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Solvation effect in the thermal decomposition of 2,2'-azoisobutyronitrile. The rate of initiation of the polymerization of methyl methacrylate in *N*,*N*-dimethylformamide

Summary — Induction time (t_i) and initiation rate ($2k_d \cdot f$) of methyl methacrylate (MMA) polymerization in *N*,*N*-dimethylformamide (DMF) at 60°C, initiated with 2,2'-azobisisobutyronitrile (AIBN), as functions of a monomer (M)/solvent (S) ratio [expressed as monomer mole fraction *i.e.* x_M = M/(M + S)] have been studied. It has been stated that ($2k_d \cdot f$) = f(x_M) dependence is linear in the whole range of x_M variability. This dependence has been compared with the dependence of initiator's thermal decomposition constant k_d as a function of x_M, which is curvilinear and shows a minimum in the range of x_M = 0.2—0.3. There was also determined the initiation efficiency — as a function of x_M, which results from formerly discussed dependence's *i.e.* ($2k_d \cdot f$) = f(x_M) and (k_d) = f(x_M), and shows — according to the expectations — characteristic maximum in the range x_M = 0.2—0.3. The courses of all three discussed dependence's have been interpreted on the base of a model of initiator solvation by monomer (IM) and solvent (SIS) as well as mixed solvation (MIS).

Key words: methyl methacrylate radical polymerization, thermal initiation, 2,2'-azoisobutyronitrile thermal decomposition, initiator solvation.

In the MMA/DMF/AIBN/60°C system [1—4] the solved forms of the initiator I exist, such as IM, MIS, and SIS (where I — initiator, M — monomer, S — solvent), which are characterized by the values K_M = 408.3, K_{MS} = 126.57, and K_{SS} = 8.17 (K_M, K_{MS} and K_{SS} are the stability constants of the respective solvated forms), k_M = $7.2 \cdot 10^{-4}$ min^{-1}, k_{MS} = $4.2 \cdot 10^{-4}$ min^{-1}, and k_{SS} = $6.45 \cdot 10^{-4}$ min^{-1} (k_M, k_{MS} and k_{SS} mean the rate constants of the thermal decomposition reactions of the respective solvated forms). Thereby the experimental relationship k_d = f(x_M) [x_M — mole fraction of methyl methacrylate in a monomer/solvent mixture (MMA/DMF)] show a distinct minimum occurring for x_M = 0.2—0.3. The minimum k_d = f(x_M) indicates a significant role of the form of mixed solvate [1].

In the light of the afore-mentioned facts the experimental determination of a dependence of the rate initiation ($2k_d \cdot f$) on the composition of monomer/solvent mixtures, *viz.* $(2k_d \cdot f)^{60}_{MMA}$ = f(x_M) within the complete range x_M (0.0—1.0) seems to be interesting.

THEORETICAL

The equation describing the thermal decomposition rate constant (k_d) of I (AIBN) as a function of the M (MMA)/S (DMF) mixture composition for the MMA/DMF/AIBN/60°C system is expressed as [4]:

$$k_d = \frac{K_M \cdot k_M \cdot \mathrm{M} + K_{MS} \cdot k_{MS} \cdot \mathrm{M} \cdot \mathrm{S} + K_{SS} \cdot k_{SS} \cdot \mathrm{S}^2}{K_M \cdot \mathrm{M} + K_{MS} \cdot \mathrm{M} \cdot \mathrm{S} + K_{SS} \cdot \mathrm{S}^2} =$$

$$= \frac{k_M \cdot \mathrm{M} + H_M \cdot k_{MS} \cdot \mathrm{M} \cdot \mathrm{S} + H'' \cdot k_{SS} \cdot \mathrm{S}^2}{\mathrm{M} + H_M \cdot \mathrm{M} \cdot \mathrm{S} + H'' \cdot \mathrm{S}^2} = \tag{1}$$

$$= k_M [\mathrm{IM}]_r + k_{MS} [\mathrm{MIS}]_r + k_{SS} [\mathrm{SIS}]_r$$

where:

$$[\mathrm{IM}]_r = \frac{\mathrm{M}}{\mathrm{M} + H_M \cdot \mathrm{M} \cdot \mathrm{S} + H'' \cdot \mathrm{S}^2} = \frac{x_M}{\mathrm{C}(x_M)} \tag{2}$$

$$[\mathrm{MIS}]_r = \frac{H_M \cdot \mathrm{M} \cdot \mathrm{S}}{\mathrm{M} + H_M \cdot \mathrm{M} \cdot \mathrm{S} + H'' \cdot \mathrm{S}^2} = \frac{G}{[(Q-P) \cdot x_M + P]} \cdot \frac{H_M \cdot x_M \cdot (1 - x_M)}{\mathrm{C}(x_M)} \tag{3}$$

$$[\mathrm{SIS}]_r = \frac{H''\cdot \mathrm{S}^2}{\mathrm{M}+H_M\cdot \mathrm{M}\cdot\mathrm{S}+H''\cdot\mathrm{S}^2} = \frac{G}{\left[(Q-P)\cdot x_M+P\right]}\cdot \cdot\frac{H''\cdot(1-x_M)^2}{\mathrm{C}(x_M)} \tag{4}$$

$$K_{MS}/K_M = H_M \tag{5}$$

$$K_{SS}/K_M = H'' \tag{6}$$

and

$$\mathrm{C}(x_M) = \left\{x_M + \frac{G}{\left[(Q-P)\cdot x_M+P\right]}\cdot\left[H_M\cdot x_M\cdot(1-x_M) + H''\cdot(1-x_M)^2\right]\right\} \tag{7}$$

In eqns. [(1)—(4)] x_M = M/(M + S), M and S mean concentrations (mol · dm^{-3}) of the monomer MMA and the solvent DMF, and

$$\mathrm{M} = \frac{G\cdot x_M}{\left[(Q-P)\cdot x_M+P\right]} \tag{8}$$

$$\mathrm{S} = \frac{G\cdot(1-x_M)}{\left[(Q-P)\cdot x_M+P\right]} \tag{9}$$

where: $P = M_S \cdot d_M$, $Q = M_M \cdot d_S$, *and* $G = d_M \cdot d_S$.

In the equations the densities (d_M, d_S) and the molecular weights (M_M, M_S) of monomer M and solvent S, respectively, were used.

On the basis of eqns. [(2)—(4)] and taking into account eqns. (8) and (9) at known values of H_M = 0.31 and H'' = 0.02 [2, 4] for the MMA/DMF/AIBN/60°C system (determined P, Q, and G), the dependences of the relative contents $[\mathrm{IM}]_r$, $[\mathrm{MIS}]_r$, $[\mathrm{SIS}]_r$, ($[\mathrm{IM}]_r + [\mathrm{MIS}]_r + [\mathrm{SIS}]_r = 1$) of the solvated forms occurring in this system on the monomer/solvent mixture composition were calculated *via* Marquardt's algorithm [5] and presented in Fig. 1. This figure shows even stronger relation as a function of the monomer mole fraction (x_M). A characteristic maximum for the mixed solvate MIS also occurs. The mutual ratio of the relative contents of the solvated forms ($[\mathrm{IM}]_r$:$[\mathrm{MIS}]_r$:$[\mathrm{SIS}]_r$) presented in Fig. 1 is also a function of x_M. In the system the solvated forms with the monomer exist primarily, that is, IM and MIS, whereas the SIS form occurs in a negligible amount. The courses of the relation [IM], [MIS], and [SIS] (mol · dm^{-3}) = f(x_M) can be obtained ([IM] + [MIS] + [SIS] = I_0, where I_0 is the overall initial concentration of the initiator).

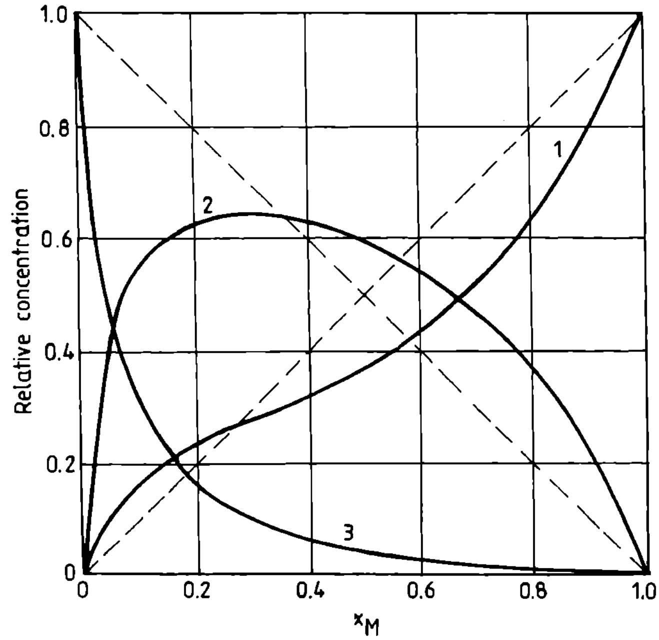

Fig. 1. The MMA/DMF/AIBN/60°C system. The relative concentrations of solvated forms $[IM]_r$ (curve 1), $[MIS]_r$ (curve 2) and $[SIS]_r$ (curve 3) according to eqs. (2)—(4) as a function of methyl methacrylate (M) mole fraction; $x_M = M/(M + S)$, $H_M = 0.31$, $H'' = 0.02$, $k_M = 7.2 \cdot 10^{-4}$ min^{-1}, $k_{MS} = 4.2 \cdot 10^{-4}$ min^{-1} and $k_{SS} = 6.45 \cdot 10^{-4}$ min^{-1}; $[IM]_r + [MIS]_r + [SIS]_r = 1$

Figure 1 reveals the significant role of the mixed solvate MIS, which resulted from the assumptions that the initiator is solvated by monomer M and solvent S [1]. These assumptions [1] for the MMA/DMF/AIBN/60°C system [2, 4] denote the replacement of the thermal decomposition of AIBN in the "free" form by the thermal decomposition of its respective solvated forms, that leads to the changes in the kinetic scheme of polymerization in a comparison with the classical kinetic scheme. The solution of a new kinetic scheme is an issue of a significant importance, for the determination of the initiation rate by the method of inhibited polymerization.

A new kinetic scheme of polymerization of the MMA/DMF/AIBN/60°C system is as follows:

— the decomposition of solvated forms of the initiator I and the rate of initiation:

$$[\mathrm{IM}] \xrightarrow{k_M} 2\mathrm{R}^{\cdot}_{0.M} + 2\mathrm{M} \xrightarrow{k_M\cdot f_M^0} 2\mathrm{R}^{\cdot}_{M}$$
$$V_{in.M} = 2k_M \cdot f_M^0 \cdot [\mathrm{IM}] \tag{10}$$

$$[\mathrm{MIS}] \xrightarrow{k_{MS}} 2\mathrm{R}^{\cdot}_{0,MS} + 2\mathrm{M} \xrightarrow{k_{MS}\cdot f_{MS}^0} 2\mathrm{R}^{\cdot}_{MS}$$
$$V_{in.MS} = 2k_{MS} \cdot f_{MS}^0 \cdot [\mathrm{MIS}] \tag{11}$$

$$[\mathrm{SIS}] \xrightarrow{k_{SS}} 2\mathrm{R}^{\cdot}_{0,SS} + 2\mathrm{B} \xrightarrow{k_{SS}\cdot f_{SS}^0} 2\mathrm{R}^{\cdot}_{SS}$$
$$V_{in.SS} = 2k_{SS} \cdot f_{SS}^0 \cdot [\mathrm{SIS}] \tag{12}$$

— inhibition:

$$\mathrm{R}^{\cdot}_M + \mathrm{BR} \rightarrow P \quad k_{t,M} \tag{13}$$

$$\mathrm{R}^{\cdot}_{MS} + \mathrm{BR} \rightarrow P \quad k_{t,MS} \tag{14}$$

$$\mathrm{R}^{\cdot}_{SS} + \mathrm{BR} \rightarrow P \quad k_{t,SS} \tag{15}$$

where: BR — *inhibitor (hero Bunfield's radical).*

— reinitiation and reinhibition by the BR:

$$\mathrm{BR} + \mathrm{M} \rightarrow \mathrm{R}^{\cdot} \quad k_{p,M} \tag{16}$$

$$\mathrm{BR} + \mathrm{R} \rightarrow \mathrm{P} \quad k_{tr,MR} \tag{17}$$

where: [IM] = $I_0 \cdot [\mathrm{IM}]_r$, [MIS] = $I_0 \cdot [\mathrm{MIS}]_r$ and [SIS] = $I_0 \cdot [\mathrm{SIS}]_r$.

Additionally, the equation set [(10)—(12)] corresponds to the well-known equation in the classical scheme:

$$\begin{gathered} I \xrightarrow{k_d} 2\mathrm{R}_0^{\bullet} \\ 2\mathrm{R}_0^{\bullet} + 2\mathrm{M} \xrightarrow{k_d \cdot f} 2\mathrm{R}^{\bullet} \end{gathered} \tag{18}$$

$$V_{in} = (2k_d \cdot f) \cdot \mathrm{I}_0 \tag{19}$$

The entire rate of initiation (resulting from the total initiator concentration) is equal to the initiation rate of the respective solvated forms:

$$\begin{gathered} (2k_d \cdot f)\mathrm{I}_0 = \left(2k_M \cdot f_M^0\right)\cdot[\mathrm{IM}] + \left(2k_{MS} \cdot f_{MS}^0\right)\cdot[\mathrm{MIS}] + \\ + \left(2k_{SS} \cdot f_{SS}^0\right)\cdot[\mathrm{SIS}] \end{gathered} \tag{20}$$

or

$$\begin{gathered} (2k_d \cdot f) = \left(2k_M \cdot f_M^0\right)\cdot[\mathrm{IM}]_r + \left(2k_{MS} \cdot f_{MS}^0\right)\cdot[\mathrm{MIS}]_r + \\ + \left(2k_{SS} \cdot f_{SS}^0\right)\cdot[\mathrm{SIS}]_r \end{gathered} \tag{21}$$

where: f_M^0, f_{MS}^0, f_{SS}^0 — *constant coefficients of the initiation efficiency (independent on the composition of a monomer/solvent mixture) of the respective solvated forms IM, MIS, and SIS.*

The application of the equation set [(10)—(17)] for the determination of equation describing the consumption of the inhibitor (BR) during the inhibited polymerization, leads to the induction period (t_i) given by [6, 7]:

$$t_i = \frac{1}{(2k_d \cdot f)} \log_e \left(1 + \alpha \frac{\mathrm{BR}_0}{\mathrm{I}_0}\right) \tag{22}$$

and the (relative) participation of the inhibitor (α) in the initiation:

$$\alpha = \frac{k_{p,M} \cdot \mathrm{M}_0}{k_d \cdot f} - \frac{1}{2f} \tag{23}$$

Various types of the solvated forms of initiator considered in the equation set [(10)—(17)] do not influence [eq. (22)] the method of determination of the initiation rate ($2k_d \cdot f$) *via* the measurements of the induction times [7].

The determination of ($2k_d \cdot f$) for the MMA/DMF/AIBN/60°C system, by the method of the inhibited polymerization, as a function of the mixture composition, M/S and the previously performed determinations of $k_d = \mathrm{f}(x_M)$, by the volumetric method of N_2 quantity, allow the computation of the global coefficient of initiation efficiency (f) from the dependence:

$$\frac{(2k_d \cdot f)_{\exp}}{(2k_d)_{\exp}} = f = \mathrm{f}\,(x_M) \tag{24}$$

The entire coefficient of the initiation efficiency (f) was determined from eq. (24), however, for the boundary conditions $x_M = 0$ and $x_M = 1$, expressed as:

$$\left.\frac{(2k_d \cdot f)}{2k_d}\right|_{x_M = 0} = f_{SS}^0 \tag{25}$$

and analogously:

$$\left.\frac{(2k_d \cdot f)}{2k_d}\right|_{x_M = 1} = f_M^0 \tag{26}$$

The value of ($2k_d \cdot f$) for $x_M = 0$ is obtained by a linear extrapolation of the relation $2k_d \cdot f = \mathrm{f}(x_M)$ to the zero concentration of the monomer M, whereas the k_d values in eq. (25) is the value determined in pure solvent (DMF). The boundary values for the relation $f = \mathrm{f}(x_M)$ are the approximations of the characteristic constants for the solvated forms, that is f_M^0 [eq. (26)], and f_{SS}^0 [eq. (25)] for the forms IM and SIS. The acceptance of these values enables the estimation of f_{MS}^0 on the basis of eqs. (20) or (21).

EXPERIMENTAL

Methyl methacrylate and *N,N*-dimethylformamide were purified by standard methods [7, 8]. The inhibitor Banfield's radical (BR) {*N*-[1,1-dimethyl-3-(*N*-oxidophenylimino)butyl]-*N*-phenylaminyl oxide} was synthesized using a method described in the literature [9] and subsequently modified [6]. The product of the synthesis was twice crystallized from *n*-octane.

The inhibited polymerizations for the MMA/DMF/AIBN/60°C system were carried out in dilatometers of 25 cm^3 capacity. Based on the dilatometric measurements (error of this method is equal to ±2% [10]) the conversion of monomer into polymer (p) after time (t) was calculated from the expression [11]:

$$p = \frac{\Delta V_M^T}{V_M^T \cdot L_M^T} \tag{27}$$

where: ΔV_M^T — *volumetric monomer contraction,* V_M^T — *volume of the monomer (M),* L_M^T — *coefficient of the volume contraction for the conversion p = 1 at measurement temperature.*

For the MMA/DMF/AIBN/60°C system L_M^T equals to 0.2353.

RESULTS AND DISCUSSION

The primary goal of the experimental part of this work is the determination of the rate of initiation, that is, a value $2k_d \cdot f$ in the entire range of variations of the monomer (MMA) concentration (x_M). The accurancy of the determined rate of initiation is equal to ±3%.

The initiation is the second elementary reaction of the polymerization, beside the decomposition of the initiator, which can be directly observed by the independent methods (maximum relative error 3% [12]). The initiation rate is convenient to be measured by the method of inhibited polymerization.

The Banfield's radical (BR) proved to be a very effective inhibitor of the MMA polymerization. In the presence of BR the induction periods are marked distinctly.

The rate of polymerization (a_1) and the induction times (t_i) were calculated from the following linear function:

$$\log_e\left(\frac{1}{1-p}\right)=a_1t+a_0\,;\quad t_i=-\frac{a_0}{a_1} \tag{28}$$

The polymerization rate of MMA, after the consumption of the inhibitor is characterized by the same value as that for the noninhibited polymerization. The induction times (t_i) determined for the inhibited polymerization of MMA for the selected values of the mixture composition which were expressed by the mole fraction of MMA (x_M) were compiled in Table 1. These results show that t_i is practically proportional to the inhibitor (BR) concentration. This means that the side reaction initiated by the Banfield's radical can be omitted, thereby, the rate of initiation $V_{in,M}$ by the AIBN initiator in the MMA/DMF/AIBN/60°C system is equal to the rate of the inhibitor consumption during the induction period, that is:

$$V_{in,M}=(2k_d\cdot f)\cdot \mathrm{I}_0=\frac{\mathrm{BR}_0}{t_i}\ \text{ or }\ (2k_d\cdot f)=\frac{1}{t_i}\cdot\frac{\mathrm{BR}_0}{\mathrm{I}_0} \tag{29}$$

Table 1. The induction times (t_i) of the inhibited polymerization of MMA by the Banfield's radical (BR) in MMA/DMF mixtures[*)]

No	$BR_0/AIBN_0 \cdot 10^2$	t_i, min for x_M:			
		0.686	0.813	0.886	1.000 (in bulk)
1	8.33	103	101	99	97
2	16.67	205	201	198	194
3	20.83	256	251	246	242
4	25.00	307	301	295	289
5	33.00	404	395	387	379
6	42.13	515	503	491	480
7	51.85	632	616	600	585
8	62.50	760	738	718	698
	$10^4 \cdot (2k_d \cdot f)$exp =	8.10	8.21	8.43	8.40
	$10^4 \cdot (2k_d \cdot f)$calc**) =	8.09	8.26	8.35	8.50

*) Initial concentration of AIBN₀ = 0.08 mol · dm^{-3}; x_M = M/(M+S).

**) Experimental equation $10^4 \cdot (2k_d \cdot f) = 7.22 + 1.28\,x_M$ (see text).

This means that eq. (29) replaces eq. (22) [6].

Values of the initiation rate ($2k_d \cdot f$) for x_M (Table 1) determined this way and other values in the whole range of x_M are presented in Fig. 2. The relation $2k_d \cdot f = f(x_M)$ is linear and may be described by empirical equation:

$$10^4 \cdot (2k_d \cdot f) = 1.28x_M + 7.22 \tag{30}$$

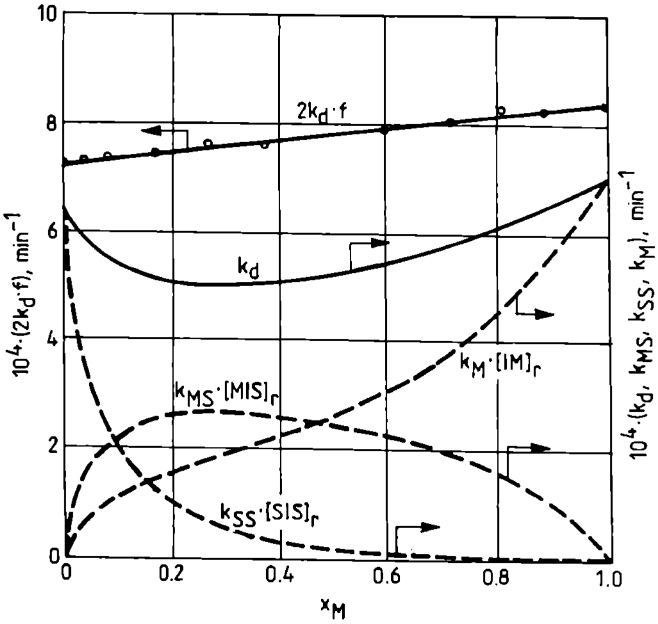

Fig. 2. The MMA/DMF/AIBN/60°C system. The initiation rate ($2k_d \cdot f$) according to eqs. (20) or (21), the decomposition rate constant (k_d) according to eq. (1), and the rate constants of decomposition of the initiator solvated forms according to eqs. (2)—(4) (dashed lines) as a function of methyl methacrylate (M) mole fraction (x_M) in MMA/DMF mixtures; for k_M, k_{MS}, k_{SS} see Fig. 1, o — experimental values of $2k_d \cdot f$

For $x_M = 0$ we obtain the value $2k_d \cdot f = 7.22 \cdot 10^{-4}$ min^{-1} (linearly extrapolated), whereas for $x_M = 1$ the value $2k_d \cdot f = 8.50 \cdot 10^{-4}$ min^{-1}.

The dependence $2k_d \cdot f = f(x_M)$ was compared with $k_d = f(x_M)$ (Fig. 2) and with the components $k_M[IM]_r$, $k_{MS}[MIS]_r$, and $k_{SS}[SIS]_r$, calculated for the constants $k_M = 7.2 \cdot 10^{-4}$ min^{-1}, $k_{MS} = 4.2 \cdot 10^{-4}$ min^{-1}, and $k_{SS} = 6.45 \cdot 10^{-4}$ min^{-1} according to eqs. (2)—(4) for $H_M = 0.31$ and $H'' = 0.02$. Figure 2 shows that for the linear dependence $2k_d \cdot f = f(x_M)$ and for $k_d = f(x_M)$ with a minimum in the region $x_M = 0.2$—0.3, the relation $f = f(x_M)$ should show a maximum for the same range of x_M, as illustrated in Fig. 3.

Figure 3 also shows that the relation $f = f(x_M)$ may be factorized into the partial dependences $f \cdot [MIM]_r$, $f \cdot [MIS]_r$, and $f \cdot [SIS]_r$ being also a function of x_M. The factorizing of the global value $f = f(x_M)$ into the partial ones was performed utilizing the fraction of the initiator solvated forms $[IM]_r$, $[MIS]_r$, and $[SIS]_r$ shown in Fig. 1.

The character of these dependences from Fig. 3 is corresponding to equation (24) and equation given below:

$$f=f\cdot[\mathrm{IM}]_r+f\cdot[\mathrm{MIS}]_r+f\cdot[\mathrm{SIS}]_r=\frac{(2k_d\cdot f)_{\exp}}{(2k_d)_{\exp}} \tag{31}$$

However, if equation (31) is fulfilled in the form (32):

$$f=f_M^0\cdot[\mathrm{IM}]_r+f_{MS}^0\cdot[\mathrm{MIS}]_r+f_{SS}^0\cdot[\mathrm{SIS}]_r \tag{32}$$

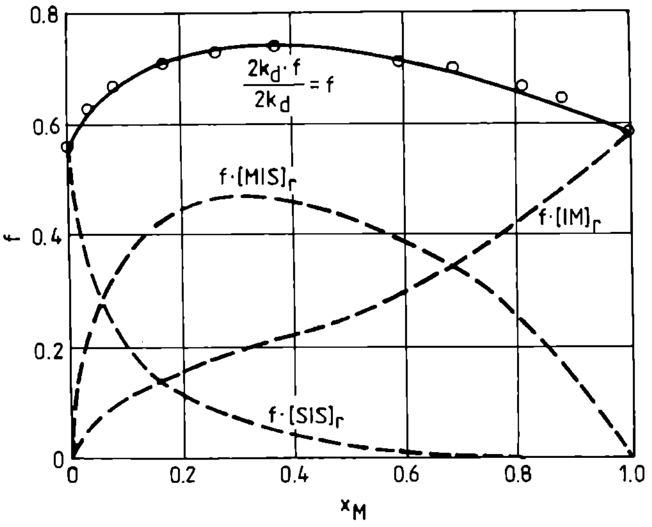

Fig. 3. The MMA/DMF/AIBN/60°C system. The global initiation efficiency coefficient (f) according to eq. (24) and the contribution of the partial initiation efficiency coefficients of the initiator solvated forms according to eq. (31) as a function of the methyl methacrylate (M) mole fraction (x_M) in MMA/DMF mixtures; for k_M, k_{MS}, k_{SS} see Fig. 1, ○ *— experimental values of f*

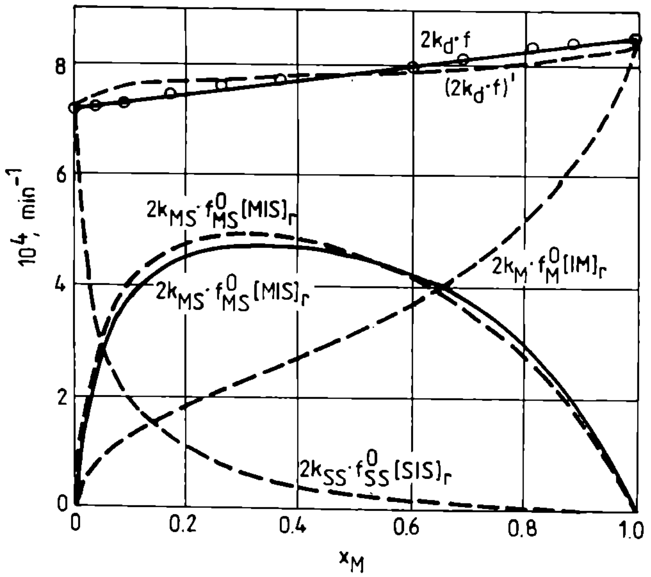

Fig. 4. The MMA/DMF/AIBN/60°C system. The initiation rate $(2k_d \cdot f)_{exp}$ (solid line) and the initiation rate $(2k_d \cdot f)'$ (dashed line) according to eq. (21) for f^0_M = 0.58, f^0_{SS} = 0.56, f^0_{MS} = 0.84—0.99 and f^0_M = 0.58, f^0_{SS} = 0.56, and f^0_{MS} equal average values 0.9023, respectively (Table 2); ○ *— experimental values of $2k_d \cdot f$*

then eq. (21) as resulting from the equation set (10)—(17) is valid.

The constant values f^0_M and f^0_{SS} were calculated from the boundary conditions:

$$\left.\frac{(2k_d \cdot f)_{\text{exp}}}{(2k_d)_{\text{exp}}}\right|_{x_M=0} = f^0_{SS} = 0.56 \tag{33}$$

$$\left.\frac{(2k_d \cdot f)_{\text{exp}}}{(2k_d)_{\text{exp}}}\right|_{x_M=1} = f^0_M = 0.58 \tag{34}$$

For f^0_{SS} = 0.56 and f^0_M = 0.58, the latter one f^0_{MS} was calculated from eq. (21) and given in Table 2.

Equation (21) was presented in Fig. 4 in the two alternative versions, which differ with the values of f^0_{MS}:

$$(2k_d \cdot f)_{\text{exp}} = 2k_M \cdot f^0_M [\text{IM}]_r + 2k_{MS} \cdot f^0_{MS} [\text{MIS}]_r + \\ + 2k_{SS} \cdot f^0_{SS} [\text{SIS}]_r \tag{35}$$

$$(2k_d \cdot f)' = 2k_M \cdot f^0_M [\text{IM}]_r + 2k_{MS} \cdot f^0_{MS} [\text{MIS}]_r + \\ + 2k_{SS} \cdot f^0_{SS} [\text{SIS}]_r \tag{36}$$

Equation (35) contains changing values (0.84—0.99) of f^0_{MS} (Table 2) and eq. (36) contains a constant, average value f^0_{MS} given in Table 2, but the values f^0_M = 0.58, and f^0_{SS} = 0.56 are the same in both equations (35) and (36). The difference between these dependences is small, and it does not exceed the accuracy of the determination of $2k_d \cdot f$. Therefore, it can be concluded that the global initiation rate of the system consists of the initiation rate of the respective solvated forms, thereby the equation set (10)—(17) was confirmed. We obtain the confirmation of the eq. set (10)—(17) in spite of using the preliminary evaluated values f^0_{MS} and f^0_{SS}.

CONCLUSION

The adoption of solvation of AIBN by the components of the mixture [1] in the system MMA/DMF/AIBN/60°C allow to propose the kinetic scheme, in which the sum of the partial initiation rates of the solvated forms determines the entire initiation rate. The partial initiation rates are determined for the system by the characteristic thermal decomposition rate constants of the solvated forms, their relative concentrations and

Table 2. Determination of the initiation efficiency coefficient (f^0_{MS}) for solvated form MIS of initiator as function of the MMA mole fraction (x_M) in MMA/DMF mixtures

x_M	0.000	0.042	0.084	0.174	0.269	0.371	0.597	0.686	0.813	0.886	1.000
f^0_{MS} *)	—	0.84	0.84	0.86	0.87	0.88	0.92	0.93	0.96	0.99	—

*) From eq. (21) for $(2k_d \cdot f)_{\text{exp}}$, f^0_M = 0.58, f^0_{SS} = 0.56, $k_M = 7.2 \cdot 10^{-4}\ \text{min}^{-1}$, $k_{MS} = 4.2 \cdot 10^{-4}\ \text{min}^{-1}$, $k_{SS} = 6.45 \cdot 10^{-4}\ \text{min}^{-1}$, $[\text{IM}]_r$, $[\text{MIS}]_r$, $[\text{SIS}]_r$ *acc.* eqs. (2)—(4); the average of values f^0_{MS} = 0.902.

the characteristic constants of the initiation efficiency (in the latter case with accuracy of their estimation).

The problem of the assessment of the individual initiation efficiency coefficients is similar to the determination of the individual thermal decomposition rate constants of the solvated forms, which was the subject of works [2, 4].

However, the acceptance of the initially estimated values of the initiation efficiency coefficients of the solvated forms let explain the course of $(2k_d \cdot f)_{exp} = f(x_M)$, and respectively $f = f(x_M)$ of the relation with a distinct maximum in terms of solvation of the initiator by monomer and solvent. This enables the observation of the polymerization kinetics in the system MMA/DMF/AIBN/60°C based on the equation set (10)—(17).

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