Chiral Amplification in Macromolecular Helicity Assisted by Noncovalent Interaction with Achiral Amines and Memory of the Helical Chirality

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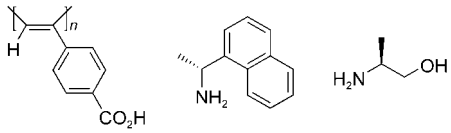
Abstract: Poly[(4-carboxyphenyl)acetylene] (poly-**1**) exhibits an intense induced circular dichroism (ICD) in the UV-visible region upon complexation with excess (*R*)-1-(1-naphthyl)ethylamine ((*R*)-**2**), owing to the formation of a predominantly single-handed helical conformation of the polymer backbone. In the presence of a small amount of (*R*)-**2**, poly-**1** showed a very weak ICD due to the lack of a single-handed helical conformation. However, we have found that the co-addition of the excess bulky, achiral 1-naphthylmethylamine (**5**) with a small amount of (*R*)-**2** caused a dramatic increase in the ICD magnitude, comparable to the full ICD induced by excess (*R*)-**2**. This indicates that an almost single-handed helix can be induced on poly-**1** upon complexation with a small amount of (*R*)-**2** assisted by achiral **5**. Furthermore, the induced single-handed helical poly-**1** could be successfully memorized by the replacement of (*R*)-**2** and **5** with achiral 2-aminoethanol or *n*-butylamine.

Keywords: chiral amplification · circular dichroism · helical structures · polymers

Introduction

Chiral amplification is a significantly interesting phenomenon in connection with not only the origin of biomolecular homochirality in nature,[1] but also the development of ideal methods to produce optically active compounds.[2] Pioneering studies on chiral amplification in synthetic polymers were performed on polyisocyanates by Green and co-workers.[1a,3] Polyisocyanates are typically stiff and dynamic helical polymers, whose helix-sense readily inverts in solution as a result of the relatively small barrier energy for helical reversals in these polymers. Therefore, copolymerization of achiral isocyanates with a small amount of optically active ones can produce optically active polymers with a prevailing single-handed helical conformation. This cooperative phenomenon named "sergeants and soldiers rule" by Green and co-workers can also be observed in other helical polymers[4] and supramolecular architectures.[5]

We previously reported that *cis–transoidal*, optically inactive poly[(4-carboxyphenyl)acetylene] (poly-**1**) forms a predominantly one-handed helix upon complexation with optically active amines and amino alcohols, such as (*R*)-(+)-1-(1-naphthylethyl)amine ((*R*)-**2**) and (*S*)-2-amino-1-propanol ((*S*)-**3**), and the complexes exhibit a characteristic induced circular dichroism (ICD) in the polymer backbone region.[6]



poly-**1** (*R*)-**2** (*S*)-**3**

The Cotton effect sign reflects the absolute configuration of the chiral amines, so that (*R*)-**2** and (*S*)-**3** induce a one-handed helical poly-**1** with an opposite helix-sense. Furthermore, we found that the macromolecular helical chirality of poly-**1** induced by (*R*)-**2** can be memorized when (*R*)-**2** is completely removed and replaced by various achiral amines and amino alcohols.[6c,7] This methodology is useful for constructing new supramolecular assemblies with various functional achiral amines arranged in a single-handed helical array along the polymer backbone. However, in order to induce the complete single-handed helix on poly-**1** prior to the memory of the helical chirality of poly-**1**, a large excess (*R*)-**2** or slight excess (*S*)-**3** was required, since a prevailing single-handed helix is induced on poly-**1** through a noncovalent acid–base interaction that involves an equilibrium between the free acid and base, the ion pairs, and free ions. Apparently, the ion pair formation of the carboxy groups of

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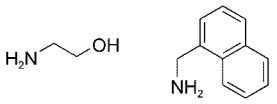
poly-**1** with chiral amines is essential for the helicity induction, and, therefore, excess chiral amines or amino alcohols are necessary for the predominant ion-pairing formation.[6b,c]

Previously, we also found that the slight excess of single-handed helix-sense of poly-**1** induced by a small amount of (*S*)-**3** was amplified by the co-addition of achiral 2-aminoethanol (**4**), thus resulting in an increase in the ICD magnitude of poly-**1**.[6b] This can be considered as a typical example of the chiral amplification in a polymer through a noncovalent interaction. However, a complete amplification of the helical chirality of poly-**1** induced by a small amount of (*S*)-**3** and achiral **4** was difficult at that time.[6b] Furthermore, it is difficult to completely remove (*S*)-**3** and replace it with other achiral amines or amino alcohols to memorize the induced helical conformation of poly-**1**, because (*S*)-**3** has a very high affinity to the carboxy groups of poly-**1**.[8] Here we report that partially induced helical chirality of poly-**1** by a small amount of (*R*)-**2** is amplified to almost the complete single-handed helix by the co-addition of a bulky achiral amine **5**, and that the amplified macromolecular helicity of poly-**1** can be successfully memorized by replacing (*R*)-**2** and **5** with achiral amines and amino alcohols. The helicity induction and memory process in poly-**1** is now possible starting with a rather small amount of chiral amines.



4 **5**

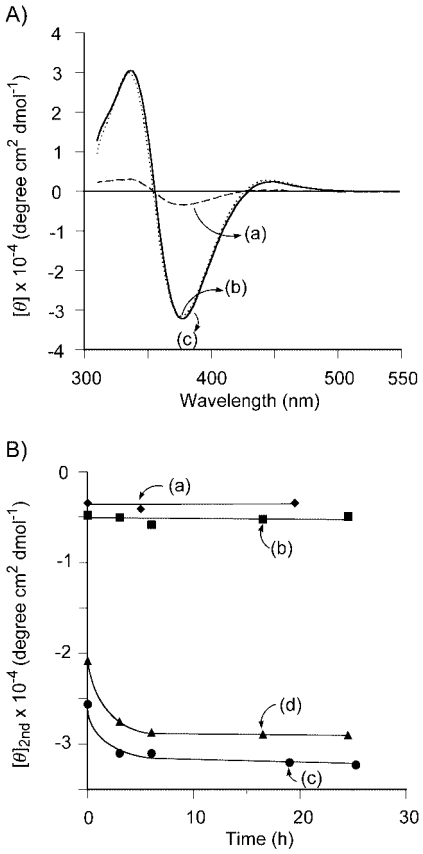


Figure 1. A) CD spectra of the poly-**1**-(*R*)-**2** complexes in the absence ([(*R*)-**2**]/[poly-**1**] = 0.5 (a) and 10 (b)) and presence ([(*R*)-**2**]/[poly-**1**]/[**5**] = 0.5/1/2.5 (c)) of **5**. Changes in the second Cotton intensity ($[\theta]_{2nd}$) in the complexation of poly-**1** (3 mg mL^{-1}) with (*R*)-**2** in the absence and presence of **5** in DMSO at ambient temperature (24–26 °C) are also shown in B; the molar ratio of **5** to poly-**1** was a) 0, b) 1.0, c) 2.5, and d) 4.5.

Results and Discussion

Chiral amplification: As previously reported, poly-**1** exhibits a split-type ICD in the UV-visible region in the presence of (*R*)-**2** in dimethyl sulfoxide (DMSO) due to the predominantly single-handed helix formation.[6] The ICD intensity increased with an increase in the concentration of (*R*)-**2** and reached a maximum value of $[\theta]_{max} = -3.1 \times 10^4$ for the second Cotton signal with excess (*R*)-**2** ([(*R*)-**2**]/[poly-**1**] = 10) (b in Figure 1A) under the condition of [poly-**1**] = 3 mg mL^{-1}. Therefore, in the presence of a small amount of (*R*)-**2** ([(*R*)-**2**]/[poly-**1**] = 0.5), poly-**1** showed a very weak ICD (a in Figure 1A); the second Cotton ICD intensity ($[\theta]_{2nd}$) was only approximately one-tenth of the $[\theta]_{max}$ due to the lack of a single-handed helical conformation of poly-**1**; that is, a small amount of (*R*)-**2** bound to poly-**1** can not induce the same helix on the major free monomeric carboxy units. However, the co-addition of the excess bulky achiral amine **5** ([(*R*)-**2**]/[poly-**1**]/[**5**] = 0.5/1/2.5) caused a dramatic increase in the ICD intensity. The ICD intensity was time-dependent and increased with time to reach a constant value ($[\theta]_{2nd} = -3.23 \times 10^4$) after 3 h; the $[\theta]_{2nd}$ value was comparable to that of $[\theta]_{max}$ (see, c in Figure 1A and B). These results indicate that the slight excess of single-handed helical chirality of poly-**1** induced by a small amount of (*R*)-**2** was significantly amplified by the co-addition of excess achiral **5** to give poly-**1** with almost the complete single-handed helix.[9] The ICD intensity of the poly-**1**-(*R*)-**2** complex ([(*R*)-**2**]/[poly-**1**] = 0.5) increased with increasing concentration of **5** and reached the maximum value at [**5**] [poly−**1**] = 2.5. However, further addition of **5** caused a slight decrease in the ICD intensity (d in Figure 1B), probably because the excess amount of **5** prevents the interaction of (*R*)-**2** with poly-**1**. When (*S*)-**2** is used instead with achiral **5** ([(*S*)-**2**]/[poly-**1**]/[5] = 0.5/1/2.5), poly-**1** with the opposite single-handed helicity is observed (entry 9 in Figure 2). We note that even at [(*R*)-**2**]/[poly-**1**] = 0.3 and 0.1, the co-addition of achiral **5** remarkably induced an excess of a single-handed helix on poly-**1** ($[\theta]_{2nd}/[\theta]_{max} = 0.94$ and 0.43, respectively; see entries 7 and 6 in Figure 2). It is worth noting that a mixture of poly-**1**, (*R*)-**2**, and **5** ([(*R*)-**2**]/[poly-**1**]/[**5**] = 0.05/1/2.95) showed a relatively intense ICD ($[\theta]_{2nd}/[\theta]_{max} = 0.23$), whereas poly-**1** exhibited almost no ICD under the same conditions in the absence of **5** (see entries 5 and 1 in Figure 2).[10]

Similar chiral amplification in macromolecular helicity of the poly-**1**-(*R*)-**2** complex at [(*R*)-**2**]/[poly-**1**] = 0.5 was also observed when other achiral amines (**4** and **6**–**9**) were used instead of **5**, as evidenced by the increase in optical activity. The best results using the optimum concentration of the

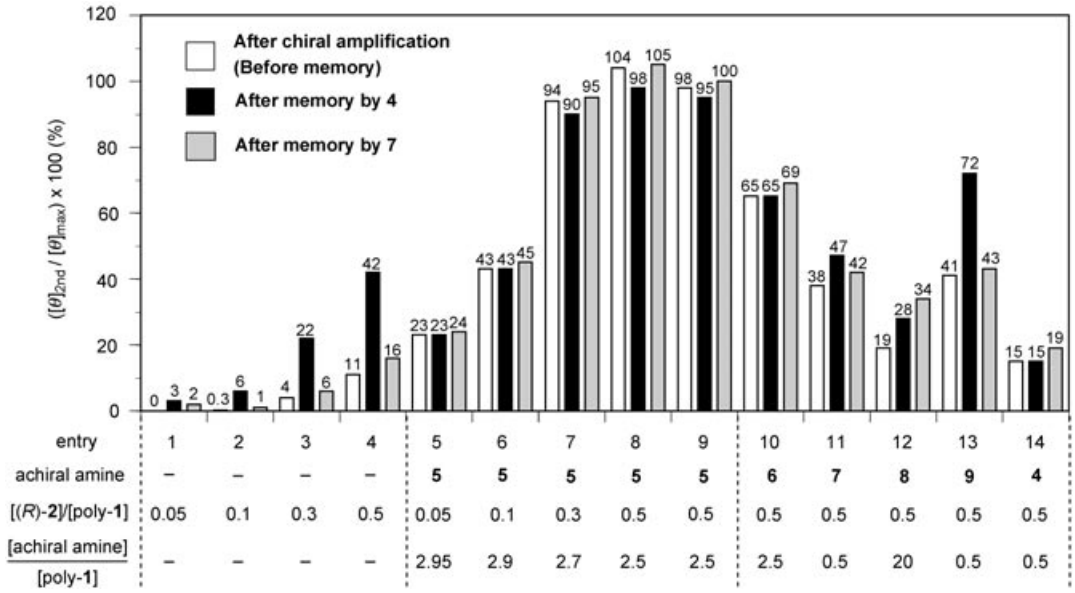
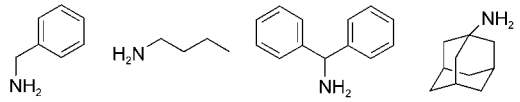


Figure 2. Results of chiral amplification in macromolecular helicity of poly-**1** by achiral amines (white bar) and memory of the helical chirality with **4** (black bar) and **7** (gray bar). $[\theta]_{max} = -3.1 \times 10^4$ was used as the maximum value for the poly-**1**-(*R*)-**2** complex ([(*R*)-**2**]/[poly-**1**] = 10). In entry 9, (*S*)-**2** was used instead of (*R*)-**2**. In entries 10–14 show the optimum concentrations of achiral amines examined for chiral amplification. In entry 13, a larger amount of **9** could not be used because of the solubility limit of **9** in the presence of poly-**1** in DMSO. The fractionation of poly-**1** from the mixture of poly-**1**, (*R*)-**2**, and achiral amines by SEC was performed by using a solution of **4** (0.8 M) or **7** (0.008 M) in DMSO after the samples had been allowed to stand at ambient temperature (24–26 °C) for 19.5 (entries 1–4), 25 (entries 5–8), 20 (entries 9, 10, and 12), and 41 h (entries 11, 13, and 14).



6 **7** **8** **9**

achiral amines for the chiral amplification are summarized in Figure 2 (entries 10–14) (see also Table S1 in the Supporting Information). Although all achiral amines more or less enhanced the ICD values, the extent of macromolecular helicity amplification in poly-**1** was not as significant as that of **5** and was dependent on the structures of the achiral amines. The ICD values tended to increase with an increase in the bulkiness of the achiral amines in the order **4** < **7**, **9** < **6** ≪ **5**, except for **8**, which has two bulky substituents at the α position. A steric repulsion between the bulky (*R*)-**2** and achiral amines complexed with poly-**1** must facilitate the induction of the predominantly single-handed helical conformation on poly-**1**, probably because the population of the helical reversals between the interconverting right- and left-handed helical segments of the poly-**1** chains may be reduced upon complexation with the bulky chiral and achiral amines. This tendency is in good agreement with the previously reported results.[11] Among the achiral amines tested, **6**, **7**, and **9** showed a relatively high chiral amplification, but the co-addition of an achiral amino alcohol **4**, which acted as an excellent achiral amine for the chiral amplification of poly-**1** with a small amount of (*S*)-**3**,[6b] showed almost no enhancement of the ICD. The reason for this is not clear at present, but the combination of chiral and achiral amines may be important.

Memory of the amplified macromolecular helicity of poly-1: We then investigated whether the macromolecular helicity of poly-**1**, induced by a small amount of (*R*)-**2** followed by amplification in the presence of **5**, could be memorized by replacing (*R*)-**2** and **5** with achiral amines, such as 2-aminoethanol (**4**) and *n*-butylamine (**7**), which were good chaperoning molecules for assisting in the memory of the helical conformation of poly-**1** induced by excess (*R*)-**2**.[7a] The memory experiments were performed in the same way as previously reported,[6c,7a] and the results are summarized in Figure 2. The memorized poly-**1** was isolated from the mixture of poly-**1**, (*R*)-**2**, and **5** ([(*R*)-**2**]/[poly-**1**]/[**5**] = 0.5/1/2.5) by size exclusion chromatography (SEC) by using a solution of **4** (0.8 M) and **7** (0.008 M) in DMSO as the eluent. During the SEC fractionation, the (*R*)-**2** and **5** complexed with poly-**1** were completely separated from poly-**1**.[12] The poly-**1** fractions containing an excess achiral **4** and **7** showed an intense ICD ($[\theta]_{2nd}/[\theta]_{max} = 0.98$ (**4**) and 1.05 (**7**)), comparable to that measured before the SEC fractionation ($[\theta]_{2nd}/[\theta]_{max} =$ 1.04) (entry 8 in Figure 2). These results indicate that the macromolecular helicity of the poly-**1** induced by a small amount of (*R*)-**2** and subsequently amplified by **5** is almost completely memorized in the presence of achiral **4** or **7**. When (*S*)-**2** was used instead, the macromolecular helicity with the opposite helix-sense was retained in the same manner (entry 9 in Figure 2). The macromolecular helicities of poly-**1** amplified by **4** and **6**–**9** were also efficiently memorized by replacing with **4** and **7** (entries 10–14 in Figure 2).

As previously reported, the memory of macromolecular helicity of poly-**1** induced by an excess (*R*)-**2** was maintained for a long time at ambient temperature after complete replacement of (*R*)-**2** with achiral **4**.[6c,7a] We further investigated the stability of the helical poly-**1** induced by a small amount of (*R*)-**2** and various achiral amines (**4**–**9**) and memorized by **4** and **7**. As shown in Figure 3A, the $[\theta]_{2nd}$ values

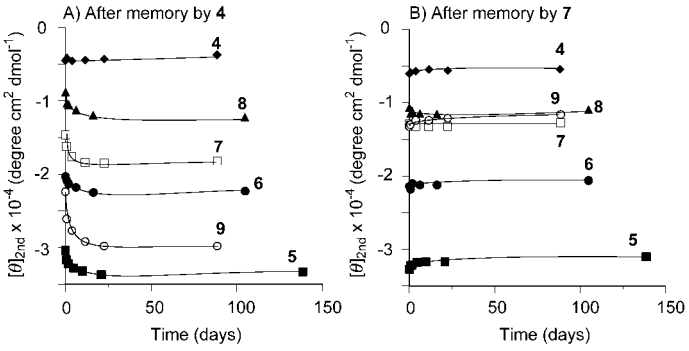
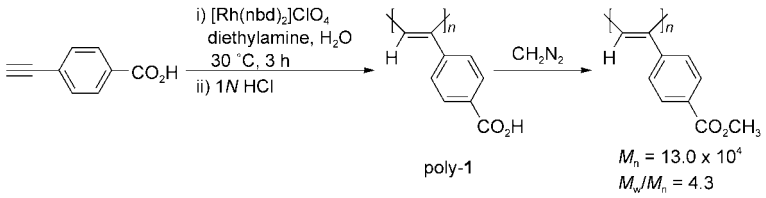


Figure 3. ICD intensity (2nd Cotton) changes of the fractionated poly-**1** from [poly-**1**-{(*R*)-**2** + achiral amines (**4**–**9**)}] (see entries 8, 10–14 in Figure 2) by SEC by using solutions of **4** (0.8 M) (A) and **7** (0.008 M) (B) in DMSO as the mobile phase component at ambient temperature.

of the isolated poly-**1** complexed with **4** further increased with time, except for poly-**1** chirally amplified by **4** before the memory. The CD intensities reached almost constant values after approximately 2–4 weeks and were maintained for about three months at ambient temperature. The memorized helical conformation of poly-**1** by **7** did not show such a further increase in their CD intensities; the $[\theta]_{2nd}$ values hardly changed over three months at ambient temperature.



Scheme 1.

Conclusion

In summary, we have, for the first time, demonstrated that the slight excess of the single-handed helical sense of poly-**1** induced by a small amount of (*R*)-**2** was dramatically amplified by the co-addition of achiral **5** to give the almost complete single-handed helix and the amplified helical chirality was memorized by replacing (*R*)-**2** and **5** with various achiral amines.[13] These results indicate that the chiral amplification followed by the memory of the helical chirality process can be used as a promising method to construct novel, functional helical polymers with the desired pendant in a single-handed helical array using a small amount of optically active compounds as a helix inducer. The same process but with a catalytic amount of a chiral amine should be more versatile and further studies along this line are now in progress.

Experimental Section

Materials: (*R*)-**2** and (*S*)-**2** were kindly supplied from Yamakawa Chemical (Tokyo, Japan), distilled under reduced pressure, and stored under nitrogen. Anhydrous DMSO (water content $<0.005\%$), 1-naphthylmethylamine (**5**), diphenylaminomethane (**8**), and 1-adamantaneamine (**9**) were purchased from Aldrich. The amines, **5** and **8** were purified by distillation under reduced pressure, and stored under nitrogen. 2-Aminoethanol (**4**) (Kishida, Osaka, Japan) was dried over calcium oxide under nitrogen and distilled under reduced pressure. Benzylamine (**6**) (TCI, Tokyo, Japan) and *n*-butylamine (**7**) (Kishida) were dried over calcium hydride and distilled under nitrogen. These amines were stored under nitrogen.

***cis–transoidal* Poly-1**: *cis–transoidal* Poly-**1** was prepared by the polymerization of 4-ethynylbenzoic acid with $[Rh(nbd)_2]ClO_4$ (nbd = norbornadiene; Aldrich) in water in the presence of diethylamine at 30 °C for 3 h according to the previously reported method (Scheme 1).[14] The stereoregularity of the obtained polymer was examined by measuring ^{1}H NMR and laser Raman spectroscopy and found that it was almost complete *cis–transoid*.[15] The molecular weight (M_n) and the distribution (M_w/M_n) of poly-**1** were estimated to be 13.0×10^4 and 4.3, respectively, as its methyl ester by size exclusion chromatography (SEC) with polystyrene standards using chloroform as the eluent. Conversion of poly-**1** into the methyl ester was carried out by using diazomethane in diethyl ether according to the previously reported method.[6b]

Instruments: NMR spectra were measured on a Varian VXR-500S (500 MHz for ^{1}H) spectrometer in [D$_6$]DMSO with the solvent residual peak as the internal standard. Laser Raman spectra were taken on a Jasco NRS-1000 spectrophotometer. Absorption and CD spectra were measured on a Jasco V-570 spectrophotometer and a Jasco J-725 spectropolarimeter (Hachioji, Japan) in a 0.1 or 4.0 mm quartz cell, respectively. The concentration of poly-**1** was calculated based on the monomer units, and was corrected using the ε (molar absorptivity) of poly-**1** ($\varepsilon_{400}=3180$). SEC was performed with a Jasco PU-980 liquid chromatograph equipped with a UV-visible (254 nm; Jasco UV-970) detector at 40 °C. A Tosoh TSKgel MultiporeH_{XL}-M SEC column was connected and chloroform was used as the eluent at a flow rate of 1.0 mL min^{-1}. The molecular weight calibration curve was obtained with polystyrene standards (Tosoh).

CD measurements—chiral amplification experiments: A typical experimental procedure is described below. Stock solutions of (*R*)-**2** (33 μL mL^{-1}, 205 mM) and **5** (60 μL mL^{-1}, 408 mM) in DMSO were prepared. Aliquots 100, 250, and 450 μL of the stock solution of **5** were transferred to three 1 mL flasks equipped with a stopcock using a Hamilton microsyringe. A 100 μL aliquot of the stock solution of (*R*)-**2** was added to the flasks and the solutions were diluted with DMSO, giving 40.8, 102, and 184 mM solutions of **5** containing (*R*)-**2** (20.5 mM). A 12 mg/2 mL (41 mM) stock solution of poly-**1** was also prepared and aliquots 400 μL of the solution were transferred to four vessels with a screwcap by using a Hamilton microsyringe. Aliquots 400 μL of the stock solutions of **5** (40.8, 102, and 184 mM) in DMSO containing (*R*)-**2** (20.5 mM) ([(*R*)-**2**]/[poly-**1**] = 0.5 and [**5**]/[poly–**1**] = 1.0, 2.5, and 4.5) and a 400 μL of the stock solution of (*R*)-**2** (20.5 mM) were added to the four vessels, respectively, and absorption and CD spectra were then taken for each sample at appropriate time intervals. The same procedure was performed in the experiments with (*R*)-**2** and achiral **4** and **6**–**9** and (*S*)-**2** and **5**.

Memory of macromolecular helicity—SEC fractionation of poly-1: SEC fractionation was performed using a Jasco PU-980 liquid chromatograph equipped with a UV (300 nm; Jasco UV-970) detector. A Shodex KF-806 L SEC column was connected, and a solution of **4** (0.8 M) or **7** (0.008 M) in DMSO was used as the mobile phase at a flow rate of 1.0 mL min^{-1}. A hundred microliter of the solution of the poly-**1**-((*R*)-**2**+**5**) complex was injected to the SEC system, and the poly-**1** fraction was collected. The CD spectrum of the fractionated poly-**1** was measured in a 4 mm quartz cell. The same procedure was performed for the SEC

fractionations of poly-**1** complexed with (*R*)-**2** or (*S*)-**2** and achiral amines (**4** and **6**–**9**).

Acknowledgments

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[8] Acid–base binding constants (K_s) of (*S*)-**3** and **4** with vinylbenzoic acid as a model compound of poly-**1**, obtained by ^{1}H NMR titration experiments in [D$_6$]DMSO, are 509 ± 30 and $1050\pm60\,\text{M}^{-1}$, respectively. These are much larger than that of (*R*)-**2** (57 ± 2); see references [6b, 6c, 7a].

[9] The binding constant (K) of **5** with vinylbenzoic acid, estimated by ^{1}H NMR titration experiments in [D$_6$]DMSO, was $123\pm2\,\text{M}^{-1}$, which was larger than that of (*R*)-**2** (57 ± 2). Therefore, poly-**1** exhibited a full ICD in the presence of 2.5 equiv **5** and 0.5 equiv (*R*)-**2**. The chiral amplification was found to be sensitive to the addition order of (*R*)-**2** and **5** with poly-**1**; the addition of 0.5 equiv (*R*)-**2** to the poly-**1** solution in DMSO, followed by the addition of 2.5 equiv **5** resulted in almost the same CD spectrum as that shown in b in Figure 1A. However, the reversed addition order of (*R*)-**2** and **5** caused a significant decrease in the ICD intensity; the initial $[\theta]_{2nd}$ value was -6.0×10^3 at ambient temperature, which gradually increased with time. After 40 h, the ICD intensity of the solution reached -1.9×10^4 and further increased slowly with time. These results indicate that the induced helix of the poly-**1** is dynamic in nature, the helix-sense and its proportion are determined by the chirality of **2**, and (*R*)-**2** complexed with poly-**1** can exchange slowly with **5**, probably with maintaining the induced macromolecular helicity.

[10] Water may affect an acid–base complexation in DMSO, and the effect of water on the ICD of poly-**1** in the presence of (*R*)-**2** and **5** ([(*R*)-**2**]/[poly-**1**]/[**5**] = 0.5:1:2.5) was investigated. The ICD intensity gradually decreased with an increase in the amount of water, but the effect is negligible when the water content was less than 5%.

[11] The ICD intensities of the copolymers of an optically active phenylacetylene derivative bearing an (*R*)-(1-phenylethyl)carbamoyloxy group at the *para* position and achiral comonomers prepared with a rhodium catalyst increased with an increase in the bulkiness of the substituents on the comonomers.[4a,f] Moreover, the magnitude of the ICD induced on poly-**1** with chiral amines had a similar tendency and increased with an increase in the bulkiness of the chiral amines.[6]

[12] The poly-**1** isolated from the poly-**1**-(*R*)-**2** complex ([poly-**1**] = 3 mg mL^{-1}, [(*R*)-**2**]/[poly-**1**] = 10) by SEC using pure DMSO as the eluent showed no ICD and more than 99% of the (*R*)-**2** was found to be recovered based on the UV spectrum of the (*R*)-**2** fraction.[6c,7a] Similarly, we confirmed that more than 99% of the **5** was recovered from the poly-**1**–**5** complex ([poly-**1**] = 3 mg mL^{-1}, [**5**]/[poly-**1** = 10) by the SEC fractionation by using pure DMSO as the eluent. These results indicate that both (*R*)-**2** and **5** complexed with poly-**1** are completely removed during the SEC fractionation.

[13] Recently, chiral amplification has been combined with the chiral memory concept for the successful formation of enantiomeric assemblies; see reference [7k].

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