

Properties of Oligomers Present in Poly(ethylene Terephthalate)

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Synopsis

Heat treatment of polyester yarns induces the selective crystallization of the cyclic trimer [(GT)₃] in the form of polygonal solids on the fiber surfaces. At the temperature studied, namely, 200°C, the diffusion rate of (GT)₃ appears to be very rapid. Small quantities of the cyclic tetramer were also found. The total extractable oligomer content of the samples is reduced considerably after annealing at 200°C, mainly due to solid phase polymerization. Exposure to methylene chloride vapor also causes cyclic oligomers to diffuse to the fiber surface. The migration of (GT)₃ is again very rapid. Larger cyclics also diffuse to the surface in appreciable quantities. Solvent exposed samples, unlike annealed ones, exhibit irregular crystal shapes and sizes on their surfaces. The moisture regain of the extracted oligomers is less than that of the polyester. It is suggested that this is due to the oligomers being in a crystalline form.

INTRODUCTION

Commercial poly(ethylene terephthalate) (PET) contains small amounts of cyclic oligomers which can affect deleteriously various textile processes.¹ Consequently, a considerable amount of research has been performed on the oligomers, especially the cyclic trimer, cyclo-tris-ethylene-glycol terephthalate [(GT)₃] since it is present normally in greater amounts than any other oligomer in PET. However, the interrelations between the oligomers and PET do not appear to have been fully explored.

Goodman and Nesbitt² have described three different mechanisms of oligomer formation during polymerization: (1) cyclization of short chain oligomers; (2) "back-biting" or cyclodepolymerization from chain ends; and (3) exchange-elimination reactions occurring randomly within or between polymer chain ester groups. They suggested the third mechanism was the most plausible of the three. However, Peebles et al.³ have shown that the rate of oligomer formation depends on the concentration of the hydroxyl end groups present in the polymer and hence indicated that cyclic oligomers are formed primarily by cyclodepolymerization. The same conclusion was drawn by Ha and Choun⁴ from their work on the kinetics of oligomer formation.

Several methods have been developed to determine the oligomer content of polyester. Isolation procedures can be classified into two groups. First, those involving extraction, usually by soxhlet, with such solvents as chloroform,^{5,6}

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dioxane,^{2,6} xylene,^{3,6} and methylene chloride.⁷ Secondly, those involving dissolution followed by precipitation, in solvents like trifluoroacetic acid,⁶ 1-methylnaphthalene,⁸ and dimethylformamide.⁴ The amount of oligomer obtained is dependent largely upon the method used as well as the type, drawing, and thermal history of the PET. Dissolution methods are the more efficient as illustrated in the studies of both Cooper and Semlyen⁸ and Luttringer et al.¹ However, both groups report that extraction removes practically all (GT)₃, and it is the larger-ring cyclics which are removed incompletely.

Various methods for separation of cyclic oligomers have been developed also. Earlier workers used solvent separation on the basis of differences of solubility and gravimetric analysis. More recently, highly efficient methods utilizing thin-layer chromatography (TLC),^{3,4,6,7,9} gel-permeation chromatography (GPC),^{5,8} high-performance liquid chromatography (HPLC),^{1,6} and spectroscopic techniques,¹ have been employed. Many different solvent systems have been found for separation of individual oligomers.

During dyeing, the predominant (GT)₃ migrates to fiber surfaces and crystallizes, thus resulting in uneven dyeing. White crystalline deposits appear on packages.¹⁰⁻¹⁷ Crystallization of cyclic oligomers on polymer surfaces can also be induced by heat treatments¹⁸⁻²⁰ or by exposure to solvent vapors, and may change significantly the electrical properties of PET films.¹⁸ Heat treatment of polyester films at temperatures up to 200°C resulted in the formation of hexagonal crystals on their surfaces, whereas cylindrically shaped crystals were formed upon exposure of the films to methylene chloride vapor.^{18,19} Solvents such as perchloroethylene,¹ dioxane,^{1,9} and methylene chloride/isopropanol mixtures⁹ have been found effective for extraction of surface oligomers. Luttringer et al. found that perchloroethylene extractions carried out below 70–80°C for up to 9 h are particularly suitable for the isolation of surface oligomers.¹ They also determined that (GT)₃ is the major oligomer present on the PET surface.

The objective of this study was to study the diffusivity, morphology, thermal properties, and moisture regain of PET oligomers and to relate such properties to those of the polymer itself.

EXPERIMENTAL

Materials

Polyester chips (PM7741) were supplied by Eastman Kodak. The intrinsic viscosity of the polymer was stated to be about 0.60, and it contained neither optical brighteners nor toners and had a very low level of TiO₂.²¹ Bright Dacron yarn type 55 (TiO₂ content about 0.1%) and semidull type 56 (TiO₂ content about 0.3%) were obtained from E. I. DuPont de Nemours. In each case, the yarn denier was 70 and it contained 34 filaments. Dioxane, perchloroethylene, and hexane were HPLC grade. Other solvents were reagent grade.

Procedures

Oligomer Extraction from Polyester Chips. Chloroform was chosen for a large scale extraction of polyester chips which were first ground in a Tekmar Model A-20 Universal Mill. The finely powdered polymer (150 g) was soxhlet-

extracted for 24 h with 500 mL of chloroform. After filtration, oligomers were obtained by flash evaporation of the solvent.

Oligomer Content of Polyester Yarns. To determine the surface oligomer content of untreated and treated yarns, samples (0.5 g) were Soxhlet-extracted for 12 h with perchloroethylene. The solvent was then removed using a rotary evaporator. The extract was taken up with chloroform and diluted to a known volume (usually 25 mL) before HPLC injections. Chloroform was used to determine either the total extractable oligomer content of the PET yarn or the residual extractable oligomer content after perchloroethylene extraction. Otherwise, the procedure was similar to that just described.

Treatment of Polyester Yarn. Heat treatment of PET yarns was carried out in an air oven at either 200 or 240°C for specified periods of time. Other samples were exposed to methylene chloride vapor at 21°C in a desiccator saturated with solvent vapor.

Analyses. HPLC analysis of oligomer extracts was carried out with a Perkin-Elmer Series 10 Liquid Chromatograph. Separation procedures were essentially similar to those described by East and Girshab.²² A Lichrosorb Si60, 5 μ (250 \times 4.6 mm) normal phase column was used with hexane/dioxane (60/40 v/v) as the mobile phase at 1 mL/min flow rate. Detection was by UV at 254 nm (Perkin-Elmer LC-15 UV spectrometer). Pure (GT)₃ was used for calibration. A linear relation was obtained between peak area versus amount injected (or % concn). Chromatographic data was collected and analyzed with a Perkin-Elmer 3600 Data Station using Chromatographics 2 (Part C; Rev. 2) software.

Differential thermal analysis (DTA) traces were taken on a Mettler TA2000M Thermal Analysis system using 3 mg samples in a nitrogen atmosphere at a heating rate of 10°C/min. Scanning electron microscope (SEM) procedures have been described previously.²³ Adsorption moisture regains were obtained at 59% RH and 21°C using a desiccator/weighing bottle procedure.²⁴ Densities of samples were determined by using a density gradient column.²⁵

RESULTS AND DISCUSSION

Oligomer Content

The chloroform extract from PM 7741 polyester powder was 1.48% on weight of the polymer (owp). Up to 20 components were detected by HPLC separation of the mixture (Figs. 1 and 2). The most predominant peak (no. 3) is identified as (GT)₃ from calibration runs using pure (GT)₃. Peak nos. 2–9 are assigned as cyclic dimer (GT)₂, trimer, tetramer (GT)₄, pentamer (GT)₅, etc. The plot of log (retention time) against ring size for these peaks is linear (Fig. 3), which should be the case for a homologous series of cyclics under the separation conditions used. Assuming all the cyclic species have the same detector response per unit weight, the total cyclic oligomer contents of the three different PET samples used in this study are presented in Table I. The values are close to those reported in the literature for similar extractions. No attempt was made to identify the peaks other than those assigned for the cyclics. However, as reported by Hudgins et al.,⁶ the other peaks probably correspond to cyclic species containing diethylene glycol residues as well as linear oligomers.

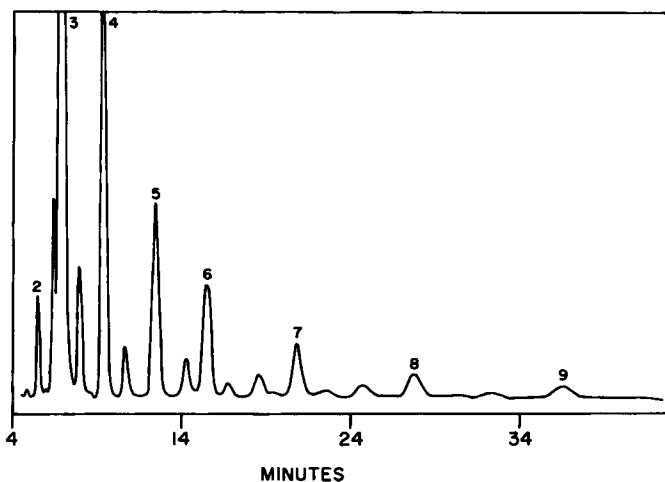


Fig. 1. HPLC separation of oligomers extracted with chloroform from PM7741 polyester powder.

Effect of Annealing

The surface of untreated yarn samples was relatively smooth and did not show any special features (Fig. 4). After heat treatment at 200°C crystalline deposits were observed on the surfaces. The crystals were not well defined for 15-min-treated samples (Fig. 5), but as treatment time increased their polygonal shapes became clearer and sizes increased (Figs. 6 and 7). Samples treated for 15 min and 1 h showed a relatively uniform distribution of crystalline deposits along the surface. As the treatment time was further increased, the deposits became unevenly distributed, but the sizes of individual crystals had increased considerably.

The analyses of perchloroethylene extractions are presented in Table II. Untreated samples had less than 0.1% oligomeric deposit on the surface with

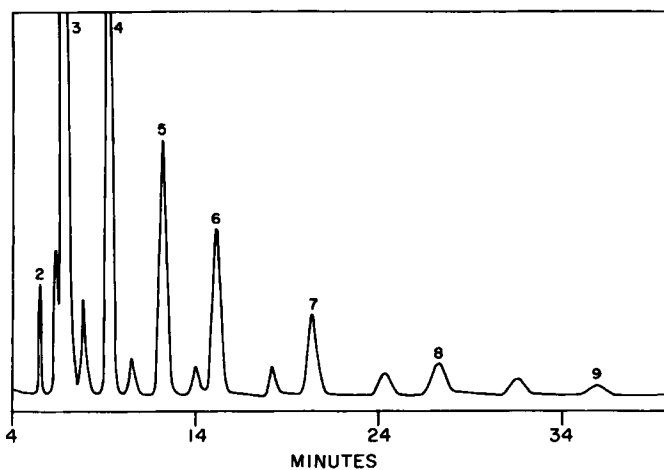


Fig. 2. HPLC separation of oligomers extracted with chloroform from semidull polyester yarn.

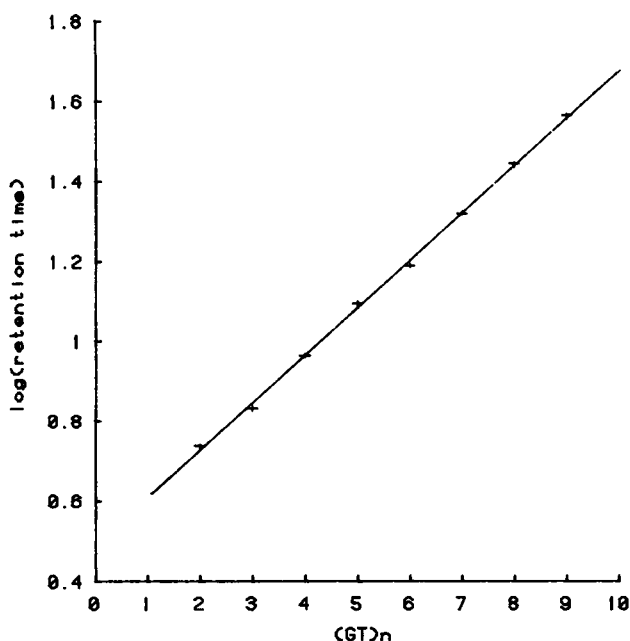


Fig. 3. Relation between log retention time and ring size for cyclic oligomers of ethylene glycol terephthalate [(GT)_n].

(GT)₃ being the major component together with small quantities of (GT)₂ and (GT)₄ (Fig. 8). Upon heat treatment the (GT)₃ content on the surface increased considerably, but the effect on (GT)₄ was not as pronounced (Fig. 9). Crystal deposits were not observed on the surface of perchloroethylene-extracted samples (Fig. 10), indicating that this solvent had successfully removed the oligomers from the fiber surfaces, confirming the findings of Luttringer et al.¹ One notable feature was the presence of relatively light circles on the extracted fiber surfaces. A closer examination revealed the presence of small spherical deposits at these regions (Fig. 11). It is possible that these are the sites where migration of (GT)₃ to the surface had occurred, and where a very small amount of further migration might have taken place while the fibers were being dried (50°C, *in vacuo*, overnight) after the perchloroethylene extraction.

TABLE I
Cyclic Oligomer^a Contents of Various Poly(ethylene Terephthalate) (PET) Samples

		(GT) ₂	(GT) ₃	(GT) ₄	(GT) ₅	(GT) ₆	(GT) ₇	(GT) ₈	(GT) ₉
PET powder	% of extract	1.11	66.62	7.61	4.38	2.99	1.71	0.86	0.49
	% owp ^b	0.015	0.99	0.11	0.07	0.04	0.03	0.01	< 0.01
Bright PET yarn	% owp	0.015	1.04	0.14	0.08	0.06	0.04	0.02	< 0.01
Semidull PET yarn	% owp	0.015	1.01	0.13	0.075	0.06	0.035	0.02	< 0.01

^a(GT)_n = cyclic oligomers of ethylene glycol terephthalate.

^bowp = on weight of polymer.

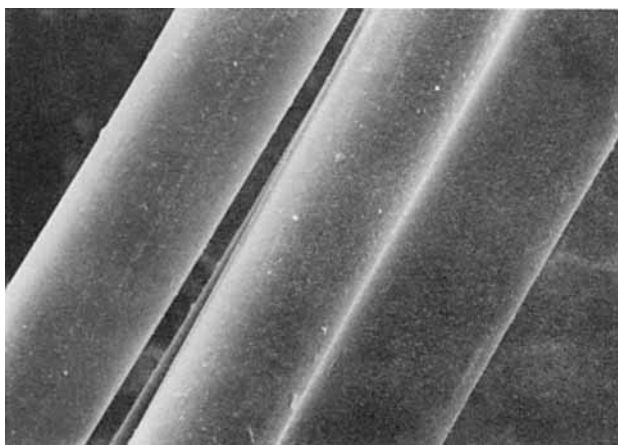


Fig. 4. Scanning electron micrograph of untreated bright polyester fiber ($\times 1200$).

The $(GT)_3$ content on the surface reached its maximum after 5 h treatment (Table II). After perchloroethylene extraction the samples were further extracted with chloroform to determine the extractable oligomer content within the fibers. When perchloroethylene and chloroform extracted oligomers are added and compared with that of the nonheated samples, it appears that up to 20% loss of $(GT)_3$ occurred due to the heat treatment. The effect on other cyclics and linear oligomers was even greater. Only very small quantities of $(GT)_4$ and $(GT)_5$ were extracted.

We suggest that the drop in cyclic oligomer content observed after heat treatments is essentially due to the solid state polymerization of cyclic species observed by Cooper and Semlyen⁸ and others.^{26,27} It may also be partially due to a reduced case of extraction of the remaining cyclics caused by increases in crystallinity of the fiber. Two further experiments were carried out to support the importance of the solid state reaction. A sample of bright PET yarn was

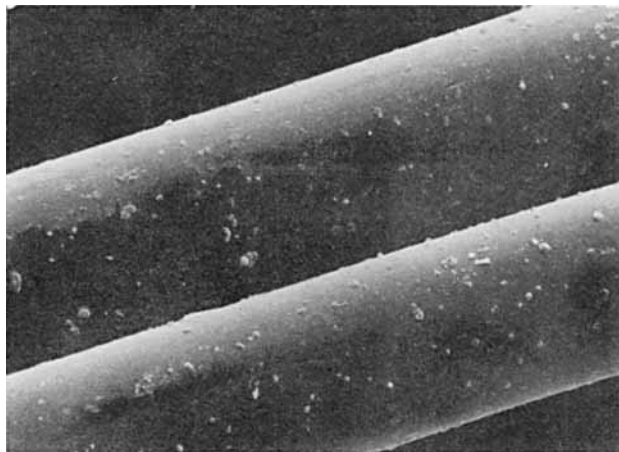


Fig. 5. Scanning electron micrograph of semidull polyester fiber heated at 200°C for 15 min ($\times 1340$).

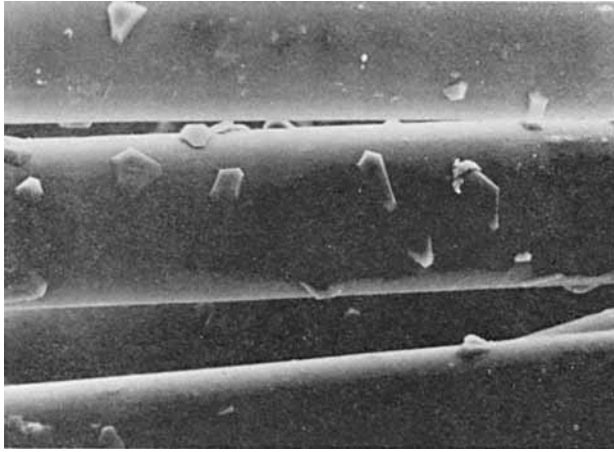


Fig. 6. Scanning electron micrograph of bright polyester fiber heated at 200°C for 1 h ($\times 1250$).

heat-treated at 240°C for 20 h and extracted with chloroform. Some thermal degradation of the sample occurred, and no crystalline deposits were observed on fiber surfaces. The $(GT)_3$ extracted was now 0.07% owp, and, apart from a small quantity ($< 0.01\%$) of $(GT)_4$ and traces of $(GT)_2$ and $(GT)_5$, no other oligomeric components were extracted. Secondly, a sample of oligomer extracted from PET powder was heat treated at 300°C for 20 h in a nitrogen atmosphere. This led to the formation of a slightly discolored, viscous melt. The DTA curve of the quenched product is similar to that of disordered polyester in showing a glass transition at 79°C, a crystallization exotherm consisting of a shoulder at 130°C and a peak at 137°C, and a melting endotherm at 255°C [Fig. 12(a)].

DTA curves obtained from the untreated extract and that of the same extract after quenching from the melt are presented in Figures 12(b) and (c)

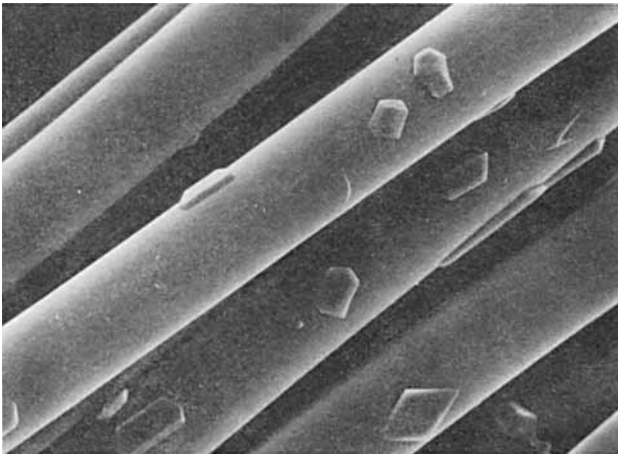


Fig. 7. Scanning electron micrograph of bright polyester fiber heated at 200°C for 5 h ($\times 860$).

TABLE II
Surface Oligomer^a Contents of Heat-Treated Poly(ethylene Terephthalate) Yarn (% owp)^b

Treatment	(GT) ₂	(GT) ₃	(GT) ₄	(GT) ₅	(GT) ₆	(GT) ₇	(GT) ₈	(GT) ₉
<u>Bright PET</u>								
None	< 0.01 (0.01) ^c	0.07 (0.98)	< 0.01 (0.13)	— (0.08)	— (0.06)	— (0.04)	— (0.015)	— (< 0.01)
200 ± 2°C, 1 h	— (< 0.01)	0.59 (0.24)	T ^d (0.03)	— (< 0.01)	—	—	—	—
200 ± 2°C, 5 h	— T	0.68 (0.19)	0.01 (0.02)	T (< 0.01)	T	—	—	—
200 ± 2°C, 20 h	— —	0.67 (0.14)	0.01 (0.015)	T (< 0.01)	T	—	—	—
<u>Semidull PET</u>								
None	< 0.01	0.045	< 0.01	—	—	—	—	—
200 ± 2°C, 15 min	T (0.01)	0.18 (0.78)	< 0.01 (0.05)	T (0.01)	— (< 0.01)	— T	— T	—

^aSee footnote a, Table I.

^bSee footnote b, Table I.

^cFigures in parentheses correspond to cyclic oligomers extracted by chloroform (24 h) subsequent to the perchloroethylene extraction used to extract the surface oligomers.

^dT = trace (< 0.001%).

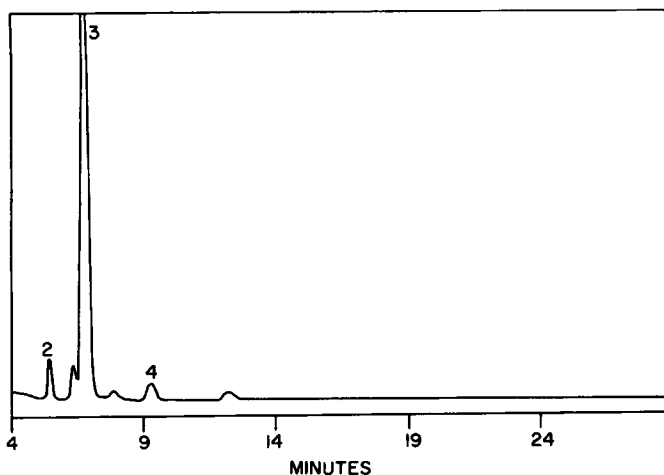


Fig. 8. HPLC separation of oligomers extracted with perchloroethylene from untreated bright polyester yarn.

for comparison. The untreated extract surprisingly showed endotherms at 188, 270, and 307°C [Fig. 12(b)]. While the endotherm at 307°C can be attributed to the melting of (GT)₃, the endotherms at 188 and 270°C are not easily assigned. It is interesting to note, however, that Oswald et al.²⁸ found a middle endotherm peak between 130 and 234°C in the DSC curves of thermally treated drawn PET yarns. They attributed it to the melting of very small crystallites (nuclei) located in the highly extended anisotropic amorphous fraction of the fibers. It is tempting to speculate that the endotherm found at 188°C in the oligomers extracted from PET may be related to the MEP reported by Oswald et al. It can be deduced from the DTA curve obtained on

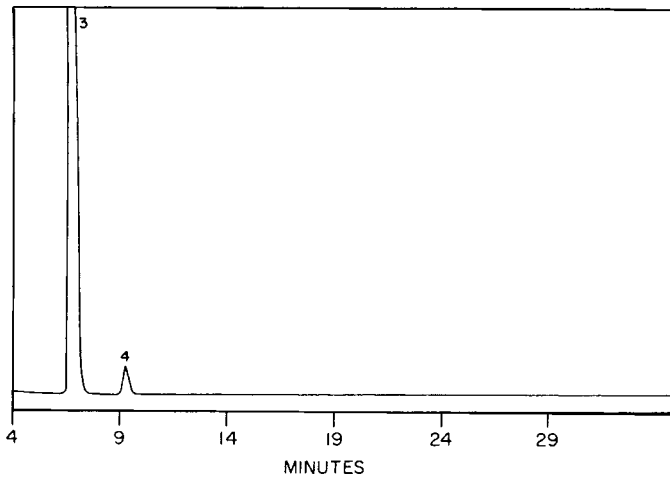


Fig. 9. HPLC separation of oligomers extracted with perchloroethylene from bright polyester yarn annealed at 200°C for 20 h.

the extracted oligomers which had been subjected to an initial run in the thermal analyzer to a temperature of 350°C and then quenched that some polymerization of the extract had resulted from the initial DTA run since the subsequent DTA trace exhibits transitions which are attributed as follows: a glass transition at 64°C, a crystallization exotherm at 113°C, a melting endotherm peaking at 247°C due to PET, and a melting endotherm at 312°C due to (GT)₃. It will be noted that the endotherm peaking at 247°C is very broad and appears to begin at about 190°C. Thus remnants of the endotherm found at 188°C in Figure 12(b) may still be present.

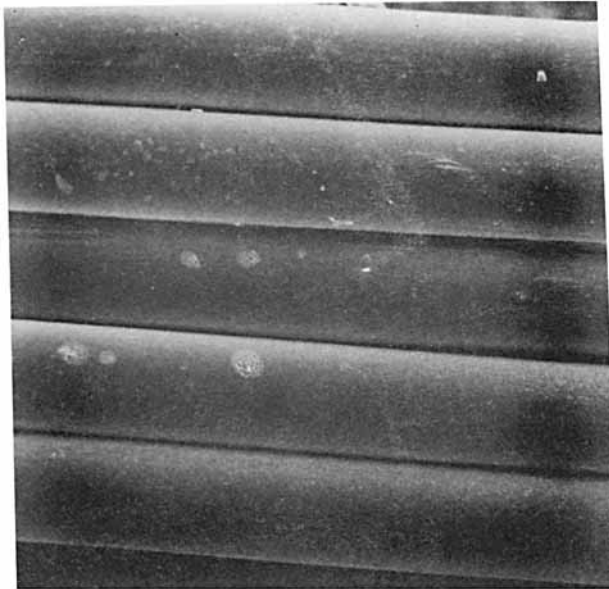


Fig. 10. Scanning electron micrograph of bright polyester fiber annealed at 200°C for 20 h and then extracted with perchloroethylene ($\times 890$).

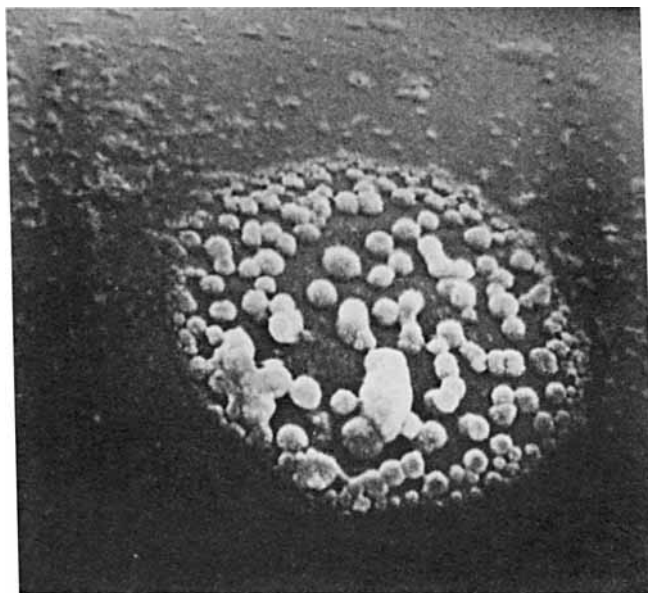


Fig. 11. Scanning electron micrograph at higher magnification of features present on bright polyester fiber annealed at 200°C for 20 h and then extracted with perchloroethylene ($\times 11,600$).

Effect of Solvent Exposure

Exposure of the yarn to methylene chloride also induced diffusion and crystallization of oligomers on the fiber surfaces (Figs. 13 and 14). By determining the oligomer concentration of the perchloroethylene extract it was established that $(GT)_3$ was again the most plentiful oligomer on the fiber surfaces (Table III). However, unlike annealing, methylene chloride exposure also resulted in migration of higher cyclic species to the surfaces (cf. Tables II and III). About 50% of the total $(GT)_3$ in a fiber diffuses to its surface within 4 h of methylene chloride exposure. Further amounts of $(GT)_3$ diffuse out with longer exposure. Significant increases were obtained in the amount of $(GT)_4$, $(GT)_5$, and $(GT)_6$ present on surfaces as exposure time was increased from 4 to 48 h. Peaks other than those assigned for cyclic oligomers also showed on HPLC traces and increased time of exposure also increased their amounts (Table III and Fig. 15).

The differences between annealing and methylene chloride exposure can be observed also on SEM micrographs. Perovic and Murti¹⁸ reported the presence of long cylindrical needle shaped crystals on the surface of semicrystalline oriented PET films, upon exposure to methylene chloride vapor. They attributed the different crystal shapes obtained by annealing and by solvent exposure to the two possible conformations of $(GT)_3$. Very few rodlike crystals were observed on the surfaces of our samples (Fig. 13). Some of the small crystals observed on the surfaces after 4 or 12 h methylene chloride exposure were polygonally shaped similar to those found on the annealed samples (cf. Fig. 13 or 14 and Fig. 6 or 7). After 48 h methylene chloride exposure, however, the main features were what appeared to be large quantities of amorphous deposits (Fig. 16), though, in fact, they may be rodlike crystals which became

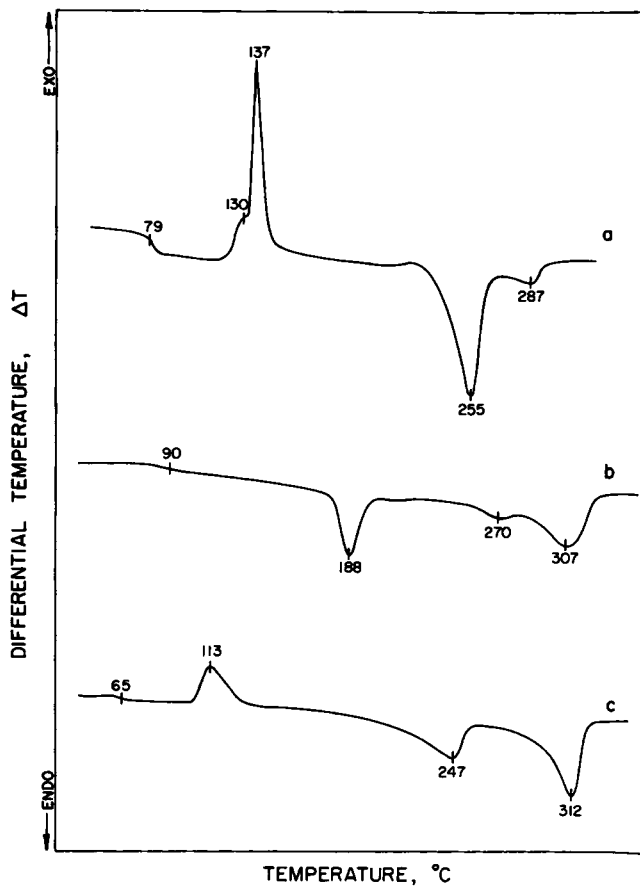


Fig. 12. DTA curves of polyester oligomers: (a) extract heated at 300°C for 20 h and then quenched; (b) untreated extract; (c) untreated extract taken from the thermal analyzer, after the temperature reached 350°C, and quenched.

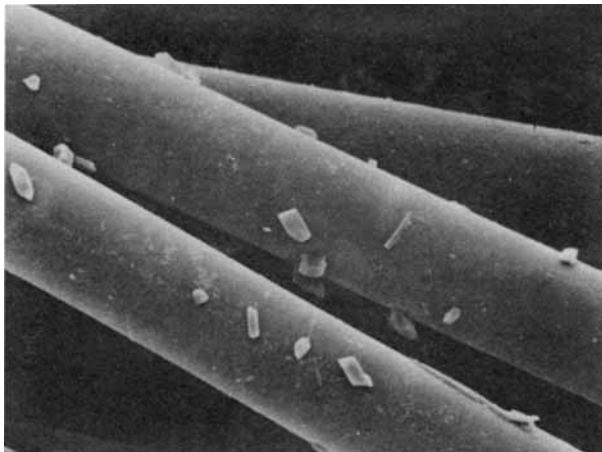


Fig. 13. Scanning electron micrograph of semidull polyester fiber exposed to methylene chloride vapor for 12 h ($\times 885$).

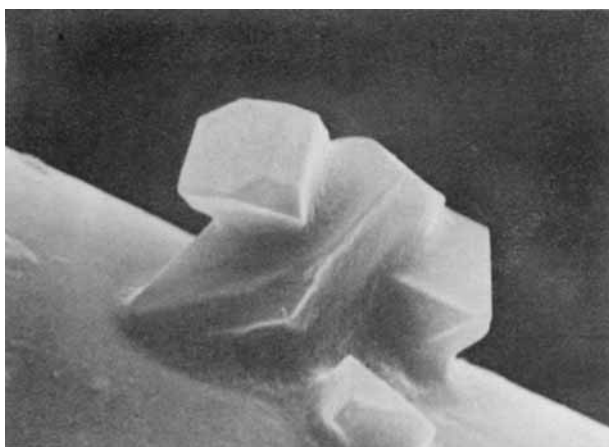


Fig. 14. Higher magnification scanning electron micrograph of oligomers present on semidull polyester fiber exposed to methylene chloride vapor for 12 h ($\times 8970$).

TABLE III
Surface Oligomer^a Contents of Poly(ethylene Terephthalate) Yarn
Exposed to Methylene Chloride Vapor for Various Periods of Time (% owp)^b

Time (h)	(GT) ₂	(GT) ₃	(GT) ₄	(GT) ₅	(GT) ₆	(GT) ₇	(GT) ₈	(GT) ₉
4	0.01	0.58	0.02	< 0.01	< 0.01	—	—	—
12	0.01	0.84	0.04	0.01	< 0.01	T ^c	—	—
48	0.01 (< 0.01) ^d	0.87 (0.13)	0.08 (0.05)	0.05 (0.02)	0.03 (0.03)	< 0.01 (0.03)	— (0.01)	— (< 0.01)

^aSee footnote a, Table I.

^bSee footnote b, Table I.

^cSee footnote d, Table II.

^dSee footnote c, Table II.

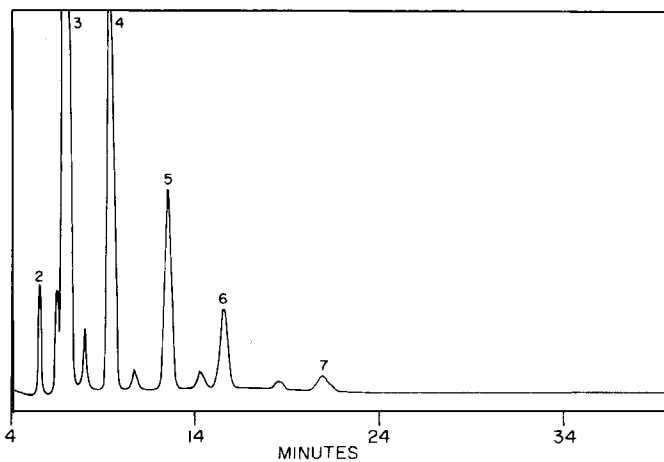


Fig. 15. HPLC separation of oligomers extracted with perchloroethylene from bright polyester yarn after methylene chloride exposure for 48 h.

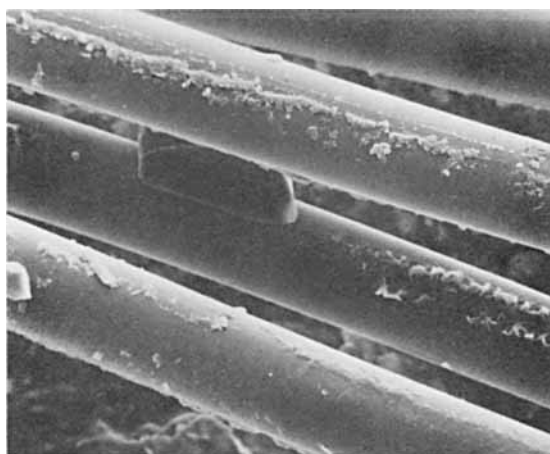


Fig. 16. Scanning electron micrograph of bright polyester fiber exposed to methylene chloride vapor for 48 h ($\times 810$).

attached as increased amounts of oligomer came to the surface (Fig. 17). The presence of increased amounts of the larger cyclics after the longer exposure may also be having an effect on the morphology of the deposits.

Moisture Regain

The adsorption moisture regain at 59% RH and 21°C for bright PET yarn, PET chips, and the oligomers extracted from the PET chips was 0.52, 0.51 and 0.29%, respectively. The lower moisture regain of the extract is not due to it consisting mostly of cyclic oligomers. The degree of polymerization of the PET samples is high (about 100); thus end groups will not make a significant contribution to the moisture regain. The difference in the regains is more likely due to the oligomers being in a crystalline form and only the crystal

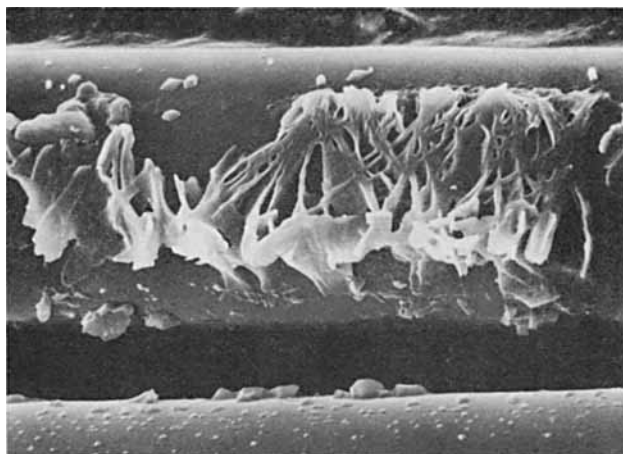


Fig. 17. Higher magnification scanning electron micrograph of bright polyester fiber exposed to methylene chloride vapor for 48 h ($\times 2460$).

surfaces being accessible to water. It was found that the DTA curve of the oligomer extract did not include a crystallizing exotherm [Fig. 12(b)], while the same sample after quenching contained such an exotherm [Fig. 12(c)]. From density determinations it appears that the PET yarn is about 64% crystalline and the PET chips are amorphous. Their densities were 1.414 and 1.340 g/cm³, respectively. The degree of crystallization (c) was calculated from the relation given by Morton and Hearle²⁹

$$c = \frac{\rho - \rho_{\text{am}}}{\rho_{\text{cr}} - \rho_{\text{am}}}$$

where ρ = density of the fiber in the PET yarn, ρ_{am} = density of amorphous PET, and ρ_{cr} = density of crystalline PET = 1.455 g/cm³.³⁰ The density of amorphous polyester has been reported to be 1.335 g/cm³.³⁰ It is interesting to note that a significant difference was not found between the moisture regains of the PET yarns and chips, although they differed markedly in crystallinity.

CONCLUSIONS

1. Heat treatment of polyester yarns induces the selective crystallization of (GT)₃ in the form of polygonal solids on the fiber surfaces. At the temperature studied, namely, 200°C, the diffusion rate of (GT)₃ appeared to be very rapid. Small quantities of the cyclic tetramer were also found.

2. The total extractable oligomer content of the samples is reduced considerably after annealing at 200°C. This is believed to be mainly as a result of solid phase polymerization.

3. Exposure to methylene chloride vapor also causes cyclic oligomers to diffuse to the fiber surface. The migration of (GT)₃ is again very rapid. Larger cyclics also diffuse to the surface in appreciable quantities. Solvent-exposed samples, unlike annealed ones, exhibit irregular crystal shapes and sizes on their surfaces.

4. The moisture regain of the extracted oligomers is less than that of the polyester. It is suggested that this is due to the oligomers being in a crystalline form.

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