

Copolymerization of 4-Nitrophenyl Acrylate with Glycidyl Methacrylate: Synthesis, Characterization, and Reactivity Ratios

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ABSTRACT: 4-Nitrophenyl acrylate (NPA) was prepared and characterized by IR and NMR spectroscopic techniques. Poly(4-nitrophenyl acrylate) [poly(NPA)] and copolymers of glycidyl methacrylate (GMA) and NPA having various feed compositions in a 2-butanone solution using benzoyl peroxide as an initiator at $65^{\circ}\text{C} \pm 0.5^{\circ}\text{C}$ were prepared. Copolymer compositions were determined by ¹H-NMR analysis. The monomer reactivity ratios were determined by Fineman–Ross, Kelen–Tudös, and extended Kelen–Tudös methods. The molecular weights of the polymers were determined by gel permeation chromatography. Thermogravimetric analysis of the polymers was performed in air and their thermal stability was studied. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **65**: 1285–1291, 1997

INTRODUCTION

Acrylic polymers find extensive applications in leather, textile, and building materials. In particular, phenyl acrylate polymers by the incorporation of an active group in the phenyl ring enhance not only the thermal stability of the polymers but also have several potential industrial applications. For example, they help in studying the kinetic parameters of a macromolecular reaction in peptide synthesis, as electroactive polymers and metal chelates.^{1–6}

Epoxy adhesives are a class of thermosetting adhesives which have excellent thermosetting properties at low temperatures.⁷ Polymer supports based on glycidyl methacrylate (GMA) are noteworthy as they find versatile applications due

to the presence of oxirane groups.^{8,9} In particular, GMA crosslinked with ethylene methacrylate has been employed for the immobilization of enzymes, DNA, catalysts, and biomolecules.^{10–13} The copolymer composition of the acrylate system was determined by NMR spectroscopy.¹⁴

The present work was undertaken with a view to develop heat-resistant adhesive polymers for leather to leather, rubber to leather, and rubber to rubber based on phenyl acrylate and GMA copolymers. The article describes the synthesis, characterization, and reactivity ratios by Fineman–Ross (F–R), Kelen–Tudös (K–T), and extended K–T methods. Thermal properties of all the polymers were analyzed by TGA and DSC.

EXPERIMENTAL

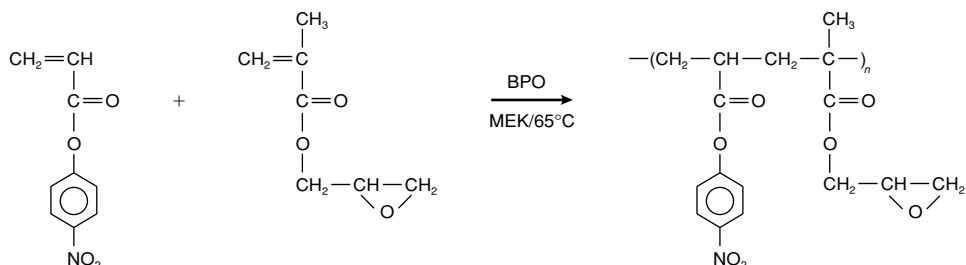
Materials

Acrylic acid (Aldrich), benzoyl chloride (BDH), 4-nitrophenol (Sigma), triethylamine (BDH), 2-

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Scheme 1

butanone (S.D. Fine Chem.), and methanol (BDH) were purified by standard procedures. Glycidyl methacrylate (GMA, Aldrich) was distilled before use. Benzoyl peroxide (Sigma) was recrystallized from a chloroform–methanol (1 : 1) mixture. 4-Nitrophenol (Sigma) was recrystallized from ethanol.

Synthesis of Monomer

Acryloyl chloride was prepared by reacting acrylic acid with benzoyl chloride following the procedure of Stempel et al.¹⁵ 4-Nitrophenyl acrylate (NPA) was synthesized using acryloyl chloride and 4-nitrophenol. Freshly distilled acryloyl chloride (0.12 mol) was added slowly to the stirring 4-nitrophenol (0.1 mol) in a chloroform solution in the presence of triethylamine (0.1 mol) at 0–2°C. One hour after completion of the addition, the reaction mixture was washed with water to remove quaternary ammonium salt formed and the unreacted NPA was then removed by washing with 5% aqueous NaOH. The organic layer was then dried with anhydrous Na_2SO_4 and the monomer was recovered after solvent evaporation. The resulting product was recrystallized from petroleum ether. Yield 58%; mp 74–76°C. The product was further confirmed by IR and NMR spectroscopic methods.

Copolymerization

Copolymerization reactions were carried out in 2-butanone at 65°C using benzoyl peroxide as a free-radical initiator (Scheme 1). Appropriate quantities of NPA and GMA with 2-butanone and benzoyl peroxide (1% w/w) were mixed in a reaction tube and purged with nitrogen gas for 20 min. The tube was tightly sealed and kept in a thermostatic water bath at 65°C \pm 0.5°C. After the desired

time, copolymerization was stopped at low conversions (<10% wt). These copolymers were precipitated into excess methanol, filtered, and dried *in vacuo* at 40°C.

Spectral Measurements

IR spectra of the polymers were recorded on a Hitachi 270-50 spectrophotometer using the potassium bromide pellet technique for solids. ^1H -NMR spectra of the copolymers were run on a JOEL 400 MHz spectrometer at room temperature in CDCl_3 and TMS was used as the internal standard. ^{13}C -NMR spectra were run on Bruker 270 MHz. The protons were decoupled by broadband irradiation. Thermogravimetric analysis was performed using a Mettler TA 3000 thermal analyzer at a heating rate of 20°C/min in air. Molecular weights (\bar{M}_w and \bar{M}_n) of the polymers were determined by a Waters 501 gel permeation chromatography instrument equipped with a refractometer index detector. Tetrahydrofuran was used as an eluent at a flow rate of 10 mL/min and polystyrene standards were employed for calibration.

RESULTS AND DISCUSSION

The copolymerization of NPA with GMA in a 2-butanone solution was studied for various feed ratios with a mol fraction of NPA ranging from 0.10 to 0.90 in the monomer feed. The data for the composition of feed and copolymer are shown in Table I. The characterization of monomeric units in the copolymer was carried out by both IR and NMR spectroscopy. The copolymers were soluble in tetrahydrofuran, chloroform, dimethylformamide, and dimethyl sulfoxide but insoluble in nonpolar solvents like hexane, benzene, and

Table I Low Conversion Copolymerization of NPA-GMA System

Sample No.	Feed Composition in Copolymer		Conversion %	Intensity of Aromatic Protons (I_A)	Intensity of Total Aliphatic Protons (I_a)	C	Copolymer Composition in Mol Fraction		Molecular Weights		
	M_1	M_2					m_1	m_2	$\bar{M}_w \times 10^{-4}$	$\bar{M}_n \times 10^{-4}$	\bar{M}_w/\bar{M}_n
	1	0.10					0.90	8.91	0.5	13.2	0.0379
2	0.20	0.80	5.67	1.1	1.25	0.0880	0.191	0.809			
3	0.35	0.65	6.38	1.9	9.9	0.1912	0.359	0.641			
4	0.50	0.50	7.02	2.9	8.6	0.3372	0.530	0.470	2.63	1.62	1.62
5	0.65	0.35	9.81	3.8	7.1	0.5352	0.691	0.309			
6	0.80	0.20	7.64	4.8	6.65	0.7934	0.831	0.169	3.24	1.98	1.64
7	0.90	0.10	6.98	5.4	5.3	1.0189	0.915	0.085			

Solvent: MEK; temperature: 65°C; initiator: BPO (1% wt of the monomers).

toluene and protic solvents like methanol and ethanol.

IR Spectroscopy

The IR spectrum of the poly(NPA-co-GMA) system is shown in Figure 1. The copolymer shows the characteristic bands of both monomer units. The bands at 3050–2880 cm^{-1} are due to the aromatic and aliphatic stretching vibrations. The keto- and ester-carbonyl groups of the NPA unit gave sharp peaks at 1765 and 1650 cm^{-1} , respectively. The ester carboxyl of GMA appeared at 1730 cm^{-1} . The intense peak at 1600 cm^{-1} corresponds to the aromatic >C=C< vibration, while the absorption bands at 1530 and 1360 cm^{-1} are due to C—N stretching vibrations. The appearance of a band at 910 cm^{-1} explains the incorporation of the GMA unit in the copolymer and also confirms the participation of the double bond in copolymerization.

^{13}C -NMR Spectroscopy

The proton-decoupled ^{13}C -NMR spectra of poly(NPA-co-GMA) (0.53 : 0.47 mol %) is shown in Figure 2. The ester carbonyl of both the acrylates appeared at 176.3 and 171.3 ppm. The aromatic carbons of NPA appeared as four peaks at 150.7, 129.6, 121.2, and 135.7 ppm, which are due to ^1C , $^3\text{C}/^5\text{C}$, $^2\text{C}/^6\text{C}$, and ^4C atoms, respectively. The well-resolved peak at 65.6 ppm is due to the O—CH₂ group. The less intensive peaks at 48.61 and 54.1 ppm are due to the epoxy ring carbons of GMA. The α -methyl carbon of GMA appeared at 19.1 ppm. The disappearance of 131.20 and 128.4 ppm peaks of vinylic carbons of the monomer also explains the polymerization of both the monomeric units. Thus, the incorporation of the two monomeric units in the copolymer was confirmed by the upfield shift for the CH₂=CH group carbons.

^1H -NMR Spectroscopy

The proton NMR spectrum of the poly(NPA) shows doublet signals at 8.20 and 7.45 ppm due to the two types of protons present in the benzene ring. The multiplets at 1.58 and 2.30 ppm are due to methine and methylene protons.

^1H -NMR spectra of poly(NPA-co-GMA)

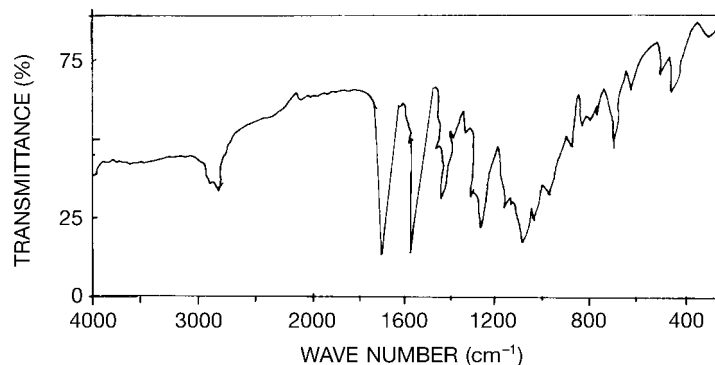


Figure 1 Infrared spectrum of poly(NPA-co-GMA); $m_1 : m_2$: 0.53 : 0.47.

(0.53 : 0.47 mol %) is shown in Figure 3. Aromatic protons of the NPA unit appeared at 8.2 and 7.41 ppm as doublets. The signals at 4.25–3.51, 3.5–3.14, and 3.13–2.21 ppm are due to the O—CH₂, methylene, and methine protons of the epoxy group, respectively. The backbone protons of NPA overlapped with the backbone protons of GMA.

Determination of Copolymer Composition

The ¹H-NMR technique is a well-established method for the determination of the copolymer composition. The distribution of protons in the two units is an important means of identifying a monomer in the copolymer chains. Thus, the mol fraction of NPA in the copolymer chain was determined from the integrated intensities of well-separated aromatic protons of NPA with

the rest of the aliphatic protons of NPA and GMA units:

$$C = \frac{\text{integrated intensities of aromatic protons } (I_A)}{\text{integrated intensities of total aliphatic protons } (I_a)} \quad (1)$$

This method of calculation was earlier employed by Soundararajan and Reddy¹⁶ for the accurate determination of copolymer composition by ¹H-NMR spectroscopy. The equation is based on the fact that there are four aromatic and three aliphatic protons in NPA and 10 aliphatic protons in GMA. Let m_1 be the mol fraction of NPA and $m_2 = (1 - m_1)$ be that of GMA; the following equation was derived:

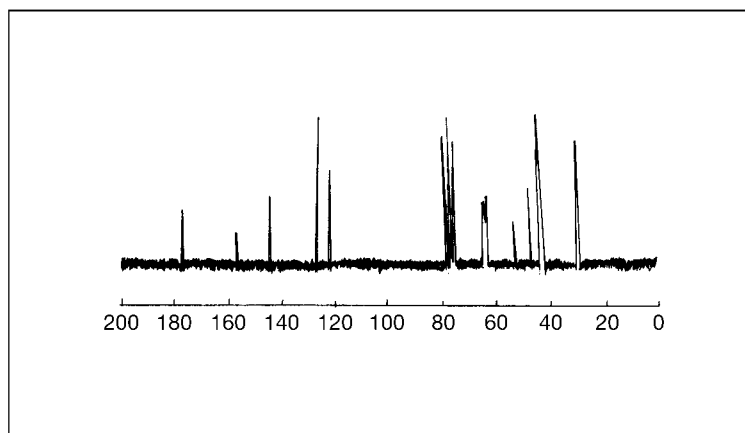


Figure 2 Proton decoupled ¹³C-NMR spectrum of poly(NPA-co-GMA); $m_1 : m_2$: 0.53 : 0.47.

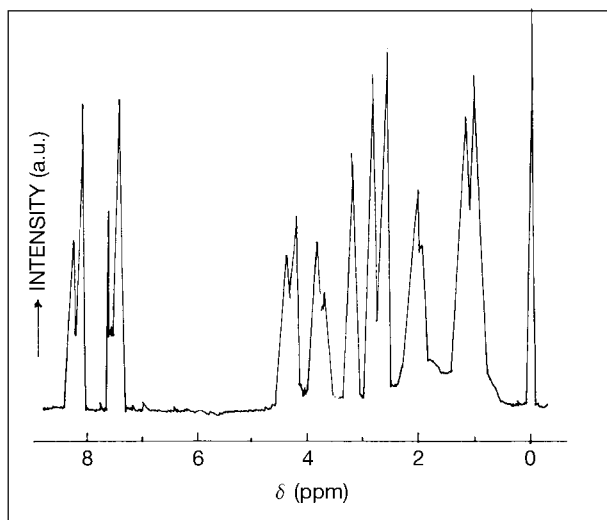


Figure 3 $^1\text{H-NMR}$ spectrum of poly(NPA-co-GMA); $m_1 : m_2$: 0.53 : 0.47.

$$m_1 = \frac{10C}{7C + 4} \quad (2)$$

The copolymer compositions and the values of C are presented in Table I. A plot of feed versus copolymer composition (Fig. 4) indicates the formation of an azeotrope at an NPA : GMA = 34.5 : 65.5 mol % composition.

Reactivity Ratios

From the copolymer composition and monomer feed ratios, the reactivity ratios of NPA and GMA were determined by F-R,¹⁷ K-T,¹⁸ and extended K-T¹⁹ methods. The K-T equation was better over the F-R method as the experimental values distribute symmetrically be-

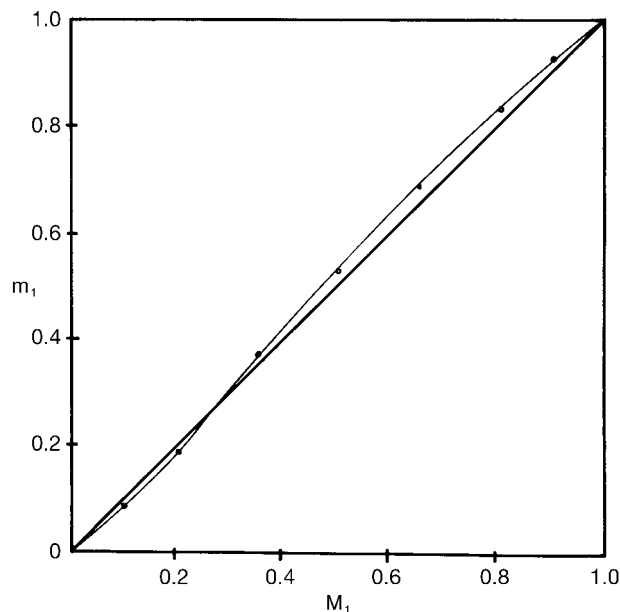


Figure 4 Composition curves of NPA-GMA copolymer system.

tween zero and one. A least-square fit method was adopted for the determination of reactivity ratios. The parameters for the F-R and K-T methods are presented in Table II. Figure 5 represents the K-T plot of the poly(NPA-co-GMA) system. The 95% confidence intervals were also calculated as per the procedure given by K-T. r_1 and r_2 determined by the three methods are given for comparison in Table III.

From the value of $1/r$, the tendency of the NPA radical to polymerize with its own monomer preferentially than with the addition of GMA was predicted. The S-shaped curve from the plot of feed versus copolymer composition confirms the forma-

Table II F-R and K-T Parameters on NPA and GMA Copolymer System

Sample No.	$F = M_1/M_2$	$f = m_1/m_2$	$G = F(f - 1)/f$	$H = F^2/f$	$\xi = G/\alpha + H$	$\eta = H/\alpha + H$
1	0.1111	0.0977	-1.0261	0.1263	-0.9317	0.1147
2	0.2500	0.2361	-0.8089	0.2647	-0.6525	0.2135
3	0.5385	0.5605	-0.4223	0.5173	-0.2830	0.3467
4	1.0000	1.1277	0.1132	0.8866	0.0608	0.4763
5	1.8571	2.2363	1.0267	1.5423	0.4079	0.6127
6	4.0000	4.9172	3.1865	3.2539	0.7535	0.7694
7	9.0000	10.7647	8.1637	7.5246	0.9605	0.8853

$$\alpha = \sqrt{0.1263 \times 7.5246} = 0.975017.$$

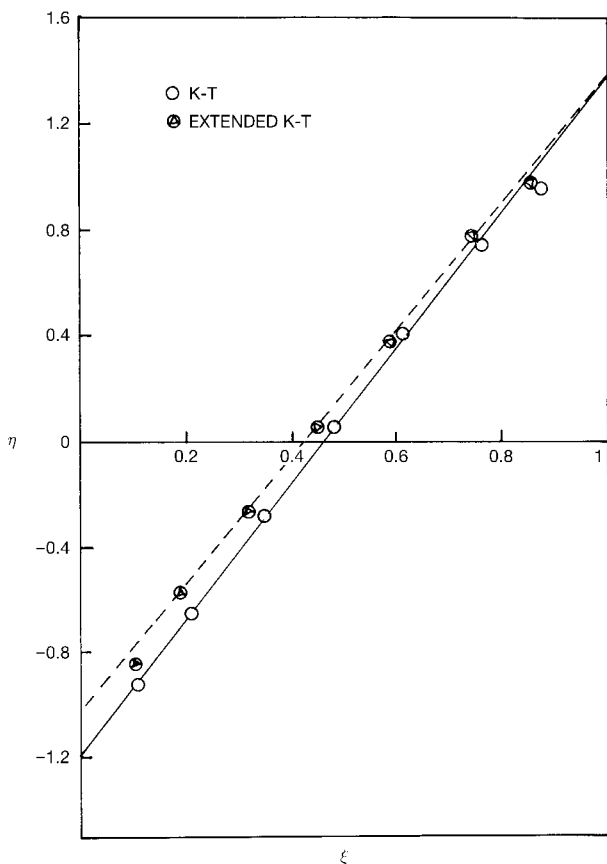


Figure 5 K-T and extended K-T plots of poly(NPA-co-GMA).

tion of an alternate copolymer system having a higher NPA concentration in the copolymer. The product r_1r_2 indicates the existence of an azeotropic composition in the polymer chain with a tendency for alternation.

Molecular Weights

The weight-average (\bar{M}_w) and number-average (\bar{M}_n) molecular weights and the polydispersity indices of poly(NPA) and the copolymers determined by GPC are presented in Table I. The theo-

Table III Comparison of Reactivity Ratios by Various Methods for Poly(NPA-co-GMA)

Methods	r_1	r_2	r_1r_2
F-R	1.44 ± 0.04	1.18 ± 0.05	1.699
K-T	1.37 ± 0.05	1.15 ± 0.02	1.576
Extended K-T	1.38 ± 0.03	1.11 ± 0.05	1.532

retical value of \bar{M}_w/\bar{M}_n for polymers produced via radical recombination and disproportion are 1.5 and 2.0, respectively.²⁰ The value of \bar{M}_w/\bar{M}_n is 1.66 for poly(NPA) and the copolymer suggests that there is a strong tendency for the system to terminate via disproportion as reported in the case of other acrylates.²⁰ The polydispersity indices of the copolymer increases with increase in the NPA unit.

Thermogravimetric Analysis

Thermogravimetric analysis (Fig. 6) was used to estimate the percent weight loss of the copolymer which underwent decomposition. The TGA data for poly(NPA) and different copolymer samples are shown in Table IV. The actual decomposition range depends on the composition of the copolymers. There are two stages in the decomposition of poly(NPA), whereas in the copolymer, only single-stage decomposition is observed. The initial decomposition temperature of the copolymers vary between the poly(NPA) on the lower-temperature side and poly(GMA) on the higher-temperature side. In copoly(NPA-GMA), initial decomposition occurred around 190–225°C, depending on the NPA monomer content. The initial decomposition increases with increase in the GMA concentration, thereby forming a thermally more stable copolymer than its homopolymer. The glass transition temperatures of poly(NPA) is 73°C,

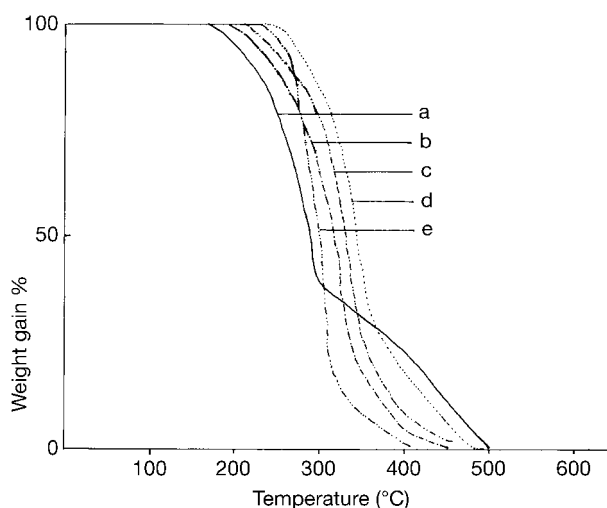


Figure 6 Thermogravimetric analysis (TGA) curves in air for poly(NPA-co-GMA) mol fractions of NPA in the copolymer: (a) 1.00, (b) 0.19, (c) 0.53, (d) 0.83; (e) poly(GMA).

Table IV Thermogravimetric Analysis of Copolymers of NPA with GMA

Copolymer Composition		Decomposition Temperature (°C)		Temperature (°C) of Weight Loss (%) of Copolymers				
m_1	m_2	Stage I	Stage II	10	25	50	75	90
1.000	0.000	165–300	300–505	218	260	290	386	485
0.190	0.809	190–450		245	307	316	338	377
0.530	0.470	210–420		258	285	330	352	392
0.831	0.169	245–475		285	318	345	378	435
0.000	1.000	225–410		290	280	300	320	340

and of copoly(NPA–GMA) (0.53 : 0.47 mol %), 82.1°C.

CONCLUSIONS

Nitrophenyl acrylate was synthesized and characterized. Copolymers of NPA–GMA of different compositions were prepared. IR and NMR spectra confirmed the presence of both monomeric constituents in the copolymer structure. The reactivity ratios from F–R, K–T, and extended K–T methods are within the experimental error, i.e., $r_1 = 1.39$ and $r_2 = 1.18$ indicates that NPA is more reactive and the copolymer structure was found to be alternate in nature. This is confirmed by the feed vs. copolymer composition curve. The thermal stability of the copolymers were compared.

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