

# Determination of Carboxyl End Groups in a Polyester, Polyethylene Terephthalate

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A semimicroprocedure for the rapid determination of the carboxyl end groups of the polyester, polyethylene terephthalate, entails dissolving the polymer in benzyl alcohol rapidly at a high temperature (203° C.), then quickly mixing the solution with chloroform, and titrating with the aid of a phenol red indicator and sodium hydroxide. About 10 minutes is required for an analysis, including weighing. An additional 5 or 10 minutes may be required if the polymer sample needs grinding. To aid precise dispensing of the reagents, a new and simple automatic pipet or buret is used.

A RAPID indicator titration method for the determination of carboxyl end groups in polyethylene terephthalate has been devised. Previously described methods (1, 3, 12, 14) for the titration of polyester acidic end groups or other polymer acidic end groups are inapplicable because of the insolubility at room temperature of polyethylene terephthalate in any but acidic, phenolic solvents which obscure indicator action. The excellent hot benzyl alcohol titration method for nylon developed by Taylor and Waltz (16) proved inapplicable because of the instability of the polyester in hot basic solutions. It was found, as a result of the present work, that a hot benzyl alcohol solution of polyethylene terephthalate could be poured into chloroform to yield either a cold metastable solution, or a fine suspension which can be satisfactorily titrated with alkali. Nitrobenzene, 1-methylnaphthalene, and tetramethylene sulfone, in addition to benzyl alcohol, can act as "high temperature solvents" for this polymer at temperatures about 175° to 210° C. Benzyl alcohol was chosen because of its preferred odor, stability with base, and low relative toxicity.

Essentially, the procedure consists of:

Dissolving the polymer rapidly at high temperature (203° C.) in benzyl alcohol and subsequently quenching the hot solution.

Adding the clear polymer solution, while it is at about 140° C., to chloroform. This yields a clear metastable solution at near room temperature which is capable of reacting rapidly and quantitatively with the base and indicator. Such solutions can also be made with other solvent combinations such as benzyl alcohol and ethyl alcohol or tetrachloroethane.

Determining and correcting for the slight decomposition caused by the dissolving procedure.

## SPECIAL APPARATUS

The aluminum block heater for test tubes is a block drilled with several large holes, close-fitting to the test tube, painted inside with a black graphite compound—e.g., Aquadag—to increase heat transfer to the tubes, and provided with thermostated electrical heating, regulated to  $215^{\circ} \pm 1^{\circ}$  C. The equivalent heating may be obtained using a boiling benzyl alcohol bath (203° C.) with direct immersion of the test tube. This, however, offers some hazard due to bumping.

Small mechanically driven stainless steel stirrers fit in the tubes, operated at about 1700 r.p.m., and controlled by a variable voltage transformer. The propeller is smooth-surfaced, so as to hold a minimum of entrapped sample. Below the stirrer is a clamp for mounting the test tube in position. The test tube and stirrer are mounted to be moved as a unit.

An automatic pipet (optional) to deliver 10 ml. of chloroform or 5 ml. of benzyl alcohol, is shown diagrammatically in Figure 1. Automatic refilling requires no squeeze bulbs or vacuum lines. Stopcocks A, B, and C are closed during filling of the main supply bulb through D, then tightly restoppered at D. Stopcocks B and C are then opened and A is turned to allow the pipet section to fill. The liquid then drains from the supply bulb to the constant level at E, filling the pipet to a reproducible level. A is then

manipulated to drain the pipet as desired. Turning A back to the refill position will again allow a constant volume refilling. The instrument may also be used as an automatically refilling buret. Alternative attachments for this purpose are readily interchanged, such as pipet bulbs of 5-, 10-, and 20-ml. capacity, or graduated burets. The precision of volume delivered is dependent on the size of the capillary at the top of the pipet, on the verticality of the instrument, and to some extent on the surface tension of the solution; low surface tension means small bubbles and better reproducibility. The level generally repeats to  $\pm 1$  mm. or better, when a 1-mm. capillary and any common organic liquid are used. The reproducibility is therefore  $\pm 0.008$  ml. and in the use of the 10-ml. volume gives a precision of 8 parts in 10,000, which is acceptable for many analytical purposes.

## REAGENTS

Benzyl Alcohol, FFC Grade. The material used in this work was from the Trubek Laboratories, Inc., East Rutherford, N. J. It was distilled in a simple column, the middle 0.8 fraction being retained for use. The blank on a 10-ml. sample of freshly purified material should not exceed 6  $\mu$ l. of 0.1N sodium hydroxide after the sample is heated for 1.8 minutes at 203° C.

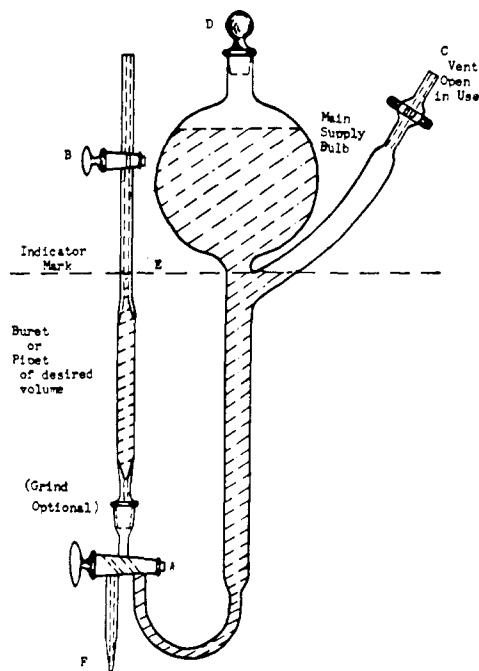


Figure 1. Automatic Pipet

- A. Three-way stopcock
- B, C. Stopcocks
- D. Refill port, closed in use
- E. Constant level
- F. Drain

Chloroform, c.p. grade. If the blank on 10 ml. exceeds 2.0  $\mu$ l. of 0.1N sodium hydroxide, the chloroform is redistilled until it passes the test. Washing with alkali, such as sodium bicarbonate, followed by distillation might also serve, but redistillation is easy, giving a more anhydrous product.

Ethyl Alcohol, c.p. grade.

Phenol Red Indicator, prepared as a neutral solution of 0.1% in alcohol.

Sodium Hydroxide, 0.1N, in Benzyl Alcohol. Into a 100-ml. beaker is weighed  $0.41 \pm 0.05$  gram of sodium hydroxide pellets

and 0.4 ml. of water is added to dissolve it. The solution is rinsed into a 100-ml. volumetric flask with 10 ml. of pure methanol, then diluted with benzyl alcohol to 100 ml. After mixing, it is standardized against hydrochloric acid of known normality, by using 2 drops of the phenol red indicator. This solution requires restandardization at the most about once a week. Alternatively the base may be made up in ethyl alcohol.

Sodium hydroxide, 0.1N, in denatured ethyl alcohol is prepared as for benzyl alcohol solution.

#### PROCEDURE

The polymer is, if necessary, finely ground in a Wiley mill to pass a 20-mesh screen. About 0.100 to 0.200 gram (to the nearest 0.0001 gram) of the prepared yarn or pulverized polymer is transferred into a small Pyrex brand test tube (15 × 125 mm.). (Difficultly soluble samples are ground to pass 40 mesh.) To the tube is added 5 ml. of benzyl alcohol from the automatic pipet. The tube is then clamped under the mechanical stirrer apparatus and transferred to the hot bath ( $215^{\circ} \pm 1^{\circ} \text{C.}$ ) for  $1.8 \pm 0.05$  minutes (105 to 110 seconds). It is important that the tube be inserted into the hot bath to a distance of 4 to 5 cm. during the heating. The stirrer should not scrape the test tube wall.

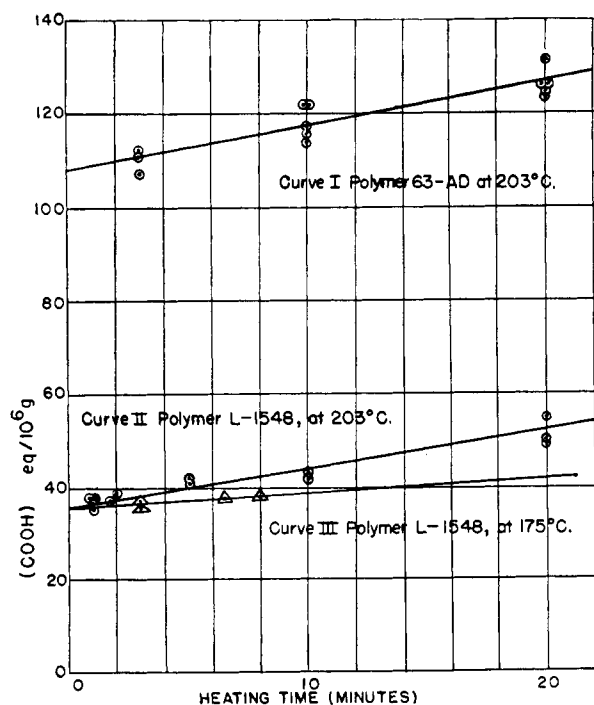


Figure 2. Rate of Increase of Carboxyl End Group on Heating

Polyethylene terephthalate in pure benzene alcohol

When the sample has been in the bath for the required length of time, the test tube in its frame is lifted quickly out of the bath and lowered immediately into a beaker of cool water ( $20^{\circ}$  to  $30^{\circ} \text{C.}$ ) to quench the sample for 6 to 7 seconds. The solution should not be overquenched, as this makes removal difficult. After quenching, the sample is immediately poured into a 50-ml. beaker containing 10 ml. of chloroform. The chloroform acts as a liquefier and dispersant and prevents too thick a gel formation. A rinse of 5 ml. of benzyl alcohol is added from the automatic pipet to the test tube, so that it runs down the walls and washes loose all gel.

The test tube containing the rinse is put in the  $215^{\circ} \text{C.}$  bath for  $60 \pm 5$  seconds, and then its contents are carefully but quickly added to the rest of the sample and stirred. Two drops of the indicator solution are added and the mixture is titrated from a Gilmont (5) ultramicroburet with 0.1N sodium hydroxide dissolved in either benzyl alcohol or ethyl alcohol. Use of the benzyl alcohol solution of this base is preferred because of higher volatility of the ethyl alcohol solution. The solution is rather vigorously stirred during titration and is illuminated by a microscope substage daylight lamp. The tip of the buret and the stirrer should be immersed and near the bottom of the beaker.

Stirring should not be done so rapidly as to cause bubbling but should effect rapid and thorough mixing. The titration is carried to the first discernible pink color throughout that persists for 10 seconds. A refinement of bubbling pure nitrogen through the liquid may be employed but is not generally necessary, presumably because the chloroform vapor barrier prevents entrance of carbon dioxide from the air. A wash bottle containing neutral denatured alcohol (Type 2B containing 0.5% benzene by volume) is used to clean the buret tip and both stirrers.

A blank is run on the benzyl alcohol-chloroform mixture. The reagents are repurified if this blank exceeds 15  $\mu\text{l.}$  of 0.1N sodium hydroxide.

The result is usually expressed in equivalents per million grams. A "standard" correction of 1.6 equivalents per  $10^6$  grams is subtracted from the result to allow for degradation, provided the analysis has been done as described.

**Example.** Ten small divisions on the 0.1-ml. capacity ultramicroburet used in this example are equivalent to 1  $\mu\text{l.}$  When 0.1500 gram of a certain polymer is titrated, 350 scale divisions or 35.0  $\mu\text{l.}$  of 0.1N sodium hydroxide is required; a blank of the heated benzyl alcohol plus chloroform requires 50 scale divisions or 5.0  $\mu\text{l.}$  The net titer is therefore 30.0  $\mu\text{l.}$  The base is 0.1050 equivalent per liter. The polymer then would be said to contain

$$\frac{(35.0 - 5.0) \text{ liters} \times 10^{-6} \times 0.1050 \text{ equivalent per liter}}{0.1500 \text{ gram}} =$$

21.0 equivalents per  $10^6$  grams (uncorrected)

and 19.4 equivalents per  $10^6$  grams, corrected for degradation during solution.

#### VARIABLES AFFECTING THE METHOD

The principal factors affecting the precision of the method are the degree of degradation to additional carboxyl groups and the precision of the titration. Because the degradation is mainly confined to that experienced during the preparation of the polymer solution prior to titration, the factors contributing to that action were given close scrutiny in an effort to minimize their effect.

**Preparation of Polymer Solution.** **CONDITION OF POLYMER.** Fiber cut to 2-cm. lengths or shorter, or powder of less than 20-mesh size, was generally readily soluble under the test conditions. Fibers of all available crystallinities proved to be readily soluble; but certain polymer powders of a high degree of crystallinity required more than 1.8 minutes. One such polymer oven dried at  $150^{\circ} \text{C.}$  for 12 hours proved soluble under test conditions if ground to pass 40 mesh. The most extreme sample required 2.9 minutes. No clearly marked solubility rate difference was noted between samples of low or high intrinsic viscosity ( $\eta = 0.4$  to  $0.8$  measured in an "excellent" solvent—i.e., a mixture of phenol and 2,4,6-trichlorophenol in a 3 to 1 mole ratio).

Table I. Carboxyl Content of Polymer Dissolved in Minimum Dissolving Times

$T, ^{\circ} \text{C.}$	Minimum Observed Dissolving Time, Min.	[COOH] Observed at $t_{\text{min.}}$ , Eq./ $10^6 \text{ G.}$	[COOH] Extrapolated at $t = 0$ , Eq./ $10^6 \text{ G.}$
175	3.0	36.4	35.5
183	2.0	36.0	35.5
193	1.25	36.1	35.5
203	0.9	36.8	35.5

**DISSOLVING PROCEDURE.** The effects of the time and temperature of dissolving, the rate of sample heating, stirring, and quenching were examined. The effects of time and temperature during dissolving are briefly summarized in Table I and in Figure 2. The data were obtained using a single ground polymer source and

a standardized dissolving procedure. Constant temperature baths using boiling *p*-cymene (175° C.), propylene glycol (183° C.), acetonylacetone (190° C.), and benzyl alcohol (203° C.) were used to heat the sample tube for the required times.

The results prompt the tentative suggestion that there is a principle of perhaps broad application underlying the action of dissolving or plasticizing a given polymer sample which can undergo decomposition during the period of dissolution or plasticization: For a given polymer and diluent pair, the amount of degradation is independent of the temperature, provided that the high temperature exposure is the minimum necessary for complete solution.

The results also showed that the degradation under fixed dissolving conditions is the same for all samples of polyethylene terephthalate investigated, regardless of source or initial carboxyl group content. Figure 2 also shows the typical degradation rate results for two polymers of widely different carboxyl group content. Examination of a large number of polymer samples showed that all but a very few could be dissolved in benzyl alcohol in 1.8 minutes, when the tube was immersed in a bath at the temperature of boiling benzyl alcohol (or its equivalent, the 215° C. aluminum block heater). Accordingly, all samples dissolved under the test conditions would be expected to undergo approximately 1.6 equivalents per 10<sup>6</sup> grams increase in carboxyl in this period, since the average degradation rate found was 0.88 equivalents per (10<sup>6</sup> grams) (per minute) and the heating lasts 1.8 minutes (see Figure 2). As all polymers are treated alike, this error is corrected for by subtracting 1.6 equivalents per 10<sup>6</sup> grams from the result found by the titer. Where solution is incomplete in 1.8 minutes, longer heating is employed, but correction is made for the increased degradation, either by further experiment or by use of the observed average factor:  $\frac{\Delta(\text{COOH})}{\Delta t_{\text{min}}} = 0.88$  equivalent per 10<sup>6</sup> grams at 203° C. Examination of the rate curves indicates that the degradation process in this solvent occurs with an activation of some 15 kcal. per mole.

Because the present method of dissolving is recognizedly empirical, and the dissolution and degradation of the polymer are dependent on the rate of heating of the test-tube contents, variables such as depth of immersion of the test tube in the hot bath, rate of stirring, test-tube dimensions, volume of solvent, and rate and duration of quenching are of some importance. The procedure given should be followed carefully. Selection of the lightest (11.3 grams) and the heaviest (14.7 grams) from 48 test tubes (15 × 125 mm. borosilicate glass Corning Glass works) for test led to the conclusion that variable test-tube thickness introduced no significant difference in the result (48.5 vs. 48.6 equivalents per 10<sup>6</sup> grams on five samples each). Without stirring, dissolution was usually incomplete; with either moderate or vigorous stirring, solution was rapid and led to no appreciable difference in the carboxyl content (48.5 vs. 48.6 equivalents per 10<sup>6</sup> grams on five samples each).

The purpose of immediately "quenching" the hot mixture after heating it 1.8 minutes in the 215° ± 1° C. bath is to bring the solution quickly down from the high-temperature and high-degradation rate range, and to increase the precision of the heating time. In practice it was found best to swing the stirrer-test tube assembly up out of the hot bath directly and quickly into the cold water quench bath, leave it there 6 or 7 seconds, then quickly pour the still clear solution into 10 ml. of chloroform. This yielded a clear metastable solution of the polymer at about 60° C. Generally this clear condition remained throughout the titration though it was found experimentally that it was not necessary to have a perfectly clear solution for the titer. Quenching the benzyl alcohol solution for longer periods generally produced a cloudy and gelatinous precipitation, giving trouble in the titration. Without quenching, erratic results are obtained.

**Titration.** The chloroform is necessary as a diluent to confer low viscosity and easy titrability. Excessive dilution, however,

reduces the sharpness of the end point. The 10 ml. of chloroform gives maximum fluidity compatible with sharpness of end point. Tests showed that the titration was unaffected by temperature in the range 25° to 60° C.

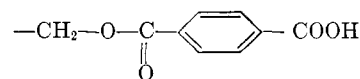
#### PRECISION AND RELIABILITY OF METHOD

A series of ten separate determinations on a single polymer showed it to contain 48.6 equivalents per 10<sup>6</sup> grams with a standard deviation of 0.86, and a coefficient of variation of 1.78%—i.e., approximately a 1.8% scatter about the mean. Further work on a routine basis involving several hundred duplicates bears out in general the above level of precision, though only the more careful work on a routine scale achieves high precision.

The reliability of the method for determining the absolute value of the carboxyl content of this polymer was checked in two ways: by comparing the value found when using this indicator method with that found when using a conductometric titration with a solvent consisting of *m*-cresol containing 2% hydroquinone as degradation inhibitor, and by titrating for a known added amount of *p*-nitrobenzoic acid in the benzyl alcohol.

The results of five indicator titrations of one polymer sample gave 35.5 equivalents per 10<sup>6</sup> grams ( $\sigma = 0.86$  equivalent per 10<sup>6</sup> grams) corrected for degradation. Those of four conductometric titrations gave 36.1 equivalents per 10<sup>6</sup> grams ( $\sigma = 1.70$  equivalents per 10<sup>6</sup> grams). The agreement is within experimental error.

The results of the titrations on *p*-nitrobenzoic acid (chosen from a number of available acids for the similarity of its dissociation constant to that of the polymer end groups) averaged 60.3  $\mu\text{l.}$ ; theoretical was 60.0. The dissociation constants for the polymer end group



and for *p*-nitrobenzoic acid were calculated using the method of Hammett (6) as  $5.1 \times 10^{-4}$  and  $6.3 \times 10^{-4}$ , respectively. It was concluded that the present method is acceptably reliable as to the absolute magnitude of the carboxyl content and offers useful precision.

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