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KINETICS OF RADICAL POLYMERIZATION—XXXVII

INVESTIGATION OF MOLECULAR-INHIBITORS IN THE RADICAL POLYMERIZATION OF ACRYLONITRILE

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Abstract—The effect of molecular inhibitors with different reactivities was studied for the homogeneous (solution) and heterogeneous bulk-polymerization of AN. *p*-Nitro-acetophenone, which acts as a weak retarder in solution, strongly decreases the accelerating character of the bulk polymerization. Aromatic nitroso-compounds are strong inhibitors in both homogeneous and heterogeneous polymerizations. The length of the inhibition period depends linearly on the inhibitor concentration. The character and kinetics of the polymerization after the inhibition period are not affected by the nitroso compounds. A novel method has been introduced to determine the length of inhibition period for accelerating heterogeneous polymerization. In every studied system, a considerable stoichiometric anomaly was observed, and attributed to the hot radical effect.

INTRODUCTION

The polymerization of acrylonitrile (AN) proceeds homogeneously if the initial concentration of monomer (m_0) does not exceed 4 mol/l in dimethylformamide (DMF) solution. The polymerizing system AN/DMF becomes heterogeneous over 5.5 mol/l because of the decreasing solubility of polyacrylonitrile. Between these concentrations, there is a transition region [1]. In the various solubility ranges, there are also qualitative differences in the kinetics of the process. In the heterogeneous system, the importance of physical factors increases and they may even dominate chemical factors.

For the homogeneous and heterogeneous systems, differences were observed also in the inhibition processes. According to Bagdasaryan [2], weak inhibitors (aniline, naphthalene, nitrobenzene derivatives) do not decrease the rate of polymerization in the homogeneous phase, while anthracene, benzoquinone dimethylaniline and diphenylamine have a slight retarding effect. These compounds exert quite a different effect in the heterogeneous polymerization, as found by Glasdyshev [3, 4] with phenol, pyrogallol and hydroquinone, and by Bamford [5] with *n*-butylmercaptan. These compounds, when applied in increasing concentration, decrease or stop the accelerating character of the polymerization, with simultaneous decrease in the molecular weight of the resulting polymer.

The present paper refers to the behaviour of strong molecular inhibitors and compares it with the effect of weak inhibitor in the homogeneous and heterogeneous polymerizations of AN.

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EXPERIMENTAL

AN (Fluka, pure grade) was purified by triple fractional distillation as already described [6]. Purification of AIBN and of DMF have also been described [6, 7]. The inhibitors *p*-nitroso-*m*-cresol, *p*-nitroso-dimethylaniline and *p*-nitroso-diphenylamine were described previously [10]. *p*-Nitro-acetophenone and *p*-nitroso-diethylaniline were recrystallized from absolute ethanol before use (m.p. 80–81° and 84° respectively).

Polymerizations were carried out in bulk and in DMF solution at 50°, in sealed dilatometers filled with nitrogen. Internal diameters of the ampoules were 5 up to 15 mm. The samples were deoxygenated by the freeze and thaw method, in three cycles. For the calculation of the conversion, the factor $\Phi_D^{50°} = 2.36\, g_{AN}$ was used [6].

EXPERIMENTAL RESULTS AND THEIR EVALUATION

1. Effect of a weak inhibitor on the radical polymerization of AN

p-Nitroacetophenone is a very weak retarder of the homogeneous AN polymerization (3.8 mol/dm^3 solution in DMF). The experimental data are listed in Table 1. In bulk, the same inhibitor decreases significantly the accelerating character of the heterogeneous polymerization even in low concentration ($z_0/x_0 = 0.08$, where z_0 and x_0 are the initial concentrations of inhibitor and initiator respectively), and also has a weak retarder effect, as in homogeneous polymerization. This feature is well illustrated by the log m_0/m vs t kinetic curves in Fig. 1 and by the data listed in Table 1; m_0 is the initial monomer concentration and m is that at time t.

2. Effect of strong inhibitors on the radical polymerization of AN

Inhibition effect of aromatic C-nitroso compounds. Aromatic C-nitroso compounds are strong inhibitors

Table 1. The effect of *p*-nitro-acetophenone on the polymerization of AN

m_0 (mol/l)	No.	x_0 (mol/l)	z_0 (mol/l)	$10^2\, z_0/x_0$	W_{rel}
3.77	1	2.33×10^{-2}	0	0	1.00*
	2	2.33×10^{-2}	1.68×10^{-3}	7.2	0.97
	3	2.34×10^{-2}	5.81×10^{-3}	24.9	0.95
	4	2.33×10^{-2}	12.17×10^{-3}	52.3	0.94
14.57 (bulk)	5	2.69×10^{-4}	0	0	—
	6	2.74×10^{-4}	2.31×10^{-5}	8.4	—
	7	2.62×10^{-4}	3.47×10^{-5}	13.3	—
	8	2.62×10^{-4}	7.60×10^{-5}	29.0	—
	9	2.62×10^{-4}	17.38×10^{-5}	66.4	—

* $K_{Br} = 8.56 \times 10^{-3}\ mol^{1/2}\, l^{-1/2}\, min^{-1}$.

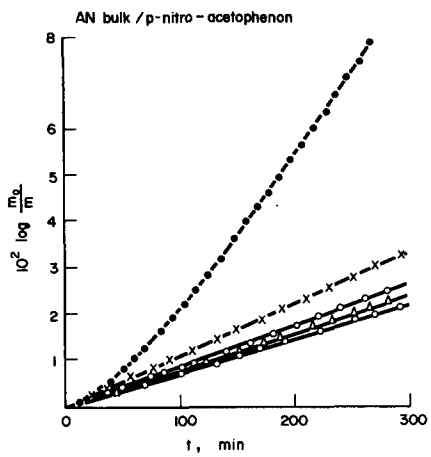

Fig. 1. Effect of *p*-nitroso-acetophenone on the bulk polymerization of AN. (designations as in Table 1).

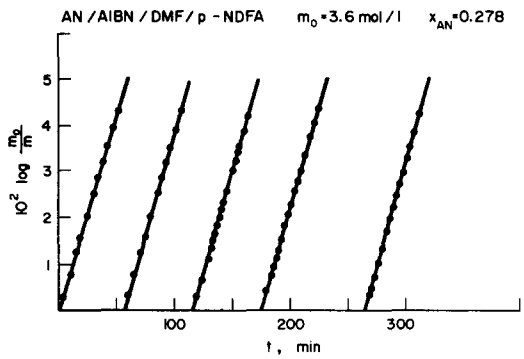

Fig. 2. Effect of *p*-nitroso-diphenylamine on the system AN/AIBN/DMF with concentrations according to designations in Table 2.

of the polymerizations of styrene, methyl methacrylate [8], vinyl acetate [9] and methyl acrylate [10]. For our inhibition kinetic measurements with AN, 6-nitroso-*m*-cresol and *N*-substituted derivatives of *p*-nitroso-aniline (such as *p*-nitroso-dimethylaniline, *p*-nitroso-diethylaniline and *p*-nitrosodiphenylamine) were chosen. All of them were found to be strong inhibitors. In the homogeneous system, after an inhibition period proportional to the inhibitor concentration, the polymerization reached a steady rate equal to that without inhibitor, as indicated by the characteristic log m_0/m vs t curves in Fig. 2.

While the *N*-substituted *p*-nitroso-analines are such strong inhibitors of AN polymerization that no chain propagation can be observed during the inhibition period, 6-nitroso-*m*-cresol does not suppress the polymerization completely (see Fig. 3). In this case, the inhibitor can be characterized by the ratio of the rate constants for the inhibition and chain propagation reactions i.e. by the relative reactivity k_5/k_2.

According to Bartlett and Kwart [11], the value of relative reactivity can be determined by the following

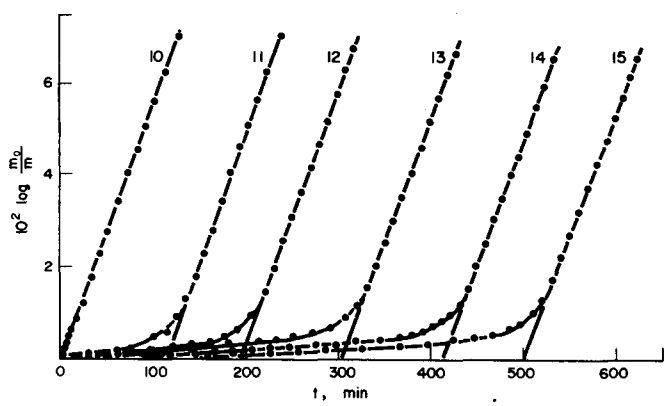

Fig. 3. The inhibition effect of 6-nitroso *m*-cresol on the system AN/AIBN/DMF. Concentrations as indicated in Table 3.

Table 2. The inhibition effect of nitroso compounds on the homogeneous polymerization of AN

Inhibitor	Sample No.	m_0 (mol/l)	10^2x_0 (mol/l)	10^4z_0 (mol/l)	t_i (min)	k_5/k_2	μ
6-nitroso-*m*-cresol	10	3.70	1.94	0	0		
	11	3.70	1.94	2.15	115	206	
	12	3.70	1.94	3.67	193	208	
	13	3.70	1.94	5.60	303	205	204 ± 5%
	14	3.70	1.94	7.44	411	197	
	15	3.70	1.94	8.93	495	202	
p-nitroso-dimethylaniline	16	3.78	5.07	0	0	—	1.60 ± 0.04
	17	3.78	5.07	3.94	73	—	
	18	3.78	5.07	8.58	157	—	
	19	3.78	5.07	12.93	228	—	
	20	3.78	5.07	15.64	276	—	
p-nitrosodiphenylamine	21	3.604	4.88	0	0	—	1.81 ± 0.05
	22	3.604	4.88	2.75	57	—	
	23	3.604	4.88	5.46	116	—	
	24	3.604	4.88	8.24	175	—	
	25	3.604	4.88	12.39	265	—	

The value $2k_1f = 1.76 \cdot 10^{-4}\ \text{min}^{-1}$ was used for calculation of the rate of initiation [7].

relationship

$$\log \frac{m_0}{m} = \frac{k_5}{k_2} \log \frac{z_0}{z} \tag{1}$$

for the value of z_0/z, the following approach can be used

$$\frac{z_0}{z} = \left\{1 - \frac{t}{t_i}\right\}^{-1} \tag{2}$$

where z is the inhibitor concentration at time t and t_i is the length of inhibition period. The relative reactivity values calculated with equations (1) and (2) are listed in Table 2.

Having measured the inhibition periods and with knowledge of the rate of initiation ($W_1 = 2k_1fx_0$), the number of macroradicals deactivated by one inhibitor molecule, i.e. the stoichiometric coefficient (μ) was determined:

$$t_i = \frac{\mu}{2k_1f} \frac{z_0}{\bar{x}} \tag{3}$$

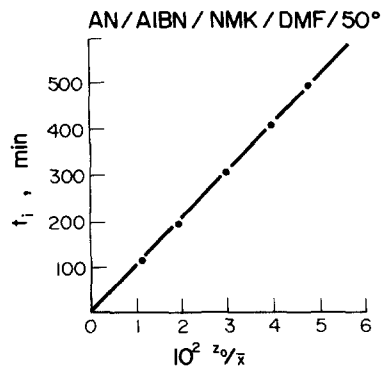

Fig. 4. Δt_i vs z_0/x plot of the experimental data listed in Table 2.

where $\bar{x}$ stands for the integral average value of initiator concentration during the inhibition period. Plots of experimental data according to equation (3) were linear (see, e.g. Fig. 4).

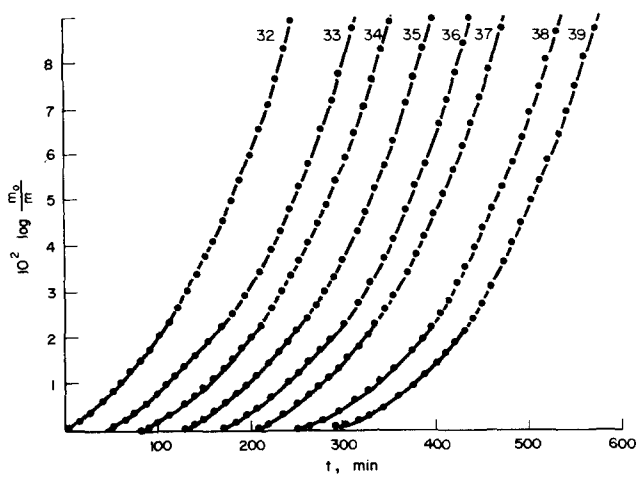

Fig. 5. The effect of *p*-nitroso-dimethylaniline on the bulk polymerization of AN. (see Table 3).

The μ values calculated from the slopes of the straight lines are listed in Table 2.

Inhibition kinetic measurements similar to those referred to above were carried out also in heterogeneous bulk polymerization. Owing to the accelerating character of the heterogeneous polymerization, the inhibition periods cannot be determined as usual, i.e. by the extrapolation of the linear section of log m_0/m vs t curve to zero conversion. Therefore, a novel method has been introduced for determination of t_i in bulk polymerization. After 4–5% conversion subsequent to the inhibition period, in the ideal case and with equal initiator concentrations, the log m_0/m vs t curves are laterally shifted corresponding to the inhibitor concentration, i.e. to the inhibition period. If t_z denotes a polymerization time for a given log m_0/m value $\sqrt{1}$ of inhibited system and t_0 denotes a polymerization time corresponding to the same conversion. $\sqrt{2}$ without inhibition, the shift of the curves can be determined by the following expression:

$$\Delta t = t_z - t_0 = f\left(\log \frac{m_0}{m}\right). \tag{4}$$

By means of this quantity, the length of the inhibition period can be defined by the following limit value:

$$t_i = \lim \Delta t \quad \log m_0/m \to 0. \tag{5}$$

In the ideal case, i.e. if the conversion curves are strictly parallel,

$$t_i = \Delta t. \tag{6}$$

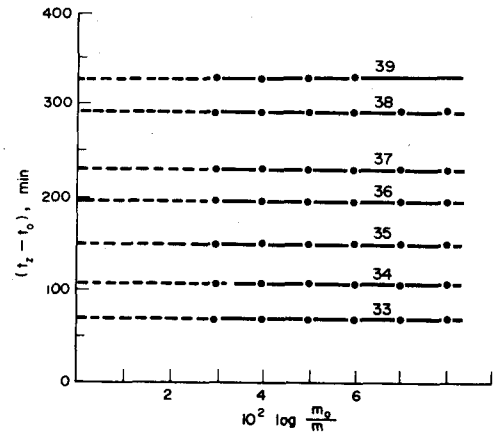

Fig. 6. The polymerization kinetic data shown in Fig. 4, plotted according to equation (4).

For example, Fig. 5. illustrates the log m_0/m vs t kinetic curves in bulk polymerization, in the case of *p*-nitroso-dimethylaniline.

Plotted according to equation (4), the experimental data gave straight lines (see Fig. 6).

The straight lines are horizontal, indicating that the investigated nitroso compound yields products inert in radical reactions. During the inhibition period, the inhibitor is quantitatively consumed, after which the heterogeneous polymerization proceeds as if no inhibitor had been present.

A strict condition of this method for determination

Table 3. The inhibition effect of nitroso compounds on the bulk polymerization

Inhibitor	Sample No.	$10^2 x_0$ (mol/l)	$10^4 z_0$ (mol/l)	t_i (min)	k_5/k_2		μ
6-nitroso-*m*-cresol	26	5.53	0	0	—	255 ± 15%	1.34 ± 0.05
	27	5.53	4.59	52	293		
	28	5.53	10.47	147	265		
	29	5.53	15.85	233	245		
	30	5.53	20.39	310	232		
	31	5.53	26.19	405	238		
p-nitroso-dimethyl-aniline	32	5.28	0	0			0.87 ± 0.06
	33	5.28	5.67	68	—		
	34	5.28	9.27	106	—		
	35	5.28	14.29	149.5	—		
	36	5.28	18.31	194	—		
	37	5.28	22.86	228	—		
	38	5.28	28.45	289	—		
	39	5.28	32.84	327	—		
p-nitroso-diethyl-analine (measured in ampoules of 5 mm diameter)	40	44.4	0	0	—		1.23 ± 0.06
	41	43.7	53.8		81	—	
	42	42.7	79.0	126	—		
	43	49.4	104.2	155	—		
	44	44.3	136.3	240	—		
	45	51.2	189.1		276	—	
p-nitroso-diphenyl-amine	46	6.51	0	0	—		0.86 ± 0.07
	47	6.51	4.59	39	—		
	48	6.51	7.83	61	—		
	49	6.51	12.57	103	—		
	50	6.51	17.46	138	—		

The value $2k_1 f = 1.64 \cdot 10^{-4}$ min^{-1} was used for the calculations [6].

of inhibition times is (for heterogeneous polymerization of AN) the equality of initiator concentrations within a series. Furthermore, the heat transmission coefficient of the ampoules should be approximately equal, otherwise the acceleration of the polymerization varies because of the overheating effect [12] (which anyway must be kept in a minimum), and the simple method of dealing with the curves cannot be applied.

If the shift of conversion curves with increasing inhibitor concentration is not parallel even when the above conditions are fulfilled i.e. the curves have positive slopes when plotted according to equation (4), then the effect is caused by chemical factors. The character of the anomaly can be easily decided by investigation of the system also in homogeneous conditions using a solvent. If, after the inhibition period, the rate of the polymerization gradually decreases with increase of inhibitor concentration in solution, then the inhibition is accompanied by secondary retardation.

If, however, no secondary retardation can be observed after the inhibition period in the homogeneous polymerization, then the anomaly found in the heterogeneous system can be attributed to other factors, e.g. to molecular weight decrease due to chain transfer.

The stoichiometric coefficient was determined by equation (3) also from the bulk polymerization data (see Table 3).

As can be seen, in bulk polymerization the μ values are in all cases considerably lower than in solution, although even the latter do not reach the theoretical value of 2 [8]. The stoichiometric anomaly can be interpreted in terms of the hot radical theory [13].

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