Semicontinuous Emulsion Copolymerization of Acrylonitrile, Butyl Acrylate, and Styrene

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Synopsis

Semicontinuous emulsion copolymerization of acrylonitrile (M_1), butyl acrylate (M_2), and styrene (M_3) was investigated. The copolymerization proceeded under the conditions used with a high degree of conversion, whereby a stationary state characterized by a constant monomer mixture composition and a constant composition of the arising copolymer was achieved. From the analytically estimated free monomers and arising copolymer compositions, the reactivity ratios for the pair AN/BA r_{12} = 0.71, r_{21} = 1.17 and for the pair AN/Sty r_{13} = 0.06, r_{31} = 0.28 were calculated. The applicability of the reactivity ratios found was verified also for the ternary system acrylonitrile/butyl acrylate/styrene.

INTRODUCTION

In technical practice, products of copolymerization having a uniform copolymer composition are often important. One of the routes of obtaining them in emulsion polymerization is the use of the so-called semicontinuous processes, where the monomers are gradually fed into the reactor. At suitable monomer feeding rates and at sufficiently high polymerization rates, a steady state may be reached at which the rate of polymerization is practically equal to that of the monomer feeding. Under these conditions, a free monomer concentration is formed in the system which produces the same copolymer composition as that of the monomer feed.[1,2] In a previous paper,[3] the semicontinuous copolymerization of styrene and butyl acrylate was studied. It was found that the relationship between the free monomer composition in the reaction mixture and the composition of the arising copolymer is governed by the monomer feeding rate or, subsequently, by the immediate polymerization conversion. The possibility of diffusion control in the copolymerization at a high degree of conversion was assumed.

In this paper, the semicontinuous emulsion copolymerization of acrylonitrile with butyl acrylate and acrylonitrile with styrene and the terpolymerization of the ternary system acrylonitrile/butyl acrylate/styrene was investigated.

EXPERIMENTAL

Copolymerizations were carried out in a 2-liter steel reactor at 70°C in a nitrogene atmosphere from the following materials:
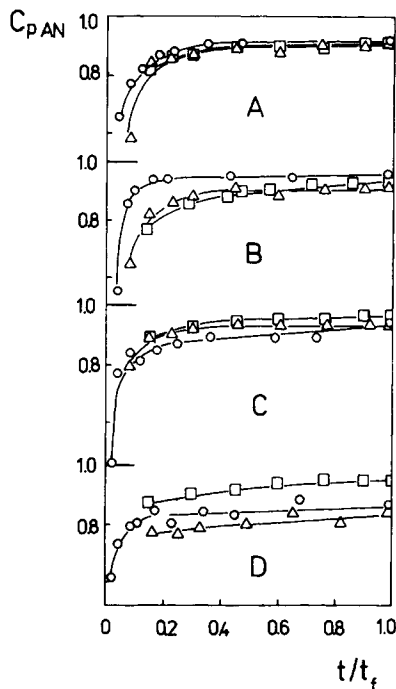
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Fig. 1. Conversion of acrylonitrile during feeding of monomer emulsion in relation to feeding rate R_f (mole/kg·sec). (A) Weight ratio AN/Sty = 400/400: (O) R_{fAN} = 2.575 × 10^{-4}, R_{fSty} = 1.318 × 10^{-4}; ($\triangle$) R_{fAN} = 0.9838 × 10^{-3}, R_{fSty} = 0.5035 × 10^{-3}; ($\square$) R_{fAN} = 1.9976 × 10^{-3}, R_{fSty} = 1.0224 × 10^{-3}. (B) Weight ratio AN/Sty = 160/640: (O) R_{fAN} = 0.9550 × 10^{-4}, R_{fSty} = 1.9560 × 10^{-4}; ($\triangle$) R_{fAN} = 0.3995 × 10^{-3}, R_{fSty} = 0.8178 × 10^{-3}; ($\square$) R_{fAN} = 0.7534 × 10^{-3}, R_{fSty} = 1.5424 × 10^{-3}. (C) Weight ratio AN/BA = 400/400: (O) R_{fAN} = 2.6900 × 10^{-4}, R_{fBA} = 1.1190 × 10^{-4}; ($\triangle$) R_{fAN} = 1.0141 × 10^{-3}, R_{fBA} = 0.4216 × 10^{-3}; ($\square$) R_{fAN} = 1.9976 × 10^{-3}, R_{fBA} = 0.7305 × 10^{-3}. (D) Weight ratio AN/BA = 160/640: (O) R_{fAN} = 0.9990 × 10^{-4}, R_{fBA} = 1.6610 × 10^{-4}; ($\triangle$) R_{fAN} = 0.4322 × 10^{-3}, R_{fBA} = 0.7188 × 10^{-3}; ($\square$) R_{fAN} = 0.7990 × 10^{-3}, R_{fBA} = 1.3288 × 10^{-3}.

Charge A: Distilled water 300g, Etoxon AF-5 16.

Charge B: Distilled water 10 g, ammonium persulfate 2.4, sodium metabisulfite 1.2.

Charge C: Distilled water 640 g, Etoxon AF-5 37.4, Slovafol 920 32.0, ammonium persulfate 5.6.

Charge D: Monomers 800 g.

Charge E: Distilled water 50 g, sodium metabisulfite 2.8.

Charge A was heated in the reactor to 70°C in a nitrogene atmosphere; then charge B was added, and the emulsion prepared from charges C and D was immediately added. Charge E was fed into the reactor simultaneously with the emulsion, the time of the addition being the same as the feeding time of the monomer emulsion feed.

Acrylonitrile of Ugilor; butyl acrylate of BASF; styrene of Kaučuk Kralupy; Etoxon AF-5 ($C_9H_{19}C_6H_4(OCH_2CH_2)_5OSO_3Na$) (30% act. matter) of Spolek pro chemickou a hutní výrobu Boletice; and Slovafol 920 ($C_9H_{19}C_6H_4(OCH_2CH_2)_{20}OH$) of CHZWP Nováky were used. Ammonium persulfate and sodium metabisulfite p.a. were supplied by Lachema Brno, ČSSR. The monomers were freshly distilled.
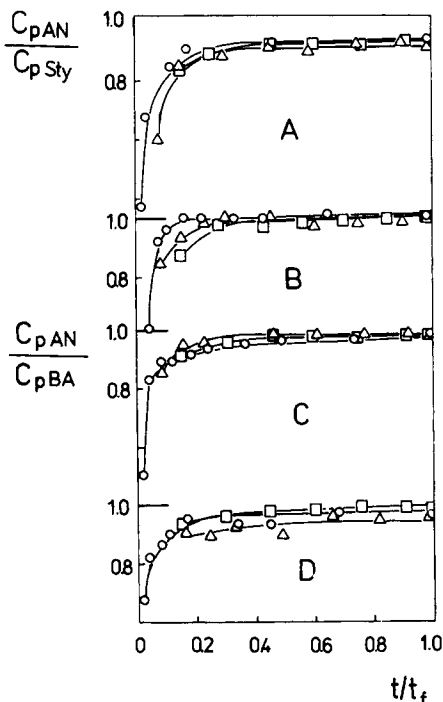
Fig. 2. Acrylonitrile/styrene and acrylonitrile/butyl acrylate conversion ratios during feeding of monomer emulsion in relation to feeding rate.   Weight ratios and feeding rates are marked in the same manner as in Fig. 1.

Free monomers were analyzed during the copolymerization by GLC analysis. Samples taken from the reaction system were precipitated in methanol containing 500 ppm hydroquinone.   Toluene was used as an internal standard.

RESULTS AND DISCUSSION

The copolymerizations were carried out with two different compositions of the acrylonitrile (M_1)–butyl acrylate (M_2) and acrylonitrile (M_1)–styrene (M_3) mixtures.   The feeding rates R_f were chosen so that the whole monomer emulsion charge was fed within t_f about 0.5, 1.0, and 4.0 hr, respectively, which corresponded to an R_f range of 2×10^{-3} to 4×10^{-4} mole/kg·sec.   Unlike the BA/ styrene copolymerizations, which exhibited a strong dependence on the feeding rate,[3] the copolymerizations of AN/BA and AN/styrene were found to be much less sensitive to the feeding rate, as illustrated in Figure 1.   Acrylonitrile exhibited a lower polymerization reactivity in copolymerization, but even at a relatively high R_f, also high immediate conversion of this monomer was found. The conversion ratios c_{pAN}/c_{pBA} and c_{pAN}/c_pSty were practically constant and converged to unity beginning around 20% of feed, as shown in Figure 2.   This means that even at high feeding rates, formation of a steady state is to be expected, as which the polymerization rate R_p equals the feeding rate R_f.   The high copolymerization rate of acrylonitrile with styrene found agrees with the results of other authors[4–6] who had ascertained that the total R_p increased with in-
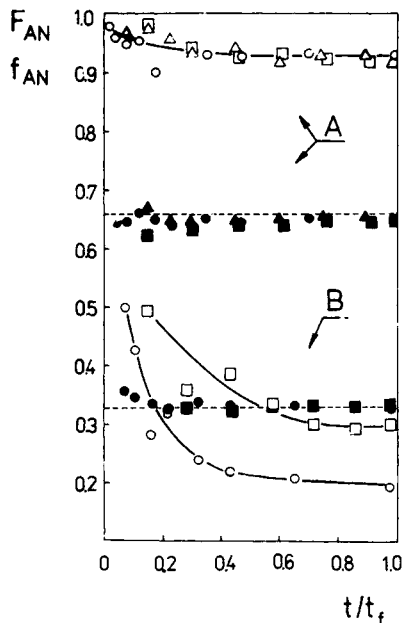
Fig. 3. Mole ratio of acrylonitrile in free monomers in the reaction mixture (○△□) and in the arising copolymer (●▲■) during feeding of monomer emulsion. Weight ratios and feeding rates are marked in the same manner as in Fig. 1. Dashed lines mark mole ratios of acrylonitrile in the AN/Sty monomer emulsion feed.

creasing content of AN in styrene. The results showed that the copolymerization rate of AN/BA at the chosen conditions was also high and, even at the highest feeding rates used, did not exceed the maximum polymerization rate $R_{p\mathrm{max}}$ of the system.[7,8]

Figures 3 and 4 show the changes of free monomer compositions in the reaction mixtures and the instant copolymer composition as a function of the feeding rate. The free monomer compositions in the reactor at the feed monomer ratios (wt/wt) of AN/Sty = 400/400 and AN/BA = 160/640 were practically independent of feeding rate; the curves of the free monomer composition versus reduced feeding time t/t_f were almost identical. On the other hand, for the feed monomer ratios (wt/wt) of AN/Sty = 160/640 and AN/BA = 400/400, different free monomer compositions were found at high feeding rates in comparison with those found at the low feeding rates. A similar relationship was found for the BA/Sty copolymerization.[3] The instantaneous copolymer composition was in all cases practically identical to the monomer feed composition. This fact was a consequence of the high polymerization conversion during the feeding period, where $R_p = R_f$ was practically achieved. Toward the end of the feeding period, the systems exhibited constant values of the free monomer ratios in the reaction vessel. For the low feeding rates, the "effective" reactivity ratios were calculated; they are to be regarded as the values valid only for the given system and copolymerization method, because the partial water solubility of acrylonitrile was not considered. Further, the copolymerization may be influenced at high conversion also by the monomer diffusion in the growing polymer particles. The free monomer concentrations and instantaneous copolymer compositions used for the reactivity ratios calculation are summarized in Table I. The calculated
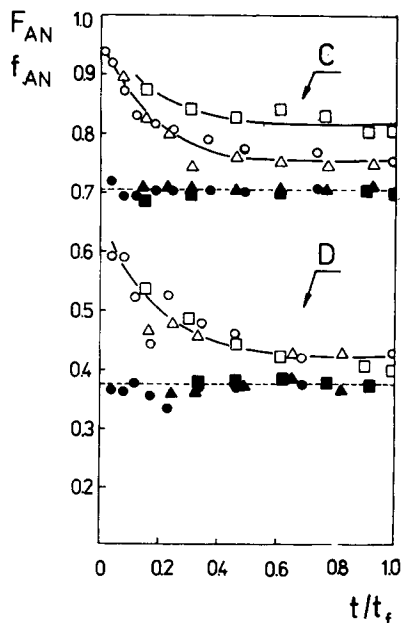
Fig. 4. Mole ratio of acrylonitrile in free monomers in the reaction mixture (O△□) and in the arising copolymer (●▲■) during feeding of monomer emulsion. Weight ratios and feeding rates are marked in the same manner as in Fig. 1. Dashed lines mark mole ratios of acrylonitrile in the AN/BA monomer emulsion feed.

reactivity ratios as well as the values found for the BA/styrene copolymerization are given in Table II.

In the following experiments, the terpolymerization of acrylonitrile, butyl acrylate, and styrene was investigated and the validity of the reactivity ratios estimated for the above binary systems was verified. In accordance with the estimated reactivity ratios, styrene exhibited the highest reactivity. Its con-

TABLE I

Monomer Concentrations at Steady State Used for the Calculation of Reactivity Ratios

| | Mole fractions of acrylonitrile in copolymerizations | |
	AN/BA	AN/Sty
Monomer emulsion feed	0.706 0.376	0.661 0.328
Free monomers in reaction mixture	0.760 0.425	0.932 0.213
Instant copolymer	0.703 0.371	0.645 0.335

TABLE II

Reactivity Ratios Estimated for Binary Systems AN/BA, AN/Sty, and BA/Sty[a]

| $r_{12} = 0.708$ | $r_{13} = 0.062$ | $r_{23} = 0.470$ |
| $r_{21} = 1.170$ | $r_{31} = 0.276$ | $r_{32} = 0.660$ |

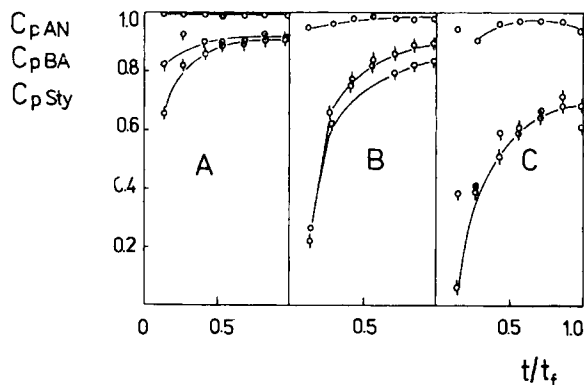[a] M_1 = AN, M_2 = BA, M_3 = Sty.

C_{pAN}
C_{pBA}
C_{pSty}

Fig. 5. Terpolymerization of acrylonitrile (ϕ), butyl acrylate (φ), and styrene (O). Conversion of monomers during feeding of monomer emulsion; R_f in mole/kg·sec. (a) Weight ratio AN/BA/Sty = 480/160/160, $R_{fAN} = 2.198 \times 10^{-3}$, $R_{fBA} = 0.304 \times 10^{-3}$, $R_{fSty} = 0.375 \times 10^{-3}$. (b) Weight ratio AN/BA/Sty = 240/240/320, $R_{fAN} = 1.130 \times 10^{-3}$, $R_{fBA} = 0.470 \times 10^{-3}$, $R_{fSty} = 0.771 \times 10^{-3}$. (c) Weight ratio AN/BA/Sty = 160/480/160, $R_{fAN} = 0.753 \times 10^{-3}$, $R_{fBA} = 0.940 \times 10^{-3}$, $R_{fSty} = 0.386 \times 10^{-3}$.

version exceeded the value of 90% even in the initial reaction interval. The course of acrylonitrile and butyl acrylate during the feeding period was similar, as shown in Figure 5.

The courses of the instantaneous copolymer composition in a batch process calculated using the estimated reactivity ratios are shown in Figure 6. The dashed lines mark the initial monomer compositions, i.e., the monomer feed compositions in the semicontinuous process. Figure 6 allows one to assume that the experimentally estimated instantaneous compositions of the terpolymers arising during the semicontinuous process are practically identical with the monomer feed and that they are highly constant during the whole feeding time. The free monomer compositions and the instantaneous terpolymer compositions estimated at steady state can be read from Table III, in which the corresponding monomer feed and the theoretical free monomer compositions calculated by means of the reactivity ratios from Table II are also given. From the data in Table III the applicability of the reactivity ratios estimated for the binary systems to the corresponding ternary system at the same processing conditions is evident. The calculated and the experimentally estimated free monomer compositions are very close, which is well illustrated by the ternary diagram in Figure 7.

CONCLUSIONS

The semicontinuous emulsion copolymerization of arylonitrile with styrene and of acrylonitrile with butyl acrylate reached a high degree of conversion at the investigated feeding rate range. The conversion ratio of both monomers stabilized approximately after about 20% of monomers had been fed, and its value was near unity. In the stationary state, a free monomer composition was formed which produced a copolymer identical in composition with the composition of the feeding monomer mixture. Homogeneous copolymers then resulted from the process. The reactivity ratios estimated for the binary mixtures from the corresponding monomer and the instantaneous copolymer compositions in the
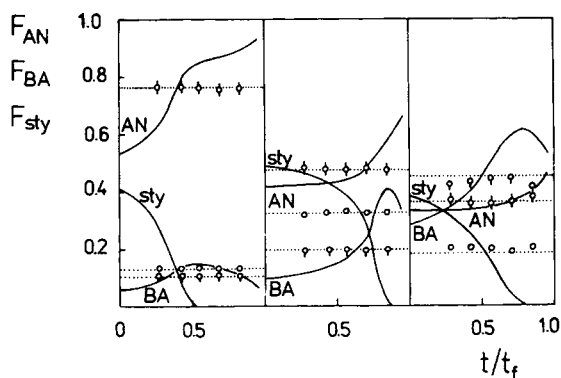
Fig. 6. Hypothetic instantaneous terpolymer composition in batch terpolymerization and experimentally estimated instantaneous terpolymer composition in semicontinuous process. Dashed lines mark mole fractions of respective monomers in the initial polymerization mixture or in the monomer emulsion feed. Monomers and feeding rates are marked in the same manner as in Fig. 5.

stationary state can be applied also for the characterization of the ternary system acrylonitrile/butyl acrylate/styrene.

Appendix

The free monomer composition corresponding to the given composition of the instantaneous terpolymer was calculated by the use of the searching procedure using the ternary copolymerization

TABLE III
Free Monomers and Instant Terpolymer Compositions in Terpolymerization of Acrylonitrile (M_1), Butyl Acrylate (M_2), and Styrene (M_3)

|	t/t_f	f_1	f_2	f_3	F_1	F_2	F_3
Monomer emulsion feed	0.4167	0.908	0.092	~0	0.767	0.100	0.133
$f_1 = 0.764$	0.5556	0.871	0.126	0.004	0.760	0.105	0.135
$f_2 = 0.106$	0.6944	0.895	0.101	0.003	0.757	0.109	0.133
$f_3 = 0.130$	0.8333	0.904	0.096	~0	0.763	0.104	0.133
Calculated free monomers							
$f_1 = 0.883$							
$f_2 = 0.102$							
$f_3 = 0.015$							
Monomer emulsion feed	0.4286	0.650	0.305	0.045	0.482	0.195	0.324
$f_1 = 0.477$	0.5714	0.634	0.336	0.030	0.479	0.189	0.332
$f_2 = 0.198$	0.7143	0.604	0.343	0.053	0.481	0.191	0.328
$f_3 = 0.325$	0.8571	0.572	0.355	0.072	0.476	0.198	0.326
Calculated free monomers							
$f_1 = 0.578$							
$f_2 = 0.311$							
$f_3 = 0.110$							
Monomer emulsion feed	0.2857	0.439	0.528	0.033	0.369	0.427	0.204
$f_1 = 0.362$	0.4286	0.449	0.530	0.021	0.359	0.435	0.206
$f_2 = 0.452$	0.5714	0.430	0.555	0.015	0.353	0.444	0.203
$f_3 = 0.186$	0.7143	0.453	0.531	0.017	0.369	0.439	0.192
Calculated free monomers							
$f_1 = 0.444$							
$f_2 = 0.527$							
$f_3 = 0.029$							
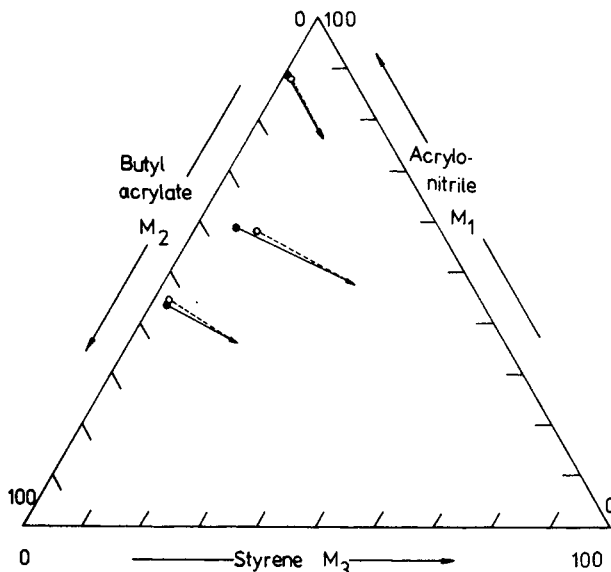
Fig. 7. Ternary diagram for semicontinuous emulsion terpolymerization of acrylonitrile, butyl acrylate, and styrene. Arrowhead indicates the instantaneous terpolymer composition from the monomer composition indicated by tail end of arrow: (●) experimentally estimated free monomer composition in the reaction mixture; (○) hypothetic free monomer composition calculated with the use of the reactivity ratios found for binary mixtures.

equation. Each searching step was tested by means of the comparison of the absolute value $|(F_1/F_2)_{calc} - (F_1/F_2)_{given}|$ with that for the previous step, directed to minimize the testing value.

The terpolymer mixture composition as a function of the conversion C with the batch copolymerization technique was calculated by solving the first-order differential equation system

$$\frac{df_1}{dC} = \frac{f_1 - F_1}{1 - C} \qquad \frac{df_2}{dC} = \frac{f_2 - F_2}{1 - C}$$

using the standard Runge–Kutta method of the IIIrd order. At a sufficient step density (100–200 steps in the conversion range from 0 to 1), it is possible to calculate the changing composition of the monomer mixture, of the instantaneously arising copolymer, and of the cumulative (integral) copolymer.

The numerical calculations were carried out on a Hewlett–Packard HP 9100 A table calculator with extended memory EM 9101.

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