

Polymer Communication

## Stereospecific interaction of one-handed helical polycations with chiral anions

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### Abstract

Optically active polyamide helices were obtained by the reaction of axially dissymmetric (*R*)- or (*S*)-6,6'-dibromo-2,2'-diethoxy-1,1'-binaphthyl, 3,6-diaminoacridine (proflavine), and carbon monoxide using a palladium catalyst. The acridine units in the chiral backbone were protonated with chiral 10-camphorsulfonic acid. Circular dichroism measurements revealed that (*R*)-(-)-camphorsulfonate anion ((*R*)-(-)-CSA<sup>-</sup>) is more easily incorporated into the protonated right-handed polyamide helix than (*S*)-(+)-camphorsulfonate anion ((*S*)-(+)-CSA<sup>-</sup>) and that the left-handed cationic helix preferentially interacts with (*R*)-(-)-CSA<sup>-</sup> to (*S*)-(+)-CSA<sup>-</sup>. © 2002 Elsevier Science Ltd. All rights reserved.

*Keywords:* Helical polyamide; 3,6-Diaminoacridine; Camphorsulfonic acid

### 1. Introduction

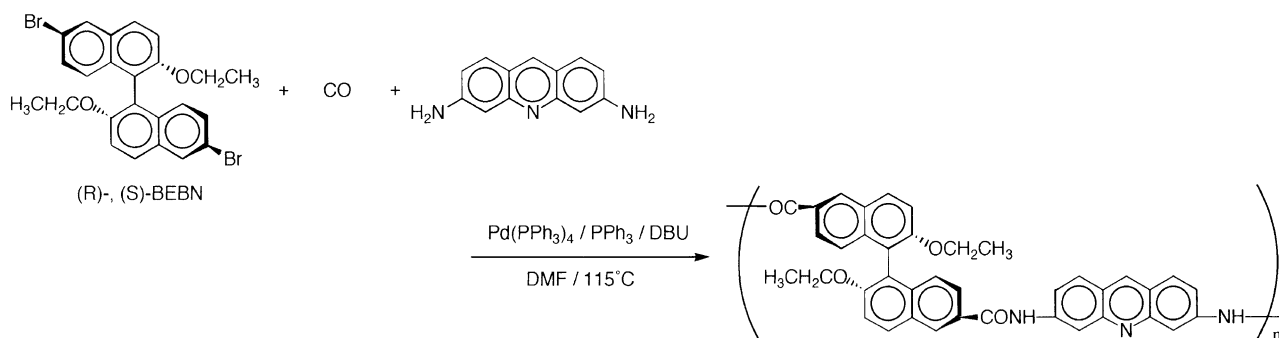
Synthetic helical polymers have been widely investigated [1]. Most of helical polymers such as polymethacrylates, polyisocyanates, and polyisocyanides were synthesized by chain reactions. To investigate the properties of helical polymers, we synthesized new types of helical polymers by step reactions, in which axially dissymmetric biphenylene or binaphthalene joints were connected with rigid aromatic segments [2–4]. These polymers have helical structures because of the chiral dissymmetric joints in their main chains. In our reports, we showed reversible photo-induced transformation of the helical structures of aromatic polyamides consisting of axially dissymmetric biphenylene or binaphthalene joints and azobenzene segments. Pu and co-workers reported conjugated polymers, whose structure was called 'propeller-like', containing dissymmetric binaphthalene units in the backbone [5], and examined electroluminescent and nonlinear optical properties of the conjugated polymers [6]. Takata et al. [7] synthesized a helical aromatic polycarbonate having C<sub>2</sub>-chiral binaphthalene units in the backbone and showed asymmetric catalysis of a one-handed helical

poly(metalo complex) [8]. Kawakami et al. [9] reported optically active polyamides that have (*R*)-spiro[3.3]heptane in the main chain. We also synthesized helical polyamides containing (1*R*,2*R*)-1,2-diaminocyclohexane units [10] or chiral tartaric acid units [11] in their backbones. Connection of functional segments with a dissymmetric joint interests us because the introduction of such segments into a helical backbone is expected to afford specific functional materials. We have already synthesized some helical polyamides having crown ether [12] and 2,2'-bipyridyl segments [13] in the main chain to examine their functional properties, in addition to the photoresponsive helical polyamides containing azobenzene segments [2–4].

3,6-Diaminoacridine (proflavine) has functions to act as a redox mediator and as a photosensitizer. Various polymers that have acridine moieties in the side chain [14] or in the main chain [15,16], and their photo-induced redox responsibilities were investigated. Since acridine is an aromatic base to act as a proton acceptor, the interaction of acridine segments oriented in a chiral helix with chiral acids is of much interest. Therefore, we synthesized a chiral helical polyamide by connecting acridine segments with chiral dissymmetric binaphthalene joints, and the interaction of the one-handed helical basic polymer with chiral 10-camphorsulfonic acid (CSA) was investigated.

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Scheme 1.

## 2. Experimental

### 2.1. Materials

3,6-Diaminoacridine free base (proflavine) was prepared by dehydrohalogenation of 3,6-diaminoacridine hydrochloride (Aldrich Chemical Co.) using an aqueous sodium hydroxide solution [16]. (*R*)- and (*S*)-6,6'-dibromo-2,2'-diethoxy-1,1'-binaphthyl (BEBN) were prepared from optically pure (*R*)- or (*S*)-1,1'-bi-2-naphthol according to the literature [17]. *N,N*-dimethylformamide (DMF) was purified by distillation. Triphenylphosphine was recrystallized from *n*-hexane. 1,8-Diazabicyclo[5.4.0]-undec-7-en (DBU), tetrakis(triphenylphosphine) palladium(0), (*R*)-(-)- and (*S*)-(+)-10-camphorsulfonic acid (CSA), and methanesulfonic acid (MSA) were used without further purification.

### 2.2. Polymerization

(*R*)- or (*S*)-BEBN (0.5 mmol), proflavine (0.5 mmol), tetrakis(triphenylphosphine) palladium(0) (0.03 mmol), triphenylphosphine (0.12 mmol), DMF (2 ml), and a magnetic stirring bar were placed in a 25 ml glass tube with two necks, and the one neck was equipped with a reflux condenser that was connected with a carbon monoxide balloon on its top through a stop cock and the other neck was stoppered with a rubber septum. The tube was cooled in liquid nitrogen and after evacuation carbon monoxide was introduced by opening the cock, and then DBU (1.1 mmol) was added using a syringe through the septum. The reaction solution was kept at 115 °C for 12 h with stirring, and the formed polymer was precipitated in methanol and separated out by filtration.

### 2.3. Characterization

NMR measurements of the polymer obtained were performed with a JEOL 270 MHz spectrometer. <sup>1</sup>H NMR (270 MHz, δ ppm, DMSO-*d*<sub>6</sub>): 1.06 (t, 6H, CH<sub>3</sub>), 4.16 (m, 4H, CH<sub>2</sub>), 7.10 (d, *J* = 9 Hz, ArH), 7.75 (d, *J* = 8 Hz, ArH), 7.85 (d, *J* = 8 Hz, ArH), 7.95 (d, *J* = 9 Hz, ArH), 8.13 (d, *J* = 9 Hz, ArH), 8.31 (d, *J* = 8 Hz, ArH), 8.74 (s, 4H, ArH),

8.93 (s, 1H, ArH), 10.8 (s, 2H, amide). UV–vis spectra were recorded on a JASCO V-560. Optical rotation was obtained on a JASCO DIP-1000 polarimeter at 589 nm. Circular dichroism (CD) spectra were recorded on a JASCO J-720WI at a room temperature: around 25 °C. Molecular weights were determined by GPC using a TOSOH HLC-8120GPC (Column: TSKgel GMH<sub>HR</sub> + TSKgel G2000H<sub>XL</sub>).

### 2.4. Computational studies

The most stable helical conformations of the polymers were computed as follows: Force field molecular modeling was performed with the PCFF force field implemented by Cerius2 Version 3.0 (Molecular Simulations Inc., San Diego, CA) software.

## 3. Results and discussion

The aromatic polyamides that have axially dissymmetric main chains were prepared by the reaction of (*R*)- or (*S*)-BEBN with carbon monoxide and proflavine using a palladium catalyst according to the method of Yoneyama et al. [18] (Scheme 1), and the properties of the polymers obtained are shown in Table 1. Wholly aromatic polyamides (aramides) are insoluble; however, the polyamides obtained were soluble in DMF and *N,N*-dimethylacetamide. Imai et al. [19] reported that the aromatic polyamides containing kinked biphenylene or binaphthylene moieties in the main chain are soluble, because the conjugated coplanar arrangement of the aromatic rings is hindered by the axially dissymmetric units.

Fig. 1 shows the most stable conformation computed for

Table 1  
Synthesis of polyamides containing BEBN joints and acridine segments

Polyamides	BEBN	Yield (%)	$M_n^a$	$M_w^a$	$[\alpha]_D^{25} (^\circ)^b$
I	( <i>R</i> )-(+)-	86	5700	11600	-190
II	( <i>S</i> )-(-)-	83	4900	9100	+196

Polymerization conditions are presented in Section 2.

<sup>a</sup> Molecular weights were obtained by GPC using standard polystyrenes.

<sup>b</sup> Specific rotations were measured in DMF (*c* = 0.06 g/dl).

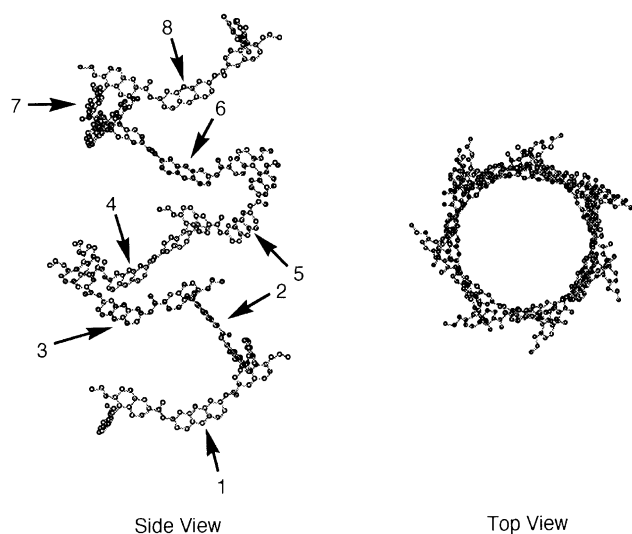


Fig. 1. The most stable conformation of the polyamide-II. Arrows with numbers indicate acridine moieties in the helix.

polyamide-II. Since chiral binaphthalene joints in the polymer main chain twist in one direction, this polymer has one-handed helical structure. Polyamide-I forms a right-handed P helix, and polyamide-II left-handed M helix.

The mirror imaged CD spectra of the polyamide-I and II shown in Fig. 2 indicate that the two polymers have symmetric structures with opposite helical senses to each other. The absorption around 390 nm in the UV-vis spectrum of the polyamides is due to  $\pi-\pi^*$  transition of the acridine chromophore in the main chain; therefore, the Cotton effect in this absorption area indicates that the achiral chromophores are arranged in a chiral, that is, a one-handed helical structure.

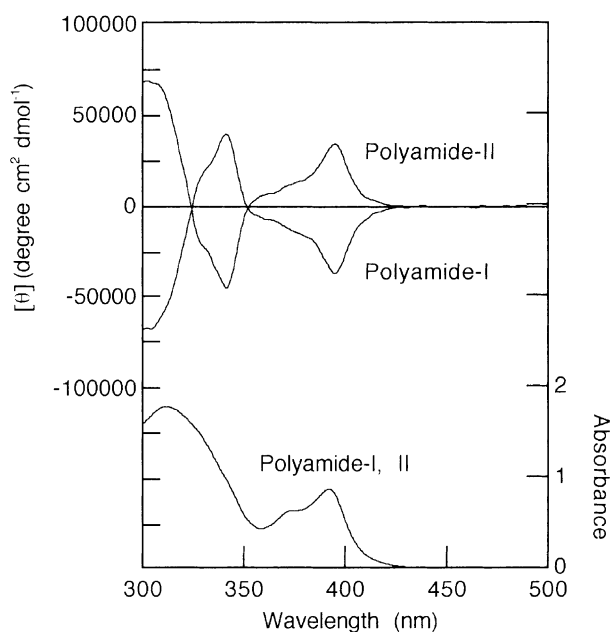


Fig. 2. CD and UV-vis spectra of polyamide-I and II in DMF. Polymer concentrations were  $2.4 \times 10^{-5}$  M based on the repeating unit.

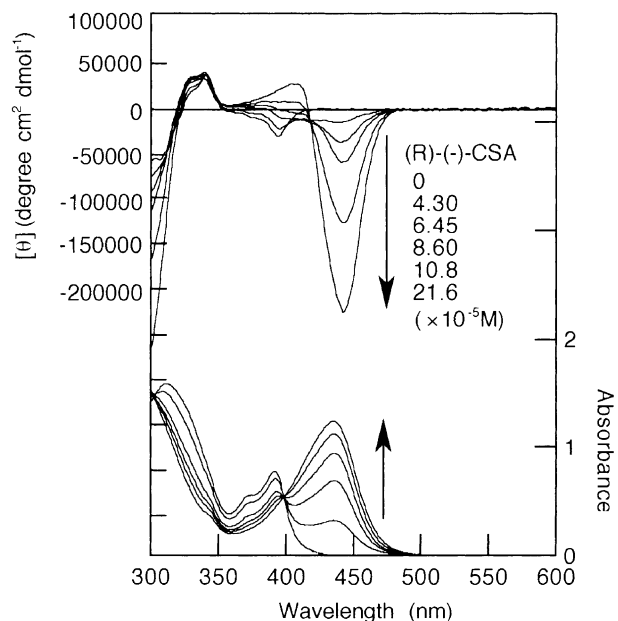


Fig. 3. The change in CD and UV-vis spectra of the polyamide-I on addition of (*R*)-(-)-CSA in DMF. Polymer concentrations were  $2.4 \times 10^{-5}$  M based on the repeating unit.

Acridine chromophore is an aromatic base that is easily protonated by protonic acids. Das et al. [14] reported the protonation of polymers containing acridine chromophores in the side chain using trifluoroacetic acid. The interaction of the chromophore fixed in a chiral structure with a chiral protonic acid attracts us. Fig. 3 shows changes in CD and UV-vis spectra of the polyamide-I in DMF in the presence of (*R*)-(-)-CSA. Changes in optical rotation were also observed on addition of (*R*)-CSA because (*R*)-camphorsul-

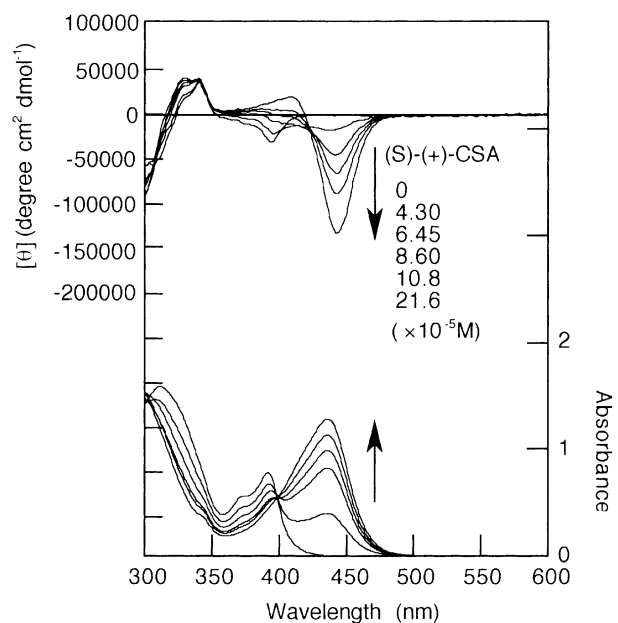


Fig. 4. The change in CD and UV-vis spectra of the polyamide-I on addition of (*S*)-(+)-CSA in DMF. Polymer concentrations were  $2.4 \times 10^{-5}$  M based on the repeating unit.

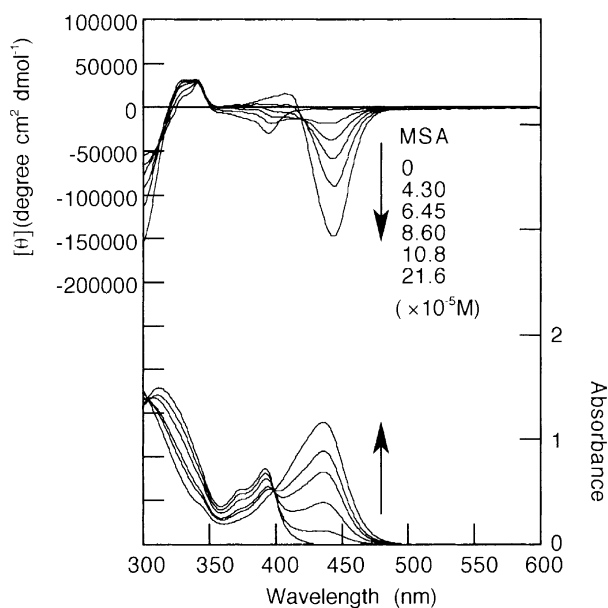


Fig. 5. The change in CD and UV-vis spectra of the polyamide-I on addition of MSA in DMF. Polymer concentrations were  $2.4 \times 10^{-5}$  M based on the repeating unit.

fonate anion was incorporated in the cationic polyamide-I. The absorption band that appeared around 435 nm on addition of the chiral acid is ascribed to protonated acridine chromophores [20,21]. The CD ellipticity in this absorption area increased with the increasing absorbance according to  $(R)$ -(-)-CSA concentrations. This indicates that the protonated acridine segments have chiral orientation in the helix. In the case of  $(S)$ -(+)-CSA that has inverse chirality,

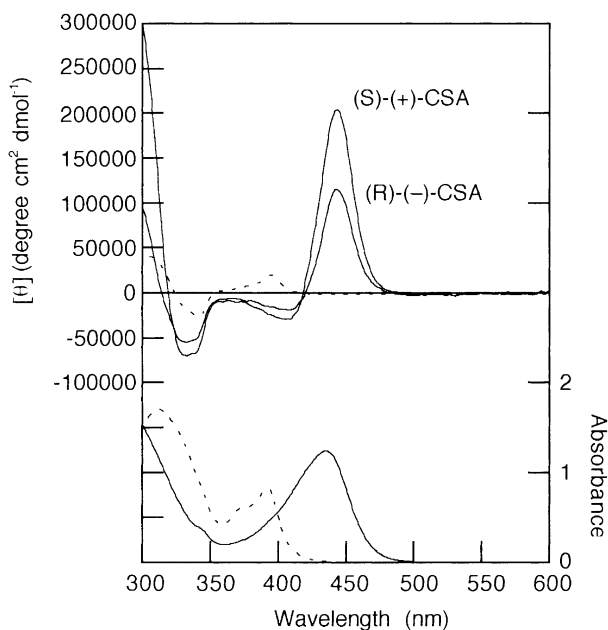


Fig. 6. CD and UV-vis spectra of the polyamide-II in the presence of  $(R)$ -(-)- or  $(S)$ -(+)-CSA ( $21.6 \times 10^{-5}$  M) (—) and in the absence of the acid (---) in DMF. Polymer concentrations were  $2.4 \times 10^{-5}$  M based on the repeating unit.

as shown in Fig. 4, the increase in the Cotton effect observed for the polyamide-I was less than in the case of  $(R)$ -(-)-CSA. This difference can be explained as follows:  $(R)$ -(-)-camphorsulfonate ion ( $(R)$ -(-)-CSA<sup>-</sup>) is sterically more suitable for the space around the polyamide-I helix than  $(S)$ -(+)-camphorsulfonate ion ( $(S)$ -(+)-CSA<sup>-</sup>); therefore, the former ion incorporated into space of the protonated polyamide helix as a counter anion suppress thermally wriggling molecular motion of the helix in DMF to stabilize the helical conformation; consequently, CD ellipticity due to the helical structure is enhanced. When the polymer solutions were cooled to 0 °C, the difference of the Cotton effect observed for two cases with each CSA enantiomer increased, suggesting that the stereospecific interaction of the one-handed helical polycation with the chiral anions become distinct at low temperature because of depressed molecular motion of the polymer.

CD spectra of polyamide-I with lower concentrations of racemic CSA appeared between a spectrum of the polyamide with  $(R)$ -(-)-CSA and that with  $(S)$ -(+)-CSA. However, at a relatively high concentration of the racemic acid, eight times the acridine unit in the polymer, the CD spectrum was almost identical with that observed in the presence of  $(R)$ -(-)-CSA, which interacts more intimately with the polyamide than  $(S)$ -(+)-CSA, because  $(R)$ -(-)-CSA<sup>-</sup> competitively excludes  $(S)$ -(+)-CSA<sup>-</sup> from the space around the helix.

Fig. 5 shows the changes in CD and UV-vis spectra of polyamide-I on addition of methanesulfonic acid (MSA). The Cotton effect in the presence of this small acid was very similar to that observed in the case of  $(S)$ -(+)-CSA. These results suggest that  $(S)$ -(+)-CSA<sup>-</sup> as a counter anion is sterically rather difficult to fit into the space around the polymer to stabilize the helical form and small achiral methanesulfonate ion is also considered to have little effect for the stabilization. The case of polyamide-II with left-handed helical structure was then examined to compare with the case of polyamide-I.

Fig. 6 shows the changes in CD and UV-vis spectra when  $(R)$ -(-)- or  $(S)$ -(+)-CSA were added to polyamide-II solution in DMF. In contrast to the case of polyamide-I, CD ellipticity of protonated polyamide-II was more enhanced by  $(S)$ -(+)-CSA than by  $(R)$ -(-)-CSA. This observation indicates that  $(S)$ -(+)-CSA<sup>-</sup> can stabilize the helical conformation of polyamide-II more effectively than  $(R)$ -(-)-CSA<sup>-</sup>, supporting the assumption described earlier. This stereospecific stabilization is interesting because stereoselective interaction of the one-handed cationic helical polymers with chiral anions seems to be useful for chromatography.

Decades ago, a polyamide containing optically active binaphthalene units in the main chain was synthesized for the first time by Schulz and Jung [22], and optical properties of the polymer were investigated. Similar dissymmetric polyamides consisting of chiral biphenylene units were also reported by Overberger et al. [23,24]. Okamoto [25]

reviewed helical polymers investigated recently referring to their chiral functions. Chromatographic applications [1] and catalytic activities for asymmetric synthesis [7,26] have already been reported. The helical polymers we prepared using axially dissymmetric joints are thermally so stable that no change in specific rotation is observed for hours above 100 °C; therefore, we are interested in such polymers as have inherently dissymmetric backbones because of their stereospecific functions at high temperature. Hence, further investigations on the functions are in progress.

#### 4. Conclusion

One-handed basic helical polyamides was synthesized by combining axially dissymmetric binaphthalene units with acridine units. The experimental results indicated that the acridine-containing chiral polyamides stereospecifically interact with (*R*)-(–)- and (*S*)-(+)-CSA. The cationic one-handed helical conformation can be stabilized by incorporated counter anions depending on their chirality. This stereospecific interaction is expected to be used for chromatography.

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