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Photodegradation of Polyimides. 5. An Explanation of the Rapid Photolytic Decomposition of a Selected Polyimide via Anhydride Formation

C. E. Hoyle,*,† E. T. Anzures,† P. Subramanian,‡ R. Nagarajan,† and D. Creed‡

Department of Polymer Science, University of Southern Mississippi,
Hattiesburg, Mississippi 39406-0076, and Department of Chemistry and Biochemistry,
University of Southern Mississippi, Hattiesburg, Mississippi 39406-5043

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ABSTRACT: The photolytic decomposition in air of a polyimide film based on a dianhydride and a diarylamine with hexafluoroisopropylidene 6F bridging groups is extremely rapid, leading to efficient chain cleavage and subsequent photooxidative decomposition. Only relatively short photolysis times with an unfiltered medium-pressure mercury lamp are required to give a clean photoablation of the 6F–6F polyimide films in air. IR difference spectroscopy shows the appearance of anhydride groups on photolysis in air, indicating a photooxidation process via decomposition of the arylimide linkage. A photophysical and photochemical analysis of several model *N*-arylphthalimides indicates that both solvent polarity and electron-withdrawing/donating substituents can greatly alter the efficiency of the photolysis process. The formation of the triplet state is also dependent on the substituents and solvent polarity. In general, an increase in the CT character of the excited state by either substituent or solvent effects leads to a reduction in both the photolysis and intersystem crossing quantum yields.

Introduction

In a recent series of papers, we reported the result of an extensive investigation of the photodegradation of aryl polyimides.[1-5] The polyimides studied were based on a variety of dianhydrides with oxydianiline (ODA) and methylenedianiline (MDA). In all of the polyimides investigated in our laboratory to date, work has focused on the effect of a bridging group such as carbonyl, oxygen, or hexafluoroisopropylidene on the inherent photostability of the polyimide structure.[1-5] In general, we find that replacement of the pyromellitic dianhydride (PMDA) used to generate, along with oxydianiline (ODA), the PMDA–ODA polyimides [which are the basis of the high-temperature-resistant arylimide films known as Kapton (DuPont)] with the 6F dianhydride leads to a lowering of resistance to light exposure from the unfiltered output of a medium-pressure mercury lamp. The photooxidative stability of the PMDA–ODA polyimide film may be related in part to the charge-transfer nature[6-12,14] of the excited state as well as the effect of the pyromellitimide moiety on the stability of reactive intermediates formed. Since the pyromellitimide group is a strong electron acceptor, it is not unreasonable to suspect that the strong charge-transfer excited state formed could alter both the radiative and nonradiative reactivities of the excited state. In addition, the dark reactions subsequent to primary photochemical events may be altered by differences in the components comprising the basic arylimide unit.

In the present paper, we focus attention on the nature of the electron donor properties of the diamine portion of the polyimide. We find that by altering the substituents on the aryl moiety of model *N*-arylphthalimides, both photophysical properties such as absorption and emission maxima, triplet yields, and chemical properties such as photoproduct formation, are greatly altered. The effect of electron-donating and electron-withdrawing bridging groups on the diamine part of a hexafluoroisopropylidene (6F) dianilinyl dianhydride based polyimide will be discussed in relation to the model compounds and with respect to the ultimate photolability of the polymer film.

Experimental Section

All solvents were obtained from Burdick and Jackson and used as received. Model compounds were synthesized by a procedure analogous to that described in the previous paper in this series.[5] Elemental analysis performed by Galbraith Laboratories was in excellent agreement for each model compound. The polyimide synthesis and film preparation have already been described thoroughly.[1-5] Polymer film photolysis was conducted with an unfiltered 450-W Canrad Hanovia medium-pressure mercury lamp in air or nitrogen, as appropriate. The films were placed approximately 9 cm from the lamp, and no attempt to measure the flux of the unfiltered broad-band light source was made for this phase of the investigation. The intensity of the source did not vary greatly between runs. This allows for relative, but not absolute, rate comparisons. Gel permeation chromatography was performed for all polymers with a THF mobile phase on a Waters system using 100-, 500-, 10^4-, and 10^5-Å columns. All molecular weights are reported relative to polystyrene standards. For model compound quantum yield measurements, band-pass filters were used to isolate a specific line from a medium-pressure mercury lamp. Samples were irradiated in a 1-cm path-length cell, and the light intensities were determined by ferrioxalate actinometry. Product formation was followed by comparison of gas chromatography retention times with those of authentic samples. Details are given in the previous paper in this series.[5]

A Perkin-Elmer 1600 Fourier transform infrared (FT-IR) spectrometer was used for recording infrared spectra. UV spectra were obtained on a Perkin-Elmer Lambda 6 UV-vis spectrophotometer. Fluorescence spectra were obtained on a Spex Fluorolog-2 with 1.5-mm slits.

The laser flash photolysis experiments were carried out in a unit consisting of a Lumonics HyperEX 440 excimer laser excitation source and an Applied Photophysics xenon lamp/monochromator/PMT monitoring system. The signal from the PMT is sent to a Phillips Model PM 3323 programmable digital oscilloscope. Data are transferred from the oscilloscope to an Archimedes desktop computer (Acorn Computers Ltd., U.K.) via the IEEE-488 instrument interface bus, which also sends control to the digital oscilloscope and LASER software package. The xenon lamp monitoring source (right-angle arrangement) was momentarily pulsed to achieve a high-intensity monitoring beam that was of near constant intensity for about 200 μs. The laser was operated at 248 nm (KrF*) for direct excitation and

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† Department of Polymer Science.
‡ Department of Chemistry and Biochemistry.

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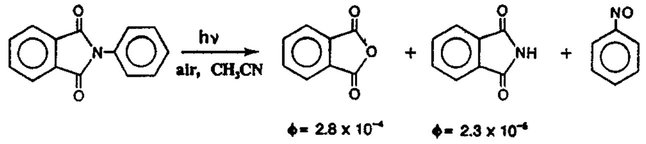
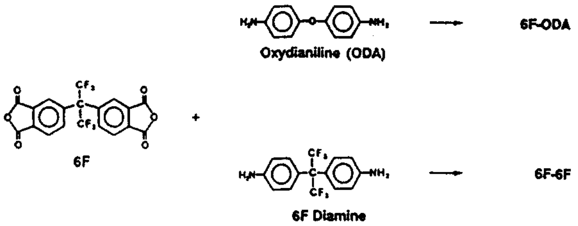
Scheme I



351 nm (XeF*) for benzophenone-sensitized experiments. Nominal outputs were 80 mJ/pulse at 248 nm and 60 mJ/pulse at 351 nm. In the laser flash photolysis experiments, all samples were contained in a 1-cm × 1-cm × 4-cm quartz fluorescence cell. In order to ensure oxygen-free samples, solutions were bubbled with nitrogen prior to the experiment. All the solutions had absorbances of approximately 1.0 at the wavelength of excitation. The data analysis system is a complete data acquisition and analysis system for the Applied Photophysics LKS.50 laser flash photolysis spectrometer. Time-resolved absorption spectra of transient intermediates were compiled from the individual wavelength encoded kinetic data files using Applied Photophysics software. Extinction coefficients of the triplet states were determined by the energy-transfer method from benzophenone, as described by Carmichael and Hug.[13] Absolute intersystem crossing quantum yields (Φ_{ISC}) were determined relative to benzophenone (Φ_{ISC} = 1.0) by laser flash photolysis at 248 nm.

Results and Discussion

The results will be presented in three parts. In the first part, we consider the effect of substituents in the para position of *N*-arylphthalimides on the resulting photochemistry and photophysics in air-saturated solutions. In addition, the spectroscopic and photolytic consequences of the polarity of the solvent on the photolysis process of *N*-phenylphthalimide (designated PA–A) are presented. On the basis of these results, the rapid photolytic degradation of polyimide films made from the hexafluoroisopropylidene-containing dianhydride (6F dianhydride) shown below and two dianilines with oxygen and hexafluoroisopropylidene (6F diamine) bridging groups (see structures and the appropriate designations for the polymers) is interpreted.



Photophysics and Photochemistry of *N*-Arylphthalimides. In a previous report,[5] we showed that photolysis of *N*-phenylphthalimide (PA–A) in an air-saturated acetonitrile solution resulted in the formation of phthalic anhydride and phthalimide as identifiable primary photoproducts (Scheme I) in a ratio of about 10:1. Although we could not obtain absolute identification, we have circumstantial evidence for the formation of nitrosobenzene as a primary product: nitrobenzene was identified and probably forms from the efficient photooxidation of nitrosobenzene. As indicated in Scheme I, the quantum yields for product formation in air-saturated acetonitrile are relatively low. However, they are reasonable values when compared to the extremely low yields for product formation of bis(*N*-arylpyromellitimides): the quantum yield for disappearance of bis(phenylpyromellitimide) is estimated to have a lower value in acetonitrile. The stability of the pyromellitimide may result, in part, from the significant charge-transfer character of the excited states. PA–A thus serves as a reasonable model for the repeat unit in 6F–ODA which does not possess as strong an electron acceptor as the pyromellitimide group of PMDA–ODA polyimides.

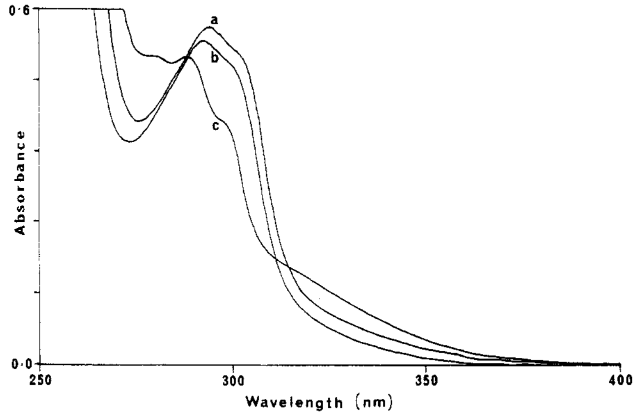


Figure 1. Absorption spectra of PA–A in several solvents: (a) 3.6×10^{-4} M in cyclohexane; (b) 3.7×10^{-4} M in CH_2Cl_2; (c) 3.8×10^{-4} M in CH_3CN.

We know that increasing the electron-accepting ability of the dianhydride-based portion of the imide repeat unit results in increased photostability of the polymer as well as a shift in the charge-transfer absorption band to the red accompanied by a decrease in the energy of charge-transfer emission. We might expect that altering the electron-donating ability of the aromatic diamine based portion of the polyimide repeat unit might well result in changes in spectroscopic (absorption, emission) and photochemical properties of the repeat unit. We might also expect that any changes in the polarity of the environment (e.g., solvent) in which the polyimide repeat unit, or an appropriate model compound, is located should also alter the spectroscopic and photochemical properties. Thus, by exploring the effect of the electron-donating ability of the *N*-aryl groups and the effect of solvent polarity, it should be possible to better define factors which lead to photoreactivity in the polyimide.

We begin by exploring the effect of solvents on the absorption and fluorescence spectra of *N*-phenylphthalimide (PA–A). The absorption spectra of PA–A in acetonitrile (ϵ = 37.7), dichloromethane (ϵ = 9.08), and cyclohexane (ϵ = 2.023) above 260 nm have two features worthy of note (Figure 1). There is a structured band at higher energies and absorption tailing above 350 nm. The absorption characteristics of PA–A and its response to solvent polarity are probably complicated, involving both conventional transitions and charge-transfer states, all of which are subject to solvent effects. Evidence for a charge-transfer (CT) excited state in PA–A comes from the broad structureless fluorescence of PA–A (Figure 2) that is red shifted from 505 to 530 to 540 nm as the solvent becomes more polar in changing from cyclohexane to dichloromethane to acetonitrile. The large Stokes shift between the absorption and emission spectra suggests this CT state has a geometry quite different from that of the vertical or Franck–Condon state formed at the instant of excitation. This relaxed CT state may be a twisted intramolecular CT state of the type proposed for (*N*,*N*-dimethylamino)-benzonitrile[14] and suggested by Frank et al.[10-12,14] to perhaps be partly responsible for the fluorescence of polyimides. In addition to being red shifted, this fluorescence becomes much weaker in acetonitrile presumably because it is increasingly solvent stabilized. Its energy is lowered, and nonradiative decay competes more effectively with fluorescence.

In considering rate processes affected by the solvent polarity, the intersystem crossing from the singlet to the

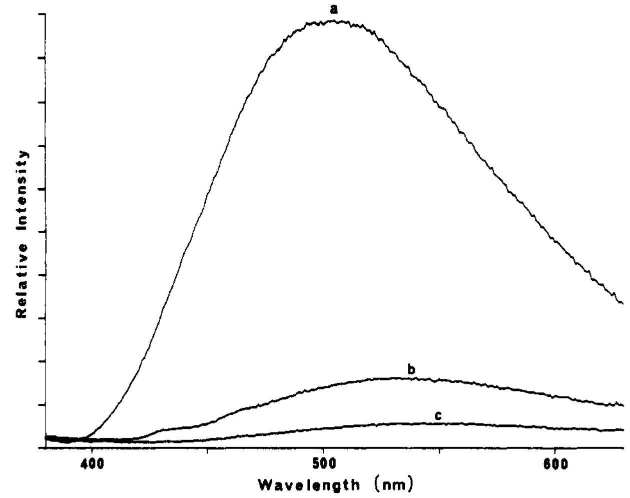


Figure 2. Fluorescence spectra (λ_{ex} = 325 nm) of PA–A in several solvents: (a) 1.49×10^{-3} M in cyclohexane; (b) 1.51×10^{-3} M in CH_2Cl_2; (c) 1.54×10^{-3} M in CH_3CN.

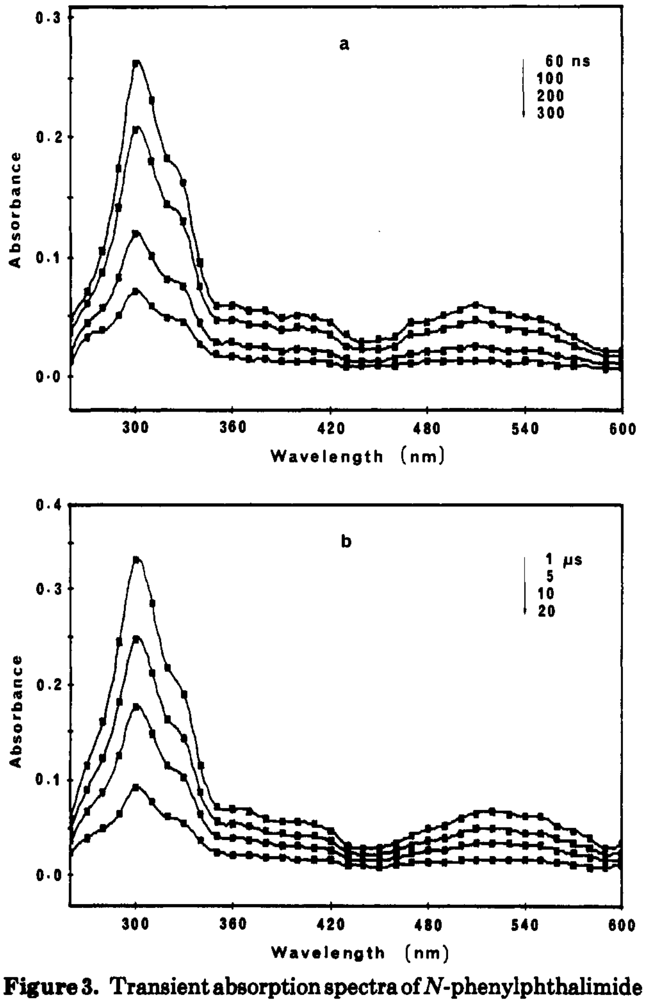


Figure 3. Transient absorption spectra of *N*-phenylphthalimide in cyclohexane at different time intervals after the flash: (a) air saturated; (b) nitrogen saturated.

Table I
Quantum Yields, Triplet Yields, and Fluorescence Emission Maxima of *N*-Phenylphthalimide in Different Solvents

solvent	Φ_{loss}[a]	Φ_{PhAnh}[a]	Φ_{ISC}[b]	fluorescence λ_{max},[c] nm
acetonitrile	6.3×10^{-4}	2.8×10^{-4}	0.03	540
dichloromethane	8.2×10^{-4}	3.2×10^{-4}	0.04	530
cyclohexane	9.3×10^{-3}	5.0×10^{-3}	0.17	505

[a] ±20%. λ_{ex} = 313 nm. [b] ±20% relative to benzophenone (Φ_{ISC} = 1.0). [c] λ_{ex} = 325 nm.

triplet excited state should be considered. Transient absorption spectra are formed by 248-nm excitation of PA–A. Figure 3 shows the transient absorption spectra of PA–A in air- and nitrogen-saturated cyclohexane solution. Similar transients were obtained in dichloromethane and acetonitrile solutions. The transient absorption spectra under nitrogen are characterized by two higher energy peak maxima at approximately 300 and 330 nm and a broad absorption band centered around 500 nm. Decay constants obtained by fitting the decay of the transient spectra to a single exponential decay function are about 8.5×10^4 s^{-1} at wavelengths from 300 to 500 nm for a nitrogen-saturated PA–A solution. All of the structural features decay with approximately the same exponential rate constant; i.e., all have a lifetime of approximately 11.5 μs. This is quite consistent with decay of a single transient species with strong absorption at 300–330 nm and weaker absorption at 470–530 nm.

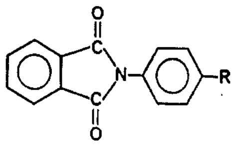
In attempting to identify the transient species responsible for the absorption bands in Figure 3, we first note that oxygen effectively quenches all of the structural features uniformly (Figure 3a). This suggests that the transient arises from either a radical species, which is efficiently quenched by oxygen, or a triplet state. Addition of low concentrations of cyclohexadiene (1×10^{-3} M or less) results in the uniform lifetime quenching of all transient peaks in a nitrogen-saturated dichloromethane solution of PA–A. A Stern–Volmer plot of the ratio of the transient lifetime before and after adding quencher as a function of the cyclohexadiene concentration is linear and the slope affords an essentially diffusion-controlled quenching rate constant of 6.0×10^9 L mol^{-1} s^{-1}. This is reasonable for quenching of a triplet state by cyclohexadiene, which has a lowest triplet state with an energy of only 54 kcal/mol. If the transient spectra resulted from a radical or biradical species, a diffusion, or near diffusion, controlled quenching rate would certainly not be expected. Results of both oxygen and cyclohexadiene quenching experiments suggest that the transient spectra in Figure 3 are due to a triplet intermediate with a lifetime of 11.5 μs. Further evidence that these spectra are due to the triplet state of PA–A comes from benzophenone sensitization experiments. The transients can also be generated by 351-nm excitation of benzophenone in the presence of PA–A, under conditions where PA–A is not directly excited. This energy-transfer quenching of benzophenone triplet can be used to determine the extinction coefficients[13] of PA–A in different solvents. The quantum yield of intersystem crossing (Φ_{ISC}) was then determined relative to benzophenone (Φ_{ISC} = 1.0) using the 248-nm laser pulse. We find that Φ_{ISC} in cyclohexane is much greater than in dichloromethane or acetonitrile (Table I). This result nicely parallels the red shifts and reductions in intensity of fluorescence observed (Figure 2) in going from cyclohexane to the two more polar solvents. Presumably, solvent stabilization of the relaxed CT state accelerates nonradiative decay processes, thereby reducing the probability of intersystem crossing to the triplet as well as the probability of fluorescence.

It is of interest to consider that the polarity of the solvent might have a significant effect on the product yields. Photolysis of PA–A was therefore conducted using the 313-nm line of a medium-pressure mercury lamp. The light intensity was measured with ferrioxalate actinometry, and the product yields and loss of reactant were determined by gas chromatographic analysis of the samples photolyzed in different solvents. The quantum yields for disappearance (Φ_{loss}) and the quantum yields for phthalic anhydride formation (Φ_{PhAnh}) in air-saturated solutions are given in Table I as well as fluorescence emission maxima and triplet yields. Only results for the primary photooxidation product quantum yield are given. The most noticeable result is the increase in product quantum yield, disappearance yield, and triplet yield in cyclohexane, a nonpolar solvent. Since the major products formed in cyclohexane are identical to those in acetonitrile, no significant alteration in the mechanism for decomposition is indicated. The high quantum yield for reactant loss in cyclohexane may result from changes in the population and nature of the excited state as well as effects of a nonpolar solvent on processes subsequent to the primary photochemical reaction.

It is worth considering the effect of solvent on the relative population of excited states. At 313 nm, the wavelength of excitation in the quantum yield experiments, there is the possibility of absorbance due to both conventional transitions as well as a charge-transfer transition. The solvent polarity may well alter the absorbing states at the 313-nm excitation wavelength, as well as the related excited-state energy and the processes occurring from the relaxed state or states. Subsequent dark reactions may also be subject to solvent effects. For purposes of this paper, we simply note that the solvent alters the quantum efficiency of the photooxidation process significantly. Differentiation between and quantitation of the various factors which solvent polarity can affect, as well the spin multiplicity of the precursor excited state leading to product formation, will be covered in a separate paper. Since multiple states are involved in the absorption process, wavelength-dependent photochemistry is possible and will be explored.

Having established the effects of reduced solvent polarity (a blue shift in the emission wavelength and an increase in triplet formation and product yield), we investigated the effect of para substituents on the spectroscopic/photochemical properties of *N*-phenylphthalimide (see structures and appropriate designations).

R	Designation
H	PA-A
OPh	PA-POA
CN	PA-CNA
Cl	PA-ClA



The absorption and emission spectra are given in Figures 4 and 5. The absorption spectra are complex and difficult to interpret although the quite different absorption spectrum of PA–POA is almost certainly due to the additional conjugation afforded by the phenoxyaryl moiety. The fluorescence maxima (Table II) leave no doubt that the relaxed CT state is stabilized by electron-donating groups (e.g. PhO–) on the *N*-aryl group and destabilized by electron-withdrawing groups (e.g. CN) in the same position. Thus, the phenoxy substituent shifts the emission to the red of that of PA–A (the emission also becomes very weak) and the cyano group shifts it to the blue. The *N*-aryl group, not surprisingly, is the donor component in the CT state! The effect of reducing CT stabilization by changing the *N*-aryl substituent from PhO to H to CN roughly parallels the effect of reducing solvation of the CT state by changing the solvent for PA–A fluorescence from acetonitrile to dichloromethane to cyclohexane.

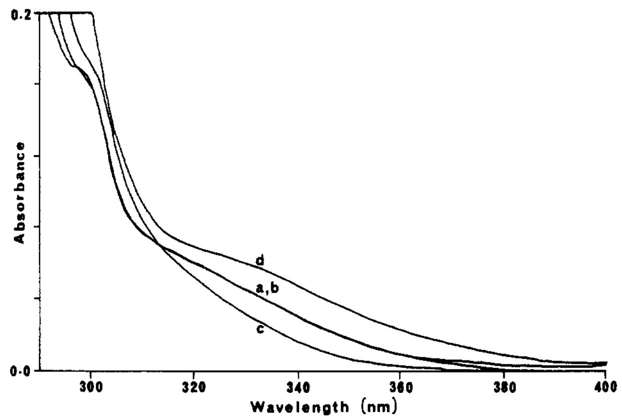


Figure 4. Absorption spectra of *N*-arylphthalimide model compounds in cyclohexane: (1) 1.56×10^{-4} M, PA–A; (b) 1.54×10^{-4} M, PA–ClA (c) 1.45×10^{-4} M, PA–CNA; (d) 1.52×10^{-4} M, PA–POA.

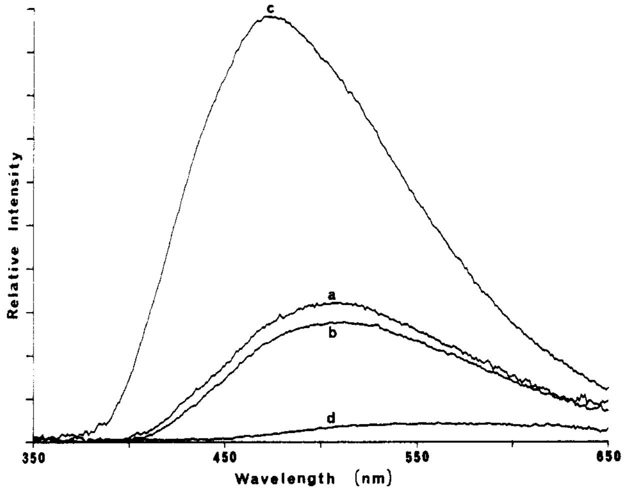


Figure 5. Fluorescence spectra ($\lambda_{ex} = 325$ nm) of *N*-arylphthalimide model compounds in cyclohexane: (a) 1.56×10^{-4} M, PA–A; (b) 1.54×10^{-4} M, PA–ClA (c) 1.45×10^{-4} M, PA–CNA; (d) 1.52×10^{-4} M, PA–POA.

Table II
Fluorescence Emission Maxima, Quantum Yields, and Triplet-Yields of Substituted *N*-Phenylphthalimides

compd	fluorescence λ_{max},[a] nm	Φ_{loss}[b]	Φ_{PhAnh}[b]	Φ_{ISC}[d]
PA-A	505 (538)	8.2×10^{-4}	5.2×10^{-4}	0.04
PA-POA	550 (too weak)	8.8×10^{-5}	1.4×10^{-5} [c]	0.02
PA-ClA	525 (546)	8.3×10^{-4}	2.8×10^{-4}	[e]
PA-CNA	470 (513)	1.3×10^{-2}	5.5×10^{-3}	0.16

[a] Determined in cyclohexane. $\lambda_{ex} = 325$ nm. Similar trend noted (in parentheses) when determined in dichloromethane, except maxima are shifted and lower in intensity. [b] ±20%. Except where noted, determined in dichloromethane. $\lambda_{ex} = 313$ nm. [c] Determined in acetonitrile. $\lambda_{ex} = 313$ nm. [d] ±20% in dichloromethane relative to benzophenone ($\Phi_{ISC} = 1.0$). [e] Not determined.

The disappearance quantum yields (Φ_{loss}) and quantum yields for phthalic anhydride formation (Φ_{PhAnh}) upon photolysis at 313 nm are also given in Table II. The phenoxy substituent leads to a decrease in the disappearance quantum yield by about 1 order of magnitude, while the electron-withdrawing cyano group has the opposite effect. In addition, the triplet yields in dichloromethane in Table II also show an increase for the cyano group, paralleling the increased starting material disappearance and product formation quantum yields. Again, the substitution of electron-withdrawing groups at a para position appears to have the same effect as decreasing solvent polarity on both triplet and product yields. The magnitudes of the increase are, however, not the same for both. The large difference in product quantum yield

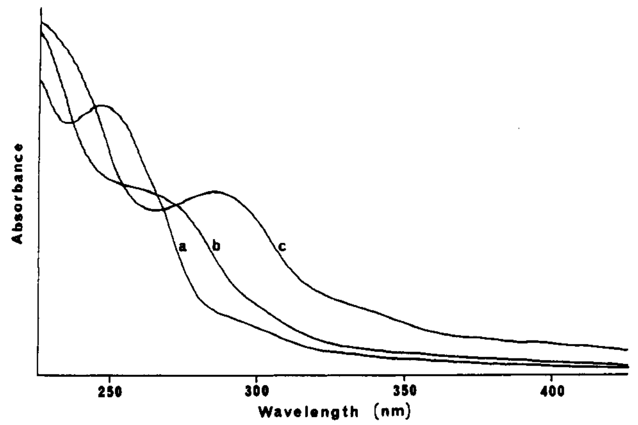


Figure 6. Absorption spectra of thin polyimide films on a quartz slide: (a) 6F–6F; (b) 6F–ODA; (c) PMDA–ODA.

between PA–POA and PA–CNA is dramatic: about 2 orders of magnitude! Thus, the effect of electron-donating and -withdrawing groups and their role in the nature and reactivity of the excited state, as well as any effect they have on subsequent dark reactions, must be taken into account in the photooxidation of polyimides. Since the primary reaction of the excited *N*-arylphthalimides may be an α-cleavage of the N–CO bond to give a diradical which can react with oxygen,[5] the rate of diradical ring closure versus interception by oxygen could well be affected by the substituents.

Photolysis of Polyimide Films Based on 6F Dianhydride. We have established that the electron-donating/withdrawing effects of para substituents can significantly alter the photochemical and spectroscopic properties of *N*-arylphthalimides. It is therefore reasonable to speculate that the chemical structure of the diamine moiety might have a profound effect on the resultant photochemistry of polyimide films. We have already reported[1–4] that any structural feature which alters the electron-accepting ability of the dianhydride-based chromophore (termed the acceptor) can markedly alter the photodecomposition of the polyimide film. For example, replacement of pyromellitic dianhydride by the 6F dianhydride results in a dramatic decrease in the photooxidative stability of the resultant polyimide film. Model compound studies indicate that the more stable pyromellitimide repeat unit is characterized by a more well-defined charge-transfer state. In the present paper, the photooxidation of the model compound, *N*-phenylphthalimide, is enhanced by a para electron-withdrawing group. Therefore, we chose to investigate the photolysis of polyimide films derived from the same 6F dianhydride repeat unit, but with diamines based on oxydianiline (ODA) and the 6F diamine, i.e., the 6F–ODA and 6F–6F polyimides. Since the bridging hexafluoroisopropylidene group is probably a much better electron-withdrawing moiety than oxygen, one might expect that 6F–6F polyimide films would be less stable than 6F–ODA polyimide films. The latter have already been shown to be photooxidatively unstable (relative to PMDA–ODA films) when exposed to the unfiltered output of a medium-pressure mercury lamp in air.

Comparative absorption spectra of thin 6F–6F, 6F–ODA, and PMDA–ODA films (Figure 6) show that the shift to the blue of the tail of the charge-transfer absorption band occurs in the order 6F–6F, 6F–ODA, PMDA–ODA. If we based a prediction of the photooxidative rate of the three polyimide films strictly on the intensity of the absorption bands, we might speculate that for a given film thickness the PMDA–ODA film would degrade at a faster rate than 6F–ODA and 6F–6F films since it has a higher absorbance at a given wavelength. However, FT-IR spectra indicate that 6F–6F degrades substantially faster than 6F–ODA when irradiated with an unfiltered medium-pressure mercury lamp. After only 3 h, the 6F–6F film shows decreases in most bands. After greater than 4 h of exposure, the 6F–6F films are essentially decomposed and reliable IR spectra cannot be obtained. The 6F–ODA films also show similar losses in all IR bands but require much longer photolysis times (>20 h) for similar absorbance loss. Clearly, the 6F–6F films are being photooxidized at a much higher rate. Photolysis of 6F–6F or 6F–ODA films in a nitrogen atmosphere leads to almost no loss of IR bands for up to 96 h of irradiation time, thus indicating the crucial role of a photooxidative process, as previously discussed.[4,5] GPC analysis (Figure 7) of 6F–6F films photolyzed in air (initial molecular weight at peak maximum of 56 700 compared to polystyrene standards) indicates a marked loss in molecular weight after photolysis for 1 h. Comparison with similar data for 6F–ODA films (Figure 7) shows that 6F–6F films are degraded to extremely low molecular weights in much less than 5 h, consistent with the observation that photolysis for longer than 4 h results in 6F–6F films which are severely decomposed and experience large weight losses. It takes well over 20 h of exposure of 6F–ODA films to the same unfiltered light source to achieve a comparable degree of decomposition and weight loss. These results can be taken as a relative comparison of decomposition rates of 6F–6F and 6F–ODA films.

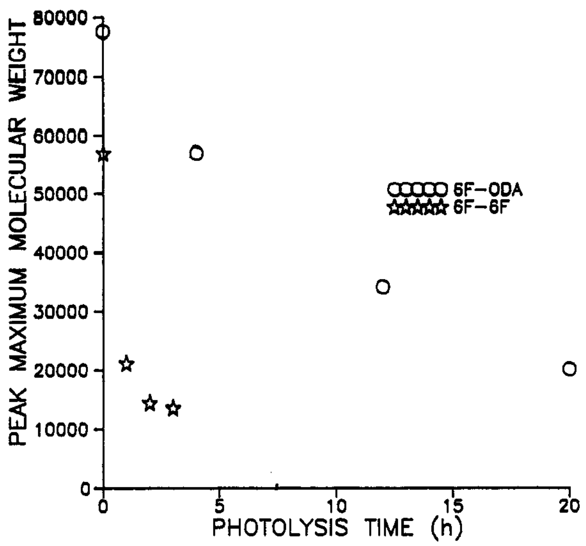


Figure 7. Plot of molecular weight of 6F–ODA (○) and 6F–6F (*) films at peak maxima (compared to polystyrene) versus photolysis time with an unfiltered medium-pressure mercury lamp in air.

As indicated previously for 6F–ODA, the loss of molecular weight and film weight are both the result of efficient photooxidation processes. Weight loss requires photolysis with wavelengths of light less than 300 nm for maximum efficiency. GPC analysis of 6F–6F and 6F–ODA irradiated for up to 96 h under nitrogen indicates no detectable change in molecular weight. This is in accordance with the IR results described previously. The photooxidative degradation process of 6F dianhydride based polyimides has been postulated,[5] on the basis of the model compounds, to proceed via a primary photooxidation step yielding phthalic anhydride. The generation of anhydride groups upon photolysis of 6F (as well as other) dianhydride based polyimides is a viable mechanism for the initiation of the series of photochemical events that eventually leads to the ultimate ablative decomposition of the polyimide film. Indeed, as for the 6F–ODA films,[4] FT-IR analysis of a gas cell of the collected products produced by the photoablation of 6F–6F films indicates that extensive amounts of carbon monoxide, carbon dioxide, and water are produced in addition to some small molecule fluorinated (probably CF_3H) compounds.

One puzzle, at least from our previous work, is the lack of evidence for anhydride formation in the actual polyimide film photolysis. As reported earlier,[1] the photooxidation of 6F–ODA films results in an "ablation" of the film and uniform decrease in all the IR absorption bands. No evidence for any new functional groups, such as anhydrides, is observed for the photolyzed 6F–ODA films. However, the studies of model *N*-phenylphthalimides indicate phthalic anhydride as the major photoproduct in air. In addition, a preliminary investigation of the model diimide made from the 6F dianhydride and aniline indicates that photolysis in an air-saturated solution yields the 6F dianhydride as one product. A simple explanation for the lack of observation of the anhydride absorbance, expected at ca. 1850, 1780, and 900 cm^{-1} in the IR of photolyzed 6F–ODA films, is based on the relative efficiencies of anhydride formation and loss in the model compounds. The quantum yields for loss of *N*-phenylphthalimide (R = H) and *N*-(*p*-phenoxyphenyl)phthalimide (R = OPh), models for the 6F–ODA repeat unit, are 8.2×10^{-4} and 8.8×10^{-5} in air-saturated dichloromethane. The exact quantum efficiencies vary with the polarity of the medium, which in the solid polyimide film might be quite different from dichloromethane. However, the quantum yields are probably a reasonable indication of the relative photolability of the imide repeat unit in the 6F–ODA film. Neglecting for a moment the phthalimide type product, which one might expect would be very difficult to differentiate in the IR from the parent *N*-arylphthalimide group, we consider the relative stability of phthalic anhydride groups subjected to the same photolysis conditions, namely an unfiltered mercury lamp in an air-saturated environment. The quantum efficiency for photolysis of phthalic anhydride in air-saturated dichloromethane at 280 nm (it has no appreciable absorbance at 313 nm where the quantum yields for the model *N*-arylphthalimides were determined) is 5.3×10^{-2}. This is essentially 2 orders of magnitude greater than the quantum yield for its formation from *N*-phenylphthalimide (PA–A) and 3 orders of magnitude greater than its formation from *N*-(*p*-phenoxyphenyl)phthalimide. If these values are representative of the respective efficiencies in the film, then for 6F–ODA we would expect that any phthalic anhydride groups formed would be immediately photolyzed in the presence of oxygen and thus observation in the IR would be impossible. In other words, the rate-determining step in the photooxidation process is the formation of phthalic anhydride moieties: the phthalic anhydride end groups would be rapidly consumed by photooxidation at a much faster rate than their formation.

The behavior of 6F–6F films is somewhat different than that of 6F–ODA films. The IR difference spectrum of 6F–6F before and after 3 h of photolysis with an unfiltered lamp (Figure 8) shows an increase in peaks at 1853, 1770, and 900 cm^{-1}, all characteristic of the phthalic anhydride moiety. All other peaks show distinct losses. By contrast, a difference spectrum (not shown) for 6F–ODA shows loss of all structural features in the IR bands: no new bands appear. The anhydride functionality may be on the end of a polymer chain or present in small molecule fragments in the irradiated polymer.

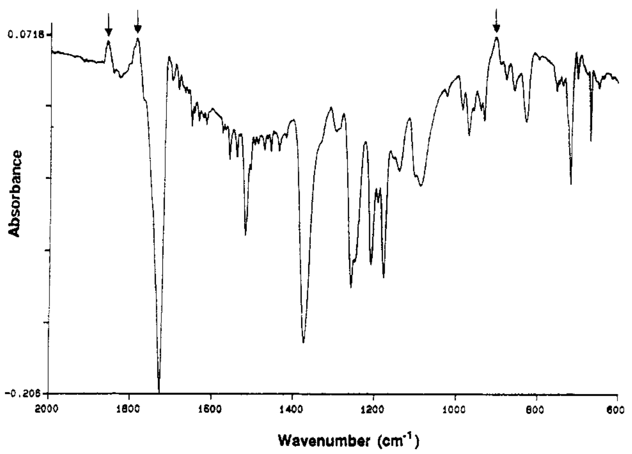


Figure 8. IR difference spectrum of 6F–6F film photolyzed with an unfiltered medium-pressure mercury lamp in air for 3 h.

The results for the 6F–6F film shown in Figure 8 are quite reasonable if account is taken of the electron-withdrawing nature of the hexafluoroisopropylidene moiety. We can speculate that the rate of anhydride formation upon photolysis of 6F–6F films might increase significantly perhaps to the point where the efficiency for formation of the anhydride is of the same order of magnitude as the efficiency for its decomposition in air. Under these circumstances we would expect to see a steady-state concentration of anhydride in the photolyzed 6F–6F films, as is shown in Figure 8.

Two other facts are important in the overall photodecomposition process. First, the phthalimide group, formed to a lower extent in the initial photolysis step, has a quantum efficiency for decomposition (0.047) comparable to that for phthalic anhydride. Also, nitrosobenzene (assuming that it is formed) and subsequently formed nitrobenzene, are readily photooxidized. In addition, one of the primary photooxidation products of phthalic anhydride is benzoic acid which would rapidly oxidize by decarboxylation under aerobic photolysis conditions. Thus, all of the primary and secondary photoproducts, once formed, rapidly photooxidize to give small molecule products such as carbon dioxide, carbon monoxide, etc., provided that the proper wavelength of light is employed. It has been demonstrated previously that phthalic anhydride, nitrobenzene, and phthalimide end groups require exposure to light of wavelength less than about 300 nm to effect rapid photooxidative decomposition.[5] Therefore, even though light of wavelength greater than 300 nm can induce chain cleavage via photooxidation of the basic phthalimide chromophore, wavelengths of light less than 300 nm, such as are obtained with an unfiltered medium-pressure mercury lamp, are required in order to complete the rapid photooxidative ablation process. This is true even for the photolabile 6F–6F polyimide.

Conclusions

In this paper, we have shown the effect of solvent polarity and electron-withdrawing and electron-accepting groups on the photochemistry/photophysics of *N*-arylphthalimides. Electron-withdrawing groups at the para position of the *N*-phenyl ring enhance the photooxidation process and phthalic anhydride formation by 2 orders of magnitude compared to electron-donating groups substituted at the same position. An increase in the same direction is found for the intersystem crossing yield of triplet state. The implication of the small molecule model study for polyimides is that electron-withdrawing groups substituted at the para position of the *N*-phenyl unit should result in enhanced photolability. Indeed, this is the case for the highly photooxidatively unstable 6F–6F polyimides. Complete photooxidation of 6F–6F films can be accomplished in a matter of a few hours with an unfiltered medium-pressure mercury lamp. In addition, the ablation is a very clean process leading to no surface pitting which often occurs when polyimides are ablatively etched with a laser. Apparently, anhydride groups which have been identified in this study by difference IR spectroscopy, are formed on the surface and subsequently photooxidized in a series of steps to produce carbon monoxide, carbon dioxide, water, and small molecule fluorocarbons.

Finally, we conclude by noting that although the processes may not be directly related, the present work may well have implications for laser-induced etching of polyimides. This is currently being investigated.

Future papers will address the spin multiplicity of the excited state leading to the initial photochemical process, and will also focus on sensitized decomposition of both model arylimides and the corresponding polyimides.

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Registry No. PA–A, 520-03-6; PA–POA, 19357-24-5; PA–CNA, 40101-61-9; PA–ClA, 7386-21-2; (6F)(6F diamine) (copolymer), 29896-40-0; (6F)(6F diamine) (SRU), 32036-79-6; (6F)(ODA) (copolymer), 32240-73-6; (6F)(ODA) (SRU), 39940-16-4.