High-Pressure Synthesis and Optical Limiting Property of Cyclic Diphenylacetylene Oligomer

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ABSTRACT: New conjugated oligomers were synthesized by reacting diphenylacetylene under high pressure of 0.13–0.76 GPa at 250 and 300°C for 1–10 h. The number-average molecular weight $\bar{M}_n$, and the weight-average molecular weight $\bar{M}_w$ increased with pressure, but those values were independent of temperature and time ($\bar{M}_n$, 320–490; $\bar{M}_w$, 350–580). Elementary analysis, field desorption mass spectrometry, Fourier transform infrared, and ^{13}C nuclear magnetic resonance experiments revealed that the oligomer above and including pentamer was a new compound having cyclic structure. Toluene solutions of the oligomer (400 $\bar{M}_n$) contained within a quartz cell were irradiated with the pulse from a frequency-doubled Nd : Yag laser at 532 nm. The transmittance of the solution decreased with input fluence, and we observed an optical limiting property with saturated output fluence. As the concentration of the oligomer increased, the saturated output fluence decreased. The optical limiting property was analyzed according to the reverse saturable absorption mechanism. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 68: 129–135, 1998

Key words: high pressure; diphenylacetylene; cyclic oligomer; optical-limiting property; reverse saturable absorption

INTRODUCTION

Polyacetylene is an insoluble conjugated polymer and can be obtained by using conventional Ziegler–Natta catalysts.[1–3] Phenylacetylene having bulky phenyl groups on the acetylene carbons produces an oligomer not exceeding a number-average molecular weight of 7500 and insoluble products by use of the Ziegler–Natta catalyst.[4,5] Catalysts based on Mo and W are effective in the polymerization of monosubstituted acetylene.[4,6] Disubstituted acetylene, such as diphenylacetylene, produces an insoluble polymer by use of the WCl_6–Ph_4Sn or $TaCl_5$–Et_3SiH catalyst.[7,8] In general, polymerization of the unsaturated compound starts from an initiator or catalyst, and a linear polymer is formed.[4,9] The application of pressure is well known to influence the reaction of substances.[10–12] In the previous articles, new cyclic phenylacetylene oligomers, which have optical limiting property, were synthesized in the absence of initiator or catalyst by oligomerization of phenylacetylene under high pressure.[13,14]

In this study, cyclic conjugated oligomers were synthesized by reacting diphenylacetylene under high pressures of 0.13–0.76 GPa at 250 and 300°C for 1–10 h. The optical limiting property of the cyclic diphenylacetylene oligomer was investigated.

EXPERIMENTAL

Materials

Diphenylacetylene (178.23 molecular weight) in the form C_6H_5—$C\equiv C$—C_6H_5 (Sigma–Aldrich

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Japan) was used for the reaction without further purification. Reaction of diphenylacetylene under high pressure was carried out using a high-hydrostatic-pressure reactor.[15] The specimen (1.2–1.6 g) was packed into a polytetrafluoroethylene cell (8 mm inside diameter, 40 mm length). After closing the cell, it was introduced into the high-pressure vessel. The specimen was compressed at various pressures in the range of 0.13–0.76 GPa by hand oil pump, substantially annealed at 250 and 300°C for a constant time of 1–10 h, with a pressure-transmitting medium (silicone oil). The specimens were annealed at a heating ratio of 10°C/min. After reaction under high pressure, the product was cooled to room temperature, decompressed, and removed from the cell.

Characterization

The molecular weight of the product was determined by gel permeation chromatography (GPC) with a liquid chromatograph (Japan Analytical Industry Co., Ltd. LC-08) consisting of a refractive index detector and a polystyrene gel column. Chloroform was used as a mobile phase at a flow rate of 3 mL/min on the column. It was also used as a solvent, and the concentration of the product solution was 3% (w/v). The product was a mixture of diphenylacetylene oligomer and monomer, as shown later.

Visible (vis) absorption spectra of the oligomer solution in toluene was recorded on an ultraviolet (UV)–vis (UV–vis) recording spectrophotometer (Shimadzu UV-2100). The spectrum in 400–800 nm was measured. Elementary analysis was made using an instrument of combustion analysis (Perkin–Elmer Elemental Analyzer 240C) for carbon and hydrogen. The oligomer and the monomer of 1.5 mg were used for the analysis. The thermal property of diphenylacetylene and the oligomer under atmospheric pressure was investigated using a differential scanning calorimetry (DSC) calorimeter from Perkin–Elmer (DSC 7) at a heating rate of 10°C/min. The endothermic peak of the DSC thermogram was identified as the melting temperature. X-ray diffraction (XRD) measurement of the oligomer was conducted with $CoK\alpha$ radiation from a Rigaku Denki Rad-B.

After separation of four components by GPC, the characterization of the diphenylacetylene oligomer was performed by infrared (IR), field desorption mass (FDMS) spectra, and ^{13}C nuclear magnetic resonance (NMR) spectrum. A Fourier transform infrared (FTIR) spectrophotometer (Japan Spectroscopic Co., Ltd. FT/IR-5M) was used for IR studies in the wavenumber from 4000 to 600 cm^{-1}. Specimens in powder form were mixed with KBr (0.7–0.9 mg of specimen with 200 mg of KBr), and tablets were formed by applying pressure. The field desorption mass (FDMS) spectra were obtained on a mass spectrometer (VG Analytical Co., Ltd. ZAB-SE) using field desorption ionization. ^{13}C-NMR spectra of the specimens were obtained on a spectrometer (Japan Electron Optics Laboratory JNM-FX90Q) at 22.53 MHz (^{13}C). The chemical shifts of the NMR spectra for the specimens in chloroform were calibrated relative to tetramethylsilane (TMS) [$(CH_3)_4Si$].

Optical Limiting Properties

The experimental arrangement to characterize the optical limiting property is the same as reported earlier by us.[16] 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 a near-Gausian transverse profile. The laser was operated at 10 Hz. The quartz cell, which contained the solution, was irradiated with the pulses of 8 mm in diameter from the Nd : Yag laser at 532 nm. The optical limiting property was obtained by varying the input energy with an increase in the delay time of Q-switch from 304 to 434 μs. Input and output energies per pulse were obtained with a power meter (Gentec : PSV-3103), and the transmitted energy through toluene was identified as an input energy.

RESULTS AND DISCUSSION

High-pressure differential thermal analysis (DTA) thermograms of diphenylacetylene indicated the melting temperature, the temperature of crystal transformation, and the broad exothermic peak temperature (reaction temperature).[17] The melting temperature of diphenylacetylene increased linearly with increasing pressure, and the pressure dependence of the melting temperature changed abruptly at 0.52 GPa because of the crystal transformation [melting temperature (atmospheric pressure), 59°C; pressure, 0.01–0.93 GPa; melting temperature, 62–303°C].

Reaction of diphenylacetylene was carried out at 250 and 300°C under high pressure (0.13–0.76 GPa). It is revealed that diphenylacetylene is mainly in a liquid phase at the annealing temper-
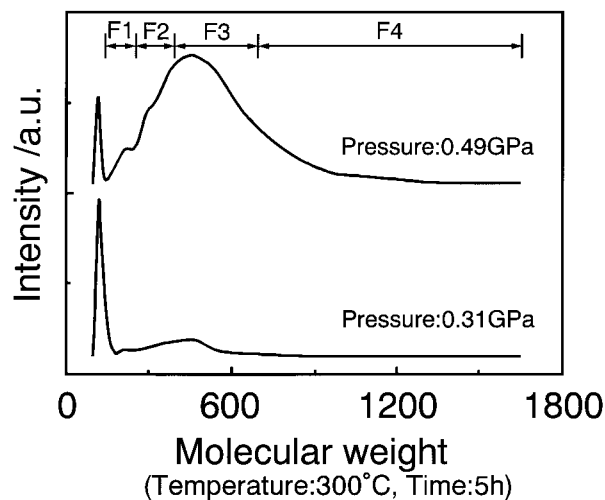
Figure 1   Molecular weight distribution of products.

Figure 3   Influence of pressure and temperature on oligomer yield O_y.

ature under the high pressure. The products obtained are easily soluble in usual organic solvents, such as chloroform and toluene, giving yellow solutions. GPC was used to estimate the molecular weight of the products in chloroform. Based on the polystyrene calibration, the molecular weight distribution was obtained. The molecular weight distribution of the products reacted at 0.31 and 0.49 GPa is shown in Figure 1. Oligomerization is accelerated by pressure. The temperature dependence of the number-average molecular weight $\bar{M}_n$ as a function of pressure is potted in Figure 2. Pressure accelerates $\bar{M}_n$ of the diphenylacetylene oligomer, but the value is independent of temperature. The number-average molecular weight ($\bar{M}_n$) and the weight-average molecular weight ($\bar{M}_w$)
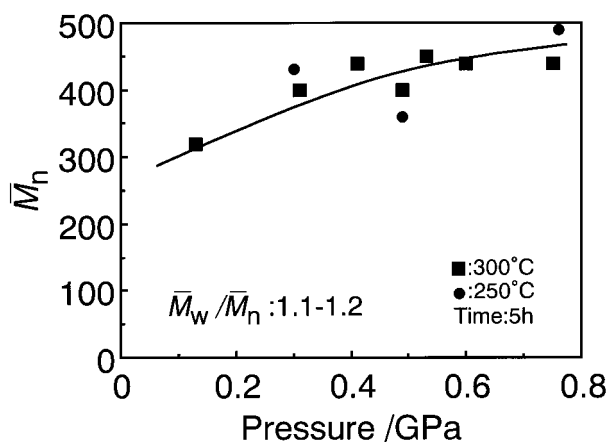
increased with increasing pressure (pressure, 0.13–0.76 GPa; $\bar{M}_n$, 320–490; $\bar{M}_w$, 350–580, the time at 5 h). $\bar{M}_w/\bar{M}_n$ of the oligomer had an approximately constant value (1.1–1.2). The oligomer yield was determined by the area ratio of the chromatograms of the monomer and the oligomer. The oligomer yield (O_y) at various temperatures as a function of pressure is plotted in Figure 3. As the pressure and the temperature increase, O_y increases and has the maximum value of 85% under 0.53 GPa at 300°C. The pressure corresponded to that of the crystal transformation. Reaction time increased the oligomer yield (time, 1–10 h; $\bar{M}_n$, 390–410; $\bar{M}_w$, 440–460; O_y, 19–94%; pressure, 0.49 GPa; temperature, 300°C).

The results of the elementary analysis showed that the H/C ratio of the oligomer agreed with that of diphenylacetylene (0.72 H/C). There was a continuous absorption for the oligomer in the vis region from 400 to 800 nm. The absorbance was weaker at a longer wavelength. The solution of diphenylacetylene was a colorless, transparent liquid and had no absorption in the visible region. This suggests that oligomer has a number of chromophores, which have different absorption maximums according to the length of the conjugated system. The oligomer showed a broad XRD peak at 2θ of 23° (0.063 rad half-width) and no melting behavior over the temperature of room temperature to 400°C from the DSC thermogram, probably owing to the amorphous structure.

The characterization of the oligomer synthesized under 0.49 GPa at 300°C for 5 h was carried out by separation of four components, F1–F4, shown in Figure 2. IR spectroscopy yields the structural information. Figure 4 shows the IR ab-

Figure 2   Influence of pressure and temperature on number-average molecular weight of diphenylacetylene oligomer $\bar{M}_n$.

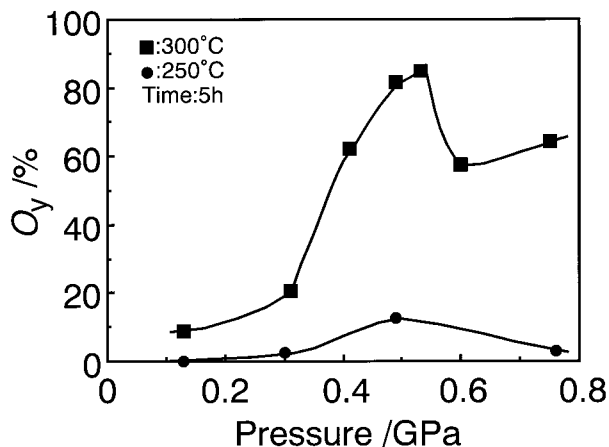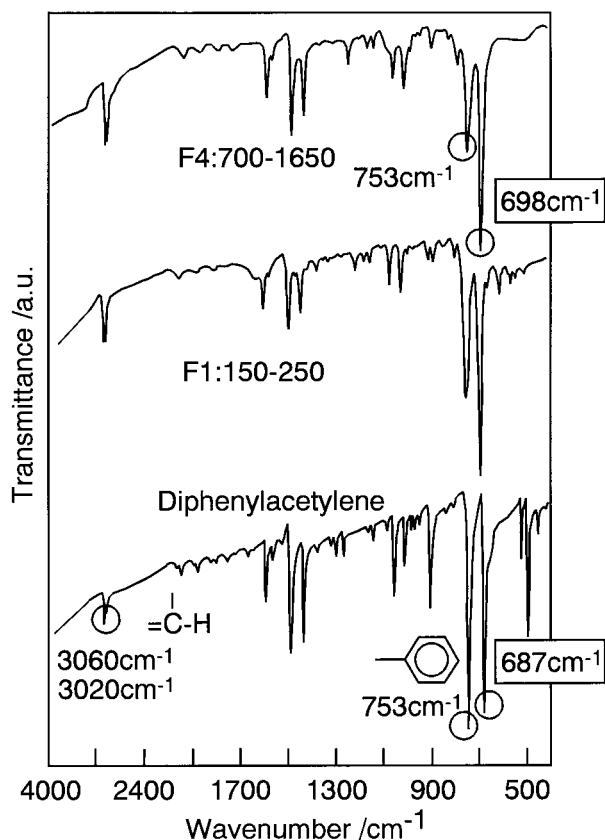**Figure 4** IR absorption spectra of diphenylacetylene oligomer (components F1 and F4) and diphenylacetylene.

sorption spectra of the diphenylacetylene oligomer of components F1 (150–250 molecular weight) and F4 (700–1650 molecular weight), together with the original diphenylacetylene. The $=\overset{|}{C}-H$ stretching vibrations of the original diphenylacetylene occur at 3060 and 3020 cm^{-1}.[18] For the oligomer of components F1 and F4, the bands at 753 and 698 cm^{-1} indicate the monosubstituted benzene structure ($-C_6H_5$).[18] The band at 687 cm^{-1} of the monomer shifts to 698 cm^{-1} by oligomerization. The IR spectra of components F2 (200–400 molecular weight) and F3 (400–700 molecular weight) corresponded to the IR spectra of F1 and F4.

Figure 5 shows the ^{13}C-NMR spectra for components F1 and F4 together with diphenylacetylene. Broad and sharp peaks observed over 125–145 ppm in the ^{13}C-NMR spectra of the components come from the sp^2-carbon ($-\overset{|}{C}=$).[19,20] The sp^3-carbon ($-\overset{|}{\underset{|}{C}}-$) was absent in the region of 0–60

ppm.[19,20] In the spectrum of diphenylacetylene, peaks for sp^2-carbon ($-\overset{|}{C}=$) and sp-carbon ($-C\equiv$) appear over 120–135 ppm (123.2, 128.2, and 131.5 ppm), and 89.4 ppm, respectively.[20] It is assumed that the NMR spectra of components F1–F4 that appeared at 135–145 and 125–135 ppm are assigned to the sp^2-carbon bonded to the sp^2-carbon ($=\overset{|}{C}-\overset{|}{C}=$) and the sp^2-carbon bonded to the hydrogen atom ($=\overset{|}{C}-H$) of the oligomer, respectively.[19,20] It is expected that the ratio of the sp^2-carbon bonded to the sp^2-carbon and the sp^2-carbon bonded to the hydrogen ($=\overset{|}{C}-\overset{|}{C}=/=\overset{|}{C}-H$) of diphenylacetylene oligomer is constant and independent of the molecular weight. The experimental ratio of components F1–F4 (0.38–0.43) was approximately in agreement with the calculated value of diphenylacetylene oligomer (0.4).

Figure 6 shows the FDMS spectrum of component F3 (400–700 molecular weight). As the error
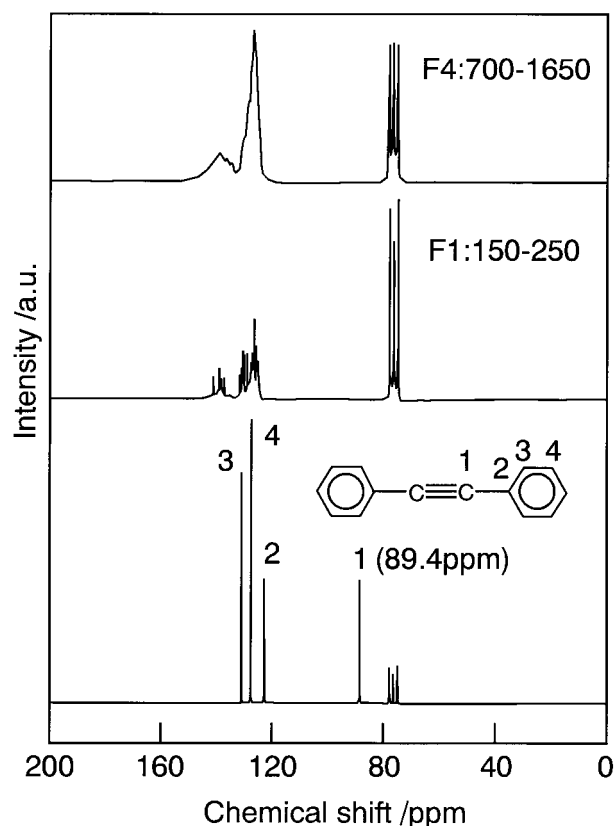

Figure 5 ^{13}C-NMR spectra of diphenylacetylene oligomer (components F1 and F4) and diphenylacetylene.
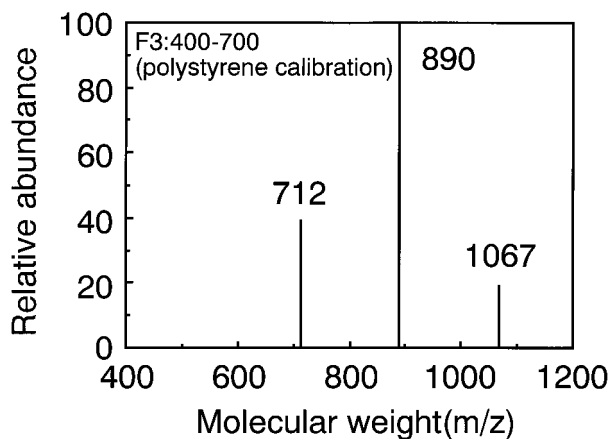
Figure 6 FDMS spectrum of diphenylacetylene oligomer (component F3).

Figure 7 Structure models of diphenylacetylene oligomers.

of the FDMS spectrum is mass of ±1, we can accurately obtain the absolute molecular weight of the oligomer. The molecular weight of diphenylacetylene monomer composed of ^{12}C and ^{1}H is 178.07,[19] and the FDMS spectrum of component F3 shows the presence of oligomers from tetramer (712 absolute molecular weight) to hexamer (1067 absolute molecular weight). On the polymerization of acetylene using a catalyst, the polymer has a linear structure owing to the presence of end groups.[4] For the oligomer having the linear structure, the molecular weight should be above a multiple of the monomer because of the existence of the end groups. However, the molecular weight of the oligomer is a multiple of the monomer according to the FDMS spectrum. Moreover, the oligomer had a compact structure because of the large absolute molecular weight at the peak intensity of the FDMS spectrum (890 molecular weight; Fig. 6) compared with the molecular weight based on the polystyrene calibration at the peak intensity of the molecular weight distribution (460 molecular weight; Fig. 1). We found that the diphenylacetylene oligomer synthesized under high pressure had a cyclic structure. Figure 7 shows the structure models of the trimer and the cyclic hexamer. The cyclic dimer and tetramer have been synthesized by Sardel and Freedman.[21] Furthermore, the cyclic trimer of diphenylacetylene (hexaphenylbenzene) is reagent. However, there is no report on above tetramer. Thus, above the degree of polymerization of 4, the diphenylacetylene oligomers are new compounds having cyclic structure.

Figure 8 shows the input–output response of the toluene solutions of the oligomer ($400\ M_n$). At
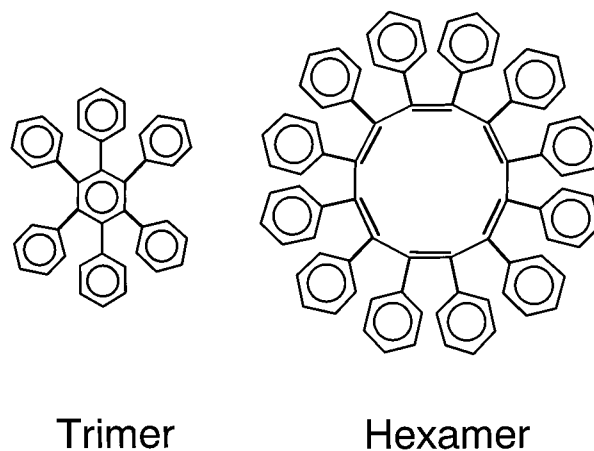
low input fluence, the transmittance of the solution, defined as the ratio of the input fluence to output fluence, obeys the Beer–Lambert law. The transmittance is constant and agrees well with that obtained by spectrophotometer. At high input fluence, the transmittance of the solution decreases with input fluence, and we observe an optical limiting property. Furthermore, the saturation of the output fluence occurs for the solutions. The saturated output fluence of the toluene solution of the oligomer was estimated from the output fluence at an input fluence of 0.6 J cm^{-2}. The saturated output fluence decreased from 0.30 to 0.13 J cm^{-2} with an increase of the concentration of the toluene solution (5 and 10 wt %). The input–output response did not depend on the rise and fall of the input fluence. This observation in-
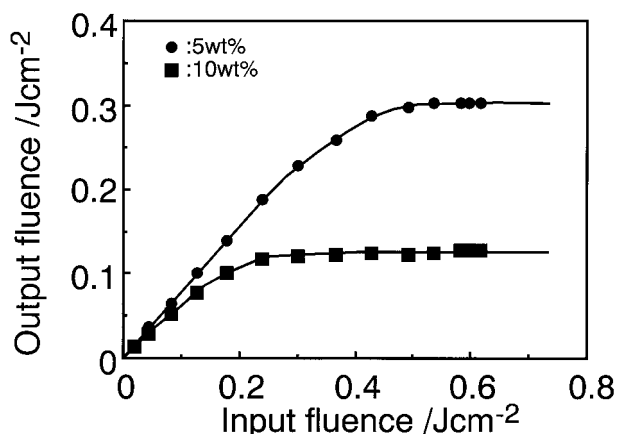

Figure 8 Relationship between output fluence and input fluence of solutions of oligomer in toluene to 532 nm optical pulse (5 and 10 wt % concentration).

dicates that there is no photodegradation of the oligomer by irradiation of the laser beam. It has been reported that π-electron conjugated systems, such as the polyacene-based oligomer,[16] the phenylacetylene oligomer,[14] and C_{60},[22] have optical limiting properties. The toluene solution of C_{60} shows the optical limiting property with saturated output fluence lower than those reported for other optical limiting materials in use.[22] The inverse of the saturated output fluence, which is one of the optical limiting properties, of the oligomer at a 70% transmitting solution was 175, 85, and 35% of those of polyacene-based oligomer, phenyacetylene oligomer, and C_{60}, respectively.

Several mechanisms have been proposed for optical limiting, including reverse saturable absorption (nonlinear absorption, such as sequential single photon absorption),[22,23] nonlinear scattering,[24] thermal blooming[25] and multiphoton absorption.[26,27] The reverse saturable absorption mechanism by a five-level energy diagram yielded a reasonable explanation for optical limiting of the π-electron conjugated system, such as C_{60},[28] polyacene-based oligomer,[16] and phenylacetylene oligomer.[14] As the diphenylacetylene oligomer also has a π-electron conjugated system, the optical limiting behavior can be described using the five-level energy diagram shown in Figure 9. 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 origi-
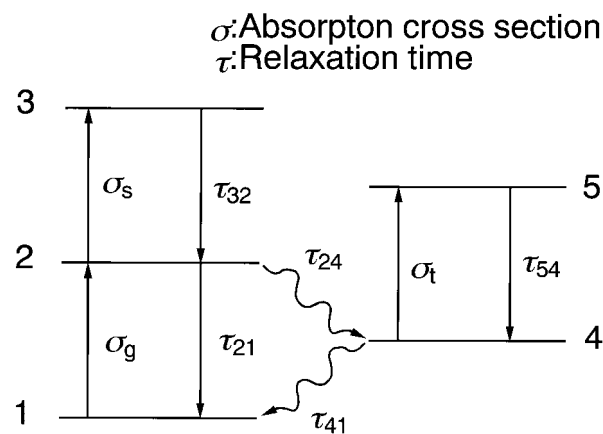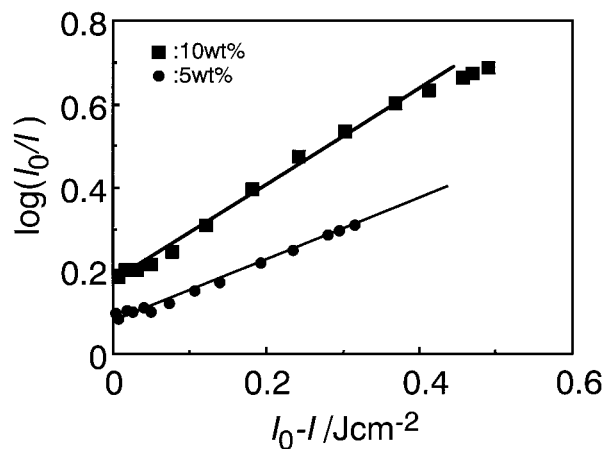
Figure 10 Plots of $\log(I_0/I)$ versus $(I_0 - I)$, (5 and 10 wt % concentration).

nal ground state, excite to the highest singlet state (level 3), or transfer to the lower level of a triplet state (level 4) by intersystem crossing, where singlet to triplet relaxation time is τ_{24}. The triplet state absorption takes place between levels 4 and 5. To obtain an optical limiting property, the upper singlet and lower triplet of the oligomer must have larger absorption cross sections of σ_s and σ_t than the ground state σ_g.

The optical limiting characteristics of the oligomer are computed based on the five-level energy diagram shown in Figure 9. The following equation was obtained approximately between input and output fluences per pulse I_0 and I:[16]

$$\log(I_0/I) = K(I_0 - I) + A_g \qquad (1)$$

Here, I_0 is the input fluence, I is the output fluence, K is the parameter depending on the absorption cross section and the relaxation time, and A_g is the absorbance of the ground state. Figure 10 shows $\log(I_0/I)$ as a function of $(I_0 - I)$ for various toluene solution of the oligomer. The linear relation between $\log(I_0/I)$ and $(I_0 - I)$ of the diphenylacetylene oligomer is demonstrated. It is represented that the optical limiting property is explained by the five-level energy diagram. The values of A_g are estimated as 0.079 (5 wt %) and 0.17 (10 wt %). These values agree well with those obtained by the spectrophotometer [0.071 (5 wt %) and 0.15 (10 wt %)]. We find that K is not constant and increases from 0.72 to 1.17 with concentration. It is presumed that τ_{21} increases with concentration because of the reabsorption of the fluorescence in the deep solution.[29]

Figure 9 Five-level energy diagram of a cyclic diphenylacetylene oligomer.

CONCLUSION

Reaction of diphenylacetylene under high pressure was carried out to synthesize a new conjugated polymer. It was indicated that cyclic diphenylacetylene oligomers were synthesized under high pressure. The diphenylacetylene oligomers of pentamer or more were new compounds having a cyclic structure. We found that the toluene solutions of the cyclic diphenylacetylene oligomer had optical limiting properties.

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