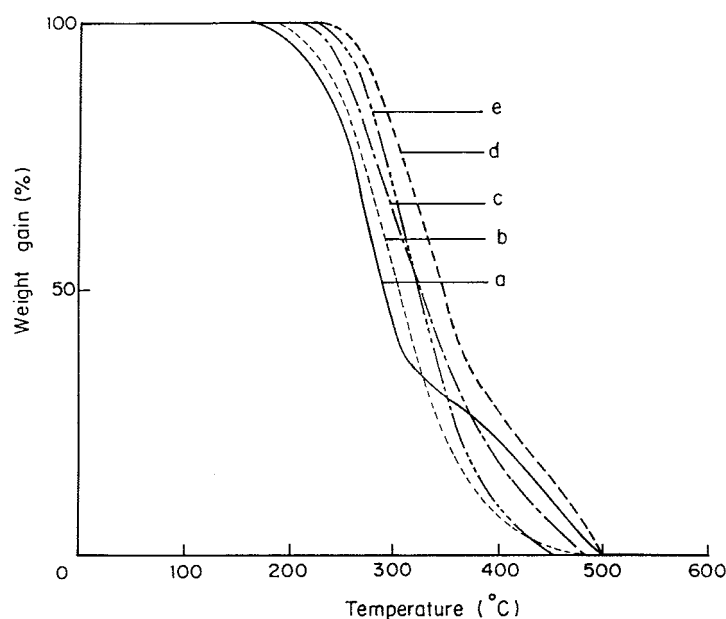


Figure 5 Thermogravimetric analysis curves in air of poly(NPA-co-BMA). Mole fraction of NPA in the copolymer: (a) 1.00; (b) 0.17; (c) 0.44; (d) 0.75; (e) 0.00.

mal stability of the different systems showed that the IDT is maximum (240°C) when the NPA:BMA ratio is 0.747:0.253. The glass transition temperature of the system with a mole ratio of NPA and BMA (0.44:0.56) is 97.2°C.

References

1. Kim, W. S.; Seo, K. H.; Chang, W. S. *Macromol Rapid Commun* 1996, 17, 835.
2. Zupan, M.; Kaanje, P.; Stauber S. *J Polym Sci Part A Polym Chem* 1996, 34, 2325.
3. Eichenbaum, G. M.; Kieser, P. F.; Simon, S. A.; Needham, D. *Polym Mater Sci Eng* 1998, 79, 479.
4. Ivanov, A. E. *J Macromol Sci Pure Appl Chem A* 1999, 36, 1981.
5. Nishi Kubo, T. *Jpn. Kokai Tokkyo koho JP* 145 228, 1995.
6. Chupov, V. V.; Lisovtseva, N. A.; Zvereva, G. F.; Noah, O. V.; Plate, N. A. *Vestn Mosk Univ Ser 2, Khim* 1992, 33, 276.
7. Feno, Z.; Wang, J.; Wang, Y. Ye, C., *Synth Met* 1993, 57, 3945.
8. Pearson, J. M. *Polym News* 1987, 13, 6.
9. Miyazaki, K.; Horibe, T. *J Biomed Mater Res* 1988, 22, 1011.
10. Kloosterboer, J. G.; Litjen, G. F. C. M. *Polym Mater Sci Eng Proc* 1987, 56, 759.
11. Peppas, N. A.; Moynihan, H. J.; Lucht, L. M. *J Biomed Res* 1985, 19, 397.
12. Thamizharasi, S.; Venkata Rami Reddy, A.; Balasubramanian, S. *Eur Polym J* 1998, 34, 1605.
13. Vogel, A. I. *Text Book of Practical Organic Chemistry*, 4th ed.; ELBS: London, 1980.
14. Stempel, G. H.; Cross, R. P.; Mariella, R. P. *J Am Chem Soc* 1950, 72, 2299.
15. Chern, C. S.; Lin, F. Y.; Chen, Y. C.; Lin, C. H. *J Appl Polym Sci* 1996, 62, 85.
16. Hild, G.; Lamps, J. P.; Rempp, P. *Polymer* 1993, 34, 2875.
17. Smith, P.; Eisenberg, A. *Macromolecules* 1994, 27, 545.
18. Spyros, A.; Davis P.; Heatley, F. *Macromolecules* 1994, 27, 5845.
19. Thamizharasi, S., Gnanasundaram, P.; Balasubramanian, S. *J Macromol Sci Pure Appl Chem A* 1999, 36, 1949.
20. Kelen, T.; Tudos, F. *J Macromol Sci Chem A* 1975 9, 1.
21. Kelen, T.; Tudos, F.; Turesanyi, B.; Kennedy, J. P. *J Polym Sci Part A Polym Chem* 1977, 15, 3041.
22. Tudos, F.; Kelen, T. *J Macromol Sci Chem A* 1981, 26, 1283.
23. Ramireddy, C.; Tuzar, A.; Prochazko, K.; Weber, S. E.; Munk, P. *Macromolecules* 1992, 25, 2541.
24. Nishioka, N.; Yamaoka, M.; Haneda, H.; Kawakami, K.; Uno, M. *Macromolecules* 1993, 26, 4694.
25. *Polymer Handbook*; Brandrup, J.; Immergut, E. H., Eds.; Wiley: New York, 1989.