Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Feherværi, A. , Foldes-berezsnich, T. and Tüdöss, F.(1982) 'Kinetics of Free Radical Copolymerization. V. Copolymerization of Ethyl Acrylate with Styrene. Composition of Copolymers', Journal of Macromolecular Science, Part A, 18: 3, 337 — 346

To link to this Article: DOI: 10.1080/00222338208056504

URL: http://dx.doi.org/10.1080/00222338208056504

J. MACROMOL. SCI.–CHEM., A18(3), pp. 337-346 (1982)

Kinetics of Free Radical Copolymerization. V. Copolymerization of Ethyl Acrylate with Styrene. Composition of Copolymers

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ABSTRACT

The composition of copolymers formed at 50°C in ethyl acrylate/styrene/azo-bis-isobutyronitrile/benzene systems of different composition was investigated. The experimental composition data (based on the elementary analysis of copolymers) were evaluated by the η-ξ transformation method. Finite monomer conversions were taken into account. The classical composition equation was found to describe the system under investigation. The reactivity ratios are $\rho_1 = 0.152 \pm 0.006$; $\rho_2 = 0.787 \pm 0.023$.

The free radical copolymerization of ethyl acrylate and styrene has been investigated in benzene solution at 50°C. Our results on the initiation kinetics were disclosed in our recent publication [1]. Now we are reporting on our studies concerning the composition of ethyl acrylate/styrene copolymers.

EXPERIMENTAL

The inhibitor was extracted from the monomers ethyl acrylate (EA) and styrene (St), Fluka purum grade, by 10% aqueous KOH solution. The monomers were neutralized by washing with distilled water, dried over anhydrous $CaCl_2$, and fractionated in reduced pressure (EA: $n_D^{20} = 1.4068$, St: $n_D^{20} = 1.5465$).

The initiator, azo-bis-isobutyronitrile (AIBN), Fluka purum grade, was purified by crystallization from a chloroform-ether mixture (mp. 104°C).

The solvent, benzene (Bz) reagent grade, was purified by a standard method [2].

Copolymerization experiments were performed in sealed dilatometric tubes under N_2 atmosphere. Oxygen was previously removed from the samples by freezing-thawing cycles [3].

Copolymers were precipitated in a 15-fold excess of chilled methanol (with higher St content) or petroleum benzine b.r. 40-60°C (with higher EA content). After separation and drying, copolymers were dissolved in methyl ethyl ketone and repeatedly precipitated on the surface of boiling distilled water.

After drying to constant weight, the composition of the copolymers was determined by elementary analysis (C, H, O).

RESULTS AND DISCUSSION

The composition of copolymers is given by the copolymerization composition equation for low monomer conversions [4, 5]:

$$\frac{dm_1}{dm_2} = \frac{m_1}{m_2} \frac{m_2 + m_1\rho_1}{m_1 + m_2\rho_2} \tag{1}$$

where m_1 and m_2 are the concentrations of the monomers, dm_1/dm_2 is the ratio of monomer incorporation at the given m_1 and m_2 concentrations, and ρ_1 and ρ_2 are the reactivity ratios.

At low monomer conversion dm_1/dm_2 is approximately equal to the ratio $y = \Delta m_1/\Delta m_2$ calculated from the copolymer composition (Δm_1 and Δm_2 are the moles of monomers incorporated in the copolymer).

Introducing $dm_1/dm_2 = y$ and $m_1/m_2 = x$, the composition equation is

$$y = x \frac{1 + x\rho_1}{\rho_2 + x} \tag{2}$$

Reactivity ratios are determined by numerical or graphical methods using Eq. (2).

Kelen and Tüdős [6] gave a detailed account on the advantages and imperfections of the most widely used evaluation methods, and they derived a new linear equation for graphical or numerical evaluation which transforms Eq. (2) into

$$\eta = (\rho_1 + \rho_2/\alpha) - \rho_2/\alpha \tag{3}$$

where

$$\eta = \frac{y - 1}{x\left(\alpha + \dfrac{y}{x^2}\right)} \qquad \text{and} \qquad \xi = \frac{y}{x^2\left(\alpha + \dfrac{y}{x^2}\right)} \tag{4}$$

and α is an arbitrary constant.

A few of the advantages of the method are:

1. In contrast to the Finemann-Ross method, it is invariant to the indexing of monomers.
2. ρ_1 and ρ_2 reactivity ratios of equal accuracy can be determined by selecting the α transformation constant appropriately (the relative errors are rendered the same).
3. The validity of composition equation (1) can be directly and simply verified through the validity of the experimental η-ξ linear relation.

This fast and simple linear method is as dependable as the most accurate nonlinear least-squares method, provided that a proper experimental design is followed [8].

Composition equation (1) is exact only at infinitely low monomer conversions since the ratio $y = \Delta m_1/\Delta m_2$ obtained at the final conversion can be determined experimentally from the composition of copolymers, and the composition of the copolymerization mixture is continuously changing during the experiment.

The integrated form of composition equation (1) [9] can be readily used at high conversion, but it requires complex computation.

In our studies we used the approximative integrated form of the composition equation (1) [10]. This method is based on the approximative integration of the composition equation by Walling and Briggs [9], who considered the expression

$$z = \frac{1 + \rho_1 x}{\rho_2 + x} \tag{5}$$

constant as a first approach. This condition is met only if $\rho_1 \rho_2 = 1$ or in azeotropic polymerization. The integration of the differential equation (1) resulted in

$$\frac{m_1}{m_1^0} = \left(\frac{m_2}{m_2^0}\right)^z \tag{6}$$

where m_1^0 and m_2^0 are the initial monomer concentrations. The ratios m_1/m_1^0 and m_2/m_2^0 can be expressed in terms of the partial molar conversions ζ_1 and ζ_2:

$$m_1/m_1^0 = 1 - \zeta_1 \tag{7}$$

$$m_2/m_2^0 = 1 - \zeta_2 \tag{8}$$

The partial molar conversions can be calculated if the molar conversion (ζ), the composition of copolymer (y), and the initial composition of the copolymerization system (x_0) are known:

$$\zeta_2 = \zeta \frac{1 + x_0}{1 + y} \tag{9}$$

$$\zeta_1 = \zeta_2 y/x \tag{10}$$

From Eqs. (6), (7), and (8), it follows that

$$z = \frac{\ln (1 - \zeta_1)}{\ln (1 - \zeta_2)} \tag{11}$$

Substituting Eq. (11) for z in Eq. (5), the copolymerization parameters ρ_1 and ρ_2 can be determined. According to Walling and Briggs, the initial monomer ratio (x_0) was applied in Eq. (5) for x, and as a consequence this method provides results more accurate than Eq. (1) only at low monomer conversions.

This method was improved to provide a good approximation at high monomer conversions (up to 50%) as well [10] as by introducing an average value for x over the (0, ζ) conversion range:

$$x = y/z \tag{12}$$

Equation (12) was substituted in Eq. (5) to give

$$y = z\frac{1 - \rho_2 z}{z - \rho_1} \tag{13}$$

Equation (13) can be transformed into linear equation (3) where the η and ξ variables take the form

$$\eta = \frac{y - 1}{z\left(\alpha + \frac{y}{z^2}\right)}; \qquad \xi = \frac{y}{z^2\left(\alpha + \frac{y}{z^2}\right)} \tag{14}$$

Our experimental results, presented in Table 1, were evaluated accordingly. The value of the α transformation constant was selected to render the relative error in the value of the reactivity ratios ρ_1 and ρ_2 equal [7]:

$$\alpha = \rho_2/\rho_1 \tag{15}$$

(ρ_1 and ρ_2 were determined in preliminary experiments and gave satisfactory agreement with previous results [11, 12].) In ethyl acrylate/styrene copolymerization, $\alpha = 4.5$ on the basis of Eq. (15).

The ρ_1 and ρ_2 constants determined as a function of overall monomer concentration are summarized in Table 2. The values of ρ_1 and ρ_2 at different monomer concentrations are constant within the limits of experimental error and no systematic trend can be observed. Consequently ρ_1 and ρ_2 are real constants independent of dilution in this copolymerization system, and joint evaluation of all experimental data is permissible. Our copolymer composition data according to the η-ξ linearization method are presented in

TABLE 1. Copolymer Composition in the EA/St/AIBN/Bz System (the overall concentration of monomers, the initial monomer ratio in the reaction mixture, the monomer ratio in the copolymer samples, and the final monomer conversion are given)

$m_{EA} + m_{St}$ (mol/dm^3)	$x_0 = m_{EA}/m_{St}$	$Y = \Delta m_{EA}/\Delta m_{St}$	ζ (%)
0.965	4.728	1.651	12.3
	2.789	1.260	12.69
	1.880	0.9251	12.28
	1.300	0.7569	12.48
	0.9096	0.6060	11.77
	0.5668	0.4402	12.30
	0.3797	0.3483	11.32
	0.2188	0.2388	12.34
	0.07891	0.1156	12.18
1.43	8.360	2.378	10.73
	5.479	1.865	10.64
	3.756	1.400	10.35
	2.217	1.030	10.13
	1.509	0.7782	10.13
	0.9533	0.5942	9.91
	0.5601	0.4285	9.48
	0.2312	0.2503	9.92
	0.1643	0.1919	10.12
	0.1011	0.1241	9.37
2.09	11.27	2.777	8.87
	5.787	1.494	8.10
	3.402	1.217	6.69
	2.138	0.9914	7.99
	1.521	0.8903	7.69
	1.171	0.7793	7.80
	0.9249	0.6421	7.72
	0.7356	0.5246	8.06
	0.5057	0.4195	8.08
	0.3468	0.3168	7.89
	0.2056	0.2222	7.39
	0.1095	0.1560	8.31
2.83	53.54	11.05	8.25
	16.21	3.873	8.01
	7.544	2.191	7.09
	4.696	1.543	8.20
	2.391	1.056	7.53

(continued)

TABLE 1 (continued)

$m_{EA} + m_{St}$ (mol/dm^3)	$x_0 = m_{EA}/m_{St}$	$y = \Delta m_{EA}/\Delta m_{St}$	ζ (%)
	1.422	0.7738	7.77
	0.9444	0.6066	7.99
	0.5678	0.4366	7.62
	0.3318	0.3046	7.74
	0.2295	0.2258	7.79
	0.1433	0.1408	7.84
	0.06716	0.08519	7.86
3.85	22.70	5.069	10.85
	10.29	2.723	9.96
	5.010	1.617	9.80
	3.725	1.334	9.76
	2.414	0.9871	9.30
	1.377	0.7339	9.01
	0.8006	0.5235	8.52
	0.4665	0.3763	7.85
	0.2275	0.2371	7.06
	0.1017	0.1446	6.38
5.23	30.74	5.935	7.35
	14.82	3.390	7.43
	6.915	1.956	7.03
	3.976	1.307	7.17
	2.106	0.9441	7.28
	1.241	0.7243	7.09
	0.8153	0.5630	7.60
	0.4941	0.4038	7.34
	0.3017	0.2761	7.38
	0.1618	0.1697	7.61
	0.07203	0.08814	7.23
6.64	0.1511	0.1898	3.87
	0.3496	0.3395	4.63
	0.6132	0.4670	4.19
	1.009	0.6491	4.66
	1.688	0.8650	4.75
	3.015	1.163	4.53
	5.150	1.584	4.23
	7.880	2.130	4.05
	15.03	3.237	4.72
	25.66	4.860	3.97

(continued)

TABLE 1 (continued)

$m_{EA} + m_{St}$ (mol/dm^3)	$x_0 = m_{EA}/m_{St}$	$y = \Delta m_{EA}/\Delta m_{St}$	ζ (%)
Bulk	52.23	12.63	13.39
	26.24	6.266	13.56
(8.86-8.45)	9.594	2.662	12.57
	4.409	1.450	16.30
	2.522	1.118	16.81
	1.053	0.6561	18.52
	0.6842	0.5038	17.02
	0.4200	0.3466	16.43
	0.2600	0.2526	15.12
	0.1121	0.1413	19.32

TABLE 2. Reactivity Ratios in the EA/St/AIBN/Bz Copolymerization System as a Function of Overall Monomer Concentration (the regression coefficient of η-ξ linear is given in the last column; $\alpha = 4.5$)

$m_{EA} + m_{St}$ (mol/dm^3)	ρ_1	ρ_2	r
0.965	0.176 ± 0.046	0.741 ± 0.112	0.952
1.43	0.163 ± 0.027	0.785 ± 0.089	0.990
2.09	0.135 ± 0.026	0.737 ± 0.085	0.986
2.83	0.163 ± 0.012	0.831 ± 0.045	0.997
3.85	0.148 ± 0.021	0.817 ± 0.088	0.993
5.23	0.145 ± 0.010	0.809 ± 0.037	0.998
6.64	0.148 ± 0.012	0.743 ± 0.058	0.997
Bulk	0.157 ± 0.018	0.811 ± 0.082	0.994

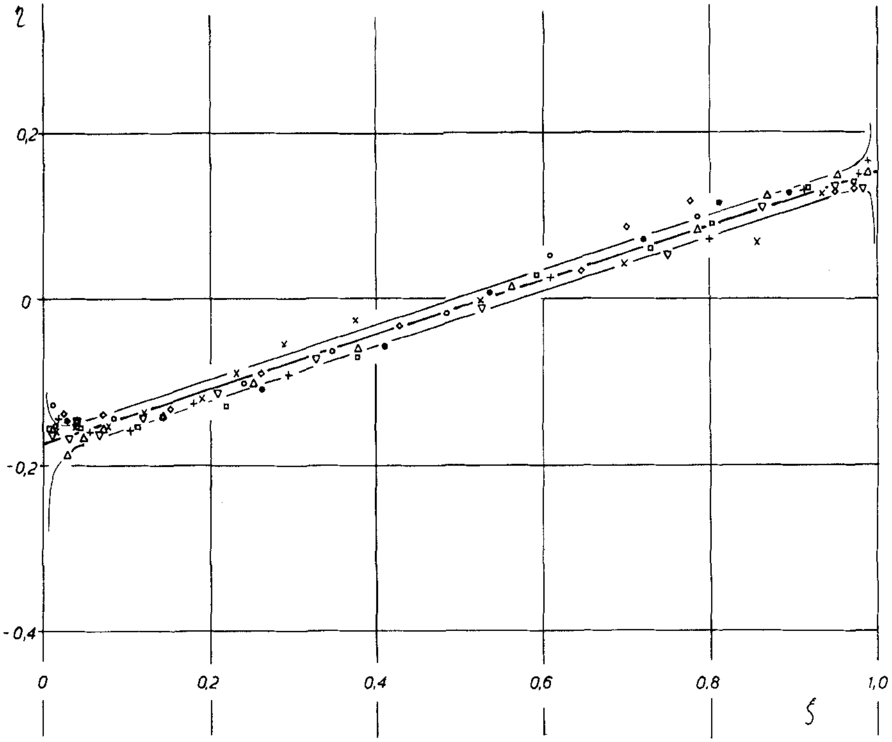

FIG. 1. Evaluation of EA/St copolymer composition by the η-ξ transformation method, $\alpha = 4.5$. The regression coefficient of the η-ξ straight line is 0.992. The contours correspond to the error in elementary analysis.

Fig. 1. The experimental data fall on a straight line, the intercept and slope of which give the reactivity ratios

$$\rho_1 = 0.152 \pm 0.006; \qquad \rho_2 = 0.787 \pm 0.023$$

(the 95% confidence intervals are given as determined in Ref. 13).

The contours corresponding to the error in the elementary analysis are also shown on Fig. 1 (±0.33% calculated from the standard deviation of C, H, O analysis of homopolymer samples).

According to earlier investigations, the reactivity ratios in ethyl acrylate/styrene copolymerization at 50°C are $\rho_1 = 0.19$, $\rho_2 = 0.79$ [11], and $\rho_1 = 0.19$, $\rho_2 = 0.78$ [12], respectively. The errors in ρ_1

and ρ_2 are not given in these references, and in Ref. 11 even the primary composition data are not available. The composition data presented in Ref. 12 were evaluated by the same procedure outlined in the foregoing to yield the reactivity ratios

$$\rho_1 = 0.161 \pm 0.033 \qquad \text{and} \qquad \rho_2 = 0.721 \pm 0.105$$

With the limits of experimental error, these values are in satisfactory agreement with our substantially more accurate results determined from numerous experimental data.

ACKNOWLEDGMENTS

Assistance in the experiments by technician Maray Klára and accurate elementary analysis by technician Balogh Zsigmondné are acknowledged.

REFERENCES

[1] A. Fehérvári, T. Földes-Berezsnich, and F. Tüdős, J. Macromol. Sci.–Chem., A16, 993 (1981).

[2] Organic Solvents, Interscience, New York, 1955.

[3] F. Tüdős, T. Földes-Berezsnich, and M. Azori, Acta Chim. Hung., 24, 91 (1960).

[4] F. R. Mayo and F. M. Lewis, J. Am. Chem. Soc., 66, 1594 (1944).

[5] G. Goldfinger and T. Kane, J. Polym. Sci., 3, 462 (1948).

[6] T. Kelen and F. Tüdős, J. Macromol. Sci.–Chem., A9, 1 (1975).

[7] F. Tüdős and T. Kelen, In Press.

[8] R. C. McFairlane, P. M. Reilly, and K. F. O'Driscoll, J. Polym. Sci., Polym. Chem. Ed., 18, 251 (1980).

[9] C. Walling and E. R. Briggs, J. Am. Chem. Soc., 67, 1774 (1945).

[10] F. Tüdős, T. Kelen, T. Földes-Berezsnich, and B. Turcsányi, J. Macromol. Sci.–Chem., A10, 1513 (1976).

[11] E. H. Riddle, Monomeric Acrylic Esters, Reinhold, New York, 1954, p. 94. Ref. 154.

[12] P. Wittmer, Angew. Makromol. Chem., 39, 35 (1974).

[13] T. Kelen, F. Tüdős, and B. Turcsányi, Polym. Bull., 2, 71 (1980).

Accepted by editor July 13, 1981
Received for publication August 4, 1981