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Kinetics of Radical Copolymerization. XII. Investigation of the Rate of Polymerization of the System Styrene-Butyl Acrylate-Benzene

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Kinetics of Radical Copolymerization. XII. Investigation of the Rate of Polymerization of the System Styrene-Butyl Acrylate-Benzene

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ABSTRACT

The classical copolymerization rate equation does not describe the copolymerization rate in the styrene-butyl-acrylate-azoisobutyronitrile-benzene-50°C system appropriately. The cross-termination coefficient (Φ), calculated according to the classical rate equation, shows a strong monomer and solvent concentration dependence. The experimental results cannot be interpreted by the diffusion theory, penultimate effect, or the theory of charge transfer complexes. However, Φ was found to be constant over the whole concentration range by the hot radical theory. Our kinetic data were consistently described by this theory, and its 13 parameters, characteristic of the copolymerization, were determined.

In 1953 Bradbury and Melville found that the cross-termination factor (Φ) in the classical rate equation of copolymerization shows a nearly 100-fold increase with the composition of the monomer mix-

ture in the system styrene-butyl acrylate-benzene (St-BA-Bz) [1]. In the calculation of Φ , the authors attempted to consider the dependence of δ values characteristic to the homopolymerizations of St and BuA in solution ($\delta = \sqrt{k_4/k_2}$, where k_4 and k_2 are the rate constants of chain termination and chain propagation, respectively), as well as the solvent dependence of the rate of initiation.

The dependence of the cross-termination factor on the composition of the monomer mixture was also observed in other copolymerization systems [2-5]. Such an intensive solvent dependence of Φ , however, cannot be interpreted by the classical theory of copolymerization. Neither does the classical theory of radical copolymerization explain the dependence of Φ values on dilution.

Different theories attempt to explain the anomalies observed in the homo- and copolymerizations of different monomers. In our earlier studies of homopolymerizations of St and BA in solution, it was pointed out [10, 11] that among the different theories, neither the classical kinetic treatment [6], nor the diffusion theory of North [7], nor the theory of electron donor acceptor complexes [8] is applicable for these systems. However, their kinetic behavior could be adequately described by the hot radical theory [9].

Explanations of the dependence of Φ on the composition of the monomer mixture, which has been observed in different copolymerization systems, is tried in the above theories and, recently, by the penultimate effect applied to the chain termination step. These attempts, however, disregard the fact that this effect should also manifest itself in the copolymer composition.

For the investigation of the applicability of the above listed theories in the St-BA system and for its complex kinetic evaluation, the few data published by Bradbury and Melville are insufficient. Therefore, we felt it necessary to determine the dependence of the rate of initiation, copolymer composition, and rate of polymerization on monomer composition and solvent concentration in the whole composition range.

The rate measurement data of homopolymerizations of St and BA in solution [10, 11], as well as our results obtained for the rate of initiation of copolymerization and for the copolymer composition [12], were described earlier. In the present paper the dependence of the copolymerization rate in the system St-BA-Bz on the monomer concentration and composition are investigated, and applicabilities of different theories on the interpretation of the relationships obtained are studied.

EXPERIMENTAL

Purification of BA, St, Bz, and AIBN was carried out as described earlier [10-12].

The rate of copolymerization was measured dilatometrically. The dilatometric constant was determined gravimetrically. According to

the gravimetric measurements, the dilatometric constant changes linearly with the copolymer composition, between those of St ($D_1^{50^\circ\text{C}} = 6.115$ [13]) and of BA ($D_2^{50^\circ\text{C}} = 6.376$ [44]). The measurements were carried out at 50°C . The experiments were planned so that only the ratio of monomer concentrations would change within a series of experiments, the overall monomer concentration being kept constant.

EXPERIMENTAL RESULTS AND THEIR EVALUATION

Our measurement data concerning the rate of copolymerization are collected in Table 1. Since the dependence of the initiation rate constant of the copolymerization system on the composition of a reaction mixture was determined earlier, the rate measurement data "normed" by the rate of initiation (W_1) are listed in Table 1. In addition to $W_2/W_1^{0.5}$ data, the initial concentrations of St (m_1), of BA (m_2), and of Bz (s) are also given. In Fig. 1 the $W_2/W_1^{0.5}$ values are plotted against the partial molar fraction of St ($\chi_1 = m_1/(m_1 + m_2)$) and against the overall monomer concentration ($m_1 + m_2$). Figure 1 shows that the rate of copolymerization changes considerably with the initial overall concentration and the composition of the monomers. The change is especially strong in the region of low St content.

The classical rate equation contains five parameters: the copolymerization constants (ρ_1 and ρ_2), the δ_1 and δ_2 values which can be determined by the homopolymerization of the monomers, and the Φ factor characterizing cross termination:

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

With knowledge of δ_1 , δ_2 , ρ_1 , and ρ_2 , Φ can be calculated. For the determination of Φ , the δ_1 and δ_2 values are generally calculated from homopolymerization (usually bulk polymerization) data and the ρ_1 and ρ_2 values as determined from the copolymer composition are used. According to classical theory, these are constants and should yield constant Φ values for rates belonging to different compositions. The reactivity ratios of the St-BA system were earlier determined by investigation of the copolymer composition, and ρ_1 and ρ_2 were found to

TABLE 1. Kinetic Data of the Copolymerization System St-BA-AIBN-Bz-50°C

m_1^0 , mol/dm ³	m_2^0 , mol/dm ³	s , mol/dm ³	$W_2/W_1^{0.5}$, mol ^{1/2} /dm ^{3/2} ·min ^{1/2}
8.129	0.261	0	1.192
7.496	0.768	0	1.329
6.500	1.568	0	1.406
5.531	2.340	0	1.487
3.433	4.036	0	1.574
2.204	5.018	0	1.752
1.650	5.668	0	1.896
0.660	6.259	0	2.364
0.309	6.542	0	3.502
0.135	6.681	0	6.402
5.531	0.134	3.744	0.8057
5.059	0.271	3.922	0.8232
4.877	0.535	3.735	0.8721
4.360	1.084	3.524	0.9509
3.789	1.621	3.399	0.9415
3.325	2.173	3.110	1.087
2.456	2.99	2.920	1.221
1.665	3.842	2.575	1.302
1.073	4.278	2.639	1.4030
0.490	4.854	2.449	1.818
0.316	5.170	2.185	2.059
0.101	5.462	2.307	3.580
3.702	0.114	6.106	0.6311
3.602	0.229	6.061	0.5581
3.318	0.343	6.308	0.5553

(continued)

TABLE 1 (continued)

m_1^0 , mol/dm ³	m_2^0 , mol/dm ³	s , mol/dm ³	$W_2/W_1^{0.5}$, mol ^{1/2} /dm ^{3/2} ·min ^{1/2}
3.012	0.760	5.979	0.5927
2.673	1.116	5.860	0.6548
2.250	1.546	5.694	0.7313
1.704	2.063	5.609	0.7838
1.075	2.694	5.311	0.8443
0.769	3.036	5.217	0.9247
0.380	3.492	4.917	1.2150
0.231	3.551	5.030	1.479
0.082	3.733	4.990	2.913
2.880	0.087	7.018	0.3799
2.764	0.181	7.017	0.3830
2.664	0.288	6.973	0.4132
2.399	0.589	6.829	0.4648
2.012	0.951	6.750	0.4829
1.865	1.314	6.359	0.5206
1.368	1.587	6.561	0.5356
0.898	2.103	6.340	0.6399
0.569	2.403	6.283	0.6930
0.198	2.784	6.151	1.055
0.115	2.858	6.140	1.341
2.329	0.108	7.689	0.2982
2.123	0.245	7.738	0.3124
1.975	0.500	7.518	0.3639
1.646	0.775	7.503	0.3867
1.448	0.956	7.470	0.4009
1.217	1.236	7.315	0.4365
1.110	1.296	7.359	0.4421

(continued)

TABLE 1 (continued)

m_1^0 , mol/dm ³	m_2^0 , mol/dm ³	s , mol/dm ³	$W_2/W_1^{0.5}$, mol ^{1/2} /dm ^{3/2} ·min ^{1/2}
0.954	1.418	7.367	0.4458
0.728	1.657	7.272	0.4950
0.501	1.964	7.071	0.5666
0.253	2.117	7.147	0.6520
0.122	2.277	7.057	0.8390
1.848	0.053	8.387	0.2231
1.683	0.113	8.513	0.2103
1.600	0.193	8.496	0.2502
1.387	0.380	8.490	0.2384
1.198	0.593	8.369	0.3125
0.771	1.053	8.179	0.3262
0.577	1.353	8.028	0.3885
0.361	1.533	7.942	0.4312
0.172	1.726	7.889	0.5220
0.033	1.880	7.801	1.2750
0.934	0.059	9.550	0.1055
0.866	0.099	9.586	0.1116
0.766	0.190	9.568	0.1205
0.665	0.285	9.547	0.1198
0.387	0.581	9.492	0.1301
0.486	0.484	9.458	0.1413
0.435	0.526	9.458	0.1488
0.384	0.580	9.437	0.1539
0.287	0.674	9.410	0.1633
0.201	0.760	9.383	0.1832
0.106	0.870	9.437	0.1951
0.057	0.919	9.315	0.2650

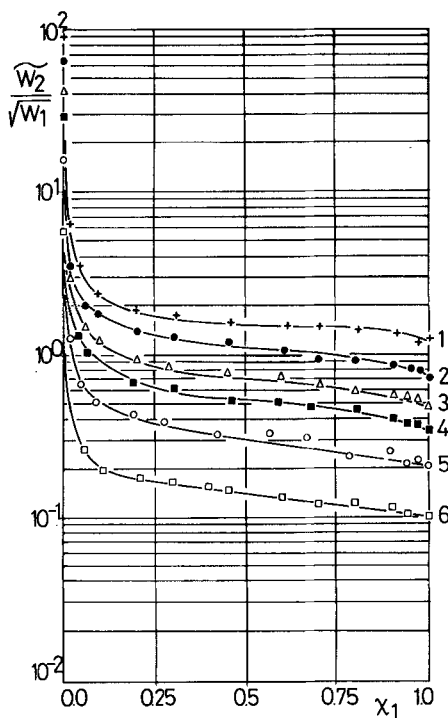


FIG. 1. The $W_2/\sqrt{W_1}$ value plotted against the partial mole fraction of styrene, with constant total monomer concentrations. System: St-BA-AIBN-Bz-50°C. Full line: theoretical curve $m_1 + m_2 = (+)$ bulk, (\bullet) 5.40 mol/dm³, (Δ) 3.70 mol/dm³, (\blacksquare) 2.90 mol/dm³, (\circ) 1.80 mol/dm³, (\square) 0.90 mol/dm³.

be constant values, independent of dilution [12]. The constancy of δ_1 and δ_2 as assumed by classical theory is, however, fulfilled neither in the homopolymerization of St nor in that of BA (both in solution) [1, 10, 11, 33]. Thus, if Φ is calculated using the δ values relating to bulk polymerization, i.e., if their dependence on dilution is neglected, a Φ value strongly dependent on the concentration and composition is obtained (see Fig. 2). Figure 2 shows that the dependence of the cross-termination factor on the medium increases with a decrease of the overall monomer concentration. The change of Φ in bulk copolymerization is small compared to that at the highest dilution.

The Φ values were also calculated by taking into account the dilution dependence of δ_1 and δ_2 values determined in homopolymerization

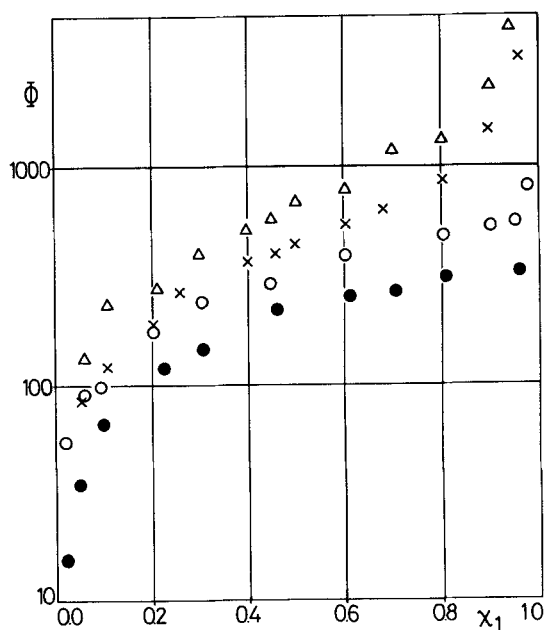


FIG. 2. The Φ values, calculated from the classical rate equation, plotted against the partial mole fraction of styrene (χ_1), with constant total monomer concentrations. $m_1 + m_2 = (\bullet)$ bulk, (\circ) 5.40 mol/dm³, (\times) 1.80 mol/dm³, (Δ) 0.90 mol/dm³.

by assuming identical dilution dependence of the δ values in homopolymerization and in copolymerization. The data thus obtained are shown in Fig. 3. According to this figure, the Φ values relating to bulk copolymerization and belonging to different overall monomer concentrations change in the same way with the monomer composition. With an increase of the partial molar fraction of St, the cross-termination factor shows a 15-fold increase both in bulk and in various dilutions. This change is the same as that determined by Bradbury and Melville in bulk copolymerization [11].

In the majority of publications dealing with the investigation of the solvent dependence of Φ , the dependence of δ values on dilution are treated as though they are independent of the course of copolymerization [1, 15-18]. In fact, the value of δ depends not only on the concentration of solvent but also on the conditions of copolymerization [34]. Only the hot radical theory takes into account the possibility of such a complex dependence of δ on the medium [24]; the other theories neglect this possibility.

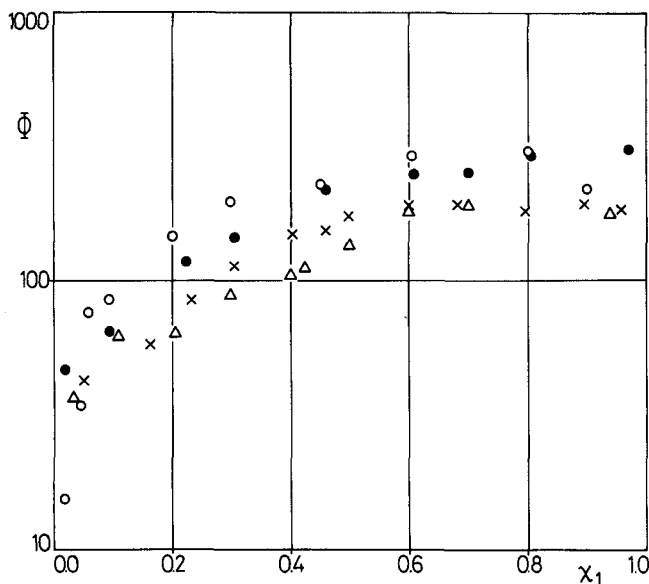


FIG. 3. The Φ values, calculated with consideration of the dilution dependences of δ_1 and δ_2 values determined in homopolymerization, plotted against χ_1 , with constant total monomer concentrations. $m_1 + m_2 = (\bullet)$ bulk, (\circ) 5.40 mol/dm³, (\times) 1.80 mol/dm³, (Δ) 0.90 mol/dm³.

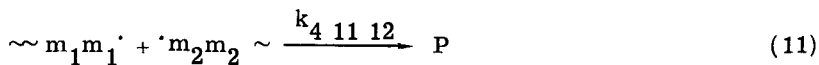
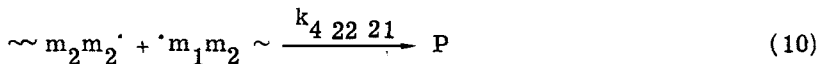
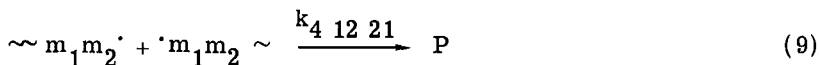
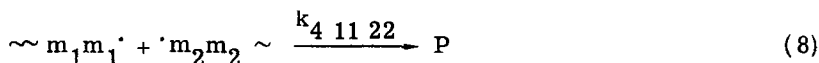
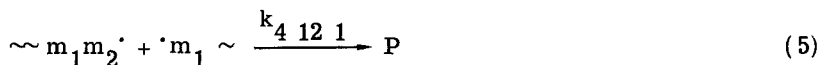
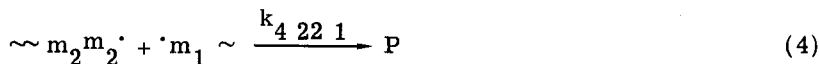
The dependence of the cross-termination factor is explained primarily by the restricted mobility of the polymer chain. The restricted mobility of the copolymer chain is generally accounted for by the penultimate effect assumed for the chain termination step [16-18]. For example, the equation derived by Arlman [16] for the dependence of Φ on the medium is

$$\Phi = \frac{m_1 \frac{k_{412} k_{11}}{k_{422} k_{11}} + \rho_2 m_2}{m_1 + \rho_2 m_2} \frac{k_{422} k_{11}}{\sqrt{k_{411} \cdot k_{422}}} \quad (2)$$

and the equation of Ito [17] is

$$\Phi = \frac{k_{4\ 11\ 22}}{\bar{k}_{4\ 12}} + \frac{k_{4\ 12\ 21}}{\bar{k}_{4\ 12}} \frac{1}{\rho_1 \rho_2} + \frac{k_{4\ 22\ 21}}{\bar{k}_{4\ 12}} \frac{1}{\rho_1} \frac{m_2}{m_1} + \frac{k_{4\ 11\ 12}}{\bar{k}_{4\ 12}} \frac{1}{\rho_2} \frac{m_1}{m_2} \quad (3)$$

where $\bar{k}_{4\ 12} = \sqrt{k_{4\ 11} \cdot k_{4\ 22}}$ and the chain termination rate constants in the equations belong to the following reactions:



Equation (2) can, by minor transformation, be brought into the following form

$$\Phi \left[1 + \rho_2 \frac{m_2}{m_1} \right] = \frac{k_{4\ 12\ 1}}{\sqrt{k_{4\ 11} \cdot k_{4\ 22}}} + \rho_2 \frac{m_2}{m_1} \frac{k_{4\ 22\ 1}}{\sqrt{k_{4\ 11} \cdot k_{4\ 22}}} \quad (12)$$

By plotting the quantity on the left-hand side of the equation against the molar ratios of the monomers, the measurement data should fall

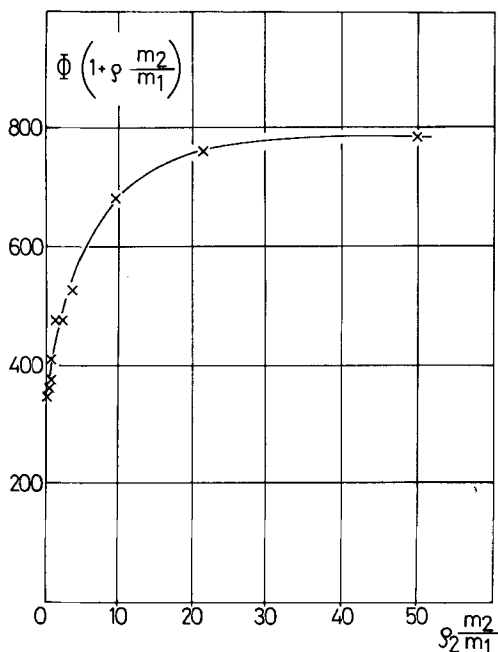


FIG. 4. Evaluation of the copolymerization system St-BA-AIBN-Bz-50°C according to Arlman (see Eq. 12).

on a straight line, provided Eq. (2) is valid. Our data show, however, absolutely no linearity when these data are plotted (see Fig. 4).

The three parameter relationship (Eq. 3) of Ito cannot be applied to the system under study because the Φ values belonging to high or to low m_1/m_2 values should fall on straight lines when plotted against m_1/m_2 or m_2/m_1 , respectively, and both lines should have the same intercept (see Fig. 5). Neither Arlman's nor Ito's equation is suitable for describing the dependence of calculated Φ values on composition.

The equation derived by Russo and Munari [18], which considers the effect of the penultimate member on the termination step, is also formally different from the classical rate equation:

$$W_2 = \frac{(m_1 + m_2)W_1^{1/2}}{X_1 + 1} \frac{\rho_1^2 X_1^3 + 3\rho_1 X_1^2 + 2X_1 + \rho_1 \rho_2 X_1 + \rho_2}{\rho_1^2 X_1^2 \delta_{11} + \rho_1 X_1 \delta_{21} + \frac{\rho_2 X_1 (\rho_1 X_1 + 1)}{\rho_2 + X_1} \delta_{12} + \frac{\rho_2^2 (\rho_1 X_1 + 1)}{\rho_2 + X_1} + \delta_2} \quad (13)$$

where $x_1 = m_1/m_2$.

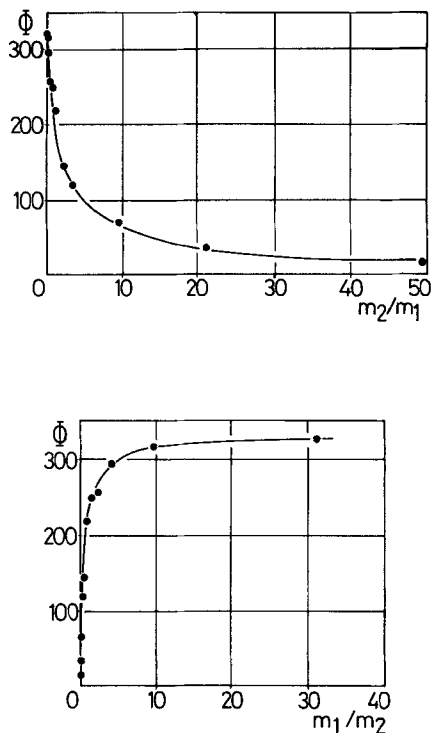


FIG. 5. Evaluation of the copolymerization system St-BA-AIBN-Bz-50°C according to Ito's three parameter relationship.

With minor alterations, Eq. (13) can be brought to the following form:

$$\frac{W_2}{W_1^{1/2}(m_1 + m_2)} = - \frac{\rho_1^2 X_1^3 + 3\rho_1 X_1^2 + \rho_1 \rho_2 X_1 + \rho_2}{\left[(X_1 + 1) (\rho_1^2 X_1^2 \delta_1 + \rho_1 X_1 \delta_{21}) + \frac{\rho_2 X_1 (\rho_1 X_1 + 1)}{\rho_2 + X_1} \delta_{12} + \frac{\rho_2^2 (\rho_1 X_1 + 1)}{\rho_2 + 1} \delta_2 \right]} \quad (14)$$

In the right-hand side of the equation, only the X_1 variable independent of the dilution is included. Consequently, with constant X_1 values, the quantity in the left-hand side of the equation should be constant and independent of the overall monomer concentration. This is, however, not true for the system under study (see Fig. 6). This figure

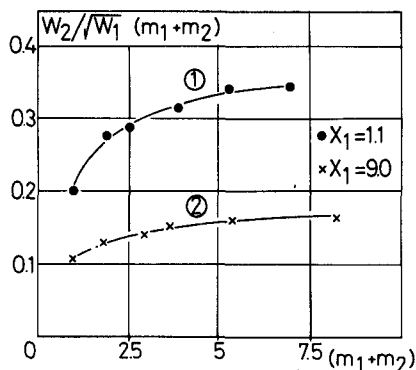


FIG. 6. $W_2/\sqrt{W_1} (m_1 + m_2)$ plotted against the overall monomer concentration. System: St-BA-AIBN-Bz-50°C.

shows the rate data measured with $X_1 = 9$, and 1.1 monomer compositions, and different overall monomer concentrations against the $m_1 + m_2$ value. The figures show that the $W_2/W_1^{0.5} (m_1 + m_2)$ value decreases with increasing dilution, and this change is different for the two monomer compositions. This presentation demonstrates the deficiencies of both the classical rate equation and the rate equations investigated so far, since according to all these equations, the value of $W_2/W_1^{0.5} (m_1 + m_2)$ should be independent of the dilution. In investigations of the applicability of rate Eq. (13) for the system EA-St-Bz, it was pointed out that the values of δ_{12} and δ_{21} calculated using the experimental data of the system change systematically with the monomer concentration [20]. Since nowadays the equation of Russo and Munari is used for the kinetical evaluation of the system St-BA, our experimental data were also plotted by the linearized form of Eq. (13) [19], which serves for the calculation of δ_{12} and δ_{21} (see Fig. 7):

$$\underline{A} = \delta_{21} + \underline{B}\delta_{12} \quad (15)$$

and

$$\underline{A} = \frac{(m_1 + m_2)W_1^{1/2}}{(X_1 + 1)W_2} \left\{ \rho_1 X_1^2 + 3X_1 + \frac{2}{\rho_1} + \rho_2 + \frac{\rho_2}{\rho_1} X_1 \right\} - \rho_1 X_1 \delta_1 - \frac{\rho_2^2 (\rho_1 X_1 + 1)}{\rho_1 X_1 (\rho_2 + X_1)} \delta_2 \quad (16)$$

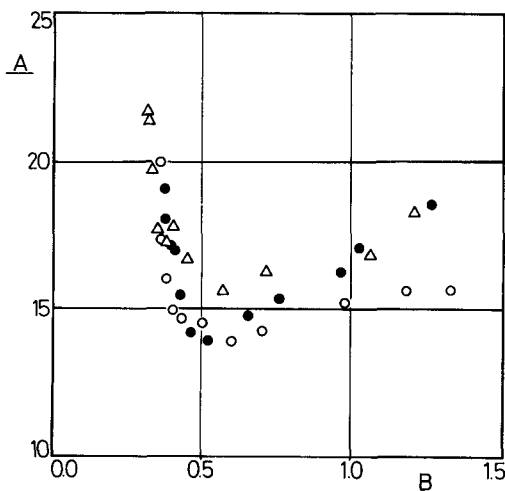


FIG. 7. Evaluation of the copolymerization system St-BA-AIBN-Bz-50°C according to the equation of Russo and Munari (Eqs. 15-17).

$$\bar{B} = \frac{\rho_2 (\rho_1 X_1 + 1)}{\rho_1 (\rho_2 + X_1)} \quad (17)$$

In addition to the bulk copolymerization data, the experimental data belonging to two different dilutions are also indicated in Fig. 7, where they are plotted according to Eq. (15). For the calculations of \bar{A} and \bar{B} values, ρ_1 and ρ_2 as determined earlier investigations were used [12], and the dilution dependence of δ_1 and δ_2 was taken into account. The experimental data indicated in Fig. 7 do not show any linearity, with the δ_1 and δ_2 values changing from point to point. Consequently, the equation of Russo and Munari cannot be applied to the St-BA-Bz system either.

The theories outlined so far have attempted to explain the diffusion-controlled behavior of the chain termination by considering the effect of the penultimate member. In contrast to them, Atherton and North [21] assumed that the rate of chain termination depends on the composition of the polymer chain. The rate equation derived by the authors does not include the cross-termination factor:

$$W_2/\sqrt{W_1} = \frac{\rho_1 m_1^2 + 2m_1 m_2 + \rho_2 m_2^2}{k_4^{1/2}(12) \left[\rho_1 \frac{m_1}{k_{11}} + \rho_2 \frac{m_2}{k_{22}} \right]} \quad (18)$$

The value of $k_{4(12)}$ in this equation depends on the homopolymerization chain termination rate constants ($k_{4,11}$, $k_{4,22}$), on the rate constant characterizing cross termination ($k_{4,12}$), and on the radical concentrations (r_1 and r_2) according to the following equations:

$$k_{4(12)} = k_{4,11} X_{r_1}^2 + k_{4,12} X_{r_1} (1 - X_{r_1}) + k_{4,22} (1 - X_{r_1})^2 \quad (19)$$

where

$$X_{r_1} = \frac{r_1}{r_1 + r_2} \quad (20)$$

According to the authors, the change of $k_{4,12}$ can be described in ideal case by the homopolymerization chain termination rate constants ($k_{4,11}$ and $k_{4,22}$) and by the composition of the copolymer formed:

$$k_{4(12)} = k_{4,11} X_{p_1} + k_{4,22} X_{p_2} \quad (21)$$

where X_{p_1} and X_{p_2} are the molar fractions of monomers 1 and 2 incorporated in the polymer chain.

The value of $k_{4(12)}$ was later defined differently by other authors. For example, O'Driscoll [22] proposed the following relationship:

$$k_{4(12)} = f_1 (k_{4,11} f_{11} + k_{4,21} f_{21}) + f_2 k_{4,22} \quad (22)$$

where f_{11} and f_{12} are the molar fractions of 11- and 12-type terminal diads, respectively; and f_1 and f_2 are the molar fractions of chains

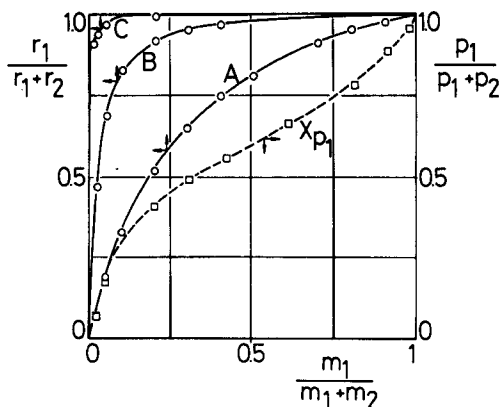


FIG. 8. The copolymer composition (X_{p_1}) and the mole fractions of radical concentrations plotted against the initial monomer composition. The supposed k_{22}/k_{11} values are: (A) $k_{22}/k_{11} = 1$, (B) $k_{22}/k_{11} = 10$, (C) $k_{22}/k_{11} = 1000$.

ending with monomer units 1 and 2, respectively. Chiang and Rudin [23] gave another relationship for $k_{4(12)}$:

$$k_{4,12} = k_{4,11}X_{p_1}^2 + k_{4,12}X_{p_1}(1 - x_{p_1}) + k_{4,22}(1 - X_{p_1})^2 \quad (23)$$

Comparison of Eq. (19) with Eqs. (21), (22), and (23) shows that various authors have tried to describe the ratio of radical concentrations by the polymer composition. In Eq. (23), $X_{r_1} = X_{p_1}$ is assumed. These assumptions are, however, valid for ideal copolymerization systems only, where $\rho_1 = \rho_2 = 1$.

In the other systems the molar ratios of radical concentrations are different from those of copolymer compositions. This is illustrated by Fig. 8 where the copolymer composition and the molar fractions of radical concentrations are plotted against the initial monomer composition, using the data of the St-BA system. For the calculation of the molar fraction of radical concentrations, the following equation, derived from the theory of short sequences, was used:

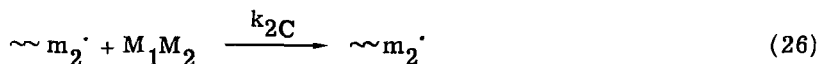
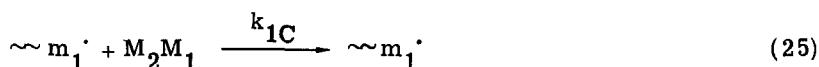
$$\frac{r_1}{r_2} = \frac{k_{22}\rho_1 m_1}{k_{11}\rho_2 m_2} \quad (24)$$

The ρ_1 and ρ_2 values relating to the system St-BA were determined earlier [12]. Curves A, B, and C in Fig. 8 are related to the cases $k_{22}/k_{11} = 1, 10, \text{ and } 1000$, respectively.

The different paths of curves A, B and C and of the curves describing the copolymer composition prove clearly that Eqs. (21), (22), and (23) are not applicable to the copolymerization system studied.

In contrast to the diffusion theory, the theories subsequently investigated do not attribute the observed anomalies to the chain termination step, but they try to describe the dependence of δ and Φ on the medium by a mechanism more complex than that assumed by classical theory.

According to the theory of electron donor-acceptor complexes [25-27], the chain propagation step can take place not only with the monomer but also with monomer molecule associates formed via secondary value forces. Thus, in addition to the four chain propagation steps assumed in copolymerization, the following chain propagation reactions should also be considered:



Consequently, the copolymer composition is determined by the relative rates of six chain propagation reactions; i.e., a relation more complicated than presented in the classical composition equation. Our earlier investigations showed that the copolymer composition in the system St-BA-Bz can be described by the classical composition equation [12]; i.e., the comonomer complexes have no demonstrable effect on the composition. Also, the comonomer complexes should have an effect on the rate of polymerization; at a certain monomer composition the rate of polymerization should have a maximum [28]. The dependence of $W_2/W_1^{0.5}$ on the monomer composition (Fig. 1) does not verify this assumption either, so it is established that the theory of electron donor-acceptor complexes cannot be applied to the system studied. It was pointed out earlier that this theory is not suitable for describing the kinetic anomalies observed in the homopolymerizations of St and of BA [10, 11].

The formation of donor-acceptor complexes can, in some cases, have a considerable effect on the rates of elementary radical reactions. Some interesting examples were found in our investigations among the inhibition reactions of radical polymerization. With chloroquinones a considerable chain regeneration was found, and its extent increased with the number of chlorine atoms. The extent of complex formation

between St and various chlorine-substituted p-benzoquinones increases in the same direction [36]. The kinetic effect observed could be theoretically interpreted as the effect of complex formation on the transmission coefficient of the reaction [37]. However, a very serious theoretical objection can be raised against the reaction of EDA complexes according to Eqs. (25) and (26); such an elementary reaction cannot occur consistent with the theory of microscopic reversibility, which means that such an elementary reaction cannot exist.

In terms of the hot radical theory, we succeeded earlier in explaining the rules of homopolymerizations of some monomers [10, 11, 29] and in describing the kinetic behavior of the systems AN-MA-DMF, EA-St-Bz, and ethyl maleate-St-Bz [20, 24, 30]. According to this theory, from among the five parameters in the classical rate equation, four can be concentration dependent and only the cross-termination factor can be regarded as really constant. The concentration dependence of the values of ρ_1 , ρ_2 , δ_1 , and δ_2 are given by the following equations:

$$\begin{aligned} \tilde{\rho}_1 &= \rho_1 \frac{1 + D_1}{1 + \rho_1/\rho_1^* D_1}, & \tilde{\rho}_2 &= \rho_2 \frac{1 + D_2}{1 + \rho_2/\rho_2^* D_2} \\ \tilde{\delta}_1 &= \frac{\delta_1}{1 + D_1}, & \tilde{\delta}_2 &= \frac{\delta_2}{1 + D_2} \end{aligned} \quad (27)$$

where ρ_1^* and ρ_2^* are the reactivity ratios of the hot radicals and ρ_1 and ρ_2 are those of the cool radicals, δ_1 and δ_2 are the $\sqrt{k_4/k_2}$ values relating to infinite dilution, and D_1 and D_2 are the deactivation functions defined by the hot radical reaction scheme of copolymerization:

$$\begin{aligned} D_1 &= \frac{m_1 + m_2/\rho_1}{\gamma_{11}m_1 + \gamma_{12}m_2 + \gamma_1 s} \\ D_2 &= \frac{m_1/\rho_2 + m_2}{\gamma_{22}m_2 + \gamma_{21}m_1 + \gamma_2 s} \end{aligned} \quad (28)$$

where s stands for the solvent concentration.

The values γ_{11} , γ_{12} , γ_1 , γ_{21} , γ_{22} , and γ_2 in Eq. (28) are the deactivation parameters of the hot radicals:

$$\gamma_{11} = k_{7,11}/k_{11}^*, \quad \gamma_{12} = k_{7,12}/k_{11}^*, \quad \gamma_1 = k_{7,1}/k_{11}^* \quad (29)$$

$$\gamma_{22} = k_{7,22}/k_{22}^*, \quad \gamma_{21} = k_{7,21}/k_{22}^*, \quad \gamma_2 = k_{7,2}/k_{22}^* \quad (30)$$

(The superscript asterisks denote the rate constants of the hot radicals.)

The concentration dependence of the Φ value found in different copolymerization systems can be explained in terms of the hot radical theory by the variation of $\tilde{\rho}_1$, $\tilde{\rho}_2$, $\tilde{\delta}_1$, and $\tilde{\delta}_2$ parameters with the composition and dilution in each experiment. If these variations are neglected, their effect will cumulate in the Φ value.

According to this theory, the concentration dependence of the effective values $\tilde{\delta}_1$ and $\tilde{\delta}_2$ is different in homo- and copolymerization since, in the latter case, the deactivation of the hot radical can also proceed with the comonomer (deactivation "cross" effect). Thus, the $\tilde{\delta}_1$ and $\tilde{\delta}_2$ values measured in the homopolymerization of monomer and belonging to different dilutions should not be substituted in the rate equation of copolymerization, since in this case the dependence of the $\tilde{\delta}$ values on the comonomer are not considered. This is illustrated by Fig. 3 where the Φ values calculated with consideration of the dilution dependence of $\tilde{\delta}_1$ and $\tilde{\delta}_2$ values found in homopolymerization are plotted against the composition of the monomer mixture. It was found that although the changes of Φ values calculated this way are independent of solvent concentration, they increase considerably with the mole fraction of styrene. From the 13 parameters necessary for the description of the polymerization rate in the copolymerization system St-BA-Bz in terms of the hot radical theory, the values of six constants (δ_1 , γ_1 , γ_{11} , δ_2 , γ_2 , γ_{22}) were determined earlier from homopolymerization experiments (see Table 2).

In the investigation of copolymer composition, it was pointed out [23] that the reactivity ratios can be regarded as constants within the limits of experimental error, i.e., their values were found to be independent of dilution over the solvent concentration range studied. Thus, it can be supposed initially that

$$\rho_1 = \rho_1^* = 0.70, \quad \rho_2 = \rho_2^* = 0.16$$

The three other parameters (γ_{12} , γ_2 , and Φ) necessary for a description of the copolymerization system in terms of the hot radical theory were calculated with the use of experimental data from the nonlinear least squares method. The parameter set thus obtained is collected in Table 2. The table contains the confidence intervals of the parameters and also data on the EA-St copolymerization system.

TABLE 2

St/BA/Bz	Values otherwise determined	St/EA/Bz [20]
$\rho_1 = 1.58 \pm 0.07$		0.828
$\rho_1^* = 0.23 \pm 0.13$		0.796
$\delta_1 = 11.78 \pm 0.14$	11.6 [10]	11.8
$\gamma_{11} = 1.44 \pm 0.09$	1.48 [10]	1.7
$\gamma_{12} = 4.9 \pm 0.6$		1.40
$\gamma_1 = 0.52 \pm 0.07$	0.521 [10]	0.435
$\rho_2 = 0.83 \pm 0.11$		0.194
$\rho_2^* = 0.19 \pm 0.03$		0.187
$\delta_2 = 1.08 \pm 0.033$	1.08 [11]	1.09
$\gamma_{21} = 9.7 \pm 1.3$		8.81
$\gamma_{22} = 0.063 \pm 0.021$	0.086 [11]	0.107
$\gamma_2 = 0.0104 \pm 0.0016$	0.0117 [11]	0.0126
$\Phi = 11.5 \pm 4.5$		11.5

In Fig. 1 the theoretical curve calculated by the 13 parameters is given as a line. The curve fits very well (within $\pm 10\%$ error) the experimentally determined dependence of $W_2/W_1^{0.5}$ on composition and dilution. Remarkable, the Φ value was found to be completely independent of the monomer composition and the dilution, as was theoretically expected.

In spite of expectations, the supposed identities of ρ_1 and ρ_1^* and of ρ_2 and ρ_2^* were not fulfilled; however, the composition of the copolymer can be completely given by the calculated parameters (see Fig. 9). This figure shows the copolymer composition data of the series of 2.9 mol/dm³ total monomer concentration in the usual η - ξ representation. At each data point the error interval calculated from the error of elemental analysis is also given. The solid line represents the theoretical curve calculated with the parameters given in

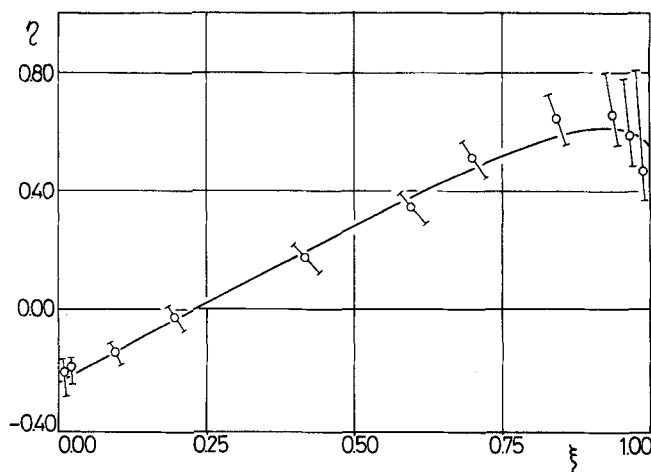


FIG. 9 The η vs ξ representation of the copolymer composition data ($m_1 + m_2 = 2.9 \text{ mol/dm}^3$).

Table 2. The deviation of the theoretical curve in Fig. 9 from a straight line is within the limits of experimental error determined by elemental analysis; thus the deviation due to the difference between ρ and ρ^* values cannot be experimentally detected.

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