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## Copolymerization of 2-Hydroxypropyl Methacrylate with Alkyl Methacrylates

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### ABSTRACT

2-Hydroxypropyl methacrylate (2 HPMA) has been copolymerized with ethyl methacrylate (EMA), n-butyl methacrylate (BMA), and 2-ethylhexyl methacrylate (EHMA) in bulk at 60°C using benzoyl peroxide as initiator. The copolymer composition has been determined from the hydroxyl content. The reactivity ratios have been calculated by the YBR method. For copolymerization of 2-HPMA ( $M_1$ ) with EMA ( $M_2$ ), the reactivity ratios are:  $r_1 = 1.807 \pm 0.032$ ,  $r_2 = 0.245 \pm 0.021$ ; with BMA ( $M_2$ ) they are  $r_1 = 2.378 \pm 0.001$ ,  $r_2 = 0.19 \pm 0.01$ ; and with EHMA the values are  $r_1 = 4.370 \pm 0.048$ ,  $r_2 = 0.103 \pm 0.006$ . Since the reactivity ratios are the measure of distribution of monomer units in a copolymer chain, the values obtained are compared and discussed. This enables us to choose a suitable copolymer for synthesizing thermoset acrylic polymers, which are obtained from cross-linking of hydroxy functional groups of HPMA units, for specific end uses.

### INTRODUCTION

Acrylic polymers containing hydroxy functional groups as side chains have become increasingly important in recent years for

various applications such as adhesives, coatings, and binders [1]. Linear polymers of this type, though satisfactory in many ways, afford poor resistance to strong solvents and a tendency to flow at high temperatures, because of their thermoplastic nature, i.e., they exhibit poor physical properties. This has been eliminated by reacting them with suitable cross-linking agents depending on the end use. For instance, for 2-hydroxypropyl methacrylate-methyl methacrylate copolymer, the cross-linking agents used are diethylene glycol dimethacrylate for medical use [2] and diisocyanates for adhesives [3]. The thermomechanical properties of the thermosets have been found to be dependent on the amount of HPMA copolymer [4]. To optimize the physical properties, it was necessary to control the cross-linkable units. With this objective, the copolymerization of 2-HPMA with EMA, BMA, and 2-EHMA was done, and the reactivity ratios were determined.

## EXPERIMENTAL

The monomers ethyl methacrylate (BDH), butyl methacrylate (BDH), and 2-ethylhexyl methacrylate (Fluka AG) were freed from inhibitor by washing with 10% sodium hydroxide and then with water and finally dried over anhydrous magnesium sulfate. The purified monomers were distilled under reduced pressure over 4 Å molecular sieves.

2-Hydroxypropyl methacrylate (E. Merck) was purified by distillation at 84-85°/5 mmHg.

Benzoyl peroxide (BDH) was purified by crystallization from methanol. A stock solution of 2% benzoyl peroxide in chloroform was prepared and stored at room temperature.

### Copolymerization

The required amounts of 2-HPMA, alkyl methacrylate, and benzoyl peroxide were charged in a Pyrex glass tube, cooled in liquid air, and sealed in a vacuum system. The sealed tubes were placed in a constant temperature bath at  $60 \pm 0.1^\circ\text{C}$ . Since the differential form of the copolymer equation was used, the conversion was limited to 10% in all cases. After the requisite time, the contents of the tube were poured into a large amount of petroleum ether (40-60°C) and washed several times in petroleum ether. The purified polymers were dried at 50°C under vacuum to constant weight.

The composition of the polymers was determined from the hydroxyl content estimated by acetylation [5] with a mixture of acetic anhydride and pyridine (1:3 v/v).

TABLE 1. Copolymerization of 2-Hydroxypropyl Methacrylate [ $M_1$ ] and Ethyl Methacrylate [ $M_2$ ]<sup>a</sup>

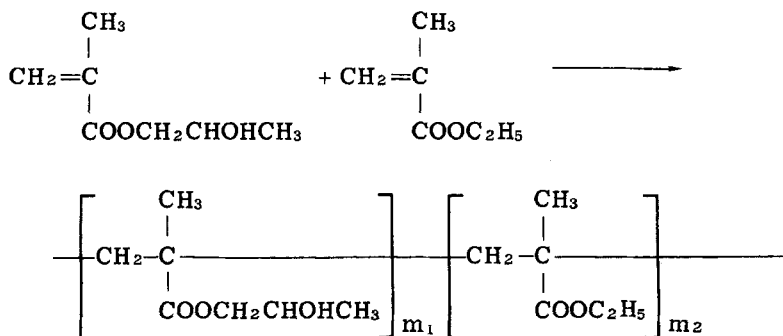
Initial monomer mixture		Copolymer composition			
Mole fraction of $M_1$	Mole fraction of $M_2$	Copolymer yield, % by wt of monomers	% OH content	Mole fraction of $m_1$	Mole fraction of $m_2$
0.10	0.90	6.7	4.793	0.2599	0.7401
0.20	0.80	10.2	5.548	0.4124	0.5876
0.30	0.70	9.4	6.930	0.5295	0.4705
0.50	0.50	4.8	8.719	0.6910	0.3090
0.70	0.30	9.5	10.117	0.8259	0.1741
0.80	0.20	8.8	10.723	0.8868	0.1132

<sup>a</sup>Polymerization conditions: catalyst, benzoyl peroxide (0.2% by wt of monomers); temperature,  $60 \pm 0.1^\circ\text{C}$ .

## RESULTS AND DISCUSSION

### Reactivity Ratios in Copolymerization of 2-Hydroxypropyl Methacrylate ( $M_1$ ) with Ethyl Methacrylate ( $M_2$ )

Copolymerization of 2-hydroxypropyl methacrylate with ethyl methacrylate is represented by



The reaction conditions and results are summarized in Table 1. From these data the monomer reactivity ratios were found by using

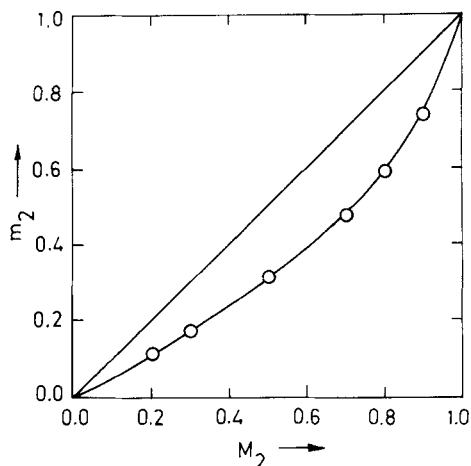


FIG. 1. Plot of mole fraction of EMA ( $m_2$ ) in copolymer versus mole fraction of EMA ( $M_2$ ) in monomer feed: (○) experimental values, (—) curve calculated from copolymer equation using reactivity ratios determined by the YBR method.

analytical method of Yezrielev, Brokhina, and Roskin (YBR method) [6], which was based on the differential form of the copolymer equation. Joshi [7] has recently reviewed various published methods of calculating  $r_1$  and  $r_2$  where he has mentioned that the linear YBR method is an outstanding method to obtain reactivity ratio values with greater accuracy than the Tidwell and Mortimer method [8] because of the symmetrical nature of the copolymer equation. The reactivity ratios for this system were found to be

$$r_1 = 1.807 \pm 0.032$$

$$r_2 = 0.245 \pm 0.021$$

Figure 1 shows the copolymer composition data as a function of monomer feed. As can be seen from the graph, the theoretical curve closely represents the experimental data. This is further reflected in the small deviations obtained for reactivity ratios. The higher value of  $r_1$  as compared to  $r_2$  indicates that the copolymer containing large blocks of 2 HPMA units is interspersed by EMA units.

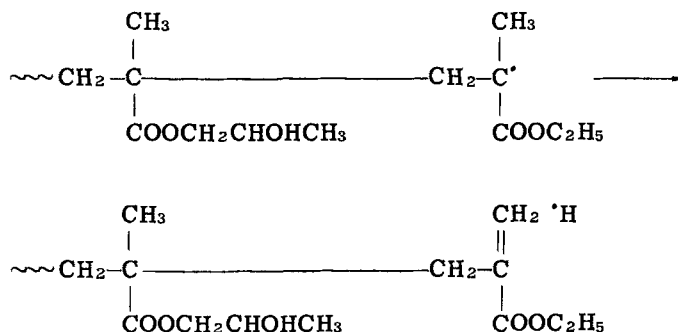
The effect of an  $\alpha$ -methyl group on the reactivity ratios of HPMA-EMA and hydroxypropyl methacrylate-ethyl acrylate (HPMA-EA) [9] gave an interesting observation. The  $1/r_1$  values of HPMA-EMA and HPMA-EA are 0.55 and 0.08, respectively, indicating greater reactivity of ethyl methacrylate than ethyl acrylate toward the

TABLE 2. Copolymerization of 2-Hydroxypropyl Methacrylate [ $M_1$ ] and n-Butyl Methacrylate [ $M_2$ ]<sup>a</sup>

Initial monomer mixture		Copolymer composition			
Mole fraction of $M_1$	Mole fraction of $M_2$	Copolymer yield, % by wt of monomers	% OH content	Mole fraction of $m_1$	Mole fraction of $m_2$
0.10	0.90	9.7	3.810	0.3197	0.6803
0.20	0.80	6.5	5.743	0.4831	0.5169
0.30	0.70	8.3	6.854	0.5772	0.4228
0.50	0.50	4.6	8.753	0.7388	0.2612
0.60	0.40	7.6	9.499	0.8025	0.1975

<sup>a</sup>Polymerization conditions: catalyst, benzoyl peroxide (0.2% by wt of monomers); temperature,  $60 \pm 0.1^\circ\text{C}$ .

poly(HPMA) radical. This may be due to the stability of the growing ethyl methacrylate radical resulting from hyperconjugation with respect to the  $\alpha$ -methyl group besides carbonyl conjugation. This is represented as



### Reactivity Ratios in Copolymerization of 2-Hydroxypropyl Methacrylate ( $M_1$ ) with n-Butyl Methacrylate ( $M_2$ )

The conditions and results of experiments for the copolymerization of this pair of monomers are given in Table 2. The reactivity ratios calculated by using the YBR method were found to be

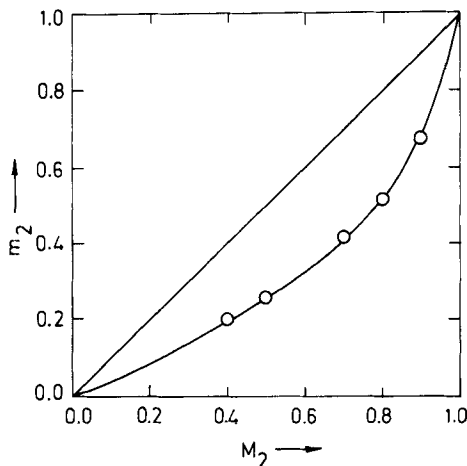


FIG. 2. Plot of mole fraction of BMA ( $m_2$ ) in copolymer versus mole fraction of BMA ( $M_2$ ) in monomer feed: ( $\circ$ ) experimental values, (—) curve calculated from copolymer equation using reactivity ratios determined by the YBR method.

$$r_1 = 2.378 \pm 0.001$$

$$r_2 = 0.190 \pm 0.010$$

The copolymer composition curve, i.e., monomer feed vs copolymer feed, was calculated from  $r_1$  and  $r_2$  values and is shown in Fig. 2 along with experimental data. Since  $r_1 > 1$  and  $r_2 < 1$ , the copolymer consists of larger blocks of 2-HPMA units interrupted with a few n-butyl methacrylate comonomer units.

Comparison of  $1/r_1$  values of the HPMA-BMA system with the HPMA-butyl acrylate (HPMA-BA) copolymer [9] reveals the higher reactivity of butyl methacrylate toward the poly(HPMA) growing species. The  $1/r_1$  values are

$$\text{HPMA-BMA} = 0.42$$

$$\text{HPMA-BA} = 0.19$$

Further, the increase in reactivity of BMA as compared to BA toward the poly-HPMA radical is only twofold. On the other hand the reactivity of EMA is five times more than EA toward the poly-HPMA radical. This clearly reveals that the former system is influenced by steric factors.

TABLE 3. Copolymerization of 2-Hydroxypropyl Methacrylate [ $M_1$ ] and 2-Ethylhexyl Methacrylate [ $M_2$ ]<sup>a</sup>

Initial monomer mixture		Copolymer composition			
Mole fraction of $M_1$	Mole fraction of $M_2$	Copolymer yield, % by wt of monomers	% OH content	Mole fraction of $m_1$	Mole fraction of $m_2$
0.10	0.90	6.0	3.379	0.4412	0.5588
0.20	0.80	9.1	4.344	0.5868	0.4132
0.30	0.70	6.4	5.004	0.6931	0.3069
0.40	0.60	6.5	5.481	0.7735	0.2265
0.50	0.50	4.6	5.816	0.8314	0.1686
0.60	0.40	10.4	6.076	0.8772	0.1228

<sup>a</sup>Polymerization conditions: catalyst, benzoyl peroxide (0.2% by wt of monomers); temperature,  $60 \pm 0.1^\circ\text{C}$ .

#### Reactivity Ratios in Copolymerization of 2-Hydroxypropyl Methacrylate ( $M_1$ ) with 2-Ethylhexyl Methacrylate ( $M_2$ )

Table 3 shows the experimental conditions and results of the copolymerization of 2-hydroxypropyl methacrylate. As above, the monomer reactivity ratios were found to be

$$r_1 = 4.370 \pm 0.048$$

$$r_2 = 0.103 \pm 0.006$$

Because  $r_1$  (HPMA)  $> 1$  and  $r_2$  (EHMA)  $< 1$ , the hydroxypropyl methacrylate is more reactive than EHMA toward both propagating species. The polymer, therefore, is richer in HPMA than in EHMA (Fig. 3).

A perusal of the reactivity ratio data (Table 4) reveals that the reactivity of comonomer in copolymerization depends on steric factors and the polarity of the molecule. The reactivity of the comonomer is influenced by the size and the number of substituents attached to the unsaturated C=C linkage. The relative reactivity of alkyl methacrylate comonomer toward the poly(HPMA) radical is of the order EMA  $>$  BMA  $>$  EHMA. Although the influence of the  $\alpha$ -methyl group on the polarization of an unsaturated bond is the same, the length and degree



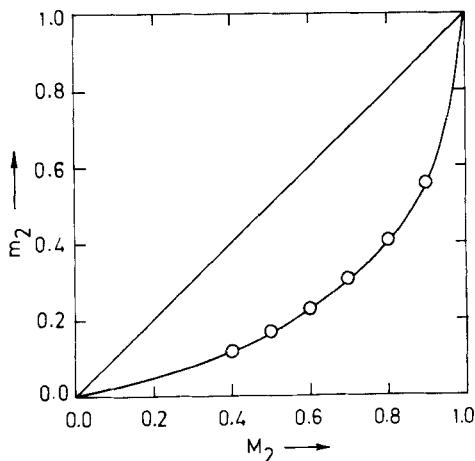


FIG. 3. Plot of mole fraction of 2-EHMA ( $m_2$ ) in copolymer versus mole fraction of 2-EHMA ( $M_2$ ) in monomer feed: ( $\circ$ ) experimental values, (—) curve calculated from copolymer equation using reactivity ratios determined by the YBR method.

TABLE 4. Reactivity Ratios for Copolymerization of 2-Hydroxypropyl Methacrylate with Alkyl Methacrylates

Monomer $M_1$	Monomer $M_2$	$r_1 \pm \Delta r_1$	$r_2 \pm \Delta r_2$
2-Hydroxypropyl methacrylate	Ethyl methacrylate	$1.807 \pm 0.032$	$0.245 \pm 0.021$
	n-Butyl methacrylate	$2.378 \pm 0.001$	$0.19 \pm 0.01$
	2-Ethylhexyl methacrylate	$4.370 \pm 0.048$	$0.103 \pm 0.006$

of branching of the alkyl radical exerts a certain influence on the reactivity of alkyl methacrylate in copolymerization with HPMA. The reactivity ratio of alkyl methacrylate is in accordance with the size of alkyl group and is also higher than the methyl methacrylate value reported by us earlier [9].

## SUMMARY AND CONCLUSIONS

In this investigation a different approach to obtain thermoset acrylic polymers, which can yield better mechanical properties, has been reported. Thus, 2-hydroxypropyl methacrylate has been copolymerized with alkyl methacrylates using free-radical initiators. Conversion was limited to less than 10% in all cases. A wide range of initial monomer feed ratios was chosen to give equal weightage to both the monomers as seen from the dependence curves.

The reactivity ratios for all systems have been evaluated by using the YBR method. These values have been compared with the corresponding HPMA-alkyl acrylate copolymers reported earlier. Since the reactivity ratios indicate the distribution of monomer units in a polymer chain, this can aid in choosing the desired composition of copolymers for specific end-use requirement. The copolymers selected could be used for cross-linking by using suitable cross-linking agents, such as aliphatic and aromatic diisocyanates, to obtain good mechanical properties. Our investigations on these aspects are under way.

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