

## Photochemical Reactions in a Commercial Poly(ether Sulfone)

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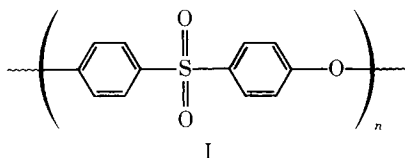
### Synopsis

A commercial poly(ether sulfone) has been examined by electronic spectroscopy, continuous photolysis, and laser flash techniques. The spectroscopic experiments indicate that the chromophoric species primarily responsible for light absorption in the region 290–350 nm is the diphenyl sulfone unit. The laser flash experiments give direct evidence of bond scission at the ether linkage on the polymer backbone.

### INTRODUCTION

Poly(ether sulfones) readily undergo deterioration in both appearance and physical properties on exposure to sunlight. The change in properties takes the form of the development of a yellow-brown discoloration and a marked reduction in tensile strength. Despite their poor light stability, however, the poly(ether sulfones) represent an important class of commercially useful polymers because of their high thermal stability.

Although several aspects of the mechanism responsible for photodegradation have received attention,<sup>1-4</sup> there is little information on the spectroscopic properties of the polymers and how these directly affect the formation of "macroradical" species within the polymer matrix. To this end, therefore, we report here a study of the electronic absorption and emission spectroscopy and the laser flash photolysis of a commercial poly(ether sulfone) of the following structure:



### EXPERIMENTAL

#### Materials

Samples of the poly(ether sulfone) (pressed out to a film 100  $\mu$  thick) and the starting material for its manufacture, 4,4'-dichlorodiphenyl sulfone, were supplied by I.C.I. Plastics Division.

### Apparatus

The ultraviolet absorption spectra were obtained using a Unicam SP800 spectrophotometer.

The luminescence spectra and phosphorescence lifetimes were obtained using a Hitachi Perkin-Elmer MPF-4 spectrofluorimeter.

The continuous photolysis experiments were carried out in a Xenotest-150 (45°C; 40% relative humidity).

The laser flash photolysis experiments were carried out using a frequency doubled ruby flash source (347 nm; 20 nsec), and the samples of polymer film were flashed using the same method as described in our recent work on a commercial MDI (diphenylmethane 4,4'-diisocyanate) elastomer.<sup>5</sup>

## RESULTS AND DISCUSSION

### Absorption and Emission Spectra

The absorption spectrum of the poly(ether sulfone) film showed no distinctive features except that the absorbance at wavelengths below about 330 nm increases markedly with decreasing wavelength (Fig. 1). The polymer is thus capable of absorbing much of the range of ultraviolet radiation present in sunlight that is known to be most damaging to light-sensitive commercial polymers (290–350 nm).<sup>1</sup>

Figures 2 and 3 show that the dichlorodiphenyl sulfone compound and the poly(ether sulfone) exhibit very similar fluorescence and phosphorescence spectra. It is also seen that both fluorescence and phosphorescence emissions have very similar excitation spectra, with maxima at about 320 nm. Further,

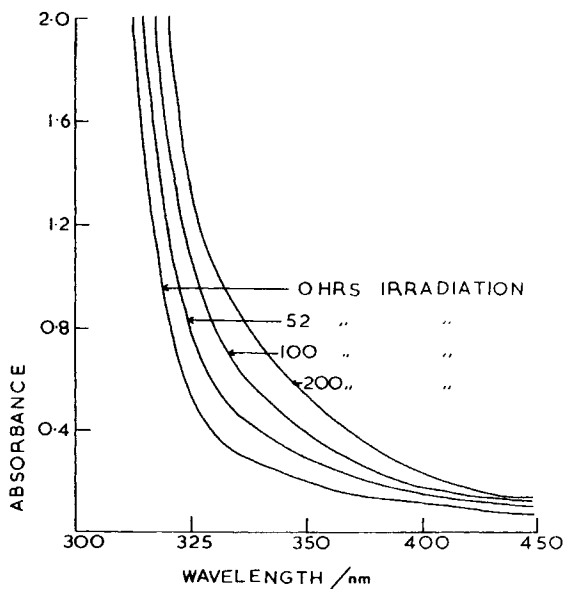
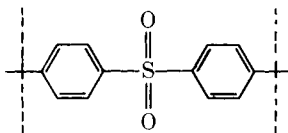


Fig. 1. Changes in ultraviolet absorption of the poly(ether sulfone) film (100  $\mu$ ) on photo-oxidation in the Xenotest-150.

no wavelength shift in the  $\lambda_{\max}$  values of the fluorescence or phosphorescence emissions was observed when the wavelength of the exciting light was varied.

These results indicate two important features concerning the absorption and emission properties of the polymer: (i) The same chromophoric species is responsible for both fluorescence and phosphorescence. (ii) The chromophoric species responsible is the diphenyl sulfone unit



and not some impurity species introduced into the commercial polymer during polymerization and/or processing, as in the case with many other commercially important synthetic polymers.<sup>6-8</sup>

The mean lifetime of the phosphorescence from the polymer was  $50 \pm 5$  msec, while that from the diphenyl sulfone compound was  $200 \pm 5$  msec. Although this indicates some difference between the polymer and the monomeric unit, the values obtained are nevertheless of a similar order of magnitude. Phosphorescence lifetimes are very sensitive to the nature of the environment of the emitting species,<sup>8</sup> and the environments of the diphenyl sulfone chromophores in the two experiments are quite different (polymer matrix and solid crystals, respectively, at 77°K; see legend for Fig. 3).

### Continuous Photolysis

Figure 1 shows that continuous photolysis of the polymer film under sunlight-simulated conditions results in a gradual increase in light absorption

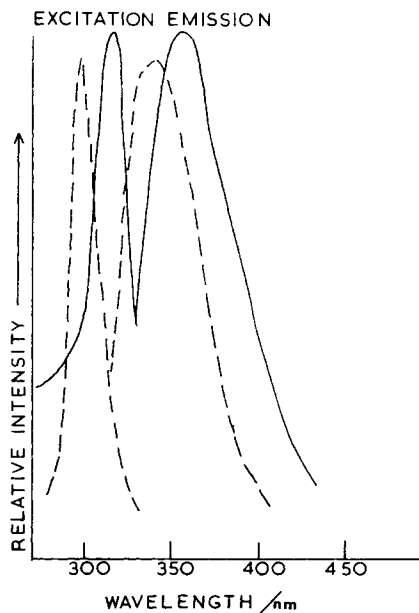


Fig. 2. Fluorescence excitation and emission spectra of (—) poly(ether sulfone) film and (---) 4,4'-dichlorodiphenyl sulfone in toluene at 300°K.

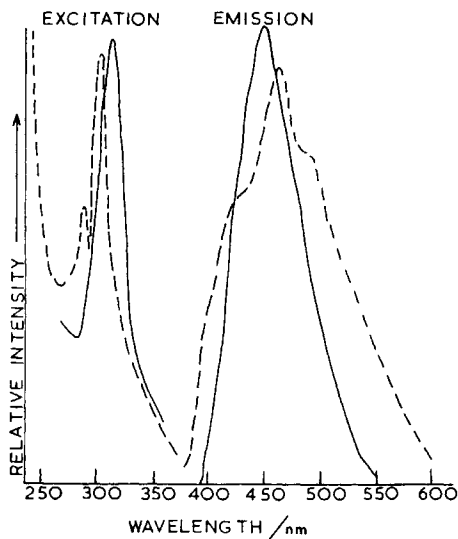


Fig. 3. Phosphorescence excitation and emission spectra of (—) poly(ether sulfone) film (---) 4,4'-dichlorodiphenyl sulfone crystals at 77°K.

throughout the near-ultraviolet region and extending into the visible region of the spectrum. This increasing absorption to longer wavelength thus accounts for the development of the yellow-brown discoloration that becomes apparent to the eye following prolonged irradiation of the film. The development of this discoloration is evidently due to the formation of a conjugated  $\pi$ -electron system.

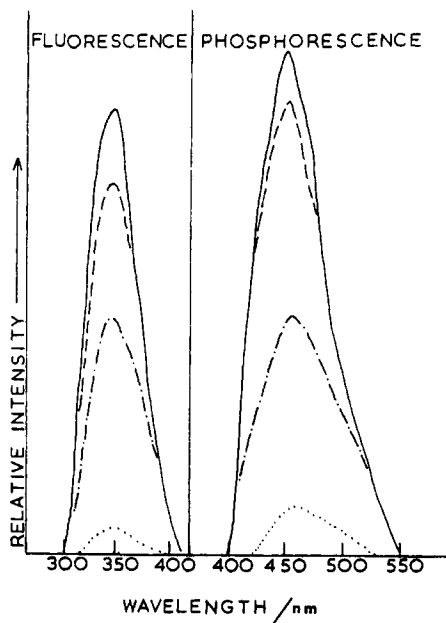


Fig. 4. Decrease in fluorescence and phosphorescence emission intensities after (—) 0 hr, (---) 52 hr, (- · - ·) 100 hr, and (.....) 200 hr of photo-oxidation in the Xenotest-150.

Figure 4 illustrates a further feature of the continuous photolysis experiments. It is seen that the intensity of both fluorescence and phosphorescence emissions gradually decreases with increasing irradiation time. Further, the rate of decrease is very similar; this observation is thus consistent with the conclusion above that both emissions are from the same chromophoric unit in the polymer. Although it is seen from the figure that the relative intensity of the emission is greatly decreased during irradiation, this decrease at the later stages is probably due more to screening or reabsorption effects by the strongly absorbing products rather than photochemical conversion of the diphenyl sulfone units.

### Laser Flash Photolysis

Figure 5 shows the end of pulse transient species formed on flashing the polymer film. The transient has  $\lambda_{\max}$  values at about 435, 465, and 605 nm and decays with a half-life of about  $5 \times 10^{-5}$  sec. ESR studies<sup>2-4</sup> have shown that bond scission can occur either at the phenyl-oxygen bond or at the phenyl-sulfone bond (see reaction scheme I). Chain scission at the former would result in the formation of phenoxy "macroradicals" along the polymer backbone. The spectra of two simple phenoxy radicals, taken from the work of Land and Porter,<sup>9</sup> are shown in Figure 5, and it is seen that they have the same basic features as those of the polymer transient. Interestingly, the absorption bands of the polymer transient display a distinct "red shift" compared with those of the simple phenoxy radicals. A similar "red shift" was observed in our recent laser flash work on an MDI elastomer when the corresponding "macroradical" and simple radical spectra were compared.<sup>5</sup>

The starting material 4,4'-dichlorodiphenyl sulfone was also flashed under a wide variety of conditions, but no transient species were observed. The lack

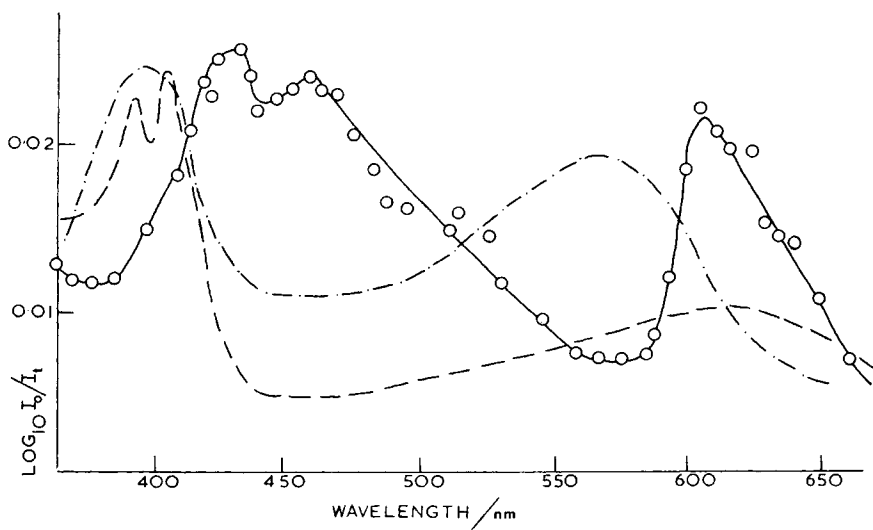


Fig. 5. End of pulse transient absorption observed on laser flash photolysis of poly(ether sulfone) film (100  $\mu$ ) (O) compared with (---) absorption spectrum of a phenoxy radical ( $\phi\text{O}\cdot$ ) in liquid paraffin and (-.-.-) absorption spectrum of a 2,4,6-triphenoxyl radical in 50% ethanol + 50% water.

of transient species from this compound is very significant to the above assignment of the polymer transient for the following reasons:

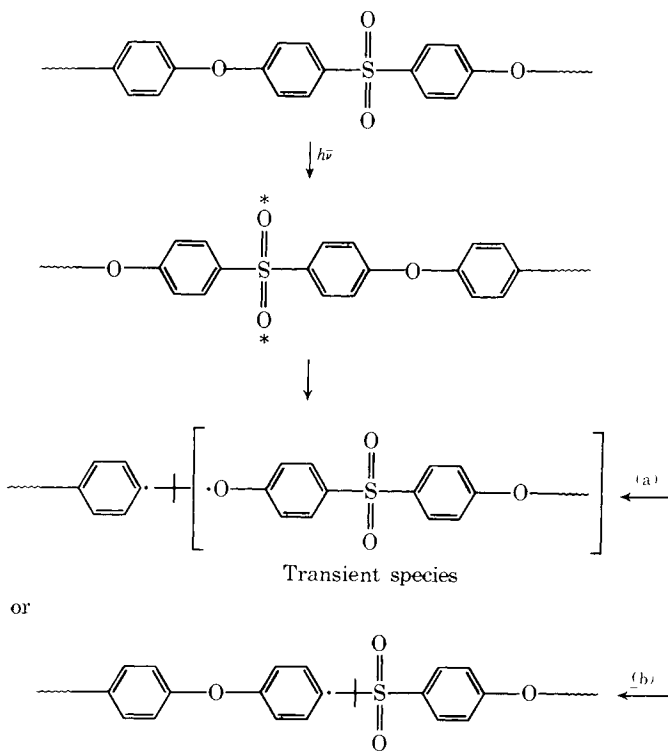
1. Although several bond-scission processes are possible with the diphenyl sulfone, and these may also occur in the polymer,<sup>2-4</sup> none gives rise to the formation of phenoxy radicals. In fact, unlike the polymer, the dichlorodiphenyl sulfone does not contain an ether linkage. Therefore, the transient observed on flashing the polymer must be due to chain scission at the phenyl-oxygen bond and not a combination of radical spectra through scission at other linkages.

2. The closely similar spectroscopic properties of the diphenyl sulfone and the polymer, section (a) in scheme I, indicate that some similarity may be expected in the absorption spectra of their photo-excited states.

Since no transients were detected in the range 400-650 nm with the diphenyl sulfone, this indicates that, even allowing for a "red shift" effect, the corresponding photo-excited states of the polymer do not absorb significantly in this wavelength region either.

### CONCLUSIONS

The spectroscopic experiments show that, unlike many other commercial polymers (polyolefins, polyamides, etc.)<sup>6-8,10</sup> whose instability to sunlight is due to the presence of photoactive impurities, the chromophoric species responsible for light absorption in the photoactive region of sunlight is the diphenyl sulfone unit which comprises the basic backbone structure of the polymer:



The laser flash photolysis experiments provide direct evidence for process (a) in reaction scheme I. They do not indicate that scission process (b) does not occur; indeed, there is sound ESR evidence to show that it does.<sup>2-4</sup> The experiments do suggest, however, that our laser flash photolysis apparatus was incapable of detecting the products formed from process (b).

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