

# Synthesis and Optical Properties of Novel Through-Space $\pi$ -Conjugated Polymers Having a Dithia[3.3]metacyclophane Skeleton in the Main Chain

Yasuhiro MORISAKI, Tamao ISHIDA, and Yoshiki CHUJO<sup>†</sup>

Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University,  
Yoshida, Sakyo-ku, Kyoto 606–8501, Japan

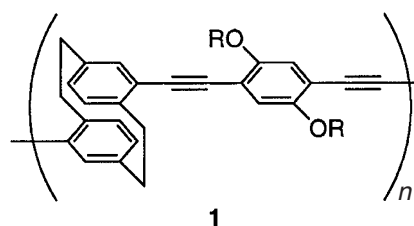
(Received December 27, 2002; Accepted April 7, 2003)

**ABSTRACT:** Palladium-catalyzed polymerization of 6,15-dibromo-2,11-dithia[3.3]metacyclophane **5** and 2,5-dialkoxy-1,4-diethynylbenzenes **6a–b** was carried out to give the corresponding polymers **7a–b** having dithia[3.3]metacyclophane as a repeating unit. The structures of the polymers were supported by <sup>1</sup>H, <sup>13</sup>C NMR, and IR spectra. The polymers obtained were soluble in common organic solvents such as tetrahydrofuran (THF), CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, and toluene. The polymer **7b** showed an extension of  $\pi$ -delocalization *via* the through-space with  $\pi$ - $\pi$  stacking according to the UV-vis absorption spectrum in comparison with those of the model compounds **8** and **9**. In the fluorescence emission spectrum of **7b** in chloroform solution, an intense emission peak was observed at 439 nm ( $\Phi = 0.51$ ) in the visible blue region. The monomer **5**, polymers **7a–b**, and the model compound **9** adopted the *syn* conformation of the dithia[3.3]metacyclophane moieties according to the <sup>1</sup>H NMR spectra.

**KEY WORDS** Through-Space /  $\pi$ - $\pi$  Stacking /  $\pi$ -Conjugated Polymer / Dithia[3.3]metacyclophane / *syn* Conformation / Blue Emission /

Recently, attention has been paid to the structure, reactivity, and physical properties of [n,n]meta- or paracyclophanes, in which two aromatic rings are faced one another in proximity.<sup>1</sup> Several cyclophane derivatives have been prepared and their physical properties derived from the transannular interactions have been investigated in detail.<sup>2</sup> In addition, several polymers having a paracyclophane unit in the main chain (in the course of developing new processes for cross-linking resins)<sup>3</sup> or in the side chain<sup>4</sup> have been studied to date. However, few  $\pi$ -conjugated polymers using the longitudinal  $\pi$ - $\pi$  interactions of cyclophane as a repeating unit have been reported so far.<sup>5–7</sup> In 1985, Mizogami and Yoshimura reported that the first synthesis of polymetacyclophane achieved by a polycondensation reaction using an oxidative dimer of 8,16-dihydroxy[2.2]metacyclophane, which exhibited a conductivity of 0.25 S cm<sup>-1</sup> by doping with H<sub>2</sub>SO<sub>4</sub> vapor.<sup>8</sup> Recently, we reported the synthesis and physical properties of the first well-defined [2.2]paracyclophane-containing  $\pi$ -conjugated polymers<sup>7</sup> based on poly(*p*-phenylene-ethynylene)s (PPEs) and poly(*p*-phenylenevinylene)s (PPVs). In these study, we demonstrated that the polymer **1** was capable of extended  $\pi$ -delocalization *via* the through-space with  $\pi$ - $\pi$  stacking of [2.2]paracyclophane.<sup>7a</sup>

In addition, dithia[3.3]cyclophanes have played an important role in cyclophane chemistry as synthetic intermediates for [2.2]cyclophanes (through sulfur elimination), and also for [2.2]cyclophane-dienes.<sup>1</sup> Fur-



Polymer 1

thermore, dithia[3.3]metacyclophane in solution involves a *syn/anti* conversion of the aromatic rings and a chair/boat conversion of the -CH<sub>2</sub>-S-CH<sub>2</sub>-bridging framework, while as a crystal, it constitutes both *syn* conformation and a chair/chair conformation.<sup>1,9–11</sup> Although the conformational behavior of [3.3]metacyclophane derivatives is not straightforward, dithia[3.3]metacyclophane appears to be a promising candidate for the aryl unit of through-space  $\pi$ -conjugated polymers. Changing the conformations of the [3.3]metacyclophane moiety by varying the temperature can fine-tune the optical and electrochemical properties of the resulting polymers. This paper reports the synthesis and properties of novel through-space  $\pi$ -conjugated polymers based on PPEs having a dithia[3.3]metacyclophane skeleton in the main chain as a repeating unit.

## EXPERIMENTAL

### General

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a JEOL JNM-EX270 instrument at 270 and 67.5 MHz, respec-

<sup>†</sup>To whom correspondence should be addressed.

tively. The chemical shift values were expressed relative to Me<sub>4</sub>Si as an internal standard. IR spectra were obtained on a PerkinElmer 1600 spectrometer. UV-vis spectra were obtained on a JASCO V-530 spectrophotometer, and samples were analyzed in CHCl<sub>3</sub> at room temperature. Fluorescence emission spectra were recorded on a PerkinElmer LS50B luminescence spectrometer, and samples were analyzed in CHCl<sub>3</sub> at room temperature. Gel permeation chromatography was carried out on a TOSOH UV-8020 and RI-8020 (TOSOH TSK-GEL  $\alpha$ -3000 column) using THF as an eluent after calibration with standard polystyrene. Analytical thin-layer chromatography (TLC) was performed with silica gel 60 Merck F<sub>254</sub> plates. Column chromatography was performed with Wakogel C-300 silica gel. Elemental analysis was performed at the Microanalytical Center of Kyoto University.

### Materials

THF was distilled from sodium benzophenone ketyl. NEt<sub>3</sub> was distilled from KOH. Toluene was distilled from CaH<sub>2</sub>. Methanol, ethanol, and benzene were used without purification. NaBH<sub>4</sub>, NaOH, CuI, 5-bromo-*m*-xylene, thiourea, PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, PPh<sub>3</sub>, and Bu<sup>n</sup><sub>4</sub>NF (1.0 M in THF solution) were obtained commercially, and used without further purification. Pd(PPh<sub>3</sub>)<sub>4</sub> was prepared as described in the literature.<sup>12</sup> 5-Bromo-*m*-xylene dibromide **4**,<sup>13</sup> 2,5-dialkoxy-1,4-diethynylbenzenes (**6a** and **6b**),<sup>14</sup> and 1,4-bis(phenylethynyl)-2,5-didodecyloxybenzene **8**<sup>14a</sup> were also prepared as described in the literature. 6,15-Dibromo-2,11-dithia[3.3]metacyclophane **5** was prepared as described in the literature with minor modification.<sup>15</sup> All of the new products are characterized below.

*1,3-Bis(isothiuroniummethyl)-5-bromobenzene Dibromide 2.* A mixture of 5-bromo-*m*-xylene dibromide **4** (2.0 g, 5.8 mmol), thiourea (0.99 g, 13 mmol), and ethanol (10 mL) was placed in a 100 mL Pyrex flask equipped with a magnetic stirring bar under a flow of nitrogen. The reaction mixture was refluxed for 2 h with stirring. After cooling, the white solid precipitated. The product was separated by filtration, washed with ethanol, and dried under vacuum to give **2** (2.7 g, 5.5 mmol, 94%). A white solid; mp 254–255 °C. <sup>1</sup>H NMR (270 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  4.50 (s, 4H), 7.45 (s, 1H), 7.63 (s, 2H), 9.05 (s, 4H), 9.20 (s, 4H); <sup>13</sup>C NMR (67.5 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  33.2, 121.8, 128.5, 131.1, 138.5, 168.6. Anal. calcd for C<sub>10</sub>H<sub>15</sub>Br<sub>3</sub>N<sub>4</sub>S<sub>2</sub>: C 24.26; H 3.05; found: C 24.41; H 2.99.

*6,15-Dibromo-2,11-dithia[3.3]metacyclophane 5.* To a solution of **2** (4.9 g, 10 mmol) in 100 mL of methanol was added NaBH<sub>4</sub> (1.5 g, 40 mmol) slowly

with rapid stirring to generate thiol. This solution and a solution of **4** (3.4 g, 10 mmol) in 100 mL of ethanol-benzene (4:1) were added dropwise simultaneously to a boiling solution of NaOH (0.79 g, 20 mmol) in 100 mL of ethanol. After the complete addition (24 h), the solution was refluxed for additional 24 h. The reaction mixture was allowed to cool to room temperature and evaporated. The residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub>. The organic layer was washed with water and dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed under vacuum and the crude product was subjected to column chromatography on SiO<sub>2</sub> with CH<sub>2</sub>Cl<sub>2</sub> as an eluent to give the compound **5** (1.8 g, 4.2 mmol, 42%). A white solid; mp 187–189 °C. <sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>):  $\delta$  3.73 (s, 8H), 6.96 (s, 2H), 7.05 (s, 4H); <sup>13</sup>C NMR (67.5 MHz, CDCl<sub>3</sub>):  $\delta$  37.6, 122.3, 130.0, 130.2, 139.0. Anal. calcd for C<sub>14</sub>H<sub>14</sub>Br<sub>2</sub>S<sub>2</sub>: C 44.67; H 3.28; found: C 44.38; H 3.19.

### Polymerization

A typical procedure is as follows. A 50 mL Pyrex flask was charged with **5** (126 mg, 0.29 mmol), **6** (0.29 mmol), Pd cat. (0.014 mmol), PPh<sub>3</sub> (16 mg, 0.060 mmol), CuI (3.9 mg, 0.020 mmol), toluene (3.0 mL), NEt<sub>3</sub> (3.0 mL), and a magnetic stirring bar under a flow of nitrogen. The reaction was carried out at 80 °C for 48 h with stirring. After the reaction mixture was cooled, the precipitated ammonium salts were filtered off and washed with THF. The filtrate was concentrated and poured into methanol (50 mL) to precipitate the polymer. The polymer was separated by filtration, washed with methanol, and dried in vacuo to give the polymer **7** as an orange powder.

*Polymer 7a.* Yield: 107 mg, 62%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 270 MHz):  $\delta$  0.92 (br, 6H), 1.37 (br, 8H), 1.52 (br, 4H), 1.82 (br, 4H), 3.74 (brs, 8H), 3.98 (br, 4H), 6.85–7.11 (m, 6H), 7.34–7.60 (m, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 67.5 MHz):  $\delta$  14.0, 22.6, 25.6, 29.0, 31.5, 37.3, 37.6, 69.7, 85.8, 95.1, 117.6, 122.4, 130.2, 130.4, 137.0, 139.0, 154.8. IR (KBr): 2203 cm<sup>-1</sup>. Anal. calcd for C<sub>38</sub>H<sub>42</sub>O<sub>2</sub>S<sub>2</sub>: C 76.72, H 7.12; found: C 78.30, H 7.30.

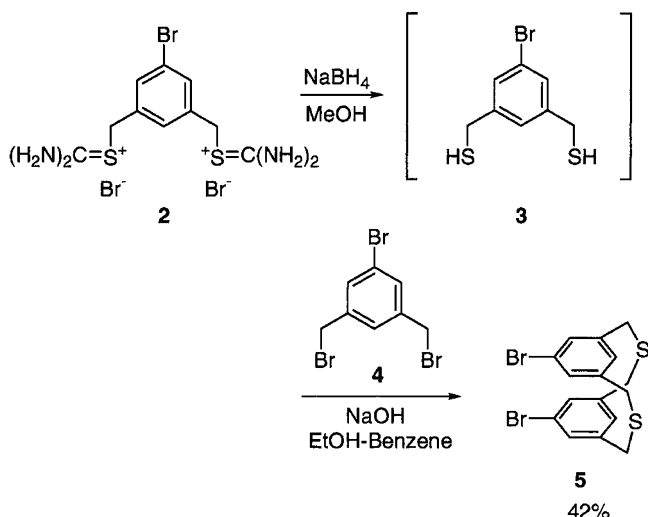
*Polymer 7b.* Yield: 128 mg, 58%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 270 MHz):  $\delta$  0.85 (br, 6H), 1.24 (br, 32H), 1.52 (br, 4H), 1.82 (br, 4H), 3.72 (brs, 8H), 3.98 (br, 4H), 6.84–7.11 (m, 6H), 7.30–7.45 (br, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 67.5 MHz):  $\delta$  14.1, 22.7, 25.9, 26.1, 29.4, 29.7 (overlapping signals), 31.9, 37.3, 37.6, 69.6, 85.9, 94.4, 116.9, 122.4, 130.2, 130.4, 136.9, 139.0, 153.5. IR (KBr): 2206 cm<sup>-1</sup>. Anal. calcd for C<sub>50</sub>H<sub>66</sub>O<sub>2</sub>S<sub>2</sub>: C 78.69, H 8.72; found: C 77.20, H 7.82.

*Model Compound 9.* A mixture of **5** (152 mg, 0.35 mmol), 1,4-didodecyloxy-2-ethynyl benzene<sup>14</sup> (333 mg, 0.71 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (46 mg, 0.040 mmol),

$\text{Bu}^n_4\text{NF}$  (1.0 mL, 1.0 M solution in THF), and THF (7.0 mL) was placed in a 50 mL Pyrex flask equipped with a magnetic stirring bar under a flow of nitrogen.<sup>16</sup> The reaction mixture was refluxed for 3 d. After cooling, the reaction mixture was diluted with  $\text{CHCl}_3$ , washed with water, and the organic layer was dried over  $\text{Na}_2\text{SO}_4$ . The solvent was evaporated and the crude product was subjected to column chromatography on  $\text{SiO}_2$  with  $\text{CH}_2\text{Cl}_2$ /hexane (1:1) as an eluent to give the compound **9** (199 mg, 0.16 mmol, 47%). A yellow solid; mp 45–47 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 270 MHz):  $\delta$  0.88 (m, 12 H), 1.27 (br, 76 H), 1.50 (br, 8 H), 1.82 (m, 4 H), 3.71 (s, 8 H), 3.82 (t,  $J = 6.5$  Hz, 4 H), 3.95 (t,  $J = 6.2$  Hz, 4 H), 6.65 (s, 2 H), 6.77 (s, 4 H), 6.93 (s, 2 H), 7.20 (s, 4 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 67.5 MHz):  $\delta$  14.1, 22.7, 26.0, 26.1, 29.3, 29.4, 29.5, 29.6 (overlapping signals), 31.9, 36.9, 68.6, 69.9, 86.1, 93.0, 113.7, 114.2, 116.6, 118.1, 124.0, 130.4, 131.7, 137.0, 152.8, 154.1. Anal. Calcd for  $\text{C}_{80}\text{H}_{120}\text{O}_4\text{S}_2$ : C 79.41; H 10.00. Found: C 79.16; H 10.11.

## RESULTS AND DISCUSSION

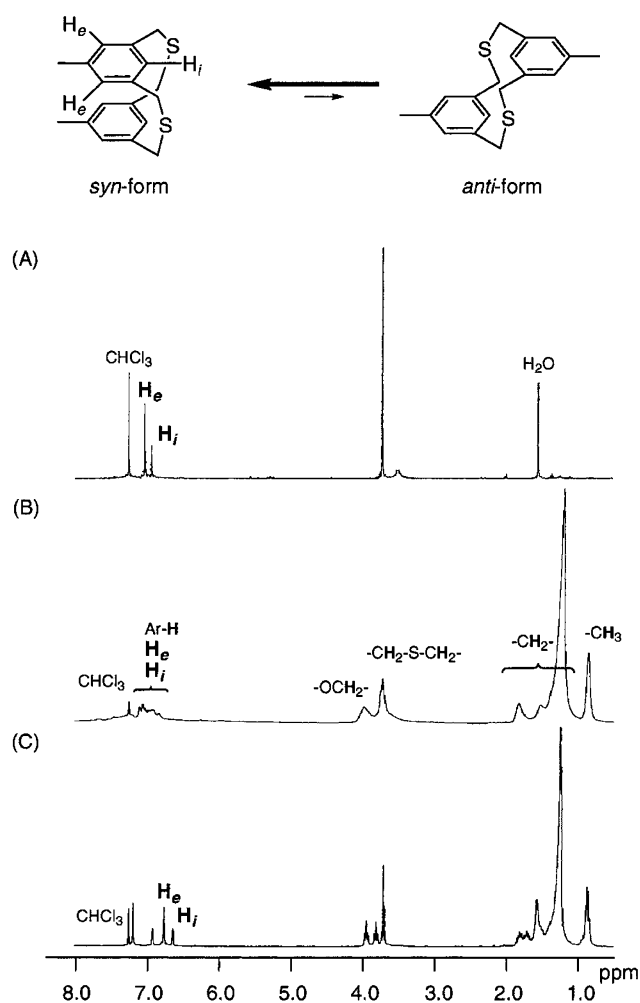
The synthesis of 6,15-dibromo-2,11-dithia[3.3]metacyclophane **5**<sup>15</sup> and polymers **7a–b** is shown in Scheme 1. The key monomer **5** was synthesized by direct coupling of 5-bromo-1,3-benzenedimethanethiol **3**, generated by reduction of 5-bromo-1,3-bis(isothio-uroniummethyl)benzene dibromide **2**, with 5-bromo-1,3-bis(bromomethyl)benzene **4** in 42% yield. Assignment of the *syn* conformation of **5** in solution at 25 °C was confirmed by the  $^1\text{H}$  NMR spectrum.<sup>10</sup> The internal aromatic proton of **5** was not affected by the transannular shielding and appeared at  $\delta = 6.96$  ppm in the normal range (Figure 1A). In the case of the *anti*-conformers, inner protons  $\text{H}_i$  are shifted



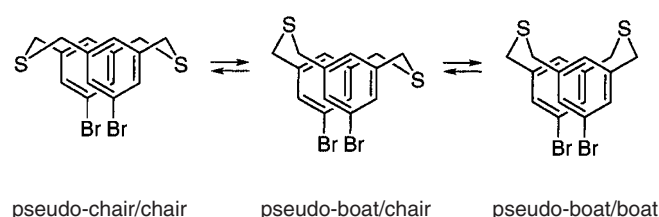
**Scheme 1.**

up-field ( $\delta = 4\sim 5$  ppm), and can be used to assign the two conformers.<sup>1</sup> In addition, the bridge protons appeared as a singlet at  $\delta = 3.73$  ppm in  $^1\text{H}$  NMR spectrum, indicating **5** likewise exists in three rapidly interconverting isomeric forms, *i.e.*, pseudo-chair/chair, pseudo-boat/chair, pseudo-boat/boat, in solution at 25 °C (Scheme 2). Comonomers **6a–b** were prepared as described in the literature.<sup>14</sup>

The procedure for the synthesis of the polymer proceeded as follows (Scheme 3),<sup>17</sup> and the results are



**Figure 1.** Schematic representation of the conformers of the dithia[3.3]metacyclophane moiety, and  $^1\text{H}$  NMR spectra (270 MHz) in  $\text{CDCl}_3$  solution at 25 °C; (A) monomer **5**, (B) polymer **7b**, and (C) model compound **9**.  $\text{H}_i$  and  $\text{H}_e$  stand for the internal and external aromatic protons of the dithia[3.3]metacyclophane moieties, respectively.

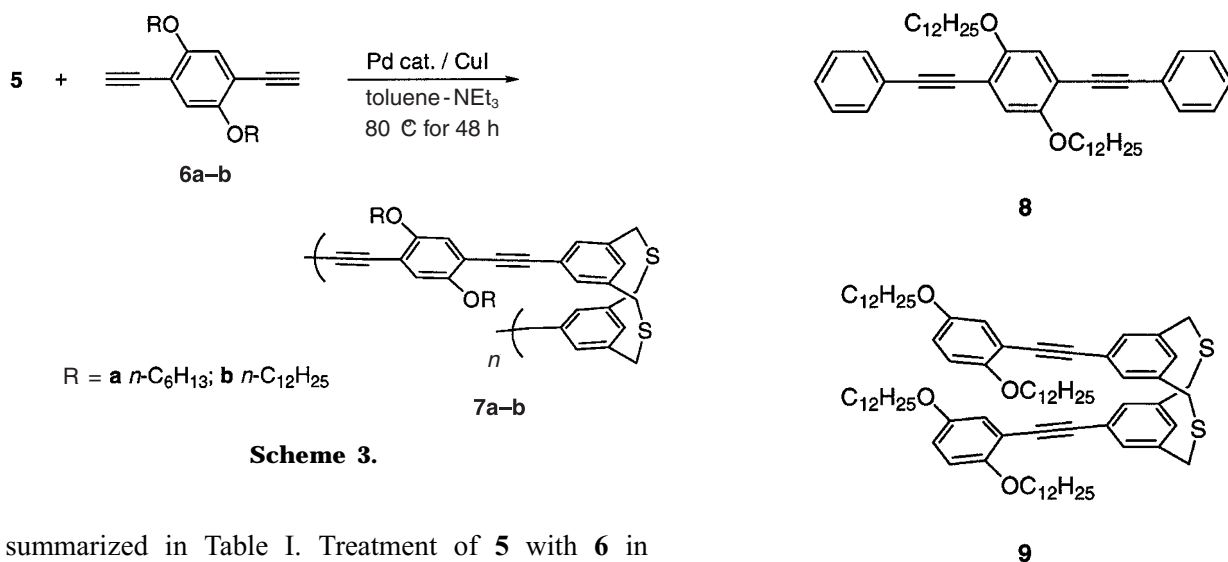


**Scheme 2.**

**Table I.** Synthesis and Optical Properties of the Polymers **7a–b**

entry	R	Pd cat.	additive	polym.	yield/% <sup>a</sup>	$M_w^b$	$M_n^b$	$M_w/M_n^b$	UV $\lambda_{max}/nm^c$	$\epsilon^c$	PL $\lambda_{max}/nm^{c,d}$
1	<i>n</i> -C <sub>6</sub> H <sub>13</sub> ( <b>6a</b> )	PdCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>	PPh <sub>3</sub>	<b>7a</b>	62	7600	4900	1.6	377	16000	440
2	<i>n</i> -C <sub>12</sub> H <sub>25</sub> ( <b>6b</b> )	PdCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>	PPh <sub>3</sub>	<b>7b</b>	58	13500	7500	1.8	373	29900	439
3	<i>n</i> -C <sub>12</sub> H <sub>25</sub> ( <b>6b</b> )	Pd(PPh <sub>3</sub> ) <sub>4</sub>	none	<b>7b</b>	47	14000	7600	1.9	372	27500	438

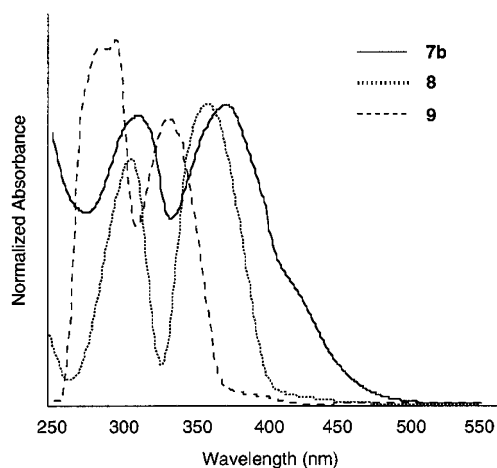
<sup>a</sup>Isolated yields after reprecipitation into MeOH. <sup>b</sup>GPC (THF), polystyrene standards. <sup>c</sup>Absorption and emission spectra were recorded in dilute CHCl<sub>3</sub> solutions at room temperature. <sup>d</sup>Excited at 375 nm ( $1.0 \times 10^{-5}$  M).



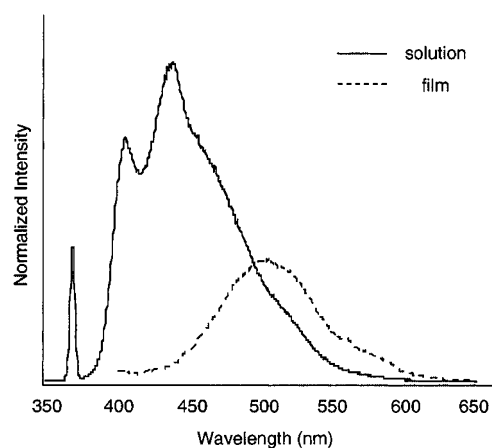
summarized in Table I. Treatment of **5** with **6** in the presence of a catalytic amount of PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (2.5 mol% to an acetylene unit), PPh<sub>3</sub>, and CuI in toluene–NEt<sub>3</sub> (v/v = 1:1) at 80 °C for 48 h under a nitrogen atmosphere gave dark fluorescent solutions. After the reaction was complete, inorganic by-products were filtered off and the filtrate was reprecipitated into a large amount of MeOH to obtain the corresponding titled polymers **7a–b** in moderate yields as an orange powder. The polymers obtained were readily soluble in common organic solvents such as THF, CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, and toluene. A self-standing thin film of the polymer was obtained easily by casting from a CHCl<sub>3</sub> solution. All polymers were thermally stable as well as air stable, both in solution and the solid state. The molecular weight measurements were performed by gel permeation chromatography (GPC) in THF eluent using a calibration curve of polystyrene as the standard (Table I). The polymer **7b** had a number-average molecular weight ( $M_n$ ) of 7500, which corresponded to a degree of polymerization of 10 (Table I, entry 2). The Pd(PPh<sub>3</sub>)<sub>4</sub>/CuI system showed almost the same catalytic activity for this polymerization, giving **7b** in a 47% isolated yield with  $M_n$  = 7600 (Table I, entry 3). All polymers were characterized by <sup>1</sup>H NMR and IR spectra. For example, in **7b**, the aryl protons of the alkoxybenzene and metacyclophane units appeared broadly at  $\delta$  = 7.30~7.60 and  $\delta$  = 6.75~7.15, respectively. The internal protons of dithia[3.3]metacyclophane in the polymer ( $\delta$  = 6.75~7.15) were not shifted upfield (Figure 1B). It

is implied that the dithia[3.3]metacyclophane units in the polymer backbone exist predominantly in the *syn* conformation in solution at room temperature. The acetylenic moiety of **7b** was characterized by <sup>13</sup>C NMR spectrum ( $\delta$  85.9 and 94.4 ppm) and by IR spectrum ( $\nu_{C\equiv C}$  = 2206 cm<sup>-1</sup>), respectively.

The optical properties of the polymers **7a–b** obtained above were examined, and the results are also summarized in Table I. The UV-vis absorption spectra of **7a–b** in a dilute CHCl<sub>3</sub> solution at room temperature exhibited absorption maxima at around 310 and 375 nm. The polymer **7b** exhibited strong absorption peaks at 311 and 373 nm, which agreed with the absorption of the PPEs backbone (Table I, entry 3). As shown in Figure 2, the UV-vis spectrum of **7b** was compared with those of two model compounds **8** and **9**. The internal proton H<sub>i</sub> of the compound **9** appeared at  $\delta$  = 6.65 ppm (Figure 1C), indicating **9** likewise adopts the *syn* conformation in solution at room temperature. The UV-vis spectrum of the compound **8** was already reported,<sup>14a</sup> but we wish to show here our own result. The spectra showed a red shift of 12 nm for the absorption of **7b** ( $\lambda_{max}$  = 373 nm) relative to **8** ( $\lambda_{max}$  = 361 nm) and 42 nm relative to **9** having a dithia[3.3]metacyclophane core ( $\lambda_{max}$  = 331 nm). Furthermore, the absorption edges were also red-shifted about 100 nm, as shown in Figure 2. These results



**Figure 2.** Absorption spectra of the polymer **7b** and the model compounds **8** and **9** in  $\text{CHCl}_3$ .



**Figure 3.** Fluorescence spectra of the polymer **7b** in dilute  $\text{CHCl}_3$  solution and in the film state (excitation wavelength at 375 nm).

suggest the extension of  $\pi$ -delocalization length only *via* the through-space based on the two benzene rings of 2,11-dithia[3.3]metacyclophane. The lone pairs of the two sulfur atoms in dithia[3.3]metacyclophane were not involved in the  $\pi$ -conjugated system because they were remote from the benzene rings. In addition, the absorption spectra of **7a–b** in the solid state were very similar to those in solution.

In the fluorescence emission spectra of the polymers **7a–b** in dilute  $\text{CHCl}_3$  solution at room temperature on excitation at 375 nm, the emission peaks were observed near 440 nm in the visible blue region (Table I, Figure 3). The polymer solutions showed high quantum efficiency; for example, **7b** had an efficiency of 0.51 in  $\text{CHCl}_3$  solution at room temperature, as demonstrated by using 9-anthracenecarboxylic acid in  $\text{CH}_2\text{Cl}_2$  as a standard ( $\Phi = 0.442$ ).<sup>18</sup> In the solid thin film of **7b**, the weak emission peak maximum at 502 nm was redshifted about 60 nm from that in solution. This result indicates relatively strong  $\pi$ - $\pi$  stacking, *i.e.*, ex-

cimer formation.<sup>19</sup> For polymers **7a** and **7b**, the physical properties were almost the same and independent on the length of the alkoxy side chain.

## CONCLUSION

Novel  $\pi$ -conjugated polymers having dithia[3.3]-metacyclophane in the main chain have been designed, synthesized, and characterized. The monomer, polymers, and the model compound adopted the *syn* conformation of dithia[3.3]metacyclophane units as shown by the  $^1\text{H}$  NMR spectra. The extension of  $\pi$ -conjugation *via* the through-space was observed according to the UV-vis absorption spectral data in comparison with those of the model compounds. The polymers emitted bright blue light ( $\lambda = 440$  nm,  $\Phi = 0.51$ ) in solution. Further studies of the electronic properties, thermal properties, and thermochromism accompanying the *syn/anti* conformational changes of dithia[3.3]metacyclophane moieties in the polymer backbone are now underway.

## REFERENCES AND NOTES

- For recent reviews, see:
  - F. Vögtle, "Cyclophane Chemistry", John Wiley & Sons, New York, N.Y., 1993.
  - J. Shultz and F. Vögtle, *Top. Curr. Chem.*, **42**, 172 (1994).
- Bazan, Mukamel, and co-workers recently reported the unique photophysical properties of a series of stilbenoids having a [2.2]paracyclophane core. See:
  - G. C. Bazan, W. J. Oldham Jr., R. J. Lachicotte, S. Tretiak, V. Chernyak, and S. Mukamel, *J. Am. Chem. Soc.*, **120**, 9188 (1998).
  - S. Wang, G. C. Bazan, S. Tretiak, and S. Mukamel, *J. Am. Chem. Soc.*, **122**, 1289 (2000).
  - J. Zyss, I. Ledoux, S. Volkov, V. Chernyak, S. Mukamel, G. P. Bartholomew, and G.C. Bazan, *J. Am. Chem. Soc.*, **122**, 11956 (2000).
  - G. P. Bartholomew and G. C. Bazan, *J. Am. Chem. Soc.*, **124**, 5183 (2002).
- R. A. Meyers, J. W. Hamersma, and H. E. Green, *J. Polym. Sci., Polym. Lett. Ed.*, **10**, 685 (1972).
  - K. P. Sivaramakrishnan, C. Samyn, I. J. Westerman, D. T. Wong, and C. S. Marvel, *J. Polym. Sci., Polym. Chem. Ed.*, **13**, 1083 (1975).
  - D. M. Chang and C. S. Marvel, *J. Polym. Sci., Polym. Chem. Ed.*, **13**, 2507 (1975).
  - S. Lin and C. S. Marvel, *J. Polym. Sci., Polym. Chem. Ed.*, **21**, 1151 (1983).
- J. Furukawa and J. Nishimura, *J. Polym. Sci., Polym. Lett. Ed.*, **14**, 85 (1976).
  - D. T. Longone and D. T. Glatzhofer, *J. Polym. Sci., Polym. Chem. Ed.*, **24**, 1725 (1986).
  - D. T. Longone and J. H. Glans, *J. Polym. Sci., Polym. Chem. Ed.*, **26**, 405 (1988).

- d) S. Iwatsuki, T. Itoh, M. Kubo, and H. Okuno, *Polym. Bull.*, **32**, 27 (1944).
5. D. M. Collard and B. Lee, *Polym. Prepr.*, (*Am. Chem. Soc., Div. Polym. Chem.*), **41** (1), 241 (2000).
  6. Independently, synthesis of the  $\pi$ -conjugated polymers having thiophene and [2.2]paracyclophane as a repeating unit by electrochemical polymerization has been reported.
    - a) L. Guyard and P. Audebert, *Electrochem. Commun.*, **3**, 164 (2001).
    - b) L. Guyard, D. A. M. Nguyen, and P. Audebert, *Adv. Mater.*, **13**, 133 (2001).
    - c) F. Salhi and D. M. Collard, *Polym. Mater. Sci. Eng.*, 222 (2002).
    - d) F. Salhi and D. M. Collard, *Adv. Mater.*, **15**, 81 (2003).
  7.
    - a) Y. Morisaki and Y. Chujo, *Macromolecules*, **35**, 587 (2002).
    - b) Y. Morisaki and Y. Chujo, *Chem. Lett.*, 194 (2002).
    - c) Y. Morisaki, T. Ishida, and Y. Chujo, *Macromolecules*, **35**, 7872 (2002).
    - d) Y. Morisaki and Y. Chujo, *Polym. Bull.*, **49**, 209 (2002).
    - e) Y. Morisaki, F. Fujimura, and Y. Chujo. *Organometallics*, in press.
  8. S. Mizogami and S. Yoshimura, *J. Chem. Soc., Chem. Commun.*, 1736 (1985).
  9.
    - a) W. Anker, G. W. Bushnell, and R. H. Mitchell, *Can. J. Chem.*, **57**, 3080 (1979).
    - b) M. F. Semmelhack, J. J. Harrison, D. C. Young, A. Gutiérrez, S. Raffi, and J. Clardy, *J. Am. Chem. Soc.*, **107**, 7508 (1985).
  10. R. H. Mitchell, *J. Am. Chem. Soc.*, **124**, 2352 (2002).
  11. Unusual boat/boat conformation of the bridging framework of *syn*-[3.3]metacyclophanes in the crystal has been reported.
    - a) G. J. Bodwell, J. N. Bridson, T. J. Houghton, and B. Yarlaga, *Tetrahedron Lett.*, **38**, 7475 (1997).
    - b) G. R. Newkome, S. Pappalardo, and F. R. Fronczek, *J. Am. Chem. Soc.*, **105**, 5152 (1983).
    - c) K. Sako, H. Tatemitsu, S. Onaka, H. Takemura, S. Osada, G. Wen, J. M. Rudzinski, and T. Shinmyozu, *Liebigs Ann.*, 1645 (1996).
  12. D. R. Coulson, *Inorg. Synth.*, **13**, 121 (1972).
  13. M. Ashram, D. O. Miller, J. N. Bridson, and P. E. Georghiou, *J. Org. Chem.*, **62**, 6476 (1997).
  14.
    - a) H. Li, D. R. Powell, R. K. Hayashi, and R. West, *Macromolecules*, **31**, 52 (1998).
    - b) M. Moroni and J. L. Moigne, *Macromolecules*, **27**, 562 (1994).
  15. T. Kawashima, S. Kurioka, Y. Tohda, M. Ariga, Y. Mori, and S. Misumi, *Chem. Lett.*, 1289 (1985).
  16.
    - a) A. Mori, J. Kawashima, T. Shimada, M. Suguro, K. Hirabayashi, and Y. Nishihara, *Org. Lett.*, **2**, 2935 (2000).
    - b) A. Mori, T. Kondo, T. Kato, and Y. Nishihara, *Chem. Lett.*, 286 (2001).
  17.
    - a) H. A. Dieck and R. F. Heck, *J. Organomet. Chem.*, **93**, 259 (1975).
    - b) K. Sonogashira, Y. Tohda, and N. Hagihara, *Tetrahedron Lett.*, **16**, 4467 (1975).
  18. The absorbance of each sample was below 0.05 at the excitation wavelength at 375 nm, in the measurement of the fluorescence quantum yield. The quantum yield ( $\Phi_{\text{unk}}$ ) of unknown sample was calculated by the following equation:  $\Phi_{\text{unk}} = \Phi_{\text{std}}[A_{\text{std}}F_{\text{unk}}/A_{\text{unk}}F_{\text{std}}][n_{\text{D,unk}}/n_{\text{D,std}}]^2$  where  $A_{\text{std}}$  and  $A_{\text{unk}}$  are the absorbance of the standard and unknown sample, respectively,  $F_{\text{std}}$  and  $F_{\text{unk}}$  are the corresponding relative integrated fluorescence intensities, and  $n_{\text{D}}$  is the refractive index [ $\text{CH}_2\text{Cl}_2$  ( $n_{\text{D}} = 1.424$ ) and  $\text{CHCl}_3$  ( $n_{\text{D}} = 1.446$ ) were used].
  19. For review on excimer formation and luminescence in conjugated polymers, see:
    - E. Conwell, *Trends Polym. Sci.*, **5**, 218 (1997). See also:
      - a) H. Li, D. R. Powell, R. K. Hayashi, and R. West, *Macromolecules*, **31**, 52 (1998).
      - b) J. Cornil, D. A. dos Santos, X. Crispin, R. Silbey, and J. L. Bredas, *J. Am. Chem. Soc.*, **120**, 1289 (1998).
      - c) C. E. Halkyard, M. E. Rampey, L. Kloppenburg, S. L. Studer-Martinez, and U. H. F. Bunz, *Macromolecules*, **31**, 8655 (1998).