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Abstract

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THERMAL DEGRADATION OF POLYETHYLENE TEREPHTHALATE

The thermal degradation of polyethylene terephthalate has been investigated by a number of authors (^{1,2}); however, the existing disagreements in the explanation of the degradation mechanism and the lack of data on the influence of various structural changes on thermal stability prompted the present work.

It is known that, in the degradation of polymers according to the law of chance, the number of broken bonds α at any moment of time is determined by the following expression (^{3}): $\alpha = 1 - e^{-kt}$.

After differentiation and subsequent logarithmation we obtain: $\lg d\alpha/dt = \lg k - kt/2.3$, i.e., the dependence of the logarithm of the rate of change in the number of broken bonds on the degradation time, for a random character of bond rupture, should be expressed by a straight line. The values of α for various moments of degradation can be determined from the equation of Montroll and Simha (^{4}):

$$N_\omega = \frac{\alpha^2 N_0 + 2(1-\alpha)\left[(1-\alpha)^{N_0} + \alpha N_0 - 1\right]}{\alpha^2 N_0},$$

where N_0 is the initial chain length, N_ω is the chain length at any moment of time, and α is the number of broken bonds corresponding to N_ω.

The change in the chain length of polyethylene terephthalate during degradation was determined by us by measuring the intrinsic viscosity of samples in a tetrachloroethane-phenol solution (1 : 1), degraded in Pyrex ampoules evacuated to 10^{-4} mm Hg, for various intervals of time at 333°. The molecular weight was calculated from the formula (^{5}): $[\eta] = 2.1 \cdot 10^{-4} M^{0.82}$.

Figure 1 presents a plot of molecular weight versus degradation time, and Fig. 2 the dependence of $\lg(d\alpha/dt)$ on degradation time. The rectilinear character of the dependence of $\lg(d\alpha/dt)$ on t indicates that the decrease in molecular weight during the degradation of polyethylene terephthalate occurs as a result of bond scission according to the law of chance.

Goodings (^{2}) and Ritchie (^{6}) found that, in the pyrolysis of glycol dibenzoate, which is a low-molecular-weight analogue of polyethylene terephthalate, benzoic acid and vinyl benzoate are formed in equimolecular amounts:

Fig. 1. Dependence of the molecular weight of polyethylene terephthalate on degradation time at 333°

Figure 1: Fig. 1. Dependence of the molecular weight of polyethylene terephthalate on degradation time at 333°

$$C_6H_5 \cdot CO \cdot OCH_2CH_2O \cdot CO \cdot C_6H_5 \rightarrow C_6H_5COOH + C_6H_5 \cdot CO \cdot OCH = CH_2.$$

Analysis of the degradation products of polyethylene terephthalate showed that the solid sublimate consists of terephthalic acid and oligomers of polyethylene terephthalate, while the gaseous products consist of CH_3CHO, CO, CO_2, and a small amount of CH_4.

We investigated the kinetics of degradation of glycol dibenzoate by the amount of benzoic acid formed upon heating samples weighing 0.1-0.2 g in Pyrex ampoules evacuated to 10^{-4} mm Hg for various times, and the kinetics of volatilization of polyethylene terephthalate on modified MacBain balances with continuous recording of weight change, having a sensitivity of 10^{-5} g, owing to which it was possible to work with sufficiently small samples of ~ 0.005 g. The results are given in Figs. 3 and 4. Polyethylene terephthalate with molecular ···

with a weight of 18,200, recrystallized from nitrobenzene, thoroughly washed and dried in vacuum at 100° for one week. To prevent adsorption of moisture, it was stored in a vacuum desiccator over P_2O_5. Although the rates of degradation of glycol dibenzoate and polyethylene terephthalate are different at the same temperatures, the activation energies calculated from degradation-rate data at different temperatures have similar values. Thus, the activation energy of degradation of glycol dibenzoate is 44 kcal/mole, and that of polyethylene terephthalate is 47 kcal/mole.

These data give grounds for assuming that the degradation of polyethylene terephthalate proceeds through random cleavage of ester bonds with the formation of carboxyl and vinyl ester groups.

Analysis of the kinetics of volatilization of polyethylene terephthalate shows that the rate of volatilization increases at the beginning of the reaction and, after passing through a maximum, decreases. The increase in rate is apparently associated with a decrease in the molecular weight of the polymer, since this increases the probability of rupture of ester bonds adjacent to the chain end, leading to the formation of terephthalic acid, which is evolved during degradation. It should also be noted that the rate of decomposition of an ester bond located adjacent to a carboxyl group is somewhat higher, probably owing to the inductive effect. This was established in studying the degradation rates of diethyl and monoethyl terephthalate.

Fig. 1. Dependence of the molecular weight of polyethylene terephthalate on

Fig. 2. Dependence of lg(da/dt) on degradation time

Figure 2: Fig. 2. Dependence of lg(da/dt) on degradation time

Fig. 3. Degradation of polyethylene terephthalate at different temperatures

Figure 3: Fig. 3. Degradation of polyethylene terephthalate at different temperatures

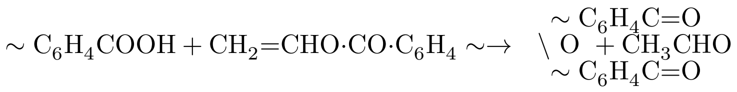
degradation time at 333°
Axis labels: $M \cdot 10^{-3}$; hours.

Fig. 2. Dependence of lg(da/dt) on degradation time
Axis labels: lg $\frac{da}{dt}$; hours.

Fig. 3. Degradation of polyethylene terephthalate at different temperatures
Axis labels: Loss in weight, %; min.
Curves: 391°, 370°, 353°, 333°.

Fig. 4. Degradation of glycol dibenzoate at different temperatures
Axis labels: Degradation, %; hours.
Curves: 395°, 379°, 362°.

The carboxyl and vinyl ester groups formed can interact with each other, with formation of anhydride groups and acetaldehyde (7):



$$\sim C_6H_4COOH + CH_2{=}CHO{\cdot}CO{\cdot}C_6H_4 \sim\rightarrow \begin{array}{l}\sim C_6H_4C{=}O\\ \backslash\ O\ \ + CH_3CHO\\ \sim C_6H_4C{=}O\end{array}$$

Spectroscopic analysis of destructed samples of polyethylene terephthalate shows that anhydride groups do in fact accumulate in the course of destruction. Apparently, owing to this reaction, the molecular weight of the polymer does not fall continuously, as would be expected in the case of random decomposition, but only down to a certain limit (Fig. 1).

Vinyl ether groups can also polymerize under the conditions of destruction of polyethylene terephthalate, with formation of polyvinyl benzoate derivatives. However, the compound formed is unstable under these conditions and readily decomposes with formation of a polyene chain and acids, analogously to polyvinyl acetate. The polyene chains formed cause the coloration of polyethylene terephthalate. Since the polymerization of vinyl ether groups proceeds by a radical mechanism, it is of interest to study the influence of radicals on the

Fig. 4. Degradation of glycol dibenzoate at different temperatures

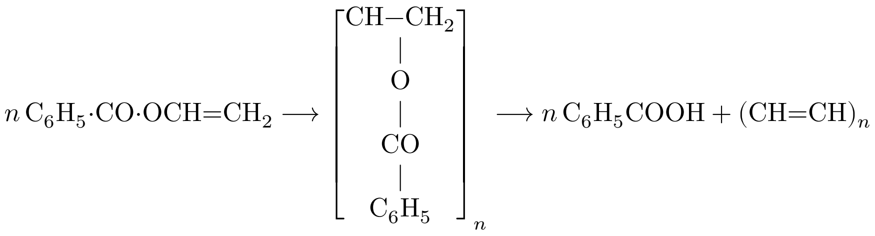
Figure 4: Fig. 4. Degradation of glycol dibenzoate at different temperatures

destruction process. It was found that, during destruction of glycol dibenzoate at 282° in the presence of azoethane, which is a source of ethyl radicals, the yield of benzoic acid and CO_2 increases sharply; this can probably be explained by abstraction of hydrogen by the radical from the glycol chain, followed by decomposition of the radical formed:

$$C_6H_5CO{\cdot}OCH_2CH_2O{\cdot}CO{\cdot}C_6H_5 + R{\cdot} \longrightarrow C_6H_5CO{\cdot}OCH_2\dot{C}HO{\cdot}CO{\cdot}C_6H_5 + RH$$

$$C_6H_5CO{\cdot}OCH_2\dot{C}HO{\cdot}COC_6H_5 \longrightarrow C_6H_5COO{\cdot} + C_6H_5{\cdot}CO{\cdot}OCH{=}CH_2$$

$$C_6H_5COO{\cdot} \longrightarrow C_6H_5{\cdot} + CO_2$$



$$n\,C_6H_5{\cdot}CO{\cdot}OCH{=}CH_2 \longrightarrow \left[\begin{array}{c} CH{-}CH_2 \\ | \\ O \\ | \\ CO \\ | \\ C_6H_5 \end{array}\right]_n \longrightarrow n\,C_6H_5COOH + (CH{=}CH)_n$$

In the gaseous products of destruction of polyethylene terephthalate and glycol dibenzoate there is a considerable amount of CO_2, despite the fact that decarboxylation of aromatic acids (terephthalic, benzoic) practically does not occur up to 400°. This may be explained by decarboxylation of the acids under the action of radicals:

Table 1

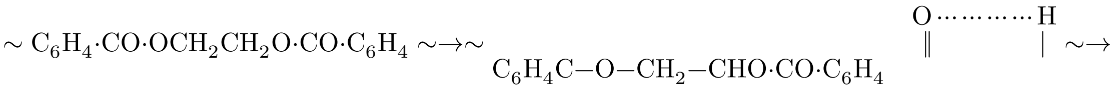
Amount of benzoic acid, g	Amount of benzoic acid, mol	Amount of added azoethane, mol	Destruction conditions	Decarboxylation, %
0.1200	$9.84 \cdot 10^{-4}$	–	298°, 2 h 30 min	0.4
0.0933	$7.66 \cdot 10^{-4}$	$1.53 \cdot 10^{-4}$	298°, 2 h 30 min	36.0

$$\sim C_6H_4COOH + R{\cdot} \longrightarrow \sim C_6H_4COO{\cdot} + RH,$$

$$\sim C_6H_4COO\cdot \longrightarrow\sim C_6H_4\cdot + CO_2.$$

The possibility of this reaction is confirmed by the fact that, on heating benzoic and trifluoroacetic acids with azoethane at 270–300°, the degree of decarboxylation increases sharply (Table 1), and when deuterated benzoic acid C_6H_5COOD was used, mass-spectrometric analysis detected C_2H_5D in the reaction products in an amount comparable with the amount of CO_2 formed.

The reaction of cleavage of the ester bond in polyethylene terephthalate apparently proceeds through an intermediate six-membered complex:



$$\sim C_6H_4\cdot CO\cdot OCH_2CH_2O\cdot CO\cdot C_6H_4 \sim\to\sim C_6H_4C{-}O{-}CH_2{-}CHO\cdot CO\cdot C_6H_4 \begin{array}{ccc} O & \cdots\cdots\cdots & H \\ \| & & | \end{array} \sim\to$$

$$\to\sim C_6H_4COOH + CH_2{=}CHO\cdot CO\cdot C_6H_4\sim.$$

We studied the influence of the nature of the acid and of the length of the glycol chain on the rate of this process. The kinetics of the destruction of ethyl acetate, ethyl benzoate, and ethyl trifluoroacetate was investigated. The investigation was carried out by two methods: by heating the named compounds in evacuated and then sealed Pyrex ampoules, followed by titration of the acid formed, and in a flow system using helium as the carrier gas, followed by analysis of the amount of ethylene formed on an KhL-3 chromatograph. The results of both methods agree satisfactorily.

Table 2

Ester	Acid dissociation constant	Destruction rate constant at 335°, min^{-1}
$CH_3COOC_2H_5$	$1.75\cdot10^{-5}$	0.00121
$C_6H_5COOC_2H_5$	$6.27\cdot10^{-5}$	0.00240
$CF_3COOC_2H_5$	$5.5\cdot10^{-1}$	0.00632

Table 3

Ester	Destruction conditions	Conversion, %
Glycol dibenzoate	60 min at 392°	29.2
Tetramethylene glycol dibenzoate	60 min at 392°	90.7
Tetramethylene glycol dibenzoate	45 min at 316°	73.5
Hexamethylene glycol dibenzoate	60 min at 392°	92.3
Hexamethylene glycol dibenzoate	45 min at 316°	69.0

Table 2 gives the destruction rate constants of the esters studied at 335°.

From the data in Table 2 it is evident that esters of stronger acids decompose at a higher rate. An increase in acid strength is usually associated with an increase in the electronegativity of the radical attached to the carboxyl group, which should in turn lead to an increase in the withdrawal of electrons from the carbon atoms in the ester group. The more positive the charge arising on the β-carbon atom, the lower the strength of the C—H bond will be and, consequently, the higher the rate of ester destruction.

To determine the influence of the length of the glycol chain, a comparison was made of the destruction rates of glycol dibenzoate, tetramethylene glycol dibenzoate, and hexamethylene glycol dibenzoate. The results are given in Table 3.

From the data in Table 3 it is evident that increasing the length of the hydrocarbon chain in the glycol from two to four carbon atoms causes a sharp increase in the destruction rate. However, a further increase in the length of the hydrocarbon chain has practically no effect on the destruction rate. This may be explained by an increase in the strength of the C—H bond in glycol dibenzoate owing to the fact that the inductive effects of the two ester groups are directed in opposite directions. Increasing the chain length to four carbon atoms practically eliminates the mutual influence of the ester groups. The increase in the destruction rate with increasing length of the glycol chain is confirmed by comparison of the destruction rates of polyethylene terephthalate and polyhexamethylene terephthalate. Thus, the initial destruction rate of polyethylene terephthalate at 325° is 0.0742%/min, whereas the destruction rate of polyhexamethylene terephthalate under the same conditions is 0.865%/min.

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Note: Figure translations are in progress. See original paper for figures.