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

Calorimetric Method for the Investigation of Copolymerization Kinetics

S. I. Kuchanov[a]; M. Y. Gelfer[a]
[a] Polymer Chemistry Department, Moscow State University, Moscow, Russia

To cite this Article Kuchanov, S. I. and Gelfer, M. Y.(1993) 'Calorimetric Method for the Investigation of Copolymerization Kinetics', Journal of Macromolecular Science, Part A, 30: 8, 571 — 581

To link to this Article: DOI: 10.1080/10601329308009431

URL: http://dx.doi.org/10.1080/10601329308009431

J.M.S.—PURE APPL. CHEM., A30(8), pp. 571–581 (1993)

CALORIMETRIC METHOD FOR THE INVESTIGATION OF COPOLYMERIZATION KINETICS

S. I. KUCHANOV* and M. Y. GELFER

Polymer Chemistry Department
Moscow State University
Moscow 119899, Russia

ABSTRACT

A calorimetric method for measurement of the copolymerization rate over a wide range of conversions has been derived. The well-known methyl methacrylate–styrene system was used as the example to prove the efficiency of the approach proposed.

INTRODUCTION

Isothermal calorimetry is widely applied for the measurement of the homopolymerization rate [1, 2]. The main idea of this method is based on the simple relationships

$$W_T = H \times W_P, \qquad q = H \times p \tag{1}$$

According to these equations, the monomer consumption rate W_P is related to the rate of heat evolvement, W_T, by the constant factor H, which is equal to the molar enthalpy of polymerization. H is also related to the integral heat evolvement q and the molar monomer conversion p. Relationships (1) give an opportunity to draw kinetic curves using the experimental dependence of the quantity W_T on the reaction time t.

For m-component copolymerization, there are m^2 elementary reactions of chain propagation

$$\overline{\mathrm{M}}_i + \mathrm{M}_j \xrightarrow{k_{ij}} \overline{\mathrm{M}}_i\overline{\mathrm{M}}_j \qquad (i, j = 1, 2, \ldots, m) \qquad (r_{ij} = k_{ii}/k_{ij}) \tag{2}$$

Every such reaction is characterized by a particular molar enthalpy H_{ij} [3, 4], whose values, along with the probabilities of directed dyads $P\{\overline{M_i}\overline{M_j}\}$, enable determination of the effective value of the instantaneous copolymerization enthalpy H_{ef}:

$$W_T = H_{ef} \times W_p, \qquad H_{ef} = \sum_{i=1}^{m} \sum_{j=1}^{m} H_{ij} P\{\overline{M_i}\overline{M_j}\} \tag{3}$$

Molar fractions of dyads $P\{\overline{M_i}\overline{M_j}\}$ can be found either experimentally (for example, by NMR techniques [5; 6, p. 266]) or calculated theoretically in the framework of some kinetic model of copolymerization [6, pp. 39–66]. Such calculations were performed for binary [7, 8] and ternary [9] copolymerization under low conversions only, with the simplified kinetic model used for terpolymerization.

In the present work we propose an approach suitable for the investigation of the copolymerization of any number of monomers over a wide range of conversions. This approach allows the dependence of the copolymerization rate on conversion to be determined, provided that the rate of heat evolvement dependence on the time of the synthesis has been experimentally measured. Such an approach might prove to be a rather powerful tool for investigation of kinetics of radical copolymerization [10, 11]. Essentially, no information on elementary reactions of initiation and termination is required in the framework of the treatment proposed. We will first formulate the general algorithm and then demonstrate its application by using the methyl methacrylate–styrene system as an example. In conclusion, a similar approach for a dilatometric investigation of the copolymerization kinetics will be described.

GENERAL ALGORITHM

In order to extend the description of the process to the region of intermediate and high conversions, the following correlation

$$q = \langle H_{ef} \rangle \times p \tag{4}$$

should be used instead of Eq. (1), where $\langle H_{ef} \rangle$ stands for the average value of the molar enthalpy of the copolymerization

$$\langle H_{ef} \rangle \equiv \frac{1}{p} \int_0^p H_{ef}(p')dp' = \sum_{i=1}^{m} \sum_{j=1}^{m} H_{ij} \langle P\{\overline{M_i}\overline{M_j}\} \rangle \tag{5}$$

Here, the average fraction of dyads, $\langle P\{\overline{M_i}\overline{M_j}\} \rangle$, in the copolymer formed within the whole range of conversions preceding p equals, by definition,

$$\langle P\{\overline{M_i}\overline{M_j}\} \rangle \equiv \frac{1}{p} \int_0^p P\{\overline{M_i}\overline{M_j}\}dp' \qquad (i, j = 1, 2, \ldots, m) \tag{6}$$

Fractions of dyads (Eq. 6) can be calculated in the regular way within the framework of the chosen kinetic model. In particular, for the well-known terminal model, the sequence distribution is easy to describe by a simple Markov chain. In this case, instantaneous dyad fractions might be calculated by the equations [6, p. 75; 12]

$$P\{\overline{M_i}\overline{M_j}\} = \pi_i \nu_{ij}, \qquad \nu_{ij} = r_{ij}^{-1} x_j / \sum_{j=1}^{m} r_{ij}^{-1} x_j \tag{7}$$

where ν_{ij} are transition probabilities, which can be expressed according to Eq. (7) through the reactivity ratios r_{ij} and the monomer feed composition as parameters. The latter is determined by molar fractions $x_1, x_2, \ldots, x_i, \ldots, x_m$ of each monomer $M_1, M_2, \ldots, M_i, \ldots, M_m$ and values of reactivity ratios, which are tabulated for hundreds of monomer pairs [13, 14].

According to ordinary terminal model of copolymerization, the copolymer instantaneous composition is characterized by vector $\vec{X}$ with the components $X_1, X_2, \ldots, X_m$ equal to fractions of proper monomer units $M_1, M_2, \ldots, M_m$ in the copolymer. Then the vector of instantaneous composition of the copolymer coincides with the stationary vector $\vec{\pi}$ of the Markov chain, whose components π_i represent the solution of a set of linear equations [12]:

$$\sum_{i=1}^{m} \pi_i \nu_{ij} = \pi_j, \qquad \sum_{i=1}^{m} \pi_i = 1 \tag{8}$$

For binary and ternary copolymerization, this solution can be reduced respectively to the well-known Mayo-Lewis [15] and Alfrey-Goldfinger [16] equations for copolymer composition. When the number of components $m \geq 4$, it is possible to use the Walling-Briggs results [17] or an algorithm based on graph theory [18, 19]. In order to determine the dependence of the dyad fractions $<P\{\overline{M_iM_j}\}>$ on the conversion, Expressions (7) are to be completed by the dependence of the monomer feed composition $\vec{x}$ on p. Components x_i of vector $\vec{x}$ are calculated from the solution of the following equations [19]:

$$(1 - p)\frac{dx_i}{dp} = x_i - \pi_i(\vec{x}), \qquad x_i(0) = x_i^0 \qquad (i = 1, 2, \ldots, m) \tag{9}$$

Therefore, Eqs. (5)-(7) allow one to find the dependence of $<H_{ef}>$ on the conversion p for the copolymerization of any number of monomers. So, in order to plot the kinetic curve $W_p(p)$ by using the calorimetric curve $W_T(t)$, the following procedure should be used:

1. Integrate the experimental curve $W_T(t)$ to replot W_T versus q, i.e., to draw the function $W_T = \omega(q)$.
2. Calculate the dependence of H_{ef} and $<H_{ef}>$ on p to plot the theoretical curve $q(p)$.
3. Put the latter dependence into $\omega(q)$ to determine the dependence of W_T on p.
4. Use Relation (3) to draw the kinetic curve $W_P(p)$.

To apply this algorithm, one is supposed to know values of such parameters as the reactivity ratios r_{ij} for each monomer pair, molar enthalpy of the homopolymerization for each of the m monomers, and the heat H_{ij} of the alternating copolymerization for all $m(m - 1)$ monomer pairs. If the direct measurement of any H_{ij} is hampered, it can be found by using the experimental data on the dependence of the effective heat of the copolymerization H_{ef} on the proper fraction of heterodyads $P\{\overline{M_iM_j}\}$. It is essential in this experiment that H_{ef} be measured only under low conversions when its instantaneous and average values almost coincide.

BINARY COPOLYMERIZATION

In this case the general formulas look especially simple:

$$H_{ef} = H_{11}P\{\overline{\mathrm{M}}_1\overline{\mathrm{M}}_1\} + H_{22}P\{\overline{\mathrm{M}}_2\overline{\mathrm{M}}_2\} + (1/2)(H_{12} + H_{21})P(\overline{\mathrm{M}}_1\overline{\mathrm{M}}_2) \tag{10}$$

$$P\{\overline{\mathrm{M}}_1\overline{\mathrm{M}}_1\} = \frac{r_{12}x_1^2}{x_1(r_{12}x_1 + x_2) + x_2(r_{21}x_2 + x_1)}$$

$$P\{\overline{\mathrm{M}}_2\overline{\mathrm{M}}_2\} = \frac{r_{21}x_2^2}{x_2(r_{21}x_2 + x_1) + x_1(r_{12}x_1 + x_2)}$$

$$P\{\overline{\mathrm{M}}_1\overline{\mathrm{M}}_2\} = P\{\overline{\mathrm{M}}_2\overline{\mathrm{M}}_1\} = \frac{x_1x_2}{x_2(r_{21}x_2 + x_1) + x_1(r_{12}x_1 + x_2)}$$

$$P(\overline{\mathrm{M}}_1\overline{\mathrm{M}}_2) = 2P\{\overline{\mathrm{M}}_1\overline{\mathrm{M}}_2\} = 2P\{\overline{\mathrm{M}}_2\overline{\mathrm{M}}_1\} \tag{11}$$

According to Expression (4), the value of H_{ef} is equal to the slope of the curve $q(p)$ at point $p = 0$, thus H_{ef} can be found from data of experiments performed at low conversions. By determining H_{ef} for a number of initial monomer feed compositions x_1^0, one can calculate by means of Relationship (10) the enthalpy of alternating copolymerization $(1/2)(H_{12} + H_{21})$ proceeding from the slope of the curve, which corresponds to the dependence of $Y = H_{ef} - H_{11}P\{\overline{\mathrm{M}}_1\overline{\mathrm{M}}_1\} - H_{22}P\{\overline{\mathrm{M}}_2\overline{\mathrm{M}}_2\}$ on $P(\overline{\mathrm{M}}_1\overline{\mathrm{M}}_2)$. Expression (5) for $<H_{ef}>$ looks like Relationship (10), but instead of the instantaneous fraction of dyad $P(\overline{\mathrm{M}}_1\overline{\mathrm{M}}_2)$, the average value $<P(\overline{\mathrm{M}}_1,\overline{\mathrm{M}}_2)>$ is used.

EXPERIMENTAL

In order to examine experimentally the algorithm proposed, the thoroughly investigated system methyl methacrylate (MMA)–styrene (St) has been chosen. In the present work, all experiments were carried out in bulk at 60°C, and AIBN with a concentration equal to 0.3 g/L was used as the initiator in all experiments. The monomers were purified by the conventional method, and the purification quality was verified by ^{1}H NMR. AIBN was recrystallized from ethanol. The kinetics was investigated by isothermal calorimetry (calorimeter DAK 1A). A standard spheric dilatometer was used for the dilatometric investigations. To determine conversion, the copolymer samples were dissolved in benzene in the presence of the inhibitor TEMPO (1,2,6,6-tetramethyl-piperidyl-oxyl). Then the copolymer was reprecipitated into methanol. The copolymer composition was determined by ^{1}H-NMR techniques by the integration ratio of the peak at 7.5 ppm (phenyl group [5]) and the overall proton signal. NMR spectra were measured with a Bruker MSL 90 impulse spectrometer.

COPOLYMERIZATION OF METHYL METHACRYLATE WITH STYRENE

To apply the present approach, one has to be sure that the kinetic model chosen is valid over the whole range of conversions under investigation. As shown in Table 1, the system MMA–St obeys the terminal model with reactivity ratio values of $r_{12} \equiv r_1 = 0.46$ and $r_{21} \equiv r_2 = 0.52$ presented in a handbook [13].

TABLE 1. Dependence of the Calculated $<X_2^c>$ and Experimentally Determined $<X_2^e>$ Composition of Copolymer MMA + St on the Conversion p for the Bulk Copolymerization at T = 60°C and Initial Monomer Feed Composition $x_1^0 = 0.7$ (MMA), $x_2^0 = 0.3$ (St)

p	$<X_2^c>$	$<X_2^e>$
0.18	0.37	0.37
0.37	0.36	0.36
0.70	0.34	0.34
0.92	0.32	0.32

To determine the molar enthalpy of homopolymerization, the integral heat evolvement q was measured by the calorimetry technique under low conversions p, whose values were determined gravimetrically. Then H_{11} and H_{22} were calculated from the expression $H = q/p$ (Eq. 1). The molar enthalpy of alternating copolymerization, $\frac{1}{2}(H_{12} + H_{21})$, was found from the dependence of H_{ef} on the fraction of heterodyads in the copolymer. In order to measure H_{ef}, we recorded the initial part of the calorimetric curve (when the rate of the heat evolvement is approximately constant), then the integral heat evolvement and conversion (by gravimetry techniques) were found. Under low conversions ($p \leq 5\%$), the instantaneous value of the enthalpy of copolymerization almost coincides with the average one ($H_{ef} = <H_{ef}>$) and does not depend on the conversion. Therefore, H_{ef} can be calculated from the expression $H_{ef} = q/p$. We measured H_{ef} for a number of copolymer compositions, and then, by using H_{11} and H_{22} values (determined from our preliminary experiments), as well as fractions of dyads $P\{\overline{M_1M_1}\}$, $P\{\overline{M_2M_2}\}$, and $P(\overline{M_1M_2})$ [calculated from Formulas (11)], the dependence of Y on P $(\overline{M_1M_2})$ was plotted

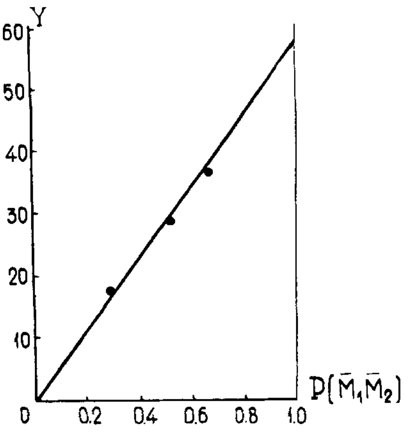

FIG. 1. Dependence of Y $[= H_{ef} - H_{11}P\{\overline{M_1M_1}\} - H_{22}P\{\overline{M_2M_2}\}$ (kJ/mol)] on the fraction of heterodyads $P(\overline{M_1M_2})$ for the copolymerization of methyl methacrylate (MMA) and styrene (St) at initial conversions.

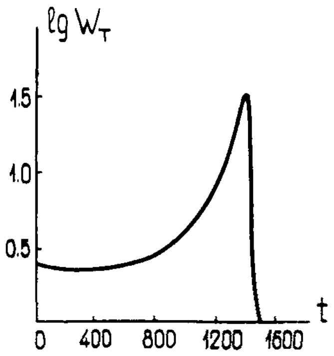

FIG. 2a. The dependence of the rate of heat evolvement W_T (J/L·s) on time t (min) for MMA + St copolymerization: x_1^0 (MMA) = 0.8, x_2^0 (St) = 0.2.

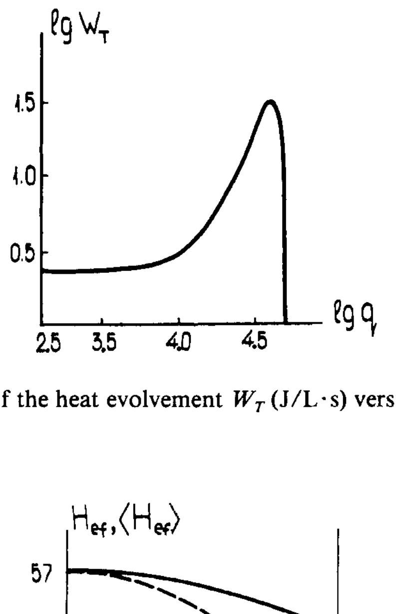

FIG. 2b. The rate of the heat evolvement W_T (J/L·s) versus the integral heat evolvement q (J/mol).

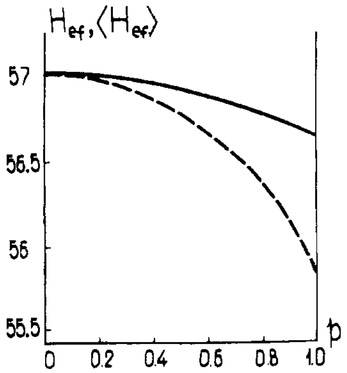

FIG. 2c. Calculated dependence of the instantaneous H_{ef} (dashed line) and averaged $<H_{ef}>$ (solid line) values of effective molar enthalpies of copolymerization (kJ/mol) on the conversion p.

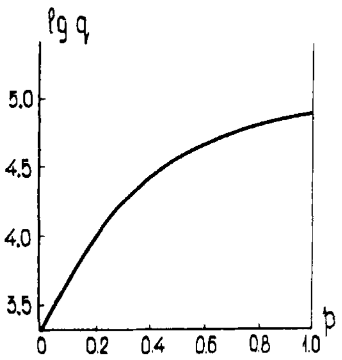

FIG. 2d. Calculated dependence of the integral heat evolvement q (J/mol) on the conversion p.

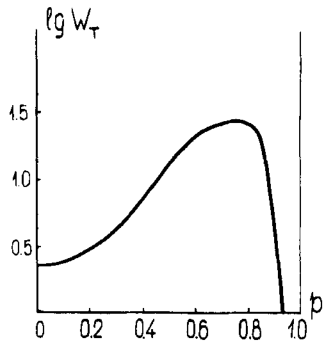

FIG. 2e. The rate of the heat evolvement W_T (J/L·s) versus the conversion p.

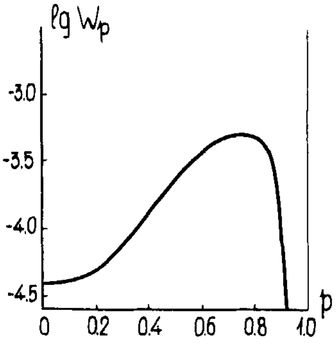

FIG. 2f. Kinetic curve for the MMA + St copolymerization.

(Fig. 1). By measuring the slope of this straight line, we found the enthalpy of alternating copolymerization: $(H_{12} + H_{21})/2 = 57.8$ kJ/mol. This value noticeably differs from that encountered in the literature [20], whereas values of H_{11} and H_{22} have been found to be very close to those obtained earlier [3, 20].

We used the aforementioned set of parameters to investigate the copolymerization kinetics for a number of initial monomer feed compositions [x_1^0 (MMA), x_2^0(St)] under a whole range of conversions. The application of the approach proposed is illustrated below in detail for this system with the initial composition $x_1^0 = 0.8$, $x_2^0 = 0.2$.

By numerical integration of the calorimetric curve (Fig. 2a), the curve $\omega_T(q)$, expressing the dependence of W_T on q, was plotted (Fig. 2b). Since the system obeys the terminal model under a whole range of conversions, values of H_{ef} as well as $<H_{ef}>$ were obtained from Eqs. (3), (5), (6), (7), (10), and (11) (Fig. 2c). Proceeding from the calculated dependence of $<H_{ef}>$ on p and using Relationship (4), the connection between q and p was determined and the curve $q(p)$ was plotted (Fig. 2d). Putting this dependence into $\omega_T(q)$, we determined the connection between W_T and p (Fig. 2e). The usage of the dependence $H_{ef}(p)$, presented in Fig. 2c, and the account of Formula (8) allowed us to plot the kinetic curve $W_P(p)$ (Fig. 2f). Kinetic curves analogous to the one described above for a series of initial monomer feed compositions are presented in Fig. 3. Values of the initial rates of copolymerization (Table 2) determined via the proposed algorithm conform rather well with published data [21, 22]. Gravimetric analysis of the MMA-St copolymerization has been carried out as the independent control. Results obtained by this technique convincingly support the calorimetric data (Fig. 4).

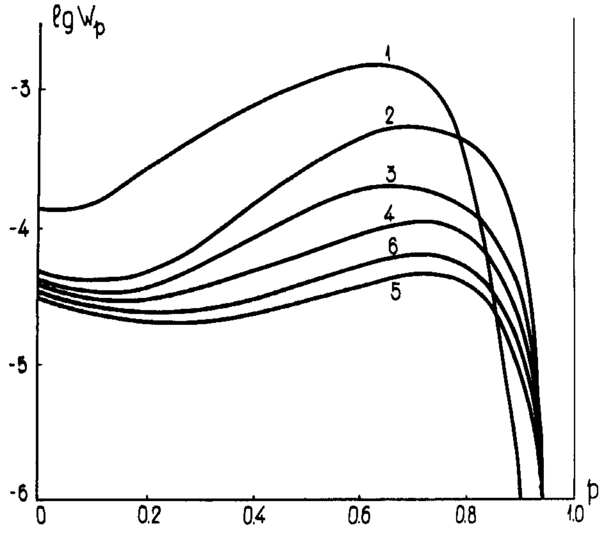

FIG. 3. Kinetic curves for the MMA + St copolymerization in the system x_1^0 (MMA) = (1) 1.00, (2) 0.80, (3) 0.70, (4) 0.48 (azeotrope composition), (5) 0.20, (6) 0.00.

TABLE 2. Dependence of Initial Rates of the Copolymerization in System MMA + St on the Monomer Feed Composition x_2^0(St)

	$W_p \times 10^5$ mol/L·s			
			Literature data	
x_2^0(St)	Calorimetry data	Dilatometry data	[21]	[22]
0.0	13.65	14.00	3.80	13.80
0.10	5.87	5.75	5.60	5.70
0.20	4.03	4.08	4.00	3.90
0.48	–	–	3.40	3.40
0.52	3.30	–	–	–
0.70	–	–	2.70	2.70
0.80	2.70	–	–	–
1.00	3.08	–	3.00	–

DILATOMETRIC METHOD

It should be mentioned that the approach described above can be applied to the dilatometric analysis of copolymerization kinetics over a wide range of conversions.

It is known that the dilatometric method of kinetic investigation of homopolymerization is based on the linear dependence of the conversion p on the relative change of the system volume $\Delta V/V$ (contraction):

$$p = \frac{1}{K} \times \frac{\Delta V}{V} \tag{12}$$

where K is the contraction coefficient.

In the case of copolymerization, coefficient K usually depends on the distribution of the dyads, which can change with conversion in the course of the process [23]. Therefore, the effective contraction coefficient K_{ef} is to be used instead of K.

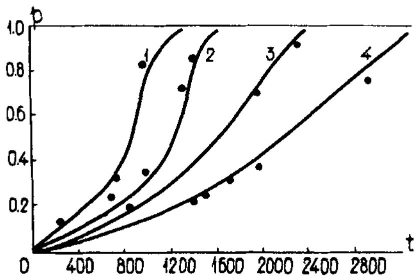

FIG. 4. Dependence of the conversion p on the time t (minutes). Points and solid lines indicate results obtained by gravimetry and calorimetry techniques, respectively. x_1^0 (MMA) = (1) 0.90, (2) 0.80, (3) 0.70, (4) 0.48 (azeotrope composition).

For the binary system, K can be expressed by a formula analogous to Relation (10):

$$K_{ef} = K_{11}P\{\overline{M}_1\overline{M}_1\} + K_{22}P\{\overline{M}_2\overline{M}_2\} + K_{12}P(\overline{M}_1\overline{M}_2) \tag{13}$$

Hereinafter, K_{11} and K_{22} will be contraction coefficients for the homopolymerization of each monomer M_1, M_2, while K_{12} will be the contraction coefficient for their alternating copolymerization. Equation (13) is applicable to investigation of copolymerization under low conversions when the drift of the monomer feed composition is negligibly small. The expression for $<K_{ef}>$ averaged over all conversions preceding a given p is to be used for the description of the process under high conversions:

$$<K_{ef}> = K_{11}<P\{\overline{M}_1\overline{M}_1\}> + K_{22}<P\{\overline{M}_2\overline{M}_2\}> + K_{12}<P(\overline{M}_1\overline{M}_2)> \tag{14}$$

To find the kinetic curve on the basis of the experimentally measured dependence of the contraction $\Delta V/V$ on the time t, one has to perform the following procedure:

1. Calculate the dependence of the contraction on conversion p by using Eqs. (12) and (14).
2. Set this dependence into the experimentally detemined $\Delta V/V$ versus t relationship to determine the dependence $p(t)$.
3. The kinetic curve $W_P(t)$ can be plotted by numerical differentiation of the curve $p(t)$. By using the obtained curves $p(t)$ and $W_P(t)$, one can calculate the dependence of the copolymerization rate on the conversion.

Within the present work we applied the dilatometry technique to investigate the copolymerization kinetics for a number of initial monomer feed compositions under low conversions, resorting to data on contraction coefficients ($K_{11} = 0.17$, $K_{22} = 0.267$, $K_{12} = 0.227$) presented in an earlier paper [23]. The values of the rate of copolymerization, measured by the dilatometry technique, are presented in Table 2.

CONCLUSION

Good agreement between the results obtained by different experimental methods convincingly proves the applicability of Eqs. (5) and (14) for effective enthalpy and contraction coefficients of copolymerization. In our opinion, this testifies to the possibility, in principle, of measuring the copolymerization kinetics with rather high accuracy. Thus, when the kinetic model of the chain propagation reaction is specified, the proposed algorithm allows one to investigate the copolymerization kinetics for various systems over a wide range of conversions with any number of reaction components. The practical realization of the approach introduced is implied in the application of a small number of parameters available from experimental data and having an explicit physical meaning. The validity of this approach was demonstrated for the MMA-St system by three experimental methods.

ACKNOWLEDGMENTS

We are pleased to thank Prof. V. A. Kabanov for useful discussions and Dr. B. A. Korolev for his careful assistance in the experimental work.

REFERENCES

[1] G. P. Gladyshev, *Radical Polymerization to High Conversion*, Akademie Verlag, Berlin, 1978 (in German).
[2] M. Stickler, "Experimental Techniques," in *Comprehensive Polymer Science*, Vol. 3 (G. Allen and J. C. Bevington, Eds.), Pergamon Press, Oxford, 1989, pp. 85-97.
[3] R. M. Joshi and B. J. Zwolinski, In *Vinyl Polymerization*, Vol. 1, Part 1 (G. E. Ham, Ed.), Dekker, New York, 1967, Chap. 8.
[4] H. Sawada, *Thermodynamics of Polymerization*, Dekker, New York, 1976, Chap. 9.
[5] F. A. Bovey, *High Resolution NMR of Macromolecules*, Academic Press, New York, 1972, Chap. 10.
[6] J. L. Koenig, *Chemical Microstructure of Polymer Chains*, Wiley-Interscience, New York, 1980.
[7] T. Alfrey and C. Lewis, *J. Polym. Sci., 4*, 221 (1949).
[8] H. Sawada, *Ibid., A2*, 3095 (1964).
[9] F. R. Mayo and F. M. Lewis, *J. Am. Chem. Soc., 9*, 1594 (1944).
[10] P. Wittmer, *Makromol. Chem., Suppl., 3*, 129 (1979).
[11] D. Braun and W. K. Czerwinski, "Rates of Copolymerization," in *Comprehensive Polymer Science*, Vol. 3 (G. Allen and J. C. Bevington, Eds.), Pergamon Press, Oxford, 1989, pp. 207-218.
[12] F. P. Price, *J. Chem. Phys., 36*, 209 (1962).
[13] H. Mark, B. I. Immergut, et al., in *Polymer Handbook* (J. Brandrup and E. H. Immergut, Eds.), Wiley-Interscience, New York, 1965.
[14] R. Greenley, *J. Macromol. Sci.—Chem., A14*, 445 (1980).
[15] F. R. Mayo and F. M. Lewis, *J. Am. Chem. Soc., 9*, 1594 (1944).
[16] T. Alfrey and J. Goldfinger, *J. Chem. Phys., 12*, 322 (1944).
[17] C. Walling and E. L. Briggs, *J. Am. Chem. Soc., 10*, 1774 (1945).
[18] S. I. Kuchanov, *Vysokomol. Soedin., B28*, 234 (1986).
[19] S. I. Kuchanov, *Adv. Polym. Sci., 103*, 1 (1992).
[20] M. Suzuki, H. Miyama, and S. Fujimoto, *J. Polym. Sci., 31*, 212 (1958).
[21] W. G. Barb, *Ibid., 11*, 117 (1953).
[22] J. C. Bevington, H. W. Melville, and R. P. Taylor, *Ibid., 14*, 463 (1954).
[23] W. Brawn and G. Disselhof, *Polymer, 18*, 963 (1977).

Received March 24, 1992
Revision received December 11, 1992