Articles

New Soluble Poly(aryleneethynylene)s Consisting of Electron-Accepting Benzothiadiazole Units and Electron-Donating Dialkoxybenzene Units. Synthesis, Molecular Assembly, Orientation on Substrates, and Electrochemical and Optical Properties

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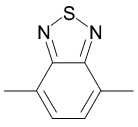
ABSTRACT: A new class of poly(aryleneethynylene)s containing an aryl heterocyclic structure were prepared in the yield of higher than 80% by polycondensation between 4,7-dibromo-2,1,3-benzothiadiazole and 2,5-dialkoxy-1,4-diethynylbenzenes with different long side chains using $Pd(PPh_3)_4$ and CuI as the catalysts in the presence of triethylamine. All these polymers had a number-average molecular weight, M_n, higher than 12 000 and showed good solubility in chloroform. The polymers were photoluminescent in chloroform and showed metallic luster in the solid state. X-ray diffraction patterns of the powder and cast film (on a platinum plate) of the polymers revealed that the polymers assumed a π-stacked structure in the solid state, and the polymer molecules in the film were ordered on the surface of the platinum plate.

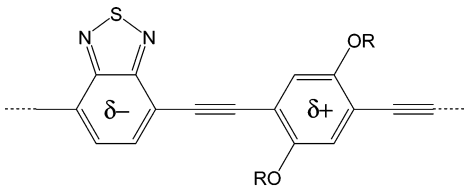
Introduction

Of various π-conjugated polymers, poly(aryleneethynylene)s (PAEs) have received much attention in the past two decades because of theoretical interest and potential applications in electronic and photonic devices.[1] Therefore, a lot of investigations on this kind of polymers containing various aromatic structures in the polymers have been carried out.[1−7] In recent years, the interest in molecular chips and new information storage materials using PAE oligomers has also been drawn.[8] π-Conjugated polymers consisting of aryl heterocyclic units such as pyrrole, pyridine, and thiophene units have been synthesized, and some of them have found industrial use. Among the aryl heterocyclic units, a 2,1,3-benzothiadiazole unit



is a typical electron-accepting unit,[9] and its homopolymer and copolymers have been synthesized; the benzothiadiazole unit[9,10] is useful to tune electronic states of π-conjugated polymers as in the cases of the copolymers with fluorenes, carbazole, and thiophene.[10b,c]

Previously, Bunz's group and our group separately reported synthesis and some properties of a new aryl heterocyclic PAE containing 2,1,3-benzothiadiazole and 2,5-dialkoxy-*p*-phenylene units in communication forms.[10d,11] The new PAE showed a strong tendency to form a stacked and ordered assembly in the solid state, presumably owing to the presence of the electron-accepting 2,1,3-benzothiadiazole unit and electron-donating dialkoxyphenylene unit to give an intermolecular CT (charge transfer) interaction.



PAE-1

Because of the molecular assembly, the polymer showed interesting optical properties. To reveal the chemical properties of PAE-1, we have prepared a series of PAE-1 type polymers by varying the length of the −OR group and investigated their chemical properties. Herein, we report the results.

Experimental Section

Materials. 1,4-Dihexyloxy-2,5-diethynylbenzene (**1a**),[1g,11b] 1,4-didodecyloxy-2,5-diethynylbenzene (**1c**),[3c] and 4,7-dibromo-2,1,3-benzothiadiazole (**2**)[9] were prepared as previously reported. 1,4-Dinonyloxy-2,5-diethynylbenzene (**1b**) and 1,4-dioctadecyloxy-2,5-diethynylbenzene (**1d**) were synthesized analogously. $[Bu_4N]BF_4$ (Bu = butyl) was purified by recrystallizing three times from ethyl acetate and dried over P_2O_5 under vacuum at room temperature for 5 days.

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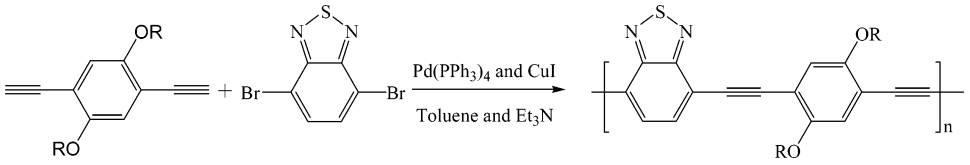
Scheme 1



1a-d **2** **3a-d**

R = *n*-C_6H_{13} (**1a**)
R = *n*-C_9H_{19} (**1b**)
R = *n*-$C_{12}H_{25}$ (**1c**)
R = *n*-$C_{18}H_{37}$ (**1d**)

Yield = 80-87%
*M*n =12600-30000
[η] = 0.42-1.44 dLg^{-1}

Table 1. Synthetic Results and Optical Data of 3a−3d

				UV−vis λ_{max}, nm		PL[e] λ_{EM} (λ_{EX})	
polymer	yield (%)	mol wt[a]	[η],[b] dL g^{-1}	in $CHCl_3$ (log ε)[c]	in film[d]	in $CHCl_3$	in film
3a	87	12 600 (3.4)	0.68	512 (4.52)	564	564 (513)	673 (565)
3b	81	30 000 (5.3)	1.44	514 (4.46)	564	565 (515)	675 (565)
3c	87	18 400 (2.7)	0.78	513 (4.62)	561	565 (516)	673 (565)
3d	80	13 200 (2.9)	0.42	512 (4.42)	560	565 (513)	673 (565)

[a] Number-average molecular weight (M_n) determined by GPC (polystyrene standards). The values in parentheses are polydispersity index (PI = M_w/M_n). [b] The intrinsic viscosity, [η], was measured in $CHCl_3$ at 30 °C. dL = 100 mL. [c] Molar absorption coefficient. Molarity is based on the repeating unit, $C_{16}H_4N_2S(OR)_2$. [d] Cast on a quartz glass plate at room temperature using chloroform as the solvent. [e] Photoluminescent data. Positions of the emission peak, λ_{EM}, and the peak in the excitation spectrum, λ_{EX}, are given.

Polymerization. To a 200 mL Schlenk flask, charged with **2** (388 mg, 1.32 mmol), 1,4-dialkoxy-2,5-diethynylbenzene (**1a**−**d**, 1.32 mmol), $Pd(PPh_3)_4$ (154 mg, 0.133 mmol), and CuI (25 mg, 0.13 mmol), were added triethylamine (50 mL) and toluene (75 mL) under nitrogen. The mixture was stirred for 0.5 h at room temperature and then heated at 60 °C for 5 h. After being cooled to room temperature, the deep red solution was poured into methanol (1 L). The precipitate was separated by filtration and washed with methanol and hexane. After being dissolved in 10 mL of hot chloroform, the polymer solution was poured into 200 mL of cool methanol to reprecipitate the polymer. **3a**−**d** with metal luster were obtained by filtration and drying under vacuum.

Measurements. IR spectra were recorded on a JASCO FT/IR 410 plus spectrophotometer using KBr pellets. ^1H and $^{13}C\{^1H\}$ NMR spectra were obtained with a JEOL P-300 spectrometer (300 MHz). The molecular weight was measured by gel permeation chromatography (GPC) using a Shimadzu LC-9A liquid chromatograph equipped with a UV detector (eluent = chloroform). The data were relative to polystyrene standards. UV−vis absorption spectra were measured with a Shimadzu UV 3000 spectrophotometer. Photoluminescence was measured with a Hitachi model F4010 fluorescence spectrophotometer. X-ray diffraction patterns were recorded with a Rigaku RINT 2000 Ultima +/PC X-ray diffractometer. Thermal stability of the polymers was determined on a Shimadzu TGA-50 thermogravimetric analyzer at a heating rate of 10 °C min^{-1} in nitrogen. The data collection and treatment were carried out on a Shimadzu TA-50WS thermal analyzer. Cyclic voltammograms for the cast polymer films on a platinum plate (1 cm × 1 cm) were obtained in an acetonitrile solution of $[Bu_4N]BF_4$ (0.10 M) under N_2 using (0.10 M $AgNO_3$)/Ag and platinum wire as reference and counter electrodes, respectively. A Solartron S-1260 analyzer was used for the cyclic voltammetry.

Results and Discussion

Synthesis and Characterization of the Polymers. By employing the previously reported method,[11] four polymers were synthesized from 4,7-dibromo-2,1,3-benzothiadiazole and 2,5-dialkoxy-1,4-diethynylbenzenes (see Scheme 1). Yields of the four polymers were higher than 80%, and the number-average molecular weight, M_n, of the polymers determined by GPC vs polystyrene standards ranged from 12 600 to 30 000, as shown in Table 1. The polymer showed an intrinsic viscosity [η] of 0.42−1.44 dL g^{-1}.

All these polymers exhibited golden green luster in the solid state.[10d,11] They were easily soluble in chloroform and exhibited orange-red color. Very thin films of the polymers made by the cast method were semitransparent and flexible and showed the color like copper.

The chemical structure of the polymers was characterized by FTIR, ^1H and $^{13}C\{^1H\}$ NMR, and elemental analysis, and the data of the four polymers are listed in Table 2. The strong ν(C≡CH) peak near 3290 cm^{-1} of the monomers disappeared on the polymerization, and a new ν(C≡C) peak appeared at about 2200 cm^{-1} (cf. the Supporting Information). ^1H NMR data summarized in Table 2 were consistent with the proposed structure of the polymers. Compared with the ^1H NMR peaks of monomers, those of the polymers were broadened and somewhat shifted to a lower magnetic field.

Optical Properties. The chloroform solution of the four polymers was red-orange and gave a strong orange-yellow photoluminescence under the irradiation with long UV light (336 nm). Figure 1 shows the UV−vis spectra of **3a** and **3d** in chloroform and in the solid state. The UV−vis data of **3a**−**3d** are included in Table 1. The UV−vis peak of **3a**−**3d** is shifted by about 160 nm to a longer wavelength from that of **1a**−**1d** due to expansion of the π-conjugation system. Films of the polymers show the UV−vis peak at a considerably longer wavelength than that in chloroform, suggesting the presence of strong intermolecular interaction due to stacking of the polymers in the solid state, similar to the cases of regioregular head-to-tail poly(3-alkylthiophene), HT-P3RTh.[11−14] Stacking of poly(aryleneethynylene)[1f,3c] with a CT structure[2e] was also reported previously, and it caused shift of the UV−vis absorption band of the polymer.

Thicker films of **3a**−**3d** shone like a metallic foil.[10d,11b] The reflection spectrum of **3a** (the dotted curve in Figure

Table 2. Characterization of 3a−3d

			analysis, %[b] calcd (found)				
polymer	IR, cm^{-1}	^1H NMR,[a] δ	C	H	N	S	Br
3a	2924, 2855, 2201, 1214, 1466, 1415	7.66−7.87 (m, 2H) 7.17 (s, 2H) 4.13 (t, 4H) 1.92 (m, 4H) 1.26−1.59 (m, 12H) 0.92 (t, 6H)	70.71 (70.66)	6.54 (6.83)	6.05 (5.81)	6.91 (6.37)	1.12 (1.44)
3b	2922, 2852, 2203, 1216, 1466, 1416	7.56−7.80 (m, 2H) 7.18 (s, 2H) 4.12 (t, 4H) 1.92 (m, 4H) 1.26−1.60 (m, 24H) 0.87 (t, 6H)	72.90 (72.81)	7.77 (7.72)	5.07 (4.92)	5.80 (5.25)	0.48 (0.50)
3c	2922, 2851, 2204, 1217, 1467, 1416	7.56−7.80 (m, 2H) 7.20 (s, 2H) 4.11 (t, 4H) 1.93 (m, 4H) 1.26−1.60 (m, 36H) 0.88 (t, 6H)	74.79 (74.92)	8.58 (8.55)	4.45 (4.29)	5.09 (4.59)	0.62 (0.46)
3d	2921, 2850, 2205, 1218, 1468, 1417	7.56−7.80 (m, 2H) 7.17 (s, 2H) 4.12 (t, 4H) 1.92 (m, 4H) 1.24−1.55 (m, 60H) 0.87 (t, 6H)	76.58 (76.67)	9.75 (9.70)	3.59 (3.34)	4.10 (3.72)	0.98 (0.87)

[a] In $CDCl_3$ at 23 °C. [b] **3a**, calcd for $Br-(C_{28}H_{30}N_2O_2S\cdot 0.6H_2O)_{30}-C_6H_2N_2SBr$. **3b**, calcd for $Br-(C_{34}H_{42}N_2O_2S\cdot 0.8H_2O)_{60}-C_6H_2N_2SBr$. **3c**, calcd for $Br-(C_{40}H_{54}N_2O_2S\cdot 0.6H_2O)_{40}-C_6H_2N_2SBr$. **3d**, calcd for $Br-(C_{52}H_{78}N_2O_2S\cdot 0.6H_2O)_{20}-C_6H_2N_2SBr$.

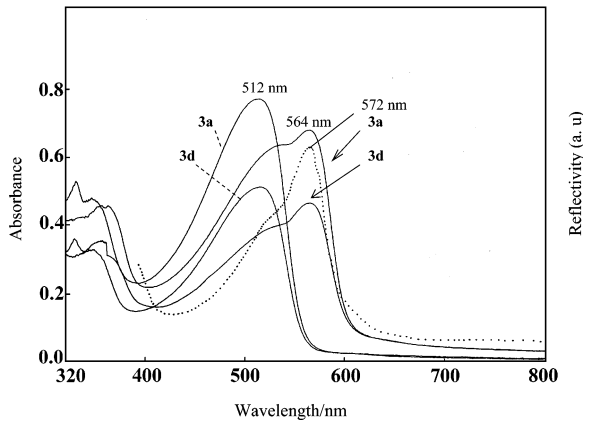


Figure 1. UV−vis spectra of **3a** and **3d** in chloroform (- - -) and in the solid state (→, cast film on a quartz glass plate). The dotted curve shows the reflection spectrum of the film of **3a**; cf. the Supporting Information for reflection spectra of **3b**−**3d**.

1) exhibits a peak at 572 nm near the absorption peak, with a peak reflectivity of about 20%. The reflection peak position is comparable to that of *cis*-polyacetylene and is located at a shorter wavelength than that of *trans*-polyacetylene.[15] **3b**−**3d** gave analogous reflection spectra as shown in the Supporting Information. When a film of **3c** was formed from a chloroform solution, it had bright metallic luster with green-yellow. On the other hand, the film formed from a mixture of chloroform and chlorobenzene (8:2, v/v) had metallic luster with red-yellow; however, a significant difference in the reflection spectrum was not observed between the two films.

3a−**3d** showed photoluminescence with an emission peak at about 565 nm, which agreed with the onset position of the absorption band as usually observed with π-conjugated polymers. Photoluminescence data are given in Table 1 and the Supporting Information.

Analyses of X-ray Diffraction (XRD) Data. One of the interesting properties of **3a**−**3d** is their strong tendency to form self-assembled structure in the solid state, which was revealed by XRD patterns of the polymers in three forms (powder, cast film on a Pt plate, and the crushed film obtained after peeled from the plate), as shown in Figures 2 and 3. For the four polymers, the peak appearing in a small-angle region (2θ(Cu Kα) < 7° in Figure 2) is assigned to the intermolecular distance d_1 between two main chains separated by the long side chains, similar to the cases of rigid π-conjugated polymers with long side chains.[12−14] Scheme 2 exhibited a packing model of the polymers. There is a good liner relationship between the d_1 value and the number of the carbon atoms in the OR group in the polymer, as exhibited in the inset in Figure 2, which is consistent with the packing structure. The slope of the linear line, 1.18 Å/carbon, is considerably smaller than that (1.8 Å/carbon) observed with HT-P3RTh. Since the number density of the side chain along the main chain of **3a**−**3d** is considerably smaller than that in HT-P3RTh and the slope is comparable to or somewhat smaller than the height of the $-CH_2-$ unit (1.25 Å/carbon), **3a**−**3d** are considered to assume an interdigitation packing mode in the solid, in contrast to the case of HT-P3RTh, which takes an end-to-end packing mode.[14]

The smaller number density of the side chain seems to allow the interdigitation packing. The d_2 distance of ca. 3.65 Å for **3a** in Figure 2 may be assigned to a face-to-face packing distance as depicted in Scheme 2, the value being comparable to those (3.5−3.8 Å) of face-to-face packing distance reported for π-conjugated poly-

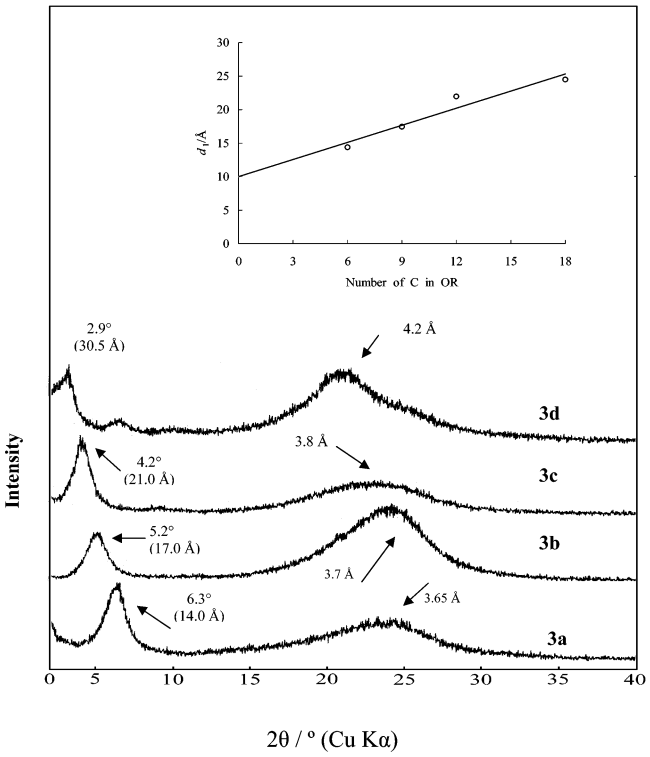


Figure 2. XRD powder patterns of **3a**−**3d**. The inset shows plots of d_1 vs number of carbon in the alkoxy side chain. The peak of **3d** at about 6° may be assigned to the second peak of the peak at 2θ of about 2.9°.

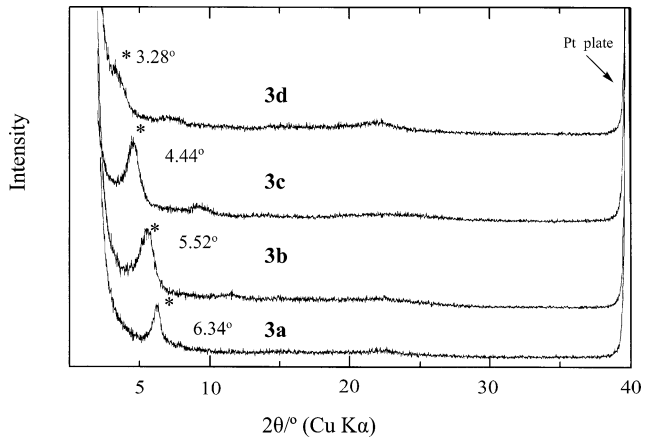


Figure 3. XRD patterns of the films of **3a**−**3d** on a Pt plate. The XRD patterns obtained by crushing the films of **3a**−**3d** peeled from the Pt plate are given in the Supporting Information.

mers such as HT-P3RTh and head-to-head poly(4-alkylthiazole).[11−14] When the side chain OR becomes longer as in **3d**, a peak at about 4.2 Å, corresponding to a side-to-side interchain distance[16] between the loosely packed alkyl chain, becomes stronger as seen from the top chart shown in Figure 2; the d_2 XRD peak (cf. Scheme 2) seems to be hidden under the strong peak due to the side-to-side packing of the alkyl chain.

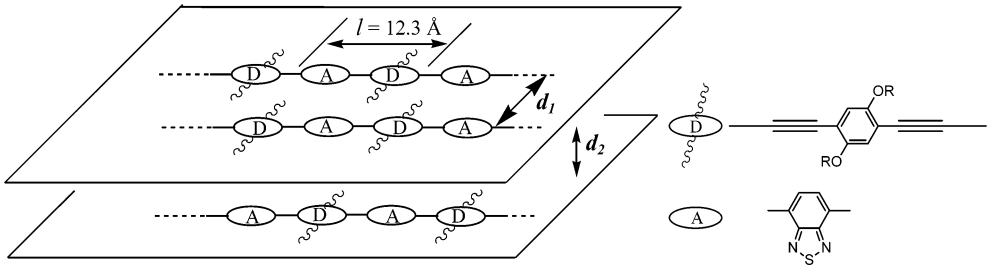
To investigate further the structure of the polymers in the solid state and confirm the packing model shown in Scheme 2, the density of **3a**−**3d** was determined and compared with the calculated data obtained by using the XRD data and a Chem 3D software (Cambridge Co.) for estimation of the length, l, of the repeating unit in Scheme 2; l thus calculated was 12.3 Å. The d_2 distance (cf. Scheme 2) estimated from the XRD data of **3a** (d_2 = 3.65 Å) is used for the calculation of the density of **3a**−**3d**.[17] The polymer solid seems to contain water (see Table 2) as the solvent of crystallization. The calculated density of **3a**−**3d** (ρ/g cm^{-3}: **3a**, 1.24; **3b**, 1.19; **3c**, 1.12; **3d**, 0.98) agrees with the observed density (ρ/g cm^{-3}: **3a**, 1.24; **3b**, 1.18; **3c**, 1.12; **3d**, 0.92) within experimental error, giving additional support for the proposed packing structure. The density decreases from **3a** to **3d** with increase in the proportion of the alkyl chain having a lower density.

For polymer films cast on a Pt plate, weaker d_2 peaks were observed. For example, the d_2 peak of **3a** at near 24° became to very weak in the cast film XRD pattern. Comparison of Figure 3 with Figure 2 and the XRD patterns obtained by crushing the films of **3a**−**3d** peeled from a Pt plate (cf. the Supporting Information) would give an assumption that the polymer molecules are oriented (or partly oriented) on the Pt plate. Similar phenomena have been reported for poly(3-alkylthiophene)s with long side chains.[11a,12] According to the strong tendency to form the stacked structure, the polymer formed spherulite of a dimension of 0.3 mm and showed solvatochromism when a poor solvent, CH_3OH, was added to a chloroform solution of the polymer.[11b]

Redox Properties. The electrochemical properties of the polymers were characterized by cyclic voltammetry (CV) with their cast films, and the results are shown in Figure 4. As depicted in Figure 4, scanning in a range from 1.5 to −2.2 V vs Ag^+/Ag showed redox peaks with color changes. It is seen that electrochemical reduction (or n-doping) of **3a** starts at about −1.5 V Ag^+/Ag and gives two n-doping peaks at −1.59 and −2.06 V vs Ag^+/Ag, respectively (peaks a and b in Figure 4). The color of the film changed from deep red to green on reduction.

Of the two aromatic units (the 2,1,3-benzothiadiazole and benzene units), the 2,1,3-benzothiadiazole unit receives the reduction at higher potential (e.g., n-doping peak of poly(thiadiazole) = −1.9 V vs Ag^+/Ag)[9] than the benzene ring [e.g., n-doping peak of poly(*p*-phenylene) (PPP) = −2.6 V vs Ag^+/Ag].[19] Consequently, peaks a and b in Figure 4 are considered to be mainly concerned with the reduction of the 2,1,3-benzothiadiazole unit and the benzene unit, respectively, although the generated

Scheme 2. Schematic Formula of the Polymers in the Solid State



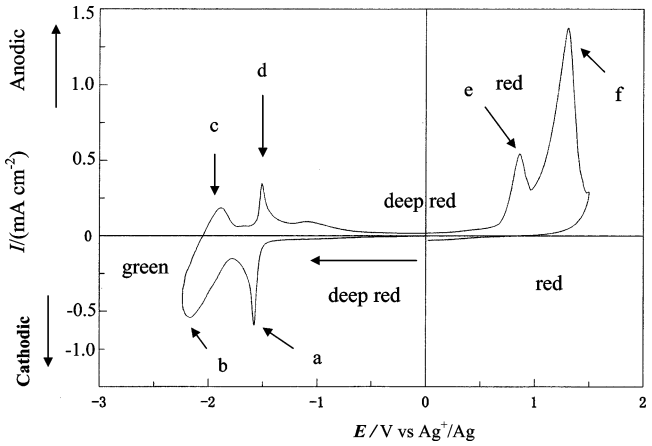


Figure 4. CV chats ofthe cast film of **3a** on a Pt electrode (1 cm × 1 cm) in an acetonitrile solution of 0.10 M $[Bu_4N]BF_4$ (Bu = butyl). (The values of peaks a, b, c, d, e, and f for **3a**−**3d** are given in the Supporting Information.)

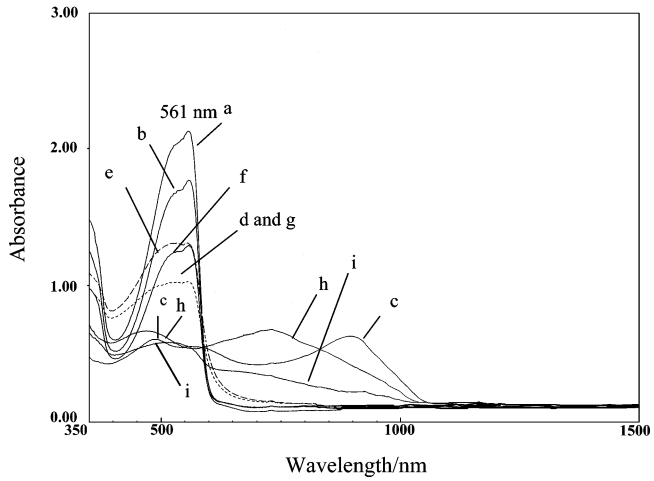


Figure 5. Changes in the UV−vis spectrum of a film of **3c** on an ITO glass electrode at various applied potentials vs Ag^+/Ag. Curve a shows the UV−vis spectrum of the cast film of **3c**. Applied potential in the n-doping (or reduction)→ n-dedoping → p-doping (oxidation) sequence (V): a (0.0) → b (−1.7) → c (−2.3) → d (−1.8) → e (−1.5) → f (0.0) → g (0.6) → h (1.2) → i (0.0). In an acetonitrile solution of $[Bu_4N][BF_4]$ (0.10 M). Curves d and g are superposed upon each other.

negative change seems to be delocalized along the polymer chain to some extent. The corresponding n-dedoping peaks appear at −1.90 and −1.49 V vs Ag^+/Ag, respectively (peaks c and d in Figure 4). The color of the film reversibly changed from green to deep red. In a range from 0.0 to −2.2 V vs Ag^+/Ag, the film revealed stable in repeated scanning of CV, giving same CV curves. However, sweeping from 0.0 to 1.5 V vs Ag^+/Ag only gave two irreversible peaks at 0.76 and 1.32 V, respectively (peaks e and f in Figure 4). Since the benzene unit is more susceptible to oxidation (e.g., p-doping peak of PPP = 1.1 V vs Ag^+/Ag)[19] than the 2,1,3-benzothiadiazole unit (p-doping peak of poly(2,1,3-benzothiadiazole) = 1.35 V vs Ag^+/Ag)[9] and the electron-donating property of the benzene unit is enhanced by the OR groups in **3a**, the first oxidation peak, peak e, is associated with the oxidation of the benzene ring and the second oxidation peak is to oxidation of the thiadiazole unit. Such irreversibility in the electrochemical processes has been reported for several π-conjugated polymers including those having OR substituents.[20] Electrochemical redox behavior of **3b**−**3d** was similar to that of **3a** (cf. the Supporting Information).

Optoelectrochemical spectra of the coated film of the polymer on the ITO glass plate were measured in an acetonitrile solution of 0.10 M $[Bu_4N]BF_4$ by applying the desired potential. All the polymers showed essentially the same electrochromic data, and the data obtained with **3c** are shown in Figure 5. When the applied potential was −1.7 V, the absorption bands of the film was not changed much (chart b in Figure 5), revealing that the first reduction in Figure 4 did not bring about severe changes in the optical state of the polymer. At the applied potential of −2.3 V, the absorption band at 561 nm disappeared, and a new absorption band was clearly observed at about 930 nm (chart c), which was characteristic of doped-π-conjugated polymers and suggested formation of polaron and/or bipolaron states in the polymer chain. On applying the reverse potential (−1.8 V), the absorption band at about 930 nm in the chart c disappeared and the peak at 561 nm appeared again as shown by curve d in Figure 5.

In the oxidation region, no significant changes were observed at 0.6 V vs Ag^+/Ag (chart g). However, when the applied potential was increased to 1.2 V, a new absorption band at about 720 nm was clearly observed (chart h). On applying the reverse potential (0.0 V), chart h in Figure 5 did not return to curve g, which supported irreversibility of the electrochemical oxidation in the region of 0−1.3 V as described above.

Conclusion

A series of new poly(aryleneethynylene)s with an aryl heterocyclic structure were prepared in high yields by polycondensation between 4,7-dibromo-2,1,3-benzothiadiazole and 2,5-dialkoxy-1,4-diethynylbenzenes with different long side chains using transition metal catalysts. All these polymers were photoluminescent and electrochemically active and showed metallic luster in the solid state. The polymers assumed a π-stacked structure in the powder state, and the polymer molecules in the film were ordered on the surface of the platinum plate with the alkoxy side chains directed to the surface of the platinum plate.

Poly(aryleneethynylene) type polymer is expected to be a key material in future electronic and optical devices such as nonlinear optical devices for rapid switching and manipulation of light (e.g., to construct effective optical communication systems).[21] The CT structure along the π-conjugated polymer chain and the molecular assembly[21] are expected to render excellent nonlinear optical properties to the poly(aryleneethynylene) type polymers.

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Supporting Information Available: IR spectra (Figure S1), ^{13}C {^1H} NMR spectrum of **3a** (Figure S2), reflection spectra (Figure S3), PL spectra (Figure S4), XRD patterns obtained by crushing the films of **3a**−**3d** peeled from the Pt plate (Figure S5), CV data for the cast films of **3a**−**3d** (Table

S1), and TGA data (Figure S6). This material is available free of charge via the Internet at http://pubs.acs.org.

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