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Synthesis and Helicity Induction of Poly(phenylacetylene)s Bearing Crown Ether Pendants. Reversible On-Off Switching of the Induced Helical Chirality Tunable with Temperature

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Summary: Cis-transoidal poly(phenylacetylene)s bearing 15-crown-5 (**2a**) and 18-crown-6 (**2b**) were prepared by stereoselective polymerization using Rh(nbd)BPh_4. In the circular dichroism (CD) spectrum of **2a** in the presence of the perchloric acid salt of L-phenylglycine (L-Pgly· $HClO_4$), a characteristic induced CD (ICD) was observed in the absorption range corresponding to the polymer backbone. On the contrary, the **2b**/L-Pgly · $HClO_4$ system did not show such an ICD spectrum. The ICD intensity of the **2a**/L-Pgly · $HClO_4$ system drastically depended on temperature, i.e., the ICD disappeared at 30 °C or higher. Thus, the on-off switching of the ICD of **2a** was controllable by either the temperature modulation or the doping/undoping process of the chiral guest.

Keywords: chiral; crown ether; helical polymers; host-guest systems; polyacetylenes; stimuli-sensitive polymers

Introduction

The dual-stimuli-responsive property in macromolecular and supramolecular systems has the potential for use in a wide variety of applications that have been never achieved by a molecule capable of responding to just one kind of stimulus.[1] A dynamic helical polymer generally changes the helical conformation in the main chain in response to external stimuli or by changing the external condition, producing a drastic change in the chiroptical property.[2,3] Thus, there have been many efforts to design and synthesize helical polymers that have a potential application as stimuli-responsive materials. For example, we reported that polyisocyanates and polyacetylenes bearing various types of crown ether units formed a one-handed helical structure triggered by the host-guest complexation with chiral guest molecules.[4–6] Additionally, we also revealed that poly(phenylacetylene) bearing a polycarbohydrate ionophore as graft chains exhibited a helix inversion in response to the addition of metal cations with an ionic radius greater than 1.16 Å.[7] However, there are a few studies regarding the design and construction of a dual-stimuli-responsive helicity system, i.e., the chiroptical property of the macromolecular helicity preorganized by the first external stimulus is tuned by the second external stimulus.[8–10] We now report the design, synthesis, and helicity induction of poly(phenylacetylene)s bearing two different sizes of crown ether pendants, i.e., 15-crown-5 (**2a**) and 18-crown-6 (**2b**), in order to develop a macromolecular helicity system with the dual-stimuli-responsive property (Scheme 1). Polymer **2a** could form a one-handed helical structure when the presence of a suitable chiral guest and temperature control were simultaneously satisfied, so that **2a**

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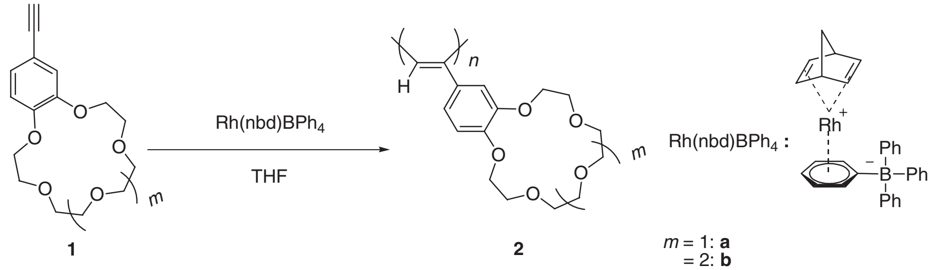

Scheme 1.
Synthesis of poly(phenylacetylene)s bearing 15-crown-5 (**2a**) and 18-crown-6 (**2b**).

should be categorized as a novel dual-stimuli-responsive material based on the macromolecular helical chirality.

Experimental Part

Materials

4′-Ethynylbenzo-15-crown-5 (**1a**),[11] 4′-ethynylbenzo-18-crown-6 (**1b**),[12] Rh^+(2,5-norbornadiene)[(η^6-C_6H_5)B^-(C_6H_5)$_3$] (Rh (nbd)BPh$_4$),[13] and the perchloric acid salt of L-phenylglycine (L-Pgly · $HClO_4$)[14] were synthesized by previously reported methods. THF was dried over sodium benzophenone ketyl and then vacuum transferred from CaH_2. Dry acetonitrile (purity >99.5%, water content <0.005 vol%) and chloroform for the spectroscopy (>99.0%) were obtained from the Kanto Chemical and used without further purification.

Measurements

The ^{1}H NMR spectra were recorded using a JEOL JNM-A400II instrument. The size exclusion chromatography (SEC) was performed at 40 °C using a Jasco high performance liquid chromatography (HPLC) system equipped with a Shodex Asahipak GF-310 HQ column and a Shodex Asahipak GF-7M HQ column in DMF containing lithium chloride (0.01 M) at a flow rate of 0.4 mL · min^{-1}. The number-average molecular weight (M_n) and polydispersity (M_w/M_n) of the polymer were calculated on the basis of a polystyrene calibration. Circular dichroism (CD) spectra were measured in a 1 mm path length using a Jasco J-720 spectropolarimeter.

Polymerization

The polymerizations of **1a** and **1b** were carried out in a dry Schlenk flask under an argon atmosphere. An example of the procedure is described for the preparation of polymer **2a** (run 1). In a glovebox (under moisture- and oxygen-free argon atmosphere, H_2O, $O_2 < 1$ ppm), Rh(nbd)BPh$_4$ (5.3 mg, 10 μmol) was weighed into a flask and dissolved in dry THF (2.1 mL). To the solution was added a solution of **1a** in dry THF (0.33 mol L^{-1}, 3.0 mL, 1.0 mmol). The concentrations of the monomer and the rhodium catalyst were 0.2 mol · L^{-1} and 0.002 mol · L^{-1}, respectively. After stirring at 25 °C for 24 h, the reaction was terminated by adding triphenylphosphine (16 mg, 62 μmol), and the mixture was then poured into a large amount of ether. The precipitate was purified by reprecipitation with chloroform/ether and then dried in vacuo to give polymer **2a** as a yellow powder. Yield, 0.25 g (83%). $M_n = 2.5 \times 10^4$, $M_w/M_n = 2.1$. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.30 (m, 3H, aromatic), 5.76 (s, 1H, =CH), 3.69 (m, 16H, –CH_2–).

Results and Discussion

Synthesis and Characterization of Poly(phenylacetylene)s Bearing Crown Ether Pendants

Table 1 lists the results for the polymerization of 4′-ethynylbenzo-15-crown-5 (**1a**) and 4′-ethynylbenzo-18-crown-6 (**1b**). The polymerization of **1a** with Rh(nbd)BPh$_4$ successfully afforded a polymeric product with a molecular weight of 2.5×10^4 (run 1). In contrast, the polymerization of **1b** involved a difficulty in increasing the molecular weight. For the polymerizations of **1b** with Rh(nbd)BPh$_4$, the polymeric product was obtained in a yield of 73%, while the molecular weight of the resulting product was relatively low, 3.6×10^3 (runs 2). In order to increase the molecular weight, we performed the polymerization under the condition where the amount of initiator was larger than that in run 2 (runs 3 and 4). However, a clear improvement in the molecular weight was not accomplished in both runs, though the yield increased with an increasing amount of rhodium catalyst.

The ^{1}H NMR spectrum of the product resulting in the polymerization of **1a** showed a characteristic signal at 5.76 ppm due to the main chain protons along with those at 6.30 ppm due to aromatic protons and at 3.69 ppm due to the methylene protons in the crown ether moiety. Therefore, the product was assignable to poly (phenylacetylene) bearing 15-crown-5 ether pendants, **2a**. On the basis of the sharpness and the region of the signal due to the main chain proton, it was found that **2a** possessed a highly cis-transoidal structure as the main chain configuration. A similar result was also observed in the ^{1}H NMR spectrum of the product resulting from **1b**, and thus this product was assigned to cis-transoidal poly(phenylacetylene) bearing 18-crown-6, **2b**.

Macromolecular Helicity Induction

We examined the potential of the macromolecular helicity induction in polymers **2a** and **2b** driven by the host-guest interaction with chiral guests. Figure 1A shows the circular dichroism (CD) and absorption spectra of **2a** and **2b** in the presence of L-Pgly · HClO$_4$ at −30 °C. The CD spectrum of the **2a**/L-Pgly · HClO$_4$ system exhibited a characteristic induced CD (ICD), i.e., a split-type Cotton effect, in the range from 300 to 550 nm corresponding to the absorption of the conjugated polymer backbone. Therefore, this result clearly indicated that **2a** formed a helical structure with an excess single screw sense triggered by the host-guest complexation with L-Pgly · HClO$_4$. In sharp contrast, the **2b**/L-Pgly · HClO$_4$ system did not show such a characteristic ICD, suggesting that **2b** did not form a stable one-handed helical structure. The reason for this is probably the low molecular weight of **2b**. Hereafter, for further investigations on macromolecular helicity induction, we focused on that for **2a**.

Figure 1B shows the CD spectra of the **2a**/L-Pgly · HClO$_4$ system in the temperature range from −30 to 30 °C. The ICD intensity of **2a** significantly decreased with the increasing temperature. In particular, the characteristic CD spectrum completely disappeared at 30 °C or higher, indicating that the one-handed helical structure of **2a** collapsed in this temperature range. Therefore, polymer **2a** should be categorized as a thermoresponsive material with the on-off switching property based on the helical chirality.

Table 1.
Polymerization results of **1a** and **1b**.[a)]

Run	Monomer	[M]/[I]	yield[b)] (%)	$M_n \times 10^{-4}$ [c)]	M_w/M_n[c)]
1	**1a**	100	83	2.5	2.1
2	**1b**	100	73	0.36	3.3
3	**1b**	50	88	0.26	3.1
4	**1b**	20	98	0.30	3.5

[a)] Initiator, Rh(nbd)BPh$_4$; solvent, THF; [M] = 0.2 M; time, 24 h; temp., 25 °C.
[b)] Diethyl ether-insoluble part.
[c)] Determined by SEC in DMF containing LiCl (0.01 M).

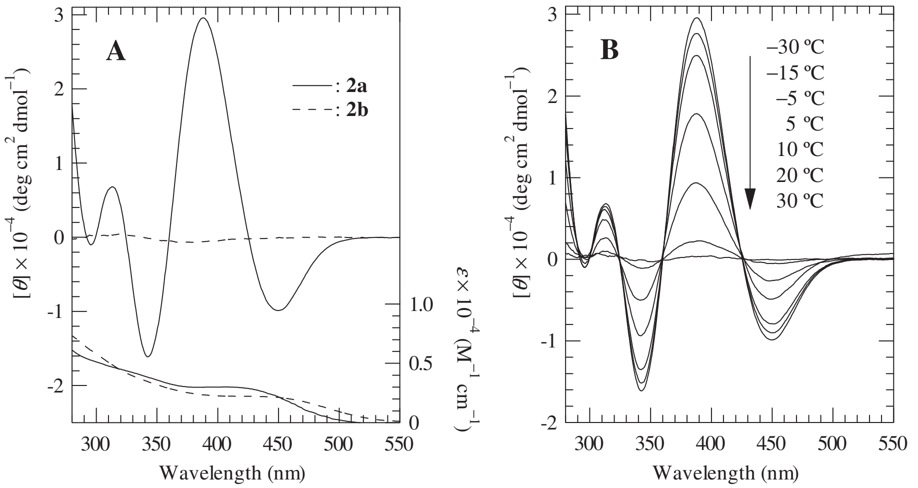

Figure 1.

CD and absorption spectra of **2a** and **2b** in the presence of 1 equiv. of L-Pgly · $HClO_4$ at −30 °C (A) and temperature dependence of CD spectrum of the **2a**/L-Pgly · $HClO_4$ system (B). CD measurements were performed in chloroform/acetonitrile (1/1, v/v). The concentrations of **2a** and **2b** were 3.4 and 3.0 mmol · L^{-1}, respectively.

The on-off switching of the ICD of the **2a**/L-Pgly · $HClO_4$ system was reversibly tunable with temperature, as shown in Figure 2. The characteristic ICD of **2a** did not appear by only adding 1.0 equiv. of L-Pgly · $HClO_4$ at 30 °C (a in Figure 2). Subsequently, the temperature change from 30 to −30 °C caused the full ICD to occur (b in Figure 2), which disappeared by changing the temperature to 30 °C once more (c in Figure 2). Additionally, the further alternate temperature modulation between −30 and 30 °C brought about the appearance and disappearance of the ICD, respectively.

The addition of L-Pgly · $HClO_4$ as the chiral guest is the essential driving force for inducing the one-handed helical structure into **2a**. Thus, we expected that the construction and collapse of the helical structure of **2a** was also tunable with the doping/undoping process of the chiral guest. The characteristic ICD of the **2**/L-Pgly · $HClO_4$ system at −30 °C almost completely disappeared with the addition of 2.0 equiv. of 18-crown-6, which is a host capable of binding L-Pgly · $HClO_4$ more strongly than **2a** (d in Figure 2). Further addition of 2.0 equiv. of L-Pgly · $HClO_4$ relative to **2a** brought about the recovery of the ICD (e in Figure 2). It should be noted that both the temperature modulation and the doping/undoping process of the chiral guest could control the on-off switching of the ICD of **2a**. Consequently, polymer **2a**

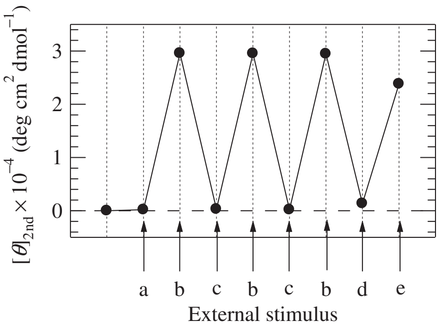

Figure 2.

Plots of the $[\theta]_{2nd}$ values of **2a** upon continuous external stimuli. The first plot is the $[\theta]_{2nd}$ value for the solution of **2a** in chloroform/acetonitrile (1/1, v/v) at 30 °C ([**2a**] = 3.4 mmol · L^{-1}). The stimuli (a–e) represent the addition of 1.0 equiv. of L-Pgly · $HClO_4$ relative to **2a** at 30 °C (a), changing the temperature to −30 °C (b), changing the temperature to 30 °C (c), the addition of 2.0 equiv. of 18-crown-6 relative to **2a** (d), and the further addition of 2.0 equiv. of L-Pgly · $HClO_4$ relative to **2a** (e).

has a great potential to be applied as a dual-stimuli-responsive material.

Conclusion

We have reported the synthesis and helicity induction of poly(phenylacetylene)s bearing two different sizes of crown ether, i.e., 15-crown-5 (**2a**) and 18-crown-6 (**2b**). In particular, for the construction of an induced one-handed helical structure into **2a**, it was essential that both the presence of a suitable guest molecule and temperature control were simultaneously satisfied. Thus, **2a** has the potential to operate as a molecular AND logic gate capable of exhibiting the characteristic induced circular dichroism.

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