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π-Conjugated Soluble Poly(aryleneethynylene) Type Polymers. Preparation by Palladium-Catalyzed Coupling Reaction, Nonlinear Optical Properties, Doping, and Chemical Reactivity

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ABSTRACT: Palladium-catalyzed polycondensation between dihalo aromatic compounds X—Ar—X (3-hexyl-2,5-diiodothiophene, 2,5-dibromoselenophene, and 3,4-dinitro-2,5-dibromothiophene) and diethynyl aromatic compounds HC≡C—Ar′—C≡CH (2,5-diethynylpyridine, 3-hexyl-2,5-diethynylthiophene, and *p*-diethynylbenzene) in the presence of triethylamine gives soluble π-conjugated poly(aryleneethynylene) (PAE) type polymers $(\text{-Ar—C≡C—Ar}'\text{—C≡C-})_n$ when Ar and/or Ar′ contains the long alkyl substituent and/or pyridine ring. The PAE type polymers are obtained in high yields (86–100%), have molecular weights of 9.6×10^4–69×10^4 and ρ_v (degree of depolarization) values of 0.005–0.034 as determined by the light scattering method, and show absorption bands in the range 350–462 nm, which are shifted from the absorption bands of the corresponding aromatic units (HArH and HAr′H), indicating the occurrence of π-conjugation along the polymer chain. The polymers exhibit fluorescence in solutions, and the λ_{max} position of the fluorescence is shifted to a longer wavelength in films of the polymers, suggesting the formation of excimer-like adducts in the solid state. The polymer films give a $\chi^{(3)}$ (third-order nonlinear optical susceptibility) value of about 5×10^{-11} esu when the Ar group has the hexyl group. Cyclic voltammetry of the PAE type polymers indicates that they receive reduction (n-doping) at about −2 V vs Ag/Ag$^+$ whereas oxidation (p-doping) of the polymer is difficult presumably due to the electron-withdrawing effect of the -C≡C- group. HBr addition to the -C≡C- group of the polymer gives a polymer having a -CH=CH(Br)- group, which can be further converted into ester and amide groups.

Introduction

Preparation of new π-conjugated polymers and revealing their chemical and physical properties are the subject of recent interest.[1] Among the π-conjugated polymers, poly(arylenevinylene) (PAV) type polymers have attracted special attention[1a,2–5] due to their interesting optical properties (e.g., large $\chi^{(3)}$ values[2] and photo- and electroluminescence[3]) and ease in the preparation of their films from their processable precursor polymers.

In contrast to the PAV type polymers, poly(aryleneethynylene) (PAE) type polymers having structures similar to those of the PAV type polymers have received much less attention,[6–10]

$$\underset{\text{PAV}}{(\text{-Ar—CH=CH-})_n} \qquad \underset{\text{PAE}}{(\text{-Ar—C≡C-})_n}$$

although the following Pd-catalyzed preparation methods easily give the PAE type polymers[6–8] and they may also show interesting optical and doping properties and good processability.

$$n\text{X—Ar—X} + n\text{HC≡C—Ar}'\text{—C≡CH} \xrightarrow[\text{NR}_3]{\text{catalyst}} \underset{\text{PAE}}{(\text{-Ar—C≡C—Ar}'\text{—C≡C-})_n} \quad (1)$$

$$n\text{X—Ar—X} + n\text{BrMgC≡C—Ar}'\text{—C≡CMgBr} \xrightarrow{\text{catalyst}} \underset{\text{PAE}}{(\text{-Ar—C≡C—Ar}'\text{—C≡C-})_n} \quad (2)$$

X = halogen; catalyst = Pd complex + CuI (eq 1) or Pd complex (eq 2)

Actually, it has been recently reported by us that the π-conjugated PAE type polymers with the arylene unit (Ar, Ar′) having an alkyl or another substituent are processable due to their good solubility in organic solvents[6d–f] and they exhibit large third-order nonlinear optical susceptibility $\chi^{(3)}$.[6d]

We here report details of the preparation and chemical and physical properties (including the optical third harmonic generation, fluorescence, doping, and addition reaction to the C≡C bond) of the soluble π-conjugated PAE type polymers. A part of the results has been reported in communications.[6d–f]

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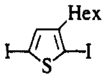
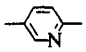
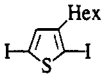
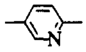
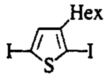
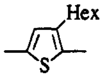
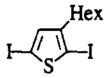
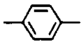
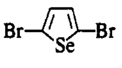
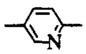
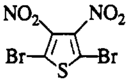
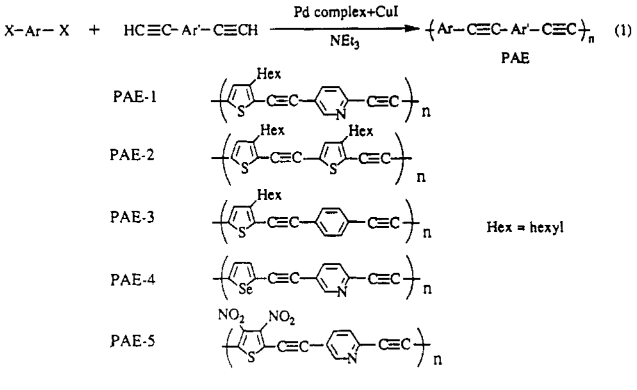
Table 1. Preparation of PAE Type Polymers by Pd-Catalyzed Polycondensation of X—Ar—X and HC≡C—Ar—C≡CH

polymer	X—Ar—X[a]	-Ar'-[b]	reaction conditions:[c] catalyst temp (°C), time (h)	yield[d] (%)	$10^{-4}M_w$[e]	ρ_v[f]	$\Delta n/\Delta c$[g] (cm^3 g^{-1})
PAE-1			PdL_4(1),CuI(2) 110,2.5	100	48 ($CHCl_3$)	0.034	0.38
PAE-1			PdL_4(1),CuI(2) 50,1.5	100	43 ($CHCl_3$)	0.093	0.36
PAE-2			PdL_4(5),CuI(4) 60,5	88	19 ($CHCl_3$)	0.002	0.26
PAE-3			PdL_4(1),CuI(2) 110,2	93	9.6 ($CHCl_3$)	0.011	0.34
PAE-4			PdL_4(2),CuI(5) 60,2	100			
PAE-5			PdL_4(2),CuI(2) 60,19	86	69 (HCOOH)	0.005	0.28

[a] Hex = hexyl. [b] Hex = hexyl. 1.0 mol of HC≡C—Ar'—C≡CH per 1.0 mol of X—Ar—X was added. [c] PdL_4 = tetrakis(triphenylphosphine)palladium(0), $Pd(PPh_3)_4$. The number in parentheses is the mol % of catalyst added per X—Ar—X. An excess amount of NEt_3 was added, and polymerization was carried out in toluene (cf. Experimental Section). [d] Based on carbon recovered. [e] Weight-average molecular weight determined by the light scattering method. The solvent used for the measurements are shown in parentheses. [f] Degree of depolarization. [g] Refractive index increment.

Results and Discussion

Preparation. Application of the Pd-catalyzed polycondensation expressed by eq 1 to the monomers X—Ar—X and HC≡C—Ar'—C≡CH containing a substituted (e.g., alkyl-substituted) arylene or pyridine-2,5-diyl unit gives the soluble PAE type polymers in high yields, as shown in Table 1. It has been reported that use of an alkyl-substituted arylene[6a,11] and/or pyridine-2,5-diyl unit[12] in poly(arylene) type polymers enhances solubility of the polymers in organic solvents.



The Pd-catalyzed polycondensation expressed by eq 1 is based on the Pd-catalyzed coupling reaction between acetylene compounds and organic halide,[13,14]

$$RX + R'C{\equiv}CH \underset{NR''_3}{\xrightarrow{\text{Pd complex, CuX}}} RC{\equiv}CR' \qquad (3)$$

and reaction 3 seems to proceed most probably through oxidative addition of RX to the Pd complex (eq 4), formation of copper acetylide (eq 5), transmetalation of the acetylide ligand to the Pd complex (eq 6), and reductive elimination of Pd (eq 7). The oxidative addition of RXto

$$RX + PdL_m \rightarrow L_mPd(R)X \qquad (4)$$

$$R'C{\equiv}CH + CuX \rightarrow R'C{\equiv}C{-}Cu \qquad (5)$$

$$R'C{\equiv}C{-}Cu + L_mPd(R)X \rightarrow L_mPd(R)(C{\equiv}CR') + CuX \qquad (6)$$

$$L_mPd(R)(C{\equiv}CR') \rightarrow RC{\equiv}CR' \qquad (7)$$

zerovalent PdL_m with neutral ligand L (eq 4),[14] strong affinity of copper compounds toward an acetylene compound to form the acetylides (eq 5),[15] and reductive elimination from a diorganopalladium complex (eq 7)[16] are well-known, and recently, an example of the transmetalation reaction (eq 6) has been also shown.[17]

The PAE type polymers have good solubility in various organic solvents. For example, PAE-1, -2, and -3 are soluble in the usual organic solvents such as $CHCl_3$, CH_2Cl_2, THF, DMF, and toluene. On the other hand, the PAE type polymers containing only the pyridine-2,5-diyl unit (PAE-4 and PAE-5) as the solubilizing unit are soluble only in formic acid among organic solvents tested, similarly to the case of poly(pyridine-2,5-diyl) (PPy).[12] Removal of formic acid from the solutions by evaporation gives the original PAE-4 and -5 as proved by IR spectroscopy, indicating that formic acid essentially serves as a solvent similarly to the case of the formic acid solution of PPy.[12]

As shown in Table 1, the PAE type polymers have relatively high molecular weights as measured by the light scattering method.[18] PAE-1 exhibits an η_{sp}/c value of 0.47 dL g^{-1} at c = 0.080 g dL^{-1}. All the PAE type polymers shown above give mechanically strong films by casting from their solutions.

The polymers show non-zero ρ_v (degree of depolarization)[18] values (Table 1); however, the ρ_v values are considerably lower than that (ρ_v = 0.33) of rigidly linear poly(pyridine-2,5-diyl) with a degree of polymerization of about 50.[12] Bowing of the long PAE type polymers in solution may be the reason for such a relatively low ρ_v value; it is reported that an increase in the molecular weight of poly(1,4-phenyleneterephthalimide) leads to the decrease in ρ_v.[18c] The PAE type polymers exhibit relatively large refractive index increments $\Delta n/\Delta c$ (Table 1) of 0.32 ± 0.06 cm^3 g^{-1} compared with those ($\Delta n/\Delta c$ = 0.1–0.2 cm^3

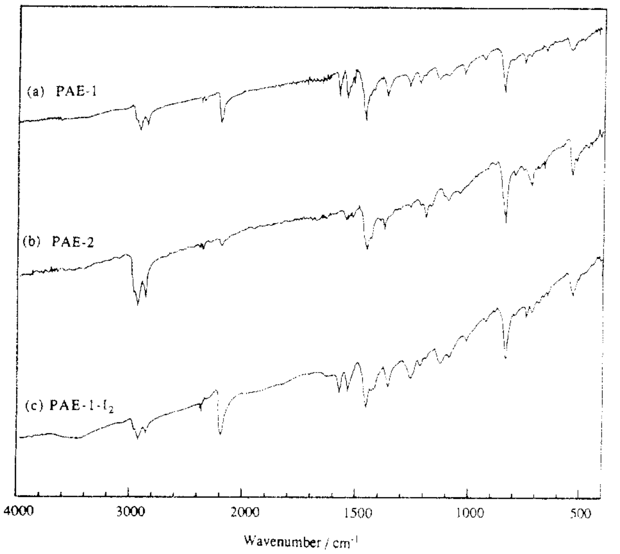


Figure 1. IR spectra of (a) PAE-1, (b) PAE-2, and (c) iodine-treated PAE-1. Signals at about 2400 cm^{-1} are due to CO_2 in air.

g^{-1}) of the usual nonconjugated polymers; the $\Delta n/\Delta c$ values are comparable to that of poly(3-alkylthiophene-2,5-diyl).[11f]

Figure 1 shows IR spectra of PAE-1 and PAE-2. By the polycondensation, the $\nu(C{\equiv}C)$ band of the original HC≡C—Ar′—C≡CH at 2120–2130 cm^{-1} is shifted to a higher frequency to about 2180–2200 cm^{-1} (Table 2, last column), consistent with a known trend that disubstituted acetylenes RC≡CR′ give rise to the $\nu(C{\equiv}C)$ band at a frequency higher than monosubstituted acetylenes RC≡CH.[19] The IR spectra of all the PAE type polymers shown above exhibit neither observable $\nu(C{\equiv}C)$ and ν-(C—H) (at about 3150 cm^{-1}) bands of the terminal -C≡CH nor a ν(C—halogen) band (e.g., 980 cm^{-1} for 3-hexyl-2,5-diiodothiophene,[11f] the monomer for PAE-1), indicating that the polycondensation gives the polymers with sufficient molecular weight. On the other hand, use of other combinations of X—Ar—X and HC≡C—Ar′—C≡CH in the present polymerization (e.g., a combination with Ar = pyridine-2,5-diyl and Ar′ = 6-hexylpyridine-2,5-diyl), sometimes, has so far given the polymer with relatively low molecular weight showing the $\nu(C{\equiv}C)$ and ν(C—H) bands of terminal -C≡CH. IR spectra of PAE-3, -4, and -5 are also reasonable for their structures. PAE-5 shows bands of the NO_2 group at 1540 and 1310 cm^{-1}.

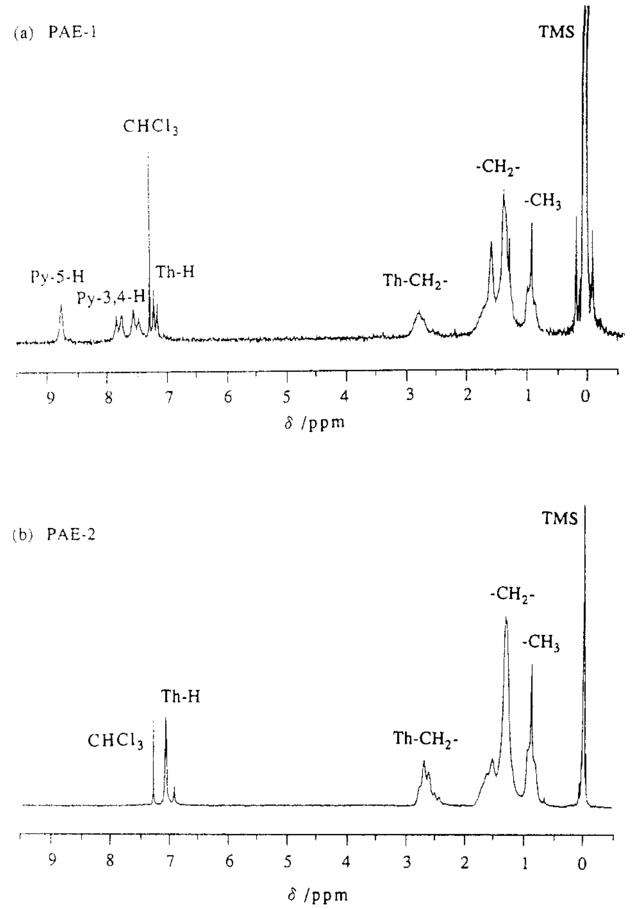


Figure 2. ^{1}H-NMR (100 MHz, $CDCl_3$) spectra of (a) PAE-1 and (b) PAE-2.

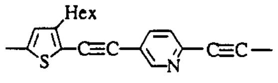
^{1}H-NMR spectra of the PAE type polymers are also reasonable for their structures. Figure 2 shows the ^{1}H-NMR spectra of PAE-1 and PAE-2. The peak area ratios among CH_3, $-CH_2-$, thiophene ring (Th) attached $-CH_2-$ (Th–CH_2–), aromatic Th–H, and pyridine (Py) hydrogens agree with the structure of PAE-1. The splitting of the Th–H absorption into two peaks at δ 7.13 ppm (relative

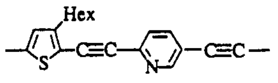
Table 2. UV–Vis, Fluorescence, $\chi^{(3)}$, and IR ($\nu(C{\equiv}C)$) Data for PAE Type Polymers

polymer	absorption[a] λ_{max} (nm)	$E(\pi\pi^*)$[b] (eV)	E_g[c] (eV)	fluorescence[d] λ_{max} (nm)	excitation spectrum[e] λ_{max} (nm)	$10^{11}\chi^{(3)}$[f] (esu)	$\nu(C{\equiv}C)$ (cm^{-1})
PAE-1	426 ($CHCl_3$)	2.91	2.61	465 (2.66 eV), 495* (2.50 eV) ($CHCl_3$)	403	4.2 (220 Å)	2194
	432 (film)			592 (2.09 eV) (film)			
PAE-2	438 ($CHCl_3$)	2.83	2.38	510 (2.43 eV), 538* (2.30 eV) ($CHCl_3$)	452	4.7 (230 Å)	2182
	446 (film)			529 (2.34 eV), 558* (2.22 eV) (film)			
PAE-3	403 ($CHCl_3$)	3.07	2.67	455 (2.72 eV), 485* (2.55 eV) ($CHCl_3$)	405	2.1 (210 Å)	2192
	410 (film)			582 (2.13 eV) (film)			
PAE-4	462 (HCOOH)	2.68	2.41	523 (2.37 eV) (HCOOH)	470		2194
	460 (film)			520 (2.38 eV), 550 (2.25 eV), 575 (2.15 eV) (film)			
PAE-5	360[g] (HCOOH)	3.44	2.10	430 (2.88 eV) (HCOOH)	360		2200
	350 (film)			*h*			

[a] Solvent or the state of measurement is shown in parentheses. [b] π–π^* transition energy estimated from λ_{max} in the absorption spectrum. [c] Band gap estimated from the onset position of the absorption band. [d] In the same solvent indicated by footnote *a*. Energy (in eV) corresponding to λ_{max} is given in the parentheses. The value with * is for the subpeak (see the text). [e] Monitored at λ_{max} of the fluorescence. In cases of PAE-1, -2, and -3, monitoring at the two fluorescence peaks gives the same λ_{max} in the excitation spectrum. In the same solvent indicated by footnote *a*. [f] Thickness of the film for the estimation is given in parentheses. Value estimated with irradiated laser with wavelength of 1.5 μm. [g] Shoulder peak. [h] Not observable with the film of PAE-5.

area = 0.4) and 7.20 ppm (relative area = 0.6) suggests the presence of the two types of units A and B. Compared


Unit A


Unit B

with the Th–H proton, chemical shifts of the pyridine ring-attached protons (δ 7.5–8.8 ppm) are less sensitive to the difference in the mode of the joining between unit A and unit B to give rise to a relatively simple absorption pattern. The ^{1}H-NMR spectrum of PAE-2 (Figure 2b) is also reasonable for the structure.

PAE-1 through PAE-5 are stable under air. For example, leaving PAE-1 under air at room temperature for 1.5 years leads to no observable IR change. The PAE type polymers prepared previously in our group[6a–c] are also stable under air, showing no observable IR change after 14 years. The polymers are thermally stable and their TGA curves (measured under N_2) generally show start of weight loss at about 280–300 °C; the residual weight of PAE-1 at 600 °C is 74%. PAE-1 is amorphous as judged from its powder X-ray diffraction pattern, and it has the density of 1.05 g cm^{-3}.

Optical Properties. Table 2 summarizes optical properties of the PAE type polymers. They exhibit π–π^* absorption bands in the visible or near ultraviolet region. MOPAC calculation indicates that the Ar and Ar′ units essentially have coplanarity in the PAE molecule and the molecule has an extended π-conjugation system. It is reported that diphenylacetylene takes the coplanar structure.[20a] The polymers exhibit fluorescence in the visible region.

Figure 3 shows comparison of the UV–visible spectrum (Figure 3a), fluorescence spectrum (Figure 3b,b′), and excitation spectrum (Figure 3c) of PAE-1. The position of the π–π^* absorption band is considerably shifted to a longer wavelength compared with those (230–250 nm) of thiophene and pyridine, indicating the presence of an extensive π-conjugation system along the polymer chain.

As shown in Figure 3b, the fluorescence spectrum of PAE-1 exhibits a main peak at 465 nm and a subpeak at 495 nm. The transition energy ($E(\pi\pi^*)$, Table 2) of the absorption band of PAE-1 is 2.91 eV, and the band gap E_g of PAE-1 (2.61 eV) estimated from the onset position of the absorption essentially agrees with the λ_{max} value (465 nm or 2.66 eV) of the main fluorescence peak, indicating that the fluorescence takes place by migration of electrons in the conduction band to the valence band. The subpeak at 495 nm is tentatively assigned to a fluorescence coupled with a vibration; the energy difference (0.16 eV or 1290 cm^{-1}) suggests the coupling with certain aromatic skeletal vibrations. Various organic molecules including diphenylacetylene give rise to fluorescence bands coupled with vibration, and observation of a similar substructure in the fluorescence spectra of PAV type polymers has been reported.[3d] The shape of the fluorescence spectrum is essentially unvaried over a relatively wide range of concentrations (1×10^{-7}–1×10^{-3} M of the repeating unit of PAE-1). Monitoring with the 465 and 495 nm fluorescences gives the same excitation spectrum shown in Figure 3c; the peak position of the excitation spectrum agrees with the peak position of the absorption spectrum, as usually observed with various fluorescent molecules. The strength of the emissions from the solutions of PAE-1, -2, -3, and -4 appears to be stronger than that from the solutions of π-conjugated poly(pyridine-2,5-diyl) and its derivatives[21a] at similar concentrations.

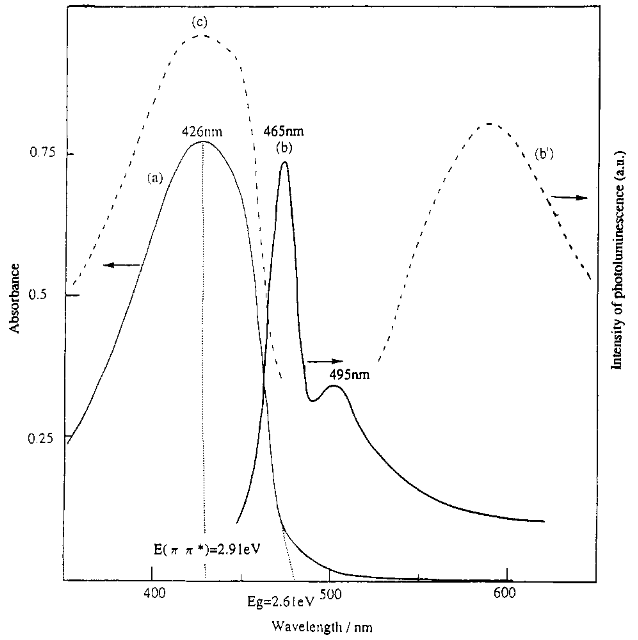


Figure 3. (a) Absorption spectrum of PAE-1 in $CHCl_3$. (b) Fluorescence spectrum of PAE-1 (1×10^{-7} M monomer unit) in $CHCl_3$. (b′) Fluorescence spectrum of the film of PAE-1. (c) Excitation spectrum of PAE-1 (in $CHCl_3$) monitored at 465 nm. Monitoring at 495 nm gives essentially the same excitation spectrum (see the text).

The film of PAE-1 exhibits the fluorescence peak at a position (Figure 3b′) much different from that of the PAE-1 solution. It is known that films of linear π-conjugated polymers such as poly(pyridine-2,5-diyl) (PPy) and poly(2,2′-bipyridine-5,5′-diyl) (PBpy) exhibit fluorescence peaks at positions much different (at a longer wavelength by 130 nm in the cases of PPy and PBpy) from those of their solutions, and the shift of the fluorescence band to the longer wavelength in the film has been attributed to the formation of an excimer-like adduct between the linear π-conjugated polymer molecules in the film on irradiation with UV light.[21] The shift of the fluorescence band in the film of PAE-1 is also reasonably accounted for by assuming a similar formation of such an excimer-like adduct in the film on irradiation with UV light; in the film, the PAE-1 molecule seems to have a direct interaction with another PAE-1 molecule to make the formation of the excimer-like molecule easier. It has been reported that diphenylacetylene exhibits excimer fluorescence on irradiation with γ-rays.[20b]

The film of PAE-3 also exhibits such a shifted fluorescence band. On the other hand the film of PAE-2 shows the fluorescence band at essentially the same position as that of the PAE-2 solution (Table 2). The presence of a hexyl group in higher density in PAE-2 may prevent the formation of the excimer-like adduct between the π-conjugated molecules. The fluorescence spectrum of the film of PAE-4 also shows such shifted fluorescence bands at 550 and 575 nm. However, in this case, these shifted fluorescence bands are overlapped with a fluorescence band at about 520 nm originated from the PAE-4 single molecule (cf. data in HCOOH in Table 2). The larger van der Waals radius of Se (1.90 Å) than that of S (1.80 Å) may prevent complete formation of the excimer-like adduct from proceeding in the case of PAE-4 containing the selenophene unit. In the case of PAE-5, it gives only a weak fluorescence in HCOOH, and the fluorescence was not observable with the PAE-5 film (Table 2).

Table 2 shows $\chi^{(3)}$ values of PAE-1, -2, and -3. The $\chi^{(3)}$ value is enhanced in the three-photon resonance region,

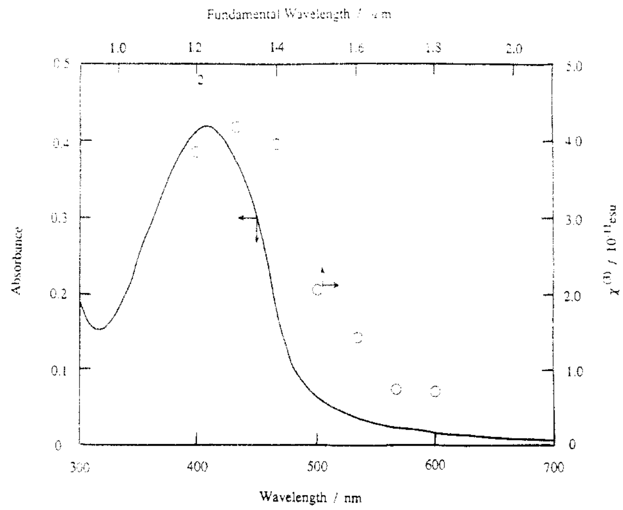


Figure 4. $\chi^{(3)}$ profile of PAE-3 film (thickness = 210 Å).

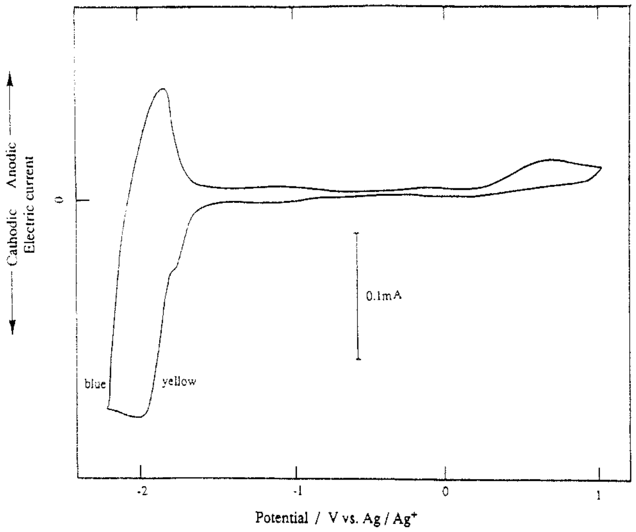
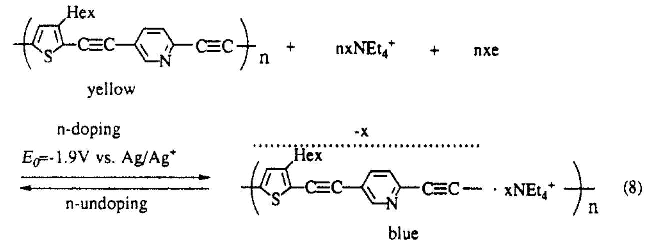


Figure 5. Cyclic voltammogram of PAE-1 film laid on a Pt plate in an CH_3CN solution of $[NEt_4][ClO_4]$ (0.1 M) (at 50 mV s^{-1} at room temperature).

as usually observed with π-conjugated polymer material. Thus, the wavelength dependence of the $\chi^{(3)}$ values of PAE-1, -2, and -3 indicates that all of the polymer films exhibit the $\chi^{(3)}$ value of (0.7–0.9) × 10^{-11} esu at a near resonant region ($\lambda_f/3\lambda_{max}$ = 1/0.7; λ_f = fundamental wavelength) and (4–5) × 10^{-11} esu at a resonant region ($\lambda_f/3\lambda_{max}$ = 1/0.9).[22] The $\chi^{(3)}$ values are comparable to that of poly(phenylenevinylene) and considerably larger than those of the usual poly(arylene)s such as poly(2,2′-bypyridine-5,5′-diyl) and poly(thiophene-2,5-diyl) which give $\chi^{(3)}$ values of about 2 × 10^{-11} esu at the resonant region.[2,21a] Figure 4 shows the dependence of the $\chi^{(3)}$ value of PAE-3 film on wavelength. Because of the large $\chi^{(3)}$ value and good processability of the PAE-type polymers, the polymers seem to be of usefulness to make interesting optical devices. The film of PAE-3 (thickness = 2000 Å) shows no distinct absorption in a range 1300 through 1700 nm, where the laser light for telecommunication may be used.

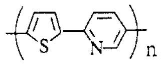
Doping Behavior. Figure 5 exhibits the cyclic voltammogram (CV chart) of the film of PAE-1 laid on a Pt plate. As shown in Figure 5, the CV chart shows a distinct redox cycle at about −1.9 V vs Ag/Ag+. The reduction (or n-doping) of PAE-1 starts at about −1.8 V and gives a peak at about −2.0 V vs Ag/Ag+ and changing the sweeping direction causes oxidation (or n-undoping) of the reduced PAE-1 with a peak anode potential E_p at about −1.8 V vs Ag/Ag+. The E_0 value estimated from an average of the peak cathode potential E_c and E_p is about −1.9 V vs Ag/Ag+. The doping level x per the repeating unit estimated from the area of the redox cycle at about −1.9 V vs Ag/Ag+ is about 0.35(±0.05). According to the n-doping, the color of PAE-1 changes from yellow to blue, as shown in eq 8 and Figure 5.

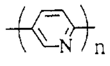


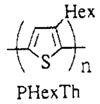
(8)

In contrast to the observation of a clear redox cycle in the reduction region, scanning to the oxidation region (beyond 0 V vs Ag/Ag+) gives no obvious redox cycle, revealing oxidation (or p-doping) of PAE-1 is difficult.

Comparison of the CV chart of PAE-1 with previously reported CV data for (a) the copolymer of pyridine and thiophene without the −C≡C− group (PTpy),[23] (b) poly(pyridine-2,5-diyl) (PPy),[21a] and (c) poly(3-hexylthiophene-2,5-diyl) (PHexTh)[11f,24] or poly(thiophene-2,5-diyl) (PTh)[25] reveals the following characteristics (i) and (ii) of the doping of PAE-1.


PTpy


PPy

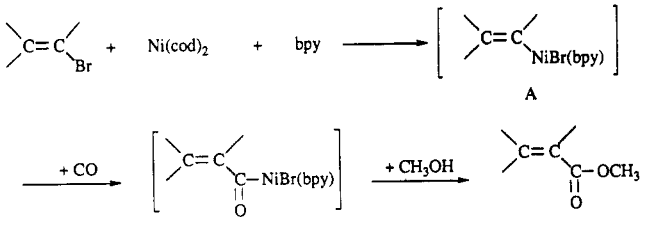


PHexTh

(i) The pyridine ring has an electron-deficient nature, whereas the thiophene ring has an electron-excessive nature.[6a,26] Therefore, PPy exhibits an n-doping–n-undoping redox cycle at E_0 = −2.11 V vs Ag/Ag+, whereas PTh and PHexTh show a p-doping–p-undoping redox cycle at E_0 = about 0.5–0.6 V vs Ag/Ag+. The copolymer PTpy gives rise to two couples of redox cycles, which show the occurrence of the reduction of the pyridine ring at E_{pc} (peak cathode potential) = −2.25 V vs Ag/Ag+ and the oxidation of the thiophene ring at E_{pa} (peak anode potential) = about 0.5 V vs Ag/Ag+, respectively. In contrast to these poly(arylene)s, PAE-1 shows only one distinct redox cycle at E_0 of −1.9 V vs Ag/Ag+ (eq 8). This seems to be ascribable to the known strong electron-withdrawing effect of the −C≡C− group,[27] which will make the whole PAE-1 molecule electron-deficient to make its n-doping easy and p-doping difficult. A small redox couple (Figure 5) with E_{pa} of about 0.6 V vs Ag/Ag+ and E_{pc} of about −1.8 V vs Ag/Ag+ (shoulder) may be attributable to partial occurrence of p-doping of the thiophene ring and its undoping; however, the peak area indicates such a redox takes place only to a minor extent.

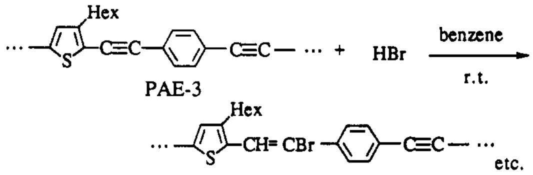
Even the CV chart of PAE-3, which does not contain the electron-deficient pyridine ring, shows the n-doping–n-undoping redox cycle at E_0 = −2.2 V vs Ag/Ag+ as a sole distinct redox cycle presumably due to the strong effect of the −C≡C− group.

(ii) The E_0 value of −1.9 V vs Ag/Ag+ for PAE-1 is negatively smaller than the E_0 values for the n-doping–n-undoping cycle of PPy and PTpy by about 0.2 V, indicating the reduction of PAE-1 takes place more easily than those of PPy and PTpy. This is also ascribable to the electron-withdrawing effect of the −C≡C− group. Due to the difficulty of oxidizing PAE-1, treatment of PAE-1 with iodine causes no obvious change in its IR spectrum, Scheme 1



as shown in Figure 1c, in contrast to a profound change of the IR spectra of PTh and PHexTh by the treatment with iodine (p-doping of the polymers).[11f] Sodium-doped PAE-1 exhibits an electrical conductivity of 10^{-7} S cm^{-1}.

Addition Reaction to the -C≡C- Bond. Since PAV type polymers exhibit interesting electric and optical properties as described above, conversion of the PAE type polymers into PAV type polymers by addition reaction to the C≡C bond is intriguing. Treatment of PAE-3 with dry HBr (20 mol/mol of C≡C bond) leads to smooth addition of HBr to the C≡C bond.



(9)

The fairly strong ν(C≡C) band in the IR spectrum of PAE-3 is considerably weakened after 30 min. The ^{1}H-NMR spectrum of the HBr-added polymer shows overlapped signals of the aromatic and olefin protons in the range δ 6.7–8.0 ppm in CD$_2$Cl$_2$, and the relative area of the signals in this range against that of the Hex group (13) increases from 5 for PAE-3 to 6 after the HBr addition. The increase in the relative area of the signals in the range δ 6.7–8.0 ppm corresponds to conversion of 50% of the -C≡C- groups into the -CH=CBr- group.

The olefin C–Br group formed by the reaction (eq 9) can be further converted to an ester group by treatment with a zerovalent nickel complex (a 1:1 mixture of bis(1,5-cyclooctadiene)nickel(0) (Ni(cod)$_2$) (ca. 4 mol/mol of C–Br) and 2,2′-bipyridine (bpy)) and carbon monoxide (1 atm) in THF at room temperature, which is followed by treatment with methanol (Scheme 1).

The ester group thus formed gives rise to a fairly strong ν(C=O) band at 1720 cm^{-1}. Addition of aniline, instead of methanol, in Scheme 1 leads to the formation of the amide group. A similar transformation of the usual organic halides[28] and a polymeric organic halide (poly(vinyl chloride))[29] to esters and amides by using the Ni complex as well as the basic reaction for the conversion of an A type nickel complex (Scheme 1) to the corresponding ester and amide[30] has been reported. Conversion of the -C≡C- group of the PAE type polymers to a -CH=CH- group by addition of H$_2$ or reduction (e.g., reaction with H$_2$ over Pd/C catalyst and reduction with hydrazine derivatives) seems to take part; however, this type of conversion seems to be not as easy as that carried out for the usual organic acetylenes.

Conclusion and Scope

The Pd-catalyzed polycondensation between X—Ar—X and HC≡C—Ar′—C≡CH gives a versatile way to prepare the soluble PAE type polymers, which show large $\chi^{(3)}$ values, strong fluorescence, and n-doping properties. The polymers are potentially usable as starting materials for various PAV type polymers. By selection of suitable reaction conditions and combinations of the monomers, the scope of the polycondensation and application of the polymers will be expanded.

Experimental Section

Materials. 3-Hexyl-2,5-diiodothiophene,[11f] 2,5-dibromoselenophene,[31] 3,4-dinitro-2,5-dibromothiophene,[32] 3-hexyl-2,5-diethynylthiophene,[33] Pd(PPh$_3$)$_4$,[34] and Ni(cod)$_2$[35] were synthesized by literature methods. 2,5-Diethynylpyridine was prepared by modifying a reported method.[36] *p*-Diethynylbenzene was used as purchased. Solvents were dried, distilled under N$_2$, and stored under N$_2$.

Polymerization. Polymerization was carried out in a manner similar to that previously reported by using standard Schlenk techniques.[6b] For example, the preparation of PAE-1 was carried out as follows.

Dry toluene (12 mL) was added to a mixture of 2,5-diethynylpyridine (273 mg, 2.15 mmol), Pd(PPh$_3$)$_4$ (23 mg, 0.02 mmol), CuI (8 mg, 0.04 mmol), and triethylamine (1.5 mL) in a Schlenk tube under nitrogen. 3-Hexyl-2,5-diiodothiophene (902 mg, 2.15 mmol) was then added to the mixture, and the brown reaction mixture was stirred at 110 °C for 2.5 h to obtain a deep black solution. GLC analysis of the solution indicated that all of the monomers were consumed.

Cooling the reaction mixture gave a brown precipitate and an orange solution. The reaction mixture was poured into methanol to obtain a brown precipitate, which was collected by filtration, washed with methanol repeatedly, and dried under vacuum to obtain 626 mg (100%) of a brown powder of PAE-1. Other polymerizations were carried out analogously.

Reaction of PAE Type Polymers. Dry HBr (about 20 mol/mol of the C≡C bond of PAE-3) prepared by a reaction of KBr and concentrated H$_2$SO$_4$ was introduced to PAE-3 in benzene by using a vacuum line. After the reaction mixture was stirred for 30 min at room temperature, HBr and benzene were removed under vacuum to obtain the HBr-added product. To a THF solution containing the HBr-added product, Ni(cod)$_2$ (4 mol/mol of the C—Br bond), and bpy (4 mol/mol of C—Br) was added an excess amount of carbon monoxide (1 atm). After the reaction mixture was stirred for 14 h at room temperature, an excess amount of methanol was added to the deep red reaction mixture. After further stirring for 3 h at room temperature, the precipitated polymer was collected by filtration, washed repeatedly with HCl-acidic methanol, and dried under vacuum. When an excess amount of aniline was added, the reaction mixture was stirred for 2 h at room temperature. Hexane was added to the reaction mixture to obtain the precipitated polymer, which was collected by filtration, washed repeatedly with HCl-acidic methanol and methanol in this order, and dried under vacuum.

Measurement and Doping. IR spectra were recorded on a JASCO IR-810 spectrometer. NMR spectra were taken using a JEOL JNM-FX-100 spectrometer. X-ray diffraction patterns were recorded on a Philips PS-1051 instrument. TGA curves, UV–visible spectra, and photoluminescence spectra were measured with a Shimadzu thermoanalyzer, a Hitachi Model 200-20 spectrometer, and a Hitachi F4010 spectrometer, respectively. Molecular weight measurement as well as measurement of ρ_v and $\Delta n/\Delta c$ (Table 1) was carried out as previously reported.[18] The density of PAE-1 was measured by addition of powdery PAE-1 to solutions whose density was measured with an areometer.

Cyclic voltammetry was carried out with a Hokuto Denko HA-501 galvanostat/potentiostat and a Hokuto Denko KB-104 function generator. The film of the PAE type polymer was laid on the Pt electrode (1.0 cm × 1.0 cm) by painting the electrode with a CHCl$_3$ solution of the polymer and then evaporating CHCl$_3$.

The third-order nonlinear susceptibility $\chi^{(3)}$ was determined by third harmonic generation (THG) measurement using the Maker fringe interferometric technique. The $\chi^{(3)}$ value was calibrated to that of quartz. The polymer film samples were prepared by spin-coating on a glass substrate from CHCl$_3$ solutions. The fundamental laser beam (1.2–1.8 μm) was obtained by using an optical parametric oscillator (GWU, BBO-OPO). The laser beam was focused on the film sample which was mounted on a gonimeter in such a way that the sample film was on the photomultiplier tube (PMT) side of the glass substrate. The third harmonic light was detected by PMT, and the gain was integrated with a boxcar averager. The $\chi^{(3)}$ values were calculated from THG intensities and the film thickness using fused silica glass ($\chi^{(3)} = 2.8 \times 10^{-14}$ esu[37]) as a reference and were corrected for absorption at a third harmonic wavelength using equations reported earlier.[38] When the sample film was mounted to face the focusing lens, the opposite direction to the way mentioned above, a larger $\chi^{(3)}$ value was measured. This is considered to be part of the reason for the larger $\chi^{(3)}$ value reported previously.[6d] Sodium doping of PAE-1 was carried out by treatment of powdery PAE-1 (30 mg) with a THF (30 mL) solution of sodium naphthalenide, which was prepared by a reaction of naphthalene (200 mg, 1.56 mmol) with sodium (500 mg, 21.7 mmol), at room temperature for 12 h under vigorous stirring. The sodium-doped black powder was collected over a glass filter, washed with THF, and dried under vacuum. Electrical conductivity of the sodium-doped PAE-1, as a compressed powder, was measured with a Sanwa CDS-820 digital multimeter.

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