

## Self-quenching of the triplet state of a semifluorinated polyimide in solution

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### Abstract

Triplet lifetimes of semifluorinated polyimides and related model compounds were determined using laser flash photolysis. It was found that the triplet lifetimes of polyimides in relatively good solvents were about 10 times less than those of *N*-arylphthalimide models. The significant reduction in the triplet lifetimes of the polymers is attributed to an intrachain self-quenching process of the triplet state via interaction between main chain chromophores. Triplet lifetimes of one of the semifluorinated polyimides polymers in a variety of solvents of varying solvent powers were measured. In relatively poor solvents, more than a 10-fold reduction in the triplet lifetimes was observed compared to the lifetimes in relatively good solvents, suggesting that intrachain self-quenching readily occurs due to enhanced coiling of the polymer in the poor solvents. © 2000 Elsevier Science S.A. All rights reserved.

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### 1. Introduction

When active chromophores are incorporated into the backbone of polymer chains, it is generally expected that the photochemical and photophysical properties of the excited states created as a result of traditional absorption processes have similar behavior to those of small molecule models. One potential difference, however, is the possibility for excited state groups in polymer systems to interact with identical ground state moieties of the same chemical structure in the same polymer chain. If the process entails interaction of an excited triplet state with a ground state singlet, the 'self-quenching' process should result in a decrease in the measured triplet lifetime. As far as we are aware, such a 'self-quenching' process has not been conclusively demonstrated for interactions between chromophoric groups incorporated into the main chain of a polymer in dilute solution. The use of soluble aromatic polyimides affords an excellent opportunity for direct observation of this phenomenon via transient laser flash photolysis.

Polyimides having a hexafluoroisopropylidene (6F) moiety in the backbone have been identified as potential candi-

dates for applications requiring high thermal stability [1–5]. A particularly interesting property, germane to the present study, of 6F containing polymers is their solubility in common solvents. In the past, a series of 6F polyimides and appropriate models (see structures) were synthesized in our laboratory and their photochemical behavior studied extensively [6–13]. During the course of this photodegradation study, we conclusively demonstrated that the resultant photochemical reactions resulted from a bond cleavage from an excited triplet ( $T_1$ ) state between nitrogen and the carbonyl carbon to give a biradical. Subsequently, when we identified triplet states of the polymers and model compounds [13] using laser flash photolysis and determined their lifetimes, we noted that the triplet lifetimes of the polymers were about an order of magnitude less than those of the corresponding model compounds. In this communication we specifically address this interesting phenomenon and provide new results demonstrating the marked effect of the solvent on the polymer triplet lifetime. The results are readily interpreted in terms of self-quenching involving the excited triplet *N*-arylimide repeat unit and a ground state *N*-arylimide group. This is the first report that we are aware of which directly demonstrates intrachain self-quenching of the triplet state in a main chain polymer system in dilute solution.

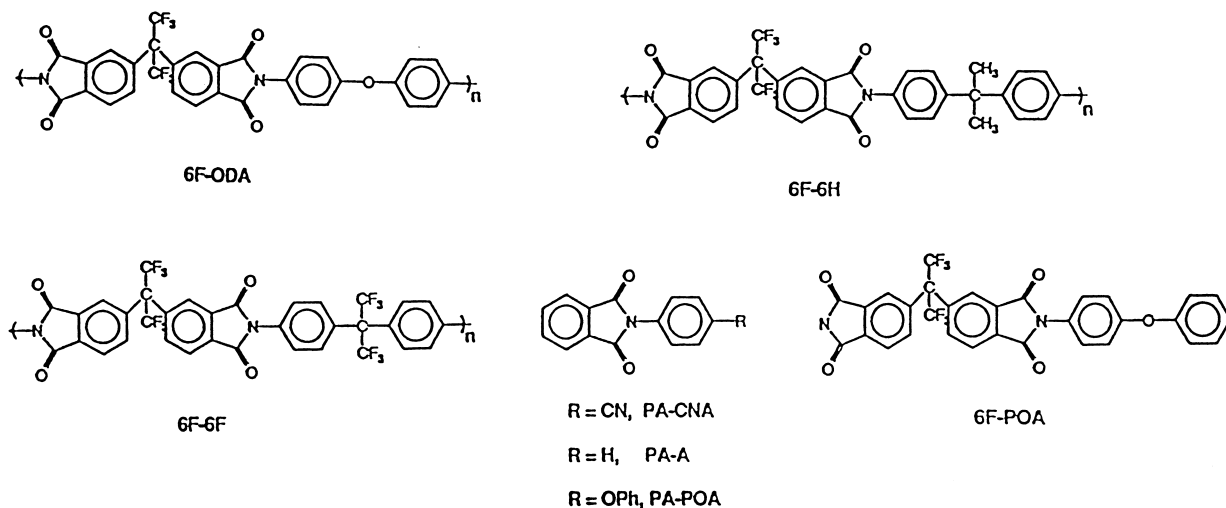
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## 2. Materials and methods

Synthetic methods for making all materials used have been published [6–13]. Solvents were used as received from Burdick and Jackson. Transient spectra were recorded on an Applied Photophysics laser flash photolysis apparatus using a pulsed excimer laser source.

## 3. Results and discussion

In a previous paper, we reported the triplet lifetimes of a variety of *N*-arylphthalimides and semifluorinated (6F) polyimides. For the sake of clarity we have reproduced the lifetimes of a number of these compounds in Table 1. The structures of the compounds listed in Table 1 and their acronyms are given below. It can be seen from Table 1 that all of the model compounds have triplet state lifetimes of about 10  $\mu\text{s}$  in cyclohexane and dichloromethane, whereas the two polymers (6F-ODA and 6F-6F) have triplet lifetimes of about 0.7  $\mu\text{s}$  in dichloromethane, an approximate 10-fold decrease in the triplet lifetime compared to the model compounds. We propose that this reduction in triplet lifetimes is due to an intrachain self-quenching process in the polymer, resulting from interaction of the triplet state of an *N*-arylphthalimide repeat unit with a ground state singlet on the same chain (i.e. an intramolecular quenching process).



In order to provide additional evidence for intramolecular self-quenching, laser flash photolysis experiments were carried out specifically on the 6F-ODA polymer and the model 6F-POA. The latter has essentially the same structure as the repeat unit of 6F-ODA and is a more exact model than the *N*-arylimides in Table 1 for which data was previously reported. The triplet–triplet transient absorption spectra of the 6F-ODA polymer and the 6F-POA model are shown in Figs. 1 and 2, and the observed triplet lifetimes in  $\text{CH}_2\text{Cl}_2$  are given in Table 2. It can be seen that while the spectral shapes

Table 1

Properties at transient species measured by laser flash photolysis ( $\lambda_{\text{ex}} = 248 \text{ nm}$ )<sup>a,b</sup>

Compound	Solvent	$\tau$ ( $\mu\text{s}$ )
PA-CNA	Methylene chloride	2.6
	Cyclohexane	8.0
PA-A	Methylene chloride	10.8
	Cyclohexane	12.4
PA-POA	Methylene chloride	9.0
	Cyclohexane	9.3
6F-ODA	Methylene chloride	0.73
6F-6F	Methylene chloride	0.65

<sup>a</sup> Reproduced in part from data in [13].

<sup>b</sup> Nitrogen degassed solutions used for all lifetime measurements.

are identical, the triplet lifetime of the polymer (6F-ODA) is a factor of 10 less than that of the model (6F-POA), in agreement with results in Table 1. In order to study the lifetime reduction in more detail, additional experiments were carried out aimed at determining the effect of solvent on the triplet lifetime of the polymer. The rationale for these studies is as follows. If intrachain self-quenching occurs in the 6F-ODA polymer, then in a good solvent, where the polymer chain is extended, the triplet lifetime should be higher than in a poor solvent where the polymer chains are coiled and intrachain self-quenching facilitated. The results of this investigation (Table 2) indeed show a remarkable reduction

in the triplet lifetime when changing from the relatively good solvent,  $\text{CH}_2\text{Cl}_2$ , to a poorer solvent mixture comprised of  $\text{CH}_2\text{Cl}_2$  and cyclohexane (cyclohexane is essentially a non-solvent for the 6F-ODA polymer). Apparently, intrachain self-quenching is indeed quite efficient in these systems. A similar dependence of the triplet lifetime on the solvent is *not* observed for the model compounds (Table 1), indicating that changes in the solvent polarity have little effect on the inherent triplet lifetime of the *N*-arylimide repeat

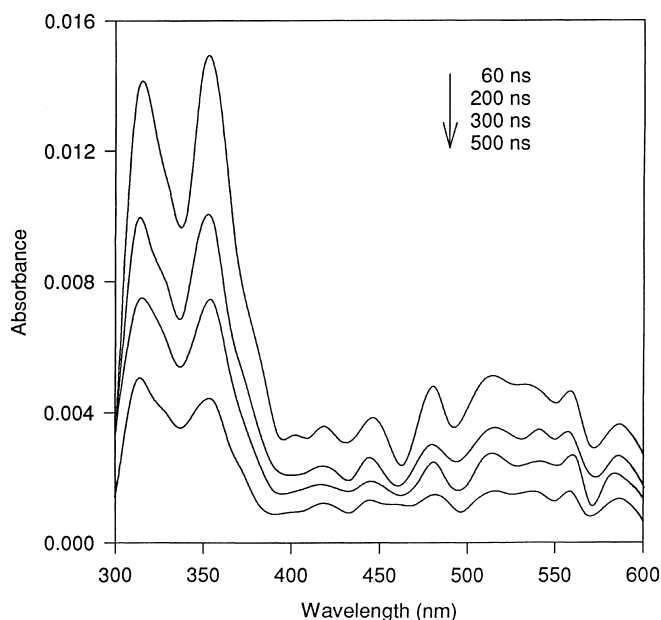


Fig. 1. Transient absorption spectra ( $\lambda_{\text{ex}} = 248 \text{ nm}$ ) of 6F-ODA in nitrogen-saturated methylene chloride solution ( $A_{248} \approx 0.8$ ) at different time intervals after the flash.

units under investigation. We were unable to observe the triplet–triplet absorption spectrum of a 6E-ODA film. This may result from self-quenching of both  $T_1$  and  $S_1$  as well as from inherent experimental difficulties in making transient measurements of films.

In order to assess the effect of conducting photolysis of the 6F-based polyimides in poor solvents, such as mixtures of  $\text{CH}_2\text{Cl}_2$  and cyclohexane (non-solvent for 6F-based

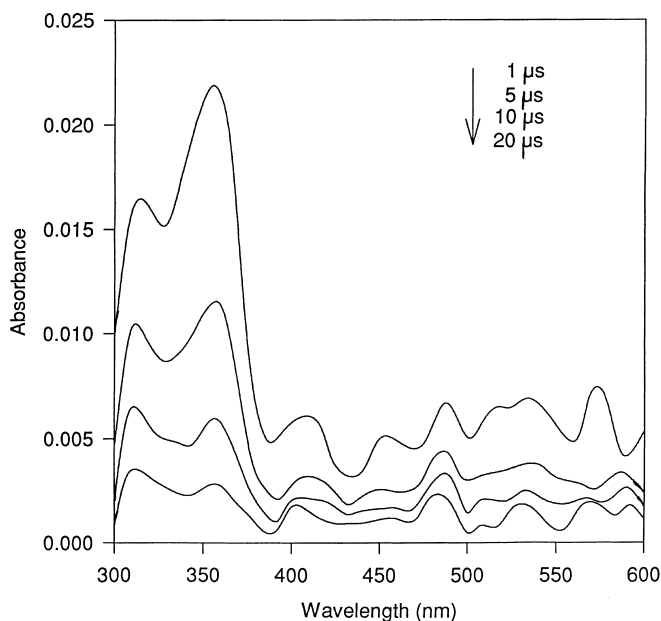


Fig. 2. Transient absorption spectra ( $\lambda_{\text{ex}} = 248 \text{ nm}$ ) of 6F-POA in nitrogen-saturated methylene chloride solution ( $A_{248} \approx 0.8$ ) at different time intervals after the flash.

Table 2

Triplet lifetimes of 6F-POA and 6F-ODA in different solvents ( $\lambda_{\text{ex}} = 248 \text{ nm}$ )<sup>a</sup>

Polymer/model compound	Solvent	$\tau_T$
6F-POA	$\text{CH}_2\text{Cl}_2$	6.3 $\mu\text{s}$
6F-POA	Cyclohexane	4.0 $\mu\text{s}$
6F-ODA	$\text{CH}_2\text{Cl}_2$	730 ns
6F-ODA	$\text{CH}_2\text{Cl}_2$ : cyclohexane :: 90 : 10	498 ns
6F-ODA	$\text{CH}_2\text{Cl}_2$ : cyclohexane :: 75 : 25	50 ns
6F-ODA	$\text{CH}_2\text{Cl}_2$ : cyclohexane :: 50 : 50	23 ns
6F-ODA	$\text{CH}_2\text{Cl}_2$ : cyclohexane :: 25 : 75	17 ns

<sup>a</sup> Nitrogen degassed solutions used for all lifetime measurements.

polyimides), 6F-6F was selected for photolysis studies and evaluation of the accompanying molecular weight changes. Interestingly, there seems to be little effect of the solvent quality ( $\text{CH}_2\text{Cl}_2$  versus  $\text{CH}_2\text{Cl}_2$  : cyclohexane mixtures) on the decrease in the molecular weight of 6F-6F (as observed by GPC) upon irradiation in solution. This may be initially surprising since one might expect that increased triplet self-quenching would reduce the quantum yield of chain cleavage in poor solvent mixtures with cyclohexane present (unless self-quenching leads to chain cleavage via a mechanism that is as efficient as the triplet state radical degradation mechanism we have previously reported [13]). However, we have also observed a dramatic increase in apparent initial intersystem crossing yield to the triplet state ( $\phi_{\text{ISC}}$  measured by the initial triplet–triplet absorbance) for the 6F-based polyimide polymers and model compounds in non-polar solvents [13]. This increased triplet yield in non-polar solvents (resulting from cyclohexane being mixed with  $\text{CH}_2\text{Cl}_2$ ) presumably acts to counterbalance the increased triplet state self-quenching that leads to the decrease in triplet lifetime observed in the poor solvent mixtures with higher cyclohexane content.

#### 4. Conclusions

We have shown that intrachain self-quenching of the triplet state of semifluorinated polyimides is operative in a main chain polyimide system in dilute solution. The self-quenching process is enhanced in poor solvents which force imide chromophores into close proximity.

#### Acknowledgements

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