NOTES

Synthesis and Optical Properties of Soluble Isoxazole-Containing Poly(*p*-phenylene)-Related Polymer

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Polymeric light-emitting diodes (LEDs) have recently attracted attention.¹ These polymers composed of highly π -deficient heterocycles such as pyridine and oxadiazole ring are typically *n*-dopable with high electron affinity showing greater tendency for transporting electrons.^{2,3} Although isoxazole derivatives are π -deficient heterocycles, polymeric materials having isoxazole ring have been paid less attention. Several poly(isoxazole)s have been prepared by 1,3-dipolar polycondensations of dinitrile *N*-oxide compounds with diynes⁴ and by reaction of poly(diethylbenzene) with hydroxylamine.⁵ However, examples of soluble polymers having isoxazole unit in the main chain are limited. Preparation of soluble polymers by 1,3-dipolar polycondensation was reported by Kanbara *et al.*⁶ This note describes the synthesis and optical properties of a soluble isoxazole-containing poly(*p*-phenylene)-related polymer by palladium-catalyzed cross-coupling reaction of an isoxazole monomer with dioctylbenzene-1,4-bisboronic acid.

EXPERIMENTAL

Measurements

¹H NMR and ¹³C NMR spectra were obtained with a JEOL JNM-EX270 spectrometer (270 MHz for ¹H NMR and 67.9 MHz for ¹³C NMR). TGA was performed on a Shimadzu DT-30 instrument (10°C min⁻¹). UV spectrum was recorded on a JASCO V-530 spectrophotometer. Fluorescence spectrum was obtained on a Perkin Elmer LS50B luminescence spectrometer. Gel permeation chromatographic analysis was carried out on a Tosoh G4000H_{XL} column using tetrahydrofuran (THF) as an eluent with calibration using standard

polystyrene samples. DSC analysis was carried out on a Seiko DSC200 instrument using 6 mg exactly weighed sample.

Materials

Unless stated otherwise, all reagents and chemicals were obtained from commercial sources and used without further purification. Toluene was distilled under nitrogen over CaH₂. 3,5-Bis(4-bromophenyl)isoxazole (**1**) was synthesized from 4'-bromo-2-(4-bromobenzoyl)acetophenone according to a literature.⁷ Dioctylbenzene-1,4-bisboronic acid (**2**) was prepared as reported.⁸

Polymerization

To a solution of **1** (77.8 mg, 0.205 mmol), **2** (80.0 mg, 0.205 mmol), and Pd(PPh₃)₄ (2.0 mg, 3.7 × 10⁻⁶ mol) in toluene (3.0 ml) were added 1.5 ml of 2 M Na₂CO₃ under nitrogen. The mixture was stirred for 2 days under reflux. The product mixture was poured into 100 ml methanol–water (4:1, v/v) and the precipitate was filtrated. To separate traces of inorganic salts, the polymer was extracted with toluene in a Soxhlet apparatus for 12 h. The resulting solution was evaporated in vacuo to give 94.8 mg (0.182 mmol, yield 89%) of the polymer (**3**). ¹H NMR (CDCl₃): δ 0.85 (CH₃, t, 6H), 1.20 (CH₂, br, 24H), 2.63 (Ph-CH₂, br, 4H), 6.96 (isoxazole, s, 1H), 7.20 (Octyl-C₆H₂-Octyl, s, 2H), 7.54 (C₆H₄, m, 4H), 7.97 (C₆H₄, m, 4H). ¹³C NMR (CDCl₃): δ 14.41, 23.11, 29.62, 29.99, 31.39, 32.30, 33.14, 97.88, 126.09, 127.04, 128.12, 130.48, 131.36, 132.67, 138.13, 140.83, 144.26, 163.32, 170.85. Anal. Calcd for C₃₇H₄₅NO: H 8.73; C 85.5; N 2.69; O 3.08. Found: H 8.71; C 83.25; N 2.47; O 3.19.

Scheme 1.

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Figure 1. ^1H NMR spectrum of **3** in CDCl_3 .

RESULTS AND DISCUSSION

Polymerization was carried out by palladium-catalyzed cross-coupling reaction of the isoxazole monomer (**1**) with dioctylbenzene-1,4-bisboronic acid (**2**). Equimolar amounts of **1** and **2** were treated with 2 mol% $\text{Pd}(\text{PPh}_3)_4$ in a heterogeneous system of water (Na_2CO_3)/toluene under reflux condition. The mixture was poured into a large quantity of methanol–water (4:1, v/v). After the precipitate was extracted with toluene in a Soxhlet apparatus, polymer (**3**) was obtained in 89% yield. The polymer was soluble in common organic solvents such as CHCl_3 and THF. The polymer was dissolved in THF and subjected to GPC measurement. The number-average molecular weight (M_n) and molecular weight distribution (MWD) of the polymer were $M_n = 74000$ and $\text{MWD} = 3.37$, respectively.

Reduction of the amount of the catalyst decreased the yield and molecular weight of the polymer. Polymerization of equimolar amounts of **1** and **2** with 1 mol% of $\text{Pd}(\text{PPh}_3)_4$ in a water (Na_2CO_3)/toluene under reflux condition for 2 days gave the polymer in 48% yield. The number-average molecular weight of the polymer was 7000.

Elemental analysis data of the polymer were in agreement with calculated values for the ideal structure. The structure of the polymer was supported by ^1H and ^{13}C NMR. Figure 1 shows the ^1H NMR spectrum of the polymer. The peak attributable to 4-H proton of the isoxazole ring was observed at 6.9 ppm. Peak areas agreed with structure. The ^{13}C NMR spectrum of the polymer shows three peaks at 163.32, 170.85, 97.88 ppm due to the carbons of isoxazole ring.

Thermogravimetric analysis (TGA) for **3** showed relatively high thermal stability with 5% weight loss of the polymer at 352°C under nitrogen. The differential scanning calorimetry (DSC) thermogram of the polymer showed no melting point below 200°C.

The UV-Vis absorption spectrum of the polymer showed a peak due to the π – π^* transition at 380 nm. Under ultraviolet light irradiation, the polymer was strongly fluorescent with purple emission. Figure 3 displays a fluorescence emission spectrum of the polymer recorded in chloroform with excitation wavelength of

Figure 2. Fluorescence emission spectrum of **3** in chloroform at room temperature (excitation wavelength at 350 nm).

350 nm. The fluorescence spectrum exhibited the emission maximum at 423 nm. Although poly(arylene)s containing isoxazole units as well as optical active carbazole units show strong fluorescence with peaks at 340–490 nm,⁶ our results indicate for the first time of a fluorescent soluble isoxazole-containing poly(*p*-phenylene)-related polymer. Electron transfer from *p*-phenylene unit to π -deficient isoxazole unit may thus occur in excited states of the polymer.

REFERENCES

1. M. Strukelj, F. Papadimitrakopoulos, T. M. Miller, and L. J. Rothberg, *Science*, **267**, 1969 (1995).
2. Q. Pei and Y. Yang, *Chem. Mater.*, **7**, 1568 (1995).
3. A. J. Epstein, J. W. Blarchford, Y. Z. Wang, S. W. Jessen, D. D. Gebler, L. B. Lin, T. L. Gustafson, H.-L. Wang, Y. W. Park, T. M. Swager, and A. G. MacDiarmid, *Synth. Met.*, **78**, 253 (1996).
4. Y. Iwakura, K. Uno, S.-J. Hong, and T. Hongu, *Polym. J.*, **2**, 36 (1971).
5. W. Bracke, *J. Polym. Sci., Part A-1*, **10**, 983 (1972).
6. T. Kanbara, T. Ishii, K. Hasegawa, and T. Yamamoto, *Polym. Bull.*, **36**, 673 (1996).
7. O. Dann, H. Fick, B. Pietzner, E. Walkenhorst, R. Fernbach, and D. Zeh, *Liebigs Ann. Chem.*, 160 (1975).
8. M. Rehahn, A. D. Schlüter, and G. Wegner, *Makromol. Chem.*, **191**, 1991 (1996).