

SHORT COMMUNICATIONS

**A New Type of Poly(thiophene-2,5-diyl) Having a Crown Etheral Subunit. Strong Interaction of the Subunit with Cationic Dopants to Exhibit Unique Doping-Undoping Behavior**

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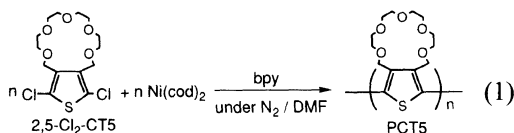
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$\pi$ -Conjugated polymers are the subject of recent interest.<sup>1</sup> On the other hand, macrocyclic ligands such as crown ethers and cyclams have received strong attentions<sup>2</sup> and electrochemical behaviors of their metal complexes have been reported. However,  $\pi$ -conjugated electrically conducting polymers having macrocyclic ligand unit(s) have been paid much less attention.

We now report synthesis of a new type of poly(thiophene-2,5-diyl) having a crown etheral subunit as well as its unique doping-undoping behavior presumably due to a strong interaction of cationic dopants with the subunit.



The above polymer, poly(3,6,9,12,15-pentaoxa-19-thiabicyclo[15.3.0]-eicosa-1(20),17-diene-18,20-diyl) (abbreviated as PCT5, cf. eq 1) was prepared according to dehalogenation polycondensation of the corresponding monomer, 18,20-dichloro-3,6,9,12,15-pentaoxa-19-

thiabicyclo[15.3.0]-eicosa-1(20),17-diene (abbreviated as 2,5-Cl<sub>2</sub>-CT5)<sup>3</sup> using nickel(0) complex.<sup>4</sup> Stirring 1.11 g (3.00 mmol) of 2,5-Cl<sub>2</sub>-CT5 with a mixture of 1.10 g (4.00 mmol) of bis(1,5-cyclooctadiene)nickel (Ni(cod)<sub>2</sub>), 0.3 cm<sup>3</sup> of 1,5-cyclooctadiene and 0.624 g (4.00 mmol) of 2,2'-bipyridine (bpy) in 30 cm<sup>3</sup> of *N,N*-dimethylformamide for 48 h at about 60°C afforded a dark-brown solution. The reaction mixture was poured into methanol (500 cm<sup>3</sup>) and stirred for 1 h. The solvent was evaporated to dryness, and the residual mass was dissolved in chloroform. The solution was washed with dilute HCl, aqueous solution of ethylenediaminetetraacetic acid, aqueous ammonia, dilute HCl, and distilled water, successively. After removal of the solvent, the residue was dried under vacuum. Light brown powder of PCT5 was obtained in good yield (86%).

The polymer was characterized by microanalysis and spectroscopic data: Found: C, 55.43%; H, 6.79%; Cl, 0.00%. Calcd for PCT5 (C<sub>14</sub>H<sub>20</sub>O<sub>5</sub>S)<sub>n</sub> (300.4)<sub>n</sub>: C, 56.00%; H, 6.67%; Cl, 0.00%.

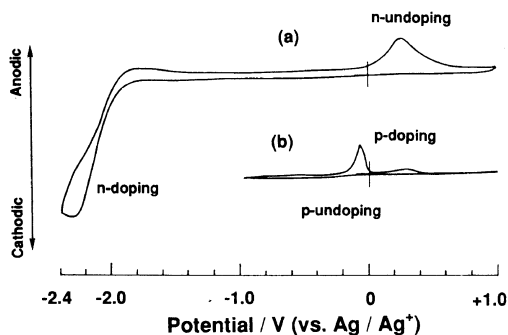
<sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 3.67 (8H; OCH<sub>2</sub>-

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CH<sub>2</sub>O), 3.74 (8H; OCH<sub>2</sub>CH<sub>2</sub>O) and 4.63 (4H; CH<sub>2</sub> attached to thiophene ring). The <sup>1</sup>H NMR pattern of PCT5 is essentially the same as that of the monomer (2,5-Cl<sub>2</sub>-CT5).<sup>3</sup> IR (KBr): 2860 (ν<sub>C-H</sub>); 1460 (skeletal) and 1100 cm<sup>-1</sup> (ν<sub>C-O-C</sub>).

The obtained PCT5 is readily soluble in most of the organic solvents such as chloroform, benzene, and acetonitrile. PCT5 has large *M<sub>w</sub>* (weight-average molecular weight) value of 7.4 × 10<sup>5</sup> (degree of polymerization = 2460) as determined by the light scattering method in benzene.

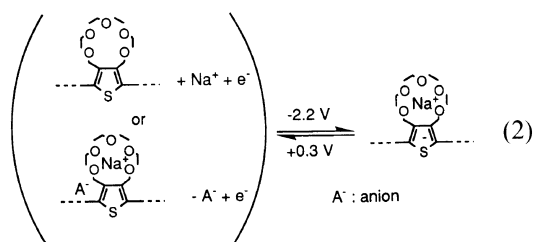
The λ<sub>max</sub> value of the π-π\* absorption band of PCT5 (λ<sub>max</sub> = 332 nm) is comparable to that of poly(3,4-dimethylthiophene) (λ<sub>max</sub> = 340 nm),<sup>5</sup> however, it is considerably different from those of polythiophene (abbreviated as PTh) (λ<sub>max</sub> = ca. 450 nm), poly(3-alkylthiophene) (PRTh) (λ<sub>max</sub> = 380–400 nm),<sup>1,3,4</sup> and poly(3,4-dimethoxythiophene) (PDMeOTh) (λ<sub>max</sub> = 470 nm),<sup>6</sup> indicating that PCT5 has a shorter effective π-conjugation system than PTh, PRTh, and PDMeOTh due to the steric hindrance of the bulky crown ethereal subunit. The π-π\* absorption peak of PCT5 lies between those of bithiophene α-2T (λ<sub>max</sub> = 302 nm) and terthiophene α-3T (λ<sub>max</sub> = 355 nm),<sup>7</sup> suggesting PCT5 has an effective conjugation length comparable to that of α-2T and α-3T. PCT5 takes a random-coil structure



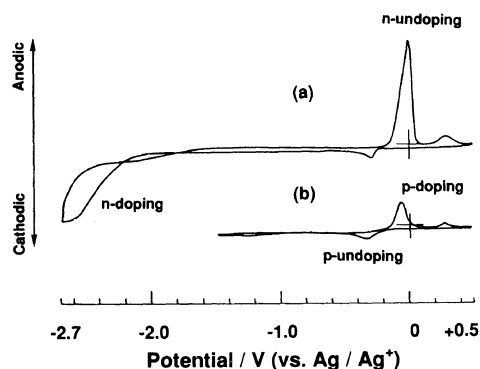
**Figure 1.** Cyclic voltammograms of PCT5 in 0.1 M NaClO<sub>4</sub>/CH<sub>3</sub>CN: (a) sweep range = -2.4 V ~ +1.0 V; (b) sweep range = -1.0 V ~ +1.0 V. PCT5, 0.05 M of monomer units; scan rate, 50 mV · s<sup>-1</sup>; WE (working electrode), Pt wire; CE (counter electrode), Pt plate.

in benzene as revealed by its degree of depolarization,<sup>8</sup> ρ<sub>v</sub> = 0.

Figure 1 shows cyclic voltammogram (CV curve) of PCT5 in an acetonitrile solution of NaClO<sub>4</sub>.<sup>9</sup> As shown in Figure 1a, the n-doping of PCT5 occurs at reducing potential comparable to that (ca. -2.45 V vs. Ag/Ag<sup>+</sup>) of PRTh.<sup>10</sup> In the case of PRTh, its n-undoping takes place near the doping potential (undoping potential = ca. -2.05 V vs. Ag/Ag<sup>+</sup>).<sup>10</sup> However, in contrast to PRTh, the undoping of PCT5 requires much higher potential as about 0.3 V vs. Ag/Ag<sup>+</sup> due to a strong interaction of Na<sup>+</sup> dopant with the crown ethereal subunit.



In the course of undoping, the Na<sup>+</sup> dopant may come out from the polymer (the upper undoped state) or anion A<sup>-</sup> may come into the polymer (the lower undoped state) due to the strong interaction of Na<sup>+</sup> with the crown ethereal unit. These two types of n-doping processes are presumably overlapped to give the undoping electric current shown in Figure 1a. Although some polythiophenes with ethereal alkoxy substituents also exhibit large difference (|doping potential - undoping potential| = ca. 1.6 V) between the n-doping potential and n-undoping potential, which is also accounted for by the interaction of cationic dopant with the ethereal oxygen,<sup>11</sup> such a large potential difference as 2.5 V has no precedent. Such high stability of the n-doped state up to 0.3 V vs. Ag/Ag<sup>+</sup> (or about 0.65 V vs. SCE and about 0.9 V vs. NHE) has no precedent, either. When CV measurement of PCT5 is carried out only in an oxidation range (Figure 1b), the CV shows p-doping peak(s) usually observed for PTh's though the p-



**Figure 2.** Cyclic voltammograms of PCT5 in 0.1 M  $\text{Et}_4\text{NClO}_4/\text{CH}_3\text{CN}$ : (a) sweep range =  $-2.7\text{ V} \sim +0.5\text{ V}$ ; (b) sweep range =  $-1.5\text{ V} \sim +0.5\text{ V}$ . PCT5, 0.05 M of monomer units; scan rate,  $50\text{ mV} \cdot \text{s}^{-1}$ ; WE, Pt wire; CE, Pt plate.

undoping process is obscured. However, after the electrochemical n-doping is carried out, no clear p-doping peak is observed presumably due to overlapping with the n-undoping peak or great change of the electrochemical property of PCT5 after the n-doping.

Use of  $[\text{Et}_4\text{N}][\text{ClO}_4]$  as the electrolyte also gives the large difference between the n-doping and n-undoping potentials as shown in Figure 2a. However, the n-doping and n-undoping potentials are somewhat shifted from those observed for the system using  $\text{NaClO}_4$ , and the p-doping and p-undoping peaks are obviously observed in this case, suggesting a somewhat different mode of interaction of the  $\text{Et}_4\text{N}^+$  cation with the crown etheral subunit.

Chemical Na-doping of PCT5 with metallic sodium in tetrahydrofuran by vigorous stirring affords brown Na-doped powdery PCT5, which has electrical conductivity of  $2 \times 10^{-4}\text{ S} \cdot \text{cm}^{-1}$ . The IR spectrum of the Na-doped PCT5 indicates weakening of the C–O–C vibration band at  $1100\text{ cm}^{-1}$  and appearance of a strong new band at about  $1450\text{ cm}^{-1}$  which is considered to originate from the  $\text{Na}^+$ -coordinated crown etheral subunit and/or skeletal vibration of n-doped thiophene ring.<sup>4f</sup> Treatment of the Na-doped PCT5 with dil. HCl gives undoped light brown PCT5, whose IR is

identical to that of original PCT5 indicating that Na-doping does not cause chemical change involving cleavage of covalent bond.

Due to the high stability of the Na-doped PCT5 as shown in Figure 1a, the chemical Na-doped PCT5 has good chemical stability under dry air at room temperature. No obvious color change of the brown chemically Na-doped PCT5 to light brown original PCT5 was observed even after 1 month, and furthermore, the electrical conductivity as well as IR spectrum of the Na-doped sample did not vary after 1 month. This is in sharp contrast to general high instability of Na-doped or n-doped  $\pi$ -conjugated polymers under air,<sup>1,3</sup> usual n-doped polymers are undoped in few seconds when exposed to air although the polythiophenes with etheral alkoxy substituents<sup>11</sup> also show some stability for several minutes under air. Iodine doping of PCT5 (saturation doping) at room temperature gives a semiconducting material with conductivity of  $1.5 \times 10^{-3}\text{ S} \cdot \text{cm}^{-1}$ .

As described above, the new type of polythiophene having crown etheral subunit has unique doping-undoping behavior and stable n-doped state, and these types of conducting polymers with such a crown etheral subunit will show interesting electrochemical behaviors related to ion recognition by the subunit.

## REFERENCES AND NOTES

1. E.g., (a) T. A. Skotheim, Ed., "Handbook of Conducting Polymers," Vol. I and Vol. II, Marcel Dekker, New York, 1986. (b) W. R. Solaneck, D. L. Clark, E. J. Samuelsen, Ed., "Science and Applications of Conducting Polymers", Adam Hilger, New York, 1990. (c) T. Shimidzu, *Reactive Polymers*, **6**, 221 (1987). (d) E. Tsuchida, Ed., "Macromolecular Complexes," VCH Publishing, New York, 1991.
2. E.g., (a) D. H. Busch, K. Farmery, V. Goedken, V. Katovic, A. G. Melnyk, G. R. Sperati, and N. Tokel, *Adv. Chem. Ser.*, **100**, 44 (1971). (b) A. Riesen, T. A. Kaden, W. Ritter, and H. R. Mäcke, *J. Chem. Soc., Chem. Commun.*, **1989**, 460 (1989). (c) R. M. Musau and A. Whiting, *ibid.*, **1993**, 1097 (1993). (d) M. H. Schmidt, G. M. Miskelly, and N. S. Lewis, *J. Am.*

- Chem. Soc.*, **112**, 3420 (1990).
3. T. Sone, K. Sato, and Y. Ohba, *Bull. Chem. Soc., Jpn.*, **62**, 838 (1989).
  4. (a) T. Yamamoto, T. Ito, and K. Kubota, *Chem. Lett.*, **1988**, 153 (1988). (b) T. Yamamoto, A. Morita, Y. Miyazaki, T. Maruyama, H. Wakayama, Z.-H. Zhou, Y. Nakamura, T. Kanbara, S. Sasaki, and K. Kubota, *Macromolecules*, **25**, 1214 (1992). (c) T. Yamamoto, *Progr. Polym. Sci.*, **17**, 1153 (1992). (d) Z.-H. Zhou, and T. Yamamoto, *J. Organomet. Chem.*, **414**, 119 (1991). (e) T. Yamamoto, S. Wakabayashi and K. Osakada, *ibid.*, **428**, 223 (1992). (f) Y. Miyazaki and T. Yamamoto, *Chem. Lett.*, **1994**, 41 (1994).
  5. G. Horowitz, G. Tourillon, and F. Garnier, *J. Electrochem. Soc.*, **131**, 151 (1984).
  6. (a) T. Yamamoto, A. Kashiwazaki, and K. Sanechika, *Denki Kagaku*, **58**, 898 (1988). (b) T. Yamamoto, A. Kashiwazaki, and K. Kato, *Makromol. Chem.*, **190**, 1649 (1989).
  7. F. Charra, D. Fichou, J.-M. Nunzi, and N. Pfeffer, *Chem. Phys. Lett.*, **192**, 566 (1992).
  8. K. Kubota, H. Urabe, Y. Tominaga, and S. Fujime, *Macromolecules*, **17**, 2096 (1984).
  9. Casting of PCT5 on plates (*e.g.*, Pt-, ITO-, and Teflon-plates) gives good films with good mechanical strength, and preparation of free standing film with good quality is also possible. However, taking CV curve of the film has not been possible due to the high solubility of PCT5 in organic solutions.
  10. M. Onoda, Y. Manda, S. Morita, and K. Yoshino, *Jpn. J. Appl. Phys.*, **31**, 2265 (1992).
  11. Y. Miyazaki, T. Kanbara, K. Osakada, and T. Yamamoto, *Chem. Lett.*, 415 (1993).