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Kinetics of Free Radical Copolymerization. VII. Kinetic Analysis of Ethyl Acrylate-Styrene Copolymerization in Inert Solvent

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ABSTRACT

The copolymerization kinetics of the ethyl acrylate/styrene/azobis-isobutyronitrile/benzene/50°C system was found to deviate from the classical rate equation of copolymerization. The experimental results could not be interpreted by the diffusion theory, the penultimate effect, or the theory of electron donor-acceptor complexes. Our kinetic data were consistently described by the theory of hot radicals, and the 13 parameters characteristic for the copolymerization system were determined from an adequate number of data at different compositions by a nonlinear least-squares method.

As early as the kinetic investigation of copolymerization began, several systems were reported to deviate from the classical treatment of copolymerization. The value of the Φ constant in the rate equation of copolymerization indicated that the rate equation (1) does not properly describe certain copolymerization systems:

$$W_2 = \frac{W_1^{1/2} (\rho_1 m_1^2 + 2m_1 m_2 + \rho_2 m_2^2)}{(\rho_1^2 \delta_1^2 m_1^2 + 2\Phi \rho_1 \rho_2 \delta_1 \delta_2 m_1 m_2 + \rho_2^2 \delta_2^2 m_2^2)^{1/2}} \quad (1)$$

where m_1 and m_2 are the concentrations of the monomers, ρ_1 and ρ_2 are the reactivity ratios, δ_1 and δ_2 are the ratios $k_4^{1/2}/k_2$ in the homopolymerization of both monomers, whereas k_2 and k_4 are the rate constants of chain propagation and chain termination.

The most striking deviation was observed in the copolymerization of styrene with butyl acrylate [1, 2] where the value of Φ , calculated on the basis of Eq. (1) from experimental data, increased two orders of magnitude in the function of monomer composition.

Such phenomena were interpreted in different terms. The most prevalent theories are:

1. North diffusion theory [3] which relates the rate constant of termination to the viscosity of the reaction mixture.
2. The theory of electron donor-acceptor complexes [4] which attributes the deviation from Eq. (1) to the formation of comonomer complexes and their role in chain propagation.
3. According to the theory of penultimate effect, the reactivity of the growing radical depends on the structure of the last two monomer units on the chain end [5-7].
4. The theory of hot radicals [8] which considers the reactions of vibrationally excited, so-called hot radicals which are produced in the chain propagation reaction and have an excess energy arising from the reaction heat and activation energy.

The kinetic description of ethyl acrylate/styrene copolymerization was attempted on the basis of these theories, and the agreement between the different kinetic models and the experimental data was checked. Our earlier results concerning the kinetics of homopolymerization of both monomers [9, 10], the kinetics of initiation in ethyl acrylate/styrene copolymerization [11], and the composition of copolymers [12] were used as complementary data in the analysis.

The homopolymerization kinetics of ethyl acrylate and styrene in solution was shown to be in contradiction with the conventional kinetic treatment, the North diffusion theory, and the theory of electron donor-acceptor complexes. We were successful in describing the kinetics of these systems on the basis of the theory of hot radicals.

Our results on the homopolymerization of monomers unambiguously indicate that the free radical copolymerization of ethyl acrylate

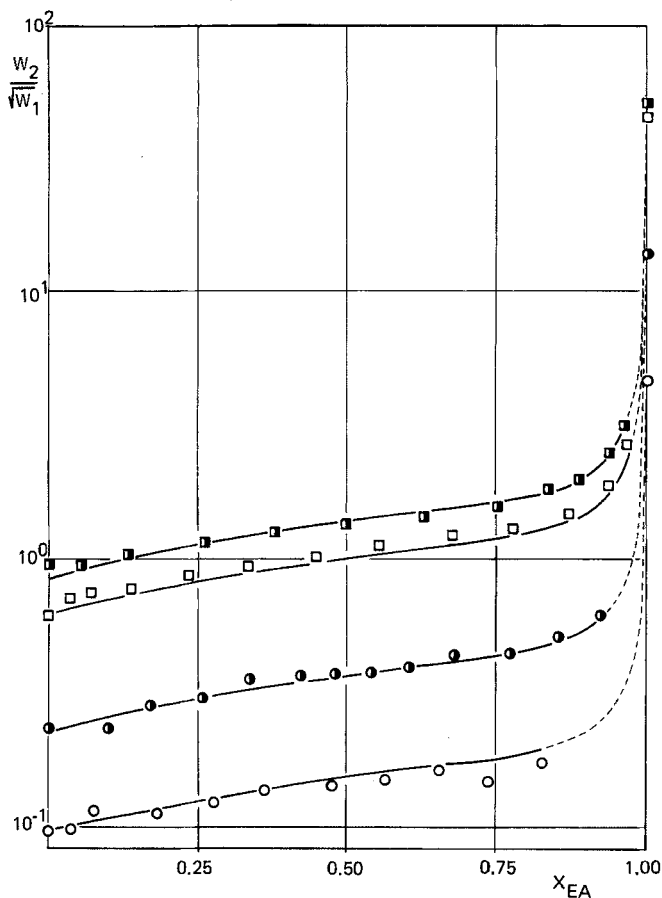


FIG. 1. $W_2/W_1^{1/2}$ as a function of the molar fraction of ethyl acrylate at constant overall monomer concentrations in EA/St/AIBN/Bz/50°C copolymerization. Solid line: Theoretical curve, $m_1 + m_2$: (○) 0.965 mol/dm³, (◐) 2.09 mol/dm³, (◑) 3.85 mol/dm³, (◒) 6.64 mol/dm³.

with styrene cannot be interpreted by either the diffusion theory or the theory of electron donor-acceptor complexes.

RESULTS

Our experimental process was described earlier [12]. The rate of copolymerization was determined by dilatometry. The dilatometric

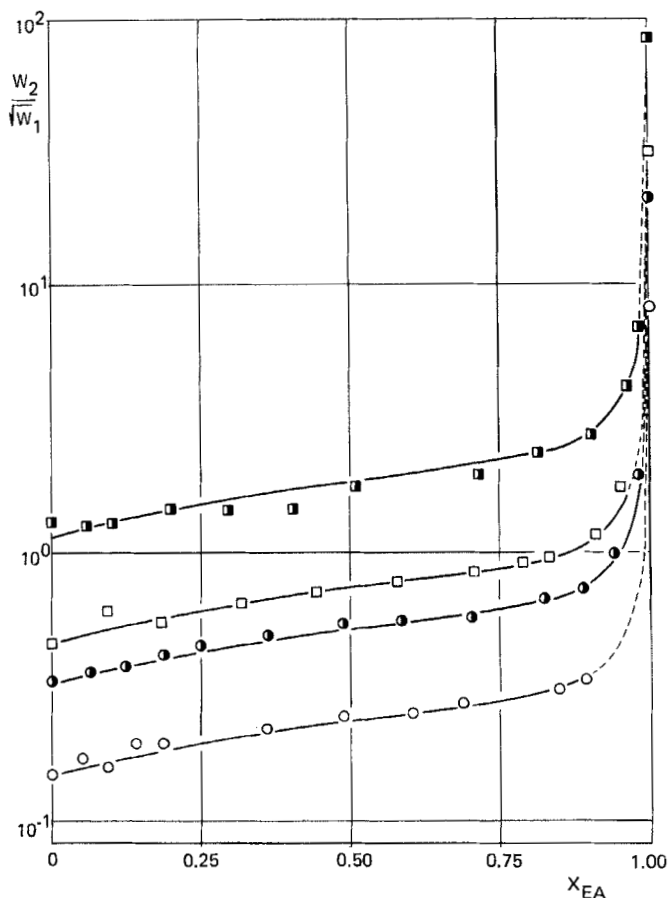


FIG. 2. $W_2/W_1^{1/2}$ as a function of the molar fraction of ethyl acrylate at constant overall monomer concentrations in EA/St/AIBN/Bz/50°C copolymerization. Solid line: Theoretical curve, $m_1 + m_2$: (○) 1.43 mol/dm³, (●) 2.83 mol/dm³, (□) 5.23 mol/dm³, (■) bulk.

constants were calculated according to Wittmer's method [13]. The molar ratio of monomers was gradually increased at constant overall monomer concentration within one series of experiments. The overall monomer concentration was varied between 0.965 and 8.86 or 8.45 mol/dm³. Copolymerization rates at different compositions are shown in Figs. 1 and 2. The values of W_2 normalized to uniform $W_1 = 1$ initiation rates are shown as a function of the molar fraction of

ethyl acrylate

$$(\chi_{EA} = \frac{m_{EA}}{m_{EA} + m_{St}})$$

at different overall monomer concentrations.

DISCUSSION

The numerical values of Φ as a function of monomer composition, calculated from experimental data on bulk copolymerization on the basis of Eq. (1), indicate that the classical rate equation does not correctly describe this copolymerization system (see Table 1). The same fact is reflected by Fig. 3, where the values of $W_2/W_1^{1/2}(m_1 + m_2)$ are shown as a function of overall monomer concentration at constant χ_{EA} . The trend is in inherent contradiction with Eq. (1), which can be rearranged to yield

$$\frac{W_2}{W_1^{1/2}(m_1 + m_2)} = \frac{\rho_1 \chi_1^2 + 2\chi_1(1 - \chi_1) + \rho_2(1 - \chi_1)^2}{(\rho_1^2 \delta_1^2 \chi_1^2 + 2\Phi \rho_1 \rho_2 \delta_1 \delta_2 \chi_1(1 - \chi_1) + \rho_2^2 \delta_2^2 (1 - \chi_1)^2)^{1/2}} \quad (2)$$

The right side of this equation contains only one independent variable χ_1 , and if χ_1 is constant, the expression calculable from experimental data on the left side of Eq. (2) should also be constant.

The deviation observed cannot be explained by the formation and reactions of electron donor-acceptor comonomer complexes.

In the presence of such complexes the greatest degree of deviation, both in the composition of copolymers and in the rate of copolymerization, occurs at the monomer composition corresponding to the composition of the comonomer complexes. Our experimental results clearly show that this kinetic model is not valid in EA/St copolymerization (see Ref. 12 and Figs. 1 and 2).

The penultimate effect on the reactivity of growing radicals in chain propagation should be detected in the composition of copolymers. Our experimental copolymer composition data, however, could be described by the classical composition equation [12], indicating, that

TABLE 1. Φ Values as a Function of Composition Calculated According to Eq. (1) in the Bulk Copolymerization System of EA/St/AIBN/50°C ($\delta_{EA} = 0.106$, $\delta_{St} = 6.92$, $\rho_{EA} = 0.152$, $\rho_{St} = 0.787$)

m_{EA} (mol/dm ³)	m_{St} (mol/dm ³)	Φ
8.69	0.166	25.6
8.52	0.325	38.7
7.99	0.832	44.6
7.16	1.63	69.1
6.26	2.48	99.9
4.44	4.22	153
3.50	5.12	196
2.53	6.03	182
1.76	6.77	191
0.856	7.64	333
0.479	7.99	417

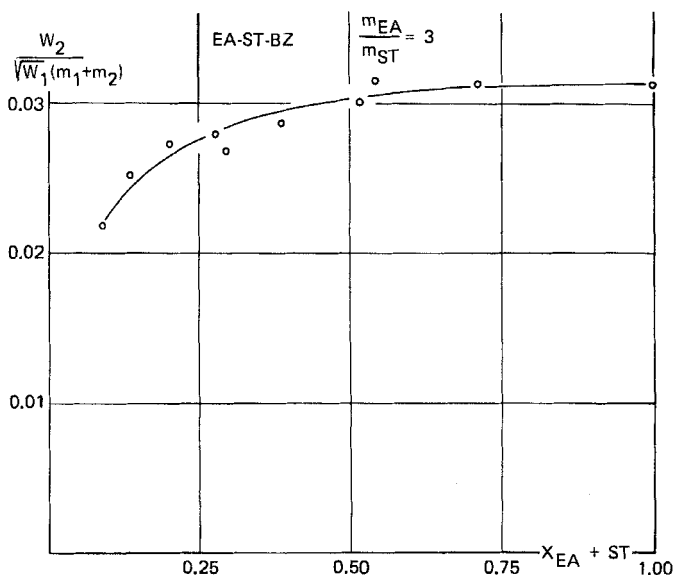


FIG. 3. $W_2/W_1^{1/2} (m_1 + m_2)$ as a function of the overall monomer concentration in EA/St/AIBN/Bz/50°C system at constant $m_{EA}/m_{St} = 3$.

the effect of the penultimate monomer unit on the reactivity ratios is negligible in this system; that is, $\rho_1 = \rho_1'$ and $\rho_2 = \rho_2'$.

The penultimate effect on the flexibility of chain end and on the reactivity of growing radicals in chain termination are considered by the following rate equation by Russo et al. [6, 7]:

$$W_2 = \frac{(m_1 + m_2)W_2^{1/2}}{x + 1} \left\{ \frac{\rho_1^2 x^3 + 3\rho_1 x^2 + \rho_1 \rho_2 x + \rho_2 + 2x}{\rho_1^2 x^2 \delta_1 + \rho_1 x \delta_{21} + \frac{\rho_2 x (\rho_1 x + 1)}{\rho_2 + x} \delta_{12} + \frac{\rho_2^2 (\rho_1 x + 1)}{\rho_2 + x} \delta_2} \right\} \quad (3)$$

where $x = m_1/m_2$.

Equation (3) can be rearranged to contain only the x variable independent of dilution in its right side:

$$\frac{W_2}{W^{1/2} (m_1 + m_2)} = \frac{\rho_1^2 x^3 + 3\rho_1 x^2 + 2x + \rho_1 \rho_2 x + \rho_2}{(x + 1) (\rho_1^2 x^2 \delta_1 + \rho_1 x \delta_{21} + \frac{\rho_2 x (\rho_1 x + 1)}{\rho_2 + x} \delta_{12} + \frac{\rho_2^2 (\rho_1 x + 1)}{\rho_2 + x} \delta_2)} \quad (4)$$

As a consequence, the expression on the left side of Eq. (4) should not depend on the overall monomer concentration provided the ratio of monomer concentrations is constant. According to Fig. 3, this condition is not met in our system. In other words, the rate of copolymerization is different from that given by Eq. (4). Considering the fact, however, that this model was reported to be valid in some systems, among others in ethyl acrylate/styrene/azo-bis-isobutyronitrile/benzene (EA/St/AIBN/Bz) copolymerization [13], we attempted to apply this kinetic form to our results.

The constant δ_{12} and δ_{21} can be determined from the linear form of Eq. (3) [6] as shown in Eq. (5). All our experimental data are presented according to Eq. (5) on Fig. 4. In the calculations the constants ρ_1 and ρ_2 , determined earlier [12], and the constants δ_1 and δ_2 , obtained in the bulk homopolymerization of both monomers [9, 10], were utilized. The constants δ_{12} and δ_{21} , determined by linear

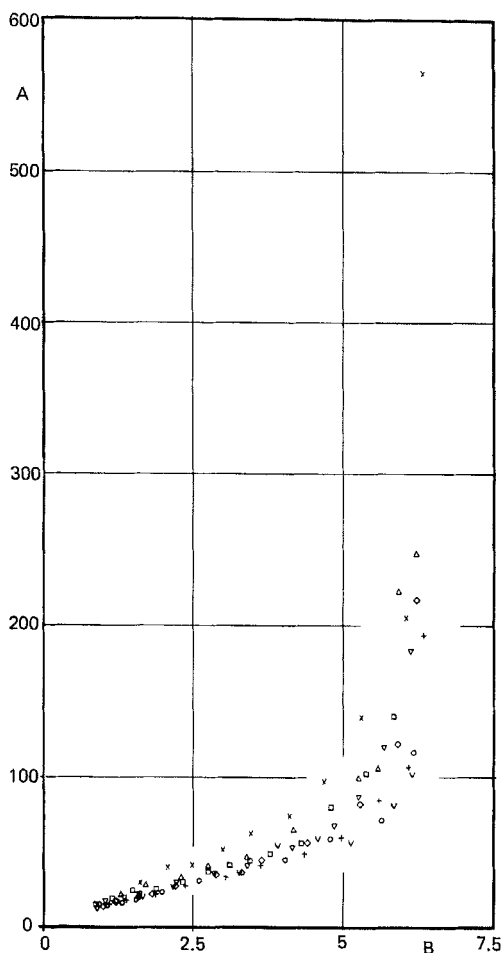


FIG. 4. Evaluation of EA/St/AIBN/Bz/50°C copolymerization system according to the penultimate theory,

$$A = \frac{W_1^{1/2} (m_1 + m_2)}{W_2(x + 1)} (\rho_1 x^2 + 3x + 2/\rho_1 + \rho_2 + \rho_2/\rho_1 x - \rho_1 x \delta_1 - \{ \rho_2^2 (\rho_1 x + 1)/\rho_1 x (\rho_2 + x) \} \delta_2)$$

$$B = \rho_2 (\rho_1 x + 1) / \rho_1 (\rho_2 + x)$$

$m_1 + m_2$: (x) 0.965 mol/dm³, (Δ) 1.43 mol/dm³, (□) 2.09 mol/dm³, (∇) 2.83 mol/dm³, (◇) 3.85 mol/dm³, (+) 5.23 mol/dm³, (○) 6.64 mol/dm³, (∨) bulk.

$$\delta_{21} = \frac{(m_1 + m_2)W_1^{1/2}}{(x + 1)W_2} (\rho_1 x^2 + 3x + 2/\rho_1 + \rho_2 + \rho_2/\rho_1 x) - \rho_1 x \delta_1 - \frac{\rho_2^2(\rho_1 x + 1)}{\rho_1 x(\rho_2 + x)} \delta_2 - \frac{\rho_2(\rho_1 x + 1)}{\rho_1(\rho_2 + x)} \delta_{12} \quad (5)$$

regression as the slope and intercept, are summarized in Table 2. The regression coefficient is also given at each overall monomer concentration. Both Fig. 4 and the data in Table 2 prove that the penultimate model is not valid in our copolymerization system. The experimental data according to Eq. (5) on Fig. 4 do not fall on a straight line, and the constants δ_{12} and δ_{21} systematically decrease as a function of the overall monomer concentration. The constant δ_{21} is even negative, which is impossible. Figure 4 also indicates that deviation from the straight line can be observed only in the region of molar fractions $\chi_{EA} < 0.2$, and it is especially significant at low overall monomer concentrations. As a consequence, if the investigation is not extended to these regions, no deviation from the straight line occurs and Eq. (3) seems to describe the rate of copolymerization.

TABLE 2. δ_{12} and δ_{21} Constants Calculated as a Function of Overall Monomer Concentration on the Basis of Eq. (5) Using the Constants $\delta_1 = 0.106$, $\delta_2 = 6.80$, $\rho_1 = 0.152$, $\rho_2 = 0.787$

$m_1 + m_2$ (mol/dm ³)	δ_{12}	δ_{21}	r
0.965	73.0	-155.8	0.748
1.43	37.0	-50.3	0.866
2.09	22.0	-20.3	0.928
2.83	23.7	-20.4	0.884
3.85	27.6	-31.0	0.862
5.23	22.3	-22.0	0.845
6.64	15.7	-6.99	0.939
Bulk	14.2	-3.05	0.964
3.0 ^a	31.5	-38.1	0.861
5.0 ^a	25.7	-28.2	0.878

^aData by Wittmer [13].

The kinetic interpretation of EA/St/AIBN/Bz copolymerization was successful on the basis of the theory of hot radicals. This is also in accord with our results on the homopolymerization of both monomers described in terms of this theory. Likewise, the copolymerization kinetics of acrylonitrile/methyl acrylate/dimethylformamide and diethyl maleate/styrene/benzene systems, where the homopolymerization of the monomers was evaluated on the basis of the theory of hot radicals [9, 15, 16], could be interpreted by this theory [8, 14].

According to the theory of hot radicals [8], eight elementary reactions constitute the chain propagation of copolymerization. Besides the four chain propagation reactions of the classical kinetic model, it also considers the four chain propagation reactions of the vibrationally excited, hot radicals. The rate equation of copolymerization is formally identical to the classical Eq. (1) [8]:

$$W_2 = \frac{W_1^{1/2} (\tilde{\rho}_1 m_1^2 + 2m_1 m_2 + \tilde{\rho}_2 m_2^2)}{(\tilde{\delta}_1^2 \tilde{\rho}_1^2 m_1^2 + 2\tilde{\phi} \tilde{\rho}_1 \tilde{\rho}_2 \tilde{\delta}_1 \tilde{\delta}_2 m_1 m_2 + \tilde{\rho}_2^2 \tilde{\delta}_2^2 m_2^2)^{1/2}} \quad (6)$$

In contrast to the classical rate equation, however, this equation contains four parameters ($\tilde{\delta}_1$, $\tilde{\delta}_2$, $\tilde{\rho}_1$, $\tilde{\rho}_2$) which are by definition dependent on concentration:

$$\begin{aligned} \tilde{\delta}_1 &= \delta_1 / (1 + D_1), & \tilde{\delta}_2 &= \delta_2 / (1 + D_2) \\ \tilde{\rho}_1 &= \rho_1 \frac{(1 + D_1)}{1 + \frac{\rho_1}{\rho_1^*} D_1}, & \tilde{\rho}_2 &= \rho_2 \frac{(1 + D_2)}{1 + \frac{\rho_2}{\rho_2^*} D_2} \end{aligned} \quad (7)$$

where D_1 and D_2 are the deactivation functions defined by the expressions:

$$\begin{aligned} D_1 &= \frac{m_1 + m_2 / \rho_1}{\gamma_{11} m_1 + \gamma_{12} m_2 + \gamma_{1S}} \\ D_2 &= \frac{m_1 / \rho_2 + m_2}{\gamma_{22} m_2 + \gamma_{21} m_1 + \gamma_{2S}} \end{aligned} \quad (8)$$

Accordingly, the copolymerization is characterized by the 13 parameters below:

Reactivity ratios:

$$\begin{aligned} \rho_1 &= k_{11}/k_{12}, & \rho_2 &= k_{22}/k_{21}, & \rho_1^* &= k_{11}^*/k_{12}^*, \\ & & & & \rho_2 &= k_{22}^*/k_{21}^* \end{aligned} \quad (9)$$

Deactivation parameters of hot radicals:

$$\begin{aligned} \gamma_{11} &= k_{7,11}/k_{11}^*, & \gamma_{12} &= k_{7,12}/k_{11}^*, & \gamma_1 &= k_{7,1}/k_{11}^* \\ \gamma_{22} &= k_{7,22}/k_{22}^*, & \gamma_{21} &= k_{7,21}/k_{22}^*, & \gamma_2 &= k_{7,2}/k_{22}^* \end{aligned} \quad (10)$$

Ratios of termination and propagation rate constants in the polymerization of the two monomers:

$$\delta_1 = k_{4,1}^{1/2}/k_{11}, \quad \delta_2 = k_{4,2}^{1/2}/k_{22} \quad (11)$$

And the Φ constant containing the rate constants of chain termination:

$$\Phi = k_{4,12}/k_{4,1}^{1/2} \cdot k_{4,2}^{1/2} \quad (12)$$

A rearrangement of Eq. (6) into a form identical to Eq. (2) would yield an equation containing the $\tilde{\delta}_1$, $\tilde{\delta}_2$, $\tilde{\rho}_1$, $\tilde{\rho}_2$ dilution-dependent parameters in its right side. As a consequence, our experimental data presented in Fig. 3 are not in contradiction with the hot radical theory, whereas they do not fit the classical or the penultimate copolymerization model.

A closer examination of Expressions (7) shows that in certain conditions the classical composition equation may apply for a system [12] where in the chain propagation the reactions of hot radicals have to be considered. It follows from the Expressions (7) defining the effective reactivity ratios $\tilde{\rho}_1$ and $\tilde{\rho}_2$ that they are independent of dilution provided that $\rho_1 = \rho_1^*$ and $\rho_2 = \rho_2^*$.

The 13 copolymerization parameters of the EA/St/AIBN/Bz system were calculated by a nonlinear least-squares method from all experimental data available on this system: rate of initiation and copolymerization, composition of copolymers, and rate of homopolymerization of both monomers. Including the kinetic data reported earlier by Wittmer [13], the data of 112 copolymerization mixtures of different composition were analyzed. The parameters obtained are summarized in Table 3 along with the parameters (where available) determined earlier by different methods (by investigation of homopolymerization kinetics and copolymer composition). A satisfactory agreement between parameters by two different methods is established. According

TABLE 3. Copolymerization Determined in the EA/St/AIBN/Bz/50°C Copolymerization System on the Basis of Eq. (6)

	Calculated	Obtained by different method	
ρ_1	0.194	0.152	[12]
ρ_1^*	0.187		
δ_1	1.09	0.926	[10]
γ_{11}	0.107	0.129	[10]
γ_{12}	8.81		
γ_1	0.0126	0.0162	[10]
ρ_2	0.828	0.787	[12]
ρ_2^*	0.796		
δ_2	11.8	11.6	[9]
γ_{21}	1.40		
γ_{22}	1.77	1.48	[9]
γ_2	0.435	0.521	[9]
Φ	11.5		

to our computation, $\rho_1 = \rho_1^*$ and $\rho_2 = \rho_2^*$, and consequently the reactivity ratios are independent of the overall monomer concentration, in agreement with our earlier results [12]. On the other hand, a reasonable value of 11.5 was obtained for the constant Φ independent of dilution.

On the basis of the 13 copolymerization parameters, the theoretical $W_2/W_1^{1/2}$ functions were calculated and are shown as solid lines in Figs. 1 and 2. The deviation of experimental points from the theoretical curve is within $\pm 10\%$.

In conclusion, the kinetics of EA/St/AIBN/Bz copolymerization, like the homopolymerization kinetics of EA/AIBN/Bz and St/AIBN/Bz systems, are consistently described by the theory of hot radicals.

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