

# The Accessibility of Sulphonic Acid Groups in Basic Dyeable Polyester Fibers. I. The Prevention of Fiber Hydrolysis during Dyeing

W. INGAMELLS, S. H. LILOU, and R. H. PETERS, *Department of Polymer and Fiber Science, The University of Manchester Institute of Science and Technology, Manchester M60 1QD, United Kingdom*

## Synopsis

The rate of acid hydrolysis of a basic dyeable polyester in water, before and after heat-setting, has been investigated. Intrinsic viscosity measurements and chemical analysis have been used to establish experimental conditions under which the hydrolysis is inhibited. It is suggested that the critical step of the hydrolysis mechanism is the exchange of sodium ions from the sulphonate groups in the fiber for hydrogen ions.

## INTRODUCTION

Polyester fibers containing acid groups are produced commercially using compounds such as 5-sulpho isophthalic acid as a comonomer during polymerization. When their dyeing properties are compared with those of normal polyester fibers dyed with disperse dyes, improvements are observed and in addition they may be dyed with water-soluble cationic dyes.

There are also difficulties reported for practical dyeing which are due to unlevelness of dyeings, poor reproducibility of shades,<sup>1</sup> and the chemical instability of the fibers under some of the hydrolytic conditions encountered in dyeing processes.<sup>2,3</sup>

The relative hydrolytic stabilities of poly(ethylene terephthalate) fibers and anionically modified polyesters have already been considered in relation to the rate of hydrolysis of model compounds under alkaline conditions.<sup>4</sup> The alkaline hydrolysis of hydroxyethyl diesters of terephthalic acid (representing PET) and of sulpho isophthalic acid (representing the anionically modified polyester fiber) were compared and the corresponding results proved that neither the sulphonate or the carboxyl groups catalyzed the hydrolysis of the esters. However, since the results were obtained in a homogeneous system at alkaline pH values, they do not necessarily represent the situation of a fiber immersed in an acidic dye-bath. In this case the accessibility of both the ester and sulphonate groups may be a controlling factor in a situation where disorders in the fine structure imposed by the bulk of the sulphonate groups influences the approach of the attacking ions.

Evidence supporting this conclusion is given by the variation of the saturation values of a basic dye with temperature on the powder obtained by reprecipitation of the dissolved modified polyester powders.<sup>5</sup>

The complete accessibility of the sulphonate groups anticipated for the polymer in this physical form is not supported by the saturation values. They

increase in a linear manner with increasing temperature, and stoichiometric agreement between the acid group content of the polymer and the saturation values is not achieved until a temperature of at least 90°C is used. High temperature dyeing at 120°C was required by another worker<sup>6</sup> before achieving full saturation of the dye sites in Tesil 31 basic dyeable polyester fiber. It is apparent therefore that the accessibility of the dye sites in anionically modified polyesters is a function of both the polymer morphology and temperature.

### PURPOSE OF THE INVESTIGATION

The study described here is concerned with defining experimental conditions under which the hydrolysis reaction takes place and with the action necessary to prevent the hydrolysis occurring in subsequent dye saturation measurements.

Changes in the accessibility of the sulpho groups caused by processing conditions as distinct from the hydrolysis reaction are defined in part II of the investigation.

### EXPERIMENTAL

Two experimental difficulties were encountered during the investigation. One was due to the instability of the dye over the long dyeing times required to reach equilibrium in an infinite dyebath and the other to the hydrolysis of the fiber. The former was overcome by periodic replacement of the dye liquor over the long dyeing times and the latter by the use of electrolyte in the dyebath. The course taken in the development of satisfactory dyeing conditions for experimental purposes is indicated in the experimental sections below.

### MATERIALS

*Dacron T65* 4 denier semidull fibers with a staple length of 5 cm were supplied by E. I. Du Pont de Nemours Inc. (Leicester U.K. Division). About 0.5% of the fiber weight was present as finishing agents. This was removed before use by refluxing with petroleum ether at 60°C for 2 h. After vacuum drying overnight at the same temperature, the fibers were scoured in an aqueous solution of 1 g/L Symperonic N (ICI) for 1 h at 60°C and dried again in a desiccator over calcium chloride.

#### Basic Dye (C.I. Basic Red 14)

A commercial sample of Synacryl Red 4G (ICI) powder was used. Before use, the powder was purified by soxhlet extraction with dry ethanol and diethyl ether. The crystals were washed with fresh ether and dried in a vacuum oven for 48 h at room temperature. The process was repeated until a constant value of the extinction coefficient was obtained.

### Viscosity Measurements

Phenol (ANALAR) and 1,1',2,2'-tetrachloroethane (10:90 by weight) were used to dissolve the fiber for intrinsic viscosity measurements.

### *m*-Cresol

Freshly distilled *m*-cresol was used to dissolve the dyed fibers before colorimetric estimation.

### Dyeing Experiments

Dyeing experiments were carried out in the apparatus described elsewhere.<sup>7</sup> Only a few details of the dyebath preparation are given here since the only reason for the experiment was to determine the reliability of the results under the starting conditions. Fuller details are given in Paper II, where more detailed results are presented.

Purified C.I. Basic Red 14 was dissolved at 60°C in water and the solution boiled for 15 min to ensure complete dissolution. The pH value of the dyebath was adjusted to a value of 4.5–4.8 by the addition of approximately 0.2 mL of 25% acetic acid to the total volume of dyebath. The liquor ratio was approximately 6000:1, and the pH value was monitored throughout. Compensation for the small changes was made by the addition of small amounts of acetic acid. The use of buffer salts was deliberately avoided because of the need to study the effect of electrolytes on the hydrolysis of the fibers.

The results shown in Figure 1 confirm that the results for the uptake of dye were erratic when obtained under the conditions used. Similar problems have also been encountered in commercial dyeing,<sup>1</sup> and there is therefore a real need to define the effect of the dyebath on the fiber more precisely.

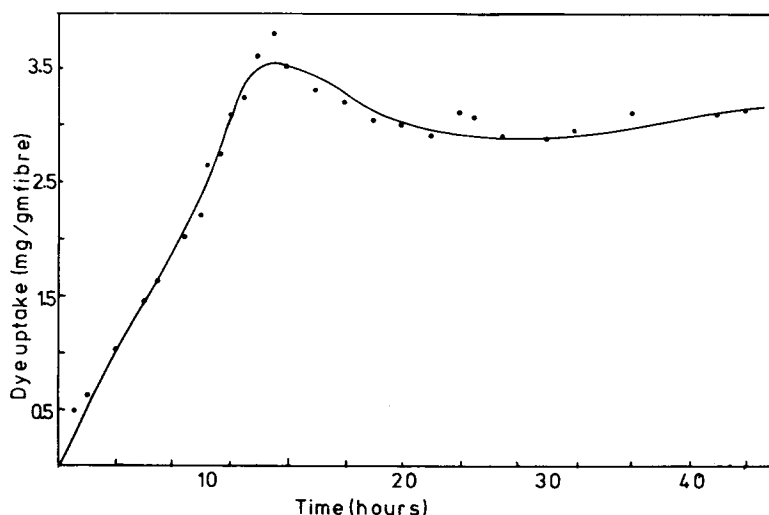


Fig. 1. C.I. Basic Red 14: rate of dyeing of Dacron T65 without salt.

### Heat Setting

Heat setting of the fibers was carried out in exactly the same manner as described in a recent publication.<sup>8</sup>

### Fiber Damage under Dyeing Conditions

Hydrolysis of the fibrous polymer will reduce the molecular weight. This in turn will be reflected by a decrease in viscosity of the solution of a known weight of fiber dissolved in the appropriate solvent.

The relation between the intrinsic viscosity  $[\eta]$  and the molecular weight of the polymer is given by the empirical Mark-Houwink equation

$$[\eta] = KM_n^\alpha$$

where  $K$  and  $\alpha$  are constants characteristic of the polymer solvent system at a given temperature and  $M_n$  represents the number-average molar mass. A decrease in  $\eta$  therefore represents a reduction in the size of the polymer molecule.

### Measurement of the Intrinsic Viscosity of the Fibrous Polymer Procedure

1 g of fiber was dissolved at 90°C in 100 mL of a solvent mixture comprising (phenol: 1,1',2,2'-tetrachloroethane) (10:90 by weight). 15 min was allowed for the dissolution.

The dissolved sample was centrifuged at 3,000 rpm for 30 min to remove the  $\text{TiO}_2$ . Final clearing of the solution was then achieved by filtering the supernatant liquid through an FGLP 0.2  $\mu\text{m}$  Floropore filter (Millipore Corporation, Bedford, MA). The flow time of the liquid was then measured in a Sofica viscometric automatic viscometer. This involves the use of an Ubbelohde viscometer and a timing device recording with an accuracy of 0.001 s. The temperature was maintained constant at 25°C  $\pm$  0.01°C by water circulation.

The specific viscosity ( $\eta_{\text{sp}}$ ) is given by

$$\eta_{\text{sp}} = \frac{t - t_0}{t_0}$$

where  $t$  = flow time of the solution of concentration  $C$  and  $t_0$  = flow time of the solvent.

$\eta_{\text{sp}}/C$  is plotted against concentration and extrapolated to zero concentration to obtain the intrinsic viscosity  $[\eta]$ .

Measurements were made using fiber before and after heat-setting at different temperatures as well as after immersion in blank dyebaths.

### Hydrolysis of the Fiber

2 L of distilled water were made acidic by the addition of acetic acid (pH 4.5–4.8). About 100 g of fiber were added and refluxing was allowed to take place for times of up to 72 h, the duration of the hydrolysis depending on the subsequent operations. Thus for intrinsic viscosity measurements the effect of a range of hydrolysis times was examined, but for examination of the material extracted from the fiber during hydrolysis times of up to 72 h were used.

Although some fiber still remained towards the end of the long refluxing periods, the liquor took on a cloudy appearance and the residual fiber which settled out on cooling was collected by filtering through a weighed No. 3 sintered glass crucible, which was then dried and reweighed.

After concentration of the filtrate to 200 mL by evaporation, a precipitate was obtained when the liquor was left overnight in a refrigerator. The precipitate was filtered off and dried overnight in a vacuum oven at 90°C. The various fractions were then subjected to analysis.

## CHEMICAL ANALYSES

### Elemental Analysis

#### *Sulphur*<sup>9</sup>

A sample of fiber (20–30 mg) was burned in an oxygen flask and the combustion products collected in 5 mL of 0.1*N* sodium nitrite. The gaseous products were absorbed by sodium nitrite solution in which all SO<sub>2</sub> and SO<sub>3</sub> were converted to sulphate. Absorption took 30–45 min. The solution was then cooled, the pH adjusted to between 4–6.5 with dilute sodium hydroxide, and 30 mL of 1.4 dioxane added.

A potentiometric titration was then carried out with 0.01*M* lead perchlorate [Pb(ClO<sub>4</sub>)<sub>2</sub>] using a lead ion activity electrode together with a double junction reference electrode. The percentage of sulphur present was calculated from the end point.

#### *Sodium and Other Metal Ions*

30–40 mg of fiber was digested in a mixture of 3 mL concentrated sulphuric acid and 0.5 mL HClO<sub>4</sub> to dissolve the fibre in a micro-Kjeldahl apparatus. The solution so formed was cooled and diluted to 100 mL with water. The metal was determined by emission spectroscopy using a flame photometer. An external standard was used for each metal being analyzed. An air acetylene mixture was used as a source of fuel.

## RESULTS AND DISCUSSION

### **The Effect of Refluxing in Water on the Intrinsic Viscosity of Dacron T65 Fibers**

Intrinsic viscosity measurements prove that the hydrolytic degradation which takes place when Dacron T65 is refluxed in a blank dyebath at pH 4.5 becomes significant after only 2 h and thereafter the degradation accelerates with time (Fig. 2).

It is likely that the sulphonate groups are involved in this hydrolysis because the conditions of the experiment are favorable for conversion of the sodium sulphonate groups to the free acid by ion exchange. This is a potentially dangerous situation because the free acid is very strong and could become the cause of an internal acid hydrolysis mechanism. Fortunately, it is easy to prevent this

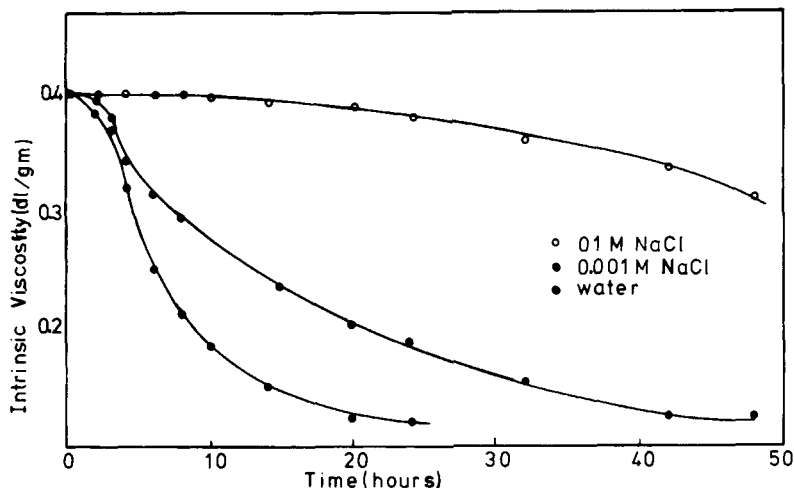


Fig. 2. Effect of electrolyte on the hydrolysis of Dacron T65 at pH 4.5. (O) 0.1M NaCl; (●) 0.001M NaCl; (●) water.

situation from arising by use of the common ion effect, and consequently the importance of the free acid in the degradation can be proved experimentally.

#### The Effect of Sodium Chloride on the Hydrolysis of the Fiber

Relatively small amounts of sodium chloride reduce the hydrolytic damage significantly (Fig. 2) and a concentration of 0.1 mol/L NaCl is sufficient to restrain the degradation for at least 10 h (Fig. 2). The use of electrolyte for inhibiting the hydrolysis of the fiber is an established practice, but the magnitude of the effect is defined in this work for experimental purposes.

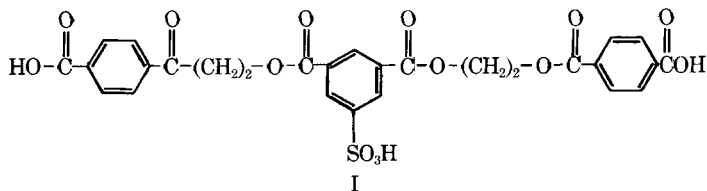
#### The Effect of Heat-Setting Temperature on the Hydrolysis

Similar measurements on fibers heat-set at different temperatures show the stability of the fibers for up to 10 h refluxing in the presence of 0.1M NaCl to be independent of the heat-setting temperature. Even beyond 10 h the effect is only small (Fig. 3).

#### Sulphur Loss on Hydrolysis

Location of the sulphur after hydrolysis is in line with the findings of other workers.<sup>10</sup> The results given in Table I show that a large proportion of the sulphur ends up in the hydrolyzing liquor. Most of the sulphur has therefore been removed from the fiber as a water soluble compound.

Speculation on the basis of the elemental analysis (Table II) suggests that its formula is near to the trimer depicted below rather than that for free 5-sulpho isophthalic acid, but more refined analysis is required for confirmation:



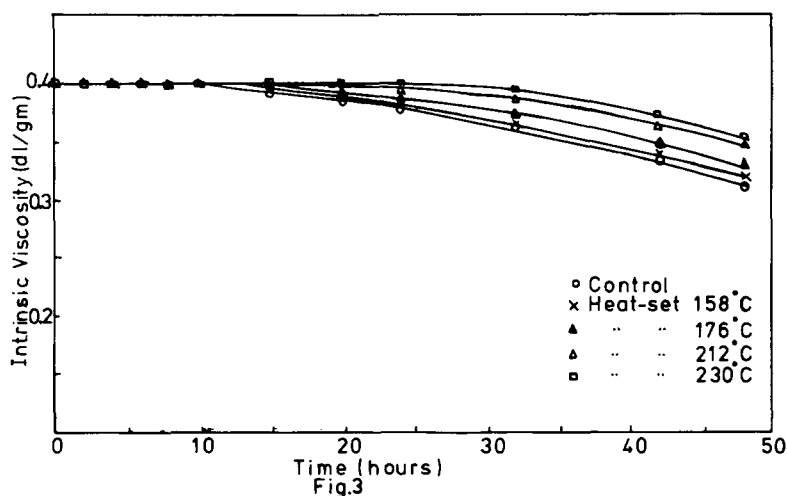


Fig. 3. The rate of hydrolysis of Dacron T65 in 0.1M NaCl. (○) Control; (×) heat-set 158°C; (▲) heat-set 176°C; (△) heat-set 212°C; (◻) heat-set 230°C.

Sodium is included in the theoretical results of Table II, because, although it is originally removed into the hydrolysis liquid, it is retained when the hydrolysis liquor is evaporated.

## CONCLUSIONS

The foregoing discussion shows that the first step in the hydrolysis of Dacron T65 is the exchange of sodium ions for hydrogen. The experimental conditions for preventing the exchange in subsequent experiments are defined precisely,

TABLE I  
Sulphur Analysis on Dacron T65 before and after Hydrolysis for 72 h at pH 4.5 in the Absence of Electrolyte

Material	Fiber, mmol/kg	Total sulphur, %
Starting material	14.4	100.0
Sulphur in the substance dissolved in the hydrolysis liquor	11.88	82.5
Sulphur in the fibrous material remaining intact	1.31	9.1
Sulphur in the precipitate filtered from the hydrolysis liquor before evaporation	1.11	7.7
Total accounted for	14.30	99.3

TABLE II  
Comparison of Experimental Values  
Elemental Analysis with the Theoretical Values for Compound I

	Found experimentally, %	Theoretical for I, %	Theoretical for sodium salt of I, %
S	4.4	5.20	5.01
O	41.8	38.81	37.48
C	46.1	52.44	50.64
H	3.9	3.56	3.28
Na	3.8	—	3.59

and it is safe to conclude that when dyeings are carried out in the presence of electrolyte of at least 0.1M in strength, any observed variations in dyeing properties are due to structural changes in the polymer rather than hydrolysis.

We wish to acknowledge the cooperation of Mr. J. M. Bather of the Chemistry Department, U.M.I.S.T., with the analysis.

### References

1. W. Beckman, *Chemiefasern*, **22**, 436 (1973).
2. H. Beutler, *Melliand Textilber.*, **51**, 1189 (1970).
3. D. H. Abrahams, *Am. Dyestuff Rep.*, **59**, 36 (1970).
4. H. Grobe, D. Nissen, and V. Rossbach, *Makromol. Chem.*, **176**, 2839-52 (1975).
5. V. Rossbach, H. Muller, and D. Nissen, *Textil Veredlung*, **9**, 339-43 (1974).
6. I. Ruzicka, J. Prikryl, L. Burget, and R. Avramova, *Faserforsch. Textil Tech.*, **29**(4), 281-5 (1978).
7. Z. Gur-Arieh, W. Ingamells, and R. H. Peters, *J. Soc. Dyers Col.*, **92**, 332 (1976).
8. W. Ingamells and H. Sherkat, *J. Soc. Dyers Col.*, **93**, 306 (1977).
9. W. Selig, *Mikrochem. Acta (Weiss)*, Suppl. 4, 168-75 (1970).
10. L. Burget, J. Prikryl, and I. Ruzicka, *Faserforsch Textil Tech.*, **29**(6), 426-30 (1978).

Received January 13, 1981

Accepted April 22, 1981