4786 *Macromolecules* **2003,** *36,* 4786−4789

Synthesis and Properties of Ion-Conducting Poly(anthrylacetylene) Derivatives

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Received January 10, 2003; Revised Manuscript Received April 28, 2003

ABSTRACT: Poly(anthryacetylenes) bearing oligooxyethylene units were synthesized from 10-ethynyl-9-[3,6-dioxaheptyl]oxycarbonylanthracene (**1**) and 10-ethynyl-9-[3,6,9,12-tetraoxatridecyl]oxycarbonylanthracene (**2**) by using a transition metal catalyst, WCl_6, in 30% and 34% yields, respectively. Both of the polymers were black solids and soluble in chloroform, tetrahydrofuran, acetone, etc., but insoluble in alcohols, aliphatic hydrocarbons, etc. The UV−vis spectra of the polymers showed absorption maxima and band edges at around 570 and 750 nm, respectively, indicating that the polymer chains possess highly extended conjugation. These polymers exhibited blue emission (emission maxima $\approx$470 nm) upon photoexcitation at 380 nm. Poly(**2**) showed a fairly large ionic conductivity (4.1×10^{-5} S/cm) at 80 °C upon doping with $Li(CF_3SO_2)_2N$.

Introduction

Ion-conducting polymers are interesting materials for its potential application in microelectronic devices. Their applications include solid-state batteries, smart windows, components in solid-state sensors, and solid-state transistors.[1,2] Poly(ethylene oxide) is one of the most well-known ion-conducting polymers, but its high crystallinity, which impairs the ionic conductivity unless used at temperature above its melting point, and poor mechanical properties preclude room temperature application.[3] However, several strategies have been developed to overcome these deficiencies, and amorphous polymers containing oxyethylene units have been synthesized. These include formation of block or random copolymers,[4] cross-linked network structures,[5] and the use of comb-branch polymers with oligomeric ethylene oxide side chains,[6] The major role of oxyethylene units in these polymers is to take part in ion transport which is the crucial part in ion-conducting polymers.

Substituted polyacetylenes have attracted much attention as promising functional materials because of their unique properties such as gas permeability, semiconductivity, photoconductivity, photo- and electroluminescence, nonlinear optical properties, etc.[7,8] These properties are based on their molecular architechture featuring stiff and conjugated main-chain structure and various side groups and can be tuned through both the control of main-chain geometric structure and the judicious choice of side groups. Among substituted polyacetylenes, those obtained from monosubstituted acetylenes with condensed aromatic rings are especially interesting from the viewpoint that they provide extended conjugation to show large third-order susceptibility in nonlinear optics along with other properties.[9−11] Incorporation of oligooxyethylene units onto the condensed aromatic rings of substituted acetylenes may lead to the development of novel functional polymers by exerting properties stemming from their ion-conducting and conjugative properties. To our knowledge, there is no report on substituted polyacetylenes containing oxyethylene units. Thus, it is interesting to study the synthesis and properties of substituted polyacetylenes, especially ring-substituted poly(arylacetylenes) having oligooxyethylenes.

In this paper, we report the synthesis of novel poly(anthrylacetylenes) with oligooxyethylene side chains. Properties of the resulting polymers are further discussed.

Experimental Section

General. All the reagents used in monomer synthesis were commercially obtained and used as received. The solvents used in the experiments were purified by the usual methods.

Synthesis of Monomers. *10-Bromo-9-anthracenecarbonyl Chloride* (**a**).[12] Into a suspension of 9,10-dibromoanthracene (50.7 g, 151 mmol) in dry ether (400 mL) was added dropwise a 1.6 M *n*-butyllithium solution in hexane (151 mmol) at −78 °C. After the reaction mixture was stirred for 30 min at −78 °C and then at 0 °C for another 30 min, the suspension was transferred into an excess amount of dry ice (ca. 500 g) and allowed to stand overnight. The resulting lithium salt of 10-bromo-9-anthracenecarboxylic was collected as a solid after removing ether by filtration. The salt was then dispersed in water (500 mL) and acidified with 2 N HCl to precipitate 10-bromo-9-anthracenecarboxylic acid. The resulting carboxylic acid was isolated by filtration and dried under reduced pressure. A chloroform suspension (400 mL) containing 20 g (66.4 mmol) of 10-bromo-9-anthracenecarboxylic acid and thionyl chloride (20 mL) was heated under reflux until the mixture became homogeneous. The solution was concentrated in vacuo to give 21.2 g (yield 100%) of 10-bromo-9-anthracenecarbonyl chloride as a yellow solid. The crude product was used for the following reaction without further purification. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.60−7.77 (m, 4H), 8.02−8.09 (m, 2H), 7.60−7.77 ppm (m, 2H).

10-Bromo-9-[3,6-dioxaheptyl]oxycarbonylanthracene (**b**). To a solution of diethylene glycol monomethyl ether (3.6 g, 30 mmol) and pyridine (4.0 mL, 50 mmol) in dry chloroform (120 mL) was slowly added solid 10-bromo-9-anthracenecarbonyl chloride (8.0 g, 25 mmol) with a spatula at room temperature, and the solution was stirred overnight at ambient temperature

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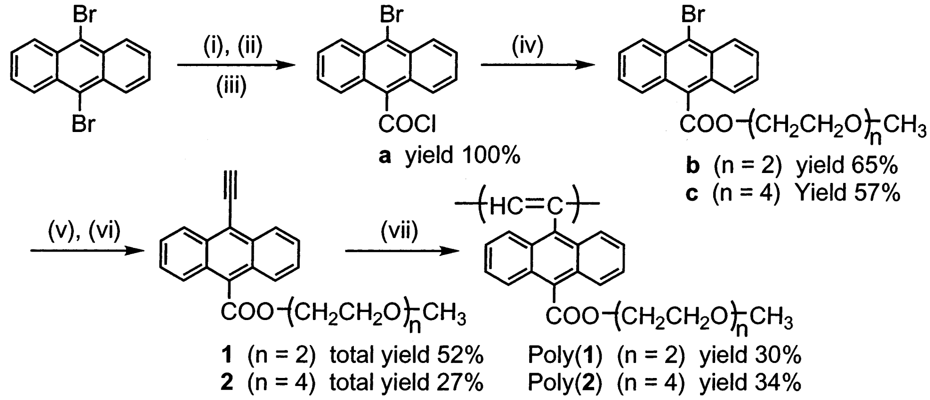
10.1021/ma030019x CCC: $25.00

Scheme 1[a]



[a] (i) BuLi (1 equiv)/Et_2O/−78 °C; (ii) CO_2/H^+; (iii) $SOCl_2/CHCl_3$; (iv) HO−$(CH_2CH_2O)_n$−CH_3/pyridine/$CHCl_3$; (v) (trimethylsilyl)acetylene/Pd/Cu/Et_3N/THF; (vi) n-Bu_4NF/THF; (viii) WCl_6/toluene/80 °C.

in a nitrogen atmosphere. After removing chloroform by evaporation, the residue was extracted with benzene, washed with 2 N HCl followed by water and then with brine, dried over $MgSO_4$, and concentrated to give a crude product. Purification was carried out by SiO_2 column chromatography (hexane/ethyl acetate = 1/1). Yellowish liquid. Yield 65% (6.6 g). ^1H NMR (400 MHz, $CDCl_3$) δ: 3.37 (s, 3H), 3.57 (t, 2H, J = 4.4 Hz), 3.69 (t, 2H, J = 4.4 Hz), 3.92 (t, 2H, J = 4.8 Hz), 4.77 (t, 2H, J = 4.8 Hz), 7.53−7.58 (m, 4H), 8.07 (d, 2H, J = 8.0 Hz), 8.58 ppm (d, 2H, J = 8.0 Hz).

10-Bromo-9-[3,6,9,12-tetraoxatridecyl]oxycarbonylanthracene (**c**). This compound was prepared in the same manner as 10-bromo-9-[3,6-dioxaheptyl]oxycarbonylanthracene. Yellowish liquid. Yield 57%. ^1H NMR (400 MHz, $CDCl_3$) δ: 3.30 (s, 3H), 3.33−3.71 (m, 12H), 3.92 (t, 2H, J = 4.8 Hz), 4.78 (t, 2H, J = 4.8 Hz), 7.52−7.62 (m, 4H), 8.09 (d, 2H, J = 8.0 Hz), 8.58 ppm (d, 2H, J = 8.0 Hz).

10-Ethynyl-9-[3,6-dioxaheptyl]oxycarbonylanthracene (**1**). A dry THF (120 mL) solution containing 10-bromo-9-[3,6-dioxaheptyl]oxycarbonylanthracene (5.8 g, 14.4 mmol), triethylamine (3 mL, 21.5 mmol), (trimethylsilyl)acetylene (4 mL, 28.3 mmol), $PdCl_2(PPh_3)_2$ (330 mg, 0.5 mmol), and CuI (95 mg, 0.5 mmol) was kept stirring at room temperature for 10 days. The Pd catalyst (ca. 200 mg) was added several times during the reaction, and the reaction was monitored using ^1H NMR. After removing the solvent, ether was added to the residue. The resulting mixture was filtered, and the filtrate was washed with water and then with brine, dried over $MgSO_4$, and concentrated to give 10-(2-trimethylsilylethynyl)-9-[3,6-dioxaheptyl]oxycarbonylanthracene. This crude product was dissolved in dry THF (80 mL) and treated with a 1.0 M THF solution of tetrabutylammonium fluoride (17 mL) at 0 °C for 15 min. Ethereal working up of the solution gave **1** as viscous yellow liquid. Purification was carried out by SiO_2 column chromatography (hexane/ethyl acetate = 1/1). The yield of **1** based on **b** was 80%. ^1H NMR (400 MHz, $CDCl_3$) δ: 3.37 (s, 3H), 3.57 (t, 2H, J = 4.4 Hz), 3.69 (t, 2H, J = 4.4 Hz), 3.92 (t, 2H, J = 4.8 Hz), 4.05 (s, 1H), 4.77 (t, 2H, J = 4.8 Hz), 7.53−7.58 (m, 4H), 8.07 (d, 2H, J = 8.0 Hz), 8.58 (d, 2H, J = 8.0 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 58.73, 68.97, 70.22, 71.90, 79.90, 89.60, 125.4, 126.70, 126.80, 126.89, 127.05, 127.68, 129.20, 132.50, 169.10 ppm. IR (KBr): 3285, 3063, 2878, 1724, 1282, 1207, 1140, 1028, 663 cm^{-1}. Mass spectrum (FAB): Calcd for $C_{22}H_{20}O_4$: m/e 348.1360. Found: m/e 348.1362.

10-Ethynyl-9-[3,6,9,12-tetraoxatridecyl]oxycarbonylanthracene (**2**). This compound was prepared using the same procedure as for 10-ethynyl-9-[3,6-dioxaheptyl]oxycarbonylanthracene. Viscous yellow liquid. Yield based on **c**: 48%. ^1H NMR (400 MHz, $CDCl_3$) δ: 3.30 (s, 3H), 3.33−3.71 (m, 12H), 3.92 (t, 2H, J = 4.8 Hz), 4.05 (s, 1H), 4.78 (t, 2H, J = 4.8 Hz), 7.52−7.62 (m, 4H), 8.09 (d, 2H, J = 8.0 Hz), 8.58 ppm (d, 2H, J = 8.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 58.65, 64.67, 68.99, 70.40, 70.49, 70.60, 71.80, 79.80, 89.66, 125.56, 125.89, 126.71, 126.82, 126.87, 127.05, 127.68, 129.30, 132.39, 169.08 ppm. IR (KBr): 3283, 3065, 2876, 1724, 1282, 1207, 1107, 1030, 663 cm^{-1}. Mass spectrum (FAB): Calcd for $C_{26}H_{28}O_6$: m/e 436.4969. Found: m/e 436.4951.

Polymerization. Polymerizations were performed in a Schlenk tube equipped with a three-way stopcock under a nitrogen atmosphere. Unless otherwise specified, the polymerizations were carried out in toluene at 80 °C for 24 h; the initial monomer concentration was 400 mM, and the catalyst concentration was 20 mM. Polymers were collected by repeated precipitation either in methanol or in hexane, and the yields of the polymers were determined by gravimetry.

Polymer Characterization. The molecular weights of polymers were estimated by gel permeation chromatography (GPC) with $CHCl_3$ as an eluent and with polystyrene (PSt) standards. IR spectra, ultraviolet−visible (UV−vis) spectra, emission spectra, and NMR spectra were recorded on a Shimadzu FTIR-8100 spectrophotometer, a Shimadzu UV-2200 spectrophotometer, a JASCO FP-750 spectrophotometer, and a JEOL EX-400 spectrometer, respectively. Thermogravimetric analyses (TGA) were conducted in air on a Perkin-Elmer TGA7 thermal analyzer.

Preparation of Solid Polymer Electrolytes. Lithium bis(trifluoromethanesulfonyl)imide ($Li(CF_3SO_2)_2N$) was used as an electrolyte salt for solid polymer electrolytes. Poly(**1**) and poly(**2**), which had been dried under high vacuum at room temperature for 24 h and stored in a glovebox (VAC, $[O_2] < 1$ ppm, $[H_2O] <1$ ppm), were used as a matrix of the solid polymer electrolytes. A given amount ([lithium]/[ether unit] = 0.08) of $Li(CF_3SO_2)_2N$ and either poly(**1**) or poly(**2**) were dissolved in anhydrous THF to form a homogeneous solution. The mixed solution was cast on a poly(tetrafluoroethylene) (PTFE) plate. The solvent was allowed to slowly evaporate at room temperature in the glovebox for 12 h and then completely removed under high vacuum for 24 h to obtain the polymer electrolyte film.

Ionic Conductivity Measurement. Ionic conductivity was determined by means of the complex impedance measurements, using a computer-controlled Hewlett-Packard 4192A LF impedance analyzer over the frequency range from 5 Hz to 1 MHz The polymer electrolytes film was cut into disks of 13 mm in diameter. The polymer electrolyte films, sandwiched between mirror-finished stainless steel electrodes, were sealed in PTFE containers in the glovebox and were subjected to the complex impedance measurements. The measurements were carried out with heating from 40 to 130 °C, and the samples were thermally equilibrated at each temperature for at least 1.5 h before the measurements.

Results and Discussion

Synthesis of Monomer. Scheme 1 illustrates the synthetic route for the substituted PEO-containing

Table 1. Polymerization of 1 and 2 with WCl_6 (in Toluene, 80 °C, 24 h (48 h for 2); $[M]_0 = 400$ mM, [Cat] = 20 mM)

monomer	yield, %[a]	$M_n \times 10^{-3}$ [b]	M_w/M_n [b]	color	solubility[c]
1	30	33.2	3.2	black	soluble
2	34	4.1	2.1	black	soluble

[a] By the gravimetric method. [b] Measured by GPC (eluent $CHCl_3$, PSt standards). [c] In THF, toluene, $CHCl_3$, DMF, acetone, etc.

anthrylacetylene monomers. The monomers were prepared starting from commercially available 9,10-dibromoanthracene via several steps. 9,10-Dibromoanthracene was transformed into the corresponding monoacid chloride, which was then converted into the bromoester. The Sonogashira coupling of the bromoester with (trimethylsilyl)acetylene followed by desilylation with tetrabutylammonium fluoride gave the monomers **1** and **2** in 52% and 27% total yields, respectively.

Polymerization. Proper selection of catalysts for the polymerization of substituted acetylenes is crucial.[8a,13] For example, W, Mo, and Rh catalysts are suitable for monosubstituted acetylenes, but they are hardly effective in the polymerization of sterically crowded disubstituted acetylenes. On the other hand, Nb and Ta catalysts are effective for the polymerization of disubstituted acetylenes while they induce only cyclotrimerization for monosubstituted acetylenes. Further, among Mo, Rh, and W catalysts, W catalysts are particularly efficient in the polymerization of aromatic monosubstituted acetylenes bearing substituents with large steric hindrance. It has been found in our previous study that the WCl_6 catalyst is the most suitable for the polymerization of anthrylacetylenes.[10b] In this study, therefore, we chose only WCl_6 as a catalyst for the polymerization reactions. The results of the polymerization are shown in Table 1. When polymerized with WCl_6, both of the monomers underwent polymerization smoothly to provide black solids soluble in common organic solvents. The yields of poly(**1**) and poly(**2**) were 30% and 34%, respectively. According to GPC, the number-average molecular weights (M_n) of poly(**1**) and poly(**2**) were 33.2 × 10^3 ($M_w/M_n = 3.2$) and 4.1 × 10^3 ($M_w/M_n = 2.1$), respectively.

Characterization. The characterization of poly(**1**) and poly(**2**) was performed by using IR and NMR spectroscopies. In the IR spectra of monomers **1** and **2**, an absorption peak due to the stretching vibration of C≡C bond was observed at around 2100 cm^{-1}. The stretching and bending vibrations of the ≡C−H group were clearly observed at 3280 and 660 cm^{-1}, respectively, in the IR spectra of both monomers. On the other hand, these signals completely disappeared in the spectra of the polymers. In the ^1H NMR spectra of the polymers, the signals at around 4.1 ppm assigned to the acetylenic proton (≡CH) of the monomers were undetectable. Similarly, the signals at around 80 and 89 ppm due to the acetylenic carbons of the monomers disappeared in the ^{13}C NMR spectra of the polymers. All of these results indicate that opening of the triple bonds of the monomers occurred during the polymerization, and the polymer backbones are composed of alternating double bonds.

Highly stereoregular cis polymers formed from phenylacetylenes in the presence of Rh catalysts are known to show a sharp signal based on the olefinic protons in the main chain around 6−7 ppm in ^1H NMR.[8a,13] On the other hand, the present polymers gave olefinic and aromatic protons as very broad signals in this region. These polymers, thus, do not possess a selective cis structure. A general feature of W catalysts is that it provides trans-rich polymers from acetylenes, suggesting that the present polymers possess trans-rich geometrical structure.

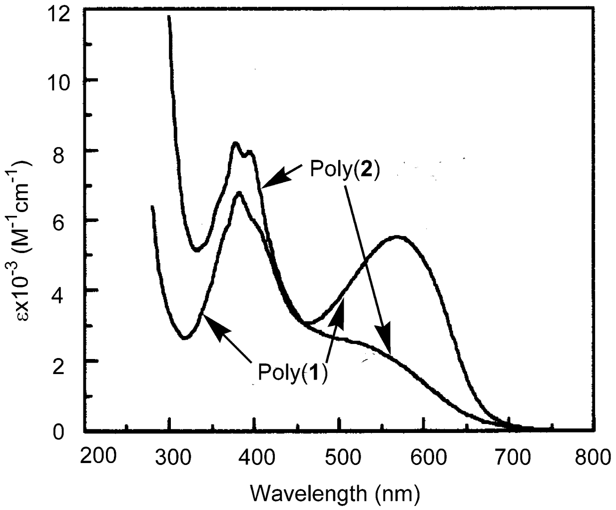


Figure 1. UV−vis spectra of poly(**1**) (1.0×10^{-4} M) and poly(**2**) (5.7×10^{-5} M) in chloroform at room temperature.

Polymer Properties. The obtained polymers did not show glass transition temperatures according to DSC measurements in the range of −30 to 100 °C. These polymers were soluble in common organic solvents such as toluene, acetone, chloroform, tetrahydrofuran (THF), dimethyl sulfoxide (DMSO), and *N*,*N*-dimethyformamide (DMF) but were insoluble in hexane, higher alkanes, and alcohols.

The weight loss of poly(**1**) and poly(**2**) in air started at 327 and 239 °C, respectively, in thermogravimetric analyses (TGA) whereas the onset temperature of weight loss of poly(phenylacetylene) is known to be around 250 °C.[10a] These results suggest that poly(**1**) is superior but poly(**2**) is inferior to poly(phenylacetylene) in thermal stability. The TGA curves of poly(**1**) and poly(**2**) showed inflection points at around 450 and 480 °C, respectively, which are presumably due to the cleavage of pendant ester groups, because the values of percent weight loss agree with those of the pendant molecular weights (ca. 49% and 58%). The reason for lower onset temperature of poly(**2**) than that of poly(**1**) is not clear at this stage; however, since the patterns of the TGA curves are the same, it is reasonable to think that the longer flexible ethylene oxide chain is responsible for it.

The UV−vis spectra of poly(**1**) and poly(**2**) are shown in Figure 1. The absorption bands tailing from 450 to 750 nm can be attributed to the $\pi-\pi^*$ electronic transition associated with the π-conjugated polymer backbones. The peaks below 450 nm are due to the absorption resulting from the electronic transition by the anthryl groups. The absorption maximum of poly(**1**) was found to be at 570 nm ($\epsilon = 5.4 \times 10^3$ M^{-1} cm^{-1}), while poly(**2**) showed an absorption maximum at around 530 nm ($\epsilon = 2.5 \times 10^3$ M^{-1} cm^{-1}). The absorption band edges were observed at around 750 nm for poly(**1**) and 720 nm for poly(**2**), which are quite red-shifted compared with that of poly(phenylacetylene) (band edge ∼ 600 nm) prepared by the same catalyst.[10c] These results suggest that the conjugation lengths of the main chain of the present polymers are extremely extended.[14]

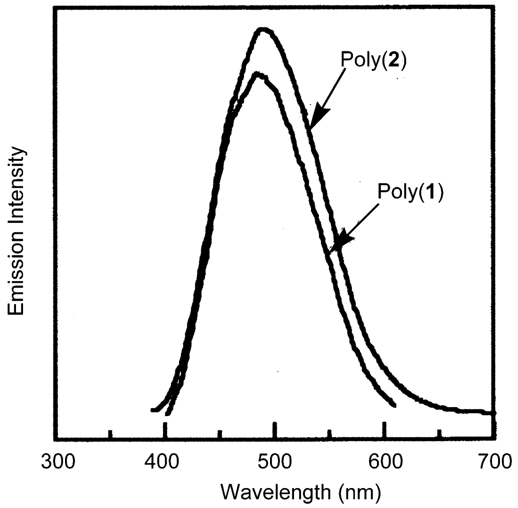


Figure 2. Emission spectra of poly(**1**) (1.0×10^{-4} M) and poly(**2**) (5.7×10^{-5} M) (excited at 380 nm) in chloroform at room temperature.

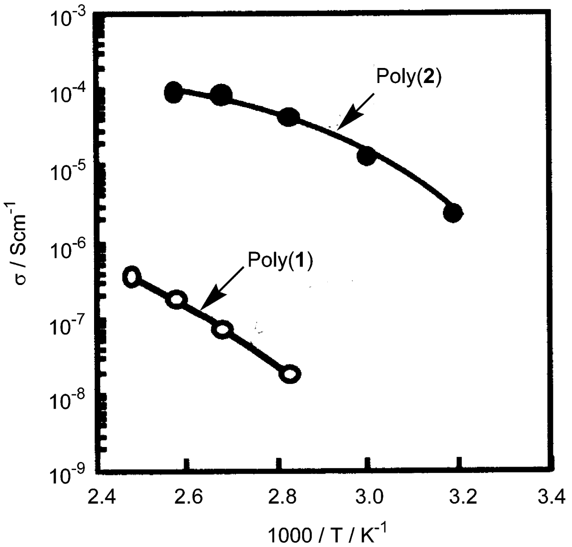


Figure 3. Relationships between reciprocal of temperature and ionic conductivity of poly(**1**) and poly(**2**) ($[LiN(SO_2CF_3)_2]/[O] = 0.08$).

When poly(**1**) was excited at the absorption based on the main-chain chromophore, no emission peak was observed. However, a clear emission peak centering at around 470 nm was detected by photoexciting at 380 nm in chloroform. This emission peak corresponds to a blue color emission which can be recognized with the naked eye (Figure 2). A similar phenomenon but even stronger luminescence was observed with polymer **2** when excited at 380 nm (Figure 2).[14] These emissions are attributable to the excimer between pendants, which indicates that the stacking of pendant anthryl ring is possible.

An interesting feature of the polymers is that they exhibit relatively high ionic conductivity upon doping with $Li(CF_3SO_2)_2N$. Figure 3 shows the relationships between reciprocal of temperature and ionic conductivity of poly(**1**) and poly(**2**) containing $Li(CF_3SO_2)_2N$. Both of the plots of the ionic conductivity exhibited positively convex profiles, as seen in conventional polyether-based polymer electrolytes.[1−6] Poly(**2**) showed much higher ionic conductivity than poly(**1**), reaching 4.1×10^{-5} S/cm at 80 °C. It is clear that four oxyethylene units in the side chain of poly(**2**) are preferable, compared to two oxyethylene units of poly(**1**), in terms of lithium ion solvation as well as their faster molecular motion. The ion-conducting property together with the conjugated structure allowing to exhibit strong fluorescence may open up new applied fields of these polymers.

Conclusion

In the present study, we have demonstrated the first example of the synthesis of polylacetylenes with oligooxyethylene in the side chain. WCl_6 catalyst provided black solid polymers soluble in common organic solvents. The resulting polymers were widely conjugated and exhibited fluorescence that could be recognized with the naked eye. Poly(**2**) showed relatively high ionic conductivity upon doping with $Li(CF_3SO_2)_2N$, reaching 4.1×10^{-5} S/cm at 80 °C.

Acknowledgment. The authors are grateful to Dr. H. Ushitora for the measurement of mass spectra. We acknowledge the financial support by KAWASAKI STEEL 21st Century Foundation for the present study. This work was partly supported by a Grant-in-Aid for Scientific Research on Priority Areas from the Japanese Ministry of Education, Culture, Sports, Science, and Technology.

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(14) UV−vis and emission spectra of the polymers were also taken in THF, but no solvent effect was observed.

MA030019X