

# Semicontinuous Emulsion Copolymerization of Ethyl Acrylate and Butyl Acrylate at High Conversions

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## Synopsis

Semicontinuous emulsion copolymerization of ethyl acrylate and butyl acrylate was studied at conversions higher than 0.9. It was found that, in the cases in which the mole fraction of ethyl acrylate in the reaction mixture was over 0.65, the copolymerization diagram differs from the one given by the reactivity ratios. It was suggested that this deviation was caused by the diffusion control of the process. This suggestion was also supported by the differences in the free-monomer composition of the systems with and without seed latex, respectively, at the beginning of the copolymerization.

## INTRODUCTION

A batch emulsion polymerization of water-insoluble monomers proceeds in three intervals<sup>1</sup>: In interval I a nucleation of the polymer particles occurs (emulsifier in a micellar form, drops of free monomer, and growing particles are present in the reaction mixture), in interval II a growth of the nucleated particles takes place (drops of monomer and growing particles swollen by the monomer are present), and in interval III the polymerization is finished by the reaction of the monomer in the swollen polymer-monomer particles. There are somewhat different reaction conditions in the case in which monomers (and frequently also emulsifiers) are fed into the polymerization reactor gradually during the process, i.e., in the case of the so-called semicontinuous process.<sup>2</sup> In such a case, supposing a sufficiently low rate of the monomer addition, the polymerization rate is limited by this monomer addition rate and the reaction proceeds at high immediate conversion, mostly over 90%. The reaction then relates to interval III, but, at suitable concentration of emulsifier in the monomer emulsion feed, new particles may be nucleated during all the feeding time. The interior of the polymer particles is usually quite viscous during the polymerization.<sup>3</sup> Consequently, there is the possibility that diffusion of a monomer from the surface to the interior of the particles may be slower than the polymerization rate. This case is probable especially at a high conversion, because the number of radicals per particle is liable to increase (particles increase in size and the viscosity increases as the monomer is depleted, leading to a lowering of the termination constant), and it is much higher than 0.5.<sup>4,5</sup> The effect of a diffusion control of the polymerization rate should appear especially in copolymerization due to the different diffusion rates of comonomers. The results of previous work<sup>6</sup> indicate the effect of diffusion on the values of "effective" reactivity ratios found in copolymerization of butyl acrylate and styrene. The values of these reactivity ratios was influenced by an immediate conversion of the polymerizing system. In this work, the copolymerization of ethyl acrylate and butyl acrylate was studied at conversions higher than 90%.

## EXPERIMENTAL

Materials, butyl acrylate and ethyl acrylate (BASF), were used fresh distilled, Fenopon EP 120 (34% active matter)—ammonium salt of nonylphenolpolyethyleneglycol sulfate (GAF) was used without purification. Sodium metabisulfite p.a., ammonium persulfate p.a. (Lachema, USSR), and distilled water were used. Seed latices were prepared from these materials in the same manner as the copolymerization without seed latex, as shown below.

Copolymerizations were carried out in a 2-L steel reactor at 70°C in a nitrogen atmosphere. The rate of the monomer emulsion addition was 2.28 g/min. The charge compositions were as follows:

Initial reactor charge (experiments without seed latex): Fenopon EP 120 5.2 g, sodium metabisulfite 6, ammonium persulfate 0.5, distilled water up to 200.

Initial reactor charge (experiments with seed latex): Fenopon EP 120 26 g, sodium metabisulfite 6, ammonium persulfate 0.5, polymer dispersion (50% solids) 150, distilled water up to 200.

Monomer emulsion: Monomers 800 g, Fenopon EP 120 26, ammonium persulfate 12, distilled water 500.

The copolymerization was followed by the estimation of free monomers in the reaction mixture during the polymerization. The gas chromatography analyses were performed on a Carlo Erba model GV chromatograph. The experimental detail were as follows: flame ionization detector, 2-m column 4-mm i.d., support silanized Chromosorb W AW, stationary phase 15% Apiezon L, carrier gas N<sub>2</sub> at 58 mL/min. Temperature program: 6 min isotherma 47°C, then increasing 7 deg/min to the upper isotherma 85°C. The temperature of the sample inlet device as well as of the detector was 175°C.

## RESULTS AND DISCUSSION

The copolymerizations of ethyl acrylate ( $M_1$ ) and butyl acrylate ( $M_2$ ) were carried out at very low rate of the monomer emulsion addition. Under these conditions practically stationary composition of free monomers in the reaction mixture as well as in the arising copolymer formed after some period. The values of mole fractions of free ethyl acrylate in the reaction mixture  $f_{EA}$ , mole fractions

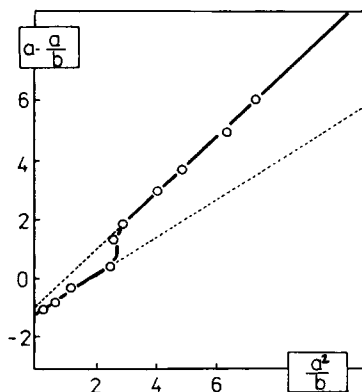


Fig. 1. Fineman and Ross relation for the copolymerization of ethyl acrylate ( $M_1$ ) and butyl acrylate ( $M_2$ ) at high conversions. (—)  $r_1 = 0.94$ ,  $r_2 = 0.95$ ; (---)  $r_1 = 0.65$ ,  $r_2 = 1.20$ .

TABLE I  
Mole Fractions of Free Ethyl Acrylate in the Reaction Mixture ( $f_{EA}$ ) and in the Arising Copolymer ( $F_{EA}$ ) in Copolymerization of Ethyl Acrylate ( $M_1$ ) and Butyl Acrylate ( $M_2$ )

Wt fraction of EA in the monomer emulsion feed	$f_{EA}$	$F_{EA}$	Average immediate wt conversion of monomers within the interval 50-90-min reaction	$a$	$b$	$a - a/b$	$a^2/b$
0.8438	0.8757	0.8736	0.95	7.0450	6.9114	6.03	7.18
0.8125	0.8563	0.8472	0.97	5.9589	5.5445	4.88	6.40
0.7813	0.8252	0.8204	0.95	4.7208	4.5679	3.69	4.88
0.7500	0.7982	0.7933	0.96	3.9554	3.8379	2.92	4.08
0.6875	0.7431	0.7379	0.94	2.8926	2.8153	1.87	2.97
0.6250	0.7050	0.6807	0.93	2.3898	2.1319	1.27	2.68
0.5000	0.6427	0.5610	0.94	1.7988	1.2779	0.39	2.53
0.3750	0.4848	0.4343	0.92	0.9410	0.7677	-0.28	1.15
0.2500	0.3613	0.2990	0.92	0.5657	0.4265	-0.76	0.75
0.1250	0.1861	0.1545	0.93	0.2788	0.1827	-1.62	0.29

TABLE II  
Reactivity Ratios of Ethyl Acrylate ( $M_1$ ) and Butyl Acrylate ( $M_2$ )

Reactivity ratio	Calculated from $Q, e^8$	Experimentally estimated	
		$f_{EA} < 0.7$	$f_{EA} > 0.7$
$r_1$	0.77	0.65	0.94
$r_2$	1.30	1.20	0.95

of ethyl acrylate in the arising copolymer  $F_{EA}$ , and the average weight conversions of monomers within the interval 90–150 min of the reaction are summarized in Table I. The reactivity ratios were calculated using the Fineman–Ross relation.<sup>7</sup> The relationship  $(a - a/b)$  vs.  $a^2/b$ , where  $a = f_{EA}/(1 - f_{EA})$  and  $b = F_{EA}/(1 - F_{EA})$  is shown in Figure 1. This relationship should give a straight line with the slope  $r_1$  and the intercept  $-r_2$ . In this case, however, two different values of  $r_1$  and  $r_2$  were found for the copolymerizations with low and high ethyl acrylate to butyl acrylate ratios respectively. The reactivity ratios (see Table II) found in the region of ethyl acrylate concentrations up to  $f_{EA} \sim 0.65$  were practically equal to the values calculated from the  $Q, e$  schema ( $Q_1 = 0.34$ ,  $e_1 = 0.58$ ;  $Q_2 = 0.43$ ,  $e_2 = 0.58$ <sup>8</sup>). In the region of  $f_{EA} > 0.75$  are both reactivity ratios close to 1. The character of copolymerization in relation to the monomer composition documents also the copolymerization diagram shown in Figure 2. The reactivity of ethyl acrylate is lower in comparison with that of butyl acrylate, and calculated and experimentally estimated copolymerization diagrams are practically identical up to  $f_{EA} \sim 0.65$ . At higher values of  $f_{EA}$ , however, an “increase of relative reactivity” of ethyl acrylate appears. The copolymerization diagram is then diagonal, which corresponds to  $r_1 \sim r_2 \sim 1$ . We suppose that this anomalous behavior of the studied monomer pair may be caused by a diffusion control of the process, especially by the better mobility of ethyl acrylate molecules under these conditions. The mobility of a diluent molecule in a given medium depends upon the probability that the molecule finds in its neighbor a hole which is large enough to permit a considerable displacement of it. The mobility depends primarily upon the size and shape of the diluent molecule.<sup>9</sup> The value of thermodynamic diffusion coefficient is the function of the diluent mobility as well as of its concentration, because the concentration and properties of diluent (or mixture of diluents) impedes the character of the polymer network.

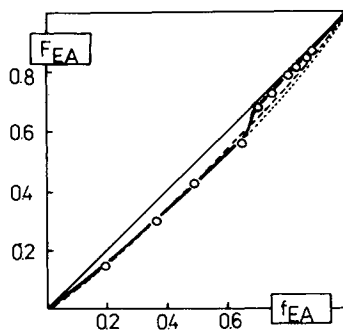


Fig. 2. Copolymerization diagram for copolymerization of ethyl acrylate ( $M_1$ ) and butyl acrylate ( $M_2$ ), a comparison of calculated and experimentally estimated copolymerization curves. (---)  $r_1 = 0.77$ ,  $r_2 = 1.30$ ; (- - -)  $r_1 = 0.67$ ,  $r_2 = 1.20$ .

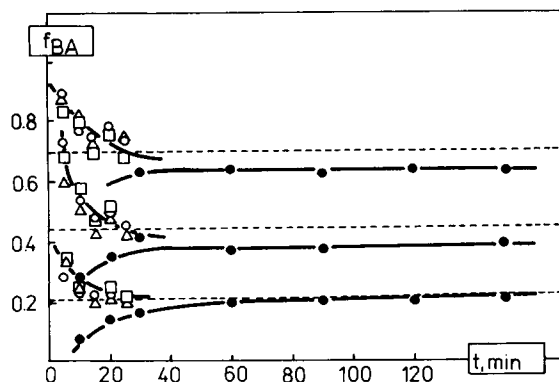


Fig. 3. Changes in free monomer ratios at the beginning of ethyl acrylate/butyl acrylate copolymerizations in presence of seed latices and without them. Dashed lines represent mole fractions of butyl acrylate in the monomer feed. Seed latex: (○) poly(BA); (△) poly(EA), (□) copoly(BA/EA); (●) without seed latex.

The suggestion of diffusion control of the copolymerization at high immediate conversions is borne also by the results obtained in copolymerizations in the presence of seed latex, i.e., at the initial conversion 100%. In Figure 3 the courses of free monomers compositions are shown for poly(ethyl acrylate), poly(butyl acrylate), and copolymer ethyl acrylate/butyl acrylate seed latices, and these are compared with courses of free monomer compositions of systems without seed latex. It is evident, that in systems with seed latices the consumption of ethyl acrylate at the beginning is much more rapid than the consumption of butyl acrylate, despite the higher reactivity of the latter. Practically no differences were found in copolymerizations with different seed latices, but the steady state formation (from the point of view of free monomer ratios), in systems with and without seed latex respectively, are quite different.

## CONCLUSIONS

The products arising from semicontinuous emulsion copolymerization, supposing a sufficiently low feeding rate of monomers, are very homogeneous in their composition. A steady state free-monomer ratio forms, which produces copolymer composition identical to that of the monomer feed. The steady ratio of free monomers depends upon the reactivity ratios of the monomers, and in the case of a high conversion reaction is probably affected also by the ratio of diffusion rates of the monomer pair.

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