Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Version of record first published: 04 Oct 2006.

To cite this article: Shujiokada Takanori Doi , Naoto Kikuchi , Kikuko Hayamizu , Hiro Matsuda & Hachiro Nakanishi (1994): A Polydiacetylene From an Asymmetrically-Substituted Octatetrayne Compound for Nonlinear Optics, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 247:1, 99-109

To link to this article: http://dx.doi.org/10.1080/10587259408039195

Mol. Cryst. Liq. Cryst. 1994, Vol. 247, pp. 99–109
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Printed in the United States of America

A POLYDIACETYLENE FROM AN ASYMMETRICALLY-SUBSTITUTED OCTATETRAYNE COMPOUND FOR NONLINEAR OPTICS

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Abstract Since solid-state polymerization reaction of symmetrically-substituted octatetrayne derivatives can start from both 1,4- and 5,8-positions in the same column of the monomers in crystals, deterioration of crystallinity seemed to occur to some extent in the course of polymerization. Thus, an asymmetrically-substituted octatetrayne, i.e. 13-(4-butyl-2,3,5,6-tetrafluorophenyl)-6,8,10,12-tridecatetraynyl *N*-(butoxycarbonylmethyl)-carbamate (5BCMU-4A-BTFP), was synthesized and its polymerization site was examined using high resolution solid-state ^{13}CNMR spectroscopy. And it was shown that asymmetrical substitution of octatetrayne is effective for site-selective 1,4-addition polymerization. Absorption spectrum and third-order nonlinear optical properties of the 5BCMU-4A-BTFP polymer were also investigated.

INTRODUCTION

π-Conjugated polymers are considered to be one of the promising materials for third-order nonlinear optical applications.[1-3] Among them, polydiacetylenes are very unique because they are prepared from butadiyne monomers with proper substituents by solid-state polymerization and obtained as single crystals.[4] Since one-dimensionally conjugated polymer backbones are aligned completely in one direction in single crystals, the maximal component of the third-order susceptibilities ($\chi^{(3)}$s) can be used in a bulk scale.[1] Thus, for improvement of the $\chi^{(3)}$ values of conventional polydiacetylenes, we have investigated novel polydiacetylenes with π-conjugated substituents directly bound to the main chain[5,6] because increasing the number of π-electrons per repeating unit seemed to be effective.

In the series of studies, we have found that octatetraynes give polydiacetylenes with butadiynyl groups directly bound to the main chain,[7,8] and effective $\chi^{(3)}$ of the π-conjugated moiety, i.e. polydiacetylenes with butadiynyl substituents, was greater than conventional polydiacetylenes without π-conjugation between polymer backbone and substituents.[9] However, in the case of the solid-state polymerization of symmetrically-substituted octatetraynes studied so far, polymerization reaction can start from both 1,4- and 5,8-positions even in the same column of the octatetrayne monomers in crystals as shown in FIGURE 1 where R equals to

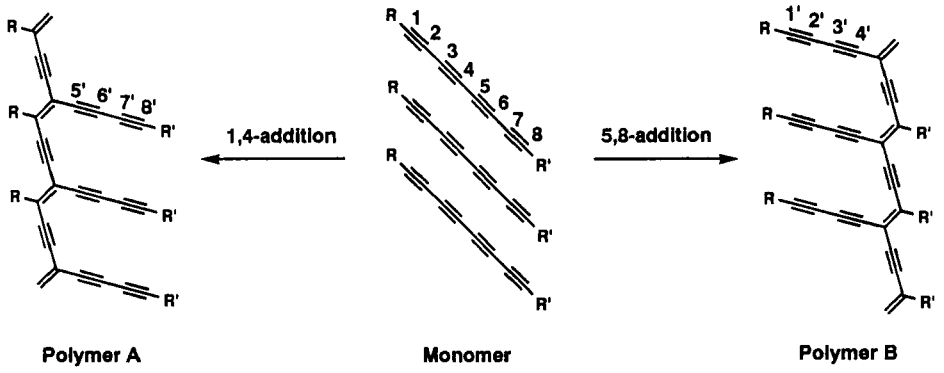

FIGURE 1 Solid-state polymerization schemes of octatetraynes.

R'. This site difference of polymerization leads deterioration of crystallinity to some extent. From the point of view for avoidance of this polymerization disorder, asymmetrically-substituted octatetrayne seemed to be interesting because different polymerizability between 1,4- and 5,8-positions was expected. It was the reason why an asymmetrically-substituted octatetrayne was synthesized. Among the octatetrayne compounds studied so far, 6,8,10,12-octadecatetrayne-1,18-diyl bis(*N*-(butoxycarbonylmethyl)carbamate) (5BCMU-4A in FIGURE 2) was highly polymerizable and showed sharp exitonic bands.[9] Thus, its substituent was selected for one of the asymmetric octatetrayne substituents. Since flexible linear substituents seemed to allow atomic movements required for the polymerization to attain high conversion, another substituent was selected from rather rigid structures such as aryl groups. Some of diarylbutadiynes have been reported to be polymerized,[5,10] and the substituent of bis(4-butyl-2,3,5,6-tetrafluorophenyl)butadiyne (BTFP) was chosen among them.

Thus, in the present study, an asymmetrically-substituted octatetrayne, i.e. 13-(4-butyl-2,3,5,6-tetrafluorophenyl)-6,8,10,12-tridecatetraynyl *N*-(butoxycarbonylmethyl)carbamate

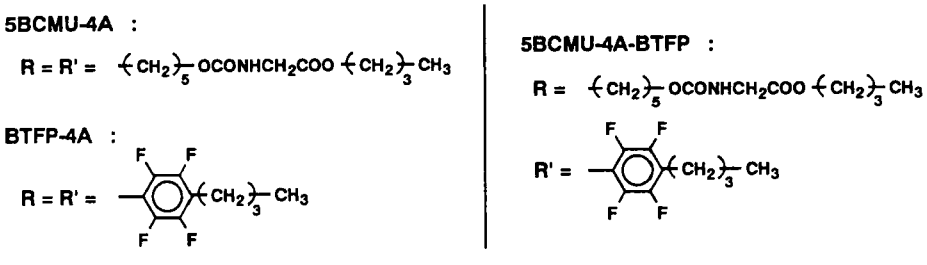

FIGURE 2 Abbreviations and chemical structures of octatetrayne derivatives. R and R' are the substituents of the monomer shown in FIGURE 1.

(5BCMU-4A-BTFP in FIGURE 2), was synthesized and its polymerization behavior was investigated using high resolution solid-state ^{13}CNMR spectroscopy. Linear and nonlinear optical properties of the polymer were also studied.

EXPERIMENTAL

Spectroscopic Measurement

UV, Visible and near IR spectra were measured using a Shimadzu UV-3100. IR spectra were recorded on a JASCO IR-810. NMR spectra in solution were measured using a JEOL PMX-60SI or a JEOL GSX-270. Those in solid state were obtained using a JEOL GSH-200 with the cross-polarization (CP)/ magic angle spinning (MAS) method. Dipolar-dephasing method was also performed for assignment.

Synthesis of an Asymmetrically-Substituted Octatetrayne Derivative

5BCMU-4A-BTFP were prepared according to the scheme shown in FIGURE 3. In the final step, we used simple cross coupling reaction to give 5BCMU-4A and bis(4-butyl-2,3,5,6-tetrafluorophenyl)octatetrayne (BTFP-4A in FIGURE 2) as well. Details of the synthetic procedure are described below.

4-(Pentafluorophenyl)-2-methyl-3-butyn-2-ol **2**. To a solution of pentafluoroiodobenzene

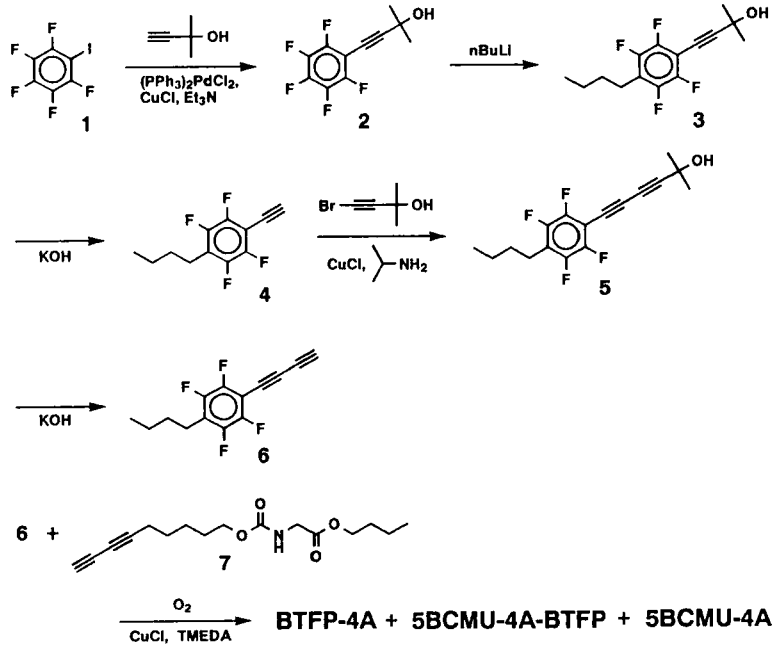

FIGURE 3 Synthetic scheme of 5BCMU-4A-BTFP.

1 (5.30 g, 18 mmol), 2-methyl-3-butyn-2-ol (1.68 g, 20 mmol) and triethylamine (40 cm^3), crushed bis(triphenylphosphine)palladium(II) chloride (420 mg, 0.2 mmol) and copper(I) chloride (60 mg, 0.6 mmol) were added under a nitrogen atmosphere and stirred for 3 days at 60 °C. Then, ether was added and the mixture was filtered. The filtrate was washed with diluted hydrochloric acid and water, and dried with anhydrous magnesium sulfate. The solid part was filtered and the filtrate was evaporated under reduced pressure. The residue was purified using column chromatography (silica gel, chloroform) and recrystallized from hexane to give 2.98 g (66 %) of **2** as colorless crystals: Mp 73.5-74 °C, IR (KBr), 3268, 2994, 2941, 2247, 1522, 1497, 1379, 1366, 1227, 1176, 1148, 1137, 1007, 991, 959 cm^{-1}; ^{1}HNMR ($CDCl_3$), δ = 1.62 (6H, s), 2.79 (1H, s).

4-(4-Butyl-2,3,5,6-tetrafluorophenyl)-2-methyl-3-butyn-2-ol **3**. To a solution of **2** (1.30 g, 5.2 mmol) and anhydrous ether (30 cm^3), 6.3 cm^3 of 1.65 M butyl lithium hexane solution was added dropwise for 30 min at 0 °C, and stirring was continued over night at ambient temperature. Then, saturated ammonium chloride solution was added, and the resulting mixture was extracted with ether. The ether layer was dried with anhydrous magnesium sulfate and filtered. From the filtrate, ether was removed under reduced pressure. The residue was purified by column chromatography (silica gel, chloroform) to give 1.31 g (87 %) of **3** as pale yellow oil: IR (film), 3350, 2967, 2933, 2874, 2242, 1484, 1379, 1364, 1222, 1166, 1137, 1105, 979, 944, 909 cm^{-1}; ^{1}HNMR (60 MHz, $CDCl_3$), δ = 0.93 (3H, t, J = 5.8 Hz), 1.15-1.75 (4H, m), 1.56 (6H, s), 2.51 (1H, s), 2.65 (2H, m).

4-Butyl-1-ethynyl-2,3,5,6-tetrafluorobenzene **4**. To a refluxed solution of **3** (3.70 g, 12.8 mmol) and benzene (200 cm^3), 360 mg of crushed potassium hydroxide was added, and reflux was continued for 3 h. The mixture was filtered and the filtrate was vacuum-evaporated. The residue was purified by column chromatography (silica gel, hexane) to give 2.59 g (88 %) of **4** as pale yellow oil: IR (film), 3322, 2967, 2941, 2882, 1486, 1292, 1114, 978, 916 cm^{-1}; ^{1}HNMR (60 MHz, $CDCl_3$), δ = 0.90 (3H, t, J = 6.4 Hz), 1.10-1.90 (4H, m), 2.66 (2H, m), 3.45 (1H, t, J = 0.6 Hz).

6-(4-Butyl-2,3,5,6-tetrafluorophenyl)-2-methyl-3,5-hexyn-2-ol **5**. To a solution of **4** (2.58 g, 11.2 mmol), copper(I) chloride (100 mg), 2-aminopropane (40 cm^3) and methanol (40 cm^3), 2-methyl-4-bromo-3-butyn-2-ol (3.65 g, 22 mmol) was added dropwise for 1 h at ambient temperature under a nitrogen atmosphere. When the solution became blue by the addition, a sufficient amount of hydroxylamine hydrochloride was added until the solution became yellow. After finishing addition, the solution was stirred for 1 h and the solvent was removed under reduced pressure. Diluted 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, chloroform) to give 2.94 g (84%) of **5** as pale yellow oil: IR (film), 3344, 2959, 2933, 2874, 2242, 2160, 1484,1180, 977 cm^{-1}; ^{1}HNMR (60 MHz, $CDCl_3$), δ = 0.92 (3H, t, J = 6.4 Hz), 1.40-1.75

(4H, m), 1.54 (6H, s), 2.39 (1H, s), 2.67 (2H, m).

1-Butadiynyl-4-butyl-2,3,5,6-tetrafluorobenzene **6**. To a solution of **5** (900 mg, 2.9 mmol) in benzene (80 cm^3), crushed potassium hydroxide (160 mg) was added and refluxed for 30 min. After filtration and removing the solvent under reduced pressure, the residue was purified by column chromatography (silica gel, hexane) to give 670 mg (90 %) of **6** as pale yellow oil: IR (film), 3311, 2967, 2941, 2882, 2237, 1486, 1314, 1163, 1116, 984, 912 cm^{-1}; ^{1}HNMR (270 MHz, $CDCl_3$), δ = 0.94 (3H, t, J = 7.3 Hz), 1.38 (2H, tq, J = 7.3, 7.3 Hz), 1.59 (2H, tt, J = 7.3, 7.6 Hz), 2.67 (1H, s), 2.75 (2H, tt, J = 7.6, 1.7 Hz); ^{13}CNMR ($CDCl_3$), δ = 13.58, 22.33, 22.88, 31.23, 60.47, 67.11, 74.32, 83.87 (t, J_{CF} = 3.4 Hz), 100.07 (t, J_{CF} = 10.3 Hz), 123.28 (t, J_{CF} = 18.6 Hz), 144.74 (dddd, J_{CF} = 244.5, 12.2, 7.5, 4.7 Hz), 146.08 (dddd, J_{CF} = 254.3, 15.7, 3.5, 3.5 Hz).

Cross coupling reaction of **6** and 6,8-nonadiynyl *N*-(butoxycarbonylmethyl)carbamate[11] **7**. Butadiynes **6** (1.19 g, 4.7 mmol) and **7** (1.50 g, 5.1 mmol) were added to deep blue solution of *N,N,N',N'*-tetramethylethylenediamine (TMEDA) (230 mg, 2 mmol) and copper(I) chloride (200 mg, 2 mmol) in acetone (80 cm^3). While it was stirred for 12 h at ambient temperature, oxygen was bubbled into the solution. After evaporating the solvent under reduced pressure, diluted hydrochloric acid solution was added to the residue and it was extracted with ether. The ether layer was dried with anhydrous magnesium sulfate and filtered. The solvent of the filtrate was evaporated under reduced pressure and the residue was purified by column chromatography (silica gel). When hexane was used as eluent, the first portion contained 790 mg of BTFP-4A: Mp. 165-167 °C; IR (KBr), 2959, 2941, 2874, 2212, 1484, 1168, 980, 918 cm^{-1}; ^{1}HNMR ($CDCl_3$), δ = 0.94 (6H, t, J = 7.2 Hz), 1.37 (4H, tq, J = 7.3, 7.2 Hz), 1.58 (4H, tt, 7.3, 7.5 Hz), 2.75 (4H, t, J = 7.5 Hz); ^{13}CNMR ($CDCl_3$), δ = 13.68, 22.34, 23.04, 31.21, 63.49 (t, J_{CF} = 4.5 Hz), 63.93, 69.39, 84.15 (t, J_{CF} = 3.6 Hz), 99.70 (tt, J_{CF} = 17.2, 2.9 Hz), 124.66 (t, J_{CF} = 18.8 Hz), 144.81 (dddd, J_{CF} = 244.1, 11.9, 7.3, 4.6 Hz), 148.26 (dddd, J_{CF} = 255.4, 16.2, 3.5, 3.5 Hz). Found: C, 66.57; H, 3.72 %. Calcd for $C_{28}H_{18}F_8$: C, 66.41; H, 3.58 %. The second portion was eluted by chloroform. After evaporation of the solvent, the residue was recrystallized from the mixture of ether and hexane to give 680 mg of 5BCMU-4A-BTFP: Mp 91-92 °C; IR (KBr), 3322, 2967, 2933, 2874, 2227, 1757, 1684, 1541, 1490, 1299, 1200 cm^{-1}; ^{1}HNMR (270 MHz, $CDCl_3$), δ = 0.94 (6H, t, J = 7.3 Hz), 1.33-1.68 (14H, m), 2.38 (2H, t, J = 6.8 Hz), 2.74 (2H, t, J = 7.6 Hz), 3.96 (2H, d, J = 5.6 Hz), 4.10 (2H, t, J = 6.4 Hz), 4.17 (2H, t, J = 6.8 Hz), 5.26 (1H, broad); ^{13}CNMR ($CDCl_3$), δ = 13.56, 18.96, 19.41, 22.21, 22.86, 25.05, 27.38, 28.31, 30.45, 31.10, 42.59, 59.05, 59.61, 60.80 (t, J_{CF} = 4.4 Hz), 64.83, 65.24, 65.64, 66.17, 70.41, 82.85, 84.53 (t, J_{CF} = 3.4 Hz), 99.89 (tt, J_{CF} = 17.6, 2.9 Hz), 124.05 (t, J_{CF} = 19.1 Hz), 144.57 (dddd, J_{CF} = 246.0, 12.2, 7.9, 4.4 Hz), 148.13 (dddd, J_{CF} = 254.3, 15.7, 3.9, 3.9 Hz), 156.45, 170.14. Found: C, 66.02; H, 5.88; N, 2.58 %. Calcd for $C_{30}H_{31}NO_4F_4$: C, 66.05; H,5.73; N, 2.57 %. The third portion eluted by chloroform contained 1.10 g of 5BCMU-4A.[11]

Solid-State Polymerization

Photopolymerization was stimulated by UV irradiation at ambient temperature. Samples were irradiated by an 8 W UV lamp (Tokyo Kogaku Kikai K.K., PUV-1A) at a distance of 2 cm. Thermal polymerization was carried out in the temperature-controlled oven (YAMATO DN-41) at 50 °C. γ-Ray irradiation from ^{60}Co whose dose rate was ca. 1.5 kGy/h were also used for polymerization.

Evaluation of Third-Order Nonlinear Susceptibilities

Third-order nonlinear optical susceptibilities ($\chi^{(3)}$s) of the polymer were determined by Maker fringe method of third harmonic generation (THG). Fundamental laser beams between 1.5 μm and 2.1 μm were obtained by difference frequency generation of Nd:YAG and tunable dye lasers (Spectra Physics tunable laser system pumped by Nd:YAG DCR-20). Incident light was always passed through the sample thin film first, and then the substrate. Polymer thin film samples for the measurement were prepared by spin-coating of the monomer chloroform solution onto quartz substrates and following polymerization. The thickness of the films was measured using a Talystep (Talor-Hobson). The $\chi^{(3)}$ values were evaluated from the equation reported by Tomaru et al.[12] with absorption correction of THG.[8,9] The $\chi^{(3)}$ value of 1.0×10^{-14} esu was used for a reference fused quartz plate at any pumping wavelength.[13]

RESULTS AND DISCUSSION

Solid-State Polymerization of 5BCMU-4A-BTFP

Among three octatetrayne compounds obtained by the last oxidative coupling reaction, BTFP-4A did not show solid-state polymerizability. Asymmetrically-substituted 5BCMU-4A-BTFP could be polymerized in solid state to give blue-colored polymer. Thus, the polymerization scheme of 5BCMU-4A-BTFP was investigated by high-resolution solid-state ^{13}CNMR spectroscopy.

At first, assignment of the monomer was carried out. FIGURE 4 summarizes ^{13}C chemical shifts in solution and solid states for 5BCMU-4A, BTFP-4A and 5BCMU-4A-BTFP. Hereafter we use *5BCMU* and *BTFP* as the substituents for 5BCMU-4A and BTFP-4A, respectively. Acetylenic carbons of symmetrically-substituted octatetraynes in solution state could be basically assigned from the magnitude of coupling constants. In the case of octatetraynes substituted by methylene chains like 5BCMU-4A, the acetylenic ^{13}C peaks from lower to higher field can be assigned from the outer most to the inner most carbons in the same order since proton-undecoupled ^{13}C spectrum showed long-range coupled signals of acetylenic carbons with the methylene protons.[7] The two acetylenic carbons near *BTFP* also showed split signal due to long range coupling with fluorines at the benzene ring in *BTFP*. The carbons with no coupling constants in BTFP-4A were assigned by comparison of the chemical shifts with the compound **6** using the relation of the chemical shifts between the compound **7** and 5BCMU-4A. Even in the case of the 5BCMU-4A-BTFP spectrum, acetylenic carbons were also assigned by the

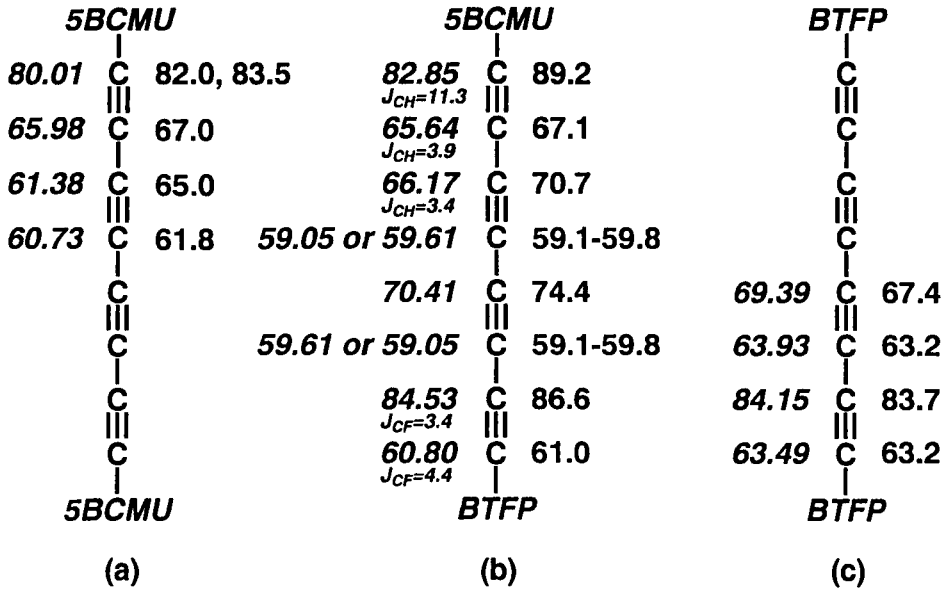

FIGURE 4 ^{13}C chemical shifts of 5BCMU-4A (a), 5BCMU-4A-BTFP (b) and BTFP-4A (c) in solution (left side of compounds) and solid state (right side). Chemical shifts and coupling constants are in ppm and Hz, respectively.

difference in coupling constants and referring the chemical shifts of symmetrically-substituted octatetraynes as shown in FIGURE 4. Among them, there was possibility of assignment replacement of the peaks at 59.64 and 59.06 ppm. The ^{13}C chemical shifts in solid state were also assigned essentially according to the order of the chemical shifts in solution. However, the peaks at 89.2 and 86.6 ppm in solid state were assigned to the carbons that showed the chemical shifts in solution at 82.85 and 84.53 ppm, respectively, because the chemical shift differences between solid and solution states of 5BCMU-4A were rather large compared with those of BTFP-4A, and the large difference for the *5BCMU* side is more favorable than that for the *BTFP* side.

FIGURE 5 shows ^{13}C CP/MAS spectra obtained for 5BCMU-4A-BTFP monomer and after γ-ray irradiation of 0.40 and 1.60 MGy. The peaks for four carbons with fluorines in the benzene ring were observed as very broad ones in 135-155 ppm because of large coupling constants between ^{13}C and F atoms. After 1.60 MGy irradiation, almost complete conversion of the monomer into the polymer was confirmed by very few soluble part to chloroform in the sample. Polymerization rate of 5BCMU-4A-BTFP was very slow and more than ten times of γ-ray dose for complete conversion of 5BCMU-4A was necessary. Though peaks became broad during polymerization, the characteristic peak patterns for carbons corresponding to polydiacetylenes substituted by butadiynyl groups were observed, i.e. the peaks at 151.8 and 110.0 ppm

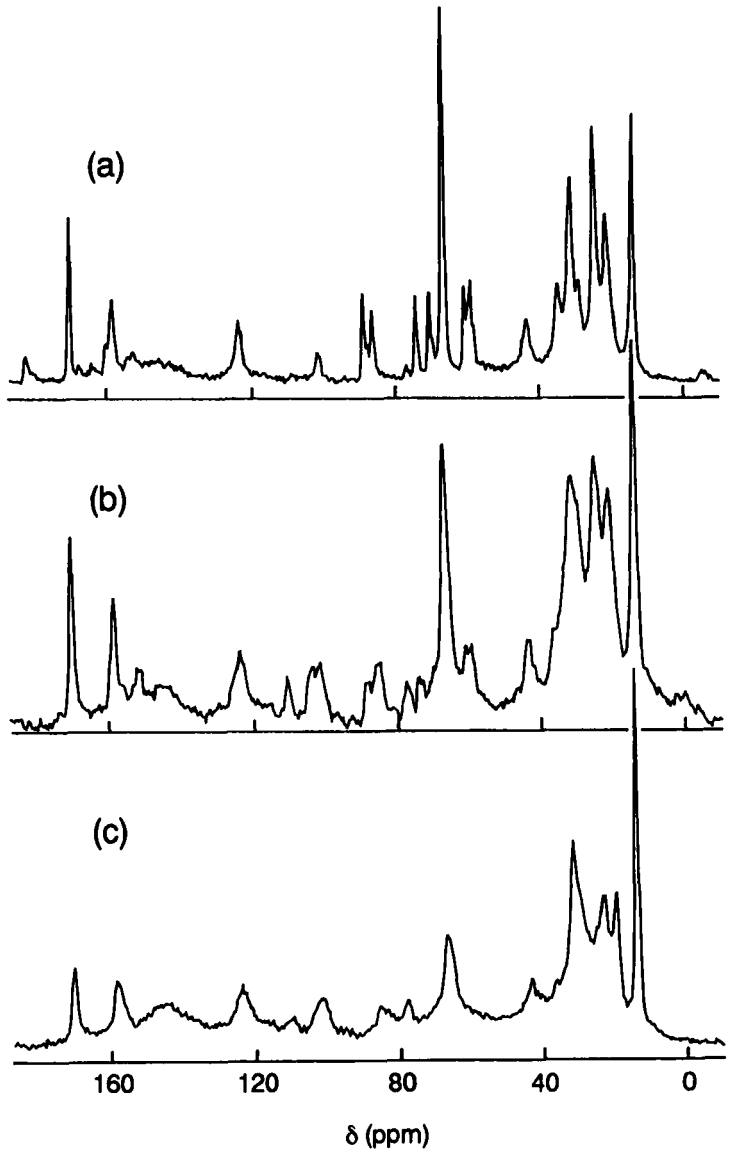

FIGURE 5 ^{13}C CP/MAS spectra obtained for 5BCMU-4A-BTFP before γ-ray irradiation (a) and after γ-ray irradiation of 0.40 (b) and 1.60 MGy (c).

correspond to two olefinic carbons of the polymer backbone and those at 101.6 ppm to overlapped two acetylenic carbons of the polymer backbone, as clearly shown in the spectrum (b) in FIGURE 5. Since the peaks for remained acetylenic carbons in the polymer side chain were rather ambiguous in the spectrum (c) in FIGURE 5, those were found using dipolar-dephasing

method at 85.1, 77.1 and 65.7 ppm. Among them, the peak at 85.1 ppm seemed to be superposed two peaks. Detection of four peaks for acetylenic carbons in side chain suggested that polymerization proceeded either 1,4- or 5,8-addition in FIGURE 1.

In order to determine the polymerization site, the chemical shifts of acetylenic carbons in side chain were compared with predicted values. TABLE I lists up chemical shift changes from the carbons 5-8 to the carbons 5'-8' in FIGURE 1 when R equals to R'. Since the chemical shift changes among these compounds were almost agreed at each position, the values were averaged and averaged ones were added to the chemical shifts of the 5BCMU-4A-BTFP monomer to give predicted chemical shifts of the polymer side chain. When we put *5BCMU* and *BTFP* as R and R' indicated in FIGURE 1, respectively, predicted chemical shifts from the carbons 5' to 8' due to 1,4-addition and those from the carbons 1' to 4' due to 5,8-addition became as shown in FIGURE 6. In polymer A, predicted chemical shifts were about 68, 76 and 85 (two carbons) ppm, and these were in good agreement with observed values. On the other hand, if polymer B was considered to be synthesized, there should be a peak around 96 ppm corresponding to the carbon attached to the methylene chain. However, in actual spectrum, chemical shifts did not coincide with the predicted values for polymer B including the peak near 96 ppm, clearly indicating that the structure of the 5BCMU-4A-BTFP polymer is not polymer B but polymer A. This result reasonably explains that 1,4-addition polymerization of octatetrayne derivatives starts from the site substituted by more flexible side chain, e.g. alkyl-type side chain.

TABLE I ^{13}C chemical shift changes ($\Delta\delta$) of carbons 5-8 of monomers to carbons 5'-8' of the polymers in FIGURE 1 when R=R'.

	$\Delta\delta$			
Substituent of octatetrayne	5 to 5'	6 to 6'	7 to 7'	8 to 8'
$-(CH_2)_{13}CH_3$	+10.7	+18.6	-1.8	+7.5
$-(CH_2)_4CONHCH_2CO_2(CH_2)_3CH_3$	+11.1	+16.3	-0.8	+7.0
$-(CH_2)_5CONHCH_2CO_2(CH_2)_3CH_3$	+9.8	+15.3	-2.0	+6.6
Average	+10.5	+16.7	-1.5	+7.0

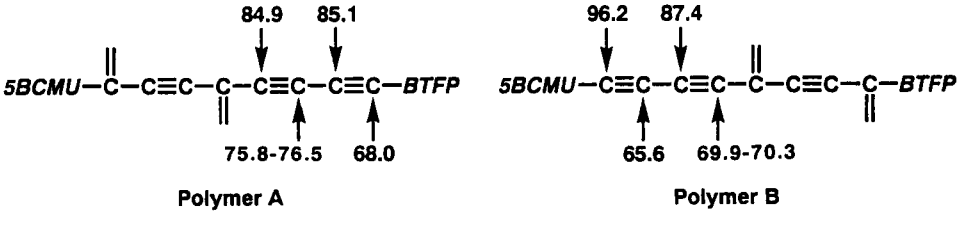

FIGURE 6 Predicted chemical shifts of the side chain carbons for polymer A and B.

Optical Properties of the Polymer of 5BCMU-4A-BTFP

UV, visible and near IR absorption spectra for 5BCMU-4A-BTFP spin-coated films were recorded

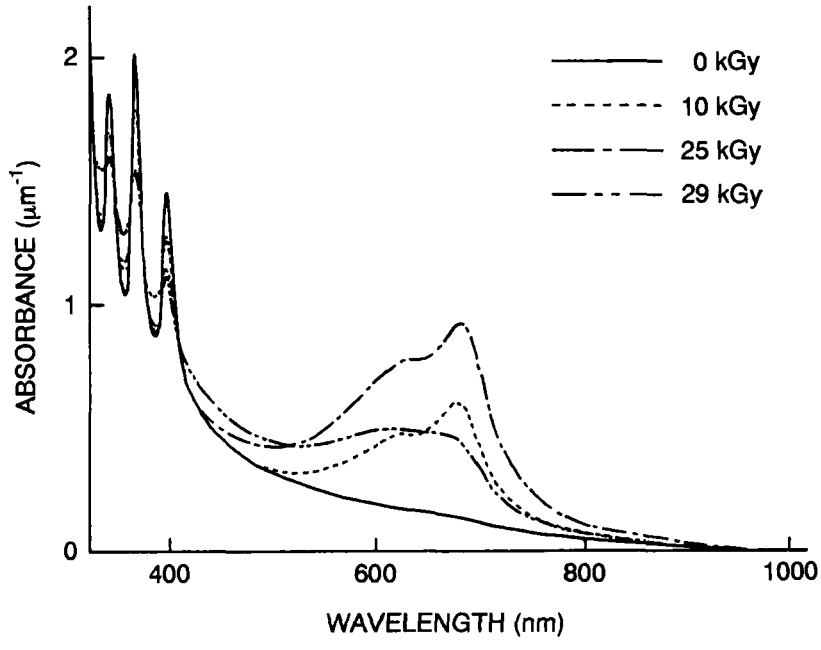

FIGURE 7 Absorption spectral change depending on the dose of γ-ray.

during UV-irradiation, thermal treatment and γ-ray irradiation. For example, absorption spectral change in the course of γ-ray induced polymerization was shown in FIGURE 7. All the polymers showed exitonic absorption maximum around 680 nm. Absorption of this band increased at first, and then it decreased after reaching the maximum value. The absorption peaks at 340, 365 and 395 nm decreased monotonously during polymerization. Normalized exitonic absorbance to film thickness at maximum of UV irradiated and heated ones were about one tenth and half, respectively, of that of γ-ray irradiated one. Thus, γ-ray irradiation was considered to be more advantageous for solid-state polymerization of 5BCMU-4A-BTFP.

The $\chi^{(3)}$ values were evaluated for the sample with 25 kGy of γ-ray dose. TABLE II summarizes the polymer's $\chi^{(3)}$ values for main chain direction of 5BCMU-4A-BTFP together with those of 5BCMU-4A.[9,14] Those values were calculated by multiplication of the correction factor 8/3 to the $\chi^{(3)}$ values for spin-coated films because X-ray diffraction patterns of the spin-coated

TABLE II $\chi^{(3)}$ values of the main chain direction of polymers from octatetraynes.

Polymer	Thickness	$\chi^{(3)}\times10^{11}$ (esu) Pumping wavelength (μm)					
	(μm)	1.50	1.62	1.74	1.86	1.98	2.10
5BCMU-4A-BTFP	0.09	2.3	2.6	3.1	2.8	3.2	3.7
5BCMU-4A	0.10	9.8	8.9	8.3	16	15	21

films showed that the polymer backbones were in the plane parallel to the substrate, and their observation under a polarizing microscope revealed that crystal domains much smaller than the laser beam spot were not oriented in that plane. The $\chi^{(3)}$ values of 5BCMU-4A-BTFP polymer were in the order of 10^{-11}, and rather small compared with other polymers from symmetrically-substituted monomers. The maximum absorption per thickness of 5BCMU-4A-BTFP was about one third of that of 5BCMU-4A. Thus, smaller $\chi^{(3)}$ value of 5BCMU-4A-BTFP is considered to be mainly due to small exitonic absorption. The reason for small exitonic absorption of 5BCMU-4A-BTFP was thought as follows: In the course of 1,4-polymerization, linear and rigid phenylbutadiynyl group have to move and this large motion seems to cause strain, resulting in slow polymerization rate and undulation of polymer backbone.

In conclusion, it was shown that methodology of asymmetrical substitution of octatetrayne is valid for site-selective 1,4-addition polymerization. Though the $\chi^{(3)}$ values were rather low in this compound due to small exitonic absorption, it may be improved by changing too rigid butyltetrafluorophenyl group into more flexible substituents.

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14. Since the $\chi^{(3)}$ values of the polymers in ref. 9 were calculated using 3.0×10^{-14} esu as a $\chi^{(3)}$ value for a reference quartz plate, those in TABLE 1 were changed into one third of the reported ones according to the revision of the $\chi^{(3)}$ value of quartz.