

Macromolecular Helicity Induction on a Poly(phenylacetylene) with C_2 -Symmetric Chiral [60]Fullerene-Bisadducts

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Abstract: Three chiral *N*-methylfulleropyrrolidine bisadducts were prepared, isolated, and completely resolved into each enantiomer using a chiral HPLC column, which were then converted to the corresponding optically active, cationic C_{60} -bisadducts to investigate if they could act as a macromolecular helicity inducer in a poly(phenylacetylene) bearing an anionic monoethyl phosphonate pendant (poly-1) in aqueous solution. Upon complexation with the chiral C_{60} -bisadducts, only the *trans*-3 bisadduct exhibited the characteristic induced circular dichroism (ICD) in the UV–visible region of the polymer backbone in dimethyl sulfoxide–water mixtures due to the predominantly one-handed helix formation of poly-1, while the *trans*-2 and *cis*-3 bisadducts induced almost no apparent CD in the same region. These results indicate that the helicity induction on poly-1 is highly sensitive to the structure and geometry of the cationic C_{60} -bisadducts with a different distance between the separated charges.

Introduction

Recently, much attention has been paid to the design and synthesis of C_{60} -containing polymers with a well-defined structure because of their possible applications in the fields of material¹ and biological sciences.² Varieties of C_{60} -based polymers have been usually prepared by the polymerization or copolymerization of the corresponding C_{60} -based monomers or by the reaction of functional C_{60} derivatives with polymers, through which C_{60} molecules can be incorporated in the polymer main chain or the pendants, and their structures and properties then investigated in the bulk state or as thin films.^{1,2} We have previously developed useful methods for constructing novel helical poly(phenylacetylenes) with pendant C_{60} molecules in a one-handed helical array; one is the copolymerization of an achiral C_{60} -bound phenylacetylene with optically active phenylacetylenes³ and the other is the helicity induction on a C_{60} -based optically inactive, but dynamically racemic helical

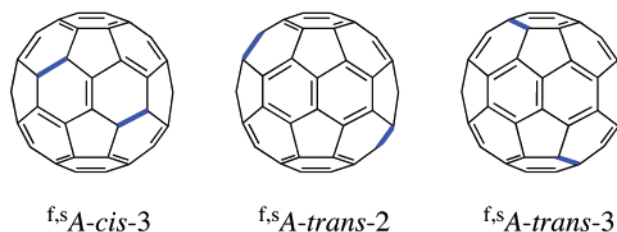


Figure 1. Double-addition patterns of chiral C_{60} -bisadducts.

poly(phenylacetylene) bearing a bulky 18-crown-6 ether pendant upon complexation with *L*- or *D*-amino acids.⁴ These C_{60} -containing polymers formed a predominantly one-handed helical structure induced by the covalently bonded optically active substituents or noncovalent bonding chiral interactions between the crown ether pendants and amino acids, respectively, and the pendant fullerenes arranged in a helical array along the polymer backbones, thus exhibiting a characteristic induced circular dichroism (ICD) in the achiral fullerene chromophore region as well as in the main chain region.

Here we report a novel method to construct a helical array of C_{60} molecules along a polymer backbone using optically active, cationic C_{60} -bisadducts as a helicity inducer in a dynamically racemic helical poly(phenylacetylene) with an anionic phosphonate pendant capable of interacting with the C_{60} -bisadducts.

The preparation and characterization of the C_{60} -bisadducts have aroused considerable interest in the field of fullerene chemistry and advanced materials science.⁵ The C_{60} -bisadducts have

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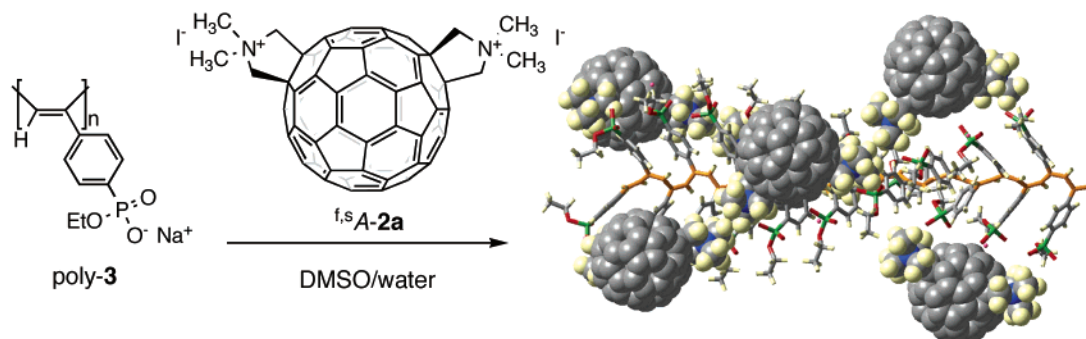


Figure 2. Schematic representation of the macromolecular helicity induction on poly-3 with optically active $f,sA-2a$ (*trans-3*).

eight regioisomers in principle, and among them, the *trans-3*, *trans-2*, and *cis-3* regioisomers have a C_2 -symmetry and are chiral due to their addition pattern (Figure 1). The complete isolation and characterization of eight regioisomers for the C_{60} -benzynes bisadducts have been achieved,⁶ and several enantiomerically pure *trans-3*, *trans-2*, and *cis-3* bisadducts were obtained by using a tether-constraint method⁷ or by chromatographic enantioseparation using chiral HPLC columns.⁸ The unique chiroptical properties of the chiral C_{60} -bisadducts and their availability stimulated us to synthesize optically active, cationic C_{60} -bisadducts (**2**) and investigate if such optically active C_{60} -bisadducts **2** could induce macromolecular helicity on an optically inactive poly(phenylacetylene) bearing an anionic monoethyl phosphonate residue (poly-**3**)⁹ in aqueous solution (Figure 2). Poly-**3** is highly sensitive to the chirality of amines and amino acids in organic solvents¹⁰ and water,⁹ respectively, and the complexes show ICDs in the polymer backbone region; the Cotton effect signs corresponding to the helix-sense of poly-**3** can be used as a novel probe for the chirality assignments of the chiral molecules.^{9,10} We anticipated that the cationic quaternary ammonium ions of the bis-*N,N*-dimethylfulleropyrrolidinium ammonium iodide (**2**) can bind to the oppositely charged polyelectrolyte poly-**3** through electrostatic interactions in aqueous solutions, leading to an excess of the one-handed helical sense in the polymer backbone induced by the chirality of the bound C_{60} -bisadducts, which simultaneously results in a helical array of the C_{60} -bisadducts along the polymer backbone with a predominant screw-sense. A similar helical array of achiral and cationic C_{60} -monoadducts through electrostatic interactions with the phosphate groups along the DNA backbone was reported by Tour and co-workers.^{2b} However, the chiroptical property of the complex has not yet been reported.

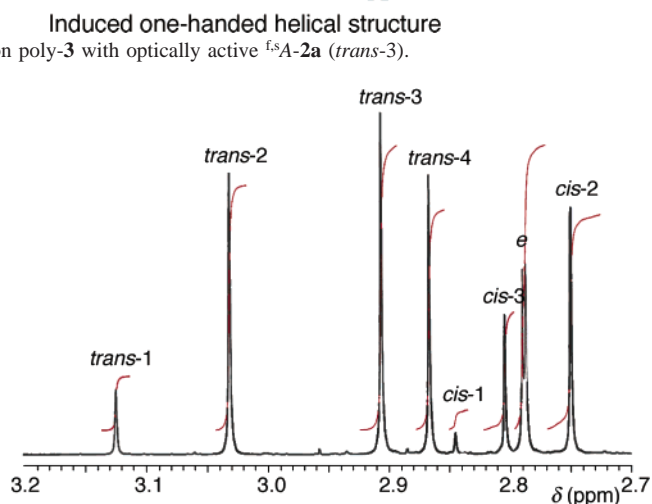


Figure 3. 1H NMR spectrum of the bisadduct **1** mixture before isolation.

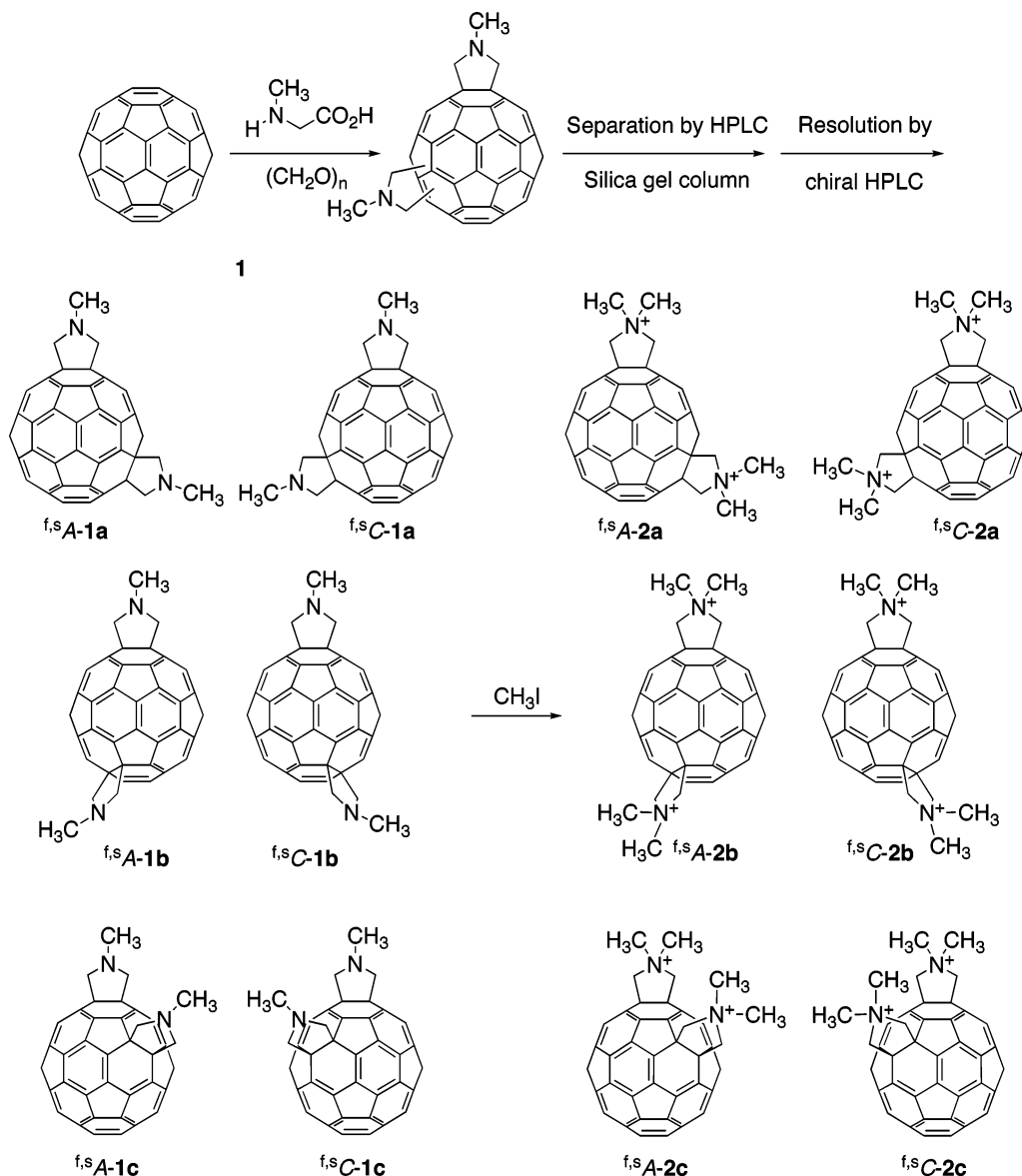
Results and Discussion

Synthesis and Isolation of Chiral C_{60} -Bisadducts. Optically active *trans-3*, *trans-2*, and *cis-3* C_{60} -bisadducts (**2**) were prepared according to Scheme 1. The *N*-methylfulleropyrrolidinium bisadducts (**1**) were synthesized by the Prato reaction of C_{60} in the presence of sarcosine and paraformaldehyde, from which the chiral regioisomers, **1a** (*trans-3*) and **1b** (*trans-2*), were isolated by HPLC according to the procedure reported by Prato et al.¹¹

However, the chiral **1c** (*cis-3*) regioisomer was not isolated in the literature,¹² although three similar chiral bisadducts including a *cis-3* of *N*-(triethylene glycol mono methyl ether)-fulleropyrrolidinium (*N*-mTEG) prepared by a similar Prato reaction were successfully isolated.¹² We then carefully examined the 1H NMR spectrum of the C_{60} -bisadducts (**1**) before separation into the regioisomers. The 1H NMR spectrum of the bisadduct mixture (**1**) showed nine proton peaks (two for *e*) in their *N*-methyl proton resonance regions (Figure 3). This clearly indicates that all eight possible regioisomers of the bisadducts including the *cis-3* (**1c**) might be produced during the Prato reaction (Chart 1). We then tried to isolate each regioisomer using a recycling HPLC system and successfully isolated the eight regioisomers including the *cis-3* and *cis-1*. The assignments were performed with 1H NMR, UV-visible, and mass spectroscopies. The FAB-MS measurements of all eight regioisomers gave a molecular ion peak of $m/z = 834$ corresponding to the desired bisadduct. Therefore, the eight *N*-methyl proton peaks

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Scheme 1. Synthesis of ^{f,s}A- and ^{f,s}C-**2a** (*trans*-3), **-2b** (*trans*-2), and **-2c** (*cis*-3)

in Figure 3 can be finally assigned. On the basis of the integral ratio of the *N*-methyl proton resonances, the relative yields of

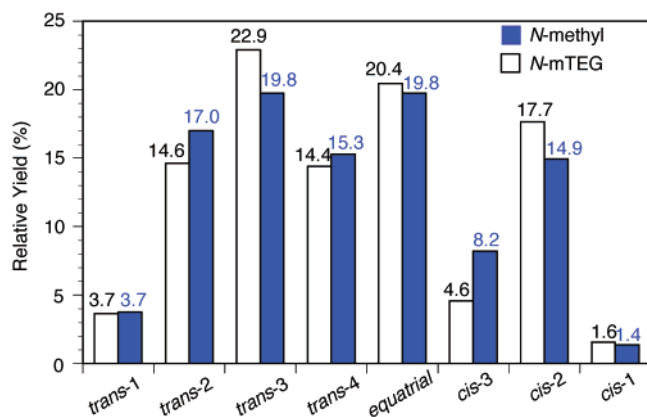


Figure 4. Relative yields of the C₆₀-bisadducts, *N*-methylfulleropyrrolidine (**1** in Scheme 1) and *N*-(triethylene glycol mono methyl ether)fulleropyrrolidine (*N*-mTEG). The relative yields of **1** were estimated by the integral ratio of their *N*-methyl proton resonances in the ¹H NMR spectrum of the mixture (Figure 3) and those of *N*-mTEG were cited from ref 12.

the C₆₀-bisadducts in the Prato reaction are estimated to be *trans*-1:*trans*-2:*trans*-3:*trans*-4:*equatorial*:*cis*-3:*cis*-2:*cis*-1 = 3.7:17.0:19.8:15.3:19.8:8.2:14.9:1.4 (Figure 4). This regioselectivity in the formation of the *N*-methyl Prato reaction was similar to that of the previously reported *N*-mTEG (Figure 4).¹²

The isolated racemic **1a**, **1b**, and **1c** were completely resolved into their enantiomers (^{f,s}A- and ^{f,s}C-enantiomers) by chiral HPLC using Chiralpak AD-H¹³ as the chiral stationary phase.⁸ The representative chromatograms for the resolution of each chiral bisadduct are shown in Figure 5. The separation factors (α) are 1.28 (**1a**), 1.30 (**1b**), and 1.96 (**1c**), respectively, and the base-line separation of the enantiomers was attained for all the regioisomers. The resolved enantiomers were then treated with an excess amount of iodomethane to give the corresponding quaternary ammonium salts, **2a**, **2b**, and **2c** (Scheme 1),¹⁴ which

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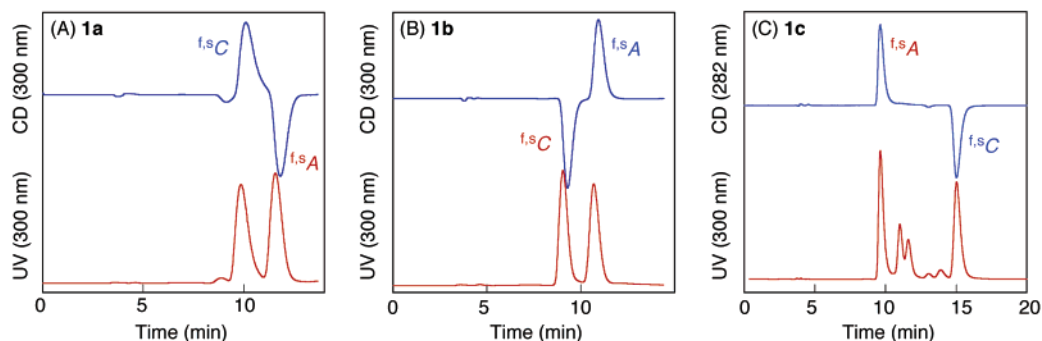


Figure 5. HPLC chromatograms for the enantioseparation of C_{60} -bisadducts **1a** (A), **1b** (B), and **1c** (C) using a chiral column (Chiralpak AD-H) with hexane/2-propanol (9/1 (v/v)) as the eluent.

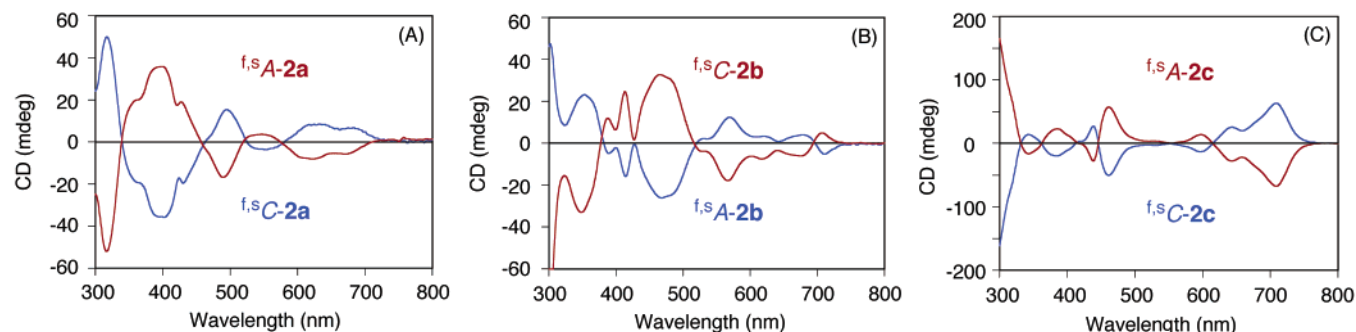
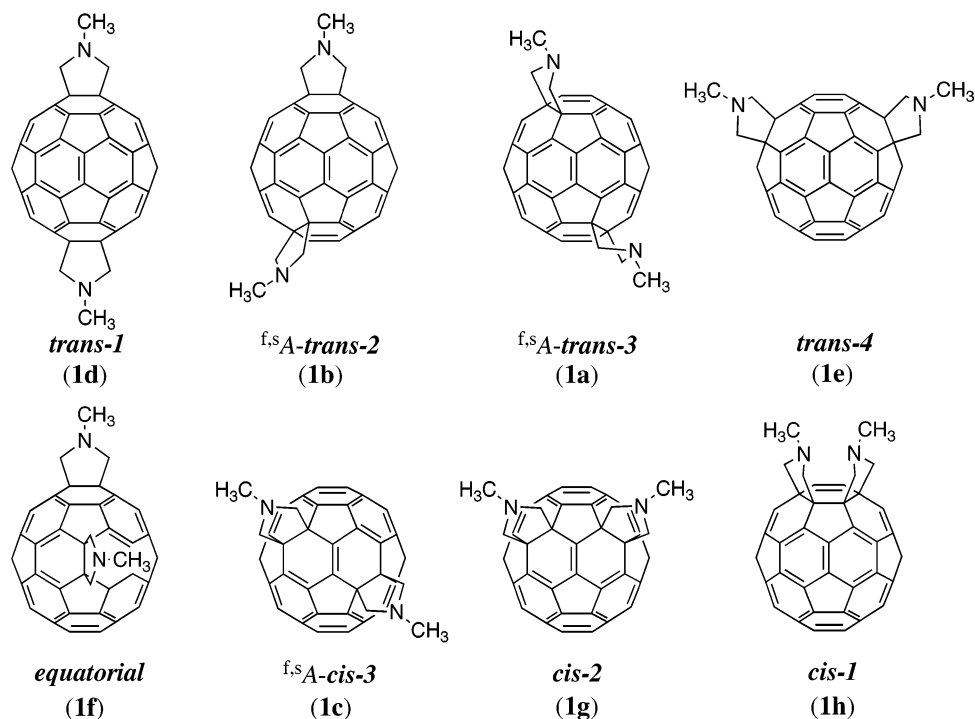


Figure 6. CD spectra of the f,sA - and f,sC -enantiomers of **2a** (A), **2b** (B), and **2c** (C) in DMSO (0.5 mg/mL) at 25 °C.

Chart 1. Structures of the possible eight regioisomers of **1**



are soluble in dimethyl sulfoxide (DMSO) and DMSO–water mixtures, but insoluble in pure water. The CD spectra of these optically active, cationic C_{60} -bisadducts **2a**, **2b**, and **2c** in DMSO are shown in Figure 6. Each pair of enantiomers clearly exhibited mirror image CDs from each other. The absolute configurations of the enantiomeric pairs of **1a**, **1b**, and **1c** were assigned as shown in Figures 5 and 6 on the basis of their CD patterns of the optically pure *trans*-3, *trans*-2, and *cis*-3 C_{60} -benzyne bisadducts, since the CD patterns of the chiral

bisadducts are determined by the addition pattern, independent of the substituents.⁸

Helicity Induction on a Poly(phenylacetylene) with Chiral C_{60} -Bisadducts. We then measured the CD spectra of poly-**3** (its number average molecular weight was 1.9×10^4)^{9,10} in the presence of f,sA - and f,sC -**2a** ($[2a]/[\text{poly-3}] = 0.1$) in a DMSO–water mixture (1/1 (v/v)) (Figure 7A). Figure 7B shows the differential CD spectra, where the contributions arising from the CD absorption due to the optically active **2a**'s themselves

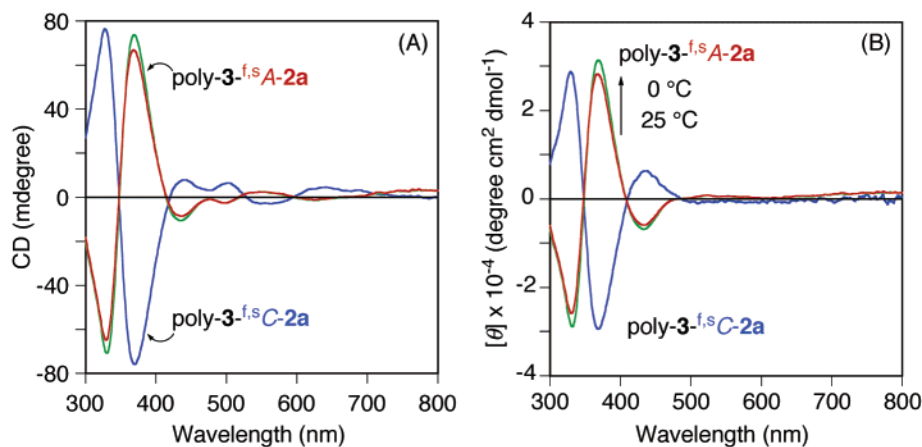


Figure 7. CD spectra of poly-3 (A) in the presence of f^sC-2a at 25 °C (blue line) and f^sA-2a at 25 (red line) and 0 °C (green line) ($[2a]/[poly-3] = 0.1$, $[poly-3] = 0.5$ mg/mL) in DMSO–water (1/1 (v/v); pH 9.5) and the differential CD spectra (B) between the poly-3– $2a$ complexes and the corresponding f^sC-2a at 25 °C (blue line) and f^sA-2a at 25 (red line) and 0 °C (green line).

are subtracted from the observed CD spectra of the poly-3– $2a$ complexes in Figure 7A. The poly-3 complexed with f^sA-2a and f^sC-2a exhibited intense and characteristic ICDs in the π -conjugated polymer backbone region (300–500 nm) in the DMSO–water mixture (1/1 (v/v)), and the ICDs are mirror images of each other (Figure 7B). The differential CD spectral patterns are in fair agreement with those of the helical poly-3 induced by optically active amines and amino acids in DMSO and water, respectively.¹⁰ Moreover, the differential CD magnitude of the poly-3– f^sA-2a complex in the polymer backbone region increased with the decreasing temperature, whereas the CD spectra of the f^sA-2a hardly changed with temperature. These results indicate that a predominantly one-handed helical conformation is induced on poly-3 through a noncovalent bonding interaction with the chiral C₆₀-bisadducts and the single-handedness excess in poly-3 also increased with the decreasing temperature, although the temperature effect was not significant. Previously, we demonstrated that dynamic helical poly(phenylacetylene)s including poly-3 are highly sensitive to a chiral environment, and a small chiral bias, such as the addition of a small amount of chiral molecules that can interact with the polymer's side groups, significantly enhances the macromolecular helicity with a large amplification.^{4,9,15}

The CD titration using f^sA-2a was then performed in order to investigate if such a chiral amplification process during the helix induction in the polymer backbone of poly-3 with $2a$ could be possible, resulting in the helical array of $2a$ (Figure 8). The CD intensity derived from the induced helical poly-3 increased with an increase in the concentration of f^sA-2a and reached an almost constant value at $[f^sA-2a]/[poly-3] = 0.2$. Plots of the differential CD intensities of the second Cotton at 370 nm ($[\theta]_{370}$) of the poly-3– f^sA-2a complex as a function of the concentration of f^sA-2a gave a saturation binding isotherm. The Hill plot analysis of the data resulted in the apparent binding

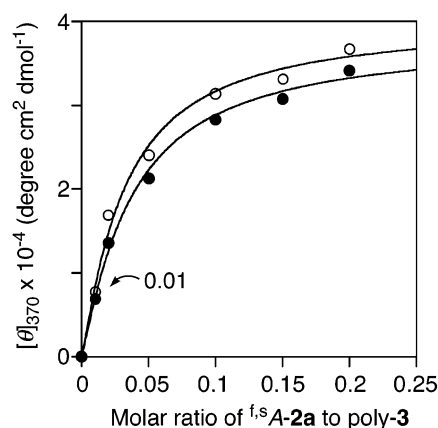


Figure 8. Plots of $[\theta]_{370}$ for the induced helical poly-3 (0.5 mg/mL) versus the concentration of f^sA-2a in DMSO–water (1/1 (v/v); pH 9.5) at 25 °C (●) and 0 °C (○). The pH was adjusted with NaOH at room temperature. A curve in the plots at 25 °C was calculated using parameters determined from the fits to the solid lines in the Hill plots.

constant (K) of 5.0×10^4 M⁻¹ at 25 °C with a Hill coefficient of 1.14.¹⁶

On the other hand, the magnitude of the ICD in the poly-3 main chain region decreased by adding NaCl and was significantly influenced by the pH as shown in Figure 9A, B, respectively, which indicates that the nature of the interaction between poly-3 and $2a$ may be mainly ionic rather than hydrophobic in an aqueous solution.^{9,17}

A possible model for the induced helical structure of poly-3 complexed with f^sA-2a is shown in Figure 2, in which the fullerenes arrange in a helical array along the polymer backbone. The molecular model indicates that the two quaternary ammonium ion residues on the C₆₀ surface bind to the oppositely charged phosphonate pendants of poly-3 in a chelation-type binding manner through electrostatic interactions (Figure 10A).

We then performed the same helicity induction experiments for poly-3 using the other chiral C₆₀-bisadducts ($2b$ and $2c$). However, the addition of the optically active *trans*- $2-2$ (f^sA- or f^sC-2b) to poly-3 ($[2b]/[poly-3] = 0.1$) resulted in the precipita-

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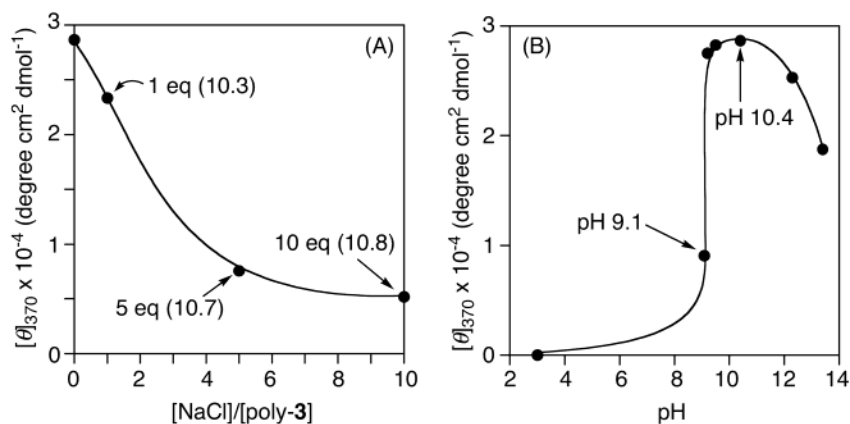


Figure 9. (A) Dependence of ICD intensity ($[\theta]_{370}$) of the induced helical poly-3 on NaCl concentration in the complexation of poly-3 (0.5 mg/mL) with $^{f,s}A-2a$ ($[^{f,s}A-2a]/[\text{poly-3}] = 0.1$) in DMSO–water (1/1 (v/v)) at 25 °C. The solution pH values are shown in the parentheses. (B) The pH dependence of ICD intensity ($[\theta]_{370}$) of the induced helical poly-3 in the complexation of poly-3 (0.5 mg/mL) with $^{f,s}A-2a$ ($[^{f,s}A-2a]/[\text{poly-3}] = 0.1$) in DMSO–water (1/1 (v/v)) at 25 °C. The pH was adjusted with HCl and NaOH aqueous solution at room temperature.

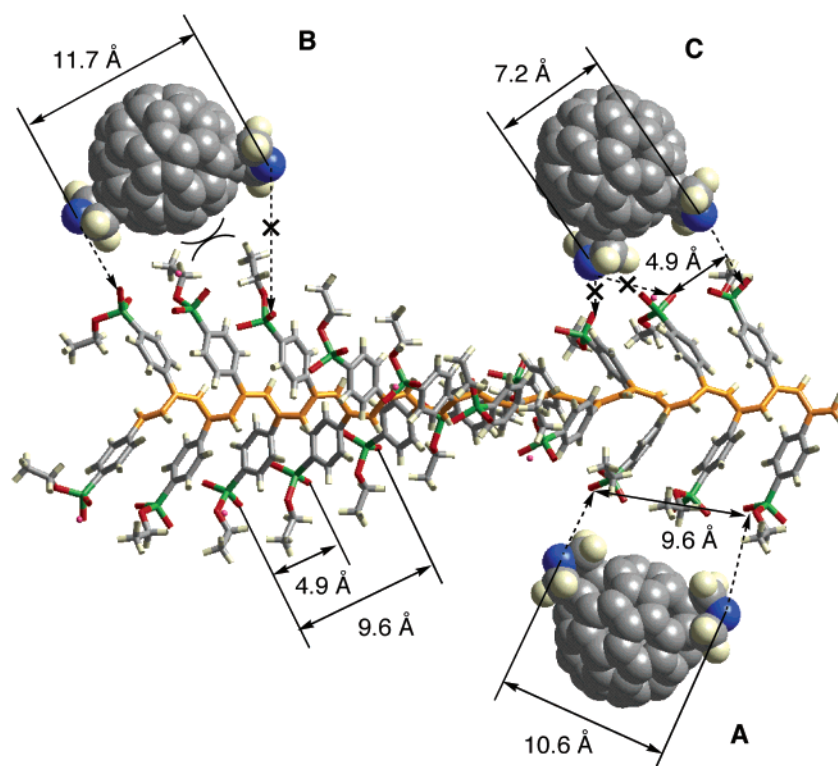


Figure 10. Possible interaction models of poly-3 with optically active $^{f,s}A-2a$ (trans-3) (A), $^{f,s}C-2b$ (trans-2) (B), and $^{f,s}A-2c$ (cis-3) (C). The methyl groups on the nitrogens are omitted for clarity.

tion of the poly-3–**2b** complex in DMSO–water mixtures. This may be because the two cationic quaternary ammonium groups of **2b** are separated from each other, and a similar chelation-type binding to the poly-3 pendants as seen in the poly-3–**2a** complex seems to be difficult, so that **2b** may intermolecularly interact with poly-3, which leads to the precipitation of the complexes. The mixture was then diluted ($[\text{poly-3}] = 0.02 \text{ mg/mL}$; $[\mathbf{2b}]/[\text{poly-3}] = 0.1$) to measure the CD of the transparent solution, but we could not observe any apparent CD in the polymer backbone region. We note that the poly-3–**2a** complex exhibited almost the same CD spectrum under the same diluted conditions.

The *cis*-3 bisadduct **2c** was first considered to be more effective than **2a** for the helicity induction on poly-3, since the two quaternary ammonium groups of **2c** are more closely

located together. The poly-3–**2c** complex ($[\text{poly-3}] = 0.5 \text{ mg/mL}$; $[\mathbf{2c}]/[\text{poly-3}] = 0.1$ and 0.7), however, did not show any CD in the polymer backbone region in a DMSO–water mixture (1/1 (v/v)). The reason for this is not clear at this time, but molecular modeling studies suggest that the chirally arranged, two ammonium groups of **2c** may not be favorably located to form a complex with poly-3 in such a way that both of the two ammonium groups form simultaneous ionic bonding to the neighboring two phosphonate groups of poly-3 like the poly-3–**2a** complexation (Figure 10A). Probably, only one ammonium group of **2c** may participate in the ionic complexation with one phosphonate group in poly-3 (Figure 10C), because the distance of the two ammonium groups in **2c** is 7.2 Å (Figure 10C), which is longer than that of the nearest adjacent two phosphonate groups of poly-3 (4.9 Å) and shorter than that

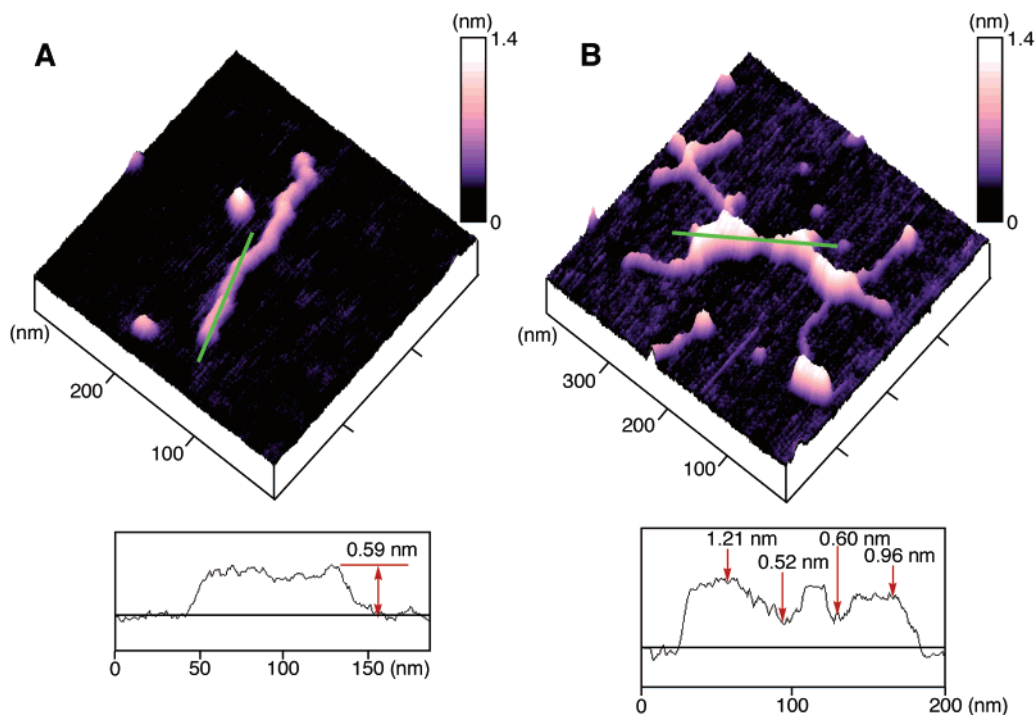


Figure 11. Tapping-mode AFM height images of poly-3 (A) and poly-3-^{f,s}C-2a complex (B) cast from a dilute solution (0.02 mg/mL (A) and 0.05 mg/mL (B)) in a DMSO–water mixture (1/1 (v/v)) on mica. The height profiles measured along the green lines in the images are also shown (bottom).

of the two phosphonate groups of poly-3 (9.6 Å; Figure 10). Similarly, for the *trnas-2* bisadduct (2b), the distance of the two ammonium groups of which (11.7 Å) is too long to form a geometrically fitted, chelation-type complexation with the two phosphonate groups in poly-3 (Figure 10B). Since these bisadducts are rigid and have no flexibility, and a structural specificity or geometric fitness is required for the C₆₀-bisadducts to form a complex with poly-3, resulting in an induced macromolecular helicity with a one-handed helical array of the bisadducts.¹⁸

Atomic force microscopy (AFM) measurements were carried out to gain an insight into the structure and morphology of the poly-3-^{f,s}C-2a complex. Figure 11 shows typical AFM images of poly-3 with and without ^{f,s}C-2a deposited on a freshly cleaved mica surface. Individual polymer chains can be seen in each image. The height profiles of the cross-sections of the complexes in Figure 11B are uneven; low (0.5–0.6 nm) and high (1.0–1.2 nm) segments were observed. Since the average height of a single poly-3 molecule on mica was 0.58 ± 0.06 (Figure 11A), the segments with the higher height values may involve the ^{f,s}C-2a molecules complexed with the poly-3 pendants. Although a helically arranged chiral C₆₀-bisadduct could not be clearly observed in the present complex images, a further study using scanning tunneling microscopy (STM) may be useful to obtain direct information about the helical array of the chiral C₆₀-bisadducts.

Conclusions

In summary, we have found that the geometrically favorable, chiral cationic C₆₀-bisadduct can be used as a novel helicity

inducer to produce a predominantly one-handed helical poly-(phenylacetylene) in DMSO–water mixtures. This is the first example of the prevailing helix formation of an optically inactive polymer induced by chiral C₆₀-bisadducts through noncovalent bonding interactions, which further results in a helical array of the C₆₀-bisadducts with a predominant screw-sense along the polymer backbone. We have recently reported that the macromolecular helicity of poly-3 induced by chiral amines can be effectively “memorized” when the chiral amines are replaced by achiral amines.^{10a} Therefore, this memory effect combined with the present results implies that the macromolecular helicity of poly-3 induced by chiral C₆₀-bisadducts may be memorized by achiral C₆₀ derivatives, which will offer another useful method to arrange C₆₀ molecules in a helical array with a predominantly one-handed screw-sense.

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Supporting Information Available: Full experimental details including resolution of chiral C₆₀-bisadducts, synthesis, and spectroscopic data of bis-*N,N*-dimethylfulleropyrrolidine ammonium iodides (^{f,s}A- and ^{f,s}C-2a, -2b, and -2c), CD measurements and CD titration, effect of NaCl and pH on ICD, molecular modeling and calculations, AFM measurements, UV–vis spectra of 1c, and characteristic ¹H NMR spectral data of all C₆₀-bisadducts (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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