Photostability of organic electro-optic polymer under practical high intensity continuous-wave 1550 nm laser irradiation

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Received February 17, 2021; revised August 3, 2021; accepted September 1, 2021; published online September 17, 2021

1. Introduction

Organic electro-optic (EO) polymers have excellent characteristics, such as low dielectric constants and high EO coefficients (\(r_{33} > 100 \text{ pm V}^{-1}\)), compared with inorganic EO materials and are expected to be widely applied in optical communication devices, such as high-speed and low-power-consumption optical modulators,\(^1\) optical phased arrays,\(^2\) optical interconnects,\(^3\)\(^–\)\(^6\) terahertz wave generation and detection applications,\(^7\)\(^–\)\(^9\) and electric-field sensors.\(^10\)\(^–\)\(^14\)

One of the main subjects for the development of practical devices using EO polymers is thermal and photochemical stability. In terms of thermal stability, side-chain\(^1\)\(^–\)\(^3\) and cross-linked EO polymers,\(^14\)\(^–\)\(^17\) with a high glass transition temperature (\(T_g\)), have been recently developed, and temporal stability measurements of poled EO film at high temperatures demonstrated that the polymers have excellent thermal stability.

With regard to the photochemical stability of organic EO materials, different photodegradation mechanisms, such as trans-cis isomerization, photooxidation via photoexcited singlet oxygen, and photolysis, have been suggested.\(^18\)\(^–\)\(^26\)

The photobleaching behavior of EO polymers with typical chromophores, such as 4,4′-dimethylamino-4′ nitrostilbene (DANS) and Disperse Red 1, have been extensively investigated. Galvan-Gonzalez et al. have reported studies on the photobleaching of DANS in guest–host and side-chain polymers. Specifically, the effects of excitation laser wavelength, temperature, ambient environment, and local molecular environment were investigated.\(^21\)\(^–\)\(^23\)

A continuous-wave (CW) laser at different wavelengths between 442 and 1320 nm was used as the excitation laser, and the wavelength dependence of the photobleaching that occurred under resonant and non-resonant excitation of the EO chromophore was obtained. It was shown that the photobleaching was dependent strongly on the wavelength of the excitation laser, and photostability was improved when the wavelength of the excitation laser was far from the absorption peak of DANS. It was also shown that the photobleaching ratio increased with temperature. Furthermore, the photobleaching rate of DANS in the side-chain polymer was approximately one order of magnitude smaller than that of DANS in the guest–host polymer. Thus, it was established that the photobleaching pathways of EO polymers containing DANS are complex, with many photobleaching pathways being identified; however, photooxidation was found to be the dominant mechanism. Zhang et al. reported that for the photoexcitation of DANS guest–host polymers at an intensity of 10 kW cm\(^−2\), one-photon excitation photobleaching was dominant due to weak absorption within the tail of the absorption band, even though the excitation was not resonant with the majority of the bandwidth of the absorption band. In addition, in this experiment, photobleaching by two-photon excitation was negligible.\(^20\)

The maximum two-photon absorption coefficient for DANS side-chain polymer was found to be 5.5 cm GW\(^−1\), in these two-photon absorption spectrum measurements, which were conducted using an open-aperture Z-scan method with a mode-locked Ti:Sapphire laser having a pulse width of 3 ps. It was shown that the contribution of two-photon absorption was small at the experimental intensity (10 kW cm\(^−2\)).

DeRosa et al. investigated the photobleaching of various CLD-type chromophores with large hyperpolarizabilities by means of pump–probe measurements using an optical fiber with a mode-field diameter (MFD) of 10 \(\mu\)m.\(^24\)

The photobleaching measurements conducted under the non-resonant excitation condition involved irradiating the sample with CW lasers at wavelengths of 1550 nm, as the pump beam, and 660 nm, as the weak probe beam, which was less intense. The probe wavelength was chosen to be within the absorption bands of CLD-type chromophores. It was found that the photobleaching rate was dependent linearly on the irradiation power in a range that extended up to 100 mW (125 kW cm\(^−2\)), suggesting that one-photon photobleaching was dominant. It was also found that photostability was dependent on molecular structure. Furthermore, the photobleaching rate in an argon atmosphere was reduced by between one or two orders of magnitude with respect to that in an ambient atmosphere.

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atmosphere, and that photostability was further improved in the presence of a singlet-oxygen quencher. Therefore, a photobleaching pathway involving photogenerated singlet oxygen was suggested. Oh et al. investigated the long-term photostability of EO polymer modulators using guest–host polymers containing FTC and CLD chromophores by monitoring the half-wave voltage, \( V_{\pi} \), of a Mach–Zehnder modulator.23 It was found that the photostabilities of the EO polymer modulators in an argon atmosphere were significantly improved compared with those measured in ambient air.

Although many studies on the photobleaching of EO polymers have been reported, few photobleaching studies at higher intensities used in practical devices have been conducted. With the recent increase in the capacities of fiber-optic communication systems, the input power introduced to the optical modulator has increased, and further miniaturization of optical modulators is required. The intensity used in practical optical modulators is now 1 MW cm\(^{-2}\) or more. In this study, we constructed a photostability evaluation system using a smaller diameter optical fiber in which intensities of 1 MW cm\(^{-2}\) or more were obtained, and we intensively investigated the photochemical stability of an EO polymer at 85 °C under irradiation by a CW laser at a wavelength of 1550 nm. It was found that the photobleaching rate was proportional to the square of the pump intensity, suggesting a dominant photodegradation pathway involving two-photon absorption.

2. Experimental methods

Figure 1(a) shows the molecular structure of the EO polymer used in this study. The PMMA-based side-chain polymer includes an EO chromophore with a large hyperpolarizability, \( \beta \) (\( \beta_{\text{EO}} = 1767 \times 10^{-30} \) esu at 1550 nm).27 The EO chromophore consists of an electron-acceptor unit based on a tricyanofuran derivative, an amino-benzene-based electron-donor unit with a benzyloxy group at the meta position, and thiethyl-di-vinylene-based \( \pi \)-conjugated system.27 The chromophore concentration in the EO polymer is 30 wt%.

A sample was prepared by forming a film on a quartz substrate by means of spin coating, using a cyclohexanone solution of the EO polymer. The thickness of the quartz substrate was 1 mm, and the thickness of the EO polymer film was about 600 nm. Figure 1(b) shows the UV–Vis–NIR absorption spectrum of the EO polymer thin film. A strong absorption band with peak wavelength of 791 nm is assigned to that of the EO chromophore in the EO polymer.

Figure 2 shows a schematic diagram of the optical fiber-based photostability evaluation system. A CW laser (Thorlabs MCLS1) with a wavelength of 1550 nm is used as the pump beam after amplified by an optical fiber amplifier (SDO Communications FEAP1BB1S8003A), and another CW laser with a wavelength of 830 nm, which is close to the EO chromophore absorption peak, is used as the probe beam. These beams are combined via a wavelength division multiplexing coupler. The MFD of the optical fiber is converted from 10 to 3.2 \( \mu \)m by means of the MFD conversion thermally diffused expanded core (TEC) optical fiber (Ishihara Sangyo). The maximum optical intensity at the fiber tip is 1.49 MW cm\(^{-2}\). This optical intensity at the tip of the MFD conversion fiber is comparable to that in a silicon slot waveguide. As shown in Fig. 2, the tip of the MFD conversion TEC fiber is brought into contact with the surface of the EO polymer thin film, and the intensity of the probe beam transmitted through the sample is measured using an integrating sphere and a Si photodetector. This measurement allows us to evaluate the photostability of the EO polymer under irradiation of 1550 nm pump laser. Because there is almost no absorption by the EO polymer at 1550 nm [Fig. 1(b)], it is difficult to directly measure changes in absorption at 1550 nm. Therefore, an 830 nm probe beam was used to evaluate the photostability. The absorbance was measured by turning off the pump beam every 30 min and irradiating the sample with the probe beam for several seconds. It was confirmed that photobleaching by the probe beam was negligibly small under the experimental conditions used in this study. The temperature of the thermostatic chamber was maintained at 85 °C, and the pump power dependence of the photobleaching of the EO polymer was determined.

3. Results and discussion

Figures 3(a)–3(d) show the time dependence of the normalized absorbance of the EO polymer thin film under irradiation with each of four different pump powers (intensities), 49 mW (0.61 MW cm\(^{-2}\)), 63 mW (0.78 MW cm\(^{-2}\)), 100 mW (1.24 MW cm\(^{-2}\)), and 120 mW (1.49 MW cm\(^{-2}\)) at 85 °C as well as the fit results for these data obtained using Eq. (1). The normalized absorbance is defined in Eq. (1). As the temporal change in normalized absorbance cannot be expressed as a single exponential decay, the analysis was performed...
assuming a two-component exponential decay

\[
\frac{\text{Normalized absorbance}}{\text{log} \left( \frac{T(t)}{T_\infty} \right) - \log \left( \frac{T(0)}{T_\infty} \right)} = f_1 \exp \left[-b_1 t\right] + f_2 \exp \left[-b_2 t\right].
\]

Here, \( T(t) \) is the transmittance at time \( t \), \( T_0 = T(0) \), \( T_\infty \) is the transmittance of the uncoated quartz substrate. Further, \( f_1 \) and \( f_2 \) are the proportions of the two photobleaching processes, and \( b_1 \) and \( b_2 \) are their respective rate constants. The experimental results are well-described by the two-component exponential decay function. The fit parameters for each pump intensity are listed in Table I. Here, \( n_0 \) is the photon flux density (in \( \text{m}^{-2} \cdot \text{s}^{-1} \)), and \( \chi^2 \) is the residual sum of squares. We found that the rate constant \( b_1 \), with a high photobleaching rate, is dominant, and the proportion \( f_1 \) is greater than 0.9. The rate constant \( b_1 \) is not linear with respect to the pump intensity. To understand the dependence of this rate constant on the pump intensity in more detail, further experiments were conducted. The number of measurements was increased to include a wider range of pump intensities.

Figure 4 shows the experimentally obtained dependence of the rate constant \( b_1 \) on photon flux density, alongside linear (blue dashed line) and quadratic (red dotted line) fits. Interestingly, it is apparent that the rate constant \( b_1 \) is proportional to the square of the pump intensity. This result suggests that a photodegradation process associated with two-photon absorption is dominant under these experimental conditions. So far photodegradation associated with two-photon absorption has not been observed in previous studies on the photostability of EO polymers under CW laser irradiation.

| Pump power (mW) | Intensity (MW cm\(^{-2}\)) | \( n_0 \times 10^{28} \text{ m}^{-2} \cdot \text{s}^{-1} \) | \( f_1 \) | \( b_1 \times 10^{-5} \text{ s}^{-1} \) | \( f_2 \) | \( b_2 \times 10^{-5} \text{ s}^{-1} \) | \( \chi^2 \) |
|-----------------|-----------------------------|-----------------------------|-----------|-----------------------------|-----------|-----------------------------|-----------|
| 49              | 0.61                        | 4.76                        | 0.92      | 4.09                        | 0.082     | 0.40                        | 0.017     |
| 63              | 0.78                        | 6.11                        | 0.93      | 6.83                        | 0.086     | 0.49                        | 0.019     |
| 100             | 1.24                        | 9.71                        | 0.91      | 13.43                       | 0.079     | 0.60                        | 0.013     |
| 120             | 1.49                        | 11.65                       | 0.92      | 20.57                       | 0.060     | 0.25                        | 0.013     |

Fig. 2. (Color online) Schematic of photostability evaluation system with mode-field diameter (MFD) conversion thermally diffused expanded core (TEC) optical fiber. The sample was maintained at 85 °C in the chamber.

Fig. 3. (Color online) Time-dependent normalized absorbance of EO polymer thin film for irradiation with pump power (intensity) of (a) 49 mW (0.61 MW cm\(^{-2}\)), (b) 63 mW (0.78 MW cm\(^{-2}\)), (c) 100 mW (1.24 MW cm\(^{-2}\)) and (d) 120 mW (1.49 MW cm\(^{-2}\)) at 85 °C in an ambient atmosphere (blue points). Fits to the experimental data obtained using Eq. (1) are also plotted (red lines).

Fig. 4. (Color online) Rate constant \( b_1 \) as a function of photon flux density at 85 °C (black circles). The blue dashed line indicated a fit to the experimental data using a linear function, and the red dotted line is a fit using a quadratic function.
Figure 5 shows the wavelength dependence of the absorption coefficients of the EO polymer and its base polymer in the range of 1200–1900 nm. To perform these measurements, both the EO polymer films and the base polymer films with a thickness of several hundred micrometers were prepared. The obtained absorption coefficient of the EO polymer at 1550 nm is small (0.80 cm⁻¹). Considering the thickness of the EO polymer used in the photostability experiment (600 nm), the absorption of the polymer at 1550 nm in the experiment is negligible. Thus, we believe that the photodegradation rate associated with one-photon absorption is very low.

In order to investigate the effect of oxygen, we examined the photodegradation under argon atmosphere. Figure 6 shows the temporal change in the normalized absorbance of the EO polymer thin film when irradiated with the pump laser at 85 °C in argon and ambient air. EO polymer was hardly photodegraded by CW laser irradiation under argon atmosphere. This result indicates that the presence of oxygen is significantly involved in the photodegradation process of EO polymer.

We propose the following photodegradation mechanism for the EO polymer. (1) A singlet excited state of the EO chromophore is produced by two-photon absorption upon irradiation with the pump beam at 1550 nm. (2) A triplet excited state of the EO chromophore is produced via intersystem crossing. (3) Excited singlet oxygen is generated via energy transfer from the triplet excited state of the EO chromophore to oxygen in its ground triplet state. (4) The excited singlet oxygen is responsible for the photodegradation of the EO polymer.

Recently, we reported on the photostability of a different EO polymer designed for O-band. In contrast to the results at a wavelength of 1550 nm in the present study, b₁ at 1310 nm showed a linear dependence against the pump power, suggesting the involvement of photodegradation by one-photon absorption. The photon energy at a wavelength of 1310 nm is 0.946 eV, which is slightly smaller than the energy required for the generation of the excited singlet oxygen (0.975 eV). If we add the energy at the temperature of 85 °C (0.031 eV) to the photon energy at 1310 nm (0.946 eV), the total energy slightly exceeds 0.975 eV. Therefore, the excited singlet oxygen may be generated efficiently. On the other hand, the photon energy at a wavelength of 1550 nm is 0.800 eV. Even if we add the energy at the temperature of 85 °C (0.031 eV) to the photon energy at 1550 nm (0.800 eV), the total energy is 0.831 eV. Therefore, excited singlet oxygen is hardly generated by one-photon absorption and two-photon absorption is necessary to produce the excited singlet oxygen. These results also suggest that oxygen plays a major role in the photodegradation of EO polymer.

In the future, we plan to examine the temperature, ambient-environment, and excitation-wavelength dependences of photodegradation. It is expected that a detailed understanding of these aspects of the photodegradation behavior will lead to the development of an evaluation index for photochemical stability, which is required for the practical application of devices incorporating EO polymers.

4. Conclusions

In this study, we constructed a photostability evaluation system with an MFD conversion fiber. This enabled us to increase the intensity of a pump beam and investigate the temporal and pump intensity dependence of the photobleaching of an EO polymer under CW laser irradiation at a wavelength of 1550 nm, at 85 °C. The temporal dependence of the absorbance of the EO polymer cannot be expressed as a single exponential decay, which suggests the existence of multiple pathways in the overall photodegradation process. In the dominant photodegradation pathway, the photobleaching rate was proportional to the square of the pump intensity, and hence we conclude that photobleaching occurs via two-photon absorption under the experimental conditions of our study. As a possible photodegradation mechanism, we proposed the generation of singlet oxygen by two-photon absorption. Our results provide new insight into a photobleaching mechanism that is activated under non-resonant CW laser excitation. Clearly, our new findings are also important for the estimation of lifetimes in accelerated photodegradation testing, as well as for assessing the photodegradation of various practical devices that incorporate EO polymers. Further studies on photodegradation mechanisms will help improve the photostability of EO polymer devices.

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![Figure 5](https://orcid.org/0000-0001-5563-0083)

Fig. 5. (Color online) Wavelength dependence of absorption coefficients for EO polymer and its base polymer (without the EO chromophore side chains) in the range of 1200–1900 nm.

![Figure 6](https://orcid.org/0000-0001-5563-0083)

Fig. 6. (Color online) Temporal dependence of normalized EO polymer absorbance for pump power (intensity) of 100 mW (1.24 M cm⁻²) at 85 °C in argon and ambient air.
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