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KINETICS OF RADICAL POLYMERIZATION—XLVII. MOLECULAR MASS AND POLYDISPERSITY IN THE INHIBITED POLYMERIZATION

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INTRODUCTION

In earlier kinetic investigation of the inhibition system styrene–benzene-thymoquinone–azobisisobutyronitrile–50°C (St–Bz–TQ–AIBN), it was pointed out that the value of k_5/k_2 (where k_5 and k_2 are the rate constants of inhibition and chain propagation, respectively) determined from the relationship by Bartlett and Kwart [1], as well as the stoichiometric constant (μ), depend on the monomer concentration [2]. The experimentally determined μ values were in all cases smaller than the theoretical value of 2. These anomalies could be consistently explained and the dilution dependences of k_5/k_2 and μ could be described in terms of the hot radical theory.

In the present paper, we deal with the investigation of molecular mass and molecular mass distribution of the polymer formed in the polymerization of styrene initiated by AIBN and inhibited by TQ.

EXPERIMENTAL

Purifications of St, Bz and AIBN were carried out as given earlier [4–6]. TQ (2-isopropyl-5-methyl-benzoquinone-1,4) was synthesized from thymol [7] and the product was recrystallized from an ethanol–water mixture.

Polymerizations were carried out in dilatometer ampoules at 50°C. Oxygen was removed by the usual freeze and thaw method. Polymerization was carried to 0.5–1% conversion. Unreacted monomer was removed by drying *in vacuo*, in the presence of stable free radical. The molecular masses of polymers were determined by GPC using a Waters ALC/GPC 201 type high pressure instrument with tetrahydrofuran solvent, at room temperature on μ-styragel columns (10^6, 10^5, 10^4, 10^3, 500, 100 Å).

MOLECULAR MASS AND POLYDISPERSITY IN INHIBITED POLYMERIZATION

In terms of the hot radical theory, the following reaction scheme can be given for the inhibited polymerization:

the $R_1^{\cdot}$ radicals formed in the initiation step can participate in chain propagation

$$R_1^{\cdot} + M \xrightarrow{k_2} R_2^{\cdot} \qquad (1)$$

in inhibition

$$R_1^{\cdot} + Z \xrightarrow{k_5} Y_1^{*} \qquad (2)$$

and in termination [see Eqn (6)]. In terms of the hot radical theory, the excess of vibrational energy released in step (2) can act as a source of energy in the further reaction of the intermediate radical (Y_1^{*}) [3], and the reactive intermediate radical thus formed can undergo chain reaction

$$Y_1^{*} + M \xrightarrow{k_6^{*}} R_2^{\cdot} \qquad (4)$$

By colliding with a monomer molecule, Y_1^{*} can of course also lose its excess energy

$$Y_1^{*} + M \xrightarrow{k_8^{*}} Y_1 + M \qquad (5)$$

In the case of quinones, this reaction step is followed by a recombination with another macroradical [8, 9]:

$$Y_1^{\cdot} + R_n^{\cdot} \xrightarrow{k_5'} P_{n+1} \qquad (6)$$

where $R_n^{\cdot}$ denotes a macroradical of any length ($n = 1 - \infty$). Due to reaction (4), the number of inhibitor molecules incorporated in the polymer chain will be greater than expected; accordingly, a smaller stoichiometric coefficient (μ) can be observed than expected theoretically. This is in accordance with the experimental results [2, 3].

From (4) and (5), the probability of chain regeneration of the hot intermediate radical ($1 - \alpha$) can be given by the following relationship

$$1 - \alpha = \frac{k_6^{*} y^{*} m}{k_6^{*} y^{*} m + k_8^{*} y^{*} m} = \frac{k_6^{*}}{k_6^{*} + k_7^{*}} \qquad (7)$$

and, for the system under study, the stoichiometric coefficient obviously is

$$\mu = 2\alpha \qquad (8)$$

In the above reaction scheme, chain termination of the type

$$R_n^{\cdot} + R_1^{\cdot} \rightarrow P_{n+1} \qquad (9)$$

was not considered, because for strong inhibitors or weak inhibitors in high concentration, the above reaction can be neglected. Obviously, a similar scheme can be given for the $R_2^{\cdot}$ formed in chain propagation step (1) and for the further $R_n^{\cdot}$ macro-

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radicals of various lengths. The set of differential equations for the individual radical concentrations has the following form:

$$\frac{\mathrm{d}r_1}{\mathrm{d}t} = W_1 - k_2 r_1 m - k_5' \sum_{n=1}^{\infty} y_n r_1 - k_5 z r_1 \tag{10}$$

$$\frac{\mathrm{d}r_2}{\mathrm{d}t} = k_2 r_1 m - k_2 r_2 m - k_5' \sum_{n=1}^{\infty} y_n r_2 - k_5 z r_2 + k_6^* y_1^* m \tag{11}$$

$$\frac{\mathrm{d}r_n}{\mathrm{d}t} = k_2 r_{n-1} m - k_2 r_n m - k_5' \sum y r_n - k_5 z r_n + k_6^* y_{n-1}^* m \tag{12}$$

From the differential equation system given for the individual y_n^* and y_n concentrations, the following relationships can be obtained by application of the Bodenstein principle:

$$y_n^* = \frac{(1-\alpha) k_5 z r_n}{k_6 m} \tag{13}$$

and

$$y_n = \alpha \frac{k_5 z r_n}{k_5 r} \tag{14}$$

where

$$r = \sum_{n=1} r_n.$$

Using the Bodenstein principle, from Eqns (10–12), the individual radical concentrations can be expressed, using Eqns (13) and (14):

$$r_1 = \frac{W_1}{k_2 m + \alpha k_5 z + k_5 z} \tag{15}$$

$$r_2 = \frac{k_2 m + (1-\alpha) k_5 z}{k_2 m + (1+\alpha) k_5 z} r_1 \tag{16}$$

$$r_n = \beta r_{n-1} = \beta^{n-1} r_1 \tag{17}$$

where β is the probability of chain propagation:

$$\beta = \frac{k_2 m + (1-\alpha) k_5 z}{k_2 m + (1+\alpha) k_5 z} \tag{18}$$

Summing up the differential Eqns (10–12) of individual radical concentrations, we obtain

$$\frac{\mathrm{d}r}{\mathrm{d}t} = W_1 - k_5' y r - k_5 z r + k_6^* y^* m \tag{19}$$

By the use of relationships obtained by application of the stationary principle and by summing (13) and (14) from 1 to ∞, we obtain the relationship

$$W_1 = 2\alpha k_5 z r \tag{20}$$

Substituting Eqn (20) into Eqn (15) yields

$$r_1 = (1-\beta) r \tag{21}$$

and by the use of Eqns (21) and (17) we obtain

$$r_n = (1-\beta)\beta^{n-1} r \tag{22}$$

In our case, the probability of the formation of a polymer chain with p length (γ_p) is given by the following expression:

$$\gamma_p = \frac{\sum_{l=1}^{p=1} k_5' y_l r_{p-l}}{\sum_{p=2}^{\propto} \sum_{l=1}^{p=1} k_5' y_l r_{p-l}} \tag{23}$$

which, by the use of Eqns (14) and (22), yields

$$\gamma_p = \frac{\sum_{l=1}^{p=1} \alpha k_5 z r^2 (1-\beta)\beta^{l-1}(1-\beta)}{\alpha k_5 z r^2} \tag{24}$$

and this leads to the well known expression

$$\gamma_p = (1-\beta)^2 \beta^{p-2}(p-1) \tag{25}$$

If β is known, the number-average ($\bar{P}_n$), the weight-average ($\bar{P}_w$) and the Z average ($\bar{P}_z$) polymerization degrees can be calculated by the following well-known equations:

$$\bar{P}_n = \frac{2}{1-\beta} \tag{26}$$

$$\bar{P}_w = \frac{2+\beta}{1-\beta} \tag{27}$$

$$\bar{P}_z = \frac{4 + 7\beta + \beta^2}{2+\beta} \frac{1}{1-\beta} \tag{28}$$

Using Eqn (18) for the probability of chain propagation, the following relationship can be obtained from Eqn (26) for the number-average polymerization degree:

$$\bar{P}_n = \frac{1}{\frac{1}{2}\mu \frac{k_5}{k_2} \cdot \frac{z}{m}} + \frac{1}{\alpha} - 1 + 2 \tag{29}$$

The term ($1/\alpha - 1$) gives the number of monomer molecules incorporated in the polymer chain by hot radical chain regeneration. For the system studied, $\mu = 0.99$ for bulk polymerization [2], i.e. $\alpha = 0.50$, which means that, on average, one monomer molecule is incorporated in the polymer chain with hot radical chain regeneration. The number 2 in the right side of Eqn (29) gives the number of initiating radicals incorporated, which is two for recombination. The curious feature of the above relationship is that it does not contain the rate of initiation, meaning that the polymerization degree does not depend on the rate of initiation.

Of course, this independence is valid only until the chain termination reaction given in Eqn (9) is really negligible. The error resulting from this neglect can be estimated by the expression [1]

$$W_{\mathrm{rel}}^2 = \left[\frac{W_{\mathrm{inh}}}{W_{\mathrm{o}}}\right]^2 \tag{30}$$

where W_{inh} is the rate of inhibited polymerization and W_o is that for the polymerization free of inhibitor. Thus, in the case $W_{\mathrm{rel}} = 0.1$, the error is 1%.

Table 1. The data for the system St–TQ–AIBN–50

	$z_0 \times 10^3$ (mol·dm^{-3})	W_{inh} (mol·dm^{-3} min^{-1})	$\mu \cdot k_5/k_2$	β	Conversion (%)
1	2.01	2.03×10^{-3}	59.6	0.9849	0.85
2	4.15	1.06×10^{-3}	62.7	0.9698	1.25
3	6.04	6.86×10^{-4}	67.9	0.9573	0.61
4	14.84	2.77×10^{-4}	65.2	0.8965	0.29
5	31.92	1.42×10^{-4}	53.4	0.8338	0.34
	$W_1 = 3.39 \times 10^{-5}$ (mol·dm^{-3} min^{-1}); $x_0 = 19.58 \times 10^{-2}$ (mol·dm^{-3})				
6	1.48	5.43×10^{-4}	67.8	0.9888	0.68
7	2.64	3.73×10^{-4}	57.0	0.9803	0.68
8	4.70	2.06×10^{-4}	60.0	0.9661	0.71
9	18.60	6.00×10^{-5}	51.7	0.8881	0.22
10	33.28	2.85×10^{-5}	60.9	0.8292	0.26
	$W_1 = 6{,}83 \times 10^{-6}$ (mol·dm^{-3} min^{-1}); $x_0 = 3.95 \times 10^{-2}$ (mol·dm^{-3})				

Table 2. The measured and calculated values of $\bar{M}_w$ and dispersity

	$(\bar{M}_w)_{calcd}$	$(\bar{M}_w)_{meas}$	$\left[\frac{\bar{M}_w}{\bar{M}_n}\right]_m$	$\left[\frac{\bar{M}_w}{\bar{M}_n}\right]_c$	$\left[\frac{\bar{M}_w}{\bar{M}_n}\right]_m$	$\left[\frac{\bar{M}_w}{\bar{M}_n}\right]_c$
1	20590	19700	1.93	(1.49)	1.75	(1.33)
2	10200	9370	1.79	(1.49)	1.62	(1.33)
3	7180	7560	1.80	(1.48)	1.75	(1.33)
4	2910	3050	1.55	(1.45)	1.50	(1.32)
5	1770	1770	1.40	(1.42)	1.36	(1.31)
6	27800	27600	2.20	(1.49)	1.70	(1.33)
7	15700	16300	1.84	(1.49)	1.61	(1.33)
8	9100	9360	1.89	(1.48)	1.71	(1.33)
9	2690	2790	1.51	(1.44)	1.47	(1.32)
10	1730	1830	1.66	(1.42)	1.56	(1.31)

EXPERIMENTAL RESULTS AND THEIR EVALUATION

Polymerizations were carried with two initiator concentrations and with five inhibitor concentrations for each series of experiments. The experimental data are listed in Table 1. The table contains also the $\mu k_5/k_2$ values calculated from the initial rate of inhibited polymerization.

Our earlier measurements on the system St–TQ–AIBN yielded a stoichiometric coefficient of 0.99 for bulk polymerization [2]; thus knowing α, the chain propagation probabilities for each measuring point could be calculated by Eqn (18) (see Table 1).

In Table 2, the measured and calculated mass average molecular masses are listed. The latter were calculated by Eqns (26) and (28), using the β values. The table contains also the measured and (in parentheses) the calculated dispersities.

For comparison of measured and calculated values, the $\bar{M}_w$ data were chosen because, since the GPC method was used, these can be considered as direct data. The $\bar{M}_w$ and $\bar{M}_z$ values are transformed and, due to the error of reading, can be strongly distorted [10].

The excellent agreement of measured and calculated $\bar{M}_w$ values in Table 2 supports the validity of the equation derived for the polymerization degree. The measured dispersity values, however, show increasing deviation from the theoretical values as the molecular mass increases; this effect may be due to error in the evaluation of GPC curves or may be a consequence of higher conversions.

From the comparison of both series with different initiator concentrations, it can be established that the degree of polymerization is really independent of the rate of initiation, as expected.

SUMMARY

The effect of molecular inhibitors on the molecular mass of homopolymers was investigated for the styrene/thymoquinone system. Equations for the weight-average molecular mass and polydispersity were derived on the basis of the reaction scheme of inhibited homopolymerization. The derived equations were suitable for the description of the experimental data.

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