

Copolymerization of Glycidyl Methacrylate with Alkyl Acrylate Monomers

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Synopsis

A newer approach to obtaining acrylic thermoset polymers with adequate hydrophilicity required for various specific end uses is reported. Glycidyl methacrylate (GMA) was copolymerized with *n*-butyl acrylate (*n*-BA), isobutyl acrylate (*i*-BA), and 2-ethylhexyl acrylate (2-EHA) in bulk at 60°C, with benzoyl peroxide as free radical initiator. The copolymer composition was determined from the estimation of epoxy group. Reactivity ratios were calculated by the Yezrielev, Brokhina, and Roskin method. For copolymerization of GMA (M_1) with *n*-BA (M_2) the reactivity ratios were $r_1 = 2.15 \pm 0.14$, $r_2 = 0.12 \pm 0.03$; with *i*-BA (M_2) they were $r_1 = 1.27 \pm 0.06$, $r_2 = 0.33 \pm 0.031$; and with 2-EHA (M_2) they were $r_1 = 2.32 \pm 0.14$, $r_2 = 0.13 \pm 0.009$. The reactivity ratios were the measure of distribution of monomer units in a copolymer chain; the values obtained are compared and discussed.

INTRODUCTION

Acrylic polymers that contain epoxy functional groups as pendant units have become increasingly important in applications for coatings and biomaterials.^{1,2} The copolymers of GMA and organotin acrylic monomers provide better control of fouling on ship hulls and other surfaces in contact with the environment and have better mechanical properties after crosslinking epoxy pendant groups.³ Our investigations of the physicommechanical properties of GMA-alkyl acrylates showed promising results.⁴ This article aims at a comparison of the trend of the relative reactivities of different alkyl acrylates toward GMA radical.

EXPERIMENTAL

Materials

The monomers *n*-butyl acrylate, isobutyl acrylate, and 2-ethylhexyl acrylate (all Fluka AG) were freed from inhibitor with 10% sodium hydroxide,⁵ followed by distillation under reduced pressure over 4-Å molecular sieves. Glycidyl methacrylate (Fluka AG) was purified by vacuum distillation.

Benzoyl peroxide (BDH) was purified by crystallization from methanol and a stock solution was made with chloroform.

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TABLE I
Copolymerization of Glycidyl Methacrylate (M_1) and *n*-Butyl Acrylate (M_2)^a

Initial monomer mixture Mole fraction of M_1	Copolymer yield by weight of monomers (%)	Epoxy content (%)	Copolymer composition Mole fraction of m_1
0.184	6.2	14.32	0.447
0.184	5.5	14.42	0.450
0.375	7.2	21.79	0.698
0.474	6.1	23.77	0.767
0.474	5.8	23.67	0.764
0.575	8.1	24.41	0.789
0.677	5.4	25.22	0.818
0.677	6.6	25.36	0.821

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

Copolymerization

All copolymerization reactions were carried out in reaction tubes after charging the predetermined amounts of GMA, alkyl acrylates, and benzoyl peroxide, followed by repeated evacuation at liquid nitrogen temperature in a cooling and thawing procedure.⁶ The reactions were made at $60 \pm 0.1^\circ\text{C}$ in a thermostat water bath. The differential form of the copolymer equation was used and conversions in all cases were limited to 10%. For checking the accuracy of the experimental procedure the reactions for the *n*-BA and *i*-BA systems were done in duplicate with identical mole ratios of feed monomer. After attaining the desired conversions the contents were poured into methanol and the purification was made by repeated precipitation and dissolution in methanol and chloroform, respectively. The purified polymers were dried at 50°C under vacuum to constant weight.

The copolymer compositions were determined by estimating the epoxy group by the hydrochloric acid-dioxane reagent method.⁷ The reaction conditions and results are summarized in Tables I-III for these bulk polymerizations.

TABLE II
Copolymerization of Glycidyl Methacrylate (M_1) and Isobutyl Acrylate (M_2)^a

Initial monomer mixture Mole fraction of M_1	Copolymer yield % by weight of monomers (%)	Epoxy content (%)	Copolymer composition Mole fraction of m_1
0.279	7.4	14.41	0.449
0.279	6.8	14.32	0.446
0.474	6.5	19.65	0.625
0.474	6.9	19.73	0.627
0.677	7.2	23.47	0.756
0.677	7.5	23.38	0.753

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

TABLE III
Copolymerization of Glycidyl Methacrylate (M_1) and 2-Ethylhexyl Acrylate (M_2)^a

Initial monomer mixture Mole fraction of M_1	Copolymer yield by weight of monomers (%)	Epoxy content (%)	Copolymer composition Mole fraction of m_1
0.245	5.5	13.33	0.504
0.463	6.2	20.75	0.738
0.564	7.5	23.17	0.808
0.751	6.5	26.24	0.893
0.921	6.4	28.88	0.964

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

RESULTS AND DISCUSSION

The reactivity ratios were calculated (Table IV) from the copolymer composition data by the Yezrielev (YBR) method.⁸

A perusal of the reactivity ratio data reveals that the rate of reaction increased with an increase on GMA concentration in the monomer feed. Further GMA-2-EHA and GMA-*n*-BA copolymers show a much higher content of GMA than the feed, whereas for GMA-*i*-BA the system tends toward random copolymerization (Figs. 1-3).

The rate of polymerization depended on the nature of the alkyl group of the

TABLE IV
Reactivity Ratios for Copolymerization of Glycidyl Methacrylate and Alkyl Acrylates

Monomer M_1	Monomer M_2	$r_1 \pm \Delta r_1$	$r_2 \pm \Delta r_2$
Glycidyl methacrylate	<i>n</i> -Butyl acrylate	2.15 ± 0.14	0.12 ± 0.03
	Isobutyl acrylate	1.27 ± 0.06	0.33 ± 0.03
	2-Ethylhexyl acrylate	2.32 ± 0.14	0.13 ± 0.04

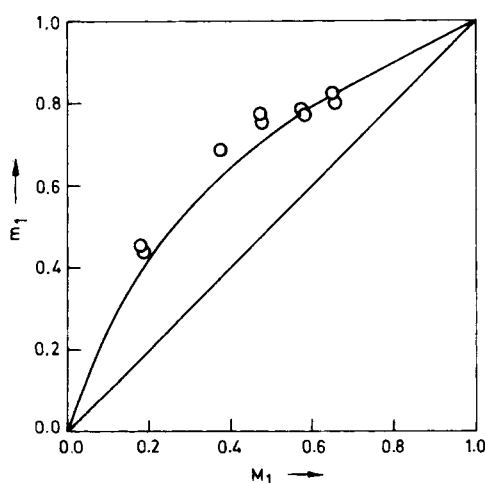


Fig. 1. Plot of mole fraction of GMA (m_1) in copolymer versus mole fraction of GMA (M_1) in monomer feed in GMA-*n*-BA copolymerization. (O) Experimental value; (—) curve calculated from copolymer equation using reactivity ratios determined by YBR method.

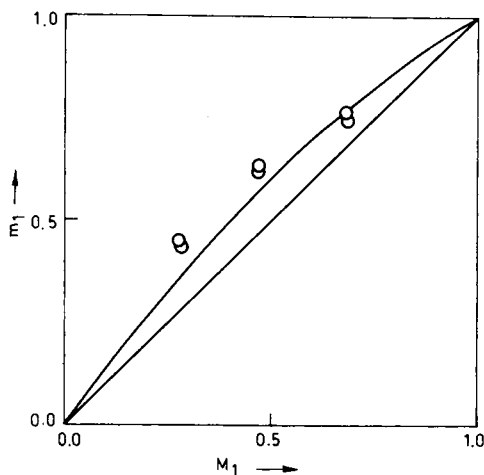


Fig. 2. Plot of mole fraction of GMA (m_1) in copolymer versus mole fraction of GMA (M_1) in monomer feed in GMA-*i*-BA copolymerization.

comonomer. This can best be understood from the $1/r_1$ values that give a measure of the relative reactivity of the acrylates towards the poly(GMA) radical; the higher the values of $1/r_1$, the greater the chance that the acrylate will add to the poly(GMA) radical. The order of reactivity of the alkyl acrylates toward GMA radical is *i*-BA > *n*-BA > 2-EHA.

The relative reactivities of the acrylates toward the GMA radical are governed by steric factors, the polarities of monomers and the resonance stabilization of radicals. It is shown that as the size of the alkyl group in alkyl acrylate (*n*-BA, 2-EHA) increased the tendency to react with GMA decreased. This may be attributed to the steric factors. Surprisingly, the low r_1 value for GMA-*i*-BA, compared with GMA-*n*-BA and GMA-2-EMA, suggests greater reactivity of *i*-BA toward poly(GMA) radical despite the bulky isobutyl group. The poor reactivities of *n*-BA and 2-EHA compared with *i*-BA may be attributed to the

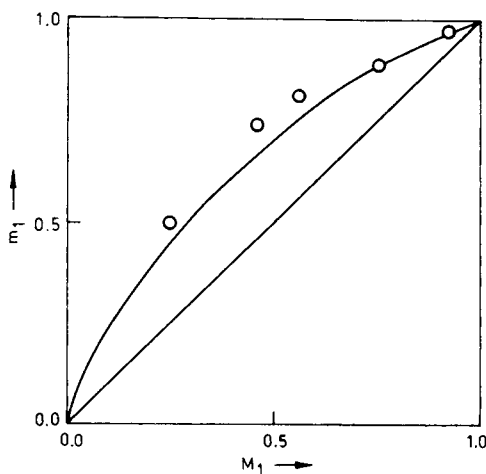


Fig. 3. Plot of mole fraction of GMA (m_1) in copolymer versus mole fraction of GMA (M_1) in monomer feed in GMA-2-EHA copolymerization.

shielding effect arising from *n*-butyl and 2-ethylhexyl side groups of the corresponding radicals due to the flexibility and free movement associated with the side alkyl groups. This would hinder the approach of incoming monomer to react with the radical. As for the attack by *n*-BA and 2-EHA macroradicals on GMA, the geometry in the transition state of both species appears to be decisive for the occurrence of steric hindrance. The reaction will have a lower activation energy if the side groups of radical and monomer in the transition state are in a syndiotactic position.

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