Precise Synthesis and Properties of Poly(isocyanide)s Bearing Porphyrins as a Pendant Group

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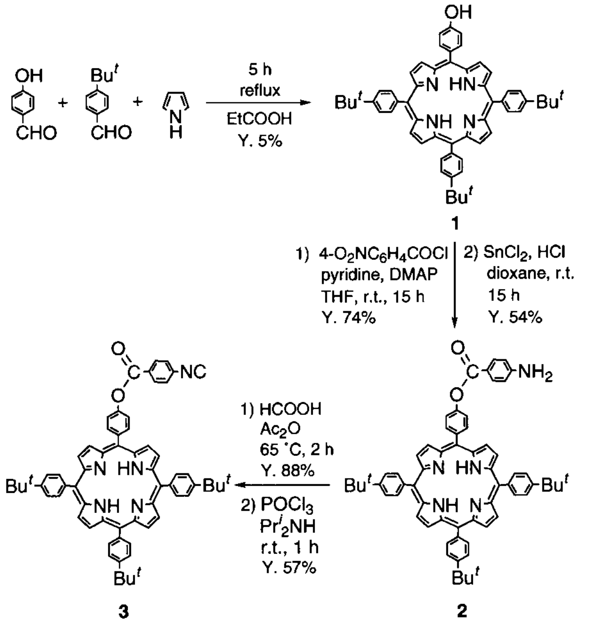
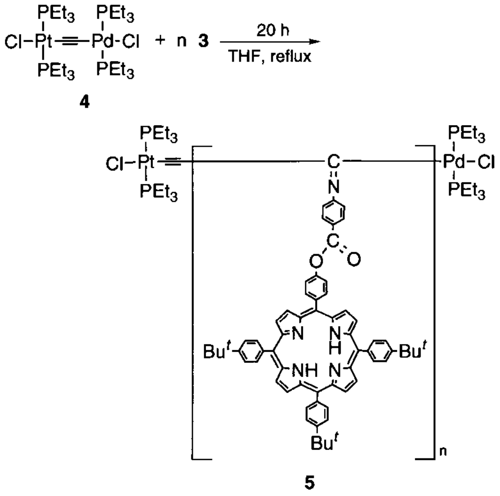
Aryl isocyanide bearing porphyrin has been prepared and polymerized by Pd–Pt μ-ethynediyl complex as an initiator to produce novel polymers. The UV–VIS absorption spectra suggest that porphyrin groups in their side chains are regularly arranged by the helical main chain of poly(isocyanide)s.

Porphyrin is a representative functional organic molecule having a wide range of potentials applicable to optoelectronics, fluorescence materials and oxidation catalysts.[1] In order to develop new materials incorporating prominent properties of porphyrin, many oligomers and polymers have been prepared.[2] However, limited numbers of reports on polymers bearing porphyrin moieties in their side chain are found in the literature.[3] It is known that poly(isocyanide)s having bulky substituents keep a rigid helical conformation even in solution.[4] Thus, poly(isocyanide)s containing porphyrins are of special interest since porphyrin groups may regularly be arranged due to the rigid main chain. Although Nolte and coworkers tried to prepare such polymers by a macromolecular reaction of poly(isocyanide)s with porphyrin moieties, the porphyrin contents were fairly low.[5] Previously we have reported the living polymerization of aryl isocyanides using Pd–Pt μ-ethynediyl complexes as an initiator.[6,7] This reaction has a wide scope of applications to various kinds of aryl isocyanides. Thus we successfully applied our system to the precise polymerization of aryl isocyanides with a porphyrin pendant group to produce novel poly(aryl isocyanide)s bearing porphyrin in their side chains.

The synthetic route for an isocyanide monomer bearing a porphyrin group is shown in Scheme 1. Monohydroxy tetraphenylporphyrin derivative **1**, which was prepared by the mixed condensation reaction of *p*-*t*-butylbenzaldehyde and *p*-hydroxybenzaldehyde with pyrrole, was treated with *p*-nitrobenzoyl chloride followed by reduction using $SnCl_2$–HCl to give *p*-aminobenzoate derivative **2**. After transformation into *N*-formamide by the treatment with formic acid in acetic anhydride, dehydration using $POCl_3$–Pr^i_2NH yielded isocyanide monomer **3**. Resulting porphyrin isocyanide **3** is relatively stable in air, and is slightly soluble in common organic solvents.



Scheme 1.



Scheme 2.

Then, we performed the polymerization of **3** by Pd–Pt μ-ethynediyl complex **4** (Scheme 2). Although isocyanide monomer **3** has a very large substituent, the polymerization smoothly proceeded in quantitative conversions to give poly(isocyanide)s **5a**–**5e** in good isolated yields. Resulting polymers **5a**–**5e** are appreciably soluble in common organic solvents such as THF, benzene and dichloromethane in contrast to monomer **3**. The results of the polymerization are summarized in Table 1. The polymers prepared in this study have a narrow molecular weight distribution, suggesting that the reaction is a living polymerization. The living nature of the present system was supported by the proportional relationship between the molecular weight of resulting polymers and the ratio of monomer **3** / initiator **4** (Figure 1).

In order to obtain information on the conformation of porphyrin groups in the side chain, the UV–VIS absorption spectra of polymers **5a**–**5e** were measured. Figure 2 shows the UV–VIS spectra of **5b** (n = 30) and **5e** (n = 100) along with those of monomer **3** and dimer **5f** (n = 2), the latter of which was prepared by the reaction of **4** with 2 equiv of **3** in 75% yield and was fully characterized by spectral analyses. Monomer **3**

Table 1. Polymerization of porphyrin isocyanide **3** by Pd-Pt μ-ethynediyl complex **4**[a]

Polymer	[**3**]$_0$/[**4**]$_0$	Yield / %	M_n[b]	M_w/M_n[b]
5a	20	80	8000	1.04
5b	30	83	10900	1.06
5c	50	89	15500	1.09
5d	70	85	18300	1.14
5e	100	94	25000	1.14

[a] Standard conditions: initiator (**4**) 2.0 μmol, THF 15 mL, reflux, 20 h. The resulting polymers were purified by reprecipitation with methanol. [b] M_n and M_w/M_n were determined by GPC analyses (mobile phase: THF) using polystyrene standards.

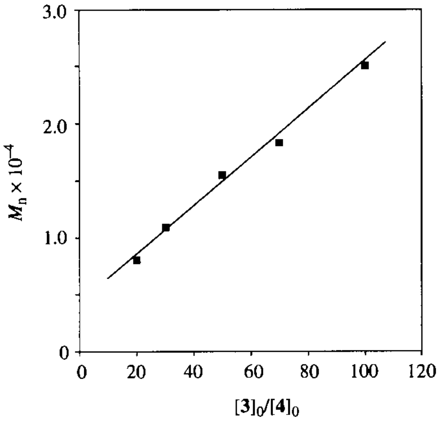


Figure 1. M_n values of poly(isocyanide)s **5** as a function of the initial ratio of monomer **3** / initiator **4**.

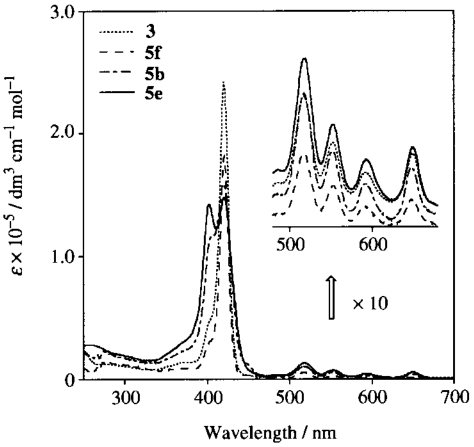


Figure 2. UV-VIS spectra of monomer **3**, dimer **5f** and polymers **5b** and **5e** in chloroform at room temperature using a 10 mm quartz cell.

showed a Soret band at 420 nm (half-band width 13 nm) and Q bands at 518, 553, 593, and 650 nm. The absorption spectrum of dimer **5f** was similar to that of monomer **3**. In contrast, polymers **5b** and **5e** exhibited broad split Soret bands (λ_{max} = 407 and 420 nm, half-band width 35 nm for **5b**; λ_{max} = 402 and 420 nm, half-band width 40 nm for **5e**), due to the exciton coupling of porphyrin groups.[8] No significant differences in λ_{max} values were observed in the region of the Q band though the absorbances were different from each other. The important point to note is that the increase in molecular weights of the polymers showed a hypochromic shift with a hyperchromic effect in the higher-energy component of the Soret band. The splitting energy ΔE, that is a function of distance and relative orientation of porphyrins,[9] corresponds to 761 cm^{-1} for **5b** and 1066 cm^{-1} for **5e**. Although such split Soret bands were often observed in oligomers containing porphyrin moieties in the main chain,[2] but not in polymers containing porphyrins in their side chains. Poly(acrylate)s and poly(methacrylate)s, of which main chains are flexible to form a random coil, containing porphyrin moieties in their side chains showed broad single Soret bands.[3] On the other hand, porphyrin oligomers with a slipped cofacial structure showed the split Soret bands as observed in our poly(isocyanide)s prepared in this study.[10] Since the UV–VIS spectrum of **5e** was independent of polymer concentration in the region from 1.13×10^{-9} to 1.13×10^{-7} M, the split Soret band was not due to the intermolecular interaction but the intramolecular one of the porphyrin chromophore. Thus, the porphyrin groups in the side chains would be regularly arranged by the helical main chain of poly(isocyanide)s though the detail of the conformation of porphyrin groups is not clear at present. The polymers prepared in this study may have a potential of molecular devices and other speciality materials.

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