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RESEARCH ARTICLE

SYNTHESIS, CHARACTERIZATION OF POLY (4- BENZYLOXYPHENYLMETHACRYLATE) AND ITS COPOLYMER WITH ACRYLONITRILE AND DETERMINATION OF MONOMER REACTIVITY RATIOS

Somu Mageswari, Narayanan Nisha, John Santhosh Kumar and Kathavarayan Subramanian*

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

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ABSTRACT

The monomer 4-benzyloxyphenylmethacrylate (4-BOPMA) was synthesized by reacting 4-benzyloxy phenol dissolved in methylethylketone (MEK) with mathacryloyl chloride in the presence of triethylamine. The homopolymer and various copolymers of 4-BOPMA with acrylonitrile (AN) were synthesized by the free radical polymerization in MEK at 70 ± 1°C in nitrogen atmosphere using benzoylperoxide as initiator. The homopolymer and copolymers were characterized by various spectral techniques like IR, ^{1}H-NMR, ^{13}C-NMR spectroscopic techniques. The molecular weights of the polymers were determined by gel permeation chromatography. The glass transition temperature of the polymers were determined by differential scanning calorimetry. The thermal stability of the polymers were performed by thermogravimetric analysis in inert atmosphere. The monomer reactivity ratios were determined using the conventional linearization methods such as Fineman – Ross (r_1 = 0.5858, r_2= 0.2263), Kelen Tüdös (r_1 = 0.5726, r_2 = 0.1517) and extended Kelen Tüdös (r_1 = 0.5691, r_2 = 0.1880).

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INTRODUCTION

Acrylic polymers which include methyl methacrylate and acrylate esters have acquired prime importance in various fields of industrial applications [1-3]. The acrylates and methacrylates esters in copolymerization reaction have great interest in commercial applications due to the well known characterstics of optical clarity and durability. By variation in composition, the basic copolymer system has been adapted to a wide variety of other applications which include coating of paper, leather and cement shingles, pigment binders in cellulose sponge and laminating adhesives. They find application mainly in dyeing of textiles. The other applications of these polymers are canvas finishing, flame proofing, water and oil repellency, transparent coating, positive and negative photoresist and electroconductive coating. Acrylic and methacrylic copolymers are widely used as binders in protective coatings because of excellent durability, water white color and transparency [4-7]. The other important applications of these resins are as primers for automotive finishes, clean lacquers for household applications like washing machines, refrigerators etc. Methacrylate copolymers are used in drug delivery system and in immobilization techniques [8-9]. Adhesives based on acrylic and methacrylic copolymers are widely used in wood, composite and leather industries because of their versatility and high performance characteristic [10]. These copolymers also find applications in the manufacture of high gloss shoes. Copolymers of long chain alkyl methacrylates are added to petroleum and synthetic lubricants to lower the pour point and improve the viscosity index. In the study of copolymerization, monomer reactivity ratios are very important quantities allowing prediction of the copolymer composition for any starting feed. In the past few decades, ^{1}H-NMR spectroscopic analysis has been established as a powerful tool for the determination of copolymer composition [11-14] and determination of monomer reactivity ratios is significant for tailor made copolymers with required physical and chemical properties and evaluating the specific end application of the copolymers. The main aim in commercial polymerization is to achieve a desirable product composition. Knowledge about the reactivity ratios of the comonomers help in this connection. We have reported many polymethacrylate polymers and copolymers which were published in reputed journals [15–19]. The monomer reactivity ratios were determined using the conventional linearization methods such as Fineman–Ross [20] Kelen-Tudos and Extented Kelen–Tudos [21, 22]. The present paper reports the synthesis, characterization of monomer reactivity ratios for 4-benzyloxyphenylmethacrylate copolymers with Acrylonitrile. Since there are no reports have been found about this copolymer system in chemical abstracts.

EXPERIMENTAL

Materials

4–Benzyloxy phenol (Aldrich) was used as received. Acrylonitrile(AN) fluka was purified by distillation under reduced pressure. Benzoylperoxide (fluka) was recrystallized

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***Corresponding author:** kathsubramanian@yahoo.com

from chloroform-methanol (1:1) mixture. All solvents purified by distillation.

Synthesis of 4–benzyloxyphenylmethacrylate

Methacryloyl chloride was prepared from methacrylic acid and benzoyl chloride using the procedure of Stampel *et al.* [23]. For the synthesis of 4-BOPMA, a three necked round bottomed flask (500ml) fitted with thermometer, stirrer, dropping funnel containing of 4-benzyloxyphenol (10.012g), triethylamine (7.65 ml), hydroquinone(0.5 g) and 2-butanone (300 ml) was cooled at -5 ºC to 0ºC. Methacryloyl chloride (5.4 ml) dissolved in 2-butanone (30 ml) was added slowly with stirring and the temperature maintained at -5 ºC to 0 ºC (Scheme 1). The stirring was continued for one hour. The reaction mixture was stirred for another 2 hours at room temperature and precipitated quaternary ammonium salt was filtered off. The unreacted contents and hydroquinone were removed by successive extraction with 5% sodium hydroxide and distilled water. After drying over anhydrous sodium sulphate, methylethylketone (MEK) was evaporated on rotatory evaporator. The crude product was recrystallized from ethanol to give 12 grams (yield 70%) of pale yellow crystals. Melting point is across 99-100 ºC.

Homopolymerization

Five grams of 4-BOPMA and BPO (0.5% wt of monomer) in 20 ml MEK was taken in a polymerization tube and O_2 free N_2 was purged through the solution for 20 min. Then the solution was thermostated at 70ºC. After 8 hrs the polymer was precipitated in methanol. It was purified by repeated reprecipitation by methanol in MEK. The polymer was then dried in vaccum at 50°C (Scheme 2).

Copolymerization

Predetermined quantities of 4-BOPMA, AN, MEK and BPO were placed in a standard reaction tube (100 ml) and the mixture was flushed with O_2 free N_2 for 20 min. The tube was tightly sealed and immersed in a water bath at 70 ± 1°C. After the required time (7-10 hrs) the polymer was precipitated in methanol. The precipitated polymer was filtered off and purified by repeated reprecipitation from chloroform solution using methanol and finally dried in vacuum at 50°C for 24 hrs. The copolymer conversions were restricted to less than 10% (Scheme 3).

Characterization techniques

Elemental analysis was recorded using Heraeus-CHN-analyzer. UV spectra were recorded in Hitachi RS1 spectrophotometer. IR spectra were recorded with a Nicolet Avatar 360 FT-IR spectrophotometer as KBr pellets. ^{1}H-NMR spectra of all the monomer and polymer samples in $CDCl_3$ were recorded on a Bruker 500 MHz FT-NMR spectrometer at room temperature using tetramethylsilane as internal standard. The proton-decoupled ^{13}C-NMR spectrum was run on the same instrument operating at 500MHz at room temperature and the chemical shifts were recorded under similar conditions. The molecular weights (M_w and M_n) were determined using a Cirrus gel permeation chromatograph. Tetrahydrofuran was used as an eluent with polystyrene standards for calibration. Thermogravimetric analysis was performed with a Setaram TG STSYS 16/18 thermal analyzer in air at a heating rate of 20°C / min. The glass transition temperature was determined with a DSC Q10 V9.0.thermal analyzer at a heating rate of 10°C /m in nitrogen.

Solubility studies

The solubility of the homopolymer and the copolymers were tested by mixing 20 mg of the polymer with 2 ml of various solvents in test tubes. After setting aside the closed tubes for one day the solubility was noticed.

RESULTS AND DISCUSSION

Characterization of monomer

The monomer was examined by elemental analysis, FT-IR, ^{1}H-NMR, Spectra. Elemental analysis (%): C = 75.89(found), 75.90 (calcd); H= 6.37 (found), 6.38 (calcd). IR (KBr, cm^{-1}): 1730 (ester; >C=O); 1250, 1140 (ether; C-O-C); 1503 (aromatic; C==C); 1638 (C=C);2938, 2950 ($-CH_2$, CH_3) ^{1}H-NMR ($CDCl_3$, δ): 7.3-6.8(m): - Ar-H; 5.0(s): $-O-CH_2Ph$; 2.5-2.0: $-CH_2$ 1.4-1.6: $-CH_3$

Characterization of homopolymer

Solubility parameters

The polymers were soluble in polar aprotic solvents like tetrahydrofuran, dimethyl formamide, dimethyl sulphoxide. It is soluble in chloroform, methylene dichloride etc. They are also soluble in hydrocarbons such as benzene, xylene, toluene, and hydroxyl group containing solvents such as methanol, ethanol and 2-propanol.

IR Spectra

IR spectrum of homopolymer is shown in fig1. Absorption at 3465 cm^{-1} corresponds to aromatic C-H stretching. C=C aromatic stretching absorption is observed at 1503 cm^{-1} and out of plane bending absorption in the region 690–900 cm^{-1}. The strong absorption peak at 1746 cm^{-1} is due to ester carbonyl C=O stretching vibrations. C-O stretching frequency of alcoholic part of ester is observed at 1008 cm^{-1} and the acid part at 1188 cm^{-1} and 1297 cm^{-1} respectively. C-O-C stretching frequency of ether is observed in the region 1247 cm^{-1} and 1103 cm^{-1}. The bending vibrations of methylene and methyl group are observed at 1453 cm^{-1} and 1382 cm^{-1}. The peak at 2933 cm^{-1} and 2878 cm^{-1} corresponds to symmetrical and asymmetrical stretching due to methyl and methylene groups. Peak at 500 cm^{-1} corresponds to C=C out of plane bending vibrations.

^{1}H-NMR spectra

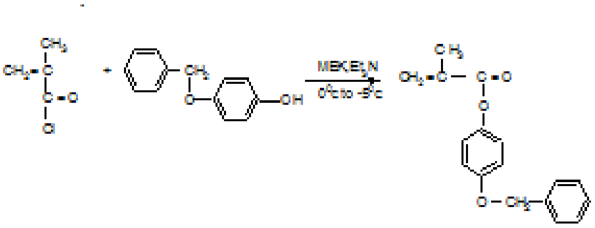
^{1}H-NMR spectra of the homopolymer is shown in fig 2. The multiplet in the region 7.3-6.8 ppm corresponds to aromatic protons. The resonance signal at 5 ppm corresponds to benzyloxy protons. The group of signals between 2.5-2.0 and 1.4-1.6 are due to the presence of backbone CH_2 and CH_3 protons.

^{13}C-NMR spectra

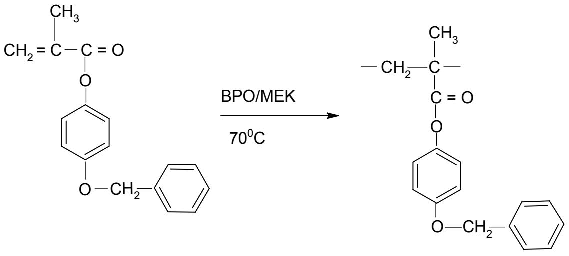
The proton decoupled ^{13}C NMR spectra of homopolymer is shown in figure 3. The resonance signals at 175.30 – 176.18 ppm correspond to ester carbonyl carbon. The aromatic

Scheme

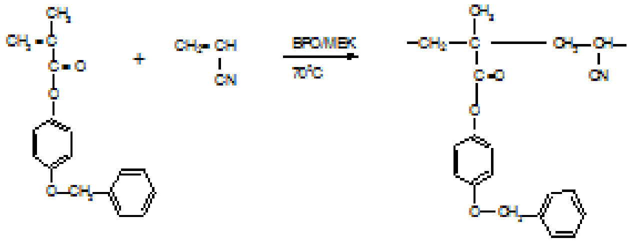
Scheme 1: Synthesis of 4-BOPMA



Scheme 2: Synthesis of poly (4-BOPMA)



Scheme 3: Synthesis of poly (4-BOPMA-co-AN)



resonance signals are observed at 115 – 144.30 ppm. Signals at 54.74, 45.94 ppm are assignable to backbone carbon CH_2, -C -. α – methyl carbon of the methacrylate polymers appear at 18 – 20 ppm. In addition the benzyloxycarbon resonance signal is observed at about 70.42 ppm.

Molecular weights

The weight (M_w) and number (Mn) average molecular weight of the homopolymer determined by gel permeation chromatography is found to be 136839, 91320 respectively and the polydispersity indice (M_w/M_n) is found to be 1.49. The polydispersity index of methacrylate polymers is closer to 1.5. Usually the polydispersity index of polymethacrylates prepared by free radical polymerization of the monomers depends, among other factors on chain termination mechanism. The theoretical values of M_w/M_n for polymers reduced via radical recombination and this disproportionation are 1.5 and 2 respectively [16].

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Ultra violet spectra

The homopolymer exhibits UV absorption maxima in chloroform solution at 277 – 299 nm. The bathochromic shift of UV absorption maxima might be due to the presence of electron donating benzyloxy group.

Thermogravimetric analysis

Thermogravimetric analysis was used in estimating the percentage weight loss of the copolymer against temperature. The initial decomposition temperature (IDT) of poly (4-BOPMA) is 220ºC. Poly (4-BOPMA) undergoes two stage decomposition, showing first stage decomposition between 220 ºC - 350 ºC with a weight loss of 40% and second stage decomposition between 351 ºC - 450 ºC with a weight loss of 80%.

Glass transition temperature

The glass transition temperature of polymer is determined by differential scanning calorimetry. The polymers show single glass transition temperature, thus indicating the absence of formation of block copolymers or a mixture of homopolymer. The T_g value of poly (4-BOPMA) is 95.26 ºC. The relatively high value of T_g for the homopolymer is due to α – methyl group introduced into the backbone which leads to chain entanglement and shows amorphous nature of the homopolymer.

Characterization of copolymer

Solubility parameters

The copolymer was soluble in polar aprotic solvents like tetrahydrofuran, dimethyl formamide, dimethyl sulphoxide. It is soluble in chloroform, methylene dichloride etc. They are also soluble in hydrocarbons such as benzene, xylene, toluene, and hydroxyl group containing solvents such as methanol, ethanol and 2-propanol.

IR spectra

The IR spectrum of the copolymer is shown in figure 4. The IR spectrum shows the characteristics bands of both the unit. The less intense peak at 2250 cm^{-1} is due to the presence nitrile group of AN unit. The ester group peak appeared at 1751cm^{-1} along with C-O-C stretching at 1250 and 1191 cm^{-1}. The peak at 1509 cm^{-1} is due to C=C aromatic stretching vibrations. The peaks between 614 – 900 cm^{-1} corresponds to aromatic C-H stretching frequency and out of plane bending frequency respectively. The peak at 1384 cm^{-1} corresponds to CH_3 bending. . The peak at 2940 cm^{-1} and 2958 cm^{-1} corresponds to symmetrical and asymmetrical stretching due to methyl and methylene groups. Peak at 525cm^{-1} corresponds to C=C out of plane bending vibrations.

Molecular weights of copolymers

The weight (M_w) and number (M_n) average molecular weight and the polydispersity index (M_w/M_n) of the copolymer determined by gel permeation chromatography is found to be 16649, 9969 and 1.67 respectively. The polydispersity index of methacrylate polymers is closer to 2. Usually the poly dispersity index of polymethacrylates prepared by free radical polymerization of the monomers depends, among other factors on chain termination mechanism. The theoretical values of M_w/M_n for polymers produced via radical recombination and this disproportionation are 1.5 and 2 respectively.

^{1}H - NMR spectra

Figure 5 show the ^{1}H NMR spectra of the copolymers in deutrated chloroform solutions. The chemical shift assignments for the copolymers are shown in table 3.16. The multiplet signals between 6.9-7.3 ppm correspond to aromatic

Table 1. Thermal Studies for the copolymers of Poly (4-BOPMA-co-AN) TGA and DSC

Polymer	M_1	T_g	IDT	Temperature (°C) at different weight loss (%)				
				10	25	50	75	90
Poly (4-BOPMA)	1.00	95.3	220	280	325	390	425	450
Poly (AN)	1.00	87	197	225	245	290	345	375
Poly (4-BOPMA-co-AN)	0.65	91.9	225	330	360	385	400	445
	0.5	93.2	222	310	339	382	390	440
	0.35	92.5	223	300	337	380	388	442

Table 2. Composition data for copolymerization of 4-BOPMA with AN

Solvent : Methylethylketone initiator :BPO (0.25% by weight of monomer)
Temp : 70 °C

Sl. No	Feed composition (in molefraction)		Conversion %	I_A	I_T	C	Copolymer composition in molefraction	
	4-BOPMA M_1	AN M_2					4-BOPMA m_1	AN m_2
1	0.9016	0.0984	8.34	4.32	7.91	0.5461	0.8622	0.1378
2	0.8066	0.1234	7.86	4.30	8.10	0.5309	0.7590	0.241
3	0.6512	0.3488	9.05	4.29	8.39	0.5113	0.6519	0.3481
4	0.5049	0.4951	6.89	4.24	8.6	0.4930	0.5708	0.4292
5	0.3501	0.6499	8.23	4.35	9.24	0.4708	0.4908	0.5092
6	0.1476	0.8524	7.17	4.15	9.97	0.4162	0.3479	0.6521

I_A: Intensity of aromatic protons in ^1H NMR spectra of copolymers; I_T: Intensity of total protons in ^1H NMR spectra of copolymers.

Table 3. Fineman–Ross (F –R) and Kelen-Tudos (K–T) Parameters for the copolymerization of 4-BOPMA with AN

Copolymer No.	$F = M_1/M_2$	$f = m_1/m_2$	F – R Parameters		K – T Parameters	
			$G = F(f-1)/f$	$H = F^2/f$	$\eta = G/(\alpha + H)$	$\xi = H/(\alpha + H)$
1	9.1626	6.2569	7.6982	13.4177	0.5389	0.9392
2	4.1706	3.1494	2.8463	5.5229	0.4453	08641
3	1.867	1.8727	0.87	1.8613	0.3187	0.6819
4	1.0198	1.3299	0.253	0.782	0.1533	0.4738
5	0.5387	0.9639	-0.0202	0.3011	-0.0173	0.2575
6	0.1732	0.5335	-0.1514	0.0562	-0.1637	0.0608

$\alpha = \sqrt{(H_{min} \times H_{max})} = 0.8684$

M_1 and M_2 are the mole fractions of 4-BOPMA and AN, respectively in the feed; m_1 and m_2 are the mole fractions of 4-BOPMA and AN, respectively in the copolymer

Table 4. Extended K–T parameters for 4-BOPMA–AN copolymer system

Sl. No of Copolymer	1	2	3	4	5	6
ζ_2	0.1209	0.1026	0.0903	0.0549	0.0522	0.0363
ζ_1	0.0826	0.0775	0.0906	0.0716	0.0934	0.1118
Z	0.6691	0.7452	1.0035	1.3157	1.829	3.2064
F	9.3512	4.2262	1.8662	1.0108	0.527	0.1664
H	13.9758	5.6713	1.8597	0.7683	0.2881	0.0519
G	7.8567	2.8843	0.8697	0.2507	-0.0197	-0.1455
η	0.5161	0.4169	0.2799	0.1244	-0.0128	-0.112
ξ	0.9181	0.8197	0.5985	0.3812	0.1876	0.0399

$\alpha = \sqrt{(F_{min} \times F_{max})} = 1.2474$; $\mu = 0.1972$

Table 5. Copolymerization Parameters of Poly (4-BOPMA-co-AN)

Copolymers	Methods	Reactivity Ratios	
		r_1	r_2
Poly (4-BOPMA-co-AN)	F-R	0.5858	0.2263
	K-T	0.5726	0.1517
	Ext. K-T	0.5691	0.1880

protons. Signals at 5.0 ppm and at 4.9 ppm correspond to OCH_2 protons bonded to benzene ring and OCH_2 bonded to butoxy group respectively. Group of muliplet singles in the region of 1.086– 1.60 ppm corresponds to CH_3 protons. Signals at 2.08-2.894ppm arise due to CH_2 protons of both the co-monomer units.

^{13}C - NMR spectra

Figure 6 show the ^{13}C NMR spectra of the copolymer. The resonance signal at 175 – 176 ppm are assignable to ester C=O of both the monomeric units. Signals at 115.45 – 156.41 ppm corresponds to aromatic carbon.The benzyloxy carbon appears

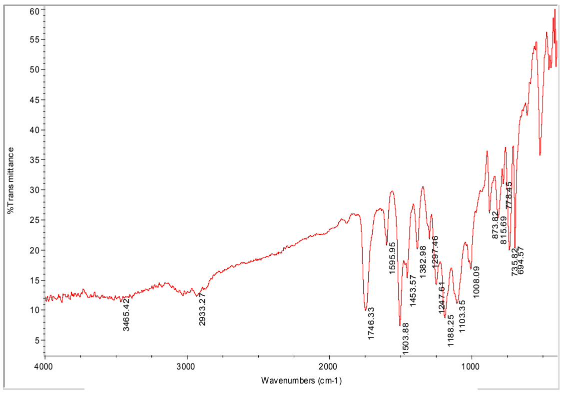

Figure 1. IR spectrum of poly (4-BOPMA)

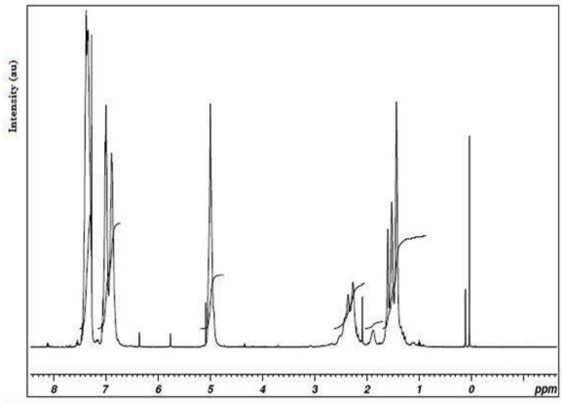

Figure 2 . ^{1}H NMR spectrum of poly (4-BOPMA)

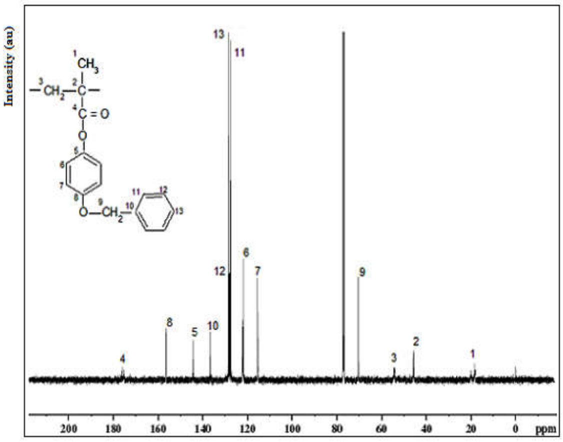

Figure 3. ^{13}C-NMR spectrum of poly (4-BOPMA)

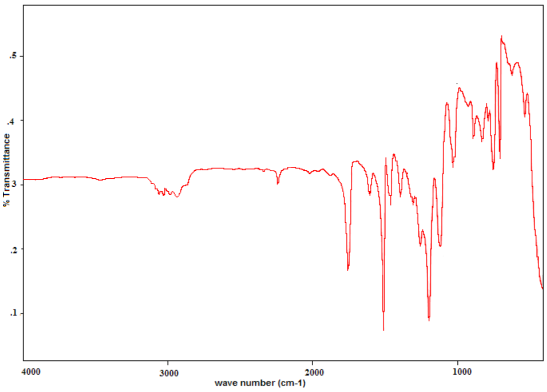

Figure 4. IR spectrum of Poly (4-BOPMA-co-AN)

in the region 70.39 ppm. The methyl carbons appears at 18.41ppm. Backbone methylene and quaternary carbons appear at 45.31-55 ppm.

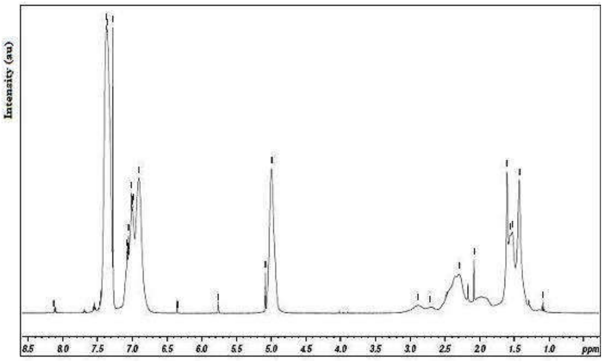

Figure 5. ^{1}H NMR spectra of Poly (4-BOPMA-co-AN)

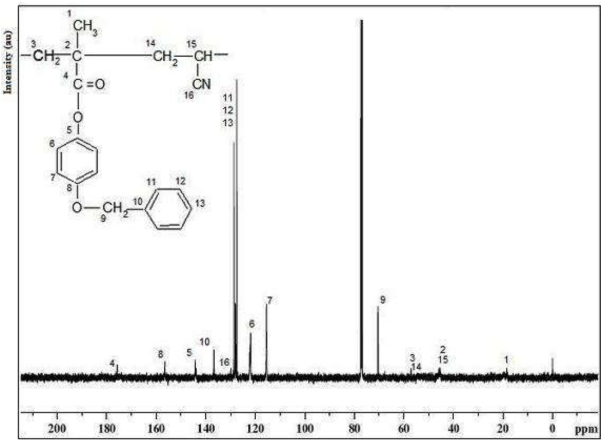

Fig 6: ^{13}C- NMR spectra of Poly (4-BOPMA-co-AN)

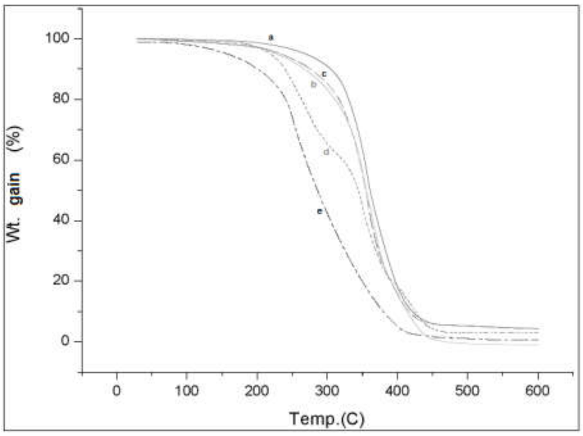

Fig 7. TGA curves of (a) poly (4-BOPMA-co-AN) (0.65:0.35), (b) poly (4-BOPMA-co-AN) (0.5:0.5), (c) poly (BOPMA-co-AN)(0.35:0.65), d) poly(4-BOPMA), (e) poly (AN)

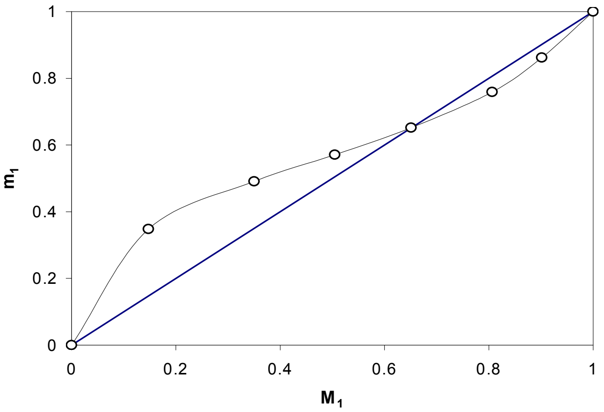

Figure 8. Plot of mole fraction of BOPMA in the feed Vs that in poly (BOPMA-co-AN)

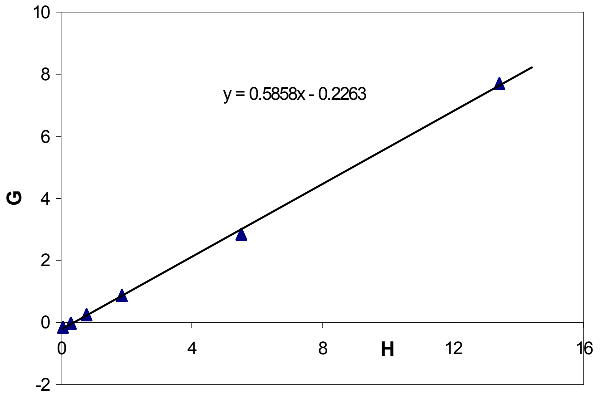

Figure 9a. F-R plot for BOPMA-AN copolymer system

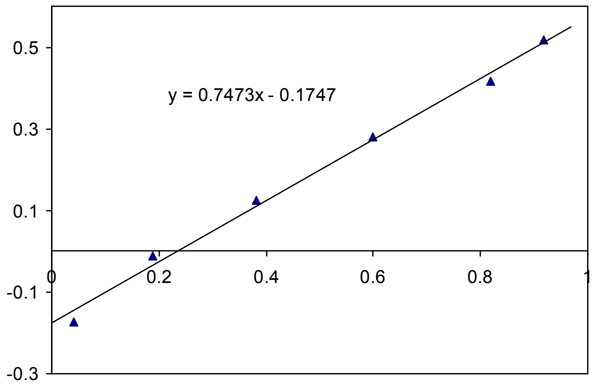

Figure 9b. K-T plot for BOPMA-AN copolymer system

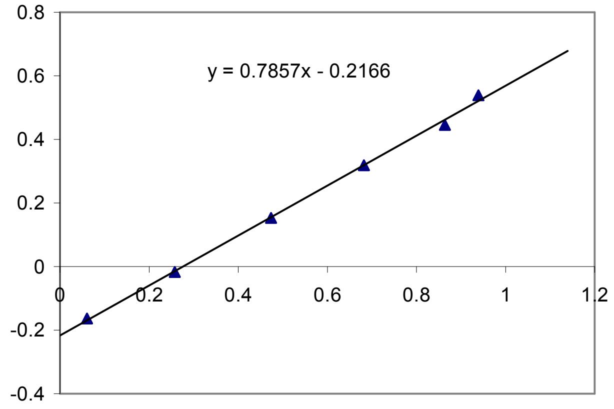

Figure 9c. Ext.K-T plot for BOPMA-AN system

Thermogravimetric analysis of copolymer poly (4-BOPMA-co-AN)

Thermogravimetric analysis was used to estimate the percentage weight loss of the copolymer against temperature. The TGA curve of poly (4-BOPMA), poly (AN) and poly (4-BOPMA-co-AN) are presented in figure 7. Table 1 shows percentage weight loss at different temperature. The initial decomposition temperature (IDT) of poly (4-BOPMA) is 220ºC and that of poly (AN) is 197 ºC. Poly (4-BOPMA) has higher IDT and thus it shows higher thermal stability. Poly (AN) shows one stage decomposition whereas Poly (4-BOPMA) shows two stage decomposition. The copolymers, BOPMA-AN shows only one stage decomposition and their IDT is higher than both the homopolymers. The weight loss of copolymers at temperatures higher than homopolymers indicates higher thermal stability.

Glass transition temperature of copolymer (DSC)

The glass transition temperature of monomers and copolymers were determined by differential scanning calorimetry. The Tg values of all the copolymers were presented in table 3.18. All the copolymers show single glass transition temperature, thus indicating the absence of formation of block copolymers or a mixture of homopolymers.The T_g value of poly (4-BOPMA), poly (AN) are found to be 95.3 ^{o}C and 87 ^{o}C. The variation of T_g of copolymers of poly (4-BOPMA-co-AN) with the mole fraction of BOPMA is shown in table1. The T_g of copolymers are in between that of T_g of the homopolymers. The relatively high value of T_g for the homopolymer and copolymer is due to α – methyl group introduced into the backbone which leads to chain entanglement

Copolymer composition

The average compositions of the copolymer samples were determined from the ^{1}H-NMR spectra. The assignment of the resonance peaks in the ^{1}H-NMR spectrum leads to the accurate evaluation of the content of each kind of monomer. The mole fraction of BOPMA in the copolymer chain was calculated from measuring the integrated peak areas of aromatic protons of 4-BOPMA and total protons. The following expression is used to determine the composition of copolymers. Let 'm_1' be the mole fraction of 4 – BOPMA and '$(1 – m_1)$' that of AN in the copolymer. There are 9 aromatic protons and 19 total protons (16H in 4 – BOPMA and 3H in AN). Hence

$$\frac{9m_1}{16m_1+3\,(1-m_1)} = \frac{\text{Intensity of aromatic protons}}{\text{Intensity of total protons}} = C \qquad (1)$$

$$m_1 = \frac{3C}{9-13C} \qquad (2)$$

From Eq. (2), the mole fractions of 4-BOPMA in the copolymers were determined by measuring the integrated peak areas of the aromatic and aliphatic proton signals. Table 2 gives the values of C and the corresponding mole fractions of BOPMA in the copolymers. The plot of mole fraction of BOPMA (M_1) in the feed Vs that in the copolymer (m_1) is shown in Fig 8. It indicates that the system undergoes azeotropic composition at a particular composition. The azeotropic composition,

$$N_1 = \frac{1-r_1}{2-r_1-r_2} = 0.6566$$

When the mole fraction of monomer in feed is 0.6566, the copolymer formed will have the same composition as that of feed. When the mole fraction of feed is less than 0.6566 with respect to 4-BOPMA, the copolymer is relatively richer in this monomer than the feed. When the mole fraction of 4-BOPMA in feed is above 0.6566, the copolymer is relatively richer in AN units than in feed.

Monomer reactivity ratios

From monomer feed ratios and the copolymer compositions, the reactivity ratios of 4-BOPMA and AN in the copolymer were determined by the application of Fineman-Ross (F-R)[17], Kelen Tüdös s (K-T)[18] and Extended Kelen Tüdös s [Ext (K-T)][19] methods and these parameters are shown in table 3 and 4 and their respective plots in figure 9a, 9b, 9c.The values of monomer reactivity ratio obtained by different methods are shown in table 5. The values of $r_1$and r_2 are less than 1. The values of the product $r_1$and r_2 is much lower than 1, which indicates that the system shows a strong alternating tendency.

Conclusion

The homopolymer and copolymers of 4-BOPMA and AN having various compositions were synthesized in solution by free radical polymerization. The structure of the homo and copolymer was confirmed by FT-IR, ^{1}H-NMR and ^{13}C-NMR spectroscopic techniques. The homopolymer and copolymers soluble in polar aprotic solvents like tetrahydrofuran, dimethyl formamide, dimethyl sulphoxide. It is soluble in chloroform, methylene dichloride etc. They are also soluble in hydrocarbons such as benzene, xylene, toluene, and hydroxyl group containing solvents such as methanol, ethanol and 2-isopropanol.The polydispersity indices of poly(BOPMA), and poly (4-BOPMA-co-AN) obtained from GPC suggest a stronger tendency for chain termination by disproportionation than combination. T_g values depends on the composition of copolymer. Thermal studies indicates that Poly (4-BOPMA) show two stage decomposition while Poly (4-BOPMA-co-AN) show single stage decomposition. The weight loss of the copolymers at various temperatures indicates higher thermal stability. The copolymer compositions were calculated by 1H NMR analysis of the polymers. The monomer reactivity ratios were determined by F-R, K-T and Ext K-T methods. The reactivity values obtained for the poly (4-BOPMA-co-AN) were found to be $r_1 = 0.5758$ and $r_2 = 0.1887$.. The reactivity value and decomposition curves suggest that this system gave azeotropic composition at 0.6566 moles in feed with respect to the monomer 4-BOPMA.

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