

SHORT COMMUNICATIONS

Synthesis and Optical Activity of Polyamides Derived from Optically Active Spiro[3.3]heptane-2,6-dicarboxylic Acid

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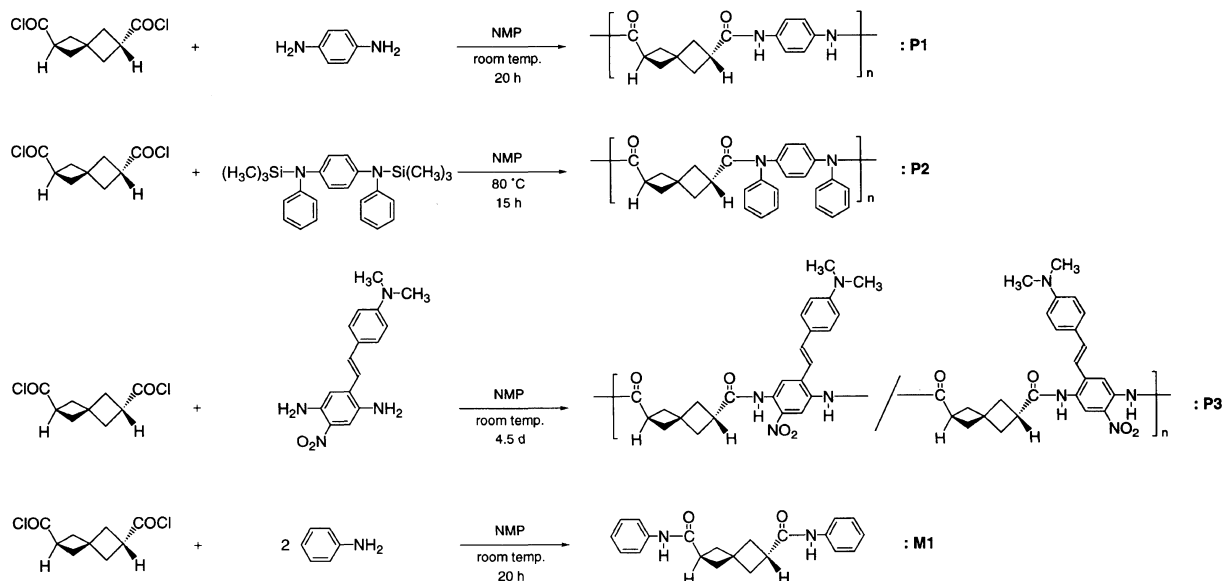
Optically active polymers are usually prepared by asymmetric polymerization, in which optical activity is induced *via* polymerization reaction using optically active catalyst or initiator from racemic or prochiral monomer or *via* that which gives conformational chirality excess in one handed sense. Optically active polymers based on the asymmetric conformation is a topic currently attracting much attention in various fields as catalysts, and photo- and electroactive materials. These polymers have been reported to be formed from various type of monomers such as isocyanates,¹ isocyanides,² chlorals,³ and methacrylates.⁴

Polycondensation of optically active monomers is another effective method to synthesize optically active polymers with rigid conformation. Overberger reported that optically active polyamides derived from *trans*-cyclopropanedicarboxylic acids showed some ordered conformation even in solution.⁵ Shulz reported the synthesis of optically active polyamide derived from optically active 1,1'-binaphthyl-2,2'-diamine.⁶ Optically active polyamides obtained from (*R*)- or (*S*)-6,6'-dimethylbiphenyl-2,2'-dicarboxylic acid chloride and azodianiline or from optically active 6,6'-dibromo-2,2'-

dimethoxy-1,1'-binaphthyl, carbon monoxide and azo-dianiline in the presence of palladium catalyst were also reported by Kondo.⁷ Pu synthesized optically active polymers containing binaphthyl units for catalysts application.⁸

(*R*)-(+)-Spiro[3.3]heptane-2,6-dicarboxylic acid chloride ((*R*)-(+)-SHDAC) has two cyclobutane rings inevitably twisting 90° each other and can be obtained by the optical resolution with brucine ($[\alpha]_D^{25} = +4.6$ ($c = 5.6$, acetone)).⁹ It is of interest that a novel class of optically active polyamides and polyesters can be synthesized by using it as a novel optically active dicarboxylic acid unit. Moreover, it is expected that the polyamide chains prepared from the spiran derivative would twist 90° unit by unit and form some ordered conformation even in solution depending on the structure of the diamine component. We report here the synthesis and optical properties of polyamides derived from (*R*)-(+)-SHDAC and three diamine derivatives.

Spiro[3.3]heptane-2,6-dicarboxylic acid (SHDA),⁹ *N,N'*-diphenyl-*N,N'*-bis(trimethylsilyl)-*p*-phenylenediamine,¹⁰ and 2',5'-diamino-4-(dimethylamino)-4'-nitrostilbene (DDANS)¹¹ were synthesized according to the



Scheme 1. Synthesis of polymer P1–3 and M1 from (*R*)-(+)-SHDAC.

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Table I. Synthesis of optically active polyamides^a

| Polymer | Concentration | Time | Yield | M_n^b | DP | PDI | $[\alpha]_D^{25}$ |
|-----------------------|----------------------|-------|-------|---------|----|-----|--|
| | mol dm^{-3} | | | | | | % |
| P1 | 0.36 | 20 h | 94 | — | — | — | +47.0 ^c |
| P2^d | 0.15 | 15 h | 21 | 15000 | 37 | 1.2 | -8.1 ^e |
| P3 | 0.40 | 4.5 d | 90 | 24300 | 55 | 1.5 | +278.5 ^f |
| M1^g | — | — | — | — | — | — | +17.0 ^h -10.1 ⁱ -13.8 ^j |

^aThe diamines are *p*-phenylenediamine (for **P1**), and *N,N'*-bis(trimethylsilyl)-*p*-phenylenediamine (for **P2**), and DDANS (for **P3**). Reaction was carried out at room temperature. ^bDetermined by SEC (eluent: DMF containing 0.01 M of LiCl, polystyrene standard). ^c $c=0.17$, conc. H_2SO_4 . ^dReaction was carried out at 80°C. ^e $c=0.69$, THF. ^f $c=0.0079$, DMAc. ^g**M1**=model compound: (*R*)-2,6-bis(*N*-phenylamido)-spiro[3.3]heptane. ^h $c=0.57$, conc. H_2SO_4 . ⁱ $c=0.48$, THF. ^j $c=0.57$, DMAc.

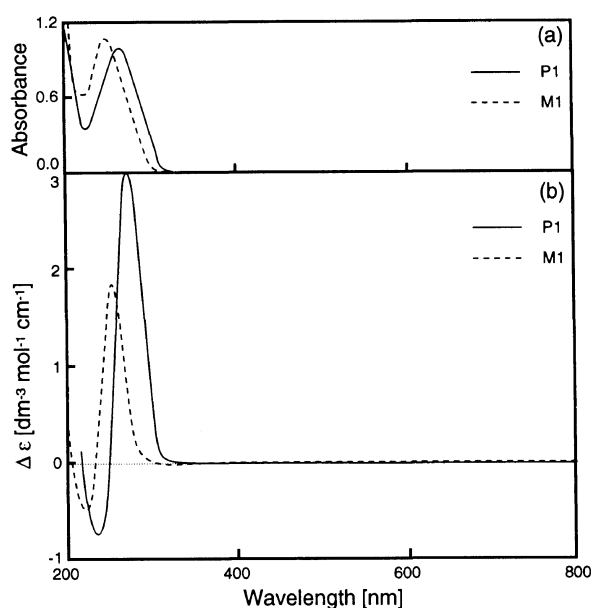


Figure 1. Electronic absorption (a) and circular dichroism (b) spectra of **P1** and **M1** in sulfuric acid. The CD spectra were measured in a 0.2 cm quartz cell with concentration of 0.3 mmol dm^{-3} .

literature. (*R*)-(+)-SHDA was treated with excess thionyl chloride to give (*R*)-(+)-SHDAC.¹²

The synthetic scheme of the polymers, **P1–P3**, and a model compound, (*R*)-2,6-bis(*N*-phenylamido)-spiro[3.3]heptane (**M1**), is shown in Scheme 1. The results of polymer synthesis are shown in Table I together with a model compound, **M1**.

The polycondensation to give polymer **P1** was a fast reaction. When the acid chloride solution in 1-methyl-2-pyrrolidinone (NMP) was added to the *p*-phenylenediamine solution in NMP, precipitation occurred immediately. The polymer **P1** is not soluble in common organic solvents such as acetone, dimethyl sulfoxide (DMSO), *N,N*-dimethylacetamide (DMAc), *N,N*-dimethylformamide (DMF), but soluble in strong inorganic acid like concentrated sulfuric acid.

Electronic absorption and circular dichroism (CD) spectra of **P1** in sulfuric acid solution are shown in Figure 1. Electronic absorption spectrum of **P1** showed one λ_{max} at 265 nm, which is assigned to $\pi\text{-}\pi^*$ transition of

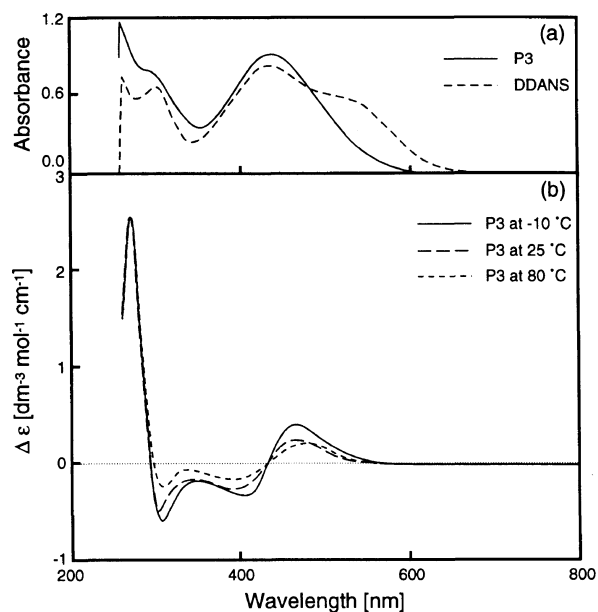


Figure 2. Electronic absorption (a) and circular dichroism (b) spectra of **P3** in DMF at -10°C , 25°C , and 80°C . The CD spectra were measured in a 0.2 cm quartz cell with concentration of 0.4 mmol dm^{-3} .

phenylene unit. This absorption band showed a larger positive Cotton effect (Figure 1 (b)), which exhibits the existence of the clockwise exciton coupling of the phenylene groups. The amplitude is about 1.5 times larger than that of the model compound, **M1**. Although more detailed investigation is needed, these results, especially, positive Cotton effect at 265 nm, might show that this polymer has some ordered structure, possibly a helical structure even in sulfuric acid.

The solubility of a synthesized polymer is very important not only for characterization but also for its application. In order to prepare a soluble polyamide from (*R*)-(+)-SHDAC having a rigid backbone, a secondary diamine *N,N'*-diphenyl-*p*-phenylenediamine was considered, and the polymer was synthesized through activated monomer as a *N*-silyl derivative.¹⁰ The resulting polymer **P2** was found to be soluble in common organic solvents such as tetrahydrofuran, NMP, DMAc, DMSO, DMF, and characterized by SEC, FT-IR and ^1H NMR. However, the yield of the resulting polymer was much lower than that of **P1**.

Polymer **P3**¹³ from (*R*)-(+)-SHDAC and DDANS has a large dye chromophore as a pendant group, and it is soluble in common polar organic solvents. Electronic absorption spectrum of **P3** in solution (Figure 2 (a)) showed a similar spectrum to that of DDANS, which has two λ_{max} s at 435 and 260 nm. In the CD spectrum (Figure 2 (b)), the absorption band having λ_{max} at 438 nm showed a positive Cotton effect as is in case of **P1**, which shows the existence of the clockwise exciton coupling of the dye chromophores. This result suggests that **P3** has some ordered structure in similar to the case of **P1**. Thus, the introduction of rigid and bulky pendant group allowed good solubility in organic solvents without loss of an ordered structure.

We also investigated the temperature dependency of CD spectra of **P1** and **P3**. Unfortunately, **P1** in sulfuric acid solution was decomposed when the solution

was heated at 80°C. CD spectra of **P3** in DMF solution were successfully measured at -10°C, 25°C, and 80°C. The Cotton effect becomes larger at lower temperature, and is still observed even at 80°C. This temperature dependency suggests that the polymer has a coil-like structure in solution.

The optical rotations of the polymers, **P1**—**P3**, and the model compound, **M1**, are also summarized in Table I. **P1** and **P3**, which are obtained from primary diamines, showed larger optical rotation, $[\alpha]_D^{26} = +47.0$ and $+278.5$, respectively, than that of the model compound, while **P2** showed a small optical rotation. These results suggest the importance of hydrogen bonding in taking the ordered structure. Among them, the optical rotation of **P3**, which has the rigid and bulky pendant group, was strikingly high. It may suggest that the rigid and bulky substituent fix the chiral axis more tightly than **P1** by preventing free rotation around the amide bond.

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12. ¹H NMR spectrum (500 MHz, δ ppm, CDCl₃): 2.32–2.54 (m, methylene, 8H), 3.44 (q, methine, 2H). ¹³C NMR spectrum (75.4 MHz, δ ppm, CDCl₃): 35.0, 37.9, 38.2, 43.9, 175.5.
13. ¹H NMR spectrum (500 MHz, δ ppm, DMSO-*d*₆): 2.20 (broad, methylene, 4H), 2.33 (broad, methylene, 4H), 2.81 (m, methine, 2H), 2.94 (s, N(CH₃)₂, 6H), 6.74 (broad, phenylene-*H*, 2H, *J*=8.7 Hz), 7.03 (d, *trans*-vinylene-*H*, 1H, *J*=15.9 Hz), 7.20 (d, *trans*-vinylene-*H*, 1H, *J*=15.9 Hz), 7.48 (broad, phenylene-*H*, 2H, *J*=8.7 Hz), 8.01 (broad, trisubstituted phenylene-*H*, 1H), 8.18 (broad, trisubstituted phenylene-*H*, 1H), 9.66 (broad, amide, 1H) 10.05 (broad, amide, 1H). ¹³C NMR spectrum (75.4 MHz, δ ppm, DMSO-*d*₆): 34.27, 35.86, 36.00, 36.15, 36.88, 37.33, 37.60, 112.40, 116.86, 120.95, 122.27, 124.44, 128.91, 129.13, 131.35, 134.50, 137.92, 139.56, 151.10, 173.41, 174.02.