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KINETICS OF RADICAL COPOLYMERIZATION—XI

INVESTIGATION OF THE RATE OF INITIATION AND COPOLYMER COMPOSITION OF THE SYSTEM STYRENE–BUTYL ACRYLATE–BENZENE

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Abstract—The initiation rate constant and the composition of copolymers formed at 50° in St–BA–AIBN–Bz systems of various compositions were investigated. The initiation rate constant was linearly dependent on the composition of monomers ("additive behaviour"). The experimental composition data were evaluated by the η-ξ transformation method and the reactivity ratios determined accordingly are dilution independent values: $\rho_1 = 0.698 \pm 0.033$, $\rho_2 = 0.164 \pm 0.017$.

INTRODUCTION

In our previous publications [1–4] the kinetics of the polymerization of butyl acrylate and styrene were examined. The present paper deals with the rate of initiation in the copolymerizations of these monomers in solution and with the compositions of the copolymers.

EXPERIMENTAL

Purifications of butyl acrylate (BA) styrene (St), benzene (Bz) and azobisizobutyronitrile (AIBN) were carried out as stated previously [5–7].

The rate of initiation was determined by the inhibition method [9]. The stable free radical triphenyl veradzyl (TPV) was synthesized and purified as already described [8].

Copolymerizations were run up to 5–10% conversion at 50° in dilatometric ampoules. Before the measurements, oxygen was removed by the usual freeze and thaw method [2]. Having finished a copolymerization, the product was precipitated in 15-fold excess of cold methanol. After drying, it was redissolved in methyl ethyl ketone and reprecipitated by pouring the solution onto boiling water. After drying to constant weight, the composition of the copolymer was determined by very accurate elemental (C, H, O) analysis.

EXPERIMENTAL RESULTS AND THEIR EVALUATION

According to earlier measurements, the initiation rate constant ($2k_1f$) of the polymerization system St–AIBN–Bz at 50° changes linearly with the initial mole fraction of St (χ_{St}) and this solvent dependence can be given by the following equation [2]:

$$2k_1f = (1.58 + 0.15 \cdot \chi_{St})\ \text{min}^{-1}. \quad (1)$$

In the system BA–AIBN–Bz at 50°, however, the value of $2k_1f$ was independent of the dilution [4] as for the systems methyl acrylate (MA)–Bz and ethyl acrylate–Bz [4, 10].

The rate of initiation in the copolymerization system St–BA–AIBN–Bz was measured by Bradbury and Melville [11] at 60° using ^{14}C-labelled AIBN. The $2k_1f$ values determined by these authors have large experimental error, so the data can be regarded as indicative only.

The inhibition method makes the more direct and much more precise determination of $2k_1f$ possible. Therefore, the initiation rate constants for various feed compositions were measured by the inhibition method, using triphenyl verdazyl (TPV) stable free radical. The inhibitor consuming side-reaction between St and TPV was considered as described previously [2]. The results listed in Table 1 and shown in Fig. 1 indicate a linear change of $2k_1f$ with the partial mole fraction of St for copolymerizations both in bulk and in solution. The partial mole fraction of St (χ_{St}) is given as follows:

$$\chi_{St} = \frac{m_1}{m_1 + m_2}$$

Table 1. Initiation rate constants of the copolymerization system BA–ST–AIBN at 50°, in bulk and in solution

$m_1^0 + m_2^0$ (mol/dm^3)	χ_{St}	$2k_1f \cdot 10^4$ (min^{-1})	Reference
Bulk	1.00	1.639	2
Bulk	0.75	1.635	
Bulk	0.50	1.638	
Bulk	0.25	1.610	
Bulk	0.00	1.608	4
2.80	1.00	1.730	2
2.80	0.83	1.750	
2.80	0.62	1.694	
2.80	0.51	1.610	
2.80	0.10	1.609	
2.80	0.049	1.555	
2.80	0.00	1.62	4

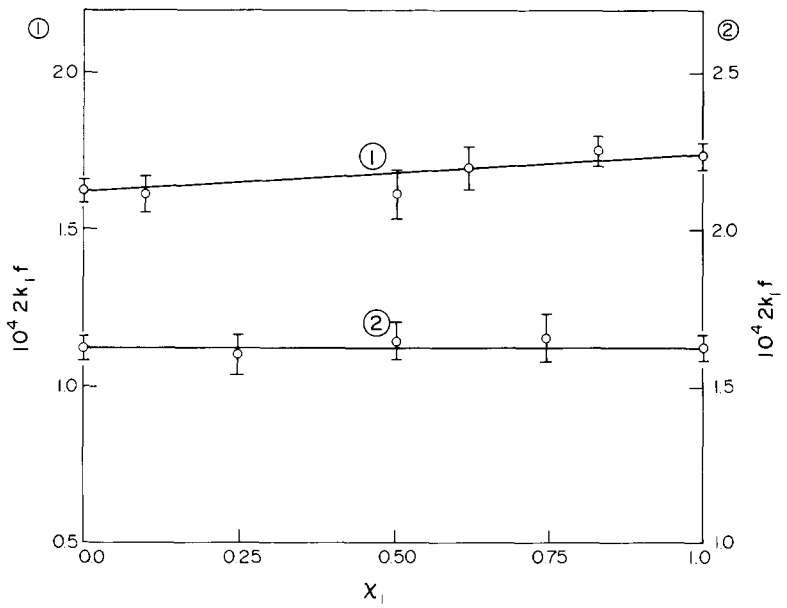

Fig. 1. The initiation rate constant of the system ST–BA–AIBN–Bz plotted against the composition of monomer mixture. 1. bulk; 2. $m_1^0 + m_2^0 = 2.90$ mol/dm^3.

where m_1 and m_2 are the concentrations of St and BA, respectively.

For the EA/St copolymerization system, the initiation rate constants change similarly with the monomer mixture composition [12].

INVESTIGATION OF THE COPOLYMER COMPOSITION

The reactivity ratios ρ_1 and ρ_2 can be calculated from the copolymer composition and monomer concentrations by the classical composition equation:

$$\frac{dp_1}{dp_2} = \frac{m_1}{m_2} \cdot \frac{m_1\rho_1 + m_2}{m_2\rho_2 + m_1} \tag{2}$$

where m_1 and m_2 are the concentrations of monomers in the feed and p_1 and p_2 are those in the copolymer.

Kelen and Tüdős [13] proposed for the simple, graphic determination of ρ_1 and ρ_2 following, transformed equation (2):

$$\eta = \rho_1\xi - \frac{\rho_2}{\alpha}(1 - \xi) \tag{3}$$

where

$$\eta = \frac{G}{\alpha - F}; \quad \xi = \frac{G}{\alpha + F}.$$

The values of F and G can be calculated at higher conversions by equation (4) [14]:

$$F = \frac{\rho_1}{\rho_2}\left(\log\frac{m_2^0 - p_2}{m_2^0} \Big/ \frac{m_1^0 - p_1}{m_1^0}\right)^2 \tag{4}$$

and

$$G = \frac{p_1 - p_2}{p_2}\left(log\frac{m_2^0 - p_2}{m_2^0} \Big/ \frac{m_1^0 - p_1}{m_1^0}\right)$$

where the quantities with subscript 0 denote initial concentrations. The optimal value of α within a series of measurements is the geometric mean of the lowest

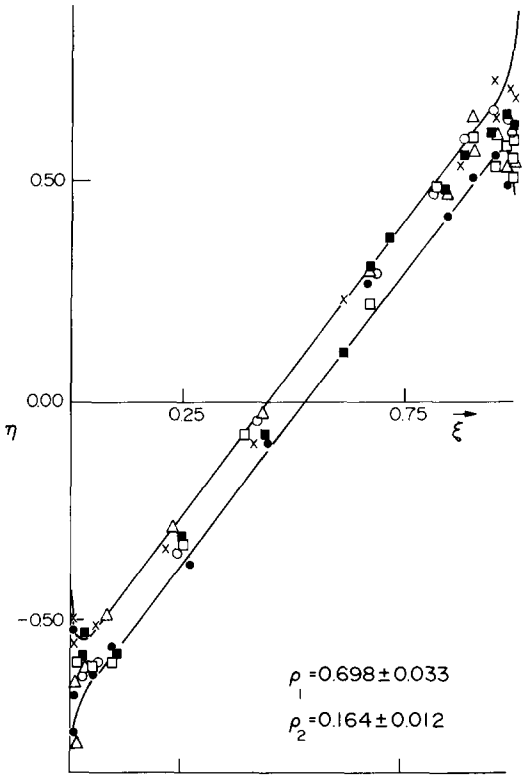

Fig. 2. The $\eta - \xi$ transformation representation of copolymer composition data belonging to different dilutions. × $m_1^0 + m_2^0$ = bulk (8.70–6.79 mol/dm^3); ○ $m_1^0 + m_2^0$ 5.40 mol/dm^3; ● $m_1^0 + m_2^0$ 3.70 mol/dm^3; □ $m_1^0 + m_2^0$ 2.90 mol/dm^3; ■ $m_1^0 + m_2^0$ 2.40 mol/dm^3; △ $m_1^0 + m_2^0$ 1.80 mol/dm^3.

Table 2. Copolymer composition in the system St–BA–AIBN–Bz. Overall monomer concentration, molar ratio of monomer in the initial mixture and in the copolymer; and conversion

$m_1^0+m_2^0$ (mol/dm^3)	m_1^0/m_2^0	p_1/p_2	ξ (%)
Bulk 8.70–6.79	31.258	18.382	5.20
Bulk 8.70–6.79	9.753	6.363	6.33
Bulk 8.70–6.79	4.155	3.632	6.23
Bulk 8.70–6.79	2.356	2.703	6.00
Bulk 8.70–6.79	1.564	1.891	5.92
Bulk 8.70–6.79	0.852	1.365	5.84
Bulk 8.70–6.79	0.439	0.968	6.16
Bulk 8.70–6.79	0.245	0.710	6.20
Bulk 8.70–6.79	0.105	0.418	6.02
Bulk 8.70–6.79	0.047	0.207	5.95
Bulk 8.70–6.79	0.020	0.084	5.68
5.40	39.634	18.332	5.37
5.40	18.668	10.972	5.95
5.40	9.111	5.639	6.20
5.40	4.022	3.386	5.50
5.40	2.337	2.318	6.54
5.40	1.530	1.760	5.28
5.40	0.821	1.330	4.86
5.40	0.433	0.897	4.85
5.40	0.251	0.659	3.44
5.40	0.101	0.383	4.19
5.40	0.061	0.257	4.54
5.40	0.019	0.090	5.65
3.70	32.474	18.376	8.86
3.70	15.728	10.523	8.31
3.70	9.673	6.817	8.85
3.70	3.963	3.224	8.63
3.70	2.395	2.601	9.07
3.70	1.455	1.855	8.96
3.70	0.826	1.272	8.76
3.70	0.399	0.917	8.29
3.70	0.253	0.681	7.49
3.70	0.109	0.376	7.33
3.70	0.065	0.266	7.44
3.70	0.022	0.095	8.36
2.90	33.103	19.931	7.18
2.90	15.271	10.627	6.72
2.90	9.250	7.168	7.20
2.90	4.073	3.856	7.27
2.90	2.116	2.427	6.88
2.90	1.419	1.817	6.42
2.90	0.862	1.364	6.72
2.90	0.427	0.949	6.53
2.90	0.237	0.663	6.68
2.90	0.071	0.290	6.01
2.90	0.040	0.180	6.21
2.40	21.727	14.679	9.62
2.40	8.615	6.917	9.74
2.40	3.951	3.584	9.34
2.40	2.125	2.348	9.74
2.40	1.513	1.871	9.35
2.40	0.984	1.511	9.01
2.40	0.859	1.376	9.26
2.40	0.675	1.116	8.81
2.40	0.439	0.921	8.88
2.40	0.256	0.698	8.54
2.40	0.120	0.401	8.81
2.40	0.054	0.249	8.52
1.80	34.868	25.861	11.04
1.80	14.894	11.975	12.25
1.80	8.290	6.689	12.53
1.80	3.650	3.870	12.97
1.80	2.020	2.466	12.12
1.80	0.732	1.273	11.24
1.80	0.426	0.904	12.18
1.80	0.235	0.660	12.48
1.80	0.100	0.376	13.38
1.80	0.018	0.084	15.28

Table 3. Reactivity ratios of the system St–BA–AIBN–Bz at different overall monomer concentrations. The values calculated by the non-linear method are indicated in parentheses

$m_1^0+m_2^0$ (mol/dm^3)	ρ_1	ρ_2
Bulk	0.663 ± 0.099	0.164 ± 0.044
	(0.721 ± 0.090)	(0.16 ± 0.02)
5.40	0.633 ± 0.079	0.169 ± 0.045
	(0.68 ± 0.08)	(0.18 ± 0.03)
3.70	0.723 ± 0.085	0.182 ± 0.034
	(0.76 ± 0.08)	(0.19 ± 0.02)
2.90	0.682 ± 0.057	0.163 ± 0.042
	(0.77 ± 0.04)	(0.16 ± 0.02)
2.40	0.691 ± 0.033	0.161 ± 0.020
	(0.72 ± 0.02)	(0.15 ± 0.01)
1.80	0.744 ± 0.081	0.145 ± 0.038
	(0.80 ± 0.08)	(0.13 ± 0.02)

and highest F values:

$$\alpha = \sqrt{F_{\min} \cdot F_{\max}} \tag{5}$$

Our copolymer composition results obtained for the system St–BA–AIBN–Bz at 50° are collected in Table 2. Figure 2 illustrates the results in an $\eta - \xi$ plot. The data were evaluated by equation (3) and the ρ_1 and ρ_2 values for different dilutions were determined by the least squares method. The ρ_1 and ρ_2 values belonging to the different overall monomer concentrations are listed in Table 3, together with the 95% confidence intervals calculated as already described [14]. The good fitting of reactivity ratios belonging to different dilutions indicates that their values do not change with the dilution by benzene within the limits of experimental error.

In the $\eta - \xi$ plot, slight curvature can be observed at high ξ values (see Fig. 2) therefore the ρ_1 and ρ_2 values were determined also by the method of non-linear least squares. These calculated values are, together with the 95% confidence intervals, indicated in parentheses in Table 3. The good fitting of reactivity ratios obtained by the linear method and by that of the non-linear least squares indicates that the use of linear evaluation is justified and the copolymer composition equation (2) can be applied to the system studied.

Because of the good fitting of reactivity ratios belonging to different overall monomer concentrations, the data were also evaluated together to give

$$\rho_1 = 0.698 \pm 0.033 \quad \text{and} \quad \rho_2 = 0.164 \pm 0.017$$

For the above values, the 95% common intervals (the "error ellipses") were also determined. In Fig. 3, the full line indicates the error intervals of values determined by the linear method, and the dotted line indicates those determined by the non-linear method. The agreement between the values calculated in two different ways is supported also by the almost complete coincidence of both error curves.

Considering the error of elemental analysis ($\pm 0.33\%$, [16]), the error contour curve belonging to ρ_1 and ρ_2 values obtained by the use of all data is calculated; it is indicated in Fig. 2 by a full line.

The dependence of reactivity ratios of the system St–BA on dilution was investigated earlier by Bradbury and Melville [11]. The authors found a slight dependence on dilution in an $\eta - \xi$ representation,

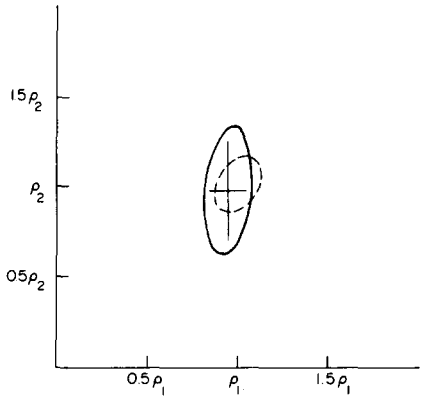

Fig. 3. The 95% common error intervals ("error ellipses") belonging to the values $\rho_1 = 0.698$ and $\rho_2 = 0.164$. (Full line: linear estimation; dotted line: non-linear estimation.)

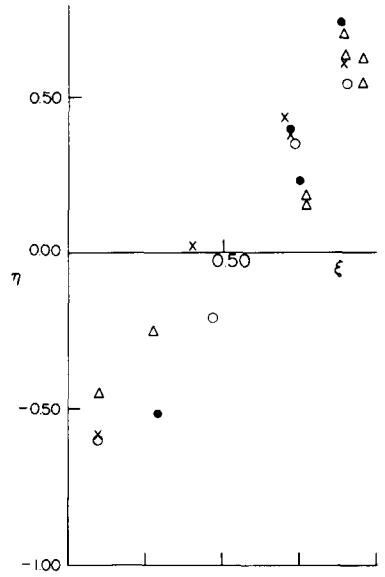

Fig. 4. The St–BA copolymer composition data of Bradbury and Melville [11] in the $\eta - \xi$ representation.

their values show a rather large, statistical scatter, therefore can be approximated by a single straight line (see Fig. 4). The reactivity ratios calculated from all their data ($\rho_1 = 0.704 \pm 0.15$ and $\rho_2 = 0.168 \pm 0.07$) agree excellently with those determined from our much more numerous and precise data.

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