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Qiang Zhang
University of Central Florida

Michael Canva
University of Central Florida

George Stegeman
University of Central Florida

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Wavelength dependence of 4-dimethylamino-4′-nitrostilbene polymer thin film photodegradation

Qiang Zhang, Michael Canva,[a)] and George Stegeman
Center for Research and Education in Optics and Lasers (CREOL), P.O. Box 162700-4000 Central Florida Boulevard, University of Central Florida (UCF), Orlando, Florida 32816-2700

The polymeric electro-optical stilbene material, 4-dimethylamino-4′-nitrostilbene (DANS), was illuminated at wavelengths ranging from the visible to near-infrared in order to quantify its photodegradation processes. Photodegradation due to one-photon and two-photon absorption was studied. The quantum efficiency of the chromophore degradation is found to be strongly wavelength and absorption mechanism dependent. This suggests that, in different regions of the spectrum, different excited states or different mechanisms are involved in the degradation process. In the near-infrared spectral region, operation lifetimes of electro-optic devices made from this chromophore are expected to be around only few hundreds hours, dramatically shorter than it was previously believed. © *1998 American Institute of Physics.* [S0003-6951(98)03933-3]

Polymers have a very promising and diversified future in photonics. However, all the different applications envisioned have to face the common problem of photochemically induced degradation of the organic materials, especially of the chromophores that usually confer to the materials their desirable properties. While great improvements have been achieved for making polymeric optical waveguiding devices a reality, there are only few papers reporting on the damage of such waveguides by infrared (IR) light in the telecommunication band (i.e., 1300 and 1550 nm) and also in the 800–900 nm range. Even though the absorption of IR light is very weak compared to the absorption of ultraviolet and visible radiation, such an induced photodegradation process has noticeable long-term destructive effects on electro-optic (EO) devices.[1,2] Large changes in both the refractive indices of materials and waveguide propagation losses due to long time IR illumination were observed.[1–4] These effects could drastically limit the lifetimes of dye-doped polymeric optical devices and therefore pose a serious long-term problem to solve for their use in applications outside research laboratories. To better characterize such photodegradation phenomenon requires systematic studies of very low efficiency photochemical events.

Although the exact microscopic mechanisms of all chromophore photodegradation processes are not well known, several mechanisms have been suggested, such as photoassisted oxidation and reductive cleavage of bonds by incident photons.[2,5,6] However, to forecast device operational device lifetime, it is necessary to quantify the efficiency of the absorption processes and photochemical reaction of the specific photons and chromophores in a given host system, which leads to the irreversible dye bleaching.

Thus, our research was aimed at quantifying the photodegradation processes of dye-doped polymer in the so-called transparent IR band and at comparing it to similar processes taking place in the visible absorption band of the chromophores. We also wanted to separate effects induced by one- (1PA) versus two-photon absorption (2PA), and provide some information about the degradation mechanisms. In this letter, we report mainly on the wavelength dependence of the 1PA induced degradation of 4-dimethylamino-4′-nitrostilbene (DANS) side chain polymer material over a spectral range from the visible to the near IR. We interpreted the experimental results with a degradation process model in terms of 1PA and 2PA, which we shall outline briefly. This allows us to quantify the quantum efficiency of photodegradation dependence on wavelength and absorption mechanisms, and predict a maximum operational lifetime of EO devices based on such a dye-doped material.

Photobleaching with light in the absorption band of dye molecules has been studied for many years in the context of patterning waveguiding structures.[7] A phenomenological model is widely used in the literature to describe the photobleaching process and it has proven valid in or near their absorption band, i.e., in the UV and visible region of the spectrum.[8–10] The model itself does not contain any restriction to its validity in the other region of the spectrum or to any specified excitation process. Therefore, we used this model in our analysis, extending its application to describe dye transformation induced by light in any part of the spectrum, and with possibly multiphoton absorption process.

Considering the molecules to be isotropic and homogeneously distributed, we assume that each dye molecule excited at a specific energy state has a certain probability of being converted to a degraded molecule while relaxing. This probability is defined as the photodegradation quantum efficiency, B^{-1}. This modeling is independent of the mechanism that has excited the molecule in the first place, but it can be expected that this B number is going to be sensitive to the excited state that has been reached. Therefore different B parameters have to be assigned for different excitation mechanism and wavelength absorption.

Let us consider, at time $t=0$, a thin film of thickness L, of photochemically reactive molecules (specie 1), with volume density N_0. During exposure by light of wavelength λ, species 1 of absorption cross section σ_1 is progressively con-

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[a)]Electronic mail: canva@mail.creol.ucf.edu

verted to species 2, which are assumed to be photochemically stable but could be absorbing, with absorption cross section σ_2. Supposing an uniform photon flux n_0 normally incident onto the thin film, such local flux inside, at depth z and time t, can be written as

$$n(z,t) = n_0 \exp[-(\sigma_1 - \sigma_2)J_1(z,t)]\exp(-\sigma_2 N_0 z),   (1)$$

where $J_i(z,t)$ denotes the number of molecules of species i per unit surface area:

$$J_i(z,t) = \int_0^z N_i(z',t)dz'.   (2)$$

Assuming that the degradation rate is proportional to the number of molecules of species 1 being excited leads for the 1PA process to

$$\frac{\partial N_1(z,t)}{\partial t} = -B_I^{-1} \times [\sigma_1 n(z,t)N_1(z,t)],   (3)$$

where the constant B_I^{-1} is the quantum efficiency of degradation via 1PA. In 1PA processes, one excitation cycle corresponds to absorbing one photon while in 2PA case it corresponds to absorbing simultaneously two photons. Similar to 1PA process, 2PA induced molecule degradation process can be described by

$$\frac{\partial N_1(z,t)}{\partial t} = -B_{II}^{-1} \times [\sigma_1^{TP} n(z,t)N_1(z,t)/2],   (4)$$

where σ^{TP} is the equivalent 2PA cross section, which is proportional to the local intensity of the light. Hence the degradation rate in Eq. (4) is proportional to $n^2(z,t)$.

Combining Eq. (1), Eq. (3), and Eq. (4) will yield molecular density evolution as a function of time. The B parameters for 1PA and 2PA processes can be obtained by fitting the associated theoretical evolution to experimental data. In the case of characterization of 1PA induced photodegradation, the peak intensity is kept low enough so that 2PA can be neglected, and only Eq. (1) and Eq. (3) need to be considered to yield B_I. However, even using only differential Eqs. (1) and (3) does not allow an analytical solution, but an approximate one may be established if σ_2 is neglected.[9] Numerical calculation can also give the total transmission change as a function of time t or integrated input energy E, (the latter variable being more general as a parameter). Furthermore, such calculations allow the dye orientation anisotropy, light polarization (linear or circular) and light spatial distribution (uniform and Gaussian) to be taken into account. Therefore, we are able to obtain the B parameter by simply measuring the total transmission change of a beam, at any wavelength, and fitting to appropriate numerical solutions according to the polarization of the incident beam. The sensitivities of the evolution rate of the transmission as a function of E for variation of σ_1, σ_2, N_0, and B are illustrated in Fig. 2 of Ref. 9. It shows that this B parameter can be fairly accurately determined from fitting experimental to theoretical curves for the transmission evolution.

However, in the IR region of the spectrum, absorption is very weak and so is the total absorption thus making accurate recording of changes in transmission difficult. In this case, the decrease in dye concentration is better measured by use of a probe beam at the edge of the absorption band of the
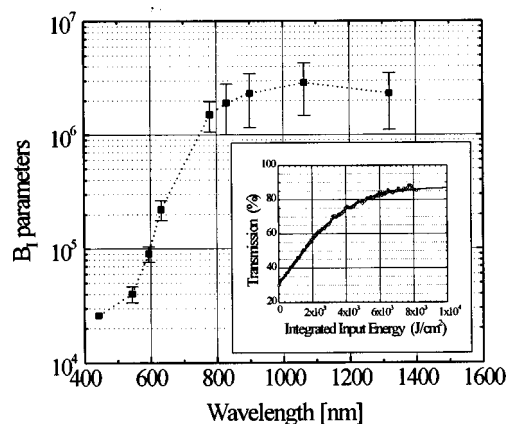

FIG. 1. B_I parameters vs wavelengths. Insert: transmission evolution through a 1 μm thick sample. A 544 nm HeNe laser was used as both a pump and probe source. (●: experimental data;—: theoretical fitting).

chromophore, where film optical transmission is a few tens of percents. In the case of 1 μm thick DANS films, a green He-Ne cw laser is conveniently used as probe (its initial transmission is about 30%), independent of the wavelength at which the material is pumped for inducing the bleaching.

The DANS polymer is chosen to conduct our experiments because of its popularity as a nonlinear dye and because both its 1PA and 2PA spectra are known.[3,11] The DANS side chain polymer sample films were made on fused silica substrates from raw material from Akzo Nobel, using standard spincoating and curing technique. The samples were about 1 μm thick and were used without any further processing, being stored in the dark in room conditions when not under test.

To shorten the experimental time, the different pump beams, that were sequentially used, were focused onto the sample, increasing the ratio E/t. A calibrated pinhole with appropriate size was put against the sample to assure a nearly uniform illumination. A 543.5 nm HeNe laser was used to probe intermittently the transmission evolution caused by pump beam. The polarized state of probe and pump beam were always the same. Special attention was paid to avoid inducing any noticeable bleaching of the sample by the probe beam.

For 1PA processes, B_I should be independent of photon flux while B_{II} should be proportional to the flux for 2PA process. Therefore, in the linear absorption study, the transmission curves for different incident powers should coincide with each other in the plot of transmission versus total integrated input energy E. Experiments for each wavelength were repeated several times with different incident powers of the light in order to assure that measurements were conducted in such conditions. Finally, B parameters were obtained by fitting first to the analytical function then to the appropriate numerical solution.

The measurements performed at different wavelengths from 443 to 1320 nm are summarized in Fig. 1, which gives the 1PA induced photodegradation quantum efficiency B_I at different wavelengths. The inset of Fig. 1 shows typical experimental data and theoretical fitting. Generally, the photodegradation quantum efficiency is thought be independent of wavelength as long as the same excited state is involved. Thus, the experimental results indicate that there may be
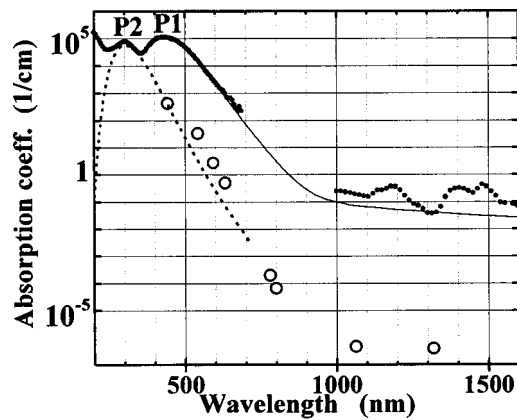
FIG. 2. Absorption spectrum of DANS polymer-experimental points (●) and first excited state fitted with a Voigt profile (—). Absorption of the second excited state assuming similar shapes of both bands (---), and back calculated values (○) from $B_I(\lambda)$ and assuming $B_I = 3 \times 10^6$ for the first excited state and $B_I = 10^2$ for the second.

TABLE I. Estimated lifetime of EO device made of DANS side chain polymer, channel transverse area is 10 μm^2 and input average power is 1 mW.

Wavelength (nm)	780	830	900	1064	1320
Lifetime (hour)	6.85	12.2	42.3	132.6	214

direction and calculated the lifetime limitation of such a structure for different operating wavelengths; 2PA induced degradation could be neglected and the lifetimes predicted are reported in Table 1. These (for example, ~200 h at 1300 nm) are much shorter than those published previously[3,4] only taking into account 2PA induced photodegradation. However, because for this material the 1PA tail is still large, the 2PA usually remains negligible, and the degradation process is ruled by 1PA.

For practical applications of polymeric EO devices to become a reality, chromophore doped materials with improved photostability need to be identified experimentally. Spectroscopic data would be needed to identify the exact mechanisms involved. We will investigate other EO polymers to check if this strong wavelength dependence of quantum efficiency of photodegradation is a general phenomenon for this type of nonlinear chromophore.

different excited states or different excited mechanisms involved. As we can see from the absorption spectrum of DANS polymer, there are two peaks (denoted as P1 and P2 in order of increasing energy) in the range from 300 to 1600 nm (Fig. 2). The first peak (P1) corresponds to the electronic transition from the ground state to the lowest energy singlet excited state (S_1) with a charge transfer character; P2 corresponds to charge transfer to another excited state (S_2) which involves large bond-order modifications and hence more pronounced geometric deformations.[12,13] The state S_2 is characterized by more lattice distortions than state S_1 and, therefore, molecules in S_2 are expected to be more reactive than those in S_1. With this in mind, the wavelength dependence of B_I could be partly explained as follows: assuming there are two excited states participating in the degradation process, i.e., S_1 and S_2, each with different but constant degradation quantum efficiency. While in the visible region, molecules can be excited to both excited states, in the near IR the absorption of the higher lying excited state virtually goes to zero and therefore the lower lying excited state is dominant. To verify this, absorption due to the higher lying excited state was calculated by assuming two different but constant B_Is for two states: the saturation value 3×10^6 for state S_1, and for fitting purposes 10^2 for state S_2. Such values allow one to obtain absorption coefficients for the $S2$ band comparable to those predicted by assuming a Voigt profile similar to the one fitting the $S1$ band (Fig. 2). Such values are plausible and so is the interpretation, although four orders of magnitude difference in quantum efficiency still remains to be explained.

With high power pulsed lasers the photodegradation quantum efficiencies of 2PA were also measured for wavelengths ranging from 800 to 1064 nm, for which 2PA coefficients are available.[3] The B_{II} value found was 2×10^4.

Having evaluated the photodegradation quantum efficiencies allows a prediction of the lifetime of systems based on such materials. By lifetime we refer to the time required for photobleaching of one half of the active molecules. Let's considered a typical channel waveguide structure 2 μm high, 5 μm wide, and 1 cm long, with a continuous 1 mW input. We assumed that bleaching was uniform along the transverse

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