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### POLYMERIZATION AND NON-LINEAR PROPERTIES OF 1-(4'-SUBSTITUTED PHENYL)-4-(4'-METHYLPYRIDINIUM)BUTADIYNE TRIFLATE

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TRIFLATE**

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**ABSTRACT**

1-(4'-Substituted phenyl)-4-(4'-methylpyridinium)butadiene triflate (**5ab**), which was prepared by the reaction of 1-(4'-Substituted phenyl)-4-(4'-pyridyl) butadiene (**4ab**) with methyl trifluoromethanesulfonate, was found to be grown into the large crystal due to the quaternized structure. The uv irradiation and thermal treatment of **5ab** gave rise to 1,4-addition polymerization to yield the polydiacetylene. The third-order nonlinear optical susceptibility ( $\chi^{(3)}$ ) of the polymer was determined by the Z-Scan method to exhibit the remarkable high value of  $1.65 \times 10^{-11}$  esu at 650 nm.

*Key Words:* 1-(4'-Substituted phenyl)-4-(4'-methylpyridinium) butadiene triflate; 1,4-solid state polymerization; Z-Scan method; Third-order nonlinear optical susceptibility ( $\chi^{(3)}$ )

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## INTRODUCTION

Polydiacetylenes have been received much attention in terms of the nonlinear properties since the  $\pi$ -conjugation net work can contribute to the increase in the third-order nonlinear optical susceptibility ( $\chi^{(3)}$ ).<sup>[1]</sup> However, most of polydiacetylenes are insoluble and prevent further investigation. Among them, poly[2,4-hexadiyne-1,6-diol-bis-(p-toluenesulfonate)]<sup>[2]</sup> and poly[1,6-bis(N-carbazolyl)-2,4-hexadiyne]<sup>[3]</sup> are reported to exhibit the highest  $\chi^{(3)}$  of the order of  $10^{-6}$ esu although most of the nonlinearity depends on the resonant region. The presence of the polarized structure in nonlinear polymers is still sluggish in conjunction with the increase in  $\chi^{(3)}$  despite the observation of the enhanced second hyperpolarizability ( $\gamma$ ) in donor-acceptor conjugated polymethine dyes.<sup>[4]</sup> Previously, we reported that polyphenyleneethynylenes substituted with donor-acceptor group as the pendant group provided only the slight increasing in  $\chi^{(3)}$ .<sup>[5]</sup> In contrast, polydiphenyldiacetylenes can be characterized with the ene-yne main chain orthogonal to the stilbene type of side chain which could have the cross-over  $\pi$ -conjugation to the main chain. So we have focused on such a diacetylene compound as 1,4-bis-(4-pyridyl)butadiyne that can be quaternized with methyl triflate. 1,4-bis-(4-alkylpyridinium)butadiyne triflate thus obtained was grown into a large single crystal that was suitable for the solid state polymerization to yield the polydiacetylene soluble in common solvents. The  $\chi^{(3)}$  was  $2.2 \times 10^{-10}$  esu at 532 nm by a pico-second DFWM method,<sup>[6]</sup> and  $1.1 \times 10^{-11}$  esu at 650 nm by a femto-second Z-scan method,<sup>[7]</sup> indicating the dependence of  $\chi^{(3)}$  on the measurements. Along with such a symmetric 1,4-bis(4-methylpyridinium)butadiyne triflate, an unsymmetric alkylpyridinium phenylbutadiyne triflate can be intrigued because the quaternization would be expected for growing a large crystal leading to a soluble polydiacetylene as well as the polarization associated with benzene ring substituted with donor or acceptor group that could contribute to  $\pi$ -conjugation of the main chain. The determination of  $\chi^{(3)}$  has been carried out so far by a variety of methods such as DFWM, THG and Z-scan in which sometimes the  $\chi^{(3)}$  values are different because of the wavelength varied with their measurements, and specifically become larger in the resonant region which is included in the wavelength for measurements. Among them, Z-scan method is widely used for the simplicity of the technique and the ease interpretation that have characteristics of both real and imaginary part of  $\chi^{(3)}$  measurements on "open or closed aperture" condition, particularly the latter is quite useful for two photon absorption detection.<sup>[8]</sup>

This paper describes the polymerization of 1-(4'-substituted phenyl)-4-(4'-pyridinium)butadiyne triflate and how the nonlinearity determined by Z-scan method can be varied with the substituents.

## EXPERIMENTAL

## Materials

4-Ethynyl Pyridine (**1**)

**1** was prepared from 4-bromopyridine and 2-methyl-3-butyn-2-ol followed by the deprotection.<sup>[9]</sup>

4-Ethynylethoxybenzene (**3a**)

4-Iodoethoxybenzene (15.5 g, 60 mmol) and 2-methyl-3-butyn-2-ol (6.22 g, 70 mmol) were refluxed in 400 mL of triethylamine in the presence of  $\text{PdCl}_2(\text{Ph}_3\text{P})_2$  (0.3 g, 0.43 mmol) and a trace amounts of CuI and  $\text{Ph}_3\text{P}$  for 2 h. After evaporating, water was added to the residue, extracted with chloroform, and dried over  $\text{MgSO}_4$ . The solvent was evaporated, the residue was distilled under reduced pressure to give 2-methyl-4-(4'-phenyl)-3-butyn-2-ol (126°C/4 torr) in 64% yield.  $^1\text{H}$  NMR (400 MHz  $\text{CDCl}_3$ ):  $\delta$  7.34–6.82 (m, 4H, Ph-H), 4.01 (q, 2H,  $\text{OCH}_2$ ), 2.17 (s, 1H, OH), 1.61 (s, 6H,  $\text{C}(\text{CH}_3)_2$ ), 1.39 (t, 3H,  $\text{CH}_3$ ). IR (KBr): 3600 ( $\nu_{\text{O-H}}$ ), 2240 ( $\nu_{\text{C}\equiv\text{C}}$ )  $\text{cm}^{-1}$ . The alcohol (8.1 g, 40 mmol) was dispersed in 200 mL of toluene under nitrogen. To the mixture was added powdered KOH (1.3 g, 25 mmol), refluxed for 1.5 h. After evaporating, water was added to the residue, extracted with chloroform, and dried over  $\text{MgSO}_4$ . The solvent was evaporated, the residue was distilled under reduced pressure to give **4a** (82°C/4 torr) in 76% yield.  $^1\text{H}$  NMR (400 MHz  $\text{CDCl}_3$ ):  $\delta$  7.44–6.83 (m, 4H, Ph-H), 4.01 (q, 2H,  $\text{OCH}_2$ ), 2.97 (s, 1H,  $\text{C}\equiv\text{CH}$ ), 1.41 (t, 3H,  $\text{CH}_3$ ). IR (KBr): 3300 ( $\nu_{\text{C-H}}$ ), 2130 ( $\nu_{\text{C}\equiv\text{C}}$ )  $\text{cm}^{-1}$ .

4-Ethynylcyanobenzene (**3b**)

4-Bromocyanobenzene (5.0 g, 27 mmol) and 2-methyl-3-butyn-2-ol (2.8 g, 33 mmol) were refluxed in 300 mL of triethylamine in the presence of  $\text{PdCl}_2(\text{Ph}_3\text{P})_2$  (0.2 g, 0.28 mmol) and a trace amounts of CuI and  $\text{Ph}_3\text{P}$  for 2 h. After evaporating, water was added to the residue, extracted with chloroform, and dried over  $\text{MgSO}_4$ . The solvent was evaporated, the residue was recrystallized from hexane to give 2-methyl-4-(4'-cyanophenyl)-3-butyn-2-ol in 90% yield.  $^1\text{H}$  NMR (400 MHz  $\text{CDCl}_3$ ):  $\delta$  7.51–7.49 (m, 4H, Ph-H), 2.79 (s, 1H, OH), 1.56 (s, 6H,  $\text{C}(\text{CH}_3)_2$ ), 1.39 (t, 3H,  $\text{CH}_3$ ). IR (KBr): 3400 ( $\nu_{\text{O-H}}$ ), 2200 ( $\nu_{\text{C}\equiv\text{C}}$ )  $\text{cm}^{-1}$ . The alcohol (3.2 g, 18 mmol) was dispersed in 200 mL of toluene under nitrogen. To the mixture was added powdered KOH (0.6 g, 11 mmol), refluxed for 45 min. After evaporating, water was added to the residue, extracted with chloroform, and dried over  $\text{MgSO}_4$ . The solvent was evaporated, the residue was recrystallized from hexane to give **3b** in 83% yield.  $^1\text{H}$  NMR (400 MHz  $\text{DMSO-d}_6$ ):  $\delta$  7.86–7.71 (m, 4H, Ph-H), 4.01 (q,

2H, OCH<sub>2</sub>), 4.66(s 1H, C≡CH). IR (KBr): 3200 ( $\nu_{\text{C-H}}$ ), 2200 ( $\nu_{\text{C}\equiv\text{N}}$ ) 2100 ( $\nu_{\text{C}\equiv\text{C}}$ )  $\text{cm}^{-1}$ .

#### 1-(4'-Ethoxyphenyl)-4-(4'-Pyridyl)Butadiyne (**4a**)

NaOH (15.2 g, 380 mmol) was dissolved in 60 mL of water and cooled 0°C. To the solution was added dropwise bromine (8 mL) followed by the addition of **1** (3.7 g, 37 mmol) dioxane (60 mL) solution under 5°C. The mixture was poured into 200 g of ice-water, extracted with dichloromethane, and dried over MgSO<sub>4</sub>. After evaporating, 1-bromo-2-(4'-pyridyl)ethyne (**2**) was obtained in 87% yield, <sup>1</sup>H NMR (400 MHz CDCl<sub>3</sub>):  $\delta$  8.58–7.83 (m, 4H, Ph-H). **3a** (4 g, 26 mmol), CuCl (0.08 g, 1 mol, NH<sub>2</sub>OH · HCl (0.06 g, 1 mmol) were dispersed in 300 mL of isopropylamine-dioxane (1:1) under nitrogen. To the mixture was added dropwise 200 mL of methanol solution containing **2** (3.1 g, 17 mmol), and stirred for 2 h at room temperature. After evaporating, diluted aqueous HCl solution was added, extracted with chloroform, and dried over MgSO<sub>4</sub>. The solvent was removed under reduced pressure, the residue was recrystallized from hexane to give **4a** in 84% yield. <sup>1</sup>H NMR (400 MHz CDCl<sub>3</sub>):  $\delta$  8.60–6.84 (m, 8H, Ph-H, Py-H), 4.04 (q, 2H, OCH<sub>2</sub>), 1.42 (t, 3H, CH<sub>3</sub>). IR (KBr): 3100 ( $\nu_{\text{C-H}}$ ), 2130 ( $\nu_{\text{C}\equiv\text{C}}$ )  $\text{cm}^{-1}$ .

#### 1-(4'-Cyanophenyl)-4-(4'-Pyridyl)Butadiyne (**4b**) **3b**

(2 g, 16 mmol), CuCl (0.08 g, 1 mol), NH<sub>2</sub>OH · HCl (0.13 g, 2 mmol) were dispersed in 300 mL of isopropylamine-methanol (10:1) under nitrogen. To the mixture was added dropwise 100 mL of methanol solution containing **2** (0.8 g, 45 mmol), and stirred for 2 h at room temperature. After evaporating, diluted aqueous HCl solution was added, extracted with chloroform, and dried over MgSO<sub>4</sub>. The solvent was removed under reduced pressure, the residue was recrystallized from hexane-ethylacetate to give **4b** in 48% yield. <sup>1</sup>H NMR (400 MHz CDCl<sub>3</sub>):  $\delta$  8.89–7.62 (m, 8H, Ph-H, Py-H). IR (KBr): 3100 ( $\nu_{\text{C-H}}$ ), 2200 ( $\nu_{\text{C}\equiv\text{N}}$ ) 2100 ( $\nu_{\text{C}\equiv\text{C}}$ )  $\text{cm}^{-1}$ .

#### 1-(4'-Ethoxyphenyl)-4-(4'-Methylpyridinium)Butadiyne Triflate (**5a**)

To the dichloromethane solution (50 mL) containing methyl trifluoromethanesulfonate (0.2 mL 2 mmol) was added dropwise the dichloromethane (100 mL) solution containing **4a** (0.4 g, 1.5 mmol) at 0°C. The precipitate was filtered, and recrystallized from acetonitrile to give pale yellow **5a** in 60% yield. <sup>1</sup>H NMR (400 MHz CD<sub>3</sub>CN):  $\delta$  8.58, 7.97, 7.57, 6.95 (m, 8H, Ph-H, Py-H), 4.20 (s, 3H, CH<sub>3</sub>), 4.08 (q, 2H, OCH<sub>2</sub>), 1.37 (t, 3H, CH<sub>3</sub>). IR (KBr): 3100 ( $\nu_{\text{C-H}}$ ), 3050 ( $\nu_{\text{C-H}}$ ), 2130 ( $\nu_{\text{C}\equiv\text{C}}$ )  $\text{cm}^{-1}$ .

## 1-(4'-Cyanophenyl)-4-(4'-Methylpyridinium)Butadiyne Triflate (5b)

To the chloroform solution (50 mL) containing methyl trifluoromethanesulfonate (0.72 mL, 7 mmol) was added dropwise the chloroform (200 mL) solution containing **4b** (1.6 g, 7 mmol) at 0°C. The precipitate was filtered, and recrystallized from acetonitrile to give colorless **5b** in 73% yield. <sup>1</sup>H NMR (400 MHz CD<sub>3</sub>CN): δ 8.62, 8.03, 7.78, 7.77 (m, 8H, Ph-H, Py-H), 4.27 (s, 3H, CH<sub>3</sub>). IR (KBr): 3100 (ν<sub>C-H</sub>), 3050 (ν<sub>C-H</sub>), 2200 (ν<sub>C≡N</sub>), 2130 (ν<sub>C≡C</sub>) cm<sup>-1</sup>.

### Polymerization

#### Thermal Polymerization

After **5ab** in a sealed tube was kept at 225°C for 1 hr, solid materials were dissolved in DMF and reprecipitated into ether. The precipitate was filtered and dried. The molecular weight and the conversion were determined by GPC analysis eluted with DMF.

#### Photopolymerization

After **5ab** was irradiated by a high pressure Hg lamp (a Eikosha EHB-W) for 72 h. Solid materials were dissolved in DMF and reprecipitated into ether. The precipitate was filtered and dried.

#### Thermal Analysis

DSC or TGA of **5ab** was monitored with a Shimadzu DSC or TGA-50 at heating rate of 10.0°C/min under nitrogen flow rate of 20 mL/min. Based on the peak area and the weight of **5ab** used, ΔH<sub>p</sub> was calculated.

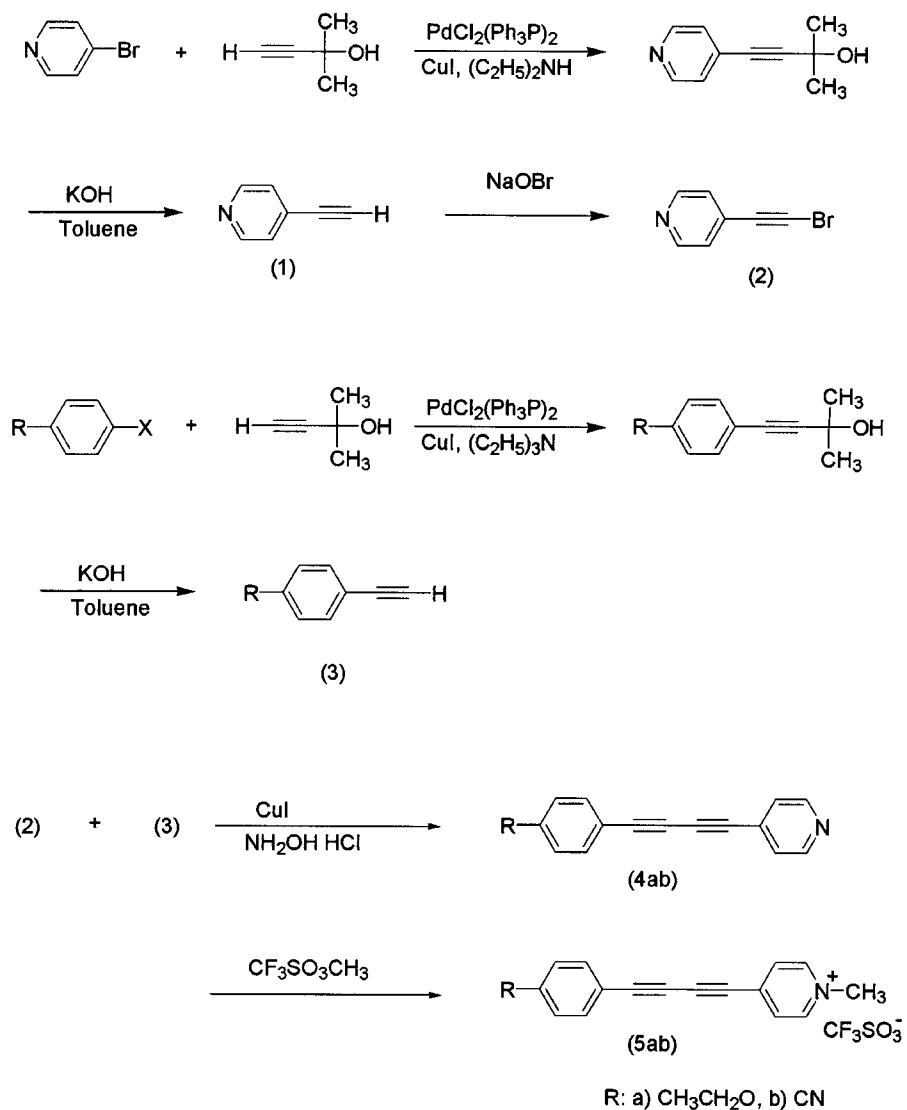
### Determination of χ<sup>(3)</sup> by Z-Scan Method

χ<sup>(3)</sup> of monomers and polymers was determined by the femto-second Z-scan method that depends on the change in the transmittance intensity in the acetonitrile solution by laser irradiation (wavelength; 650, 850 nm). The principle and the technique are described elsewhere.<sup>[8]</sup>

Real part of χ<sup>(3)</sup> for sample relative to reference is expressed as follows;

$$\text{Re}[\chi_{\text{sample}}^{(3)}] = (n_{\text{sample}}/n_{\text{ref}}) \cdot (L_{\text{eff-ref}}/L_{\text{eff-sample}}) \cdot (M_{\text{sample}}/M_{\text{ref}}) \cdot \text{Re}[\chi_{\text{ref}}^{(3)}] \quad (1)$$

where n is refractive index, L<sub>eff</sub> is effective length, and M is the deference in the transmittance intensity for sample and reference, respectively. When



Scheme 1.

acetone is used as the solvent ( $n_{\text{samp}}$ ; 1.36), the filter FD<sub>2</sub> as the reference ( $\chi_{\text{ref}}^{(3)}$ ;  $9.5 \times 10^{-14}$  (esu),  $n_{\text{ref}}$ ; 1.648) for  $L_{\text{eff.ref}}/L_{\text{eff.samp}} = 1$ , the Eq. (1) can be rewritten into (2):

$$\text{Re}[\chi_{\text{samp}}^{(3)}] = 6.47 \times 10^{-14} \cdot (M_{\text{samp}}/M_{\text{ref}}) \quad (2)$$

For the solid state of sample,

$$\chi_{\text{samp}}^{(3)} = N_{\text{samp}} \cdot f^4 \cdot \gamma \quad (3)$$

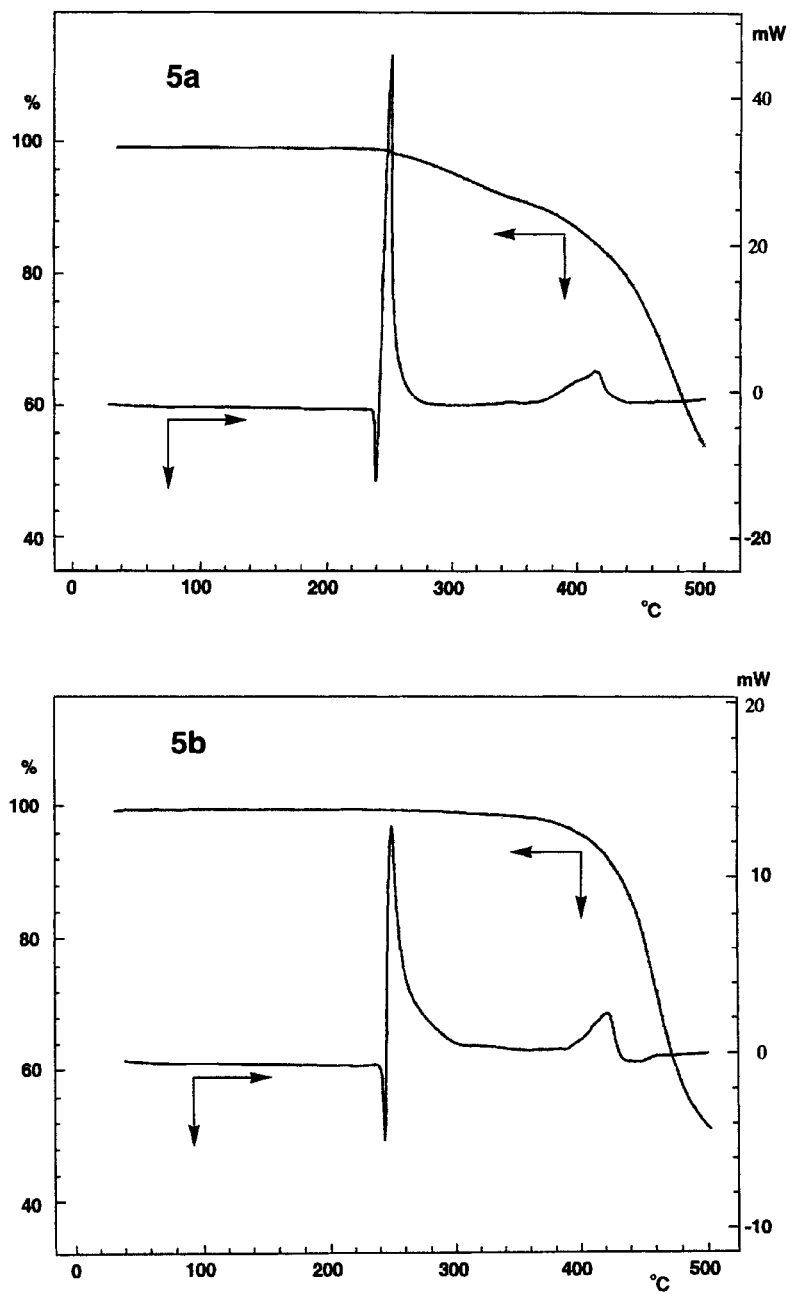


Figure 1. DSC and TGA for 5a and 5b.



where  $N_{\text{samp}}$  is equal to  $d_{\text{samp}}/M_w/N_o$  ( $d_{\text{samp}}$ ; density of sample determined by a floating method,  $N_o$ ; Avogadro's number,  $M_w$ ; molecular weight of sample),  $f$  is Lorentz's field factor ( $f = (2 + n_{\text{samp}}^2)/3$ ), and  $\gamma$  is second-order hyperpolarizability.

## RESULTS AND DISCUSSION

### Monomer Synthesis and Polymerization

4-Ethynylpyridine (**1**) and 4-substituted ethynylbenzene (**3**) were synthesized by Sonogashira's method. Subsequently, **1** was converted into the bromoethynyl compound (**2**) which was coupled with **3ab** by a modified Cadiot-Chodkiewicz method in the presence of Cu(I)Cl to afford **4ab**. Further treatment of **4ab** with methyl trifluoromethanesulfonate in dichloromethane or chloroform at 0°C provided immediately the triflates (**5ab**) (Sch. 1). Particularly, **5a** was found to be grown in acetonitrile to give the pale yellow large crystal ( $20 \times 7 \times 2$  mm) in one month at 4°C.

DSC analysis of **5a** exhibited the endothermic peak at 239°C for melting point and the exothermic peak at 248°C from which  $\Delta H$  for the heat of polymerization was estimated to 33.4 kcal/mol corresponding to the value of the conventional 1,4-addition polymerization<sup>[10]</sup> to suggest the possibility of 1,4-addition polymerization under the melting state, and followed by 415°C for the decomposition (Fig. 1 **5a**). The weight loss of the polymer started at 250°C and became 40% at 500°C as can be seen by the TGA. On the other hand, **5b** was thermally more stable than **5a** as shown in the higher temperature as the endothermic peak at 245°C and the exothermic peak at 253°C ( $\Delta H$ ; 43.5 kcal/mol) followed by 420°C for the decomposition, together with the weight loss started at 300°C (Fig. 1 **5b**). Base on these analyses, the temperature for the thermal solid state polymerization of **5ab** was set at 225°C, and carried out in a sealed tube for 1 h. In contrast, the photopolymerization under a high pressure Hg lamp irradiation was performed for 72 h at room temperature. The crystal was gradually changed into brown in the color. Poly(**5ab**)s thus obtained were found to be soluble in acetonitrile, DMSO, and DMF. Their molecular weights were determined by GPC eluted

**Table 1.** Polymerization of **5ab**

Compounds	Polymerization	$M_n \times 10^{-4}$	Conversion (%)
<b>5a</b>	225°C, 1 h	4.2	92
<b>5a</b>	UV irradiation, 72 h	17.4	20
<b>5b</b>	225°C, 1 h	7.1	96
<b>5b</b>	UV irradiation, 72 h	10	10

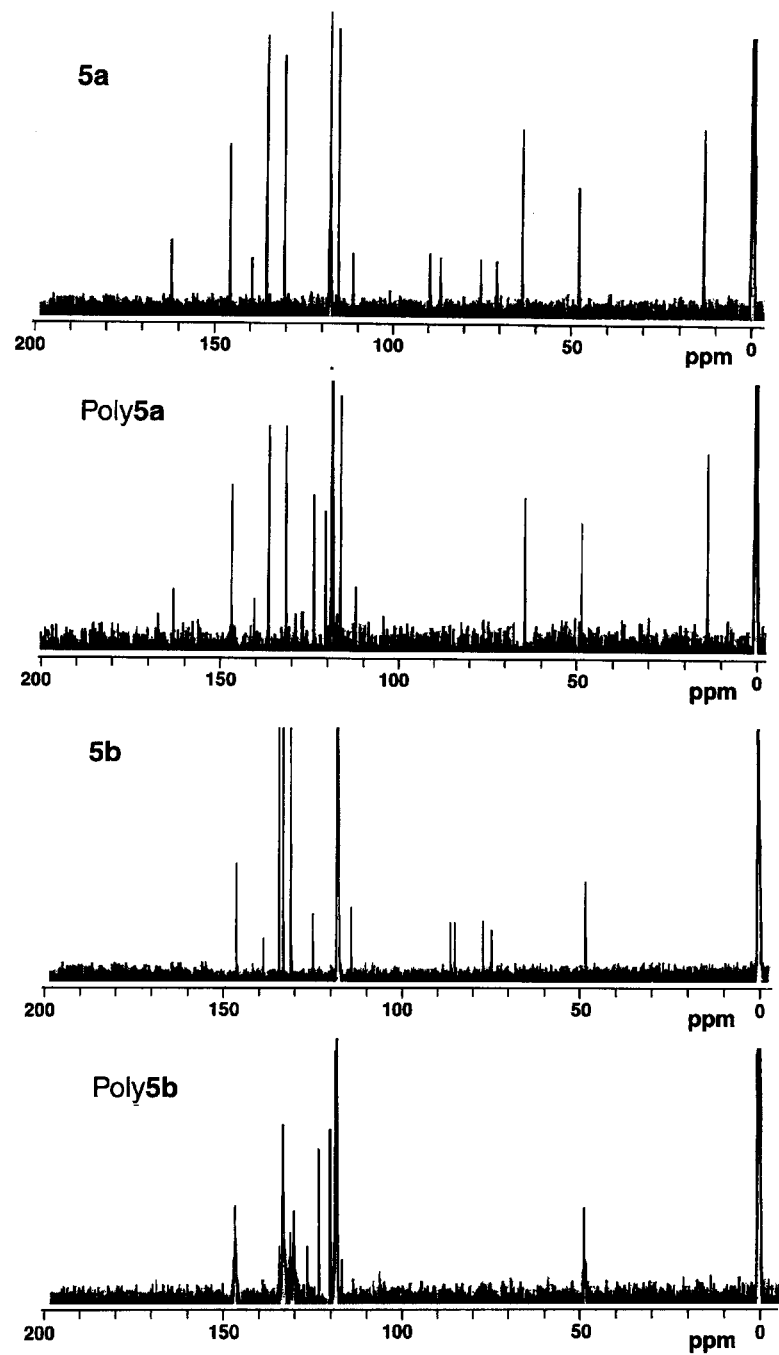


Figure 2.  $^{13}\text{C}$  NMR spectra for 5a, Poly5a, 5b, and Poly5b in  $\text{CD}_3\text{CN}$ .

**Table 2.**  $^{13}\text{C}$ -NMR Chemical Shifts (ppm) for **5ab** and Poly**5ab**

<b>5a</b>	Poly <b>5a</b>	<b>5b</b>	Poly <b>5b</b>
$\text{CH}_3\text{CH}_2\text{O}$ 14.9	14.9	CN 125.4	124.9
$\text{CH}_3\text{-Py}$ 49.7	50.0	49.4	49.6
$\text{CH}_3\text{CH}_2\text{O}$ 64.9	66.5		
$\text{C}\equiv\text{C-C}\equiv\text{C}$ 72.0, 76.6, 87.9, 90.8	$=\text{C}$ 120.2, 123.5 $\equiv\text{C}$ 105.5	$\text{C}\equiv\text{C-C}\equiv\text{C}$ 75.7, 78.0, 85.8, 87.0	$=\text{C}$ 121.3, 123.5 $\equiv\text{C}$ 107.1
$\text{CF}_3$ 111.9,	110.5	114.7,	115.5
Ph 112.2, 116.0, 139.9, 162.2	116.0, 140.4, 161.3	118.9, 133.5, 139.0	119.0, 133.5
Py 131.0, 135.9, 146.1	131.1, 136.0, 145.6	131.4, 134.4, 146.4	132.9, 146.8

118.3 ( $\text{CH}_3\text{CN}$ )

with DMF (polystyrene standard). The results are shown in Table 1. Heating crystal at 225°C for 1 h provided good conversion with fairly high molecular weight of polymers, whereas UV irradiation gave the higher molecular weight of polymer with the less conversion that reflects the polymerization limited on the crystal surface area. The structure was confirmed by the  $^{13}\text{C}$ -NMR in acetonitrile- $d_3$  that depicted the peaks at 105~107 (C $\equiv$ C) and 120~124 (C=C) ppm assigned to the common 1,4-addition polydiacetylene having the ene-yne structure<sup>[11,12]</sup> (Fig. 2). The signal assignments are summarized in Table 2.

### Determination of $\chi^{(3)}$ by Z-Scan Method

Based on the Eqs. (2) and (3),  $\chi^{(3)}$  and  $\gamma$  for **5ab** and the thermally obtained Poly**5ab** were determined at 650 and 850 nm. The results are summarized in Table 3, together with the absorption coefficient ( $\alpha$ ). Obviously, polymers exhibited larger  $|\chi^{(3)}|$  and  $|\gamma|$  than monomers due to the extended  $\pi$ -conjugation that can be related to the large  $\alpha$ . When the resonant region can

**Table 3.**  $\chi^{(3)}$  and  $\gamma$  for **5ab** and Poly**5ab** at 650 and 850 nm

	$\chi^{(3)} \times 10^{11}(\text{esu})$		$\gamma \times 10^{33}(\text{esu})$		$\alpha^a$	
	650 nm	850 nm	650 nm	850 nm	650 nm	850 nm
Poly <b>5a</b>	-1.65	-0.178	-3.07	-0.33	3760	787
<b>5a</b>	-0.009	0.120	-0.018	0.26	55	55
Poly <b>5b</b>	-1.02	-0.083	-1.73	-0.145	1640	575
<b>5b</b>	0.11	0.029	0.225	0.059	61	61

<sup>a</sup> $e^{-\alpha L} = 10^{-\epsilon cL}$ ,  $\epsilon$  = absorptivity,  $c$  = concentration,  $L$  = cell length.

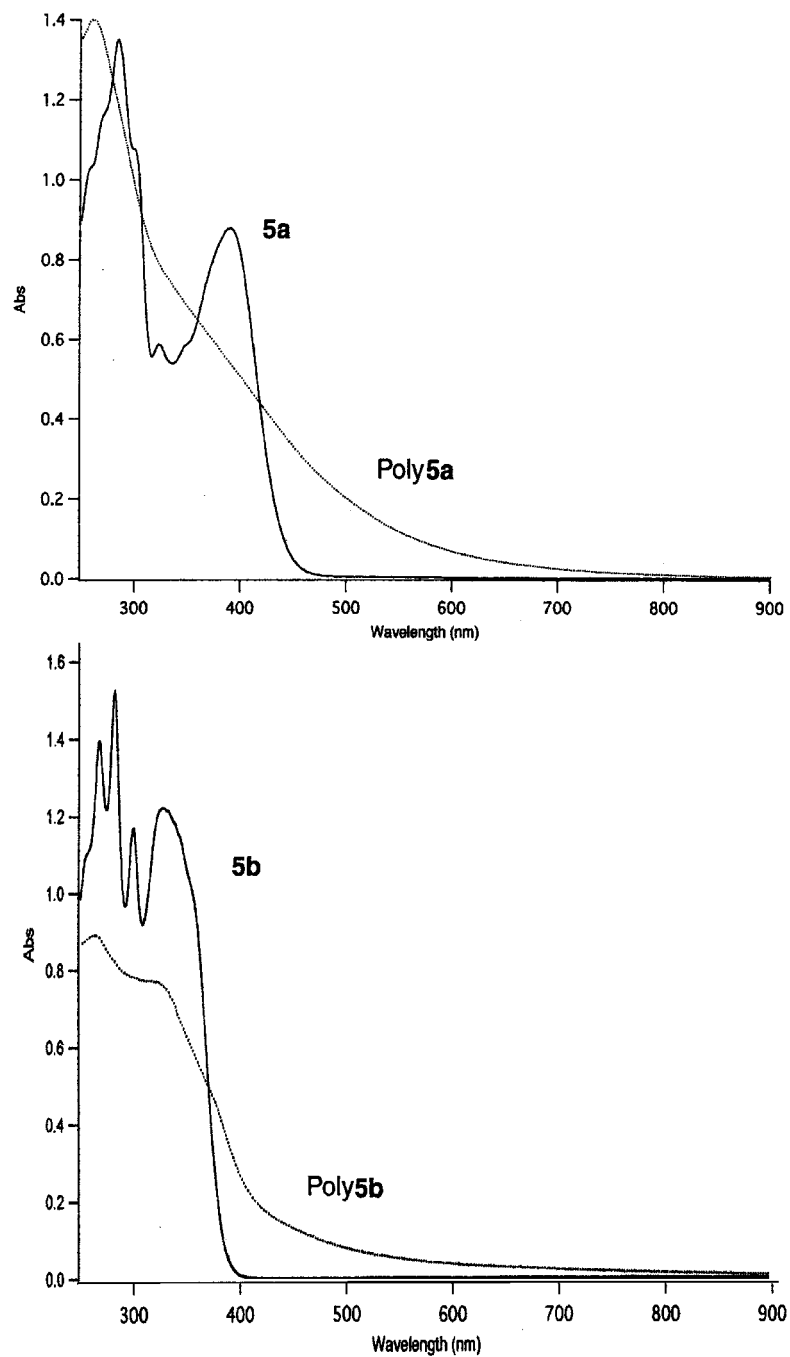


Figure 3. UV spectra for 5a, Poly5a, 5b, and Poly5b in  $\text{CH}_3\text{CN}$ .

be included in the wavelength for measurements, the values would be large and much more enhanced in the shorter wavelength. The effect of the substituent on  $|\chi^{(3)}|$  and  $|\gamma|$  appeared in the slightly large value for the donor ethoxy group substitution (Poly**5a**, **5a**) that could enhance  $\alpha$  at 650 and 850 nm in the polymer as observed in the uv spectra, suggesting the easy electron modulation between the donor ethoxy and acceptor pyridinium group through  $\pi$ -conjugation framework, although  $\epsilon$  ( $3.05 \times 10^4$  at 282 nm) at  $\lambda_{\max}$  of **5b** is larger than that of **5a**  $2.7 \times 10^4$  at 284 nm (Fig. 3ab). Furthermore, Z-scan method that is useful for two photon absorption (TPA) detection related to the imaginary part of third-order nonlinearity was also applied to poly**5ab** and **5ab** on the open aperture condition. However, no TPA was observed from 600 to 1015 nm in the wavelength indicating the importance of the symmetric  $\pi$ -conjugate structure for TPA generation.<sup>[13]</sup>

## CONCLUSION

1-(4'-Substituted phenyl)-4-(4'-methylpyridinium)butadiynes (**4ab**), which were prepared by the Cadiot-Chodkiewicz coupling reaction of 4-substituted phenylacetylene with 1-bromo-2-(4'-pyridyl)ethyne, were converted into the triflates (**5ab**) by methyl trifluoromethanesulfonate treatment in dichloromethane. **5ab** was found to be grown into the large crystal due to the quaternized structure. The uv irradiation and thermal treatment of **5ab** underwent 1,4-addition polymerization to yield the polydiacetylene. The third-order nonlinear optical susceptibility ( $\chi^{(3)}$ ) of the polymers and monomers was determined by the Z-scan method to exhibit the remarkable high value of  $1.65 \times 10^{-11}$  esu at 650 nm for the combination of the donor-acceptor substituents.

## REFERENCES

1. Chemla, D.S.; Zyss, J., Eds.; *Nonlinear Optical Properties of Organic Molecules and Crystals*; Academic Press: Orlando (FL) 1987; Vol. 2, p 3.
2. Greene, B.L.; Orenstein, J.; Millard, R.R.; Williams, L.R. *Chem. Phys. Lett.* **1987**, *139*, 381.
3. Matsuda, H.; Molyneux, S.; Kar, A.K.; Wherrett, B.S.; Okada, S.; Nakanishi, H. *J. Photopolym. Soc. Technol. Jpn.* **1993**, *6*, 261.
4. Marder, S.R.; Perry, J.W.; Bourhill, G.; Gorman, C.B.; Tiemann, B.G.; Mansour, K. *Science* **1993**, *261*, 186.
5. Koishi, K.; Ikeda, T.; Kondo, K.; Sakaguchi, T.; Kamada, K.; Tawa, K.; Ohta, K. *Macromol. Chem. Phys.* **2000**, *201*, 525.
6. Shiga, K.; Inoguchi, T.; Mori, K.; Kondo, K.; Kamada, K.; Tawa, K.; Ohta, K.; Maruo, T.; Mochizuki, E.; Kai, Y. *Macromol. Chem. Chem. Phys.* **2001**, *202*, 257.

7. Iwase, Y.; Kondo, K.; Kamada, K.; Ohta, K.J. *Polymer Sci. Part A: Polymer Chem.* **2001**, *39*, 3686.
8. Sutherland, R.L., Ed.; *Handbook of Nonlinear Optics*; Marcel Dekker: NY, 1996; p. 655.
9. Ciana, L.D.; Haim, A. *J. Heterocyclic Chem.* **1984**, *21*, 607.
10. Patel, G.N.; Chance, R.R.; Turi, E.A.; Khanna, Y.P. *J. Am. Chem. Soc.* **1978**, *100*, 6644.
11. Nava, A.D.; Thakur, M.; Tonell, A.E. *Macromolecules* **1990**, *23*, 3055.
12. Okada, S.; Hayamizu, K.; Matsuda, H.; Masaki, A.; Minami, N.; Nakanishi, H. *Macromolecules* **1994**, *27*, 6259.
13. Albota, M.; Belijonne, D.; Brédas, J.-L.; Ehrlich, J.E.; Fu, J.-Y.; Heikal, A.A.; Hess, S.E.; Kogei, T.; Levin, M.D.; Marder, S.R.; Mccord-Maughon, D.; Perry, J.W.; Röckel, H.; Rumi, M.; Subramaniam, G.; Webb, W.W.; Wu, X.-L.; Xu, C. *Science* **1998**, *281*, 1653.

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