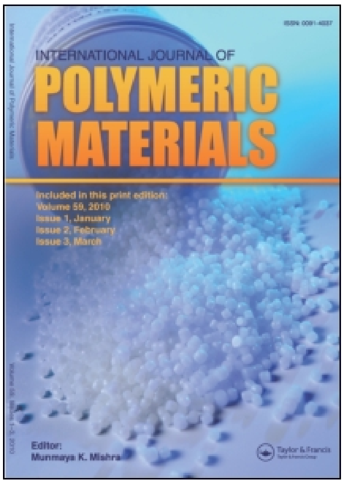

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Copolymers of Phenoxyethyl Methacrylate with Butyl Methacrylate: Synthesis, Characterization and Reactivity Ratios

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Phenoxyethyl methacrylate (POEMA) and butyl methacrylate (BMA) were copolymerized by free-radical copolymerization using α,α′-azobisisobutyronitrile (AIBN) in 2-butanone solution at $333 \pm 1K$. Copolymers were characterized by FTIR, ^{1}H-NMR and ^{13}C-NMR spectroscopic methods and by comparison of the spectra with the corresponding homopolymers. Thermogravimetric analysis of the copolymers was carried out in order to know their thermal stability. Copolymer composition was established by ^{1}H-NMR analysis. Monomer reactivity ratios (MRR) were computed using the classical Fineman – Ross (FR) and Kelen – Tüdos (KT) procedures. MRR were also estimated using a nonlinear computational fitting procedure, known as reactivity ratios error in variable model (RREVM). The mean sequence lengths of the copolymers were estimated and suggest that random copolymers were obtained.

Keywords: butyl methacrylate, comonomer sequence, copolymer characterization, monomer reactivity ratios, phenoxyethylmethacrylate

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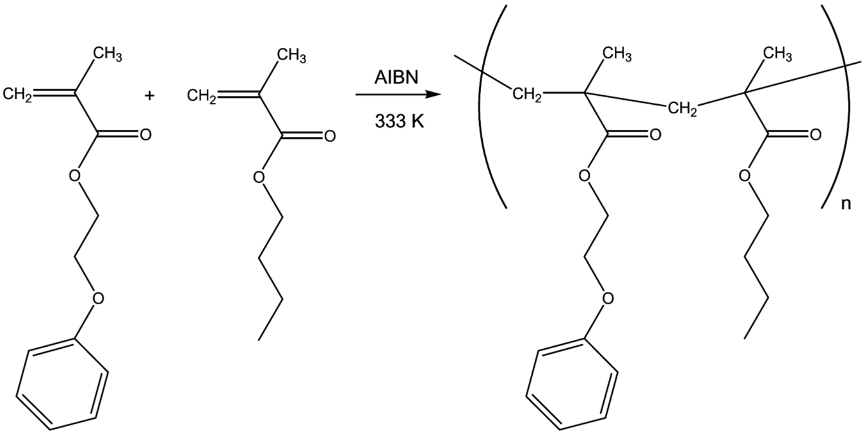
INTRODUCTION

As a part of the continuing program on the study of structure – property relationships [1] exhibited by vinyl monomers, the behavior of methacrylic esters containing phenoxy group on the β-position of the alkyl side chain is studied. The synthesis of methacrylates has been undertaken, since they have extensive applications in different fields [2–5]. Recently amorphous random copolymers of butyl methacrylates were used for fabricating dry toners [6]. Acrylates and methacrylates of phenoxy polymers are used as coating materials for optical fiber and UV-curable adhesive film [7]. They are also used as optical data storage materials [8]. Copolymerization of such methacrylates with butyl methacrylate, which has good properties such as continuous film-forming and softness, provides a simple route for the preparation of optical materials that possess good mechanical properties.

The copolymerizability of vinyl monomers with a bulky substituent that also carries a highly electronegative atom like oxygen has not been discussed so far. The possible effect of such a pendant group on the backbone with respect to reactivity is significant.

The focus of this work is the synthesis and characterization of copolymers of phenoxyethyl methacrylate (POEMA) with butyl methacrylate (BMA) (Scheme 1) of different compositions by free-radical polymerization and to establish the monomer reactivity ratios using linear [9–10] and nonlinear procedures [11–12].



SCHEME 1 Chemical structure of the monomers and copolymers.

EXPERIMENTAL

Materials

Phenoxyethyl methacrylate (POEMA, ALDRICH) and butyl methacrylate (BMA, Fluka) were purified by vacuum distillation. α,α'-azobisisobutyronitrile (AIBN) was recrystallized twice from methanol. 2-butanone, methanol and chloroform were purified by standard procedures.

Copolymerization

Copolymerization reactions were carried out in 2-butanone solutions (50 ml) in glass vessels with a inlet and outlet as previously reported for related systems [13,14]. The reaction tube containing the required amount of monomers (total concentration of the comonomer was $1.5\,\mathrm{mol\,L^{-1}}$) and initiator (1% total mass of monomer) dissolved in 2-butanone was deaerated by flushing with pure, dry nitrogen gas for 30 min prior to immersion in a waterbath kept at a temperature of 333 K. Comonomer mixtures in ratios ranging from POEMA/BMA = 20/80 to 80/20 were prepared. The reaction was carried out for 3–5 h to give conversion $<10\%$ in order to satisfy the differential copolymerization equation. The copolymer was precipitated in an excess of cold methanol. The pure white powdery mass was dissolved in chloroform and then reprecipitated in methanol to ensure the complete removal of residual monomers. It was then dried in vacuum oven at 313 K for 24 h.

Measurements

The FTIR spectra of the copolymers were recorded on a Perkin – Elmer Paragon 1000 Fourier Transform IR (FTIR) spectrophotometer, using the potassium bromide pellet technique, in the range 500–4000 $\mathrm{cm^{-1}}$. The ^{1}H-NMR spectra of the copolymers were recorded on a Jeol GSX – 400 spectrometer operating at 400 MHz at room temperature with 15–20% (w/v) solution in $CDCl_3$. Tetramethylsilane (TMS) was the internal standard. ^{1}H-NMR spectra were obtained using a spectral width of 5000 Hz, an acquisition time of 2 sec and pulse delay of 3.3 sec. Spectra were generally obtained after accumulating 32 scans. The proton noise decoupled ^{13}C-NMR spectra of the copolymers were also recorded using a Jeol GSX – 400 spectrometer operating at 100 MHz. The protons were decoupled by broad-band irradiation.

RESULTS AND DISCUSSION

Characterization of (POEMA-co-BMA) Copolymer

Scheme 1 shows the monomeric constituents of the copolymer and a representation of the copolymerization reaction. The FTIR spectra show a strong absorption at about $1731\,\mathrm{cm}^{-1}$ corresponding to ester carbonyl groups of two monomeric units. The bands due to methyl and methylene groups in both monomer units are observed in the $2800–3400\,\mathrm{cm}^{-1}$ region. The peaks at 1601 and $1498\,\mathrm{cm}^{-1}$ are attributed to the aromatic C=C stretching, similar to that reported in other polymeric compounds [15].

The FTIR spectrum of the carbonyl band was more sensitive to copolymer composition, i.e., position and shape of the carbonyl band in the IR spectra vary with the copolymer composition [16].

The ^{1}H-NMR spectrum of the copolymer is shown is Figure 1a. The signals at 6.8–7.4 ppm are assigned to the aromatic protons of POEMA unit. The characteristic signal at 3.9 ppm is assigned to $-\mathrm{OCH_2}$ methyleneoxy protons of BMA unit. Signals at 1.2–0.8 ppm are assigned to the methyl protons of POEMA. The signals at 4.4 and 4.2 ppm are due to the methylene protons of POEMA units. The multiple signals between 1.2–2.2 ppm are due to methylene and backbone protons of POEMA and BMA units. Thus the participation of both monomeric units in the copolymer is confirmed. The ^{13}C-NMR spectrum of the copolymer is shown in Figure 1b. The ester carbonyl carbons are observed at 158.3 and 154.2 ppm. The peaks at 129.4, 128.9, 121.0 and 114.5 ppm are due to 2, 3 and 4 position on the phenyl ring. The signals at 45.0 and 44.0 ppm are due to $-\mathrm{OCH_2}$ group of two monomeric units. Whereas the signal at 63.2 ppm is attributed to the carbon of $-\mathrm{OCH_2}$ carbon directly attached to the aromatic part of the POEMA unit. The backbone carbon $-\mathrm{CH_2}$ appeared at 30.05 ppm. The sharp signal at 19.2 ppm is due to the methylene carbon of BMA unit. Thus the spectrum shows the characteristic peaks of two monomeric units.

Determination of the Monomer Reactivity Ratios (MRR)

Monomer reactivity ratios were determined by using the classical procedures of Fineman and Ross [9] or Kelen Tudös [10] according to:

$$\mathrm{G} = \mathrm{Fr_1} - \mathrm{r_2} \quad \text{and} \quad \eta = \left(r_1 + \left(\frac{r_2}{\alpha}\right)\right)\xi - \frac{r_2}{\alpha},\ \alpha = \left(\frac{F_1}{F_h}\right) \tag{1}$$

where F_1 and F_h are the lowest and highest values of F.

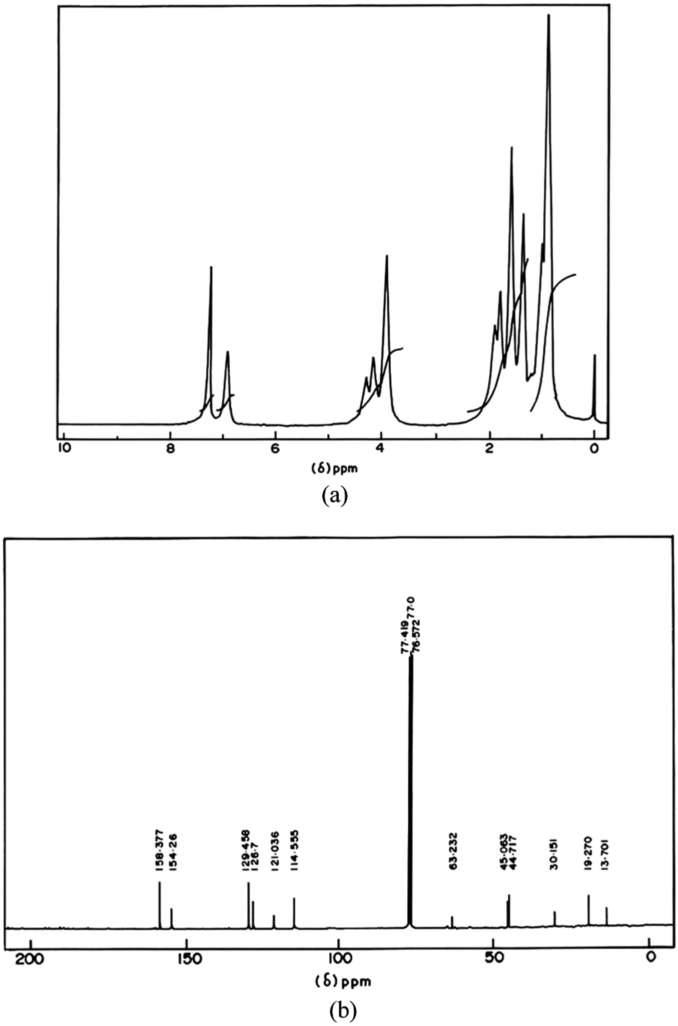


FIGURE 1 (a) ^{1}H-NMR spectrum of (POEMA-co-BMA) copolymer (0.50:0.50); (b) ^{13}C-NMR spectrum of (POEMA-co-BMA) copolymer (0.50:0.50).

These linear methods do not consider the implicit error in the variables involved for the determination of MRR. Nevertheless, they are a powerfull tool, as a first approximation, to obtain MRR. That is the reason why nowadays non-linear methods are most commonly used. These nonlinear procedures are based on the statistically valid error-in-variable model (EVM) [14,17] and allow us to take properly into account all the sources of experimental error. Likewise, the non-linear computational methods needs, as starting values, good initial monomer reactivity ratios, although these values come from straight line intersection methods such as those of Fineman and Rose [9] and Kelen Tudös [10] which could be considered as statistically invalid [14,17].

Copolymer composition was determined from the corresponding ^{1}H-NMR spectra. The mole fraction of POEMA in the copolymer chain was determined from the ratio of the integrated intensities of the aromatic protons. Protons of POEMA to those of the total aliphatic protons of POEMA and BMA units. i.e., C = Intensities of aromatic protons of POEMA (I_A)/ntensities of total aliphatic protons (Ia). Therefore $C = 5m_1/9m_1 + 14(1 - m_1)$ and by simplification $m_1 = 14C/5 + 5C$.

Based on the above procedure the mole fraction of POEMA in the copolymer system was determined. The value of C and the corresponding mole fractions of POEMA in the copolymer are complied in Table 1. A plot of mole fraction of POEMA in feed (m_1) against the composition in the copolymer (M_1) is shown in Figure 2a. There is no azeotropic copolymer composition.

The reactivity ratios of POEMA and BMA were determined by F-R, K-T and RREVM (Figures 2b, 2c and 2d) and they are presented in Table 2. Linearization methods have been commonly employed for the determination of monomer reactivity ratios. The values obtained by these methods are not accurate. In order to obtain correct values of monomer reactivity ratios, nonlinear methods are employed today with good results. The values of r_1 and r_2 by various methods are

TABLE 1 Low Conversion Copolymerization Data of (POEMA-co-BMA)

	Feed composition in mole fraction						Copolymer composition in mole fraction	
S. No.	M_1	M_2	Percentage of conversion	Intensity of aromatic protons I_A	Intensity of aliphatic protons I_a	$C = I_A/I_a$	dM_1	dM_2
1	0.20	0.80	7.2	0.404	2.934	0.1376	0.3386	0.6614
2	0.35	0.65	4.3	0.660	3.830	0.1723	0.4115	0.5885
3	0.50	0.50	8.6	0.426	1.339	0.3181	0.6757	0.3243
4	0.65	0.35	2.9	0.472	1.280	0.3687	0.7542	0.2458
5	0.80	0.20	5.1	0.215	0.470	0.4574	0.8787	0.1213

Solvent: 2-butanone, temperature 333 K ± 1 Initiator: AIBN (1% mass of the monomers).

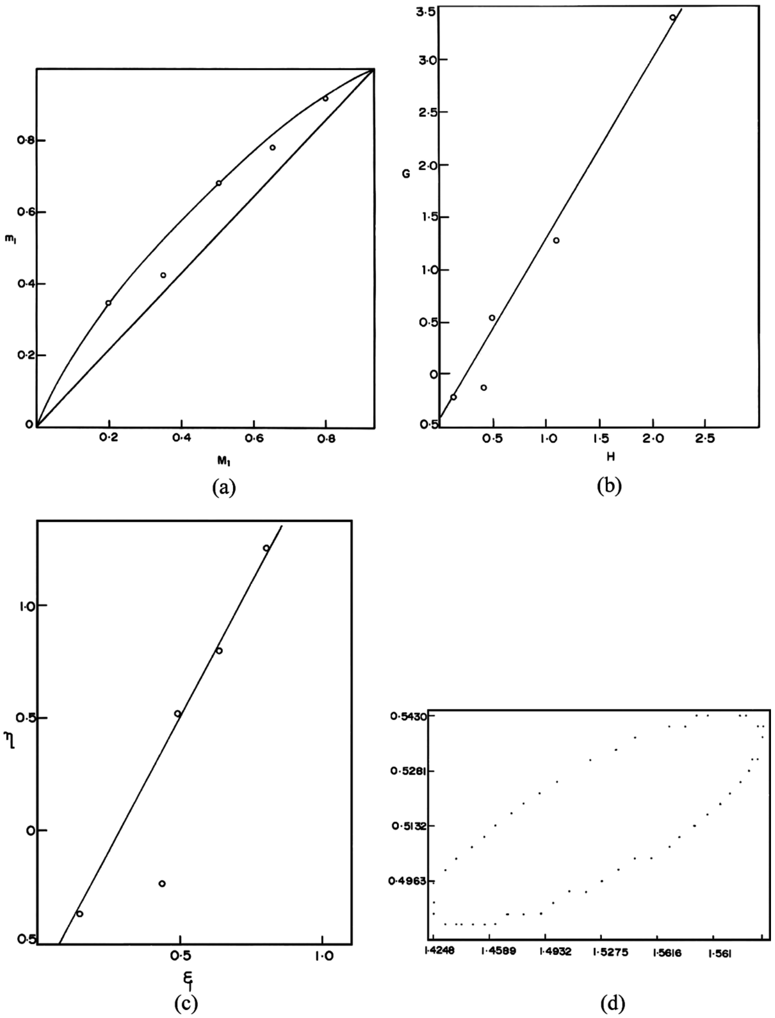


FIGURE 2 (a) Composition curves of (POEMA-co-BMA) copolymer; (b) F-R plot for the (POEMA-co-BMA) copolymer; (c) K-T plot for (POEMA-co-BMA) copolymer; (d) RREVM plot for (POEMA-co-BMA) copolymer. 95% posterior probability contor.

shown in Table 3; the higher r_1 value of POEMA confirms the higher reactivity of POEMA than that of BMA.

Based on the higher feed composition of POEMA in the feed, with the help of reactivity ratios, small block formation tendency is

TABLE 2 F-R and K-T Parameters of (POEMA-co-BMA) Copolymer

S. No.	$X = \frac{M_1}{M_2}$	$y = \frac{dm_1}{dm_2}$	$\frac{G=X(y-1)}{y}$	$F = \frac{X^2}{y}$	$\eta = \frac{G}{\alpha+F}$	$\xi = \frac{F}{\alpha+F}$
1	0.2500	0.5119	−0.2383	0.1220	−0.3717	0.1903
2	0.5385	0.6992	−0.2316	0.4147	−0.2480	0.4441
3	1.0000	2.0835	0.5200	0.4799	0.5205	0.4804
4	1.8571	3.0683	1.2519	1.1240	0.7619	0.6841
5	4.0000	7.2440	3.4478	2.2087	1.2639	0.8097

Fineman Rose equation: $G = Fr_1 - r_2$ and Kelen Tudös: $\eta = \left(r_1 + \left(\frac{r_2}{\alpha}\right)\right)\xi - \frac{r_2}{\alpha}$, $\alpha = \left(\frac{F_1}{F_h}\right)$, where F_1 and F_h are the lowest and highest values of F, respectively.

TABLE 3 Comparison of Reactivity Ratios by Various Method for (POEMA-co-BMA) Copolymer

Methods	r_1	r_2	$1/r_1$	$1/r_2$	$r_1 \cdot r_2$
F-R	1.68	0.37	0.60	2.70	0.621
K-T	1.64	0.34	0.60	2.94	0.557
RREVM	1.52	0.51	0.65	1.96	0.775

observed. This may be because the POEMA monomer is more reactive towards the growing chain regardless of whether the radical was derived from POEMA or BMA. The mean sequence length determination is shown in Table 4. This behavior is similar to other copolymers containing BMA and phenoxyethylmethacrylate [13,18].

CONCLUSIONS

Five copolymers of POEMA-co-BMA were prepared using AIBN as initiator in 2-butanone solution at 333 K. FTIR, ^{1}H and ^{13}C-NMR

TABLE 4 Mean Sequence Lengths in (POEMA-co-BMA) Copolymerization

Mole percentage of BMA in feed, M_2	$\bar{l}_1$	$\bar{l}_2$	$\bar{l}_1$:$\bar{l}_2$	Distribution
100				B
80	1.41	2.36	1:2	PBBP
65	1.88	1.63	1:1	PBB
50	2.64	1.34	2:1	PPBPP
35	4.04	1.1	4:1	PPPPBPPPP
20	7.56	1.0	7:1	PPPPPPPBPPPPPPP
0				P

spectroscopy reveal the presence of both monomeric constituents in the copolymer structure. The copolymer composition was determined by ^{1}H-NMR spectroscopy. The reactivity ratios were obtained by the F-R, K-T and RREVM methods. The reactivity ratios value indicates that POEMA is more reactive than BMA and the copolymer structure will be of random nature with some tendency to form small blocks.

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