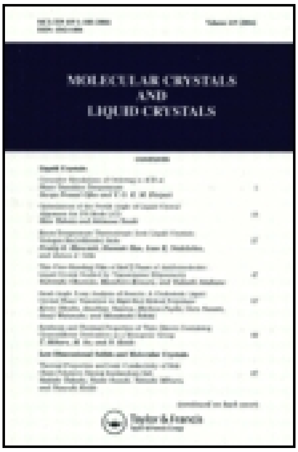

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Synthesis of Diacetylene-Substituted Polydiacetylenes with Alkoxycarbonylurethane Substtuents and Their Optical Properties

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SYNTHESIS OF DIACETYLENE-SUBSTITUTED POLYDIACETYLENES WITH ALKOXYCARBONYLURETHANE SUBSTITUENTS AND THEIR OPTICAL PROPERTIES

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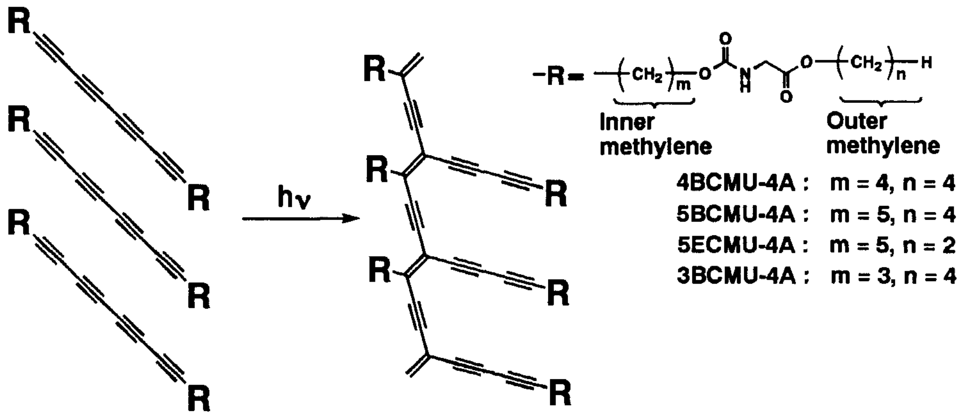
Abstract Octatetrayne monomers with urethane groups, i.e. R-C≡C-C≡C-C≡C-C≡C-R in which R=-$(CH_2)_m$-OCONH-CH_2-COO-$(CH_2)_n$-H (5ECMU-4A: m=5, n=2; 3BCMU-4A: m=3, n=4), were synthesized, and their polymerization behavior and optical properties were investigated. The polymer structures were confirmed to be diacetylene-substituted polydiacetylenes like polymers from octatetraynes studied previously. Though both of thin film polymers obtained by γ-ray and UV irradiation showed excitonic absorption around 680 nm, absorbance of γ-ray irradiated one was three times larger than that of UV-irradiated one. Thus, it was found that UV-irradiation caused not only polymerization but also deterioration of the produced polymers, and γ-ray irradiation is superior to UV irradiation for polymerization. The third-order nonlinear optical susceptibilities ($\chi^{(3)}(-3\omega)$ s) of these polymers were $(0.56\text{-}3.7)\times10^{-11}$ esu, and roughly proportional relation between $\chi^{(3)}$ s in three-photon resonant region and absorbance were found in this series of polymers.

INTRODUCTION

Polydiacetylenes are only the π-conjugated polymers obtained as single crystals via topochemical polymerization,[1] and are interesting because of their large third-order nonlinear optical properties.[2] In order to enhance their third-order nonlinear optical susceptibilities ($\chi^{(3)}$ s) further more, we have synthesized varieties of polydiacetylenes with π-conjugation between polymer backbone and substituents, and evaluated their $\chi^{(3)}$ values.[3,4] Among this series of studies, we have found that octatetrayne and dodecahexayne derivatives are polymerized to give diacetylene-substituted and tetraacetylene-substituted polydiacetylenes, respectively, in the first step of polymerization.[5-8] SCHEME 1 shows polymerization of octatetrayne compounds and their substituents. The $\chi^{(3)}$ values of third-harmonic generation (THG) in three-photon resonant region of diacetylene-substituted polydiacetylenes with urethane groups in substituents, i.e. the polymers of 4BCMU-4A[6] and 5BCMU-4A,[7] were in the order of 10^{-11} esu. And the effective $\chi^{(3)}$ values for only the π-conjugated system, i.e. diacetylene-substituted polydiacetylenes, was estimated to be near 10^{-9} esu. Thus, the $\chi^{(3)}$ values seemed to be improved by shortened substituents due to the increase of the conjugated π-electron density.

In the present study, 5BCMU-4A, whose polymer shows comparatively sharp excitonic absorption, was chosen as a basic chemical structure. And two monomers, where two methylenes were removed from the substituent of 5BCMU-4A, were synthesized. In the 5BCMU-4A monomer substituent, methylenes can be classified into the following two parts. One is the outer methylenes in the terminal alkyl groups, and the other one is the inner methylenes between acetylenes and urethane group, as shown in SCHEME 1. Thus, one of the monomer synthesized had shortened outer methylenes, i.e. 5ECMU-4A, and the other monomer had shortened inner methylenes, i.e. 3BCMU-4A. Their chemical structures are described in SCHEME 1. Polymerization behaviors by different irradiation source and optical properties including $\chi^{(3)}$ values of these polymers were investigated.



SCHEME 1 Polymerization scheme of tetrayne compounds and their substituents.

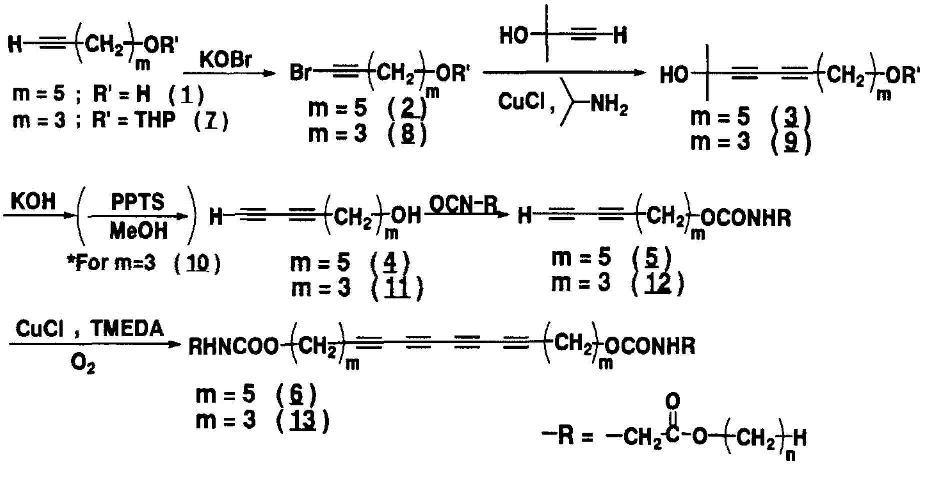
EXPERIMENTAL PARTS

Synthesis

Octatetrayne monomers (5ECMU-4A and 3BCMU-4A) were synthesized according to SCHEME 2. Experimental details are as follows.

9-(Ethoxycarbonylmethylcarbamoyloxy)-1,3-nonadiyne(5): 6,8-Nonadiyne-1-ol(4)[7] (5.03 g, 36.9 mmol), ethyl isocyanatoacetate (5.55 g, 43.0 mmol, 1.16 equiv.) and a few drops of pyridine as the catalyst in dry benzene (150 mL) were refluxed for 12h. Then, the solvent was evaporated under reduced pressure to give crude oily residue, and it was purified by flash column chromatography (silica gel, chloroform as eluent) to give 5 (9.08 g, 34.3 mmol, 99 %) as pale yellow oil : ^{1}H NMR (90 MHz, $CDCl_3$) δ= 5.43(1H, broad), 4.24 (2H, q, J= 4.8 Hz), 4.10 (2H, t, J= 4.8 Hz), 3.95 (2H, d, J= 3.6 Hz), 2.30 (2H, dt, J= 4.8 Hz, J'= 0.96 Hz), 2.03 (1H, t, J= 0.96 Hz), 1.8-1.4 (6H, m), 1.48 (3H, t, J= 4.8 Hz); IR (KBr, cm^{-1}) 3319, 3068, 2940, 2865, 2229, 2110, 1756, 1690, 1541.

5ECMU-4A(6): To a solution of CuCl(I) (0.60 g, 6.1 mmol) and N,N,N',N'-tetramethylethylenediamine (TMEDA) (0.71 g, 6.1 mmol) in acetone (200 mL), the compound 5 (9.08 g, 34.3 mmol) was added at room temperature, and it was stirred for 6 h while oxygen was bubbled. After the resulting solution was evaporated under reduced pressure, 1N HCl was added to the residue and the mixture was stirred for a few minutes. Then, it was extracted with chloroform. The organic layer was washed with 1N HCl (x2) and water, and was dried over anhydrous magnesium sulfate. After filtration, the solvent was evaporated under reduced



SCHEME 2 Synthetic scheme of 5ECMU-4A and 3BCMU-4A monomers.

pressure to give crude residue. Purification of the residue by flash column chromatography (silica gel, chloroform as eluent) provided 6 (9.00 g, 17.1 mmol, 100 %) as colorless crystals : mp 94-98 °C; ^{1}H NMR(200 MHz, $CDCl_3$) δ= 5.28 (2H, broad), 4.22 (4H, q, J= 7.7 Hz), 4.08 (4H, t, J= 4.3 Hz), 3.94 (4H, d, J= 5.6 Hz), 2.37 (4H, t, J= 6.6 Hz), 1.7-1.4 (12H, m), 1.29 (6H, t, J= 7.1 Hz); ^{13}C NMR(50MHz, $CDCl_3$) δ= 171.2, 170.2, 158.6, 68.2, 65.3, 65.1, 63.7, 60.7, 42.7, 30.6, 27.6, 21.1, 19.4, 14.1; IR(KBr, cm^{-1}) 3402, 3319, 2943, 2928, 2896, 2858, 2226, 1716, 1559 ; Anal. Calcd for $C_{28}H_{36}O_8N_2$: C, 63.61; H, 6.87; N, 5.30. Found: C,63.45; H,6.86; N,5.13.

7-(Oxacyclohexan-2-oxy)-4-pentyne(7): 4-Pentyn-1-ol (5.54 g, 65.9 mmol), pyridinium *p*-toluenesulfonate (PPTS) (1.69 g, 6.7 mmol) and 3,4-dihydro-2H-pyrane (6.97 g, 82.9 mmol) in dichloromethane (200 mL) were stirred for 4.5 h at room temperature, and the solvent was evaporated under reduced pressure. The residue was extracted with ether(x3), and the organic layer was dried over anhydrous magnesium sulfate, and was filtered. After the solvent of the filtrate was evaporated under reduced pressure, the residue was purified by flash column chromatography (silica gel, chloroform as eluent) to give 11.08 g (65.9 mmol, 100 %) of 7 as pale yellow oil; ^{1}H NMR (250 MHz, $CDCl_3$) δ= 4.59 (1H, t, J= 3.3 Hz), 3.83 (1H, td, J= 9.8 Hz, J'= 6.2 Hz), 3.47 (1H, td, J= 9.8 Hz, J'= 6.2 Hz), 3.90-3.81 (1H, m), 3.54-3.45 (m), 2.30 (2H, td, J= 2.6 Hz), 1.96 (1H, t, J= 2.6 Hz), 1.81 (2H, tt, J= 6.7 Hz), 1.77-1.46 (6H, m); ^{13}C NMR (50 MHz, $CDCl_3$) δ= 98.5, 83.7, 68.3, 65.5, 61.8, 30.4, 28.4, 25.3, 19.3, 15.1.

5-Bromo-7-(oxacyclohexan-2-oxy)-4-pentyne(8): Bromine (2.8 ml, 108.6 mmol) was added to aqueous solution (100 mL) of KOH (24.7 g, 373.5 mmol), and 7 (11.1 g, 65.9 mmol) was added to the solution. And then the mixture was mechanically stirred for 24 h at room temperature. Sodium thiosulfate aqueous solution was added to the reaction mixture, and was extracted with ether(x3). The organic layer was dried with anhydrous magnesium sulfate, and was filtered. The solvent was evaporated under reduced pressure to give 8 (14.42 g, 58.3 mmol, 89 %) as pale yellow oily residue : ^{1}H NMR (90 MHz, $CDCl_3$) δ= 4.59 (1H, broad), 3.82 (1H, td, J= 9.8 Hz, J'= 6.1 Hz), 3.45 (1H, td, J= 10.1 Hz, J'= 6.0 Hz), 4.01-3.68 (1H, m), 3.60-3.38 (1H, m), 2.43 (2H, t, J= 7.2 Hz), 1.80 (2H, tt, J= 6.6 Hz, J'= 6.6 Hz), 1.65-1.45 (6H, m).

2-Methyl-9-(oxacyclohexane-2-oxy)-3,5-nonadiyn-2-ol(9): The compound 8 (14.42 g ,58.3 mmol) in methanol (50 mL) was added dropwise to a mixture of 2-methyl-3-butyn-2-ol (6.58 g, 78.3 mmol), CuCl(I) (0.64 g, 6.4 mmol), isopropylamine (25 ml) and methanol (100 mL) under nitrogen atmosphere at room temperature. When the solution became blue by addition and stirring, a sufficient amount of hydroxylamine hydrochloride was added until the solution became yellow. The resulting solution was stirred for a day. Then the solvent was evaporated under reduced pressure, and the residue was extracted with chloroform(x3) and washed with 1N HCl(x2) quickly. The organic layer was dried with anhydrous magnesium sulfate, and was filtered. After the solvent of the filtrate was evaporated under reduced pressure, the residue was purified by flash column chromatography(silica gel, chloroform as eluent) to give 9 (16.4 g, 56.6 mmol, 88.9 %) as pale yellow oil : ^{1}H NMR (200 MHz, $CDCl_3$) δ= 4.59 (1H, t, J= 3.2 Hz), 3.92-3.73 (2H, m), 3.56-3.40 (2H, m), 2.34 (2H, t, J= 7.1 Hz), 1.80 (2H, tt, J= 6.6 Hz, J= 6.6 Hz), 1.75-1.49 (10H, m) ; IR (neat, cm^{-1}) 3420, 2943, 2871, 2252; LRMS (EI) 250 (M$^+$, 1.3%), 249 (M$^+$-1, 2.8 %), 233 (M$^+$-17, 0.6 %), 165 (M$^+$-pyran, 1.1 %), 149 (M$^+$-101, 1.9 %), 85 (pyran, 100 %).

7-(Oxacyclohexan-2-oxy)-1,3-heptadiyne(10): Powdered potassium hydroxide (1.0 g, 15.1 mmol) was added to 9 (2.63 g, 11.9 mmol) in dry benzene (100 mL). The mixture was refluxed for 5 min, and it was filtered using celite. The solvent of the filtrate was evaporated under reduced pressure. The residue was purified by flash column chromatography(silica gel, chloroform as eluent) to give 10 (1.18 g, 7.2 mmol, 60 %) as pale yellow oil : ^{1}H NMR (90 MHz, $CDCl_3$) δ= 4.58 (1H, broad), 3.95-3.70 (2H, m), 3.62-3.33 (2H, m), 2.40 (2H, td, J= 6.1 Hz, J= 1.1 Hz), 1.97 (1H, t, J= 1.1 Hz), 1.85-1.50 (6H, m) ; ^{13}C NMR (50MHz, $CDCl_3$) δ= 176.5, 129.0, 128.2, 98.8, 68.4, 65.6, 64.5, 62.2, 30.6, 28.2, 25.4, 19.4, 16.0, 15.3; IR(neat, cm^{-1}) 2944, 2872, 2298, 2227.

1,3-Heptadiyn-7-ol(11): The compound 10 (0.51 g, 2.66 mmol) and PPTS (0.15 g) in methanol (50 ml) were stirred for a day at room temperature. Then solvent was evaporated under reduced pressure, and the residue was purified by the flash column chromatography (silica gel, chloroform as eluent) to give 11 (0.27 g, 2.50 mmol, 94 %) as pale yellow oil : ^{1}H-NMR(90MHz,$CDCl_3$) δ= 3.70(2H, t, J = 6.1 Hz), 3.18 (1H, broad), 2.39 (2H, dt, J= 7.0 Hz, J'= 0.9 Hz), 2.04 (1H, t, J = 1.1 Hz), 1.78 (2H, tt, J = 5.9 Hz, J' = 6.1 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ= 77.8, 68.3, 65.0, 61.2, 60.9, 31.0, 14.9; IR (neat, cm^{-1}) 3339, 3295, 2954, 2883, 2297, 2227.

7-(Butoxycarbonylmethylcarbamoyloxy)-1,3-heptadiyne(12): A similar procedure to the synthesis of 5 was done but using 11 instead of 4 to give 12 in the yield of 84 %. : ^{1}H NMR (200 MHz, $CDCl_3$) δ=5.36 (1H, broad), 4.12 (2H, t, J= 6.1 Hz), 4.10 (2H, t, J= 6.6 Hz), 3.89 (2H, d, J= 5.7 Hz), 2.32 (2H, td, J= 7.1 Hz, J'= 1.2 Hz), 1.96 (1H, t, J= 1.2 Hz), 1.82 (2H, tt, J= 6.6 Hz, J= 6.6 Hz, 1.58 (2H, m), 1.31 (2H, m), 0.88 (3H, t, J=7.3 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ= 171.2, 170.2, 156.3, 60.4, 42.7, 30.6, 27.6, 21.1, 19.1, 14.2, 13.7; IR (neat, cm^{-1}) 3358, 3306, 3018, 2962, 2936, 2875, 2299, 2228, 1721.

3BCMU-4A(13): A similar procedure to the synthesis of 6 was done but using 12 instead of 5 to give 13 in the yield of 57 % : Mp 55.3- 57.7 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ= 5.24 (2H, t, J= 4.9 Hz), 4.14 (8H, m), 3.93 (4H, d, J= 5.6 Hz), 2.40 (4H, t, J= 7.0 Hz), 1.86 (2H, tt, J= 6.4 Hz, J'= 6.4 Hz), 1.62 (4H, tt, J= 6.6 Hz, J'= 7.3 Hz), 1.36 (4H, tq, J= 7.9 Hz, J'=7.9 Hz), 0.92 (3H, t, J= 7.2 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ= 170.0, 156.1, 78.9, 66.2, 65.3, 63.5, 61.2, 53.7, 42.6, 30.4, 27.4, 19.0, 16.2, 13.6; IR(KBr, cm^{-1}) 3442, 3365, 3020, 2964, 2936, 2876, 2228, 2160, 1721, 1519, 1365, 1215, 1061; Calcd for $C_{28}H_{36}O_8N_2$: C, 63.61%, H, 6.87%, N, 5.30%; Found: C, 63.45 %, H, 6.85 %, N, 5.26 %.

Polymerization of Monomer Thin Films

Polymer thin films composed of microcrystallites were prepared as follows. At first, chloroform solution of a monomer was spin-coated on the fused quartz. Then, UV from a UV lamp (UVC INC., UVG-11) at a distance of 2 cm, or γ-ray from ^{60}Co was irradiated to the sample at room temperature. In the case of γ-ray irradiation, samples were put under a nitrogen atmosphere.

Characterization

UV and visible absorption spectra were measured by a Shimadzu UV-220. X-ray powder diffraction patterns were recorded on a Shimadzu XD-D1 diffractmeter using CuKα line (λ= 1.542 Å). Solid-state ^{13}C NMR spectra were measured by a JEOL GSH200 with the cross-polarization / magnetic angle spinning (CP/MAS) method. Third-order nonlinear optical susceptibilities ($\chi^{(3)}$ s) were evaluated by Maker fringe method of third harmonic generation (THG).[9] The $\chi^{(3)}$ value of 1.0×10^{-14} esu was used for a reference fused quartz plate at any pumping wavelength.[10]

RESULTS AND DISCUSSION

The melting points of 5ECMU-4A and 3BCMU-4A monomers are much different in spite of the same molecular weight. The comparison of their melting points with those of 4BCMU-4A and 5BCMU-4A monomers gave the order of melting points from higher one as follows: 5ECMU-4A (94-98 °C) > 5BCMU-4A (87-88 °C) > 4BCMU-4A (85-87 °C) >> 3BCMU-4A (55-58 °C). From these data, the higher melting points tend to be shown in the compounds with longer inner and shorter outer methylene chains. The large van der Waals interactions between inner methylenes together with hydrogen bonding between urethane groups of adja-

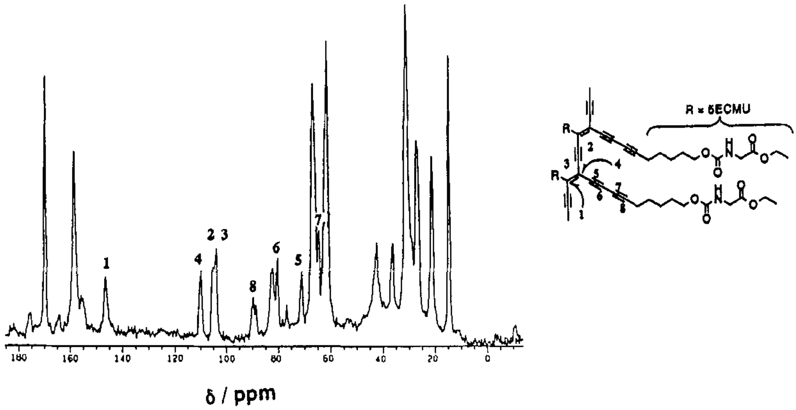


FIGURE 1 ^{13}C CP/MAS spectrum of the polymer of 5ECMU-4A.

cent molecules may cause the rigid packing, resulting in higher melting points, and the flexible structure of outer methylene chains may lower the melting points.

Both 5ECMU-4A and 3BCMU-4A monomer crystals could be polymerized by γ-ray irradiation more than 20 kGy dose in quantitative conversion. They could be also spontaneously polymerized quantitatively even by keeping them at room temperature for several months. Polymer structures were confirmed by solid-state ^{13}C NMR spectroscopy, e.g. FIGURE 1 shows the CP/MAS spectrum of 5ECMU-4A polymer obtained by keeping the monomer at room temperature for three months in darkness. The peak patterns in the region of unsaturated carbons in FIGURE 1 were almost the same as those of the polymers from octatetrayne derivatives studied previously.[5-7] Then, the peaks at 147 ppm (1), 110 ppm (4) and 105 ppm (2), (3) were assigned to the carbons in the polymer backbone, and the peaks at 89 ppm (8), 81 ppm (6), 72 ppm (5) and 65 ppm (7) were assigned to the carbons in the butadiynyl substituent, as displayed in FIGURE 1 by the numbers of peaks and an inserted chemical formula.

In order to clarify the difference in polymerization on irradiation source, thin film samples of 5ECMU-4A on quartz plates were irradiated by UV or γ-ray, and absorption spectra in the course of polymerization were investigated. In FIGURE 2, the unit of ordinate is absorbance per unit thickness. Both spectra showed increase of excitonic absorption around 680 nm depending on irradiation dose indicating that polymerization proceeded to give polydiacetylenes. However, in the case of excess UV irradiation more than 20 min, excitonic absorption remarkably decrease. The largest absorption maximum in whole irradiation procedure of γ-

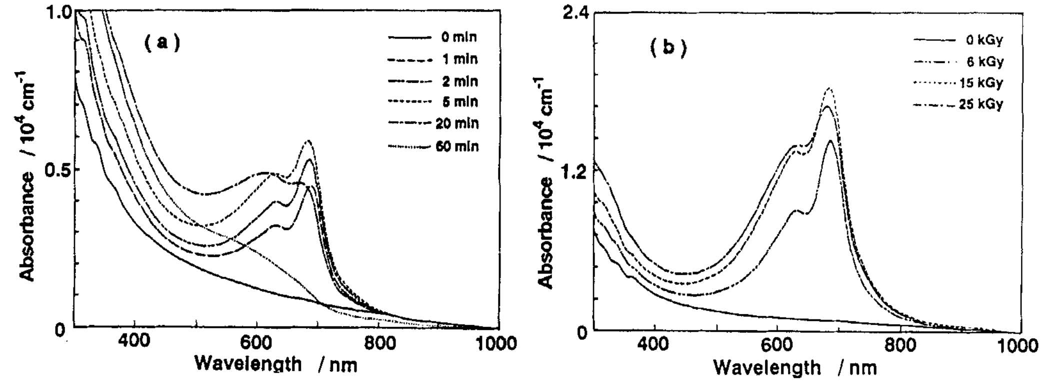


FIGURE 2 Absorption spectral change of 5ECMU-4A in the course of polymerization stimulated by UV(a) and γ-ray(b).

ray irradiated one was about three times larger than that of UV irradiated one even in the same amount of the monomer. These results pointed out that γ-ray irradiation works mainly to polymerize the monomers though UV irradiation causes simultaneously both generation and photodecomposition of the polymers. Thus, it could be concluded that γ-ray irradiation is superior to UV irradiation for polymerization of this series of compounds. Similar results were also obtained for 3BCMU-4A. The crystallinity of the 3BCMU-4A thin film samples during UV-induced polymerization was evaluated using X-ray diffractions. The samples from monomer to the polymer with the largest absorption maximum showed several crystalline diffraction peaks. However, the polymerized sample with excess UV irradiation showed no peaks. Deterioration of crystalline polymer structure, i.e. an amorphous state of the latter sample, was also confirmed by an optical microscope as dark images of compound's domains under crossed-nicols conditions.

TABLE I summarizes the $\chi^{(3)}$ values of the polymers of 5ECMU-4A and 3BCMU-4A together with those of 4BCMU-4A and 5BCMU-4A studied previously.[6,7] These values are for three-photon resonant region. In the 5ECMU-4A polymer, the $\chi^{(3)}$ values of γ-ray irradiated one was from twice to three times larger than those of UV irradiated one. This ratio almost corresponded to the ratio of absorbance between those two samples. This relation could be explained that both absorbance of the excitonic bands and the $\chi^{(3)}$ values should be proportional to the density of the π-conjugated polymer backbone.

The $\chi^{(3)}$ values of the polymers of 5ECMU-4A and 3BCMU-4A were (0.5 - 3.7)x10^{-11} esu, which were similar to those of the 4BCMU-4A polymer and a little

TABLE I $\chi^{(3)}$ values of the thin films of the polymer from octatetraynes.

		$\chi^{(3)}$ / x 10^{-11} esu					
Polymer	**Polymerization method**	**Pumping wavelength / μm**					
		1.50	**1.62**	**1.74**	**1.86**	**1.98**	**2.10**
5ECMU-4A	**UV**	**0.46**	**0.53**	**0.73**	**0.67**	**0.73**	**0.76**
5ECMU-4A	**γ-ray**	**0.77**	**1.1**	**1.7**	**1.6**	**1.7**	**2.3**
3BCMU-4A	**γ-ray**	**0.56**	**1.0**	-	**1.5**	**1.6**	**3.7**
4BCMU-4A	**γ-ray**	**1.8**	**1.7**	**2.0**	**3.3**	**3.1**	**2.3**
5BCMU-4A	**γ-ray**	**3.7**	**3.3**	**3.1**	**6.0**	**5.7**	**8.0**

smaller than those of the 5BCMU-4A polymer, though the higher $\chi^{(3)}$ values were expected because of higher polymer backbone density due to shorter substituents in 5ECMU-4A and 3BCMU-4A compared with 5BCMU-4A. Thus, absorbance per unit thickness of these polymers was investigated like the case of 5ECMU-4A polymers obtained by two different polymerization methods. Actually, the largest absorbance was found to be for the 5BCMU-4A polymer, and other polymers showed a little smaller absorbance. Thus, the $\chi^{(3)}$ values by THG in three-photon resonant region is roughly said to be in proportional correlation to the absorbance among the polymers with similar structures. In the case of degenerate four wave mixing experiment, $\chi^{(3)}$ values in one-photon resonant region of one-dimensionally conjugated polymers were reported to be proportional to the absorbance.[11]

In conclusion, 5ECMU-4A and 3BCMU-4A was synthesized as the compounds with shortened methylenes of 5BCMU-4A, and their polymer structures were confirmed to be diacetylene-substituted polydiacetylenes like polymers from octatetraynes studied previously. From the comparison of the polymerization methods between by UV and γ-ray irradiations, we found that γ-ray irradiation is more advantageous than UV irradiation because of intense deterioration of the polymer by UV. The $\chi^{(3)}$ values of the polymers were around 10^{-11} esu, and $\chi^{(3)}$ s in three-photon resonant region were found to be roughly proportional to absorbance per unit thickness in this series of compounds. The effect of shortening of methylene chains for improvement of $\chi^{(3)}$ values was not clear in the studied compounds because only four methylenes were cut from a basic structure of 5BCMU-4A. However, it may be realized by more drastic reduction of the substituent's volume and maintaining ordered polymer structures.

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