Kinetics of Radical Copolymerization. XV. Absolute Rate Constants in the Copolymerization System Styrene-Ethyl Acrylate-Benzene

A. Nagy[a]; T. Földes-Berezsnich[a]; I. Gyöngyhalmi[a]; F. Tüdös[ab]

[a] Central Research Institute for Chemistry of the Hungarian Academy of Sciences, Budapest, Hungary

[b] Institute for Chemical Technology Eötö Loránd University, Budapest, Hungary

PLEASE SCROLL DOWN FOR ARTICLE

KINETICS OF RADICAL COPOLYMERIZATION. XV. ABSOLUTE RATE CONSTANTS IN THE COPOLYMERIZATION SYSTEM STYRENE–ETHYL ACRYLATE–BENZENE

A. NAGY, T. FÖLDES-BEREZSNICH, and
I. GYÖNGYHALMI

Central Research Institute for Chemistry of the Hungarian
    Academy of Sciences
P.O.B. 17, H-1525 Budapest, Hungary

F. TÜDÖS*

Central Research Institute for Chemistry of the Hungarian
    Academy of Sciences
P.O.B. 17, H-1525 Budapest, Hungary;

Institute for Chemical Technology
Eötvös Loránd University
P.O.B. 32, H-1528 Budapest, Hungary

ABSTRACT

With the use of rate data of the system St–EA–AIBN–Bz–50°C measured earlier, the parameters of the rate equation derived in terms of the hot radical theory were determined. The reason for the reevaluation of experimental data was that the absolute values of propagation and termination rate constants could be determined in the homopolymerization of both monomers with the improved rotating sector method elaborated for nonsteady-state kinetic investigations. This enabled us to determine the rate constants of the elementary reactions and deactivation parameters (γ_{12} and γ_{21}) of the copolymerization. The rate data calcu-

lated with the new parameter set are in good agreement with the measured ones, proving the applicability of the hot radical theory. The results are represented by a steric coordination system in order to call attention to the importance of the simultaneous study of composition- and dilution-dependence in copolymerization.

INTRODUCTION

Complete kinetic analysis of the system specified in the title was reported in our earlier publications [1–3]. The rates of initiation and of copolymerization, and the compositions of copolymer mixtures in bulk and in benzene solution were studied in a range of dilutions. Our kinetic data were evaluated in terms of the hot radical theory, and the parameter values in the rate equation of copolymerization were determined by parameter estimation. The copolymerization parameters contained the chain propagation and termination rate constants in combined form. The absolute values of chain propagation and termination rate constants were determined for styrene and ethyl acrylate by the rotating sector instrument we constructed earlier [4, 5].

In the present paper the reevaluation of our earlier copolymerization data are given, based on new measurement data.

EXPERIMENTAL

The investigations reported in our earlier papers [1–5] were carried out uniformly at 50°C, in bulk, or in an inert solvent (benzene, Bz) with the application of AIBN or benzoin. Purification procedures of the materials used are given in the above references.

RESULTS AND CONCLUSIONS

A complete kinetic study of the homopolymerization of both monomers by the rotating sector method was given in our previous papers [4, 5]. These investigations revealed that the chain termination rate constant of each monomer is independent of the dilution, while the dependence of the effective chain propagation rate constant ($\bar{k}_2$) can be described by an equation derived from the hot radical theory [6]:

$$\bar{k}_2 = k_2\left[1 \ + \ 1/\left(\gamma \ + \ \gamma' \ \frac{s}{m}\right)\right] \tag{1}$$

where k_2 is the chain propagation rate constant extrapolated to infinite dilution

$\quad \gamma$ and γ' are the parameters of deactivation with monomer and solvent, respectively (detailed in Refs. 4 and 5)

$\quad s$ is the solvent concentration

$\quad m$ is the monomer concentration

We pointed out in Ref. 3 that the rate of copolymerization cannot be described by the classical rate equation. Our experimental data were in contradiction with the diffusion theory [7], with the penultimate effect [8–12], and with the copolymerization theory of EDA complexes [13–16]. Our kinetic data could be interpreted quantitatively in terms of the hot radical theory [17]. This theory describes the rate of copolymerization (W_2) by the following equation:

$$W_2 = \frac{\sqrt{W_1}\left(\tilde{\rho}_1 m_1^2 + 2m_1 m_2 + \tilde{\rho}_2 m_2^2 \right)}{\left(\tilde{\delta}_1^2 \tilde{\rho}_1^2 m_1^2 + 2\Phi \tilde{\delta}_1 \tilde{\delta}_2 \tilde{\rho}_1 \tilde{\rho}_2 m_1 m_2 + \tilde{\delta}_2^2 \tilde{\rho}_2^2 m_2^2 \right)^{1/2}} \tag{2}$$

where m_1 and m_2 are the monomer concentrations, W_1 is the rate of initiation, and

$$\tilde{\rho}_1 = \tilde{k}_{11}/\tilde{k}_{12} \tag{3}$$

$$\tilde{\rho}_2 = \tilde{k}_{22}/\tilde{k}_{21} \tag{4}$$

$$\tilde{\delta}_1 = \sqrt{k_{4,12}}/\tilde{k}_{11} \tag{5}$$

$$\tilde{\delta}_2 = \sqrt{k_{4,22}}/\tilde{k}_{22} \tag{6}$$

and

$$\Phi = \frac{k_{4,11}}{\sqrt{k_{4,11} \times k_{4,22}}} \tag{7}$$

A tilde in the rate equation refers to the possible dependence of the above parameters on dilution or composition (see later on). $\tilde{k}_{11}$, $\tilde{k}_{12}$, $\tilde{k}_{21}$, and $\tilde{k}_{22}$ are chain propagation constants, and $k_{4,11}$, $k_{4,22}$, and $k_{4,12}$ are the corresponding chain termination constants.

Equation (2) is formally identical to the classical rate equation of copolymerization. The four parameters which depend on concentration and which are defined by Eqs. (3)–(6) supply the theoretical difference. According to the hot radical theory, the concentration dependence can be defined by the so-called deactivation functions (D_1, D_2) [17]:

$$\tilde{\rho}_1 = \rho_1 \frac{1 + D_1}{1 + \dfrac{\rho_1}{\rho_1^*}D_1} \tag{8}$$

$$\tilde{\rho}_2 = \rho_2 \frac{1 + D_2}{1 + \dfrac{\rho_2}{\rho_2^*}D_2} \tag{9}$$

$$\tilde{\delta}_1 = \frac{\delta_1}{1 + D_1} \tag{10}$$

$$\tilde{\delta}_1 = \frac{\delta_1}{1 + D_1} \tag{11}$$

In terms of the reaction scheme, the deactivation functions are [17]

$$D_1 = \frac{m_1 + m_2/\rho_1}{\gamma_{11}m_1 + \gamma_{11}m_2 + \gamma_1 s} \qquad (12)$$

$$D_2 = \frac{m_2 + m_1/\rho_2}{\gamma_{22}m_2 + \gamma_{21}m_1 + \gamma_2 s} \qquad (13)$$

An asterisk in the equations refers to the reactions of hot radicals; γ_{11}, γ_{12} and γ_{22}, γ_{21} are the cooling parameters of the corresponding hot radical with the monomer, while γ_1 and γ_2 are those with the solvent. The 13 parameters in the rate equation were determined from the rate data by computer fitting [3].

For the sake of better comparability, the summary table of Ref. 3 is repeated here. The indices were defined as follows: monomer 1 is styrene and monomer 2 is ethyl acrylate, and the values of δ_1 and δ_2 are given in $L^{-1/2} \cdot mol^{1/2} \cdot s^{1/2}$ units (Table 1).

According to the data of Ref. 2, the copolymerization constants are independent of dilution in the present system, $\rho_1 \cong \rho_1^*$ and $\rho_2 \cong \rho_2^*$. Consequently, according to theory [17], $\tilde{\rho}_1 = \rho_1$ and $\tilde{\rho}_2 = \rho_2$. After these considerations, the rate equation can be written in the following form after elementary transformations:

$$\frac{W_2}{\sqrt{W_1}} = \frac{k_{11}(1 + D_1)m_1\left(1 + \dfrac{2m_2}{\rho_1 m_1} + \dfrac{\rho_2}{\rho_1}\dfrac{m_2^2}{m_1^2}\right)}{\left(k_{4,11} + 2k_{4,12}\dfrac{k_{12}}{k_{21}}\dfrac{(1 + D_1)m_2}{(1 + D_2)m_1} + k_{4,22}\dfrac{k_{12}^2}{k_{21}^2}\dfrac{(1 + D_1)^2}{(1 + D_2)^2}\dfrac{m_2^2}{m_1^2}\right)^{1/2}} \qquad (14)$$

From the parameters of the equation, ρ_1 and ρ_2 can be determined from the composition data with high accuracy (see Ref. 2). γ_{11}, γ_1, γ_{22}, and γ_2 can be determined separately in kinetic investigations of the individual monomers. Their numerical values are

TABLE 1. Parameters Calculated in Terms of the Hot Radical Theory from Data of the Copolymerization System St-EA-AIBN-Bz-50°C [3]

	Dimension	Calculated	Determined by another way	Reference
ρ_1	—	0.828	0.787	2
ρ_2^*	—	0.796	—	—
δ_1	$L^{-1/2} \cdot mol^{1/2} \cdot s^{1/2}$	91.40	89.85	18
γ_{11}	—	1.77	1.48	18
γ_{12}	—	1.40	—	—
γ_1	—	0.435	0.521	18
ρ_2	—	0.194	0.152	2
ρ_2^*	—	0.187	—	—
δ	$L^{-1/2} \cdot mol^{1/2} \cdot s^{1/2}$	8.443	7.172	19
γ_{21}	—	8.81	—	—
γ_{22}	—	0.107	0.0129	19
γ_2	—	0.0126	0.0162	19
Φ	—	11.5	—	—

$\gamma_{11} = 1.47$ [18]

$\gamma_1 = 0.520$ [18]

$\gamma_{22} = 0.129$ [19]

$\gamma_2 = 0.0162$ [19]

$\rho_1 = 0.787$ [2]

$\rho_2 = 0.152$ [2]

k_{11}, $k_{4,11}$, k_{22}, and $k_{4,22}$ are the chain propagation and termination rate constants of the individual monomers. Their numerical values are for infinite dilution:

$k_{11} = 110.7 \ L \cdot mol^{-1} \cdot s^{-1}$ [4]

$k_{4,11} = 9.85 \times 10^7 \ L \cdot mol^{-1} \cdot s^{-1}$ [4]

$k_{22} = 1680 \ L \cdot mol^{-1} \cdot s^{-1}$ [5]

$k_{4,22} = 1.45 \times 10^8 \ L \cdot mol^{-1} \cdot s^{-1}$ [5]

The remaining parameters (not more than three: $k_{4,12}$, γ_{12}, and γ_{21}) characterize an elementary reaction that is realized only in the copolymerization system. Their numerical values can be determined with sufficient accuracy from the copolymerization rate data given in Ref. 3 by using Eq. (14). The parameters were determined with the nonlinear least-squares method by a computer. The result of parameter estimation is

$k_{4,12} = 9.89 \times 10^8 \ L \cdot mol^{-1} \cdot s^{-1}$

$\gamma_{12} = 3.25$

$\gamma_{21} = 6.98$

According to Eq. (7), the value of Φ containing the chain propagation rate constant is

$\Phi = 8.29$

The rate of polymerization values calculated with the above parameter set and their percent deviations from the measured values are listed in Table 2. The error scatter is not statistically perfect, indicating that optimization of the parameters needs further iteration. This could not be done for technical reasons, but 85% of the calculated data still equals the experimental data within ±12% despite the fact that the copolymerization rate is changing quite extraordinarily at a 1:33 ratio in the whole range of dilution and composition.

The determination of absolute values of cross-propagation constants ($\tilde{k}_{12}$ and $\tilde{k}_{21}$, from the values of ρ_1 and ρ_2) and of cross-termination ($k_{4,12}$, with parameter estimation) became possible by determination of the chain propagation and termination rate constants of individual monomers. By comparison of the γ_{12}, γ_{21}, and Φ values with the data in Table 1, and considering the errors in parameter estimation and in the rotating sector method, the agreement is acceptable.

The copolymerization parameters of the systems St–MA–Bz [22] and St–EA–Bz as determined by the above procedure, are summarized in Table 3. The kinetic behavior of St–MA–Bz–50°C is very similar to that of St–EA–Bz–50°C and even to that of the earlier investigated system St–butyl acrylate–Bz–50°C [20, 21]. This

TABLE 2. Measured [3] and Calculated Copolymerization Rate Data in the System St–EA–AIBN–Bz–50°C

m_1, mol·L^{-1}	m_2, mol·L^{-1}	s, mol·L^{-1}	$W_2/\sqrt{W_1} \times 10^2$ mol$^{1/2} \cdot$L$^{-1/2} \cdot$s$^{-1/2}$ Measured	Calculated	$[(W_2/\sqrt{W_1})_{\text{calc}} - (W_2/\sqrt{W_1})_{\text{meas}}] / (W_2/\sqrt{W_1})_{\text{meas}}$ %
		$m_1 + m_2 \cong 0.97$ mol/L			
0.1675	0.7920	9.669	2.245	2.945	31.18
0.2518	0.7021	9.672	1.902	2.637	38.67
0.3372	0.6338	9.648	2.100	2.488	18.48
0.4210	0.5475	9.645	1.922	2.298	19.56
0.5047	0.4591	9.645	1.809	2.113	16.77
0.6237	0.3535	9.622	1.775	1.926	8.53
0.7050	0.2677	9.623	1.600	1.756	9.73
0.7860	0.1720	9.635	1.443	1.553	7.61
0.9409	0.03468	9.605	1.264	1.319	4.38
		$m_1 + m_2 \cong 1.4$ mol/L			
0.1526	1.276	9.103	4.385	5.187	18.30
0.2213	1.212	9.085	4.004	4.708	17.59
0.2993	1.224	9.093	3.803	4.733	24.44
0.4456	0.9881	9.073	3.539	3.940	11.33
0.5744	0.867	9.057	3.298	3.670	11.27
0.9299	0.5209	9.026	2.873	2.981	3.74
1.222	0.2008	9.046	2.525	2.311	−8.47
1.341	0.07060	9.055	2.211	2.041	−7.71
		$m_1 + m_2 \cong 2.1$ mol/L			
0.1662	1.924	8.283	7.884	8.642	9.62
0.4579	1.558	8.360	5.794	6.213	7.24
0.6664	1.425	8.230	5.653	5.932	4.93
0.9497	1.116	8.273	4.866	5.197	6.81
1.073	0.9924	8.262	4.818	4.941	2.56
1.210	0.8902	8.210	4.739	4.793	1.15
1.391	0.7034	8.207	4.543	4.409	−2.95
1.719	0.3535	8.220	3.661	3.792	3.57
1.615	0.1768	8.563	3.009	2.856	−5.08
		$m_1 + m_2 \cong 2.8$ mol/L			
0.05138	2.751	7.419	25.23	23.14	−8.30
0.1662	2.694	7.338	12.91	13.67	5.88
0.3316	2.501	7.368	9.571	10.66	11.42

TABLE 2.   Continued

m_1, mol·L^{-1}	m_2, mol·L^{-1}	s, mol·L^{-1}	$W_2/\sqrt{W_1} \times 10^2$ mol$^{1/2}$·L$^{-1/2}$·s$^{-1/2}$		$[(W_2/\sqrt{W_1})_{calc} - (W_2/\sqrt{W_1})_{meas}]$ $(W_2/\sqrt{W_1})_{meas}$ %
			Measured	Calculated	
0.8306	1.986	7.355	7.461	8.402	12.62
1.155	1.642	7.360	7.199	7.565	5.08
1.465	1.384	7.278	7.001	7.116	1.64
2.138	0.7096	7.239	5.777	5.755	−0.38
2.609	0.1758	7.292	4.571	4.565	−0.13

$$m_1 + m_2 \cong 3.0 \text{ mol/L}$$

0.1500	2.850	7.172	12.92	15.32	18.54
0.3000	2.700	7.163	9.67	11.89	22.98
0.6000	2.400	7.145	8.20	9.90	19.17
2.850	0.1500	7.011	4.74	4.90	3.46

$$m_1 + m_2 \cong 4.9 \text{ mol/L}$$

0.1647	3.738	6.064	22.37	21.96	−1.82
0.3393	3.490	6.149	15.02	16.08	7.08
0.6504	3.259	6.031	12.46	13.78	10.60
0.8268	3.080	6.025	11.92	13.01	9.12
1.135	2.740	6.048	11.08	11.94	7.72
2.595	1.210	6.038	8.338	8.551	2.56
3.082	0.7009	6.042	7.217	7.489	3.77
3.639	0.1742	5.974	6.269	6.478	3.33

$$m_1 + m_2 \cong 5.2 \text{ mol/L}$$

0.1650	5.072	4.426	34.73	34.69	−0.12
0.3310	4.907	4.416	24.40	25.40	4.08
0.5000	4.500	4.711	17.49	20.60	17.80
0.6617	4.576	4.399	19.36	20.24	4.55
1.163	4.053	4.396	16.68	17.56	5.27
1.725	3.633	4.188	15.78	16.58	5.09
2.860	2.332	4.323	13.08	13.51	3.28
4.488	0.7261	4.199	10.01	10.38	3.67
5.072	0.1771	4.121	9.13	9.34	2.31

$$m_1 + m_2 \cong 6.6 \text{ mol/L}$$

0.2500	6.415	2.679	41.60	41.20	−0.972
0.4144	6.230	2.694	32.24	32.86	1.94

(continued)

TABLE 2.   Continued

m_1, mol·L^{-1}	m_2, mol·L^{-1}	s, mol·L^{-1}	$W_2/\sqrt{W_1} \times 10^2$ mol$^{1/2}$·L$^{-1/2}$·s$^{-1/2}$		$[(W_2/\sqrt{W_1})_{calc} - (W_2/\sqrt{W_1})_{meas}]$ $(W_2/\sqrt{W_1})_{meas}$ %
			Measured	Calculated	
1.080	5.563	2.657	23.42	24.45	4.40
1.641	4.948	2.690	20.12	22.00	9.36
3.287	3.317	2.573	17.22	18.32	6.38
4.914	1.718	2.443	14.29	15.26	6.81
5.793	0.8755	2.346	13.39	13.70	2.29
6.287	0.3545	2.343	12.21	12.61	3.27

could also be expected from the similar homopolymerization kinetic behavior of the monomers MA, EA, and BA [19].

In our earlier paper on homopolymerization [22], only the hot radical theory [6, 17] was applied for the interpretation of copolymerization kinetics of the St–MA–Bz system.

The above-mentioned close kinetic similarity gives us the right to omit a detailed treatment of theories explaining the copolymerization anomalies since the authors had previously investigated all of these theories and found them unsuitable for the description of experimental data in earlier investigations of the systems St–EA–Bz [1–3], and St–BA–Bz [20, 21].

TABLE 3.   Copolymerization Parameters of the Systems St–EA–Bz–50°C and St–MA–/bz–50°C

	St–EA–Bz–50°C	St–MA–Bz–50°C [22]	Dimension
ρ_1	1.787	0.76	—
ρ_2	0.152	0.20	—
γ_{11}	1.47	1.47	—
γ_1	0.52	0.52	—
γ_{22}	0.129	0.133	—
γ_2	0.0162	0.0396	—
k_{11}	110.7	110.7	L·mol^{-1}·s^{-1}
$k_{4,11}$	9.85×10^7	9.85×10^7	"
k_{22}	1.68×10^3	2.5×10^3	"
$k_{4,22}$	1.45×10^8	2.18×10^8	"
$k_{4,12}$	9.89×10^8	2.19×10^9	"
γ_{12}	3.25	2.01	—
γ_{21}	6.98	10.2	—
k_{12}	140.7	145.5	L·mol^{-1}·s^{-1}
k_{21}	11.05×10^3	12.5×10^3	"
Φ	8.29	14.5	—
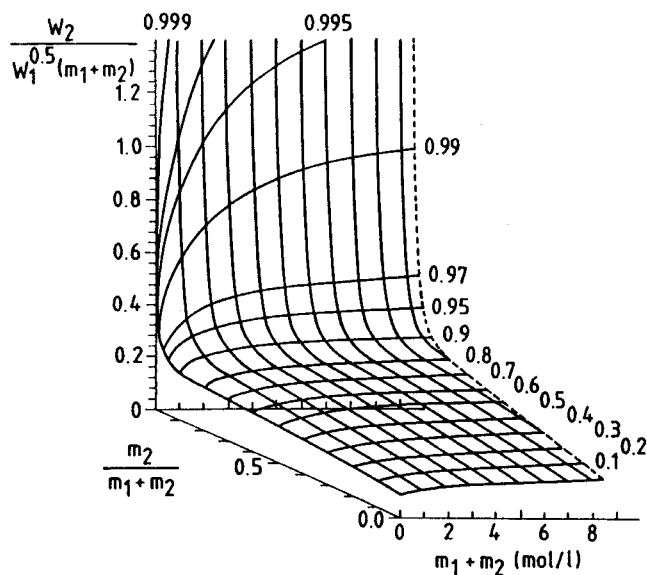
FIG. 1.   Representation of the overall rate constant (K) of the copolymerization system St–EA–Bz–50°C in steric coordinate system.
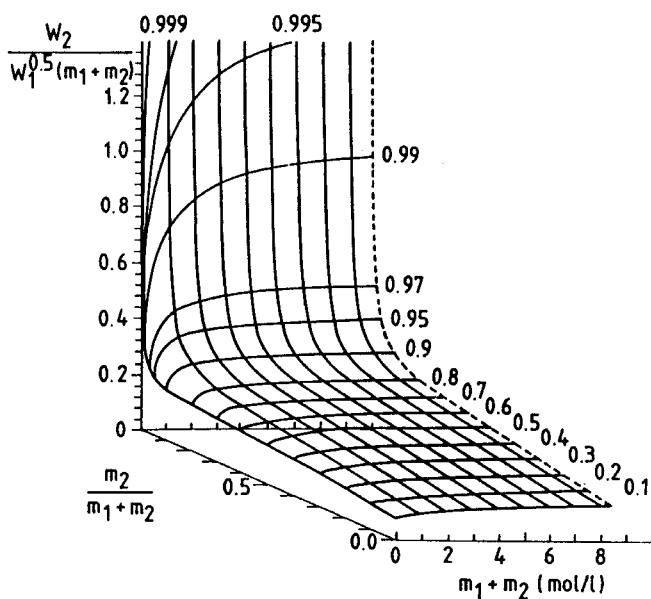
FIG. 2.   Representation of the overall rate constant of the copolymerization system St–MA–Bz–50°C in steric coordinate system.
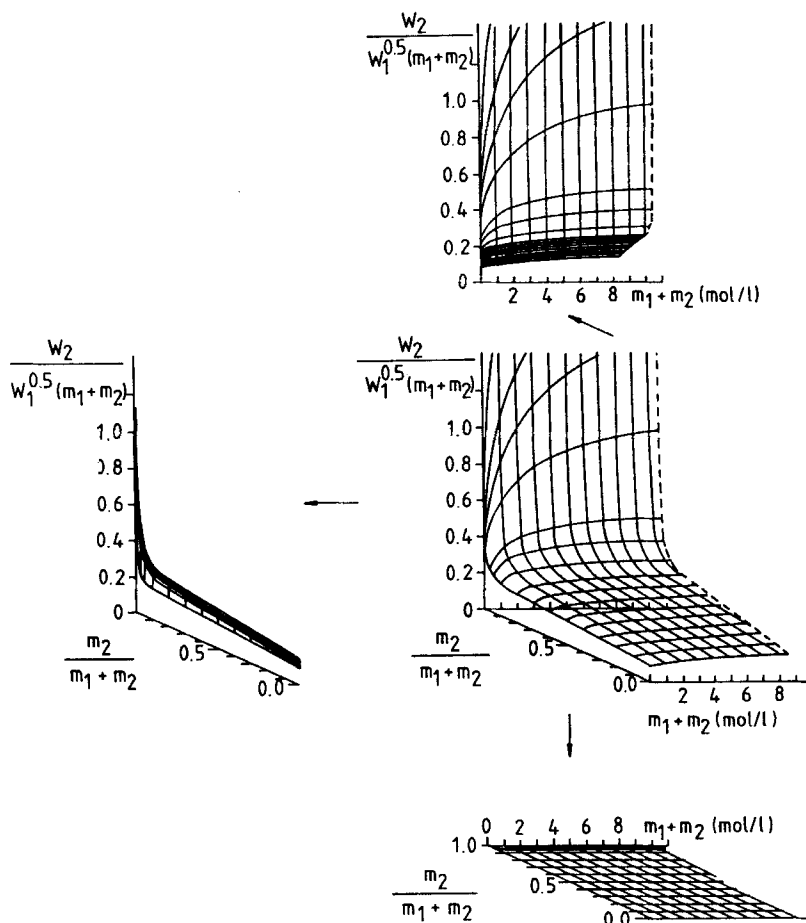
FIG. 3. Front view, side view, and view from above of the surface showing the K value of the system St–MA–Bz–50°C.

Since it was verified by our earlier studies that the kinetic investigation of a copolymerization system should be carried out in the entire composition and dilution region, the application of a steric coordination system is advisable. The two horizontal axes can represent the composition and the monomer concentration, while the vertical axis can be used for the copolymerization rate, the overall rate constant, etc.

The overall rate constant of the copolymerization can be defined by the following equation [17]:

$$\frac{W_2}{\sqrt{W_1}(m_1 + m_2)} = K$$

$$= \frac{\tilde{\rho}_1 \chi^2 + 2\chi(1 - \chi) + \tilde{\rho}_2(1 - \chi)^2}{\{\tilde{\rho}_1^2 \tilde{\delta}_1^2 \chi^2 + 2\Phi\tilde{\rho}_1\tilde{\rho}_2\tilde{\delta}_1\tilde{\delta}_2\chi(1 - \chi) + \tilde{\rho}_2^2\tilde{\delta}_2^2(1 - \chi)^2\}^{1/2}} \quad (15)$$

where

$$\chi = \frac{m_1}{m_1 + m_2} = \text{the partial mole fraction of styrene}$$

According to Eq. (15), at a constant χ value K should be constant as well if the parameters (or a part of them) are not dependent on the concentration and composition.

Figure 1 illustrates the change of the overall rate constant (K) of the copolymerization system St–EA–Bz–50°C against the total monomer concentration $(m_1 + m_2)$ and the mole fraction of EA $[m_2/(m_1 + m_2)]$. The K values were calculated with the parameters of the St–EA–Bz system (summarized in Table 3) by using Eq. (15). The direction of the plot was chosen in order to show the greatest possible part of the surface and to avoid overlapping some parts of it. Since the points fall on a curved surface, it seemed suitable to represent the netlines also: $(m_1 + m_2) = 0, 1, 2, \ldots,$ etc., and $m_2/(m_1 + m_2) = 0, 0.1, 0.2, \ldots$ The density of the netlines increased above the mole fraction $m_2/(m_1 + m_2) = 0.9$, which demonstrates the sudden change of the surface.

Since it can be seen from Table 3 that the copolymerization system St–MA–Bz–50°C can be described with a very similar parameter set, the overall rate constant of this system is also represented in the three-dimensional figure (Fig. 2).

Figure 3 shows three projection pictures of the surface. The view from above shows the interpretation region of the copolymerization system, i.e., the totality of concentration $(m_1 + m_2)$ and composition $[m_2/(m_1 + m_2)]$ value pairs that can be created by mixing two monomers and one solvent at the temperature of the investigation.

The front view shows the dependence of the overall rate constant of copolymerization on the total monomer concentration at different mole fractions, while the dependence of K on the composition can be seen at different $(m_1 + m_2)$ values in the side view. Disregarding some small deviations, these two projections are identical to $W_2/\sqrt{W_1}(m_1 + m_2) = f(\chi_2)$, and $K = f(m_1 + m_2)$ (see Figs. 2 and 3 in Ref. 22). We suggest the use of three-dimensional representations in order to call attention to the importance of studying the dependence of both composition and dilution in copolymerization.

CONCLUSION

With the use of rate data for the system St–EA–AIBN–Bz–50°C measured earlier, the parameters of the rate equation derived in terms of the hot radical theory were determined. The reason for reevaluation of the experimental data was that the absolute values of propagation and termination rate constants could be determined in the homopolymerization of both monomers with the improved rotating sector method elaborated for non-steady-state kinetic investigations. This enabled us to determine the rate constants of the elementary reactions and deactivation parameters (γ_{12} and γ_{21}) of the copolymerization. The rate data calculated with the new parameter set are in good agreement with the measured ones, proving the applicability of the hot radical theory. The results are represented by a steric coordination system in order to call attention to the importance of a simultaneous study of composition- and dilution-dependence in copolymerization.

ACKNOWLEDGMENTS

REFERENCES

[1]   Á. Fehérvári, T. Földes-Berezsnich, and F. Tüdös, *Magy. Kém. Foly.*, *85*, 205 (1979); *J. Macromol. Sci. – Chem.*, *A16*, 993 (1981).

[2]   Á. Fehérvári, T. Földes-Berezsnich, and F. Tüdös, *Magy. Kém. Foly.*, *88*, 226 (1982); *J. Macromol. Sci. – Chem.*, *A18*, 337 (1982).

[3]   Á. Fehérvári, T. Földes-Berezsnich, and F. Tüdös: *Magy. Kém. Foly.*, *88*, 267 (1982); *J. Macromol. Sci. – Chem.*, *A18*, 347 (1982).

[4]   A. Nagy, D. Szalay, T. Földes-Berezsnich, and F. Tüdös, *Eur. Polym. J.*, *19*, 1047 (1983); *Magy Kém. Foly.*, *89*, 529 (1983).

[5]   F. Tüdös, A. Nagy, and T. Földes-Berezsnich, *Angew. Makromol. Chem.*, *185/186*, 303 (1991); *Magy. Kém. Foly.*, *97*, 67 (1991).

[6]   F. Tüdös, *Acta Chim. Hung.*, *43*, 397 (1965); *44*, 403 (1965).

[7]   J. Artherton and A. M. North, *Trans. Faraday Soc.*, *58*, 2049 (1962).

[8]   F. J. Arlman, *J. Polym. Sci.*, *17*, 357 (1955).

[9]   K. Ito, *J. Polym. Sci., Part A1*, *8*, 2819 (1970).

[10] K. Ito, *Ibid.*, *9*, 869 (1971).

[11] S. Russo and S. Munari, *J. Macromol. Sci. – Chem.*, *A7*, 1321 (1968).

[12] E. Merz, T. Alfrey, and G. Goldfinger, *J. Polym. Sci.*, *1*, 75 (1946).

[13] Y. Shirota, M. Yoshimura, A. Matsumoto, and H. Mikawa, *Macromolecules*, *7*, 4 (1974).

[14] M. G. Boldwin, *J. Polym. Sci.*, *A3*, 703 (1965).

[15] T. Kukubo, S. Iwatsuki, and Y. Yamashita, *Macromolecules*, *1*, 482 (1968); *3*, 518 (1970).

[16] M. Yoshimura, T. Nogami, M. Yokoyama, H. Mikawa, and Y. Shirota, *Ibid.*, *9*, 211 (1976).

[17] F. Tüdös, T. Kelen, and T. Földes-Berzsnich, *Kém. Közl.*, *44*, 243 (1975); *J. Polym. Sci., Polym. Symp.*, *C50*, 109 (1975).

[18] T. Földes-Berezsnich, M. Szesztay, E. Boros Gyevi, and F. Tüdös, *Magy. Kém. Foly.*, *86*, 49 (1980); *J. Polym. Sci., Polym. Chem. Ed.*, *18*, 1229 (1980).

[19] Á. Fehérvári, T. Földes-Berezsnich, and F. Tüdös: *Magy. Kém. Foly.*, *86*, 54 (1980); *Eur. Polym. J.*, *16*, 185 (1980).

[20] G. Kaszás, T. Földes-Berezsnich, and F. Tüdös, *Magy. Kém. Foly.*, *89*, 154 (1983); *Eur. Polym. J.*, *20*, 395 (1984).

[21] G. Kaszás, T. Földes-Berezsnich, and F. Tüdös, *Magy. Kém. Foly.*, *89*, 345 (1983); *J. Macromol. Sci. – Chem.*, *A22*, 1571 (1985).

[22] A. Nagy, T. Földes-Berezsnich, and F. Tüdös, *Magy. Kém. Foly.*, *91*, 1 (1985); *Eur. Polym. J.*, *21*, 871 (1985).