Singlet Oxygen as a Reactive Intermediate in the Photodegradation of Phenylenevinylene Oligomers

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Singlet molecular oxygen ($a^1\Delta_g$) is shown to be the principal reactive intermediate in the photoinduced oxygen-dependent decomposition of a series of phenylenevinylene oligomers. The reaction rate between singlet oxygen and the oligomer decreases (1) with a decrease in the extent of phenylenevinylene conjugation (i.e., oligomer chain length) and (2) upon the incorporation of electron-withdrawing substituents on the oligomer. The reaction rate, however, does not appear to depend solely on the electron density of the oligomer π system, as calculated using ab initio methods. For oligomers with vinyl-substituted cyano group(s), the reaction with singlet oxygen is very slow, thus making such compounds good candidates for the production of stable electroluminescent materials.

Introduction

Phenylenevinylene polymers and oligomers have been the subject of a significant amount of recent research, principally because of their use as the active material in light emitting diodes (LEDs).[1−9] Much of this research has focused on the sensitivity of these materials to oxygen, both in an LED as well as after UV/vis irradiation.[10−16] It is now well-established that oxygen-dependent degradation of the polyene is a key factor that determines the longevity of phenylenevinylene LEDs.[1,17]

We recently established that singlet molecular oxygen ($a^1\Delta_g$) is the reactive intermediate in the photooxidative decomposition of the electroluminescent material poly(2,5-bis(5,6-dihydrocholestanoxy)-1,4-phenylenevinylene) [BCHA-PPV], both in liquid solutions and in polymer films.[10] Extensive chain scission of BCHA-PPV was proposed to proceed via reaction of singlet oxygen in a ${}_{\pi}2 + {}_{\pi}2$ cycloaddition with the double bond that connects phenylene groups in the macromolecule. Cumpston et al.[11−14] have provided significant data that are likewise consistent with such a cycloaddition. Although the reaction between the monomeric analogue of the phenylenevinylene system, stilbene, and singlet oxygen is slow,[18,19] we speculated that the increased conjugation of the polymer along with the electron-donating alkoxy substituents increased the reactivity of the bridging double bond in BCHA-PPV to singlet oxygen.[10] Subsequent reports have provided sporadic data that are consistent with these speculations.[14,16,20]

In an attempt to better understand this chemistry, we set out to systematically examine how changes in the phenylenevinylene influence the production of, and reaction with, singlet oxygen. We specifically wanted to focus on the effects of both substituents and phen-

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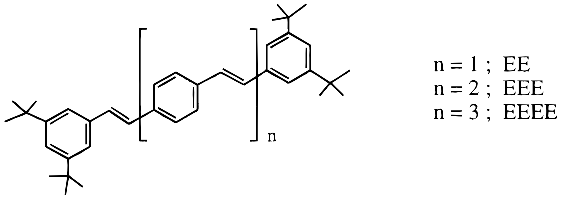
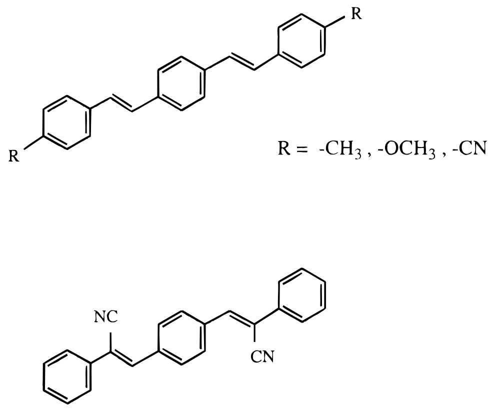
Scheme 1



Scheme 2



ylenevinylene chain length. The use of phenylenevinylene oligomers makes this study more tractable. Although singlet oxygen is the reactive intermediate responsible for the photooxidative degradation of phenylenevinylene polymers, it does not necessarily mean that it will likewise be the reactive intermediate responsible for phenylenevinylene oligomer degradation. Indeed, other mechanisms for oligomer degradation could very easily be proposed and justified, particularly since the reaction between singlet oxygen and stilbene is slow. Thus, it is first necessary to ascertain if singlet oxygen is even involved in phenylenevinylene oligomer degradation.

Like their polymeric analogues, phenylenevinylene oligomers are also electroluminescent.[21−23] Thus, the applicability of our results is not diminished, and our study should be pertinent in the quest for molecular control of the reactions that result in the degradation of electroluminescent materials.

Results and Discussion

Experiments were performed on two groups of phenylenevinylene oligomers. The effect of chain length was examined using the molecules shown in Scheme 1, where the number of linking double bonds is denoted by the letter E (entgegen).

Substituent effects were examined using the EE molecules shown in Scheme 2. EE-CH_3, EE-OCH_3, and EE-CN denote the aryl-substituted oligomers, whereas EE-vCN denotes the vinyl cyano compound.

1. General Photophysical Properties. The absorption and fluorescence spectra of the phenylenevinylenes were recorded, and the data corresponded to those already published either for the identical or similar compounds.[7,10,24−26] As expected, the respective band maxima shift to the red as the extent of conjugation increases in the series EE, EEE, EEEE, BCHA-PPV. For the EE oligomer, aryl substituent changes have only a small effect except for the cyano group which results in a ∼10 nm red shift of both the absorption and emission maxima. Although EE-CN and EE-vCN have similar spectral maxima, the shapes of the EE-vCN absorption and emission bands are significantly different, reflecting conformational changes that arise upon vinyl substitution.[7]

Table 1. Singlet Oxygen Quantum Yields, ϕ_Δ, and Relative First-Order Rate Constants, k_{rem}(rel), for the Singlet Oxygen-Mediated Photooxidation of Phenylenevinylenes[a]

molecule	ϕ_Δ	k_{rem}(rel)
BCHA-PPV	0.025[b]	8.0
EEEE	0.09	1.0
EEE	0.08	0.80
EE	0.07	0.60
EE-OCH_3	0.07	0.57
EE-CH_3	0.08	0.52
EE-CN	0.05	0.16
EE-vCN	0.002	0.01

[a] In toluene, unless otherwise noted. [b] Determined in CS_2.[10]

Like BCHA-PPV, the phenylenevinylene oligomers generally have high fluorescence quantum yields (∼0.7−1.0) and short singlet state lifetimes (∼1 ns).[10,24−26] A consequence of the latter is that oxygen-induced intersystem crossing to produce the oligomer triplet state does not play a significant role, even in oxygenated solutions. Thus, upon direct absorption of light, oligomer excited states that could sensitize the production of singlet oxygen are not produced in great yield.

BCHA-PPV has a triplet state energy, E_T, of ∼150 kJ/mol.[10] E_T in the less-conjugated oligomers is somewhat higher [E_T(EE)= ∼170 kJ/mol].[27] E_T for the monomeric analogue of these compounds, (*E*)-stilbene, is 206 kJ/mol.[28] In the absence of oxygen, the triplet-state lifetime of the oligomers exceeds 1 μs. Thus, once formed, the oligomer triplet state is (1) sufficiently long-lived to be quenched by ground-state oxygen [k_q(EE) = 5×10^9 M^{-1} s^{-1}][27] and (2) sufficiently energetic to generate singlet oxygen. Indeed, upon photolysis of the oligomers, singlet oxygen is formed and can be monitored by its characteristic 1270 nm phosphorescence. However, as expected, the quantum yields of singlet oxygen production, ϕ_Δ, are small (Table 1).

2. Oxygen-Dependent Photodegradation. As in our previous work on BCHA-PPV,[10] photoinduced degradation of the oligomers was quantified by monitoring the decrease in phenylenevinylene UV/vis absorbance as a function of elapsed photolysis time.

Upon direct irradiation in oxygenated or aerated solutions, the oligomers do degrade, albeit slowly. The

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degradation rate (1) increased upon changing the solvent from toluene to CS_2 and (2) decreased upon the addition of 1,4-diazabicyclo[2.2.2]octane (DABCO), thus implicating singlet oxygen as a reactive intermediate (singlet oxygen is longer-lived in CS_2 than in toluene, and DABCO is a known quencher of singlet oxygen).[29,30] In contrast to the experiments on BCHA-PPV, however, the rate of oligomer degradation upon direct irradiation was sufficiently slow that it was difficult to accurately quantify the data.

To better assess the reactivity of the oligomers with singlet oxygen, photosensitizers were employed to increase the singlet oxygen yield in the system. Selection criteria for the photosensitizer included (1) an absorption band sufficiently red-shifted relative to the oligomer absorption bands to ensure consistent singlet oxygen production, (2) low absorbance in the spectral region used to monitor oligomer disappearance, and (3) stability under the conditions in which oligomer degradation occurs. Although some experiments were performed with C_{60}, including those on BCHA-PPV, biacetyl proved to be the most useful sensitizer for all the oligomers.[31] Time-resolved absorption experiments indicated that, in aerated solutions, quenching of the biacetyl triplet state by the oligomers did not compete with quenching by oxygen to yield singlet oxygen. Under these photosensitized conditions, the rate of oligomer degradation increased dramatically. The degradation rate was quantified by plotting $\ln(A_t/A_0)$ vs the elapsed photolysis time t, where A_t and A_0 are the oligomer absorbances at time $= t$ and time $= 0$, respectively (Figure 1). The slope of these plots yields a first-order rate constant, k_{rem}, for oligomer removal (Table 1).

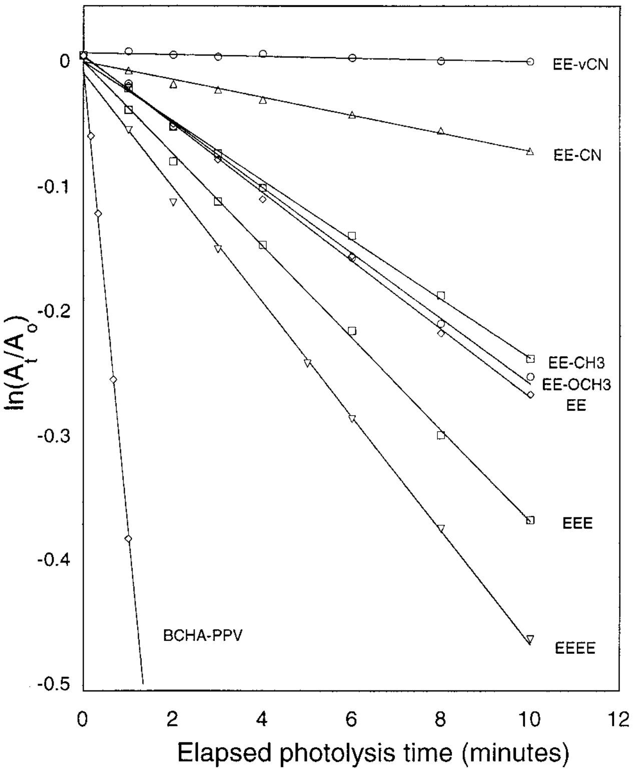

Figure 1. Plot of $\ln(A_t/A_0)$ as a function of the elapsed photolysis time for a series of phenylenevinylene oligomers, where A_t and A_0 are the oligomer absorbances at time $= t$ and time $= 0$, respectively. The solid lines are linear least-squares fits to the respective data sets.

It is important to again ascertain that, under the photosensitized conditions, the oligomers are indeed being removed as a consequence of a reaction with singlet oxygen. In this regard, (1) when the solvent was changed from toluene to CS_2, the rate of oligomer degradation increased by an amount consistent with the expected change in singlet oxygen lifetime, (2) upon the addition of DABCO, the rate of degradation decreased by an amount consistent with the expected quenching of singlet oxygen by DABCO, and (3) the time-resolved phosphorescence of singlet oxygen was monitored and the decay rate of this emission increased in the presence of oligomer.[33] The data are thus consistent with a reaction in which singlet oxygen is the reactive intermediate in the photooxidative degradation of the oligomers.[34]

As shown in Table 1 and Figure 1, results obtained in this study appear to confirm our speculations regarding the reactivity of phenylenevinylenes with singlet oxygen, as set forth in our report on BCHA-PPV.[10] Specifically, (1) a decrease in the extent of phenylenevinylene conjugation results in a decrease of reactivity and (2) withdrawal of electron density from the oligomer, as achieved for example by cyano substituents, likewise results in a significant reactivity decrease. The data also indicate that a vinyl cyano group is particularly effective at decreasing the rate of reaction. Although vinyl cyano-substituted phenylenevinylenes have

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(31) It is known that biacetyl can be labile under photooxidation conditions and that it can sensitize the radical-mediated epoxidation of olefins.[32] Under the conditions employed to quantify oligomer bleaching, however, the biacetyl absorption spectrum remained unchanged and the data were all consistent with a biacetyl-sensitized, singlet oxygen-mediated process. However, in pulsed-laser time-resolved experiments to quantify the biacetyl triplet state lifetime, where comparatively higher irradiation intensities were used, evidence of biacetyl instability became apparent.

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(33) The rate constant for quenching of singlet oxygen by the oligomer is comparatively small ($\sim 5 \times 10^4$ M^{-1} s^{-1} for EE). Thus, an appreciable amount of oligomer is required to decrease the singlet oxygen lifetime. With limited oligomer supplies, we did not undertake standard quenching studies to quantify rate constants for singlet oxygen removal.

(34) The oligomers also degrade upon irradiation of biacetyl in deoxygenated toluene solutions. Although the degradation rates at early irradiation times are approximately the same as in aerated solutions, the spectral data suggest that different reactions are occurring to form different products. As with the experiments in the presence of air, the biacetyl absorption spectrum did not change over the course of oligomer degradation. In this case, the data are consistent with a mechanism in which the biacetyl triplet state is quenched by the oligomer followed by a reaction that removes and/or changes the phenylenevinylene chromophore, possibly a 2 + 2 cycloaddition reaction between oligomers.[35] This latter reaction, however, should not be a significant problem in deoxygenated solid films where oligomer diffusion is curtailed.

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previously been studied as electroluminescent materials, the motivation for this earlier work was to provide a better match between the electron affinity of the polymer and the work function of the desired metal electrode in an LED.[4,9,36,37] It was subsequently observed that materials with electron-withdrawing vinyl substituents were in fact quite stable against photooxidation.[14,16]

It has been amply demonstrated that useful information can be obtained about phenylenevinylenes using computational methods.[5,38,39] In an attempt to further substantiate our model of phenylenevinylene reactivity with singlet oxygen, we used ab initio computations to obtain electron densities at various positions along the π system, including the vinyl carbons. The electron densities thus obtained, however, do not correlate with the experimental k_{rem} data as well as one might have expected. For example, calculations on EE, EEE, and EEEE oligomers[40] indicate that conjugation length does not significantly influence the electron density at the vinyl carbons, a point previously noted by Cumpston et al.[14] Experimental data, however, show significant differences in reactivity between these oligomers (Table 1, Figure 1). A reasonable correlation was observed between the calculated HOMO energy levels and k_{rem} for EE-OCH_3, EE-CH_3, EE-CN, and EE-vCN. However, this correlation did not extend to include EE, EEE, and EEEE oligomers. It thus appears that the singlet oxygen reaction rates may not just depend on electronic effects; other factors may also play a role. In this regard, it is important to note that our computations, as well as those of others,[7,39] indicate substituent- and chain length-dependent deviations from planarity in the oligomers. Thus, conformational and steric effects may be factors that partially influence oligomer reactivity with singlet oxygen,[41-43] perhaps by influencing the extent to which different reactions (e.g., 2 + 2 vs 2 + 4 cycloaddition)[10] contribute to the overall process.

Conclusions

Singlet oxygen ($a^1\Delta_g$) is the reactive intermediate in the photooxidative degradation of phenylenevinylene oligomers. The reaction rate between singlet oxygen and the oligomer decreases (1) with a decrease in oligomer chain length and (2) upon the incorporation of electron-withdrawing substituents. The reaction rate, however, does not appear to depend solely on the electron density of the oligomer, and other factors may play a role. Although the rate of oligomer degradation can be significantly reduced upon the addition of a singlet oxygen quencher, it is not likely that such quenchers can totally preclude degradation, particularly in solid films where solute mobility is restricted and “cage reactions” play a more important role.[10,44] Rather, it appears that the photooxidation rate is best attenuated through the use of oligomer substitution, such as a vinyl cyano group. Despite the rather inefficient production of singlet oxygen upon direct irradiation of phenylenevinylene oligomers, singlet oxygen precursors will be formed in much greater yield under electroluminescent conditions.[10] Thus, the results reported herein are pertinent in the quest for stable organic optoelectronic materials.

Experimental Section

All oligomers were prepared via Wittig reactions using standard procedures.[6,24,25,45] Biacetyl (Sigma) was used both as received and after fractional distillation.

Singlet oxygen quantum yields were obtained in aerated solutions by comparing the intensity of the 1270 nm singlet oxygen phosphorescence sensitized by the oligomer with that sensitized by C_{60}.[10] Biacetyl-sensitized degradation reactions were performed using a 150 W steady-state Xe lamp as the irradiation source. The lamp output was passed through an interference filter centered at 440 nm (fwhm 10 nm). Oligomer degradation was monitored using a Cary 17 absorption spectrometer at wavelengths where degradation products did not absorb.

General techniques used to spectroscopically monitor oxygen and organic molecule excited states are described elsewhere.[46-49] Ab initio calculations were performed using Gaussian 94 (restricted Hartree–Fock, 3-21G* basis set).

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