Polyester Formation: Aminolytic Degradation and Proposed Mechanisms of the Reaction

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Synopsis

The acid-catalyzed chemical degradation of polyesters is discussed, with emphasis on the chemistry of the reactions involved. Using primary amines as degrading agents in presence of water as the acid-ionizing medium, mechanisms consistent with the chemistry of the reaction and those of related esters are proposed.

INTRODUCTION

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

The hydrolytic and chemical degradations of simple esters have been studied, and recently, most of these studies have been extended to polyesters using poly(ethylene terephthalate) as model for the investigation.[1-6] In these various studies, attention has been focused on the chemical degradation process and the structural/morphological changes resulting from the reaction. Previous studies on the degradation process of polyester have, however, largely ignored the chemistry and mechanisms of the acid-catalyzed degradation. In this article, the chemical reactions of amine degradation of polyester investigated and the mechanisms are discussed.
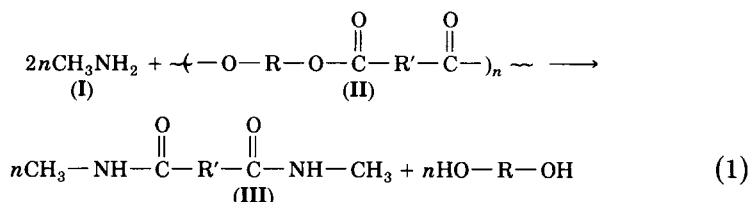
EXPERIMENTAL

Most degradation experiments carried out on polyesters have used aqueous primary amines, usually 40% aqueous methylamine to degrade poly(ethylene terephthalate) at 20°C.[5-7] In most cases, about 30–50 mg of vacuum-dried polymer was degraded in excess aqueous amine contained in an airtight tube to prevent the loss of gaseous methylamine from solution. This was done with or without mild agitation for various periods of time. On completion of degradation time, sample was filtered, carefully washed, and dried at 60°C for

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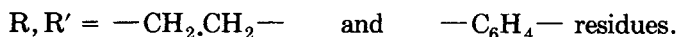
3 h, which was found sufficient to remove water and residual methylamine solution. Following the drying, both the weight loss and extent of chain scission were determined by gravimetry and viscometry runs.
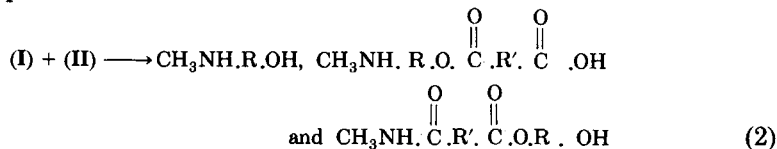
RESULTS AND DISCUSSION

Generally, the acid-catalyzed degradation of polyesters in presence of primary amines occurs in accordance with the equation:

$$2n CH_3NH_2 + (-O-R-O-\overset{\overset{O}{\|}}{C}-R'-\overset{\overset{O}{\|}}{C}-)_n \sim \longrightarrow$$
$$\text{(I)} \qquad\qquad\qquad \text{(II)}$$

$$n CH_3-NH-\overset{\overset{O}{\|}}{C}-R'-\overset{\overset{O}{\|}}{C}-NH-CH_3 + n HO-R-OH \qquad (1)$$
$$\text{(III)}$$

For poly(ethylene terephthalate)

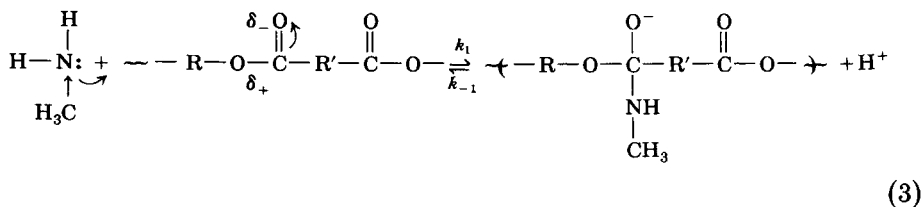$$R, R' = -CH_2.CH_2- \qquad \text{and} \qquad -C_6H_4- \text{ residues.}$$

The amide (III) is the product on final degradation of the ester. 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 degradation. The following byproducts could be proposed for the same reaction.
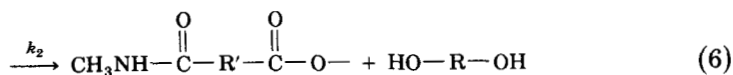
$$\text{(I) + (II)} \longrightarrow CH_3NH.R.OH, \quad CH_3NH. R.O. \overset{\overset{O}{\|}}{C}.R'. \overset{\overset{O}{\|}}{C}.OH$$

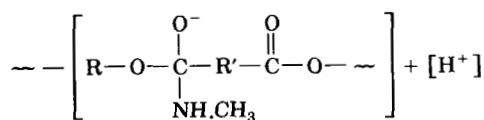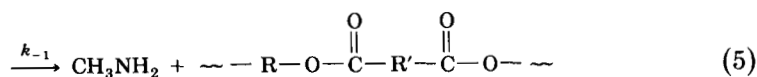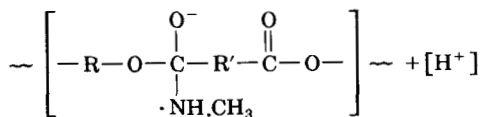$$\text{and } CH_3NH.\overset{\overset{O}{\|}}{C}.R'. \overset{\overset{O}{\|}}{C}.O.R . OH \qquad (2)$$
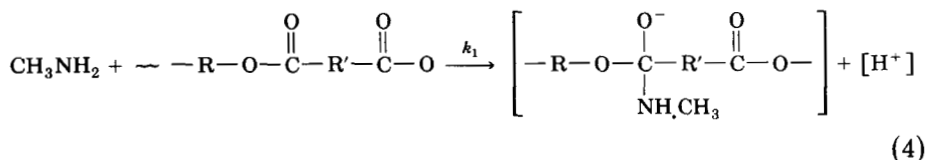
Following the degradation, there was a considerable weight loss resulting in residual weight kinetic of PET (2GT) shown in Figure 1.[7] For the residual weight kinetic shown, a corresponding sharp drop in the viscosity number, and thus the average degree of polymerization ($\overline{DP}$) of the polymer, displayed in Figure 2, occurred.[8] Indeed, a family of curves shown in broken lines b–d would be expected from the degradation depending on the strength of the degrading mixture, type of amine, and time of degradation.

Proposed Mechanisms for the Degradation

The aminolytic degradation reaction itself is catalyzed by water or any other suitable acid. In aqueous amine solutions, this is done by the water in which the gaseous amine is dissolved. In certain nonaqueous liquid such as hydroxylamine, an autocatalytic effect is obtained, leading to faster rate of degradation. The reaction of aqueous methylamine with the ester occurred according to the following steps.

$$H\underset{\underset{H_3C}{|}}{\overset{\overset{H}{|}}{-N:}} + \sim-R-O-\overset{\overset{\delta_-O}{\|}}{\underset{\delta_+}{C}}-R'-\overset{\overset{O}{\|}}{C}-O- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (-R-O-\overset{O^-}{\underset{\underset{CH_3}{\overset{|}{NH}}}{\overset{|}{C}}}-R'-\overset{\overset{O}{\|}}{C}-O-) +H^+$$

$$(3)$$

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 as proceeding via the following discrete steps:

$$CH_3NH_2 + \sim \; -R-O-\underset{\substack{\| \\ O}}{C}-R'-\underset{\substack{\| \\ O}}{C}-O \xrightarrow{k_1} \left[-R-O-\underset{\substack{| \\ NH.CH_3}}{\overset{O^-}{C}}-R'-\underset{\substack{\| \\ O}}{C}-O- \right] + [H^+]$$

(4)

$$\sim \left[-R-O-\underset{\substack{| \\ \cdot NH.CH_3}}{\overset{O^-}{C}}-R'-\underset{\substack{\| \\ O}}{C}-O- \right] \sim +[H^+]$$

$$\xrightarrow{k_{-1}} CH_3NH_2 + \sim -R-O-\underset{\substack{\| \\ O}}{C}-R'-\underset{\substack{\| \\ O}}{C}-O- \sim$$

(5)

$$\sim - \left[R-O-\underset{\substack{| \\ NH.CH_3}}{\overset{O^-}{C}}-R'-\underset{\substack{\| \\ O}}{C}-O- \sim \right] + [H^+]$$

$$\xrightarrow{k_2} CH_3NH-\underset{\substack{\| \\ O}}{C}-R'-\underset{\substack{\| \\ O}}{C}-O- + HO-R-OH$$

(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 absence of an ionizing medium, H_2O, reaction (5) takes place. However, where such medium is available, the complex proceeds into the formation of the expected amide and alcohol in accordance to reaction (6). The rate of the degradation therefore is proportional to the steady-state concentration of the conjugate-base amine/ester complex, and since this is a reactive intermediate, at steady state, the following relationship occurs:

$$\frac{d \sim \left[-R-O-\underset{\substack{| \\ NH.CH_3}}{\overset{O}{C}}-R'-\underset{\substack{\| \\ O}}{C}-O- \right] \sim}{dt}$$

$$= O = k_1 [CH_3NH_2] \sim \left[-R-O-\underset{\substack{\| \\ O}}{C}-R'-\underset{\substack{\| \\ O}}{C}-O- \right] - \sim$$

$$-k_{-1} \left[-R-O-\underset{\substack{| \\ NH.CH_3}}{\overset{O^-}{C}}-R'-\underset{\substack{\| \\ O}}{C}-O \sim \right] [H^+]$$

$$-k_2 \sim \left[-R-O-\underset{\substack{| \\ NH.CH_3}}{\overset{O^-}{C}}-R'-\underset{\substack{\| \\ O}}{C}-O- \right] \sim [H^+]$$
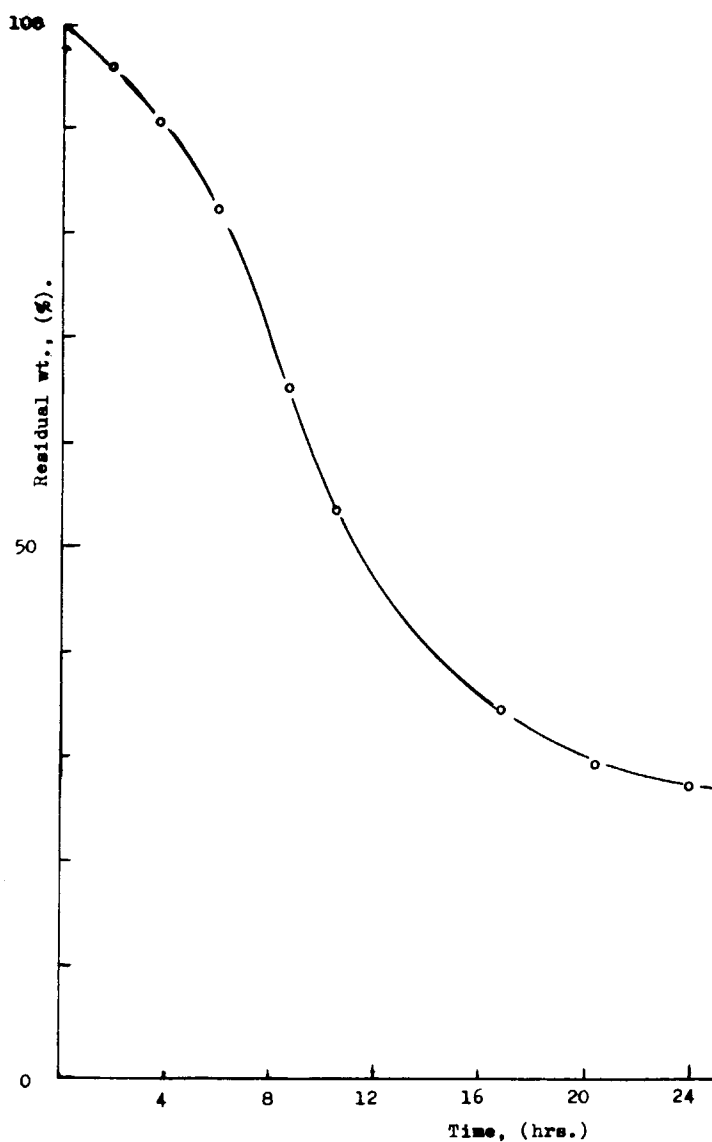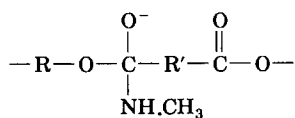
(7)

Fig. 1.   Residual wt (%) vs. time of methylamine degradation for laboratory PET fiber D.R. 5 : 1 at 20°C.

that is, the reactive intermediate

$$-R-O-\underset{\underset{NH.CH_3}{|}}{\overset{\overset{O^-}{|}}{C}}-R'-\overset{\overset{O}{||}}{C}-O-$$

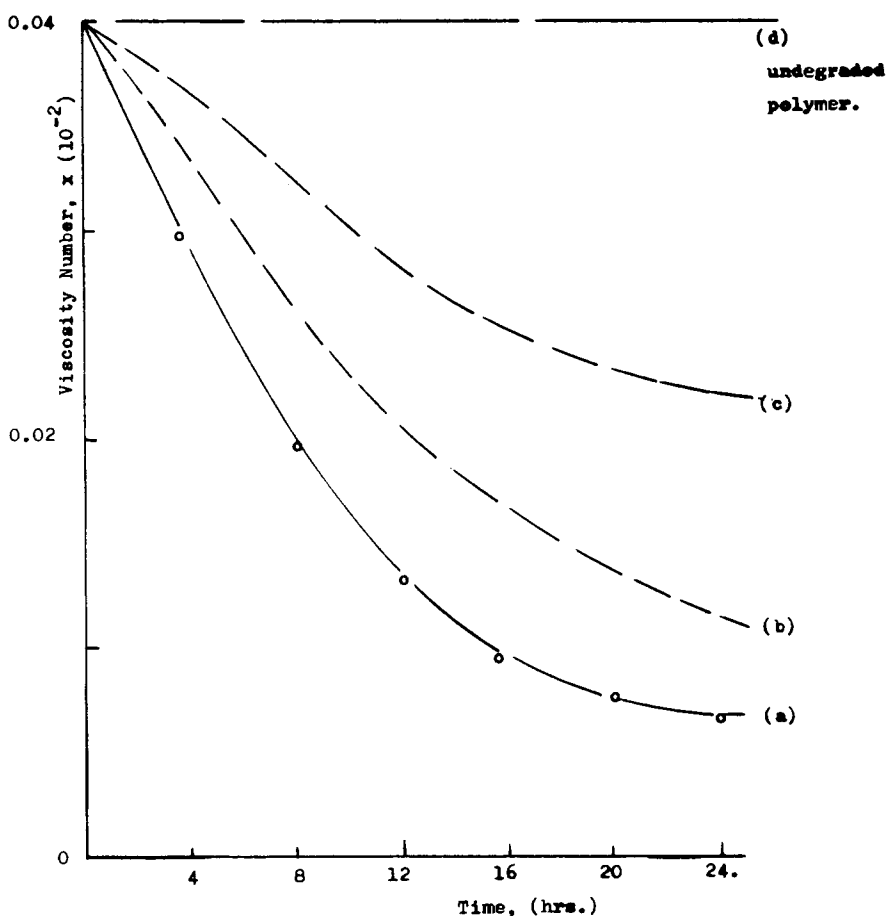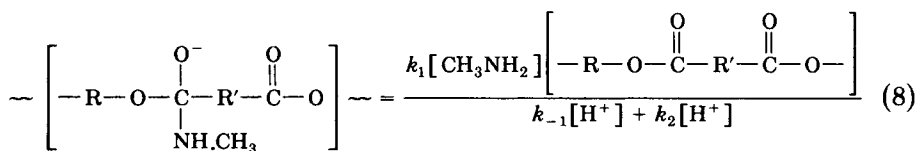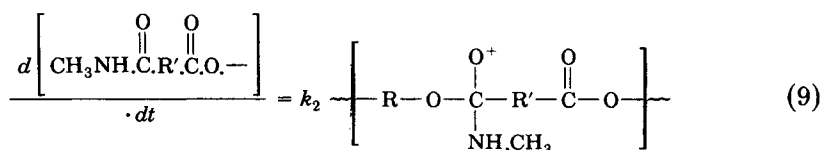is formed in reaction (4) and consumed in reactions (5) and (6). Thus the

Fig. 2. Viscosity number vs. time of methylamine degradation for (a) laboratory PET, D.R. 5 : 1 at 20°C (b & c expected curves for ethyl- and propyl-amines).
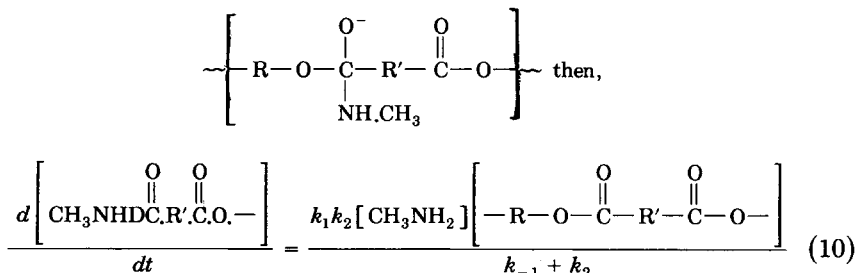
steady-state concentration of the reactive intermediate is given as:

$$\sim\left[-R-O-\overset{O^-}{\underset{NH.CH_3}{\underset{|}{C}}}-R'-\overset{O}{\overset{\parallel}{C}}-O \right]\sim = \frac{k_1[\,CH_3NH_2\,]\left[-R-O-\overset{O}{\overset{\parallel}{C}}-R'-\overset{O}{\overset{\parallel}{C}}-O- \right]}{k_{-1}[H^+] + k_2[H^+]} \quad (8)$$

and the steady rate of reaction measured by the rate of formation of the amide product is

$$\frac{d\left[CH_3NH.\overset{O}{\overset{\parallel}{C}}.R'.\overset{O}{\overset{\parallel}{C}}.O.- \right]}{\cdot dt} = k_2 \sim\left[-R-O-\overset{O^+}{\underset{NH.CH_3}{\underset{|}{C}}}-R'-\overset{O}{\overset{\parallel}{C}}-O- \right]\sim \quad (9)$$

Substituting eq. (8) for the steady-state concentration of

$$\left[\begin{array}{c} \overset{O^-}{\underset{NH.CH_3}{\mid}} \quad \overset{O}{\overset{\parallel}{}} \\ \sim\!\!\left[-R-O-\overset{\mid}{\underset{\mid}{C}}-R'-\overset{\parallel}{C}-O\!-\right]\!\!\sim \end{array}\right] \text{ then,}$$

$$\frac{d\left[\overset{O}{\overset{\parallel}{CH_3NHD}}\overset{O}{\overset{\parallel}{C}}.R'.\overset{}{C}.O.-\right]}{dt} = \frac{k_1 k_2 [\,CH_3NH_2\,]\left[-R-O-\overset{O}{\overset{\parallel}{C}}-R'-\overset{O}{\overset{\parallel}{C}}-O-\right]}{k_{-1}+k_2} \quad (10)$$

where the rate of the degradation is given in terms of the concentration of the reactants only rather than in that of the reactive intermediate.[9]

In view of the fact that water might be expected to act as an acid in solvents which are more protophilic than water itself, it would be expected to form an ammonium complex by its reaction with the amine, that is,

$$RNH_2 + H_2O \rightleftharpoons (RNH_2H^+) + OH^-$$
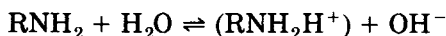
In that case, an alternative mechanistic scheme involving protonation of the ester before nucleophilic attack by the amine similar to those of acid-catalyzed degradation of cellulose esters would occur.[10]

Factors that are expected to determine the rate of the degradation will include the basicity of the amine relative to that of water. The electron density on the nitrogen affects the ease of its attack on the electrophilic carbonium center. Generally, the lower the pKb value of the amine, the greater will be the expected rate of aminolysis reaction. For a homolog of primary aliphatic amines shown in Table I, their rates of degradation on polyester will be expected to be in order

ethyl > methyl > *n*-propyl-amines
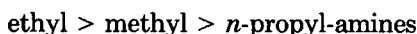
leading to a family of degradation curves a–c of Figure 2.

In actual practice, this order will not be obtained because of the steric factor of the amine/ester pair, since the size of the attacking amine is also important in 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 the degradation. A smaller size of methylamine coupled with a pKb of almost equal value to that of ethylamine makes it a

TABLE I
pKb Values of Some Primary Aliphatic Amines.

Amines	pKb	Kb
Methylamine	3.34	4.5×10^{-4}
Ethylamine	3.30	5.1
n-Propylamine	3.38	4.1

Source: Refs. 11 and 12.

faster degrading agent giving an order of relative rate of degradation shown; methyl- > ethyl- > n-propyl-amines.

CONCLUSION

The acid-catalyzed amine degradation of polyesters occurred by bimolecular nucleophilic substitution mechanism, S_N2. In view of the fact that water will behave as an acid in solvents which are more protophilic than it, 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. It is also concluded that the chemically similar ammoniolysis reaction of polyesters can be adequately explained by both the reaction scheme and the mechanism discussed.

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