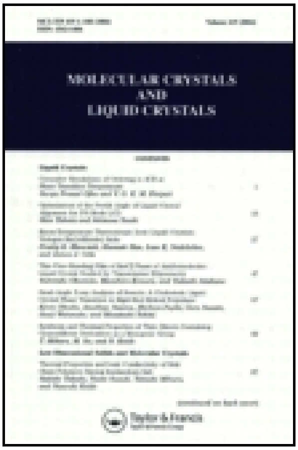

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Synthesis and Physical Properties of Poly(Phenylene Vinylene)s having Oligo(Ethylene Oxide) in the Side Chain

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SYNTHESIS AND PHYSICAL PROPERTIES OF POLY(PHENYLENE VINYLENE)S HAVING OLIGO(ETHYLENE OXIDE) IN THE SIDE CHAIN

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Oligo(ethylene oxide) chains were introduced into the phenyl ring of the poly-(phenylene vinylene) (PPV) derivatives to obtain electronic and ionic conductive liquid crystalline PPV derivatives. Thermal decomposition of all PPV derivatives occurred before isotropic melt. A typical texture of the liquid crystalline phase was not shown but birefringence was observed below the thermal decomposition temperature. Exhibition of a smectic phase for the polymers having triethylene or tetraethylene oxide chains was supported by X-ray measurements. Electronic conductivity of the PPV derivatives doped with I_2 *and ionic conductivity of the mixture of these polymers and* $LiClO_4$ *were also discussed.*

Keywords: electronic conductivity; ionic conductivity; oligo(ethylene oxide); poly(phenylene vinylene); smectic phase

INTRODUCTION

π-Conjugated polymers were extensively investigated because of their various optical and electrical functions in their main chains. In general, most π-conjugated polymers are insoluble in any solvents and infusible. However, it is well-known that the introduction of the substituted group to the side chain of the π-conjugated polymers increases solubility and fusibility of the π-conjugated polymers [1–6].

The conductivity of the π-conjugated polymers is enhanced by controlling the orientation of their polymer backbone. Stretching of the π-conjugated polymer, polymerization under magnetic field or liquid crystal field, etc are carried out to control the orientation of the polymer backbone [7]. The liquid crystalline compound oriented under magnetic field has

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been used for the medium of the acetylene polymerization [8]. The electrical conductivity of the obtained polyacetylene is about $10^4\,\mathrm{Scm}^{-1}$.

On the basis of the improvement of the solubility for polythiophene with the side chain [1–6] and the enhancement of the conductivity for the oriented polyacetylene [8], it can be expected that the conductive liquid crystalline polymers would improve their conductivity, solubility and fusibility based upon the above two aspects. The conductive liquid crystalline polymers were obtained by the introduction of the mesogenic group into the side chain of the π-conjugated polymers. Oh et al. reported that the polyacetylene with a mesogenic group in the side chain itself displays mesomorphic properties [9].

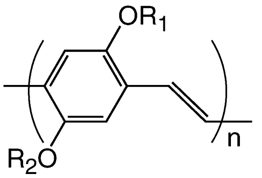
PPV is one of the π-conjugated polymers and is noticed as an optically functional material [10–15]. The backbone of PPV is consisted of phenyl rings and conjugated double bonds and the backbone is a rigid rod core. Consequently, PPV itself would be a candidate of a mesogenic group. If a flexible chain is introduced to the phenyl ring of PPV, the resultant PPV derivatives would produce a liquid crystalline phase. The exhibition of the liquid crystalline phase has the capability of the oriented polymer backbone of the PPV derivatives. The orientation of the polymer backbone would improve optical and electrical properties of the PPV derivatives.

In this study, in order to obtain electronic and ionic conductive liquid crystalline PPV derivatives, flexible oligo(ethylene oxide) (EO) chains were introduced into the phenyl ring of the PPV derivatives, as shown in Figure 1. Thermal, optical and electrical properties of the PPV derivatives were investigated.

EXPERIMENTAL

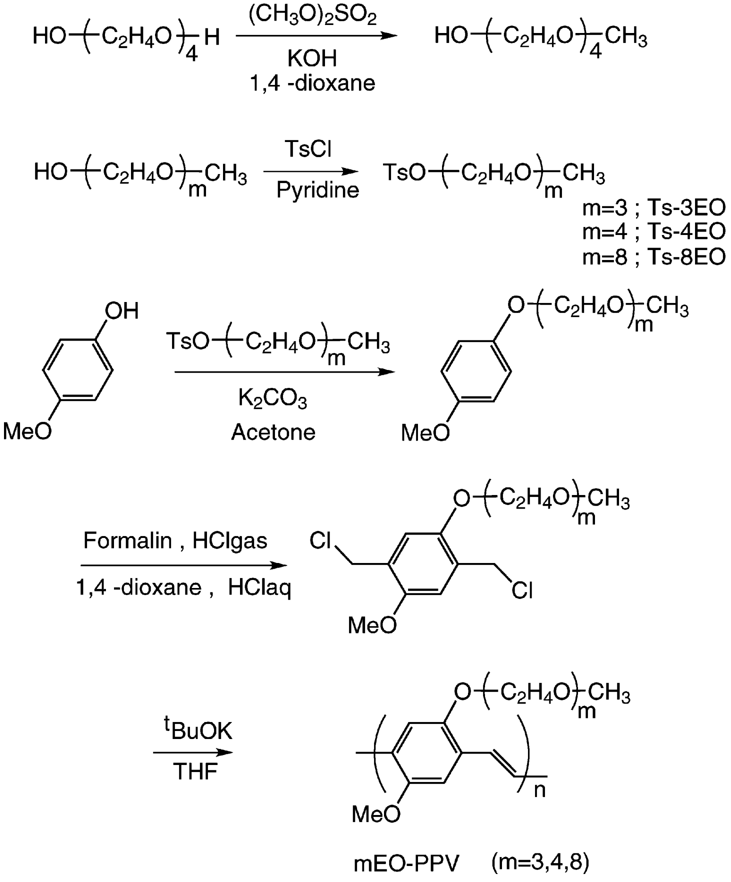
Materials

Synthetic methods of PPV derivatives were summarized in Schemes 1 and 2, respectively. Typical synthetic procedures were described below [10–15].



3EO-PPV : $R_1 = (CH_2CH_2O)_3CH_3$, $R_2 = CH_3$
4EO-PPV : $R_1 = (CH_2CH_2O)_4CH_3$, $R_2 = CH_3$
8EO-PPV : $R_1 = (CH_2CH_2O)_8CH_3$, $R_2 = CH_3$
2,5-3EO-PPV : $R_1 = R_2 = (CH_2CH_2O)_3CH_3$
2,5-4EO-PPV : $R_1 = R_2 = (CH_2CH_2O)_4CH_3$

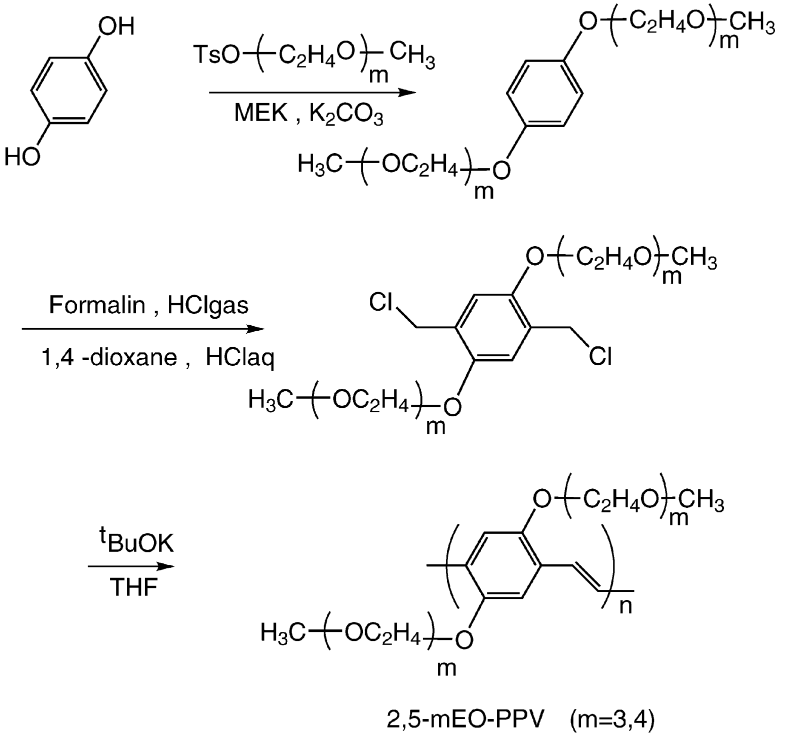
FIGURE 1 Chemical structures of PPV derivatives.



SCHEME 1 Synthesis of mEO-PPV.

Tetraethylene glycol monomethyl ether

Potassium hydroxide (110 g, 1.67 mol) and tetraethylene glycol (325 g, 1.67 mol) were dissolved in a mixed solvent of water (70 ml) and dioxane (300 ml). To the solution was added dimethylsulfate (70 g, 0.56 mol) dropwise over 6 hours at 70°C. The reaction mixture was stirred at 70°C for 10 hours. An aqueous solution of HCl was added to the reaction mixture until the pH value of the resultant mixture became about 7–8. After dioxane and water were evaporated under reduced pressure, precipitate was removed by filtration. The filtrate was extracted with chloroform. The chloroform was evaporated under reduced pressure. The residue was purified by the fractional distillation (1 mmHg, 105°C). The product was obtained in a 42% yield (116 g).



SCHEME 2 Synthesis of 2,5-mEO-PPV.

^{1}H-NMR ($CDCl_3$) δ ppm: 3.38 (s, 3H, OCH_3), 3.45–3.80 (m, 16H, OCH_2).

2-[2-(2-Methoxyethoxy)ethoxy]Ethyl tosylate: Ts-3EO

Triethylene glycol monomethyl ether (123 g, 0.75 mol) was dissolved in pyridine (200 ml). The pyridine solution was cooled to –10°C. P-Toluenesulfonyl chloride (186 g, 0.975 mol) was added to the pyridine solution and then the reaction mixture was stirred for 8 hours. Water was added to the reaction mixture, and then an aqueous solution of HCl was added to the mixture. The mixture was extracted with chloroform. The chloroform solution was washed with water. The chloroform solution was dried over magnesium sulfate. The chloroform was evaporated under reduced pressure. The residue was freeze-dried. The colorless and clear liquid was obtained in 98% yield (233 g).

^{1}H-NMR ($CDCl_3$) δ ppm: 2.44 (s, 3H, CH_3), 3.40 (s, 3H, OCH_3), 3.50–3.80 (m, 10H, OCH_2), 4.16(t, 2H, OCH_2), 7.36(d, 2H, Ar), 7.79(d, 2H, Ar).

Ts-4EO and Ts-8EO

Ts-4EO and Ts-8EO were synthesized by the similar synthetic method to Ts-3EO. Ts-4EO and Ts-8EO were obtained in 92% or 61% yield, respectively.

Ts-4EO: ^{1}H–NMR ($CDCl_3$) δ ppm: 2.50 (s, 3H, CH_3), 3.44 (s, 3H, OCH_3), 3.50–3.80 (m, 14H, OCH_2), 4.16(t, 2H, OCH_2), 7.35(d, 2H, Ar), 7.76 (d, 2H, Ar).

Ts-8EO: ^{1}H-NMR ($CDCl_3$) δ ppm: 2.40 (s, 3H, CH_3), 3.40 (s, 3H, OCH_3), 3.50–3.80 (m, 30H, OCH_2), 4.20(t, 2H, OCH_2), 7.36(d, 2H, Ar), 7.79(d, 2H, Ar).

Methoxy-4-(triethoxymethoxy)benzene

p-Methoxyphenol (25 g, 0.2 mol) was dissolved in acetone (150 ml). A potassium carbonate (83 g, 0.6 mol) was added to the acetone solution, and then the mixture was refluxed for 1 hour. An acetone solution (50 ml) of Ts-3EO (77 g, 0.24 mol) was added dropwise to the mixture. After the reaction mixture was refluxed for 12 hours, the acetone was evaporated under reduced pressure. The residue was extracted with chloroform and the chloroform solution was washed with an aqueous solution of potassium hydroxide. And then the chloroform solution was washed with water. The chloroform solution was dried over magnesium sulfate. The chloroform was evaporated under reduced pressure. The residue was purified by column chromatography (eluent; ethyl acetate: hexane = 1:3). The colorless liquid was obtained in an 86% yield (46 g).

^{1}H-NMR ($CDCl_3$) δ ppm: 3.44 (s, 3H, OCH_3), 3.55 (s, 3H, OCH_3), 3.6–3.9 (m, 10H, OCH_2), 4.08 (t, 2H, OCH_2), 6.8 (q, 4H, Ar).

Methoxy-4-(tetraethoxymethoxy)benzene and methoxy-4-(octaethoxymethoxy)benzene

Methoxy-4-(tetraethoxymethoxy)benzene and methoxy-4-(octaethoxymethoxy)benzene were synthesized similarly. Methoxy-4-(tetraethoxymethoxy)benzene was obtained in a 71% yield (22.5 g). And then methoxy-4-(octaethoxymethoxy)benzene was obtained in a 51% yield. Methoxy-4-(tetraethoxymethoxy)benzene:^{1}H-NMR ($CDCl_3$) δ ppm: 3.45 (s, 3H, OCH_3), 3.57 (s, 3H, OCH_3), 3.6–3.9 (m, 14H, OCH_2), 4.00 (t, 2H, OCH_2), 6.8(q, 4H, Ar).

Methoxy-4-(octaethoxymethoxy)benzene: ^{1}H–NMR ($CDCl_3$) δ ppm: 3.47 (s, 3H, OCH_3), 3.56 (s, 3H, OCH_3), 3.6–3.9 (m, 30H, OCH_2), 4.00 (t, 2H, OCH_2), 6.8(q, 4H, Ar).

1,4-bis(triethoxymethoxy)benzene

Hydroquinone (22 g, 0.2 mol) was dissolved in 2-methylethylketone (MEK, 250 ml) and then potassium carbonate (110 g, 0.8 mol) was added to the MEK solution. The mixture was refluxed for 1 hour and then to the mixture was added dropwise the MEK solution (50 ml) of Ts-3EO (160 g, 0.5 mol). After the reaction mixture was refluxed for 48 hours, MEK was evaporated under reduced pressure. The residue was extracted with chloroform and the chloroform solution was washed with an aqueous solution of potassium hydroxide and water. The chloroform solution was dried over magnesium sulfate. After the chloroform was evaporated under reduced pressure, the residue was purified by column chromatography (eluent; acetone: chloroform = 1:15). The colorless liquid was obtained in a 51% yield (23.5 g).

^{1}H-NMR ($CDCl_3$) δ ppm: 3.40 (s, 6H, OCH_3), 3.5–3.9 (m, 20H, OCH_2), 4.10 (t, 4H, OCH_2), 6.87(s, 4H, Ar).

1,4-Bis(tetraethoxymethoxy)benzene

1,4-Bis(tetraethoxymethoxy)benzene was synthesized similarly. This compound was obtained in an 80% yield.

^{1}H-NMR ($CDCl_3$) δ ppm: 3.40 (s, 6H, OCH_3), 3.5–3.9 (m, 28H, OCH_2), 4.12 (t, 4H, OCH_2), 6.89(s, 4H, Ar).

1,4-Bis(chloromethyl)-2-methoxy-5-(triethoxymethoxy)-benzene

Methoxy-4-(triethoxymethoxy)benzene (27 g, 0.1 mol) was dissolved in dioxane (60 ml). An aqueous solution of formaldehyde (18 ml, 0.22 mol) and an aqueous solution of hydrochloric acid (36 ml, 0.4 mol) were added to the dioxane solution. An excess hydrochloric acid gas was bubbled into the reaction mixture for 5 hours at room temperature. Furthermore after an aqueous solution of formaldehyde (18 ml, 0,22 mol) was added to the reaction mixture, an excess hydrochloric acid gas was bubbled into the reaction mixture for 6 hours. An aqueous solution of sodium hydrogen carbonate was added to the reaction mixture, and then the mixture was extracted with chloroform. The chloroform solution was washed with water and dried over magnesium sulfate. The chloroform was evaporated under reduced pressure. The residue was purified by column chromatography (eluent; ethyl acetate: hexane = 1:2). The colorless liquid was obtained in a 73% yield (27 g).

^{1}H-NMR ($CDCl_3$) δ ppm: 3.40 (s, 3H, OCH_3), 3.5–3.7 (m, 8H, OCH_2), 3.86(m, 5H, OCH_2 and OCH_3), 4.20(t, 2H, OCH_2), 4.69(d, 4H, Cl-CH_2), 6.91(s, 1H, Ar); 6.97(s, 1H, Ar).

IR (nujol) ν-cm^{-1}: 1618 and 1510 (aromatic group), 1215 (Ar-O), 1107 (C-O-C), 849 (C-H, Ar), 729 (C-Cl).

1,4-Bis(chloromethyl)-2-methoxy-5-(tetraethoxymethoxy)-benzene

1,4-Bis(chloromethyl)-2-methoxy-5-(tetraethoxymethoxy)benzene was synthesized similarly. This compound was obtained in a 69% yield.

^{1}H-NMR ($CDCl_3$) δ ppm: 3.39 (s, 3H, OCH_3), 3.5–3.7 (m, 12H, OCH_2), 3.72 (s, 3H, OCH_3), 3.86 (t, 2H, OCH_2), 4.20(t, 2H, OCH_2), 4.70(d, 4H, Cl-CH_2), 6.93(s, 1H, Ar), 6.97(s, 1H, Ar).

IR (nujol) $\nu\,cm^{-1}$: 1618 and 1510 (aromatic group), 1212 (Ar-O), 1112 (C-O-C), 849 (C-H, Ar), 734 (C-Cl).

1,4-Bis(chloromethyl)-2-methoxy-5-(octaethoxymethoxy)-benzene

1,4-Bis(chloromethyl)-2-methoxy-5-(octaethoxymethoxy)benzene was synthesized similarly and this compound was purified by recrystallization from the mixed solvent (ethanol: hexane = 1:3) after purification by column chromatography (eluent; acetone: chloroform = 1:15). This compound was obtained in a 47% yield.

^{1}H-NMR ($CDCl_3$) δ ppm: 3.39 (s, 3H, OCH_3), 3.5–3.7 (m, 28H, OCH_2), 3.89 (m, 5H, $OCH_2$and OCH_3), 4.22 (t, 2H, OCH_2), 4.73 (d, 4H, Cl-CH_2), 6.98(s, 2H, Ar).

IR (nujol) $\nu\,cm^{-1}$: 1597 and 1516 (aromatic group), 1208 (Ar-O), 1112 (C-O-C), 860 (C-H, Ar), 742 (C-Cl).

1,4-Bis(chloromethyl)-2-5-bis(triethoxymethoxy)benzene

This compound was prepared according to the synthetic method of 1,4-Bis (chloromethyl)-2-methoxy-5-(triethoxymethoxy)benzene. This compound was purified by column chromatography (eluent; acetone: chloroform = 1:15). Furthermore this compound was purified by recrystallization from the mixed solvent of ethanol and hexane (ethanol : hexane = 1:3). This compound was a white solid and was obtained in a 59% yield (29.7 g).

^{1}H–NMR ($CDCl_3$) δ ppm: 3.45 (s, 6H, OCH_3), 3.5–3.7 (m, 20H, OCH_2), 4.17 (m, 4H, OCH_2), 4.68 (d, 4H, Cl-CH_2), 6.90 (d, 2H, Ar).

IR (nujol) $\nu\,cm^{-1}$: 1601 and 1526 (aromatic group), 1218 (Ar-O), 1108 (C-O-C), 857 (C-H, Ar), 733 (C-Cl).

1,4-Bis(chloromethyl)-2-5-bis(tetraethoxymethoxy)benzene

1,4-Bis(chloromethyl)-2-5-bis(tetraethoxymethoxy)benzene was prepared according to the synthetic method of 1,4-Bis(chloromethyl)-2-5-bis (triethoxymethoxy)benzene. This compound was obtained in a 48% yield.

^{1}H-NMR ($CDCl_3$) δ ppm: 3.47 (s, 6H, OCH_3), 3.5–3.7 (m, 28H, OCH_2), 4.16 (m, 4H, OCH_2), 4.68 (d, 4H, Cl-CH_2), 6.90 (d, 2H, Ar).

IR (nujol) $\nu\,cm^{-1}$: 1612 and 1521 (aromatic group), 1215 (Ar-O), 1114 (C-O-C), 857 (C-H, Ar), 742 (C-Cl).

Poly [2-methoxy-5-(triethoxymethoxy)-1,4-phenylene-vinylene] : 3EO-PPV

^{t}BuOK (4.2 g, 37.5 mmol) was added to dry tetrahydrofuran (THF, 150 ml) in a dry vessel. THF solution (70 ml) of 1,4-Bis(chloromethyl)-2-

methoxy-5-(triethoxymethoxy)benzene (3.7 g) was added dropwise to the THF solution over 2 hours. After the reaction mixture was stirred for 48 hours at room temperature, THF was evaporated under reduced pressure. The residue was poured into water and then the precipitate was washed with water. The polymer was purified with methanol using Soxhlet extractor. The residue was extracted with chloroform. The chloroform solution was poured into methanol. The red solid was obtained in a 26% (0.75 g).

^{1}H-NMR ($CDCl_3$) δ ppm: 3.42 (s, 6H, OCH_3), 3.5–3.95 (m, 10H, OCH_2), 4.25 (s, 2H, OCH_2), 7.10 (d, 2H, vinyl), 7.49 (s, 2H, Ar).

Poly[2-methoxy-5-(tetraethoxymethoxy)-1,4-phenylenevinylene]: 4EO-PPV

Poly[2-methoxy-5-(tetraethoxymethoxy)-1,4-phenylenevinylene] was prepared according to the synthetic method of poly[2-methoxy-5-(triethoxymethoxy)-1,4-phenylenevinylene]. This polymer was obtained in a 35% yield (1.2 g).

^{1}H-NMR ($CDCl_3$) δ ppm: 3.39 (s, 6H, OCH_3), 3.5–3.85 (m, 14H, OCH_2), 4.25 (s, 2H, OCH_2), 7.13 (d, 2H, vinyl), 7.50 (s, 2H, Ar).

Poly[2-methoxy-5-(octaethoxymethoxy)-1,4-phenylenevinylene]: 8EO-PPV

Poly[2-methoxy-5-(octaethoxymethoxy)-1,4-phenylenevinylene] was prepared according to the synthetic method of poly[2-methoxy-5-(triethoxymethoxy)-1,4-phenylenevinylene]. This polymer was obtained in a 47% yield (2.4 g).

^{1}H-NMR ($CDCl_3$) δ ppm: 3.37 (s, 3H, OCH_3), 3.45–3.95 (m, 33H, OCH_2 and OCH_3), 4.21 (s, 2H, OCH_2), 7.19 (d, 2H, vinyl), 7.45 (s, 2H, Ar).

Poly[2-5-(triethoxymethoxy)-1,4-phenylenevinylene]: 2,5-3EO-PPV

Poly[2-5-(triethoxymethoxy)-1,4-phenylenevinylene] was prepared according to the synthetic method of poly[2-methoxy-5-(triethoxymethoxy)-1,4-phenylenevinylene]. This polymer was obtained in a 19% yield (0.82 g).

^{1}H-NMR ($CDCl_3$) δ ppm: 3.40 (s, 6H, OCH_3), 3.45–3.95 (m, 20H, OCH_2), 4.19 (s, 4H, OCH_2), 7.19 (d, 2H, vinyl), 7.38 (s, 2H, Ar).

Poly[2-5-(tetraethoxymethoxy)-1,4-phenylenevinylene]: 2,5-4EO-PPV

Poly[2-5-(tetraethoxymethoxy)-1,4-phenylenevinylene] was prepared according to the synthetic method of poly[2-methoxy-5-(triethoxymethoxy)-1,4-phenylenevinylene]. This polymer was obtained in a 12% yield (0.64 g).

^{1}H-NMR ($CDCl_3$) δ ppm: 3.40 (s, 6H, OCH_3), 3.45–3.95 (m, 28H, OCH_2), 4.10 (s, 4H, OCH_2), 7.14 (d, 2H, vinyl), 7.45(s, 2H, Ar).

Characterization

^{1}H-NMR was carried out with a JEOL JNM-LA 500 spectrometer using $CDCl_3$ as the solvent. Infrared spectra were recorded on a JEOL JIR 7000 spectrometer. IR Spectra were collected at 4 cm^{-1} resolution. DSC measurements were conducted with a Mettler DSC821^e. Optical microscopy was performed on a Nikon polarizing optical microscope, OPTI-PHOTO-POL, equipped with a Mettler FP80 controller and a FP82 hot stage. Thermal properties of synthesized materials were investigated by optical microscopy and DSC measurements. X-ray diffraction patterns were recorded with a RIGAKU RINT 2500 series with Ni-filtered CuKα radiation. The sample in quartz capillary (diameter 1 mm) was held in a temperature-controlled cell (RIGAKU LC high-temperature controller). Gel permeation chromatography (GPC) was carried out with a Tosoh HLC-8020 instrument using chloroform as the eluent, equipped with four columns (TSK gel G4000H$_{HR}$, G3000H$_{HR}$, G2000H$_{HR}$ and G2000H$_{HR}$). The electrical conductivity was measured with a Mitsubishikagaku Loresta HP (MCP-T410) electrometer using four-probe (Mitsubishikagaku MCP-TP06P) technique. The ionic conductivity of the mixtures was measured with a.c. impedance/gain-phase analyzer SI1260) over the frequency range 10^2–10^7Hz at temperature ranges 30–160°C. Sample temperature was controlled using a Mettler FP80 controller and a FP82 hot stage. UV-vis spectroscopy measurements were carried out with a HITACHI U-3410 spectrophotometer. Fluorescence spectroscopy measurements were carried out with a HITACHI F-4500 equipped with an optical fiber.

RESULTS AND DISCUSSION

The color of these PPV derivatives was red. These PPV derivatives were soluble in organic solvents, such as CH_2Cl_2, $CHCl_3$ and THF, etc. Thermal properties of the PPV derivatives were investigated by polarized optical microscopy, and DSC measurements. Phase structures of the PPV derivatives were examined by X-ray measurements. Thermal properties, molecular weight and polydispersity for the PPV derivatives were summarized in Table 1.

In DSC curves of all the PPV derivatives, both a remarkable glass transition and a peak cannot be detected. Thermal decomposition occurred for all the PPV derivatives before they become the isotropic melt. However, birefringence was observed for the PPV derivatives. We considered that

TABLE 1 Thermal Properties of PPV Derivatives

Polymers	Phase transition temperatures/°C	Number-average molecular weight ($\overline{\mathrm{Mn}}$)	$\overline{\mathrm{Mw}}/\overline{\mathrm{Mn}}$
3EO-PPV	M $\xrightarrow{270}$ decomp.	5700	2.6
4EO-PPV	M $\xrightarrow{250}$ decomp.	6200	3.6
8EO-PPV	M $\xrightarrow{235}$ decomp.	9900	1.9
2,5-3EO-PPV	Sm $\xrightarrow{215}$ decomp.	19000	4.5
2,5-4EO-PPV	Sm $\xrightarrow{200}$ decomp.	11000	5.4

M; mesophase, Sm; smectic phase, decomp.; thermal decomposition.

glass transition temperatures of the PPV derivatives would be lower than the starting temperature (−50°C) in DSC measurements. The flexible side chains of PPV derivatives would be in a liquid-like state. We could not detect glass transition temperatures of these PPV derivatives by DSC measurements.

X-ray measurements of the PPV derivatives were carried out to clarify the phase structure of them. A small peak in the small-angle region and a broad peak in the wide-angle region were observed for 3EO-PPV, 4EO-PPV and 8EO-PPV that have one oligo EO chain per benzene ring in the polymer backbone. These X-ray patterns supported that these PPV derivatives would exhibit some kinds of mesophases, however we could not observe clear optical textures of these PPV derivatives. Therefore we considered that these PPV derivatives exhibited a mesophase.

Figure 2 showed the X-ray patterns of 2,5-3EO-PPV. Similar X-ray patterns were also observed for 2, 5-4EO-PPV. These PPV derivatives have two oligo EO chains per benzene ring in the polymer backbone. A sharp peak in the small-angle region and a broad peak in the wide-angle region were observed in the X-ray patterns of 2, 5-3EO-PPV. These results indicated that these PPV derivatives exhibited a layer structure like a smectic phase. The d-spacing due to the sharp peak in the small-angle region was about 21 Å for 2, 5-3EO-PPV, while the calculated length of side chain for 2,5-3EO-PPV was about 12 Å. A possible mesomorphic structure model of 2, 5-3EO-PPV was shown in Figure 2.

The mixtures of the poly(ethylene oxide) (PEO) derivatives and alkali metal salts are intensively investigated for the ionic conductive material. Furthermore new functional materials would be generated by combination of ionic conductive properties and optical properties based upon π-conjugated polymers. One of the new typical functional properties would be the polymer light-emitting electrochemical cells (LEC) composed of the mixture of PPV derivative, PEO and lithium trifluoromethanesulfonate

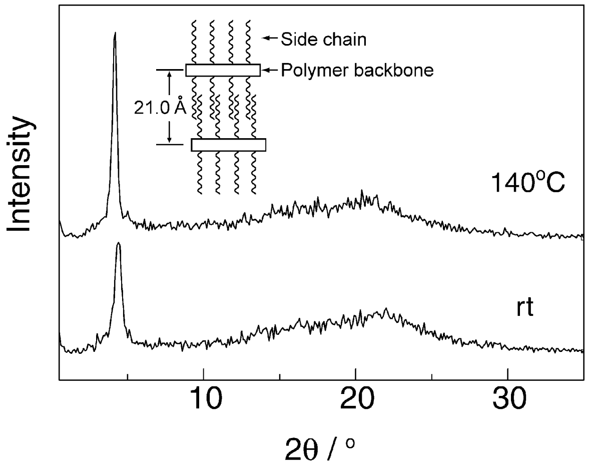


FIGURE 2 X-ray patterns of 2,5-3EO-PPV.

[16]. We expect that ionic conductivity would be enhanced in the liquid crystalline state in which ionic conductive path would be generated.

We prepared the various mixtures of $LiClO_4$ and PPV derivatives. Glass transition temperature of the mixtures was detected by DSC measurements. Glass transition temperatures of the mixtures were determined based on the shift of the baseline of DSC curves. Glass transition temperatures increased with increasing fraction of $LiClO_4$ in the mixtures as shown in Table 2. Increase in glass transition temperatures would be based upon the formation of the complex of lithium ion and oxygen atom in the EO chain. In general, glass transition temperatures are related to the

TABLE 2 Thermal Properties of Mixtures of PPV Derivative and $LiClO_4$

Polymers ($LiClO_4$)	Phase transition temperatures/°C
8EO-PPV(4%)	$\mathrm{g} \xrightarrow{?} \mathrm{M} \xrightarrow{235}$ decomp.
8EO-PPV(7%)	$\mathrm{g} \xrightarrow{?} \mathrm{M} \xrightarrow{235}$ decomp.
8EO-PPV(10%)	$\mathrm{g} \xrightarrow{-25} \mathrm{M} \xrightarrow{235}$ decomp.
8EO-PPV(20%)	$\mathrm{g} \xrightarrow{15} \mathrm{M} \xrightarrow{235}$ decomp.
2,5-3EO-PPV(4%)	$\mathrm{g} \xrightarrow{6} \mathrm{Sm} \xrightarrow{215}$ decomp.
2,5-3EO-PPV(7%)	$\mathrm{g} \xrightarrow{17} \mathrm{Sm} \xrightarrow{215}$ decomp.
2,5-4EO-PPV(4%)	$\mathrm{g} \xrightarrow{13} \mathrm{Sm} \xrightarrow{200}$ decomp.
2,5-4EO-PPV(7%)	$\mathrm{g} \xrightarrow{31} \mathrm{Sm} \xrightarrow{200}$ decomp.
2,5-4EO-PPV(10%)	$\mathrm{g} \xrightarrow{39} \mathrm{Sm} \xrightarrow{200}$ decomp.

g; glassy, M; mesophase, Sm; smectic phase, decomp.; thermal decomposition.

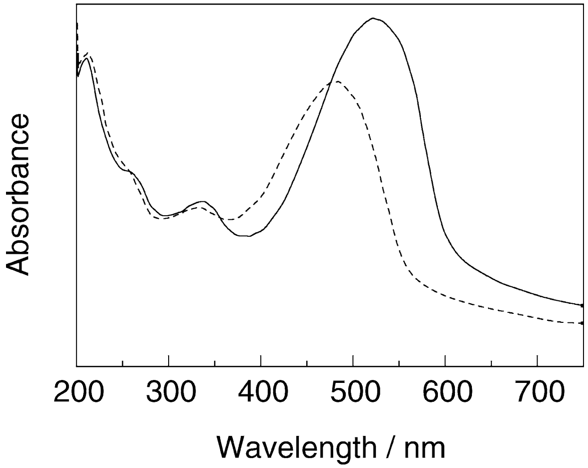


FIGURE 3 UV-vis spectra of 2,5-4EO-PPV: solid line; neat cast film, broken line; annealed film.

micro-Brownian motion of the polymer backbone. However, in our case, glass transition temperatures would be determined by the cooperative phenomenon composed of the motion of the side chain and the micro-Brownian motion of the polymer backbone. The motion of the side chain would be restricted by the formation of the complex of lithium ion and oxygen atom in the EO chain. Glass transition temperatures would increase with adding $LiClO_4$ because the complex would act as a crosslinking point. Increase in glass transition temperatures was observed for the mixtures of 8EO-PPV and $LiClO_4$, however the mixtures of 3EO-PPV or 4EO-PPV and $LiClO_4$ did not show glass transition temperatures. It would not be so easy to form the complex of lithium salt and oxygen atom in the EO chain for 3EO-PPV and 4EO-PPV, because they had the shorter length of the EO chain. At first glance, the motion of the side chain would influence glass transition temperatures of the PPV derivatives, however we considered that the effect of the motion of the side chain on glass transition temperatures would be emphasized apparently compared to that of the micro-Brownian of the polymer backbone, because the addition of $LiClO_4$ mainly influenced the motion of the side chain.

Mesomorphic phase structures of the mixtures were investigated by the X-ray measurements. A smectic phase was observed for 2, 5-3EO-PPV and 2, 5-4EO-PPV, respectively. The d-spacing of the mixtures was almost same as that of each PPV derivative. On the other hand, a typical X-ray pattern for a smectic phase was not observed for the mixtures of lithium salt and the PPV derivative (3EO-PPV, 4EO-PPV or 8EO-PPV).

TABLE 3 π-π^* Absorption Maximum and Band Gap of PPV Derivatives

	π-π^* absorption maximum (λmax)/nm			Band gap/eV	
Polymers	Solution[a]	Film[b]	Annealed film[c]	Film[b]	Annealed film[c]
3EO-PPV	482	545	525	2.00	2.05
4EO-PPV	483	524	508	1.96	2.04
8EO-PPV	488	524	514	2.03	2.10
2,5-3EO-PPV	487	545	507	2.04	2.07
2,5-4EO-PPV	484	522	482	2.03	2.17

[a] chloroform solution, [b] cast film, [c] measured after annealing.

Figure 3 showed UV spectra for the cast and annealed film of 2, 5-4EO-PPV. The wavelength of the π-π^* absorption peak and the band gap of PPV derivatives were summarized in Table 3. The values of the band gap were calculated from the wavelength of the edge of the maximal absorption peak. In the case of the chloroform solution of the PPV derivatives, the π-π^* absorption peaks were observed near 485 nm, while the π-π^* absorption peaks were shown about 520–545 nm for the cast films of the PPV derivatives. Annealing of the cast film of the PPV derivatives resulted in the blue shift of the absorption peak. This result indicated that the planarity of the polymer backbone would decrease by annealing. The value of the band gap slightly increased with annealing. These results also indicated that the planarity of the polymer backbone would decrease by annealing.

Figure 4 displayed a fluorescence spectrum of the chloroform solution of 8EO-PPV. The wavelength of the maximum emission peak for the PPV

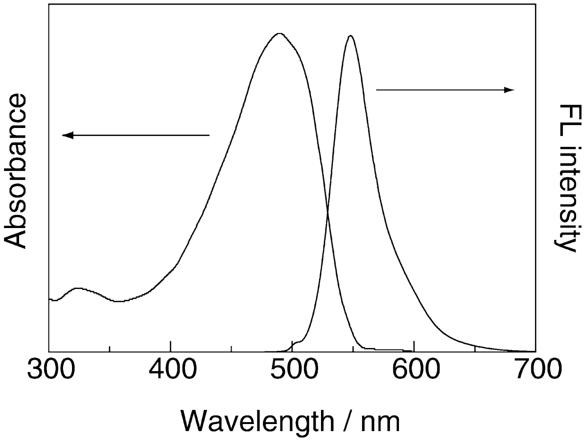


FIGURE 4 Fluorescence spectrum of 2,5-4EO-PPV in chloroform solution.

TABLE 4 Emission Maxima of PPV Derivatives in Chloroform Solution

Polymers	Emission maxima[a]
3EO-PPV	544
4EO-PPV	546
8EO-PPV	547
2,5-3EO-PPV	545
2,5-4EO-PPV	547

[a] in chloroform solution

derivatives was summarized in Table 4. The maximum emission peak of the fluorescence spectra was detected at about 545 nm for the chloroform solution of the PPV derivatives. On the other hand, the fluorescence spectra were not observed for the cast film of these PPV derivatives.

Quantum yields of the PPV derivatives in chloroform solution were summarized in Table 5. The quantum yields increased with length of the

TABLE 5 Quantum Yields of PPV Derivatives in Chloroform Solution

Polymers	Quantum yields[a]	Quantum yields[b]
3EO-PPV	19	17
4EO-PPV	28	25
8EO-PPV	45	42
2,5-3EO-PPV	21	19
2,5-4EO-PPV	30	28

[a]Rodamine B, [b]Quinine sulfate in 0.1 M H_2SO_4 solution.

TABLE 6 Electrical Conductivity of PPV Derivatives

	Electrical conductivity (S/cm)	
Polymers[a]	Neat[b]	Annealed film[c]
3EO-PPV	2.0×10^{-4}	1.6×10^{-4}
4EO-PPV	3.2×10^{-3}	3.0×10^{-3}
8EO-PPV	5.0×10^{-4}	$<10^{-7}$
2,5-3EO-PPV	8.8×10^{-3}	6.2×10^{-3}
2,5-4EO-PPV	6.0×10^{-4}	7.0×10^{-5}

[a] doped with I_2 vapor, [b]cast film, [c]measured after annealing.

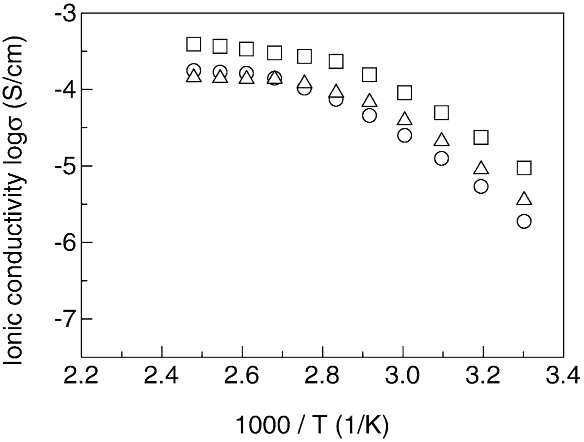


FIGURE 5 Temperature dependence of ionic conductivity for 8EO-PPV: open circle; $LiClO_4$/EO unit = 0.04, open square; $LiClO_4$/EO unit = 0.07, open triangle; $LiClO_4$/EO unit = 0.10.

EO chain. 8EO-PPV showed the largest quantum yield of them. Furthermore the quantum yield of the 2,5-3EO-PPV was larger than that of the 3EO-PPV. The same tendency was observed for the quantum yields of 4EO-PPV and 2,5-4EO-PPV. Therefore the quantum yield was affected by the number and length of the EO chain introduced into the benzene ring in the polymer backbone.

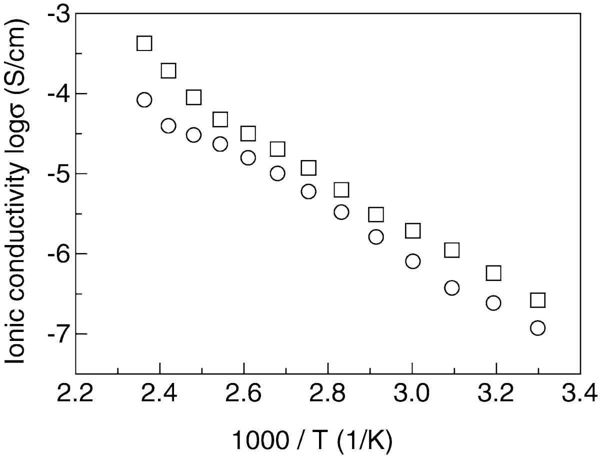


FIGURE 6 Temperature dependence of ionic conductivity for 2,5-3EO-PPV: open circle; $LiClO_4$/EO unit = 0.04, open square; $LiClO_4$/EO unit = 0.07.

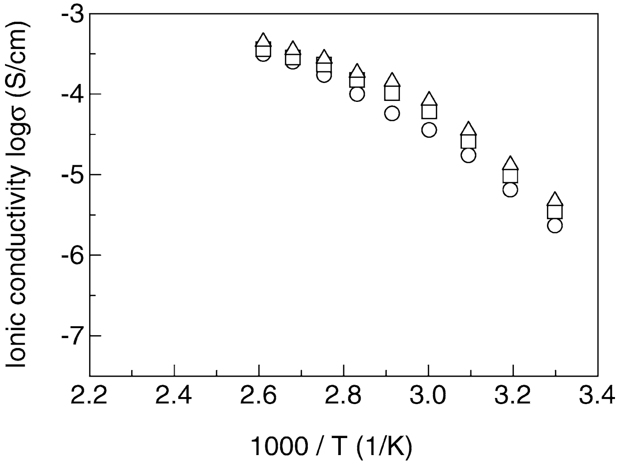


FIGURE 7 Temperature dependence of ionic conductivity for 2,5-4EO-PPV: open circle; $LiClO_4$/EO unit = 0.04, open square; $LiClO_4$/EO unit = 0.07, open triangle; $LiClO_4$/EO unit = 0.10.

Electrical conductivity of the PPV derivatives doped with I_2 vapor was summarized in Table 6. The electrical conductivity of the PPV derivatives was about 10^{-3} - 10^{-4} Scm^{-1}. The electrical conductivity of the PPV derivatives slightly decreased with annealing. These results showed that the annealing resulted in decrease in the planarity of the polymer backbone.

Ionic conductivity of the mixtures of $LiClO_4$ and 3EO-PPV or 4EO-PPV was very low. The low ionic conductivity would originate from the poor solubility of $LiClO_4$ in these PPV derivatives. The solubility of $LiClO_4$ in 8EO-PPV was higher than that in 3EO-PPV or 4EO-PPV. The solubility of $LiClO_4$ was influenced by the length of the EO chain. Thermal dependence of ionic conductivity for the mixture of 8EO-PPV and $LiClO_4$ was shown in Figure 5. The ionic conductivity for the mixture with 7% of salt concentration was higher than that with other concentration. (This salt concentration means mol% of $LiClO_4$ versus EO unit in the PPV derivatives.) In the case of the mixture with 10% of salt concentration, the mobility of ions would decrease due to the crystallization of the salt and decrease in fluidity of the mixture.

Figures 6 and 7 showed temperature dependence of the ionic conductivity for 2,5-3EO-PPV and 2,5-4EO-PPV, respectively. In both cases, large temperature dependence of the ionic conductivity was observed. The ionic conductivity of these PPV derivatives increased with temperature. Then the ionic conductivity of the mixture of PPV derivative and $LiClO_4$ increased with the $LiClO_4$ concentration.

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