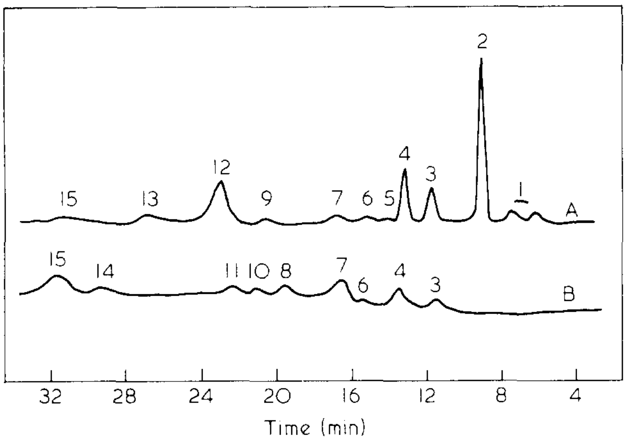

Figure 3 Gas-chromatograms of the liquid resulting after 30 h thermal treatment in vacuum at 195°C (A) and of the products released during pyrolysis of $(CH)_x$; (B) at 195°C: (1) C_5–C_6 hydrocarbons; (2) benzene; (3) toluene; (4) *m*- and *p*-xylene; (5) *o*-xylene; (6) unidentified; (7) styrene; (8) vinyl toluene; (9) indan; (10) unidentified; (11) unidentified; (12) indene; (13) divinyl benzene; (14) naphthalene; (15) methyl naphthalene

The maintainance of $(CH)_x$ at 195°C in a vacuum (7×10^{-5} torr) for long periods led to a visible degradation of the polymer, i.e. a liquid sample was collected in a cold trap (−196°C) after a prolonged degassing at 150°C. The liquid was analysed by gas chromatography and the chromatogram obtained was compared with that of the parent sample pyrolysed in the gas chromatograph at the same temperature (*Figure 3*). It can be seen that the chromatogram of the pyrolysed sample does not indicate the presence of C_5–C_6 hydrocarbons (benzene included) as decomposition products. However, benzene is the major product detected in the liquid sample collected at 195°C, suggesting that the aromatization process occurs even at this temperature.

In conclusion, the use of temperatures close to 200°C for the isomerization of *cis* $(CH)_x$, even for short periods, is not recommended, since chain defects and degradations could be induced.

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Action of far-ultraviolet radiation (185 nm) on poly(ethylene terephthalate) films: a method for controlled dry-etching

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Far-ultraviolet light (185 nm) rapidly etches poly(ethylene terephthalate) films without any subsequent processing. Both non-oxidative and oxidative mechanisms are operative.

Keywords Dry photoetching; poly(ethylene terephthalate); far-ultraviolet radiation; films; non-oxidative mechanisms; oxidative mechanisms

Introduction

In the extensive literature that exists on the action of ultraviolet light on poly(ethylene terephthalate) (PET), radiation of wavelength less than 200 nm was rarely used. This is understandable since the objective of nearly all of the investigations was the study of the degradation of the material in an adverse environment. The elegant and most exhaustive research of Wiles and coworkers[1–4] has provided a clear understanding of the reactions that take place under these conditions. We report here that far-u.v. radiation of wavelength 185 nm is highly effective in the rapid removal of PET in a controlled manner and without any subsequent treatment.

Experimental

Commercially available PET films of 250, 50 and 2.5 μ thickness were used as obtained. The sources of light were low-pressure mercury lamps of 10 W (Osram HNS 10 W/oz) or 40 W (Westinghouse G37T6VH) power. The former was enclosed in a fused-quartz well which was inserted in a water-cooled reaction chamber. The atmosphere in the chamber could be swept with air or oxygen. The 40 W lamp was used only in an air environment. The samples were placed about 0.5 cm away from the lamps. The depth and definition of the photoetching was followed by loss of weight, Taylor–Hobson Talystep measurement, and scanning electron

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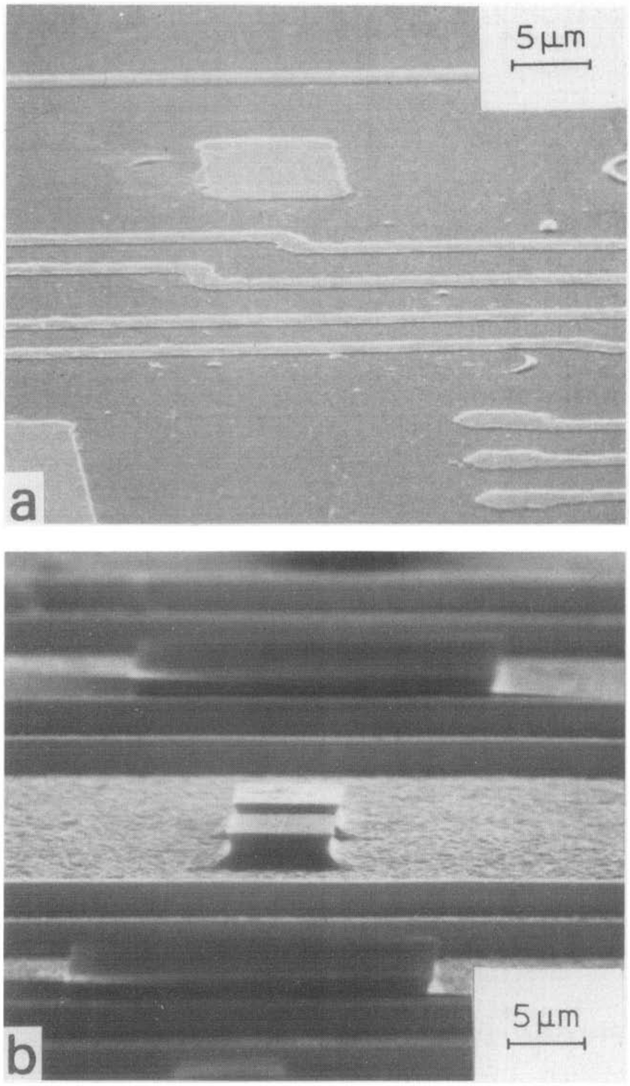

Figure 1 Scanning electron microphotographs of PET after irradiation at 185 nm. (a) 16 hours, nitrogen atmosphere, (b) 16 hours, air. The pattern is defined by a film of lead 2000Å thick. The total intensity of irradiation was the same in both cases

microscopy. A pattern of lead film (2000 Å) laid over the sample was helpful in gauging the depth of the photoetching in *SEM* photographs. I.r. spectra were obtained in transmission in one set of experiments in which 2.5 μ thick films were used.

Results

Exposure of a PET film in a nitrogen atmosphere to 185 nm radiation at a power density of 0.05 W cm^{-2} resulted in the removal of material in the exposed area at the rate of ~300 Å per hour. When the atmosphere was replaced by air, the rate of removal was 3200 Å per hour. Scanning electron micrographs of the irradiated samples (*Figure 1*) show that the removal of the material was completely defined by the path of the radiation and there was no observable particulate residue. These results can be contrasted with the earlier report[4] that at longer wavelengths ($\lambda > 220$ nm) after exposure to much more intense radiation for 1000 h, there was a noticeable shrinking of the exposed areas 'but the initially featureless surface of PET remains featureless, with the exception that small amounts of particulate debris appeared on some areas of the irradiated films'. Again, in significant contrast to earlier work, at 185 nm there was no build-up of any fluorescent material in the film that was exposed. Nevertheless, some similarities were observed. Thus the film that was irradiated at 185 nm in nitrogen turned yellow but the sample that was irradiated in air did not. The slow formation of –OH absorptions was evident in the latter case. Chemical analysis of the volatile products formed from irradiation in a vacuum showed CO and CO_2 as the important products and an equivalent quantity of a variety of other products up to C–6 compounds which could not be identified separately owing to the complexity of the mixture.

The possibility that ozone (formed by the action of 185 nm radiation on oxygen in air) was the cause of the etching that was observed[5] was ruled out because exposure of the air stream to direct 185 nm, while shielding the PET surface, led to no observable etching whatsoever.

Discussion

The importance of decreasing wavelength on the sensitivity of PET to photodegradation has been commented upon by Day and Wiles[1]. In the far-ultraviolet region the photosensitivity is greatly increased by (i) the strong absorption of the radiation by nearly every group in the polymer, (ii) the high quantum yields for bond-breaking[6], and (iii) the instability of the primary photochemical products (both non-oxidative and oxidative) to the radiation. It is therefore not surprising that although the photochemical mechanism at 185 nm may not be fundamentally different from that proposed[1] for the mid-u.v. region, the efficiency of these reactions is greatly enhanced.

The scope of the photoetching process at 185 nm as a method for the controlled milling of PET is under investigation.

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