Copolymers Derived from 4-Nitrophenyl Methacrylate (Npma) and Methyl-Methacrylate (MMA)-Synthesis, Characterization, and Reactivity Ratios

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COPOLYMERS DERIVED FROM 4-NITROPHENYL METHACRYLATE (NPMA) AND METHYL-METHACRYLATE (MMA) – SYNTHESIS, CHARACTERIZATION, AND REACTIVITY RATIOS

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ABSTRACT

The free radical copolymerization of 4-nitrophenyl methacrylate (NPMA) with methylmethacrylate (MMA) in 2-butanone was carried out with different mole ratios of NPMA and MMA. The resulting copolymers were characterized by spectral studies. The molecular weights of the copolymers were determined by gel permeation chromatography and both number average (M_n) and weight average (M_w/ molecular weights lie in the range of 1.7-1.9 x 10^4 and 3.2-3.6 x 10^4, respectively. The copolymer composition was evaluated by ^1H NMR spectroscopic technique. The reactivity ratios of the monomers in the copolymer were calculated by Fineman-Ross, Kelen-Tudos and extended Kelen-Tudos methods. The product of these values are close to each other (0.73-0.80) and suggest a random arrangement of monomers in the copolymer chain. Thermal properties of these systems investigated by TG and DSC indicate that the decomposition of all the copolymers occurs in the temperature range 175°C-535°C.

INTRODUCTION

The synthesis and study of acrylates and their copolymers is important as they find extensive application in several applied areas. Thermal and photochemical behavior of many of these systems have been investigated [1-5]. The effect of magnetic field on the radical bulk polymerization of different methacrylates has been reported [6]. The synthesis of graft polymers in high yield was achieved when PMMA bearing carboxylate anions was used as a macroinitiator after its partial saponification and subsequent complexation with 18-crown-6-potassium [7]. The photochemistry of PMMA doped with 1,1,3,3-tetraphenylacetone was reported using 266nm laser excitation [8]. The investigation on the thin film behavior of some acrylates indicated that the monolayers were shown to be sufficient to induce an oriented epitaxial crystallization [9]. Also, the TEM study of the block copolymers obtained from PMMA and STY showed the layer formation and the competitive mechanisms of swelling and diffusion were explained in these systems [10].

The present study deals with the synthesis and study of the copolymers obtained from nitrophenyl methacrylate (NPMA) and methylmethacrylate (MMA). The calculation of reactivity ratios of these systems by different methods and their thermal behavior will be discussed. The earlier report [11] in this series deals with the poly (NPMA-co-STY) system which has certain similarities to the present system.

EXPERIMENTAL

Materials

Monomers used in the present study were 4-nitrophenyl methacrylate (NPMA) and methylmethacrylate (MMA). Methylmethacrylate supplied by Fluka, stabilized with 15 ppm hydroquinone methyl ether was repeatedly washed with 5% NaOH, water and finally vacuum distilled to remove the polymerization inhibitor. The common solvents 2-butanone, methanol and chloroform were distilled prior to use [12]. Methacryloyl chloride was synthesized by the reaction of methacrylic acid with benzoyl chloride according to the reported procedure [13]. Benzoyl peroxide (Fluka) employed as an initiator was used without any purification.

Synthesis of 4-Nitrophenyl Methacrylate (NPMA)

The monomer 4-nitrophenyl methacrylate (NPMA) was synthesized as per the following method :

4-Hydroxy nitrophenol (20 g, 0.14 mol), triethyl amine (17.5 ml, 0.15 mol) and 150 ml of 2-butanone were placed in a three-necked round bottom flask fitted with a reflux condenser, stirrer and an addition funnel. The contents were cooled to 0°C by keeping the flask in a freezing mixture. Freshly distilled methacryloyl chloride (17 ml, 0.16 mol) was placed in the addition funnel and was gradually added to the reaction mixture with vigorous stirring. The stirring was continued for 1 hour at 0°C and for another 3 hours at 30°C. The product obtained was filtered, washed with water, 5% NaOH and finally with water. The organic layer was separated and dried over anhydrous Na_2SO_4. The solution was filtered and the solvent was removed to get a pale yellow colored product.

> Yield: 64% m.p. 80°C-82°C
> Anal. Calcd. for $C_{10}H_9NO_4$: C = 57.97%; H = 4.35%; N = 6.76%
> Found: C = 57.91%; H = 4.39%; N = 6.82%

Synthesis of Copolymers

The monomers NPMA and MMA were taken in seven different mole ratios (Table 2) along with 1% BPO in polymerization tubes. The solvent used was 2-butanone (10 ml). The reaction mixture was thoroughly degassed by bubbling N_2 through the solution for 30 minutes. The reaction was carried out at 65°C for 8 hours and methanol was added in excess to precipitate the product. The copolymers thus obtained were purified by dissolving in $CHCl_3$ and reprecipitating with excess methanol. The product was finally dried at 40°C under *vacuo*.

Spectroscopy

Infrared spectra of the samples were recorded on a Hitachi 270-50 infrared spectrophotometer using KBr pellets. ^{1}H and ^{13}C NMR spectra were recorded on a Jeol 400 MHZ spectrometer. The solvent used was $CDCl_3$ with TMS as internal standard and the spectra were recorded at room temperature.

Gel Permeation Chromatography

Gel permeation chromatography (GPC) was carried out with a Waters model 501 gel permeation chromatograph equipped with a RI detector. The calibration was done using polystyrene and THF was used as an eluent at a flow rate of 10 ml/min.

Thermal Studies

Thermogravimetric analysis of the samples were carried out on a Mettler 3000 TA thermal analyzer. The sample weight was about 10 mg and the heating
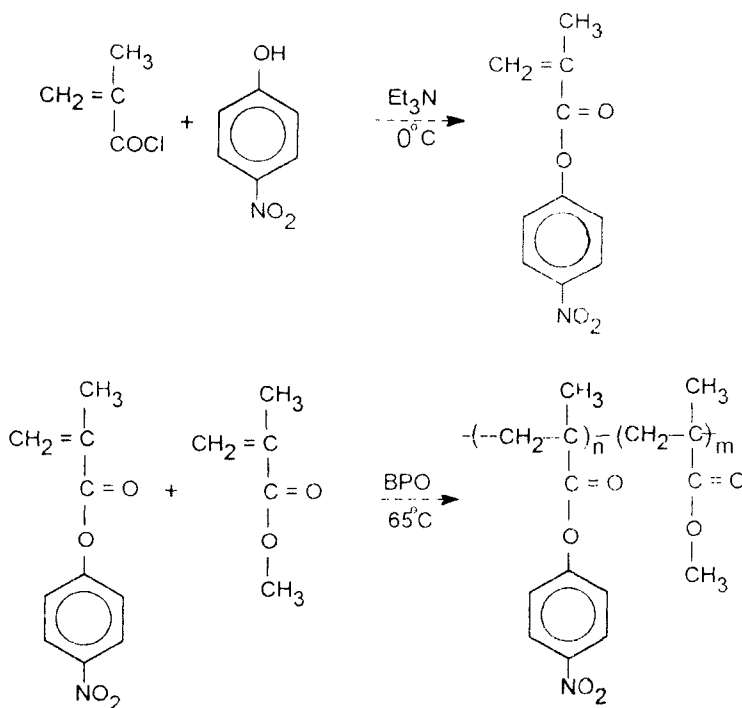
Scheme 1

rate was maintained at 20°C/min in the atmosphere of air. DSC measurements were made on a Dupont 990 thermal analyzer.

RESULTS AND DISCUSSION

The copolymers poly(NPMA-Co-MMA) were synthesized by free radical polymerization of the monomers NPMA and MMA taken in seven different mole ratios. The monomer MMA was obtained commercially, while NPMA was synthesized by the following reaction (Scheme 1).

Infrared Spectra

The infrared spectral studies have been extensively used in the characterization of homopolymer [14], copolymer [15] and blends [16] obtained from a range of acrylates and substituted acrylates. The IR spectra of the copolymers poly-(NPMA-co-MMA) recorded as Br pellets indicate important clues regarding, the
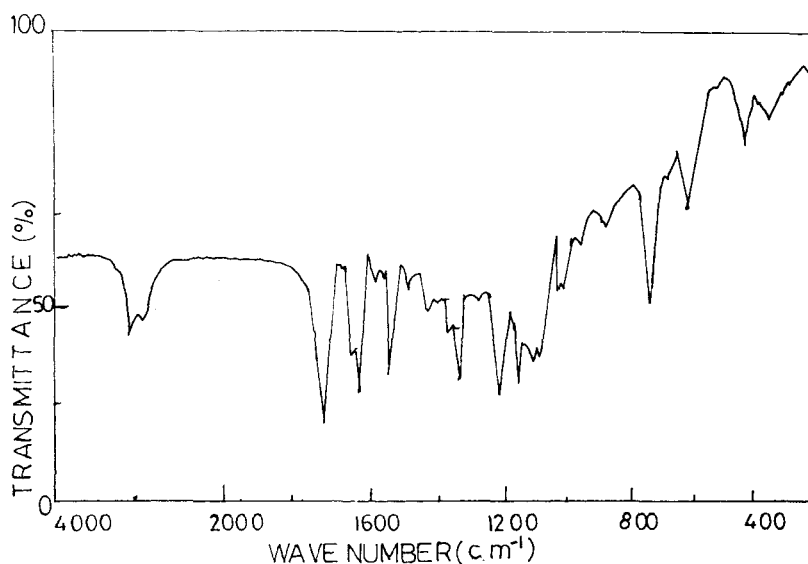
Figure 1.   Infrared spectrum of poly (NPMA-co-MMA; m_1:m_2:033:0.67).

formation of copolymers. The medium intensity bands at 3100 cm^{-1} are attributed to aromatic - CH stretching vibrations of NPMA. The strong bands due to keto and ester carbonyl are observed at 1670 cm^{-1} and 1750 cm^{-1}, respectively. The aromatic >C = C< skeletal vibrations are seen around 1610 cm^{-1}. The CH$_3$ and CH$_2$ stretching frequencies of MMA are also observed in the region 2800-3050 cm^{-1}. These assignments are in keeping with the reported values for similar organic compounds [17] [Figure 1].

NMR Spectra

The NMR spectral data of acrylate and substituted acrylate systems provide important information regarding the structure of these systems. The characterization of acrylate polymers obtained from microemulsion polymerization [18], radiolysis [19] and copolymerization [20] have been reported. The proton spectra of all copolymers were recorded in CDCl$_3$ solution. The signals observed at 7.35 δ and 8.20 δ are due to the aromatic protons of NPMA unit in the copolymer. The methoxy protons of MMA unit exhibit their signals at 3.6 δ. The peaks observed at 2.35 δ, 1.5 δ, and 1.02 δ are attributed to the methylene, methine and α-methyl protons respectively in the back bone (Figure 2).
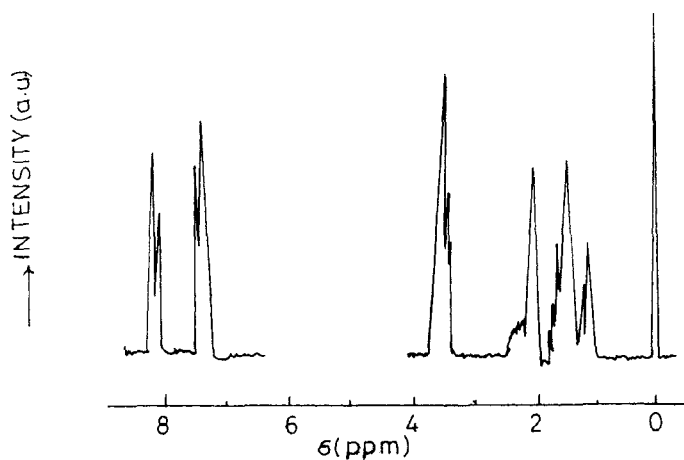
Figure 2. ^{1}H NMR spectrum of: copolymer (NPMA-c-MMA; $m_1:m_2:033:0.67$).

The ^{13}C NMR spectrum of a representative copolymer system has been reproduced (Figure 3) and the monomer structural unit is provided in this figure. The aromatic carbons of the NPMA unit appear at 121.34 ppm, 129.64 ppm, 135.87 ppm and 150.78 ppm, which are attributed to ^{2}C/^{6}C, ^{3}C/^{5}C, ^{4}C and ^{1}C carbons, respectively. The signals due to the ester carbonyls of both NPMA and MMA overlap with each other at 175.48 ppm. The α-methyl and the methyl group attached to the γ-carbon appear at 18.97 ppm and 60.02 ppm, respectively. The other peaks due to backbone carbons are observed at 48.03 ppm and 30.98 ppm (Table 1). The microstructural analysis of terpolymers obtained from STY, MMA and O_2 has been reported. The oxidative copolymerization reactivity ratios were evaluated in this study [21].

The mole fraction of NPMA in the copolymer can be determined from the ratio of the integral intensities aromatic protons of NPMA unit to those of the methoxy protono of MMA unit. If m, be the mole fraction of NPMA in the copolymer and m_2 be that of MMA. Then the term c is given by the following expression.

$$C = \frac{4m_1}{3m_2} \quad (or) \quad m_1 = \frac{3\ C}{3\ C\ +\ 4} \tag{1}$$
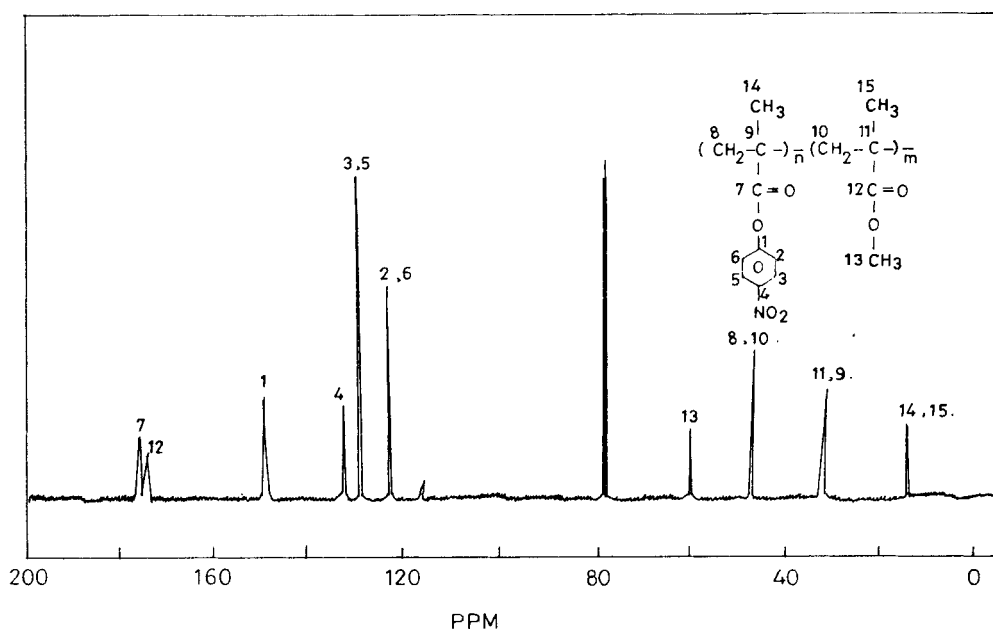
Figure 3. ^{13}C NMR spectrum of poly (NPMA-c-MMA) in CDCl₃.

Equation 1 provides the basis for the calculation of mole fraction of NPMA in the copolymer system. A plot of mole fraction of NPMA in the feed to that of the copolymer is given (Figure 4). The shape of the curve is almost similar to that of poly [NPA-co-BMA] system.

The copolymer compositional curve (Walls's diagram), wherein the mole ratio of NPMA in feed (m_1) vs. mole ratio of NPMA in the copolymer (M_1) is a sigmoidal one without any intersection at the ideal line. This type of curve clearly indicates that the feed composition and copolymer composition were not equal at any point of time during the polymerization reaction (Figure 4).

Molecular Weight

The molecular weight determinations of poly(NPMA-co-MMA) were carried out by gel permeation chromatographic method and the relevant data are tabulated (vide: Table 2). Three different polymer compositions were selected for this study. The mole ratios between NPMA and MMA are 0.111:0.889, 0.326:0.674 and 0.650:0.350. The weight average molecular weight ($\overline{M_w}$) for these systems are 3.64, 3.47 and 3.21 x 10^4, respectively, while the number average

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

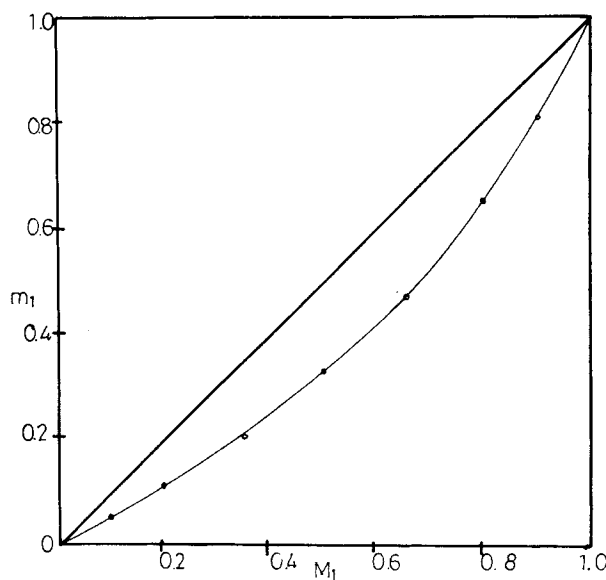| System | ¹H NMR resonances (ppm) | | | | ¹³C NMR resonances (ppm) | | | | |
	Aromatic protons	-O-CH₃	-CH₂-	-CH₃-	-O-C=O	Aromatic. ^1C, $^3C/^5C$, $^2C/^6C$	-CH₂-	-CH₃-	-C-
NPMA	8.8-8.2 (s, 2H) 7-7.42 (s, 2H)	-	6.52 (s,2H)	1.12	168.12	152.4, 129.6, 120.9	132.4	20.41	32.14
poly(NPMA)	8.05-8.2 (s, 2H) 7.2-7.4 (s, 2H)	-	2.3 (s,2H)	0.95	173.9	150.3, 129.4, 121.7	52.32	19.98	30.32
poly(NPMA-co-MMA)	8.0-8.2 (s, 2H) 7.4-7.21 (s, 2H)	3.61	2.35 (s,2H)	1.03	175.3-176.8	150.8, 129.6, 121.3	54.73	19.36	31.64

Figure 4. Composition curves of NPMA-MMA copolymer system.

molecular weight ($\overline{M}_w$) for the corresponding systems are 1.93, 1.86 and 1.76 x 10^4 respectively. The ratio between $\overline{M}_w$ and $\overline{M}_n$ lie in the range 1.82-1.89. Yasuda *et al.* [22] have reported that the number average molecular weight ($\overline{M}_n$) of PMMA, which has an extremely low polydispersity, is 10.0 x 10^4. The relatively high molecular weight in this case was achieved by the use of an organolanthanide complex viz. [Sm $(C_5 H_5)_2 H]_2$. The free radical polymerization of the systems under current investigation using BPO as initiator has yielded low molecular weight copolymers.

Reactivity Ratios

The well known methods viz. Fineman-Ross (F-R) [23] Kelen-Tudos (K.T) [24] and extended Kelen-Tudos (ext. K.T) [25] methods were employed in the calculation of reactivity ratios of the monomers 4-nitrophenyl methacrylate (NPMA) and methylmethacrylate (MMA) in the copolymer system poly(NPMA-co-MMA). However, other methods like non-linear least square fitting program that employs a modified Marquardt method has also been reported in the literature [26] for the calculation of reactivity ratios.

TABLE 2. Copolymerization Data of NPMA-MMA System

Sl. No.	Feed composition		Conversion (%)	Intensity of aromatic protons (I_α)	Intensity of methoxy protons (I_m)	$C = I_\alpha/I_m$	Copolymer composition		$\bar{M}_n \times 10^{-4}$	$\bar{M}_n \times 10^{-4}$	$\bar{M}_w/\bar{M}_n$
	M_1	M_2					m_1	m_2			
1	0.10	0.90	8.63	1.10	14.7	0.0748	0.053	0.947			
2	0.20	0.80	5.27	2.10	12.6	0.1667	0.111	0.889	3.64	1.93	1.89
3	0.35	0.65	6.92	3.30	9.3	0.3548	0.210	0.790			
4	0.50	0.50	9.87	6.50	10.1	0.6436	0.326	0.674	3.47	1.86	1.87
5	0.65	0.35	3.64	4.70	4.0	1.1750	0.468	0.532			
6	0.80	0.20	7.18	6.20	2.5	2.4800	0.650	0.350	3.21	1.76	1.82
7	0.90	0.10	8.46	6.70	1.2	5.5833	0.807	0.193			

TABLE 3. F-R and K-T Parameters of NPMA-MMA Copolymer System

Sl. 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	0.0561	-1.8703	0.2201	-0.8185	0.0923
2	0.2500	0.1249	-1.7523	0.5006	-0.6830	0.1889
3	0.5385	0.2658	-1.4873	1.0903	-0.4714	0.3445
4	1.0000	0.4837	-1.0675	2.0675	-0.2583	0.4990
5	1.8571	0.8797	-0.2540	3.9200	-0.0424	0.6352
6	4.0000	1.8571	1.8462	8.6154	0.1729	0.7886
7	9.0000	4.1814	6.8476	19.3718	0.3194	0.9077

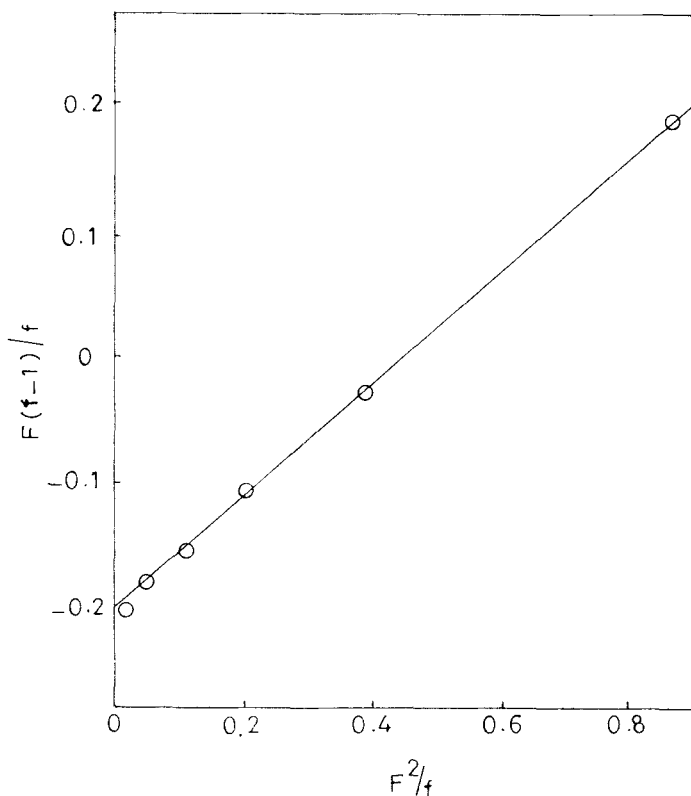$\alpha = \sqrt{0.2201 \times 19.3718} = 2.0648$

Figure 5.   Fineman-Ross plot for the poly (NPMA-MMA copolymer system.

The parameters G, H, f and F are calculated by making use of the standard equations, and they are presented in Table 3. A plot of G vs. H results in a straight line with the slope = r_1 and intercept = -r_2 (Figure 5).

The following equation has been employed in Kelen-Tudos (K-T) method.

$$\eta = \quad (r_1 + r_2/\alpha)\, \xi - r_2/\alpha \tag{2}$$

where η, ξ and α were determined from G & H. A plot of ξ vs. η also results in a straight line, where $\xi = 0$ gives the intercept (r_1) and $\xi = 1$ is equal to -r_2/α. The relevant values and the figure are provided (Table 3, Figure 6).

The parameters obtained from the extended Kelen-Tudos method has been tabulated and the plot of ξ vs. η is also given (Table 4, Figure 6). The r_1 and r_2 values obtained from all the three methods along with their products (Table 5) indicate that the values do not differ much from each other. The present system is an
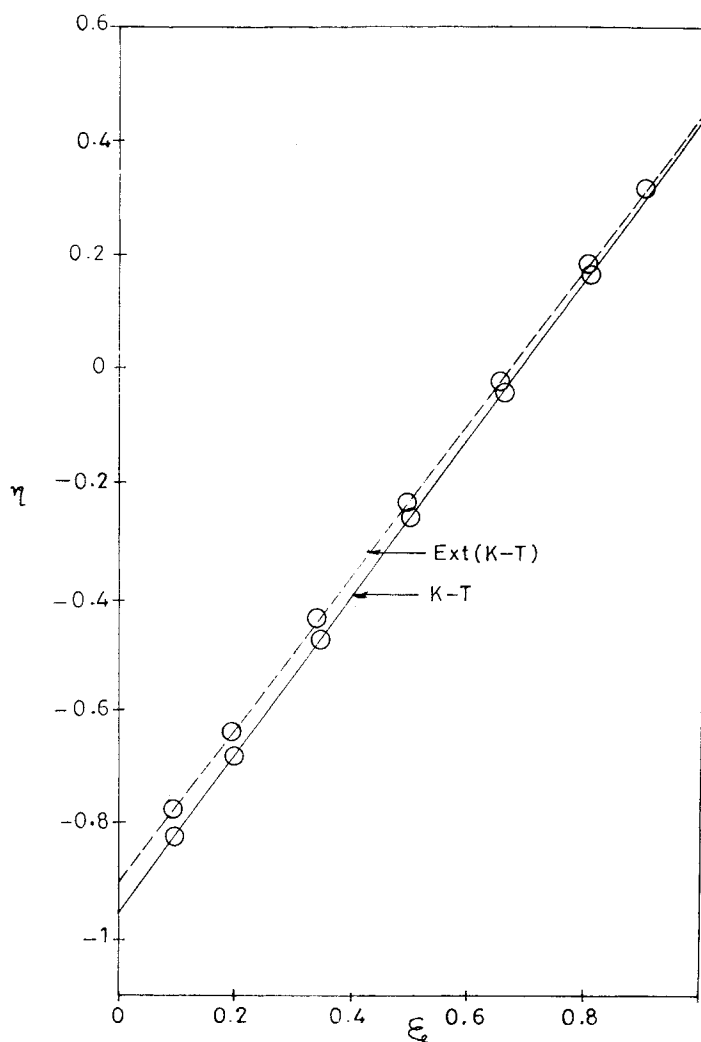
Figure 6. K-T and Ext(K-T) plots of η vs. ξ for NPMA-MMA copolymer system.

example for the case $0 > r_1 r_2 < 1$. The product $r_1 r_2$ provides valuable information regarding the arrangement of monomers in the copolymer chain. If it is close to unity a random arrangement of monomers occur, while the value which is close to zero suggests alternation of the monomers. The values obtained in the present study ranges from 0.73 to 0.80 and hence an random arrangement of monomers has been suggested.

TABLE 4. Extended K-T Parameters for NPMA-MMA Copolymer System

Sl.No.	1	2	3	4	5	6	7
ζ_2	0.0951	0.0635	0.0944	0.1514	0.0625	0.1375	0.1720
ζ_1	0.0480	0.0317	0.0466	0.0732	0.0296	0.0639	0.0799
Z	0.4925	0.4914	0.4812	0.4632	0.4657	0.4459	0.4413
F	0.1139	0.2542	0.5523	1.0441	1.8891	4.1643	9.4759
H	0.2313	0.5173	1.1478	2.2539	4.0569	9.3380	21.4745
G	-1.9167	-1.7809	-1.5273	-1.1145	-0.2596	1.9219	7.2097
α	2.2288						
ξ	0.0940	0.1884	0.3399	0.5028	0.6613	0.8073	0.9060
η	-0.7791	-0.6485	-0.4523	-0.2486	-0.0413	0.1662	0.3042
μ	0.4831						

TABLE 5. Comparison of Reactivity Ratios by Various Methods for poly(NPMA-co-MMA)

Methods	r_1	r_2	$1/r_1$	$1/r_1$	r_1r_2
Fineman-Ross (F-R)	0.70	1.15	1.44	0.87	0.80
Kelen-Tudoss (K-T)	0.67	1.12	1.49	0.89	0.75
Extended (K-T)	0.66	1.11	1.52	0.90	0.73

TABLE 6. Thermogravimetric Analysis Data of poly(NPMA-co-MMA) System

Sl.No.	Copolymer composition		Decomposition Temperature range (°C)		Temperature (°C) of weight loss (%) of copolymers				
	m_1	m_2	Stage I	Stage II	10	25	50	75	90
1	0.000	1.000	278-508	--	305	332	302	378	420
2	0.111	0.889	190-455	--	252	296	328	355	420
3	0.326	0.674	200-485	--	266	307	340	367	440
4	0.650	0.350	210-545	--	278	315	365	385	470
5	1.000	0.000	175-350	350-555	245	285	302	355	440

Thermal Studies

Thermal properties of five different polymer systems obtained from poly-(NPMA-co-NMA) have been studied by thermogravimetric analysis. The relevant values are tabulated (Table 6) and the thermograms are reproduced (Figure 7). The decomposition essentially occurs in a single stage except in the case of first system, where two distinct stages are observed. The weight loss occurs in the temperature range 175°C-545°C in the first stage, while it is observed between 350°C and 550°C in the second stage. The initial decomposition temperature (IDT) increases gradually with increase in the mole ratio of MMA in the copolymer. The first member of the series exhibits, an IDT of 175°C, wherein the concentration is zero. When the system has exclusively MMA (last member of the series), the IDT goes
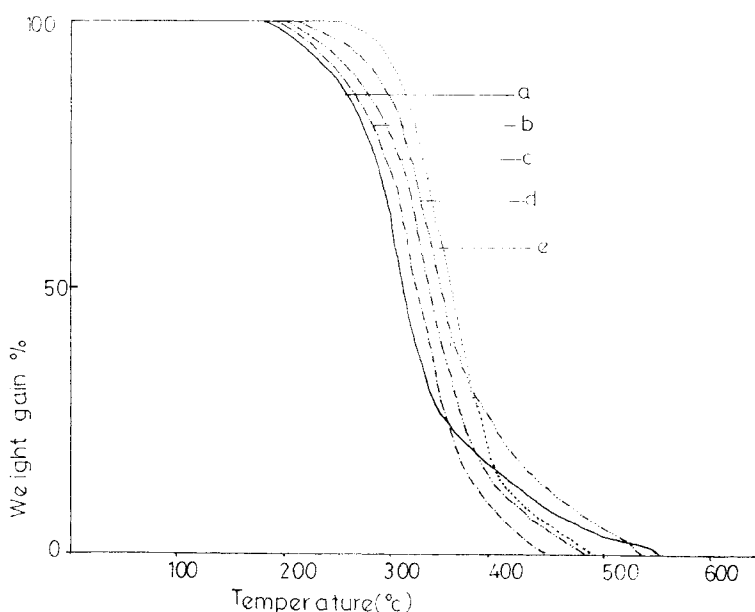
Figure 7.   Thermogravimetric analysis (TGA) curves in air of poly (NPMA in copolymer (a) 1.00; (b) 0.11; (c) 0.33; (d) 0.65, and poly (MMA).

up to 278°C. The copolymers with intermediate compositions start decomposing at 190°C, 200°C and 210°C when the MMA ratios are 0.889, 0.674 and 0.350, respectively. The temperature vs. percentage weight loss of copolymers also indicate a similar trend when the weight loss is 10% and 25% (vide: Table 6). A gradual increase in the temperature with increasing amount of NPMA has been observed in these two cases. However, when the weight loss is 50%, 75% or 90% no such gradual change has been noticed. The reason for a single stage decomposition except in the case of one system is not clear. The acrylate copolymers with styrene as well as with vinylcyclohexane were reported [27] to exhibit lesser thermal stability (310°C-340°C) when compared to the systems under investigation. The random copolymers obtained from PMMA were also reported to exhibit composition dependence of glass transition temperature [28] (T_g) and the structural relaxation of PMMA was also attributed to the change of thermodynamic and dynamic mechanical properties [29]. The glass transition temperature (T_g) of poly(NPMA-co-MMA) with a NPMA:MMA composition of 0.47:0.53 in the present study is found to be 116.3°C.

CONCLUSION

The synthesis of copolymers derived from 4-nitrophenyl methacrylate (NPMA) and methylmethacrylate (MMA) was achieved by free radical copolymerization of the above monomers with seven different mole ratios. The IR and NMR spectral data confirm the formation of copolymers. The ^{1}H NMR spectral studies are employed in the evaluation of copolymer compositions. The weight average molecular weight ($\overline{M_w}$) and the number average molecular weight of these systems are found to be 3.2 -3.6 x 10^4 and 1.7-1.9 x 10^4, respectively. The reactivity ratios are evaluated by Fineman-Ross, Kelen-Tudos and extended Kelen-Tudos methods and their product r_1, r_2 lies in the range 0.73 to 0.80 which indicates a random arrangement of monomers in the copolymer chain. Thermal studies show that the copolymers decompose in the temperature range 175°C-535°C mostly in single stage. The glass transition temperature of one of the systems with a composition of NPMA:BMA = 0.47:0.53 is found to be 116.3°C.

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