Copolymerization of Hydroxyalkyl Methacrylates with Acrylamide and Methacrylamide I. Determination of Reactivity Ratios

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ABSTRACT: The free-radical copolymerization of 2-hydroxyethyl methacrylate, 2-hydroxypropyl methacrylate, and 3-chloro-2-hydroxypropyl methacrylate with acrylamide and methacrylamide was investigated. The reactivity ratios of the monomers were determined by the Fineman–Ross and Kelen–Tüdös methods. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **64:** 1259–1265, 1997

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INTRODUCTION

Hydroxyalkyl esters of acrylic acid and methacrylic acid make the basic substrates for the production of polymers which, in turn, are the main component of water-soluble or water-thinned lacquers and varnishes.[1–4] Their reaction with isocyanates or diols give resins for the production of protective coatings for metals, fiberoptics, etc.[5–7] Their copolymerization with some vinyl monomers give products that may also be used to impregnate textiles, laminates, and paper, as well as for the production of ultraviolet-setting coatings.[8–15] The UV-setting is particularly useful for copolymers prepared from hydroxyalkyl methacrylates and isocyanates.[16–21] As follows from the data in the literature, the hydroxyalkyl methacrylates were studied mostly from the point of view of their commercial applications. The reports on the reactivity of these monomers in copolymeriza-

tion are scarce. *The Polymer Handbook,* 3rd Ed., quotes just one work on reactivity ratios of hydroxyethyl methacrylate (1) with acrylamide (2) (r_1 = 1.890; r_2 = 0.050).[22]

Worth mentioning is the work of Babu and Deshpande,[23,24] who determined reactivity ratios of hydroxypropyl methacrylate with methyl methacrylate or butyl methacrylate and 2-ethylhexyl methacrylate. Lebduska and Snuparek[25] studied the copolymerization of styrene with 2-hydroxyethyl methacrylate in polar solvents like dimethylformamide, 2-propanol, and 1-butanol, and in nonpolar solvents, e.g., in toluene. Such copolymers are used to prepare laquers and varnishes,[26,27] and the presence of acrylamide units in macromolecules normally improves thermostability of coatings.[28] In the present article, a bulk copolymerization of hydroxyethyl methacrylate (HEMA), hydroxypropyl methacrylate (HPMA), and 3-chloro-2-hydroxypropyl methacrylate (CHPMA) with acrylamide and methacrylamide has been investigated. The reactivity ratios of the comonomers have been determined.

EXPERIMENTAL

Monomers

Acrylamide (AA), pure (Fluka A.G., Switzerland), was purified by recrystallization from benzene (m.p. = 357 to 359 K). The content of nitrogen determined by Kjeldahl's method[29] was 19.58% (19.70% theoretical).

Methacrylamide (MA), pure (Fluka A.G., Switzerland), was purified by recrystallization from benzene (m.p. = 383 to 384 K). The content of nitrogen was 16.52% (16.47% theoretical).

Benzoyl peroxide (BP), pure (Argon, Łódź, Poland), had the reactivity of 86 wt %.[30] Hydroxyalkyl methacrylates were obtained by the following procedure.

In a 750 cm^3 three-necked flask fitted with a mechanical stirrer, a reflux condenser [in the reactions with ethylene oxide (EO), a special reflux condenser containing dry ice as a cooling medium was used], and a thermometer, 258 g of methacrylic acid (3 mol), 2.5 g of phenothiazine, and 14.4 g of N,N-dimethylaniline were placed and mixed. Next, 192 g (3.3 mol) of propylene oxide (PO) or 278 g (3 mol) of glycerol epichlorohydrin (ECH) was added (EO was added in 1 mol (44 g) portions). The reaction mixture was brought to gentle boiling and maintained at that temperature until the reaction was over (the extent of reaction was controlled by titration of unreacted methacrylic acid). Then, the product was distilled off under reduced pressure. The distillation conditions were as follows.

HEMA, p = 266.6 Pa, t = 81–85°C; HPMA, p = 400.0 Pa, t = 77–78°C; CHPMA, p = 533.2 Pa, t = 92–95°C. From unsymmetrical oxiranes (R ≠ H), e.g., from PO (R = —CH$_3$) or ECH (R = —CH$_2$Cl), the mixture of constitutional isomers was formed, as follows.

The mixtures were used without separation of isomers.[28]

Copolymerization

The copolymerization of hydroxyalkyl methacrylates with acrylamide or methacrylamide, using BP as the initiator, were carried out in bulk as follows. The required amounts of comonomers were weighed and, after dissolving the initiator, poured into 10 cm^3 glass ampules. The ampules were closed and placed in a water thermostat at 60 ± 1°C. The time of the copolymerization was experimentally established, to obtain conversion of the monomer not exceeding 10%. The glass ampules were removed from the bath, cooled to room temperature, and broken. The content was poured into a beaker containing 40 cm^3 of a suitable precipitant. The copolymer was separated, dissolved in methanol, and then precipitated again with ethyl acetate. The purification procedure was repeated twice. Isopropyl alcohol was used as the solvent for HPMA-AA and HPMA-MA copolymers. The precipitant was ethyl acetate, heptane, or ethyl acetate–heptane mixture (2 : 1 v/v) for HEMA-AA and HEMA-MA, HPMA-AA and HPMA-MA, or CHPMA-AA and CHPMA-MA copolymers, respectively.

Finally, the copolymers were dried *in vacuo* at room temperature to constant weight.

Copolymer Analysis

The copolymer compositions were calculated from the nitrogen contents by Kjeldahl's method. Each copolymer was analyzed three times. The results of the copolymerization experiments are shown in Tables I–VI. For each pair of comonomers, two series of measurements for six compositions were made. Mean values for two experiments are given in the tables.

Computations

The reactivity ratios of the monomers are determined using the Fineman–Ross (F-R)[31] and Kelen–Tüdös (K-T)[32-34] methods. Reactivity ratios are usually calculated from the differential form of the well-known monomer-copolymer composition equation, as follows:

$$\frac{dM_1}{dM_2} = \frac{M_1}{M_2} \frac{r_1 M_1 + M_2}{r_2 M_2 + M_1} \tag{1}$$

Table I   Experimental Data for Copolymerization of HEMA (Monomer 1) with AA (Monomer 2) in the Presence of BP (0.008 wt %)

Composition of Starting Mixture (mol %)		Polymerization Time (min)	Conversion (wt %)	N Content in Copolymer (wt %)	Fraction of AA in Copolymer (mol %)	Ratio of HEMA/AA Units in Copolymer
M_1	M_2					
95	5	8.4	5.93	0.25	2.30	42.5 : 1
90	10	7.6	4.41	0.61	5.52	17.1 : 1
85	15	6.5	4.27	0.82	7.37	12.6 : 1
80	20	6.0	6.66	1.05	9.35	9.7 : 1
75	25	5.8	5.34	1.30	11.46	7.7 : 1
70	30	5.5	4.74	1.57	13.68	6.3 : 1
65	35	5.2	6.21	1.87	16.11	5.2 : 1
60	40	5.0	4.54	2.24	19.02	4.3 : 1
55	45	4.6	3.64	2.55	21.40	3.7 : 1
50	50	4.0	3.34	2.85	23.65	3.2 : 1
45	55	3.4	5.25	3.00	24.75	3.1 : 1
40	60	3.0	4.48	3.37	27.43	2.6 : 1

where M_1 and M_2 are the molar concentration of the monomers 1 and 2, respectively. In the monomer feed, $r_1 = k_{11}/k_{12}$ and $r_2 = k_{22}/k_{21}$ are the reactivity ratios of monomers 1 and 2. At low conversions, dM_1/dM_2 is equal to the concentration ratio of the copolymer components. Equation (1) was linearized by Fineman and Ross,[31] as follows:

$$\frac{F}{f}(f - 1) = \frac{F^2}{f}(r_1 - r_2) \qquad (2)$$

where $f = m_1/m_2$ and $F = M_1/M_2$.

M_1 and M_2 are the molar concentrations in the monomer feed, and m_1, and m_2 are the molar concentrations in the final copolymer.

In Kelen–Tüdös method (Fig. 1), the reactivity ratios are determined from the following equation:

$$\eta = \left(\frac{r_1 + r_2}{\alpha}\right)\xi - \frac{r_2}{\alpha} \qquad (3)$$

by plotting η as a function of ξ, in which

$$\eta = \frac{g}{(\alpha + m)} \quad \text{and} \quad \xi = \frac{m}{(\alpha + m)}$$

Table II   Experimental Data for Copolymerization of HEMA (Monomer 1) with MA (Monomer 2) in the Presence of BP (0.02 wt %)

Composition of Starting Mixture (mol %)		Polymerization Time (min)	Conversion (wt %)	N Content in Copolymer (wt %)	Fraction of MA in Copolymer (mol %)	Ratio of HEMA/MA Units in Copolymer
M_1	M_2					
95	5	17.2	2.36	0.38	3.48	27.7 : 1
90	10	13.0	2.41	0.71	6.45	14.5 : 1
85	15	11.0	4.37	1.09	9.79	9.2 : 1
80	20	9.6	3.01	1.49	13.22	6.6 : 1
75	25	8.6	3.08	1.81	15.90	5.3 : 1
70	30	7.5	4.41	2.29	19.58	4.1 : 1
65	35	6.5	2.14	2.67	22.85	3.4 : 1

Table III Experimental Data for Copolymerization of HPMA (Monomer 1) with AA (Monomer 2) in the Presence of BP (0.03 wt %)

Composition of Starting Mixture (mol %)		Polymerization Time (min)	Conversion (wt %)	N Content in Copolymer (wt %)	Fraction of AA in Copolymer (mol %)	Ratio of HPMA/AA Units in Copolymer
M_1	M_2					
95	5	9.3	5.04	0.22	2.24	43.7 : 1
90	10	8.0	4.09	0.48	4.82	19.7 : 1
85	15	8.5	6.21	0.70	6.96	13.4 : 1
80	20	7.3	4.59	0.98	9.60	9.4 : 1
75	25	6.8	3.63	1.25	12.1	7.3 : 1
70	30	6.3	5.84	1.56	14.87	5.7 : 1
65	35	5.0	4.24	1.83	17.20	4.8 : 1
60	40	5.5	3.24	2.17	20.07	4.0 : 1
55	45	4.5	5.11	2.52	22.94	3.4 : 1
50	50	3.3	4.73	2.89	25.86	2.9 : 1
45	55	2.0	5.57	3.32	29.14	2.4 : 1

$$g = F\left(\frac{f-1}{f}\right) \quad m = \frac{F^2}{f}$$

$$\alpha = (m_{min} \cdot m_{max})^{1/2}$$

where m_{min} and m_{max} are the minimum and the maximum values of m, respectively, for a given series of measurements. Thus, a straight line is obtained which, when extrapolated to $\xi = 0$ and $\xi = 1$, gives r_2/α and r_1.

RESULTS AND DISCUSSION

The reactions of methacrylic acid with EO, PO, and with ECH leads to hydroxyalkyl esters. These functional esters are able to copolymerize in the presence of BP with AA and MA. AA and MA are considered as effective comonomers in the preparation of different coatings. The influence of the content of acrylamide and methacrylamide in copolymers on some properties of copolymers will be discussed in a forthcoming publication. In introductory experiments, we have found AA and MA to dissolve sufficiently in hydroxyalkyl methacrylates; therefore, the copolymerization could be carried out in bulk. The copolymerization was studied by evaluating the content of nitrogen in the resulting copolymers. The reactivity ratios are shown in Table VII. The values of r_2 were found to be equal or close to 0, whereas r_1 ranged from 1.11 to 2.17. Therefore, one may assume that in all cases a radical of hydroxyalkyl methacrylate
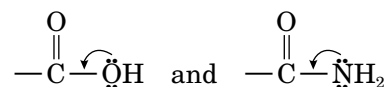
Table IV Experimental Data for Copolymerization of HPMA (Monomer 1) with MA (Monomer 2) in the Presence of BP (0.025 wt %)

Composition of Starting Mixture (mol %)		Polymerization Time (min)	Conversion (wt %)	N Content in Copolymer (wt %)	Fraction of MA in Copolymer (mol %)	Ratio of HPMA/MA Units in Copolymer
M_1	M_2					
95	5	11.1	5.32	0.31	3.15	30.7 : 1
90	10	10.0	4.25	0.64	6.42	14.6 : 1
85	15	9.0	5.28	1.01	9.98	9.0 : 1
80	20	8.5	3.46	1.40	13.61	6.3 : 1
75	25	7.8	5.70	1.84	17.58	4.7 : 1
70	30	7.0	5.71	2.30	21.59	3.6 : 1
65	35	6.0	5.38	2.85	26.19	2.8 : 1

Table V   Experimental Data for Copolymerization of CHPMA (Monomer 1) with AA (Monomer 2) in the Presence of BP (0.02 wt %)

Composition of Starting Mixture (mol %)		Polymerization Time (min)	Conversion (wt %)	N Content in Copolymer (wt %)	Fraction of AA in Copolymer (mol %)	Ratio of CHPMA/ MA Units in Copolymer
M_1	M_2					
95	5	16.3	7.31	0.32	3.98	24.2 : 1
90	10	15.0	4.52	0.62	7.54	12.3 : 1
85	15	13.5	2.15	0.95	11.27	7.9 : 1
80	20	12.5	2.40	1.30	15.05	5.6 : 1
75	25	10.5	7.73	1.67	18.86	4.3 : 1
70	30	10.0	7.80	1.89	21.01	3.8 : 1
65	35	8.0	6.49	2.14	23.40	3.3 : 1
60	40	7.1	4.29	2.45	26.26	2.8 : 1
55	45	6.3	5.63	3.01	31.14	2.2 : 1
50	50	4.9	7.02	3.60	35.92	1.8 : 1

reacts more easily with its own monomer than with amide monomer. The fastest reaction takes place between HEMA radical and AA monomer. At $r_2 = 0$, an amide radical does not react with its own monomer but only with hydroxyalkyl methacrylate monomer. This has been observed for the following pairs of comonomers: HEMA-AA, HPMA-AA, CHPMA-AA, and CHPMA-MA. Therefore, the copolymers are, at the beginning, enriched with units of corresponding hydroxyalkyl methacrylate.

The results are in good agreement with the effects of electron shifts in comonomers used. A molecule of ester or amide has the same number of mesomeric structures, but the latter is more stabilized mesomerically. It results from smaller elec-

tronegativity of the nitrogen atom compared to the oxygen one. The nitrogen atom is a better donor of nonbonding electrons, as follows:

$$
\begin{array}{ccc}
\overset{\displaystyle O}{\underset{\displaystyle \|}{}} & & \overset{\displaystyle O}{\underset{\displaystyle \|}{}} \\
-C \overset{\frown}{\leftarrow} \ddot{O}H & \text{and} & -C \overset{\frown}{\leftarrow} \ddot{N}H_2
\end{array}
$$

This leads to the conclusion that the radical is easily formed from hydroxyalkyl methacrylate molecule and reacts easily with its own monomer. Also, the amide radical chooses to react the more reactive molecule, i.e., the hydroxyalkyl methacrylate molecule. This causes the enrichment of copolymer with hydroxyalkyl methacrylate units

Table VI   Experimental Data for Copolymerization of CHPMA (Monomer 1) with MA (Monomer 2) in the Presence of BP (0.02 wt %)

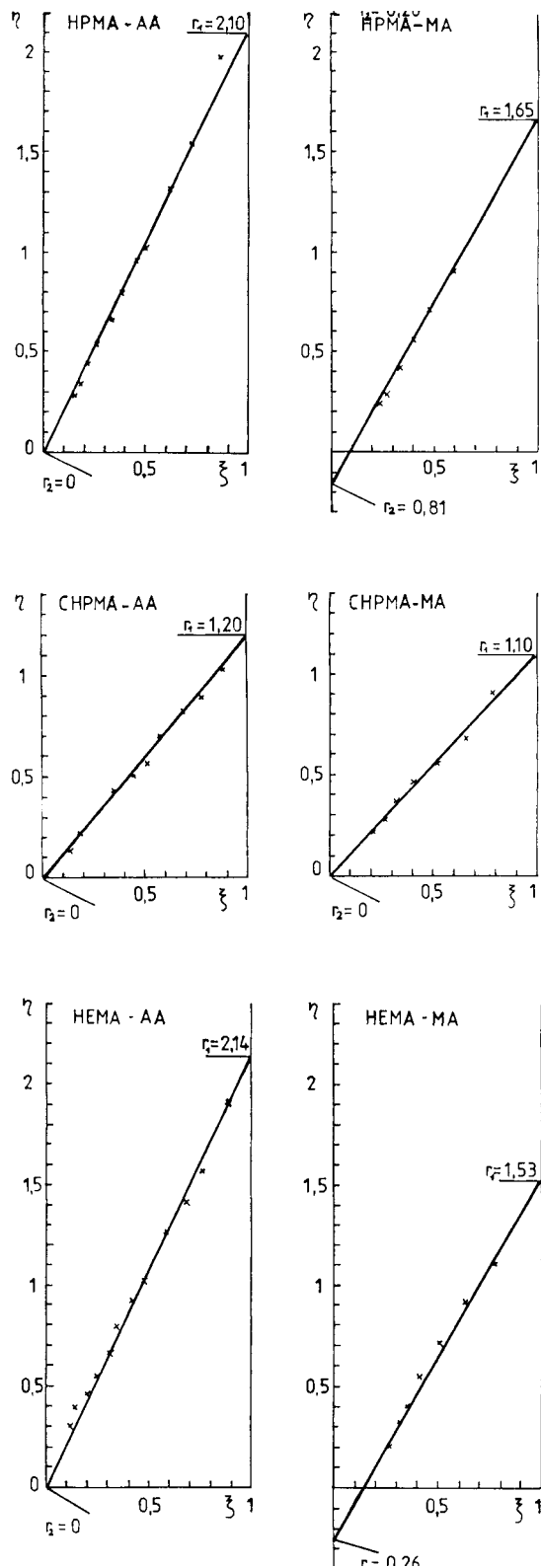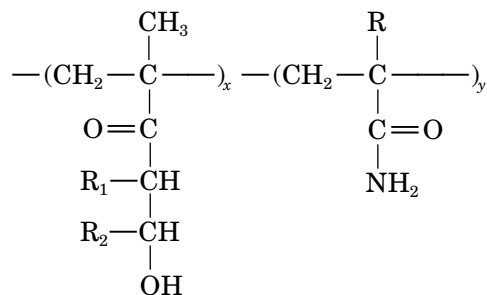| Composition of Starting Mixture (mol %)		Polymerization Time (min)	Conversion (wt %)	N Content in Copolymer (wt %)	Fraction of MA in Copolymer (mol %)	Ratio of CHPMA/ MA Units in Copolymer
M_1	M_2					
95	5	16.8	3.29	0.33	4.11	23.3 : 1
90	10	15.5	2.71	0.73	8.85	10.3 : 1
85	15	14.0	2.52	1.01	12.04	7.3 : 1
80	20	13.0	1.99	1.31	15.33	5.5 : 1
75	25	10.5	3.91	1.62	18.61	4.4 : 1
70	30	10.0	3.82	2.01	22.56	3.4 : 1
65	35	9.0	3.85	2.35	25.86	2.8 : 1

Figure 1 Plot of η versus ξ for the systems of hydroxy-alkyl methacrylates with AA and MA (Kelen–Tüdös method).

as compared with the initial mixture of comonomers. The reactivity differences of acrylates and methacrylates may be explained by the stabilizing the inductive effect of the methyl group present in MA. To summarize, the rate of reaction of hydroxyalkyl methacrylate radical with AA is faster than that with MA monomer, and the MA radical reacts faster with its own monomer than does the AA radical. This is one of the conclusions that can be drawn by observing a decrease of r_1 and, at the same time, an increase of r_2 for the hydroxyalkyl methacrylate/MA pair compared to hydroxyalkyl methacrylate/AA one (Table VII). The composition of copolymers may be shown in the form of the following general scheme:

$$-(CH_2-\underset{\underset{\underset{OH}{R_2-CH}}{\underset{R_1-CH}{\underset{O=C}{\overset{CH_3}{C}}}}{C}}-)_x -(CH_2-\underset{\underset{NH_2}{C=O}}{\overset{R}{C}}-)_y$$

where R = —H, —CH$_3$; R$_1$ = R$_2$ = —H; R$_2$ = —H, if R$_1$ = —CH$_3$, —CH$_2$Cl; and R$_2$ = —H, if R$_1$ = —CH$_3$, —CH$_2$Cl.

The average values of x and y are shown in Tables I–VI.

The composition of several copolymers presented in these tables was verified by ^{1}H-NMR (solvent DMSO-d$_6$, spectrometer ^{1}H-NMR type BS 587A of Tesla). It was established by comparing the integrated signals from protons of —NH$_2$ groups at 7.4 ppm (MA) or 6.8 ppm (AA) with those from methyl groups at 1.05 ppm (HPMA) or chloromethyl groups at 3.30 ppm (CHPMA).

CONCLUSIONS

The hydroxyethyl methacrylate monomers readily copolymerize with acrylamide or methacrylamide to yield colorless glassy polymers. The relativity ratios of the comonomers indicate that at the beginning of polymerization, the copolymers are richer in hydroxyalkyl methacrylate units compared to initial monomer mixture. The AA and MA monomers can therefore be used as modifiers of hydroxyalkyl methacrylate polymers.

Table VII   Reactivity Ratios of Hydroxyalkyl Methacrylates with AA and MA

Comonomers	Method	Fineman–Ross		Kelen–Tüdös	
		r_1	r_2	r_1	r_2
HEMA	AA	2.17	0.00	2.14	0.00
HEMA	MA	1.53	0.30	1.53	0.26
HPMA	AA	2.10	0.00	2.10	0.00
HPMA	MA	1.60	0.80	1.65	0.81
CHPMA	AA	1.20	0.00	1.20	0.00
CHPMA	MA	1.12	0.00	1.10	0.00

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