Copolymerization of 2-(*N*-Phthalimido)ethyl Methacrylate with Glycidyl Methacrylate: Synthesis, Characterization, and Monomer Reactivity Ratios

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ABSTRACT: A phthalimido group containing methacrylate based monomer 2-(*N*-phthalimido)ethyl methacrylate (NPEMA) was synthesized by reacting 2-(*N*-phthalimido)-ethanol (NPE) with methacryloyl chloride. NPE was prepared by reacting phthalic anhydride dissolved in dimethyl formamide (DMF) with ethanolamine. Homopolymer of NPEMA and copolymers of NPEMA and glycidyl methacrylate (GMA) having various feed compositions were synthesized in methyl ethyl ketone (MEK) solution using benzoyl peroxide as an initiator at $70 \pm 1°C$. The polymers were characterized by IR and ^{1}H-NMR spectral studies. The composition of the copolymers was also determined by ^{1}H-NMR analysis. The reactivity ratios of the monomers were determined by the application of Fineman-Ross and Kelen-Tüdös methods. The molecular weights ($\bar{M}_w$ and $\bar{M}_n$) and polydispersity index of the polymers were determined using gel permeation chromatography. Thermogravimetric analysis of the polymers was carried out in air and their thermal stability was studied. The solubility and intrinsic viscosity of the homo- and copolymers were also studied. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 81: 96–103, 2001

Key words: 2-*N*-(phthalimido)ethyl methacrylate; glycidyl methacrylate; copolymerization; reactivity ratio

INTRODUCTION

Methacrylic copolymers have gained great importance in various fields of industry.[1] Copolymers of glycidyl methacrylate (GMA) with methacrylic monomers could be used for overhead projector (OHP) sheets due to their transparent nature.[2] Copolymers containing the phthalimide derivatives have been used as optical brightening agents.[3] Copolymers of phthalimidomethyl methacrylate and sodium methacrylate have been used as ion exchanging polymer stabilizer.[4]

Phthalimido-group-containing polymers have excellent heat resistance and transparency properties. Epoxy-group-containing compounds are used as excellent thermosetting adhesives.[5] Polymer supports based on GMA are found to have versatile applications due to the presence of an oxirane group.[6] Copolymers of methyl *N*-phthalimido acrylate with methacrylic monomer have good thermal stability.[7] The estimation of copolymer composition and determination of reactivity ratios are significant for tailor-making properties. The copolymer composition and reactivity ratios of the methacrylate system were determined by ^{1}H-NMR spectroscopy.[8–10]

The aim of the present work involves the development of heat resistant adhesive polymers for leather and rubber finishing purposes, and also for

various specific applications, based on 2-(N-phtha-limido)ethyl methacrylate and GMA copolymers. The present paper deals with the synthesis, characterization, and determination of reactivity ratios by the Fineman-Ross and Kelen-Tüdös methods. Thermal stability of the polymers was also identified.

EXPERIMENTAL

Materials

Phthalic anhydride (Ranbaxy) dried under vacuum was used without further purification. Ethanolamine (BDH) was purified using the standard method.[11] Methacryloyl chloride was prepared using the method described by Stempel et al.[12] The monomer, GMA (Acros, USA), was purified by adopting the conventional method,[13] and was finally distilled under reduced pressure. Benzoyl peroxide (BPO, Merck) was recrystallized from a 1:1 chloroform-ethanol mixture. Fractionally distilled solvents were used for all reactions.

### Synthesis of 2-(N-Phthalimido)ethanol (NPE)

Phthalic anhydride (20 g, 0.135 mol) dissolved in DMF (80 mL) was put into a 250-mL three-necked RB flask equipped with a stirrer, a reflux condenser, and a nitrogen inlet. Ethanolamine (8.1 mL, 0.135 mol) was then added dropwise to the reaction vessel, which was kept cool in an ice bath. After the addition was completed, the contents were heated in an oil bath at 130°C for 12 h in nitrogen atmosphere. Then most of the DMF was distilled off and the solution was transferred to a beaker. On cooling, a solid product was obtained. The final product was filtered and recrystallized with rectified ethanol. It had a melting point of 126°C and the yield was 80%. The compound formed was characterized by IR and ^{1}H-NMR spectroscopy.

IR (cm^{-1}): 3480 (OH stretching), 3090 (aromatic C—H stretching), 2960 and 2890 (asymmetric and symmetric C—H stretch, respectively, due to the methylene group), 1720 (C=O stretch due to the phthalimido group), 1450 (aromatic C=C stretch), 995 and 725 (C—H stretch due to out-of-plane bending).

^{1}H-NMR (ppm): 7.90–7.65 (4H) (aromatic protons), 4.48 (1H) (OH), 4.32 (2H)(—CH$_2$—O—), and 3.90 (2H) (>N—CH$_2$—).

Synthesis of 2-(N-Phthalimido)ethyl Methacrylate (NPEMA)

NPE (9.6 g, 0.05 mol) dissolved in MEK (100 mL) and triethylamine (6.9 mL, 0.05 mol) were put
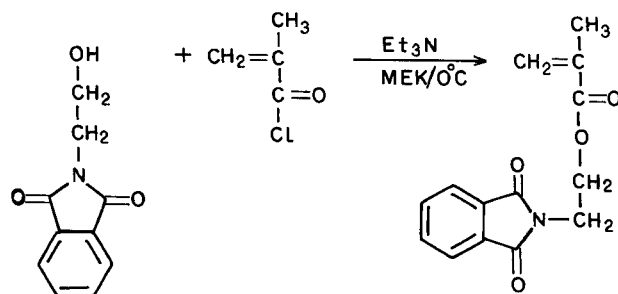
Scheme 1

into a 500 mL three-necked flask equipped with a stirrer, a nitrogen inlet, and a dropping funnel. The temperature of the reactants was maintained at 0 to 5°C using an ice bath. A mixture of 4.9 mL (0.05 mol) of methacryloyl chloride and 20 mL of MEK was then added slowly from a dropping funnel to the reactant with constant stirring and cooling. After stirring the reaction mixture for 1 h, the ice bath was removed and the mixture was stirred for another hour at room temperature. The triethylamine hydrochloride salt formed was filtered off and the filtrate was mixed with hydroquinone and evaporated in a rotary evaporator. The final product (white solid) was washed with 0.05% NaOH and recrystallized from ethanol. The yield was found to be 60% (Scheme 1). The formation of the monomer was confirmed by IR and ^{1}H-NMR spectroscopic techniques.

IR (cm^{-1}): 3090 (aromatic C—H stretching), 2960 and 2885 (asymmetric and symmetric C—H stretch, respectively, due to methylene and methyl protons), 1760 (C=O stretch due to the ester group), 1720 (C=O stretch due to the phthalimido group), 1640 (C=C stretch), 1615 and 1460 (aromatic C=C stretch), 1180 (C—O stretch of the ester group), and 990 and 715 (C—H out-of-plane bending).

^{1}H-NMR(ppm): 7.95–7.74 (4H) (aromatic protons), 5.55 (1H) and 6.13 (1H) (olefinic protons), 4.40 (2H) (—CH$_2$—O—), 3.96 (2H) (>N—CH$_2$—), and 1.94 (3H) methyl.

Homopolymerization

NPEMA, MEK, and BPO were put into a standard tube (100 mL) and deaerated by passing oxygen free nitrogen gas for 25 min. The reaction tube was closed and kept in a thermostat at 70°C for 10 h. The contents were then cooled and poured over methanol. The precipitated poly(N-PEMA) was filtered, washed with methanol, and purified by dissolving in DMF, and was then re-

precipitated by the addition of methanol. The purified polymer was dried under vacuum at 40°C for constant weight.

Copolymerization

Copolymers with different feed compositions of NPEMA and GMA were synthesized in MEK solution using BPO as a free radical initiator. Predetermined quantities of NPEMA, GMA, BPO (0.4 wt %, with respect to the monomer), and MEK were mixed in a polymerization tube, and the mixture was purged with oxygen free nitrogen for 30 min, sealed, and kept in a thermostat at 70 ± 1°C. After the desired time (<10% conversion), the copolymer was precipitated by pouring the contents into excess methanol. The precipitated polymer was filtered, washed with methanol, and purified by repeated precipitation from the solution of polymer in DMF by methanol. The polymer was finally dried in a vacuum at 45°C.

Spectral Measurements

The IR spectra of the samples were recorded with a Hitachi 270-50 IR spectrophotometer on solid samples as KBr pellets. NMR spectra were run on a Hitachi 200 MHz NMR spectrometer and the spectra were recorded at room temperature as 15–20% (w/v) solutions in CDCl$_3$. TMS was used as the internal standard. Thermogravimetric analysis was carried out with a Mettler 3000 Thermal Analyzer at a heating rate of 15°C/min in air. The molecular weight ($\bar{M}_n$ and $\bar{M}_w$) of the polymers was determined using water 510 gel permeation chromatography with polystyrene standards and THF as the eluent. The intrinsic viscosity of the polymers was determined in DMF solvent at 30 ± 1°C using an Ubbelohde viscometer.

RESULTS AND DISCUSSION

Copolymers of NPEMA with GMA in EMK solution were studied for different mole fractions of NPEMA (0.1 to 0.9) in the feed. The reaction time was restricted to give conversions less than 10% in order to obtain polymer samples with homogeneous composition. The chemical structure of the copolymer is shown in Scheme 2.

Characterization

The solubility of the homopolymer and the copolymers was tested in several solvents in cold con-
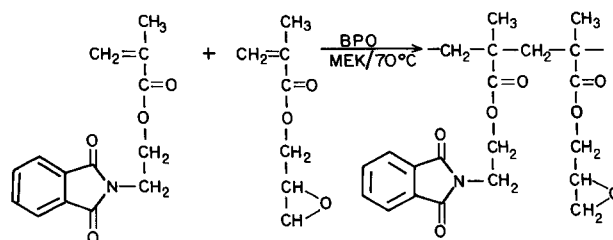
Scheme 2

ditions. The homopolymers and copolymers were soluble in chloroform, DMF, dimethyl sulfoxide, MEK, and THF. They were insoluble in hydroxy-group-containing solvents like methanol, ethanol, isopropanol, and water, and nonpolar solvents like benzene, toluene, and hexane.

A thin layer of film was prepared by evaporating the copolymer solution (dissolved in chloroform) that had been poured over a glass plate. The transparency of the films was tested using a laser diode. The films prepared from the copolymer samples showed good transparency, and the transparent nature increased with an increase in the NPEMA content of the copolymer.

The IR spectrum of poly(NPEMA-co-GMA) is shown in Figure 1. The absorption peak at 3080 cm^{-1} is due to aromatic C—H stretching. The peaks at 2940 and 2860 cm^{-1} are due to C—H stretching of methyl and methylene groups. The strong absorption peaks at 1770 and 1720 cm^{-1} are due to the carbonyl stretching of the ester group and the phthalimido group, respectively. The peaks at 1600 and 1465 cm^{-1} correspond to the C=C stretching of the aromatic ring. The medium absorption peaks at 1235 and 1190 cm^{-1} are attributed to the C—O stretch of the epoxide group and the ester group, respectively. The peak at 720 cm^{-1} is due to the out-of-plane C—H bending vibration of ortho disubstituted benzene.

The ^{1}H-NMR spectrum of poly(NPEMA-co-GMA) (0.53:0.47) (Fig. 2) is consistent with its chemical structure. The resonance signals between 7.98–7.67 ppm correspond to the aromatic protons of the NPEMA unit. The signals at 4.32 and 4.12 ppm are due to the methylenoxy protons of the ester groups of the NPEMA and GMA units, respectively. The signal at 3.94 ppm is due to —NCH$_2$— protons. The signal at 3.74 ppm is due to methylenoxy protons of the epoxy group in the GMA unit. The signal at 3.21 ppm corresponds to ring methyne protons of the GMA unit. The backbone methylene protons of the two comonomer units are observed between 2.23–1.67 ppm. The
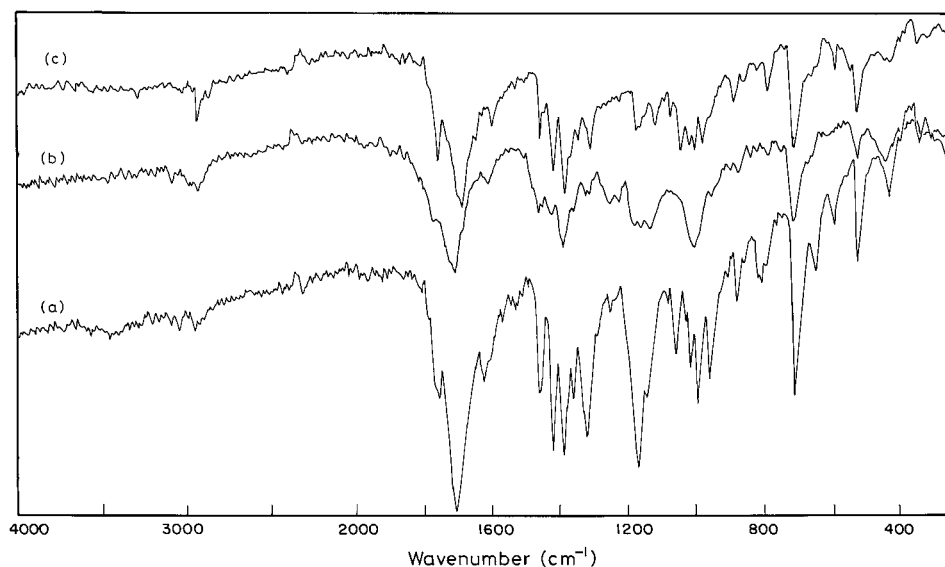
Figure 1 IR spectrum of: (a) NPEMA, (b) poly(NPEMA), and (c) poly(NPEMA-*co*-GMA) (0.53:0.47).

signal between 1.26–0.85 ppm is due to the methyl protons of the NPEMA and GMA units.

Copolymer Compositions

Copolymer composition was determined by ^{1}H-NMR spectral analysis of the copolymers. The resonance signals shown between 7.98–7.67 ppm correspond to the four aromatic protons of the NPEMA unit, and that between 0.86–4.32 ppm corresponds to the total aliphatic protons in the copolymer. Hence, it is possible to determine the composition of the copolymer by comparing the intensities of aromatic protons and the intensities of total aliphatic protons of the copolymer.

The following expression was applied to the copolymers. Let m_1 be the mole fraction of

Figure 2 ^{1}H-NMR spectrum of poly(NPEMA-*co*-GMA) (0.53:0.47).

NPEMA and $(1 - m_1)$ be that of GMA. The NPEMA unit contains four aromatic protons and nine aliphatic protons. The GMA unit contains 10 aliphatic protons.

$$C = \frac{\text{Intensities of aromatic protons}}{\text{Intensities of aliphatic protons}}$$

$$= \frac{4m_1}{9m_1 + 10(1 - m_1)} \quad (1)$$

Simplification of the equation results in eq. (2):

$$m_1 = \frac{10C}{(4 + C)} \quad (2)$$

By measuring the intensities of the aromatic proton signals and the total aliphatic proton signals from the spectra of copolymer samples, the mole fraction of NPEMA in all the copolymers was calculated using eq. (2). Table I gives the values of C and the corresponding mole fraction of NPEMA in the copolymers. The plot of mole fraction of NPEMA (M_1) in the feed versus that in the copolymer (m_1) indicates the copolymerization behavior of the monomers (Fig. 3).
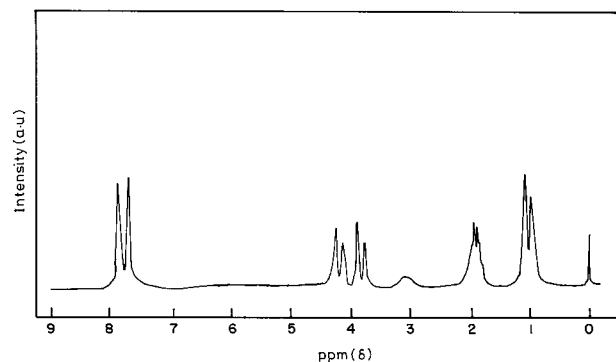
Reactivity Ratios

The knowledge of the reactivity ratio is essential for the preparation of any copolymers having a definite composition. The reactivity ratio of

Table I   Composition Data for the Free Radical Polymerization of NPEMA(1) with GMA(2) in MEK Solution at 70 ± 1°C

Feed Composition		Intensities of Protons			Copolymer Composition
$M_1{}^a$	Conversion %	I_{Arom}	I_{Ali}	C	$m_1{}^b$
0.10	8.3	6.5	122.0	0.0532	0.131
0.20	7.1	10.0	108.0	0.0925	0.226
0.35	6.9	15.0	93.5	0.1604	0.386
0.50	9.2	18.0	80.0	0.2250	0.533
0.65	8.6	20.5	70.5	0.2908	0.677
0.80	5.8	26.0	71.0	0.3662	0.838
0.90	7.5	30.0	74.0	0.4054	0.920

[a] The mole fractions of NPEMA in the feed.
[b] The mole fractions of NPEMA in the copolymer.

NPEMA and GMA was evaluated from the monomer feed ratios and the copolymer compositions by the application of the Fineman-Ross (F-R)[14] and Kelen-Tüdös (K-T)[15] methods (Table II). The reactivity ratio related to monomer 1 (NPEMA) is r_1, and that of monomer 2 (GMA) is r_2. The reactivity ratios of the monomers are obtained by plotting F-R and K-T parameters separately using the reported methods. The values of r_1 and r_2 obtained from the F-R plot (Fig. 4) and the K-T plot (Fig. 5) are: F-R method: $r_1 = 1.049 \pm 0.04$, $r_2 = 0.775 \pm 0.03$; K-T method: $r_1 = 1.002 \pm 0.02$, $r_2 = 0.722 \pm 0.04$.

The value of r_1 is more than 1 and that of r_2 is less than 1; however, the product of r_1 and r_2 remain less than 1, thus indicating that the system follows a random distribution of the monomeric units. The values of r_1 and r_2 suggest that the mole fraction of NPEMA in the copolymer would be always higher than that in the feed.

Molecular Weights

The number average, weight average molecular weights ($\bar{M}_n$, $\bar{M}_w$), and the polydispersity index of homopolymer as well as copolymer samples were determined by gel permeation chromatography and are given in Table III. The polydispersity index of poly(NPEMA) is very close to 2. The theoretical value of $\bar{M}_w/\bar{M}_n$ for polymers produced through radical combination and disproportination were 1.5 and 2, respectively.[16] This suggests that poly(NPEMA) was produced mainly via termination of growing chain by disproportination. With an increase in the composition of NPEMA in the feed, the tendency for chain termination by disproportination increases.

The intrinsic viscosity of the polymers was obtained by plotting η_{sp}/C versus concentration and extrapolating the straight line to zero concentration. The intercept gave the intrinsic viscosity [η] of the polymers. The intrinsic viscosity (Table III) of the copolymer ranges between 0.28–0.38 dL/g. The change in viscosity with the change in composition of the polymer is random.

Thermal Analysis

TG traces of the polymers are shown in Figure 6. The thermal stability of the polymers was identi-
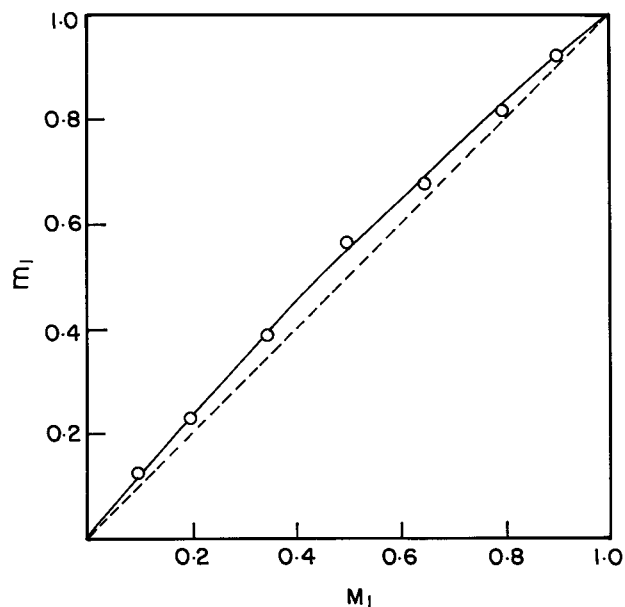

Figure 3   The plot of mole fractions of NPEMA in the feed versus that in the copolymer.

Table II   F-R and K-T Parameters for the Copolymers of NPEMA with GMA

$F = M_1/M_2$	$f = m_1/m_2$	$G = F(f - 1)/f$	$H = F^2/f$	$\eta = G/(\alpha + H)$	$\xi = H/(\alpha + H)$
0.1111	0.1507	−0.6260	0.0819	−0.7439	0.0973
0.2500	0.2920	−0.5975	0.2119	−0.6151	0.2181
0.5385	0.6287	−0.3180	0.4612	−0.2605	0.3778
1.0000	1.1413	0.1238	0.8762	0.0756	0.5356
1.8571	2.0959	0.9710	1.6455	0.4037	0.6842
4.0000	5.1728	3.2267	3.0930	0.8375	0.8028
9.0000	11.500	8.2174	7.0434	1.0531	0.9029

Alpha is equal to 0.7595.

fied by estimating the percentage weight loss of the polymers on thermal decomposition. The TGA data for poly(NPEMA), poly(GMA), and different copolymer samples are shown in Table IV. The actual decomposition temperature range depends upon the composition of the constituent monomeric units in the copolymers. The thermogram of all polymers shows that all three systems undergo decomposition in single stage. The initial decomposition temperature of poly(NPEMA-*co*-GMA) (0.53:0.47) was 258°C, and that of poly(N-PEMA) and poly(GMA) was 325 and 206°C, respectively. Incorporation of a NPEMA unit in the copolymer chain increases the thermal stability of the copolymers.

Application of the Copolymers as Leather Adhesive

Poly(NPEMA-*co*-GMA) samples having two different compositions (0.53:0.47 and 0.22:0.78) were chosen in order to study the adhesive property on leather. These copolymers were individually crosslinked using 40% ethanolamine (based on
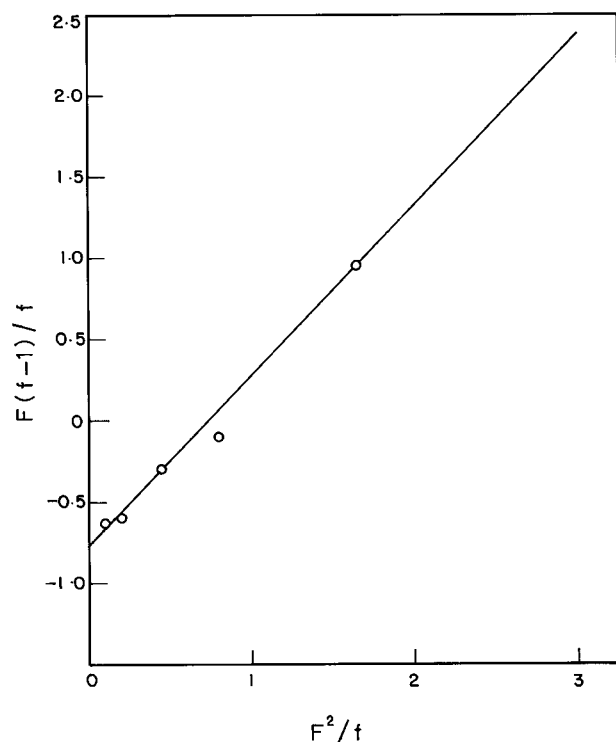
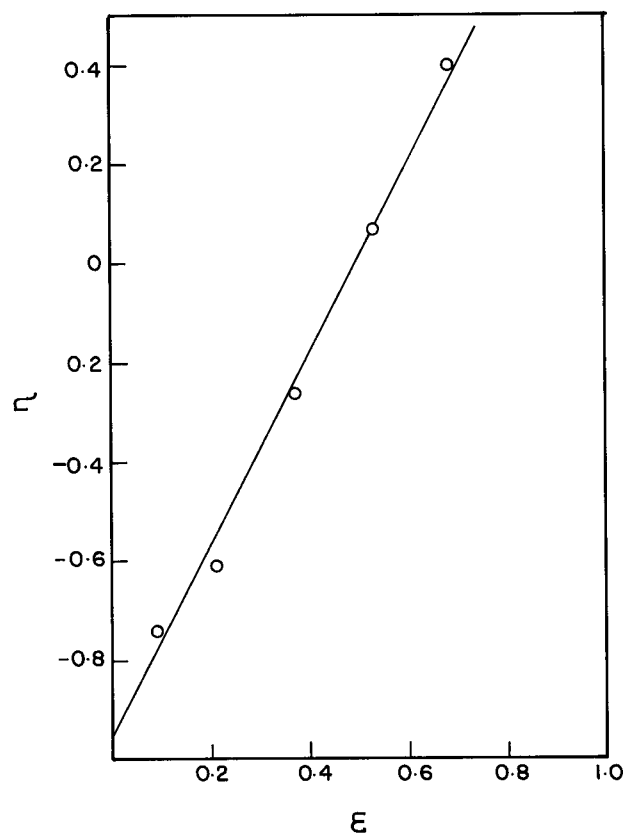**Figure 4**   F-R plot for NPEMA-GMA copolymer system.

Figure 5   K-T plot for NPEMA-GMA copolymer system.

Table III Molecular Weight and Intrinsic Viscosity Data for Polymers of NPEMA and GMA

| Polymers | m_1[a] | Molecular Weights | | | Intrinsic Viscosity $[\eta]$ (dL/g) |
		$\overline{M}_w \times 10^{-4}$	$\overline{M}_n \times 10^{-4}$	$\overline{M}_w/\overline{M}_n$	
Poly(NPEMA)	1.00	2.89	1.48	1.95	0.28
Poly(NPEMA-*co*-GMA)	0.920	3.24	1.68	1.93	0.30
	0.838	3.55	1.80	1.94	0.33
	0.677	3.28	1.71	1.92	0.30
	0.533	3.55	1.88	1.89	0.34
	0.386	4.13	2.21	1.87	0.38
	0.226	3.70	2.02	1.83	0.36
	0.131	3.94	2.13	1.85	0.37
Poly(GMA)	0.00	4.11	2.25	1.83	0.35

[a] The mole fraction of NPEMA in the polymers.

the weight of GMA) in chloroform. The peel strength for the adhesive prepared from the co-polymer having 47% GMA was 0.6 and 1.0 N/mm at 50 and 90°C, respectively. The corresponding values for the adhesive prepared from the copolymer containing 78% GMA was 0.9 and 1.4 N/mm. The enhanced peel strength of the latter is due to higher epoxy group content in the copolymer. These compositions showed good adhesive characteristics even at room temperature.
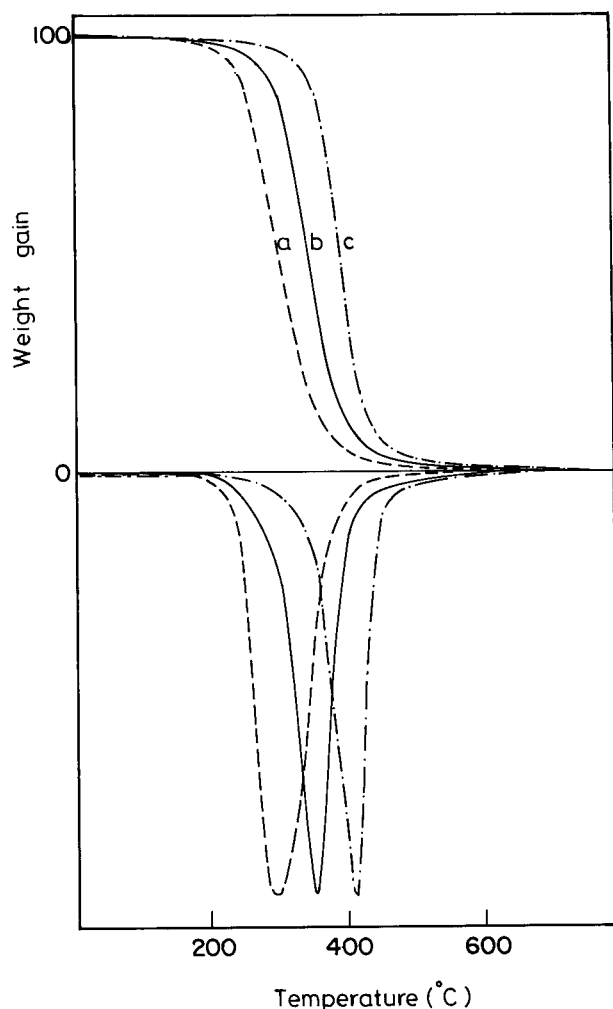
CONCLUSIONS

NPEMA was synthesized and characterized. Poly(NPEMA) and the copolymers of NPEMA and GMA with different compositions were synthesized. The presence of both monomeric units in the copolymers was confirmed by IR and ^{1}H-NMR spectra. The composition of the copolymers was calculated from the ^{1}H-NMR spectra of the polymers. The reactivity ratios determined from F-R and K-T methods ($r_1 = 1.049 \pm 0.04$, 1.002 ± 0.02, respectively; $r_2 = 0.775 \pm 0.03$, 0.722 ± 0.04, respectively) are in good agreement. The r_1 values of both methods are greater than 1, and r_2 values are less than 1, which indicates that NPEMA is more reactive than GMA. The value of r_1 and r_2 is less than 1, which indicates the random distribution of monomeric units in the copolymers. TGA studies concluded that the thermal stability of the copolymers increases with an increase of NPEMA unit in the copolymer chain. The intrinsic viscosity of the polymers was in the range 0.28–0.38 dL/g.

Figure 6 TGA curves for: (a) poly(GMA), (b) poly(NPEMA-*co*-GMA) (0.53: 0.47), and (c) poly(NPEMA).

Table IV   TGA Data of Homo- and Copolymers of NPEMA and GMA

Polymers	Copolymer Composition		IDT[a] °C	Temperature (°C) at Different Weight Loss (%)				
	m_1	m_2		10%	30%	50%	70%	90%
Poly(PEMA)	1.00	0.00	325	368	394	406	427	462
Poly (PEMA-*co*-GMA)	0.68	0.32	304	345	378	389	408	447
	0.53	0.47	258	291	324	359	381	434
	0.39	0.61	227	262	301	333	356	408
Poly(GMA)	0.00	1.00	206	254	284	302	334	381

[a] Initial decomposition temperature.

REFERENCES

1. Payene, H.F. Organic Coating Technology; Wiley: New York, 1965; p 1.
2. Ihara, K.; Sasaki, K.; Kuvachi, I. Jpn. Pat. JP-11 105205, 1999.
3. Konstantinova, T.N.; Garbechev, I.K. Polym Int 1998, 43, 39.
4. Kaidov, A.A.; Ericv, O.M. Akad Nank Resp Uzb 1997, 11, 39.
5. Arshady, A.; Atherton, E.; Sheppard, R.C. Tetrahedron Lett 1979, 1521.
6. Kalal, J. J Polym Sci, Polym Symp 1978, 62, 251.
7. Manlyanov, Kh. N.; Eriev, O.M.; Maulanov, B.A.; Khasanov, G.P. Uzb Khim 1997, 5, 59.
8. Tacx, J.F.; Vander Velden, G.P.M.; German, A.L. Polymer 1988, 29, 1675.
9. Balaji, R.; Nanjundan, S. Eur Polym J 1999, 35, 1133.
10. Thamizharasi, S.; Gnanasundaram, P.; Reddy, B.S.R. J Appl Polym Sci 1997, 65, 1285.
11. Balaji, R.; Sivakumar, N.; Nanjundan, S. J Polym Mater 2000, 17, 207.
12. Stempel, G.H.; Cross, R.P.; Mariella, R.P. J Am Chem Soc 1950, 72, 2299.
13. Balaji, R.; Nanjundan, S. J Macromol Sci Chem 1998, A(35)9, 1527.
14. Fineman, M.; Ross, S.D. J Polym Sci 1950, 5, 259.
15. Kelen, T.; Tüdös, F. J Macromol Sci Chem 1975, A9, 1.
16. Teramachi, S.; Hasegeva, A.; Akatsuka, M.; Yamashita, A.; Takemoto, N. Macromolecules 1978, 11, 1206.