



Opposite effects of a singlet oxygen quencher on photochemical degradation of dicyano-substituted poly(phenylenevinylenes) with different side chains



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ABSTRACT

RO-diCN-PPV and C8-diCN-PPV, poly(1,4-phenylene-1,2-dicyanovinylene) with alkoxy and octyl side chains, have recently been shown to photodegrade via a singlet oxygen mechanism, and RO-diCN-PPV is seven times more stable. To improve photostability, 1,4-diazabicyclo[2.2.2]octane (DABCO), a singlet oxygen quencher, was used as a dopant. To our surprise, DABCO exhibited opposite effects on their photodegradation. With 15 mol% DABCO, degradation rate of C8-diCN-PPV decreased by 65%, while that of RO-diCN-PPV increased by 246%. The DABCO content in C8-diCN-PPV film remained unchanged during 20 min of illumination, but mostly disappeared in RO-diCN-PPV in only 5 min due to decomposition. IR and MW analysis results suggest that DABCO slowed down degradation of C8-diCN-PPV without altering the mechanism, but accelerated RO-diCN-PPV photodegradation by initiating a radical process. C8-diCN-PPV's HOMO energy is lower than that of DABCO by 1.78 eV, a gap too wide for efficient electron transfer to happen. On the other hand, the HOMO of RO-diCN-PPV is only lower by 1.14 eV, allowing DABCO to donate electron to photoexcited RO-diCN-PPV to initiate a radical process that damaged the polymer and destroyed DABCO itself. It was also found that, in RO-diCN-PPV, radical decomposition takes very different paths from those of RO-PPVs and produce very different products.

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1. Introduction

Π -Conjugated organic materials have many (potential) applications such as photovoltaics, light emitting diodes, solid-state dye lasing, biological imaging and sensing, and chemical sensing. However, photochemical stability is a major concern for these materials [1–5]. For electron-rich polymers, such as poly(3-hexylthiophenes) and poly(p-phenylene-vinylenes) (PPV), a radical degradation mechanism has been established [6–9]. When illuminated in the presence of oxygen, the polymer donates an electron through charge transfer to an oxygen molecule to form a polymer cation and a superoxide radical anion. In the case of PPVs, the superoxide radical anion can abstract a hydrogen from a side chain to form a carbon radical [8]. It can also attack a vinylene unit in the backbone to produce a peroxide anion and a carbon radical [8]. Hoke et al. and Dam et al. have shown that the LUMO (lowest unoccupied molecular orbital) energy of a polymer is directly

related to the rate of photodegradation [10,11]. In our earlier reports, poly[2,5-bis(decyloxy)-1,4-phenylene-1,2-dicyanovinylene] (RO-diCN-PPV), and poly(2,5-dioctyl-1,4-phenylene-1,2-dicyanovinylene) (C8-diCN-PPV) (Fig. 1) [12,13] were shown to have photostability up to 250 times that of RO-PPV, due to reduced LUMO energy, -3.54 eV and -3.69 eV as compared to -2.91 eV of RO-PPV. Superoxide radical generation was shut down in these two polymers [13], however, singlet oxygen mechanism, though less aggressive, still limited their photostability, and C8-diCN-PPV degraded seven times faster due to faster $^1\text{O}_2$ generation in the polymer.

For organic materials that undergo photodegradation via radical oxidation mechanisms, radical scavengers can be used to slow down the processes [14,15]. For materials that are sensitive to singlet oxygen, $^1\text{O}_2$ quenchers such as 1,4-diazabicyclo[2.2.2]octane (DABCO) [16] and other tertiary amines [17] are effective antioxidants and can be used to improve the lifetime of dyes in dye lasers and fluorescence microscopy [18], as they can physically remove the excitation energy from $^1\text{O}_2$ without undergoing permanent change themselves and convert the energy to heat [19].

In this work, the effects of DABCO on the photostability of RO-

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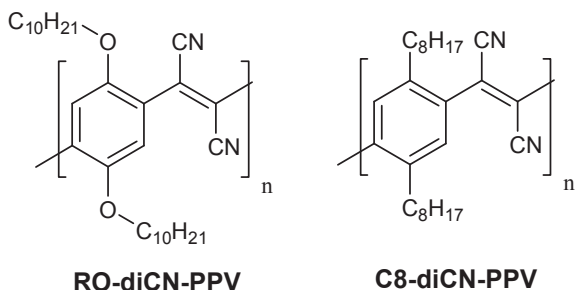


Fig. 1. Chemical structures of two diCN-PPV polymers.

diCN-PPV and C8-diCN-PPV were investigated. To our surprise, the singlet oxygen quencher affected photodegradation of the two similar polymers in opposite ways, a situation not have been found in the literature. The differences in the mechanisms are elucidated with the help of UV–vis absorption and infrared spectroscopic methods, and molecular weight analysis.

2. Experimental

The polymer films were spin-coated from polymer solutions in *o*-dichlorobenzene on glass substrates for UV–vis measurements and drop casted on KBr plates for IR measurements. The optical density of the films on glass substrate was kept between 0.2 and 0.3, except when shown otherwise. Films on KBr plates are about 10 times thicker as polymer absorption is about one order of magnitude weaker in the infrared ($4000 - 650 \text{ cm}^{-1}$) than in the visible region.

A high power Newport light source (model 66903) equipped with a 300 W xenon arc lamp and a Newport power supply (Model 69911) was used for the photostability study. The xenon lamp produces light of broad spectrum from 200 nm to IR. The unfiltered output was focused on sample to generate an intensity of 2200 mW/cm^2 , 22 times the intensity of one standard sun. UV–vis or IR analyses were performed immediately after illumination.

UV–vis spectra were obtained from an Agilent 8453 photodiode array UV–vis absorption spectrophotometer. Infrared spectra were obtained on a PerkinElmer Spectrum Two FT-IR spectrometer with a DynaScan interferometer, KBr optics and a temperature-stabilized DTGS detector. Molecular weights were determined using an Agilent 1100 series HPLC system, equipped with a diode array detector and two GPC columns (PL1110-6500, PLGel 5 mm MIXED-C $7.5 \times 300 \text{ mm}$). Polystyrenes were used as the standards for conventional calibration and tetrahydrofuran as the solvent.

3. Results and discussion

3.1. Photostability

Photooxidation of the polymer film samples was monitored using UV–vis absorbance (Fig. 2 and Fig. 3). Since the light intensity and oxygen concentration are constant, the photodegradation follows the first order rate law [13].

$$\log \frac{A}{A_0} = -Kt, \quad (1)$$

where K is the effective polymer photodegradation constant, A_0 is the initial peak absorbance, and A/A_0 is the normalized peak absorbance. $\log(A/A_0)$ is plotted as a function of time in Fig. 4. The absolute values of the slopes are the effective degradation constants. Since decomposition product can have absorption tailing

into the peak region of the polymer and causes the data points to deviate from a linear dependence as the illumination continues. This effect is much more significant in the pristine C8-diCN-PPV film than other samples. Therefore, in Fig. 4, only the data points in the first 5 min are used to calculate the slope for C8-diCN-PPV. The initial photooxidation rate of C8-diCN-PPV is 7 times greater than that of RO-diCN-PPV.

With 15 mol% DABCO doping, the degradation rate of C8-diCN-PPV film decreased by 65% (Figs. 2 and 4), in consistency with the singlet oxygen mechanism. The effect of DABCO in RO-diCN-PPV may not appear significant when comparing the top two charts of Fig. 3. After the spectra are magnified (Fig. 3 bottom), it becomes clear that, with DABCO doping, the degradation of RO-diCN-PPV was much faster in the first 3 min of illumination and then slowed. Comparing the slopes of doped RO-diCN-PPV in the first 3 min and the undoped (Fig. 4), the initial decay rate of doped sample was faster by 246%.

3.2. Characterization of photodegradation products

To understand the different effects of DABCO, IR spectroscopy was used to examine components and functional groups evolution during the course of illumination.

C8-diCN-PPV. IR spectra of the undoped and doped films with different illumination time are in shown in Fig. 5, and the following observations are made:

- 1) The integrated area of the C–H peaks of the doped sample during 20 min of illumination remained constant, just as the undoped sample, consistent with a singlet oxygen mechanism.
- 2) The formation of COOH (with C=O at 1716 cm^{-1} and OH at 3425 cm^{-1}) and oxo-acetonitrile [C(O)CN with C≡N at 2244 cm^{-1} and C=O at 1768 cm^{-1} , a product of $^1\text{O}_2$ cleavage of the dicyanovinylene and the precursor of COOH [13]] and the loss of the vinylenyl CN (2223 cm^{-1}) are all slower in the doped sample (Fig. 5B) in agreement with the slower degradation observed in the UV–vis measurements. This further supports the singlet oxygen mechanism because DABCO is a singlet oxygen quencher and there is no report on its ability to inhibit a radical process.
- 3) The DABCO in the doped sample was not consumed during the 20 min of illumination, in stark contrast to the fate of DABCO in RO-diCN-PPV. This observation also helps exclude the involvement of a radical process as it is known that DABCO reacts with oxygen and other free radicals [20].
- 4) The C(O)CN carbonyl peak (1768 cm^{-1}) is as strong as the COOH carbonyl peak (1716 cm^{-1}) in both samples, while the same signal in the earlier report [13] of the undoped sample only appeared as a shoulder of the COOH carbonyl peak. This is because C(O)CN is not stable in film and IR measurements in this study were performed with less delay after illumination ($<1 \text{ min}$ opposed to 5–10 min). Previously, it was noted that C(O)CN hydrolyzed completely when the illuminated films were transferred from slides to KBr plates using a solvent (CH_2Cl_2) [13].

RO-diCN-PPV. The IR spectra of the pristine and 15 mol% DABCO-doped polymer samples with different illumination time are shown in Fig. 6. Hardly any change happened to the undoped RO-diCN-PPV, showing again the excellent photostability of this polymer [13].

The following changes happened to the doped sample after illumination:

- 1) 80% loss of DABCO after 5 min of the illumination and complete loss at 20 min.

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