Synthesis of a Novel Ionic Liquid Crystalline Polythiophene Having Viologen Side Chain

Masashi Kijima,* Kenichi Setoh, and Hideki Shirakawa
Institute of Materials Science, University of Tsukuba, Tsukuba, Ibaraki 305-8573

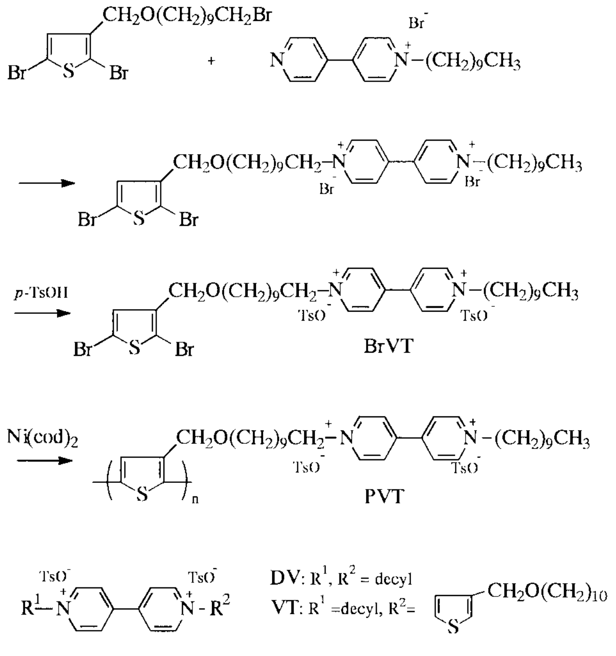
(Received May 17, 2000; CL-000482)

A novel polythiophene having an ionic viologen mesogenic side chain at the 3-position was synthesized from a 2,5-dibromothiophene derivative by dehalogenative polycondensation using Ni(cod)$_2$. Redox function of the viologen moiety in the polymer was confirmed by cyclic voltammetry. The polymer showed liquid crystalline, electrical conductive and photoelectrical properties.

Recent great advance of optoelectronic devices fabricated with conjugated polymers has been received considerable attention in the field of functional polymer materials with non-linear optical, photosensitive and light emitting properties. On making devices, an alignment of conjugated main chain of the polymers may furnish novel functions such as polarized electroluminescence[1] due to a strengthening of intrinsic electrical and optical properties. Along this purpose, we have synthesized[2,3] thermotropic liquid crystalline conjugated polymers whose conjugated main chain can be aligned by appropriate manners. Viologen, *N*,*N*'-dialkyl-4,4'-bipyridinium, has been recognized as a useful molecule in material chemistry for its electrochromic, photochromic, radical generation, and reversible electron transport properties. Recently, viologen was found to exhibit liquid crystalline properties.[4,5] Since intermolecular ionic force in viologen assembly is greater than van der Waals interaction in common liquid crystals, introduction of a mesogenic viologen side chain into conjugated polymers may attain effective alignment of the rigid polymers via formation of a liquid crystalline state. Furthermore combination of conjugated polymer systems with the viologen moiety must promote multifunctions such as photovoltaic property observed in viologen doped poly(*p*-phenylene vinylene).[6] So far synthesis of conjugated polymers having viologen moieties is succeeded only as immobilized thin films on electrode in the field of electrochemistry.[7]

Thus we report in this paper for the first time synthesis of a soluble and fusible polythiophene having a viologen side chain and its basic properties.

Synthetic route of a polythiophene having viologen side chain at the 3-position (PVT) and chemical structure of related viologens are shown in Scheme 1. Dibromothiophene monomer (BrVT) was prepared by reaction of 2,5-dibromo-3-(2-oxa-12-bromodecyl)thiophene[8] with equimolar of 1-decyl-4-(4-pyridyl)pyridinium bromide in DMF at 70 °C for 24 h and successive work up of ion exchange from EtOH–H$_2$O containing excess *p*-toluenesulfonic acid (TsOH). PVT was synthesized from BrVT by dehalogenative polycondensation using Ni(cod)$_2$[9] in DMF at 70 °C for 12 h. The product well soluble in MeOH was purified by reprecipitation from MeOH–aq TsOH solution and washing with H$_2$O and ether, respectively, for several times, affording pure PVT as a brown solid. Alternatively, *N*,*N*'-didecyl-4,4'-bipyridinium ditosylate (DV) and *N*-decyl-*N*'-(10-(3-thienylmethoxy)decyl)-4,4'-bipyridinium ditosylate (VT) were similarly prepared as reference models for PVT.



Scheme 1.

Presence of TsO$^-$ and the bipyridinium structure in PVT was confirmed from typical ^{1}H NMR signals at 9.12, 8.53 (bpy$^+$) and 7.56, 7.10 (TsO$^-$) ppm and IR absorptions at 1639 ($\nu_{C=N}$) and 1191, 1036 (ν_{SO_2}) cm^{-1}. Other ^{1}H NMR signals and IR peaks were satisfactory to identify the chemical structure of PVT.[10] The polymerization was suggested[11] from a newly appeared UV–Vis absorption band around 350 nm due to π–π* transition of conjugated main chain of PVT as shown in Figure 1. From an absorption edge of a casting film, HOMO–LUMO gap of PVT was estimated[12] to be 2.2 eV, which was somewhat larger than those of polythiophenes.[13]

Redox function of the viologen moiety in PVT was confirmed by cyclic voltammetry. All of DV, VT, and PVT in DMF containing 0.1 mol dm^{-3} of tetrabutylammonium perchlorate (TBAP) as an electrolyte showed typical two reversible redox waves: DV, –0.23 (E$_1$), –0.69 (E$_2$); VT, –0.22 (E$_1$), –0.62 (E$_2$); PVT, –0.21 (E$_1$), –0.61 (E$_2$) V (vs SCE), respectively, comparable for usual viologens.[14] When tetraethylammonium tosylate (TEAT) was used as an electrolyte in place of TBAP, the redox potentials were anodically shifted: DV, 0.20 (E$_1$), –0.11 (E$_2$); VT, 0.21 (E$_1$), –0.17 (E$_2$); and PVT, 0.16 (E$_1$), –0.23 (E$_2$). The anodic shift led to spontaneous one-electron reduction (E$_1$) when the viologens were only dissolved in the DMF–TEAT solution. The one-electron reduction resulted in generation of a viologen cation radical that was confirmed by

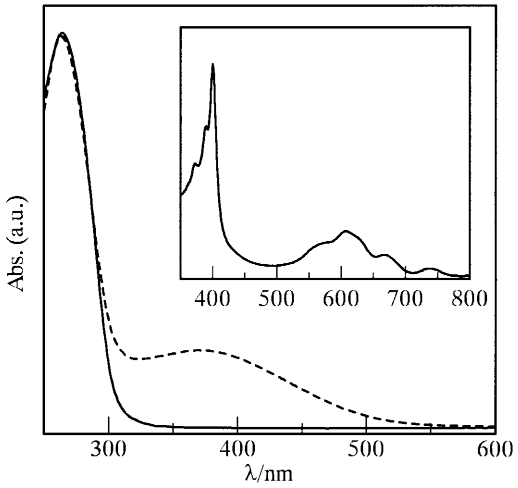


Figure 1. UV-Vis absorption spectra of TV (———) , PTV (-------) in MeOH, and PTV in DMF containing TEAT (inset).

blue coloration. An absorption spectrum of the PVT solution is shown in Figure 1 (inset). The typical two absorption bands with λ_{max} at 401 and 607 nm similar to those of DV and VT correspond the formation of viologen cation radical.[15] These results suggest that the viologen moiety of PVT remain the intrinsic function after the polymerization process.

Thermotropic liquid crystalline behavior of PVT was compared with those of DV, VT and BrVT using thermo-controlled polarizing optical microscopy (POM) and differential scanning calorimetry (DSC). In case of VT, a mesophase appeared between an isotropic liquid phase (> 205 °C) and a higher-ordered smectic phase (< 140 °C). Similar enantiotropic phase-transitions were observed for DV and BrVT.[16] It is noteworthy that the observation of the liquid crystalline phase for BrVT is in contrast to the results that 2,5-dibromo thiophene and pyrrole monomers having a non-ionic mesogenic side chain prepared so far never exhibit liquid crystalline phases.[3,8] The mesophase was assigned as smectic A (S_A) from a fan-shaped texture observed by POM and an X-ray diffraction (XRD) pattern typical of S_A with an intense peak suggesting a layer distance of 27 Å. Likewise the molecular arrangement of diphenylviologen suggested previously,[4] VT molecules are assumed to take an intricate S_A ordering. Below 140 °C, a higher-ordered smectic phase showing a striped fan-shaped texture and a complex XRD pattern appeared, that was distinguished from a crystalline state by DSC. In case of PVT, a polygonal texture consisting of very fine domains appeared first in the cooling process from an isotropic liquid state (>160 °C), then it changed to a bâtonnet texture on annealing at 125 °C. Furthermore the texture changed to a striped one by annealing at 90 °C. Although PVT shows the similar tendency to DV, VT and BrVT, a DSC thermogram without apparent peaks, a broad XRD pattern, slow domain formation, and ambiguous phase transitions disable further characterizations. It is thought that presence of the rigid polymer main chain in PVT makes difficult to take the intricate S_A molecular arrangement observed for DV and VT. In addition to the thermotropic liquid crystalline property, PVT exhibited a lyotropic liquid crystalline property in some alcoholic solvents.

Electrical conductivity of PVT in a form of film was measured by four-probe method. Conductivity of the as-prepared sample was an order of 10^{-7} S cm^{-1} that increased to 3.5×10^{-3} S cm^{-1} after saturated doping of I_2. It should be noted that the doping effect is more remarkable than that of polythiophenes having a non-ionic mesogenic side chain.[8] Furthermore, the conductivity of the as-prepared sample was increased about two times by irradiation of visible light (W lamp).

In conclusion, we succeeded to synthesize a polythiophene having an ionic viologen side chain at the 3-position. The polymer was soluble in alcohol and fusible on heating that was appropriate for material processing. The viologen side chain in the polymer functioned not only as a redox moiety but also as an effective mesogenic group for appearance of thermotropic and lyotropic liquid crystalline behaviors. The photosensitivity of PVT may open ways to photoelectrical device applications.

The authors are grateful to the Chemical Analysis Center, University of Tsukuba, for NMR spectral and elemental analyses data.

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10 Analytical data of PVT: ^{1}H NMR (δ in ppm); 9.12(d, 4H); 8.53(d, 4H); 7.56(d, 4H); 7.09(d, 4H); 7.3–6.8(br, 1H); 4.75(m, 4H); 4.35(m, 2H); 3.35(t, 2H); 2.23(s, 6H); 1.93(br, 4H); 1.46(br, 2H); 1.4–0.8 (br, 26H); 0.79(t, 3H). IR (cm^{-1}): 3054, 2926, 2854, 1639, 1448, 1191, 1123, 1036, 1012, 817, 684, 568.

11 P. Bäuerle et al. (in ref 7) reported a similar absorption pattern. Degree of polymerization (*n*) was preliminary estimated to be about 5 from elemental analysis data that must require further investigations; Elemental analysis of PVT: Found: C, 63.5; H, 7.7; N, 3.0 %. Calacd for $(C_{49}H_{66}N_2O_7S_3)_5{\cdot}Br_2$: C, 63.75; H, 7.2; N, 3.0 %.

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16 Phase transition temperatures of DV and BrVT are summarized following: DV: $C{\cdot}160{\cdot}S_x{\cdot}175{\cdot}S_A{\cdot}255{\cdot}I$ (in the heating process), $I{\cdot}210{\cdot}S_A{\cdot}160{\cdot}S_x{\cdot}140{\cdot}C$ (in the cooling process), BrVT: $(C)S_x{\cdot}140{\cdot}S_A{\cdot}220{\cdot}I$ (in the heating process), $I{\cdot}200{\cdot}S_A{\cdot}120{\cdot}S_x(C)$ (in the cooling process), where C, S_x, and I mean crystalline, non-characterized higher-ordered smectic, and isotropic liquid phases, respectively.