Preparation of Poly(9,10-dihydrophenanthrene-2,7-diyl) Consisting of a Chiral C_2-Symmetrical Monomeric Unit and Optical Properties of the Polymer

Takayuki Iijima and Takakazu Yamamoto*
Chemical Resources Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503

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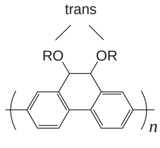
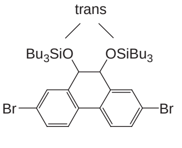
Poly(9,10-dihydrophenanthrene-2,7-diyl) consisting of chiral 9,10-dihydro-9,10-bis(tributylsilyloxy)phenanthrene-2,7-diyl units has been prepared. Film of the polymer showed a very large circular dichroism with a peak value of −6 deg/μm at 411 nm.

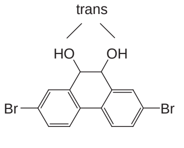
Poly(*p*-phenylene)s such as poly(fluorene)s[1] and poly(tetrahydropyrene)s[2] show strongly light emitting properties and are considered to be candidates as materials for polymer-based light emitting diodes. Previously, we reported synthesis of a new family of poly(*p*-phenylene), poly(9,10-dihydrophenanthrene-2,7-diyl)s, and their strong light emitting feature (e.g., almost 100% quantum yield in photoluminescence for PH_2Ph(9,10-OR) with R = $SiBu_3$ (Bu = butyl)).[3]



PH_2Ph(9,10-OR)



Momomer-1



di-OH compound

The polymers were synthesized by organometallic polycondensation of dibromo monomers such as Monomer-1. The monomer was synthesized via the above shown di-OH compound[3] formed by reaction of the corresponding dialdehyde (Mukaiyama reaction),[4] which usually gives trans configuration for the two OH groups. Consequently, the di-OH compound was considered to be a mixture of (*S*),(*S*)- and (*R*),(*R*)-isomers with C_2 symmetry.

If optically resolved monomer is obtained, the monomer will give a chiral polymer consisting of chiral aromatic monomeric units with C_2 symmetry. Chiral compounds with C_2 symmetry are centrally important compounds in the modern asymmetric chemistry.[5] Synthesis of chiral and helical polymers are the subject of recent interest.[6,7] However, preparation of such a π-conjugated poly(*p*-phenylene) type chiral polymer consisting of the aromatic chiral monomeric unit with C_2 symmetry has no precedent to our knowledge. Herein, we report preparation of the chiral aromatic π-conjugated polymer and strong dichroism observed with a film of the polymer.

The di-OH compound was optically resolved to a (+)-di-OH compound and a (−)-di-OH compound by HPLC using a chiral column at Sumika Chemical Analysis Service, Ltd. The optical purity of the (+)-di-OH compound and the (−)-di-OH compound was estimated at 98.6 and 98.5%, respectively, from the HPLC curve. The obtained (+)-di-OH compound and (−)-di-OH compound gave $[\alpha]_D$ of +33.84 and −33.02°, respectively, in methanol. Slow natural evaporation of solvents from solutions of (+)- and (−)-di-OH compounds gave band-like crystals, however, crystals suited for single crystal X-ray analysis have not been obtained. From the (+)-di-OH compound, (+)-Monomer-1 was prepared.[3] Figure 1 exhibits circular dichroic (CD) spectrum of (+)-Monomer-1; the CD spectrum shows peak at 289 nm which correspond to the UV–vis peaks of (+)-Monomer-1.

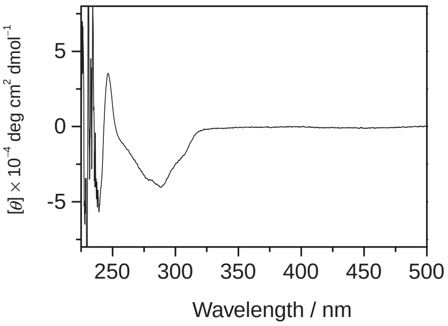


Figure 1. CD spectrum of (+)-Monomer-1 in chloroform. [(+)-Monomer-1] = 4.3×10^{-5} M.

Dehalogenative polycondensation of (+)-Monomer-1 with a zerovalent nickel complex, similar to the preparation of racemic $PH_2Ph(9,10\text{-}OSiBu_3)$,[3] gave (+)-$PH_2Ph(9,10\text{-}OSiBu_3)$. The polymer showed a number average molecular weight and a weight average molecular weight of 4800 and 5800, respectively, in GPC analysis. (+)-$PH_2Ph(9,10\text{-}OSiBu_3)$ was also strongly photoluminescent, and IR, ^1H NMR, and UV–vis data (including molar absorption coefficient) of (+)-$PH_2Ph(9,10\text{-}OSiBu_3)$ were the same as those of racemic $PH_2Ph(9,10\text{-}OSiBu_3)$. Casting a chloroform solution of (+)-$PH_2Ph(9,10\text{-}OSiBu_3)$ gave a smooth film, whereas analogous casting procedure for racemic-PH_2Ph-(9,10-$OSiBu_3$) afforded a brittle film with cracks. There data suggest the presence of a stronger intermolecular interaction

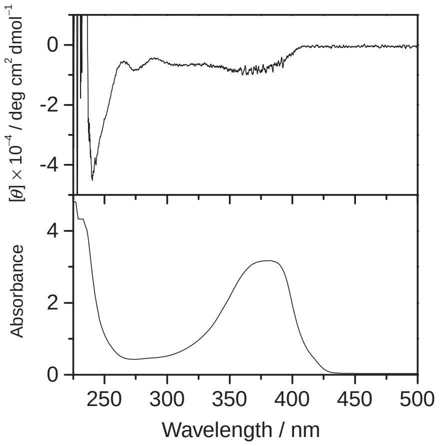


Figure 2. UV–vis and CD spectra of the chloroform solution of (+)-$PH_2Ph(9,10\text{-}OSiBu_3)$.

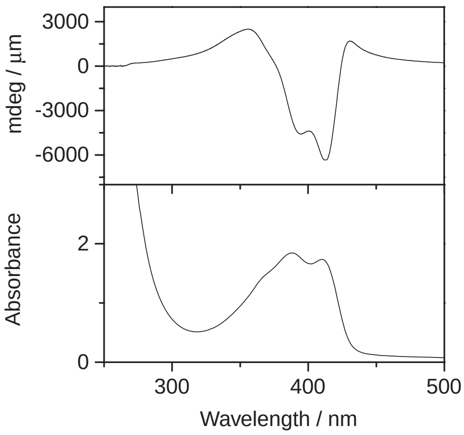


Figure 3. UV–vis and CD spectra of the cast film (thickness = 320 nm) of (+)-PH_2Ph(9,10-$OSiBu_3$). The CD data are given in the degree per the thickness of the film. The film was cast on a non-fluorescent glass plate.

between the (+)-PH_2Ph(9,10-$OSiBu_3$) molecules. One of the interesting features of (+)-PH_2Ph(9,10-$OSiBu_3$) is that the polymer exhibits a very strong circular dichroism in the film. Figures 2 and 3 depict the UV–vis and CD spectra of a chloroform solution and the cast film of (+)-PH_2Ph(9,10-$OSiBu_3$), respectively.

As seen from Figure 2, (+)-PH_2Ph(9,10-$OSiBu_3$) showed no significant CD peak related to the π–π^* transition of the poly(*p*-phenylene) type polymers at about 370 nm which occurs along the polymer main chain.[1,2,8] On the contrary, the cast film exhibits a strong CD peak(s) at about 400 nm,[9] suggesting formation of an ordered structure (possibly a helical structure) in the cast film. Strong CD of films has been reported for some chiral polymers.[6,7] The observed mdeg/µm value shown in Figure 3 is very large. Both the solution and film, which afford the data exhibited in Figures 2 and 3, have a comparable absorbance indicating the presence of a comparable amount of the polymer in the path of light, however, the CD effect is much stronger (by more than 10^3 times) for the film. Addition of a small amount (e.g., 10 vol %) of methanol (poor solvent) to the chloroform solution of the polymer caused no obvious change; no significant CD was observed. However, when a larger amount of methanol, more than 20 vol %, was added, UV–vis absorption peak shifted to a longer wavelength and a new peak appeared at about 410 nm. When the large amount of methanol was added, CD was clearly observed. At 40 vol %, a peak CD value of 5.3×10^5 deg cm^2 dmol^{-1} was obtained at 390 nm. The peak CD value saturated at about 40 vol % of methanol and addition of 50 volume % of methanol gave a similar CD value. Addition of a larger amount of methanol caused precipitation of the polymer. These results suggest that addition of methanol leads to aggregation of the (+)-PH_2Ph(9,10-$OSiBu_3$) molecules and the aggregated particles afford the strong CD. Although CD data of cast films of chiral polymers have been reported,[6,7] such a large degree/µm value of the CD peak as shown in Figure 3 has no precedent to our knowledge.

As described above, a new light-emissive (+)-PH_2Ph(9,10-$OSiBu_3$) constituted of the chiral aromatic monomeric unit with C_2 symmetry has been prepared and the polymer gives very strong CD in film.

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References and Notes

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9 The π–π^* peaks of π-conjugated polymers often show a shift to a longer wavelength in films.[8]