Optical Limiting Property of a Polyacene-Based Oligomer Synthesized under High Pressure

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ABSTRACT: The optical limiting property of a new polyacene-based diphenyldiacetylene oligomer was investigated. The oligomer was synthesized by reaction of diphenyldiacetylene under high pressure. Toluene solutions of the oligomer contained within a quartz cell were irradiated with the pulse from a frequency-doubled Nd:YAG laser at 532 nm. At low input fluence, the transmittance of the toluene solution obeyed the Beer–Lambert law. The transmittance was constant and agreed well with that obtained by a spectrophotometer. At high input fluence, the transmittance decreased with input fluence. The oligomer had an optical limiting property. As the concentration of the oligomer increased, the threshold for optical limiting and the saturated output fluence decreased. The inverse of saturated output fluence of the oligomer was about $^1/_5$ of that of C_{60}. According to the reverse saturable absorption mechanism, the following equation was obtained between the absorbance $\log(I_0/I)$ and $I_0 - I$; $\log(I_0/I) = K(I_0 - I) + A_g$, where I_0 is the input fluence, I is the output fluence, K is a parameter depending on the absorption cross section and the relaxation time, and A_g is the absorbance of the ground state.

Introduction

Optical limiters act to limit the intensity to a fixed value above an intensity-dependent threshold.[1] Optical sensors used with lasers and arc welders must be protected from damaging light levels by use of optical limiters. Optical limiters can be fabricated in a variety of ways. The simplest limiter makes use of materials whose optical transmittance decreases at a high light level. The optical limiting property was first discovered by Giuliano and Hess for the compounds Indanthrone and Sudanschwarz B.[2] Since then, many other compounds were shown to possess the optical limiting property.[3-11] These compounds were termed reverse saturable absorbers[2] or optical limiting materials.[9] It has been reported that π-electron conjugated systems such as metallophthalocyanine,[4,5] diphenylpolyenes,[8] C_{60},[9] and C_{70}[9] have optical limiting properties. The toluene solution of C_{60} shows the optical limiting property with saturated output fluences lower than those reported for other optical limiting materials in use.[9]

In the previous paper, we have synthesized a new class of conjugated oligomers with a polyacene-based structure by reaction of diphenyldiacetylene under high pressure.[12] The oligomer is a π-electron conjugated system. It was expected that the toluene solution of the oligomer has the optical limiting property. In this paper, the objective is to study optical limiting properties of a polyacene-based oligomer.

Experimental Section

Materials. The polyacene-based oligomer was made by reaction of diphenyldiacetylene under high pressure. The reaction was carried out using a high hydrostatic pressure reactor (Rigaku-Denki) in a presence of 0.13 GPa at 250 °C for 5 h.[12] Based on polystyrene calibration, the number-average molecular weight of the oligomer was 1270 by gel permeation chromatography (GPC). The oligomer of 0.1–0.5 wt % was dissolved in toluene. A 0.12 wt % toluene solution of C_{60} was prepared as a reference. C_{60} (C_{60}: 99.9%) from MER Corp. was used without further purification. The toluene solution of the specimen was poured into a quartz cell (specimen path length, 1 mm; width, 40 mm; length, 40 mm) to estimate the optical limiting.

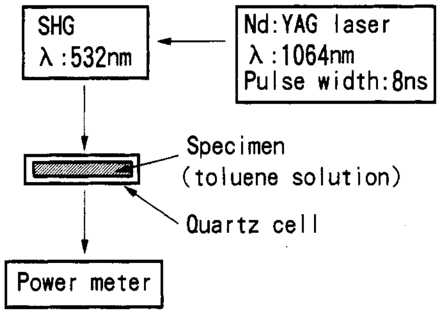

Figure 1. Experimental configuration used to measure optical limiting.

Optical Limiting Properties. The experimental arrangement to characterize the optical limiting property is shown in Figure 1. The optical limiting tests were performed with a Continuum frequency-doubled Nd:YAG laser that produces about 400 mJ/pulse of 8-ns pulse width. The beam was near a Gaussian transverse profile. The laser was operated at 10 Hz. The quartz cell which contained the solution was irradiated with pulses of 8 mm in diameter from the Nd:YAG laser at 532 nm. Apertures and focusing optics were not used. The optical limiting property was obtained by varying the input energy with an increase in the delay time of the Q-switch from 304 to 474 μs. Input and output energies per pulse were obtained from a power meter (Gentec: PSV-3103), and the transmitted energy through toluene was identified as an input energy. Absorption spectra were recorded on a double-beam spectrometer (Shimadzu UV-2100).

Results and Discussion

Figure 2 presents the visible absorption spectrum of the oligomer in a toluene solution between 400 and 800 nm. There is continuous absorption in the visible region. The absorption intensity is stronger at shorter wavelength. Such a behavior can be attributed to an oligomer in which a number of chromophores exist, each having different absorption maxima according to the length of the conjugated system. The transmittance at

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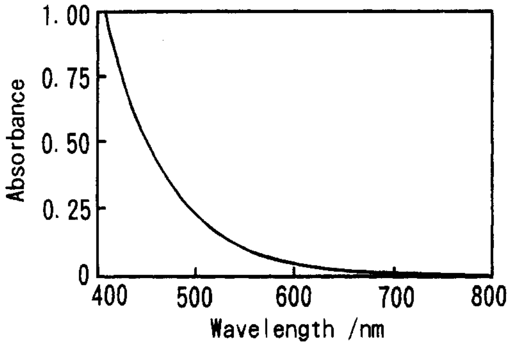

Figure 2. Absorption spectrum of a diphenyldiacetylene oligomer in a toluene solution (concentration: 0.12 wt %).

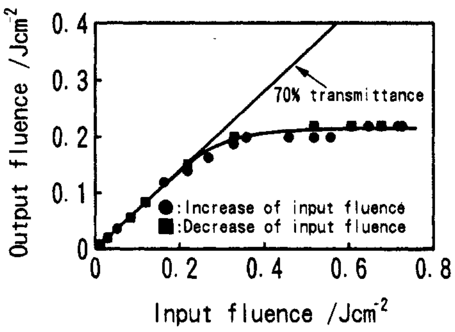

Figure 3. Relationship between output fluence and input fluence of a 70% transmitting solution of an oligomer in toluene to 532 nm optical pulse (concentration: 0.12 wt %).

532 nm decreases from 74 to 21% with increasing concentration (0.1–0.5 wt %). The decrease in the intensity of the light as it passes through an absorbing material is proportional to the intensity of light. The absorption of light through the specimen is usually characterized by the following Beer–Lambert law.

$$\log(I_0/I) = \epsilon CL \tag{1}$$

where I_0 is the input fluence and I is the output fluence, and $\log(I_0/I)$ is called the absorbance. ϵ, C, and L are the molar absorption coefficient, concentration, and specimen thickness, respectively. The law implies that the transmittance (I/I_0) is a constant independent of the input fluence. Figure 3 shows the input–output response of the toluene solution of the oligomer at a concentration of 0.12 wt %. At low input fluence, the transmittance obtained by the ratio of the input fluence to output fluence obeys the Beer–Lambert law. The transmittance is constant (70%) and agrees well with that obtained by the spectrophotometer. At high input fluence, the transmittance decreases with input fluence and we observe an optical limiting property with saturated output fluence. The saturated output fluence of the toluene solution of the oligomer was estimated by the output fluence at an input fluence of about 0.6 J/cm^2. The saturated output fluence decreased from 0.25 to 0.033 J/cm^2 with an increase of the concentration of the toluene solution (0.1–0.5 wt %). Figure 3 also shows that input and output response does not depend on increase and decrease of the input fluence. After measurement of the optical limiting property, the visible absorption spectrum was consistent with that shown in Figure 2. These observations indicate that there is no photodegradation of the oligomer by irradiation of the laser beam. Figure 4 shows the dependence of the absorbance [$\log(I_0/I)$] on input fluence. Below the threshold for optical limiting, the absorbance is constant. The absorbance begins to increase above the nonlinear threshold. The toluene solution is becoming a strong absorber. The increase in absorbance is based on excited-state absorption as shown later. The nonlinear thresholds for each of the toluene solutions of the oligomer were obtained. As the concentration of the oligomer increases from 0.1 to 0.5 wt %, the threshold shifts from 0.3 to 0.1 J/cm^2. This shows that the threshold is inversely proportional to the concentration. The nonlinear threshold and the saturated output fluence seem to be affected by the molecular interaction of the oligomer in the toluene solution.

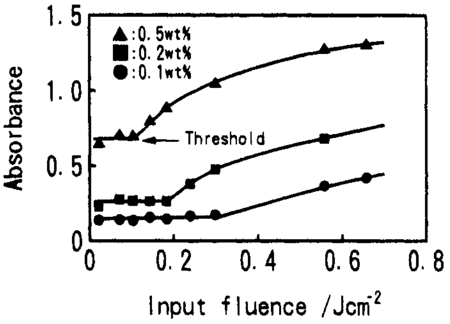

Figure 4. Dependence of absorbance on input fluence.

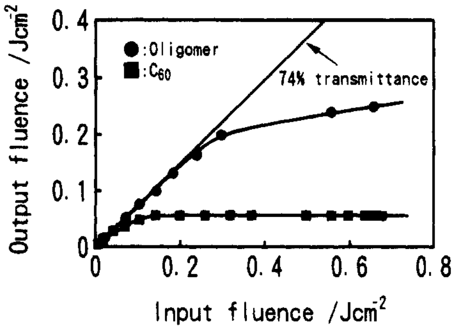

Figure 5. Comparison of optical limiting properties of solutions of oligomer and C$_{60}$.

Figure 5 is a comparison of the performance of the oligomer and C$_{60}$ with 74% transmittance. The inverse of saturated output fluence of C$_{60}$, which is one of the optical limiting properties, is the highest.[9] It is indicated that the optical limiting property of the oligomer at a 74% transmitting solution is about $^1/_5$ of that of C$_{60}$.

Several mechanisms have been proposed for optical limiting including reverse saturable absorption (nonlinear absorption such as sequential single photon absorption),[6,9] nonlinear scattering,[13] thermal blooming,[14] and multiphoton absorption.[1,15] The reverse saturable absorption mechanism by a five-level energy diagram yielded a reasonable explanation for optical limiting of a π-electron conjugated system such as C$_{60}$ below the input fluence of 1 J/cm^2.[16] As the polyacene-based oligomer also has a π-electron conjugated system, the optical limiting behavior can be described using the five-level energy diagram shown in Figure 6.[6] It is well-known that numerous organic chromophores exhibit absorption from excited electronic states to higher electronic states subsequent to excitation. This excited-state absorption involves singlet–singlet or triplet–triplet transition. The initial absorption is from a ground state (level 1), typically a singlet, to an excited singlet state (level 2). This excited state can relax to its original ground state, be excited to a higher singlet state (level 3), or transfer to the lower level of a triplet state (level 4) by intersystem crossing. The triplet state

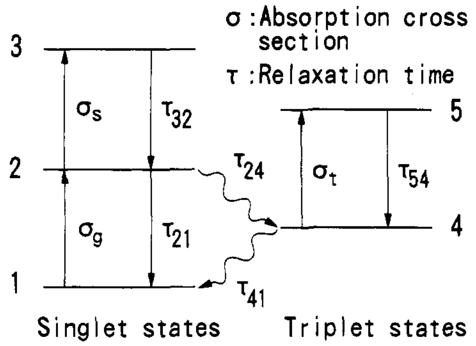

Figure 6. Five-level energy diagram of a polyacene-based oligomer.

absorption takes place between level 4 and level 5. To obtain an optical limiting property, the upper singlet and lower triplet must have larger absorption cross sections of σ_s and σ_t than the ground state σ_g. Those absorption cross sections have units of square centimeters. It is assumed that the relaxation times between levels 3 and 2, τ_{32}, and between levels 5 and 4, τ_{54}, are extremely fast. The upper singlet level and lower triplet level should have large relaxation times of τ_{21} and τ_{41} compared with relaxation times τ_{32} and τ_{54}.

The optical limiting characteristics of the oligomer are computed based on the following analysis.[17,18] Let N_s be the molecular density (cm^{-3}) of the oligomer in the excited state (level 2), let $[N - (N_s + N_t)]$ be the molecular density in the ground state of level 1, and let N_t be the concentration of the oligomer in the excited state of level 4. Then the change in intensity of light i (number of photons/cm^2 s) with distance x is

$$\mathrm{d}i/\mathrm{d}x = -\sigma_g[N - (N_s + N_t)]_i - \sigma_s N_s i - \sigma_t N_t i \quad (2)$$

The time rates of changes of N_s and N_t are

$$\mathrm{d}N_s/\mathrm{d}t = \sigma_g[N - (N_s + N_t)]i - N_s/\tau_{21} - N_s/\tau_{24} \quad (3)$$

$$\mathrm{d}N_t/\mathrm{d}t = N_s/\tau_{24} - N_t/\tau_{41} \quad (4)$$

where τ_{21}, τ_{24}, and τ_{41} are relaxation times. We suspect that τ_{21} and τ_{24} are on a nanosecond scale.[4,5,16] τ_{41} must be long compared to the relaxation times τ_{21} and τ_{24}, as well as pulse duration. Under these conditions, N_s and N_t vary with time. The transmitted power measured through the specimen was constant and independent of time. This exhibits that the molecules in the excited states of levels 2 and 4 relax to the ground state below 100 ms (interval between two pulses). It is reasonable to assume the quasi-steady state.[19] $\mathrm{d}N_s/\mathrm{d}t$ and $\mathrm{d}N_t/\mathrm{d}t$ vanish in the quasi-steady state. Thus,

$$N_s = N/[1 + \tau_{41}/\tau_{24} + 1/(\sigma_g i)(1/\tau_{21} + 1/\tau_{24})] \quad (5)$$

$$N_t = (\tau_{41}/\tau_{24})N/[1 + \tau_{41}/\tau_{24} + 1/(\sigma_g i)(1/\tau_{21} + 1/\tau_{24})] \quad (6)$$

Substituting eqs 5 and 6 into eq 2, the differential equation is given by

$$\mathrm{d}i/\mathrm{d}x = -\sigma_g N i\left[1 - \frac{(1 - \sigma_s/\sigma_g) + (1 - \sigma_t/\sigma_g)(\tau_{41}/\tau_{24})}{(1 + \tau_{41}/\tau_{24}) + 1/(\sigma_g i)(1/\tau_{21} + 1/\tau_{24})}\right] \quad (7)$$

The solution is

$$\ln(i_0/i) - \sigma_g NL = D/E \ln[(1 + EFi_0)/(1 + EFi)] \quad (8)$$

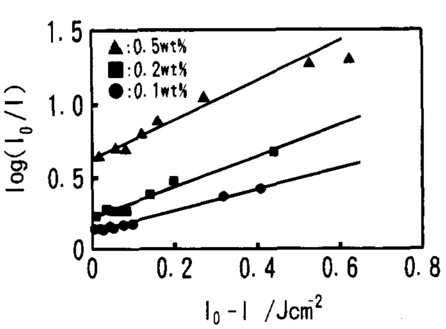

Figure 7. Plots of $\log(I_0/I)$ versus $(I_0 - I)$.

Here, i_0 and i are the input and output intensities, L is the specimen path length, $D = (\sigma_s/\sigma_g - 1) + (\sigma_t/\sigma_g - 1)(\tau_{41}/\tau_{24})$, $E = (\sigma_s/\sigma_g) + (\sigma_t/\sigma_g)(\tau_{41}/\tau_{24}$, and $F = 1/[1/\sigma_g(1/\tau_{21} + 1/\tau_{24})]$. According to Maclaurin's series of $\ln(1 + EFi_0)$ and $\ln(1 + EFi)$, eq 8 approximately becomes

$$\ln(i_0/i) = DF(i_0 - i) + \sigma_g NL \quad (9)$$

The absorption cross section σ_g of the ground state is expressed by eq 10.

$$\sigma_g = A_g \ln 10/(NL) \quad (10)$$

where A_g is the absorbance of the ground state. Furthermore, input and output fluences per pulse I_0 and I have units of joules per square centimeter. As the laser is operated at 10 Hz, the values i_0 and i are expressed by eqs 11 and 12.

$$i_0 = 10I_0/(h\nu) \quad (11)$$

$$i = 10I/(h\nu) \quad (12)$$

where h and ν are Planck's constant and the frequency of the laser beam, respectively. The following equation is obtained by substituting eqs 10–12 into eq 9.

$$\log(I_0/I) = K(I_0 - I) + A_g \quad (13)$$

Here, $K = 10DF/(h\nu \ln 10)$. Equation 13 shows that the relation between $\log(I_0/I)$ and $I_0 - I$ should be linear. Figure 7 shows $\log(I_0/I)$ as a function of $I_0 - I$ for various toluene solutions of the oligomer. The linear relation between $\log(I_0/I)$ and $I_0 - I$ is demonstrated. It is represented that the optical limiting property is explained by the five-level energy diagram. The plot of $\log(I/I_0)$ vs $I_0 - I$ looks like it may be rolling off and not strictly linear. This is due to the fact that eq 13 is an approximate linear relation between $\log(I_0/I)$ and $I_0 - I$. The values of A_g are estimated as 0.12–0.64. These values agree well with those obtained by the spectrophotometer (0.13–0.68). We find that K is not constant and increases from 0.8 to 1.3 with concentration. It is presumed that τ_{21} increases with concentration because of the reabsorption of the fluorescence in the relatively thick solution.[20] $\log(I_0/I)$ of C_{60} also linearly increased with $I_0 - I$ in the low values below 0.07 J cm^{-2}. The value of K of C_{60} at the 74% transmitting solution was about 5 times that of the oligomer. It is suggested that the oligomer has the smaller relative excited-state absorption σ_s/σ_g and σ_t/σ_g and smaller values of τ_{41}/τ_{24}, τ_{21}, and τ_{24} for optical limiting. Absorption cross sections and relaxation times of a polyacene-based oligomer seem to be changed by the molecular weight and the substituents on the polyacene carbon. We support the idea that high-pressure oligomerization of many diacetylenes gives a variety of polyacene-based oligomers, whose optical limiting properties depend on the molecular weight and the substituents.

Conclusion

We found that toluene solutions of the polyacene-based oligomer had optical limiting properties. The nonlinear threshold and the saturated output fluence of the toluene solution of the oligomer decreased with increasing concentration. The optical limiting property at the 74% transmitting solution of the oligomer was about $^1/_5$ of that of C_{60}. The optical limiting property was described by the five-level energy diagram.

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