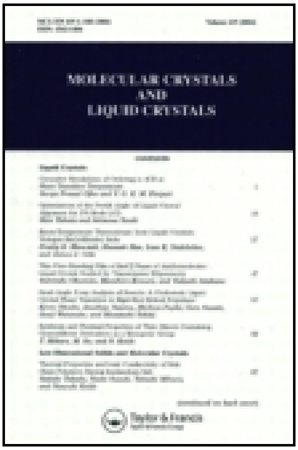

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Synthesis of Novel Ionic Liquid Crystalline Pyrrole Derivatives Having a Viologen Moiety

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A novel liquid crystalline N-substituted pyrrole having an ionic viologen side chain was synthesized, and was polymerized by a $FeCl_3$ method. Thermotropic liquid crystalline behavior of the pyrrole and the polymerized material were investigated by DSC, thermo-controlled polarizing optical microscopy, and XRD. The pyrrole derivatives showed two smectic phases between isotropic and crystalline (solid) phases. Viologen functions of redox and cation-radical generation for the pyrrole derivatives were confirmed by cyclic voltammetry with UV-Vis spectroscopy.

Keywords: N-substituted pyrrole derivatives; ionic liquid crystal; viologen; polymerization

INTRODUCTION

Ionic liquid crystals have been received considerable attention for a novel molecular assembly capable of molecular arrangement by ionic interactions. Viologen, *N,N'*-dialkyl-4,4'-bipyridinium, has been recognized not only as a useful molecule in materials chemistry for its reversible redox and radical generation properties with photosensitivity but also as an ionic liquid crystal [1]. Combination of conjugated

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polymers with the ionic viologen may arise multifunctions such as, a photovoltaic property observed in PPV-viologen system [2] and multiconducting properties participated both electrons and ions, in a highly ordered structure induced by an effective alignment with the strong ionic interactions. So far there is no reports along the line except for our recent attempt on synthesis of liquid crystalline polythiophene having a viologen moiety [3]. Pyrroles have been known as a useful monomer easily polymerized to a conjugated polymer by oxidative manners, but there was no investigations about synthesis and properties of liquid crystalline pyrrole derivatives having a viologen moiety.

Thus, in this report, we synthesized for the first time an *N*-substituted pyrrole having a viologen side chain as an ionic liquid crystalline monomer, and investigated its liquid crystalline property and the polymerization.

EXPERIMENTAL

General

Liquid crystalline behaviors of viologen-pyrrole derivatives were investigated by thermo-controlled polarizing microscopy (POM), DSC and XRD. Redox behaviors of the viologen moiety were investigated by cyclic voltammetry with Pt plates as the working and counter electrodes, a saturated calomel electrode (SCE) as the reference electrode in DMF containing tetrabutylammonium perchlorate (TBAP) and tetraethyl ammonium tosylate (TEAT) as the supporting electrolyte under Ar.

Synthesis of *N*-substituted pyrrol derivatives having a viologen side chain

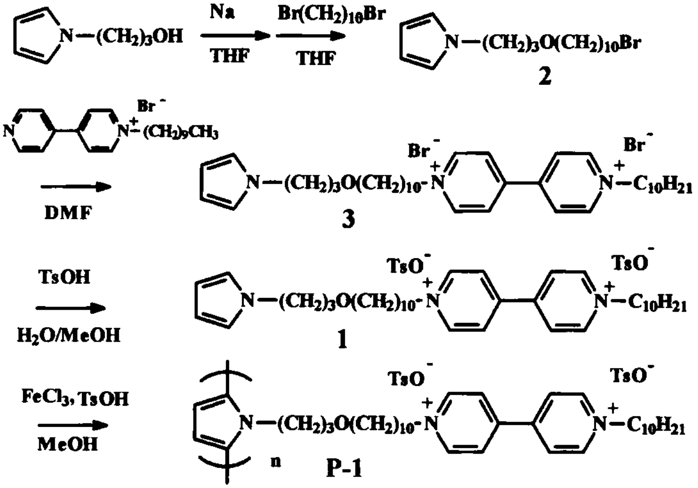
Synthesis of monomer **1** was carried out according to a route summarized in Scheme 1. First, a THF solution (30 mL) of 3-(1-pyrolyl)propanol (18.4 mmol)[4] reacted with Na (20 mmol) under reflux for 24 h in advance was added dropwise into a solution of 1,10-dibromodecane in THF (13 mL), affording 10-bromodecyl 3-(1-pyrrolyl)propyl ether **2** in 30 % yield.

The ether **2** (4 mmol) was reacted with 1,1'-decyl-4-(4-pyridyl) pyridinium bromide (4.4 mmol) in DMF at 70 °C for 48 h with an addition of small amount of KI, affording a viologen dibromide **3** in 60 % yield.

Ion exchange of **3** with *p*-toluenesulfonic acid (TsOH) gave a pyrrole monomer **1** in a quantitative yield.

Spectral data for **1**: ^{1}H NMR in $CDCl_3$; (δ) in ppm 9.18 (d, 4H, pyridinium-α), 8.78 (d, 4H, pyridinium-β), 7.68 (d, 4H, TsO^--α), 7.09 (d, 4H, TsO^--β), 6.63 (s, 2H, pyrrole-α), 6.12 (s, 2H, pyrrole-β), 4.57 (t, 4H, CH_2-N^+), 4.00(t, 2H, CH_2-N), 3.40 (m, 8H, CH_2-O and CH_2-CH_2N^+), 2.27 (s, 6H, Me of TsO^-), 2.0-1.0 (br, 28H, CH_2), 0.87 (t, 3H, Me); ^{13}C NMR in $CDCl_3$ (ppm): 148.7, 146.2, 143.5, 139. 6, 128.9, 127.3, 125.8, 120.5, 107.9, 71.1, 67.1, 62.0, 46.3, 31.9, 31.6, 29.8, 29.5, 29.4, 29.3, 26.2, 26.1, 22.7, 21.3, 14.1; IR (KBr); 1642 ($\nu_{C=N}$), 1213,1167, 1034 (ν_{SO2}), 1120 ($\nu_{C\text{-}O\text{-}C}$) cm^{-1}.

Pyrrole monomer **1** (0.7 mmol) was polymerized with $FeCl_3$ (1.4 mmol) in MeOH (22 mL) containing TsOH (2.1 mmol) at 40 °C for 12 h. After the reaction, most of the solvent was evaporated. The concentrated solution was poured into water containing TsOH, affording a product (**P-1**) as a powdery precipitate. A soluble part of the product was purified by the precipitation procedure.

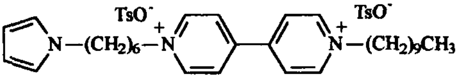


SCHEME 1

RESULTS AND DISCUSSION

Synthesis of liquid crystalline pyrrole monomer having an ionic viologen side chain

Choice of an appropriate length of spacer, terminal group, and counter ion of viologen is quite important for synthesis of ionic liquid crystalline pyrrole monomers having the viologen moiety. Since polymeric viologens having a spacer longer than decamethylene and a counter ion of tosylate have realized a stable liquid crystalline property [5], these spacers and the counter anion were used for the synthesis. Moreover, a viologen substituent is introduced at the *N*-position of pyrrole as an initial work of this studies, because *N*-substituted pyrroles can be easily prepared. Firstly we synthesized a pyrrole having a viologen moiety with hexamethylene spacer, decyl terminal group, and tosylate counter anions as shown below. However, this compound did not show any liquid crystalline behaviors, although *N*,*N*'-didecylviologen ditosylate had a stable smectic phases with a good fan-shaped texture [3]. Thus, a longer spacer than the hexamethylene is considered to be introduced into the pyrrole. According to the Scheme 1, pyrrole monomer **1** was successfully synthesized.



Thermotropic liquid crystalline behavior of 1

The pyrrole **1** shows enantiotropic liquid crystalline phases. In a cooling process from an isotropic temperature (> 210 °C), a mesophase showing a fan-shaped texture appears at 190 °C, and succesively another mesophase showing a striped fan-shaped texture appear at 140 °C. The POM textures are shown in Figure 1, respectively.

Phase transition temperatures of **1** were determined by DSC and POM observations. The DSC thermograms are shown in Figure 2. From the textures and enthalpy changes (ΔH= 7-10 kJ/mol) of a phase transition between two mesophases, the mesophases are assigned to be smectic. Further, XRD patterns shown in Figure 3 suggest that the mesophese observed in the higher temperature range is smectic A with a layer distance of 26 Å, and another is a highly ordered smectic

FIGURE 1 Polarizing optical micrographs of **1** at 170 °C (A) and at 144 °C (B).
See Color Plate XXXI at the back of this issue.

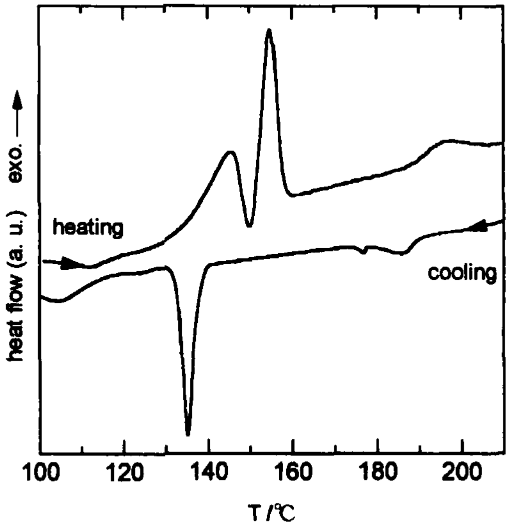


FIGURE 2 DSC thermograms of 1

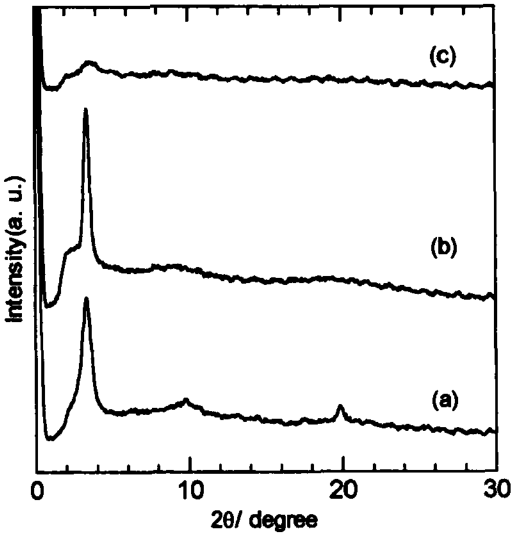


FIGURE 3 XRD patterns of 1 at r. t. (a), 150 °C (b) and 190 °C

phase. The observed layer distance shorter than an estimated molecular length (about 35-40 Å) suggests that **1** takes an intricate smectic order [1, 3].

$$C \underset{110}{\overset{130}{\rightleftharpoons}} S_X \underset{140}{\overset{150}{\rightleftharpoons}} S_A \underset{190}{\overset{195}{\rightleftharpoons}} I$$

Polymerization of 1 by $FeCl_3$

Oxidative polymerization of **1** was attempted by $FeCl_3$. UV-Vis absorption spectrum of the polymerized sample **P-1** shows a new absorption band with λ_{max} of 464 nm (Figure 4), which may be due to a π-π^* transition of conjugated main chain of polypyrrole. In POM observations, **P-1** has mesophases but the textures are polygonal. Phase transition temperatures and XRD patterns were similar to those of monomer. Since other supporting data for the polymerization is not observed for NMR and IR, **P-1** may be an oligomer. The large ionic substituent may disturb the polymerization.

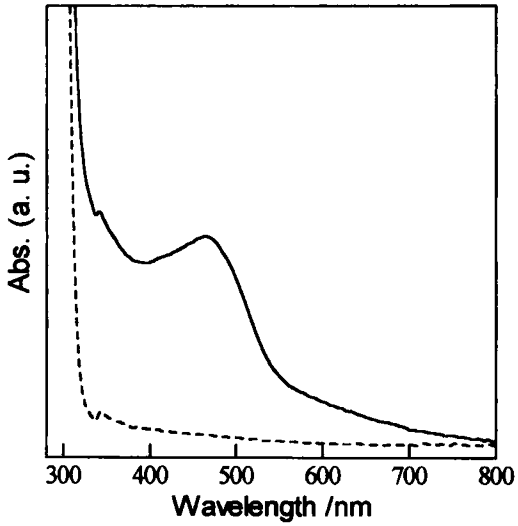


FIGURE 4 UV-Vis spectra of **1** (----) and **P-1** (——) in MeOH

Redox properties

Redox properties were investigated by cyclic voltammetry in DMF containing TBAP. Both **1** and **P-1** showed two reversible redox waves (E_1= –0.4, E_2 =–0.79 V for **1** and E_1= –0.77, E_2= –1.19 V for **P-1**) in a cathodic region. When the supporting electrolyte is replaced to TEAT, the redox potentials are anodically shifted. The shift induces spontaneous one-electron reduction of the viologen moiety that is confirmed by blue coloration of the solution. These results suggest that **1** and **P1** have intrinsic properties of viologen such as an electron-transfer mediator. In case of **P-1**, redox potentials were cathodically shifted. These behaviors are similar to those of the polythiophene-viologen system[4].

CONCLUSION

We synthesized, for the first time, a liquid crystalline *N*-substituted pyrrole having an ionic viologen side chain, which should be polymerized by an appropriate manner. The pyrrole exhibited stable enantiotropic smectic phases. The appearance of the liquid crystalline properties with other preliminary results must open a way for materials applications.

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