

Study on the Kinetics of Thermodestruction of Copolymers of Trioxane with Phenylglycidylether

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Synopsis

The kinetics of destruction of copolymers of trioxane (TO) and phenylglycidylether (PhGE) at different rates of heating was investigated. The thermogravimetric investigations were carried out on Perkin-Elmer thermograph using the thermogravimetric balance TGS-2. The experimental curves are bimodal. For the calculations the methods of Rabek and Reich were applied and compared. The most probable values of the determinations done are found by approximation of the experimental results. The effect of the quantity of PhGE incorporated on the rate of destruction, the activation energy, and the order of reaction was established. It was supposed to be a probable mechanism of destruction of the copolymers on the basis of TG investigations, mass spectroscopic, and DSC analyses.

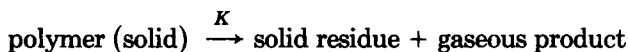
INTRODUCTION

One of the well-known and most practiced methods for thermostabilization of polyoxymethylene (POM) is the copolymerization by inserting the —C—C— bond into the polymer —C—O—C— chain to prevent the autocatalytic destruction under the action of the split CH_2O .¹

It is quite natural to suppose that the rate of thermodestruction of these copolymers depends on the quantity of the comonomer incorporated and its distribution alongside the chain as well as on the type of the copolymer.

On the basis of trioxane (TO) and phenylglycidylether (PhGE) copolymers with a different degree of polymerization were synthesized. There were no data and studies on the thermostability of copolymers of TO and PhGE. It was interesting to study the influence of the quantity of PhGE incorporated on the thermostability of copolymers as well as the kinetics of thermodestruction to establish the order and mechanism of reaction. The methods of thermogravimetry were chosen for the study of thermodestruction.

In our case the nonisothermal method of Rabek² and the method of Reich,³ for comparison, were chosen. In polymers the destruction most often occurs according to the scheme:



The rate of decreasing the masses (K) according to the equation of Arrhenius is

$$K = \frac{dW}{dt} = A W^n \cdot e^{E/RT} \quad (1)$$

$$\ln K = \ln \frac{dW}{dt} = \ln A + n \ln W - \frac{E}{RT} \quad (2)$$

where W = mass of the residue, n = order of the reaction, dW/dt = rate of the reaction (mg/s), and E = activation energy (kcal/mol K).

If we take thermogravimetric curves with different heating rates and all the other conditions remain unchanged, having two different rates, we can write

$$\Delta \ln(dW/dt) = n(\ln W_1 - \ln W_2) - E/RT [\Delta(1/T)] \quad (3)$$

In this case from $\ln(dW/dt)$ vs. $1/T$ the slope of the straight lines (that is, the tangent) will give E/R . The order of the reaction (n) when $\ln K = 0$ is determined by eq. (2), which adopts the following expression:

$$E/RT_0 = \ln A + n \ln W \quad (4)$$

When plotting the dependences E/RT_0 vs. $\ln W$, n is determined from the tangent of the slope.

EXPERIMENTAL

The copolymerization of TO and PhGE was carried out in nitrobenzene, $T = 60^\circ\text{C}$, and catalyzed by $\text{BF}_3\text{Et}_2\text{O}$ (Fluka product). The quantity of PhGE varied from 5 up to 40%. Copolymers were isolated by selective precipitation and washed out, so that only the copolymer remained on the filter. Their structure was studied by the elemental analysis, IR and NMR spectra.

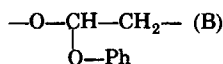
DSC and TG curves were recorded in nitrogen on Perkin-Elmer TGS-2 type apparatuses.

Mass-spectra were taken down on a KB 2091 apparatus with voltage 20 and 70 eV and acceleration 3.5 eV.

RESULTS AND DISCUSSION

According to the requirements of the method for heating at different rates, the thermogravimetric curves of destruction of TO/PhGE copolymers were determined. The course of the curves is shown in Figure 1. It is seen that the rate of destruction when PhGE = const is a function with the rate of heating and with its increase the rate of destruction falls abruptly, which corresponds to the known data about other polymers and copolymers.

The rate of destruction (defined by the slope of the curves) taken down at one and the same heating rate at a nonisothermal regime depends, to a great extent, on the ratio of the comonomer units CH_2O (A) from TO and



from PhGE (Figs. 2 and 3).

When B units are more in the polymer chain, the rate of destruction observed is less.

The activation energy (E_a) of destruction calculated according to eq. (2) and the data of thermogravimetric studies show that, in polymers containing a considerable content of B units, the E_a of destruction is considerably higher, resp. their thermostability, too. On the basis of these data we can conclude

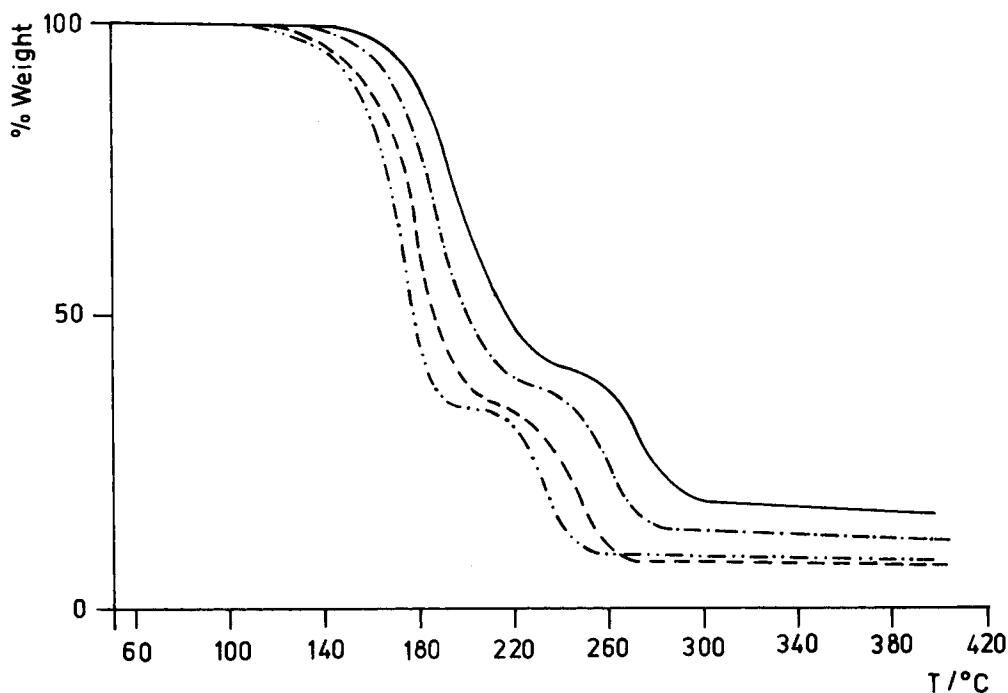


Fig. 1. Thermogravimetric curves of destruction of copolymers of TO/PhGE at different heating rates: (—) 40°C/min.; (---) 20°C/min.; (-·-·-) 10°C/min.; (-··-) 5°C/min. PhGE incorporated is 7.1 mol %.

that the incorporation of monomer units such as PhGE into the chain of polyoxymethylene leads to the decrease of the tendency to thermal destruction. In order to examine the validity of the chosen method,² the data of the activation energy were compared with those calculated by another method of Reich³ according to which the dependence between E_a of destruction and T is given by the equation

$$E_a = 2.303 \log \left[\frac{RH_2}{RH_1} \left(\frac{T_1}{T_2} \right)^2 \right] \left(\frac{1}{T_1} - \frac{1}{T_2} \right)^{-1} \quad (5)$$

where RH = heating rate, $T_{s1}/T_{s2} = T_1/T_2$, T_s is the temperature at which $W/W_0 = 1/e$, W_0 = mass of initial substances, $W = W_0/e$ = instant value of mass.

The results calculated according to both methods are compared in Table I.

The values of E_a of destruction using the methods of Reich and Rabek obtained for both sections of the bimodal curves for samples with different content of incorporated PhGE are compared in Table I.

It is evident that there is a difference between the values calculated by the two methods, but they are of one and the same order. This fact assures us that the methods are correctly chosen.

In order to find the most probable values of all measured quantities, we used the method of approximation of experimental data.

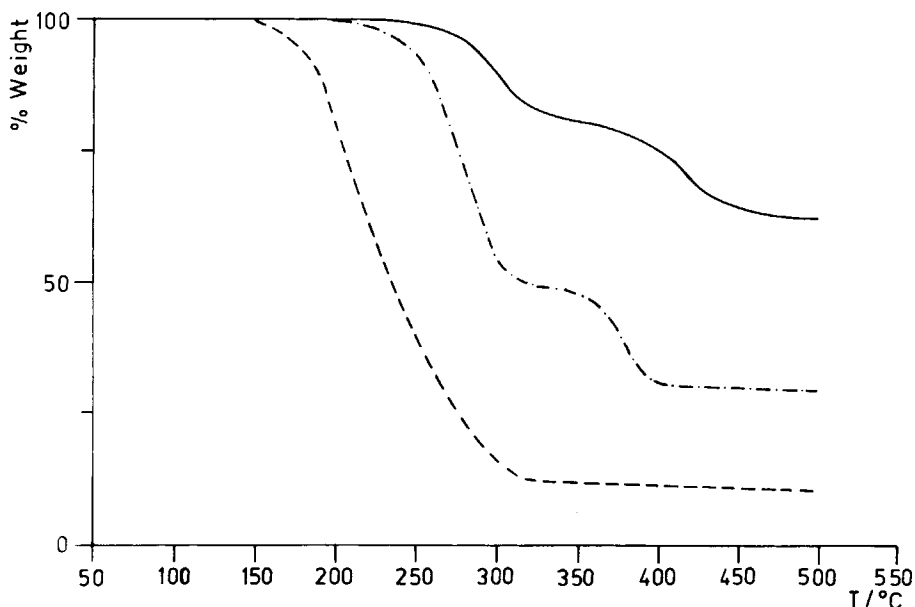


Fig. 2. Thermogravimetric curves of destruction of TO/PhGE copolymers at different quantities of PhGE incorporated: (—) 41.5 mol %; (-·-) 7.1 mol %; (---) 4 mol %. Heating rate 20°C/min.

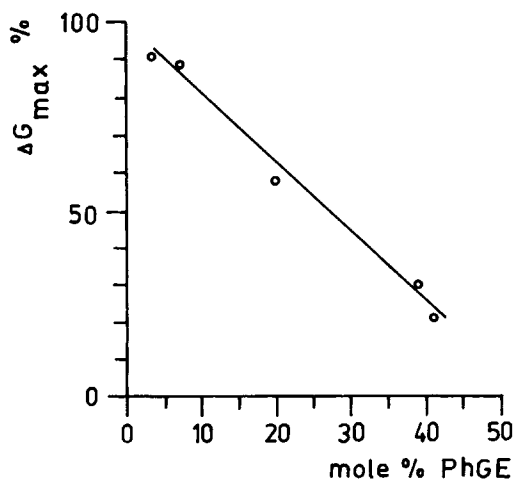


Fig. 3. Rate of destruction depending on the quantity of PhGE incorporated at constant heating rate 20°C/min.

Using the method, it was established that the most probable values of the two samples are as follows (Table II).

The bimodality of the curves of thermodestruction most probably is due to different kinds of destruction processes taking place at different temperatures.

The range between 50 and 150°C seems to be the first section. In this range E_a of destruction is lower in comparison with the second one. The second section includes the range 150–300°C. The greater the contents of B units in

TABLE I
Activation Energy of Destruction of TO/PhGE Copolymers

Content of PhGE in copolymer (mol %)	E_a by the method of Reich ³ (kcal/mol K)	E_a by the graphic method of Rebek (kcal/mol K)	% Loss	Section of TG curves
$P_1 = 7.1$	22.165	22.799	12.5	I
		21.808	25.0	
		21.780	27.5	
		25.020	69.9	II
		24.630	75.0	
		24.620	80.8	
		23.430	10.0	
$P_2 = 41.5$	23.588	23.325	20.0	I
		23.031		
		31.046	47.1	
		30.798	52.3	II
		30.698	54.9	

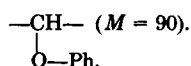
TABLE II
Most Probable Values of E_a of Destruction of TO/PhGE Copolymer

Content of PhGE (mol %)	E_a of destruction in I section (kcal/mol K)	E_a of destruction in II section (kcal/mol K)
$P_1 = 7.1$	22.129	24.756
$P_2 = 41.5$	23.203	31.070

the polymer chain, the greater will be the differences in the values of E_a of destruction.

We can suppose that in the first section, where the temperature range is 50–150°C, the bond —C—O— is mainly affected which is more unstable in comparison with the bond —C—C— ($E_{a-C-C} = 82.60$ kcal/mol and $E_{a-C-O-C} = 77$ kcal/mol). This results in the separation of a considerable quantity of CH_2O . This supposition is confirmed by the mass-spectroscopic investigations (Fig. 4). Considerable quantities of substances with molmass 30–40 and, to a smaller degree, substances with higher molmass 40–60 (such as $M_{(CH_2O)_2} = 60$) were separated.

The reaction of destruction is autocatalyzed by the separation of CH_2O , which can explain the sharp slope of the first section and the smaller value of E_a of destruction. At higher temperatures (150–300°C), due to destruction of —C—C— bonds, products with higher molmass $M = 90$ are eliminated in higher quantities (Fig. 4), most probably due to fragments of



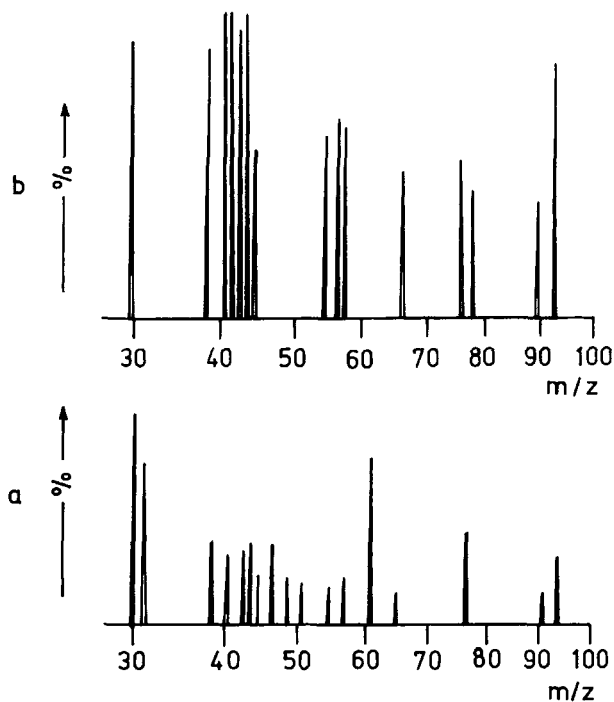


Fig. 4. Mass spectrum of TO/PhGE copolymers at different temperatures: (a) 160°C; (b) 270°C.

On the basis of eq. (4) the order of the reaction was determined (Table III). From Table III it is seen that the order of reaction in both sections of the curves are different, which means that the mechanism of destruction is different. This is confirmed by mass spectroscopy. The mechanism of destruction also depends on the quantity of the incorporated B units (samples P_1 and P_2). On the basis of DSC investigations of the polymer samples, it was established that at lower contents of PhGE the variation of ΔH and ΔT_m is proportional to PhGE incorporated in the polymer chain of POM (about 18 mol %). At a higher degree of incorporation this dependence disappears and ΔH and ΔT_m do not practically change with the alteration of the incorporated quantities of PhGE.⁴

In the first case this is due to the statistic distribution of PhGE (B units) (Scheme 1), and at a higher content of PhGE (B units) a block-statistic distribution is present (Scheme 2):

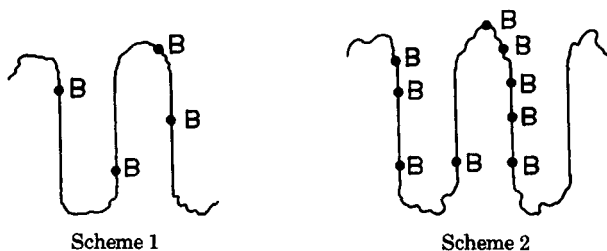


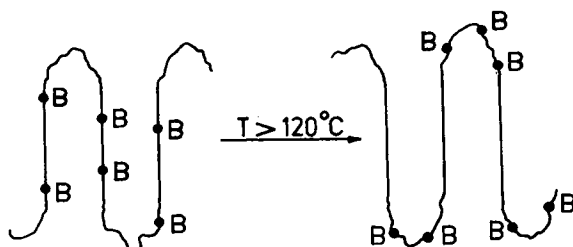
TABLE III
Order of Reaction of Thermodestruction of TO/PhGE Copolymers

Sample	Order of reaction	Section of the curve
$P_1 = 7.1 \text{ mol \% PhGE}$	1.57	I
	1.30	II
$P_2 = 41.5 \text{ mol \% PhGE}$	2.08	I
	1.81	II

MECHANISM OF DESTRUCTION

When heating at lower temperature, the amorphous regions are first affected, because they are more mobile. At lower contents of PhGE (that is, B units) (Scheme 1) the groups CH_2O — will be mainly broken. They are predominant and more thermally unstable, which is shown in Figure 4.

At the same temperature because of the predominant B units, (Scheme 2) and especially at temperatures 150 – 160°C (the I section of TG curve), a possibility for recrystallization appears, and B units are thrown out into the amorphous region (the crystals turn from stretched into folded ones—Scheme 3):



Scheme 3

It is seen in Figure 1 that only 10% of the copolymer is destroyed at the temperature of 150°C ; therefore, only a small part of the sections with $-\text{C}-\text{O}-$ bonds are destroyed. At temperatures 150 – 160°C together with crystallization processes a destruction of the $-\text{C}-\text{O}-\text{C}-\text{O}-$ bond takes place, but to a considerably lower degree. The reason is that, because of recrystallization, mainly B-B units move to the amorphous region and they are with a higher thermostability.

At temperatures higher than the melting point of the crystals 180 – 190°C , the crystal lattice does not exert any influence. Only the fact that destruction stops at $-\text{C}-\text{C}-$ bonds is important.

References

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Received April 1, 1986

Accepted October 6, 1986