

KINETICS OF THE RADICAL COPOLYMERIZATION OF STYRENE AND 2-METHOXYETHYL METHACRYLATE

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Dedicated to Academician O. Wichterle on the occasion of his 70th birthday.

Twenty low-conversion statistical copolymers of styrene and 2-methoxyethyl methacrylate with various composition were prepared. The dependence of the copolymer composition, molecular weight, initiation efficiency and other parameters on the composition of the monomer mixture is discussed. Kinetic data are correlated by means of various models of the copolymerization kinetics. The best fit with experimental data is provided by a diffusion-controlled termination model, especially its dyad variant suggested in this study.

The rate of the binary low-conversion radical copolymerization, R_p , of monomers A and B may be described similarly to homopolymerization in terms of the molar concentrations of the two monomers, $[A]$ and $[B]$, and of the rate of initiation $R_i = 2k_d f[I]$, where k_d is the decomposition constant of the initiator, f is the initiation efficiency, and $[I]$ is the molar concentration of the initiator:

$$R_p = - \frac{d([A] + [B])}{dt} = \frac{k_{po}}{k_{to}^{1/2}} ([A] + [B]) R_i^{1/2}. \quad (1)$$

The formally introduced overall rate constants of propagation and termination, k_{po} and k_{to} , are not genuine constants, but parameters depending on the composition of the monomer mixture.

The overall rate constant of propagation is given by¹

$$k_{po} = \frac{r_A y_A^2 + 2y_A y_B + r_B y_B^2}{r_A y_A / k_{pAA} + r_B y_B / k_{pBB}}, \quad (2)$$

where $y_A = 1 - y_B$ is the composition of the monomer mixture expressed by the mole fraction of monomer A, r_A and r_B are the monomer reactivity ratios, and k_{pAA} , k_{pBB} are the propagation rate constants for corresponding homopolymerizations.

For the classical model of chemically controlled termination^{2,3} we have

$$\frac{k_{po}}{k_{t0}^{1/2}} = \frac{r_A^2 y_A^2 + 2y_A y_B + r_B^2 y_B^2}{(r_A^2 \delta_A^2 y_A^2 + 2\phi r_A r_B \delta_A \delta_B y_A y_B + r_B^2 \delta_B^2 y_B^2)^{1/2}}; \quad (3)$$

δ_A and δ_B are ratios of the termination and propagation rate constants of homopolymerization

$$\delta_A = \frac{k_{tAA}^{1/2}}{k_{pAA}}, \quad \delta_B = \frac{k_{tBB}^{1/2}}{k_{pBB}}. \quad (4)$$

The so-called cross-termination factor

$$\phi = \frac{k_{tAB}}{2(k_{tAA} k_{tBB})^{1/2}} \quad (5)$$

or the cross-termination rate constant, k_{tAB} , indicates to what extent the termination of different radicals is preferred to that of radicals of the same kind.

By separating expressions which contain parameters related to the propagation and termination process, we obtain from Eq. (3) for the overall termination constant

$$k_{t0} = k_{tAA} x_A^{*2} + k_{tAB} x_A^* x_B^* + k_{tBB} x_B^{*2}, \quad (6)$$

where $x_A^* = [A^{\cdot}]/([A^{\cdot}] + [B^{\cdot}])$ is the mole fraction of radicals of type A which again depends on the composition of the monomer mixture.

The experimentally determined and often very high values of the cross-termination factor ϕ and its dependence on the composition of the monomer mixture raised criticism of the chemically-controlled model⁴⁻⁷. The dependence of the rate constant of propagation k_{po} , given by Eq. (2), on the composition of the monomer mixture is – apart from the constants k_{pAA} and k_{pBB} characterizing homopolymerization – determined by the monomer reactivity ratios only. The physical meaning of the latter quantities is well established. This is why the causes of discrepancy between the predictions based on the model of chemically controlled copolymerization and experimental results were sought in the mechanism of termination.

In the light of experimental results on termination in homopolymerization, it becomes clear that also in copolymerization the rate of termination ought to be – at least partly – controlled by segmental diffusion⁸⁻¹⁰. The rate of segmental diffusion is connected with the chain flexibility. The overall termination constant may therefore be expected to be a function of the copolymer composition. Ito and O'Driscoll¹ suggested a theoretical expression for k_{t0} at the onset of polymerization, but this expres-

sion holds for chemically related monomers only, and consequently cannot be applied generally. Earlier, an empirical relation was suggested for k_{10} by Atherton and North¹¹

$$k_{10} = k_{1AA}x_A + k_{1BB}x_B, \quad (7)$$

in which x_A , x_B are mole fractions of constitutional units in the copolymer. Formally, Eq.(7) does not contain any adjustable parameter. Modification introduced by Chiang and Rudin¹²

$$k_{10} = k_{1AA}x_A^2 + k_{1AB}x_Ax_B + k_{1BB}x_B^2 \quad (8)$$

contains one adjustable parameter denoted, by analogy with Eq. (4) as k_{1AB} . The diffusion-controlled termination model does not, however, distinguish between radicals with respect to the chemical nature of their active end. Another variant suggested and tested in this study is the dyad model

$$k_{10} = k_{1AA}x_{AA} + k_{1AB}x_{AB} + k_{1BB}x_{BB}, \quad (9)$$

in which x_{AA} , x_{BB} and x_{AB} are mole fractions of homogeneous and heterogeneous dyads, respectively, in the copolymer.

Correlation of model calculations with experimental data on the rate of copolymerization R_p calls for the explicit knowledge of both rate constants of termination, k_{1AA} and k_{1BB} .

Russo and Munari¹⁰ also start from the diffusion-controlled model, but assume that the rate of termination is predominantly controlled by segmental diffusion of the active chain end which in turn is mainly affected by the chemical character of the two terminal monomer units in the radical. This means that termination is described by ten reactions, and thus by ten different termination constants the number of which has been reduced to four basic ones ($k_{1,AAAA}$, $k_{1,BBBB}$, $k_{1,ABBA}$, $k_{1,BAAAB}$) by approximating the "mixed" termination constants by the geometric average from the termination constants of identical radicals¹⁰.

For the diffusion-controlled models (including that of Russo and Munari), k_{10} is assumed to be inversely proportional to the viscosity of the medium¹³.

The experiment yields the overall rate of copolymerization R_p or the change of conversion with time. If the loss of the initiator during the conversion can be neglected, integration of Eq. (1) gives

$$\frac{k_{p0}}{k_{t0}^{1/2}} = - \frac{\ln(1 - \psi')}{R_i^{1/2}t}, \quad (10)$$

where ψ' is the molar conversion of copolymerization (if changes in the composi-

tion of the monomer mixture are small, the molar conversion may be approximated by weight conversion) and t is time.

The kinetic factor $k_{po}/k_{io}^{1/2}$ may, also independently, be calculated from the determined molecular weight of the copolymer. If the transfer reactions may be neglected, then the relation of this kinetic factor to the number average molecular weight, M_n , is given by

$$\frac{k_{po}}{k_{io}^{1/2}} = \left(1 - \frac{\varrho}{2}\right) \frac{M_n R_i^{1/2}}{M_0 [M]}, \quad (11)$$

where M_0 is the average molecular weight of the monomer unit, $[M]$ is the overall molar concentration of monomers and ϱ is the fraction of radicals terminated by recombination. The relation between $k_{po}/k_{io}^{1/2}$ and the weight average molecular weight, M_w , ensues from the polydispersity index, M_w/M_n , which is 2 or 1.5 for termination by disproportionation or recombination, respectively.

If the copolymerization conversion and the molecular weight of the copolymer are determined and a certain mode of termination is known or assumed, it is possible, by combining Eqs (10) and (11), to calculate the initiation efficiency f or the product $k_d f$, in addition to $k_{po}/k_{io}^{1/2}$.

This study has as its objective to determine basic characteristics of the statistical copolymerization of styrene with 2-methoxyethyl methacrylate and dependencies of the rate of copolymerization on the composition of monomer mixture. The experimental data are analyzed considering potential changes in the initiation efficiency and compared with predictions of various termination models.

EXPERIMENTAL

Copolymerization of Styrene with 2-Methoxyethyl Methacrylate

Styrene was a commercial product of Lachema, Czechoslovakia. 2-Methoxyethyl methacrylate was prepared¹⁴ by the esterification of methacrylic acid with 2-methoxyethanol (methyl cellosolve). Both monomers were redistilled on a laboratory column, and their purity (99.6 and 99.9 wt.%, respectively) was checked by gas chromatography. Initiator, azobisisobutyronitrile, was recrystallized twice from methanol. Benzene and some solvents of reagent grade quality (Lachema, Czechoslovakia) were checked for purity and then used without further treatment.

The copolymerizations were carried out in a 500 ml stirred glass reactor. 75 g of the mixture of monomers and most of benzene were introduced into the reactor and preheated to 60°C while at the same time a stream of nitrogen was passed through the mixture. In a separate part of the apparatus, a solution of the initiator in the small remainder of benzene was also freed from oxygen. Then, the solution of the initiator was added to the mixture of monomers, and timing began. The total amount of benzene was chosen so as to make its content 80 vol.%. The copolymerization was stopped by pouring the reaction mixture into a tenfold volume of hexane. After a quantitative isolation of the precipitated copolymer, the samples were dried *in vacuo* to constant weight at 60°C.

Characterization of Copolymers

The copolymer composition was determined by elemental analysis.

The weight average molecular weight M_w , of copolymers was determined by light scattering measurements from their solutions in butanone using a Sofica 42 000 apparatus. The refractive index increments, dn/dc , were calculated from the experimentally determined dependence

$$dn/dc = 0.108 + 0.110w \quad [\text{ml g}^{-1}] \quad (12)$$

(25°C, wavelength of light *in vacuo* 546 nm), where w is the weight fraction of styrene in the copolymer.

The number average molecular weights, M_n , were determined osmotically in butanone solutions with a Mechrolab membrane osmometer.

RESULTS AND DISCUSSION

The copolymerization time, the initial initiator concentration and the volume dilution of the mixture of monomers with benzene were optimized so that *a*) change of the initiator concentration with time could be neglected (*i.e.* decomposition below 10%); *b*) copolymerization time would be sufficiently long to neglect the effect of the initial nonstationary period of the copolymerization (heating of the reaction mixture, *etc.*); *c*) conversion of copolymerization would be in most cases below 5 wt.%; *d*) molecular weights could be determined with sufficient accuracy by light scattering and/or osmotically (*i.e.*, M_w approximately in the range between $5 \cdot 10^4$ and $5 \cdot 10^5$); *e*) the volume dilution with solvent would be sufficiently high to minimize the variation in the nature of the polymerization medium with the changing composition of the monomer mixture, *etc.*

Benzene was chosen as solvent because the transfer constants for both styrene and substituted methacrylates are very low, and the transfer reactions can therefore be neglected in the first approximation.

Monomer Reactivity Ratios

The monomer reactivity ratios were determined by the extended method of Kelen and Tüdös¹⁵ (Fig. 1), *i.e.* by a procedure which takes into account also changes in the copolymer composition with conversion: $r_A = 0.41 \pm 0.05$ (styrene), $r_B = 0.48 \pm 0.02$ (2-methoxyethyl methacrylate). Neglecting the conversion changes in the copolymer composition, the same result is obtained within the limits of experimental error ($r_A = 0.40 \pm 0.03$ and $r_B = 0.46 \pm 0.04$ by the method of Kelen and Tüdös¹⁶, and also according to Fineman and Ross¹⁷). The copolymerization parameters for the present pair of monomers given by Yokota and coworkers¹⁸ are somewhat higher ($r_A = 0.50 \pm 0.01$, $r_B = 0.58 \pm 0.04$).

Determination of $k_{po}/k_{to}^{1/2}$

From the experimental results of both homopolymerizations and copolymerizations,

$k_{po}/k_{t1}^{1/2}$, and the initiation efficiency, f , were calculated by means of Eqs (10) and (11) (Table I). The recombination of polymer radicals is assumed to be the only type of termination operative. For polystyrene this assumption is satisfied¹⁹, similarly as for poly(2-methoxyethyl methacrylate) and all copolymers, judging by the M_w/M_n values (Table I) which mostly vary in the range 1.4–1.6 (the theoretical value corresponding to the termination by recombination being 1.5).

In the homopolymerization of styrene, a comparatively good agreement between $k_{po}/k_{t1}^{1/2} = 0.0192$ (Table I) and 0.0207 given in the classical literature²⁰ can be acknowledged. Also, the initiation efficiency $f = 0.45$ calculated on the assumption that the decomposition constant of initiator is²¹ $k_d = 15.2 \mu s^{-1}$ fits well the reported data^{21,22} ($f = 0.46$ and 0.42). For the homopolymerization of 2-methoxyethyl methacrylate, $k_{po}/k_{t1}^{1/2} = 0.127$ and $f = 0.71$ were obtained. In the literature¹⁸, only values determined at 30°C were found for this monomer, viz., $k_{po}/k_{t1}^{1/2} = 0.0816$ and $f = 0.63$.

Within a broad interval of composition, the initiation efficiency f is virtually independent of the composition of the monomer mixture and corresponds to that observed for styrene. The initiation efficiency increases only in the range of low styrene contents (Table I).

The dependence of $k_{po}/k_{t1}^{1/2}$ values on the composition of the monomer mixture has a convex shape, characteristic of the vast majority of copolymerizations, with an indication of a minimum at high styrene contents (Table I, Fig. 2). A similar trend is observed with the dependences of molecular weights M_n and M_w on the composition of the monomer mixture, as follows also from Eq. (11). In all cases the molecular weights are lower than the respective linear combination of the molecular weights of homopolymers.

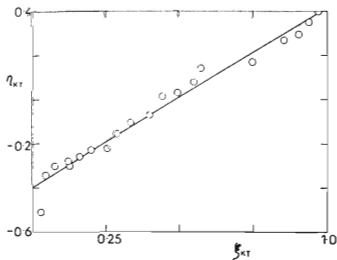


FIG. 1

Determination of the monomer reactivity ratios for styrene and 2-methoxyethyl methacrylate by the extended method of Kelen and Tüdös. Equation of the straight line: $\eta_{KT} = -0.400 + 0.814\xi_{KT}$, correlation coefficient $r = 0.985$. For meaning of symbols η_{KT} and ξ_{KT} cf. refs^{15,16}

TABLE I

Results of the copolymerization of styrene with 2-methoxyethyl methacrylate. y_A and x_A are mole fractions of styrene in the polymerization mixture and in the copolymer. $[M] = [A] + [B]$ is the total initial molar concentration of monomers, ψ is the weight conversion, R_p is the rate of copolymerization, M_n and M_w are the number and weight average molecular weight, respectively, f is the calculated initiation efficiency (for $k_d = 15.2 \mu s^{-1}$), and $k_{po}/k_{to}^{1/2}$ is the kinetic parameter. The AIBN concentration $[I] = 10^{-3} \text{ mol l}^{-1}$; 60°C ; 80 vol.% benzene. Time of copolymerization: 2 h for samples 1–4 and 3 h for the other samples

Exp	y_A	x_A	$[M]$ mol l^{-1}	ψ wt.-%	$R_p \cdot 10^6$ $\text{mol l}^{-1} \text{ s}^{-1}$	$M_n \cdot 10^{-5}$	$M_w \cdot 10^{-5}$	M_w/M_n	f	$k_{po}/k_{to}^{1/2} \cdot 10^2$
1	0.00	0.000	1.363	12.33	24.9	3.26	4.94	1.52	0.72	12.4
2	0.00	0.000	1.363	12.71	25.7	3.42	5.25	1.53	0.70	13.0
3	0.05	0.069	1.378	8.35	16.7		3.07		0.58	9.20
4	0.10	0.166	1.393	5.70	11.4	1.85	3.06	1.65	0.51	6.52
5	0.15	0.232	1.408	7.01	9.48		2.36		0.54	5.30
6	0.21	0.277	1.427	5.58	7.59		2.20		0.45	4.53
7	0.21	0.288	1.427	5.61	7.63	1.38	2.14	1.55	0.47	4.46
8	0.25	0.318	1.440	5.18	7.09		1.85		0.50	4.01
9	0.29	0.349	1.454	4.55	6.27	1.04	1.65	1.59	0.49	3.54
10	0.33	0.364	1.467	4.25	5.90		1.63		0.46	3.39
11	0.37	0.406	1.481	4.00	5.60	1.02	1.51	1.48	0.47	3.17
12	0.41	0.438	1.495	3.81	5.38		1.36		0.49	2.94
13	0.456	0.461	1.509	3.60	5.12	0.87	1.35	1.55	0.47	2.84
14	0.50	0.507	1.527	3.29	4.73	0.82	1.20	1.46	0.48	2.56
15	0.53	0.517	1.538	3.21	4.65		1.16		0.49	2.48
16	0.57	0.542	1.553	3.06	4.47	0.71	1.08	1.52	0.51	2.34
17	0.60	0.578	1.565	3.01	4.43		1.13		0.47	2.37
18	0.70	0.604	1.604	2.73	4.11		0.96		0.51	2.07
19	0.80	0.693	1.646	2.54	3.92	0.58	0.96	1.66	0.47	2.00
20	0.85	0.741	1.668	2.53	3.96		0.90		0.50	1.93
21	0.90	0.815	1.690	2.48	3.93	0.63	0.89	1.41	0.48	1.92
22	0.95	0.866	1.713	2.40	3.85		0.88		0.47	1.89
23	1.00	1.000	1.736	2.44	3.97	0.60	0.90	1.50	0.45	1.93
24	1.00	1.000	1.736	2.37	3.86	0.58	0.89	1.53	0.45	1.91
25	1.00	1.000	1.736	2.37	3.86		0.88		0.45	1.91

Correlation of Copolymerization Kinetic Data

The experimental data were correlated for the chemically controlled termination model using the experimentally obtained constants δ_A and δ_B . For all the variants of the diffusion-controlled termination model mentioned above, the rates of copolymerization relative with respect to the homopolymerization of styrene were compared,

$$\frac{R_p}{(R_p)_A} = \left(\frac{f\eta k_{iAA}}{f_A \eta_A k_{i0}} \right)^{1/2} \frac{r_A y_A^2 + 2y_A y_B + r_B y_B^2}{r_A y_A + r_B y_B k_t \delta_B / \delta_A} \frac{[M]}{[M]_A}; \quad (13)$$

η is the viscosity of the copolymerization mixture and $K_t = (k_{iAA}/k_{iBB})^{1/2}$ is the square root of the ratio of termination constants for homopolymerizations. Index A denotes (except y_A) quantities related to the homopolymerization of styrene.

Correlation by means of Eq. (13) has the advantage that the absolute values of k_{iAA} and k_{iBB} can be replaced by the ratio, K_t . Due to the lack of data on the termination constant for 2-methoxyethyl methacrylate, K_t has to be regarded as an adjustable parameter. For the cross-termination parameters which appear in Eqs (8), (9) it is assumed that $k_{iAB} = 2(k_{iAA}k_{iBB})^{1/2}$. All the models compared include then a single adjustable parameter.

A certain problem presents the knowledge of the viscosity of the copolymerization mixture, η , which depends on the composition of the monomer mixture, and especially on the conversion of copolymerization and on the molecular weight of the forming copolymer. The viscosity was estimated by simple calculation based on the theory of viscosity of dilute solutions; the parameters of the Mark-Houwink equation and the Huggins constant were supposed to assume values usual for polymers in thermodynamically good solvents and to be independent of the copolymer composition in the first approximation. The value of η/η_A varied between approx. 2.5 for the homopolymerization of 2-methoxyethyl methacrylate and, by virtue of definition,

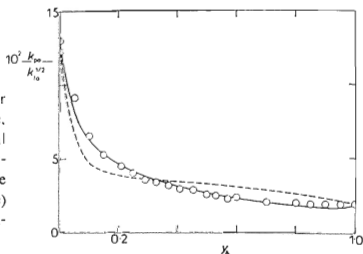


FIG. 2

Dependence of the kinetic parameter $k_{po}/k_{i0}^{1/2}$ on the mole fraction of styrene, y_A , in the monomer mixture for the statistical copolymerization of styrene with 2-methoxyethyl methacrylate and comparison with the prediction of the chemically (broken line) and diffusion (solid line) controlled termination model

1.0 for styrene. In the correlation, this viscosity factor was neglected, *i.e.*, we put $\eta/\eta_A = 1$ for all compositions of the monomer mixture. The results show that the inclusion of the viscometric correction slightly improves the correlation, the standard deviations becoming somewhat lower (Table II). Understandably, values of the adjustable parameter K_t are different in both cases.

The results also show that any variant of the diffusion-controlled termination model provides a markedly better fit between the calculated and experimental values than the chemically-controlled termination model (Table II, Fig. 2). This is in agreement with the findings collected in an extensive analysis of the reported data²³. The individual variants of the diffusion-controlled model appear to be almost equivalent (Table II) and the differences in the graphic presentation are insignificant. The relatively best results are obtained with the dyad model (Table II).

The calculation for the two-parameter model of Russo and Munari¹⁰ gives a result comparable with the one-parameter models. Similarly, the calculation by means of Eq. (8) with two adjustable parameters, K_t and k_{tAB}/k_{tAA} , provides virtually the same standard deviations as the one-parameter dyad model. The introduction of a second adjustable parameter in Eqs (8) and (9) does not lead to any important improvement. Thus, the diffusion-controlled termination model, even in its simple one-parameter variant, is able to describe satisfactorily data on the statistical copolymerization of styrene with 2-methoxyethyl methacrylate.

TABLE II
Correlation characteristics for the individual termination models of copolymer radicals using (I) and neglecting (II) the viscosity factor

Model	Equation	Standard deviation	$K_t \cdot 10^2$
Chemical control ^{2,3}	(3)	0.577	^a
Diffusion control: Atherton-North ¹¹	(7)	(I) 0.129 (II) 0.163	7.50 5.00
Chiang-Rudin ¹²	(8)	(I) 0.145 (II) 0.198	6.56 4.47
Dyad approximation	(9)	(I) 0.125 (II) 0.150	7.95 5.31

^a Cross-termination factor, $\Phi = 9.48$.

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