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Thermal decomposition of 2, 2′-azobis[2-methyl-ω-hydroxy-oligo(oxyethylene)propionate] in the acrylonitrile/*N*, *N*-dimethylformamide system

RAPID COMMUNICATION

Summary — The thermal decomposition (333 K) of initiator 2,2′-azobis[2-methyl-ω-hydroxyoligo(oxyethylene)propionate] [AIB-OOE(400)] in *N,N*-dimethylformamide (DMF), in acrylonitrile (AN) and in the mixture DMF/AN with the composition x_{AN} = 0.52 and 0.87 (x_{AN} — the mole fraction of acrylonitrile) was studied by volumetric method. A priority of the experimental determination of the order of decomposition reaction in relation to the initiator was established. It has been found, that the differential kinetic equations (7) and (9) can be used for this purpose. After the determination of the order equal to 1 for all solutions, the kinetic constant $k_d^{(I)}$ was determined from the integral equation (15). The differential equations (8) and (10) cannot be used for this purpose ($k_d^I \neq k_d^{II}$). The method used allows to avoid diversities of meaning, occurring in the literature, in determination of the reaction order and thermal decomposition rate constant for the azo-initiators.

Key words: thermal decomposition, azo-initiators, decomposition rate constant, order of azo-initiators decomposition reaction.

Technology of polymer manufacture *via* the radical polymerization requires besides the determination of the substrate and product properties, detail recognition of the process, which can comprise the basis for its modification or control. One of the posibilities of process modification is the application of new initiators *e.g.* azo-initiators or macro-azo-initiators [1—3] which varies both the process [2, 4] as well as the product properties *e.g.* polyacrylonitrile [5].

In a previous work [4] it was found that the azo-initiator 2, 2′-azobis[2-methyl-ω-hydroxyoligo(oxyethylene)propionate] causes the kinetic anomalies of polymerization of acrylonitrile in the solvent *N,N*-dimethylformamide. The reason of anomalies may be each elementary reaction of the chain polymerization process. The aim of this work is to explain the reasons of anomalies or the kinetic correctness in the important elementary reaction of decomposition of azo-initiator in a varying environment (solvent-monomer).

EXPERIMENTAL

Materials

Acrylonitrile (AN) and *N,N*-dimethylformamide (DMF) were purified by standard method. The densities at 293 K and 333 K and the coefficient of the thermal expansion were given in work [4]. Azo-initiator 2,2′-azobis[2-methyl-ω-hydroxyoligo(oxyethylene)propionate] [AIB-OOE(400)] was prepared by the Pinner's method [6, 7], whereas the conditions of synthesis and the initiator properties were described in work [8]. The molecular weight of the initiator is equal to $M_{n\,(VPO)}$ =1100 g/mol. The initiator is soluble in pure solvent (DMF), in pure monomer (AN) and the mixtures of DMF/AN with any composition (expressed by the mole fraction x_{AN}). For the mixture with the composition of x_{AN} = 0.52, the densities were d_4^{20} = 0.8864 g·cm^{-3}, and d_4^{60} = 0.8545 g·cm^{-3}, while $\alpha_{0.52} = 0.94\cdot10^{-3}$ K^{-1}, whereas for the composition of x_{AN} = 0.87 the densities were d_4^{20} = 0.8336 g·cm^{-3}, d_4^{60} = 0.7976 g·cm^{-3} and $\alpha_{0.87} = 1.13\cdot10^{-3}$ K^{-1}.

As the inhibitor of polymerization of acrylonitrile during the thermal decomposition of initiator was used 4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl (HTEMPO) without further purification.

Measurements

The thermal decomposition of the initiator [AIB-OOE(400)] is stoichiometrically associated with the volume of evolved nitrogen. Measurements of the nitrogen volume and the calculations were performed according to the method from work [9]. The solutions of the initiator in DMF, mixtures of DMF/AN and in AN were the diluted solutions. The initiator concentrations in the solutions were determined at 293 K and were then recalculated on the values at temperature 333 K.

RESULTS AND DISCUSSION

Measurement series (for 3—4 different initial concentrations of the initiator $[I]_0$) were performed for each solution, by repeating (from 2 to 4 times) the respective measurements of the volume (V_t) as a function of time. The compilation of the results was given in Table 1. The obtained relationships $V_t = f(t)$ and the calculated values of V_∞ (column 3 in Table 1) permitted to define the relative degree of initiator decomposition $\alpha(t)$ (column 4 in Table 1) and its time derivative:

$$\alpha(t) = \frac{V_t}{V_\infty} = \frac{[I]_0 - [I]_t}{[I]_0} = 1 - \frac{[I]_t}{[I]_0};\ [I]_0 \frac{d}{dt}\alpha(t) = -\frac{d}{dt}[I]_t \tag{1}$$

as well as the relative degree of unreacted initiator and its time derivative:

$$1-\alpha(t) = \frac{V_\infty - V_t}{V_\infty} = \frac{[I]_t}{[I]_0} \text{ thus } [I]_t = [I]_0 \cdot [1-\alpha(t)];$$
$$\frac{d}{dt}[I]_t = [I]_0 \frac{d}{dt}[1-\alpha(t)]t \tag{2}$$

where $[I]_t$ — *the concentration of the initiator (in mol· dm^{-3}) at the moment t at 333 K.*

The function $\alpha(t)$ is shown in Fig. 1a for four independent measurements at the constant concentration of the initiator $[I]_0$ = 0.0714 mol·dm^{-3} in DMF. A character of these dependences is the same. The linear courses with the constant slopes were achieved after a certain time of induction (t_i). These stationary states commence at about 5% decomposition of the initiator, which permits to recognize that the initial concentration $[I]_0$ was not changed during this time. All the results from Fig. 1a can be described in the stationary part by equation of single straight line (presented in Fig. 1), which the slope

Table 1. Thermal decomposition (333 K) of 2,2′-azobis[2-methyl-ω-hydroxy-oligo(oxyethylene) propionate] in the mixtures solvent — monomer (with the compositions expressed by the mole fractions x_{AN})

No	$[I]_0^{60}$ mol·dm^{-3}	V_∞ [a], cm^3	$\alpha(t) = \frac{V_t}{V_\infty}$	$10^4 \frac{d\alpha}{dt}$, min^{-1}	Δ [b]	$10^4 \frac{d}{dt}\ln\frac{1}{1-\alpha}$ min^{-1}	Δ′ [b]	$10^5 [I]_0 \frac{d\alpha}{dt}$ mol·dm^{-3}·min^{-1}	$10^5 [I]_0 \frac{d}{dt}\ln\frac{1}{1-\alpha}$ mol·dm^{-3}·min^{-1}
1	2	3	4	5	6	7	8	9	10
Solvent: DMF (x_{AN} = 0)									
1.1	0.0354	25.0160	$5.68 \cdot 10^{-4}$ t – 0.0920	5.68	-0.08	6.69	-0.04	2.01	2.37
1.2	0.0714	50.4426	$5.55 \cdot 10^{-4}$ t – 0.0609	5.55	-0.21	6.67	-0.06	3.96	4.76
1.3	0.1057	74.7463	$5.69 \cdot 10^{-4}$ t – 0.0568	5.69	-0.07	6.80	0.07	6.01	7.19
1.4	0.1407	99.4394	$6.11 \cdot 10^{-4}$ t – 0.0649	6.11	0.35	6.76	0.03	8.60	9.51
			average:	5.76		6.73			
Solvent: DMF/AN (x_{AN} = 0.52)									
2.1	0.0527	37.5328	$5.28 \cdot 10^{-4}$ t – 0.0424	5.28	-0.13	6.42	-0.19	2.78	3.38
2.2	0.0626	44.5793	$5.25 \cdot 10^{-4}$ t – 0.0143	5.25	-0.16	6.53	-0.07	3.29	4.09
2.3	0.0710	50.4966	$5.60 \cdot 10^{-4}$ t – 0.0087	5.60	0.19	6.79	0.19	3.98	4.82
2.4	0.0873	62.1514	$5.52 \cdot 10^{-4}$ t – 0.0367	5.52	0.11	6.68	0.08	4.82	5.83
			average:	5.41		6.61			
Solvent: DMF/AN (x_{AN} = 0.87)									
3.1	0.0352	25.2781	$6.38 \cdot 10^{-4}$ t – 0.0012	6.38	0.17	7.81	0.13	2.25	2.75
3.2	0.0713	50.9053	$5.91 \cdot 10^{-4}$ t – 0.0222	5.91	-0.30	7.44	-0.24	4.21	5.30
3.3	0.1059	75.2680	$6.35 \cdot 10^{-4}$ t – 0.0074	6.35	0.14	7.79	0.11	6.72	8.25
			average:	6.21		7.68			
Solvent: acrylonitrile (x_{AN} = 1)									
4.1	0.0367	26.3103	$6.09 \cdot 10^{-4}$ t – 0.0052	6.09	0.04	7.15	-0.29	2.24	2.62
4.2	0.0521	37.4620	$6.04 \cdot 10^{-4}$ t – 0.0059	6.04	-0.01	7.60	0.16	3.15	3.96
4.3	0.0702	50.0602	$6.19 \cdot 10^{-4}$ t – 0.0017	6.19	0.14	7.65	0.21	4.35	5.37
4.4	0.0861	61.9199	$5.90 \cdot 10^{-4}$ t – 0.0016	5.90	-0.15	7.36	-0.08	5.08	6.34
			average:	6.06		7.44			

[a] Calculated from the law of ideal gas for the standard conditions (1013 hPa, 333 K) and R = 82.06 cm^3·atm·mol^{-1}·K^{-1}.

[b] $\Delta = \left(\frac{d\alpha}{dt}\right)_i - \left(\frac{d\alpha}{dt}\right)_{av}$, $\Delta' = \left(\ln\frac{1}{1-\alpha}\right)_i - \left(\ln\frac{1}{1-\alpha}\right)_{av}$ — Deviations of the i-th measurement from the average of all measurements (i = 1, 2, 3, 4).

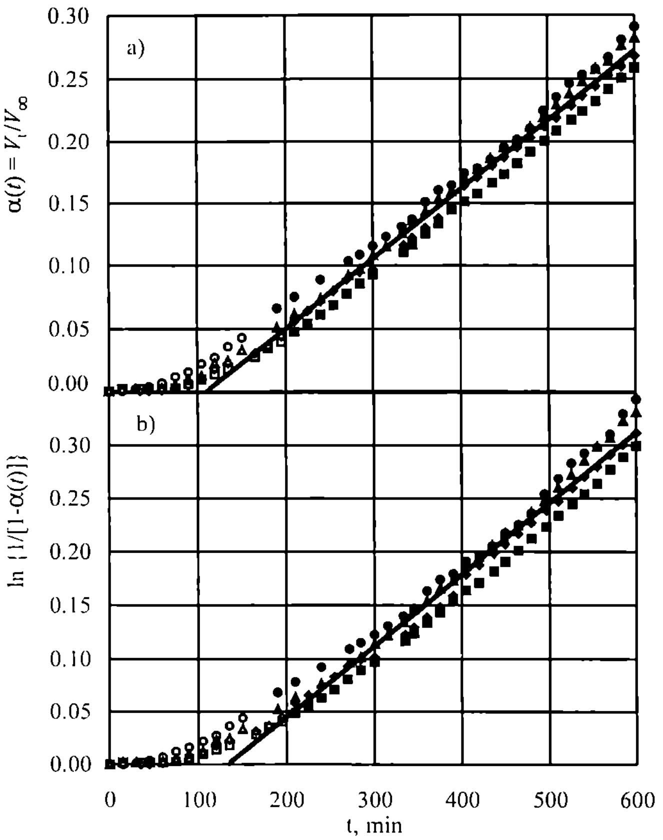

Fig. 1. Thermal decomposition (333 K) of the initiator 2,2'-azobis[2-methyl-ω-hydroxyoligo(oxyethylene) propionate] in N,N-dimethylformamide: (a) dependence of α(t) according to definition (1) as a function of time, full points — experimental points considered in equation (3), hollow points — points did not considered in equation (3); (b) dependence ln {1/[1 – α(t)]} as a function of time according to eq (4), full points — experimental points considered in equation (5), hollow points — points did not considered in equation (5)

of a straight line equal to $a_0 = 5.55 \cdot 10^{-4}$ min^{-1} determines the stationary rate of initiator decomposition (induction time t_i=110 min). This equation has the form:

$$\alpha(t) = a_0 \cdot t + a_1 \quad \text{thus} \quad \frac{d}{dt}\alpha(t) = a_0 \quad (\text{min}^{-1}) \tag{3}$$

A variable parameter α(t) can be replaced by the approximation ln [1/1 - α(t)] [10]:

$$\alpha(t) \cong \ln[1+\alpha(t)] \cong \ln\frac{1}{1-\alpha(t)} \quad \text{for} \quad 0 \le \alpha(t) \le 1 \tag{4}$$

For the same experimental data (Fig. 1 a) using the approximation (4) the equation was derived:

$$\ln\frac{1}{1-\alpha(t)} = b_0 \cdot t + b_1 \quad \frac{d}{dt}\ln\frac{1}{1-\alpha(t)} = b_0 \quad (\text{min}^{-1}) \tag{5}$$

The course of the relationship (5) is shown in Fig 1b. As can be seen, these are also the linear dependences. The slope of a straight line (5) amounts $b_0 = 6.67 \cdot 10^{-4}$ min^{-1}, and the induction time is t_i = 132 min. Both relationships (3) and (5) (Figs. 1a and 1b) determine the different rates of the decomposition of azo-initiator ($a_0 \neq b_0$), which is comprehensible, because the transformation (4) is the approximation but not an identity. The obtained information concerning the rate (a_0, b_0) of the initiator decomposition enables a classical kinetic interpretation of the process, since the classical equation combines the rate (d[I]$_t$/dt) with the instantaneous concentration of the initiator [I]$_t$:

$$-\frac{d}{dt}[\text{I}]_t = k_d^{(x)}[\text{I}]_t^x \tag{6}$$

Therefore, taking into consideration (1) and (2) in equation (6) results in the transformation of this equation to the form, which utilizes the data already obtained (3):

$$[\text{I}]_0\frac{d}{dt}\alpha(t) = k_d^{I(x)}[1-\alpha(t)]^x[\text{I}]_0^x \tag{7}$$

or

$$[\text{I}]_0 \cdot a_0 = k_d^{I(x)}[1-\alpha(t)]^x[\text{I}]_0^x \tag{8}$$

Analogously, the equation (6) by means of equations (2) and (5) can be transformed into the form:

$$[\text{I}]_0\frac{d}{dt}\ln\frac{1}{1-\alpha(t)} = k_d^{II(x)}[1-\alpha(t)]^x[\text{I}]_0^x \tag{9}$$

or

$$[\text{I}]_0 \cdot b_0 = k_d^{II(x)}[1-\alpha(t)]^x[\text{I}]_0^x \tag{10}$$

In the equations (6)—(10) the order of the reaction in relation to the initiator is denoted as x, $k_d{}^{I(x)}$, $k_d{}^{II(x)}$ — the reaction rate constants dependent on the order x, as far as the numerical values and the dimension are concerned. The differential equations (7) and (9) or their transformations (8) and (10) become the base of experimentally determined exponent x, after accomplishing the measurement series V_t = f(t) for varying [I]$_0$, because finding the logarithm transforms them to the linear dependences with the slope of a straight line x:

$$\ln R_d^I \cong \ln([\text{I}]_0 \cdot a_0) \cong \ln\left\{[\text{I}]_0\frac{d}{dt}\alpha(t)\right\} = \ln k_d^{I(x)} + x\ln[\text{I}]_0 \tag{11}$$

$$\ln R_d^{II} \cong \ln([\text{I}]_0 \cdot b_0) \cong \ln\left\{[\text{I}]_0\frac{d}{dt}\ln\frac{1}{1-\alpha(t)}\right\} = \ln k_d^{II(x)} + x\ln[\text{I}]_0 \tag{12}$$

Data in Table 1 are sufficient for the determination of the order x. The course of equation (11) is shown in Fig. 2a, in which are presented the cumulative results for various mixtures of DMF/AN. The order x of the decomposition reaction amounts 1.0017. Analogously, Fig. 2b presents the relationship (12) for which x = 0.9857. Combined Figures 2a and 2b for the mixtures entitled to the conclusion that the order of the thermal decomposition [AIB-OOE(400)] for the whole system DMF/AN (x_{AN} = 0—1) can be recognized as constant and equal to 1.00±0.02.

The determination of the reaction orders allows determining the rate constants of decomposition $k_d{}^{(x)}$

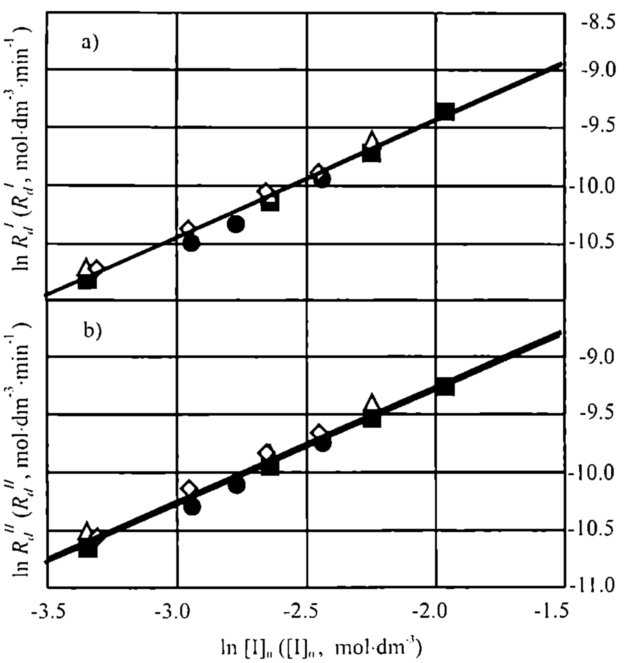

Fig. 2. Determination of the order of thermal decomposition reaction (333 K) of 2,2′-azobis[2-methyl-ω-hydroxy-oligo(oxyethylene) propionate] in the mixtures of solvent-monomer (with the compositions expressed by the mole fraction x_{AN}*)* ■ — $x_{AN} = 0$, ● — $x_{AN} = 0.52$, Δ — $x_{AN} = 0.87$ *and* ✧ — $x_{AN} = 1.0$*; (a) from the dependence* $R_d' = [I]_0 \cdot \left[\frac{d\alpha(t)}{dt}\right]$ *according to equation (11), (b) from the dependence* $R_d'' = [I]_0 \cdot \left\{\frac{d \ln[1/(1-\alpha(t))]}{dt}\right\}$ *according to equation (12)*

through the integration of the differential equations (6)—(9), which leads to the common result:

$$[I]_0 \cdot \frac{d}{dt}\left\{\frac{1}{x-1}\left[\left(\frac{1}{1-\alpha(t)}\right)^{x-1} - 1\right]\right\} = k_d^{(x)}[I]_0^x \quad \text{for } x > 1 \qquad (13)$$

and
$$\ln\frac{1}{1-\alpha(t)} = k_d^{(I)}[I]_0 \cdot t \quad \text{for } x = 1 \qquad (14)$$

The numerical values of $k_d^{(I)}$ from equation (14) for the investigated systems were summarized in Table 1 (column 7). These results indicate for the dependence of k_d on the mixed solvent composition (x_{AN}). The interpretation of the relationship $k_d = f(x_{AN})$ according to the solvatation model [11] and a comparison of the results with those for the AIBN initiator [12] will be the subject of other publication.

The equation (14), based on a definition (1), is transformed to the form most frequently used in the literature for the decompositions of AIBN and its derivatives:

$$\ln\frac{V_\infty}{V_\infty - V_t} = k_d^{(I)} \cdot t = f(t) \qquad (15)$$

Sometimes [13] the equation (2) was used for the calculation of $k_d^{(I)}$ for azo-initiators, however with the assumed $x = 1$. In the pioneer works [14, 15] the equation (15) was also used for the determination of the rate constant of decomposition with the assumed exponent $x = 1$. In the subsequent publications [16] the rectilinearity of the relationship (15) was assumed as the experimental evidence of the order $x = 1$. In such a way Walz *et al.* [7] have determined $k_d^{(I)} = 4.22 \cdot 10^{-4}$ min^{-1} for the decomposition of [AIB-OOE(300)] in *o*-xylene at temperature of 333 K.

CONCLUSIONS

An unambiguous determination of x and $k_d^{(x)}$ first requires the experimental determination of the order x followed by the determination of the decomposition rate constant $k_d^{(x)}$ from the kinetically justified equation (13). The assumed exponents x in equation (13) cannot be verified by rectilinearity of this relationship.

The reaction of thermal decomposition of the azo-initiator [AIB-OOE(400)] is the first order reaction in the studied systems DMF/AN, which comprises the kinetic correctness and support the unimolecular (homolytic) mechanism of the decomposition of azo-bond [17]. In connection with this the initiator concentration decreases according to the dependence:

$$[I]_t = [I]_0 \cdot e^{-k_d \cdot t} \qquad (16)$$

Technologically, the relationship (16) means that a variation of initiator concentration would result in proportional variations of the decomposition rate of initiator.

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