Photodegradation and Photostabilization of Poly(*p*-phenylene sulfide). 1. Laser Flash Photolysis Studies of Model Compounds

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ABSTRACT: In order to understand the mechanism of poly(*p*-phenylene sulfide) (PPS) photodegradation, eight model compounds related to the polymer and two aromatic disulfides have been studied by nanosecond laser flash photolysis. The model compounds absorb light mostly in the deep UV region and fluoresce very weakly with very short lifetimes. Laser pulse excitation of the linear oligomers in solution produces short-lived triplets that are readily quenched by oxygen, a 4-hydroxy-2,2,6,6-tetramethylpiperidinyloxy radical, biphenyl, and 1-methylnaphthalene. In particular, the quenching by O_2 occurs with unusually high rate constants ($(8–13) \times 10^9$ M^{-1} s^{-1}), suggesting dominance of charge transfer in the quenching interaction. Laser pulse excitation of the disulfides gives longer-lived thiophenoxy radicals which are essentially nonquenchable by oxygen. For the PPS oligomers, the weak character of residual absorptions following decay of triplets suggests that the C–S bond photocleavage leading to thiophenoxy radicals is an inefficient process (particularly for linear trimer and tetramer, quantum yield < 0.05). Oxygen-quenching effects establish that the photocleavage in oligomers occur from the singlet manifold and not from the lowest triplet state. Major implications of these findings to PPS photodegradation and photostabilization are 2-fold. First, in order to suppress degradation resulting from direct C–S bond cleavage, quenching should be aimed at excited singlets rather than triplets; this, however, would be difficult in view of short singlet lifetimes. Second, upon light absorption by the polymer, macromolecular triplets are expected to be formed in high yields as energy-rich, long-lived species; the quenching of these triplets by oxygen or electron-acceptor-type impurities may lead to singlet oxygen (a reactive oxidant for organosulfur compounds) or labile radical ions (potential intermediates through which C–S bond cleavage may readily occur).

Introduction

Physicochemical studies of monomers and model compounds, e.g., short-chain oligomers, are often undertaken in polymer research, because they offer themselves as relatively simple systems with tractable chemistry and yet reflect some of the basic behaviors of the complex macromolecules. For poly(*p*-phenylene sulfide) (PPS), model compound studies are especially pertinent in light of the solubility limitations of the polymer. The work described in this paper was undertaken in the context of our efforts to stabilize PPS against photodegradation. When exposed to UV light, PPS resins can undergo degradation as well as color darkening. Very little is known about the chemistry or mechanism of PPS photodegradation.

In order to shed light on the mechanism of PPS photodegradation, we have carried out a time-resolved laser flash photolysis study of several model compounds related to the polymer. Specifically, our objectives have been (1) to identify excited states and intermediates involved in the photochemistry of the PPS backbone as represented by short-chain linear oligomers, (2) to know the quenching and scavenging behaviors of phototransients from model compounds and to suggest how to utilize this information to reduce photodegradation of PPS, and (3) to determine roles, if any, played by oligomers in PPS photodegradation.

To the best of our knowledge, very little or no work has been done on the photochemistry and photophysics of thioaromatics related to poly(arylene sulfides) (PAS). Becker et al.[1] reported on the electronic spectroscopy of phenyl sulfides in low-temperature glasses and noted that, in addition to spin-orbit coupling, intramolecular exciton interaction could be a salient factor responsible for a large phosphorescence-to-fluorescence quantum yield ratio of diphenyl sulfide. The reactions of organic sulfides with singlet oxygen leading to sulfoxides and sulfones have attracted the attention of several groups of workers.[2–5]

The model compounds under study are shown in Table I.

Experimental Section

The model compounds were prepared by methods described in the literature.[6,7] Diphenyl sulfide and diphenyl disulfide were Aldrich products. The solvents used in laser flash photolysis were of spectral grades (Fisher or Aldrich). 1-Methylnaphthalene (Aldrich) was used without further purification. 4-Hydroxy-2,2,6,6-tetramethylpiperidinyloxy (HTEMPO) and biphenyl, both from Aldrich, were recrystallized from ethanol.

The ground-state absorption spectra were mostly recorded in a Hewlett-Packard Model HP8452 diode-array spectrophotometer under a band-pass of 2 nm. Some spectral measurements were also carried out using Perkin-Elmer Model 320 and Hewlett-Packard Model HP8450A instruments. The emission measurements were performed in an in-house apparatus consisting of a QUESTEK excimer laser source (Xe/HCl, 308 nm, ~20 ns, ≤100 mJ) and an OMA-III detector system from PARC.

The laser sources used for flash photolysis were a Quantel YG481 Nd:YAG system capable of producing 11-ns pulses of 1064 nm (1 J), 532 nm (300 mJ), 355 nm (100 mJ), and 266 nm (60 mJ) or a Lambda-Physik EMG 101 excimer (Xe/HCl, 308 nm, ~20 ns, 10–50 mL/pulse). For both, the laser intensities (5–15 mJ/pulse) were appropriately attenuated. The kinetic spectrometer used with the YAG system consisted of a 150-W Xe arc lamp (monitoring source), usually pulsed to high brightness during experiments, a high-intensity monochromator (Bausch & Lomb), and a Hamamatsu R928 photomultiplier tube detector with a response time on the order of 1 ns. The PMT signals were digitized in a Biomation Model 8100 waveform recorder and then processed and analyzed in a PDP 11/70 computer system. The kinetic spectrometer used with the excimer laser is similar to that described elsewhere.[8]

The flash photolysis experiments were carried out in 1 cm × 1 cm square or 0.2 cm × 1 cm rectangular quartz cells. Both right-angle and front-face geometries were employed between the directions of laser excitation and the analyzing light. The

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Table I. Model Compounds under Study[a]

1, $C_6H_5SC_6H_5$ (dimer)
2, $C_6H_5SC_6H_4SC_6H_5$ (trimer)
3, $C_6H_5SC_6H_4SC_6H_4SC_6H_5$ (tetramer)
4, *p*-$ClC_6H_4SC_6H_5$
5, *p*-$ClC_6H_4SC_6H_4Cl$-*p*
6, *p*-$BrC_6H_4SC_6H_4Br$-*p*
7, *p*-$PhCOC_6H_4SC_6H_4COPh$-*p*
8, *p*-$CH_3C_6H_4SC_6H_4SC_6HCH_3$-*p*
9, $C_6H_5SSC_6H_5$
10, *p*-$ClC_6H_4SSC_6H_4Cl$-*p*

[a] Phenylene groups ($-C_6H_4-$) are linked at *p*-positions.

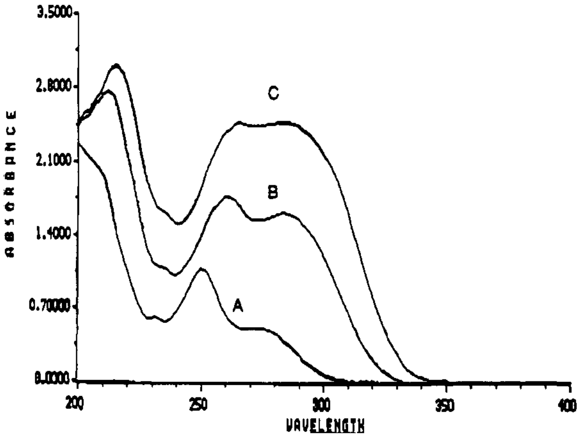

Figure 1. Absorption spectra of linear dimer, **1** (A; 0.097 mM), trimer, **2** (B; 0.10 mM), and tetramer, **3** (C; 0.099 mM), in acetonitrile. Cell path length in each case: 1 cm.

solutions were deoxygenated by bubbling oxygen-free nitrogen or argon (unless oxygen effects were meant to be studied).

Results and Discussion

The bulk of the results presented in this paper came from nanosecond laser flash photolysis experiments. In these experiments,[8,9] the sample solutions were subjected to photoexcitation via absorption of laser pulses of short duration (typically, 5–20 ns). The resultant transient species were monitored, on nano- to millisecond time scales, in terms of their absorption of an analyzing light or their emission. The photogenerated transients could be the electronically excited states (namely, lowest singlets and triplets) or short-lived products derived therefrom (e.g., radicals and radical ions). In kinetics measurements, the usual detector was a photomultiplier tube (PMT) with fast response (typically, 1 ns); with such a detector, the absorption or emission intensities of phototransients at various times following laser pulse excitation were obtained by measurements at discrete wavelengths in a point-by-point manner. Alternatively, use was made of a gated diode-array detector, Optical Multichannel Analyzer (OMA III), which allowed measurements of complete spectra at a given instant subsequent to a single laser shot.

A. UV Absorption Spectra. All of the model compounds under study absorb light in the UV region, and are colorless (except **10**, which is yellow in the solid, crystalline state). The absorption spectra of the three unsubstituted linear oligomers (**1**–**3**) are shown in Figure 1. It is noted that, with an increase in the chain length, the overall location of the lowest energy band system becomes progressively red-shifted and the corresponding molar extinction coefficient becomes higher. Furthermore, the relative intensity of the maximum of the longer-wavelength component of the two-part band systems is higher for the longer-chain oligomers. Except for nominal substituent effects on the wavelength maximum and molar absorption intensity, the chloro- and bromo-substituted diphenyl sulfides (**4**–**6**) exhibit spectral features similar to those of the parent sulfide. As shown in Figure 2, the dibenzoyl derivative (**7**), however, has its spectrum altered considerably; that is, there is a large red shift (~40 nm) in the lowest-energy maximum as well as a pronounced increase in the corresponding molar extinction coefficient (ca. 3 times). The dimethyl analog (**8**) of the linear trimer is spectrally similar to the trimer itself. The spectral data of all the compounds are summarized in Table II.

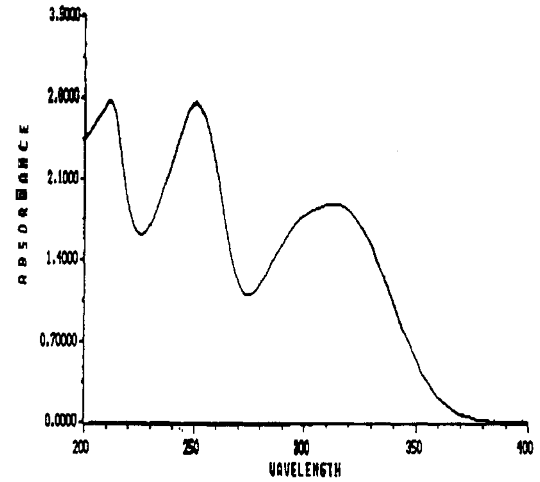

Figure 2. Absorption spectrum of a 0.100 mM solution of **7** in acetonitrile (cell path length: 1 cm).

Table II. Absorption Spectral Data in Acetonitrile at 295 K

substrate	λ_{max} (nm)	ϵ_{max} (10^3 M^{-1} cm^{-1})	ϵ_{266} (10^3 M^{-1} cm^{-1})	ϵ_{355} (10^3 M^{-1} cm^{-1})
		Oligomers		
1	251	11.6	5.6	
2	259	17.1	15.5	
3	265	23.7	24.1	~0.1
4	253	17.7	9.9	
5	256	19.9	10.8	
6	256	23.1	15.1	
7	317	19.3	16.6	4.0
8	262	20.3	18.5	
		Disulfides		
9	240	15.7	3.3	0.12
10	248	21.4	7.2	0.24

The two disulfides (**9** and **10**) included in this study are characterized by long tails of absorption covering the whole of the near-UV region (250–350 nm). The spectra are presented in Figure 3. The tail absorptions probably owe their origin to low-lying transitions arising from the configuration interaction of two isoenergetic $n \rightarrow \pi^*$ type transitions involving nonbonding and π^* orbitals of S and phenyl groups, respectively. Such weak, structureless, low-lying absorptions are also typical of organic peroxides.

B. Emission Properties of Linear Oligomers. On the basis of the low-temperature emission behavior of **1** in rigid matrices,[1] it was suspected that this compound as well as its longer-chain homologues would be weakly fluorescing at room temperature in fluid solutions. Still, attempts were made to detect emissions, if any, from **1**–**3** under ambient conditions, using 308-nm laser pulse (20-ns-wide) excitation and OMA-based detection. For each of the three homologues, very weak fluorescence could be observed in such solvents as *n*-heptane and acetonitrile at 295 K. The emission spectra (uncorrected) showed maxima at 380–400 nm. Unfortunately, these weak emissions were often distorted by contributions from impurities present in the solvent and, therefore, were not pursued in detail.

The emissions observed from **1**–**3** were maximum in intensity when the gate pulse applied to the detector was tightly synchronized with the excitation laser pulse. As the gate (i.e., time window of observation) was shifted

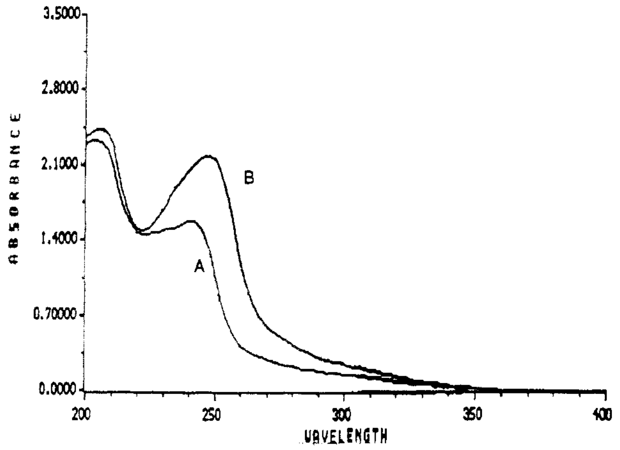

Figure 3. Absorption spectra of disulfides **9** (A; 0.10 mM) and **10** (B; 0.10 mM) in acetonitrile. Cell path length in both cases: 1 cm.

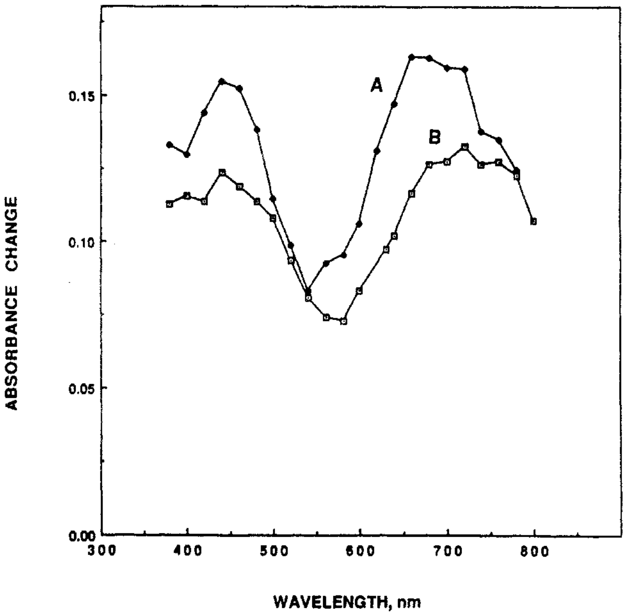

Figure 4. Transient absorption spectra observed at 300 ns following 308-nm laser pulse excitation of ca. 0.1 mM solutions of (A) trimer, **2**, and (B) tetramer, **3**, in acetonitrile (argon-saturated).

beyond the laser pulse, the emission intensities died off sharply. This result suggests that the lifetimes of the fluorescing states are short (<10 ns) for the compounds in question. PMT-based traces of emission obtained by 308-nm laser excitation showed that they followed the laser pulse profile very closely; estimated lifetimes from the traces were <5 ns.

C. Spectra and Kinetics of Laser-Induced Phototransients. Upon 266-, 308-, or 355-nm laser flash photolysis, solutions of compounds **1**–**10** produce transient species that can be monitored in terms of absorbance changes in the near-UV and visible regions. The trimer (**2**) is a representative case. The transient absorption spectrum observed at ~300 ns following 308-nm laser excitation of this compound in acetonitrile is shown in Figure 4A. The transient decays over a period of 15–20 μs and follows predominantly first-order kinetics. The best fit of the decay profile into combined first- and second-order kinetics gives $4.9 \times 10^4\ \text{s}^{-1}$ as the rate constant for first-order decay (major component). Following the completion of the decay of the primary transient, there is a weak, broad, residual absorption due to a longer-lived species which does not display any well-defined maximum. The transient phenomena from **2** in cyclohexane, from **8** in acetonitrile, and from **3** in cyclohexane, acetonitrile, and toluene are very similar to those from **2** in acetonitrile, except that the transient absorption maxima from the tetramer (**3**) and the methyl-substituted trimer (**8**) are red-shifted by 10–20 nm (see Figure 4B for **3**).

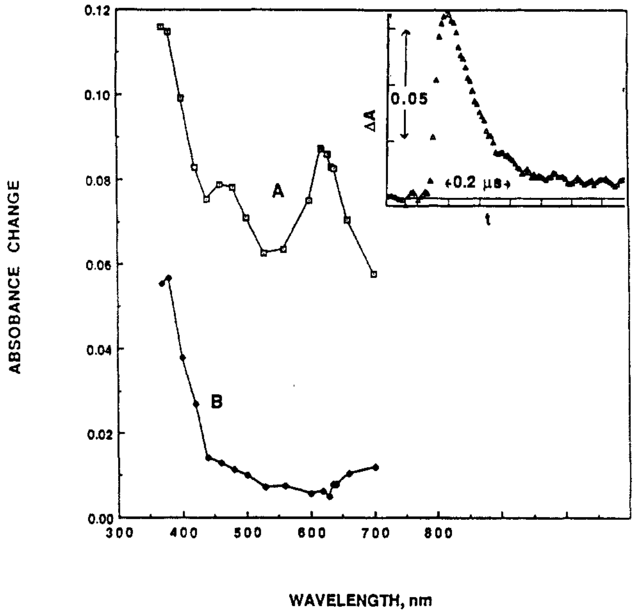

Figure 5. Transient absorption spectra observed at (A) 100 and (B) 600 ns following 308-nm laser pulse excitation of dimer, **1** (ca. 1 mM), in argon-saturated acetonitrile. Inset: kinetic trace at 635 nm.

In comparison to **2** and **3**, the initial phototransient from the dimer (**1**) is considerably shorter-lived. This is illustrated by the kinetic trace shown in the inset of Figure 5. The transient absorption spectra (Figure 5) suggest at least two photoproducts. One of these is relatively short-lived and displays maxima at 450 and 630 nm (in acetonitrile). The other corresponds to the longer-lived residual absorbance following the decay of the initial transient and shows a maximum at 380 nm. Among the three halogenated diphenyl sulfides (**4**–**6**), **4** and **5** exhibit transient behaviors reminiscent of the parent compounds, while in the case of the bromo derivative (**6**) no transient is discernible in the shortest time scale available (100 ns).

In order to know where thiophenoxy radicals absorb, the disulfides **9** and **10** were subjected to laser flash photolysis. The transient phenomena observed for these two compounds are given in Figure 6. On the basis of spectral and kinetic similarity with the transient products of photocleavage of disulfides and of photoinduced electron and/or H-atom transfer from the thiophenolate ion and thiophenol,[10] the slow-decaying ~450 and 520-nm transients (Figure 6A,B) observed in the case of **9** and **10** are identifiable as thiophenoxy and *p*-chlorothiophenoxy radicals, respectively.

Upon laser flash photolysis, the dibenzoyl derivative (**7**) behaves like a substituted benzophenone.[11,12] The initial phototransient, recognizable as the lowest triplet (see later), has its major absorption maximum located at 700 nm in acetonitrile (Figure 7). In cyclohexane, the triplet is shorter-lived, and following its decay, a second species with maxima at 350 and 550 nm becomes evident. The latter is assignable to the ketyl radical[13,14] produced as a result of hydrogen abstraction from the solvent by the ketone triplet.

Wherever appropriate, the decay profiles of the various transient intermediates were fitted into equal-concentration second-order, or combined first- and second-order,

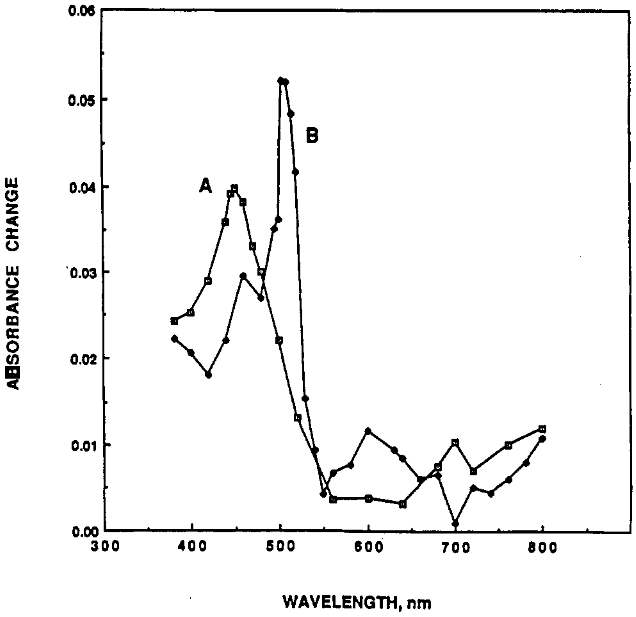

Figure 6. Transient absorption spectra observed at 300 ns following 308-nm laser pulse excitation of ca. 0.5-mM solutions of (A) 9 and (B) 10 in argon-saturated acetonitrile.

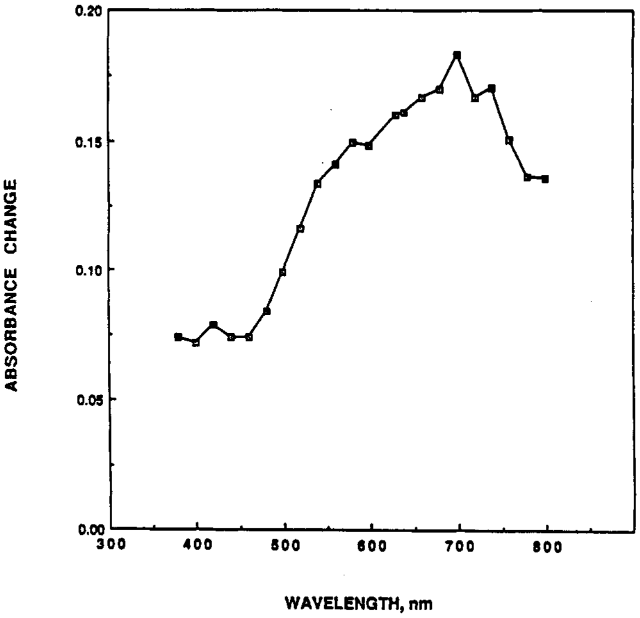

Figure 7. Transient absorption spectrum observed at 300 ns following 308-nm laser pulse excitation of 7 (ca. 0.05 mM) in argon-saturated acetonitrile.

kinetics. The kinetic and spectral data are compiled in Table III.

D. Quenching Studies: Triplet Yields. The thiophenoxy radicals from the disulfides (9 and 10), and the triplet and the ketyl radical from the ketone (7), were easily assignable through comparison with the same (or similar) species obtainable from related systems and described in the literature.[10] This was, however, not the case with the linear oligomers and their halo- and methyl-substituted analogs. In the case of the latter systems, for assignment purposes, quenching studies were carried out. The microsecond phototransients from 1–3, 7, and 8 were readily quenchable by oxygen, as indicated by pronounced enhancements of their decay kinetics in air-saturated solutions. From a comparison of the decay rate constants in air- and argon-saturated solutions, bimolecular rate constants for quenching by O_2 were measured and were found to be unusually high ($\sim 10^{10}$ M^{-1} s^{-1} in acetonitrile) for the initial phototransients from 1–3.

Table III. Transient Spectral Properties of Triplets and Primary Photoproducts Observed upon Laser Flash Photolysis of Model Compounds[a]

substrate	solvent[b]	λ^T_{max} (nm)	τ^T [c] (μs)	λ^P_{max} (nm)	$\tau^P_{1/2}$ [d] (μs)
1	ACN	450, 620	0.11	370	10
2	ACN	450, 700	9.0	380	6
3	ACN	450, 730	8.5	380	10
	TOL	480, 700	10.0		
4	ACN	460[e]	0.8	~370	
5	ACN	470[e]	0.25	~370	
7	ACN	700	22.5	370	
	CH	690	3.3	350, 560	>20
8	ACN	480[e]	11.1	380	~10
9	ACN			450	5.0
	CH			450	5.0
	TOL			450	2.0
10	ACN			520	4.5
	CH			520	4.5

[a] Laser excitation wavelengths were 266 nm for acetonitrile and cyclohexane solutions and 355 nm for toluene solutions. [b] ACN, acetonitrile; CH, cyclohexane; TOL, toluene. [c] Obtained from analysis of composite first- and second-order kinetics; the 2nd order component was minor in each case. [d] Half-lives from second-order, equal-concentration, kinetic fits. [e] The longer-wavelength maxima were not looked for in these cases.

The oxygen sensitivity points to the assignment of the transients in question as triplets, and this is corroborated by their quenching by the stable radical 4-hydroxy-2,2,6,6-tetramethylpiperidinyloxy (HTEMPO) and by the fact that they sensitize the formation of biphenyl and naphthalene triplets when 1–3 and 7 are flash-photolyzed in the presence of millimolar concentrations of biphenyl and naphthalenes. The latter compounds have realtively low triplet energies (E_T's,[15] 55–60 kcal/mol for naphthalenes and 66 kcal/mol for biphenyl) and are commonly used as efficient triplet quenchers (energy acceptors). That the sensitization by triplet energy transfer occurred was established by the facts that the transient spectra of the products of quenching matched with the triplet–triplet absorption spectra (λ_{max}'s, 360–365 nm for biphenyl and 420–430 nm for naphthalenes) given in the literature[16] and that the decay kinetics of the transients (donors) agreed with those of formation of quencher triplets (acceptors). In the case of the quenching of a triplet from 3 by 1-methylnaphthalene (MN) in toluene, the bimolecular rate constant for the quenching was calculated to be 4.7×10^9 M^{-1} s^{-1}. The fact that the quenching rate is diffusion-controlled suggests that the energy trnsfer is exothermic and that the triplet energy (E_T) of 3 is at least 10 kcal/mol higher than that of MN (E_T = 59.6 kcal/mol[15]).

Using acetonitrile solutions of 1–3, 7, and benzophenone optically matched at 308 nm, the triplet yields (ϕ_T) of the sulfide oligomers were determined under 308-nm laser flash excitation via energy transfer to biphenyl (added to the solutions at 0.1–0.2 M). In these experiments, the absorbance change due to the biphenyl triplet (monitored at 365 nm) produced as a result of essentially complete quenching of triplets of 1–3 and 7 was compared with that in the case of benzophenone. ϕ_T's were calculated based on the assumption that the ϕ_T of benzophenone (actinometer) in acetonitrile was unity. The data regarding ϕ_T and quenching by O_2 and HTEMPO are given in Table IV.

The decay characteristics of the transient absorptions attributable to thiophenoxy radicals photogenerated from 9 and 10 remain completely unchanged on going from deoxygenated to air-saturated solutions. This implies the insensitivity of the S-centered radicals to O_2 (in contrast to the C-centered radical in general[13,14]). The weak, long-

Table IV. Triplet Yields and Rate Constants for Triplet Quenching by O_2 and HTEMPO in Acetonitrile

substrate	ϕ_T[a]	k_{q,O_2},[a] 10^9 M^{-1} s^{-1}	$k_{q,HTEMPO}$,[a] 10^9 M^{-1} s^{-1}
1	0.91	7.8	1.0
2	0.92	10.7	1.4
3	0.82	13.2	1.1
7	0.77	3.2	

[a] Estimated error: ±15%.

lived, residual absorptions in the case of **1**–**3** were also similarly nonquenchable by O_2.

The 355-nm laser flash excitation of the disulfides **9** and **10**, in the presence of MN at concentrations as high as 0.071 M does not show the formation of any MN triplet. Also, the yield of the thiophenoxy radicals is practically unchanged, relative to excitation in the absence of MN. This result indicates that no reasonably long-lived triplet with energy close to or higher than that of MN is involved in the photocleavage of the disulfide bond. There is, however, the possibility that the energy of the lowest triplet of the aromatic disulfide is well below that of MN, and this would render energy transfer from the former endothermic and therefore unfavorable. The fact that oxygen at ~2 mM concentration (as available in air-saturated solutions) does not affect the thiophenoxy radical yields suggests that, even if the S–S bond cleavage occurs via a triplet pathway, the triplet(s) involved must be much shorter-lived than usual (i.e., in the nanosecond domain).

In the case of **1**–**3**, the magnitude of the residual absorbance, at the 400–500-nm region, following the decay of the initial phototransients remains practically unchanged on going from N_2-saturated to air-saturated solutions. In air-saturated solutions of **2** and **3**, the initial phototransients are almost totally quenched by O_2; partial quenching by O_2 also occurs in the case of **1**. These observations establish that the formation of thiophenoxy radicals, if any, in the case of linear oligomers does not take place through the intermediacy of the observed initial transients.

E. Identification of Phototransients: Bond Cleavage Yields. The principal transients formed in the course of laser flash photolysis of the model compounds and observed by kinetic spectrophotometry in the microsecond time regime are of two types. The first type consists of the initial, relatively rapidly decaying components which decay by predominantly first-order kinetics and are quenchable by oxygen, HTEMPO, and typical triplet energy acceptors. The second type is represented by the slower-decaying species, observed mainly in the case of the disulfides, which decay predominantly by second-order kinetics and are practically nonquenchable by oxygen at millimolar concentrations. As discussed earlier, the transients of the first type are reliably identified as thioaromatic triplets. The identification of transient photoproducts from disulfides in terms of thiophenoxy radicals is also straightforward, because their spectra and kinetics agree with those of the same radicals produced by a variety of photochemical and radiation-chemical methods.[10] A pertinent question is whether these radicals make any significant contribution to the relatively long-lived, residual absorbances observed in the case of oligomers. Spectrally, the latter are characterized by maxima at 370–380 nm whereas the thiophenoxy radicals from disulfides (**9** and **10**) show prominent maxima at 450 and 520 nm, respectively. Specifically, a comparison of transient spectra B (Figure 5) and A (Figure 6) suggest that a major part of long-lived residual absorption in the case of **1** cannot be due to the thiophenoxy radical. Nevertheless, even if we assume that all of the residual absorbance changes at 450 nm in the case of **1** are due to the thiophenoxy radical, we estimate that the yield of the primary photocleavage of the C–S bond is less than 0.1. In comparison, the corresponding yields are much lower for **2** and **3** (<0.05). Also, the spectral features of the *p*-chlorothiophenoxy radical are sharp and distinct (Figure 6B). With **5** as the substrate under 266-nm excitation in acetonitrile, we do not see any hint of the formation of the *p*-chlorothiophenoxy radical on the microsecond time scale. The C–S bond photocleavage yield in this case is <0.01.

The dominance of triplets (ϕ_T's ~ 1) in the laser-induced transient phenomena of oligomers is not surprising. Spin-orbit coupling due to the heavy atom, S, makes intersystem crossing facile. Moreover, as noted for diphenyl sulfide,[1] there is the possibility of exciton interaction between adjacent phenyl groups, rendering the lowest excited singlet state partially forbidden and, hence, intersystem crossing relatively important. Importantly, the triplets are not participants in the inefficient photocleavage process. This conclusion is based on the fact that their extensive quenching by O_2 does not make any difference in the yields of observed, longer-lived photoproducts (thiophenoxy radicals inclusive). Thus, we infer that the photocleavage (in small yields) occurs from the singlet excited states.

F. Implications to PPS Photodegradation. The two major findings from model compounds flash photolysis studies are as follows. First, for dimer (**1**), the photoinduced C–S cleavage is a low-yield, singlet-mediated process; this process becomes more insignificant on increasing the chain length (that is, on going to trimer and tetramer). Second, the intersystem crossing efficiency is close to unity for all the oligomers. The triplets, although not responsible for direct C–S photocleavage, are readily oxygen-quenchable and can act as potential sensitizers for singlet oxygen or participate as activated species in electron-transfer reactions. In fact, the unusually high rate constants for O_2 quenching, indicative of a charge-transfer mechanism[17,18] with O_2 as an acceptor, reflect a strong electron-donor nature of the thioaromatic oligomers.

The trends in the efficiencies of photocleavage and triplet formation as observed in oligomers are expected to continue to the polymer, PPS. Since the singlet energy (E_S) decreases with increasing chain length, singlet-mediated bond cleavage in the polymer would be less exothermic and, hence, less favorable. This, however, does not mean that the direct cleavage in low yields cannot be crucial in the polymer degradation process. Even a low concentration of cleavage-derived macroradicals can be potential intermediates in the photodegradation process as is often the case with relatively non-UV-absorbing polymers in which radicals from impurities act as initiators.[19]

That photocleavage in oligomers takes place from the singlet state has two implications. First, it means that to suppress chemistry ensuing from the cleavage, one can in principle attempt to quench the singlet state by, for example, long-range dipole–dipole energy transfer[20] in the polymer matrix. Such a long-range mechanism is not available to triplets, which transfer energy through a collisional mechanism (via exchange interactions). On the other hand, it is shown that the oligomer singlets, as manifested in fluorescence, are short-lived. If this trend continues to the polymer, stripping the singlets of their energy by any bimolecular mechanism would be difficult.

Although the triplets are shown not to contribute to the direct photocleavage, they can play other damaging roles significant to PPS photodegradation. Based on the behavior of the oligomers, triplets are, no doubt, also formed in high yields in the course of photoexcitation of the polymer. The polymer triplets in the rigid matrix are expected to be considerably longer-lived than the oligomer triplets in fluid solutions and hence more susceptible to interactions with O_2 and electron donor/acceptor impurities in the polymer. Such interactions would give rise to singlet oxygen and labile radical ions which in turn would initiate chemistry. The reactions of organosulfur compounds (including diphenyl sulfide) with singlet oxygen resulting in sulfoxides and sulfones are well documented.[2-5] The C–S bond energy in diphenyl sulfide decreases drastically on going from the parent substrate to the radical anion (from ca. 80 kcal/mol to ca. 4 kcal/mol[21]), making the C–S bond rupture unusually facile in the latter.

We also noted the insensitivity of thiophenoxy radicals (produced from disulfides) toward oxygen. This suggests that such radicals cannot be as reactive as C-centered radicals in forming peroxy- or oxy-type intermediates commonly implicated in polymer photooxidation.[18] However, with polymer and oligomers as substrates, the phenyl-type radicals would be coproduced and might react with oxygen, leading to oxy intermediates. Furthermore, the kinetic measurements on thiophenoxy radicals in air-saturated solutions gave only the upper limits for their reactivity with O_2 ($\leq 10^7$ M^{-1} s^{-1}). In the solid polymer matrix, the low O_2 reactivity of polymer-derived thiophenoxy radicals may very well be compensated for by their long lifetimes.

Finally, we should address the question as to whether the direct light absorption by oligomers present in PPS can be a factor in the polymer degradation. From the short-wavelength absorptions of linear and cyclic oligomers (Figure 1), it is obvious that these compounds at low concentrations cannot absorb much light, simply because the sunlight (sea level) as well as the output from a Pyrex-shielded Xe lamp in a WeatherOmeter is deficient in deep UV. Equally important, the oligomer absorptions are buried under the stronger absorption of the polymer itself. Thus, it is unlikely that the presence of oligomers would be a serious cause for PPS photodegradation. This is, in fact, borne out by the results from our experiments in which films made from a PPS resin that had been purified of oligomers by solvent extraction were UV-exposed; these films were found to be as photocolorable as those made from the unpurified resin and as those made from purified resin deliberately mixed with oligomers.

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