

Jerzy Szafko,
Barbara Pabin-Szafko

Technical University of Szczecin
Polymer Institute

Department of Physical Chemistry of Polymers

ul. Pulaskiego 10, 70-322 Szczecin, Poland

Thermal Decomposition of 2,2'-Azobutyronitrile. The Polymerisation Rate of Acrylonitrile in *N,N*-dimethylformamide

Introduction

Polyacrylonitrile is insoluble in its monomer. Therefore, polymerisation in appropriate solvents (in solution) - but not in bulk - has gained importance in the industrial manufacture of acrylic fibres [1]. *N,N*-dimethylformamide (DMF) [1,2] is frequently employed as a solvent, in which the polymerisation may exhibit a homogeneous or heterogeneous character [3] depending on monomer concentration. In both cases of solution polymerisation [4-6], as well as in the case of bulk polymerisation [7], the regularities and kinetic anomalies have not been completely explained. The classical kinetic scheme [8] assumes that the initial rate of initiation R_m by the thermal initiators (e.g. AIBN - 2,2'-azobutyronitrile) amounts to:

$$R_m = 2k_d \cdot f \cdot I_0 \text{ [mol} \cdot \text{dm}^{-3} \cdot \text{s}^{-1}] \quad (1)$$

where k_d - the thermal decomposition rate constant of initiator [s^{-1}], f - the initiation efficiency factor, I_0 - the initial initiator concentration [$\text{mol} \cdot \text{dm}^{-3}$], 2 - the factor indicates that two primary radicals are generated from one molecule of the thermal initiator.

According to the classical scheme, the initial rate of polymerisation (R_p) is given by the following relationship:

$$R_p = k_p \left(\frac{2 \cdot k_d \cdot f}{k_t} \right)^{0.5} \cdot I_0^{0.5} \cdot M = K \cdot I_0^{0.5} \cdot M \quad (2)$$

where k_p - the rate constant of the elementary process of chain propagation, k_t - the rate constant of the elementary process of the termination of macroradicals, M - monomer concentration [$\text{mol} \cdot \text{dm}^{-3}$], K - the overall rate constant [$\text{dm}^{1.5} \cdot \text{mol}^{-0.5} \cdot \text{s}^{-1}$],

$$K \equiv \frac{(2k_d \cdot f)^{0.5}}{k_t^{0.5}} = \frac{(2k_d \cdot f)^{0.5}}{\delta} = \frac{(R_i)^{0.5}}{\delta \cdot I_0^{0.5}};$$

$$K = \frac{R_p}{I_0^{0.5} \cdot M} \quad (\text{acc. equation 2}) \quad (3)$$

The kinetic anomalies of acrylonitrile polymerisation in solution are often taken into account through the incor-

Abstract

The initial rate of acrylonitrile (M) polymerisation initiated by 2,2'-azobutyronitrile (AIBN) in solutions with *N,N*-dimethylformamide (S) over the entire range of variations of the monomer-solvent mixture composition [expressed by the monomer mole fraction (x_M)] at 60°C was investigated. The polymerisation rate (R_p) was found to be given by $R_p = \tilde{K} [\text{AIBN}]^{0.5} [M]^n$, where \tilde{K} the overall rate constant is a function of x_M for $n=1$. The variability of \tilde{K} was interpreted in accordance with the model of the solvation of initiator (I) by monomer (M) and solvent (S). According to this model, three double solvated forms MIM, SIM and SIS exist in the solution, which initiate the polymerisation of acrylonitrile independently of each other. Hence, the total rate of polymerisation is the sum of the partial rates of solvated forms occurring in the system. The possibility of describing the kinetic data by other polymerisation theories (diffusion, electron-donor-acceptor (EDA) complex and 'hot radicals') has also been discussed.

Key words: homo- and heterogeneous polymerisation, polymerisation rate, solvent effect, acrylonitrile.

poration of the exponents n and m into the equation for the initial rate [1], thus:

$$R_p = k_p \cdot \frac{2k_d \cdot f}{k_t} \cdot I_0^m \cdot M^n = K' \cdot I_0^m \cdot M^n \quad (4)$$

The exponents n and m represent a measure of the kinetic anomalies for the acrylonitrile polymerisation in relation to the classical scheme [8]. A comparison of equations 3 and 4 enables the recalculation of K into K' and vice versa:

$$K' = K \cdot \left(\frac{2k_d \cdot f}{k_t} \right)^{0.5} = \frac{K^2}{k_p} \quad (5)$$

The exponents in equation 4 $m \neq 0.5$ and $n > 1$ were explained in a double way:

- by the attribution of the kinetic scheme for each particular case of the polymerisation [8-14],
- by the assumption that $m=0.5$ and $n=1.0$. Then, the constant K' from equation 4 (or thereby K in equation 5) undergoes variability:

$$R_p = \tilde{K} \cdot I_0^{0.5} \cdot M$$

$$\tilde{K} = k_p \cdot \left(\frac{2k_d \cdot f}{k_t} \right)^{0.5} = f(M) \quad (6)$$

The variability of \tilde{K} , in accordance with equation 6, requires the explanation of which of the elementary processes of polymerisation [the rate constant of propagation (k_p), termination (k_t), initiator decomposition (k_d), the initiation efficiency factor (f)] is a function of the monomer concentration M .

The diffusion theory [15-18] assumes that the termination rate constants are inversely proportional to the viscosity of the polymerisation medium. A theo-

ry of EDA complex [19-21] attributes the variability of \tilde{K} to the variability of k_p as a consequence of the formation of electron-donor-acceptor complexes with the monomer (M) and solvent (S). The 'hot radicals' theory [22,23] attributes the growth of \tilde{K} with increasing monomer concentration to a rapid reaction of the 'hot radical' with the monomer besides the reaction which proceeds in parallel propagating the thermalised radical.

In work [24], the rate of polymerisation of acrylonitrile in DMF initiated by AIBN was described by equation 4, in which $m=0.5$ and $n=3/2$ and the parameter $\delta=9.09$ was determined. In other work [25], under the same conditions (DMF, AIBN) it was determined that $m=0.5$ and $\delta=13.33$ (50°C), whereas in work [26] (DMF, AIBN) it was determined that $\delta=14.28$ and [27] (DMF, AIBN) $\delta=15.3$.

The objective of this work was to establish the mechanism and kinetics of polymerisation of acrylonitrile in *N,N*-dimethylformamide, over the entire range of monomer dilution, that is, homogeneous polymerisation (up to a concentration of 6 $\text{mol} \cdot \text{dm}^{-3}$) as well as heterogeneous polymerisation (above the concentration of 6 $\text{mol} \cdot \text{dm}^{-3}$), utilising the results obtained from the determination of the polymerisation rate of the AN/DMF/AIBN/60°C system and previously recognised experimental facts [2, 28-32]. These results were interpreted on the basis of model [29] of the solvation of the initiator AIBN (I) by monomer (M) and solvent (S).

Theoretical

It was established in our previous works [30, 31] that equation (7) describes the dependence of the thermal decomposition rate constant of AIBN (k_d) in the acrylonitrile (M) - *N,N*-dimethylformamide (S) mixtures. Equation 7 can be transformed (by means of):

$$\frac{S}{M} = \frac{1-x_M}{x_M}; x_M = \frac{M}{M+S}; X_M = (0...1) \quad (8)$$

into a more convenient form (equation 9). The relative contents of the solvated forms

$$([MIM]_r + [SIM]_r + [SIS]_r = 1)$$

amount to what is shown in equations (9a,b,c). Equation 9 very well describes the experimental dependence $k_d=f(x_M)$ for the values of

$$H'_M = K_{SM}/K_{MM} = 11.86,$$

$$H'_S = K_{SS}/K_{MM} = 8.72 \text{ and}$$

$$k_{SM} = 4.09 \cdot 10^{-4} \text{ min}^{-1}$$

at values of $k_{SS} = 6.45 \cdot 10^{-4} \text{ min}^{-1}$ and $k_{MM} = 7.2 \cdot 10^{-4} \text{ min}^{-1}$, which were experimentally determined for the boundary values $x_M = 0$ and $x_M = 1$ respectively. In this way, the experimental dependence $k_d=f(x_M)$ (equation 9) was distributed into three components: $k_{MM}[MIM]_r$, $k_{SM}[SIM]_r$, and $k_{SS}[SIS]_r$, the mutual contribution of which depends solely on the monomer mole fraction (x_M) in the solution. At low concentrations of acrylonitrile in DMF, the SIS and SIM forms prevail, and they possess the decomposition rate constants of k_{SS} and k_{SM} respectively. However, for the concen-

trated solutions of the monomer for $x_M > 0.5$, besides the previous forms, the form MIM with the highest k_{MM} begins to increase its contribution. The solvated form SIM is responsible for a minimum of $k_d=f(x_M)$, and this form exhibits the highest contribution and the lowest numerical value of k_{SM} within the range of $x_M = 0.7-0.8$.

In our work [33], the initiation rate constant ($2k_d \cdot f$) was determined over the entire range of variation of x_M (0-1) by the method of inhibited polymerisation. It appears that:

$$\frac{(2k_d \cdot f)_{\text{exp}}}{(2k_d)_{\text{exp}}} = f = f_{SS}^0 [SIS]_r + f_{SM}^0 [SIM]_r + f_{MM}^0 [MIM]_r \quad (10)$$

Expression 10 possesses a physical sense which is analogous to expression 9; namely the total initiation efficiency factor, which is a function of x_M , is composed of the constant factors characteristic of the given solvated forms (f_{SS}^0 , f_{SM}^0 and f_{MM}^0). These factors are corrected by the relative content of the solvated forms (also dependent on x_M according to equations 9a-9c). Taking equations (9a-9c) into account, in equation 10 one can obtain the expression (11). Equation 11 also indicates that in accordance with the model of the solvation [29], the dependence $f=f(x_M)$ will as a rule be a curvilinear, and will be a linear dependence only in particular cases.

The initiation rate constant ($2k_d \cdot f$) of the polymerisation of acrylonitrile in DMF can be described (according to equations 9 and 10) by the relationship (12) [33]. The experimental dependence

$2k_d \cdot f=f(x_M)$ is very well described by equation 12 for $f_{MM}^0 = 0.58$, $f_{SS}^0 = 0.63$ and $f_{SM}^0 = 1.0$. According to equations (1), (9), (10) and (12) the stationary concentrations of the radicals of each type amount to (equations 13-16), where k_t is a average constant of the termination,

$$[MIM] = [MIM]_r \cdot I_0, [SIM] = [SIM]_r \cdot I_0, \text{ and } [SIS] = [SIS]_r \cdot I_0.$$

Hence, the consumption of monomer (M) in the propagation reactions determining the initial, stationary rate of polymerisation amounts:

$$R_p = k_{p,MM} \cdot R_{MM}^* \cdot M + k_{p,SM} \cdot R_{SM}^* \cdot M + k_{p,SS} \cdot R_{SS}^* \cdot M \quad (17)$$

Taking into account equations (13-16) in equation (17) leads to (18), where

$$\delta_{MM} = \frac{k_t^{0.5}}{k_{p,MM}}; \delta_{SM} = \frac{k_t^{0.5}}{k_{p,SM}} \quad (19); \delta_{SS} = \frac{k_t^{0.5}}{k_{p,SS}}$$

We may note that if:

$$2k_{MM} \cdot f_{MM}^0 \equiv 2k_{SM} \cdot f_{SM}^0 \equiv 2k_{SS} \cdot f_{SS}^0 \equiv 2k_d \cdot f \quad (20)$$

thus (21) or (22) and (23).

If $\delta_{MM} = \delta_{SM} = \delta_{SS} = \delta$

and $[MIM]_r + [SIM]_r + [SIS]_r = 1$, then

$$\tilde{K}^S = K \cdot I_0^{0.5} = \frac{(2k_d \cdot f)^{0.5} \cdot I_0^{0.5}}{\delta},$$

which leads to classical equation 6.

Experimental

The monomer (acrylonitrile) was rectified three times in accordance with the laboratory procedure given in work [34]. The solvent *N,N*-dimethylformamide and the initiator, 2,2'-azoisobutyronitrile (AIBN) were purified by standard methods. The rate of polymerisation was determined by the dilatometric method using dilatometers with a capacity of $25 \times 10^{-3} \text{ dm}^3$. The dilatometers were filled and degassed using a vacuum line technique. The initial rate [noncorrelated (%/time)] was calculated from the angle of inclination of the dependence $10^2 \cdot \ln(1/1-p) = f(t)$, where p is the monomer conversion at time (t). A noncorrelated rate (%/time) was recalculated into the correlated (R_p) one in $\text{mol} \cdot \text{dm}^{-3} \cdot \text{s}^{-1}$.

Results and Discussion

Figure 1 shows the experimental results for determining the rate of polymerisation (R_p) of acrylonitrile (AN) in DMF at 60°C after recalculation into the overall rate constant (\tilde{K}) (according to equation

$$k_d = \frac{k_{MM} \cdot K_{MM} \cdot M^2 + k_{SM} \cdot K_{SM} \cdot S \cdot M + k_{SS} \cdot K_{SS} \cdot S^2}{K_{MM} \cdot M^2 + K_{SM} \cdot S \cdot M + K_{SS} \cdot S^2} = \frac{k_{MM} + k_{SM} \cdot H'_M \cdot \frac{S}{M} + k_{SS} \cdot H'_S \cdot \frac{S^2}{M^2}}{1 + H'_M \cdot \frac{S}{M} + H'_S \cdot \frac{S^2}{M^2}} \quad (7)$$

$$k_d = \frac{k_{MM} \cdot x_M^2 + k_{SM} \cdot H'_M \cdot x_M \cdot (1-x_M) + k_{SS} \cdot H'_S \cdot (1-x_M)^2}{x_M^2 + H'_M \cdot x_M \cdot (1-x_M) + H'_S \cdot (1-x_M)^2} = \frac{k_{MM} \cdot x_M^2 + k_{SM} \cdot H'_M \cdot x_M \cdot (1-x_M) + k_{SS} \cdot H'_S \cdot (1-x_M)^2}{(1+H'_M-H'_S) \cdot x_M^2 + (H'_M-2H'_S) \cdot x_M + H'_S} = k_{MM} \cdot [MIM]_r + k_{SM} \cdot [SIM]_r + k_{SS} \cdot [SIS]_r \quad (9)$$

$$[MIM]_r = \frac{x_M^2}{(1+H'_M-H'_S) \cdot x_M^2 + (H'_M-2H'_S) \cdot x_M + H'_S} \quad (9a)$$

$$[SIM]_r = \frac{H'_M \cdot x_M \cdot (1-x_M)}{(1+H'_M-H'_S) \cdot x_M^2 + (H'_M-2H'_S) \cdot x_M + H'_S} \quad (9b)$$

$$[SIS]_r = \frac{H'_S \cdot (1-x_M)^2}{(1+H'_M-H'_S) \cdot x_M^2 + (H'_M-2H'_S) \cdot x_M + H'_S} \quad (9c)$$

Equations 7, 9, 9a, 9b, 9c

$$f = \frac{(f_{MM}^0 + H' \cdot f_{SS}^0 - H'_M \cdot f_{SM}^0) \cdot x_M^2 + (H'_M \cdot f_{SM}^0 - 2H' \cdot f_{SS}^0) \cdot x_M + H' \cdot f_{SS}^0}{(1 + H' - H'_M) \cdot x_M^2 + (H'_M - 2H') \cdot x_M + H'} \quad (11)$$

$$(2k_d \cdot f)_{\text{exp}} = 2k_{MM} \cdot f_{MM}^0 [MIM]_r + 2k_{SM} \cdot f_{SM}^0 [SIM]_r + 2k_{SS} \cdot f_{SS}^0 [SIS]_r \quad (12)$$

$$R_{MM}^* = \frac{(R_{m,MM})^{0.5}}{k_t^{0.5}} = \frac{(2k_d \cdot f)^{0.5} \cdot [MIM]_r^{0.5}}{k_t^{0.5}} = \frac{(2k_{MM} \cdot f_{MM}^0)^{0.5} \cdot [MIM]_r^{0.5} \cdot I_o^{0.5}}{k_t^{0.5}} \quad (13)$$

$$R_{SM}^* = \frac{(R_{m,SM})^{0.5}}{k_t^{0.5}} = \frac{(2k_d \cdot f)^{0.5} \cdot [SIM]_r^{0.5}}{k_t^{0.5}} = \frac{(2k_{SM} \cdot f_{SM}^0)^{0.5} \cdot [SIM]_r^{0.5} \cdot I_o^{0.5}}{k_t^{0.5}} \quad (14)$$

$$R_{SS}^* = \frac{(R_{m,SS})^{0.5}}{k_t^{0.5}} = \frac{(2k_d \cdot f)^{0.5} \cdot [SIS]_r^{0.5}}{k_t^{0.5}} = \frac{(2k_{SS} \cdot f_{SS}^0)^{0.5} \cdot [SIS]_r^{0.5} \cdot I_o^{0.5}}{k_t^{0.5}} \quad (15)$$

$$R^* = \frac{(R_m)^{0.5}}{k_t^{0.5}} = \frac{(2k_d \cdot f)^{0.5} \cdot I_o^{0.5}}{k_t^{0.5}} \quad (16)$$

$$R_p = M \cdot I_o^{0.5} \left[\frac{(2k_{MM} \cdot f_{MM}^0)^{0.5} [MIM]_r + (2k_{SM} \cdot f_{SM}^0)^{0.5} [SIM]_r + (2k_{SS} \cdot f_{SS}^0)^{0.5} [SIS]_r}{\delta_{MM} \delta_{SM} \delta_{SS}} \right] \quad (18)$$

$$R_p = M \cdot I_o^{0.5} \cdot (2k_d \cdot f)^{0.5} \left[\frac{[MIM]_r}{\delta_{MM}} + \frac{[SIM]_r}{\delta_{SM}} + \frac{[SIS]_r}{\delta_{SS}} \right] \quad (21)$$

$$\tilde{K}^S = I_o^{0.5} \cdot (2k_d \cdot f)^{0.5} \left[\frac{[MIM]_r}{\delta_{MM}} + \frac{[SIM]_r}{\delta_{SM}} + \frac{[SIS]_r}{\delta_{SS}} \right] \quad (22)$$

$$\frac{1}{\delta} = \frac{[MIM]_r}{\delta_{MM}} + \frac{[SIM]_r}{\delta_{SM}} + \frac{[SIS]_r}{\delta_{SS}} \quad (23)$$

$$\left\{ \frac{\tilde{K}^S \cdot \left[(1 + H' - H'_M) \cdot x_M^2 + (H'_M - 2H') \cdot x_M + H' \right]}{(2k_d \cdot f)^{0.5} \cdot I_o^{0.5}} - \frac{1}{\delta_{MM}} \cdot x_M^2 \right\} \cdot \frac{1}{1 - x_M} = \left(\frac{H'_M}{\delta_{SM}} - \frac{H'}{\delta_{SS}} \right) \cdot x_M + \frac{H'}{\delta_{SS}} \quad (25)$$

Equations 11, 12, 13, 14, 15, 16, 18, 21, 22, 23, 25

4 for $m=0.5$ and $n=1.0$) as a function of the monomer concentration, expressed by the composition of the monomer-solvent mixture [$x_M=M/(M+S)$].

The relationships between the monomer concentration (M) occurring in equation 4 and the mole fraction x_M can be written as [31]:

$$M = \frac{G \cdot x_M}{[(Q-P) \cdot x_M + P]} \quad \text{and}$$

$$x_M = \frac{P \cdot M}{[G - (Q-P) \cdot M]} \quad (24)$$

where:

$P = m_S \cdot d_M = 55696 \text{ [g}^2 \cdot \text{dm}^{-3} \cdot \text{mol}^{-1}\text{]}$;
 $Q = m_M \cdot d_S = 47377 \text{ [g}^2 \cdot \text{dm}^{-3} \cdot \text{mol}^{-1}\text{]}$ and
 $G = d_S \cdot d_M = 680690 \text{ [g}^2 \cdot \text{dm}^{-6}\text{]}$;
 m_M and m_S designate the molecular weight [$\text{g} \cdot \text{mol}^{-1}$] of the monomer and solvent respectively;
 d_M and d_S designate the densities [$\text{g} \cdot \text{cm}^{-3}$] of the monomer and solvent respectively.

As can be seen from Figure 1, a pronounced dependence of the overall rate constant of polymerisation (\tilde{K}) on

the monomer concentration is visualised, which should not take place if the polymerisation of acrylonitrile is subject to the regularities of the classical scheme [in accordance with equation (2)]. The dependence in Figure 1 can be described by the derived equation (22). In this equation, the values of \tilde{K}^S , the relative concentrations of the solvated forms $[MIM]_r$, $[SIM]_r$, and $[SIS]_r$ (equations 9a - 9b) and values $(2k_d \cdot f)$ are known. Thus, determination of kinetic parameters δ_{MM} , δ_{SM} and δ_{SS} is possible. These calculations should be performed by the application of Marquardt's algorithm [35] in the non-linear least-squares method for the dependence $\tilde{K} = f(x_M)$ (Figure 1), then one obtains $\delta_{SS}=13.38$, $\delta_{SM}=7.72$ and $\delta_{MM}=7.87$. Moreover, δ_{MM} as calculated directly from the rate of acrylonitrile polymerisation in bulk amounts to 7.84.

An auxiliary method in relation to the nonlinear least-square method is the linearisation of equation 22, which leads to the expression (25). The course of dependence 25 depicts Figure 2. A straight line in this Figure (CF=0.996)

determines the values of $\delta_{SS}=13.31$ and $\delta_{SM}=7.76$ for directly determined $\delta_{MM}=7.84$ (polymerisation in bulk). Thus, both calculation methods lead to the same results:

$$\delta_{SS} = 13.31 \pm 0.07, \quad \delta_{SM} = 7.74 \pm 0.03, \\ \delta_{MM} = 7.84 \pm 0.04.$$

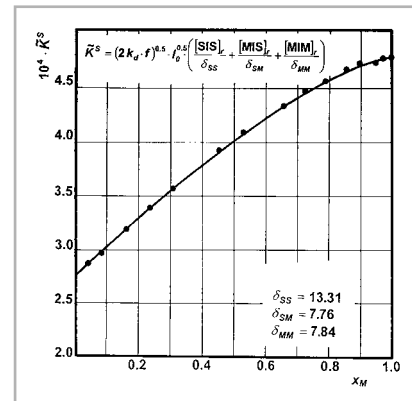


Figure 1. Dependence of the overall rate constant of polymerisation (\tilde{K}) acrylonitrile according to equation 4 on the mole fraction (x_M) of acrylonitrile. AN/DME/AIBN/60°C system; ● - experimental values of \tilde{K} .

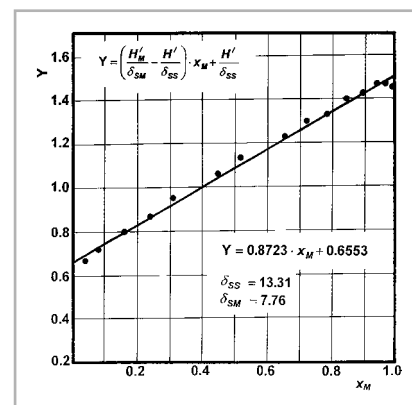


Figure 2. Determination of the kinetic parameters $\delta_{SS}=13.31$ and $\delta_{SM}=7.76$ for $\delta_{MM}=7.84$ according to equation 25, $H'_M=11.86$ and $H'=8.72$. The value $(2k_d \cdot f)$ was taken from [33].

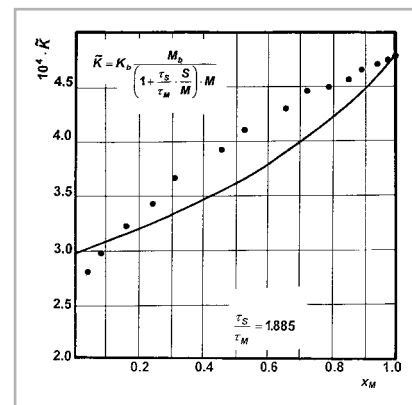


Figure 3. Determination of the kinetic parameter τ_r/τ_M according to equation 27; ● - experimental values.

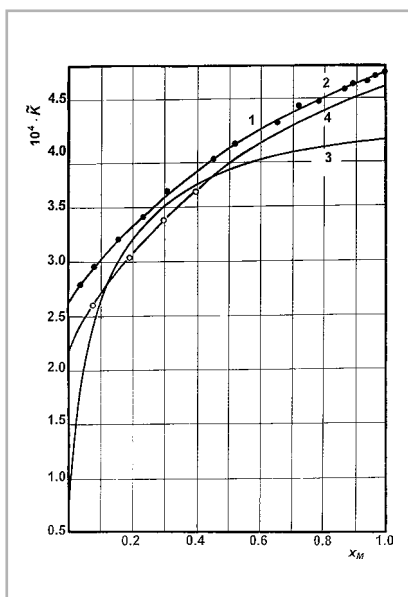


Figure 4. Determination of the kinetic parameters K_∞ , γ and γ' according to equation 29; ● - experimental values of this work, ○ - experimental values of work [38]; 1 - $K_\infty=2.64 \times 10^{-4}$; $\gamma=1.25$ and $\gamma'=0.67$ by Marquardt's method; 2 - $K_\infty=2.61 \times 10^{-4}$; $\gamma=1.24$ and $\gamma'=0.61$ by linearisation method; 3 - $K_\infty=0.818 \times 10^{-4}$; $\gamma=0.248$ and $\gamma'=0.0245$ by Simplex method; 4 - $K_\infty=2.16 \times 10^{-4}$; $\gamma=0.877$ and $\gamma'=0.383$ by Marquardt's method.

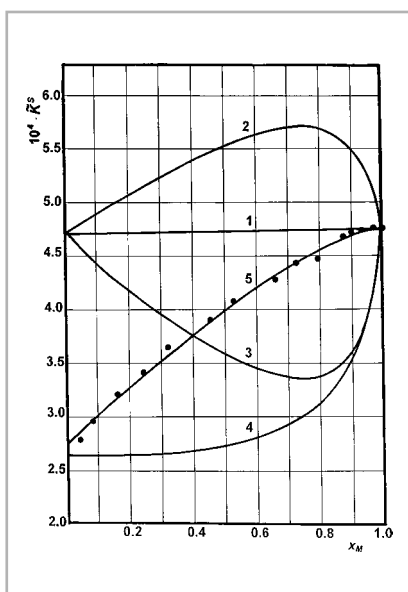


Figure 5. The dependence 22 for various values of the kinetic parameters δ_{SS} , δ_{SM} and δ_{MM} ; 1 - $\delta_{SS}=\delta_{SM}=\delta_{MM}=7.84$; 2 - $\delta_{SS}=7.84$, $\delta_{SM}=6.0$ and $\delta_{MM}=7.84$; 3 - $\delta_{SS}=7.84$, $\delta_{SM}=14.0$ and $\delta_{MM}=7.84$; 4 - $\delta_{SS}=\delta_{SM}=14.0$ and $\delta_{MM}=7.84$; 5 - $\delta_{SS}=13.38$, $\delta_{SM}=7.72$ and $\delta_{MM}=7.84$; ● - experimental points.

These values utilised in equation 22 results in the complete agreement between the \tilde{K}^S values calculated (solid line in Figure 1) and those determined from the experimental data (\tilde{K}). The numerical value

$\delta_{SS}=13.31$ demands attention, because it is significantly larger than those for δ_{SM} and δ_{MM} . This result is rather unexpected. However, one should expect a different value for δ_{SM} because the thermal decomposition rate constant of the solvated form SIM was characterised by the lowest value of $k_{SM}=4.09 \times 10^{-4} \text{ min}^{-1}$, which might affect the reactivity of radical R_{SM}^* in the reactions of propagation or termination ($\delta=k_t^{0.5}/k_{p,SM}$). This experimental fact may shed new light on the comprehension of the 'cage' effect [36].

The model of the solvation of initiator [29], which was used for the description of the experimental results of the polymerisation AN (M) in DMF (S), describes the course of polymerisation over the entire range of variations of the monomer-solvent mixture composition.

According to the diffusion theory [14-16], the value \tilde{K} (from equation 6) should increase along with the increasing dilution of the monomer, whereas the value δ should decrease. Figure 1 shows a dependence which is reciprocal to the described dependence. [The viscosity of DMF (60°C, 0.5722 cP) is higher than that of acrylonitrile (60°C, 0.3210 cP)]. The theory of EDA complex [19-21] formulates the expression which determines the overall rate constant of polymerisation in the form:

$$\tilde{K} = K_b \frac{M_b}{\left(1 + \frac{\tau_s}{\tau_m} \cdot \frac{S}{M}\right)} \cdot M \quad (26)$$

where:
 M_b - monomer concentration in bulk;
 K_b - the overall rate constant of polymerisation in bulk;
 M, S - the concentrations of monomer and solvent respectively;
 τ_m, τ_s - lifetimes of the complex of radical with the monomer and solvent respectively.

Using equation 8 for the transformation of equation 26, we have:

$$\frac{M_b \cdot K_b}{\tilde{K}} \cdot x_M = \left(1 - \frac{\tau_s}{\tau_m}\right) \cdot x_M + \frac{\tau_s}{\tau_m} \quad (27)$$

The application of equation 27 for the experimental results (from Figure 1) presents Figure 3. The EDA theory is divergent from the experimental data, although it allows determination of the constant value $\tau_s/\tau_m = 1.885$ from the straight line (CF=0.9623).

A description of the polymerisation kinetics in solvents also demonstrates the 'hot radicals' theory [22,23,37] in the form of equation:

$$\tilde{K} = K_\infty \left(1 + \frac{x_M}{\gamma \cdot x_M + \gamma' \cdot (1 - x_M)}\right) \quad (28)$$

where:
 K_∞ - is the overall rate constant extrapolated to a zero concentration of monomer ($x_M \rightarrow 0$);

γ, γ' - the ratios of kinetic constants of the reaction of 'cooling' hot radicals by solvent (γ) and monomer (γ') in relation to the rate constant of propagation (k_p) of the 'hot radical';

$$x_M = M/(M+S).$$

$$\tilde{K} = K_\infty \left(1 + \frac{x_M}{\gamma \cdot x_M + \gamma' \cdot (1 - x_M)}\right) \quad (29)$$

The application of equation 29 to the experimental results (\tilde{K} from Figure 1) shows Figure 4. From Figure 4 (line 1), it results that equation 29 with the parameters (K_∞, γ and γ') determined by the application of the nonlinear least-squares method according to Marquardt's algorithm [35], describes our experimental results correctly. In this figure (line 4), the experimental points from work [38] were also presented in which equation 29 was applied, whereas its parameters $K_\infty=2.16 \times 10^{-4}$, $\gamma=0.877$ and $\gamma'=0.383$ were calculated according to Marquardt's algorithm. Equation 29 very well describes the experimental data [38]. The course of the dependence 29 for the parameters K_∞, γ and γ' , which were determined by the authors of work [38] using the Simplex [39] method, was shown in Figure 4 (line 3). These parameters [39] applied in equation 29 mean that this equation does not describe the experimental results [38].

On the basis of Figures 1 and 4, one can conclude that both the 'hot radicals' hypotheses " and the solvation of the initiator lead to the kinetic relationships useful for describing the polymerisation (kinetics) of acrylonitrile in DMF.

The model of the solvation of the initiator describes the kinetic relationships in the elementary processes: the thermal decomposition of the initiator, the initiation (the rate and efficiency) and the rate of polymerisation (the overall constant of polymerisation \tilde{K} , and the polymerisability δ [39]). Moreover, the model of the solvation can describe the case of the increase in value \tilde{K} with dilution of the monomer, which is attested by the simulated courses of the dependence 22 plotted in Figure 5.

Table 1. Polymerization of the AN/DMF/AIBN/600C System; $AIBN = I_0 = 0.06 \text{ mol}\cdot\text{dm}^{-3}$.

No.	M	x_M	$10^4 \cdot k_d$	$10^4 \cdot 2k_d \cdot f$	f	$10^4 \cdot \bar{K} \cdot I_0^{0.5}$	$\delta = k_t^{0.5}/k_p$	k_p	$10^{-6} \cdot k_t$
	$\frac{\text{mol}}{\text{dm}^3}$		min^{-1}	min^{-1}		s^{-1}	$\frac{\text{mol}^{0.5} \cdot \text{s}^{0.5}}{\text{dm}^{1.5}}$	$\frac{\text{dm}^3}{\text{mol} \cdot \text{s}}$	$\frac{\text{dm}^3}{\text{mol} \cdot \text{s}}$
1	2	0.160	5.97	8.15	0.68	3.20	11.52	672	60
2	5	0.385	5.42	8.22	0.76	3.76	9.83	788	60
3	11	0.794	4.99	8.25	0.82	4.47	8.31	932	60
No.	$[\text{SIS}]_r$	$[\text{MIS}]_r$	$[\text{MIM}]_r$	$10^4 \cdot k_{SS}$ min^{-1}	$10^4 \cdot k_{SM}$ min^{-1}	$10^4 \cdot k_{MM}$ min^{-1}	f_{SS}^0	f_{SS}^0	f_{MM}^0
1	0.792	0.205	0.003	6.45	4.09	7.20	0.63	1.0	0.58
2	0.529	0.445	0.026	6.45	4.09	7.20	0.63	1.0	0.58
3	0.129	0.660	0.021	6.45	4.09	7.20	0.63	1.0	0.58
	δ_{SS}	δ_{SM} $\text{mol}^{0.5} \cdot \text{s}^{0.5} \cdot \text{dm}^{-1.5}$	δ_{MM}	$k_{p,SS}$	$k_{p,SM}$ $\text{dm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$	$k_{p,MM}$			
	13.38	7.72	7.84	579	1002	988			

Conclusions

The AN(M)/DMF(S)/AIBN(I)/60°C system appeared to be complex: an illustration of the homogeneous, transient and heterogeneous conditions in this system is the kinetic data compiled in Table 1 as a function of the monomer concentration (x_M).

As the concentration of acrylonitrile increases, the following relationships apply: the observed value of the thermal decomposition rate constant of initiator (k_d) decreases, the initiation rate constant ($2k_d \cdot f$) is practically constant, the initiation efficiency (f) increases, the overall rate constant of polymerisation (\bar{K}) increases, the parameter referred to as the 'polymerisability' of monomer ($\delta = k_t^{0.5}/k_p$) [39] decreases, and as a consequence the rate constant of the elementary reaction of propagation (k_p) enhances with the assumption of invariability of the rate constant of the elementary process of termination (k_t).

The data δ from Table 1 should be compared with those reported in the literature so far, which were usually obtained for one chosen monomer concentration. This magnitude is accepted as independent of the monomer concentration.

Srinivasan & Santappa [24] have determined $\delta=9.09$, Bagdasaryan [25] $\delta=13.3$, Bamford [26,27] $\delta=14.28$, Onyon [40] $\delta=9.0$, Colebourne [41] $\delta=14.1$, Bengough [42] $\delta=11.76$, and again Bamford [43] $\delta=12.35$, and Szafko in work [2] $\delta=10.45$. Part of this data is consistent with that presented in Table 1.

Similarly, the constants k_p calculated from the value of δ (Table 1) for $k_t=6 \times 10^{-7}$, are in good correlation with the literature data: $k_p=1000$ according to work [25], $k_p=660$ according to [41], $k_p=627$ [43], $k_p=658$ [42] and $k_p=1960$ [27]. The values of δ obtained in this work are as follows: $\delta_{SS}=13.38$; $\delta_{SM}=7.72$ and $\delta_{MM}=7.84$, and $k_{p,SS}=579$; $k_{p,SM}=1002$ and $k_{p,MM}=988$ (for $k_t=60 \cdot 10^{-6}$). These are the constant values for the respective solvated forms; however, their influence on the course of the polymerisation over the entire range of variations of the monomer solvent mixture composition (x_M) is variable, corrected by the relative concentrations of the solvated forms: $[\text{SIS}]_r$, $[\text{SIM}]_r$, $[\text{MIM}]_r = f(x_M)$. As a consequence, over the entire range of variations x_M the kinetics of the polymerisation of acrylonitrile is described by the derived equation 22. □

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