

Steric Effects in the Basic Hydrolysis of Poly(ethylene Terephthalate)*

C. G. G. NAMBOORI and MALCOLM S. HAITH,
*Research and Development Division, Cone Mills Corporation,
Greensboro, North Carolina 27405*

Synopsis

A comparative study of the reactivity of hydroxide and various alkoxide anions was made by determining percentage weight loss of poly(ethylene terephthalate) fiber. Regardless of the basicity of the anions, the order of reactivity was found to be hydroxide < *tert*-butoxide < *sec*-propoxide < methoxide < ethoxide. This observed order follows the nucleophilicity of the bases, and the relatively lower reactivity of *sec*-propoxide and *tert*-butoxide is assumed to be due to steric retardation during the equilibrium reactions.

Introduction

According to the literature, poly(ethylene terephthalate) fiber is stable to the action of chemical reagents such as alkalis, salts and acids at low temperature. The fiber has no apparent loss of strength upon several hours exposure to dilute solutions of hydrochloric, sulfuric, and nitric acids and sodium hydroxide at room temperature.^{1a} The fiber loses only 15% of its strength on treatment with 50% nitric acid at 40°C for 72 hr.^{1b} Treatment with 30% hydrochloric acid solution at 40°C for 48 hr or 70% sulfuric acid at 40°C for 72 hr has no effect on tensile strength.^{1b} Treatment with 4% solution of caustic soda at 100°C for 2 hr gives 30% loss in weight.^{1c} Alcoholysis with methyl alcohol decomposes poly(ethylene terephthalate) at 180°C after 3 hr, the product being dimethyl terephthalate.³

Since alkaline processes are used extensively in fabric preparation and due to the increased use of polyester fiber blended with cotton, the current study was undertaken in order to evaluate possible adverse effects. The existence of nonaqueous systems for textile processing led to further investigations on basic hydrolysis of polyester in nonaqueous media. The present investigation determines the order of reactivity of the various bases in the depolymerization of poly(ethylene terephthalate) and the nature of hydrolysis with respect to physical properties of the hydrolyzed fiber.

Experimental

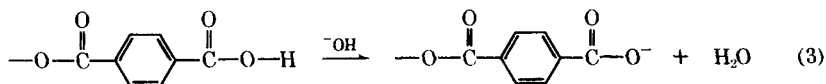
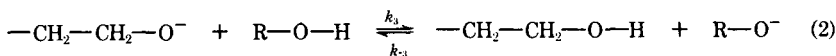
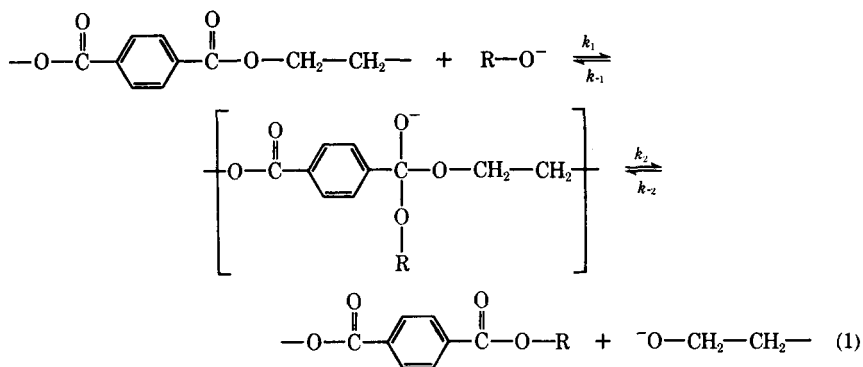
In this study sodium hydroxide in water, sodium methoxide in methanol, sodium ethoxide in ethanol, sodium isopropoxide in isopropanol, and potas-

* Presented at the 154th National Meeting of the American Chemical Society, Chicago, Illinois, September 11-14, 1967.

sium *tert*-butoxide in *tert*-butanol were employed at 60°C and at different concentrations. In the case of sodium hydroxide, additional experiments were conducted at 100°C at different concentrations. Kodel IV drawn polyester tow fiber (Eastman Kodak Co.) was used for the investigation. The fiber was dried and kept in the desiccator overnight. Samples, 2–2.5 g, were weighed accurately, and 100 cc of the anion solution was used for each experiment. The treatments were carried out in a 250-cc round-bottomed flask fitted with a reflux condenser for time periods of 10, 20, 40, and 60 min with the use of various concentrations of the anions. The temperature was maintained by immersing the flask in a constant temperature bath. After the treatments, the samples were washed with an excess of water and 10–15 cc of 1% hydrochloric acid solution followed by an excess of water until the filtrate was neutral. After suction extraction of water, the samples were collected in weighing crucibles and dried at 80–100°C in an oven for 1 hr, kept in the desiccator overnight, and reweighed to calculate the percentage weight loss. The tensile properties were measured at 70°F and 65% RH by use of an Instron tester, reported as an average of ten determinations, and denier changes were evaluated microscopically.

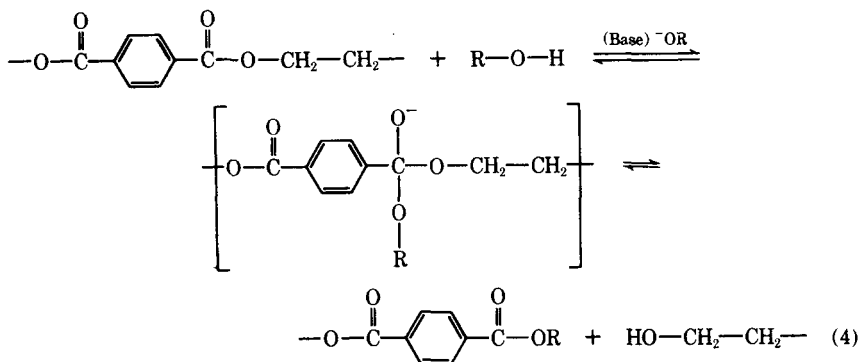
Results and Discussion

Although a complex polyester, poly(ethylene terephthalate) fiber is susceptible to basic hydrolysis similar to simple esters; the base attacks the electron deficient carbonyl carbon, forming an intermediate anion with the choice of reversing the reaction or forming the product.



According to eq. (1) the overall hydrolysis depends on the first equilibrium reaction and the base regenerated in solution as in eq. (2). In saponification the overall reaction is irreversible, since once the acid is

formed it is immediately converted to the carboxylate anion [eq. (3)], which is not further attacked by base. Hence the reaction goes to completion in the direction of hydrolysis. If a base-catalyzed ester interchange reaction is considered, it should proceed through the path shown in eq. (4), depending on the nature of the solvent.



Base-catalyzed ester interchange is analogous to the saponification reaction, except that an alkoxide base is used in catalytic amounts in place of hydroxide.² In general, esters of primary alcohols are hydrolyzed more rapidly than corresponding esters of secondary alcohols, which in turn are hydrolyzed more rapidly than esters of tertiary alcohols; if one type of ester is considered at a time, polar effects may be disregarded and differences in rate attributed to steric factors.⁴

Figure 1 shows the percentage weight loss of poly(ethylene terephthalate)

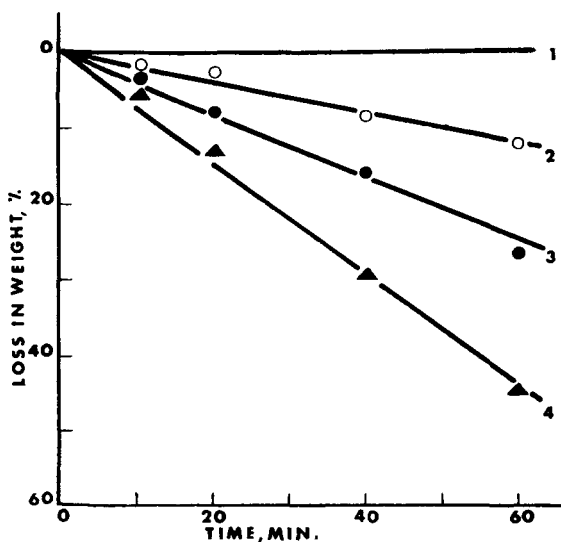


Fig. 1. Loss in weight of poly(ethylene terephthalate) fiber at 100°C; (1) water; (2) 5% NaOH; (3) 10% NaOH; (4) 15% NaOH.

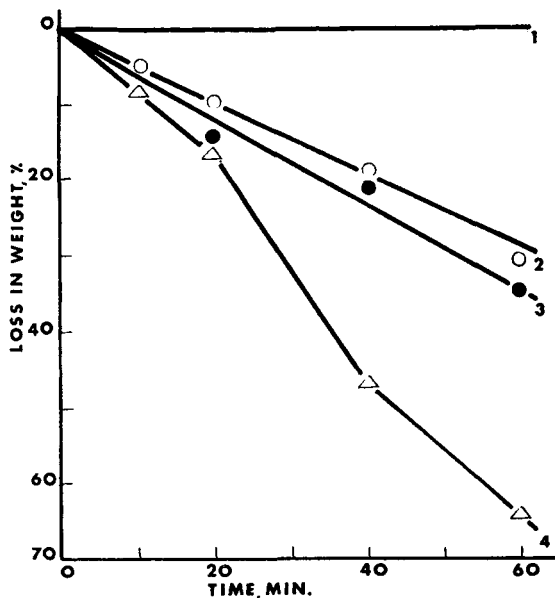


Fig. 2. Loss in weight of poly(ethylene terephthalate) fiber at 60°C: (1) methyl alcohol; (2) 0.25*M* sodium methoxide; (3) 0.5*M* sodium methoxide; (4) 0.75*M* sodium methoxide.

fiber on treatment with 5, 10, and 15% sodium hydroxide solution at 100°C for the various time periods.

It should be noticed from the figure that the saponification of poly(ethylene terephthalate) is proportional to time of treatment and the initial concentration of hydroxide ions in solution. Figure 2 is the plot of percentage weight loss of poly(ethylene terephthalate) fiber at 60°C with various concentrations of methoxide anions in methanol.

It was observed that there was no methanolysis at 60°C since there was no weight loss for a treatment time of 1 hr in methanol. The per cent weight loss at the end of 60 min was found to depend considerably on the initial concentration of methoxide anions. Figure 3 shows the per cent weight loss of poly(ethylene terephthalate) fiber on treatment with hydroxide, methoxide, ethoxide, isopropoxide, and *tert*-butoxide anions in the respective solvents at a concentration of 0.25*M* and Figure 4 for a concentration of 0.5*M* at a constant temperature of 60°C.

Considering the acidity functions (H⁻), the relative basicity of the bases used in the experimental part falls theoretically in the following way (Table I); OH⁻ < CH₃O⁻ < C₂H₅O⁻ < *sec*-C₃H₇O⁻ < *tert*-C₄H₉O⁻ (7). The acidity of the solvents is in the order: H₂O > CH₃OH > C₂H₅OH > *sec*-C₃H₇OH > *tert*-C₄H₉OH.²

From the experimental data (Figs. 3 and 4), the reactivity of the anions in the depolymerization of poly(ethylene terephthalate) falls in the order of OH⁻ < *tert*-C₄H₉O⁻ < *sec*-C₃H₇O⁻ < CH₃O⁻ < C₂H₅O⁻. This observed

order follows the nucleophilicity of the bases and the relatively lower reactivity of *sec*-propoxide and *tert*-butoxide is assumed to be due to steric retardation during the equilibrium reactions.

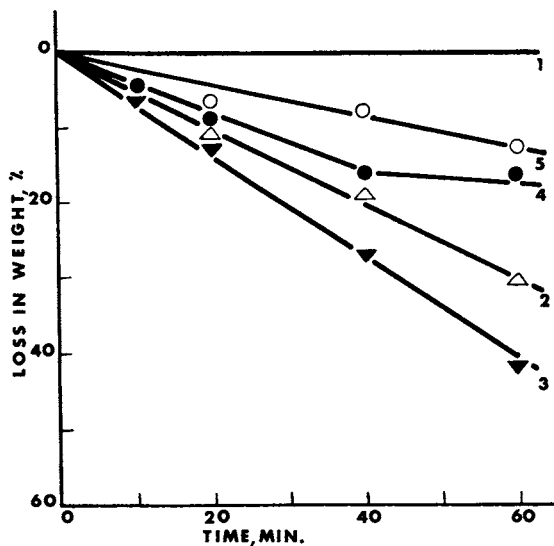


Fig. 3. Loss in weight of poly(ethylene terephthalate) fiber at 60°C: (1) 0.25M NaOH; (2) 0.25M sodium methoxide; (3) 0.25M sodium ethoxide; (4) 0.25M sodium isopropoxide; (5) 0.25M potassium *tert*-butoxide.

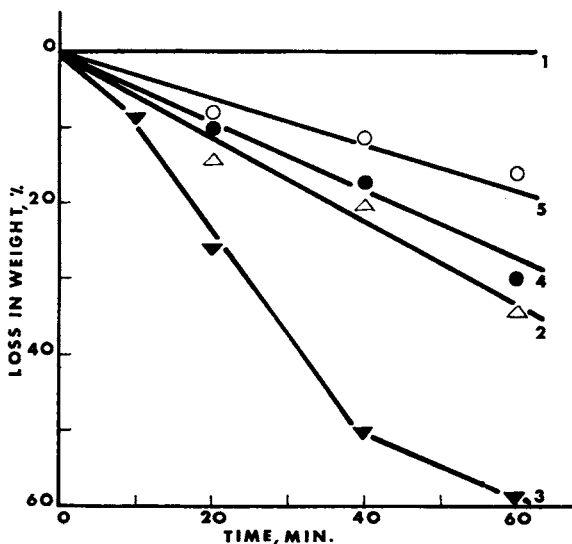


Fig. 4. Loss in weight of poly(ethylene terephthalate) fiber at 60°C: (1) 0.5M NaOH; (2) 0.5M sodium methoxide; (3) 0.5M sodium ethoxide; (4) 0.5M sodium isopropoxide; (5) 0.5M potassium *tert*-butoxide.

TABLE I
Acidity Function (H-) for 0.1M Concentration of Base at 25°C

Solvent	Base	Acidity function (H-) for 0.1M at 25°C ^a
H ₂ O	OH ⁻	—
CH ₃ OH	CH ₃ O ⁻	12.66
C ₂ H ₅ OH	C ₂ H ₅ O ⁻	14.57
<i>sec</i> -C ₃ H ₇ OH	<i>sec</i> -C ₃ H ₇ O ⁻	16.95
<i>tert</i> -C ₄ H ₉ OH	<i>tert</i> -C ₄ H ₉ O ⁻	19.14

^a Data of Bowden.⁵

The next step in the investigation was to determine the nature of hydrolysis. Table II gives the changes in tenacity, per cent elongation, and denier during hydrolysis with methoxide and ethoxide anions at 60°C. It should be observed that there are significant effects on tensile properties during the course of hydrolysis. Since denier changes are observed with respect to time of treatment, and microscopical observation shows circular cross sections, the hydrolysis is assumed to be taking place predominantly on the surface. Figure 5 shows that there is no change in specific viscosity (measured on 0.5 g in 100 ml of 1:1 tetrachloroethane-phenol mixture⁶ at 25°C) for the samples treated with 0.5M methoxide anion in methanol at 60°C for various time periods.

It is assumed that the base randomly attacks the carbonyl groups of the polymer molecules present on the surface of the fiber and removes them from the surface as short chains. These short chains are further hydrolyzed

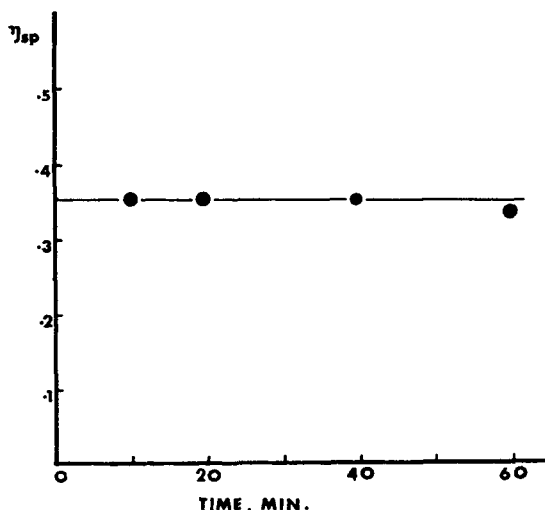


Fig. 5. Specific viscosity of poly(ethylene terephthalate) treated with 0.5M sodium methoxide at 60°C; measured with 0.5 g in 100 cc of tetrachloroethane and phenol at 25°C.

TABLE II
Changes in Tenacity, Elongation, and Denier during Hydrolysis of Poly(ethylene Terephthalate) Fiber with Methoxide and Ethoxide Anions at 60°C

Time of hydrolysis, min	0.5M MeO ⁻ /MeOH, 60°C			0.5M EtO ⁻ /EtOH, 60°C		
	Tenacity, g/den	Elongation, %	Denier	Tenacity, g/den	Elongation, %	Denier
0 (control)	—	—	—	5.1	45.7	1.5
10	4.37	29.8	1.5	4.06	32.7	1.5
20	3.66	25.0	1.5	3.60	24.5	1.25
40	3.74	23.3	1.25	2.50	12.5	1.00
60	3.74	24.3	1.25	2.50	13.7	1.00

to the salt of terephthalic acid or to its esters by the base present in solution. Since neither water nor the alcohols under consideration have any swelling and crystallizing action on poly(ethylene terephthalate),⁷ breaking of intermolecular forces by the solvent and subsequent penetration of anions inside the fiber bundle may not be considered below the second-order transition temperature.

Conclusion

It was found that the loss in weight of poly(ethylene terephthalate) fiber in the various anions studied at 60°C was in the order of hydroxide < *tert*-butoxide < *sec*-propoxide < methoxide < ethoxide. This observed order follows the nucleophilicity of the bases, and the relatively lower reactivity of *sec*-propoxide and *tert*-butoxide is assumed to be due to steric retardation during the equilibrium reactions. Since there was no change in specific viscosity and a denier change was observed, and microscopical observation shows circular cross sections, the hydrolysis is assumed to be taking place on the surface of the fiber. The attack of the base on the carbonyl groups of these surface polymer molecules is assumed to be of a random nature, removing shorter chains from the surface which are further hydrolyzed by the base present in solution.

References

1. V. V. Korshak and S. V. Vinogradova, *Polyesters*, Pergamon Press, New York, 1965, (a) p. 407; (b) p. 408; (c) p. 410.
2. J. D. Roberts and M. C. Caserio, *Basic Principles of Organic Chemistry*, Benjamin, New York, 1965.
3. B. V. Petukhov, *The Technology of Polyester Fibers*, Macmillan, New York, 1963, p. 532.
4. M. S. Newman, *Steric Effects in Organic Chemistry*, Wiley, New York, 1956, p. 220.
5. K. Bowden, *Chem. Rev.*, **66**, 119 (1966).
6. K. R. Osborn, *J. Polym. Sci.*, **38**, 357 (1959).
7. J. H. Lemons, S. K. Kaker, and D. M. Cates, *Am. Dyestuff Repr.*, **55**, 76 (1966).

Received December 22, 1967

Revised January 2, 1968