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### Copolymers of *p*-Nitrobenzyl Acrylate with Methyl Acrylate: Synthesis, Characterization, and Monomer Reactivity Ratios

E. Murugan<sup>a</sup>; S. Nanjundan<sup>b</sup>

<sup>a</sup> Department of Physical Chemistry, University of Madras, Madras, India <sup>b</sup> Department of Chemistry College of Engineering, Anna University, Madras, India

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## **COPOLYMERS OF *p*-NITROBENZYL ACRYLATE WITH METHYL ACRYLATE: SYNTHESIS, CHARACTERIZATION, AND MONOMER REACTIVITY RATIOS**

E. MURUGAN

Department of Physical Chemistry  
University of Madras  
Madras 25, India

S. NANJUNDAN\*

Department of Chemistry  
College of Engineering  
Anna University  
Madras 600025, India

### **ABSTRACT**

Copolymers of *p*-nitrobenzyl acrylate and methyl acrylate with different feed ratios are synthesized in ethyl methyl ketone using benzoyl peroxide as a free radical initiator at  $70 \pm 1^\circ\text{C}$ . The copolymers were characterized by IR and  $^1\text{H-NMR}$  spectroscopic techniques. Copolymer compositions were determined by  $^1\text{H-NMR}$  analysis of the polymers. The monomer reactivity ratios were determined by the application of conventional linearization methods such as Fineman-Ross and Kelen-Tüdös. Gel permeation chromatography was used for determining the molecular weights  $\bar{M}_n$  and  $\bar{M}_w$ , and the polydispersity index. The intrinsic viscosities and the thermal properties of the homo- and copolymers are also discussed.

## INTRODUCTION

Polymers with reactive functional groups are synthesized, analyzed, and used not only for their macromolecular properties (bulk properties of the polymers) but also for specific end applications [1]. Among the techniques available for the synthesis of a functional polymer, synthesis of a prepolymer which consists of activated acrylates and its modification with various reagents to get the desired polymers is noteworthy [2–4]. Polymers of *o*-nitrobenzyl acrylates are known to exhibit photo-hardenable properties [5]. Copolymers formed from (2-nitrophenyl)methyl acrylate, methyl methacrylate, and acrylic acid or hydroxypropyl acrylate are used in the production of printing plates and electrical circuits [6, 7]. Polymers based on *p*-nitrobenzyl methacrylate are used for the preparation of organic electrophotographic photoconductor compositions having high sensitivity, a low dark-decay rate, low toxicity and excellent durability [8, 9]. Melvin et al. [10] and David et al. [11] reported the use of *p*-nitrobenzyl acrylate (PNBA) as an ingredient in erodible ship bottom paints for control of marine fouling.

The accurate estimation of copolymer composition and determination of reactivity ratios is significant for tailor-making copolymers with required physicochemical properties and in evaluating the end applications of copolymers. In the past few decades, <sup>1</sup>H-NMR spectroscopic analysis has been established as a powerful tool for the determination of tacticity and sequence distribution as well as for the estimation of copolymer composition because of its simplicity, rapidity, and sensitivity [12–14]. The present article discusses the copolymerization behavior of *p*-nitrobenzyl acrylate (PNBA) and methyl acrylate (MA) in solution, characterization of the copolymers, and determination of monomer reactivity ratios.

## EXPERIMENTAL

Methyl acrylate was freed from inhibitor by washing with 5% aqueous sodium hydroxide solution, dried over calcium chloride, and distilled twice under reduced pressure. Benzoyl peroxide (BPO) was recrystallized from a chloroform–methanol (1:1) mixture. The solvents were purified by distillation.

### Synthesis of *p*-Nitrobenzyl Acrylate

Acryloyl chloride was prepared by reacting acrylic acid with benzoyl chloride [15]. The *p*-nitrobenzyl acrylate was synthesized by reacting *p*-nitrobenzyl alcohol (0.16 mol) with acryloyl chloride (0.16 mol) at 0 to 5°C in the presence of triethyl amine (0.16 mol) in ethyl methyl ketone solution. The quaternary ammonium salt was filtered off and the filtrate evaporated. The crude product obtained was recrystallized from ethanol, and the crystalline product melted at 81.5 to 82°C.

The formation of the monomer was confirmed by IR, and <sup>1</sup>H-NMR techniques.

IR (cm<sup>-1</sup>): 3100, 2950, 1740, 1660, 1600, 1510, 1140, 840.

<sup>1</sup>H-NMR (ppm): 8.30 (2H), 7.61 (2H), 7.3 (H), 4.9–4.6 (2H), 5.23 (2H).

### Copolymerization

Predetermined quantities of *p*-nitrobenzyl acrylate and methyl acrylate with ethyl methyl ketone (EMK) and benzoyl peroxide were placed in a standard reaction tube (100 mL) and the mixture was flushed with oxygen-free nitrogen for 20 minutes. The tube was tightly sealed and immersed in a thermostated water bath maintained at  $70 \pm 1^\circ\text{C}$ . The conversions were restricted to less than 10% by pouring the solution into excess methanol, the precipitated polymer was filtered off and purified by reprecipitation from chloroform solution using methanol, and finally dried in a vacuum oven at  $40^\circ\text{C}$  for 24 hours.

### Instrumentation

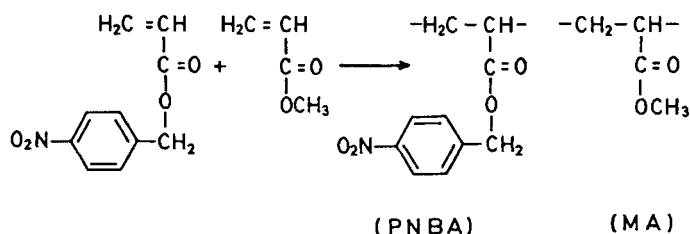
$^1\text{H-NMR}$  spectra of all the copolymer samples were run on a Hitachi-R600 60 MHz NMR spectrometer. Spectra were recorded at room temperature for 15–20% (w/v) solutions in  $\text{CDCl}_3$ , and TMS was the internal standard. The IR spectra of the copolymers were recorded on a Hitachi 270-50 IR spectrophotometer using KBr pellets. The molecular weights ( $\overline{M}_n$ ,  $\overline{M}_w$ ) of the polymers were determined by Waters 501 Gel Permeation Chromatography equipment with an RI detector and calibrated with polystyrene standards and THF as the eluent. Viscometric measurements were made in dimethylformamide (DMF) at  $30^\circ\text{C}$  with an Ubbelohde suspended level viscometer. Thermogravimetric analysis was performed with a Metler 3000 thermal analyzer at a heating rate of  $15^\circ\text{C}$  per minute in air.

## RESULTS AND DISCUSSION

Five copolymers of PNBA and MA with different feed compositions were synthesized by radical solution polymerization in EMK using benzoyl peroxide as initiator. Copolymerization was allowed to proceed to low conversion (less than 10%) in order to obtain polymer samples having a homogeneous composition as far as possible. The copolymer monomeric units are shown in Scheme 1.

### Characterization

The copolymers were soluble in chloroform, acetone, dimethylformamide, tetrahydrofuran, and dimethylsulfoxide but insoluble in nonpolar solvents like xylene, benzene, and hexane as well as hydroxy-group-containing polar solvents like water, methanol, and ethanol.



SCHEME 1.

The IR spectrum of the copolymer reveals that the PNBA unit has more prominent features than the MA. The peaks at  $3040$  and  $2960\text{ cm}^{-1}$  are due to aromatic and aliphatic C—H stretching, respectively. The strong absorption peak at  $1740\text{ cm}^{-1}$  corresponds to esteric C=O stretchings. Absorptions at  $1605$  and  $1515\text{ cm}^{-1}$  are assigned to aromatic C=C vibration, and the bands at  $1160\text{ cm}^{-1}$  may be assigned to ester C—O—C stretching. The peak at  $840\text{ cm}^{-1}$  is due to C—H out-of-plane deformation of the para-disubstituted aromatic ring.

The proton NMR spectrum of the copolymer is shown in Fig. 1. The chemical shift assignments for poly(PNBA-*co*-MA) were based on the chemical shifts observed for the respective homopolymers. The signals between  $8.61$  and  $7.53$  ppm correspond to aromatic protons of the PNBA unit. The signals at  $5.13$ – $5.1$  ppm correspond to  $-\text{OCH}_2$  protons. The resonance signals at  $3.58$ – $3.56$  ppm are due to  $\text{OCH}_3$  protons of methyl acrylate. Signals between  $2.36$  and  $1.76$  ppm are assigned to backbone methyne ( $>\text{CH}-$ ) and methylene ( $-\text{CH}_2-$ ) protons.

### Copolymer Compositions and Reactivity Ratios

Copolymer compositions were determined by  $^1\text{H-NMR}$  analysis. The assignment of the resonance peaks in the  $^1\text{H-NMR}$  spectrum allow for the accurate evaluation of the content of each kind of monomeric unit incorporated into the copolymer chains. Resonance signals at  $8.61$ – $7.53$  ppm in Fig. 1 correspond to aromatic protons (four) of PNBA, and the signals ranging from  $5.13$  to  $1.77$  ppm are due to the aliphatic protons (eleven) of the copolymer. Hence the compositions of PNBA units in the PNBA-MA copolymers were calculated by comparing the intensities of the aromatic protons of PNBA and the total aliphatic protons of the copolymer.

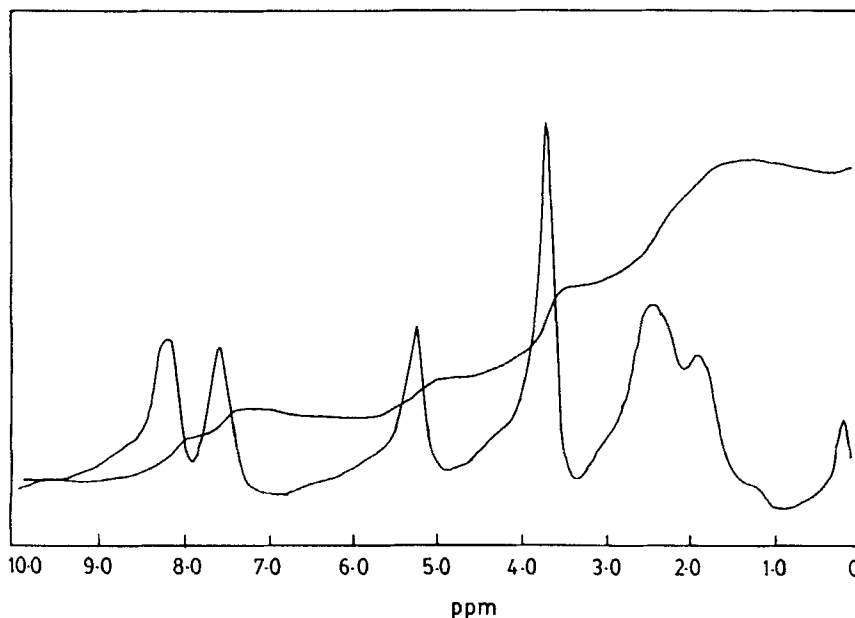


FIG. 1.  $^1\text{H-NMR}$  spectrum of PNBA-*co*-MA polymer system. (0.64:0.36).

The following expression was derived from copolymers consisting of both monomer units. Let  $m_1$  be the mole fraction of PNBA and  $(1 - m_1)$  that of MA. There are four aromatic protons and five aliphatic protons in PNBA, and six aliphatic protons in MA.

$$C = \frac{\text{intensity of aromatic protons } (I_{Ar})}{\text{intensity of aliphatic protons } (I_{Al})} = \frac{4m_1}{5m_1 + 6(1 - m_1)} \quad (1)$$

which on simplification yields

$$m_1 = \frac{6C}{4 + C} \quad (2)$$

Based on Eq. 2, the mole fraction of PNBA in all copolymers was calculated by measuring the intensities of the aromatic proton signals and aliphatic proton signals from the spectra of all copolymer samples. Table 1 gives the value of  $C$  and the corresponding mole fractions in the copolymers.

The normal kinetic behavior was determined by plotting the mole fractions of PNBA in the feed vs that in the copolymer, and the curve (Fig. 2) indicates that the distribution of the monomeric unit is random and in no case is a homopolymer formation expected.

From the monomer feed ratios and the resultant copolymer compositions, the reactivity ratios of PNBA and MA were evaluated by the methods of Fineman-Ross and Kelen-Tüdös. According to Fineman-Ross (F-R), the reactivity ratios of monomer pairs can be found by using

$$F(f - 1)/f = r_1(F^2/f) - r_2 \quad (3)$$

A graphical evaluation of the conventional linear equation suggested by Kelen-Tüdös [16, 17] was followed, and no corrections for conversion were made to determine the reactivity ratios.

$$\eta = \left[ r_1 + \frac{r_2}{\alpha} \right] \zeta - \frac{r_2}{\alpha} \quad (4)$$

TABLE 1. Composition Data for the Free Radical Copolymerization of *p*-Nitrobenzenyl Acrylate with Methyl Acrylate in EMK Solution at  $70 \pm 1^\circ\text{C}^a$

Feed composition		Conversion, %	Intensities of protons			Copolymer composition	
$M_1$	$M_2$		$I_{Ar}$	$I_{Al}$	$C = I_{Ar}/I_{Al}$	$m_1$	$m_2$
0.096	0.904	9.78	10	80.0	0.1250	0.1818	0.8182
0.250	0.750	8.14	19	68.0	0.2794	0.3917	0.6083
0.400	0.600	9.56	44	111.0	0.3964	0.5410	0.4590
0.500	0.500	8.46	48	101.0	0.4752	0.6371	0.3629
0.700	0.300	8.33	50	82.5	0.6061	0.7895	0.2105

<sup>a</sup> $M_1$  and  $M_2$  are the mole fractions of PNBA and MA, respectively, in the feed.  $m_1$  and  $m_2$  are the mole fractions of PNBA and MA, respectively, in the copolymer.

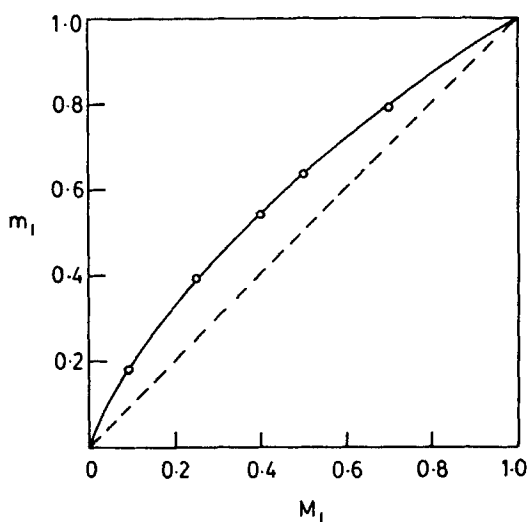


FIG. 2. Composition diagram of PNBA-MA copolymer system.

where  $r_1$  and  $r_2$  are the reactivity ratios relating to monomer 1 (PNBA) and monomer 2 (MA) respectively. The significance of parameters of F-R and K-T equations are as defined and presented in Table 2. The reactivity ratios obtained from the F-R and K-T plots (Fig. 3), are

F-R method:  $r_1 = 1.49 \pm 0.04$  and  $r_2 = 0.44 \pm 0.02$

K-T method:  $r_1 = 1.50 \pm 0.03$  and  $r_2 = 0.45 \pm 0.02$

The difference between the two measurements is well within experimental error. The value of  $r_1$  is more than 1 and that of  $r_2$  is less than 1. The product of  $r_1$  and  $r_2$  ( $r_1 r_2 = 0.675$ ), however, remains less than 1, thus indicating that the system follows a random distribution of the monomeric units. The  $r_1$  value, which is more

TABLE 2. Fineman-Ross and Kelen-Tüdös Parameters for the Copolymerization of *p*-Nitrobenzyl Acrylate with Methyl Acrylate<sup>a</sup>

$F =$ $M_1/M_2$	$f =$ $m_1/m_2$	F-R parameters		K-T parameters	
		$G =$ $F(f - 1)/f$	$H = F^2/f$	$\eta =$ $G/(\alpha + H)$	$\zeta =$ $H/(\alpha + H)$
0.1062	0.2222	-0.3717	0.0508	-1.1529	0.1576
0.3333	0.6439	-0.1843	0.1725	-0.4150	0.3884
0.6667	1.1786	0.1010	0.3771	0.1557	0.5813
1.0000	1.7556	0.4304	0.5696	0.5117	0.6771
2.3330	3.7506	1.7112	1.4516	0.9930	0.8424

<sup>a</sup> $M_1 = \text{PNBA}, M_2 = \text{MA}, (H_{\min} \times H_{\max})^{1/2} = 0.2716.$

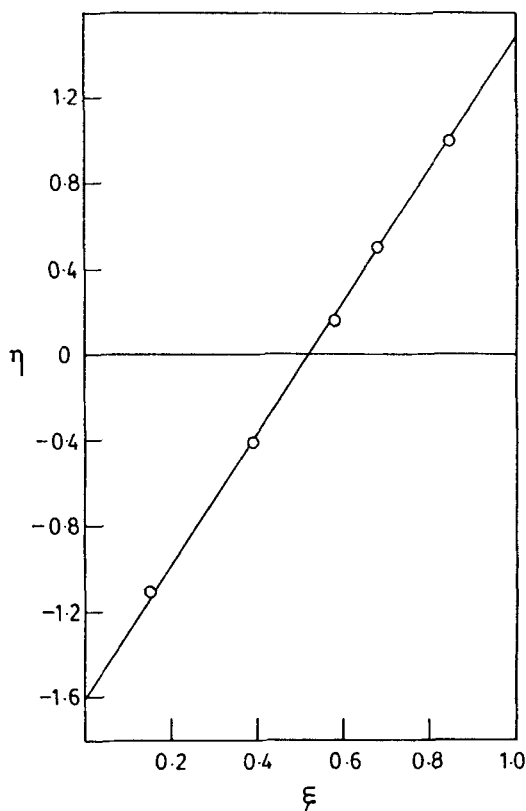


FIG. 3. K-T plot for the determination of reactivity ratios of PNBA-MA copolymer system.

than 1, indicates the presence of a higher amount of PNBA units in the copolymer than in the feed.

### Molecular Weights

The number-average, weight-average molecular weights ( $M_n$ ,  $M_w$ ), and polydispersity index of homopolymers as well as of four copolymer samples were determined by gel permeation chromatography and are given in Table 3. The polydispersity index of poly(PNBA), poly(MA), and the copolymers are very close to 1.5. The theoretical value of  $\overline{M}_w/\overline{M}_n$  for polymers produced via radical combination and disproportionation are 1.5 and 2, respectively [18]. In the homopolymerization of MA the free radicals undergo termination mainly by recombination [19]. The value of  $\overline{M}_w/\overline{M}_n$  for the poly(PNBA) and the copolymers suggests a strong tendency for chain termination by recombination.

### Viscosity Measurements

The intrinsic viscosities  $[\eta]$  were obtained by extrapolating  $\eta_{sp}/C$  to zero concentration. The data in Table 3 clearly indicates that the value of  $[\eta]$  is affected by the composition of the copolymer and the change is not uniform.



TABLE 3. Intrinsic Viscosities and Molecular Weights Data for the Copolymers of *p*-Nitrobenzyl Acrylate with Methyl Acrylate

Polymer	Copolymer composition		Intrinsic viscosity [ $\eta$ ], dL/g	Molecular weights		
	$m_1$	$m_2$		$\bar{M}_w \times 10^{-4}$	$\bar{M}_n \times 10^{-4}$	$\bar{M}_w/\bar{M}_n$
Poly(PNBA)	1.00	0.00	0.38	2.72	1.66	1.64
1	0.18	0.82	0.29	2.47	1.56	1.54
2	0.39	0.61	0.26	2.30	1.45	1.59
3	0.54	0.46	0.28	2.35	1.56	1.54
4	0.64	0.36	0.33	—	—	—
5	0.79	0.21	0.36	2.54	1.74	1.46
Poly(MA)	0.00	1.00	0.32	2.46	1.67	1.47

### Thermal Analysis

Thermogravimetric analysis curves of poly(PNBA) and two copolymer samples are presented in Fig. 4; Table 4 gives the decomposition temperatures. The data clearly show that poly(MA) undergoes decomposition in a single stage whereas poly(PNBA) and the copolymers undergo decomposition in two different stages. The initial decomposition temperatures of poly(PNBA) and poly(MA) are 350 and 255°C, respectively; those of the copolymers are intermediate. The stability of the copolymers decreases with an increase of MA in the copolymer chain.

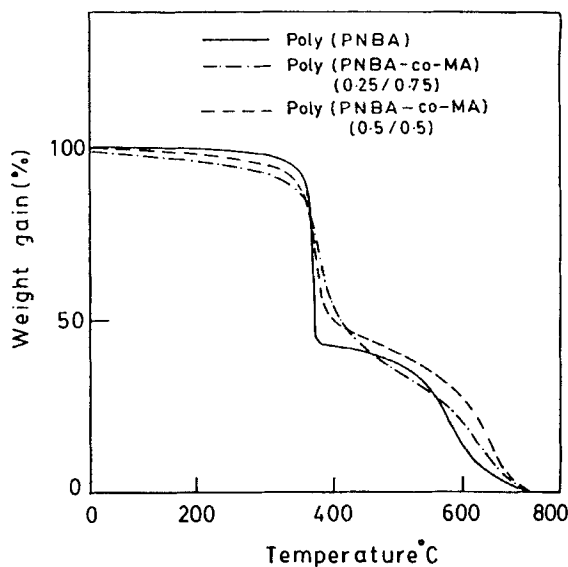


FIG. 4. TGA curves of poly(PNBA) and poly(PNBA-co-MA).

TABLE 4. TGA Data of Homo and PNBA-*co*-MA Polymer System<sup>a</sup>

Polymer	Copolymer composition		IDT	$T_{\max 1}$	$T_{\max 2}$
	$m_1$	$m_2$			
Poly(PNBA)	1.00	0.00	350	375 (57.32)	580 (71.82)
2	0.39	0.61	325	382 (40.12)	675.15 (87.80)
4	0.64	0.36	341	387.5 (46.33)	643.75 (88.75)
Poly(MA)	0.00	1.00	255	—	—

<sup>a</sup>IDT = initial decomposition temperatures in °C.

$T_{\max 1}$ ,  $T_{\max 2}$ , etc. = temperature at which maximum weight loss occurs. Figures in parentheses indicate the total weight loss (%) up to the temperatures stated.

## CONCLUSION

Poly(*p*-nitrobenzyl acrylate) and the copolymers of PNBA with MA were synthesized in solution by free radical polymerization. Characterization of PNBA and PNBA-*co*-MA were performed with IR and <sup>1</sup>H-NMR spectroscopy. Copolymer compositions were calculated by proton NMR analyses. The reactivity ratios were determined by both F-R and K-T methods, and the values obtained ( $r_1 = 1.49 \pm 0.04$ ,  $1.50 \pm 0.03$  and  $r_2 = 0.44 \pm 0.02$ ,  $0.45 \pm 0.02$ ) are in good agreement. The  $r_1$  values of both methods are greater than 1, and this indicates that PNBA is more reactive than MA. The copolymerization of PNBA with MA ( $r_1 r_2 = 0.675$ ) resulted in random distribution of the monomeric units. GPC data showed that the polydispersity index of the poly(PNBA), poly(MA), and poly(PNBA-*co*-MA) is very close to 1.5, suggesting chain termination by combination. Thermogravimetric analysis results indicated that poly(PNBA) is thermally more stable than poly(MA), and incorporation of poly(MA) reduced the thermal stability of poly(PNBA). Intrinsic viscosity values also proved the nonuniformity of the copolymer.

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