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Helix induction in an optically inactive poly[(4-carboxyphenyl)acetylene] film with chiral amines

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An optically inactive *cis-transoidal* poly[(4-carboxyphenyl)acetylene] was found to form a predominantly one-handed helical conformation upon complexation with optically active amines and amino alcohols in the solid state, resulting in a characteristic induced circular dichroism in the polymer backbone region.

Solid-state or solvent-free organic reactions are of interest not only because of their unexpectedly high reactivity and stereoselectivity but also due to being an environment-friendly process.[1] However, only a few examples have been reported regarding chiral information transfer by a solid–solid interaction. Tanaka *et al.*[2] recently reported that achiral calix[4]resorcarenes formed host–guest complexes upon interaction with chiral acids and alcohols in the solid state using a solid-state grinding procedure, and the complexes exhibited an induced circular dichroism (ICD) in the achiral host chromophore region. Similarly, the time-dependent formation of chiral supramolecular aggregates in the solid state was also reported by Borovkov *et al.*[3] for the zinc octaethylporphyrin–chiral amine systems.

Previously, we reported the helicity induction on optically inactive stereoregular *cis-transoidal* poly(phenylacetylene)s bearing functional groups in solution, which can change their structures into the prevailing dynamic one-handed helices upon complexation with specific chiral guests.[4–8] For instance, poly[(4-carboxyphenyl)acetylene] (poly-**1**, Scheme 1) can respond to the chirality of chiral amines in dimethyl sulfoxide (DMSO)[4] and water,[6] as well as in a gel,[7] and their complexes show a characteristic ICD in the UV–visible region of the polymer backbone. The Cotton effect signs corresponding to the helical sense of poly-**1** can be used as a novel probe for the chirality assignments of the chiral amines.[4–7] We now report a similar helicity induction in a poly-**1** film upon interaction with liquid and solid optically active amines.

The optically inactive poly-**1** film[†] was first interacted with a liquid optically active amine [6 μl of (*S*)-**2**, Scheme 1], but poly-**1** showed almost no ICD in the π-conjugated polymer backbone region (Figure 1, curve *1*). However, the ICD intensity gradually but dramatically increased with time and reached an almost constant value after ~60 h (Figure 1, curves *2*–*6*, and the inset). The Cotton effect pattern was similar to that of poly-**1** induced by (*S*)-**2** in DMSO,[4,5] indicating that the helical sense of poly-**1** induced in the film was the same in solution induced by the same optically active amine. When (*R*)-**2** was used instead, poly-**1** with the opposite helicity was induced in the solid state as shown in the mirror image ICD (Figure 1, curve *7*). A similar helicity induction in poly-**1** films was also possible for other liquid chiral amines **3**–**5** (see Scheme 1 and Table 1), and the complexes exhibited the same Cotton effect signs when the absolute configurations were the same.[4,5] We also measured the linear dichroism (LD) spectra of the films in the presence of these optically active amines and found that the LD contributions caused by macroscopic anisotropy are negligible.[9] Note that poly-**1** is neither soluble nor swelled in the chiral amines. These results indicate that poly-**1** can form a predominantly one-handed helical structure in the film upon complexation with liquid chiral amines.

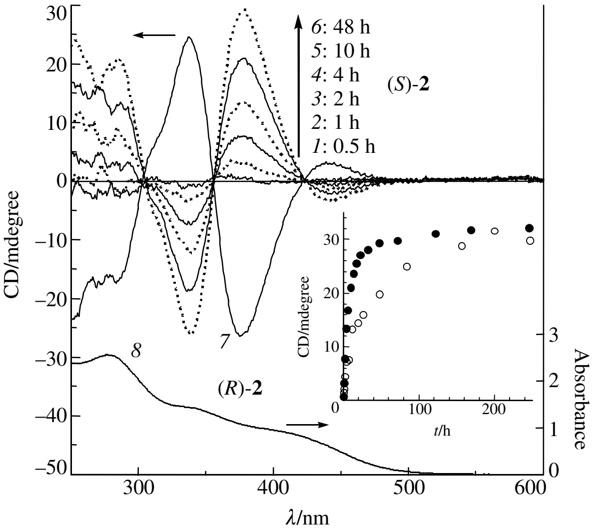
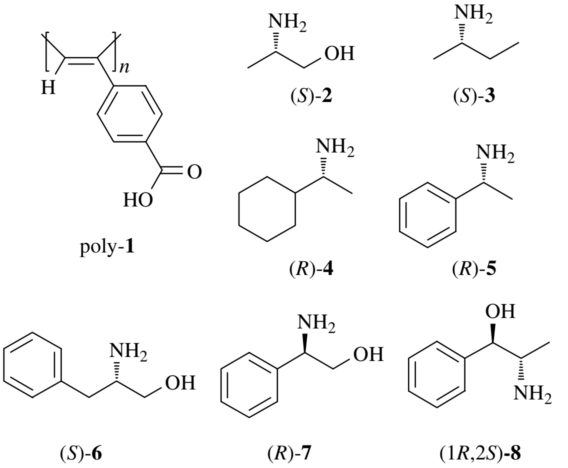


Figure 1 CD spectral changes in a poly-**1** film with (*S*)-**2** at ambient temperature (~25 °C) with time (*1*–*6*). CD and absorption spectra of a poly-**1** film with (*R*)-**2** after 49 h are also shown (*7* and *8*, respectively). Inset: the plots of ICD intensity (2nd Cotton) of the poly-**1** film with (*S*)-**2** *versus* time (●) in air and (○) in a dry box under argon atmosphere.



Scheme 1 Structures of poly-**1** and amines.

IR measurements were carried out to study the mechanism of the helicity induction in the poly-**1** film with (*S*)-**2**. Previously,

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[†] *Cis-transoidal* poly-**1** was prepared according to the previously reported method.[6] The number average molecular weight (M_n) and its molecular weihgt distribution were 3.3×10^4 and 2.8, respectively, as its methyl ester estimated by size exclusion chromatography with polystyrene standards using tetrahydrofuran as the eluent. Poly-**1** films were prepared by casting 50 or 100 μl of a DMSO solution of poly-**1** (1 or 5 mg cm^{-3}) on a cylindrical quartz plate (2 cm in diameter) or a CaF_2 plate (2 cm in diameter) for CD and IR measurements, respectively, followed by drying under reduced pressure in a desiccator. The poly-**1** film was covered with the same well-greased quartz or CaF_2 plate for CD and IR measurements with chiral amines, respectively. Absorption and CD spectra were measured on a Jasco V-570 spectrophotometer and a Jasco J-725 spectropolarimeter (Hachioji, Japan), respectively. LD spectra were measured using a Jasco J-725 spectropolarimeter with an LD attachment. IR spectra were recorded using a Jasco Fourier Transform IR-620 spectrophotometer.

Table 1 Signs of split Cotton effects for poly-**1**–amine complexes in the solid state and in DMSO.

Amine	2nd Cotton			
	Film		In DMSO[a]	
	Sign	λ_{max}/nm	Sign	λ_{max}/nm
(*S*)-**2**	+	378	+	373
(*S*)-**3**	+	378	+	378
(*R*)-**4**	–	376	–	376
(*R*)-**5**	–	386	–	376
(*S*)-**6**	–	373	+	374
(*R*)-**7**	–	382	–	374
(1*R*,2*S*)-**8**	–	375	+	372

[a] From ref. 4(*b*).

we demonstrated that the ion pair formation of poly-**1** with chiral amines is essential for the helicity induction in DMSO.[5] The poly-**1** film showed an absorption band at 1700 cm^{-1} corresponding to the free carboxylic acid band (COOH), which immediately and completely disappeared upon interacting with (*S*)-**2**, and a new band at 1582 cm^{-1} assigned to the ion-paired carboxylate band (COO$^-$) appeared.[5] These IR spectral changes indicate that liquid (*S*)-**2** easily permeates into the poly-**1** film and the carboxy groups of poly-**1** immediately changed to carboxylate ions complexed with (*S*)-**2** in the solid state. However, the conformational change of the poly-**1** film into a one-handed helix required a long time after rapid carboxylate formation at the pendants. In sharp contrast, we observed almost no time-dependent CD and IR spectral changes of poly-**1** in DMSO in the presence of chiral amines including (*S*)-**2**.[5] In order to investigate the effect of moisture in air on the helicity induction in the poly-**1** film, the same experiments were performed in a dry box under an argon atmosphere; a similar time-dependent helicity induction was also observed in the poly-**1** film (see inset in Figure 1), suggesting that the effect of water may be negligible for the conformational change (helicity induction) in the poly-**1** film by liquid amines.

We investigated a similar helicity induction in the poly-**1** film upon complexation with solid optically active amines (**6**–**8** in Scheme 1 and Table 1). Grinding poly-**1** using a mortar and a pestle in the presence or absence of a solid chiral amine caused a pressure-induced *cis*-to-*trans* isomerization of the poly-**1** main chain,[10] and this method could not be utilized in this study. Therefore, a finely ground solid chiral amine (50 mg) was placed on the poly-**1** film and a stress (0.1 kg cm^{-2}) was applied to the film by placing a weight (0.35 kg) on it. The CD and absorption spectra were then measured at ambient temperature for an appropriate time interval. Before the CD measurements, the solid amines on the film were removed using a brush. The poly-**1** film showed a weak but apparent ICD in the polymer backbone region by interaction with solid chiral amines, and the ICD intensity gradually increased with time, resulting in a maximum after about a day. Figure 2 shows the CD spectra of poly-**1** films with the chiral amines after a day (**6**–**8**; their melting points are 92–94, 75–77 and 51–53 °C, respectively). Each enantiomeric pair of chiral amine **6** induced mirror images of the split-type ICDs. Contributions from the LD were also negligible in the CD spectra. The chiral amines (**7** and **8**) exhibited rather weak ICDs in the poly-**1** film and their Cotton effect patterns were different from those of the complexes with the corresponding amines in DMSO and the poly-**1**–**6** complexes in the film. Moreover, the helical sense induced in the poly-**1** film was opposite when complexed with (*S*)-**6** and (1*R*,2*S*)-**8** (Table 1) to that in DMSO. The reason is not clear at present. Although the ICD intensities of poly-**1** were weaker in the solid state than those in solution, this study clearly indicates that a macromolecular helicity can be induced in the solid state by a solid–solid interaction. However, we found that a small amount of water molecules in moisture play an important role in the helicity induction in the poly-**1** film. When the poly-**1** film with solid (*S*)-**6** was kept in a dry box under an argon atmosphere, no apparent ICD could be detected in the poly-**1** film even after two months. The IR spectrum of the sample showed the free carboxylic acid band (COOH), and almost no band derived from the ion-paired carboxylate group (COO$^-$) was observed. However, when the same sample was exposed in air for a day, an apparent ICD in the poly-**1** chromophore region appeared as shown in Figure 2. These results indicate that, under anhydrous conditions, solid chiral amines cannot permeate into the poly-**1** film to interact with the pendant carboxy groups, so that helicity induction in the poly-**1** film could not be attained. We note that the poly-**1** film with chiral amines showed no changes, such as liquefaction and swelling, in the presence of moisture. To date, a number of examples of solid–solid reactions and host–guest complexations have been reported,[1–3] while the effects of moisture on the reactions and complexations have usually been ignored.[11] Consequently, the present results demonstrated that a one-handed helicity induction can be possible in an amorphous polymer film of a dynamically racemic helical poly(phenylacetylene) upon complexation with liquid and solid chiral amines, and in the latter complexation, a small amount of water plays a critical role in the formation of the ion-pair species, which is essential for the helicity induction. The present method is more convenient to sense the chirality of chiral amines than the solution method, and it may be applicable to other dynamic helical polyacetylenes.[12]

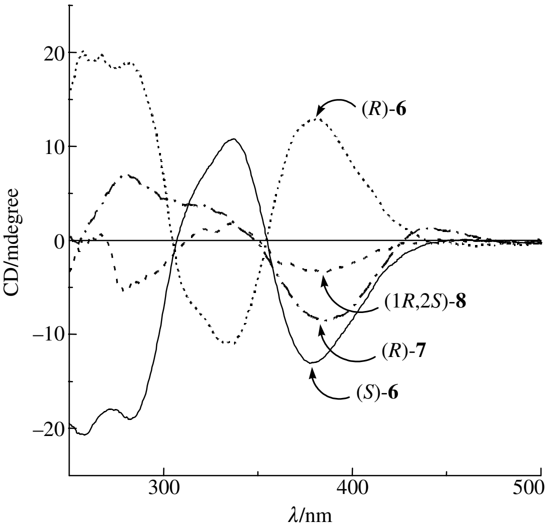

Figure 2 CD spectra of a poly-**1** film with solid optically active amines **6**–**8** in air at ambient temperature (~25 °C) after a day.

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