DIRECT FLUORINATION OF POLYESTER AND RELATED COMPOUNDS

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SUMMARY

Polyethylene terephthalate and model compounds representing various
aspects of polyethylene terephthalate have been treated with elemental
fluorine. Polyester was found to react in a manner more resembling
ethylene glycol dibenzoate than diethyl terephthalate or terephthalic
acid. The degree of fluorine incorporation increases as the aliphatic
character of the substrate is increased. The reaction was studied
using fluorine incorporation, ir, ESCA and esr techniques.

INTRODUCTION

The reaction of elemental fluorine with a variety of compounds has
been extensively reported in the literature. However, the reaction
between fluorine and polyethylene terephthalate, commonly called poly-
ester, has not been reported.

Rudge [1] was one of the earliest workers to report the reaction
between elemental fluorine and a polymer. Since that time, several workers
have shown that there are many positive results that can be obtained when
a polymer is fluorinated with elemental fluorine. Schonhorn and coworkers
[2,3] have shown that fluorination of polyethylene increases the adhesive
joint between polyethylene and an aluminum plate. Even though this increase
in adhesion was not attributed to increased wettability of the polyethylene
surface, there has been recent evidence that direct fluorination of poly-
ethylene can in fact increase the wettability of the surface under certain
conditions [4].

Polyethylene has also been shown to have improved barrier property
after fluorination [5,6]. Fluorination of polypropylene fibers has been

shown to improve the dye acceptance of the fiber towards basic dyes [7].

The fluorination of polyethylene terephthalate and related compounds with elemental fluorine was studied to provide an insight into the reaction pathways. In addition the effect of fluorination on specific physical properties, e.g., wetting properties, soil release, etc. was also determined.

EXPERIMENTAL

Polyester fabric was fluorinated in a monel reactor by first purging the reactor several times with nitrogen and then filling the reactor with a fluorine/nitrogen gas blend varying in fluorine concentration between 1% and 10% for one to fifteen minutes reaction time at ambient temperature [8].

In order to study percent fluorine incorporation versus structure of the substrate, polyester material was ground to 20 mesh using a Wiley Mill. The organic monomers were ground in a mortar and pestle and used without further purification. The substrates were placed in copper boats and then placed in a monel reactor. The reactor was purged several times with nitrogen and then filled with various fluorine/nitrogen blends at 100 cc/minute. The reaction time was taken from the time the reactor reached atmospheric pressure to the time the reactor was evacuated. The samples were either sent for fluorine analysis, washed with water, or the basic and neutral products were separated from the acidic products using standard procedures. These fractions were then analyzed by ir and vpc/mass spectrometry. The fabric was also sent for ESCA analysis [9].

Mylar® film was placed in a gas infrared cell and purged with nitrogen for several minutes. A fluorine/nitrogen blend was then admitted and ir scans were taken periodically. In some cases an untreated film was placed in the reference cell. At the conclusion of the reaction, the film was analyzed by attenuated total reflectance using a universal ATR reflectant accessory, KRS-5 crystal.

Finally, the substrates were fluorinated in an esr cavity. Polyester material was ground to 40 mesh using a Wiley Mill, washed thoroughly with trichloroethylene, and dried under a vacuum at 100°C. The organic monomers were ground with a mortar and pestle and used without further purification. The esr cell was evacuated and purged with nitrogen several times. The cell was evacuated and the fluorine/nitrogen blend was admitted to allow various

pressures between -28 inches and 0 psig to be obtained. In some cases the cell was evacuated prior to raising the pressure. The gas blend was allowed to flow through the reactor for various times. For polyester, the sample was evacuated at the end of the reaction and acrylonitrile vapors were admitted. In all cases the fluorinated samples were exposed to air to determine if there were any oxygen radicals present in the samples.

The esr instrument was a Varian 4500 ESR spectrometer equipped with an X-band and 100 Kc field modulation and employing a cylindrical cavity. The standard reference used was diphenylpicrylhydrazyl radical (dpph, g = 2.0036). The instrument was operated at 3250 gauss with a sweep width of either 250 or 500 gauss at a sweep speed of 2 inches/minute and 50 gauss/inch [10].

RESULTS AND DISCUSSION

The physical properties imparted to the polyester fabric is the subject of a separate paper [8]. In general the fabric has better soil release, soil antideposition, and wetting properties than the nonfluorinated fabric. It is known that fluorochemical treatments which have both stain repellent and soil release properties are obtained by the addition of hydrophilic segments to the fluorochemical segment [11].

Zisman and coworkers [12,13] have shown that the wettability of partially fluorinated acids show better wetting toward hydrophilic solvents than the unfluorinated acids. The perfluorinated acids exhibits poorer wetting. Thus it is evident that the extent of fluorination is important to wetting property in addition to the location and structure of the fluorinated groups.

When the wetting property of the polyester fabric was measured versus the extent of fluorination, it was found that the degree of wetting goes through a maximum. This is in agreement with Zisman's work when it is known that carboxylation accompanies fluorination of polyester [8].

In order to determine how the reaction between fluorine and polyester was giving a stable hydrophilic, oleophobic fabric, polyester, terephthalic acid, diethyl terephthalate, and the dibenzoate of ethylene glycol were fluorinated under a variety of reaction conditions and analyzed by several techniques that would allow for the determination of the reaction mechanism for the fluorination of polyester.
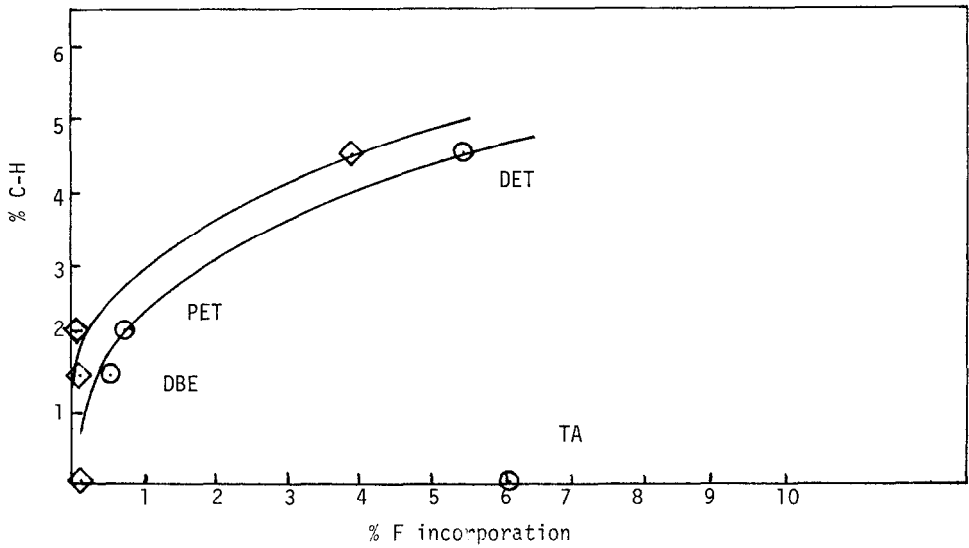
Figure 1. Fluorine incorporation versus compound structure:
○ - before wash analysis; ◇ - after wash analysis; DET = diethyl
terephthalate; PET = polyester; DBE = dibenzoate of ethylene glycol;
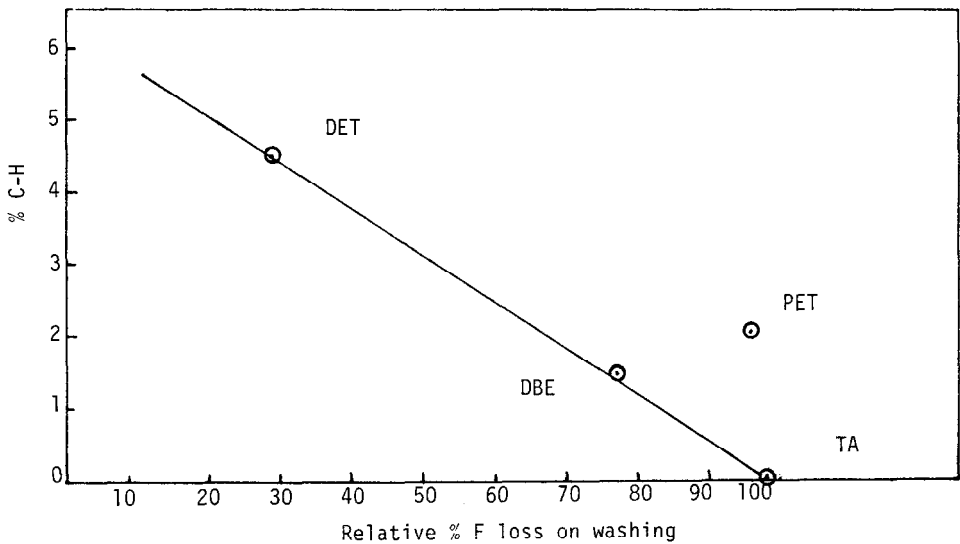TA = terephthalic acid

Figure 2. Fluorine wash stability versus compound structure: DET = diethyl
terephthalate; PET = polyester; DBE = dibenzoate of ethylene glycol; TA =
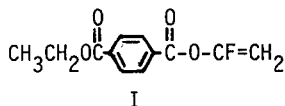terephthalic acid

These substrates were fluorinated under identical reaction conditions in a copper boat. The products were sent for fluorine analyses directly from the reactor and also after washing.
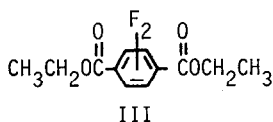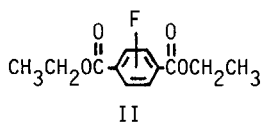
It was found that the percent fluorine incorporated increased as the aliphatic CH bonds in the molecule increased, Figure 1. Also the percent fluorine lost on washing decreases as the percent CH bonds in the molecule increases, Figure 2. It is interesting to note that both polyester and the dibenzoate of ethylene glycol show similar results of fluorine incorporation both before and after washing.

When the products of the fluorination were examined, it was found that the dibenzoate of ethylene glycol is much more resistant to fluorination than diethyl terephthalate. After either a twenty minute or one hour reaction with 50% fluorine, the ethylene glycol ester contained only 0.5% fluorine. The only product identified was the starting material. If the reaction is carried out with 100% fluorine, then in addition to starting material, benzoic acid is obtained in small amounts.
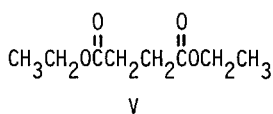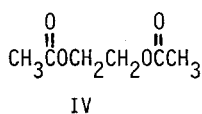
The reason for the inertness of the ethylene glycol ester to 100% fluorine may result from the experimental technique used. The reactor was filled with nitrogen when 100% fluorine was admitted. Therefore, the exact fluorine concentration at any specific time is impossible to know. However, the same experimental technique was used for all samples. In fact, in almost all cases all four substrates were fluorinated in the same reaction. Thus, they should have experienced the same reaction conditions and thus the correlations found are considered accurate.

On the other hand, diethyl terephthalate reacts with 50% fluorine in one hour to give 28% starting material, 6% monoethyl terephthalate (m/e 256, 211, 194, 193, 163, 63, and 45), and trace quantities of I (m/e 238, 177, 149, 121, and 29), II (m/e 240, 196, 195, 168, 167, 122, and 94), and III (m/e 258, 231, 213, 202, 185, 158, 141, and 113). If the reaction was run for only twenty minutes, an excess of 75% of the starting material was recovered. Structures I, II, and III are based on mass spectra data and are not isolated products.

$$CH_3CH_2O\overset{O}{\overset{\|}{C}}\!\!-\!\!\overset{}{\underset{}{\bigcirc}}\!\!-\!\!\overset{O}{\overset{\|}{C}}\!\!-\!O\!-\!CF\!=\!CH_2$$

I

$$CH_3CH_2O\overset{O}{\underset{\|}{C}}-\overset{F}{\underset{|}{\underset{}{\bigcirc}}}-\overset{O}{\underset{\|}{C}}OCH_2CH_3$$

II

$$CH_3CH_2O\overset{O}{\underset{\|}{C}}-\overset{F_2}{\underset{|}{\underset{}{\bigcirc}}}-\overset{O}{\underset{\|}{C}}OCH_2CH_3$$

III

It was hoped that the fluorination of these model compounds would give some insight into the mode of fluorination of polyester. The only information that indicates the mode of fluorination for polyester is in the fluorine incorporation data. If aromatic substitution was predominant, then it would seem that all four substrates would show similar fluorine incorporation data and especially in the % F lost on washing. Since terephthalic acid loses essentially all of the before wash fluorine, aromatic fluorination must occur as the minor reaction and aliphatic fluorination occurring as the major reaction. In addition due to the relative reactivities of diethyl terephthalate and the dibenzoate of ethylene glycol, the position of the aliphatic bonds between two ester linkages must be stabilized by these functions. It is not known what effect the aromatic ring has on the stability relative to the carbonyl linkage. That is would an aliphatic ester of the type IV be more stable than V since ethylene glycol dibenzoate is more stable than diethyl-terephthalate?

$$CH_3\overset{O}{\underset{\|}{C}}OCH_2CH_2O\overset{O}{\underset{\|}{C}}CH_3 \qquad\qquad CH_3CH_2O\overset{O}{\underset{\|}{C}}CH_2CH_2\overset{O}{\underset{\|}{C}}OCH_2CH_3$$

IV   V

The polyester fabric was sent for ESCA analysis. Figure 3 shows the spectra for both the control and the fluorinated fabric. The fluorine is located at 687.5 eV with a count of 5500. The rest of the spectra is identical to the control fabric. For comparison, Teflon® exposed under the same conditions as the fabric showed a count of 150,000. Since the fluorine line is one broad peak, the type of fluorine bond cannot be assigned. Fluorine in organic C-F compounds is usually around 689 eV.
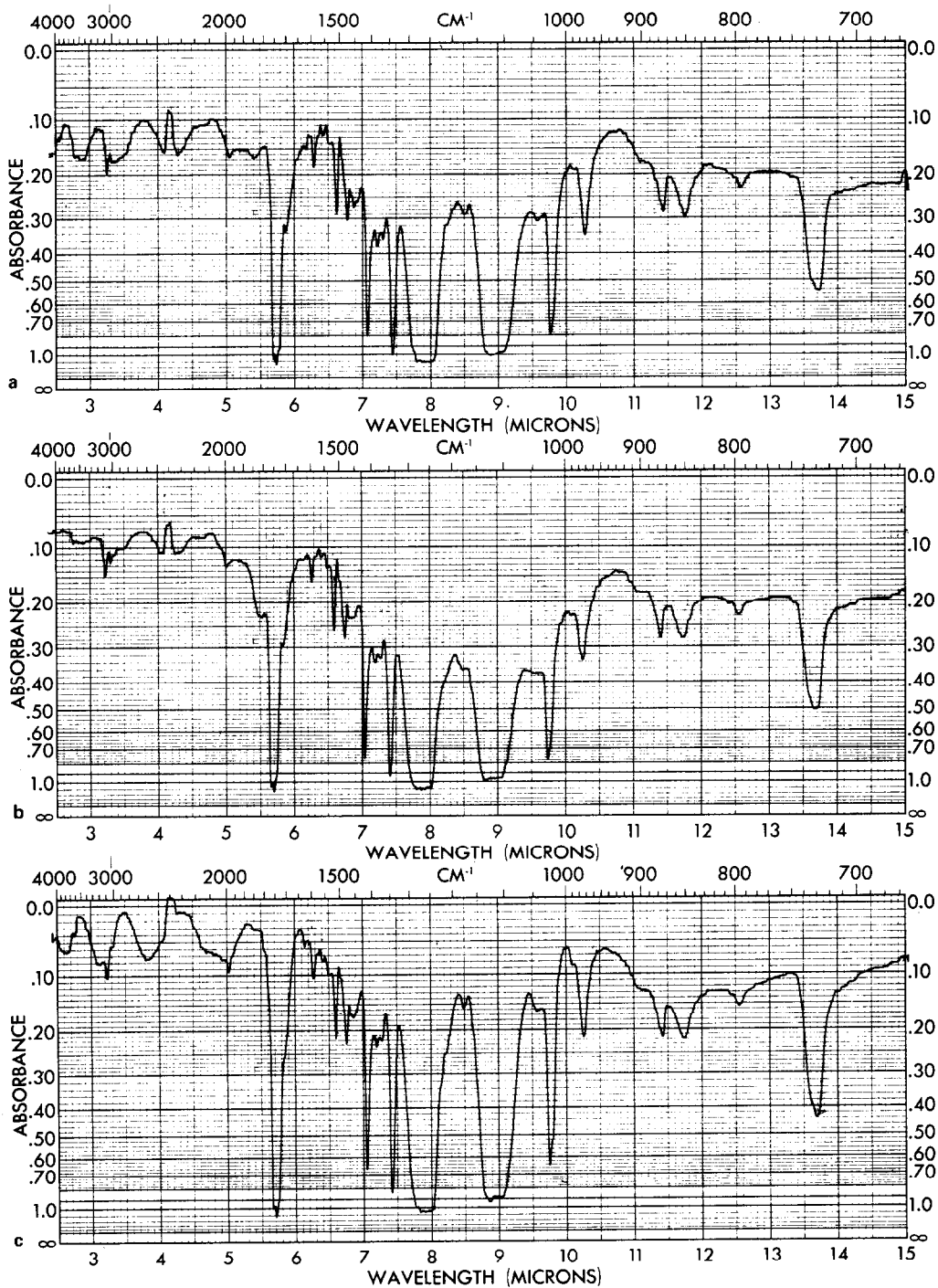
Figure 4. Infrared spectra of fluorinated polyester film. a) control; b) treated; water washed; c) treated; base washed.
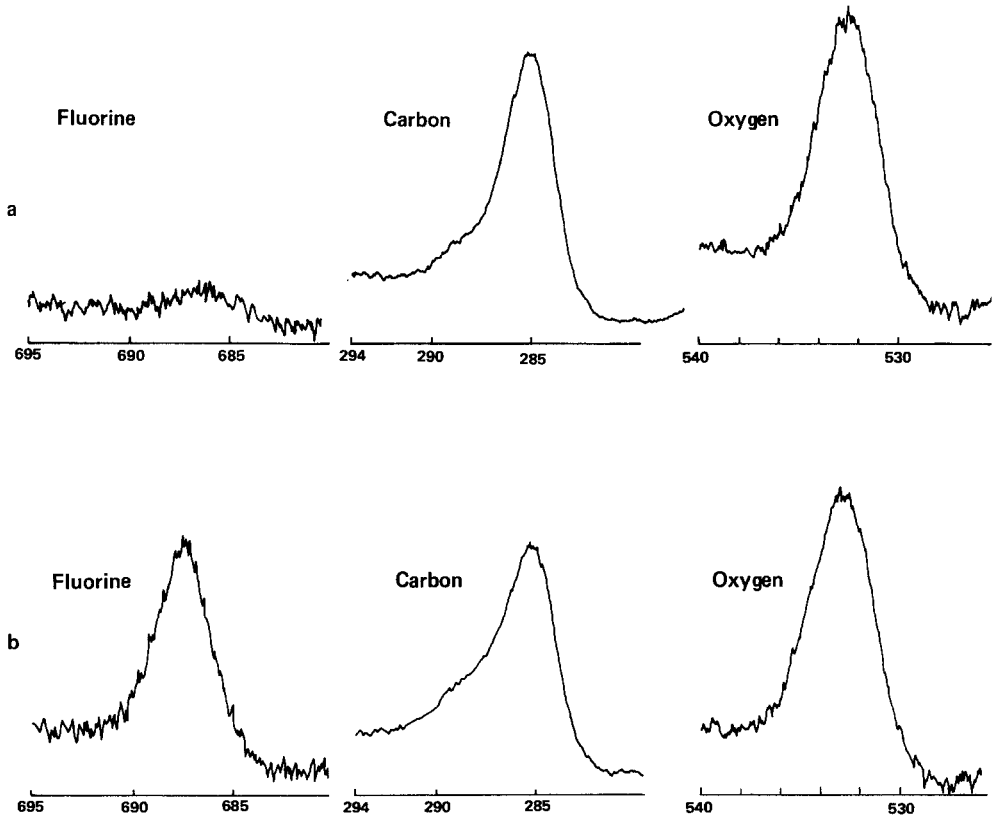
Figure 3. ESCA spectra of polyester. a) control; b) fluorinated.

The second approach used to study the mode of fluorination of poly-ester was by infrared. When a polyester film was mounted in a infrared gas cell and fluorinated, the ir spectrum shows a band forms during fluorination at about 5.6 μ . This absorption is not removed when the film is washed with water. However, it is removed by basic washing, Figure 4. If the fluorinated film is analyzed by attenuated total reflec-tance (ATR) without being washed, not only is the adsorption at 5.6 μ pre-sent, but the adsorptions at 6.78 and 7.3 μ that are present in the con-trol are reduced, Figure 5. These data along with the absence of addi-tional bonds between 11 and 18 μ indicate that minor amounts of aroma-tic fluorination occurs relative to aliphatic fluorination.
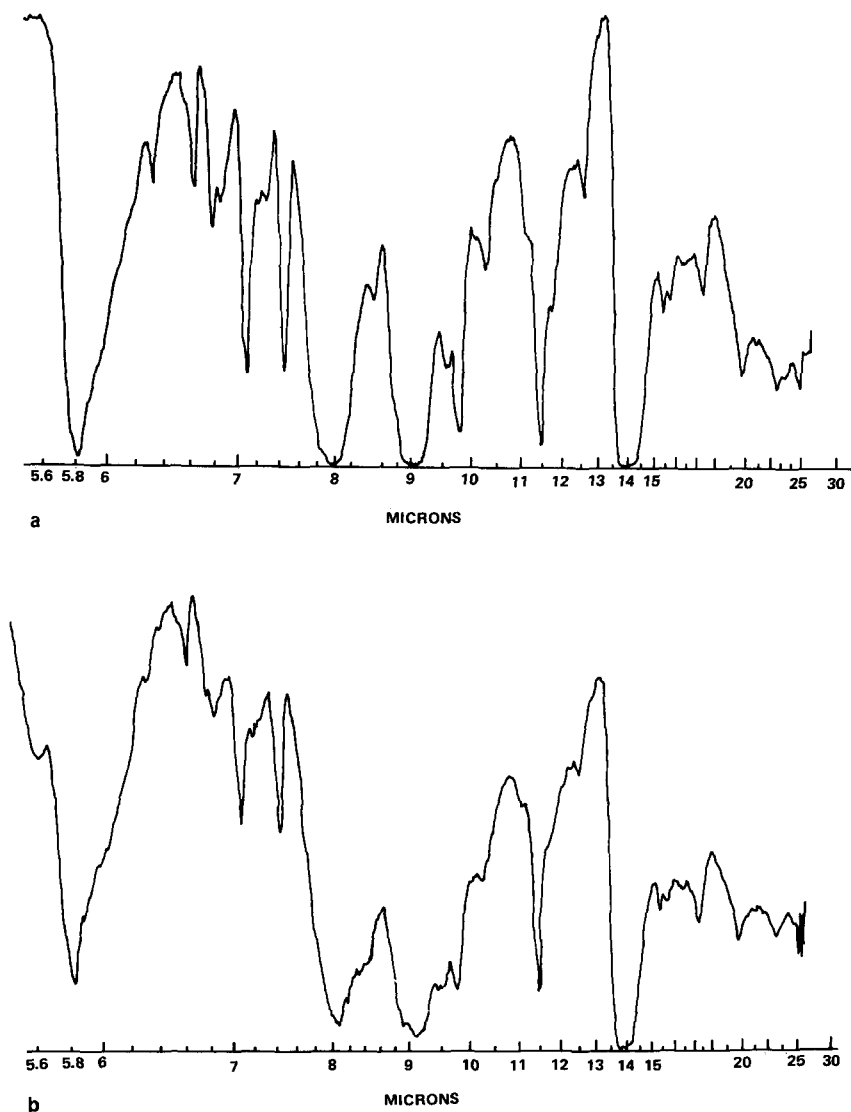
Figure 5. ATR spectrum of fluorinated polyester film. a) control; b) treated.

Since the new carbonyl bond at 5.6 μ is stable to water, the structure cannot be an acid fluoride. Fluorine substitution on the aromatic ring causes little if any shift in the carbonyl absorption. However, saturation of the aromatic ring would cause the carbonyl band to shift to higher wave numbers. Also, the formation of acid groups would cause
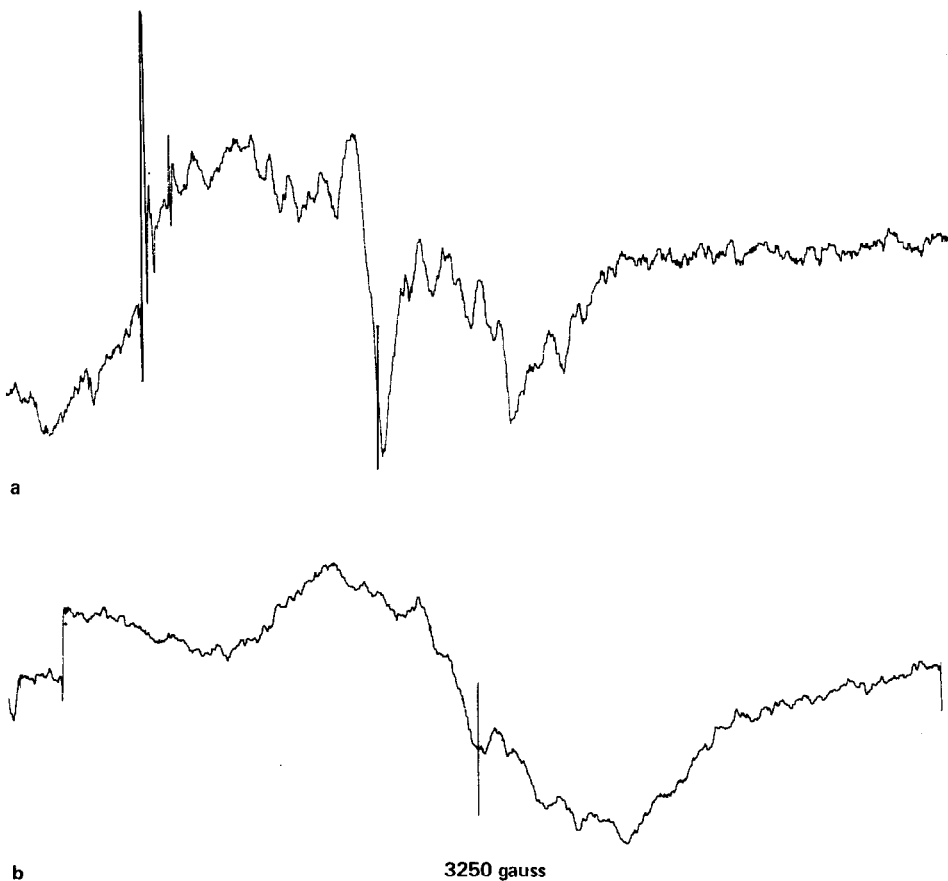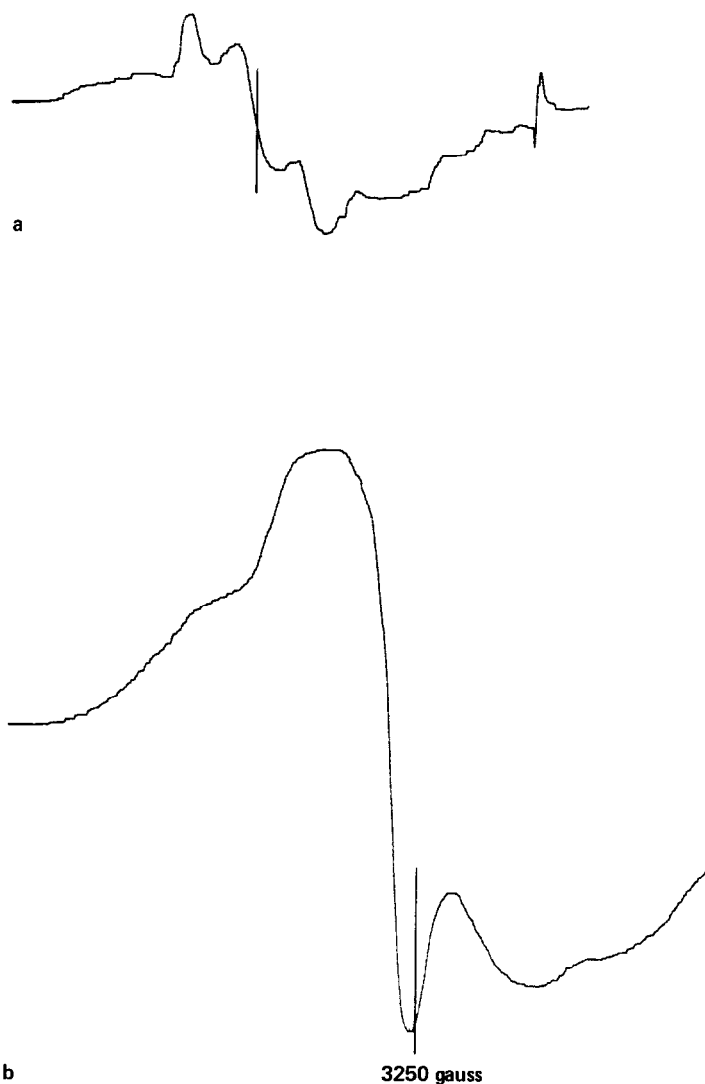
Figure 6. ESR of mildely fluorinated terephthalic acid and polyester. a) terephthalic acid; b) polyester.

the observed shifts in absorption. It is not believed that ring satura-
tion occurs, thus the data again points toward aliphatic fluorination
over aromatic fluorination.

Since the above reactions of polyester and related structures did not
provide for unambiguous results to base whether fluorination of polyester
is selective, it was decided to follow the reaction by esr.

The spectra at mild reaction conditions are all different, Figures 6
and 7. The spectra are also too complicated to obtain coupling constants
and thus the nature of the radical species cannot be identified. When the

a

b   3250 gauss

Figure 7. ESR of mildly fluorinated diethy terephthalate and dibenzoate of ethylene glycol.
a) diethyl terephthalate; b) ethylene glycol dibenzoate.

reaction is continued for a longer period, all the spectra begin to resemble
each other, Figures 8 and 9. These latter spectra are a combination of
carbon radicals and oxygen radicals. For instance, the spectra of poly-
ester is almost identical to the esr spectra obtained when the sample
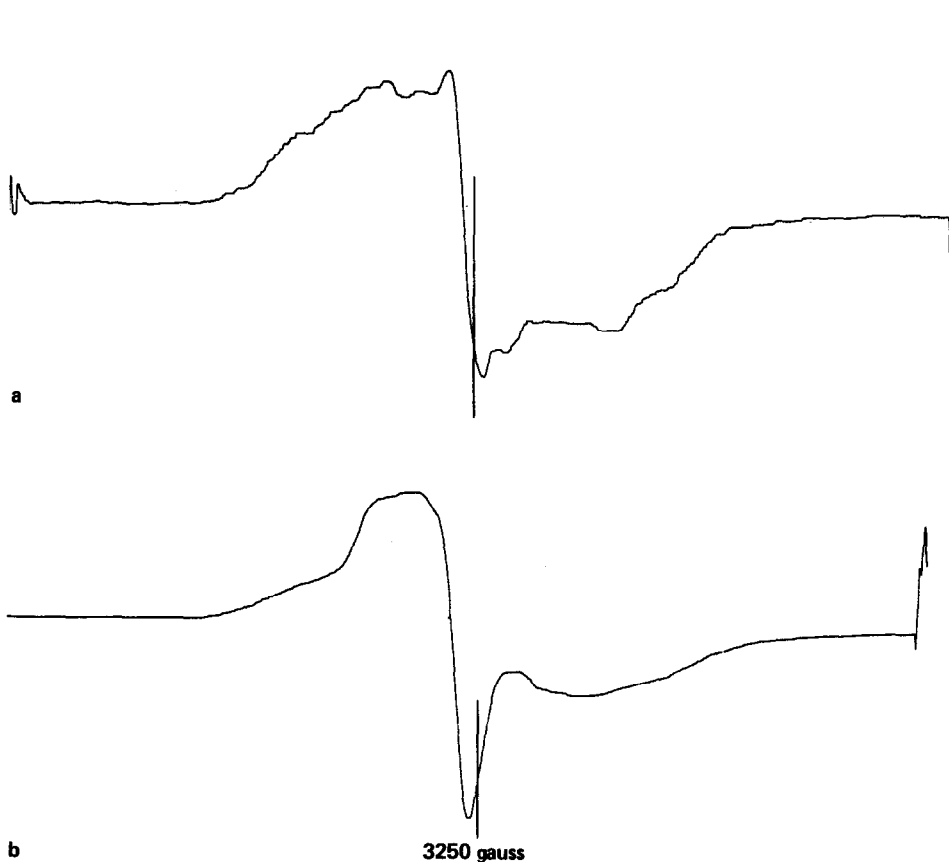
Figure 8. ESR of heavily fluorinated terephthalic acid and polyester. a) terephthalic acid; b) polyester.

was exposed to air, Figure 10. It is known that fluorine and hydrogen fluoride will react with quartz to generate oxygen. When these spectra are compared to published esr spectra of fluorinated polymer radicals, it can be seen that the oxygen radical is interfering in all cases, Figure 11.

Since acrylonitrile undergoes free radical polymerization readily, the fluorinated polyester was exposed to acrylonitrile vapors to determine if the free radicals present were available for grafting.

When the fluorinated polyester was exposed to acrylonitrile vapors, the oxygen radicals reacted first, followed by slow reaction of the carbon
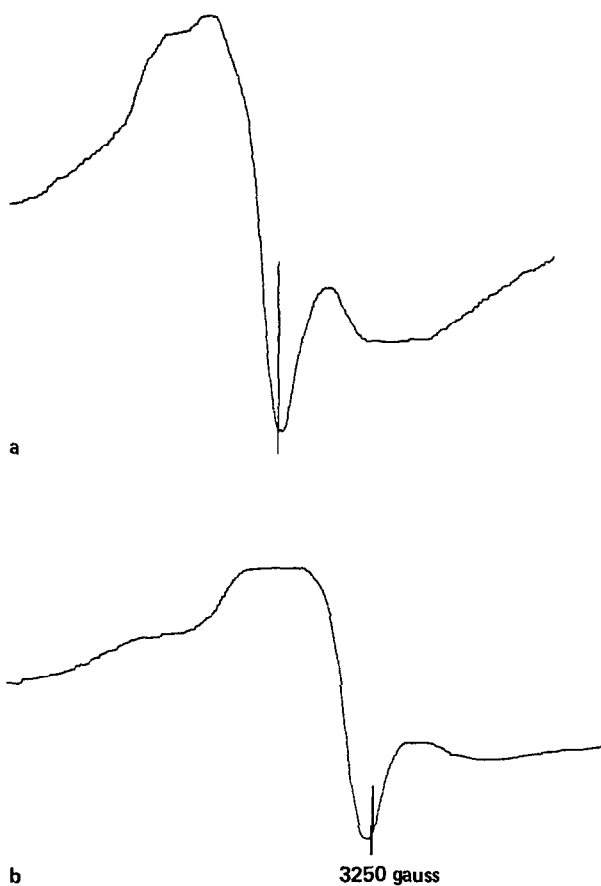
Figure 9. ESR of heavily fluorinated diethyl terephthelate and dibenzoate of ethylene glycol.
a) diethyl terephthalate; b) ethylene glycol dibenzoate.

radicals, Figure 12. Since analysis of the sample for nitrogen showed no nitrogen incorporation, the mode of termination may not be through poly-merization with acrylonitrile. It is possible, however, that not enough grafting occurred to give sufficient nitrogen incorporation to be detected by CHN analysis.

Any one of the above experiments independently gives little insight into the mechanism of direct fluorination of polyester. However, together it is believed it has been shown how polyester fabric can be converted
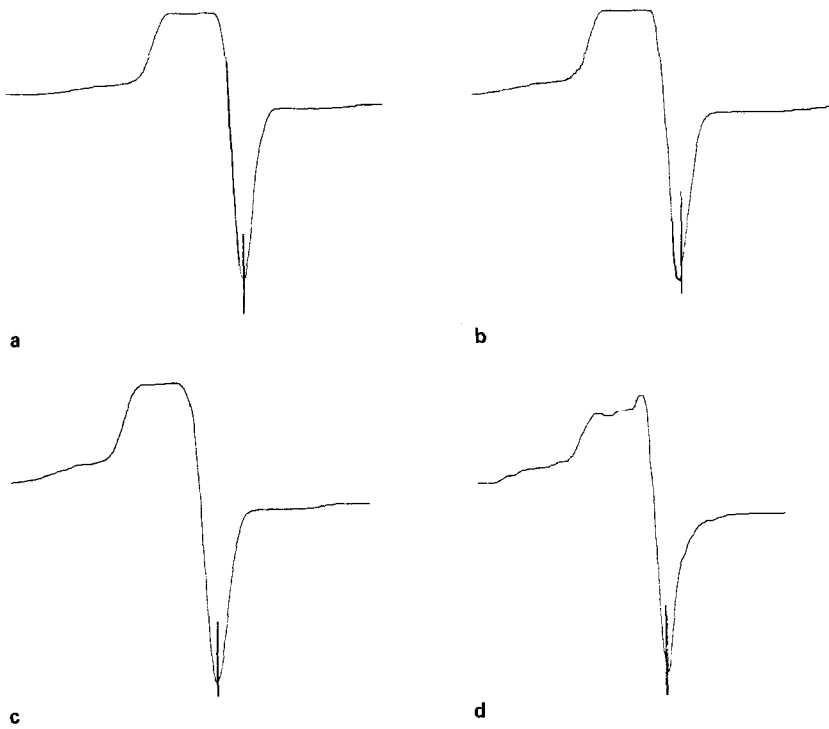
Figure 10. ESR of fluorinated compounds exposed to air. a) diethyl terephthalate; b) polyester; c) ethylene glycol dibenzoate; d) terephthalic acid.
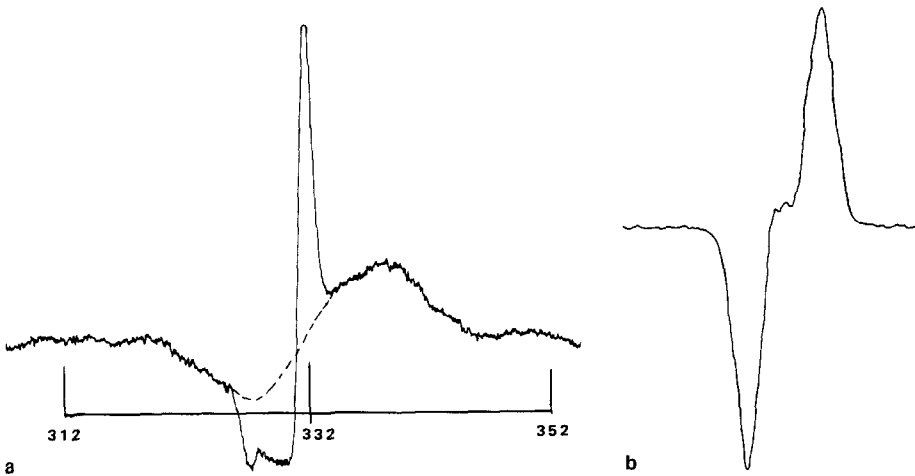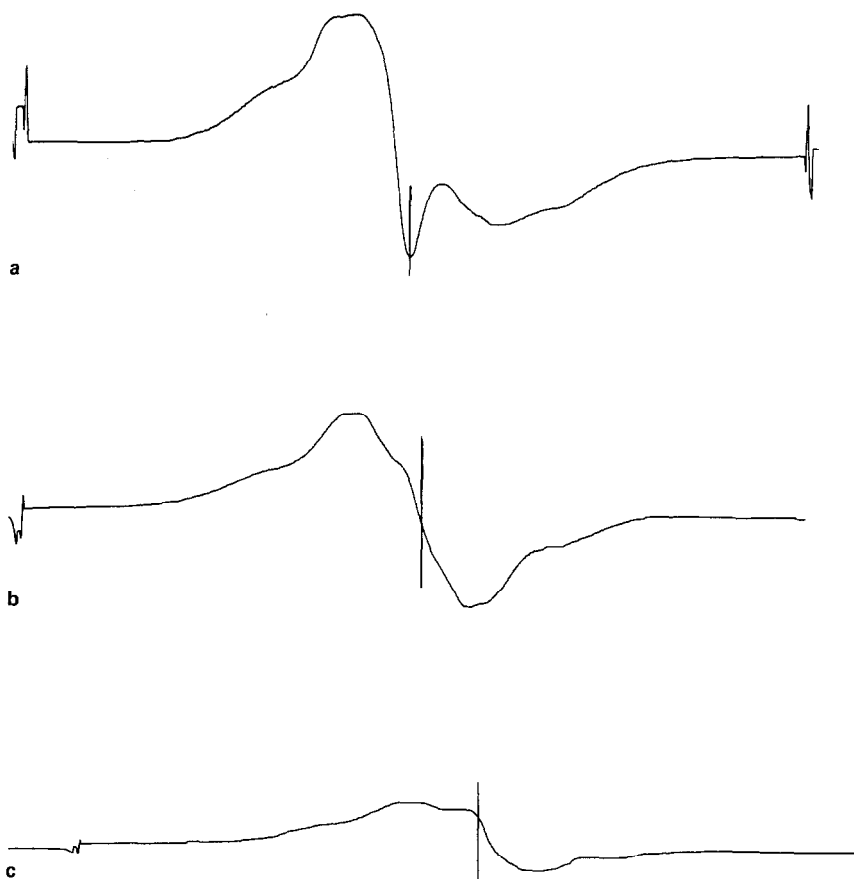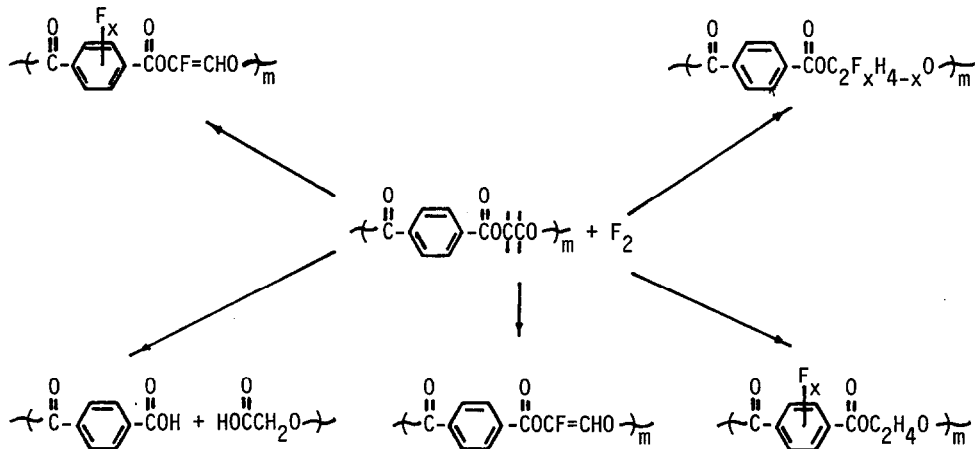

Figure 11. ESR of fluorinated polymers a) polyethylene; values in millitesla (see Reference 14); b) polyperfluorobutadiene (see reference 15).

Figure 12. ESR of fluorinated polyester exposed to acrylonitrile. All spectra were run at the same attenuation. a) fluorinated PET; b) acrylonitrile vapors added; c) b sat for 10 minutes.

from a hydrophobic, oleophilic material to a hydrophilic, oleophobic material. Polyester fabric when treated with fluorine, undergoes fluorination at both the ring position and the ethylene glycol position. The preferred attack is at the ethylene glycol position. Attack at the methylene position causes several reactions to occur. The fluorine can incorporate as stable fluorine, it can be eliminated as HF, or it can cause the molecule to cleave to form an acid molecule either directly or as a hydrolysis product, Scheme 1.

SCHEME 1

$$+C-\langle\rangle-COCF=CHO+_m \qquad +C-\langle\rangle-COC_2F_xH_{4-x}O+_m$$

$$+C-\langle\rangle-COCCO+_m + F_2$$

$$+C-\langle\rangle-COH + HOCCH_2O+ \qquad +C-\langle\rangle-COCF=CHO+_m \qquad +C-\langle\rangle-COC_2H_4O+_m$$

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