case, analysis, both Kjeldahl and Dumas, indicated that this material did not contain nitrogen. We have not yet identified this substance.

Acknowledgment.—The authors wish to thank Miss Sadie Herndon for performing the analyses incident to this research and Miss Stella Efland for skilled technical assistance.

CHAPEL HILL, N. CAROLINA RECEIVED JUNE 13, 1951

[CONTRIBUTION FROM THE CAROTHERS RESEARCH LABORATORY, E. I. DU PONT DE NEMOURS COMPANY]

The Thermal Degradation of Polyesters

BY HERBERT A. POHL

The general character of thermal degradation in hot polyesters has been examined. In particular the degradation of molten terephthalic acid/ethylene glycol polyester is shown to involve considerable main chain cracking resulting in lowered molecular weight. Study of a number of polymers of varied structure has thrown some light on the probable weak points for their thermal degradation. The carboxyl group, –CO·O–, is considered to be an active center for the degradation reaction as polymer without this group but otherwise similar in structure is considerably more stable. It is further evident that the presence of a –CH_2– group two carbon atoms removed from the ether oxygen of the carboxyl, is a key weak point and that replacing the H's by CH_3 on this β-CH_2 group considerably increases the thermal stability of the polyester.

I. General Character of Polymer Degradation

As H. Melville recently explained[1] the degradation of polymers to monomer may in general follow three courses (Fig. 1).

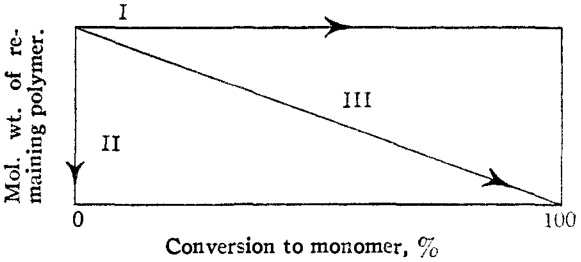

Fig. 1.

Types of Polymer Degradation.—Type I degradation, in which particular polymer molecules depolymerize practically completely to monomer while the remaining polymer molecules stay essentially unchanged in size, is common in vinyl addition polymers. It is typical of a "zipper-like" reverse polymerization preceded by activation of an end group.

Type II degradation is typical of random chain cracking where relatively few chain breaks cause a large drop in molecular weight. Thermal degradation of most polyesters which cannot form cyclic monomer and of polythene is of this type (*e.g.*, terephthalic acid/glycol polyesters).

Type III degradation is typical of main chain cracking in which the zipper effect goes in one direction only from the split, or proceeds to a limited extent to leave fragments of relatively large but reduced molecular weight together with many monomer fragments. Certain vinyl polymers degrade in this manner[1] as well as certain polyesters and polyanhydrides which produce cyclic monomer at relatively low temperatures.[2,3]

II. Broad Aspects of Thermal Degradation in Polyesters

A. Depolymerization to Monomer.—To an extent limited essentially by the end-group content, condensation polymers can in general be heated to yield small amounts of monomer. This reaction tends to increase the molecular weight, except in the cases noted where cyclic monomer can be split out in analogy to reverse addition polymerization.

For example, polyethyleneterephthalate, the monomeric unit of which cannot exist as a cyclic structure, under molecular distillation conditions yields only a few-tenths per cent. of material containing 1, 2 or 3 monomer units. On the other hand, polytrimethylene carbonate under similar conditions easily produces much larger (up to 50%) yields of cyclic monomer.[2,3]

B. Chain Cracking.—The most important mode of polymer degradation, as far as molecular weight or chain size is concerned, is chain-cracking. This may occur in polyesters as a direct thermal cracking or as a result of hydrolysis by water produced by other reactions. The chemical attack by oxygen is excluded from this discussion.

C. Conversion of Main Chain Groups.—In polyethyleneterephthalate there is good evidence that in at least two instances the nature of groups in the main chain are rather simply altered, causing only slight change in the chain length, although the by-products of these reactions may presumably act to split other chain links. In the first instance, the ester link is known in this polymer to be convertible to an anhydride link. This conclusion is based on direct chemical and on infrared spectroscopic evidence. In the second instance, color formation, the colored residues can be shown by selective solubility experiments to be converted members of the chain which are still attached to the main chain. To prove this second case, a terephthalic acid/glycol polyester, which was colored because of thermal degradation, was dissolved to form a 10% solution in liquefied phenol (*ca.* 10% H_2O). This solution was mixed with a similar 10% solution of colorless nylon (hexamethylenediamine adipamide) in the same solvent. The mixture reseparated into two layers, the lower containing the polyester. That the color of the polyester is firmly fixed onto the long polyester chains was evidenced by the observation that the color remained associated with the polyester layer instead of becoming distributed between the two layers as small molecules would do.

III. The Effect of Structure on Thermal Stability

In order to better understand the source of degradation and site of weak spots in polyesters, a number of polyesters were prepared from carefully purified intermediates and the thermal degradation studied and compared with that of a pure hydrocarbon polymer. In these experiments the degradation was determined by measurement of the rate of total gas evolution, coloration, and acid end-group formation. The hydrocarbon polymer, polyethylene of a low degree of branching, was employed as a comparison compound to allow better understanding of the role of the ester linkage in degradation.

A. Experimental

Measurement of the rate of gas produced was made in an isoteniscope. One-gram samples of polymer were placed in

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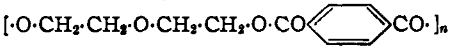
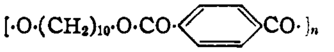
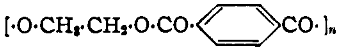
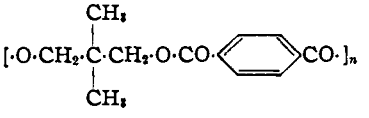
[1] H. Melville, *Science Progress*, 38, 1–9 (1950), No. 149, January.

[2] W. H. Carothers and E. W. Spanagel, *ibid.*, 58, 654 (1936).

[3] W. H. Carothers and J. W. Hill, THIS JOURNAL, 55, 5031 (1933).

TABLE I

THE THERMAL DEGRADATION OF POLYESTERS AT 307°

Polymer name	Polymer formula	Gas evolved (moles/ 10^6 g. hr.)	Color change (units/ hr.)	Acid formation equiv./ 10^6 g. hr.
Terephthalic acid/diethylene glycol polyester		231	240	242
Terephthalic acid/decamethylene glycol polyester		77	9	35
Terephthalic acid/ethylene glycol polyester		62	~10	30
Sebacic acid/ethylene glycol polyester	$[\cdot O\cdot CH_2\cdot CH_2\cdot O\cdot CO\cdot (CH_2)_8\cdot CO\cdot]_n$	60	12	31
Terephthalic acid/2,2-dimethylpropane-diol-1,3 polyester		23	10	11
Polyethylene	$-(\cdot CH_2\cdot CH_2\cdot)_n-$	5	3	...

a small Pyrex glass bulb (12–14 cc. vol.) sealed to a small empty manometer and vacuum-pressure system as shown in Fig. 2. Molten tin served as the manometer liquid in the null pressure manometer. Prior to the run, solid tin was placed in the widened section of the tube above the null pressure manometer. At the start of the run the system was highly evacuated ($10^{-4,5}$ mm.), then the vapor-bath of boiling benzophenone slowly raised first around the sample bulb, then to the solid tin which melted and ran down to seal off the bulb. In this fashion the polymer, its gaseous products, and manometer were all held at the same temperature to avoid condensation. By adjusting the pressure in the external system until the tin manometer showed equal pressures on the systems on either side of it, then noting the pressure of N_2 in the external system with the mercury manometer, the presssure changes within the polymer bulb were followed. At the conclusion of the run, the polymer color was measured by comparison with standard dye solutions and the carboxylic acid end-group content determined by titration with alcoholic NaOH using phenol red as indicator. The volume of the polymer bulb including the space up to the edge of the tin was measured and the absolute amount of gas evolution was then calculated. Plots of the pressure changes with time were linear over the entire range of 0 to 200 mm. and reproducible. A summary of the results is shown below in Table I. Each result shown is the average of at least duplicate runs.

In their study of polyethylene degradation, Oakes and Richards[4] observed a rate of chain cracking at this temperature of about 1 to 15 moles of C-bonds/10^6 g. per hr., in fair agreement with our observation of 5 moles of gas/10^6 g. per hr.

Detailed examination of the products and of polymer behavior during degradation of the terephthalic acid/ethylene glycol polymer showed the decomposition to be deep seated, yielding quantities of acetaldehyde, H_2O, CO_2 and of COOH end-groups, as well as anhydride groups. The latter, of course, were not present in appreciable numbers until after most of the active hydroxyl groups (as *e.g.*, glycol end groups) are gone. The reactions are best interpreted as involving main chain cracking to produce new end-groups and shorter chains (Type II Degradation). Additional evidence on this point is given in the accompanying communication.[6]

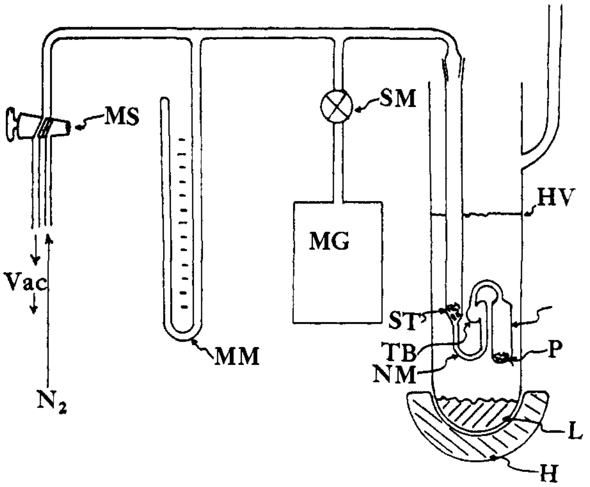


Fig. 2.—Isoteniscope assembly: MS, main stopcock Vac, conn. to vacuum systems; N_2, conn. to 10 p.s.i. N_2 pressure; MM, mercury manometer; MG, McLeod gage; SM, stopcock to MG; ST, solid tin in position before melting into null manometer; NM, null manometer; TB, trap bulb; P, polymer sample; H, heater; HV, approx. level of hot vapors; L, boiling liquids.

B. Discussion of Results

The degradation of terephthalic acid/ethylene glycol polymer is now known to involve main chain cracking to smaller molecules (Type II).

Consideration of the effect of structure on the relative stability of the polymers (Table I) indicates that (1) The polymer structure $-(CH_2\cdot CH_2)_m-$ is the most stable one examined. (2) Introduction of –COO– groups into this chain (as *e.g.*, in sebacic acid/ethylene glycol polyester) considerably reduces the thermal stability. (3) At least one principal point of weakness in the polyesters is on the CH_2 group beta to the ether oxygen atom *i.e.*,

$$-\underset{\beta}{CH_2}-\underset{\alpha}{CH_3}-O\cdot CO-R$$

weak spot

The evidence for this is that (a) replacement of the H's on this β-CH_2- by methyl groups (as in the terephthalic acid/2,2-dimethyl propane diol-1,3 polyester) increases the stability (b) introduction of more ether oxygens (as in the terephthalic acid/diethylene glycol polyester) decreases the thermal stability.

Acknowledgment.—The writer expresses his appreciation to Professor Paul J. Flory of Cornell University for his helpful interest in this work.

WILMINGTON, DELAWARE RECEIVED APRIL 27, 1951

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(4) W. G. Oakes and R. B. Richards, *J. Chem. Soc.*, 2929 (1949).

(5) H. A. Pohl, "The Kinetics of Concurrent Polycondensation and Degradation," presented at the A.C.S. Symposium on Macromolecules, April, 1951, Boston, Mass.