Preparation of Chiral Poly(dipyridylamine). Its Metal Complex-controlled Steric Structure, and Its Light Emitting Properties

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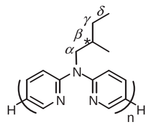
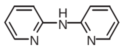
A new type of polyaniline, poly(dipyridylamine), with a coordination site and a chiral side chain was prepared. The polymer formed polymer–metal complexes, and steric structure of the polymer–metal complex was controlled by the kind of the coordinating metal species, as revealed by remarkable changes of the CD spectrum caused by coordination with the metal.

Polyaniline is one of the most attractive functional polymers,[1–3] and various derivatives of polyaniline have been synthesized.[4,5]



PDPyA(MB)

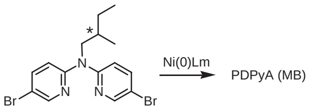


DPyA

We now report preparation of the following new type of polyaniline, PDPyA(MB), with the coordinating pyridine unit and a chiral (*S*)-2-methylbutyl (MB) side chain which might introduce an interesting structure to the polymer.

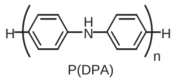
Wang reported that derivatives of di(2-pyridyl)amine (DPyA) emit blue light,[6] and Cotton, Dunbar, and Murillo found out that metal complexes of DPyA had unique crystal structures.[7] However, there has been no precedent of such a type of polyaniline with both the chelating coordination site and the chiral side chain to our knowledge. Herein we report synthesis of PDPyA(MB), its metal complex-controlled steric structure, and chemical properties of the polymer and metal complexes. Syntheses of the corresponding oligomers of PDPyA(MB) ($n = 2$ (UV–vis peak: 350 nm)–4 (UV–vis peak: 369 nm)) and their $CuCl_2$ complex and the crystal structure of the Cu complex of the dimer ($n = 2$) were previously reported by us.[8]

Dehalogenative polycondensation of *N*-(*S*)-(2-methylbutyl)bis(4-bromo-2-pyridyl)amine[8] with a zero-valent nickel complex, Ni(0)Lm, provided PDPyA(MB) in 84% yield (Eq 1). Detection of no Br in PDPyA(MB) indicated that the polymer had two C–H end groups, similar to the case of P(DPA) prepared by similar polycondensation.[9,10]



(1)

Ni(0)Lm: a mixture of bis(1,5-cyclooctadiene)nickel, Ni(cod)$_2$, and 2,2'-bipyridyl, bpy.



P(DPA)

PDPyA(MB) was soluble in chloroform and THF. Intrinsic viscosity of PDPyA(MB), 0.52 dLg^{-1} ($CHCl_3$, 30 °C, dL = 100 cm^3), was comparable to that (0.66 dLg^{-1}) of P(DPA),[9] which gave a number average molecular weight, M_n, of 6400 and a weight average molecular weight, M_w, of 20000 in GPC analysis in DMF. Light scattering analysis of PDPyA(MB) in chloroform gave an M_n value of 44000.

^{1}H NMR signals of the hydrogens at the α and β positions in PDPyA(MB) were observed at δ 4.18 and 1.99, respectively. A peak of the two CH_3 groups was located at δ 0.92. Two hydrogens at the γ position were diastereotropic and showed peaks at δ 1.21 and 1.54 in an equal intensity. Peaks of the pyridine ring hydrogens were observed in a range of δ 7.23 to 8.58. Peak intensity ratio between the MB hydrogens and the pyridine ring hydrogens agreed with the structure. The terminal C–H peak was not detected, revealing that PDPyA(MB) had enough degree of polymerization. ^{13}C NMR signals assigned to aromatic and aliphatic carbons of PDPyA(MB) appeared in ranges of δ 115.0–156.9 and of δ 11.4–54.1, respectively. PDPyA(MB) showed a π–π* absorption peak (379 nm; cf. Figure 1) at the same position (380 nm) as P(DPA).

Mixing a $CHCl_3$ solution of PDPyA(MB) with a CH_3OH solution of MCl_2 (M = Ni and Cu) in a 95:5 volume ratio caused 1:1 coordination of the metal with PDPyA(MB) to give polymer–metal-complexes, MCl_2-PDPyA(MB). By the coordination with MCl_2, the λ_{max} position is shifted to a shorter wavelength (e.g., 350 nm by coordination with Cu^{2+}) as shown in the top

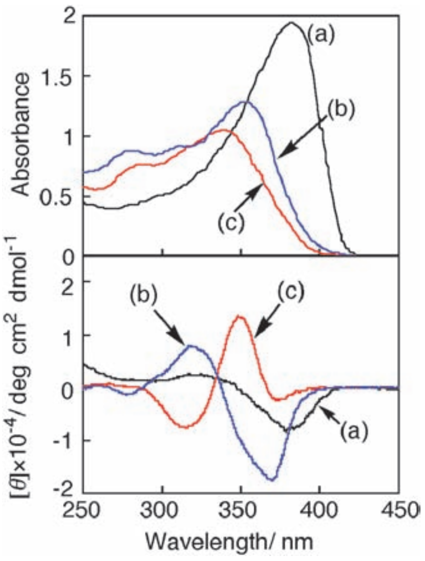


Figure 1. UV–vis (top) and CD (bottom) spectra of the 95:5 $CHCl_3$–CH_3OH solution of (a) PDPyA(MB) (0.6 mM) and the 95:5 $CHCl_3$–CH_3OH solution of PDPyA(MB) (0.6 mM) in the presence of 0.6 mM (b) $CuCl_2$ and (c) $NiCl_2$. Molarity is based on the repeating unit.

panel of Figure 1. The effective conjugation length is shortened presumably due to twisting of the polymer main chain caused by the coordination of MCl_2; however, the λ_{max} position locates at a longer wavelength than that of the π-conjugated 3,3′-bipyridyl unit in PDPyA(MB) (λ_{max} of 3,3′-bipyridyl $= 274$ nm). For $NiCl_2$ and $CuCl_2$, the change of the UV–vis spectra was almost saturated at the MCl_2/(chelating unit) ratio of 1, indicating that the complex forming reaction proceeded quantitatively. Although the formed polymer complex did not have good solubility, their basic optical properties in solutions could be followed.

Figure 1 depicts the changes of UV–vis and CD spectra of the 95:5 $CHCl_3$–CH_3OH solution of PDPyA(MB) caused by addition of MCl_2 (M = Cu and Ni). PDPyA(MB) showed a CD signal with a Cotton effect corresponding to the UV–vis peak. The $CuCl_2$ and $NiCl_2$ complexes exhibited opposite CD signals to each other, revealing that the steric structure of the PDPyA(MB) main chain was controlled by the coordination of MCl_2. The position of the Cotton effect was shifted to a shorter wavelength in accord with the shift of the UV–vis peak. The 95:5 $CHCl_3$–CH_3OH solution of PDPyA(MB) containing $CuCl_2$ and $NiCl_2$ in a Cu:Ni:DPyA(MB) unit ratio of 1:1:1 showed a CD curve similar to the CD curve obtained with the solution made of PDPyA(MB) and $CuCl_2$. These data indicate that $CuCl_2$ has much higher coordinating ability toward PDPyA(MB) than $NiCl_2$.

In contrast to the cases of $CuCl_2$ and $NiCl_2$, a solution made of PDPyA(MB) and $CoCl_2$ gave only a very weak CD signal in spite of a UV–vis shift to 350 nm by coordination with $CoCl_2$, indicating that the complex formation with $CoCl_2$ did not bring about an ordered structure of the polymer main chain. One of possible explanations about the CD data shown in Figure 1 is that PDPyA(MB) has a helical structure caused by the side chain chirality and the coordination with $NiCl_2$ and $CuCl_2$ leads to a reverse type of helical structures each other. It was reported that a helical structure of polythiophene with a chiral oxazole side chain, PTh–Oxz, was induced by metal complexation with Cu(II).[11] The peak θ value in the CD spectra of PDPyA(MB) and its $CuCl_2$- and $NiCl_2$-complexes was comparable to that of the PTh–Oxz–Cu(II) system, supporting formation of the helical structures of MCl_2–PDPyA(MB) (M = Cu and Ni) complexes in the solution.

PDPyA(MB) was photoluminescent and the photoluminescence (PL) spectrum showed a main peak and a shoulder peak at 416 and 440 nm, respectively. The position of the main peak agrees with the onset position of the UV–vis absorption band, as usually observed with aromatic compounds and polymers, and indicates that the main peak is assigned to a usual singlet-singlet emission. The PL main peak is located at a longer wavelength than that of the previously reported oligomers (409 nm for $n = 4$).[8] The shoulder PL peak of PDPyA(MB) was ascribed to a phosphorescence based on its considerably long lifetime of about 700 ms at 20 °C, which is comparable to that observed with the oligomer (682 ms for $n = 3$).[8] A life-time of the main peak was shorter than 1 ms (detection limit of the measuring system), supporting the assumption of the usual singlet–singlet emission. Figure 2 depicts PL spectra of a $CHCl_3$ solution of PDPyA(MB) at 20 °C and of a frozen $CHCl_3$ solution of PDPyA(MB) at −196 °C.

Intensity of the shoulder peak became stronger at −196 °C than that at 20 °C. Phosphorescence often shows such enhancement of the intensity at a lower temperature, supporting the assignment of the peak to phosphorescence.[12] One of possible explanations for the PL data is that the photoenergy captured by PDPyA(MB) is mainly emitted at the main PL peak, however, it is partly transferred to a triplet state to give the triplet-singlet (phosphorescent) sub-emission. PL spectra of aromatic polymers often show multiple peaks, however, observation of both the usual PL and phosphorescence is rare. Total quantum yield $\Phi_p + \Phi_f$ of PDPyA(MB) at 20 °C was 9%. The PL of the $CHCl_3$ solution of PDPyA(MB) was quenched by addition of an equimolar amount of $CuCl_2$. The quench of the PL is probably due to the existence of chloride ligands in $CuCl_2$–PDPyA(MB), which is known to quench PL through heavy atom effects. Similar quenching effect of metal complexation on PL of derivatives of DPyA has been reported.[6]

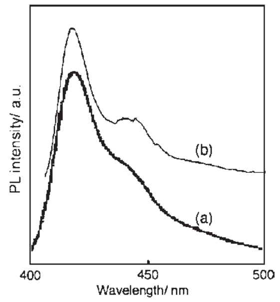


Figure 2. PL spectra of (a) the $CHCl_3$ solution of PDPyA(MB) at 20 °C and (b) the frozen $CHCl_3$ solution of PDPyA(MB) at −197 °C.

As described above, a novel polyaniline-type polymer with the chiral side chain has been prepared. The CD data indicate that the steric structure of the polymer is controlled by metal complexation.

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