

Photochemical Reactions in an MDI-Based Elastomeric Polyurethane

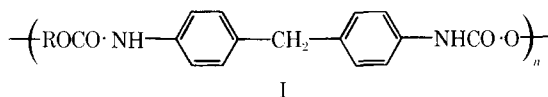
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Synopsis

Polyurethanes based on diphenylmethane 4,4'-diisocyanate (MDI) were examined by electronic spectroscopy and by continuous and laser flash photolysis. Fluorescence and phosphorescence emissions were observed, and although the source of the fluorescence could not be identified, the phosphorescence appears to originate from a benzophenone-type oxidation impurity. On laser flash photolysis, transient absorptions were observed at 375 nm and 580 nm. The latter is assigned to a ketyl radical center formed by hydrogen abstraction from the polymer matrix. Participation of these species in the photochemical reactions leading to deterioration of the MDI-based polyurethane is discussed.

INTRODUCTION

Polyurethanes prepared from aromatic diisocyanates and polyglycols and/or polyesters are known to undergo chemical reactions under the influence of light.¹⁻⁵ In the presence of air or oxygen and light, a marked change in properties takes the form of the development of a yellow-brown discoloration and a substantial amount of crosslinking coupled with a marked reduction in tensile strength. Polyurethanes synthesized with aromatic diisocyanates are more unstable to light than those synthesized with aliphatic diisocyanates.³ In particular, those commercial polyurethanes based on diphenylmethane 4,4'-diisocyanate (MDI) are the most unstable. Although the photodegradation of urethane polymers has received some attention, the light-induced reactions causing this effect are not clearly established. To this end we report here a study of the electronic spectroscopy and laser flash photolysis on several MDI-based thermoplastic block copolyester urethanes of the general structure I:



where R = aliphatic polyester residue or glycol residue.

EXPERIMENTAL

Materials

The MDI-based polyurethane films were obtained from various commercial manufacturers and, depending on the source, varied in thickness from 100 to 200 μ .

The benzophenone was purified by recrystallization from ethanol before use.

Apparatus

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

The fluorescence and phosphorescence spectra were recorded using a Hitachi Perkin-Elmer MPF-4 spectrofluorimeter. Phosphorescence lifetimes were obtained by coupling the sample intensity signal from the fluorimeter to a Tetrionix DM-64 storage oscilloscope.

The continuous photolysis experiments were carried out under simulated sunlight conditions (45% relative humidity; 40°C) using a Xenotest-150 supplied by Original Hanau, Quartzlampen G.m.b.H.

The laser flash photolysis apparatus is described elsewhere.⁶ The ruby laser (Laser Associates Model 501) was Q-switched by means of a Pockels cell and, after frequency doubling through a crystal of potassium dihydrogen phosphate, produced approximately 50 mJ pulses of 347 nm light with a half-peak width of about 20 ns. The absorption profiles and lifetimes of the transient species were recorded by mounting the polyurethane films at an angle of 45° to both excitation and monitoring light sources.

RESULTS

Absorption and Emission Spectra

All the polyurethane films examined had the same absorption and emission properties regardless of their origin of manufacture.

The absorption spectrum of the films showed no distinctive features except that the absorbance in the near-ultraviolet increased in intensity with decreasing wavelength (see Fig. 2). It was evident from their absorption spectra that the films were capable of absorbing the ultraviolet radiation present in sunlight that is damaging to most commercial polymers (290–350 nm).⁷

In contrast to their absorption spectra, the films exhibited quite distinctive fluorescence and phosphorescence emission spectra. The results obtained from a typical film are summarized in Table I. First, it is seen that the excitation wavelength maxima (λ_{max}) are different for fluorescence and phosphorescence, indicating that the same light-absorbing species cannot be responsible for both emissions. Second, while the fluorescence spectrum showed only a single wavelength maximum at about 420 nm, the phosphorescence spectrum exhibited vibrational structure in the region of 420 to 500 nm. From the examination of a number of films, values of $1621 \pm 10 \text{ cm}^{-1}$ and 20 ± 2 msec were obtained for the vibrational splitting and lifetime of the latter emission. The vibrational splitting is of a similar magnitude to that of an aromatic carbonyl group.⁸ Indeed, except for a distinctive "red shift," which will be considered later, the phosphorescence emission from the polyurethane films was found to be remarkably similar to that of benzophenone⁹ (Fig. 1, Table II).

TABLE I
Typical Luminescence Spectra from an MDI-Based Polyurethane

Excitation λ , nm	Emission λ , nm
Fluorescence	
350	420
372 max	420
390	420
Phosphorescence	
300	423,454.5,489
320 max	423,454.5,489
350	423,454.5,489

Continuous Photolysis

Figure 2 shows that on continuous photolysis under sunlight-simulated conditions, a gradual increase in light absorption in the near-ultraviolet developed. After about 50 hr of irradiation, this absorption had extended into the visible region of the spectrum (400–700 nm). This spectral shift to longer wavelengths could thus account for the yellow-brown discoloration that gradually develops with longer periods of irradiation. For example, after 400 hr of irradiation, the discoloration of the film was clearly evident to the eye.

During the period of continuous photolysis, attempts were made to monitor any change in the fluorescence and phosphorescence spectra of the irradiated film. It was found that after about 25 hr of irradiation, virtually all the fluorescence emission had disappeared while relatively little change had occurred in the phosphorescence. With longer periods of irradiation, a gradual

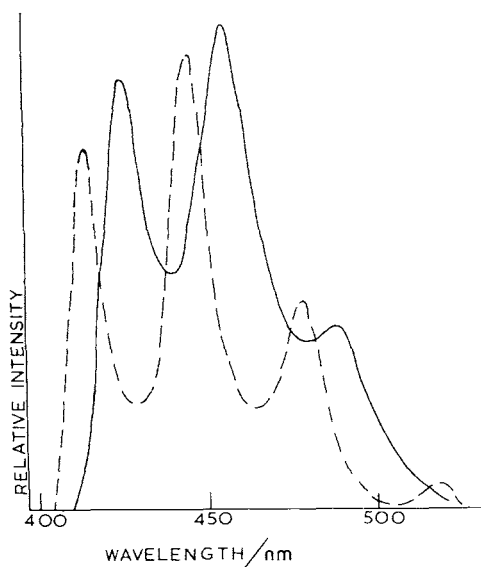


Fig. 1. Phosphorescence emission spectra of (—) on MDI-based polyurethane film and (- - -) benzophenone in 2-propanol (77°K). Excitation λ = 325 nm; band width = 2 nm.

TABLE II
Wave Numbers of Peaks in the Phosphorescence Emission Spectra of an MDI-Based Polyurethane and Benzophenone

	λ , nm	ν , $\text{cm}^{-1} \times 10^2$	$\Delta\nu$, $\text{cm}^{-1} \times 10^2$
Polyurethane	423.0	23.64	} 16.21 ± 10
	454.5	22.01	
	489.0	20.45	
Benzophenone	414.5	24.12	} 16.12 ± 10
	445	22.47	
	479	20.88	
	517	19.34	

decrease in the phosphorescence intensity was observed, but this change became difficult to monitor satisfactorily as the yellow-brown discoloration of the film developed. For example, no phosphorescence was observed from the 400-hr-irradiated film shown in Figure 2.

Laser Flash Photolysis

Figure 3 shows that two transient species were observed, with λ_{max} values of about 375 and 580 nm, respectively. Both decayed with half-lives of about 5×10^{-6} sec. Following our observation that the light-absorbing species responsible for the phosphorescence could be aromatic carbonyl in character, it is seen from the figure that, apart from a "red shift" (also noted above), the spectrum of the longer wavelength transient is similar to that of the ketyl radical observed from the flash photolysis of benzophenone.¹⁰

On repeatedly flashing the same area of polymer film, a further interesting feature can be seen from Figure 3. While the transient at 375 nm has almost

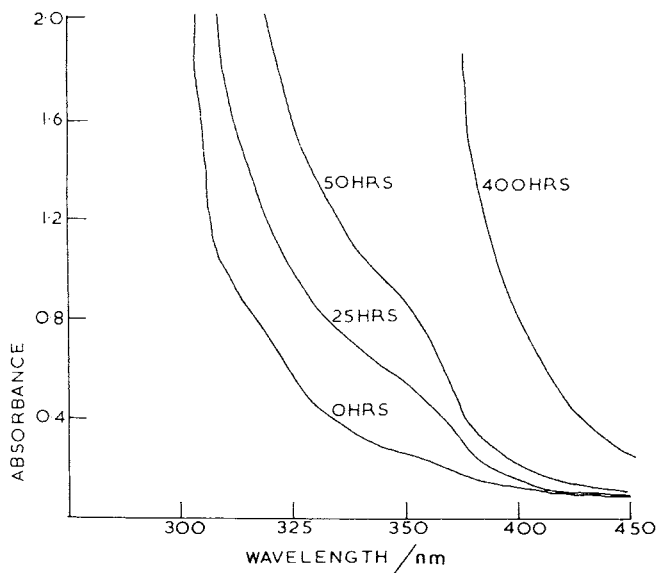


Fig. 2. Changes in the ultraviolet absorption of an MDI-based polyurethane film (200 μ) on photo-oxidation in the Xenotest-150.

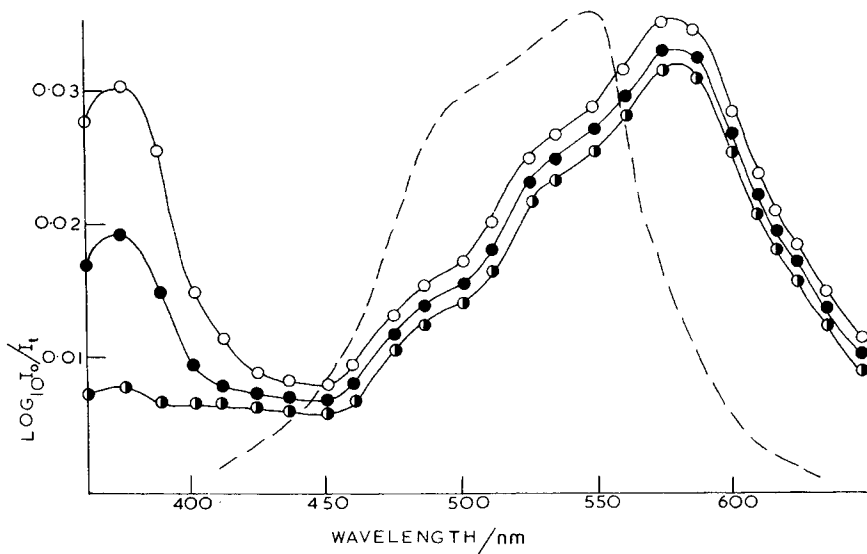


Fig. 3. End of pulse transient absorption observed on laser flash photolysis of an MDI-based polyurethane film (200 μ thickness): (O) after one flash; (●) after two flashes; (◐) after three flashes; (- - -) absorption spectrum of the benzophenone ketyl radical in alcoholic solution.¹⁰

disappeared after only three flashes, the transient at 580 nm is still clearly observed. This effect suggests that the two transients are formed from different light-absorbing species in the polymer film.

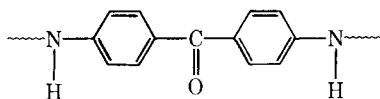
DISCUSSION

The luminescence experiments clearly demonstrate the presence of at least two distinct chromophoric species in commercial MDI-based polyurethane films. The λ_{\max} values of their excitation spectra also indicate both are capable of absorbing light in the near-ultraviolet region of the spectrum, i.e., 300 to 400 nm. Other nonluminescent chromophoric species may be present in the polymer film. Here, however, we shall restrict our discussion to the photochemical reactions involving the two luminescent species of whose existence we can be confident.

Since the fluorescence at 420 nm lacks any significant structure, there is little we can conclude as to the identity of the species responsible for this emission. However, the continuous photolysis experiments show the species to be highly fugitive to light since virtually all the emission had disappeared after only 25 hr of irradiation. Further, since an exposure time of about 50 hr was required to produce any significant change in the visible region of the spectrum (Fig. 2), it seems unlikely that it participates directly in the photochemical reactions responsible for discoloration. We cannot exclude the possibility that any products arising from photolysis of the fluorescent species may contribute to the discoloration, but from the evidence considered below the phosphorescent species appears a more likely initiator.

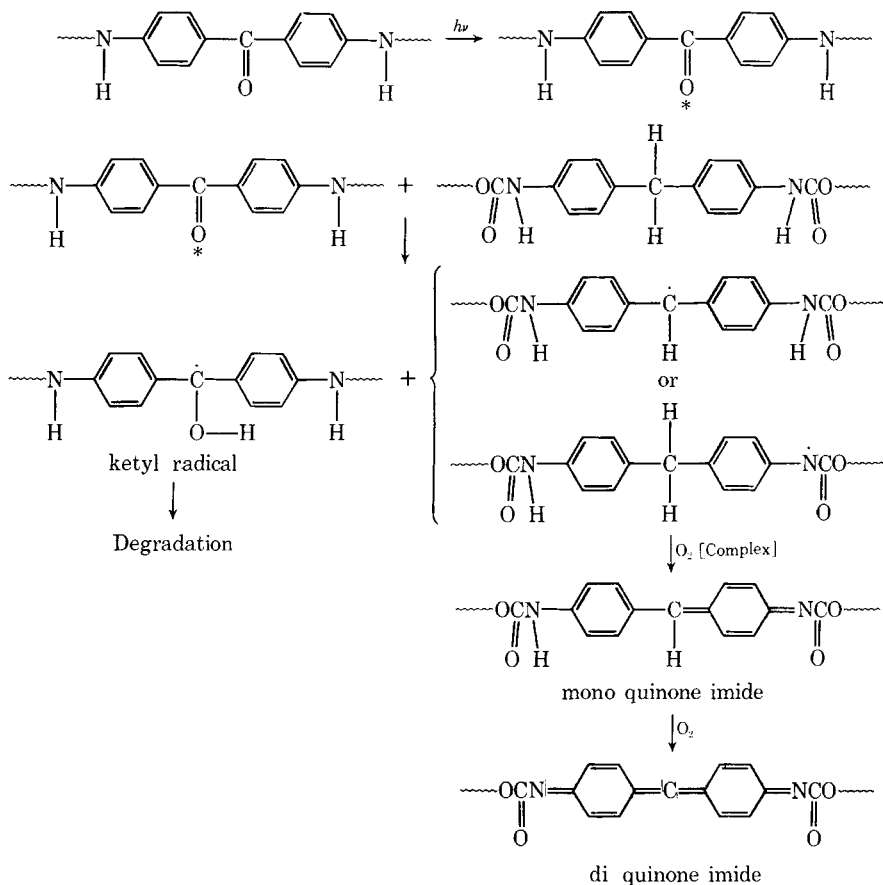
The magnitude of the vibrational splitting of the phosphorescence spectrum strongly suggests that the emission is from the triplet state of an aromatic carbonyl group (or groups) present as impurities in the polymer. The

“red shift” of the spectrum, evident when it is compared to that of benzophenone (Fig. 1), may be attributed to the presence of substituents in the para positions of the benzene rings.¹¹ For example, we can readily envisage that an impurity chromophoric species such as



may be responsible for the emission, and that this impurity could be formed as a result of oxidation of the methylene group of the MDI unit at some stage in the manufacture of the polymer or MDI. A further point consistent with this argument is that when we examined other polyurethanes made from toluene diisocyanate and isophorone diisocyanate, but containing a polyester or glycol component of the type normally used with the MDI polyurethanes, both exhibited weak phosphorescence at about 450 nm, but neither gave a distinctive structured spectrum like that in Figure 1.

The presence of such an aromatic carbonyl impurity in the MDI-based film now enables us to conclude that the transient species at 580 nm is most probably a ketyl radical center formed by the carbonyl impurity in its photoactive



triplet state abstracting a hydrogen atom from the surrounding polymer matrix. An analogous primary photochemical process is responsible for the benzophenone-sensitized degradation of other commercial polymers such as the polyolefins.^{12,13} Further, the spectrum of this ketyl radical center is "red shifted" compared to that of the ketyl radical formed from benzophenone; again, this is presumably due to the presence of substituents in the para positions of the benzene rings.

Finally, our continuous photolysis experiments indicated that the onset of the yellow-brown discoloration only becomes apparent with the consumption of the phosphorescent carbonyl species. In reaction scheme on page 1446, we outline how an interchain hydrogen atom abstraction process involving this species could result in the formation of a ketyl radical center which could itself undergo further reactions of a degradative nature to the polymer. In the scheme, we also indicate how the same hydrogen atom abstraction process could initiate color development by complex oxidation reactions resulting in the extension of quinonoid-type conjugation along the polymer chain.³

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