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Photochemical Stability of Organic Electro-Optic Polymer at 1310-nm Wavelength

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SUMMARY We investigated the photochemical stability of an electro-optic (EO) polymer under laser irradiation at 1310 nm to reveal photodegradation mechanisms. It was found that one-photon absorption excitation assisted with the thermal energy at the temperature is involved in the photodegradation process, in contrast to our previous studies at a wavelength of 1550 nm where two-photon absorption excitation is involved in the photodegradation process. Thus, both the excitation wavelength and the thermal energy strongly affect to the degradation mechanism. In any cases, the photodegradation of EO polymers is mainly related to the generation of exited singlet oxygen.

key words: *electro-optic polymer, photochemical stability, photodegradation mechanism, excitation wavelength, one-photon and two-photon absorption*

1. Introduction

In recent years, the scale of data centers has grown with the expansion of the use of big data, IoT, and cloud computing. Therefore, to increase the speed of the data center network, the optical transceivers with a higher speed, a larger capacity, and a lower power consumption are required [1], [2]. Silicon-organic hybrid optical modulators, which combine organic electro-optic (EO) polymers that enable the high speed and low power consumption operation with silicon that enables miniaturization and integration, have attracted much attention to their potential use of the optical interconnection for faster data communication [3]–[8]. EO polymers have low dielectric constant and large EO coefficients ($>$ 100 pm/V), and modulators using them are suitable for high-speed applications at the C-band or O-band [9]–[12]. Because O-band is used in data centers, EO polymers that have the absorption coefficient and EO coefficient suitable in O-band operation are required. We have developed EO polymers with small absorption coefficients and large EO coefficients in the O-band, which are promising in the future medium-to-short range communication, and optical devices based on EO polymers [13]. In this study, we investigated the photochemical stability and photodegradation mechanism of one of the EO polymers for O-band under laser irradiation at 1310 nm, which provide us with insights for the long-term operations of various optical devices with EO polymers for O-band. Furthermore, we compared the photodegradation mechanism of the EO polymer for O-band under 1310-nm irradiation with that of the EO polymer for C-band under 1550-nm irradiation in our previous studies [14].

2. Experimental Setup

Figure 1 (a) shows the chemical structure of an EO polymer used in this study. The poly methyl methacrylate-based side-chain EO polymer includes EO chromophores that comprised of perfluorophenyl tricyanofuran as the electron-acceptor unit, thienyl-di-vinylene as the π electron bridge, and aminobenzene with a benzyloxy group as the electron-donor unit. We measured the hyperpolarizability β of the EO chromophore by hyper-Rayleigh scattering [15], [16]. A relatively high hyperpolarizability value $\beta_{\mathrm{EO,zzz}}$ of 1171×10^{-30} esu at 1310 nm was obtained. The chromophore concentration in the EO polymer was 30 wt%. A sample film on a quartz substrate was prepared by spin-coating, using a cyclohexanone solution of the EO polymer. Figure 1 (b) shows the UV–Vis–NIR absorption spectrum of the EO polymer thin film coated on quartz substrate. The thickness of the quartz substrate was 1 mm, and the thickness of the EO polymer film was about 550 nm. A strong absorption band with a peak wavelength of around 730 nm due to EO chromophore in the EO polymer was observed. Figure 1 (c) shows the absorption coefficient spectrum of an EO polymer with the same chromophore in the range of 1200–1900 nm. The absorption coefficient of the EO polymer was 0.44 cm^{-1} at 1310 nm and 0.46 cm^{-1} at 1550 nm. The absorption coefficients were evaluated using thick films of the EO polymer [14], [17].

We constructed a photostability measurement system to investigate the photochemical stability of EO polymer under the irradiation of a laser at the O-band (1310 nm). The photostability measurements at 85°C were performed by using a fiber optic pump-probe beam system with continuous-wave (CW) lasers as shown in Fig. 2. The 1310 nm pump beam was irradiated on the film of the EO polymer to induce photobleaching, and the increase in transmission of the film was monitored every 5 or 10 minutes using a low power probe beam at 730 nm. The mode field diameter (MFD) of the optical fiber was converted from 10 μm to 3.3 μm to obtain a high intensity of 1.2 MW cm^{-2} at the fiber tip. The intensity can be comparable to that used in silicon-organic hybrid optical modulators. A more detailed description of

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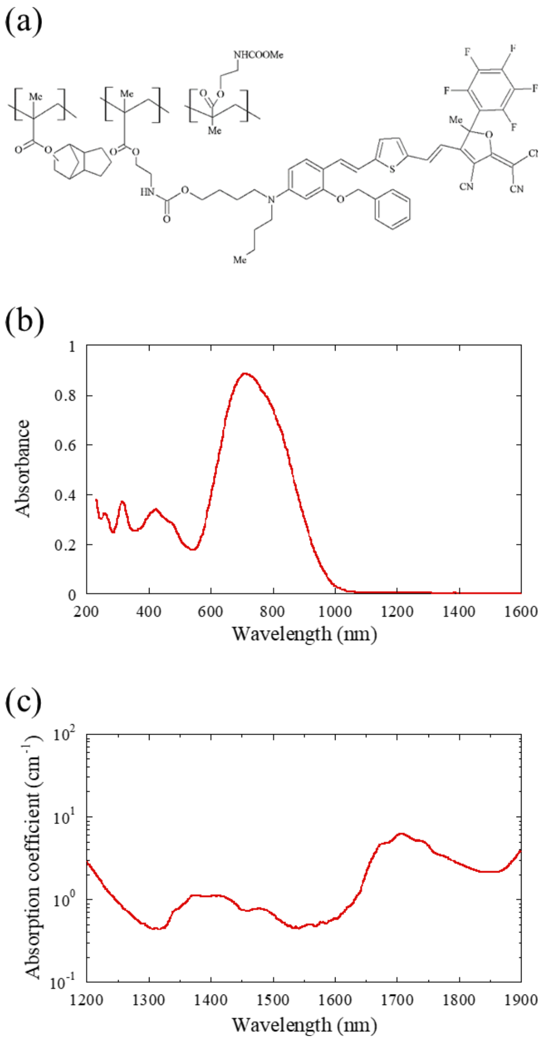

Fig. 1 (a) The molecular structure of an EO polymer. (b) The absorption spectrum of the EO polymer in the UV–Vis–NIR region. (c) The absorption coefficient spectrum in the 1200 nm to 1900 nm region for an EO polymer with the same chromophore.

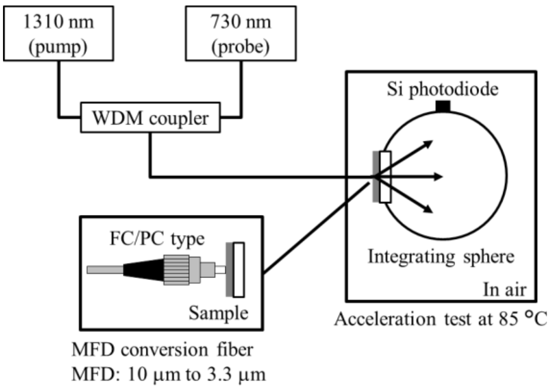

Fig. 2 Schematic diagram of the photostability evaluation system. The sample was maintained at 85°C in the atmosphere in the thermostatic chamber.

the experimental setup was reported elsewhere [14], [18].

3. Results and Discussion

Figure 3 (a)–3 (d) show the time dependence of the normalized absorbance of the EO polymer thin films at 85°C under the irradiation at various pump powers (intensities), such as (a) 19.4 mW (0.23 MW cm^{-2}), (b) 45.2 mW (0.53 MW cm^{-2}), (c) 75.8 mW (0.89 MW cm^{-2}), and (d) 103 mW (1.20 MW cm^{-2}) as well as the fitted results using the Eq. (1) as shown below. We found that the temporal change in the normalized absorbance of the EO polymer cannot be expressed by a single exponential decay. Therefore, as in our previous study, the analysis was performed assuming a two-component exponential decay in Eq. (1) [14].

$$\frac{-\log\dfrac{T(t)}{T_\infty}}{-\log\dfrac{T_0}{T_\infty}} = f_1\exp[-b_1t] + f_2\exp[-b_2t] \qquad (1)$$

Here, $T(t)$ is the transmittance at time t, $T_0 = T(0)$ and $T_\infty = T(\infty)$, where T_∞ is the transmittance on the quartz substrate only. f_1 and f_2 are the proportions of the two photodegradation processes and b_1 and b_2 are the rate constants, respectively. Table 1 shows the detail of the fitting parameters for normalized absorbance of the EO polymer thin films at each pump power (intensity). Here, n_0 is the photon flux density ($\mathrm{m}^{-2}\cdot\mathrm{s}^{-1}$) and χ^2 is the residual sum of squares. We

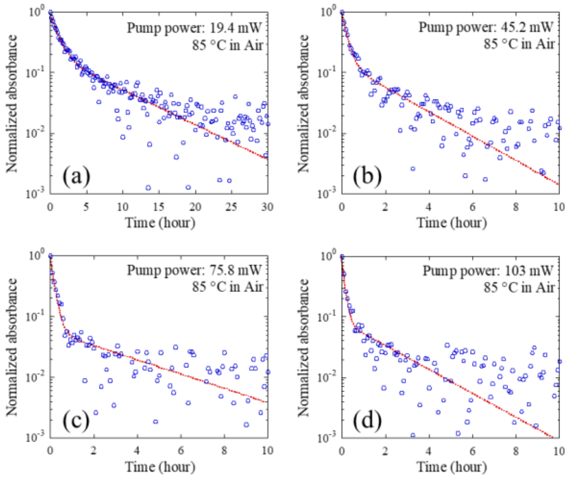

Fig. 3 Temporal dependence of normalized absorbance of EO polymer thin films for each pump power at 85°C in an atmosphere (blue points). Fits to the experimental data obtained using Eq. (1) are also plotted (red lines).

Table 1 Fitted results with Eq. (1) for data on time-dependent normalized absorbance of the EO polymer at 85°C for each pump power.

Pump power (mW)	Intensity (MW cm^{-2})	n_0 ($\times10^{28}$ $\mathrm{m}^{-2}\,\mathrm{s}^{-1}$)	f_1	b_1 ($\times10^{-5}$ s^{-1})	f_2	b_2 ($\times10^{-5}$ s^{-1})	χ^2
19.4	0.23	1.50	0.76	27.4	0.19	3.7	0.042
45.2	0.53	3.49	0.83	123.8	0.14	12.9	0.022
75.8	0.89	5.85	0.90	160.7	0.06	7.5	0.025
103.0	1.20	7.94	0.91	237.0	0.08	12.6	0.019

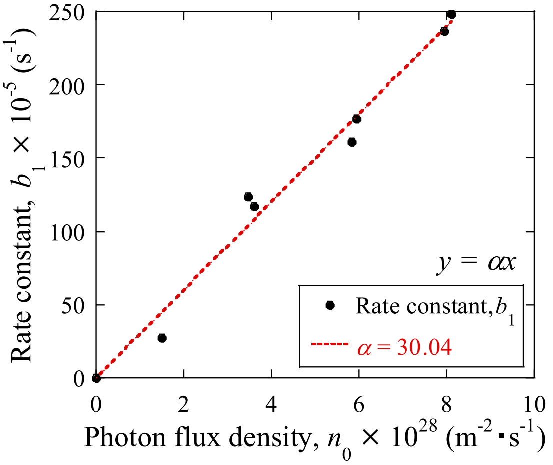

Fig. 4 Dependence of rate constant b_1 on photon flux density at 85°C.

found that the contribution of rate constant b_1 with a high photodegradation ratio is dominant as the proportion f_1 is in the range from 0.76 to 0.91. Therefore, we focus on the rate constant b_1.

The dependence of the rate constant b_1 on photon flux density are summarized in Fig. 4. It was found that the rate constant b_1 is linearly proportional to the pump intensity. This result means that a photodegradation process associated with one-photon absorption is dominant under the pump beam irradiation at 1310 nm, which is essentially different from our previous result under the pump beam irradiation at 1550 nm where a photodegradation process associated with two-photon absorption is dominant [14].

The rate constant b_1 obtained in the present study is about 30 to 40 times larger than the rate constant under the irradiation at 1550 nm in our previous study [14]. The rate constant in the case that a photodegradation process is associated with one-photon absorption is proportional to the product of one-photon absorption cross-section and photon flux density [18], [19], while the rate constant in the case that a photodegradation process is associated with two-photon absorption is proportional to the product of two-photon absorption cross-section and square of photon flux density. The large difference in the rate constant is probably related to the difference between the magnitude of the one-photon absorption cross-section and the magnitude of the two-photon absorption cross-section.

We also discuss from the viewpoint of the excited singlet oxygen generation. The photon energy at a wavelength of 1310 nm is 0.946 eV, which is slightly smaller than the energy required to generate the excited singlet oxygen (0.975 eV). By adding the thermal energy at the measurement temperature of 85°C (0.031 eV) to the photon energy (0.946 eV), the total energy (0.977 eV) exceeds the energy required to generate the excited singlet oxygen (0.975 eV). Therefore, it is considered that excited singlet oxygen can be generated even if the absorption coefficient at 1310 nm is small. Thus, temperature plays an important role in the generation of excited singlet oxygen at an excitation wavelength of 1310 nm.

On the other hand, in our previously study [14] at an excitation wavelength of 1550 nm, the photodegradation due to two-photon absorption excitation rather than one-photon absorption excitation was dominant. The photon energy at a wavelength of 1550 nm is 0.800 eV. By adding the thermal energy at the temperature of 85°C (0.031 eV) to the photon energy (0.800 eV), the total energy is 0.831 eV, which does not reach the energy required to generate the excited singlet oxygen (0.975 eV). In addition, the absorption coefficient at 1550 nm is small. Therefore, excited singlet oxygen is hardly generated via one-photon absorption excitation, and two-photon absorption excitation is required to produce the excited single oxygen. The two-photon energy at wavelength of 1550 nm is 1.600 eV that largely exceeds the energy required to generate the excited singlet oxygen (0.975 eV). Thus, the photodegradation due to two-photon absorption excitation is expected at an excitation wavelength of 1550 nm. This suggests that the external energy, such as photon energy of pump laser, temperature, required to generate the excited singlet oxygen is important in photodegradation of EO polymers. Therefore, photodegradation by the one-photon process would also occur in other EO polymers such as EO polymer used in the literature [14] under photoexcitation at a wavelength of 1310 nm and 85°C.

4. Conclusions

We have constructed a photostability measurement system using an MFD conversion fiber and investigated photochemical stability of the EO polymer at 85°C under CW laser irradiation at the O-band (1310 nm). It was found that the dominant photodegradation pathway at 85°C under the irradiation at 1310 nm is the photobleaching due to one-photon absorption excitation assisted with the thermal energy at 85°C, which is essentially different from the photodegradation pathway associated with two-photon absorption excitation under the pump beam irradiation at 1550 nm in our previous studies. We found that both the excitation wavelength and the thermal energy at the temperature strongly affect to the photodegradation mechanism. In any cases, the photodegradation of the EO polymers is strongly related to the generation of exited singlet oxygen.

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References

[1] H. Subbaraman, X. Xu, A. Hosseini, X. Zhang, Y. Zhang, D. Kwong, and R.T. Chen, “Recent advances in silicon-based passive and active optical interconnects,” Opt. Express, vol.23, no.3, pp.2487–2511, 2015. DOI: 10.1364/OE.23.002487

[2] Y. Yue, Q. Wang, and J. Anderson, “Experimental investigation of 400 Gb/s data center interconnect using unamplified high-baud-rate

and high-order QAM single-carrier signal," Appl. Sci., vol.9, no.12, p.2455, 2019. DOI: 10.3390/app9122455

[3] J. Leuthold, C. Koos, W. Freude, L. Alloatti, R. Palmer, D. Korn, J. Pfeifle, M. Lauermann, R. Dinu, S. Wehrli, M. Jazbinsek, P. Günter, M. Waldow, T. Wahlbrink, J. Bolten, H. Kurz, M. Fournier, J.-M. Fedeli, H. Yu, and W. Bogaerts, "Silicon-organic hybrid electro-optical devices," IEEE J. Selected Topics Quantum Electron., vol.19, no.6, p.3401413, 2013. DOI: 10.1109/JSTQE.2013.2271846

[4] X. Zhang, A. Hosseini, S. Chakravarty, J. Luo, A.K.-Y. Jen, and R.T. Chen, "Wide optical spectrum range, subvolt, compact modulator based on an electro-optic polymer refilled silicon slot photonic crystal waveguide," Opt. Lett., vol.38, no.22, pp.4931–4934, 2013. DOI: 10.1364/OL.38.004931

[5] S. Wolf, H. Zwickel, W. Hartmann, M. Lauermann, Y. Kutuvantavida, C. Kieninger, L. Altenhain, R. Schmid, J. Luo, A.K.-Y. Jen, S. Randel, W. Freude, and C. Koos, "Silicon-organic hybrid (SOH) mach-zehnder modulators for 100 Gbit/s on-off keying," Sci. Rep, vol.8, p.2598, 2018. DOI: 10.1038/s41598-017-19061-8

[6] C. Kieninger, Y. Kutuvantavida, D.L. Elder, S. Wolf, H. Zwickel, M. Blaicher, J.N. Kemal, M. Lauermann, S. Randel, W. Freude, L.R. Dalton, and C. Koos, "Ultra-high electro-optic activity demonstrated in a silicon-organic hybrid modulator," Optica, vol.5, no.6, pp.739–748, 2018. DOI: 10.1364/OPTICA.5.000739

[7] P. Steglich, C. Mai, C. Villringer, B. Dietzel, S. Bondarenko, V. Ksianzou, F. Villasmunta, C. Zesch, S. Pulwer, M. Burger, J. Bauer, F. Heinrich, S. Schrader, F. Vitale, F.D. Matteis, P. Prosposito, M. Casalboni, and A. Mai, "Silicon-organic hybrid photonics: an overview of recent advances, electro-optical effects and CMOS integration concepts," J. Phys.: Photonics, vol.3, no.2, p.022009, 2021. DOI: 10.1088/2515-7647/abd7cf

[8] J. Mao, H. Sato, A. Bannaron, J. Hong, G.-W. Lu, and S. Yokoyama, "Efficient silicon and side-cladding waveguide modulator with electro-optic polymer," Opt. Express, vol.30, no.2, pp.1885–1895, 2022. DOI: 10.1364/OE.447616

[9] C. Zhang, L.R. Dalton, M.-C. Oh, H. Zhang, and W.H. Steier, "Low V_π electrooptic modulators from CLD-1: chromophore design and synthesis, material processing, and characterization," Chem. Mater., vol.13, no.9, pp.3043–3050, 2001. DOI: doi.org/10.1021/cm010463j

[10] L.R. Dalton, P.A. Sullivan, and D.H. Bale, "Electric field poled organic electro-optic materials: state of the art and future prospects," Chem. Rev., vol.110, no.1, pp.25–55, 2010. DOI: 10.1021/cr9000429

[11] P. Groumas, V. Katopodis, J.H. Choi, H.-G. Bach, J.-Y. Dupuy, A. Konczykowska, Z. Zhang, P. Harati, E. Miller, A. Beretta, L. Gounaridis, F. Jorge, V. Nodjiadjim, A. Dede, A. Vannucci, G. Cangini, R. Dinu, N. Keil, N. Grote, H. Avramopoulos, and C. Kouloumentas, "Multi-100 GbE and 400 GbE interfaces for intra-data center networks based on arrayed transceivers with serial 100 Gb/s operation," J. Lightwave Technol., vol.33, no.4, pp.943–954, 2015. DOI: 10.1109/JLT.2014.2363107

[12] Y. Enami, A. Seki, S. Masuda, T. Joichi, J. Luo, and A.K.-Y. Jen, "Bandwidth optimization for mach–zehnder polymer/sol–gel modulators," J. Lightwave Technol., vol.36, no.18, pp.4181–4189, 2018. DOI: 10.1109/JLT.2018.2860924

[13] A. Otomo, I. Aoki, C. Yamada, H. Yokohama, T. Yamada, H. Tazawa, and Y. Murakami, "Development of EO polymer/Si hybrid optical modulators for use in the O-band," The 80th JSAP Autumn Meeting 2019, Hokkaido Japan, 21p-E204-2, Sept. 2019.

[14] Y. Tominari, T. Yamada, T. Kaji, C. Yamada, and A. Otomo, "Photostability of organic electro-optic polymer under practical high intensity continuous-wave 1550 nm laser irradiation," Jpn. J. Appl. Phys., vol.60, no.10, p.101002, 2021. DOI: 10.35848/1347-4065/ac235a

[15] T. Yamada, I. Aoki, H. Miki, C. Yamada, and A. Otomo, "Effect of methoxy or benzyloxy groups bound to an amino-benzene donor unit for various nonlinear optical chromophores as studied by hyper-Rayleigh scattering," Mater. Chem. Phys., vol.139, no.2-3, pp.699–705, 2013. DOI: 10.1016/j.matchemphys.2013.02.020

[16] T. Yamada and A. Otomo, "Recent progress in the evaluation of molecular nonlinear optical (NLO) properties by hyper-Rayleigh scattering (HRS) and higher-order HRS, and the development of NLO chromophores," Mol. Cryst. Liq. Cryst., vol.728, no.1, pp.82–91, 2021. DOI: 10.1080/15421406.2021.1946970

[17] S. Kamada, R. Ueda, C. Yamada, K. Tanaka, T. Yamada, and A. Otomo, "Superiorly low half-wave voltage electro-optic polymer modulator for visible photonics," Opt. Express, vol.30, no.11, pp.19771–19780, 2022. DOI: 10.1364/OE.456271

[18] M.E. DeRosa, M. He, J.S. Cites, S.M. Garner, and Y.R. Tang, "Photostability of high $\mu\beta$ electro-optic chromophores at 1550 nm," J. Phys. Chem. B, vol.108, no.25, pp.8725–8730, 2004. DOI: 10.1021/jp037907e

[19] D. Rezzonico, M. Jazbinsek, P. Günter, C. Bosshard, D.H. Bale, Y. Liao, L.R. Dalton, and P.J. Reid, "Photostability studies of π-conjugated chromophores with resonant and nonresonant light excitation for long-life polymeric telecommunication devices," J. Opt. Soc. Am. B, vol.24, no.9, pp.2199–2207, 2007. DOI: 10.1364/JOSAB.24.002199