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CHARACTERIZATION OF ACRYLONITRILE POLYMERIZATION BY DILATOMETRY AND MODELING

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SUMMARY Solution polymerization of acrylonitrile was investigated in N,N'-dimethylformamide with various azo- and peroxo-initiators. Investigations were carried out in a concentration range of initiatior from 0.0016 mol/l up to 0.0160 mol/l, constant acrylonitrile concentration of 3.8 mol/l and temperatures from 40°C up to 70°C. The computer combined dilatometric equipment for long time and high conversion investigations was used for estimation of the conversion-time-reaction. By means of obtained data a mathematical model was created. The model describes sufficiently precise acrylonitrile polymerization kinetics in N,N'-dimethylformamide with various initiators in the used range of concentrations and temperatures.

INTRODUCTION

During the last few years the importance of polyacrylonitrile and its copolymers has been increased rapidly for the development and production of filtration membranes and as a support of membranes for gas separation, vapour permeation and pervaporation. Molecular weight, molecular weight distribution, hydrophilic/hydrophobic behaviour, functional groups and functional group distribution of membrane polymer are important for membrane formation and macroscopic membrane properties. The knowledge of polymerization or copolymerization kinetics allows to synthesize tailor-made polymers in a short time and with prescribed parameters.

Therefore the aim of this work was to enlarge the knowledge about course of solution polymerizations by physico-chemical investigations using an example of the acrylonitrile homopolymerization in N,N'-dimethylformamide (DMF) with various initiators. Reaction mechanism and kinetic constants for polymerizations up to high conversions have been estimated for creating of a mathematical model.

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EXPERIMENTAL

Various initiators with different decomposition constants were synthesized (*) [1-3] and used together with commercial initiators (+) for polymerization investigations:

- 2,2'-azobisisobutyronitrile (AIBN) (+)
- di-(2-hydroxyethyl)-2,2'-azobisisobutyrate (AEG) (*)
- di-[2-hydroxy-poly(oxyethyl)$_n$]-2,2'-azobisisobutyrate (APEG200) (*)
- di-(2-hydroxydecyl)-2,2'-azobisisobutyrate (DEDA) (*)
- di-[2-poly(oxyethyl)$_n$-2-ammoniumsulphate]-2,2'-azobisisobutyrate (APEGS200) (*)
- di-(2-decyl-2-ammoniumsulphate)-2,2'-azobisisobutyrate (DEDAS) (*)
- poly[di-(2-oxyethyl)$_n$-2,2'-azobisisobutyrate]$_m$ (PAEG) (*)
- poly{di-[2-poly(oxyethyl)$_n$]-2,2'azobisisobutyrate}$_m$ (PAPEG200) (*)
- dibenzoylperoxide (DBP) (+)
- ammoniumperoxodisulphate (APS) (+)

Initiators were twice-purified by fractional crystallization from ethyl alcohol or from water (APS) respectively. Monomer and solvent were dried over calcium hydride and then distilled under nitrogen atmosphere. Monomer-initiator-solution was made and filled into reaction flask under nitrogen atmosphere, too.

Investigations were carried out within concentration range of initiatior from 0.0016 mol/l up to 0.0160 mol/l, constant acrylonitrile concentration of 3.8 mol/l and temperatures from 40°C up to 70°C. A computer combined dilatometric equipment for long time and high conversion investigations (Fig.1) was used for estimation of the conversion-time-reaction. The course of polymerizations was obtained as pressure-time-curves (every 30 seconds one value) from each reaction flask. Final conversion was determined by precipitation of polymerization solutions to ethyl alcohol and following constant-drying in a vacuum-drying chamber.

For mathematical modeling of the named polymerization systems dilatometric conversion-time-curves, gravimetrical final conversion as well as by GPC or viscosimetry obtained molecular weights were needed. In the first step pressure-time-curves were changed into so-called master curves with a reduced number of data and with final conversion into conversion-time-curves.

As a mathematical model with a chemical-physical background the classical polymerization mechanism was used [3].

Nonlinear differential equation system was solved by Runge-Kutta-Fehlberg-procedure (5. order) with self-optimizing intercept length control. Parameter optimization was made by means of Nelder-Mead-procedure (parameter search procedure for function minimization) [4]. Starting values for modeling result from ideal gross kinetics (conversion <10%) by use of classical analysis methods. Kinetic constants for initiation, propagation and solvent transfer were derived from this model [3].

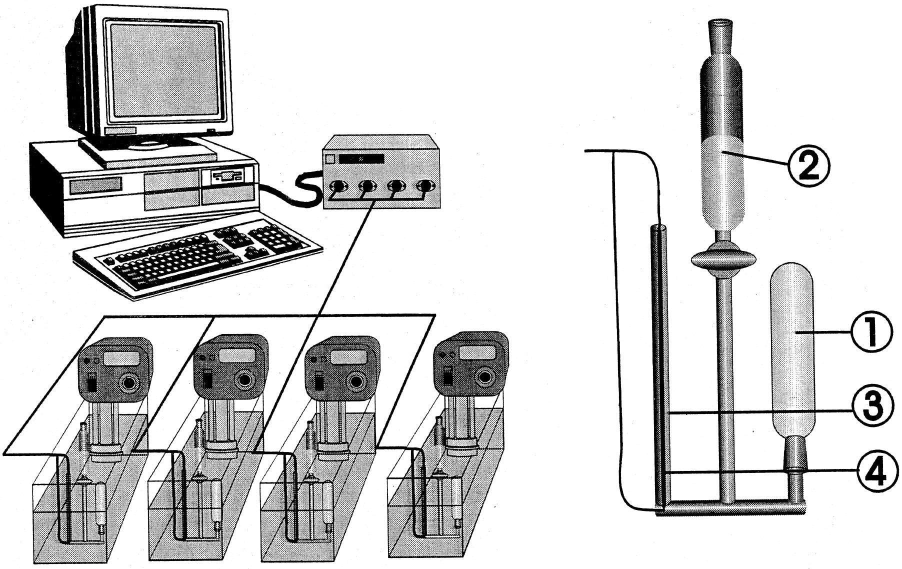

Fig.1: Principle of mercury dilatometry (1 - reaction flask, 2 - mercury storage tank, 3 - mercury measurement capillary, 4 - resistor wire)

RESULTS AND DISCUSSION

All of the used azo-initiators and DBP show a monomolecular first order decomposition corresponding to AIBN. Activation energies (E_d), exception DEDAS, and initiator effectivities (f) were lower as in the case of AIBN (Tab.1). This corresponds with the different course of conversion-time-curves in polymerization with azo-initiators in comparison to AIBN (Fig.2-5).

Table 1: Summary of the obtained initiator constants

Initiator	k_{d0} s^{-1}	E_d kJ/mol	f	$k_{d,60°C}$ 1) $10^6\ s^{-1}$	$2fk_{d,60°C}$ $10^6\ s^{-1}$
AIBN	$2.7\cdot10^{15}$	131	0.46	7.98	7.34
DBP	$1.2\cdot10^{13}$	115	0.13	11.4	2.96
APEG200	$2.6\cdot10^{12}$	110	0.08	15.0	2.40
PAPEG200	$5.6\cdot10^{11}$	105	0.07	19.6	2.74
DEDA	$3.6\cdot10^{12}$	112	0.07	10.1	1.41
AEG	$1.1\cdot10^{14}$	119	0.13	24.7	6.42
PAEG	$1.1\cdot10^{13}$	114	0.12	15.0	3.60
APEGS200	$6.7\cdot10^{13}$	118	0.05	21.6	2.16
DEDAS	$5.6\cdot10^{15}$	131	0.03	16.5	0.99
APS	k_{d0} $3.7\cdot10^{12}$	E_d 89	0.40		
	k_{f0} $1.7\cdot10^{05}$	E_f 53			
	k_{r0} $9.5\cdot10^{07}$	E_r 72			

1) $k_d=k_{d0}\cdot e(-E_d/RT)$

Furthermore APS needs for a precise description of its decomposition in DMF an initiator-solvent-complex-mechanism (eq. 1 and 2).

$$I \xrightarrow{k_d} 2R\bullet \qquad \text{eq. 1}$$

$k_d = 1.6\ 10^{-4}\ s^{-1}$ (50°C in DMF)

$$I + S \underset{k_r}{\overset{k_f}{\rightleftarrows}} \{ISC\} \qquad \text{eq. 2}$$

$k_f = 4.8\ 10^{-4}\ s^{-1}$ (50°C in DMF)*)

$k_r = 2.4\ 10^{-4}\ s^{-1}$ (50°C in DMF)

I - initiator
R• - initiator radical
S - solvent
{ISC} - initiator-solvent-complex
*) - reaction of pseudo first order, because - solvent concentration was in a large overplus

Selected results are given in Tab.2 and Fig.2-5.

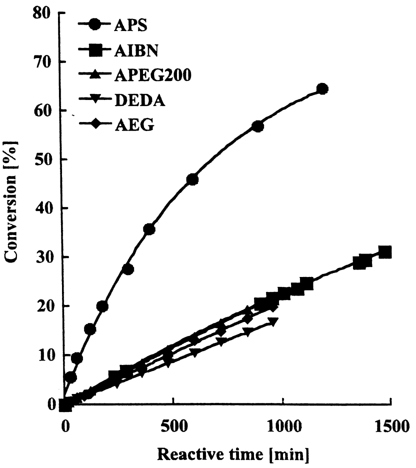

Fig.2: Comparison of experimental (marker) and modeling (solid line) values of some selected polymerizations at T=40°C ($[AN]_0$=3.8 mol/l, $[APS]_0$=0.0045 mol/l, $[AIBN]_0$, $[APEG200]_0$, $[DEDA]_0$ and $[AEG]_0$=0.008 mol/l)

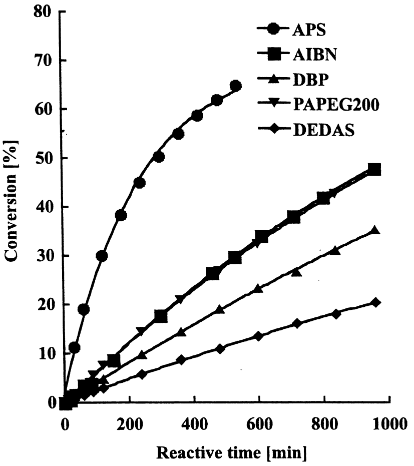

Fig.3: Comparison of experimental (marker) and modeling (solid line) values of some selected polymerizations at T=50°C ($[AN]_0$=3.8 mol/l, $[APS]_0$=0.0045 mol/l, $[AIBN]_0$, $[DBP]_0$, $[PAPEG200]_0$ and $[DEDAS]_0$=0.008 mol/l)

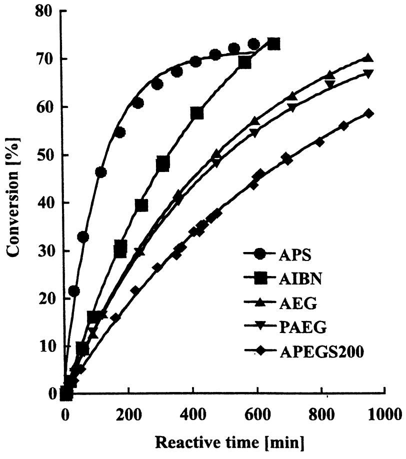

Fig.4: Comparison of experimental (marker) and modeling (solid line) values of some selected polymerizations at T=60°C ($[AN]_0$=3.8 mol/l, $[APS]_0$=0.0045 mol/l, $[AIBN]_0$, $[AEG]_0$, $[PAEG]_0$, and $[APEGS200]_0$=0.008 mol/l)

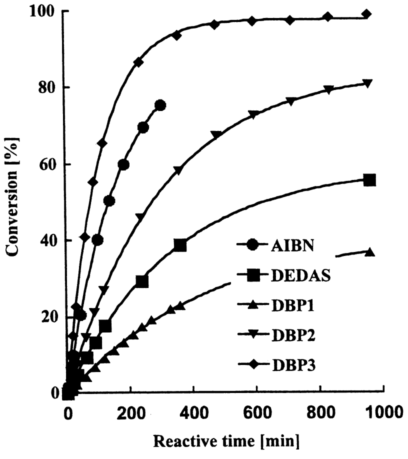

Fig.5: Comparison of experimental (marker) and modeling (solid line) values of some selected polymerizations at T=70°C ($[AN]_0$=3.8 mol/l, $[AIBN]_0$ and $[DEDAS]_0$=0.008 mol/l, $[DBP1]_0$=0.0006 mol/l, $[DBP2]_0$=0.006 mol/l, $[DBP3]_0$=0.060 mol/l)

Table 2: Comparison between experimental and model values of selected polymerization samples ($[AN]_0$=3.8 mol/l; T=60°C)

Initiator	Reactive time min.	$[I]_0$ mol/l	$Conversion_{exp.}$ %	$Conversion_{model}$ %	$M_{w,exp.}$ 10^3 g/mol	$M_{w,model}$ 10^3 g/mol
AIBN	662	0.0076	73.4	72.5	60	57
DBP	960	0.0061	65.0	62.8	66	69
APEG200	960	0.0099	69.4	67.9	63	64
PAPEG200	960	0.0129	72.0	70.4	67	62
DEDA	960	0.0080	62.7	61.3	70	69
AEG	960	0.0065	70.3	70.7	61	62
PAEG	960	0.0057	66.8	65.9	65	66
APEGS200	960	0.0107	58.8	57.4	64	72
DEDAS	960	0.0080	40.9	41.4	74	73
APS	600	0.0045	73.1	73.8	41	42

M_w – weight average molecular weight obtained by GPC

As shown in Fig.6, a significant trend of decreasing $2fk_d$-values of modified azo-initiators in comparison to AIBN in acrylonitrile polymerization was obtained. The trend correlates with decreasing solubility of initiators in N,N'-dimethylformamide [3].

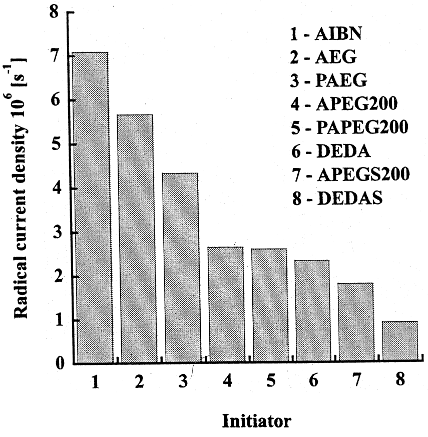

Fig.6: Dependence of radical current density ($2fk_d$) from type of initiator at 60°C

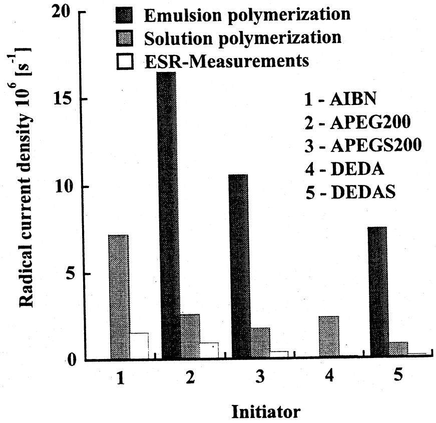

Fig.7: Dependence of radical current density ($2fk_d$) from type of polymerization and initiator at 60°C

Comparison of radical current densities of some selected initiators (Fig.7) shows for emulsion polymerization and ESR-measurement in water an analogous trend of decreasing 2fk_d-values (AIBN>APEG200>DEDA>APEGS200>DEDAS), like in the case of radical current densities in solution polymerization. That trend can lead back to structure dependence differencies in associate formation behaviour of initiators [2,3].

Gross kinetics of all polymerization systems can be discribed sufficiently precise up to high conversions by classical polymerization mechanism (Fig.2-5, Tab.2). Propagation (k_p), termination (k_t) and solvent transfer (k_{st}) constants are characterized by following Arrhenius-equations.

$$k_p = 4.92 \cdot 10^7 \cdot e^{-\left(\frac{25.8}{RT}\right)} \ 1/\mathrm{mol} \cdot \mathrm{s}$$

$$k_t = 8.11 \cdot 10^8 \ 1/\mathrm{mol} \cdot \mathrm{s}$$

$$k_{st} = 1.51 \cdot 10^7 \cdot e^{-\left(\frac{44.6}{RT}\right)} \ 1/\mathrm{mol} \cdot \mathrm{s}$$

A comparison between the obtained constants and values from literature shows a good correspondence (Tab.3).

Table 3: Comparison between own and some selected values from literature

Constant	Temperature	Own values	Literature values	Literature
k_p	50°C	3326 l/mol·s	3300 ± 300 l/mol·s	[5]
k_t	50°C	$8.11 \cdot 10^8$ l/mol·s	$12.0 \cdot 10^8 \pm 1.7 \cdot 10^8$ l/mol·s	[5]
	60°C	$8.11 \cdot 10^8$ l/mol·s	$7.82 \cdot 10^8$ l/mol·s	[6]
$C_S = k_{st}/k_p$	40°C	$2.25 \cdot 10^{-4}$	$2.30 \cdot 10^{-4}$	[7]
	50°C	$2.81 \cdot 10^{-4}$	$2.80 \cdot 10^{-4}$	[8]
			$2.83 \cdot 10^{-4}$	[9]
	60°C	$3.46 \cdot 10^{-4}$	$2.412 \cdot 10^{-4}$	[10]
			$4.494 \cdot 10^{-4}$	[7]
$k_{d,AIBN}$	50°C	$1.86 \cdot 10^{-6}$ s^{-1}	$2.00 \cdot 10^{-6}$ - $2.20 \cdot 10^{-6}$ s^{-1}	[11]
	60°C	$0.80 \cdot 10^{-5}$ s^{-1}	$1.03 \cdot 10^{-5}$ - $1.05 \cdot 10^{-5}$ s^{-1}	[12]
	70°C	$3.11 \cdot 10^{-5}$ s^{-1}	$4.14 \cdot 10^{-5}$ s^{-1}	[13]
	80°C	$1.14 \cdot 10^{-4}$ s^{-1}	$1.49 \cdot 10^{-4}$ s^{-1}	[14]
$k_{d,APS}$	50°C	$1.60 \cdot 10^{-4}$ s^{-1}	$1.15 \cdot 10^{-4}$ s^{-1}	[15]

CONCLUSION

Decomposition of all azo-initiators and dibenzoylperoxide follows a first order mechanism. The effects of azo-initiators on the acrylonitrile polymerization in N,N'-dimethylformamide restrict to smaller time conversions at same temperatures and concentrations. That can lead back on an aggregate and micell formation of initiators in the solution polymerization in N,N'-dimethylformamide, like in emulsion polymerization and ESR-measurement in water. This aggregation decreases initiator effectivity, because the cage effect in initiator micelles increases and so primary radical termination in micelles.

The mathematical polymerization model describes sufficiently precise acrylonitrile polymerization in N,N'-dimethylformamide with various initiators in the used range of concentrations and temperatures. An initiator-solvent-complex-mechanism is necessary for precise course description of polymerizations with APS as initiator.

Furthermore it is possible to reach aimed polymer parameters by choosing suitable initiators and by calculating polymerization conditions.

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