SHORT COMMUNICATIONS

π -Conjugated Copolymers of Electron-Withdrawing Pyridine and Electron-Donating Selenophene

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It has been reported that π -conjugated polymers constituted of electron-withdrawing aromatic units (*e.g.*, pyridine-2,5-diyl) and electron-donating aromatic units (*e.g.*, thiophene-2,5-diyl) exhibit interesting optical and electrochemical properties due to internal charge transfer structures of the copolymers,^{1–3} *e.g.*,

PTPy

PNS

As an extension of the research concerning such charge-transfer π -conjugated polymers, we have prepared new π -conjugated copolymers of pyridine and selenophene, the latter of which contains more soft element (Se) than S in thiophene and may give a different type of copolymer with pyridine. The copolymer has been prepared by dehalogenation polycondensation of the corresponding dihaloaromatic monomers with Ni(0) complexes, which is based on organometallic chemistry,^{1c,4} and we here report results of the preparation as well as characterization and some optical properties of the copolymers.

EXPERIMENTAL

2-Bromo-5-(5-bromo-2-pyridyl) selenophene, monomer **1**, was prepared by bromination of 2-(5-bromo-2-pyridyl)selenophene with *N*-bromosuccinimide in CCl₄. *Anal.* Found: C, 29.9%; H, 1.3%; N, 3.7%. Calcd: C, 29.5%, H, 1.4%; N, 3.8%. ¹H NMR (90 MHz, CDCl₃): δ : 7.32 (dd, 2H), 7.58 (dd, 1H), 7.76 (dd, 1H), 8.50 (dd, 1H). Reaction of the monomer **1** (370 mg, 1.0 mmol) with a mixture of bis(1,5-cyclooctadiene)nickel Ni(cod)₂ (410 mg, 1.5 mmol), 2,2'-bipyridyl bpy (240 mg, 1.5 mmol), and 1,5-cyclooctadiene cod (160 mg, 1.5 mmol) in 15 cm³ of *N,N*-dimethylformamide DMF at 60°C for 16 h with stirring under N₂ gave a brown crude precipitate of the copolymer PSePy, which was worked up in a manner similar to that previously reported^{1,4a} to obtain a brown powder of PSePy (200 mg, 94% yield). *Anal.* Found: C, 50.5%, H, 2.4%, N, 6.4%. Calcd: C, 52.4%, H, 2.4%, N, 6.8%.

Another type of copolymers of pyridine and selenophene were prepared analogously by using 1 : 1 and 4 : 1 mixtures of 2,5-dibromopyridine and 2,5-dibromoselenophene, instead of the monomer **1**, as expressed by eq 2. The molar ratio between the pyridine unit and sele-

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nophene unit (the a:b ratio in eq 2) was calculated from the C/N ratio obtained from elemental analysis. Poly(selenophene-2,5-diyl) was also prepared analogously from 2,5-dibromoselenophene by using the mixture of Ni(cod)₂, bpy, and cod as the dehalogenating reagent; yield = 63%.

RESULTS AND DISCUSSION

Dehalogenation polycondensation of the monomer **1** with the zerovalent nickel complex Ni(0)L_m (a mixture of Ni(cod)₂ and bpy) affords PSePy in a high yield.

Another type of copolymers are also obtained analogously.

As for comparison, poly(selenophene-2,5-diyl) PSe has been also prepared by a similar method.

Analytical data of PSePy are reasonable for their structures, and IR spectrum of PSe agrees with reported data of PSe,⁵ which was prepared through a Grignard reagent.^{1c} The copolymerization (eq 2) gives the copolymers containing the pyridine and selenophene units in ratios essentially agreeing with the feeding ratios of the two monomers as revealed by C/N ratios of the copolymers.

Previously reported homopolymer of pyridine, poly(pyridine-2,5-diyl) PPy,^{4a} has good solubility in formic acid and sulfuric acid, however, PSe has only very low solubility in organic and inorganic solvents tested similarly

to reported low solubility of poly(thiophene-2,5-diyl) PTh,^{1c,6}

A soluble part of PSe in CHCl₃ exhibits π - π^* absorption band with λ_{max} value of 421 nm, which is comparable to the λ_{max} value (ca. 415 nm) of the π - π^* absorption band of a CHCl₃ soluble part of PTh.⁶

In contrast to good solubility of PTPy in formic acid, PSePy has only low solubility in organic and inorganic solvents including formic acid and sulfuric acid, possibly due to lower solubilizing effect of selenophene unit than thiophene unit and/or a stronger interaction between polymers originating from the polarized structure of copolymer due to the postulated charge transferred structure,

PTPy

PSePy

PNSe11 (eq 2b) also shows low solubility in the solvents, however, PNSe41 is soluble in formic acid and η_{sp}/c value of PNSe41 follows the following equation in formic acid at 30°C: η_{sp}/c (dl g⁻¹) = 1.23 + 3.5*c* (*c* in g dl⁻¹; *c* = 0.069—0.103 g dl⁻¹). The $[\eta]$ value of 1.23 indicates that PNSe41 has sufficient molecular weight. The random copolymers of pyridine and thiophene (PNS31 and PNS11)

PNS31 (a:b = 73:27)

PNS11 (a:b = 45:55)

have been reported to have molecular weight of 5×10^4 and 5×10^6 , respectively, as determined by light scattering method,^{1b,1c} and PNS31 shows the η_{sp}/c value of 0.92. Determination of the molecular weight of PNSe41 by the light scattering method was not possible due to tail absorption of PNSe41 at the positions of Ar⁺ and He-Ne laser.

Figure 1 shows comparison of IR spectra of PPy, PSe, and the copolymers. As shown in Figure 1, the copolymers give rise to the absorption bands originated from the pyridine ring (peaks with * mark) and selenophene ring (peaks with ○ mark). Splitting of the pyridine skeletal vibration peak at about 1600 cm⁻¹ into several peaks in the IR spectrum of PNSe11 indicates the presence of pyridine-2,5-diyl units under various circumstances due to the copolymerization.

Figure 2 shows UV-vis spectra of PPy, PSe, and the copolymers. PSePy gives rise to the π - π^* absorption peak at λ_{max} = 491 nm, the position being comparable to the λ_{max} position of PTPy (490 nm).^{1a}

The appearance of the π - π^* absorption peak

of PSePy (curve (a) in Figure 2) at a longer wavelength than those of PPy (373 nm) and PSe (421 nm) supports the occurrence of the postulated intramolecular charge transfer between the electron-withdrawing pyridine ring and electron-donating selenophene ring.

PNSe41 ((b) in Figure 2) shows a main absorption band at 369 nm and shoulder at 423 nm, and these bands are considered to be originated from poly- or oligo(pyridine-2,5-diyl) and poly- or oligo(selenophene-2,5-diyl), respectively. On the other hand, PNSe11 ((c) in Figure 2) shows absorption bands originated from the PPy and PSe units and shoulder band at about 500 nm, attributed to charge transfer band. Observation of these spectra ((b) and (c) in Figure 2) is in a sharp contrast to the observation that PNS11, the copolymer of pyridine and thiophene, shows only one broad absorption band at about 470 nm ((d) in Figure 2) and suggests that PNSe rather has a block copolymer structure than a random copolymer structure whereas PNS has a random copolymer structure. The formation of a different type of copolymer between pyridine and selenophene from that of copolymer between pyridine and thiophene is attributed to the difference in electronic state and/or bulkiness between selenophene and thiophene units. For example, difference in the strength of interaction with 2,5-dibromopyridine between 2,5-dibromothiophene and 2,5-dibromoselenophene is conceivable due to the difference between the van der Waals radius⁷ of Se (1.90 Å) and that of S (1.80 Å). A considerably stronger interaction between thiophene and pyridine units than that between selenophene and pyridine units is reported in relation to excimer formation of poly(aryleneethynylene) type polymers.⁸

The UV-vis data of PPy, PSe and the copolymers are summarized in Table I. If the PNSe type copolymers take such a block copolymer structure, they may serve to design interesting optical devices utilizing such unique structure having electron withdrawing poly-

Figure 1. IR spectra of PPy, copolymers, and PSe.

or oligo(pyrine-2,5-diyl) block and electron-donating poly- or oligo(selenophene-2,5-diyl) block.

The copolymers have the electrical conductivity (σ) of $10^{-9} \text{ S cm}^{-1}$, whereas iodine doped PNSe11 and PNSe41 show the σ value

Figure 2. UV-visible spectra of copolymers: (a) PSePy; (b) PNSe41; (c) PNSe11; (d) PNS11. $\lambda_{\max}$ positions of PPY and PSe are also shown. Solvent: HCOOH for PPY, PNSe, PSePy, and PNS; CHCl_3 for PSe.

Table I. UV-vis spectra of PPY, copolymers and PSe

No.	Polymer	$\lambda_{\max}/\text{nm}$
1	PPY ^a	373
2	PSePy ^a	491
3	PSe ^b	421
4	PNSe41 ^a	369 + 423sh ^c
5	PNSe11 ^a	250 + 360 + 470 sh ^c
6	PNS11 ^a	ca. 470
7	PTPy ^{a,d}	490
8	PTh ^b	415

^a In formic acid. ^b In CHCl_3 . ^c Shoulder peak.

^d From ref 1.

of 10^{-6} and $10^{-8} \text{ S cm}^{-1}$, respectively, as measured with compressed powder at room temperature.

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