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A Model Chiral Graft Copolymer Demonstrates Evidence of the Transmission of Stereochemical Information from the Side Chain to the Main Chain on a Nanometer Scale

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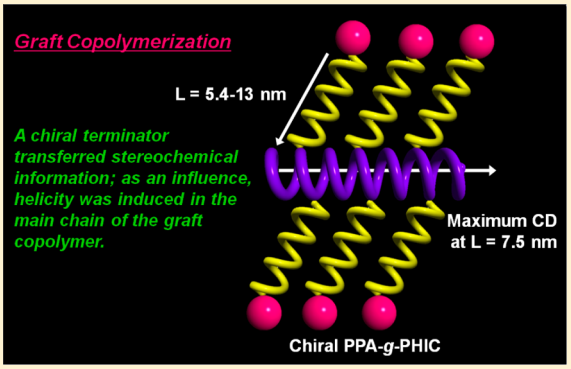
Supporting Information

ABSTRACT: A model chiral graft copolymer, poly(phenylacetylene)-*g*-poly(*n*-hexyl isocyanate) (PPA-*g*-PHIC), in which a chiral moiety is located at the end of each PHIC side chain, was synthesized. First, chiral PHIC macromonomers with a phenylacetylene end group were synthesized via living anionic polymerization using the functional initiator sodium *N*-(4-ethynylphenyl)benzamide (Na-4EPBA) and then end-capped using the chiral terminator (*S*)-2-acetoxypropionyl chloride ((*S*)-C*t*). The molecular weights (MWs) of the PHIC macromonomers were controlled based on the feed ratio of the monomer to the initiator. Subsequent polymerization of PHIC macromonomers using $Rh^{+}(2,5\text{-norbornadiene})[(\eta^{6}\text{-}C_6H_5)\text{-}B^{-}(C_6H_5)_3]$ ($Rh(nbd)BPh_4$) catalyst generated chiral PPA-*g*-PHIC graft copolymers with varying graft strand lengths. Chiral macromonomers and graft copolymers were characterized by SEC-MALLS, NMR, and CD spectroscopy. This model chiral graft copolymer provided an excellent example of the transmission of stereochemical information from the side chain to the main chain, as a preferred helicity was induced in the PPA backbone of the graft copolymer even when chiral moieties were separated from the main chain by nanometer scale distances (5.4−13 nm). Furthermore, CD spectroscopy clearly showed that the CD intensity of the PPA main chain was directly dependent on the CD intensity of the optically active PHIC side chain determined by the strand length.



INTRODUCTION

The long-range control of helical conformation has been a fascinating field of chemistry research over the past few decades. Such control can be obtained using a remote (i.e., terminal) chiral moiety to transmit stereochemical information on the nanometer scale. This approach is a promising biomimetic strategy for directing biological signaling.[1−4] A primary source of inspiration for this approach is G-protein-coupled receptors (GPCRs), which are involved in biochemical signal transmission through binding with stimulative signal molecules on the cell surface; GPCRs control key physiological functions, including neurotransmission, hormone and enzyme release from endocrine and exocrine glands, immune responses, cardiac and smooth-muscle contraction, and blood pressure regulation.[5,6] In addition to signal transmission, many sophisticated functions, such as recognition, replication, and catalytic activity, are performed by macromolecular helical structures.[7,8]

Various helical structures have been artificially constructed from self-assembled small molecules and synthetic polymers to mimic biological structures and their functions.[9,10] Polyisocyanates have been extensively studied for helicity induction due to their dynamic right-handed (P) and left-handed (M) helical conformations[11−13] and also for their ability to chemically induce a specific optical activity.[10,14] Polyisocyanates with a single-handed helical conformation can be obtained using different types of chiral moieties, such as initiators,[15−17] terminators,[17−20] monomers,[21−23] guest molecules,[24−26] and solvents.[27] The synthesis and characterization of chiral polyisocyanates have been key in understanding the chirality effects on the helical structures of other natural and synthetic polymers.[10,14] Furthermore, the use of living anionic polymerizations to synthesize the polyisocyanates with well-controlled molecular weights (MWs) and narrow molecular weight distributions (MWDs) has enabled the characterization of the qualitative helical properties of these polymers in accordance

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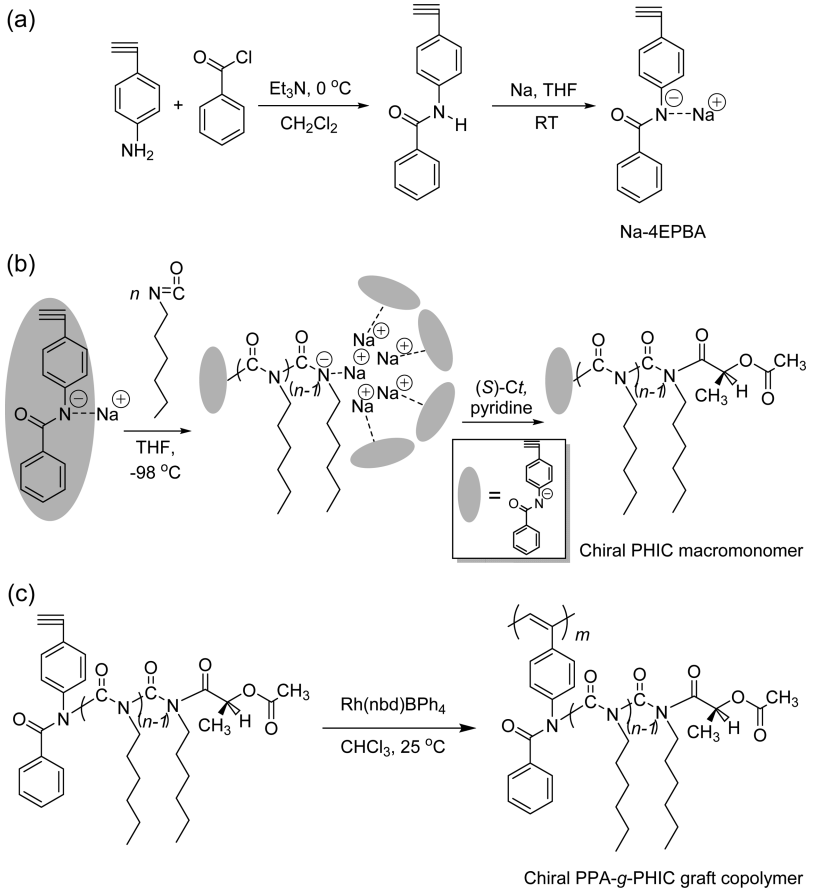
Scheme 1. Synthetic Route for Chiral PPA-*g*-PHIC Graft Copolymer: (a) Synthesis of Na-4EPBA Initiator, (b) Synthesis of Chiral PHIC Macromonomer, and (c) Synthesis of Chiral PPA-*g*-PHIC Graft Copolymer



with their chain length.[28−32] We have previously reported the helicity induction in well-defined poly(*n*-hexyl isocyanate) (PHIC) using end-capping with a chiral terminator.[17−20] According to the covalent chiral domino (CCD) effect, a chiral moiety attached to the α-end of a polymer chain can strongly contribute to the long-range control of a preferred-handed helical conformation.[10] In our work, the terminal chiral moiety of PHIC induced dynamic single-handed helicity in up to ∼36 monomer units (i.e., ∼5.0 kDa).[18] In contrast, PHIC containing a chiral initiator group showed static helicity.[17] From these different chirality effects depending on the structural types of terminal chiral moieties, we have described new helical behaviors as results from the "double covalent chiral domino (DCCD) effect".[17,19,20]

Interestingly, several groups have synthesized graft copolymers composed of helical side chains and a helical main chain.[33,34] For instance, Maeda et al. synthesized a graft copolymer containing helical poly(phenyl isocyanate) side chains and a helical poly(phenylacetylene) main chain and found that the stereochemical information on side chains determined by terminal chiral moieties could be transmitted to the main chain.[34] Circular dichroism (CD) spectroscopy confirmed that a preferred-handed helical sense of each polyisocyanate side chain, which was amplified by the CCD effect, was imparted to the PPA main chain. However, the effect of side chain length on the helicity of the backbone was unclear due to polydispersity of the polyisocyanate macromonomers, which were not synthesized by living polymerization.

In the present work, we synthesized model chiral graft copolymers with varying strand lengths, poly(phenylacetylene)-*g*-poly(*n*-hexyl isocyanate)s (PPA-*g*-PHICs), and examined their chiroptical properties to demonstrate the nanometer scale transmission of stereochemical information from the side chain to the main chain. Importantly, living anionic polymerization was used to control the MWs of the polyisocyanates and also to allow the quantitative introduction of a chiral moiety at the end of the chain through a chiral terminator.[28−32] Chiral PHIC macromonomers with different MWs were synthesized using a functional initiator, sodium *N*-(4-ethynylphenyl)-benzamide (Na-4EPBA), and a chiral terminator, (*S*)-2-acetoxypropionyl chloride ((*S*)-C*t*) (Scheme 1a,b). PHIC macromonomers containing a phenylacetylene group were polymerized using Rh^+(2,5-norbornadiene)[(η^6-C_6H_5)-$B^-(C_6H_5)_3$] ($Rh(nbd)BPh_4$) catalyst (Scheme 1c). The CD data for the helical graft copolymers with various helical strand lengths are useful in understanding of the transmission of stereochemical information on a nanometer scale. Furthermore, it is anticipated that the effect of strand length will apply to a diversity of helical polymers.

■ EXPERIMENTAL SECTION

Materials. Tetrahydrofuran (THF, Fisher Scientific, GR grade) was distilled under N_2 after refluxing with sodium (Aldrich, 99%) for 5 h and then distilled from a sodium naphthalenide (Na-Naph) solution under high vacuum (10^{-6} Torr). *n*-Hexyl isocyanate (HIC, Aldrich, 97%), pyridine (Aldrich, 99.5%), and (*S*)-2-acetoxypropionyl chloride ((*S*)-C*t*, Aldrich, 98%) were distilled over calcium hydride (CaH_2,

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Junsei, 95%) under reduced pressure and then redistilled over CaH_2 under 10^{-6} Torr. The distilled reagents were appropriately diluted with dry THF and divided in pure glass ampules equipped with break-seals under 10^{-6} Torr. 4-Ethynylaniline (Aldrich, 97%), benzoyl chloride (Aldrich, 99%), and triethylamine (Et_3N, Aldrich, 99%) were used without purification to synthesize sodium *N*-(4-ethynylphenyl)-benzamide (Na-4EPBA). Rh^+(2,5-norbornadiene)[(η^6-C_6H_5)-$B^-(C_6H_5)_3$] (Rh(nbd)BPh_4) was synthesized according to a previously reported procedure.[35]

Synthesis of Sodium *N*-(4-Ethynylphenyl)benzamide (Na-4EPBA). *N*-(4-Ethynylphenyl)benzamide (4-EPBA) was synthesized as follows: A solution of benzoyl chloride (6.00 g, 42.7 mmol) in CH_2Cl_2 was added dropwise to a solution of 4-ethynylaniline (4.50 g, 38.4 mmol) and Et_3N (6.00 g, 59.3 mmol) in CH_2Cl_2 at 0 °C under N_2. After stirring for 3 h, the organic solution was filtered, washed with the saturated solution of $NaHCO_3$ in water, and dried over Na_2SO_4. 4-EPBA was purified by recrystallization from ethanol three times and dried *in vacuo*. 4-EPBA: ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm): 3.07 (d, 1H, C*H*≡C−), 7.88 (m, 1H, −N*H*). 7.30−7.80 (8H, two aromatic rings). ^{13}C NMR ($CDCl_3$, 100 MHz), δ (ppm): 81.18 (CH≡C−), 82.42 (CH≡*C*−), 165.85 (C═O), 120.10, 126.83, 128.68, 132.01, 133.95, 135.03, 136.17, 137.52 (8C, −CH of aromatic ring). FT-IR (KBr, cm^{-1}): 3346 (−NH), 3076, 3043, 1600−1700 (C═O), 1600−1400 (C═C of aromatic ring), 846, 717. Elemental analysis, calculated values for $C_{15}H_{11}NO$: C, 81.43; H, 5.01; N, 6.33; O, 7.23. Observed values: C, 81.14; H, 5.12; N, 6.42; O, 7.32.

A solution of sodium *N*-(4-ethynylphenyl)benzamide (Na-4EPBA) was prepared via the reaction of 4-EPBA (2.12 g, 9.50 mmol) with elemental sodium (0.180 g, 7.80 mmol) in dry THF in a glass flask equipped with a break-seal at room temperature. After the color of the reaction mixture turned a light yellow, it was frozen, degassed under 10^{-6} Torr, and flame-sealed. The initiator solution was diluted with dry THF and divided in pure glass ampules equipped with break-seals under 10^{-6} Torr.

Synthesis of Chiral PHIC Macromonomer. Anionic polymerizations were carried out under 10^{-6} Torr in a sealed glass reactor using break-seal techniques. The reactor was prewashed with a solution of Na-Naph in THF prior to the polymerization. In a typical polymerization procedure (run CH-1), the initiator solution, Na-4EPBA (0.165 g, 0.68 mmol) in THF (3.6 mL) was transferred into a reaction flask through the break-seal, and the solution temperature was equilibrated to −98 °C. The polymerization was then performed by adding the monomer solution, HIC (0.630 g, 4.95 mmol) in THF (10.7 mL), to the initiator solution. After 60 min, polymerization was terminated by adding an excess of the chiral terminator, (*S*)-C*t*, with pyridine. The resulting polymer was precipitated in a large amount of methanol, filtered, and dried *in vacuo*. The polymer was obtained with a yield of 99%. The d*n*/d*c* value for the polymer was found to be 0.0906 mL/g, and the M_n and M_w/M_n values were determined to be 5.1 kDa and 1.09, respectively. Dissolution in THF and precipitation in methanol was repeated to obtain a highly pure polymer sample, which was dissolved again in benzene and freeze-dried for characterization. The methanol-soluble parts were concentrated and analyzed by ^{1}H NMR to check for the presence of remaining monomers or trimers. Chiral PHIC macromonomer: ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 0.89 (3H, −C*H*$_3$), 1.04−1.92 (8H, −(C*H*$_2$)$_4$−), 2.12 (s, 3H, COC*H*$_3$, terminator), 3.14 (d, 1H, C*H*≡C−), 3.68 (2H, N−C*H*$_2$−). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 14.01 (−CH_2CH_3), 17.26 (−CH−CH_3), 21.03 (−$COCH_3$), 23.12, 26.89, 28.72, 31.72 (−$(CH_2)_4$−), 48.41 (−N−CH_2−), 70.12 (−CH-CH_3), 157.54 (*C*═O), 170.41 (−$COCH_3$), 173.65 (−N−CO−CH−). FT-IR (KBr, cm^{-1}): 2961, 2925, 2859 (CH_2), 1712 (C═O), 1335/1304 (disubstituted amide), 1229, 1171, 1096, 788, 732 (CH_2).

Synthesis of Chiral PPA-*g*-PHIC Graft Copolymer. A mixture of PHIC macromonomer (0.44 g, 86.0 μmol) and Rh(nbd)BPh_4 catalyst (2.19 mg, 4.3 μmol) in $CHCl_3$ (0.93 mL) was placed in a glass ampule, degassed by three freeze−pump−thaw cycles under 10^{-6} Torr, flame-sealed, and stirred at 25 °C for 24 h. After polymerization, the resulting polymer was precipitated in a large amount of methanol, filtered, and dried *in vacuo*. Unreacted macromonomer was separated by three rounds of fractional precipitation in THF and methanol. The PPA-*g*-PHIC graft copolymer was obtained at an 86% yield. The d*n*/d*c* value for the polymer was observed to be 0.0887 mL/g, and the M_n and M_w/M_n values were found to be 131 kDa and 1.28, respectively (run CG-1). Chiral PPA-*g*-PHIC: ^{1}H NMR ($CDCl_3$, 300 MHz)), δ (ppm): 0.9 (3H, −C*H*$_3$), 1.0−2.0 (8H, −(C*H*$_2$)$_4$−), 3.7 (2H, N−C*H*$_2$−). ^{13}C NMR ($CDCl_3$, 75 MHz), δ (ppm): 14.5 (−CH_3), 22.5, 26.2, 28.5, 31.5 (−$(CH_2)_4$−), 48.6 (N−CH_2−), 156.8 (C═O). IR (KBr, cm^{-1}): 2958, 2931, 2860 (CH_2), 1702 (C═O), 1350/1298 (disubstituted amide), 1228, 1172, 1093, 784, 729 (CH_2).

Characterization. The ^{1}H and ^{13}C NMR spectra were measured at 25 °C using a JEOL-JNM-ECX400 NMR with $CDCl_3$ as the solvent. Chemical shifts were referenced to tetramethylsilane (TMS) at 0 ppm. The M_n and M_w/M_n values were determined using a multiangle laser light scattering detector system (MALLS) with an SEC-MALLS (OPTI LAB-DSP interferometric refractometry (478-009-690) and DAWN EOS laser photometer (113-E, Wyatt Technology)) and four columns (HR 0.5, HR 1, HR 3, and HR 4; Waters Styragel columns connected in series with column pore sizes of 50, 100, 500, and 1000 Å, respectively). THF with 2 vol % Et_3N, which was added to prevent adsorption of the hydrophilic polymer to the column, was used as the mobile phase with a flow rate of 1.0 mL/min. The d*n*/d*c* value for each polymer in THF at 40 °C was measured with an LED (Optilab DSP) source. After the d*n*/d*c*s were measured for the five different concentrations of the polymer samples, SEC-MALLS data were gained with refractive index detection at 40 °C. FT-IR spectra were collected on a PerkinElmer System 2000 using KBr pellets. Circular dichroism (CD) and ultraviolet (UV) spectra were measured on a JASCO-J-720 spectropolarimeter using a cell path length of 0.5 cm. Specific ellipticity values are expressed in molar ellipticity. All CD spectra were smoothed with a Savitzky-Golay filter within OriginPro-8.1 software. All CD samples were prepared at 1 mg/mL.

■ RESULTS AND DISCUSSION

Synthesis of Chiral PHIC Macromonomer. To prepare the phenylacetylene end-functionalized PHIC macromonomers through living anionic polymerization, it was necessary to use a functional initiator with a phenylacetylene group. Therefore, *N*-(4-ethynylphenyl)benzamide (4-EPBA) was synthesized by the reaction of 4-ethynylaniline with benzoyl chloride in the presence of Et_3N, as shown in Scheme 1a (Figure S1a,b in the Supporting Information). The reaction of 4-EPBA with sodium metal in THF produced a dark yellow solution of Na-4EPBA initiator.

Importantly, Na-4EPBA has structural similarity to sodium benzanilide (Na-BA) and was found to exhibit similar reactivity.[30] Na-BA is known to form a pentameric aggregated structure in THF at −98 °C. This aggregate performs the dual function of initiating isocyanate polymerization through one molecule and simultaneously protecting the chain-end through the other four molecules. Thus, the intrinsic efficiency of the Na-BA initiator is ∼20%.[30] For Na-4EPBA initiation here, the introduction of HIC into the Na-4EPBA solution produced a color change from dark yellow to pale yellow, indicating the formation of the living PHIC amidate anion. The optimal polymerization time of HIC in THF at −98 °C to achieve 100% yield was 60 min, and under this condition the efficiency of the Na-4EPBA initiator (efficiency of initiator = calculated M_n/observed M_n × 100%) was calculated to be 19−21%. As the anion content of Na-4EPBA was estimated to be 95% using a standard procedure,[30] this result indicates that only ∼20% of the Na-4EPBA molecules initiated polymerization. Therefore, like Na-BA, Na-4EPBA appears to possess a dual function during polymerization.

Table 1. Synthesis of Chiral PHIC Macromonomers via Living Anionic Polymerization Using Na-4EPBA Initiator and (*S*)-C*t* Terminator in THF at −98 °C

						M_n (kDa)					
run	Na-4EPBA (mmol)	HIC (mmol)	pyridine (mmol)	(*S*)-C*t* (mmol)	time (min)	calcd[d]	obsd[e]	M_w/M_n[e]	yield	DP[f] (%)	L_{PHIC}[g] (nm)
CH-1[a]	0.68	4.95	2.35	1.58	60/20[c]	1.3	5.1	1.09	99	37.3	7.5
CH-2[a]	0.42	4.47	1.67	1.48	60/20[c]	1.7	7.3	1.08	99	54.6	11
CH-3[a]	0.33	4.42	1.45	1.18	60/20[c]	2.0	8.9	1.07	98	67.2	13
CH-4[a]	0.73	4.42	2.96	1.64	60/20[c]	1.0	3.8	1.12	98	27.1	5.4
AH-5[b]	0.41	4.99			60	1.8	7.8	1.09	99	58.6	12

[a]Chiral PHIC macromonomer prepared by end-capping with a (*S*)-C*t* terminator. [b]Achiral PHIC macromonomer prepared by termination with a 20-fold excess of HCl in methanol. [c]The former is the polymerization time and the latter is the termination time. [d]M_n = {[HIC]/[Na-4EPBA] × MW of HIC} + MW of Na-4EPBA residue + MW of (*S*)-C*t* residue. [e]M_n and M_w/M_n values were determined by SEC-MALLS in THF with 2 vol % Et_3N at 40 °C. [f]DP: degree of polymerization of the PHIC macromonomer. [g]The length of the PHIC chain (L_{PHIC} = DP × 0.2 nm) was calculated assuming the length per repeat unit to be ca. 0.2 nm.

Chiral PHIC macromonomers were synthesized using a Na-4EPBA initiator and a (*S*)-C*t* terminator, as shown in Scheme 1b. As the living chain end had very poor reactivity, even with acid chloride, the end-capping was catalyzed using pyridine.[18,19] The polymerization results are summarized in Table 1. To study the effect of chain length on the optical activity, chiral PHIC macromonomers (CH-1 to CH-4) were synthesized with varying MWs (M_n = 3.8−8.9 kDa) and narrow MWDs (M_w/M_n = 1.07−1.12), as determined by SEC-MALLS. Quantitative polymer yields (∼99%) were obtained in each case. A control achiral PHIC macromonomer (AH-5) prepared without using (*S*)-C*t* and pyridine had a M_n of 7.8 kDa and a M_w/M_n of 1.09. The ^{1}H NMR spectrum of chiral PHIC macromonomer (CH-1) exhibited characteristic peaks of the acetylene group of the initiator and the methyl group of the chiral terminator at 3.14 and 2.12 ppm, respectively. No −NH peak of uncapped PHIC was observed, indicating that the introduction of the chiral moiety onto the N-terminus had proceeded to 100% (Figure 1).[18,19] Furthermore, by studying the relative peak intensities of

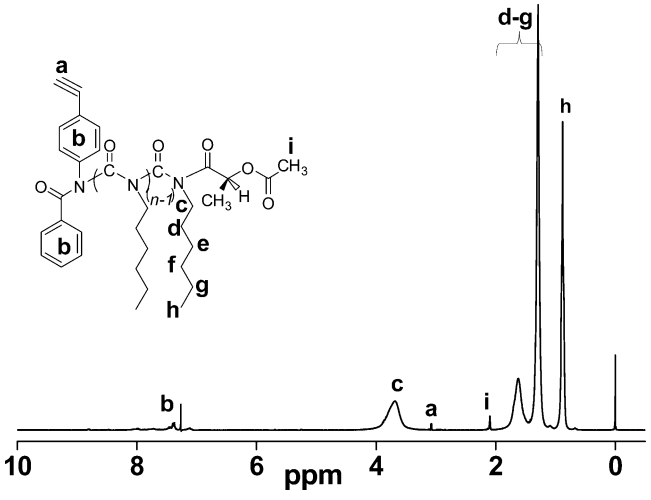

Figure 1. ^{1}H NMR of chiral PHIC macromonomer (CH-1) in $CDCl_3$.

the functional initiator, the chiral terminator, and the repeating unit, the degree of polymerization (DP) values of these chiral PHIC macromonomers were calculated to be 27.1−67.2. These DP values correspond to the chain lengths (L_{PHIC}) of 5.4−13 nm (Table 1). PHIC (CH-1) was found to have a M_n of 5.1 kDa and a DP of ∼36 by SEC-MALLS, which was in good agreement with the observed DP determined by ^{1}H NMR. Overall, these results suggest that Na-4EPBA promoted the living polymerization of HIC and produced well-defined chiral PHIC macromonomers with the quantitative acetylene and chiral end functionalities. The reactive acetylene group of Na-4EPBA did not cause any side reactions during polymerization.

Synthesis of Chiral PPA-*g*-PHIC Graft Copolymer. Model chiral graft copolymers with varying strand lengths, poly(phenylacetylene)-*g*-poly(*n*-hexyl isocyanate)s (PPA-*g*-PHICs), were synthesized by the polymerization of purified PHIC macromonomers using Rh(nbd)BPh_4 catalyst in $CHCl_3$ at 25 °C, as shown in Scheme 1c. The polymerization results are summarized in Table 2. The PPA-*g*-PHICs (CG-1 to CG-4) exhibited M_n and M_w/M_n values in a range of 64.5−263 kDa and 1.28−1.34, respectively. As a control, an achiral PPA-*g*-PHIC (M_n = 205 kDa and M_w/M_n = 1.22 for AG-5) was also prepared using achiral PHIC macromonomer (AH-5). After polymerization, a unimodal SEC curve for the graft copolymer was observed with a very small curve in the low-MW region for the unreacted macromonomer. This macromonomer was removed by fractional precipitation using THF and methanol to yield pure graft copolymer, as shown in Figure 2. Moreover, in the SEC curve, a clear MW shift was observed for the graft copolymers. Disappearance of the acetylene peak of the macromonomer after graft copolymerization was also observed by ^{1}H NMR analysis (Figure 3). A sharp peak at 5.43 ppm corresponding to a proton of the PPA backbone was also observed, indicating that the main chain of the graft copolymer possessed a highly *cis*-transoidal structure.[36]

Helicity Study of Chiral PPA-*g*-PHIC Graft Copolymer. The optical activity of chiral PHIC macromonomers and the corresponding graft copolymers were characterized by CD analysis of THF solutions in the UV/vis region (1 mg/mL; cell path length: 0.5 cm; 25 °C). The CD spectra of chiral PHIC macromonomers showed a positive Cotton effect at 255 nm due to the characteristic n−π^* transition of the polyisocyanate backbone,[14] indicating that the PHIC macromonomers had a right-handed helical sense (Figure S4 in the Supporting Information). The CD intensity of the chiral PHIC macromonomer increased when the MW increased from 3.8 to 5.1 kDa (L_{PHIC} = 5.4−7.5 nm), and it decreased gradually when the MW increased from 5.1 to 8.9 kDa (L_{PHIC} = 7.5−13 nm), as observed in a previous study.[18] These results confirmed that the (*S*)-C*t* moiety can induce a preferred-handed helicity in the chiral PHIC macromonomer in a domain (MW) up to 5.1 kDa (L_{PHIC} = 7.5 nm) through the CCD effect.

Figure 4 shows the CD spectra of chiral PPA-*g*-PHICs with varying strand lengths (L = 5.4−13 nm). CD intensities at absorption regions corresponding to the PHIC backbone

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Table 2. Synthesis of Chiral PPA-*g*-PHIC Graft Copolymers via Rh(nbd)BPh_4-Catalyzed Polymerization of Chiral PHIC Macromonomers in $CHCl_3$ at 25 °C for 24 h

			M_n (kDa)[c]/M_w/M_n[c]		
run	Rh(nbd)BPh_4 (mmol)	macromonomer (mmol)	macromonomer	graft copolymer	DP[d]
CG-1[a]	0.0043	0.086	(CH-1) 5.10/1.09	131/1.28	25.7
CG-2[a]	0.0027	0.055	(CH-2) 7.30/1.08	234/1.31	32.1
CG-3[a]	0.0022	0.045	(CH-3) 8.90/1.07	263/1.32	29.6
CG-4[a]	0.0048	0.045	(CH-4) 3.80/1.12	64.5/1.34	17.0
AG-5[b]	0.0029	0.045	(AH-5) 7.80/1.09	205/1.22	25.8

[a]Chiral PPA-*g*-PHIC prepared using a chiral PHIC macromonomer. [b]Achiral PPA-*g*-PHIC prepared using an achiral PHIC macromonomer. [c]M_n and M_w/M_n values were determined by SEC-MALLS in THF with 2 vol % Et_3N at 40 °C. [d]Degree of polymerization of the graft copolymer.

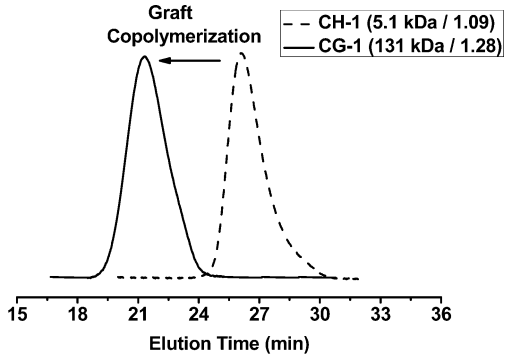

Figure 2. SEC curves of chiral PHIC macromonomer (CH-1) and chiral PPA-*g*-PHIC graft copolymer (CG-1).

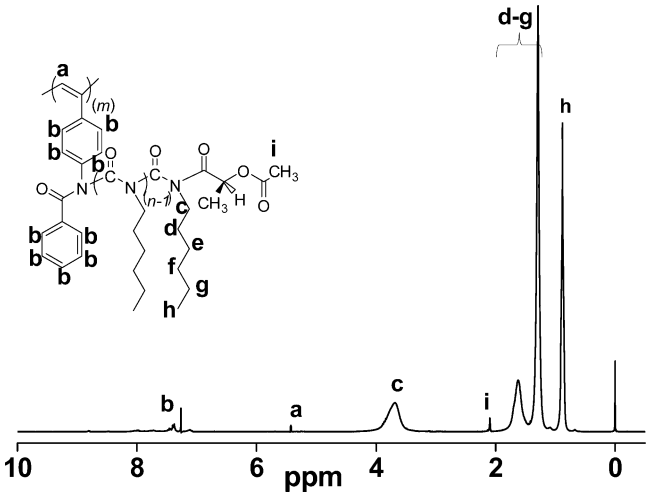

Figure 3. ^1H NMR of chiral PPA-*g*-PHIC graft copolymer (CG-1) in $CDCl_3$.

(210−300 nm) and the PPA backbone (300−475 nm) were standardized in a unit of molar ellipticity ([θ]) to compensate for the low CD intensity of the PPA backbone, which was the result of differing molar concentrations of HIC and PHIC macromonomer in a solution of the graft copolymer. The PHIC chain still retained an identical right-handed helical sense after graft copolymerization. Meanwhile, the PPA backbone adopted a left-handed helical sense presenting a negative Cotton effect at 375 nm,[37−40] although chiral moieties of (*S*)-type are present at nanometer scale distances of 5.4−13 nm. Since PPA derivatives are highly dynamic helical polymers whose helical sense can be dramatically changed by external stimuli (solvent, temperature, additive, pH, etc.),[37−40] this opposite helical sense might be a result observed in a specific

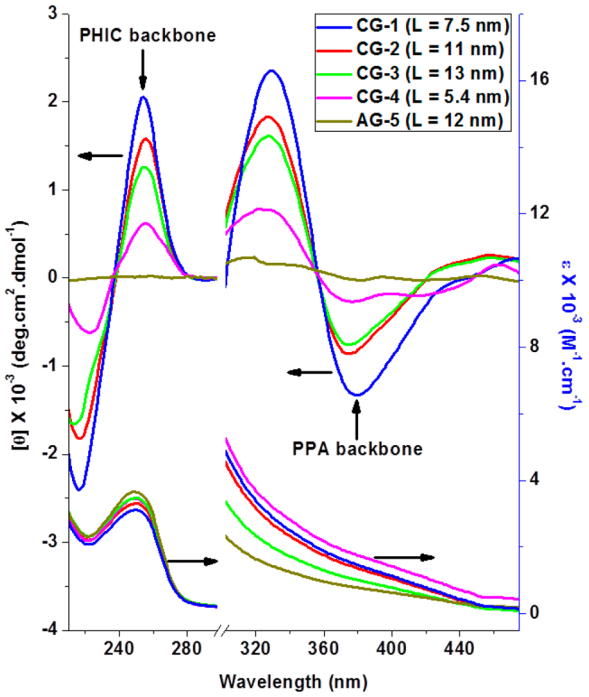

Figure 4. CD (upper) and UV (lower) spectra of chiral/achiral PPA-*g*-PHIC graft copolymers in THF (1 mg/mL; cell path length: 0.5 cm; 25 °C). The molar ellipticity ([θ]) and molar absorption coefficient (ε) were calculated using the molar concentration of HIC (210−300 nm: the absorption region of the PHIC backbone) and PHIC macromonomer (300−475 nm: the absorption region of the PPA backbone). The strand length (L), which is the distance from the chiral end group to the PPA backbone, corresponds to L_{PHIC} from Table 1.

condition (THF, 25 °C in this case). Interestingly, it was clearly observed that the CD intensity of the PPA backbone of the chiral graft copolymer was directly proportional to the CD intensity of the PHIC side chain. When the chiral PHIC (CH-1) with a M_n of 5.1 kDa and maximum CD intensity was used to make the graft copolymer, the CD intensity of the PPA backbone on its graft polymer (CG-1) with a strand length of 7.5 nm was the highest. The CD intensity of PPA induced by the chiral PHIC side chain with a lower or higher strand length than 7.5 nm decreased with decreasing CD intensity of the chiral PHIC.

Importantly, PPA derivatives do not naturally adopt a single-handed helical sense. Thus, some chiral driving force must be applied to induce a preferred helicity. Here, the driving force for helicity induction is applied by installing a terminal chiral moiety on each helical side chain, which then influences the

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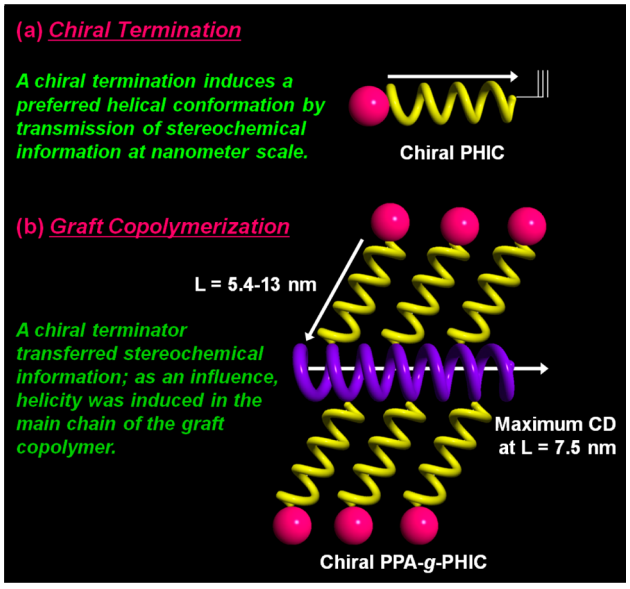
helical main chain of the graft copolymer. As the strength of the driving force for helicity induction from helical side chain to the helical main chain is tunable by varying length of the side chain, the CD intensity of the helical main chain can also be controlled. Consequently, higher CD intensity of the helical side chain translates to higher CD intensity of the helical main chain (Scheme 2). It is noteworthy that each helical strand with

Scheme 2. Transmission of Stereochemical Information from Helical Side Chain to Helical Main Chain on Nanometer Scale in Chiral PPA-*g*-PHIC Graft Copolymer



a remote chiral moiety located several nanometers away from the main chain plays a crucial role in transmitting helicity. In particular, the helical sensor's sensitivity and output responsivity to the specific stereochemical information can be tuned by controlling the strand length, which is an important prerequisite for optimal signal monitoring.

CONCLUSIONS

Chiral poly(*n*-hexyl isocyanate) (PHIC) macromonomers with controlled MWs were synthesized using a Na-4EPBA initiator and end-capped with a (*S*)-C*t* terminator by living anionic polymerization. Through the polymerization of these well-defined chiral macromonomers, model chiral graft copolymers with varying distances between the chiral end of the side chain and the main chain, poly(phenylacetylene)-*g*-poly(*n*-hexyl isocyanate)s (PPA-*g*-PHICs), were synthesized. Evidence of the transmission of stereochemical information from the helical side chain to the helical main chain was shown by CD spectroscopy, as a preferred-handed helicity was imparted to the PPA backbone by the chiral moiety, even when the distance between the chiral moiety and the main chain exceeded 10 nm. In addition, the results showed that the CD intensity of the PPA main chain was directly dependent on the strand length and optical activity of the helical PHIC side chain. The similar operations may be observed in primary cilia on the cell surface. The ciliary length is closely associated with the type of sensory function performed by the cilia, and its defects cause problems with feedback disorder and the relevant diseases.[41] It suggests that controlling the strand length is essential for signaling process in biochemistry. In future work, the present findings will provide a foundation for studies on stimuli-controlled helicity in which the fixed chiral moiety will be replaced with stimuli-responsive moieties that can be activated under the influence of light, pH, or binding materials. This work will provide insights into the sensing, transmission and output of signals in the aggregated states of biochemical receptors.

ASSOCIATED CONTENT

Supporting Information

^{1}H NMR and ^{13}C NMR of initiator, chiral macromonomer, and chiral graft copolymer; CD spectra of chiral macromonomers. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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