

Copolymerization of 2-Hydroxypropyl Methacrylate with Alkyl Acrylate Monomers

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Synopsis

2-Hydroxypropyl methacrylate has been copolymerized with methyl acrylate, ethyl acrylate, *n*-butyl acrylate, and methyl methacrylate in bulk at 60°C using benzoyl peroxide as initiator. The compositions of copolymers have been determined by the estimation of the hydroxyl group by acetylation process. The copolymerization parameters have been determined by conventional scheme of copolymerization.

INTRODUCTION

Most of the useful properties of the hydrophilic polymers derived from methacrylic acid glycol esters are directly or indirectly due to their capacity to water absorption.¹ The hydrophilic gels based on 2-hydroxypropyl methacrylate (HPMA) have been proposed for medical uses.^{2,3} Copolymers of HPMA with several vinyl monomers have been reported.^{4,5}

The objective of the present investigation was to study the free-radical copolymerization of 2-hydroxypropyl methacrylate with methyl acrylate (MA), ethyl acrylate (EA), *n*-butyl acrylate (BA), and methyl methacrylate (MMA).

EXPERIMENTAL

Materials

The monomers methyl acrylate (BDH), ethylacrylate (BDH), and methyl methacrylate (BDH) were freed from the inhibitor by washing with 10% sodium hydroxide and then with water and finally dried over magnesium sulfate. The monomers MA, EA, MMA, BA (E. Merck), and HPMA (BDH) were purified by distillation under reduced pressure. Only the middle half of the distillate was used in each case.

Benzoyl peroxide (BDH) was purified by crystallization from methanol. A stock solution of 0.2% benzoyl peroxide in chloroform was prepared and stored at room temperature.

The parameters of copolymerization were determined by bulk copolymerization with the use of free radicals for initiation. The polymerization was carried out in a two-necked flask equipped with condenser and nitrogen gas inlet. A

known volume of benzoyl peroxide solution in chloroform was transferred to the reaction flask, and then chloroform was evaporated under vacuum. The monomers of different molar ratios were introduced into the flask. The flasks were placed in an electrically controlled water bath at $60 \pm 0.1^\circ\text{C}$. The proper time of copolymerization, i.e., the time necessary to polymerize not more than 10% of the mixture, was found by trial and error. After polymerization, the flasks were cooled to room temperature, and the reaction mixture was poured in *n*-heptane (MA, EA, BA) or in carbon tetrachloride (MMA). The precipitated

TABLE I
Copolymerization of 2-Hydroxypropyl Methacrylate and Methyl Acrylate

Mole fraction of M_1 in monomer feed	Conversion, %	Mole fraction of m_1 in copolymer
0.8	5.5	0.967
0.7	6.0	0.946
0.6	7.3	0.920
0.5	6.4	0.888
0.4	6.8	0.846
0.2	8.4	0.723

TABLE II
Copolymerization of 2-Hydroxypropyl Methacrylate and Ethyl Acrylate

Mole fraction of M_1 in monomer feed	Conversion, %	Mole fraction of m_1 in copolymer
0.8	8.4	0.980
0.7	6.5	0.963
0.6	6.2	0.947
0.5	5.6	0.906
0.2	9.4	0.632

TABLE III
Copolymerization of 2-Hydroxypropyl Methacrylate and *n*-Butyl Acrylate

Mole fraction of M_1 in monomer feed	Conversion, %	Mole fraction of m_1 in copolymer
0.8	4.8	0.954
0.7	5.5	0.924
0.6	8.2	0.888
0.4	6.4	0.770
0.2	5.7	0.561

TABLE IV
Copolymerization of 2-Hydroxypropyl Methacrylate and Methyl Methacrylate

Mole fraction of M_1 in monomer feed	Conversion, %	Mole fraction of m_1 in copolymer
0.8	10.4	0.823
0.7	9.8	0.744
0.6	8.5	0.672
0.5	8.4	0.594
0.2	6.8	0.319

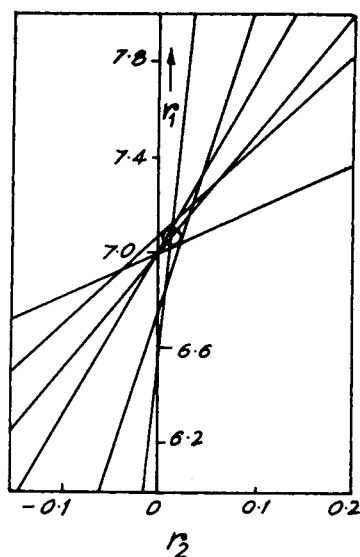


Fig. 1. Evaluation of r_1 and r_2 by intersection method for HPMA:MA pair.

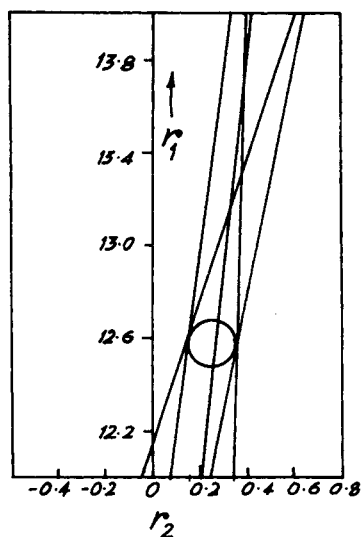


Fig. 2. Evaluation of r_1 and r_2 by intersection method for HPMA:EA pair.

polymers were filtered, purified by reprecipitation, and then dried at 50°C under reduced pressure for 24 hr.

The composition of copolymers was determined by analysis of their hydroxyl content by acetylation with a mixture of acetic anhydride and pyridine (1:3 in volume) and hydrolyzing the unreacted acetic anhydride.⁶ The reaction conditions and results are summarized in Tables I–IV for the bulk copolymerizations.

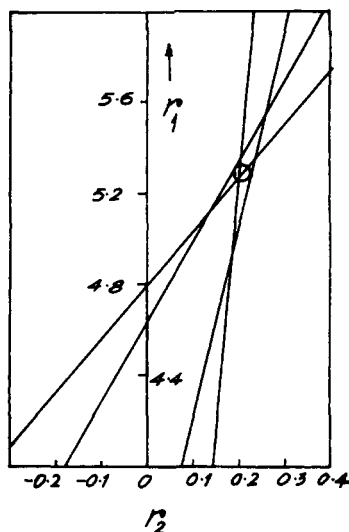


Fig. 3. Evaluation of r_1 and r_2 by intersection method for HPMA:BA pair.

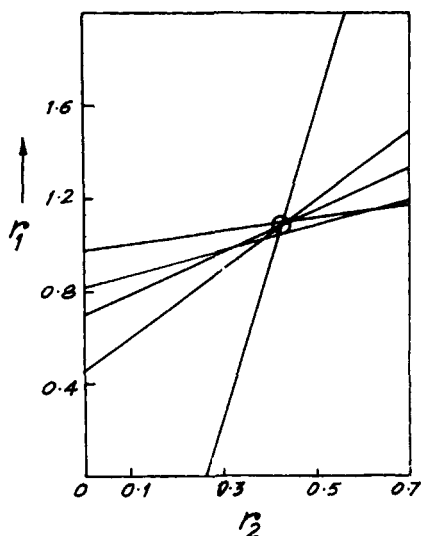


Fig. 4. Evaluation of r_1 and r_2 by intersection method for HPMA:MMA pair.

RESULTS AND DISCUSSION

The reactivity ratios r_1 and r_2 were determined by the graphical method⁷ (Figs. 1–4) by using the following equation

$$r_2 = (M_1/M_2) \{ (m_2/m_1) [1 + (M_1/M_2)r_1] - 1 \}$$

where M_1/M_2 is the ratio of the unreacted monomers and m_2/m_1 is the ratio of the two monomers in the polymer. The values obtained by Fineman–Ross⁸ by the use of the linear least-squares method is slightly lower than the values obtained by intersection method (Table V).

TABLE V
Copolymerization Parameters for 2-Hydroxypropyl Methacrylate (HPMA) with Methyl, Ethyl, and Butyl Acrylates and Methyl Methacrylate

Monomer (M_2)	Intersection method		Fineman Ross method	
	r_1 (HPMA)	r_2	r_1 (HPMA)	r_2
MA	7.08 ± 0.04	0.01 ± 0.008	7.045	0.013
EA	12.56 ± 0.10	0.24 ± 0.10	13.038	0.330
BA	5.3 ± 0.04	0.22 ± 0.02	5.170	0.190
MMA	1.16 ± 0.04	0.43 ± 0.02	1.122	0.486

A perusal of the reactivity ratio data reveals that the rate of reaction is increased with an increase of HPMA in the monomer feed. Further, in all three alkyl acrylates, the copolymers show a much higher content of HPMA than the monomer mixtures, whereas in the HPMA-MMA pair a random copolymerization is observed (Figs. 5 and 6).

The rate of polymerization was found to depend on the nature of the alkyl group of the comonomer. This may also be known from the reciprocal of r_1 values which can be used as a measure of the relative reactivity of the acrylates towards the poly(hydroxypropyl methacrylate) radical; the higher the value of $1/r_1$, the greater the chance that the acrylate will add to the poly-HPMA radical. The order of reactivity of the acrylates towards poly-HPMA radical is, therefore, as follows: MMA > EA > BA > MA.

The relative reactivities of the acrylates towards HPMA radical depend on the polarities of monomers, on the steric factors and on the resonance stabilization of the radicals. It is seen that as the size of the alkyl group in alkyl acrylate (EA, BA) is decreased the tendency to react with HPMA increases. This may be ascribed to steric factors because the variation in the reactivity of growing polymer radical due to inductive effect of various alkyl groups may not be significant. The conjugation in methyl acrylate imparts high reactivity to the monomer to react with the radical; this is because of the poor electron-releasing effect of the methyl substituent as compared to those of ethyl acrylate and *n*-

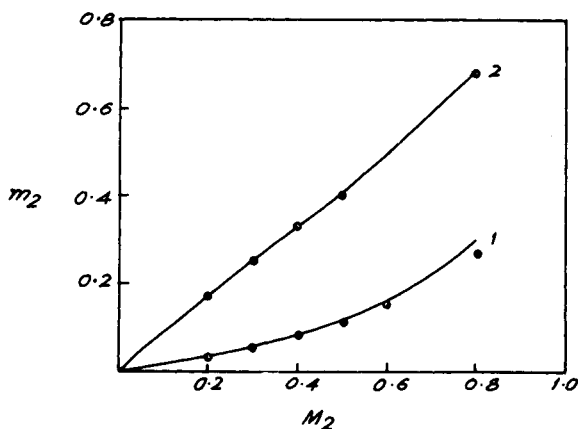


Fig. 5. Plot of mole fraction of HPMA in monomer feed against mole fraction of HPMA in copolymer: (curve 1) HPMA:MA pair; (curve 2) HPMA:MMA pair.

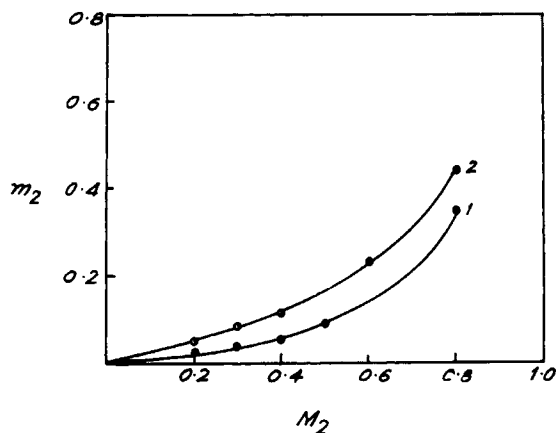


Fig. 6. A plot of mole fraction of HPMA in monomer feed against mole fraction of HPMA in copolymer: (curve 1) HPMA:EA pair; (curve 2) HPMA:BA pair.

butyl acrylate, which will render the carbonyl group less polar and thus increase the possibility of conjugation between the carbonyl and vinyl bonds in MA; this will reduce the rate constant for the steps involving the addition of MA monomer to the poly-HPMA radical; also, the value of r_1 increases. It is possible that in the alkyl acrylate having bulky substituent, there exists steric inhibition to resonance; thus, the reactivity of the growing polymer radical towards alkyl acrylate monomer increases, i.e., k_{22}/k_{21} increases.

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