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U. Senthilkumar[a]; R. Balaji[a]; R. Arun Prasath[a]; S. Nanjundan[a]
[a] Department of Chemistry, College of Engineering, Anna University, Chennai, India

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SYNTHESIS AND CHARACTERIZATION OF HOMO- AND COPOLYMER OF 2-(*N*-PHTHALIMIDO)ETHYL METHACRYLATE AND STYRENE

U. Senthilkumar, R. Balaji, R. Arun Prasath, and S. Nanjundan*

Department of Chemistry, College of Engineering, Anna University,
Chennai 600 025, India

ABSTRACT

2-(*N*-Phthalimido)ethanol (NPE) was prepared by reacting phthalic anhydride with ethanolamine in dimethy formamide medium. The NPE thus obtained was reacted with methacryloyl chloride in the presence of triethylamine to form the monomer, 2-(*N*-Phthalimido)ethyl methacrylate (NPEMA). Free radical polymerization technique was used to synthesize the homopolymers and copolymers of different composition of NPEMA and styrene in 2-butanone solution at 70°C ± 1°C using benzoyl peroxide as initiator. The monomer and the polymers were characterized by IR and ^{1}H-NMR techniques. 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 were carried out in air. The solubility of the polymers were also studied. The composition of the copolymers was inferred from the ^{1}H-NMR data obtained. The reactivity ratios of the monomers were determined by the application of FinemanRoss and Kelen-Tüdös methods.

Key Words: 2-(*N*-Phthalimido)ethyl methacrylate; Reactivity ratios copolymers; Styrene ^{1}H-NMR

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*To whom correspondence should be addressed.

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INTRODUCTION

Phthalimido group containing polymers are found to possess excellent heat resistant property, durability, and transparency. Copolymers of styrene with methacrylic monomer have been used in the automotive industry for coating purposes (1). Copolymers containing phthalimide derivatives have been used as optical brightening agents (2). Methacrylic copolymers with styrene have been widely used for the production of transparent film (3) and in paper coating (4). The composition of copolymers and the reactivity ratios of the comonomers have been determined by ^{1}H-NMR spectroscopic techniques (5–8) for evaluating the specific application of copolymers.

The present work was undertaken with a view to develop heat-resistant transparent polymer films based on the copolymer of 2-(*N*-phthalimido)ethyl methacrylate (NPEMA) with styrene. The article describes the synthesis and characterization of homopolymers and copolymers of NPEMA and styrene. It also describes the reactivity ratios and thermal stability of the polymers.

EXPERIMENTAL

Materials

Phthalic anhydride (Ranbaxy) dried under vacuum was used without further purification. Ethanolamine (BDH) was purified by the standard method. Methacryloyl chloride was prepared using the method described by Stempel et al. (9). The monomer, styrene (Fluka) was purified by adopting the conventional method and finally distilled under reduced pressure. Benzoyl peroxide (BPO, Merck) was recrystallized from 1:1 chloroform–ethanol mixture. Fractionally distilled solvents were used for all reactions.

Synthesis of 2-(*N*-Phthalimido) Ethanol (NPE)

Phthalic anhydride (14.8 g, 0.1 mol) dissolved in dimethyl formamide (DMF) (60 mL), was placed in a 250-mL three-necked flask equipped with a stirrer, reflux condenser, and a nitrogen inlet. Ethanolamine (6 mL, 0.1 mol) was then added dropwise to the reaction mixture and kept cool in an ice bath. After the addition, the contents were heated in an oil bath at 130°C for 12 h in nitrogen atmosphere. The solvent was partly distilled off and the solution was transferred into a beaker. On cooling, a solid product was obtained. The final product was filtered and recrystallized with rectified ethanol. It has a melting point of 126°C and the yield was 80%. The compound formed was characterized by IR and ^{1}H-NMR spectra.

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

NPE (12 g, 0.06 mol) dissolved in 2-butanone (100 mL) and triethylamine (8.3 mL, 0.06 mol) were placed in a 250-mL three-necked flask equipped with a stirrer, nitrogen inlet, and a dropping funnel. The temperature of the reactants was maintained at 0°C to 5°C using an ice bath. A mixture of 5.9 mL (0.06 mol) of methacryloyl chloride and 20 mL of 2-butanone 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 further for 1 hour at room temperature. The triethylamine hydrochloride salt formed was filtered off and the filtrate was mixed with hydroquione (0.5 g) and the solvent was removed in a rotary evaporator. The residue was dissolved in ether and it was washed successively with 0.05% NaOH and distilled water. The solution was dehydrated with anhydrous sodium sulphate and the ether was evoparated in a water bath. The crude product was recrystallized from ethanol. It has a melting point of 91°C and the yield was found to be 60%. The formation of the methacrylic 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 due to methylene and methyl protons), 1760 (C=O stretch due to ester group), 1720 (C=O stretch due to phthalimido group), 1640 (C=C stretch), 1600 and 1450 (aromatic C=C stretch), 1180 (C–O stretch of the ester group) and 715 (C–H out of plane bending). ^{1}H-NMR(ppm): 7.95–7.74 (4H) (aromatic protons), 6.13 (1H) and 5.55 (1H) (olefinic protons), 4.40 (2H) ($-CH_2-O-$), 3.96 (2H) ($>N-CH_2-$), and 1.94 (3H) ($-CH_3$).

Homopolymerization

NPEMA, 2-butanone, and BPO were placed in 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 ± 1°C for 10 h. The contents were then cooled and poured over methanol. The precipitated poly(NPEMA) was filtered, washed with methanol, and purified by dissolving in dimethyl formamide (DMF) and reprecipitating by the addition of methanol. The purified polymer was dried under vacuum at 40°C for constant weight.

Copolymerization

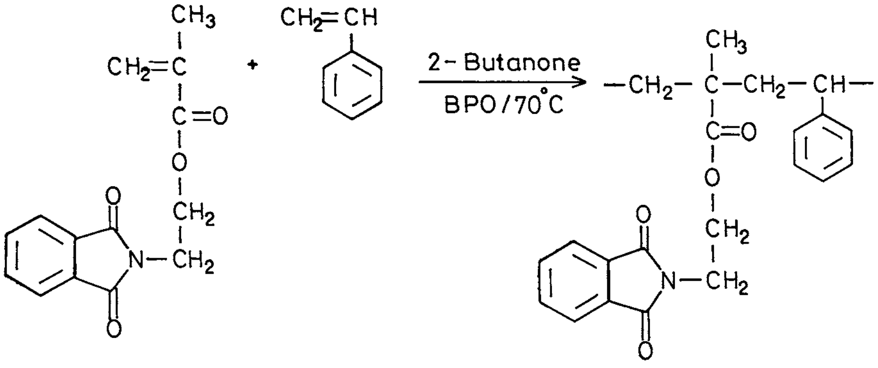
Copolymers of NPEMA and styrene, having different compositions, were synthesized in 2-butanone solution using BPO as a free radical initiator. Predetermined quantities of NPEMA, styrene, BPO (0.25% w/v) and 2-butanone were mixed in a polymerization tube, and the reaction was carried out under a nitrogen atmosphere 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 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. ^{1}H 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 DMSO-d_6. 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 ($\bar{M}_w$ and $\bar{M}_n$) of the polymers were determined using Waters 510 gel permeation chromatograph with polystyrene standards and tetrahydrofuran as the eluent.

RESULTS AND DISCUSSION

The homopolymerization of NPEMA was carried out in 2M solution of the monomer in 2-butanone at 70°C using BPO as initiator. Seven copolymers of NPEMA with styrene having different composition were prepared in 2-butanone by a free radical solution polymerization. The reaction time was restricted to low conversion so that the copolymer equation is obeyed (10). Scheme 1 shows the two monomer units present in the copolymer system.



Scheme 1.

Characterization

Solubility

The solubility of the homopolymer poly(NPEMA) and the poly(2-(*N*-phthalimido)ethyl methacrylate-*co*-Styrene) [poly(NPEMA-*co*-Sty)] were tested in several solvents under cold conditions. The homopolymer and the copolymers were found to be soluble in chloroform, DMF, DMSO, 2-butanone, and THF, but insoluble in a hydroxy group containing solvents like methanol, ethanol, isopropyl alcohol, and water, and in nonpolar solvents like benzene, toluene, and hexane.

IR Spectra

IR spectra of homopolymer of NPEMA shows a peak at 3095 cm^{-1} due to the aromatic C–H stretch. The absorption band at 2950 cm^{-1} and 2880 cm^{-1} are due to the asymmetric and symmetric C–H stretching of methyl and methylene groups. The signal at 1780 cm^{-1} and 1720 cm^{-1} are attributed to the carbonyl stretching of ester group and phthalimido group, respectively. The peak at 1600 cm^{-1} and 1450 cm^{-1} are due to the C═C stretch of the aromatic ring. The peak at 1195 cm^{-1} is due to the C–O stretch of the ester group. The peak at 700 cm^{-1} is due to the out-of-plane C–H bending vibration of the disubstituted benzene.

The IR spectrum of poly(NPEMA-*co*-Sty) shows an absorption peak at 3090 cm^{-1} due to the aromatic C–H stretching. The peaks at 2940 cm^{-1} and 2850 cm^{-1} are attributed to asymmetric and symmetric C–H stretching of methyl and methylene groups. The absorption peaks at 1775 cm^{-1} and 1720 cm^{-1} are due to the carbonyl stretching of the ester group and the phthalimido group, respectively. The peaks at 1600 cm^{-1} and 1450 cm^{-1} correspond to the C═C stretching of the aromatic ring. The peak at 1190 cm^{-1} is attributed to the C–O stretch of the ester group. The peak at 720 cm^{-1} is due to the out-of-plane C–H bending vibration of ortho-disubstituted benzene.

^{1}H-NMR Spectra

The ^{1}H-NMR spectrum of poly(NPEMA) shows a resonance signal from 7.88 to 7.56 ppm due to the aromatic protons. The peak at 4.46 ppm is due to the methyleneoxy protons. The $-NCH_2-$ protons show a peak at 3.98 ppm. The signal between 1.85 and 1.60 ppm is due to the methylene protons, while the signal from 1.25 to 0.85 ppm is due to the methyl protons.

The ^{1}H-NMR spectrum (Fig. 1) of poly(NPEMA-*co*-Sty) [0.46:0.54] shows peaks between 7.88 and 7.50 ppm due to the aromatic protons of the NPEMA unit. The signal between 7.34 and 6.80 ppm corresponds to the aromatic protons of styrene unit. The signal at 4.05 ppm is attributed to methyleneoxy proton. The signal at 3.82 ppm is attributed to $-NCH_2-$ protons. The methyne and methylene protons of NPEMA and styrene shows a broad band between 2.25 and 1.35 ppm. The peak at 0.85 ppm is due to the methyl group.

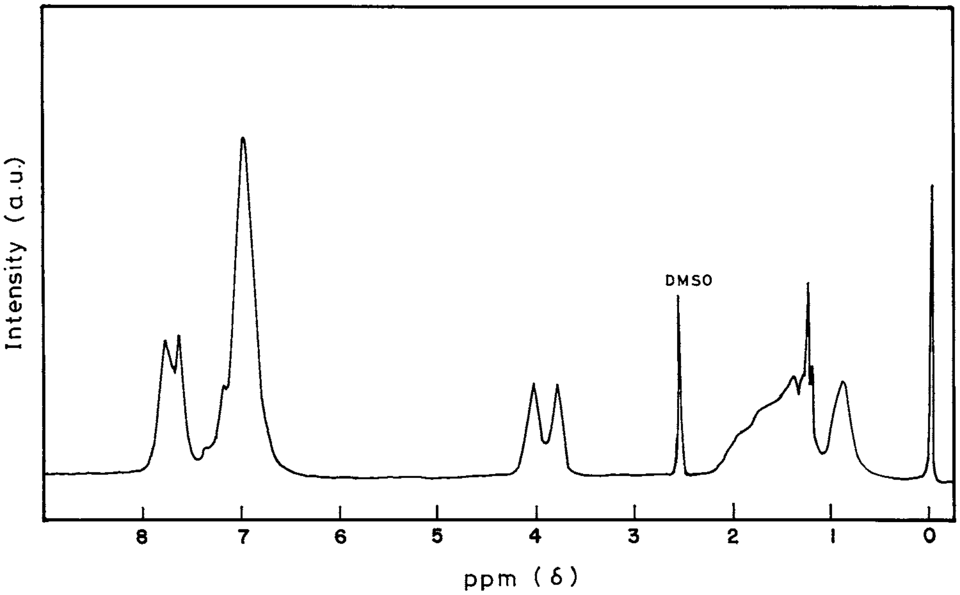


Figure 1. ^{1}H-NMR spectrum of poly(NPEMA-*co*-Sty) (0.46:0.54).

Molecular Weights

The number and weight average molecular weights ($\bar{M}_w$ and $\bar{M}_n$) and polydispersity index of homopolymers, as well as copolymers determined by gel permeation chromatography, are given in Table 1. The polydispersity index value 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 disproportionation were 1.5 and 2, respectively (11). This suggests that poly(NPEMA) was produced primarily via termination of growing chain by disproportionation. Polydispersity index values of the copolymers suggest that at lower mole fraction of styrene in the feed, the chain termination occurs predominantly by disproportionation and at higher mole fractions of styrene in the feed, the chain termination occurs predominantly by radical recombination.

Thermal Analysis

The TG and DTG traces of poly(NPEMA), poly(Sty), and poly(NPEMA-*co*-Sty) are shown in Figure 2. The thermal stability of the polymers were identified by estimating the percentage weight loss of the polymers on thermal decomposition. The TGA data for the homopolymers and the copolymers at various temperatures are shown in Table 2. The decomposition temperature of the copolymers depends on the composition of the constituent monomeric units in the copolymer. The thermogram clearly shows that polystyrene, poly(NPEMA) and poly (NPEMA-*co*-Sty) undergoes decomposition in a single stage. The initial decomposition temperature

Table 1. Molecular Weight Data for Polymers of NPEMA and Styrene

Polymers	m_1	Molecular Weights $\bar{M}_w \times 10^{-4}$	$\bar{M}_n \times 10^{-4}$	$\bar{M}_w/\bar{M}_n$
Poly(NPEMA)	1.000	5.81	2.98	1.95
Poly(NPEMA-*co*-Sty)	0.886	5.34	2.87	1.86
	0.769	5.10	2.82	1.81
	0.614	4.92	2.78	1.77
	0.457	4.68	2.72	1.72
	0.323	4.41	2.64	1.67
	0.181	4.38	2.59	1.69
	0.087	4.12	2.48	1.66
Poly(Sty)	0.000	3.83	2.34	1.64

m_1 is the mole fraction of NPEMA in the copolymer.

of poly(NPEMA-*co*-sty) (0.56:0.44) was 296°C and those of poly(NPEMA) and poly(Sty) were 325°C and 258°C, respectively. TGA results indicate that the incorporation of NPEMA unit in the copolymer chain increases the thermal stability of the copolymers.

Copolymer Compositions

The copolymer composition was determined by ^{1}H-NMR spectral analysis of the copolymer. The resonance signals shown between 7.88 and 6.8 ppm correspond to 4 aromatic protons of NPEMA unit and 5 aromatic protons of styrene unit. The signals between 4.14 and 3.71 ppm correspond to $>N{-}CH_2\ CH_2O{-}$ group. Hence, in the present investigation, the copolymer composition were determined by measuring the ratios of integrated peak intensities of aromatic protons to that of the proton in the $>N{-}CH_2\ CH_2O{-}$ group.

Table 2. TGA Data for Homopolymers and Copolymers of NPEMA and Styrene

Polymers	Copolymer Composition $m_1{}^a$	$m_2{}^a$	IDT °C^b	Temperature (°C) at Different Weight Loss (%) 10%	30%	50%	70%	90%
Poly(NPEMA)	1.00	0.00	325	368	394	406	427	442
Poly(NPEMA-*co*-Sty)	0.77	0.23	311	357	388	401	420	438
	0.46	0.54	296	342	380	394	409	434
	0.18	0.82	274	328	370	385	398	431
Poly(Sty)	0.00	1.00	258	322	364	381	392	424

[a] m_1 and m_2 are the mole fractions of NPEMA and styrene in the copolymers, respectively.
[b] IDT indicates initial decomposition temperature.

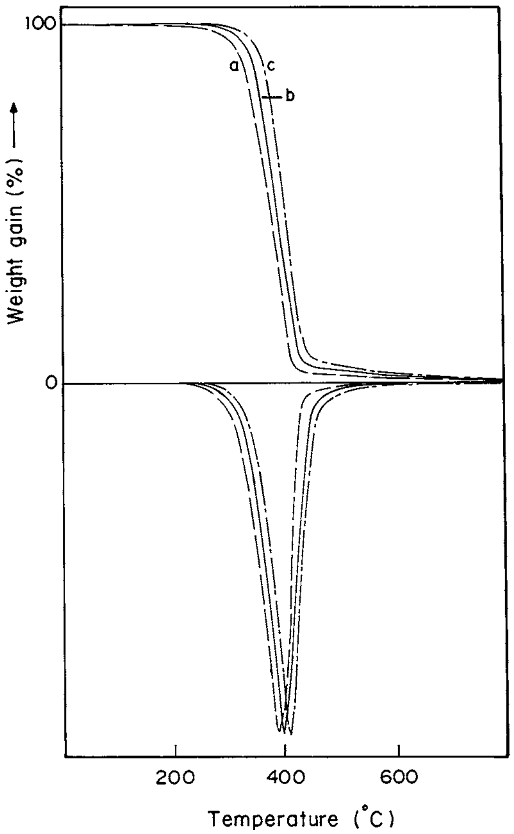


Figure 2. TG-DTG curves of: a) poly(Sty); b) poly(NPEMA-*co*-Sty) [0.46:0.54]; and c) poly(NPEMA).

If m_1 is the mole fraction of NPEMA and $(1 - m_1)$ be that of styrene, then

$$C = \frac{\text{Intensities of} >\text{N–CH}_2\text{CH}_2\text{O– protons}}{\text{Intensities of aromatic protons}} = \frac{4m_1}{4m_1 + 5(1 - m_1)} \tag{1}$$

which, on further simplification gives:

$$m_1 = \frac{5C}{4 + C} \tag{2}$$

Based on Equation (2), the mole fraction of NPEMA in all the copolymers was calculated by measuring the signal intensities of $>N–CH_2CH_2O–$ protons and aromatic protons from the spectra of all copolymers. Table 3 gives the values of C and the corresponding mole fraction in the copolymers. The kinetic behavior was determined by plotting the mole fraction of NPEMA in the feed against that in the copolymer (Fig. 3).

Table 3. Composition Data for the Free Radical Copolymerization of NPEMA with Styrene in 2-Butanone Solution at 70 ± 1°C

Feed Composition $(M_1)^a$	Conversion (%)	Intensities of Protons $I_{>NCH_2CH_2O-}$	 I_{Arom}	C	Copolmer Compostion $(m_1)^a$
0.10	7.8	5.0	70.5	0.0709	0.087
0.20	9.1	7.0	46.5	0.1505	0.181
0.35	7.3	10.5	38.0	0.2763	0.323
0.50	8.3	18.5	46.0	0.4022	0.457
0.65	5.9	21.0	37.5	0.5600	0.614
0.80	6.8	24.0	33.0	0.7270	0.769
0.90	6.3	28.0	32.5	0.8615	0.886

[a] M_1 and m_1 are the mole fractions of NPEMA in the feed and in the copolymers, respectively.

Reactivity Ratios

The type of copolymer formed will be understood from the values of reactivity ratio of the comonomers. By the application of the Fineman-Ross (F-R) (12) and Kelen-Tüdös (K-T) (13) methods, the reactivity ratios of NPEMA and styrene were evaluated from the monomer feed ratios and the resultant copolymer compositions. The significance of parameters of F-R and K-T equations are presented in Table 4. The rectivity ratios for NPEMA (r_1) and styrene (r_2) from the F-R plot (Fig. 4) and K-T plot (Fig. 5) are:

$$\text{F-R method: } r_1 = 0.88 \pm 0.03; \quad r_2 = 1.15 \pm 0.02$$

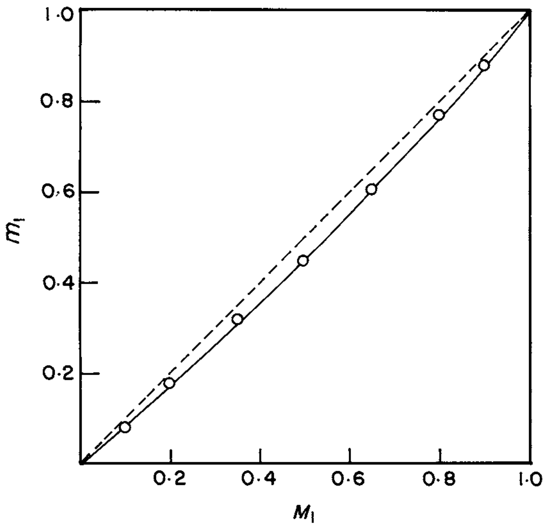


Figure 3. Composition diagram of NPEMA-Styrene copolymer system.

Table 4. F-R and K-T Parameters for the Copolymers of NPEMA with Styrene

$F = M_1/M_2$	$f = m_1/m_2$	$G = F(f-1)/f$	$H = F^2/f$	$\eta = G/(\alpha + H)^a$	$\xi = H/(\alpha + H)^a$
0.1111	0.0953	−1.0547	0.1295	−0.8167	0.1003
0.2500	0.2210	−0.8812	0.2828	−0.6099	0.1958
0.5385	0.4771	−0.5902	0.6078	−0.3335	0.3435
1.0000	0.8416	−0.1882	1.1882	−0.0800	0.5056
1.8571	1.5906	0.6895	2.1683	0.2070	0.6511
4.0000	3.3290	2.7980	4.8062	0.4688	0.8053
9.0000	7.7719	7.8420	10.422	0.6769	0.8990

[a] α is equal to 1.1618.

$$\text{K-T method: } r_1 = 0.87 \pm 0.02; \quad r_2 = 1.14 \pm 0.03$$

The value of r_1 is less than 1 and that of r_2 greater than 1, which indicates the presence of higher amount of styrene units in the copolymer than in the feed. However, the product of r_1 and r_2 remains close to 1, which indicates that the system follows a random distribution of the monomeric unit.

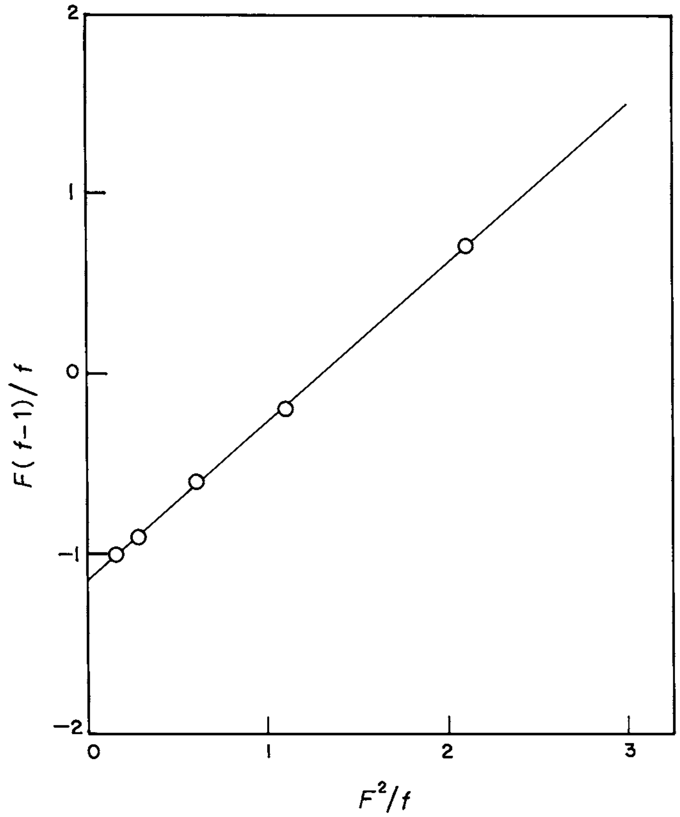


Figure 4. F-R plot for the NPEMA-Styrene copolymer system.

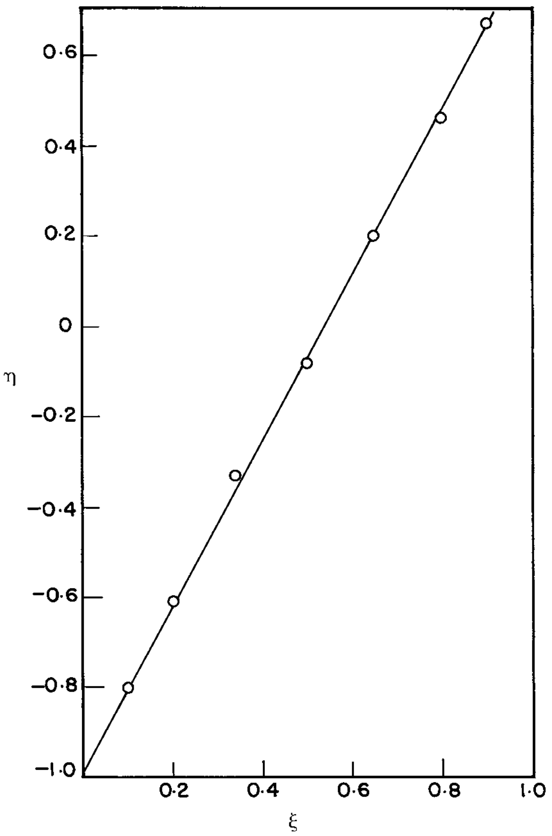


Figure 5. K-T plot for the NPEMA-Styrene copolymer system.

CONCLUSION

The methacrylic monomer, NPEMA was synthesized. Poly(NPEMA) and copolymers of NPEMA and styrene having different compositions were synthesized in solution by free radical polymerization. The formation of the monomer and the polymers was confirmed by the IR and ^{1}H-NMR spectroscopic techniques. GPC data suggest that poly(NPEMA) was produced primarily via termination of growing chains by disproportionation and with increase in the composition of NPEMA in the feed, the tendency for chain termination by disproportionation increases. Thermogravimetric analysis results indicate that the incorporation of NPEMA unit in the copolymer chain increases the thermal stability of the copolymers. The copolymer compositions were evaluated from ^{1}H-NMR spectra of the copolymers. The reactivity ratios obtained from F-R and K-T methods are in good agreement. The value of r_1 is less than 1 and that of r_2 is greater than 1 indicating that styrene is more reactive than NPEMA. The value of the product of r_1 and r_2 shows the random distribution of the monomeric units in the copolymers.

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