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Adriana Galvan-Gonzalez, Michael Canva, George I. Stegeman, Robert Twieg, Tony C. Kowalczyk, et al.. Effect of temperature and atmospheric environment on the photodegradation of some Disperse Red 1 type polymers. *Optics Letters*, 1999, 24 (23), pp.1741-1743. hal-00668315

HAL Id: hal-00668315

<https://hal-iogs.archives-ouvertes.fr/hal-00668315>

Submitted on 9 Feb 2012

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Effect of temperature and atmospheric environment on the photodegradation of some Disperse Red 1-type polymers

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Received July 28, 1999

The photodegradation of the azobenzene chromophore DR1 {4-[*N*-ethyl-*N*-(2-hydroxyethyl)amino]-4'-nitroazobenzene} incorporated as a side chain or as a guest in a poly(methyl) methacrylate host has been evaluated as a function of wavelength, temperature, and the atmospheric environment. The effects of these variables on the lifetime of DR1-based electro-optic devices is quantified. © 1999 Optical Society of America

OCIS codes: 230.0250, 250.2080, 160.4330, 230.7380, 160.5470.

The azobenzene chromophore 4-[*N*-ethyl-*N*-(2-hydroxyethyl)amino]-4'-nitrobenzene [Disperse Red 1 dye (DR1)], attached either as a side chain on a polymer or as guest in a host polymer, has been investigated for a variety of applications including electro-optics and second-harmonic generation.^{1,2} There are devices whose linear and nonlinear optical properties are required to be stable under operating conditions for periods of years. Previous stability studies have focused primarily on the effects of temperature on the loss of chromophore orientation in electric-field-poled polymers.³ Standard device operating conditions include continuous illumination with wavelengths ranging from 820 to 1600 nm under a variety of environmental conditions, including high temperatures and different gas atmospheres. However, little is known about the photostability of such materials in photonics applications.⁴⁻⁹ For the azobenzenes, photostability is critical because they have also been used for generating photoactivated functions that involve permanent changes in the refractive index for data storage, all-optical alignment, etc., primarily near the peak of the DR1 absorption peak. Fortunately, the nonlinear applications occur at longer wavelengths, far from this absorption maximum but still in regions of significant ($\sim \text{cm}^{-1}$) absorption.¹⁰⁻¹² It has been reported that the photostability of a similar chromophore, 4-*N,N*-dimethylamino-4'-nitrostilbene (DANS), has a strong wavelength dependence.^{6,7} So the key questions here are whether DR1 is photostable at active device wavelengths and how this photostability depends on a variety of environmental conditions such as temperature and atmosphere.

The nonlinear optical properties of DR1 are due to a strong charge-transfer state established by electron-donating and electron-withdrawing groups at opposite ends of the conjugated *trans* azobenzene bridge.¹³ This charge-transfer state exhibits strong absorption in the blue-green region of the spectrum, and the concentration $N_1(t)$ of nonlinear species in the

polymer is proportional to the absorption coefficient of the charge-transfer state, which we measure here in its long-wavelength tail at 544 nm. Absorption of light raises the chromophore from its ground to its first excited state, where it is more chemically active. It can either decay back to the original *trans* ground state or undergo a structural or chemical transformation. The transformation can be either reversible, as in structural *cis-trans* isomerization, or irreversible, as in chemical photo-oxidation or some other degradational process.^{14,15} In either case, the nonlinear activity is significantly diminished, the charge-transfer system is reduced, and new absorption features appear elsewhere in the spectrum, usually at much shorter wavelengths. The identity and number of specific reactions and their relative rates are influenced in a complicated way by the exact identity of the chromophore, the influence of the polymer and atmospheric environment, the excitation wavelength, the temperature, etc.¹⁶

Assuming a single dominant transformation process and a quantum efficiency B^{-1} for this to occur, the local rate of creation of the new photoproduct [concentration $N_2(t)$] can be written as

$$\frac{\partial N_2(t)}{\partial t} = -\frac{\partial N_1(t)}{\partial t} = \left[\frac{B(\lambda)}{(\lambda)} \right] N_1(t)n(t) \propto -\frac{\partial \alpha_1(t)}{\partial t}, \quad (1)$$

where $n(t)$ is the photon flux, $\sigma(\lambda)$ is the chromophore's molecular absorptivity, $\alpha_1(t)$ is the polymer absorption coefficient, and the lifetime of the active species is given by $\tau = B(\lambda)/\sigma(\lambda)n$.^{7,17} Hence $B(\lambda)/\sigma(\lambda)$ is a useful figure of merit for describing the chromophore's photostability. The larger the value, the longer the lifetime for the active species in the polymer. The experiments involve illumination of a thin film of the polymer at normal incidence with a uniform flux and periodically measuring the transmission with a weak

probe laser at 544 nm. Experiments at different intensities showed the transmission temporal change to be linear in the flux, ruling out multiphoton absorption as a significant contributing mechanism at all the intensity levels used. From relation (1), the initial slope of transmission increases with time and gives a direct measure of $B(\lambda)/\sigma(\lambda)$, and varying λ then allows the wavelength dependence of $B(\lambda)/\sigma(\lambda)$ to be evaluated. The analysis and experimental details have been described in detail elsewhere.^{6,17}

DR1, a prototype azobenzene chromophore, was investigated here both as a side-chain polymer (SCP; 24% weight fraction, glass transition temperature $T_g \cong 130^\circ\text{C}$) and as a guest-host (GH; 5% weight fraction, $T_g = 100^\circ\text{C}$) in an atactic poly(methyl) methacrylate matrix. Figure 1 shows the absorption spectrum of GH DR1 before illumination and for various periods of exposure in air at 488 nm. The decrease in the absorption that is due to the charge-transfer state at 490 nm and the growth of a new broad absorption feature at 370 nm are both clear. After 20 h there is no further significant change in the absorption. The spectrum was remeasured after a few months' storage in the dark and in air and was found to be unchanged from that observed at 20 h.

Photo-oxidation is a well-known mechanism for photodegradation, and in an azobenzene dye such as DR1 oxygen can react in a number of possible locations in the molecule.¹⁵ All the compounds were prepared in an ambient atmosphere, so the powder forms of the polymers and their constituents were all initially exposed to oxygen. To investigate the effects of atmospheric oxygen, we bubbled either pure oxygen or pure nitrogen through the solution for 2 h when the polymers were dissolved in cyclopentanone for spin coating. Then the subsequent spin coating and degradation measurements were performed in that corresponding atmosphere. Note that this procedure does not preclude the presence of some oxygen in the polymer bubbled with nitrogen.

The same final absorption spectrum for GH DR1 in an oxygen atmosphere (not shown here) was measured as shown in Fig. 1 for an air atmosphere. In neither case did all the curves pass through the same point, indicating the presence of more than one degradation pathway. However, for a nitrogen atmosphere the evolution of the absorption spectrum (Fig. 2) is much slower, leading to a broad peak at 400 nm, and all the spectra pass through a single (isobestic) point, which indicates that there is one dominant degradation channel. The pure-nitrogen results are attributed primarily to *trans-cis* isomerization.¹⁸ Therefore, for photodegradation in air and oxygen, photo-oxidation occurs in addition to the *trans-cis* isomerization process.

Measured values of B/σ versus photon energy in air are shown in Fig. 3 for both GH and SCP DR1. B/σ (and therefore the lifetime of the electro-optic activity) increases by 6 orders of magnitude as the wavelength is increased between the absorption peak in the visible and 1320 nm in both systems. This wavelength dependence is mostly a consequence of the wavelength dependence of the absorption coefficient, particularly for

wavelengths as long as 1064 nm. Although we have not measured $\alpha_1(\lambda)$ over the full range of the photostability results, there are sufficient data to permit us to evaluate the quantum-efficiency factor for degradation B^{-1} . At long wavelengths, B is equal to 10^7 in air and to 5×10^7 and 7×10^6 in nitrogen- and oxygen-enriched atmospheres, respectively. There is a difference of a factor of 2–8 between the photostability in the poly(methyl) methacrylate host polymer and in the side-chain format. This disparity shows

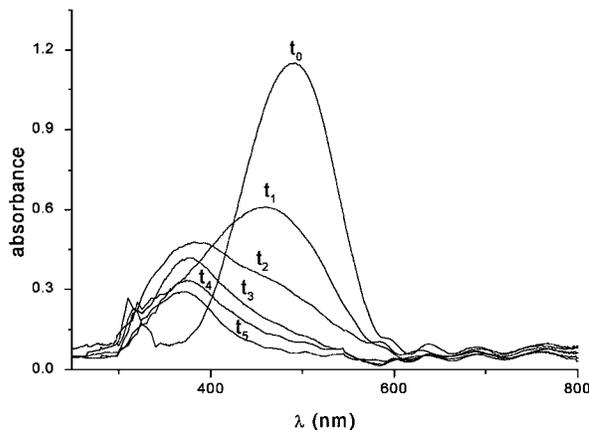


Fig. 1. Absorption spectrum of GH DR1 taken in a normal air atmosphere versus illumination time with a 488-nm pump beam of 20-W/cm² intensity. Illumination times are t_0 , 0; t_1 , 5 min; t_2 , 20 min; t_3 , 60 min; t_4 , 2 h; and t_5 , 20 h.

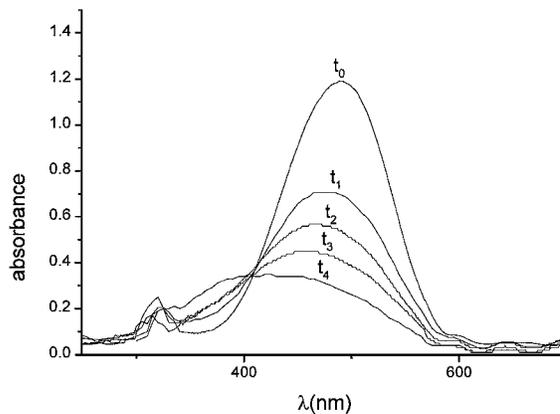


Fig. 2. Absorption spectrum of GH DR1 taken in a nitrogen atmosphere versus illumination time with a 488-nm pump beam of 20-W/cm² intensity. Illumination times are t_0 , 0; t_1 , 5 min; t_2 , 20 min; t_3 , 60 min; t_4 , 2 h.

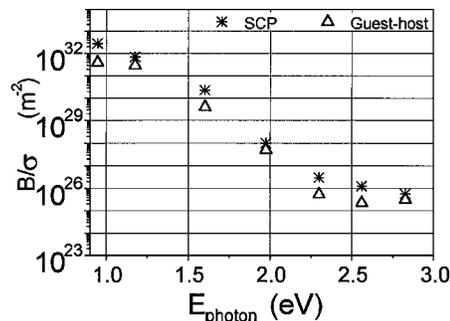


Fig. 3. Figure of merit B/σ in air plotted versus photon energy for DR1 as a GH and in a side chain.

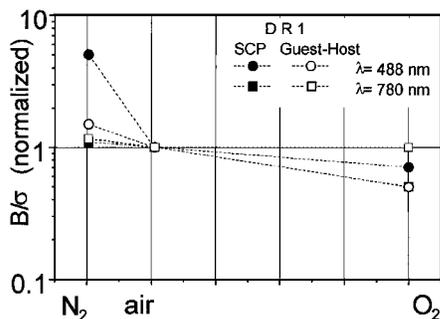


Fig. 4. Normalized figure of merit B/σ as a function of wavelength for DR1 side-chain and GH polymer films at, 488 and 780 nm, prepared and measured in three different atmospheres: nitrogen, air, and oxygen.

that side-chain systems are more stable than the corresponding GH polymers, similar to previous findings for solid-state dye lasers that use Rhodamine B.¹⁹

The effect of increasing the temperature from 25 to 95 °C on the photostability of both DR1 polymers was investigated. The decrease in the photostability was found to be less than a factor of 3 in all cases.

The difference in B/σ for pure-nitrogen, air, and pure-oxygen atmospheres is shown in Fig. 4 for the SCP and GH polymers at the wavelengths 488 and 780 nm. Replacement of air with nitrogen improved the photostability, whereas the use of pure oxygen decreased B/σ . The largest stability improvement, a factor of 5, occurred inside the absorption band for the side-chain polymer when nitrogen was substituted for air. Overall, for DR1, the amount of oxygen in the air was sufficient to cause most of the changes found in a pure-oxygen environment.

It is interesting to predict device lifetimes achievable in DR1 for electro-optic modulators in channel waveguides. For a waveguide of cross-sectional area $10 \mu\text{m}^2$, the calculated lifetimes for SCP DR1 under continuous illumination at room temperature are much better than for DANS.¹⁷ For example, at 1 mW of continuous illumination at 1320 nm a lifetime of 12 days is predicted for side-chain DR1, whereas for DANS it was ~ 3.5 days. Note, however, that lifetime scales inversely with the operating power and hence that devices operating at powers of $1 \mu\text{W}$ will have the required stability against photodegradation.

In summary, the photodegradation properties of Disperse Red 1 dye, as both a side chain and a guest-host polymer, have been measured from the visible to 1320 nm. Two processes were identified, *trans-cis* isomerization and photo-oxidation. Although the lifetime of the electro-optic active species increases by more than 6 orders of magnitude over this wavelength range, DR1 does not have the stability to last 10 years at continuous 1-mW illumination in a typical channel waveguide. Extended exposure to oxygen or operation at higher temperatures further decreases the lifetime. However, preliminary results with oxygen getters indicate that the lifetime can be significantly increased.

This research was supported at the Center for Research and Education in Optics and Lasers by the

National Science Foundation and at the Gemfire Corporation by the Ballistic Missile Defense Organization. M. Canva acknowledges support from the French Direction Generale de l'Armement under contract ERE96-1101 and a science fellowship from NATO. This research was supported by a joint U.S.–French National Science Foundation–Centre National de la Recherche Scientifique grant. G. I. Stegeman's e-mail address is george@creol.ucf.edu.

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