

# COPOLYMERIZATION OF 2-HYDROXYETHYL METHACRYLATE WITH ALKYL ACRYLATES

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**Abstract**—Copolymerization of 2-hydroxyethyl methacrylate (HEMA) with methylacrylate (MA), ethylacrylate (EA), *n*-butylacrylate (BA) and methylmethacrylate (MMA) were studied in bulk at 60° using benzoyl peroxide as initiator. The monomer reactivity ratios were determined using several methods and are briefly discussed.

## INTRODUCTION

Hydrophilic gels based on 2-hydroxyethylmethacrylate (HEMA) are finding wide application in surgery and medicine[1, 2]. Copolymers of HEMA with several vinyl monomers have been reported and the biological tolerance of the copolymers has also been investigated[3, 4].

The present work concerns copolymerization of HEMA with methyl (MA), ethyl (EA), *n*-butylacrylates (BA) and methylmethacrylate (MMA) at 60° using benzoyl peroxide as initiator. Copolymer compositions were evaluated by estimation of hydroxyl groups in the copolymers.

## EXPERIMENTAL

The monomers methylacrylate (BDH), ethylacrylate (BDH) and methylmethacrylate (BDH) were washed with 5% NaOH to remove the inhibitor, then with water, and finally were dried over anhydrous sodium sulphate (MA, EA) or calcium chloride (MMA). MA, EA, MMA, BA (E. Merck) and HEMA (BDH) were purified by distillation under reduced pressure. Benzoyl peroxide (BDH) was purified by crystallization from chloroform-methanol. A stock solution of 0.2% benzoyl peroxide in chloroform was prepared and stored at low temperature. Fresh solutions were prepared every week.

The copolymerizations of HEMA with MA, EA, BA and MMA were carried out in bulk in the presence of 0.2% benzoyl peroxide in reaction tubes. The reaction tubes were of approx. 16 cm length and 2 cm diameter, closed at one end and having a B-14 socket at the other. A constriction was made in the tube at approx. 5 cm from the socket. A known volume of benzoyl peroxide solution in chloroform was transferred to the reaction tube and then the chloroform was evaporated with a vacuum pump. A known volume of monomer was transferred to the reaction tube and the contents were degassed on a vacuum line at 10<sup>-6</sup> mm pressure by three cycles of freezing, evacuating and thawing. The tubes were then sealed off at the constriction and placed in an electrically controlled water bath at 60° ± 0.1°. After the desired interval the copolymer solution was poured in *n*-heptane (MA, EA, BA) or in carbon tetrachloride (MMA). The precipitated polymers were filtered, purified by reprecipitation and then dried at 60° for 12 hr.

The compositions of copolymers were found by estimating the hydroxyl groups by acetylation with a mixture of acetic anhydride and pyridine (1:3 in volume)[5] and hydrolysing the unreacted acetic anhydride. The mole fraction of HEMA in a copolymer was then calculated from this

hydroxyl content. The monomer reactivity ratios were calculated by Fineman-Ross, Joshi-Joshi and intersection method.

## RESULTS AND DISCUSSION

*Copolymerization of HEMA with MA, EA, BA and MMA*

The compositions of polymerization mixtures and copolymers are summarized in Table 1. A higher rate of polymerization was observed on increasing the mole fraction of HEMA in the feed. The rate of polymerization also depended on the nature of the alkyl group of the comonomer. By keeping the mole fractions of HEMA in the initial monomer feed similar for different acrylates, the following reactivity order was observed: MMA > EA > BA > MA.

Figure 1 shows the variation of mole fraction of HEMA (*m*<sub>1</sub>) in copolymer as a function of mole fraction of HEMA in the monomer feed (*M*<sub>1</sub>). A random copolymerization is observed only from HEMA-MMA; for other monomer pairs, *m*<sub>1</sub> increases more

Table 1. Copolymerization of 2-hydroxyethylmethacrylate with MA, EA, BA and MMA

Monomer ( <i>M</i> <sub>2</sub> )	Mole fraction of HEMA in monomer feed ( <i>M</i> <sub>1</sub> )	Conversion (%)	Mole fraction of HEMA in copolymer
MA	0.0765	5.3	0.5647
	0.1163	6.3	0.7056
	0.1572	9.1	0.7425
	0.2423	6.8	0.7689
EA	0.0905	10.1	0.3096
	0.1830	6.5	0.6297
	0.2299	5.2	0.7114
	0.2773	5.6	0.7385
BA	0.3253	7.3	0.8082
	0.1169	6.5	0.4931
	0.2286	8.0	0.5869
	0.3369	8.0	0.7098
MMA	0.4414	8.9	0.8319
	0.0887	7.3	0.2903
	0.1796	7.0	0.3213
	0.3689	6.3	0.4856
	0.4669	4.8	0.6172
	0.5676	5.9	0.6749

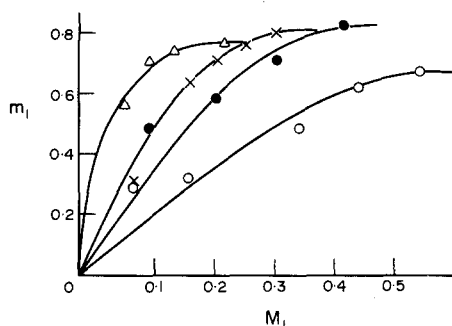
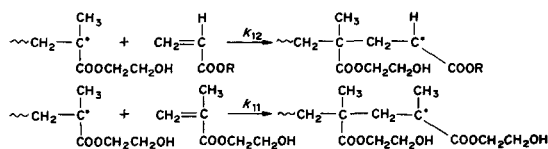


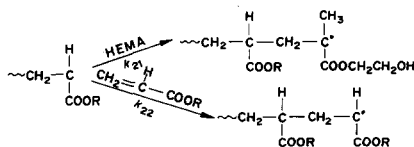
Fig. 1. A plot of mole fraction of HEMA ( $m_1$ ) in copolymer vs mole fraction of HEMA ( $M_1$ ) in monomer feed. HEMA-MMA (○); HEMA-EA (×); HEMA-MA (△).

rapidly indicating a preference of growing polymer radical for HEMA molecules.



(where  $R = -\text{CH}_3$ ,  $-\text{C}_2\text{H}_5$ ,  $-n\text{-C}_4\text{H}_9$ ).

For the alkyl acrylate monomers investigated,  $k_{11} > k_{12}$ . Another significant observation is that, as the size of the alkyl group in alkyl acrylate is decreased, the tendency to react with HEMA increases, i.e.  $k_{11} - k_{12}$  difference becomes greater. This appears to be a purely steric effect because the variation in the reactivity of a growing polymer radical due to the inductive effect of various alkyl groups may not be significant. Conjugation in monomers such as methyl acrylate imparts high reactivity for the monomer towards a radical; a low reactivity of the corresponding radical with monomers in general is, however, observed[6]. It is quite likely that, in the alkyl acrylates with bulky substituents, there is a steric inhibition to resonance, thus increasing the reactivity of the growing polymer radical towards alkyl acrylate monomer,



or  $k_{22}/k_{21}$  increases.

#### Determination of the monomer reactivity ratio

The copolymer composition is given by the well-known equation of Mayo and Lewis[7]:

$$\frac{m_1}{m_2} = \frac{r_1 M_1^2 + M_1 M_2}{r_2 M_2^2 + M_1 M_2}, \quad (1)$$

where  $m_1$  = mole fraction of monomer-1 in the copolymer,  $M_1$  = mole fraction of monomer-1 in the feed,  $r_1$  = the monomer reactivity ratio of monomer-1 (HEMA in the present work).

Fineman and Ross[8] rearranged Eqn. (1) for the evaluation of  $r_1$  and  $r_2$

$$\frac{M_1(m_2 - m_1)}{M_2 m_1} = \left( -\frac{m_2 M_1^2}{m_1 M_2^2} \right) r_1 + r_2. \quad (2)$$

A plot of

$$\frac{M_1(m_2 - m_1)}{M_2 m_1} \text{ vs } -\frac{m_2 M_1^2}{m_1 M_2^2}$$

gives a straight line with slope  $r_1$  and intercept  $r_2$ . In the present work the linear least-square procedure was applied to fit the Fineman-Ross equation; from the slope and intercept of the regression line, the reactivity ratios were evaluated (see Table 2).

The intersection method which is based on the Mayo-Lewis[7] relationships was also used for calculating  $r_1$  and  $r_2$ ; typical plots are given in Fig. 2. The Joshi-Joshi[9] equation, based on integrated copolymerization equation, was also used for evaluation of  $r_1$  and  $r_2$ . In Table 2,  $r_1$  and  $r_2$  values calculated by the different methods are given. The agreement in the values calculated by different methods

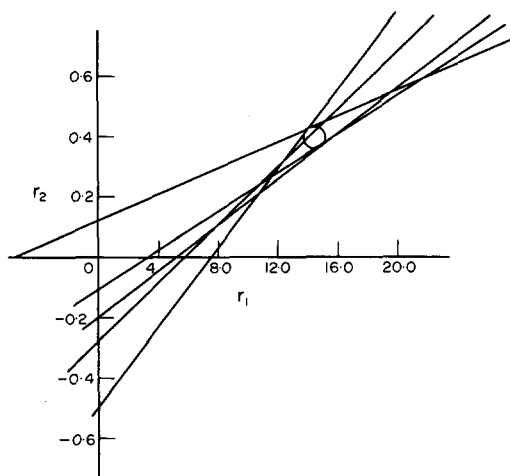


Fig. 2. Evaluation of  $r_1$  and  $r_2$  by the intersection method for HEMA-EA.

Table 2. Monomer reactivity ratios of 2-hydroxyethylmethacrylate (HEMA) with methyl, ethyl and *n*-butyl acrylates and methyl methacrylate

Monomer [2]	Fineman-Ross $r_1$ (HEMA) $r_2$		Joshi-Joshi $r_1$ (HEMA) $r_2$		Intersection method $r_1$ (HEMA) $r_2$		Q-e scheme $r_1$ (HEMA) $r_2$	
MA	7.141	0.012	7.148 ± 0.0009	0.011 ± 0.031	9.2 ± 0.800	0.03 ± 0.008	2.285	0.570
EA	13.526	0.358	13.530 ± 0.073	0.358 ± 0.043	14.5 ± 0.700	0.4 ± 0.003	1.544	0.648
BA	5.414	0.168	5.404 ± 0.039	0.167 ± 0.092	5.6 ± 0.400	0.123 ± 0.010	1.900	1.103
MMA	1.054	0.296	1.016 ± 0.036	0.284 ± 0.091	1 ± 0.100	0.25 ± 0.050	1.125	0.925

varies between the individual pairs. There is good agreement between the Joshi-Joshi and Fineman-Ross values of  $r_1$  and  $r_2$  but some deviation is observed in the intersection method.

For the pairs formed by HEMA and acrylates, the reactivity ratios were also calculated by the  $Q-e$  scheme. The parameters  $Q$  and  $e$  were taken from the literature[10]. The results thus obtained are not at all comparable with the experimental values. These calculated values for the various pairs are also given in Table 2.

It is difficult to account for the variation in the calculated and observed values of  $r_1$  and  $r_2$ . It may be that the  $e$  values of monomer and radical are not similar leading to the observed discrepancy.

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