COPOLYMERIZATION OF 4-NITROPHENYL ACRYLATE (NPA) WITH METHYL METHACRYLATE (MMA): SYNTHESIS, CHARACTERIZATION AND REACTIVITY RATIOS

S. Thamizharasi[a]; P. Gnanasundaram[a]; S. Balasubramanian[a]

[a] Central Leather Research Institute, Chennai, India

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COPOLYMERIZATION OF 4-NITROPHENYL ACRYLATE (NPA) WITH METHYL METHACRYLATE (MMA): SYNTHESIS, CHARACTERIZATION AND REACTIVITY RATIOS

S. Thamizharasi,[1] P. Gnanasundaram,[1,2] and S. Balasubramanian[1,*]

[1]Central Leather Research Institute
Adyar, Chennai - 600 020, India

[2]Department of Chemical Engineering
Anna University
Chennai - 600 025, India

ABSTRACT

4-Nitrophenyl acrylate (NPA) has been synthesized from the precursor viz 4-nitrophenol, and characterized by IR, ^{1}H and ^{13}C NMR spectroscopic methods. Homo- and copolymerization of NPA with methyl methacrylate (MMA) has been carried out in 2-butanone by free radical polymerization using benzoyl peroxide (BPO) as initiator at 70°C. Poly(NPA) and poly(NPA-co-MMA) were characterized by IR, ^{1}H and ^{13}C NMR spectral studies and their copolymer compositions were evaluated by ^{1}H NMR spectroscopy. The reactivity ratios were calculated by Fineman-Ross, Kelen-Tudos, and Extended Kelen-Tudos methods. The Q and e

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* Author to whom correspondence should be addressed.

values for NPA has been determined by using Alfrey-Price scheme. The thermal properties of the polymers have been studied by TGA and DSC analysis. The molecular

INTRODUCTION

The acrylate polymers have received considerable attention in recent times because of their versatile nature. Several studies with homopolymers, copolymers and polymer blends containing these systems have been reported [1-4]. Group transfer polymerization has also been described [5] with acrylate polymers which combines the advantage of living polymerization with the ability to carry out polymerization at room temperature and above, wherein the narrow molecular weight distribution polymers are formed in quantitative yield and the degree of polymerization is controlled by the ratio of the monomer to the initiator. Also, the incorporation of sugar into acrylates extends the application of these materials into areas such as catalysts and reagents for organic synthesis, adsorbents with specific chirality, hydrophilicity and biodegradables [6-7]. Maunu *et al.* [8] have indicated that water soluble polymers of this type occur with interpolymer compounds possessing secondary bonds. Neutron reflectometry using the kinematic approximation has been employed in the analysis of layers obtained from PMMA [9]. Kinetic studies of homopolymerization and radical copolymerization of MMA with triorganosilyl methacrylate indicates that the electronegativity of Si leads to reactivity ratios r_2 having values which were less than one [10].

The present report deals with the synthesis and characterization of poly(methyl methacrylate) and its copolymers with nitrophenyl acrylate (NPA). The reactivity ratios of these systems have been calculated by three different methods viz. Fineman-Ross (F-R), Kelen-Tudos (K-T), and Extended (Kelen-Tudos) methods. The Q-e values of NPA are determined by Alfrey-Price method. Thermal properties of these systems investigated by TG and DSC are discussed. The number and weight average molecular weight of the copolymers are also determined.

EXPERIMENTAL

Materials and Methods

Methyl methacrylate (Aldrich) was washed with 5% NaOH solution, then with distilled water to remove the inhibitor, and distilled under reduced

pressure. 4-nitrophenol was recrystallized from ethanol and benzoyl peroxide was recrystallized from methanol/ chloroform mixture. 2-Butanone (AR) and methanol were of LR grade and were used as received. Acryloyl chloride was prepared by the reaction of acrylic acid with benzoyl chloride [11].

Monomer Synthesis

Synthesis of 4-Nitrophenyl Acrylate (NPA)

4-nitrophenol (20 g, 0.15 mol) dissolved in 2-butanone was taken along with triethyl amine (17.5 ml, 0.15 mol) in a two necked round bottomed flask. The freshly distilled acryloyl chloride (15 ml, 0.16 mol) was added slowly in drops to the reaction mixture at 0°C with constant stirring. After an hour, when the addition was over, the reaction mixture was stirred at room temperature (30C). The contents were washed with water to remove the quarternary ammonium salt and the unreacted 4-nitrophenol was removed by washing with 5% NaOH solution. The organic phase was then dried with anhydrous sodium sulphate and the monomer 4-nitrophenyl acrylate was recovered after evaporation of the solvent. m.p. 76-78C, Yield 76%.

Element Analysis:

Calculated (%): C = 55.96; H = 3.63 and N = 7.25.
Experimental (%): C = 55.73; H = 3.81 and N = 7.12.

Polymerization

For the synthesis of homo- and copolymers of NPA appropriate quantities of the monomers (3.32 g/10 ml) (2 M), free radical initiator (BPO (0.0332 g) 1% wt of the monomers) and solvent chlorobenzene were placed in a polymerization tube, flushed with oxygen free nitrogen for 15 minutes, and then allowed to polymerize at a concentration of 1.0 mol at 70°C. After the desired time ($\cong 6$ to 8 hours) (<10% yield) the product was precipitated by the addition of methanol. The polymer was filtered and dried *in vacuo*.

Characterization of the Polymers

The IR spectrum for the monomer and polymers were recorded on a Hitachi 270-50 spectrophotometer as KBr pellets. The FT-NMR spectra were run on a Jeol 400-MHz instrument in CDCl3, for the monomer and polymers. TGA curves were recorded on a Mettler TA 2000 thermal analyzer. DSC curves were recorded on a Dupont 990 thermal analyzer. Samples of less than 10 mg were used at a heating rate of 20C/min for thermal studies. The molecular weight of

the samples were found out using a Waters 501 gel permeation chromatograph. The instrument was calibrated using polystyrene. The solvent employed in this experiment was THF.

RESULTS AND DISCUSSION

Synthesis of 4-nitrophenyl acrylate was carried out by a modified procedure of Schotten-Baumann reaction, which is presented in Scheme 1:
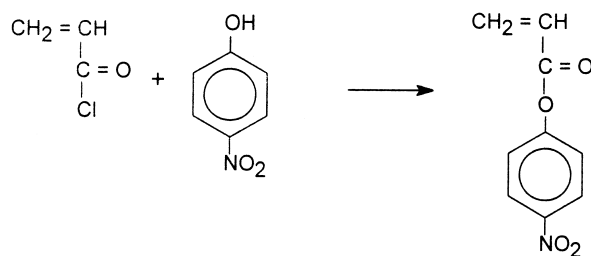
The polymerization of NPA with MMA in different mole ratios using BPO as the free radical initiator has resulted in the formation of poly(NPA-co-MMA) with seven compositions and the reaction sequence is provided in Scheme 2:
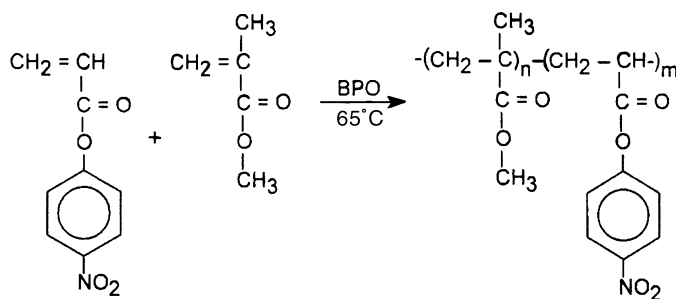
IR Spectral Studies

The formation of NPA is indicated by IR and NMR spectral studies. The aliphatic and aromatic C-H stretching vibrations are seen at 2900 and 2959 cm^{1}. The characteristic strong absorptions due to keto and ester carbonyls of simple organic compounds are found in the region 1630-1720 cm^{-1} and 1720-1770 cm^{-1} respectively [12, 13]. This trend is observed in the present case, where the frequency due to keto group is observed at 1640 cm^{-1}, while that of ester carbonyl

is seen at 1742 cm^{-1}. However, there is a considerable shift towards lower frequency (at least by 50 cm^{-1}) when there is an intramolecular H-bonding.

NMR Spectral Studies

The structural elucidation of simple organic compounds, complex natural products, polymer etc. have been achieved by ^{1}H and ^{13}C NMR spectral analysis. The proton NMR studies not only help in the elucidation of molecular structure of polymers but also the solvent self diffusion coefficient of some linear and cross linked polymers [14]. Polymer blends containing PMMA-polyoxide have also been investigated by NMR and thermal analysis [15]. The ^{1}H NMR resonance signals observed in the present study at 7.42 and 8.2 ppm are due to the aromatic protons of NPA unit. The signals due to the vinylic protons appear at 6.5-7.00 ppm in the case of poly(NPA) and the peaks at 1.0-1.3 ppm correspond to the methylene protons of the backbone (Scheme 2).

Spyros *et al.* [16] have indicated that the chain segmental motion and side chain internal rotations of poly(1-naphthylallyl acrylate) can be studied by ^{13}C longitudinal relaxation time and NOE measurements. In the ^{13}C NMR spectrum of NPA, the aromatic carbons ^{1}C, ^{3}C/^{5}C, ^{2}C/^{6}C, and ^{4}C appear at 150.7, 129.6, 120.9, and 135.3 ppm respectively, while the vinylic protons appear at 128.1 and 132.4 ppm.

Figures 1 and 2 represent spectra of copolymer with a molar composition of NPA/MMA equal to 0.46/0.54. By comparing the ^{1}H NMR spectrum of poly(NPA) with that of copoly(NPA-MMA), the additional peaks in the region 3.2-3.6 ppm are attributed to the O-CH$_3$ protons of MMA unit. Similarly, ^{13}C NMR spectra of poly(NPA) and poly(NPA-co-MMA) prove that the additional peaks in the copolymer spectra are due to MMA unit. The α-CH$_3$ and (-CH^3 carbons of MMA appear at 59.63 and 19.36 ppm respectively. The ester carbonyl of both the acrylates appear at 175.3-176.8 ppm. The back bone carbons -CH$_2$-, -CH- and -C- appear at 48.5, 54.7, and 31.6 ppm respectively (Table 1).

Copolymer Composition

The mole fraction m$_1$ of NPA in the NPA-MMA copolymer has been calculated by adopting a similar method employed by us earlier [17]:

$$C = \frac{[x \ I_{aro}]}{[y \ I_{meth}]} \tag{1}$$
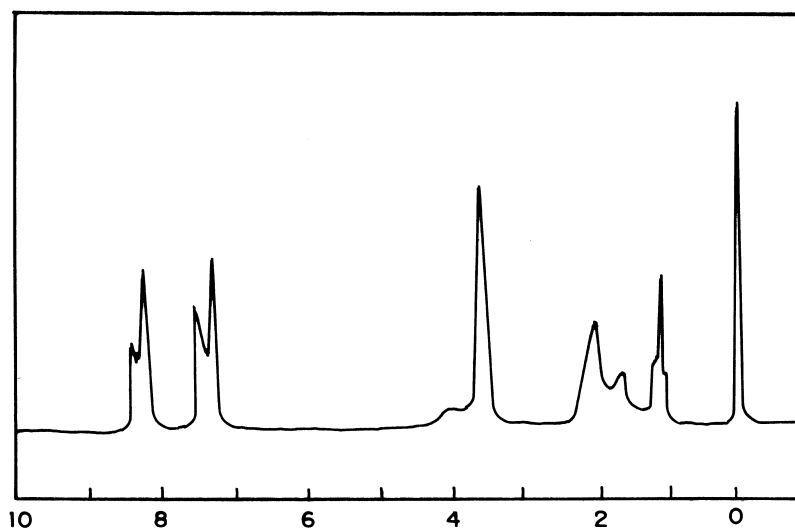
Figure 1. ^{1}H NMR spectrum of poly (NPA-co-MMA) in CDCl$_3$.
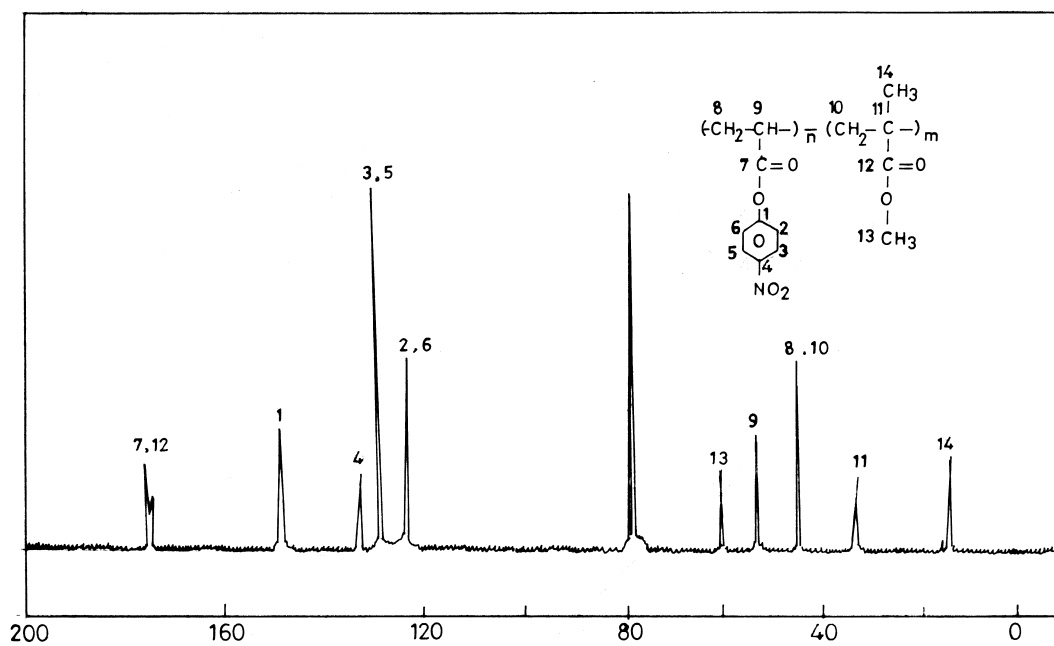
Figure 2. ^{13}C NMR spectrum of poly (NPA-co-MMA) in CDCl$_3$.

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

| System | ^{1}H NMR resonances (ppm) | | | | | ^{13}C NMR resonances (ppm) | | | | | |
	Aromatic protons	-O-CH$_3$	-CH-	-CH$_2$-	-CH$_3$-	-O-C=O	Aromatic. ^{1}C. ^{3}C/^{5}C, ^{2}C/^{6}C	-CH$_2$-	-CH-	-CH$_3$-	-C-
NPA	8.8-8.2 (s, 2H) 7-7.42 (s, 2H)	-	5.9 (s,H)	6.5 (s,2H)	-	173.12	150.7, 129.6, 120.9	128.1	132.4	-	-
poly(NPA)	8.05-8.2 (s, 2H) 7.2-7.4 (s, 2H)	-	1.58 (s,H)	2.3 (s,2H)	-	173.9	150.3, 129.4, 121.2	46.62	52.32	-	-
poly(NPA-co-MMA)	8.0-8.2 (s, 2H) 7.4-7.21 (s, 2H)	3.61	1.49 (s,H)	2.35 (s,2H)	1.03	175.3-176.8	152.4, 128.9, 120.6	48.50	54.73	19.36	31.64

where x is the total number of aromatic protons in the monomer 1 (NPA), y is the total number of methoxy protons in monomer 2 (MMA), I_{aro} is the integral intensity of aromatic protons in the copolymer and I_{meth} is the integral intensity of methoxy protons in the copolymer. Substituting x and y by 4 and 3, respectively, in Equation 1, the following equation is obtained.

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

The copolymer composition curve for poly(NPA-co-MMA) was obtained by plotting mole ratio of NPA in feed (M_1) Vs mole ratio of MMA in the copolymer (m_1). The curve tends to be sigmoidal in shape and it does not cross the ideal line indicating that the feed composition and copolymer composition do not become equal in the polymerization reaction (Figure 3).
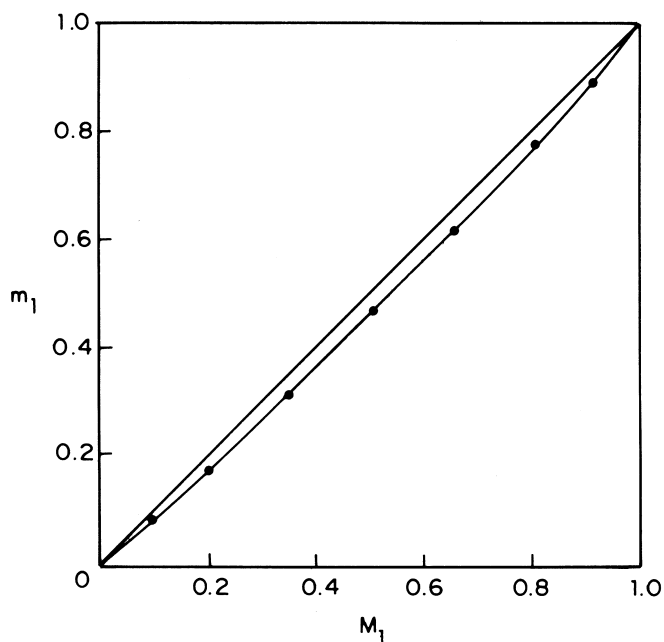
Figure 3.   Composition curves of NPA-MMA coplymer system.

Reactivity Ratios

From the monomer feed ratios and the copolymer compositions, the reactivity ratios r_1 and r_2 of NPA and MMA are computed by Fineman Ross [18], Kelen-Tudos [19], and Extended Kelen-Tudos [20] methods and the corresponding data are presented in Tables 2 and 3.

The method proposed by Fineman-Ross for calculating r_1 and r_2 involves the following equation:

$$G = Hr_1 - r_2 \tag{3}$$

Where G and H are the functions of initial compositions of the monomer and copolymer respectively. A plot of G Vs H gives a straight line with a slope equal to r_1 and intercept equal to r_2 (Figure 4).

The equation proposed by Kelen-Tudos was also worked out where η and ξ are functions involving the initial composition of monomers and final copolymer respectively

$$\eta = (r_1 + r_2\mu) \; \xi - r_2/\alpha \tag{4}$$

A plot of η against ξ gives a straight line (Figure 5) and from α ($H_{min} \times H_{max}$) and intercept $\xi = 0$, r_1 was calculated. The intercept at $\xi = 1$ gives the r_2 value (Table 4).

The reactivity ratios and microstructural determination of vinyl acetate-alkyl acrylate copolymers have recently been reported [21]. Free radical copolymerization of 2-hydroxy ethylmethacrylate with 4-(2-(methacryl-oyl)ethyl-oxy)acetamide gives rise to the reactivity ratio of $r_M = 0.673$ and $r_H = 1.391$, whereas, those of methacrylonitrile-MMA copolymers are $r_N = 0.883$ and $r_M = 0.892$ [22, 23]. A comparision of reactivity ratios by various methods in the present study is given in Table 5. The product of reactivity ratios and the nature of the copolymer sequence can also be studied from this table, the r_1r_2 values obtained by F-R, K-T and Ext(K-T) methods are 0.924, 0.961, and 0.935, respectively. In the case of present system, it has been found that, $r_1 < 1$ and $r_2 > 1$. The product of r_1 and r_2 is almost equal to one and it is within the range $0 < r_1r_2 < 1$. The value of $1/r_2$ which is less than 1 shows that the relative attack of MMA radical towards MMA monomer is greater. The $1/r_1$ value explains that the cross propagation of NPA radical is more. Since $r_2 > r_1$, the MMA concentration in the copolymer is more. As the product of reactivity ratios (r_1r_2) is close to unity, there

TABLE 2. Copolymerization Data of poly(NPA-co-MMA) System

Sl. No	Feed composition		Conver -sion (%)	Intensity of aromatic protons (I_{aro})	Intensity of methoxy protons (I_{meth})	$C = \dfrac{I_{aro}}{I_{meth}}$	Copolymer composition (mole fraction)		Molecular weight data (x 10^4)		
	M_1	M_2					m_1	m_2	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_w/\overline{M}_n$
1.	0.10	0.90	9.48	0.55	4.30	01279	0.087	0.913			
2.	0.20	0.80	11.32	1.10	3.70	0.2973	0.182	0.818	2.24	4.16	1.86
3.	0.35	0.65	7.94	2.00	3.20	0.6250	0.319	0.681			
4.	0.50	0.50	6.36	3.20	2.80	1.1529	0.461	0.539	2.53	4.48	1.77
5.	0.65	0.35	8.92	4.50	2.10	2.1429	0.616	0.384			
6.	0.80	0.20	5.14	6.75	1.45	4.6552	0.777	0.223	2.76	4.63	1.68
7.	0.90	0.10	9.13	7.20	0.70	10.2857	0.885	0.115			

Solvent : MEK;   Temperature 70°C

Initiator : BPO   C1 % wt. of the monomer).

TABLE 3. F-R and K-T Parameters of NPA-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	0.0953	-0.6259	0.0819	-0.7057	0.0923
2	0.2500	0.2225	-0.5001	0.1875	-0.5039	0.1889
3	0.5385	0.4685	-0.2473	0.4231	-0.2014	0.3445
4	1.0000	0.8553	0.1982	0.8018	0.0898	0.4990
5	1.8571	1.602	1.1023	1.4019	0.4995	0.6352
6	4.0000	5.3291	3.2494	3.0023	0.8535	0.7886
7	9.0000	10.2360	8.1208	7.9133	0.9315	0.9077

$$\alpha = \sqrt{0.0819 \times 7.9133} = 0.8050.$$

is a tendency for M_1 and M_2 to copolymerize randomly, and this has been explained by the Walls diagram of NPA-MMA copolymer system (Figure 3).

The Q and e values of NPA were determined by the Alfrey-Price method using the reactivity ratios obtained experimentally by Extended Kelen-Tudos method. The values of $e_2 = 0.4$ and $Q_2 = 0.72$ obtained from the literature for
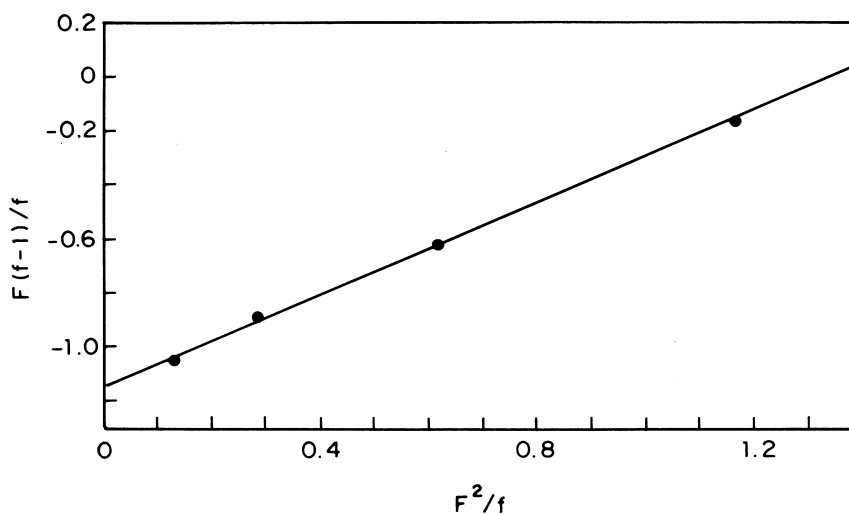
Figure 4. Fineman-Ross plot for the poly (NPA-co-MMA) system.
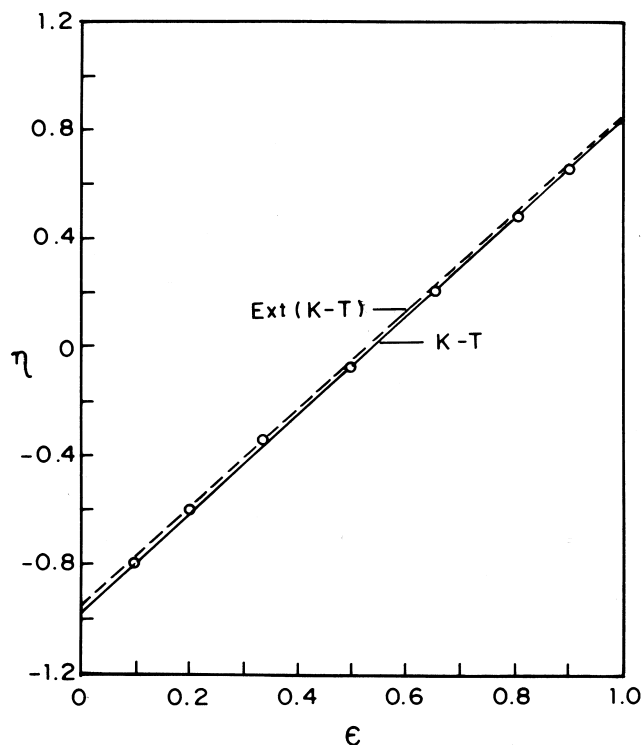
Figure 5.   KT and Ext (K–T) plots of poly (NPA-co-MMA).

MMA and $Q_1 = 0.565$ and $e_1 = 0.600$ were evaluated for NPA using the following equations.

$$e_1 = e_2 + (|\ln r_1 r_2|)^{1/2} \tag{5}$$

$$Q_2 = Q_2/r_2 \exp[e_2(e_1 - e_2)] \tag{6}$$

Molecular Weights

The molecular weight determination of three different copolymer compositions were carried out by gel permeation chromatography. The copolymer compositions of poly(NPA-co-MMA) employed in the present study are 0.20:0.80, 0.50:0.50, and 0.80:0.20. The weight average molecular weight (M_w) for these systems are 4.16, 4.48 and 4.63×10^4, respectively. The number aver-

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

S.No.	1	2	3	4	5	6	7
ζ_2	0.0980	0.1179	0.0855	0.0706	0.1002	0.0582	0.1059
ζ_1	0.0820	0.1049	0.0744	0.0605	0.0866	0.0507	0.0906
Z	0.8290	0.8837	0.8654	0.8570	0.8574	0.8676	0.8480
F	0.1121	0.2518	0.5417	1.0054	1.8710	4.0161	9.0754
H	0.1352	0.2849	0.6259	1.1819	2.1821	4.6291	10.7026
G	-1.0942	-0.8798	-0.6138	-0.1701	0.7047	2.8635	7.8962
α	1.202815						
η	-0.8178	-0.5914	-0.3326	-0.0869	0.2082	0.4910	0.6632
ξ	0.1010	0.1915	0.3423	0.4956	0.6447	0.8038	0.8990
μ	0.4456						

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

| Methods	r_1	r_2	$1/r_1$	$1/r_2$	r_1r_2
Fineman-Ross (F-R)	0.84	1.10	1.191	0.909	0.924
Kelen-Tudos (K-T)	0.85	1.13	1.177	0.885	0.961
Extended (K-T)	0.82	1.14	1.200	0.877	0.935

age molecular weight $(\overline{M_n})$ for these polymeric systems are found to be 2.24, 2.53, and 2.76 $\times$ 10^4, respectively. The ratio between weight average $(\overline{M_w})$ and number average $(\overline{M_n})$ molecular weight of these systems lie in the range 1.68-1.86. Some of the fluorinated methacrylates are found to have number average molecular weight in the range of 3.98 x 10^4-6 $\times$ 10^4 [24].

Thermal Studies

The thermal behavior of the copolymers was investigated by recording the thermograms of the copolymers. The thermal characteristics of some of the acrylate polymers both homopolymers and copolymers have been reported [25, 26]. The relevant data for copoly(NPA-MMA) system are also tabulated (vide:Table 6) and the thermograms are presented in Figure 6. The NPA-MMA

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

Sl.No.	Copolymer composition		Decomposition Temperature range (°C)		Temperature (°C) Vs weight loss (%) of copolymers				
	m_1	m_2	Stage I	Stage II	10	25	50	75	90
1	1.000	0.000	165-300	300-550	218	260	290	386	485
2	0.182	0.818	175-310	310-510	243	270	300	355	430
3	0.461	0.539	190-315	315-515	250	287	311	367	450
4	0.772	0.228	200-330	330-505	266	308	327	385	452
5	0.000	1.000	278-508	425-565	305	332	302	378	420
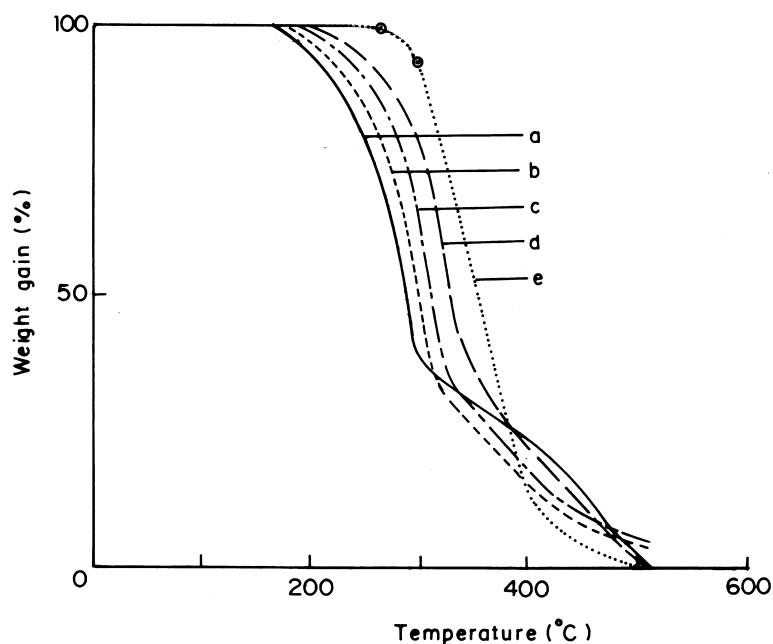
Figure 6. Thermogravimetric Analysis (TGA) curves in air of poly (NPA-co-MMA). Mole fraction of NPA in copolymer (a) 1.00, (b) 0.18, (c) 0.46, (d) 0.77 and (e) poly-MMA.

composition was varied in the range 100%:0% to 0%:100%. Copolymer samples with five different mole ratios were employed in the present study. The decomposition of the polymers was observed in two stages, while the two stages are distinct in four samples the last sample (m_1:m_2 = 0:1) exhibits only single stage. The first inflexion in the curve lies between 165°C-315°C, while the second one ranges between 165°C-550°C. There is a general increase in the decomposition temperature of the samples at the first stage with increasing concentration of MMA. For the first sample with zero MMA mole ratio, the plateau in the thermograms commences at 165°C and it gradually increases with higher concentration of MMA and finally reaches a maximum (278°C) in the case of last sample [sample no.(5)]. The trend observed in the second phase is almost identical to that of the first one. The temperatures observed at 10% and 20% weight loss percentage also indicate similar trend. However, this pattern varies above 50% weight loss, wherein, a gradual change in the decomposition temperature with

increasing concentration of MMA was not observed. The complete decomposition occurs in the range 505°C-550°C with the first sample exhibiting the maximum decomposition temperature (550°C) and the fourth one showing the lowest (505°C) temperature in the series. The glass transition temperature of PNPA is 110°C. This study clearly establishes the higher thermal stability of nitrophenyl acrylate when compared to that of MMA. The tacticity of the copolymer also plays an important role in determining the thermal stability of the compolymer (26). The glass transition temperature (T_g) was reported to decrease with increasing mole fraction of styrene in a MMA-STY copolymer (27). The glass transition temperature of poly (NPA-co-MMA) with a molar composition of NPA:MMA = 0.46:0.54 was found to be 104.4°C in the present investigation.

CONCLUSION

The copolymers poly (NPA-co-MMA) with seven different compositions were synthesized by taking different mole ratios of NPA and MMA and polymerizing them in 2-butanone using BPO as the initiator. The monomer 4-nitrophenyl acrylate was also synthesized from 4-nitrophenol and the characterization of monomer as well as the polymers was done by IR and NMR spectral studies. The formation of copolymers were ascertained by ^{1}H-NMR spectral studies. The molecular weight of the copolymers was found out by gel permeation chromatography and the number average molecular weight (M_n) of these systems lie in the range 2.2-2.7 x 10^4, while their weight average molecular weight ($\overline{M_w}$) is found to be 4.1-4.6 x 10^4. The reactivity ratios of the monomers in poly(NPA-co-MMA) evaluated by Fineman-Ross, Kelen-Tudos and Extended Kelen-Tudos methods indicate that the product of r_1-r_2 is 0.924, 0.961, and 0.935, respectively and hence the arrangement of monomers NPA and MMA in the copolymer is a random one.

The Q, e values of NPA determined by Alfrey-Price method were found to be 0.565 and 0.600, respectively. Thermal properties of these systems were also investigated by TGA and DSC. The decomposition of all the polymers occur in the temperature range 165-550°C and the initial decomposition temperature (IDT) is maximum when NPA concentration is zero, which is closely followed by the system with the composition NPA:MMA = 0.772:0.228. The glass transition temperature of one of the systems (NPA:MMA = 0.46:0.54) is found to be 104.4°C.

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