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### Kinetics of Radical Polymerization. XXIX. Kinetics of Initiation in the Polymerization of Ethyl Acrylate

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## **Kinetics of Radical Polymerization. XXIX. Kinetics of Initiation in the Polymerization of Ethyl Acrylate**

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### **ABSTRACT**

The rate of initiation has been investigated in the free-radical polymerization of ethyl acrylate at 50°C in two solvents, benzene and dimethylformamide. The rate constant of initiation and the rate constant of the decomposition of AIBN was determined by the inhibition method and nitrogen volumetry, respectively. The rate constant of initiation was found to be constant over the whole range of monomer concentration in benzene solutions, but it proved to depend on the concentration of monomer in dimethylformamide

solutions. The latter dependence is not linear. It was pointed out that the change in the rate constant of initiation is due to the solvent effect on the rate constant of decomposition of AIBN, because the factor of radical efficiency is practically constant over the whole range of monomer concentration. The observed relationship between the rate constant of initiation and the molar fraction of monomer was interpreted on the basis of the selective solvation of initiator molecules.

In kinetic studies of polymerization the solvent effect on the kinetics of initiation has seldom been investigated. Our recent results concerning this effect are disclosed in this paper.

The rate of initiation by an azo-type initiator is given as:

$$W_1 = 2k_1fx \quad (1)$$

where  $k_1$  is the rate constant of decomposition,  $x$  is the concentration of the initiator, and  $f$  is the initiation efficiency.

Early reports on free-radical polymerization initiated by azoisobutyronitrile (AIBN) usually assumed that the rate constant of initiation ( $2k_1f$ ) is independent of the composition of the reaction mixture, because the rate constant of the decomposition of AIBN was found to be the same in various solvents [1-3]. More detailed and accurate measurements proved, however, that its numerical value definitely changes in different solvents [4-9]. This solvent effect of the decomposition rate constant has not yet been successfully interpreted.

The rate constant of initiation is influenced also by the value of the initiation efficiency  $f$ . In solution, generally  $f < 1$ , owing to the primary recombination of cyanoisopropyl radicals, also known as the cage effect [10-13]. The numerical value of initiation efficiency may also be different in different solvents, as has been shown by Hammond and co-workers [12]. The solvent effect on the initiation efficiency is explained on the basis of the Noyes diffusion theory [14], which relates the probability of the recombination of the primary radicals to the viscosity of the solution. In practice, however, this interpretation does not apply for each system, presumably as a consequence of approximations used in the model [15].

Consequently, the value of initiation rate constant of a given polymerization system and its dependence on the monomer concentration cannot be predicted, but it has to be determined experimentally over the whole composition range used in the investigations.

More and more papers have been published concerning the solvent effect on the initiation kinetics of polymerization as in the homopolymerization of styrene (St) [6, 16, 21], methyl methacrylate (MMA) [17-19], cyclohexyl and cyclododecyl acrylates (CHA, CDA) [22] in solution. There have also been studies on the copolymerization of

several monomer pairs in bulk or in solution: St/diethyl maleate (DEM) [8], acrylonitrile/methyl acrylate (AN/MA) [23, 25], AN/bromophenyl acrylate (BPA) [24], and maleic anhydride with several electron-donating monomers [9].

Our present investigations have been focused on the effect of monomer concentration on the rate constant of initiation in the polymerization of ethyl acrylate in benzene and dimethylformamide solutions.

## EXPERIMENTAL

### Materials and Methods

The inhibitor was extracted from the monomer, ethyl acrylate (EA), Fluka pure grade, by 10% aqueous KOH solution. EA was neutralized by washing with distilled water, dried over anhydrous  $\text{CaCl}_2$ , and fractionated in reduced pressure ( $n_D^{20} = 1.4068$ ).

Benzene (Bz) and dimethylformamide (DMF) were reagent grade materials and were purified by standard methods [20, 26]. AIBN, Fluka pure grade, was purified as described earlier [20].

The initiation rate was determined by the inhibition method by using the stable free-radical inhibitor, triphenylverdazyl (TPV). The inhibitor was synthesized by the method of Kuhn and Trischmann [27] and purified by repeated crystallization from acetone-methanol mixture (mp 141-142°C). Rate measurements were carried out in sealed glass dilatometric tubes under atmosphere pressure of  $\text{N}_2$  at 50°C. Oxygen was previously removed from the samples by the usual procedure [20].

The rate constant of the decomposition of AIBN was determined by nitrogen volumetry [7]. Inhibitor ( $2 \times 10^{-2}$  mole/dm<sup>3</sup>) was added to the solutions to prevent polymerization during the measurements.

### Kinetic Studies

If the polymerization is inhibited by a stable free radical, the rate constant of initiation is related to the length of the inhibition period by the equation:

$$t_i = z_0 / 2k_1 f \bar{x} \quad (2)$$

where  $t_i$  is the length of the inhibition period,  $z_0$  is the initial concentration of inhibitor, and  $\bar{x}$  is the average concentration of initiator during the inhibition period.

In the inhibition kinetic investigations of more reactive monomers, besides its role as a radical trap, the stable free radical exhibited a

certain affinity towards the monomer as well, which manifested itself in an inhibitor-consuming side reaction and a decline in the  $t_i = f(z_0/\bar{x})$  function. If only this pseudounimolecular side reaction takes place in addition to the one-step inhibition reaction, the rate constant of initiation can be determined by using the following linear approximation [28, 20]:

$$\left(\frac{z_0}{x_0 t_i}\right)^{3/2} = (2k_1 f)^{3/2} \left(1 + 0.74 \frac{(2k'm - k_1)z_0}{2k_1 f x_0}\right) \quad (3)$$

where  $k'$  is the rate constant of the side reaction.

During the polymerization of ethyl acrylate inhibited by triphenylverdazyl, such a side reaction was observed between the stable free radical and the monomer. This side reaction is indicated by the slight decline in the  $t_i = f(z_0/\bar{x})$  function (Fig. 1 and Table 1). The mole fraction of the monomer is designated by  $x_{EA}$ . At lower monomer concentrations this side reaction is not detectable; in such cases the  $t_i = f(z_0/\bar{x})$  function is linear (Fig. 2 and Table 2).

Equation (3) was used in our investigations to determine the rate constant of initiation. A series of five or six experiments was performed at each monomer concentration. The method of evaluation is demonstrated for a characteristic series of experiments in Fig 3;

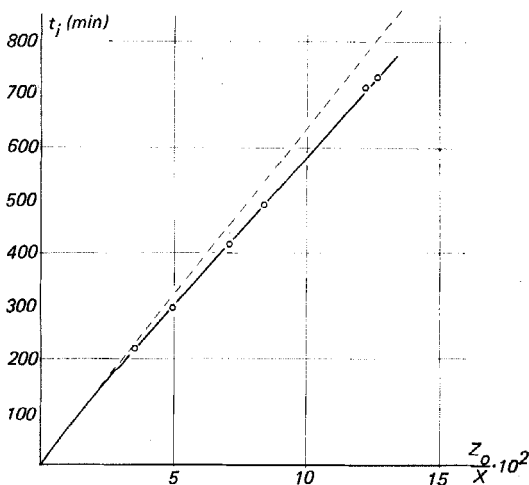


FIG. 1. Length of the inhibition period vs.  $z_0/\bar{x}$  ratio in the EA/AIBN/Bz polymerization system,  $x_{EA} = 0.9135$ .

TABLE 1. Inhibition Kinetic Data in the EA/AIBN/TPV Polymerization System at 50°C.<sup>a</sup>

| $\bar{x} \times 10^5$<br>(mole/dm <sup>3</sup> ) | $z_0 \times 10^6$<br>(mole/dm <sup>3</sup> ) | $(z_0/x_0 t_i)^{3/2}$<br>$\times 10^6$<br>(min <sup>-3/2</sup> ) | $t_i$<br>(min) | $2k_{1f} \times 10^4$<br>(min <sup>-1</sup> ) |
|--|--|--|----------------|---|
| 9.701  | 3.493  | 2.082  | 218            |   |
| 9.657  | 4.861  | 2.182  | 294            | 1.626   |
| 9.585  | 6.983  | 2.216  | 418            |   |
| 9.542  | 8.286  | 2.229  | 494            |   |
| 9.418  | 12.03  | 2.253  | 712            |   |
| 9.406  | 12.44  | 2.269  | 733            |   |

<sup>a</sup>  $m_{EA} = 8.225$  mole/dm<sup>3</sup>;  $x_{EA} = 0.9135$ ;  $x_0 = 9.829 \times 10^{-5}$  mole/dm<sup>3</sup>.

the corresponding data are presented in Table 1. Numerical values of the rate constant of initiation at different monomer concentrations are summarized in Tables 3 and 4.

The thermal decomposition of AIBN is a first-order unimolecular process [2], and its rate can be determined from the rate of N<sub>2</sub> evolution as the slope of the function

$$\ln [V_\infty / (V_\infty - V_t)] = f(t) \quad (4)$$

where  $V_t$  is the volume of N<sub>2</sub> evolved up to time  $t$  and  $V_\infty$  is the volume of N<sub>2</sub> evolved during the complete decomposition of AIBN in the sample.

## RESULTS

In the system EA/AIBN/Bz (Table 3) the rate constant of initiation is practically independent of the monomer concentration. The experimental data scatter around a mean value with a standard deviation of 4.9%. Its numerical value is  $2k_{1f} = 1.53 \times 10^{-4}$  min<sup>-1</sup>, which is in good agreement with the value [16] determined in pure benzene solution:  $2k_{1f} = 1.58 \times 10^{-4}$  min<sup>-1</sup>.

In the system EA/AIBN/DMF, as is demonstrated in Fig. 4, the numerical value of the rate constant of initiation shows a significant dependence on the molar fraction of the monomer in the mixture. This function is obviously not linear: decreasing the molar fraction

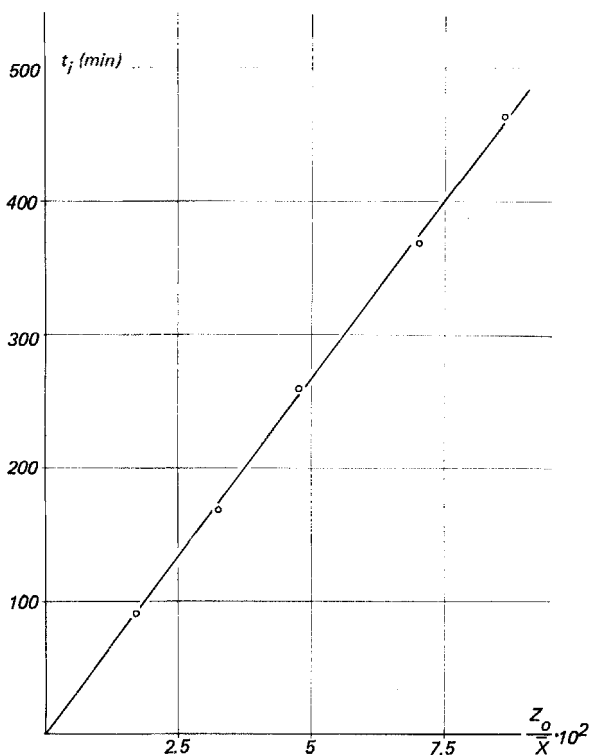


FIG. 2. Length of the inhibition period vs.  $z_0/\bar{x}$  ratio in the EA/AIBN/DMF polymerization system  $x_{EA} = 0.4456$ .

TABLE 2. Inhibition Kinetic Data in the EA/AIBN/TPV/DMF Polymerization System at 50°C<sup>a</sup>

| $\bar{x} \times 10^4$<br>(mole/dm <sup>3</sup> ) | $z_0 \times 10^5$<br>(mole/dm <sup>3</sup> ) | $t_i$<br>(min) | $2k_1 f \times 10^4$<br>(min <sup>-1</sup> ) |
|--|--|----------------|--|
| 8.788  | 1.506  | 91             |  |
| 8.738  | 2.844  | 169            | 1.867  |
| 8.679  | 4.137  | 261            |  |
| 8.611  | 6.056  | 369            |  |
| 8.552  | 7.371  | 464            |  |

<sup>a</sup>  $m_{EA} = 4.727$  mole/dm<sup>3</sup>;  $x_{EA} = 0.4456$ .

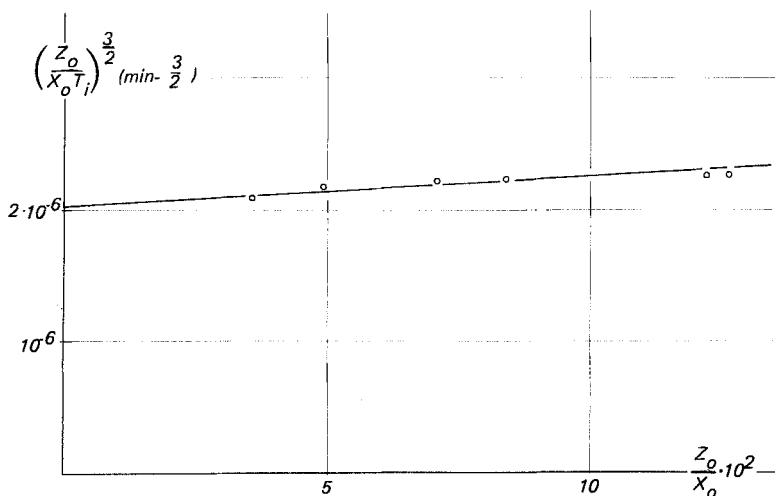


FIG. 3. Determination of the rate constant of initiation by Eq. (3) in the EA/AIBN/Bz polymerization system,  $x_{EA} = 0.9135$ .

TABLE 3. Rate Constant of Initiation in the EA/AIBN/Bz Polymerization System at Different Monomer Concentrations at 50°C

| $m_{EA}$<br>(mole/dm <sup>3</sup> ) | $x_{EA}$ | $2k_1 f \times 10^4$<br>(min <sup>-1</sup> ) |
|-------------------------------------|----------|--|
| 0                                   | 0        | 1.58 <sup>a</sup>                            |
| 2.135                               | 0.2057   | 1.607  |
| 3.702                               | 0.3695   | 1.443  |
| 4.707                               | 0.4805   | 1.50   |
| 5.637                               | 0.5881   | 1.420  |
| 6.734                               | 0.7206   | 1.498  |
| 6.730                               | 0.7206   | 1.590  |
| 7.598                               | 0.8309   | 1.579  |
| 8.225                               | 0.9135   | 1.626  |
| 8.860                               | 1.000    | 1.518  |

<sup>a</sup>Data of Tüdös [16].



TABLE 4. Rate Constant of Initiation in the EA/AIBN/DMF Polymerization System at 50°C

| $m_{EA}$<br>(mole/dm <sup>3</sup> ) | $\chi_{EA}$ | $2k_1f \times 10^4$<br>(min <sup>-1</sup> ) |
|-------------------------------------|-------------|---|
| 0.885                               | 0.0723      | 1.927                                       |
| 2.189                               | 0.1873      | 1.927                                       |
| 3.030                               | 0.2674      | 1.865                                       |
| 3.106                               | 0.2749      | 1.899                                       |
| 4.727                               | 0.4456      | 1.867                                       |
| 6.684                               | 0.6833      | 1.869                                       |
| 6.826                               | 0.7022      | 1.887                                       |
| 8.038                               | 0.8729      | 1.771                                       |
| 8.860                               | 1.000       | 1.530                                       |

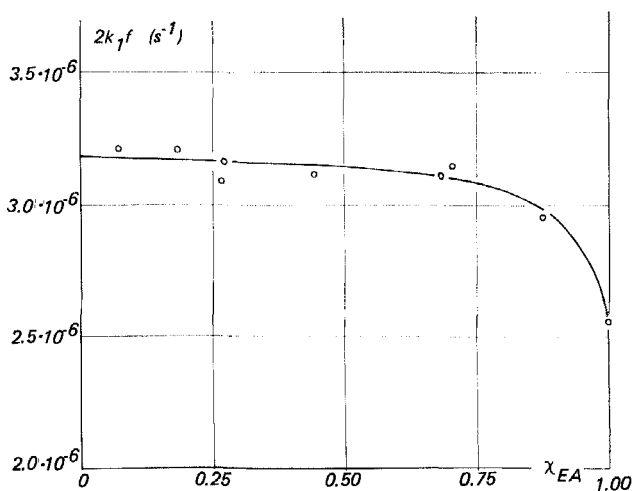


FIG. 4. Rate constant of initiation vs. molar fraction of monomer in the EA/AIBN/DMF polymerization system at 50°C.

TABLE 5. Rate Constant of Initiation, Decomposition Rate Constant of AIBN, and the Calculated Value of Initiation Efficiency at 50°C

| System      | $\chi_{EA}$ | $2k_{if} \times 10^4$<br>( $\text{min}^{-1}$ ) | $k_1 \times 10^4$<br>( $\text{min}^{-1}$ ) | f    |
|-------------|-------------|--|--|------|
| EA/AIBN/Bz  | 1.0         | 1.53   | 1.21                                       | 0.63 |
|             | 0.0         | 1.58   | 1.29 <sup>a</sup>                          | 0.61 |
| EA/AIBN/DMF | 1.00        | 1.53   | 1.21                                       | 0.63 |
|             | 0.86        | 1.77   | 1.34                                       | 0.66 |
|             | 0.74        | 1.86   | 1.56                                       | 0.60 |
|             | 0.00        | 1.91   | 1.49                                       | 0.64 |

<sup>a</sup>Data of Van Hook and Tobolsky [ 5 ].

of EA from 1 to 0.7 causes a sudden increase in  $2k_{if}$ , which becomes approximately constant in the region of molar fractions smaller than 0.7. The increase is about 25% between 0.7 and 1.

The rate constants of decomposition of AIBN in various monomer/solvent mixtures are presented in Table 5 as well as the initiation efficiency f calculated from the rate constant of decomposition and from the rate constant of initiation in the given mixture.

## DISCUSSION

Relatively few reports have been published on the free-radical polymerization of ethyl acrylate in solution.

Ratzsch and his co-workers studied the polymerization of ethyl acrylate in toluene solution, but since the polymerization was initiated by benzoyl peroxide, the kinetics of initiation was evidently different and therefore could not be compared to our findings [ 29 ].

Raghuram and Nandi [ 30 ] investigated the polymerization of ethyl acrylate in benzene solution at 50°C using AIBN as initiator. The rate constant of initiation was calculated only at one particular monomer concentration from the degree of polymerization and from the rate of polymerization (this latter was determined gravimetrically). There are two reasons why this value has to be considered only as a rough approximation: first their method, featuring gravimetry and molecular weight measurement by viscometry, is much less accurate than the inhibition method; additionally, during their investigations the polymerization started only after a considerable induction period obviously caused by some inhibiting impurity which changed the rate and the degree of polymerization as well.

The solvent effect on the kinetics of initiation by AIBN, however, has been studied in the homopolymerization and copolymerization, respectively, of several other monomers. The polymerization systems investigated so far can be divided into two groups with regard to their initiation kinetics.

In the first group, the rate constant of initiation in the mixture is a linear composition of the rate constants determined in the pure components, e. g., St/Bz or St/dioxane (Do) [16]. Those systems with rate constant of initiation constant over the whole composition range are considered limiting cases in this group, e. g., EA/Bz, AN/DMF [20], MA/DMF [31].

In the second group, the rate constant of initiation is not a linear composition of the rate constants in the pure components. The  $2k_{if} = f(\chi)$  function may exhibit different characteristics in this case: (a) the curve reaches a minimum value, e. g., DEM/St [8]; AN/BPA/DMF [24] (in copolymerization studies the overall concentration of monomer was kept constant and only the ratio of the two monomers was changed); (b) the curve reaches a maximum value, e. g., St/DMF [21]; (c) the curve reaches a plateau, a constant value in a certain region of composition, e. g., AN/MA/DMF and EA/DMF [23].

On observing the characteristic kinetic constants of initiation in the ethyl acrylate polymerization system ( $2k_{if}$ ,  $k_1$ ,  $f$ ) as a function of monomer concentration (Table 5), it is seen that the value of initiation efficiency shows a little scattering commensurable with the experimental error. The rate constant of AIBN decomposition ( $k_1$ ) and that of initiation ( $2k_{if}$ ) are practically constant in the system EA/AIBN/Bz, while in the system EA/AIBN/DMF both constants sharply decrease in the region  $\chi_{EA} = 0.7-1.0$ . Our experiments indicate that the change in the rate constant of initiation is caused by the change in the rate constant of AIBN decomposition.

The characteristic  $2k_{if} = f(\chi)$  function observed can be interpreted by the selective solvation of the initiator.

We assumed that the AIBN molecule exists in two forms in the solution: partly in "free", partly in solvated form. If the solvent mixture consists of two components and both are capable of solvating the initiator molecule, two equilibria should be taken into account:



where  $K$  and  $K'$  are stability constants characteristic of the solvation,

$$K = [XM]/x_m$$

and

$$K' = [XS]/x_s \quad (6)$$

X, M, and S are the symbols for initiator, monomer, and solvent; the corresponding concentrations are  $x$ ,  $m$ , and  $s$ .

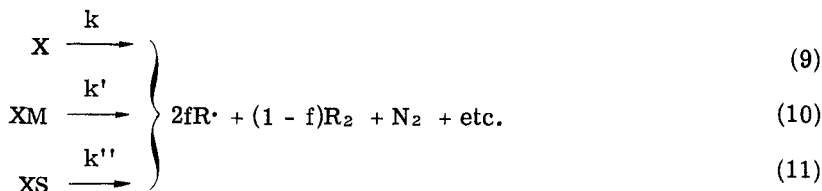
The overall concentration of initiator in the solution is:

$$x_0 = x + [XM] + [XS] \quad (7)$$

The overall rate of the decomposition of initiator in the solution:

$$-dx/dt = k_1 x_0 \quad (8)$$

is the sum of the decomposition rates of the different forms of AIBN:



$$(10)$$

$$(11)$$

In agreement with our experimental observations this mechanism assumes that the different solvated and nonsolvated forms of AIBN decompose with different rates ( $k$ ,  $k'$ ,  $k''$ ). This difference may be attributed to a slight change in either the activation energy or the frequency factor of  $k_1$ . Hence the overall rate of decomposition is:

$$-dx/dt = kx + k'[XM] + k''[XS] \quad (12)$$

The concentrations can be expressed in  $x_0$  from Eqs. (6) and (7):

$$-dx/dt = kx_0 [(1 + \alpha Km + \beta K's)/(1 + Km + K's)] \quad (13)$$

where

$$\alpha = k'/k$$

and

$$\beta = k''/k \quad (14)$$

On combining Eqs. (8) and (13) the expression for the solvent dependence of decomposition rate constant of AIBN is:

$$k_1 = k(1 + \alpha Km + \beta K's)/(1 + Km + k's) \quad (15)$$

A more general derivation of Eq. (15) in the case of solvate shells consisting of  $i$  monomer and  $j$  solvent molecules, respectively, results in the following equation:

$$k_1 = k \frac{1 + \alpha K m^i + \beta K' s^j}{1 + K m^i + k' s^j} \quad (15a)$$

Calculations performed on the EA/AIBN/DMF polymerization system according to Eq. (15a) showed that the initiator molecule is solvated by one monomer or solvent molecule only, in agreement with expression (15).

If both the monomer and the solvent molecules strongly solvate the initiator molecules the concentration of "free" AIBN is negligible and expression (15) simplifies to

$$k_1 = \frac{k' [1 + \gamma \kappa (s/m)]}{1 + \kappa (s/m)} \quad (16)$$

where

$$\gamma = k''/k$$

$$\kappa = K'/K \quad (17)$$

If  $\kappa = 1$ , that is, the solvation is equally strong with both components of the solution, the rate constant of decomposition is a linear composition of the two rate constants in the pure components.

If  $\gamma = 1$ , evidently,  $k_1 = k = k' = k''$ , and the value of the decomposition rate constant is independent of the composition.

In a general case, when both  $\kappa \neq 1$  and  $\gamma \neq 1$ , one of the components is a better solvent for the initiator and the  $k_1 = f(x)$  function is represented by a curve reaching a constant value characteristic for the better solvent.

The numerical value of  $k_1$  can be determined in the pure components

$$m = 0 \quad k_1(0) = k' \quad (18)$$

$$s = 0 \quad k_1(\infty) = k'' \quad (19)$$

and from Eqs. (18) and (19)

$$\gamma = k_1(\infty)/k_1(0) \quad (20)$$

$\kappa$  can also be calculated from experimental data on the basis of Eq. (16):

$$\kappa = [(k_1 - k')/(k'' - k_1)](m/s) \quad (21)$$

In the EA/AIBN/DMF polymerization system under investigation,  $\kappa = 15.6$  was found, which indicates that there is a considerably stronger solvation with DMF than with EA. (Calculations were performed using the experimental values of  $2k_1f$  since  $f$  is constant in this system).

The theoretical curve was calculated from Eq. (16) (solid line in Fig. 4), which is in good agreement with the experimental points.

This interpretation based on the selective solvation of initiator is applicable to  $k_1 = f(x)$  functions which are constant, linear, or saturation-type curves. Further considerations are necessary to interpret functions with a maximum or minimum value.

Consequently, investigations on the kinetics of initiation are of particular importance: on the one hand they may provide a better understanding of the mechanism and the kinetics of initiation; on the other hand by separating it from the solvent effect on chain propagation and chain termination they make a more accurate kinetic study of polymerization possible.

#### REFERENCES

- [1] C. G. Overberger, M. T. O'Shaughnessy, and H. Shalit, J. Am. Chem. Soc., **71**, 2661 (1949).
- [2] M. Talat-Erben and S. Bywater, J. Am. Chem. Soc., **77**, 3712 (1955).
- [3] M. S. Matheson, E. E. Auer, E. B. Bevilacqua, and E. J. Hart, J. Am. Chem. Soc., **73**, 1700 (1951).
- [4] J. W. Breitenbach and A. Schindler, Monatsh. Chem., **83**, 724 (1952).
- [5] J. P. Van Hook and A. V. Tobolsky, J. Am. Chem. Soc., **80**, 779 (1958).
- [6] H. G. Olivé and S. Olivé, Makromol. Chem., **58**, 188 (1962).
- [7] A. F. Moroni, Makromol. Chem., **105**, 43 (1967).
- [8] Zs. László-Hedvig, L. Sümegi, and F. Tüdös, Kinetics and Mechanism of Polyreactions, Vol. 3, 1969, p. 89.
- [9] M. Rätzsch, M. Arnold, and R. Hoyer, Mikrosymposium über Radikalische Polyreaktionen, Warszawa, 1978.
- [10] J. C. Bevington, H. W. Melville, and R. P. Taylor, J. Polym. Sci., **12**, 449 (1954).
- [11] G. S. Hammond, J. N. Sen, and Ch. E. Boozer, J. Am. Chem. Soc., **77**, 3244 (1955).

- [12] G. S. Hammond, C.-H. S. Wu, O. D. Trapp, J. Warkentin, and R. T. Keys, *J. Am. Chem. Soc.*, **82**, 5394 (1960).
- [13] R. M. Noyes, in *Encyclopedia of Polymer Science and Technology*, Vol. 2, Interscience-Wiley, New York-London-Sydney, 1965, p. 976.
- [14] R. M. Noyes, in *Progress in Chemical Kinetics*, Vol. 1, Pergamon Press, New York, 1961, p. 129.
- [15] O. Dobis, J. M. Pearson, and M. Szwarc, *J. Am. Chem. Soc.*, **90**, 278 (1968).
- [16] F. Tüdös, *MTA Kém. Tud. Oszt. Közl.*, **21**, 49, 403 (1964).
- [17] D. B. Anderson, G. M. Burnett, and A. C. Gowan, *J. Polym. Sci. A*, **1**, 1465 (1963).
- [18] G. M. Burnett, W. S. Dailey, and J. M. Pearson, *Trans Faraday Soc.*, **61**, 1216 (1965).
- [19] G. M. Burnett, G. G. Cameron, and M. M. Zafar, *Eur. Polym. J.*, **6**, 823 (1970).
- [20] I. Czajlik, T. Földes-Berezsnich, F. Tüdös, and S. Szakács, *Eur. Polym. J.*, **14**, 1059 (1980).
- [21] T. Földes-Berezsnich, M. Szesztay, E. Boros Gyevi, and F. Tüdös, *J. Polym. Sci., Polym. Chem. Ed.*, **18**, 1223 (1980).
- [22] D. Hiroshi and J. Kumantani, *Makromol. Chem.*, **176**, 2359 (1975).
- [23] I. Czajlik, T. Földes-Berezsnich, F. Tüdös, and E. Vétres, *Magyar Kémikusok Lapja*, **33**, 240 (1978).
- [24] A. Miller and J. Szafko, in *Mikrosymposium über Radikalische Polyreaktionen*, Warszawa, 1978.
- [25] J. Szafko, in *Mikrosymposium über Radikalische Polyreaktionen*, Warszawa, 1978.
- [26] A. Weissberger, Ed., *Organic Solvents (Technique of Organic Chemistry, Vol. 7)*, Interscience, New York, 1955.
- [27] R. Kuhn and H. Trischmann, *Monatsh. Chem.*, **95**, 457 (1964).
- [28] F. Tüdös, T. Földes-Berezsnich, and M. Azori, *Acta Chim. Hung.*, **24**, 91 (1960).
- [29] M. Rätzsch and I. Zschach, *Plaste u. Kautschuk*, **21**, 345 (1974).
- [30] P. V. T. Raghuram and U. S. Nandi, *J. Polym. Sci. A-1*, **5**, 2005 (1967).
- [31] I. Czajlik, T. Földes-Berezsnich, F. Tüdös, and E. Vértés, *Magy. Kem. Foly.*, **85**, 1 (1979); *Eur. Polym. J.*, in press.

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