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THERMOGRAVIMETRIC INVESTIGATIONS ON THE KINETICS OF THERMAL DEGRADATION OF POLYOXYMETHYLENES

H. ZIMMERMANN and J. BEHNISCH

Institute for Polymer Chemistry, Academy of Sciences of the G.D.R., Teltow-Seehof (G.D.R.)

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ABSTRACT

It is shown that thermogravimetric results reflect in a correct manner individual polymer characteristics for various polyoxymethylenes investigated. The results of isothermal and nonisothermal investigations can be compared only in special cases and then represent an additional criterion for the correctness of the kinetic model used. If there is disagreement between isothermal and nonisothermal results, this fact too gives further information for the interpretation of the mechanism of degradation, e.g., the kinetic reaction scheme or the deduction of the overall rate equation (especially under nonisothermal conditions) must be checked.

Furthermore, the results discussed demonstrate that in the case of a polymer with a rather uncomplicated molecular structure like POM, with an uncomplicated mechanism of depolymerization and with only one known product of destruction, some difficulties arise in evaluating experimental thermogravimetric results in order to calculate meaningful kinetic data. Therefore, it is all the more important to have sufficient chemical knowledge on the mechanism of destruction and the kind of volatile products if the degradation of polymers like polyesters or polyamides proceeds by random chain scission, accompanied by secondary reactions, resulting in various reaction products or in a change in the composition of the reaction products. In such cases the reaction could be analyzed only to very low degrees of conversion to avoid misinterpretation and to obtain, for example, reasonable data reflecting the thermal stability of a polymer by the requirements of use, and not to obtain data representing the complete pyrolysis which are mostly of no interest in relating to specific polymer properties.

INTRODUCTION

The thermal depolymerization of polyoxymethylenes (POM) proceeds by a zipper mechanism, producing formaldehyde as the only reaction product. Therefore, polyoxymethylene was chosen as a model compound for the investigation of some specific problems connected with the interpretation of thermoanalytical results of polymer degradation under isothermal and nonisothermal conditions.

The depolymerization of POM is initiated up to about 260°C at chain ends and above this temperature mainly by random chain scission. The

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kinetics of thermal degradation of POM can be realized as a combination of four elementary steps: initiation (according to the molecular mechanism proposed by Grassie and Roche [1] a cyclization at chain ends), propagation, chain transfer, and termination. According to the theory of depolymerization [2] the overall rate equation of weight loss of a sample during degradation depends on the kind of initiation, the proportion between the average zip length and the number-average degree of polymerization, molecular weight distribution of POM, and the temperature range investigated.

Particularly for short zip length it must be taken into consideration that the above mentioned deduction of an overall rate equation presumes a steady state concentration of initiated macromolecules.

Further, overall rate equations for nonisothermal conditions are obtained only by formal transformations from the isothermal cases and special deductions are demanded.

EXPERIMENTAL

The samples investigated are a polyoxymethylene dihydrate (POM-DH), a polyoxymethylene diacetate (POM-DA), and a commercial sample Delrin 500 (end-group blocked POM with an additional stabilizer). Experiments were carried out on a Mettler TA1 thermoanalyzer in a flow of nitrogen (7 l h^{-1}), with a Pt sample holder (diameter 14 mm), a Pt–Pt/Rh temperature thermocouple, and a sample weight of 10 mg (melt layer ≤ 0.15 mm).

The kinetic data for the isothermal runs were determined by plotting $\ln t(\alpha, T)$ vs. $1/T$ [$t(\alpha, T)$: time to obtain the degree of conversion at temperature T] and for nonisothermal runs by an integral method described previously [3]. Special investigations on the reproducibility showed good agreement between data evaluated from different runs, e.g., about ± 10 kJ mole^{-1} in the activation energy and one order of magnitude in the pre-exponential factor.

RESULTS AND DISCUSSION

Polyoxymethylene dihydrate (POM-DH)

A typical nonisothermal run of POM-DH degradation is shown in Fig. 1. The kinetic data obtained are summarized in Table 1. In all cases the rate law of a first-order reaction was valid. Table 1 shows that the kinetic parameters depend in both cases, isothermal (up to the temperature investigated) and nonisothermal, on the heating rate and the data are not comparable. These facts emphasize the importance of a careful analysis of the results obtained.

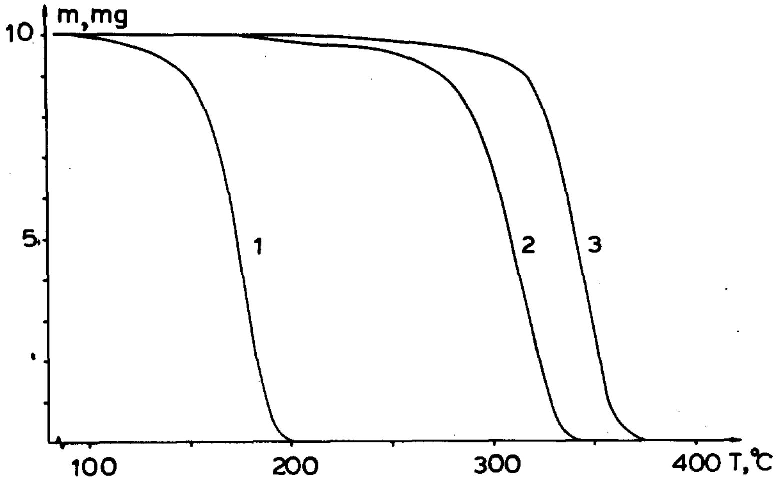

Fig. 1. Nonisothermal TG runs ($\beta = 2$ K min^{-1}) of the polyoxymethylenes investigated: 1, POM-DH; 2, POM-DA; and 3, Delrin 500.

In the temperature range investigated (up to 220°C) the depolymerization of POM-DH is exclusively end initiated. According to the results of Grassie and Roche [1], chain transfer can be neglected. Under such conditions for long zip length the overall rate is characterized only by the initiation step, that is, the kinetics of weight loss would be like that of an elementary process, but then it is not possible to interpret the described differences.

For short zip length in general we have to presume kinetics of a complex process including initiation, propagation and termination, which can explain the observed effects with less difficulty. Therefore, presuming the existence of a short zip length, we tried to obtain an overall rate equation without the necessity of assuming a steady state concentration of activated molecules mentioned before. This is possible under isothermal conditions, if, at first, summarizing the differential equations for time dependence of the number of nonactivated and activated macromolecules of n repeat units P_n and R_n and getting finally

$$\frac{\mathrm{d}m}{\mathrm{d}t} = -K_\mathrm{P} M R(t) \tag{1}$$

where m is the actual sample weight, t is the time, K_p is the rate constant for propagation, M is the molecular weight of the repeat unit, and $R(t)$ is the total number of activated macromolecules. Equation (1) can be related to the experimental fact that the kinetics of weight loss are of first order

$$\frac{\mathrm{d}m}{\mathrm{d}t} = -Km \tag{2}$$

TABLE 1

Kinetic parameters on thermal degradation of POM-DH

β (K min^{-1})	Isothermal		Nonisothermal			
	2 [a]	10 [a]	0.5	1	2	4
E (kJ mole^{-1})	175	150	357	240	148	118
A (s^{-1})	4.8×10^{17}	7.2×10^{14}	2.0×10^{39}	4.2×10^{25}	7.9×10^{13}	1.9×10^{11}

[a] Heating rate up to the temperature investigated (172.5, 183 and 192.5°C).

From eqns. (1) and (2) we get a differential equation with respect to $R(t)$

$$\frac{\mathrm{d}R(t)}{\mathrm{d}t} = -KR(t) \tag{3}$$

with the solution

$$R(t) = R_0 \exp(-Kt) \tag{4}$$

Equations (1), (2) and (3) lead to the relation

$$K = \frac{MR_0}{m_0} K_\mathrm{P} \tag{5}$$

where K is the overall rate constant obtained from TG data, R_0 and m_0 are the total number of activated macromolecules, and respective sample weight at the beginning of the isothermal run. Relation (5) renders the following two conclusions:

(1) contrary to the assumption of a steady state, the concentration of activated macromolecules exceeds a maximum during depolymerization up to the beginning of isothermal runs, since the mentioned solution of the differential equation with respect to $R(t)$ [eqn. (4)] demands an exponential decrease;

(2) the obtained activation energies are of the order of magnitude of the activation energy of propagation E_P, but differences in the relation R_0/m_0 for isothermal runs at different temperatures give some falsification. Thus, with increasing heating rate up to the isothermal run the differences in R_0/m_0 decrease and, therefore, the value $E = 150$ kJ mole^{-1}, obtained for the higher heating rate (Table 1), should be a better approximation for E_P.

Under nonisothermal conditions the situation is more complicated and there are still some unsolved problems. By the formal transformations $\mathrm{d}t \rightarrow (1/\beta)\,\mathrm{d}T$ and $R(t) \rightarrow R(T)$, eqn. (1) is also valid in the nonisothermal case (β = heating rate)

$$\frac{\mathrm{d}m}{\mathrm{d}T} = \frac{1}{\beta} K_\mathrm{P}(T) M R(T) \tag{6}$$

and the kinetics of weight loss are also of first order

$$\frac{\mathrm{d}m}{\mathrm{d}T} = \frac{1}{\beta} K(T) m \tag{7}$$

Equations (6) and (7) lead to

$$\frac{\mathrm{d}R(T)}{\mathrm{d}T} = \frac{1}{\beta} K(T)\, R(T) \left[1 + \frac{\beta}{RA}\, \frac{\mathrm{e}^{-E/RT}}{T^2}\, (E - E_\mathrm{P})\right] \tag{8}$$

but it is not possible to find a solution of this differential equation with respect to $R(T)$ only in terms of K_P, obtained in a similar way described for the isothermal case, because at the integration step the temperature dependence of K and K_P must be considered.

Comparing eqns. (8) and (3), a formal conformity in the isothermal and nonisothermal case would be established, if the second term in brackets in eqn. (8) is negligible compared with 1. However, such a conformity in the kinetic data was not found. Therefore, this second term must be taken into consideration. Thus, the dependence of $R(t)$ and of the evaluated kinetic data on the heating rate, can be shown qualitatively and the data from nonisothermal runs cannot be related to one of the elementary steps of depolymerization as was possible in the isothermal case. A more detailed discussion will be given elsewhere [4].

End-blocked polyoxymethylene

In the case of thermal degradation of end-blocked POM the two possibilities of initiation at chain ends or by random chain scission require differentiation of two independent temperature ranges. Thus, the obtained nonisothermal TG curves (Fig. 1) are in principle subdivided into two main parts, but as the Šatava plot shows (Fig. 2), there are also additional differences between both the samples investigated, viz.

(a) the subdivision of the TG curves of POM-DA degradation at all heating rates is strongly related to temperature (up to 230°C and above 260°C) with different degrees of conversions, whereas the kinetics of Delrin 500 degradation change at constant degree of conversion ($\alpha = 0.05$) at different and, moreover, higher temperatures. In our opinion the latter is caused by the stabilizer added to the commercial polymer;

(b) in the temperature range above 260°C the kinetics of POM-DA

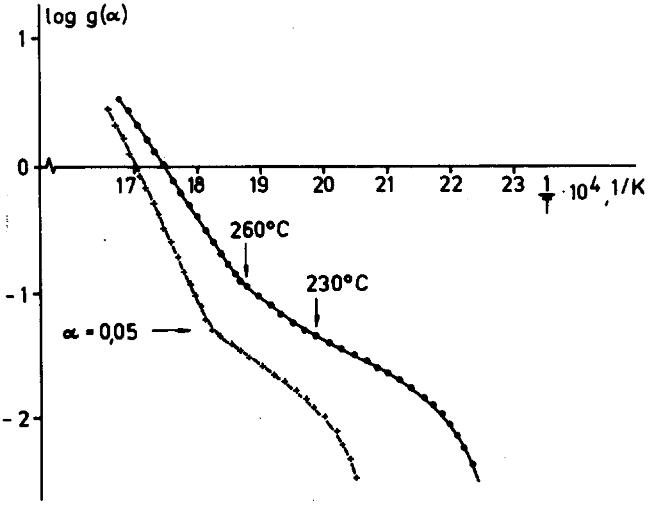

Fig. 2. Šatava plot of nonisothermal TG data of POM-DA (●) and Delrin 500 (+) degradation.

TABLE 2

Kinetic parameters on thermal degradation of end-blocked POM in initial state of degradation

β (K min^{-1})	POM-DA		Delrin 500	
	E (kJ mole^{-1})	A (s^{-1})	E (kJ mole^{-1})	A (s^{-1})
0 [a]	79	2.8×10^{3}	100	9.0×10^{4}
0.2	56	7.5×10^{0}	90	7.5×10^{3}
1	47	7.7×10^{-1}	92	2.1×10^{4}
4	48	1.8×10^{0}	81	8.7×10^{2}

[a] Isothermal runs at 210, 220 and 230°C.

degradation are of first order, whereas the kinetics of Delrin 500 degradation are of 1.5 order.

The interpretation of kinetic parameters obtained for the lower temperature range (Table 2) is complicated and is influenced by a small amount of macromolecules with unblocked hydroxyl end groups and, especially for Delrin 500, the influence of the stabilizer must be considered. However, the isothermal and nonisothermal results are in good agreement and describe the stabilizer activity in a similar manner: both isothermal and nonisothermal data give identical relations between the rate constants for POM-DA and Delrin 500 degradation, e.g., at 220°C (1×10^{-5} s^{-1} and 2×10^{-6} s^{-1}, respectively).

The relative independence of the kinetic parameters established above 260°C (Table 3) with respect to the heating rate and the satisfactory agreement with isothermal results strengthen the assumption that the weight loss is related only to one elementary reaction step. This is shown in the case of

TABLE 3

Kinetic parameters on thermal degradation of end-blocked POM above 260°C

β (K min^{-1})	POM-DA		Delrin 500	
	E (kJ mole^{-1})	A (s^{-1})	E (kJ mole^{-1})	A (s^{-1})
0 [a]	190	4.1×10^{14}	201	1.3×10^{15}
0.2	176	2.3×10^{13}	197	2.3×10^{14}
1	144	2.8×10^{10}	199	2.6×10^{14}
4	130	5.0×10^{8}	227	5.5×10^{16}

[a] Isothermal runs at 270, 280, 290 and 300°C.

long zip length, which means the overall rate equation is determined exclusively by the initiation step and the kinetic parameters listed here are valid for random chain scission.

According to the theory, the 1.5 order kinetic law for Delrin 500 degradation refers to a "most probable" molecular weight distribution, whereas the first order kinetic equation for POM-DA refers to a narrow (unimolecular) distribution. But both statements need additional experimental verification.

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