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## Local and external factors affecting the photodegradation of 4*N,N'*-dimethylamino-4'-nitrostilbene polymer films

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The photodegradation of the electro-optic chromophore 4*N,N'*-dimethylamino-4'-nitrostilbene was investigated as a function of wavelength, temperature, local atmosphere, and local molecular environment, i.e., attached as a side chain to a polymer or dissolved as a guest in a host polymer.

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The performance of nonlinear polymers as electro-optic modulators has reached record performance with >100 GHz bandwidths.<sup>1</sup> The electro-optic active materials consist of noncentrosymmetric chromophores incorporated into a polymer and aligned to produce a macroscopic nonlinearity typically by electric field poling.<sup>2</sup> The resulting devices are expected to operate under conditions of continuous illumination for periods of years under a diversity of environmental conditions. However, many organic materials are known to be susceptible to a number of photoactivated mechanisms which degrade the nonlinear activity of the polymer.<sup>3-9</sup> To date, photodegradation studies have focused on the chromophore 4*N,N'*-dimethylamino-4'-nitrostilbene (DANS), which has taken on the role of the prototype chromophore for degradation studies.<sup>3-6</sup> They have established that the photodegradation decreases by many orders of magnitude between 500 and 1064 nm, that oxygen complexation leading to an absorption feature at 1280 nm adversely affects the refractive index at 1320 nm and that the variation in the quantum efficiency associated with the degradation for  $\lambda \approx 500-600$  nm suggests that there may be multiple degradation channels present.<sup>3-6</sup> In this letter, we demonstrate that there are two charge transfer states which are photobleached, evaluate the quantum efficiency for both, investigate the temperature and environmental dependence of the photodegradation and its dependence on whether the polymer is a side chain or a guest host.

As shown in the inset of Fig. 1, the molecular structure of DANS is that of a classical stilbene chromophore. An electron donor (amino) and an acceptor (nitro) group is connected via an electron conjugated bridge consisting of two benzene rings connected by two carbons with a double bond between them. There has been some early discussion of the dominant degradation mechanism, trans-cis isomerization leading to a bent molecular geometry or photo-oxidation of the central carbon double bond.<sup>3,4,10</sup> Both are initiated by the absorption of a photon exciting the chromophore into one of its two excited charge transfer states, and the subsequent conversion to another species with a quantum efficiency

$B^{-1}$ . This results in a change in the absorption spectrum with a reduction in the absorption in the deep blue and near ultraviolet (UV), and presumably the appearance of new spectral features in the UV. As discussed previously, our technique consists of monitoring the transmission of the sample in the long wavelength tail of the charge transfer absorption peak as the film is illuminated with radiation of different wavelengths.<sup>6</sup> The measurement of the transmission evolution yields directly the ratio  $B/\sigma$  where  $\sigma$  is the molecular absorptivity. This is a key molecular parameter since the  $1/e$  lifetime of the initial population of molecules with the interesting charge transfer state is given by  $\tau = B/\sigma n_p$  where  $n_p$  is the photon flux.

The absorption spectrum shown in Fig. 1 for the side-chain polymer (SCP, 43% weight fraction) exhibits two strong peaks, both of which have been shown theoretically to have strong charge transfer character by Bredas and co-workers.<sup>11</sup> Illumination at 544 nm, in the tail of the dominant charge transfer spectral line, shows that both peaks are photobleached with time. This shows conclusively that there are at least two degradation pathways, one associated with each peak. For a photon flux of  $4.8 \times 10^{21}/\text{cm}^2$ , the dominant photodegradation effect is essentially finished in about 2 h. Further degradation occurs but at a much slower rate. It is this initial (faster) photodegradation that we study in this letter. No further changes in the spectrum of the irradiated material were observed 150 h after the completion of the photobleaching experiment showing that the photoproducts are stable.

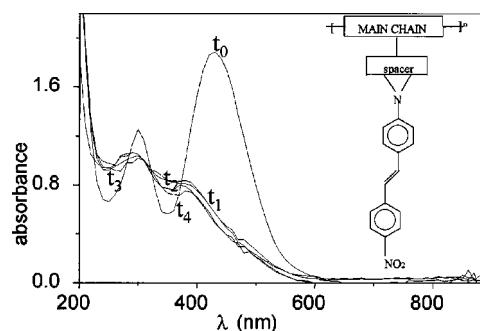


FIG. 1. The absorption spectrum of the SCP DANS in air as a function of illumination time with a 544 nm pump beam of  $0.20 \text{ W}/\text{cm}^2$ . (0, 80 min, 4, 6, 20 h).

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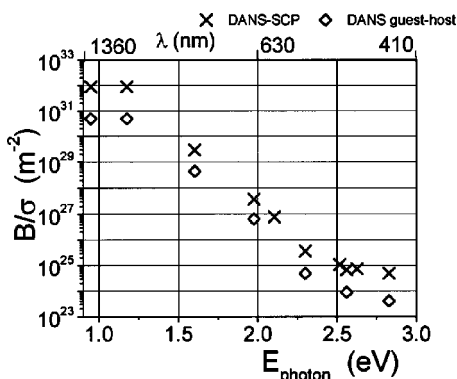


FIG. 2. The figure of merit  $B/\sigma$  is plotted vs the photon energy for SCP DANS in air as a guest host ( $\diamond$ ) and in a side chain (X).

The parameter  $B/\sigma$  was measured from 442 to 1320 nm for both the SCP and DANS as a guest in a polymethylmethacrylate host (GHP) using the techniques outlined in Ref. 6, see Fig. 2. In the guest–host case the chromophores are simply dispersed in the polymer with doping concentrations of  $<10\%$  in order to avoid aggregation effects, 4% weight fraction in our case. Clearly the large change in  $B/\sigma$  indicates that DANS is much more stable for wavelengths far from its dominant absorption peak. The trend of increasing  $B/\sigma$  with wavelength is, however, broken at 1320 nm where significant enhanced photodegradation occurs as can be seen in Fig. 2, probably due to the formation of oxygen complexes, as noted previously.<sup>4</sup> We found here that the SCP was roughly an order of magnitude more photostable than the guest–host polymer. Note that the side-chain approach should therefore be used not only for its enhanced orientational stability, but also for its superior photostability.

The absorption spectrum of DANS is known for the SCP which allows  $B$  to be evaluated from  $B/\sigma$  over a limited range of wavelengths.<sup>12</sup> A plot of  $B$  versus wavelength exhibits two plateaus where  $B$  is independent of wavelength giving  $B \approx 3 \times 10^4$  in the blue-green visible and  $B \approx 10^6$  for  $\lambda > 0.65 \mu\text{m}$ .<sup>6</sup> The photodegradation quantum efficiency of the chromophore in the guest–host system is about a factor of three higher than that in the side chain. In both cases, the quantum efficiency for the photobleaching of the higher energy charge transfer state (centered at  $\sim 300$  nm) is 30 times larger than that of the lower energy charge transfer state (centered at  $\sim 430$  nm). The charge distributions associated with these two excited states were calculated by Bredas *et al.* and Zoos *et al.*<sup>11,13</sup> The high energy peak involves larger bond-order modifications than the low energy one, and hence, more pronounced geometric deformations. Therefore, the 300 nm state is characterized by a larger lattice distortion and therefore molecules in this state are expected to be the more reactive of the two, in agreement with our results.

The temperature dependence of  $B/\sigma$  can occur due to the temperature dependence of  $B$ ,  $\sigma$ , or both. Systematic measurements in both SCP ( $T_g = 142^\circ\text{C}$ ) and GHP ( $T_g = 100^\circ\text{C}$ ) systems were performed at different wavelengths (photon energies) between 442 and 780 nm, increasing the temperature from 25 to 95 °C. Figure 3 shows representative results both inside and outside the absorption band. Increasing the temperature increases the photodegradation rate by less than an order of magnitude, with the side-chain system

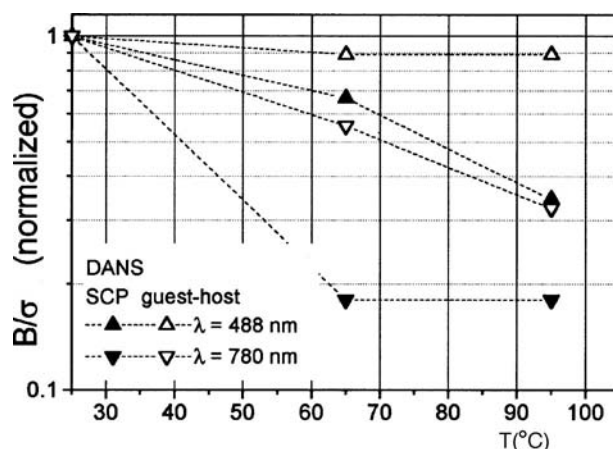


FIG. 3. Temperature dependence in air of the normalized (to data at 25 °C) figure of merit  $B/\sigma$  for the SCP ( $\blacktriangle$ ,  $\blacktriangledown$ ) and GHP ( $\triangle$ ,  $\triangledown$ ) polymers at the two wavelengths 488 ( $\triangle$ ,  $\blacktriangle$ ) and 780 nm ( $\triangledown$ ,  $\blacktriangledown$ ).

deteriorating faster than the guest host. We suspect that the temperature dependence of the inhomogeneous broadening may play an important role.

The effect of different atmospheres on the photodegradation was investigated to shed light on the dominant degradation mechanism and establish the sensitivity of the charge transfer excited states to oxygen. The powder form of the side SCP was dissolved in the solvent cyclopentanone and then either pure oxygen or nitrogen was bubbled vigorously through the solution for 2 h. Both the spin-coating and optical experiments were carried out in the respective atmospheres. A third control sample was prepared in air. Note that although this procedure does not ensure that all of the oxygen is removed when purged with nitrogen, it does give an indication of the importance of oxygen in photodegradation.

As in the previous case, both the side-chain and guest–host polymers were investigated at five wavelengths. Results at two wavelengths, 488 and 780 nm are shown in Fig. 4 for both the side-chain and guest–host polymers. It is clear that photo-oxidation is an important photodegradation mechanism: The figure of merit  $B/\sigma$  is very sensitive to oxygen concentration. It increases in nitrogen and decreases in oxy-

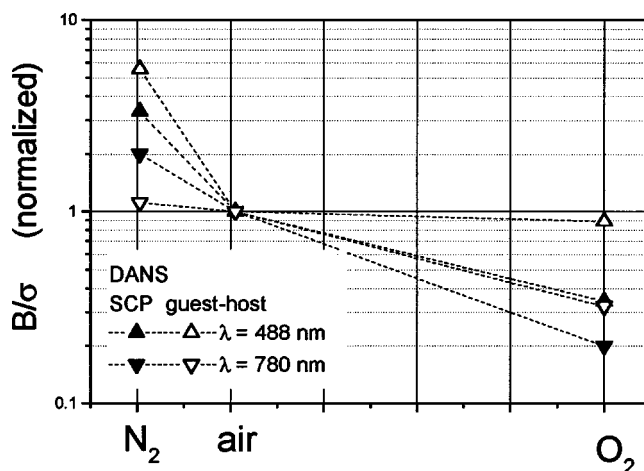


FIG. 4. Normalized (to data in air) figure of merit  $B/\sigma$  for SCP ( $\blacktriangle$ ,  $\blacktriangledown$ ) and GHP ( $\triangle$ ,  $\triangledown$ ) films prepared and measured in three different atmospheres, nitrogen, air, and oxygen at the two wavelengths 488 ( $\triangle$ ,  $\blacktriangle$ ) and 780 nm ( $\triangledown$ ,  $\blacktriangledown$ ).

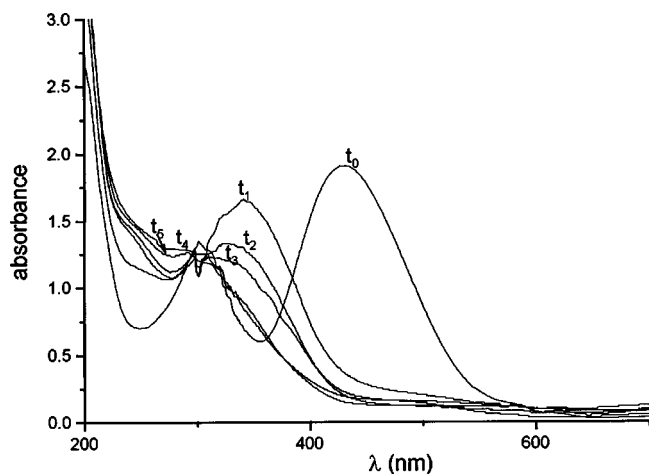


FIG. 5. Evolution of the absorption spectrum for SCP-DANS illuminated in a nitrogen atmosphere at 488 nm at an intensity of  $[20 \text{ W/cm}^2]$  in the first half hour then  $101 \text{ W/cm}^2$  for times up to 2 h]. After 2 h an oxygen atmosphere was used. Here  $t_0 \dots t_5$  are 0, 30, 90, 120, 120+10, and 120+40 min.

gen, differing by up to one order of magnitude between those two limits. We found that the decrease in  $B/\sigma$  from the nitrogen case to the small amount of oxygen present in air is larger at 488 nm than at 780 nm, showing that photo-oxidation is stronger for the 300 nm charge transfer excited states than the 430 nm charge transfer excited state. This could explain the values found for  $B$  for the two states, in qualitative agreement with theory.<sup>11</sup>

The existence of multiple photodegradation pathways was confirmed by additional measurements of the photoinduced change in the absorption spectrum of the SCP under different atmospheres. In nitrogen, air, and oxygen, the charge transfer peaks at 430 and 300 nm disappear rapidly. In nitrogen, Fig. 5, a new peak absorption peak at 330 nm, and a shoulder at about 250 nm appear, probably due to conformational changes such as cis-trans isomerization. In oxygen (results not shown here), on the same scale (30 min) the spectrum evolves directly to that obtained in Fig. 5 after illumination in nitrogen for 120 min, followed by 10 min in oxygen. This shows that when oxygen is present, photo-oxidation determines the final state of the degradation process.

In summary, many factors affect the photodegradation of DANS. This work has shown that there are multiple degradation channels involving the two charge transfer states. Of these, the higher energy one has a much higher quantum efficiency for degradation than the low energy one. At long wavelength ( $>600 \text{ nm}$ ) this quantum efficiency is deter-

mined by the dominant absorption feature and has the value  $B^{-1} \cong 10^{-6}$ . Although this seems small, it is large enough to make DANS unacceptable for long term electro-optical applications between 800 and 1320 nm, and possibly even at 1550 nm where it has not been measured yet. For example, when the propagation of 1 mW in a DANS channel of  $10 \mu\text{m}^2$  cross section is assumed under ambient conditions, the maximum lifetime predicted is of the order of 3.5 days for wavelengths up to 1320 nm. Photo-oxidation was identified as the dominant but not sole degradation mechanism and it was found that an oxygen atmosphere relative to a nitrogen one increased the degradation rate by up to an order of magnitude. It was also shown that increasing temperature from room temperature to  $100 \text{ }^\circ\text{C}$  decreased the photostability by less than one order of magnitude. Overall, we conclude that stilbenes like DANS are not good candidates for long lifetime electro-optic devices.

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