The Molecular Weight Distribution and Oligomers of Sodium Hydroxide Hydrolyzed Poly(ethylene terephthalate)

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SYNOPSIS

Methanolic sodium hydroxide reacted more quickly than aqueous sodium hydroxide with poly(ethylene terephthalate) (PET). Larger amounts of low molecular weight deposits were formed at the product surface after the former treatment, also indicating the severity of this attack. The molecular weight distribution, obtained by gel permeation chromatography for the product of methanolic NaOH hydrolysis, had a population with 2400 peak molecular weight, which was not present on the chromatograph of the aqueous sodium hydroxide hydrolyzed product. This population is hypothesized to have been crystalline material. Extraction and analysis by high performance liquid chromatography of the low molecular weight products on the surface and in the bulk of the hydrolyzed PET samples, in comparison to controls, revealed the presence of more oligomeric species after hydrolysis. Also, more oligomeric species were present in the bulk extract of the methanolic sodium hydroxide hydrolyzed sample than in the aqueous NaOH hydrolyzed product.

INTRODUCTION

From a critical review of the literature, it can be deduced that the reaction of aqueous sodium hydroxide with poly(ethylene terephthalate) (PET) has been well established as a reaction in which surface layers are successively removed by hydrolysis.[1] Weight loss of PET due to hydrolysis with methanolic NaOH has been shown to occur more rapidly than with aqueous NaOH.[2] In a recent investigation, we showed that the molecular weight distribution of the fiber after aqueous hydrolysis remained essentially unaffected to weight losses up to 90%.[3] It has been reported that hydrolyzed PET fibers contain greater amounts of oligomers than the starting product and that the oligomers on the sample surface are significantly polydisperse.[4] An analysis of the cyclic oligomers present in heatset semidull PET yarns, using extraction techniques coupled with high-performance liquid chromatography (HPLC) analysis, has been published recently.[5]

The objective of this study was to compare the molecular weight distributions and oligomeric contents of methanolic NaOH treated PET with those of aqueous NaOH hydrolyzed specimens.

EXPERIMENTAL

Materials

The starting material was a scoured heatset, semidull Dacron PET type 54 fabric (obtained from Test Fabrics, Inc., Middlesex, NJ) made of spun yarns. All chemicals used were of reagent grade, except the 1,4-dioxane, the hexane, and the chloroform, which were HPLC grade.

Procedures

Alkaline Hydrolysis

Fabric samples were treated in 2.8 M aqueous NaOH solution at 60°C (±0.1°C) by a procedure described elsewhere.[6] Additional samples were treated in 2.5

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Table I Weight Loss of Hydrolyzed and Extracted PET Samples

Sample Treatment and Treatment Time: (h)	Total Fabric Weight Loss (%)		
	Before Extraction	After Extraction	
		C_2Cl_4	$CHCl_3$
Untreated	—	−0.9	0.1
2.8 M aqueous NaOH at 60°C			
2	10.3	—	11.6
4	26.0	25.4	26.3
2.5 M Methanolic NaOH at 21°C			
Control	0.1	−0.4	1.0
1	36.1	42.7	43.7
2.3	82.8	91.1	91.4

M methanolic NaOH solution in sealed jars at 21°C (±2°C) with mild mechanical agitation. All samples were treated in a 2.5 ratio of wt/vol (g/L). The hydrolysis was terminated and the samples were dried and conditioned using the same procedure as described previously for the aqueous sodium hydroxide treatment.[6] Controls were prepared by treating PET with water at 60°C or methanol at 21°C.

Scanning Electron Microscopy (SEM)

Scanning electron micrographs were obtained in the manner described previously.[6]

Gel Permeation Chromatography (GPC)

Molecular weight distributions were determined using the HPLC equipment described below, fitted with two Waters Ultrastyragel GPC columns (sizes

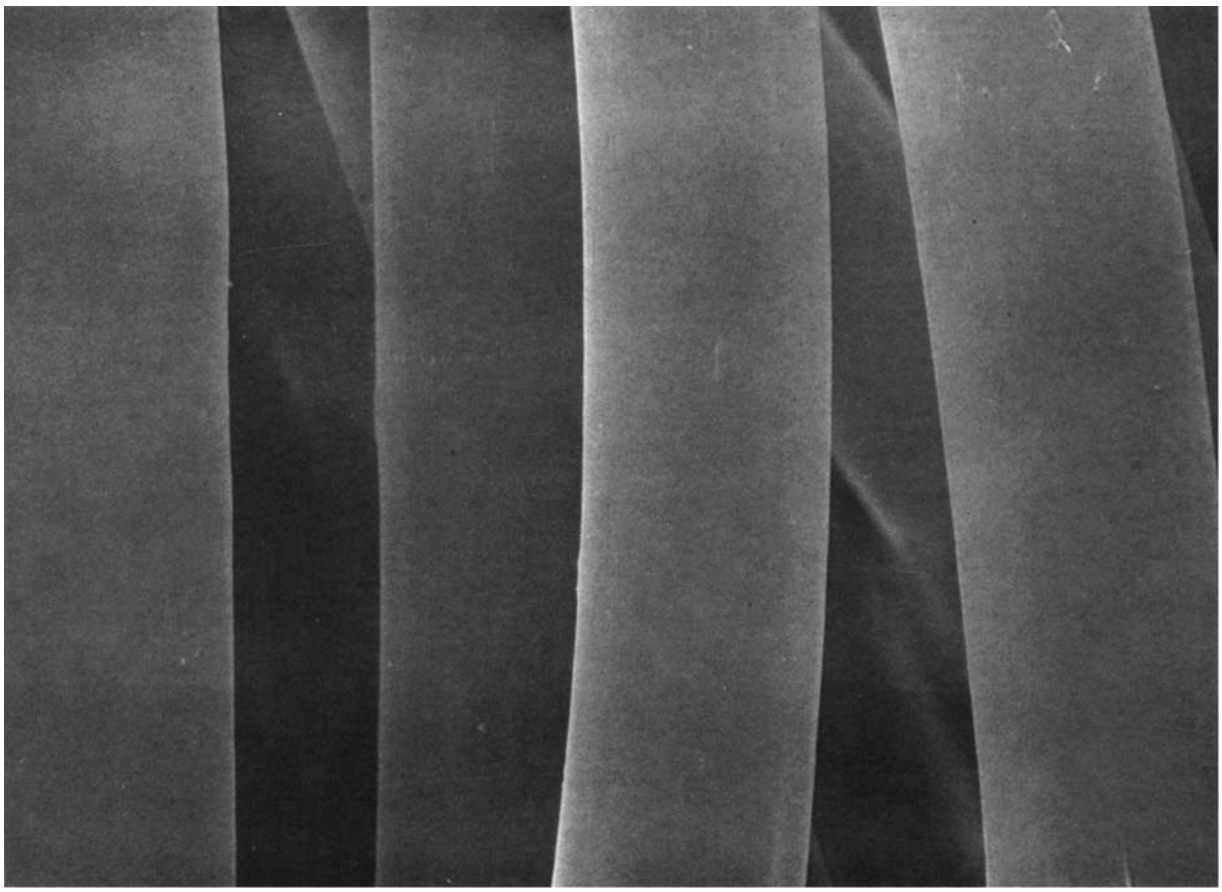

Figure 1 Scanning electron micrograph of methanol treated PET (×2640).

1000 and 50 nm), and 70/30 dichloromethane/hexafluoroisopropanol as the solvent and mobile phase. The procedures have been described in detail elsewhere.[7]

Oligomer Content of Polyester Yarns and Analyses

The fabric samples (0.5 g) were soxhlet-extracted, utilizing a previously described procedure,[5,7] which used perchloroethylene to remove surface oligomers and chloroform to remove either the total extractable oligomer content or the residual extractable oligomeric content after perchloroethylene extraction. Extracted fabrics were dried in a vacuum oven at 50°C for 24 h.

HPLC analysis to characterize the cyclic oligomeric extracts followed an established method,[5] using hexane/dioxane (60/40 v/v) as the mobile phase and chloroform as the solvent. A Perkin–Elmer (PE) Series 10 Liquid Chromatograph, operating with a Lichrosorb Si60 (250 × 4.6 mm) normal phase column, and with UV detection at 254 nm (PE LC-15 UV spectrophotometer), was used along with a 3600 PE Data Station and Chromatographics 2 software for data collection and analysis. In some instances, several peaks were observed on chromatograms in addition to the peaks assigned to the cyclic oligomers. These were probably due to cyclic species containing diethylene glycol residues as well as linear oligomers.[5,8]

Weight Loss

Weight losses of the hydrolyzed samples and of the extracted samples were calculated from the differences in the weight of the specimens before and after hydrolysis and from the differences in the weight of the starting fabric and of the extracted fabric, respectively. In all cases, samples were conditioned by exposure to an atmosphere of 65% relative humidity and 21°C before weighing.

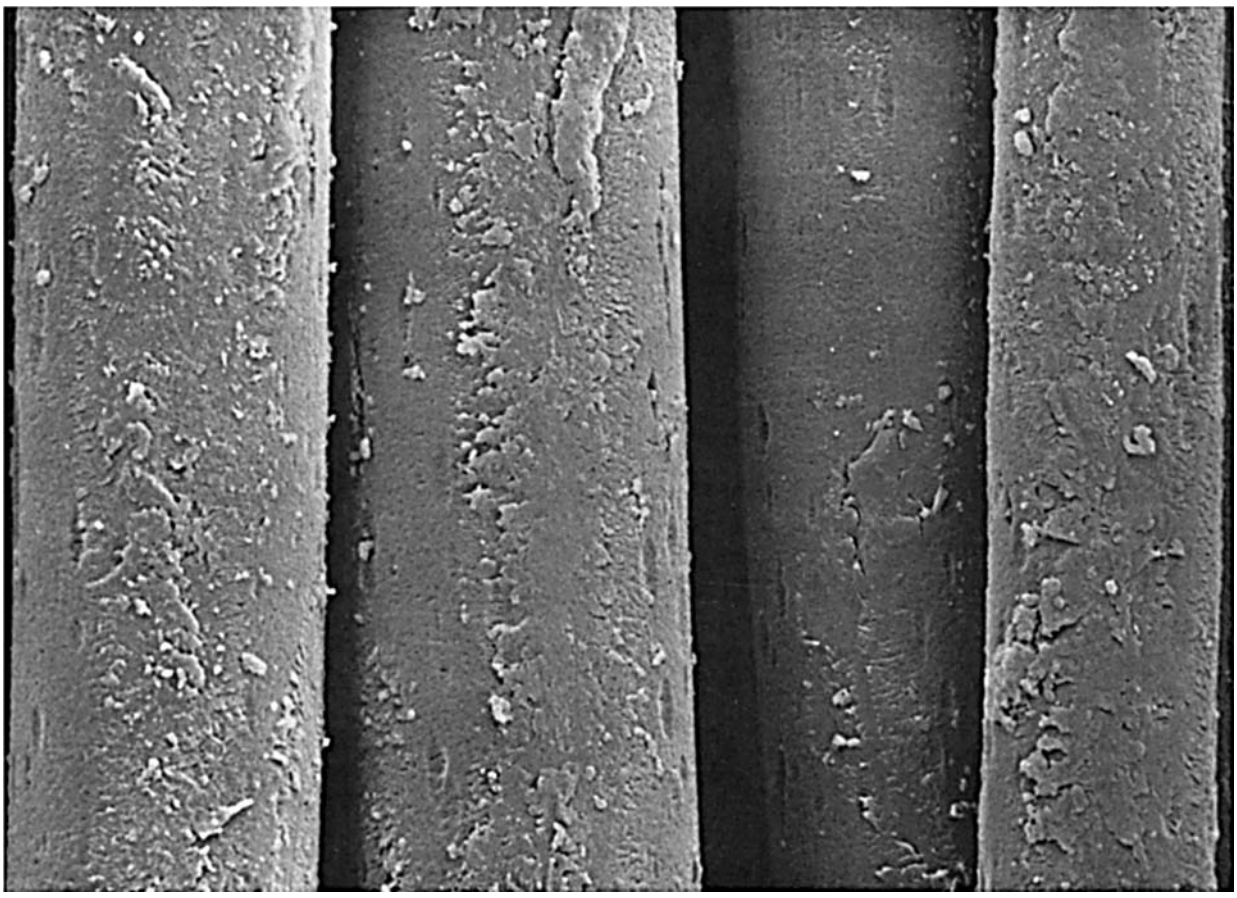

Figure 2 Scanning electron micrograph of methanolic NaOH hydrolyzed PET specimen to 26% weight loss (×2870).

RESULTS AND DISCUSSION

Product Characterization

The weight loss achieved by treatment of the PET with methanolic sodium hydroxide ranged up to 82.8%, depending on the treatment time (Table I). It will be noted that even though the reaction temperature was higher, the rate of weight loss with aqueous NaOH treatment was lower.

Perchloroethylene extractions caused small weight gains for the controls and for the aqueous NaOH hydrolyzed specimens, presumedly due to retention of the solvent by the PET. Weight losses were achieved for all samples that had been extracted with chloroform. After both surface and bulk extraction of the oligomers by the perchloroethylene and chloroform, respectively, the weight of the methanolic NaOH treated samples decreased markedly, whereas that of the aqueous NaOH hydrolyzed samples lessened by only small amounts. This difference reinforces the observation that the reaction of PET with methanolic NaOH is more severe than the reaction with the aqueous solution.

Unlike the surface of the starting PET (Fig. 1), the surface of the methanolic NaOH treated PET fibers was covered with debris (Fig. 2). These deposits were removed after extraction with perchloroethylene (Fig. 3), revealing a surface full of pits or cavities, which is similar to that of an aqueous NaOH hydrolyzed delustered PET.[1] Extraction by chloroform, either following the perchloroethylene extraction or alone, caused no additional distinguishable changes in the fiber surfaces. The surfaces of the aqueous NaOH treated specimens were not affected by extraction with either solvent.

Gel Permeation Chromatography

We have shown that the differential molecular weight distribution (DMWD) of aqueous NaOH hydrolyzed PET is essentially unchanged from the DMWD of its control up to a weight loss of 91%.[3] Unlike such samples, the chromatograph of the

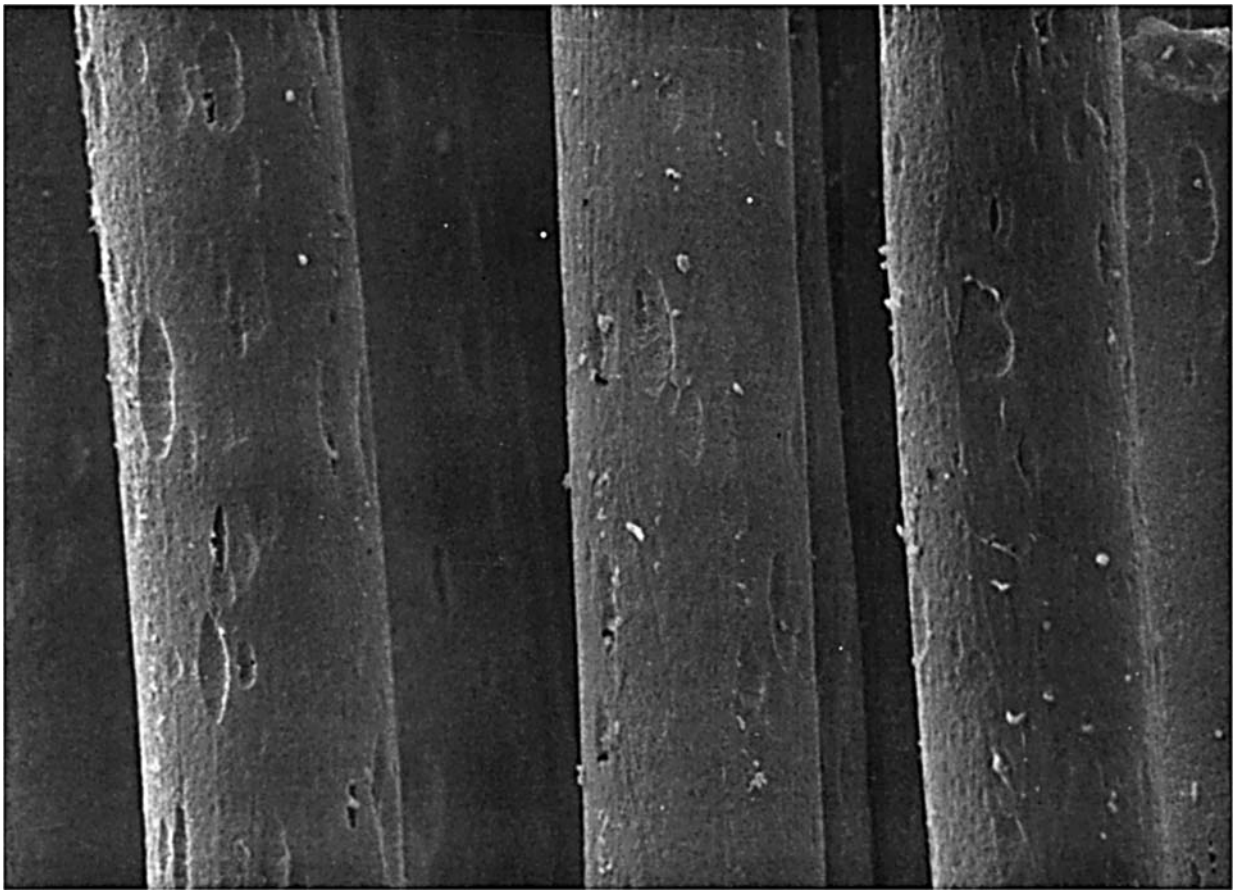

Figure 3 Scanning electron micrograph of methanolic NaOH hydrolyzed PET specimen to 26% weight loss, extracted with perchloroethylene (×3570).

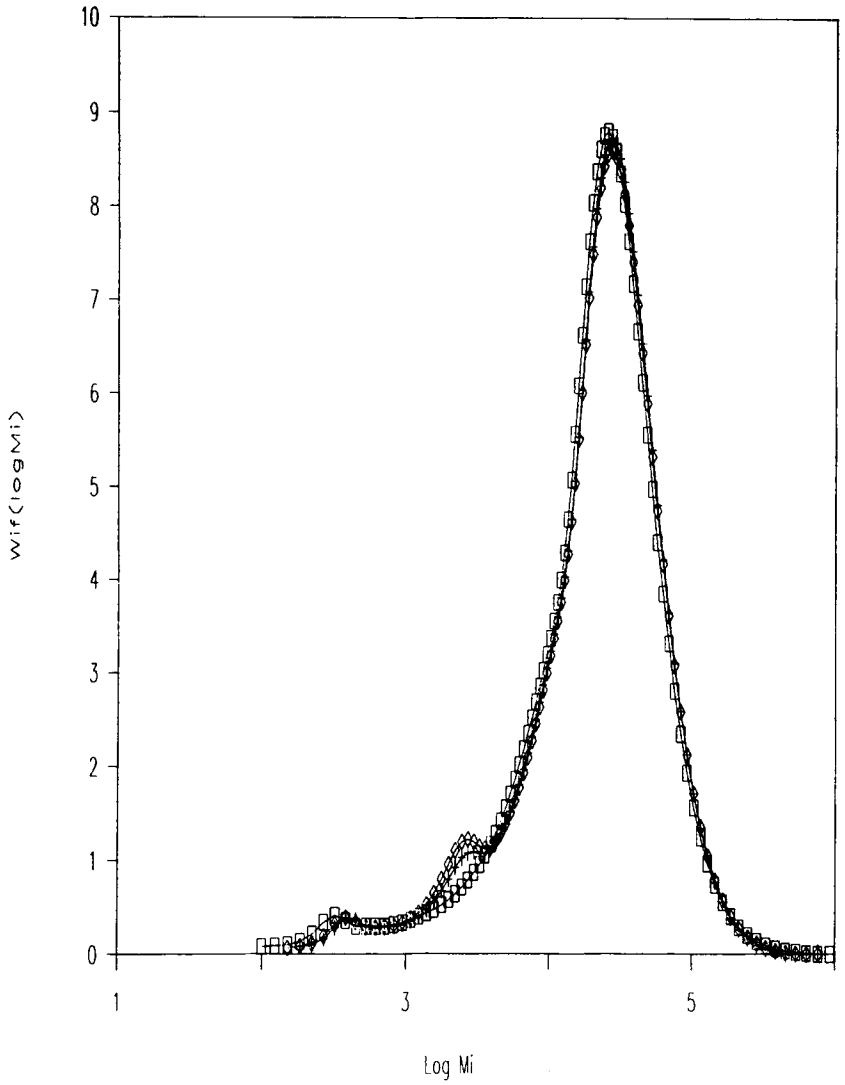

Figure 4 Differential molecular weight distributions of nonhydrolyzed PET (□), methanolic NaOH hydrolyzed PET to 36% weight loss (+) and to 83% weight loss (◇).

methanolic NaOH hydrolyzed polymer contained an additional distinct peak, which eluted before the trimer (Fig. 4). The peak was removed by extraction by perchloroethylene as well as chloroform, indicating that the species to which it can be attributed was present at the fiber surface (Fig. 5). This low molecular weight product had a peak molecular weight of approximately 2400, which is equivalent to a DP of 12–13. It is speculated that this product is degraded crystalline material (i.e., with folds cleaved) that is no longer bound by covalent bonds to the fiber. A molecular weight of 2400 would yield an extended chain length of approximately 13.4 nm, which is well within ranges given for the axial length in PET crystallites.[9,10]

Extraction with perchloroethylene or chloroform was incomplete. About 0.1% of the cyclic trimer remained, indicating that oligomers at the core of the fiber may not have been completely removed. Although some trimer was left, the higher DP fragment caused by methanolic alkaline hydrolysis was removed by extraction. Thus it is feasible that the latter product was present only near or at the fiber surface.

High-Performance Liquid Chromatography

It should be noted that there were products extracted from the methanolic NaOH hydrolyzed PET samples that precipitated on cooling, or after flash evap-

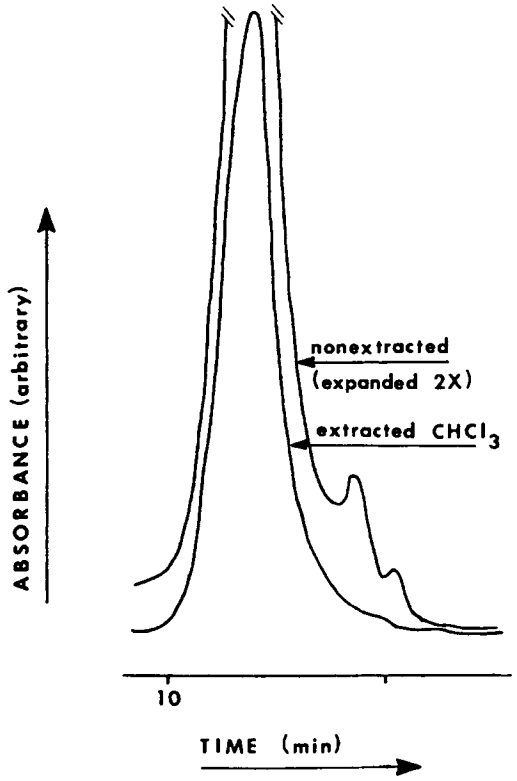

Figure 5 Gel permeation chromatogram of methanolic NaOH hydrolyzed PET to 36% weight loss and the same specimen after chloroform extraction.

oration of the solvent. These products did not completely redissolve in fresh chloroform. On heating the extracted material in fresh chloroform, some solubilization occurred, but after cooling the solutions were turbid. Filtration before HPLC analysis, however, resulted in clear solutions. The insoluble substance is thought to be the species of DP 12–13. The amount of this product was estimated as being between 3 and 7% of the sample weight from the area of the low molecular weight peak, relative to that of the total DMWD obtained by GPC.

The HPLC chromatograms of the chloroform extract of the untreated PET, the methanol control, and the 2 h aqueous NaOH treated sample were similar (Figs. 6(1) and (2) and Fig. 7b). All yielded similar amounts of oligomer, the results of which are presented in Table II as percent on-weight-polymer (% OWP). The 1 h methanolic NaOH treated PET contained a greater amount of oligomers, including greater quantities of $(GT)_4$, $(GT)_5$, and $(GT)_6$ (Fig. 6(3) and Table II). In the case of the methanolic hydrolyzed sample, there was a large discrepancy in the % OWP measured by HPLC and the weight loss, as determined after chloroform extraction (*cf.* Tables I and II). However, this discrepancy can be explained by taking into consideration the estimated weight of polymer of DP 12–13 (see above). In addition, the % OWP oligomers measured by HPLC yielded larger values for weight

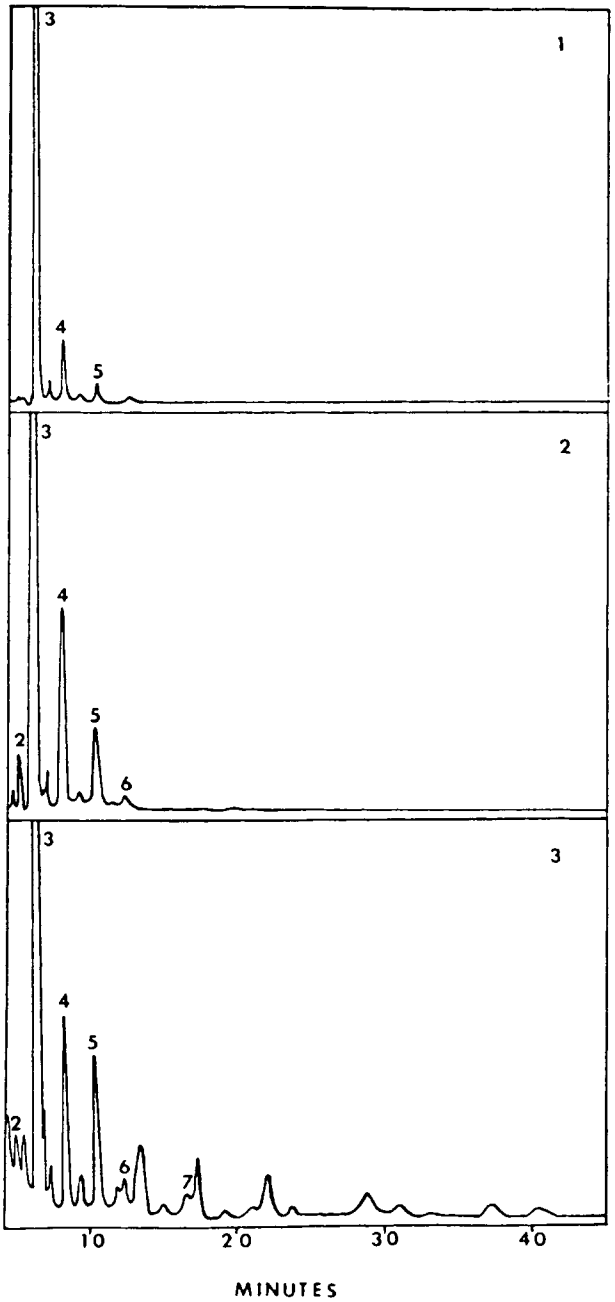

Figure 6 HPLC chromatograms of chloroform extracted oligomers of untreated and 1 h methanolic NaOH hydrolyzed PET: (1) untreated, (2) methanolic control, (3) hydrolyzed.

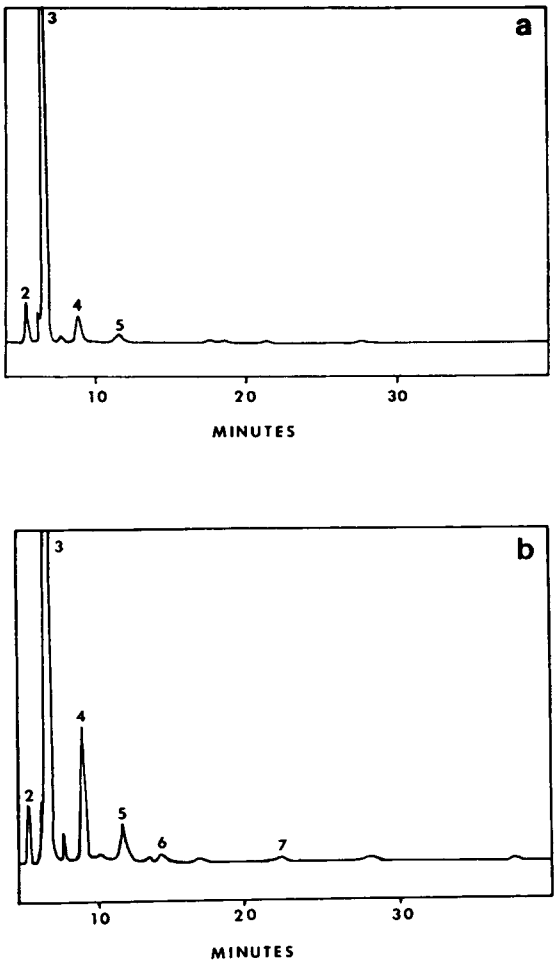

Figure 7 HPLC chromatograms of extracted oligomers of 2 h aqueous NaOH hydrolyzed PET: (a) surface extract (using C_2Cl_4), (b) bulk extract (using $CHCl_3$).

loss for the untreated PET control and the methanol treated specimen than for direct fabric measurements, which, as mentioned before, were affected by small retentions of the extracting solvent.

Methanol treatment of the starting PET appeared to cause migration of the cyclic species, predominantly the trimer, to the surface of the PET fiber (*cf.* % OWP oligomers, Table III). This is indicative of easier diffusion of the trimer to the fiber surface due to swelling of the PET.

The methanolic NaOH hydrolyzed specimen had less cyclic trimer at the surface than its control (Table III). However, the chromatograph of the bulk or chloroform extract of this hydrolyzed product contained several additional peaks, which are probably due to linear oligomers (*cf.* Figs. 8(3) and Fig. 6(3)). It also contained more oligomeric species than the bulk extract of the aqueous sodium hydroxide treated sample (*cf.* Fig. 6(3) and Fig. 7b). The latter, in turn, contained more oligomeric species than the perchloroethylene extract of its counterpart (*cf.* Figs. 7a and b).

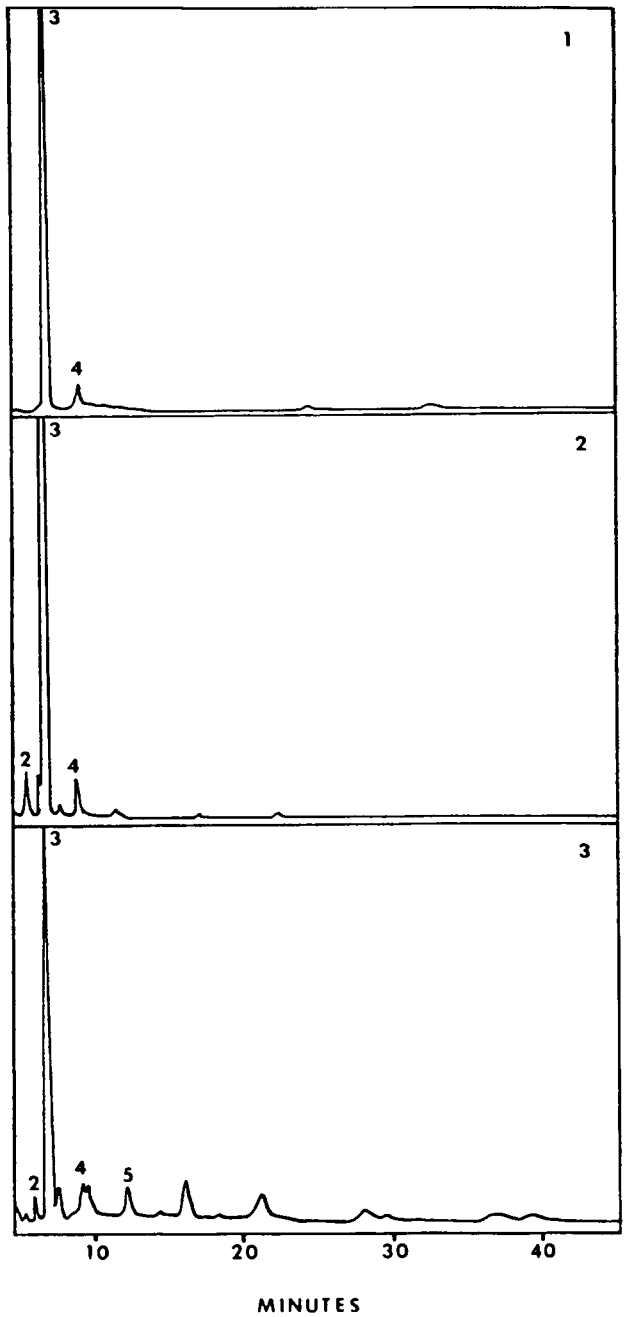

Figure 8 HPLC chromatograms of perchloroethylene extracted oligomers of untreated and 1 h methanolic NaOH hydrolyzed PET: (1) untreated, (2), methanolic control, (3) hydrolyzed.

Table II Cyclic Oligomer[a] Content of $CHCl_3$ Extract of Hydrolyzed PET Samples

Sample	Percent On-Weight-Polymer of Cyclic Species						
	$(GT)_2$	$(GT)_3$	$(GT)_4$	$(GT)_5$	$(GT)_6$	$(GT)_7$	Total
Untreated	0.02	1.14	0.08	0.01	T[b]	—	1.25
Control[c]	<0.01	1.12	0.09	0.04	<0.01	—	1.27
1 h 2.5 M me[d] NaOH	0.04	1.04	0.15	0.14	0.03	<0.01	1.41
2 h 2.8 m aqueous NaOH	0.02	1.09	0.07	0.03	0.01	T	1.22

[a] $(GT)_n$ corresponds to cyclic oligomers of ethylene glycol terephthalate.
[b] T = Trace.
[c] Untreated sample treated with methanol.
[d] Me = Methanolic.

Table III Surface Cyclic Oligomer[a,b] Content of Hydrolyzed PET Samples

Sample	Percent On-Weight-Polymer of Cyclic Species						
	$(GT)_2$	$(GT)_3$	$(GT)_4$	$(GT)_5$	$(GT)_6$	$(GT)_7$	Total
Untreated	—	0.18	0.01	—	—	—	0.19
	(0.01)[c]	(1.05)	(0.07)	(0.02)	(<0.01)	—	
Control[d]	0.01	0.42	0.02	<0.01	T[e]	—	0.46
	(<0.01)	(0.44)	(0.02)	(<0.01)	—	—	
1 h 2.5 M me[f] NaOH	—	0.15	0.02	0.02	—	—	0.19
	(<0.01)	(0.61)	(0.06)	(0.06)	(0.02)	(T)	
2 h 2.8 M aqueous NaOH	0.01	0.22	0.01	<0.01	—	—	0.25
	(<0.01)	(0.82)	(0.05)	(0.01)	(<0.01)	(T)	

[a] Determined from the perchlorethylene extract of the samples.
[b] See footnote a, Table II.
[c] Values in parentheses constitute % OWP of the perchloroethylene sample subsequently extracted with chloroform.
[d] Untreated sample treated with methanol.
[e] Trace.
[f] Me = Methanolic.

CONCLUSIONS

Methanolic sodium hydroxide reacts more rapidly with PET than does aqueous sodium hydroxide. In addition, the products of these two processes differ. Notably, the residue of the treatment with methanolic sodium hydroxide contains a population with 2400 peak molecular weight, which is not present in the product of the hydrolysis with aqueous sodium hydroxide. The former reaction also produces more oligomeric species.

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