SYNTHESIS AND CHARACTERIZATION OF COPOLYMERS OF 2-N-PHTHALIMIDO-2-METHYL PROPYL METHACRYLATE WITH METHYL METHACRYLATE AND DETERMINATION OF COPOLYMER REACTIVITY RATIOS

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ABSTRACT

2-N-Phthalimido-2-methyl propan-1-ol was prepared by refluxing phthalic anhydride dissolved in dimethyl formamide with 2-amino-2-methyl propan-1-ol. The monomer, 2-N-phthalimido-2-methyl propyl methacrylate was synthesized by reacting 2-N-phthalimido-2-methyl propan-1-ol dissolved in ethyl acetate with methacryloyl chloride in the presence of triethylamine. Free radical polymerization technique was used to synthesize the homo and copolymers of different feed composition of 2-N-phthalimido-2-methyl propyl methacrylate and methylmethac-rylate in ethyl acetate solution using benzoyl peroxide as a free radical initiator at 70°C. The IR and ^{1}H-NMR spectroscopic techniques were used for the characterization of the polymers. The compo-

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sition of the copolymers were determined by ^{1}H-NMR analysis. The reactivity ratios of the co-monomers were evaluated according to Fineman-Ross and Kelen-Tüdös methods.Thermal analysis of the polymers were carried out using TGA-DTG method. Gel permeation chromatography was used for determining the molecular weights (M_w and M_n) and polydispersity index of the polymers. The solubility and intrinsic viscosity of the homopolymer and copolymers were determined.

INTRODUCTION

Methacrylic copolymers of methyl methacrylate have gained great importance in various fields of industrial application [1]. Methacrylic copolymers are widely used as binders in protective coatings because of their durability and transparency [2]. Recently, methacrylic copolymers are used as primers for automotive finishes, clean lacquers for household appliances [3]. Polymers having phthalimido group in the main chain are having excellent heat resistance properties and transparency. Copolymers containing the phthalimide derivatives have been used as optical brightening agents [4]. Because of these properties, phthalimide copolymers are used in paint coatings and insulating products manufacturing. N-Substituted phthalimide copolymers have been used as activated drug binding materials [5].

The accurate estimation of copolymer composition and determination of reactivity ratios is significant for tailor making copolymers with required physico chemical properties and in evaluating the end applications of copolymers. For the estimation of copolymer composition, ^{1}H-NMR analysis has been used as a powerful tool [6-8]. The present research paper reports the synthesis, characterization and determination of reactivity ratios for the comonomers, 2-N-phthalimido-2-methyl propyl methacrylate (NPMPM) and methylmethacrylate (MMA).

EXPERIMENTAL

The monomer, methyl methacrylate was purified by conventional methods and then, subjected to vacuum distillation under nitrogen [9]. Benzoyl peroxide (BPO) was recrystallized from a methanol-chloroform (1:1) mixture. Phthalic anhydride (Fluka) was used as such without further purification. The

solvents were purified by standard methods. 2-Amino-2-methyl propan-1-ol was allowed to stand over anhydrous sodium sulphate, decanted and the fraction boiling at 120°C at 10 mm was collected and used for synthesis.

Synthesis of 2-N-Phthalimido-2-Methyl Propyl Methacrylate [NPMPM]

Phthalic anhydride (20 g, 0.13 mol) dissolved in 70 ml of dimethyl formamide (DMF) was placed in a 250 ml flask. 2-Amino-2-methyl propan-1-ol (13 ml, 0.13 mol) was added dropwise with constant stirring and refluxed for 8 hours at 130°C. After completion of the reaction, the solvent was removed from the product by reduced pressure distillation. The product 2-N-phthalimido-2-methyl propan-1-ol was purified by reduced pressure distillation. Methacryloyl chloride was prepared by reacting methacrylic acid with benzoyl chloride [9]. 2-N-Phthalimido-2-methyl propan-1-ol (16.4 g, 0.08 mol), triethylamine (10.5 ml, 0.08 mol) dissolved in ethylacetate (100 ml) were placed in a 500 ml three-necked flask and the temperature of the reactants was maintained around 0°C. Methacryloyl chloride (7.3 ml, 0.08 mol) dissolved in 15 ml of ethyl acetate was added dropwise to this solution with constant stirring and cooling. After 1 hour, the temperature of the reaction mixture was allowed to rise to 30°C and the contents were stirred for an additional hour. The quaternary ammonium salt formed was filtered off and the filtrate was washed with distilled water, dried over anhydrous sodium sulphate, and the solvent was evaporated in a rotary evaporator. The crude NPMPM was purified by reduced pressure distillation and the liquid boiling at 86°C at 10 mm pressure was collected. The monomer formation was confirmed by IR and 1H-NMR techniques.

IR (cm^{-1}): 3100 (aromatic =C-H stretching), 2920 and 2850 (asymmetric and symmetric C-H stretching due to CH_3 and CH_2 groups), 1745 (C=O stretching due to the ester group), 1725 (C=O stretching due to phthalimido group), 1645 (aliphatic C=C stretching), 1600 and 1450 (aromatic C=C stretching), 1380 (>CMe$_2$), 1205 (C-O stretching), 960 and 645 (out of plane C-H bending due to ortho di-substituted benzene ring).

^{1}H-NMR (ppm): 7.80-7.73 (4H) (aromatic), 6.54-6.03 (2H) (=CH$_2$), 5.50 (1H) (=CH-), 4.50 (2H) (-CH$_2$O), 1.90-1.08 (6H) (>CMe$_2$).

Copolymerization

Copolymerization were carried out in ethyl acetate solution using BPO as free radical initiator at 70°C. Appropriate amounts of NPMPM, MMA, BPO and the solvent were mixed in a polymerization tube, degassed with nitrogen,

and kept in a thermostated water bath for a predetermined period of time so as to maintain the conversion below 10%. The contents were poured into excess methanol, the precipitated polymer was filtered off and purified by reprecipitation from dimethyl formamide (DMF) solution using methanol and dried in a vacuum oven at 45°C for 12 hours.

Measurements

IR spectra of the samples were recorded with a Hitachi 270-50 IR spectrophotometer on solid samples as KBr pellets and liquid samples using NaCl flats. NMR spectra were obtained with a JEOL JNX-100 FT NMR spectrometer as 15% solution in $CDCl_3$ with TMS as internal standard. Waters 510 Gel Permeation Chromatography with polystyrene standards and THF as the eluent was used for the determination of molecular weights ($\overline{M}_w$ and $\overline{M}_n$) of the polymers. The intrinsic viscosity was measured with Ubbelohde viscometer in DMF solvent at 30°C. Thermogravimetric analysis was carried out with a Mettler 3000 Thermal Analyzer at a heating rate of 15°C/min in air.

RESULTS AND DISCUSSION

Seven copolymers of NPMPM with MMA of different feed compositions were prepared in ethyl acetate by free radical solution polymerization and the copolymerization was restricted to low conversion (less than 10%) so that the copolymer equation is obeyed. The composition data of feeds and copolymers are presented in Table 1.

Characterization

Solubility

The copolymers were soluble in dimethyl formamide, dimethylsulphoxide, dimethyl acetamide, acetone, chloroform and tetrahydrofuran but insoluble in hydroxy group containing polar solvents like water, methanol, and ethanol as well as non-polar solvents like xylene, hexane, benzene, and toluene.

IR Spectra

The IR spectrum of the copolymer of NPMPM with MMA shows peak at 3080 cm^{-1} due to the aromatic C-H stretching. The absorption bands at 2975

TABLE 1. Composition Data for the Free Radical Copolymerization of NPMPM (1) with MMA (2) in Ethyl Acetate Solution at 70°C

Sample No.	Feed Composition M_1	Conversion %	Intensities of protons		$C = \dfrac{I_{Aro}}{I_{Ali}}$	Copolymer Composition m_1
			I_{Aro}	I_{Ali}		
1	0.10	8.3	0.70	3.35	0.2090	0.1489
2	0.20	7.8	1.45	3.75	0.3867	0.2645
3	0.35	8.2	2.40	3.85	0.6233	0.4045
4	0.50	9.2	3.20	3.75	0.8533	0.5275
5	0.65	7.7	4.10	3.70	1.1081	0.6508
6	0.80	8.9	4.90	3.50	1.4000	0.7778
7	0.90	7.9	5.50	3.30	1.6667	0.8824

M_1 and m_1 are the mole fraction of NPMPM in the feed and in the copolymers respectively.

cm^{-1} and 2870 cm^{-1} were attributed to asymmetric and symmetric stretching of methyl and methylene groups. The ester carbonyl stretching was observed at 1770 cm^{-1}. The absence of strong absorption band at 1645 cm^{-1} which was present in the IR spectra of the monomer indicated that the olefinic double bond was involved in polymerization. The peaks at 1605 cm^{-1} and 1450 cm^{-1} were due to C=C stretching of the aromatic ring. The absorption peaks at 1380 cm^{-1} was attributed to the gem dimethyl group. The peak at 1210 cm^{-1} was due to C-O stretching. The absorption due to out of plane C-H bending of the ortho di-substituted benzene was observed at 980 cm^{-1} and 675 cm^{-1}.

^{1}H-NMR Spectra

The ^{1}H-NMR spectrum (Figure 1) of poly(NPMPM-co-MMA) [0.55:0.45] showed peaks between 7.79-7.72 ppm corresponding to aromatic protons of NPMPM. The characteristic signal at 4.21 ppm was due to -CH$_2$O-
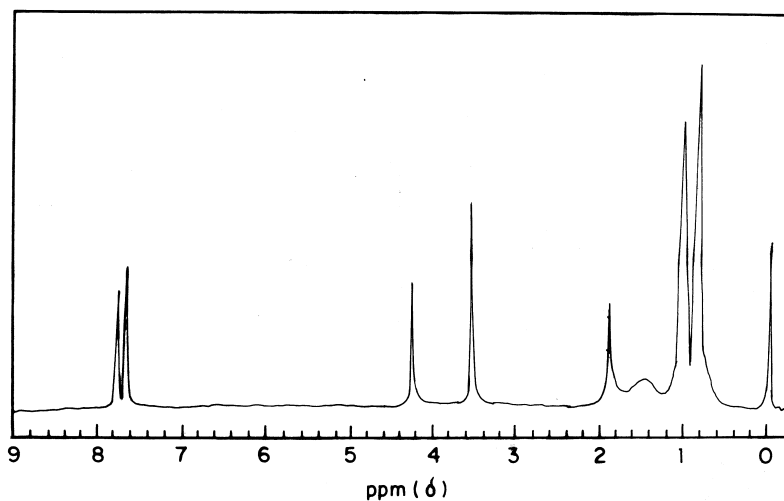
Figure 1. ^{1}H-NMR Spectrum of poly(NPMPM-co-MMA) [0.55:0.45].

group of NPMPM. The signal at 3.62 ppm was attributed to the -OCH$_3$ protons of the MMA unit. The additional broad band between 2.31-1.32 ppm was due to the methyne ($\rightarrow$CH) and methylene (>CH2) protons of the main chain which was not shown by the monomer. The gem dimethyl protons present in NPMPM unit gave signals at 0.84 ppm and 1.00 ppm. The absence of peaks at 6.35 ppm and 6.03 ppm in the NMR of copolymer, which was present in the monomer, suggested that the olefinic double bond was involved in the polymerization.

Copolymer Compositions

Copolymer compositions were determined by ^{1}H-NMR spectral analysis of the copolymers. The copolymer structure may be shown as in Scheme 1. From the resonance peaks of ^{1}H-NMR spectrum, the contents of each kind of monomeric unit incorporated into the copolymer chains were evaluated. Though methoxy and methylenoxy protons do not overlap with the signals due to methylene and methyl groups, in order to avoid about because of the closeness of their chemicals values, the mole fraction of NPMPM in the copolymer was calculated by measuring the ratio of integrated intensity of aromatic protons to that of methoxy and methylenoxy protons.
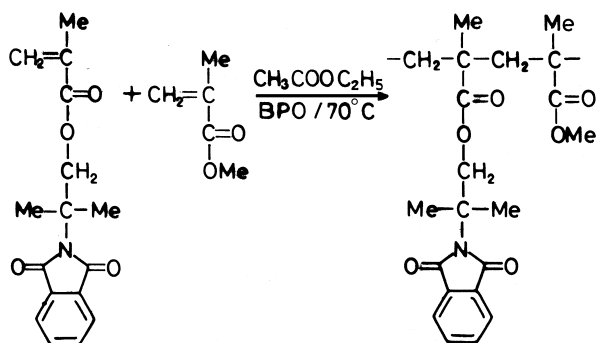
Scheme 1.

The following expression was derived from copolymers consisting of both monomeric units, Let m_1 be the mole fraction of NPMPM and $(1-m_1)$ be that of MMA. NPMPM contains 4 aromatic protons and 2 methylenoxy protons. MMA contains 3 methoxy protons.

$$C = \frac{\text{Intensities of aromatic protons}}{\text{Intensities of methoxy and methylenoxy protons}}$$

$$C = \frac{4\ m_1}{2\ m_1 + 3(1-m_1)} \tag{1}$$

On simplification it gives

$$m_1 = \frac{3C}{4+C} \tag{2}$$

Based on Equation 2, the mole fractions of NPMPM in all copolymers were calculated by measuring the intensities of aromatic, methoxy and methylenoxy proton signals from the spectra of all copolymers. Table 1 gives the values of C and the corresponding mole fractions in the copolymers. The kinetic behavior was determined by plotting the mole fractions of NPMPM in the feed vs that in the copolymer, and the curve is sigmoidal (Figure 2) which indicates
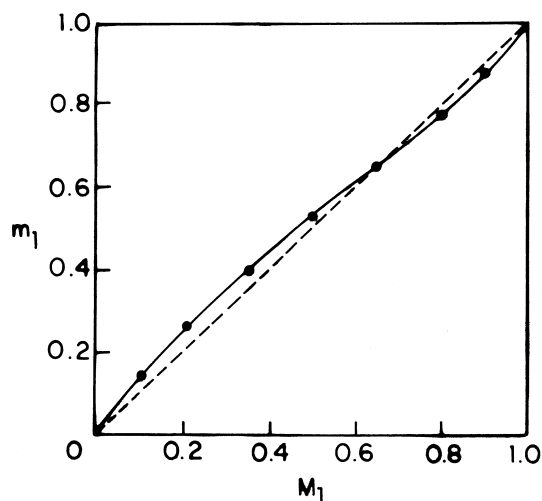
Figure 2.   Composition diagram of NPMPM-MMA copolymer system.

that the distribution of the monomeric unit is nearly statistical and azeotropic copolymerization takes place at a particular composition of the monomer feed.

Reactivity Ratios

The type of copolymer formed will be understood by the values of reactivity ratio of the comonomrs. By the application of Fineman-Ross (F-R) [11] and Kelen-Tüdös (K-T) [12] methods, the reactivity ratios of NPMPM and MMA were evaluated from the monomer feed ratios and the resultant copolymer compositions. A graphical evaluation of the conventional linear equation suggested by Kelen-Tüdös [13] was followed and no corrections for conversion were made to determine the reactivity ratios. The reactivity ratios for NPMPM (r_1) and MMA (r_2) from the F-R plot (Figure 3) and K-T plot (Figure 4) are

F-R method : $r_1 = 0.78 \pm 0.03$ and $r_2 = 0.54 \pm 0.02$

K-T method : $r_1 = 0.77 \pm 0.02$ and $r_2 = 0.55 \pm 0.03$

Since r_1 and r_2 values are less than 1, this system gives rise to azeotropic polymerization at a particular composition of the monomers which is calculated using the following equation.
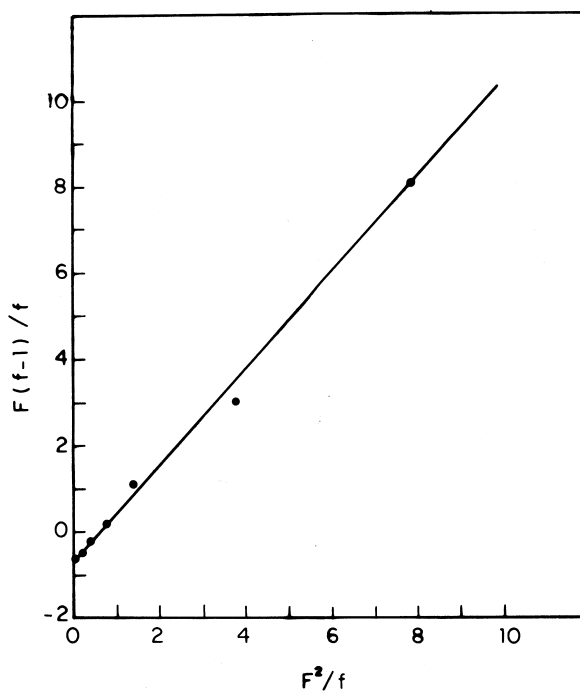
Figure 3. F-R plot for NPMPM-MMA copolymer system.

$$N_1 \quad = \quad \frac{(1\text{-}r_2)}{(2\text{-}r_1\text{-}r_2)} \quad = \quad 0.662 \tag{3}$$

When the mole fraction of the monomer, NTMPM in the feed is 0.662, the copolymer formed will have the same composition as that of the feed. When the mole fraction of the feed is less than 0.662 with respect to NTMPM, the copolymer is relatively richer in this monomer than the feed. When the mole fraction of NTMPM in the feed is above 0.662, the copolymer is relatively richer in MMA unit than in the feed. The product of r_1 and r_2 ($r_1.r_2 = 0.42$) remains much less than 1, which indicates that the system shows greater tendency to alternate.
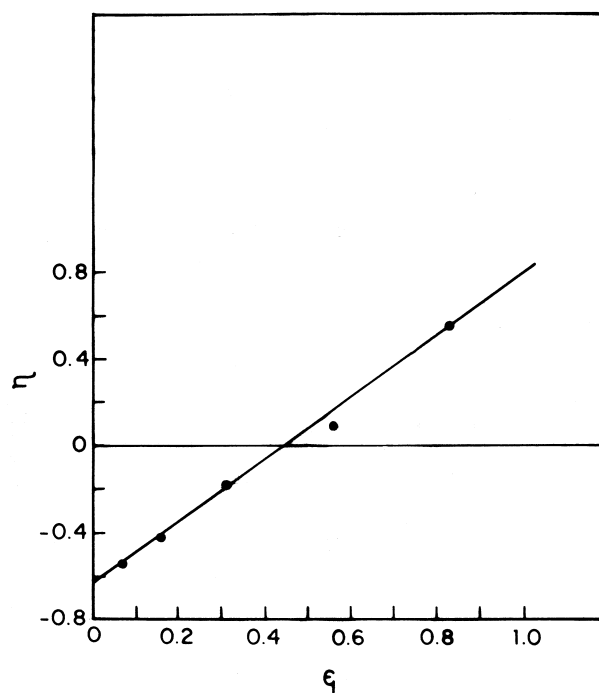
Figure 4. K-T plot for NPMPM-MMA copolymer system.

Thermal Analysis

Thermogravimetric analysis was used in estimating the percentage weight loss of the copolymer which undergoes decomposition. The actual decomposition temperature range depends upon the composition of the constitutional monomeric units in the copolymers. The TGA and DTG traces of poly(NPMPM), poly(MMA) and poly(NPMPM-co-MMA) are presented in Figure 5. Table 2 shows the data of the weight loss at various temperatures. Figure 5 clearly indicates that poly(MMA), poly(NPMPM) and the copolymer poly(NPMPM-co-MMA) undergo decomposition in a single stage.

The initial decomposition temperature of poly(NPMPM-co-MMA) [0.55/0.45] was 206°C and those of poly(NPMPM) and poly(MMA) were 152°C and 275°C, respectively. TGA results indicated that the thermal stability of the copolymers were increased by the incorporation of MMA unit with NPMPM.
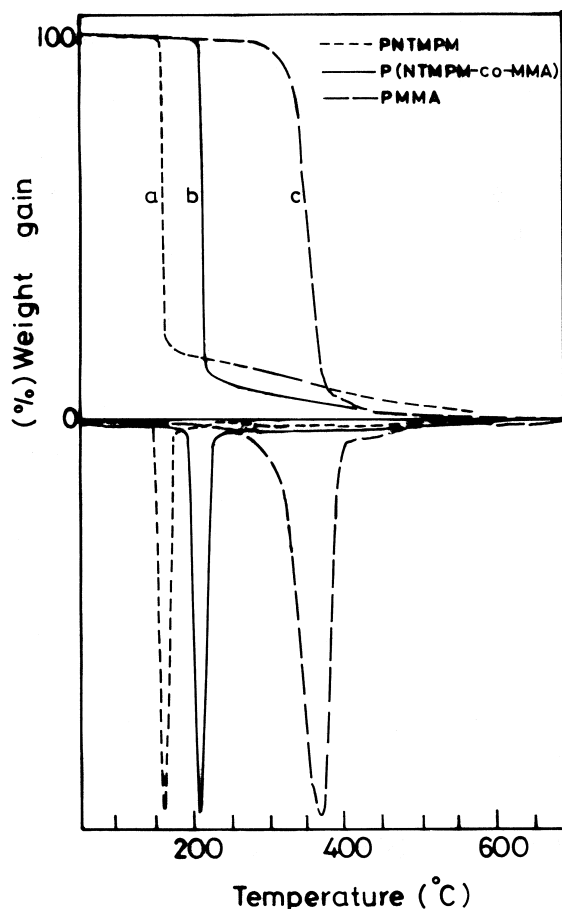
Figure 5. TGA-DTA curve of (a) Poly (NPMPM); (b) Poly(NPMPM-co-MMA) [0.55:0.45]; (c) Poly(MMA).

Molecular Weights

The number and weight average molecular weights ($\overline{M}_w$, $\overline{M}_n$) and poly-dispersity index of homopolymer as well as copolymers were determined by gel permeation chromatography and is given in Table 3. The polydispersity index of poly(NPMPM) is very close to 2. The theoretical values of $\overline{M}_w/\overline{M}_n$ for polymer produced via radical combination and disproportionation were 1.5 and 2 [14, 15]. This suggests that poly(NPMPM) was produced mainly by chain termination by disproportionation. The tendency for chain termination by disproportionation was found to increase with increase in the composition of NPMPM in the feed.

TABLE 2.   TGA Data of Homo and Copolymers of NPMPM and MMA

Polymers	Copolymer composition		IDT °C	Temperature (°C) at different weight loss (%)				
	m_1	m_2		10%	30%	50%	70%	90%
Poly(NPMPM)	1.00	0.00	152	154	200	264	337	387
Poly(NPMPM-co-MMA)	0.81	0.19	178	185	197	209	223	278
	0.55	0.45	206	210	219	225	234	307
	0.26	0.74	225	232	242	258	271	339
Poly(MMA)	0.00	1.00	275	306	338	351	363	375

IDT - Initial decomposition temperature

m_1 and m_2 are the mole fractions of NPMPM and MMA in the copolymers respectively.

Intrinsic Viscosity Measurements

A plot of $\eta sp/C$ vs concentration gave a straight line and the extrapolation of this straight line to zero concentration gave the intrinsic viscosity as the intercept. The value of intrinsic viscosity $[\eta]$ is affected by the composition of the copolymer and the change is not uniform which are clearly given in the Table 3.

CONCLUSION

Poly(NPMPM) and the copolymers of NPMPM and MMA were synthesized in solution by free radical polymerization using benzoyl peroxide initiator at $70 \pm 1°C$. The copolymers were soluble in DMF, DMSO, EMK, acetone, THF, dimethyl acetamide and chloroform and insoluble in ethanol, methanol, water, n-hexane, xylene, toluene and benzene. The characteristic behavior of polymers were confirmed by IR and [1]H-HMR spectroscopic methods. The copolymer

TABLE 3. Molecular Weight and Intrinsic Viscosity Data for Polymers of NPMPM and MMA

Polymers	Feed composition M_1	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(NPMPM)	1.00	2.64	1.34	1.97	0.23
Poly(NPMPM-co-MMA)	0.90	2.47	1.28	1.93	0.21
	0.80	2.65	1.36	1.95	0.24
	0.65	2.54	1.33	1.91	0.23
	0.50	2.38	1.25	1.90	0.20
	0.35	2.47	1.33	1.85	0.23
	0.20	2.58	1.38	1.86	0.24
	0.10	2.63	1.42	1.85	0.27
Poly(MMA)	0.00	2.41	1.31	1.84	-

M_1 is the mole fraction of NPMPM in the feed

composition were calculated from the ^{1}H-NMR spectra of the polymers. The reactivity ratios were determined by both F-R and K-T methods and the values obtained ($r_1 = 0.78 \pm 0.03$, 0.77 ± 0.02; $r_2 = 0.54 \pm 0.02$, 0.55 ± 0.03) are in good agreement. The r_1 and r_2 values of both methods are less than 1 which indicates that the system gives rise to azeotropic polymerization at a particular composition of the feed. The value of $r_1 r_2$ remains much less than 1, indicates that the system shows greater tendency to alternate. Thermogravimetric analysis showed that the thermal stability of the copolymers increased with increase in MMA units in the copolymer chain. The values of polydispersity index of poly(NPMPM), poly(NPMPM-co-MMA) and poly(MMA), obtained from GPC studies, suggest a strong tendency for chain termination by disproportionation in all cases and that the tendency increased with the increasing NPMPM content in the feed. The intrinsic viscosity of the polymers were in the range of 0.20-0.27 dl/g.

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