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Note Aminolytic Degradation of Polyesters

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NOTE
AMINOLYTIC DEGRADATION OF POLYESTERS

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INTRODUCTION

Esters are usually prepared by the acid-catalyzed reaction of alcohols and phenols with acids or acid derivatives, such as acid chlorides and anhydrides. In the presence of the reaction products, the esterification step is followed by the similar acid-catalyzed homogeneous hydrolysis of the polymer. Both the formation of the polymer and the hydrolysis reaction that follows are accompanied by considerable degradation of the polymer chain leading to deterioration of the polymer end-use properties.

The hydrolytic and chemical degradations of simple esters have long been studied, and recently these studies have been extended to polyesters by using poly(ethylene terephthalate) as the model substance [1-6]. Attention has been focused on the chemical degradation process and the structural/morphological changes resulting from it.

Since these studies have, however, largely ignored the chemistry and mechanisms of the acid-catalyzed degradation, this paper directs attention to these subjects.

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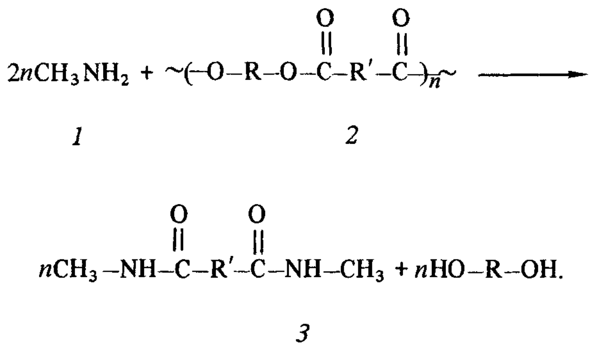
EXPERIMENTAL

Most of our polyester degradation experiments have used aqueous primary amines, usually 40% aqueous methylamine, to degrade poly(ethylene terephthalate) at 20°C [5-7]. Generally, 30-50 mg of vacuum-dried polymer was degraded in excess aqueous amine in air-tight tubes to prevent loss of the gaseous methylamine. This was done with or without mild agitation for various periods of time. On completion, the sample was filtered, carefully washed, and dried at 60°C for 3 h, which was found sufficient to remove water and residual methylamine solution. Then weight loss and extent of chain scission were determined by gravimetry and viscometry on 0.1 g samples in 100 mL of a 10:90 w/w phenol/tetrachloroethane mixture at 25°C. A modified size 2 Poulten Selfe and Lee Ltd., Ubbelohde viscometer was used.

RESULTS AND DISCUSSION

Generally, the acid-catalyzed degradation of polyesters in the presence of primary amines occurs as follows:

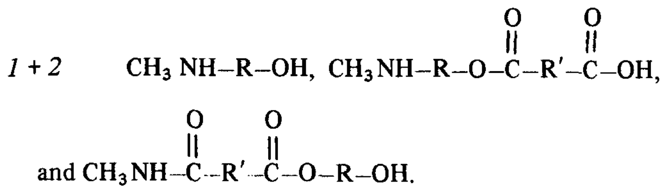


$$\underset{1}{2nCH_3NH_2} + \underset{2}{\sim\!\left(O-R-O-\overset{\overset{O}{\|}}{C}-R'-\overset{\overset{O}{\|}}{C}\right)_n\!\sim} \longrightarrow \underset{3}{nCH_3-NH-\overset{\overset{O}{\|}}{C}-R'-\overset{\overset{O}{\|}}{C}-NH-CH_3} + nHO-R-OH. \qquad (1)$$

for poly(ethylene terephthalate), R and R′ are the $-CH_2-CH_2-$ and $-C_6H_4-$ residues, respectively.

The amide (*3*) is the final degradation product. Several workers have isolated and characterized this product [2-6].

Formation of various intermediate by-products are, however, expected, depending on the mode of random chain scission occurring during the degradation. The following by-products are proposed:



$$1+2 \quad CH_3NH{-}R{-}OH,\ CH_3NH{-}R{-}O{-}\overset{O}{\overset{\|}{C}}{-}R'{-}\overset{O}{\overset{\|}{C}}{-}OH,$$

$$\text{and } CH_3NH{-}\overset{O}{\overset{\|}{C}}{-}R'{-}\overset{O}{\overset{\|}{C}}{-}O{-}R{-}OH. \qquad (2)$$

Following the degradation, there was a considerable weight loss resulting in the residual weight curve shown in Fig. 1 [7]. A corresponding sharp drop

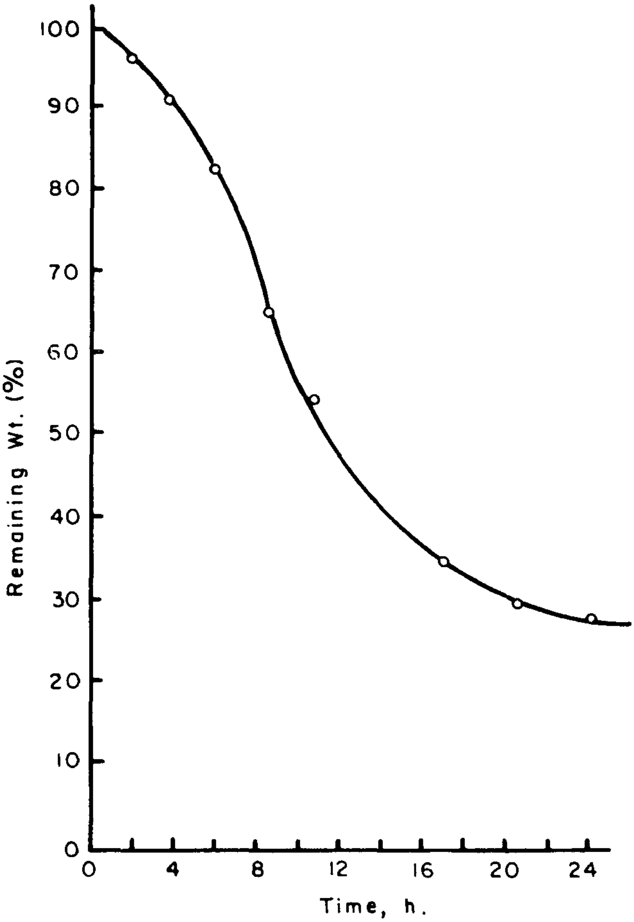


FIG. 1. Remaining polyester (in wt%) vs time for methylamine degradation of laboratory PET fiber D.R. 5:1 at 20°C.

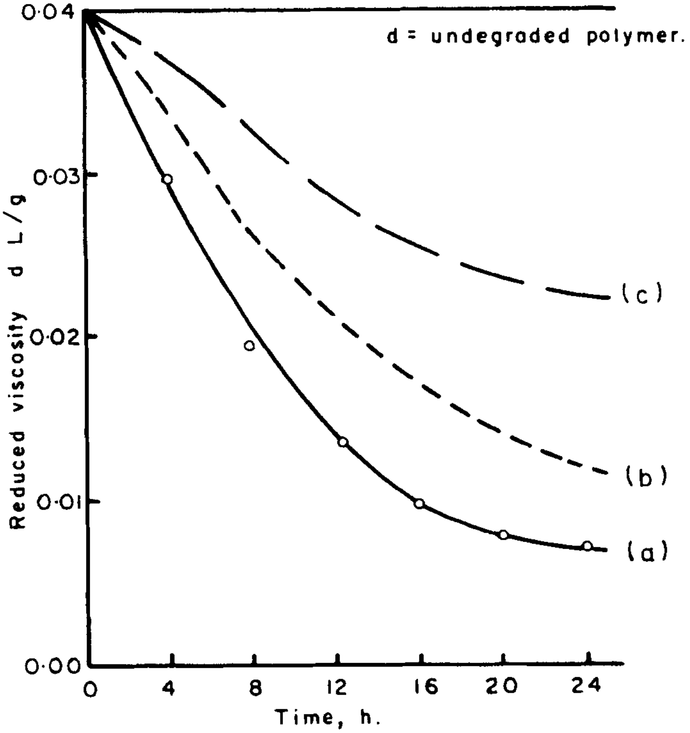
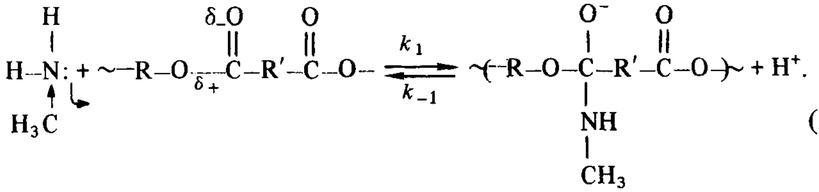


FIG. 2. Reduced viscosity vs time for methylamine degradation (a) of laboratory PET D.R. 5:1 at 20°C. Expected curves (b) and (c) are for ethylamine and propylamine, respectively.

in the reduced viscosity, and thus of the $\overline{DP}$ of the polymer, occurred (Fig. 2) [8]. Indeed, a family of similar curves would be expected depending on the strength of the degrading mixture and type of amine.

Proposed Mechanisms for the Degradation

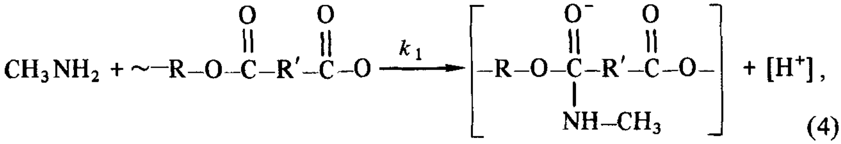
The aminolytic degradation reaction itself is catalyzed by water or any suitable acid. In certain nonaqueous liquids such as hydroxylamine, an autocatalytic effect is obtained, leading to faster degradation. The reaction of aqueous methylamine with the ester occurred according to the following steps:



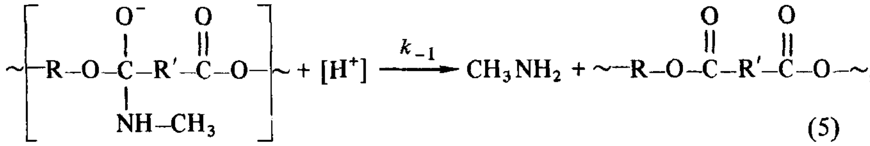
$$\mathrm{H_3C{-}\ddot{N}H_2} + \sim\mathrm{R{-}O{-}\overset{\delta-}{\overset{O}{\overset{\|}{C}}}\,{}^{\delta+}{-}R'{-}\overset{O}{\overset{\|}{C}}{-}O}\sim \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \sim\!\left(\mathrm{R{-}O{-}\underset{\underset{\underset{CH_3}{|}}{NH}}{\underset{|}{\overset{O^-}{\overset{|}{C}}}}{-}R'{-}\overset{O}{\overset{\|}{C}}{-}O}\right)\!\sim + \mathrm{H^+}. \tag{3}$$

There is a nucleophilic attack of the nitrogen on the carbonium center of the carbonyl ester. This would normally be a rapid reaction.

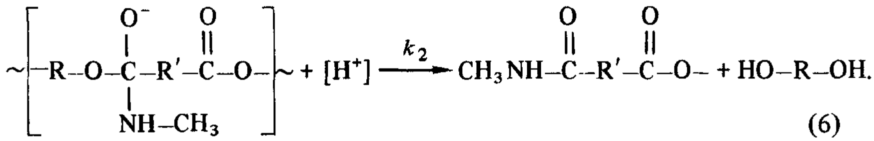
The reaction may be considered to proceed via the following discrete steps:



$$\mathrm{CH_3NH_2} + \sim\mathrm{R{-}O{-}\overset{O}{\overset{\|}{C}}{-}R'{-}\overset{O}{\overset{\|}{C}}{-}O} \xrightarrow{k_1} \left[\mathrm{{-}R{-}O{-}\underset{\underset{NH-CH_3}{|}}{\overset{O^-}{\overset{\|}{C}}}{-}R'{-}\overset{O}{\overset{\|}{C}}{-}O{-}}\right] + [\mathrm{H^+}], \tag{4}$$

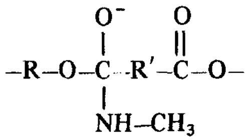


$$\sim\!\left[\mathrm{{-}R{-}O{-}\underset{\underset{NH-CH_3}{|}}{\overset{O^-}{\overset{|}{C}}}{-}R'{-}\overset{O}{\overset{\|}{C}}{-}O{-}}\right]\!\sim + [\mathrm{H^+}] \xrightarrow{k_{-1}} \mathrm{CH_3NH_2} + \sim\mathrm{R{-}O{-}\overset{O}{\overset{\|}{C}}{-}R'{-}\overset{O}{\overset{\|}{C}}{-}O}\sim, \tag{5}$$



$$\sim\!\left[\mathrm{{-}R{-}O{-}\underset{\underset{NH-CH_3}{|}}{\overset{O^-}{\overset{|}{C}}}{-}R'{-}\overset{O}{\overset{\|}{C}}{-}O{-}}\right]\!\sim + [\mathrm{H^+}] \xrightarrow{k_2} \mathrm{CH_3NH{-}\overset{O}{\overset{\|}{C}}{-}R'{-}\overset{O}{\overset{\|}{C}}{-}O{-}} + \mathrm{HO{-}R{-}OH}. \tag{6}$$

Since Reaction (3) is fast, the rate-determining step of the degradation is the reaction of the steady-state concentration of the conjugate amine/ester complex. In the absence of an ionizing medium (H_2O), Reaction (5) takes place. Otherwise, the complex proceeds to the formation of the expected amide and alcohol in accordance with Reaction (6). The rate of degradation is therefore proportional to the steady-state concentration of the conjugate base amine/ester complex. Since this is a reactive intermediate, the following relationship holds at the steady state. Since the reactive intermediate



$$\mathrm{{-}R{-}O{-}\underset{\underset{NH-CH_3}{|}}{\overset{O^-}{\overset{|}{C}}}{-}R'{-}\overset{O}{\overset{\|}{C}}{-}O{-}} \quad \text{(I)}$$

is formed in Reaction (4) and consumed in Reactions (5) and (6), its steady-state concentration is given by

$$[\mathrm{I}] = \frac{k_1\,[\mathrm{CH_3NH_2}]\left[-\mathrm{R{-}O{-}}\overset{\overset{\displaystyle \mathrm{O}}{\|}}{\mathrm{C}}\mathrm{{-}R'{-}}\overset{\overset{\displaystyle \mathrm{O}}{\|}}{\mathrm{C}}\mathrm{{-}O{-}}\right]}{k_{-1}\,[\mathrm{H^+}] + k_2}, \tag{7}$$

and the steady-rate of reaction in terms of the rate of formation of the amide product is given by

$$\frac{d\left[\mathrm{CH_3NH{-}}\overset{\overset{\displaystyle \mathrm{O}}{\|}}{\mathrm{C}}\mathrm{{-}R'{-}}\overset{\overset{\displaystyle \mathrm{O}}{\|}}{\mathrm{C}}\mathrm{{-}O{-}}\right]}{dt} = \frac{k_1 k_2\,[\mathrm{CH_3NH_2}]\left[-\mathrm{R{-}O{-}}\overset{\overset{\displaystyle \mathrm{O}}{\|}}{\mathrm{C}}\mathrm{{-}R'{-}}\overset{\overset{\displaystyle \mathrm{O}}{\|}}{\mathrm{C}}\mathrm{{-}O{-}}\right]}{k_{-1}\,[\mathrm{H^+}] + k_2}. \tag{8}$$

Since water would act as an acid in solvents that are more protophylic than itself, it would form an ammonium complex:

$$\mathrm{RNH_2 + H_2O \rightleftharpoons (RNH_2H^+) + OH^-}.$$

In that case an alternative mechanistic scheme involving protonation of the ester prior to nucleophilic attack by the amine, similar to those of acid-catalyzed degradation of cellulose esters, would apply [10].

The basicity of the amine relative to that of water would affect the degradation rate. The electron density on the nitrogen affects the ease of its attack on the electrophilic carbonium center. Generally, he lower the pK_b of the amine, the greater the expected rate of the aminolysis reaction. For the homologous primary aliphatic amines in Table 1, the rates of degradation are expected to be in the order ethyl > methyl > *n*-propyl.

In actual practice, this order might not be obtained because of steric factors of the amine/ester pair since the size of the attacking amine is also important to the orientation and attachment of the amine to the carbonium center of the carbonyl carbon. The bigger the size of the alkyl group of the amine, the lower the rate of degradation. The smaller size of methylamine coupled with a pK_b almost equal to that of ethylamine makes it a faster degrading agent, leading to the order of relative degradation rates methyl > ethyl > *n*-propyl.

TABLE 1. Basicity of Some Primary Aliphatic Amines [11, 12]

Amines	pK_b
Methylamine	3.34
Ethylamine	3.30
n-Propylamine	3.38

CONCLUSION

The acid-catalyzed amine degradation of polyesters occurs by a bimolecular nucleophilic substitution mechanism, S_N2. Since water will behave as an acid in more protophilic solvents, an onium complex is formed in the presence of amines, leading to a possible degradation mechanism involving protonation of the ester prior to nucleophilic attack by the amine.

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