# Photodegradation of Polyimides. 6. Effect of Donor-Acceptor Groups on the Photooxidative Stability of Polyimides and Model Compounds

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ABSTRACT: The photophysics of polyimides and several *N*-arylphthalimide model compounds has been investigated as part of an effort to understand the factors that control the oxidative photodegradation of these materials. Substituents that increase the donor-acceptor (D-A) character of both polymers and models cause an enhancement of the red-shifted electronic absorption and a shift to lower energy of the broad, weak fluorescence of these materials. Increasing solvent polarity causes a similar effect on the absorption and fluorescence spectra of the model compounds. Fluorescence quantum yields decrease with increasing D-A character in the series of model compounds and with increasing solvent polarity for a given compound. The triplet states of both polymers and models have been characterized in solution by laser flash photolysis, and intersystem crossing quantum yields have been determined. The triplet yields also decrease with increasing D-A character of the chromophore and with increasing solvent polarity. A comparison of fluorescence and phosphorescence spectra reveals a very small singlet-triplet energy gap. It seems likely that the lowering, by increased D-A character, of the yields of the triplet states that are intermediates in the photooxidative degradation enhances the photostability of aromatic-based polyimides.

## Introduction

Aromatic polyimides are important high-performance materials because of their superior thermal stability, excellent mechanical properties, and low dielectric constants. There are many reports of the thermal behavior of high-temperature, heat-resistant polyimides but relatively little is known about their photochemical behavior. We have recently begun a comprehensive study[1-5] of the photochemistry and photophysics of a series of polyimides exemplified by 6F-ODA and 6F-6F (see structures and appropriate designations in Chart 1), derived by reaction of a bis-aromatic dianhydride, 6F, in which two phthalic anhydride moieties are linked by a hexafluoroisopropylidene "hinge" group, with bridged (either oxygen of hexafluoroisopropylidene) aromatic diamines and by PMDA-ODA, derived from pyromellitic dianhydride and 4,4′-oxydianiline. In the course of this investigation, we also conducted a comprehensive study of a series of *N*-arylphthalimides (see structures in Chart 1 designated PA-A, PA-POA, PA-ClA, PA-MOA, and PA-CNA) with differing substituents at the *para*-position of the *N*-aryl ring.[4,5] These phthalimides model (*vide infra*) many of the photophysical and photochemical properties of the much less tractable polymers.

Broad-band mercury lamp irradiation of polymers such as 6F-ODA, 6F-6F, and 6F-6H in the presence of oxygen results in their complete degradation to small-molecule fragments. For example, 6F-ODA, when irradiated in the presence of oxygen, yields[4] photoproducts such as benzoic acid, $H_2O$, CO, $CO_2$, and $CF_3H$: Irradiation of films of 6F-ODA and 6F-6F results in progressive weight loss by clean ablation of the surface. In contrast, irradiation of 6F-ODA through a Pyrex filter results in chain breaks but no facile breakdown to small-molecule fragments or surface ablation. Upon examination of model systems, we found that irradiation of model *N*-arylphthalimides through Pyrex in the presence of oxygen affords phthalic anhydride as the major photoproduct.[4] Phthalic anhydride undergoes secondary photolysis to unknown photoproducts only under broad-band mercury lamp irradiation, which includes light of wavelength less than 300 nm. These observations have led us to propose[4] a mechanism for the extensive photooxidative degradation of fluorinated polyimides involving initial production of aryl anhydride functional groups in the irradiated polymer followed by their subsequent photolysis. We have obtained evidence for the first part of this mechanism by direct observation[5] of aryl anhydride functional groups (by their characteristic IR bands) in 6F-6F films irradiated in the presence of air.

It is clear from our previous work on photooxidative degradation of both polymers and models that the least photolabile materials are those in which the donor-acceptor (D-A) character of the chromophore is predicted to be the most pronounced. The order of stability of the polymers (as determined by weight loss) is PMDA-ODA > 6F-ODA > 6F-6F and, for the models (as determined by degradation quantum yields) is PA-POA > PA-A ≈ PA-ClA > PA-CNA. Presumably, the pyromellitimide moiety in PMDA-ODA is a more powerful electron acceptor than the 6F moiety in 6F-ODA, and the 6F bridging group in the diamine moiety of 6F-6F suppresses the D-A character of 6F-6F relative to 6F-ODA. The photostability trend for the *N*-arylphthalimide models parallels the expected electron-donating ability of the *para*-substituent, i.e., OPh > H > CN. We have also obtained evidence from quenching experiments that the triplet state is a key intermediate in PA-A photodegradation. In this paper we will report details of the D-A effect on the singlet states of 6F-based polymers and appropriate model

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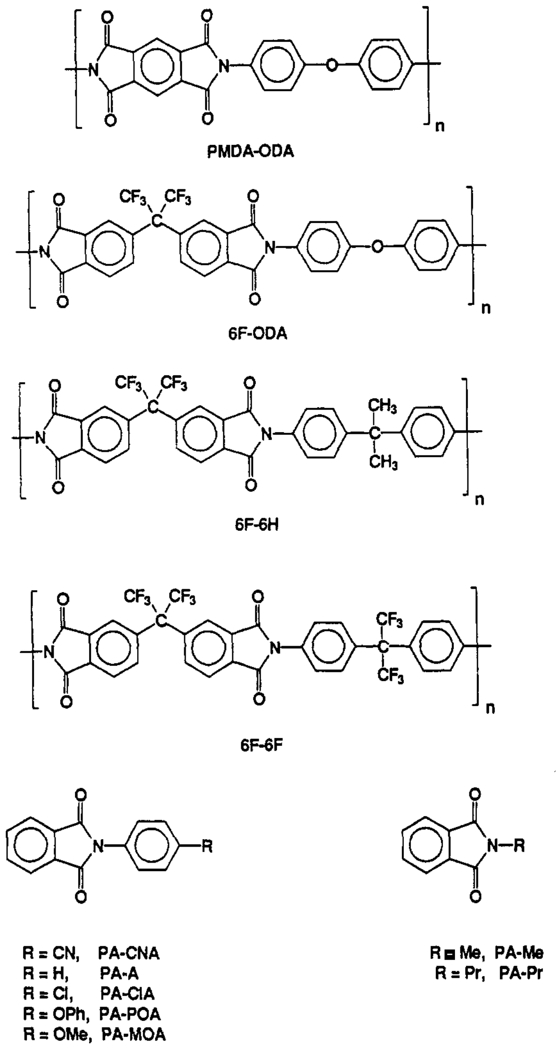
Chart 1



phthalimides, direct observation of the triplet states of these materials in fluid solution, measurements of intersystem crossing quantum yields ($\Phi_{isc}$) and, finally, low-temperature emission experiments that enable estimation of singlet–triplet energy differences. Our results suggest that D–A stabilization of the lowest singlet state of both polymers and models reduces photochemical reactivity, to a certain extent, by reduction of intersystem crossing yields.

## Experimental Section

The synthesis and purification of both polymers and model compounds have been described elsewhere.[1,4] All solvents were obtained from Burdick and Jackson and used as received. UV-vis absorption spectra were recorded on a Perkin-Elmer Lambda 6 spectrophotometer and fluorescence spectra on a Spex Fluorolog-2 spectrofluorometer. A Spex phosphorescence attachment was used to obtain phosphorescence spectra at different delay times after pulsed excitation. Fluorescence quantum yields were obtained relative to anthracene ($\Phi_F = 0.3$) in cyclohexane.[6] Laser flash photolysis experiments were carried out using a Lumonics HyperEx 440 excimer laser as an excitation source operating at 248 (KrF) or 351 nm (XeF), and an Applied Photophysics (AP) pulsed xenon lamp as monitoring source, the output from which was analyzed using an AP monochromator/fast PMT system as reported earlier.[5] Extinction coefficients of the triplet states were determined by the energy transfer method[7] from benzophenone. Intersystem crossing yields, $\Phi_{isc}$, were determined relative to benzophenone ($\Phi_{isc} = 1.0$) by laser flash photolysis at 248 nm.

Polymer molecular weights were determined from gel permeation chromatography 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.

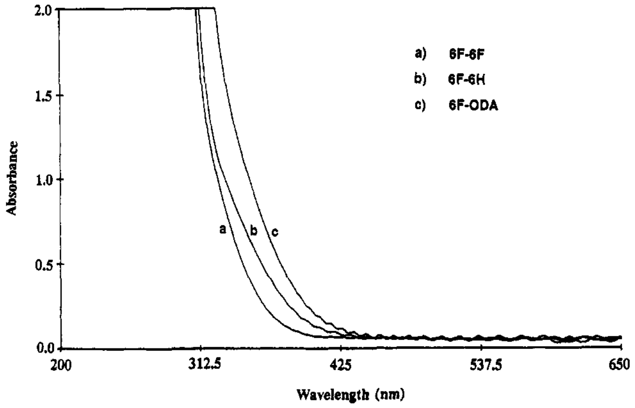


**Figure 1.** Absorption spectra of thin polyimide films cured at 300 °C: (a) 6F–6F; (b) 6F–6H; (c) 6F–ODA.

**Table 1. Fluorescence Maxima (nm) of the Polymers in Fluid Solution at Room Temperature**

| polymer | methylene chloride | tetrahydrofuran | acetonitrile |
|---|---|---|---|
| 6F–ODA | 595 | 600 | not soluble |
| 6F–6H | 575 | 580 | very weak |
| 6F–6F | 525 | 530 | 542 |

## Results and Discussion

**A. Fluorinated Polyimides: Photolysis Dependence on Amine Donor Characteristics.** The absorption and fluorescence spectra of the polyimides designated 6F–6F, 6F–ODA, and 6F–6H are similar to those previously reported[8] for related materials. UV–vis absorption spectra of thin films of these polymers (uniform film thickness) cured at 300 °C are shown in Figure 1, with the 6F–ODA film being considerably red shifted compared to 6F–6F and 6F–6H. The red shift in the absorption spectra occurs in accordance with expected increasing D–A interactions, i.e., 6F–6F < 6F–6H < 6F–ODA. Solutions and thin films of the 6F-based polymers exhibit a broad, weak fluorescence maximum. For example, 6F–6F has a maximum at 542 nm in acetonitrile, 530 nm in tetrahydrofuran, and 525 nm in $CH_2Cl_2$. The results are typical for the 6F-based polymers, all of which exhibit a red shift in the fluorescence peak maximum with increasing solvent polarity. Of particular interest in the present case is to compare the shift in the fluorescence peak maximum in a common solvent for 6F–6F, 6F–6H, and 6F–ODA. The entries in Table 1 show fluorescence emission maxima for all three polymers in at least one solvent: A shift in the peak maximum to lower energies with the expected order of increasing D–A interaction (6F–6F < 6F–6H < 6F–ODA) apparently occurs in each solvent. In addition, the intensity of the triplet spectrum of all three polymers in $CH_2Cl_2$ suggests that the intersystem crossing yield to the triplet state of the aryl imide is greatest for 6F–6F and least for 6F–ODA, with 6F–6H being intermediate. This assumes that the extinction coefficients of the triplet states are approximately equal. On the basis of the donor character expected for the amine-based component of the aryl imide repeat unit (ODA > 6H > 6F), we might expect to see the photolytic decomposition, which we will demonstrate in a subsequent section in this paper to proceed, at least to an extent, from the triplet state, to follow the same order; i.e., 6F–6F would be the more photolabile polymer. In accordance with this prediction, photolysis of 6F–6F films led to very rapid decomposition compared to 6F–6H and 6F–ODA films. The rapid decomposition

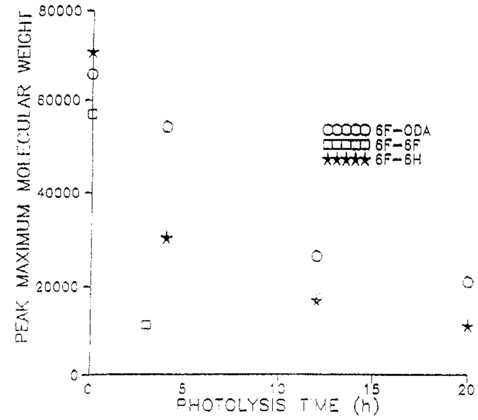


**Figure 2.** Plot of molecular weight of 6F–ODA (○), 6F–6F (□), and 6F–6H (*) films at peak maxima (compared to polystyrene) versus photolysis time with an unfiltered medium-pressure Hg lamp in air.

of 6F–6F is even more surprising when we consider that its UV–vis absorption (not shown) in the range of the photolysis source (unfiltered medium-pressure Hg lamp) is much less than for 6F–6H and 6F–ODA. Figure 2 shows changes in the molecular weight at the peak maximum for 6F–ODA, 6F–6F, and 6F–6H as a function of photolysis time in air. As indicated above, the order of decomposition is 6F–6F > 6F–6H > 6F–ODA. Obviously, the photostability of the films parallels the D–A acceptor properties of the photoreactive repeat unit and the apparent intersystem crossing yield to the triplet. However, we should point out that a rough analysis of the relative intersystem crossing yield for 6F–6F, 6F–6H, and 6F–ODA does not exactly parallel in magnitude the large difference in decomposition rate exhibited in Figure 2 for 6F–6F versus 6F–ODA and 6F–6H. While quantitative results are not available, our results seem to indicate that the substituent effect on the *N*-aryl ring ($(CF_3)_2CPh$ versus $(CH_3)_2CPh$ or OPh) not only alters the intersystem crossing yield but also has an effect on the subsequent reactions which proceed from the triplet state. Hence, any proposed photodegradation mechanism, such as depicted in Scheme 1 (suggested[5] as being consistent with our cumulative results to date for model and polymer systems having the *N*-aryl imide moiety), must reflect the possibility that the R substituent group can affect both the properties of the excited state from whence products are formed and subsequent reactions of any intermediates, such as a biradical comprised of an amidyl and a carbonyl radical, which may form. This will, of necessity, require positive identification of the spin multiplicity of the excited state leading to product formation. The rest of this paper will be directed toward identification of the effect of D–A properties on the photophysics and photochemistry of model *N*-arylphthalimides by clearly defining the spin multiplicity of the reactive states, the D–A effects on singlet emission and singlet to triplet intersystem crossing yields of *N*-arylphthalimides, the energy levels of the singlet/triplet states of *N*-arylphthalimides, and the lifetimes of the reactive states.

**B. Photophysics of Model *N*-Arylphthalimides.** Absorption spectra of the *N*-arylphthalimides (see structures) shift to longer wavelengths as the D–A character increases.[5] Furthermore, there is a measurable solvent effect on the fluorescence (first five entries in Table 2) of each of these arylphthalimide models: The emission maxima shift to lower energies with increasing solvent polarity. We note that the *N*-aryl group seems to be essential for observation of the broad, substituent and solvent sensitive band in the fluorescence spectra of the *N*-arylphthalimides, since the fluorescence of *N*-alkylphthalimides (last two entries in Table 2) is considerably blue shifted relative to the *N*-arylphthalimides and shows little solvent sensitivity. For example, the fluorescence maximum of PA–Pr in cyclohexane is at 410 nm while it is at 507 nm for PA–A. Furthermore, in contrast to PA–A, the fluorescence maximum of PA–Pr does not shift when the solvent is changed from cyclohexane to acetonitrile, although its intensity increases considerably. The fluorescence maximum of PA–A shifts from 507 to 552 nm in going from cyclohexane to acetonitrile, with a significant drop in intensity (Table 2).

**Scheme 1. Mechanism for the Photolysis of *N*-Arylphthalimides**

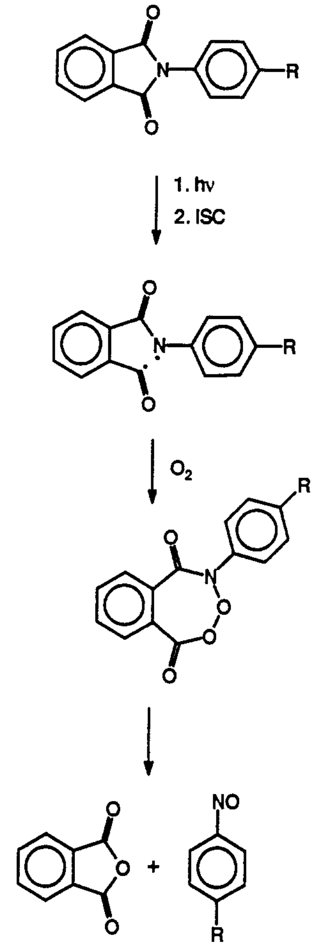


**Table 2. Fluorescence Maxima (nm) of Phthalimide Model Compounds in Fluid Solution at Room Temperature**

| compd | cyclohexane | methylene chloride | acetonitrile |
|---|---|---|---|
| PA–CNA | 471 | 493 | 512 |
| PA–A | 507 | 537 | 552 |
| PA–ClA | 509 | 540 | 555 |
| PA–POA | 555 | 606 | 610 |
| PA–MOA | 565 | 622 | *a* |
| PA–Pr | 410 | 410 | 410 |
| PA–Me | 406 | 410 | 410 |

[a] Weak emission between 610 and 650 nm.

To provide additional insight into the photophysical nature of *N*-arylphthalimides, we measured the fluorescence quantum yields ($\Phi_F$) of the models in several different solvents and at excitation wavelengths from 250 to 350 nm (Table 3): We did not observe an excitation wavelength effect on $\Phi_F$ for any of the models or polymers examined. Moreover, the fluorescence was weak in all cases, with the highest value of $\Phi_F$ being $8.3 \times 10^{-3}$ for the model compound PA–CNA in cyclohexane. Upon close examination of the

**Table 3. Quantum Yields[a] of Fluorescence of Phthalimide Model Compounds in Fluid Solution at Room Temperature**

| compd | cyclohexane | methylene chloride | acetonitrile |
|---|---|---|---|
| PA-CNA | $8.3 \times 10^{-3}$ | $4.6 \times 10^{-3}$ | $1.8 \times 10^{-3}$ |
| PA-A | $2.5 \times 10^{-3}$ | $5.6 \times 10^{-4}$ | $2.5 \times 10^{-4}$ |
| PA-ClA | $2.3 \times 10^{-3}$ | $4.9 \times 10^{-4}$ | $2.5 \times 10^{-4}$ |
| PA-POA | $3.5 \times 10^{-4}$ | $4.9 \times 10^{-5}$ | $2.8 \times 10^{-5}$ |
| PA-MOA | $3.5 \times 10^{-4}$ | $3.9 \times 10^{-5}$ | $1.8 \times 10^{-5}$ |
| PA-Pr | $5.2 \times 10^{-5}$ | $1.1 \times 10^{-3}$ | $1.0 \times 10^{-3}$ |
| PA-Me | $4.3 \times 10^{-5}$ | $9.4 \times 10^{-4}$ | $1.4 \times 10^{-3}$ |

[a] Relative to anthracene ($\Phi_F = 0.3$); ±10%.

results in Table 3, it can be seen that $\Phi_F$ diminishes for a given compound in more polar solvents and as the D–A character of the material is enhanced by electron-donating substituents. In contrast to the results for the *N*-arylphthalimides, the "isolated" phthalimide chromophore, as exemplified by PA-Pr, exhibits a marked increase in $\Phi_F$ from $5.2 \times 10^{-5}$ to $1.0 \times 10^{-3}$ in going from cyclohexane to acetonitrile. Solvent effects on the fluorescence of *N*-alkylphthalimides[9] have been attributed to an increase in $\pi,\pi^*$ character of the singlet state in solvents of increasing polarity. This seems quite reasonable to us. Obviously, the same mechanism cannot be invoked for the *N*-arylphthalimides or for the 6F–6F, 6F–6H, and 6F–ODA polymers since an increase in solvent polarity leads to a pronounced red shift in the position of the wavelength maximum and an accompanying decrease in the fluorescence intensity. This is best exemplified for 6F–6F in Table 1 since we were able to obtain fluorescence spectra in three solvents for this polymer.

From the results presented in this report, it seems obvious that D–A effects are important to the singlet-state behavior of *N*-arylphthalimides and aromatic-based polyimides. One possibility is that *N*-aryl imide groups have a twisted intramolecular charge transfer (TICT) state in which the *N*-aryl group acts as an electron donor and the phthalimide as an acceptor. Indeed, Frank et al.[12–14] have previously suggested that the red-shifted fluorescence of *N*-aryl polyimides originates from intramolecular charge transfer complexes. While there is no direct proof that *N*-arylphthalimides exhibit a TICT state, they do have a very broad, weak, structureless fluorescence that is dependent on the donor–acceptor character of the interactive components and on solvent polarity, with a large Stokes shift from the onset of absorption, all characteristic of a TICT state.[10,11] A compound forming a TICT state is also expected to have a very small singlet–triplet energy gap: Such is apparently the case for *N*-arylphthalimides. For example, the phosphorescence spectrum of PA-CNA at 77 K (Figure 3) in an ether–tetrahydrofuran glass, shows a 0–0 band at 402 nm, corresponding to a triplet energy, $E_T$, of 71.1 kcal·mol$^{-1}$. Such precise determination of the singlet energy, $E_S$, is not possible, since no vibrational structure is apparent in the fluorescence spectrum. However, taking the wavelength at which the fluorescence intensity is 10% of its value at $\lambda_{max}$ as an approximation for the position of a 0–0 band, we obtain a value for $E_S$ of *ca.* 72 kcal·mol$^{-1}$ in cyclohexane and *ca.* 70 kcal·mol$^{-1}$ in acetonitrile, identical within experimental error to the triplet-state energy obtained from the phosphorescence experiments (Table 4). Similar results are obtained for the other model compounds and for 6F–6F and 6F–ODA (Table 4).

**C. Spin Multiplicity of Reactive State.** Although we have presented data for *N*-arylphthalimides with respect to the effect of donor/acceptor substituents on the singlet state, we are ultimately interested in the triplet state, since preliminary quenching results suggest[5] that photooxidative degradation of the phthalimide model compounds proceeds from the triplet state of the imide. Therefore, we have used laser flash photolysis to characterize the lowest triplet states of the polymers and model compounds in fluid solution. Laser flash photolysis (248 nm) of the models PA-CNA, PA-A, PA-ClA, PA-POA, and PA-MOA led to observation of transients with lifetimes of several microseconds in nitrogen-saturated solvents. The transient lifetimes are greatly reduced in each case when the medium is air saturated. For example, the transient from PA-A in cyclohexane has a sharp maximum at *ca.* 300 nm and a broad maximum at *ca.* 520 nm (Figure 4). The lifetime of this transient is *ca.* 12 μs in a nitrogen-purged solution and *ca.* 150 ns in the presence of air. The decay of the transient absorption is independent, within experimental error (±10%), of the monitoring wavelength, indicating that it is due to a single species. The transient is readily quenched by cyclohexadiene ($E_T$ = 52.4 kcal·mol$^{-1}$) with a quenching rate constant of 6.0 × $10^9$ L·mol$^{-1}$·s$^{-1}$ and by naphthalene ($E_T$ = 61 kcal·mol$^{-1}$) with a quenching rate constant of 2.9 × $10^9$ L·mol$^{-1}$·s$^{-1}$. Quenching with biphenyl ($E_T$ = 66 kcal·mol$^{-1}$) is much less efficient (<2 × $10^7$ L·mol$^{-1}$·s$^{-1}$). Formation of the transient can be sensitized by 351-nm excitation in the presence of benzophenone ($E_T$ = 69 kcal·mol$^{-1}$). Similar results are obtained for the other *N*-arylphthalimide model compounds as well as the 6F–6F and 6F–ODA polymers (Figure 5) in solution, although the lifetimes of transients from the polymers in dilute solution are much shorter (nitrogen-saturated solution) than for the models (Table 5). The short lifetimes for 6F–6F and 6F–ODA suggest the possibility of intrachain self-quenching in the polymers that cannot occur in dilute solutions of the models.

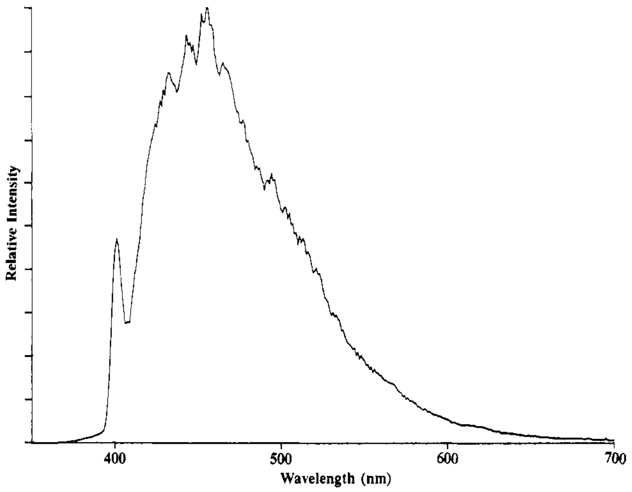


**Figure 3.** Phosphorescence spectrum ($\lambda_{ex}$ = 250 nm) of PA-CNA in ether–tetrahydrofuran glass at 77 K.

**Table 4. Excited-State Energies from Emission Spectra of *N*-Arylphthalimides and Polymers**

| | | $E_S$, kcal·mol$^{-1}$ | | | |
|---|---|---|---|---|---|
| compd | $E_T$,[a] kcal·mol$^{-1}$ | cyclohexane | acetonitrile | film | tetrahydrofuran |
| PA-CNA | 71.1[b] | 72.2[c] | 69.6[c] | | |
| PA-A | 67.6[c] | 69.6[c] | 65.4[c] | | |
| PA-POA | 67.1[c] | 64.0[c] | 58.7[c] | | |
| 6F–6F | 71.5[b] | | | 67.9[c] | 72.2[c] |
| 6F–ODA | 71.1[b] | | | 65.9[c] | *d* |

[a] Ether–tetrahydrofuran glass at 77 K. [b] Estimated from 0–0 band. [c] Estimated from onset of emission (wavelength at which intensity of corrected spectrum is 10% of maximum intensity). [d] Not determined.

From the data obtained for all of the models and polymers investigated, there seems little doubt that the

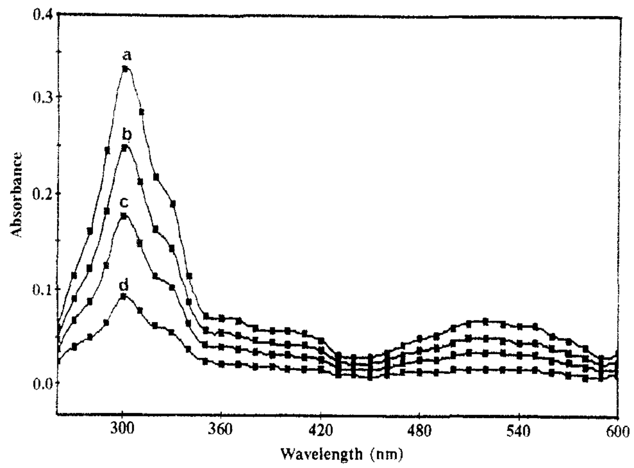


**Figure 4.** Transient absorption spectra ($\lambda_{ex}$ = 248 nm) of PA–A at room temperature in nitrogen-saturated cyclohexane solution at different time intervals after the flash: (a) 1 $\mu$s; (b) 5 $\mu$s; (c) 10 $\mu$s; (d) 20 $\mu$s.

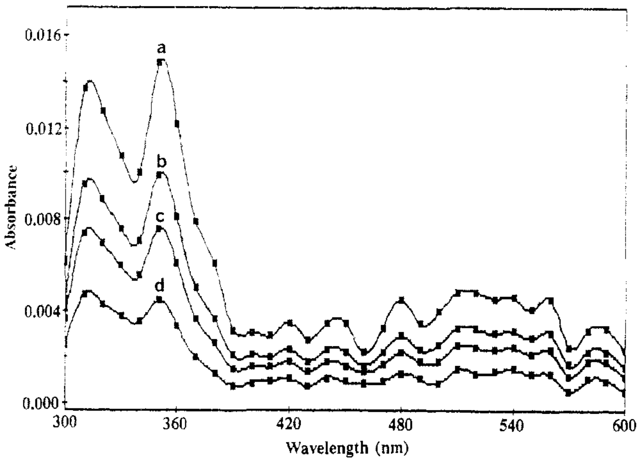


**Figure 5.** Transient absorption spectra ($\lambda_{ex}$ = 248 nm) of 6F–ODA at room temperature in nitrogen-saturated methylene chloride solution at different time intervals after the flash: (a) 60 ns; (b) 200 ns; (c) 300 ns; (d) 500 ns.

**Table 5. Properties of Transient Species Measured by Laser Flash Photolysis**

| compd | solvent | $\lambda_{max}$, nm | $\tau(N_2)$, $\mu$s | $\tau$(air), ns |
|---|---|---|---|---|
| PA-CNA | acetonitrile | 310, 340, 550 | 15.0 | 439 |
| | methylene chloride | 310, 340, 540 | 2.6 | 590 |
| | cyclohexane | 300, 340, 560 | 8.0 | 225 |
| PA–A | acetonitrile | 300, 500 | 11.4 | 116 |
| | methylene chloride | 310, 340, 500 | 10.8 | 430 |
| | cyclohexane | 300, 330, 520 | 12.4 | 155 |
| PA-POA | acetonitrile | 310, 350, 540 | 8.6 | 88 |
| | methylene chloride | 310, 350, 560 | 9.0 | 258 |
| | cyclohexane | 300, 345, 540 | 9.3 | 91 |
| 6F–ODA | methylene chloride | 310, 350, 520 | 0.73 | 135 |
| 6F–6F | methylene chloride | 310, 340, 520 | 0.65 | 127 |

transient species arising from the excitation of *N*-arylphthalimides are due to triplet states of the phthalimides with energies between 61 and 66 kcal·mol$^{-1}$ (estimated from quenching studies at room temperature) or 67–71 kcal·mol$^{-1}$ (estimated from phosphorescence spectra at 77 K). To confirm this hypothesis, energy transfer experiments were carried out using $\beta$-carotene as the energy acceptor. $\beta$-Carotene is a convenient triplet indicator since it gives no transient absorption upon direct laser photolysis due to an inherently low intersystem crossing quantum yield.[15] When PA–A is excited in the presence of $\beta$-carotene, the PA–A transient is quenched and triplet $\beta$-carotene is produced[15] with a characteristic absorption maximum around 520 nm (Figure 6). The growth of the carotene triplet and the decay of PA–A transient absorption occur on essentially the same time scale, indicating that the transient species produced on excitation of PA–A is a triplet: The 400–470-nm region in Figure 6 shows a bleaching effect due to the depletion of ground-state $\beta$-carotene absorption.

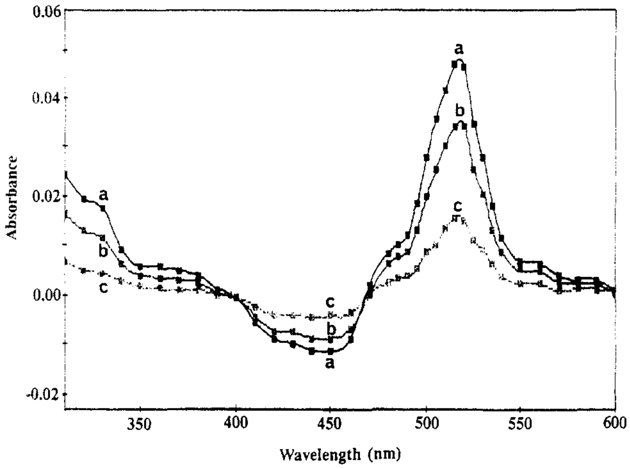


**Figure 6.** Absorption spectra ($\lambda_{ex}$ = 248 nm) of $\beta$-carotene triplet generated by energy transfer from the PA–A triplet in cyclohexane at different time intervals after the flash: (a) 6 $\mu$s; (b) 10 $\mu$s; (c) 20 $\mu$s. $\beta$-Carotene concentration is 5 × $10^{-6}$ M.

To confirm the role of the triplet state in the photooxidative degradation of *N*-arylphthalimides, photolysis experiments[4,5] (using a 450-W medium-pressure mercury lamp) were conducted using triplet quenchers and sensitizers. The photolysis of PA–A ($\lambda_{ex}$ = 313 nm, bandpass filter) in methylene chloride, resulted in the quenching of the quantum yield for phthalic anhydride formation ($\Phi_{PA}$) with a bimolecular quenching rate constant of 9.0 × $10^9$ L·mol$^{-1}$·s$^{-1}$, well within the experimental error of the quenching constant obtained by laser flash photolysis. Competitive absorption by naphthalene at 313 nm was negligible for the concentrations employed. A comparable quenching rate constant was also obtained when cyclohexadiene was used. Similarly, it was found that the extent of photolysis, as monitored by GPC, of the 6F–6F polymer when irradiated with 313-nm radiation was considerably lower when carried out in the presence of the triplet quencher, 1,3-cyclohexadiene. After 7 h of photolysis the reduction in the peak maximum molecular weight (compared to polystyrene) was only 5%, compared to a reduction of 57% in the absence of the quencher. When benzophenone was used as the triplet sensitizer for PA–A, $\Phi_{PA}$ was increased to a value of 5 × $10^{-3}$, over an order of magnitude larger than obtained by direct photolysis in dichloromethane. This is consistent with the sensitization expected by benzophenone with a triplet energy of 69 kcal·mol$^{-1}$, which is greater than either the estimated value of 67.6 kcal·mol$^{-1}$ for PA–A in an ether–tetrahydrofuran glass at 77 K (Table 4) or that estimated from the triplet quenching results at room temperature. The quenching and sensitization results provide compelling evidence that the photooxidative degradation of the model compounds proceeds from the triplet state of *N*-arylphthalimides.

To provide a comparison of the intersystem crossing efficiencies of the model *N*-arylphthalimides, intersystem crossing quantum yields ($\Phi_{isc}$) were determined by laser flash photolysis relative to benzophenone ($\Phi_{isc}$ = 1.0). The $\Phi_{isc}$ of the *N*-arylphthalimides decreases with increasing D–A character and with increasing solvent polarity as can be seen in Table 6 (some of these values were extracted from previous papers[5]). These results also parallel the observation we obtained by emission and irradiation

**Table 6. Quantum Yields[a] of Intersystem Crossing in Fluid Solution of *N*-Arylphthalimides**

| compd | cyclohexane | methylene chloride | acetonitrile |
|---|---|---|---|
| PA–CNA | 0.64 | 0.16 | 0.06 |
| PA–A | 0.17 | 0.04 | 0.03 |
| PA–POA | 0.06 | 0.02 | 0.02 |
| PA–MOA | 0.08 | 0.02 | 0.02 |

[a] ±15%; determined relative to benzophenone ($\Phi_{isc}$ = 1.0).

studies (most of which were reported in ref 5), reflecting the relative sensitivity of these compounds to photooxidative degradation: i.e., PA–CNA > PA–A > PA–POA > PA–MOA. However, as we noted in the previous paper in this series,[5] substituent effects are probably prominent not only in increasing the quantum yield for intersystem crossing to the reactive triplet state but also the subsequent reactions which occur. Interestingly, the triplet lifetime itself and hence the actual initial reaction from the triplet state is not altered appreciably by the substituent at the *para*-position of the *N*-aryl ring (see entries in Table 5). Since we find that the quantum yield for the products formed increases to a greater extent than the intersystem crossing yield upon substitution of an electron-withdrawing group on the donor portion of the molecule, it seems probable that such substituents play a role in determination of the reactivity of intermediates other than by just enhancing intersystem crossing to the triplet state. There is little question that the correlation of photochemical reactivity of *N*-arylphthalimide moieties with donor substituents on the *N*-aryl group is important.

## Conclusion

In this work, we have established the triplet multiplicity of the state responsible for the photochemistry of *N*-arylphthalimides and polyimides based on partially fluorinated polymers. The origin of the photochemical dependence of the D–A properties of the major components comprising the *N*-arylphthalimide repeat unit has been established quantitatively. A viable mechanism for the photolysis in an oxygen environment of partially fluorinated poly(aryl imides) has been postulated. Finally, the fluorescence emission of *N*-arylphthalimides from a TICT state seems feasible in view of the fluorescence solvent and substituent dependence as well as the close proximity of the singlet–triplet energy levels in *N*-arylphthalimides.

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