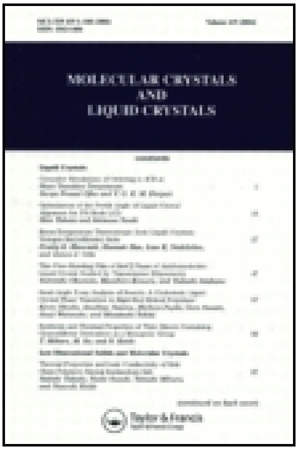

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Preparation and Nonlinear Optical Property of Polydiacetylenes from Dialkyltetraacetylene Compounds

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Preparation and Nonlinear Optical Property of Polydiacetylenes from Dialkyltetraacetylene Compounds

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To obtain polydiacetylenes with π-conjugation between polymer backbone and side chains, diacetylene monomers with acetylenic substituents, *i.e.*, dialkyltetraacetylene compounds, were synthesized. It has been found that they were highly polymerizable on UV or γ-ray irradiation and became deeply blue-colored polymers. It was confirmed that the polymerization proceed topochemically via 1,4-addition to give polydiacetylenes with acetylenic substituents. Third order nonlinear optical susceptibility of these polymers, evaluated from third harmonic generation by Maker fringe method, were larger than that of the corresponding dialkyldiacetylene polymer.

I. INTRODUCTION

Polydiacetylenes have caught much attention for their large third order nonlinear optical properties.[1,2] To achieve higher susceptibilities, polydiacetylenes having π-conjugation between polymer backbone and substituents and therefore, enlarged polarizability must be better candidates. In the series of our studies along this concept, we have already reported varieties of new monomers for polydiacetylenes with π-conjugation between backbone and aryl substituents as side chains,[3,4] and confirmed the enlarged third order susceptibilities.[5] Both theoretical calculation[6] and our recent experimental results[7] have revealed that smaller dihedral angle between aryl substituents and the polymer backbone (θ in Figure 1 (a)) makes nonlinear optical susceptibilities larger. In these aryl substituted polydiacetylene compounds, however, steric hindrance between the adjacent substituents dose not allow the aryl groups to take a coplanar configuration with respect to the polymer backbone, as is seen from Figure 1 (a). On the other hand, if acetylene groups are directly bound to the main chain (Figure 1 (b)), perfect π-conjugation between polymer backbone and the acetylenic moieties may be expected. The monomers

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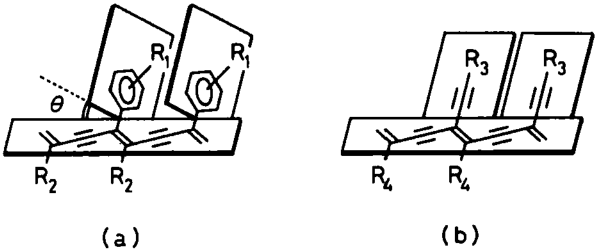


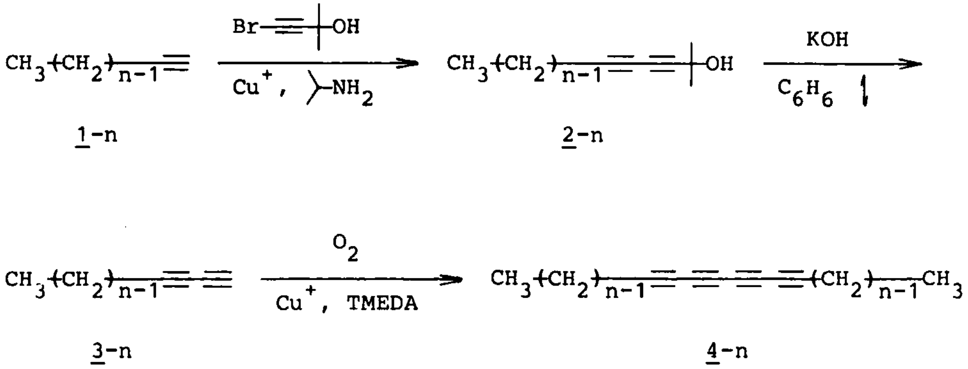
FIGURE 1 Structural models of an aryl-substituted polydiacetylene (a) and an acetylene-substituted polydiacetylene (b).

for such polydiacetylenes are oligoacetylenes like tri-[8,9] or tetra-acetylene compounds. In the present paper we report synthesis and polymerization behavior of dialkyltetraacetylenes, and third order nonlinear optical susceptibility of the polymers.

II. EXPERIMENTAL

Dialkyltetraacetylene compounds, *i.e.*, hexatriaconta-15,17,19,21-tetrayne 4-14 and tetratetraconta-19,21,23,25-tetrayne 4-18, were synthesized according to the Scheme 1. Details of the synthetic procedures were as described below.

2-methyleicosa-3,5-diyn-2-ol 2-14. To a solution of 1-14 (22.20 g, 100 mmol) in the mixture of ethanol (40 cm^3) and 2-aminopropane (40 cm^3) with 500 mg of cuprous chloride, 4-bromo-2-methylbut-3-yn-2-ol 5 (19.56 g, 120 mmol) was added dropwise for 2 h at ambient temperature under a nitrogen atmosphere. When the solution became blue by the addition of 5, a sufficient amount of hydroxylamine hydrochloride was added until the solution became yellow. After finishing addition of 5 the solution was stirred for 2 h and the solvent was removed *in vacuo*. Hydrochloric acid solution was added to the residue and it was extracted with chloroform. After being dried with anhydrous sodium sulfate chloroform was vacuum-evaporated. The residue was purified with column chromatography (silica gel,



SCHEME 1

dichloromethane) to give 11.42 g (45%) of 2-14 as colorless viscous oil: IR (film), 3367, 2933, 2857, 2252, 1468, 1379, 1364, 1263, 1172, 1157, 960 cm^{-1}; ^{1}H-NMR (360 MHz, CDCl$_3$), δ = 0.88 (3 H, t, J = 7.6 Hz), 1.10–1.45 (22 H, m), 1.45–1.63 (2 H, tt, overlapped with methyl group), 1.52 (6 H, s), 2.27 (2 H, t, J = 7.0 Hz), 3.13 (1 H, broad s); ^{13}C-NMR (CDCl$_3$), δ = 14.05, 19.19, 22.63, 28.13, 28.78, 29.04, 29.31, 29.43, 29.57, 29.60, 31.08, 31.88, 64.29, 65.42, 67.31, 79.76, 81.74.

2-methyltetracosa-3,5-diyn-2-ol 2-18. 5.56 g (20 mmol) of 1-18, 15 cm^3 of ethanol, 15 cm^3 of 2-aminopropane, 100 mg of cuprous chloride and 4.89 g (30 mmol) of 5 was used and the similar operation like described above was carried out. The residue was purified with column chromatography (silica gel, benzene). From the first portion 3.365 g of 1-18 was recovered (61%). The second portion contained 1.989 g (28%) of 2-18 as colorless crystals: IR (KBr), 3356, 2924, 2857, 2257, 1468, 1379, 1364, 1263, 1172, 1157, 960, 722 cm^{-1}; ^{1}H-NMR (360 MHz, CDCl$_3$), δ = 0.90 (3 H, t, J = 6.1 Hz), 1.08–1.46 (30 H, m), 1.46–1.66 (2 H, tt, overlapped with methyl group), 1.55 (6 H, s), 2.30 (2 H, t, J = 6.8 Hz), proton of hydroxyl group was too broad to detect; ^{13}C-NMR (CDCl$_3$), δ = 14.12, 19.25, 22.69, 28.15, 28.82, 29.08, 29.36, 29.47, 29.60, 29.69, 31.16, 31.92, 64.20, 65.53, 67.38, 79.72, 81.98.

Octadeca-1,3-diyne 3-14. To a solution of 2-14 (3.04 g, 10 mmol) in benzene (100 cm^3), powdered potassium hydroxide (224 mg) was added and refluxed for 5 h. After filtration and removing the solvent the residue was purified by column chromatography (silica gel, hexane) to give 2.085 g (85%) of 3-14 as pale yellow oil: IR (film), 3322, 2933, 2865, 2304, 2237, 1471, 1214, 727, 671, 615 cm^{-1}; ^{1}H-NMR (360 MHz, CDCl$_3$), δ = 0.88 (3 H, t, J = 6.7 Hz), 1.26 (20 H, m), 1.37 (2 H, m), 1.53 (2 H, tt, J = 7.2, 7.0 Hz), 1.95 (1 H, s), 2.25 (2 H, t, J = 7.0 Hz); ^{13}C-NMR (CDCl$_3$), δ = 14.05, 18.96, 22.69, 28.02, 28.81, 29.07, 29.39, 29.47, 29.62, 29.67, 31.93, 64.27, 64.69, 68.46, 78.21.

Docosa-1,3-diyne 3-18. 1.80 g (5 mmol) of 2-18, 50 cm^3 of benzene and 112 mg of powdered potassium hydroxide was used and the similar operations like described above were carried out to give 1.487 g (98%) of 3-18 as pale yellow viscous oil: IR (film), 3322, 2933, 2865, 2304, 2237, 1471, 1214, 727, 671, 615 cm^{-1}; ^{1}H-NMR (360 MHz, CDCl$_3$), δ = 0.88 (3 H, t, J = 6.8 Hz), 1.26 (28 H, m), 1.38 (2 H, m), 1.53 (2 H, tt, J = 7.2, 7.0 Hz), 1.95 (1 H, s), 2.25 (2 H, t, J = 7.0 Hz); ^{13}C-NMR (CDCl$_3$), δ = 14.09, 19.90, 22.73, 28.09, 28.88, 29.14, 29.46, 29.54, 29.69, 29.79, 31.99, 64.21, 64.78, 68.51, 78.08.

4-14. To a deep blue solution of N,N,N′,N′-tetramethylethylenediamine (TMEDA) (116 mg, 1 mmol) and cuprous chloride (100 mg, 1 mmol) in tetrahydrofuran (THF) (50cm^3), 3-14 (1.968 g, 8 mmol) was added. While it was stirred for 6 h at ambient temperature, oxygen was bubbled into the solution. After evaporating solvent in vacuo, hydrochloric acid solution was added to the residue and it was extracted with benzene. The benzene layer was dried with anhydrous sodium sulfate. After filtration, the solvent was evaporated in vacuo and the residue was purified by column chromatography (silica gel, benzene) and recrystallized from the mixture of hexane and benzene to give 1.236 g (63%) or 4-14: mp 58–59°C; IR (KBr), 2967, 2924, 2857, 2237, 1464, 1422, 728 cm^{-1}; ^{1}H-NMR (CDCl$_3$), δ = 0.88 (6 H, t, J = 6.0 Hz), 1.26 (40 H, m), 1.36 (4 H, m), 1.53 (4 H, tt, J = 7.8, 6.7 Hz), 2.29 (4 H, t, J = 6.7 Hz); ^{13}C-NMR (CDCl$_3$), δ = 14.12, 19.45, 22.69, 27.95, 28.82, 29.01, 29.36, 29.41, 29.57, 29.66, 29.69, 31.92, 60.60, 61.36, 65.70, 80.50. Found: C, 87.77; H, 11.95%. Calcd for $C_{36}H_{58}$: C, 88.01; H, 11.90%.

4-18. 116 mg (1 mmol) of TMEDA, 100 mg (1 mmol) of cuprous chloride, 50 cm^3 of THF and 906 mg of 3-18 was used and the similar operations like described above were carried out to give 637 mg (71%) of 4-18: mp 73–74°C. IR (KBr), 2967, 2924, 2857, 2237, 1471, 1420, 725 cm^{-1}; ^{1}H-NMR ($CDCl_3$), δ = 0.88 (6 H, t, J = 6.7 Hz), 1.25 (56 H, m), 1.37 (4 H, m), 1.53 (4 H, tt, J = 7.4, 7.0 Hz), 2.29 (4 H, t, J = 7.0 Hz); ^{13}C-NMR ($CDCl_3$), δ = 14.05, 19.36, 22.60, 27.86, 28.74, 28.92, 29.28, 29.33, 29.49, 29.62, 31.82, 60.50, 61.31, 65.60, 80.47. Found: C, 87.74; H, 11.94%. Calcd for $C_{44}H_{74}$: C, 87.63; H, 12.37%.

Visible and IR spectra were measured by a Shimadzu UV-220 and a JASCO IR-810, respectively. Absorption changes during polymerization were followed with KBr-pelletized specimens of the compounds. NMR spectra were measured by a Nicolet NT-360 and a JEOL JMN-GSX270. Transmitted X-ray diffraction patterns were recorded on a powder diffractometer (Philips PW-1700) using CuKα radiation. Polymerization was stimulated by UV irradiation with an 8 W UV lamp (Tokyo Kagaku Kikai K.K. PUV-1A) at the distance of 2 cm, or ^{60}Co γ-ray irradiation with the dose rate of ca. 0.15 Mrad/h. The susceptibilities of third harmonic generation (THG) were evaluated by Maker fringe method[5] at three different pumping wavelengths.

III. RESULTS AND DISCUSSION

Upon UV irradiation both 4-14 and 4-18 became deeply blue-colored polymers. The absorption spectra of both compounds during UV-induced polymerization are shown in Figure 2. The absorption maximum at the longest wavelength were at 700–710 nm in the initial stage of polymerization. They are 70–80 nm longer than that of the corresponding dialkyldiacetylene, *i.e.*, octacosa-13,15-diyne 5 (630 nm),[10] and 40 nm longer than that of the alkyltriacetylene with carboxylic acid, *i.e.*,

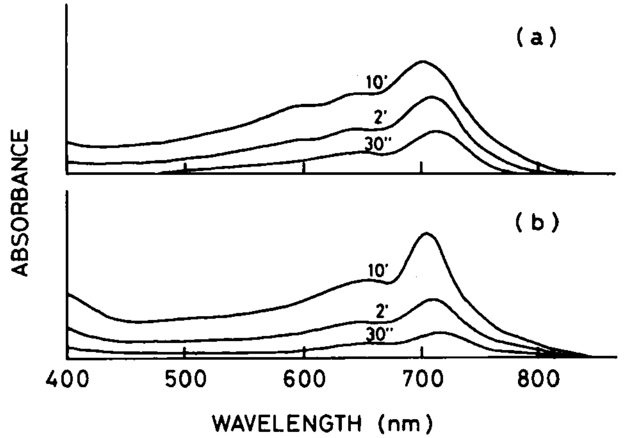


FIGURE 2 Visible spectral changes of 4-14 (a) and 4-18 (b) on UV irradiation.

nonacosa-10,12,14-triynoic acid (660–670 nm).[9] Even in the case of the aromatic-ring-substituted diacetylenes, such longer absorption maximum was rarely observed: For example, 5-(9-carbazolyl)penta-2,4-diyn-1-ol (CPDO) showed the absorption maximum at 670 nm.[3] As was expected, polymers of 4-n have more extended π-conjugation system than so-far prepared polydiacetylenes.

Polymer yields by γ-ray irradiation at the dose of 22 and 47 Mrad, which were calculated from the weight of benzene insoluble part, were 90% and 91% for 4-14 and 79% and 95% for 4-18, respectively. It seems that the shorter the alkyl chains, the higher the polymerizability of tetraacetylene derivatives becomes. In the IR spectra of monomers, the stretching band of acetylenic triple bonds appeared at 2237 cm^{-1} (Figure 3 (a)). In polymers, intensity of the band at 2237 cm^{-1} decreased and another new band appeared at 2114 cm^{-1} (Figure 3 (b)). This new band at lower wavenumber corresponds to conjugated acetylenes. When those tetraacetylene compounds were polymerized in the molten state under the reduced pressure of *ca.* 1 × 10^{-6} Torr, the polymers produced showed no IR absorptions corresponding to the acetylenic triple bonds, suggesting that the compounds were polymerized with no regularities. On the contrary in the solid state polymerization, it seems that desired structure of polymer backbone with acetylenic substituents is formed since the new acetylenic band at the lower wavenumber appears. In fact, deeply colored polymer with metallic luster is common characteristics of the polydiacetylenes via 1,4-addition polymerization in the solid-state. In the present tetraacetylene compounds two types of 1,4-addition are possible as are shown in Figure 4. However, it is difficult to identify one of those structures from IR data.

To check the crystallinity of those polymers, powder X-ray diffraction analysis were carried out on both monomers and polymers. Monomers showed several diffraction peaks between 13° and 29° in 2θ. However, the polymers showed only one broad peak around 19–20°. This peak corresponds to the spacing of about 0.45 nm indicating that polymers have a regularity only between adjacent alkyl

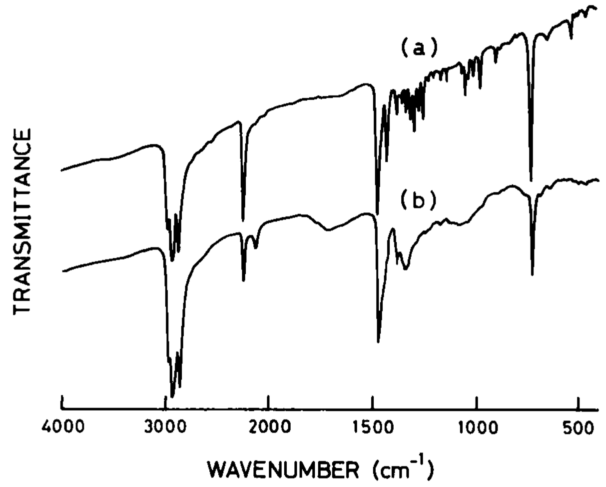


FIGURE 3 IR spectra of the monomer (a) and polymer (b) of 4-14.

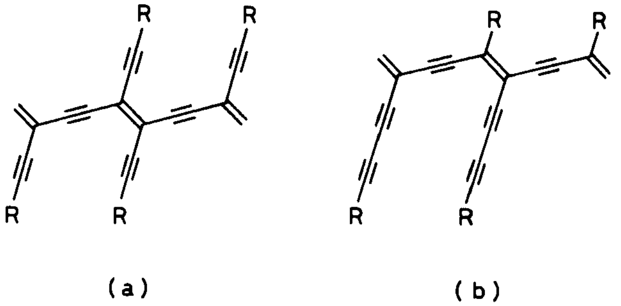


FIGURE 4 Possible 1,4-polymerization processes of tetraacetylene compounds: Symmetrical process (a) and unsymmetrical process (b).

chains. The deterioration of crystalline lattice in the course of polymerization may suggest that the polymerization proceeds via unsymmetrical 1,4-addition (Figure 4 (b)) which is apt to cause strains in the crystalline lattice. To confirm the polymer structure, high resolution solid-state ^{13}C-NMR spectroscopy is currently in progress.

$\chi^{(3)}$s of deeply blue-colored polymers of 4-n are shown in Table I. Thin film samples for the Maker fringe measurements would be obtained by recrystallization from molten state between two quartz plates. And one of the two plates was removed for the Maker fringe experiment. Physical vapor deposition of these tetraacetylene compounds was impossible because polymerization in molten state proceeded faster than evaporation. $\chi^{(3)}$s of those polymers were about $6 \times 10^{-12} - 2 \times 10^{-11}$ esu at the pumping wavelengths of resonant region. In the case of the dialkyldiacetylene derivative 5, $\chi^{(3)}$s of the highly crystalline blue-colored polymer in the resonant region were $(3\text{–}4) \times 10^{-12}$ esu[10] under the same measuring conditions. From the comparison of $\chi^{(3)}$ values of the polymers from tetraacetylene and diacetylene compounds, it is clear that the π-conjugation between acetylene moieties and polymer backbone contributes to enlarge the susceptibility.

In conclusion polydiacetylenes with complete π-conjugation between backbone and side chains, *i.e.*, acetylene substituted polydiacetylene, have been obtained by the solid-state polymerization of dialkyltetraacetylene compounds. They were deeply blue-colored with narrower band gaps as was expected. Nonlinear optical susceptibility of THG of these polymers were larger than that of the corresponding

TABLE I

$\chi^{(3)}$s of 4-n polymer

Compound	Film thickness (μm)	Pumping wavelength (μm)	$\chi^{(3)}$ (esu)
4-14 polymer	5.0	1.50	7.9×10^{-12}
		1.90	7.9×10^{-12}
		2.10	1.6×10^{-11}
4-18 polymer	0.84	1.50	6.3×10^{-12}
		1.90	1.3×10^{-11}
		2.10	1.9×10^{-11}

dialkyldiacetylene polymer. It is noted that acetylenes as substituents of polydiacetylene are also effective to enlarge nonlinear optical properties.

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