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INVESTIGATION OF POLYMERIZATION KINETICS AT HIGH CONVERSION

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Abstract

The polymerization of methyl-methacrylate was investigated in the presence of different initiators and retarders. For processing the measured data a calculation method was worked out on the basis of regression analysis. The results have shown that at high conversion only the rate constant of the chain termination reaction decreases, those of the initiation and chain propagation reactions do not change. Correlation was found between the rate constant of the chain termination reaction and the viscosity of the monomeric-polymeric system.

It was shown that the rate of reaction between the macroradical and the retarder molecule is the same at the beginning stage of polymerization and at high conversions. The amount of retardation is determined by the $\mu k_5 z$ product also at high conversions.

Calculations were made for controlling the exact suitability of the Cardenas-O'Driscoll model for describing the change of polymerization rate depending on the conversion. Our calculations pointed out that the model does not give an exact correlation between the change of polymerization rate and the conversion.

Keywords: Polymerization of methyl-methacrylate.

The polymerization of methyl-methacrylate was investigated in the presence of different initiators [1 – 3] and retarders [4, 5]. For processing the measurement data a calculation method was worked out on the basis of regression analysis [6]. The Gauss–Jordan method for solving equations in more unknown variables was applied for computer, which enabled the values of polymerization rate and time for any conversion to be determined.

The results of our testing and calculations have shown that at high conversions only the rate constant of the chain termination reaction decreases, those of the initiation and chain propagation reactions do not change. Correlation was found between the rate constant of the chain termination reaction and the viscosity of the monomeric-polymeric system. It was stated that in a large interval a linear correlation exists between the logarithm of the chain termination and the logarithm of the viscosity of the system [7].

It was shown that the rate of reaction between the macroradical and the retarder molecule is the same at the beginning stage of polymerization and at high conversions. The extent of retardation is determined by the $\mu k_5 z$ product also at high conversions [8].

CARDENAS and O'DRISCOLL [9], considering the interaction between the polymer chains gave an equation for determining the rate of polymerization also at high conversions. This was later modified by considering the chain-transfer reaction to the monomer [10].

The equation is as follows:

$$-\frac{\mathrm{d}m}{\mathrm{d}t} = k_2 m \left(\frac{W_1}{k_4}\right)^{0.5} 1 + \frac{\tau(1-\alpha)\exp(-\tau n_c)}{\tau_\varepsilon - k_{3,m}(1-\alpha)\exp(-\tau n_c)}, \tag{1}$$

where

$$\tau = k_{3,m} + \frac{2\left(\frac{W_1}{k_4}\right)^{0.5}}{k_2 m}, \tag{2}$$

and

$$\tau_\varepsilon = k_{3,m} + \frac{2\alpha\left(\frac{W_1}{k_4}\right)^{0.5}}{k_2 m} \tag{3}$$

$$n_c = \frac{K_c^2(1+\varepsilon x)^2}{x^2(1+\varepsilon)^2}. \tag{4}$$

The modified Cardenas–O'Driscoll model contains three parameters:

1) K_c refers to the interaction between the polymer chains.
2) α characterizes the decrease of radical movement.
3) $k_{3,m}$ is the rate constant of the chain transfer reaction to the monomer.

Calculations were made for controlling the exact suitability of the Cardenas–O'Driscoll model for describing the change of polymerization rate depending on the conversion. As an example the processed testing data of the system containing $4.13 \cdot 10^{-2}$ mol·dm^{-3} benzoyl peroxide polymerized at 60°C are shown in *Table 1*. The data in column 'C' of *Table 1* were calculated from *Eqs* (1) – (4). From reference data [7] the values of $k_1 = 4.374 \cdot 10^{-6}\,\mathrm{s}^{-1}$, $k_2 = 518.7\,\mathrm{dm}^3\mathrm{mol}^{-1}\mathrm{s}^{-1}$, and $k_4 = 2.603 \cdot 10^7\,\mathrm{dm}^3\mathrm{mol}^{-1}\mathrm{s}^{-1}$. The values of α, $k_{3,m}$ and K_c had been selected so — not regarding their physical meaning — as to obtain the lowest average values of percentage deviations in columns 'D' and 'E' of *Table 1*.

Table 1

Comparison of the polymerization rates calculated from the Cardenas–O'Driscoll model with the measured values. A: conversion (%), B: measured rate of polymerization ($\text{mol}\cdot\text{dm}^{-3}\text{s}^{-1}\cdot 10^4$), C: polymerization rate calculated from the Cardenas–O'Driscoll model, D: $(B-C)\cdot 100/B$, E: $(C-B)\cdot 100/C$

A	B	C	D	E
1	3.837	3.836	4.376	–4.376
2	3.799	3.798	0.024	–0.024
3	3.760	3.759	0.018	–0.018
4	3.525	3.720	–5.547	5.256
5	3.490	3.681	–5.498	5.211
6	3.478	3.644	–4.799	4.579
7	3.464	3.617	–4.441	4.252
8	3.467	3.614	–4.256	4.083
9	3.469	3.646	–5.122	4.873
10	3.481	3.718	–6.829	6.392
11	3.519	3.829	–8.830	8.113
12	3.532	3.976	–12.574	11.169
13	3.573	4.153	–16.249	13.978
14	3.574	4.358	–21.937	17.990
15	3.595	4.585	–27.560	21.605
16	3.587	4.833	–34.758	25.792
17	3.596	5.099	–41.804	29.480
18	3.604	5.380	–49.280	33.011
19	3.662	5.674	–54.945	35.461
20	3.764	5.979	–59.628	37.354
21	3.896	6.295	–61.581	38.111
22	4.272	6.619	–54.945	35.461
23	4.472	6.950	–55.425	35.660
24	5.145	7.288	–41.652	29.404
25	5.381	7.630	–41.802	29.479
26	6.279	7.976	–27.035	21.281
27	6.531	8.325	–27.478	21.555
28	7.361	8.676	–17.872	15.162
29	7.958	9.028	–13.453	11.857
30	8.204	9.380	–14.342	12.543
31	8.651	9.732	–12.495	11.107
32	8.877	10.081	–13.571	11.949
33	9.197	10.429	–13.397	11.814
34	9.461	10.773	–13.872	12.182
35	9.922	11.113	–12.011	10.723
36	10.260	11.449	–11.594	10.389
37	11.060	11.779	–6.509	6.112
38	11.900	12.104	–1.717	1.688
39	12.420	12.422	–0.016	0.016
40	13.730	12.732	7.265	–7.834
41	14.240	13.034	8.463	–9.246
42	15.780	13.328	15.535	–18.393
43	16.510	13.612	17.547	–21.282
44	18.600	13.887	25.336	–33.933

Table 1
(continued)

A	B	C	D	E
46	22.840	14.404	36.932	–58.559
47	26.640	14.646	45.021	–81.889
48	28.410	14.875	47.639	–90.982
49	33.460	15.092	54.893	–121.699
50	34.830	15.296	56.083	–127.704
51	38.690	15.486	59.973	–149.837
52	40.070	15.661	60.913	–155.845
53	41.890	15.822	62.227	–164.743
54	43.380	15.968	63.188	–171.654
55	44.260	16.099	63.626	–174.922
56	44.720	16.213	63.744	–175.822
57	44.810	16.311	63.599	–174.721

The percentage deviations had been calculated in a different way. In column 'D' the measured polymerization rate, in column 'E' the polymerization rate calculated from the model served as basis. The average value of the two deviations gives more real results, because accepting the higher values as the basis, the maximum deviation can be only 100 per cent which reduces the average value of these deviations.

From *Table 1,* it can be seen that the agreement of the measured and calculated rates of polymerization is acceptable up to 10 – 12 per cent conversion. Later on the deviations increase, then according to the optimal selection of the model parameters they will begin to decrease and at 36 – 42 per cent conversion the agreement is again acceptable. At higher conversions the deviations increase again, after 51 per cent conversion the average of the deviations is more than 100 per cent.

As a result of calculations it can be stated that with decreasing α the average of the mentioned deviations greatly decreases. A decrease in the order of a per cent arises with decreasing value of α in the range of 10^{-1} – 10^{-3}, the effect of further decrease is minimal. Changing the other two parameters has essentially less effect. The results of our calculations are given in *Table 1.* At $\alpha = 10^{-3}$ lower average deviation occurs at $K_c = 0.315$ and $k_{3,m} = 0.420$. Then the average of the absolute values of deviations given in column 'D' is 27.81%, and that of deviations in column 'E' is 41.64%, and the average of these two values is 34.73%. Similar values had been given by other initiator-concentrations and at different temperatures.

Our calculations point out that the Cardenas–O'Driscoll model does not give an exact correlation between the change of polymerization rate and the conversion.

List of Symbols

m	concentration of monomer
z	concentration of retarder
t	time
k_2	rate constant of chain propagation reaction
W_1	rate of initiation
k_4	rate constant of chain termination reaction
$k_{3,m}$	rate constant of chain transfer reaction to the monomer
x	conversion degree of polymerization
ε	dilatometric constant of monomer

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