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Saccharide-Dependent Induction of Chiral Helicity in Achiral Synthetic Hydrogen-Bonding Oligomers

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Abstract: Conformational transitions of biopolymers are well-known to be affected by noncovalent interactions with small molecules. We found that synthetic polymers, poly- and oligo(*meta*-ethynylpyridine)s, are guided to helical structures by uncharged hydrogen-bonding interactions with saccharides enclosed in the inner sphere of the polymers. Circular dichroism (CD) studies revealed that chirality of saccharide was transferred to the helical sense of the polymers. Among the *n*-octyl pyranosides of naturally important hexoses, β-glucoside induced CDs most effectively. Size-regulated 18-mer and longer oligomers also showed the induced CDs similar to those for the polymers. Furthermore, native monosaccharides were extracted into less polar organic solvent with the help of the polymers, inducing similar CD signals.

Introduction

Reversible changes between disordered and well-ordered conformational states are seen in many biopolymers such as oligonucleotides and oligopeptides.[1] The well-ordered states are represented as helices, sheets, and coils and are stabilized by the noncovalent forces from the internal and/or external functionalities. Because of the sophisticated but complex structures of biopolymers, this transition is conducted by combination of several types of individual noncovalent forces, i.e., electrostatic, hydrophobic, hydrogen-bonding, and van der Waals interactions.[2−4] While synthetic polymers and oligomers possess much simpler skeletons, such transitions can clearly be reproduced to shed light on the contribution of particular interactions.[5−7] This is also true even in the cases that the external, small molecules induce the transition. Indeed, several synthetic oligomers were developed to interact with small biological and nonbiological molecules, in which the conformational transitions of the oligomers to their well-defined states were successfully achieved by strong electrostatic and metal-coordinative interactions from the small molecules.[8,9] On the other hand, hydrogen bonds,[10] particularly from biologically important molecules such as saccharides, were hardly explored for these intermolecular processes, possibly because of the inherent weakness of the intermolecular hydrogen-bonding interactions for saccharides. A notable exception is the charged hydrogen-bonding interactions of polyelectrolytes to saccharides in their outer sphere on the defined conformation of the polymers.[11] Here we present induction of the chiral helicity on synthetic polymers and oligomers driven by uncharged hydrogen bonds in their inner sphere depending on the stereochemistry of saccharides added.[12]

We recently reported the tris(ethynylpyridine) macrocycles as synthetic receptors for ribofuranosides, deoxyribofuranosides, and glucopyranosides in less polar solvents such as CH_2Cl_2 and $CHCl_3$.[13−15] The hydrogen-bonding motifs of the macrocycles are composed of "*meta*"-tethered ethynylpyridine trimers. We thought that if the ethynylpyridine unit is polymerized, the resulting poly(*m*-ethynylpyridine) would adopt unfolded conformations because each pyridine nitrogen atom is mainly located on opposite sides of the ethynediyl bonds in order to cancel the dipoles.[15] Once the polymer meets with a saccharide, this pseudolinear conformation of the polymer will be guided to a well-ordered helical structure in order that the nitrogen atoms of the pyridine nuclei inwardly interact with peripheral saccharide-OH groups in a manner similar to those of the macrocycles (Figure 1). Thus, the chirality of saccharides added

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(10) Synthetic oligomers that form helical structures by hydrogen bonding were reported such as with cyanurates, see: Berl, V.; Krische, M. J.; Huc, I.; Lehn, J.-M.; Schmutz, M. *Chem. Eur. J.* **2000**, *6*, 1938−1946.
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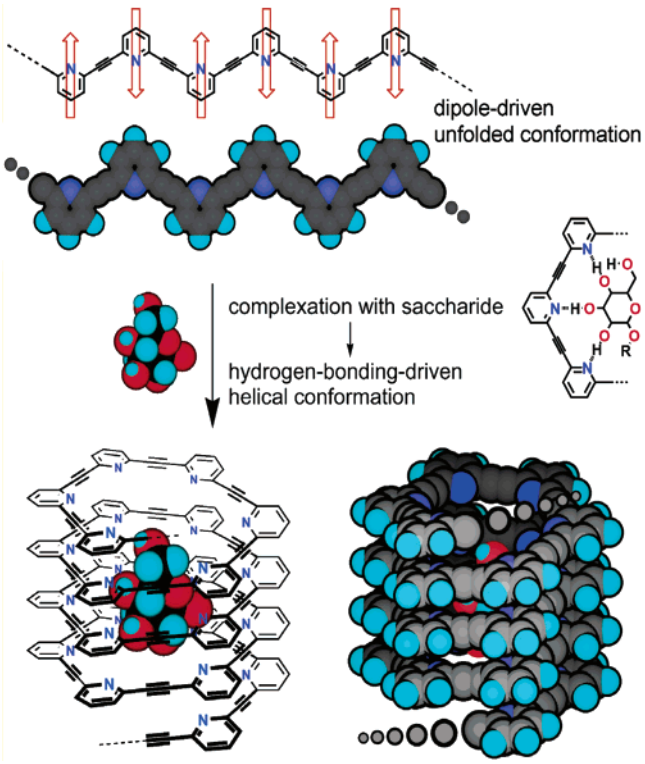


Figure 1. Conformation change of poly(*m*-ethynylpyridine) driven by the complexation with saccharide.

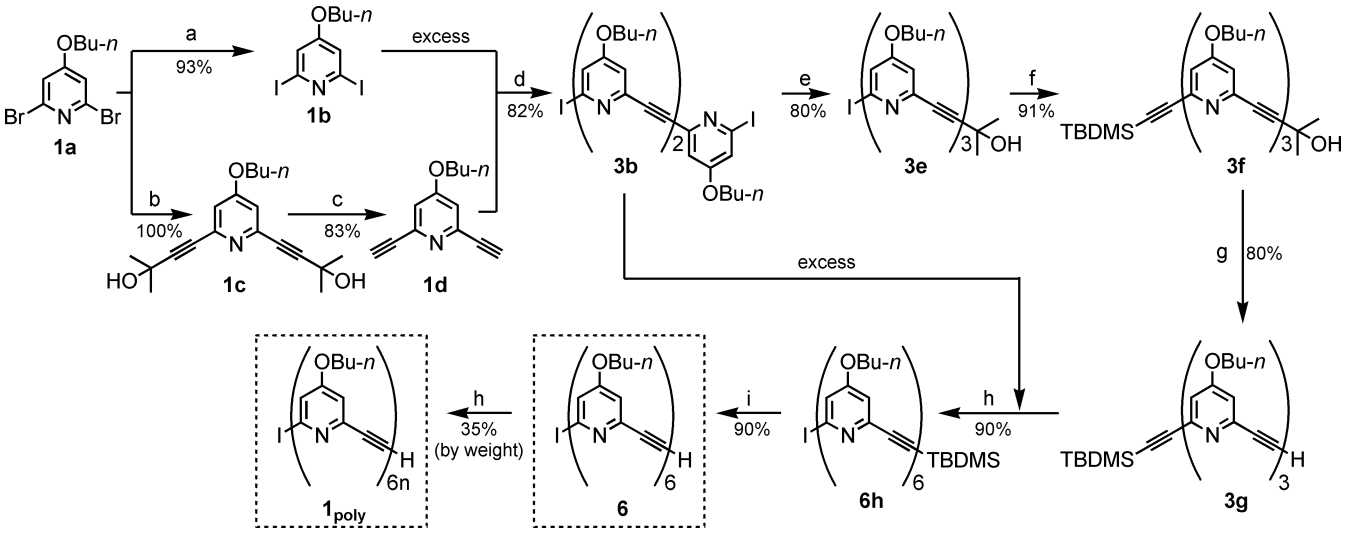
must be transferred to the helical sense of the polymer, which may be characterized on the basis of various spectroscopies.

Results and Discussion

Syntheses and Structures of Poly- and Oligo(*m*-ethynylpyridine)s. The poly(*m*-ethynylpyridine) $\mathbf{1}_{poly}$ was prepared via the polymerization of the hexameric (*m*-ethynylpyridine) **6** by use of Sonogashira acetylene coupling (Scheme 1).[16] Not only the 6-mer **6** but also 1-, 2-, 3-, 4-, 5-, 12-, 18-, and 24-mer (numbered as **1**, **2**, **3**, **4**, **5**, **12**, **18**, and **24**) were all synthesized from 2,6-dibromo-4-butoxypyridine (**1a**)[13] by repeating the Sonogashira method (Scheme 2). The use of the 6-mer **6** not **1** as a starting "monomer" for the polymerization is expected to generate polymers (≥12-mer) by a small number of the repeated reactions, resulting in the formation of relatively "clean" polymers. Indeed, ^{1}H and ^{13}C NMR of $\mathbf{1}_{poly}$ (M_n = 2200, M_w = 4500)[17] in $CDCl_3$ revealed the simple and sharp peaks of pseudo one set of a symmetrically 2,6-disubstituted 4-*n*-butoxypyridine unit, which are almost the same as those for 4-*n*-butoxy-2,6-diethynylpyridine (Figure 2). These NMR data indicated that $\mathbf{1}_{poly}$ itself could exist as a disordered conformation with high mobility in the solvent.

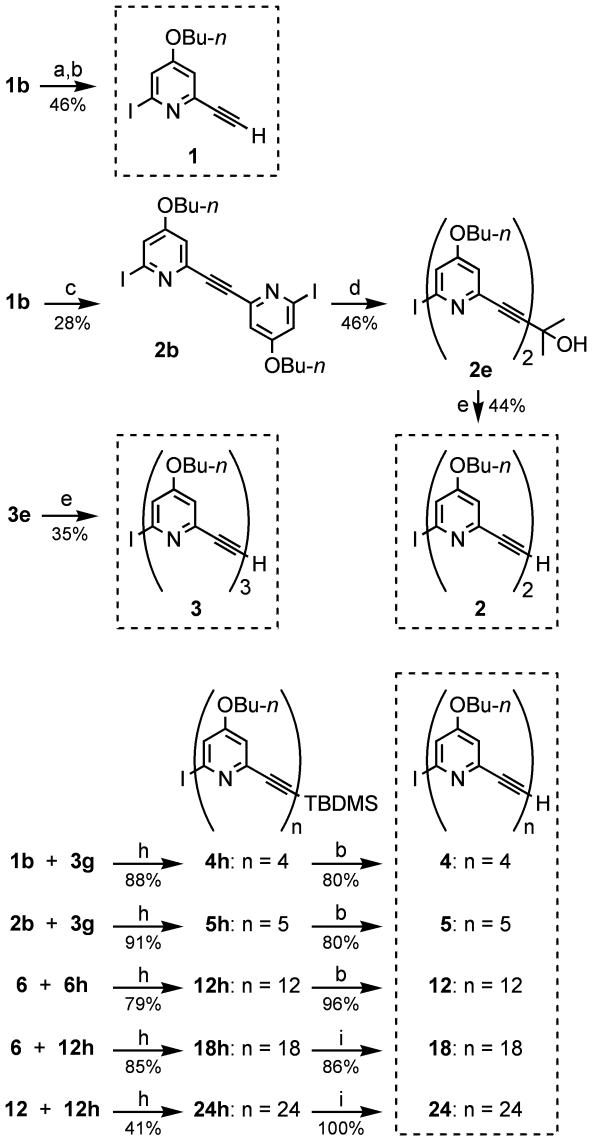
Further information for the conformation of the poly(*m*-ethynylpyridine)s was given by the UV−vis measurements of $\mathbf{1}_{poly}$ and exactly synthesized oligomers **2**−**24** (Figure 3). The UV−vis spectrum of $\mathbf{1}_{poly}$ has two absorption maxima at 275 and 323 nm in CH_2Cl_2, and the shape of the spectrum is not sensitive to its concentrations. Thus, $\mathbf{1}_{poly}$ obeyed Beer's law at $\leq 1.0 \times 10^{-3}$ M (monomer unit concentration) as judged from the changes of both the absorbances as a function of the concentration of $\mathbf{1}_{poly}$, suggesting that the intermolecular association of $\mathbf{1}_{poly}$ can be ruled out in this concentration range. Next, intramolecular interactions of the oligomers were assessed on the basis of the molar extinction coefficients for **2**−**24**. The molar extinction coefficient at the absorption maximum (275 nm; 1.0×10^{-5} M) increased linearly depending on the oligomer length up to 12-mer, while the deviations from the slope were observed at ≥18-mer (Figure 4). In this concentration, intermolecular association was negligible because each oligomer obeyed Beer's law, so that the deviation implies the presence of intramolecular π-interactions. Fluorescence emission spectra of the polymer and oligomers confirmed the intramolecular π-interactions and were recorded in CH_2Cl_2 under the identical optical density conditions that each absorbance of the solutions was 0.18 at 275 nm. Emission of **2**−**6** appeared only at 331 nm, and the intensity increased as the chain lengthened (the excitation wavelength: 300 nm). The oligomers **12**, **18**, **24**, and polymer $\mathbf{1}_{poly}$, however, exhibited another, broad featureless emission at ≥500 nm, which might be assigned as intramo-

Scheme 1. Preparation of Poly(*m*-ethynylpyridine) $\mathbf{1}_{poly}$ via 6-mer **6**[a]



[a] Key: (a) CuI, KI, DMF; (b) 2-methyl-3-butyn-2-ol, $PdCl_2(PPh_3)_2$, CuI, Et_2NH; (c) NaH, toluene; (d) $Pd_2(dba)_3$·$CHCl_3$, PPh_3, CuI, *i*-Pr_2NH; (e) 2-methyl-3-butyn-2-ol, $PdCl_2(PPh_3)_2$, CuI, *i*-Pr_2NH; (f) (*tert*-butyldimethylsilyl)acetylene, $PdCl_2(PPh_3)_2$, CuI, *i*-Pr_2NH; (g) NaH, toluene; (h) $Pd_2(dba)_3$·$CHCl_3$, PPh_3, CuI, *i*-Pr_2NH, DMF; (i) *n*-Bu_4NF, THF, H_2O.

Scheme 2. Preparation of Oligo(*m*-ethynylpyridine)s **1**−**5**, **12**, **18**, and **24**[a]



[a] Key: (a) (trimethylsilyl)acetylene, $PdCl_2(PPh_3)_2$, CuI, Et_3N; (b) *n*-Bu_4NF, THF, H_2O; (c) bis(tri-*n*-butylstannyl)acetylene, $Pd(dba)_2$, PPh_3, toluene; (d) 2-methyl-3-butyn-2-ol, $PdCl_2(PPh_3)_2$, CuI, *i*-Pr_2NH; (e) NaH, toluene; (h) $Pd_2(dba)_3$·$CHCl_3$, PPh_3, CuI, *i*-Pr_2NH, DMF; (i) *n*-Bu_4NF, THF, $CHCl_3$, H_2O.

lecular excimer emission accompanying the decrease in the monomer emission in the cases for **24** and $\mathbf{1}_{\mathbf{poly}}$ (Figure 5). This type of excimer-like emission was also observed for oligo(pyridine−pyrimidine)s[18,19] and oligo(*m*-phenylene ethynylene)s.[20] These UV−vis and fluorescence studies showed that intramolecular π-stacking interactions should at least partially exist in poly- and oligo(*m*-ethynylpyridine)s of enough molecular length.

Binding Studies of the Poly- and Oligo(*m*-ethynylpyridine)s to Saccharides. The interactions of poly- and oligo-

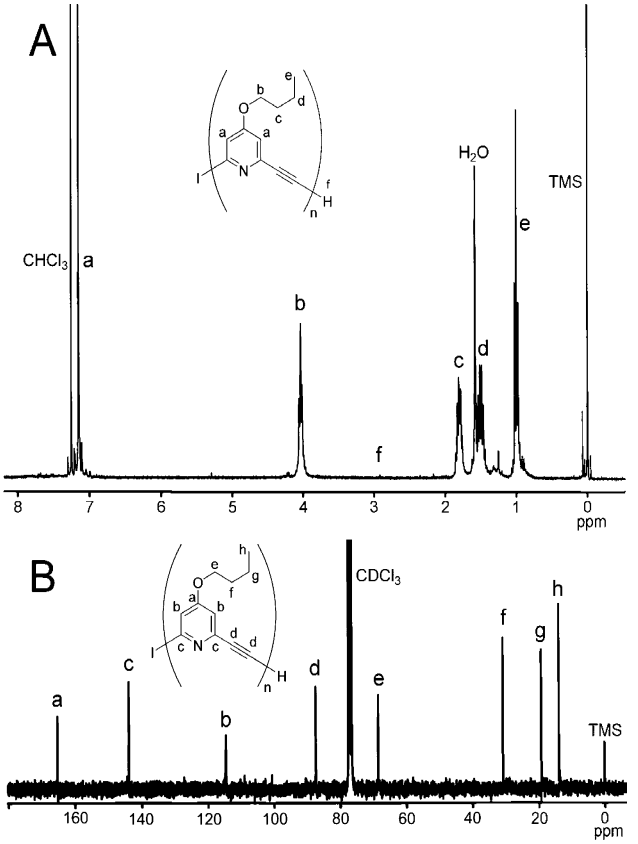


Figure 2. (A) ^1H (300 MHz) and (B) ^{13}C (75 MHz) NMR spectra of $\mathbf{1}_{\mathbf{poly}}$ in $CDCl_3$.

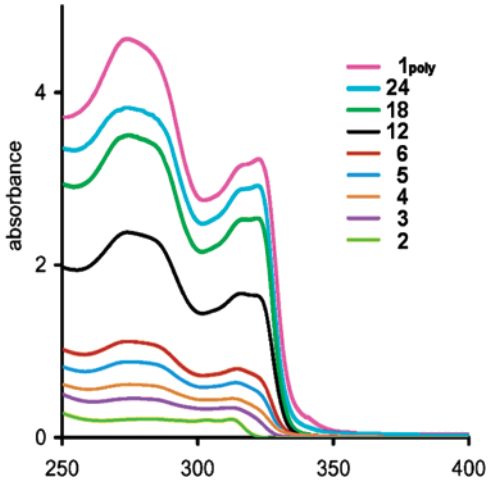


Figure 3. UV−vis spectra of $\mathbf{1}_{\mathbf{poly}}$ and **2**−**24**. Conditions: $\mathbf{1}_{\mathbf{poly}}$ (2.5×10^{-4} M, monomer unit concentration), **2**−**24** (1.0×10^{-5} M), CH_2Cl_2, 25 °C. Light-path length was 1 (for $\mathbf{1}_{\mathbf{poly}}$) or 10 mm (for **2**−**24**), normalized to the latter.

(*m*-ethynylpyridine)s with *n*-octyl pyranosides derived from monosaccharides were investigated also by UV−vis spectroscopy (Chart 1). The saccharide derivatives showed no absorption bands in the usual UV−vis region, so the changes for the spectra of the polymer will directly give the information for the interactions. When the monosaccharide ***β*-D-Glc** was added incrementally to a CH_2Cl_2 solution of $\mathbf{1}_{\mathbf{poly}}$ (1.0×10^{-3} M, monomer unit concentration), a decrease of the absorbances at 275 and 323 nm of $\mathbf{1}_{\mathbf{poly}}$ was observed (Figure S1 in Supporting Information). This hypochromism would suggest that the interaction with the saccharides caused $\mathbf{1}_{\mathbf{poly}}$ to be an ordered

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(18) Bassani, D. M.; Lehn, J.-M.; Baum, G.; Fenske, D. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1845−1847.
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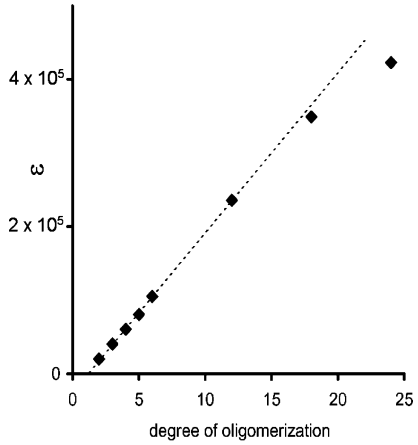


Figure 4. Plotting between the molar extinction coefficient (at 275 nm) and the degree of oligomerization for **2**−**24**. Dotted line is drawn based on linearity up to 12-mer.

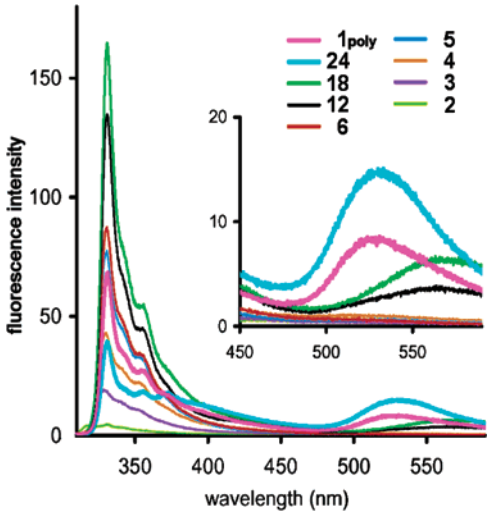


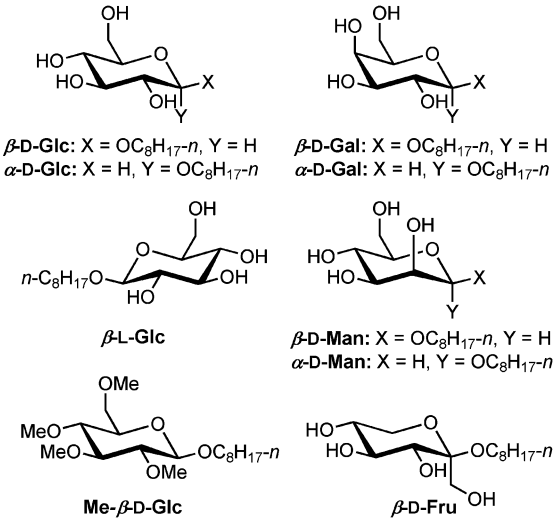
Figure 5. Fluorescence spectra of $\mathbf{1}_{\mathbf{poly}}$ and **2**−**24**. Conditions: $\lambda_{ex} = 300$ nm, $\mathbf{1}_{\mathbf{poly}}$ and **2**−**24** at the concentration of equal optical density (absorbance = 0.18), CH_2Cl_2, 25 °C. Light-path length was 10 mm. Inset expands the region of the excimer-like emmision.

helical conformation which induces intramolecular π-interaction. However, this result could not exclude other possibilities, e.g., the hypochromism was due to hydrogen bonding at individual pyridine rings; thus, the contribution of the helical conformation was small.

No spectroscopic method is as useful as circular dichroism (CD) for detecting the interactions between a chiral molecule and an achiral one.[21] In the absence of saccharides, the CD spectrum of $\mathbf{1}_{\mathbf{poly}}$ (1.0×10^{-3} M, monomer unit concentration) is silent, as expected for an achiral molecule. Upon addition of ***β*-D-Glc** (2.0×10^{-3} M), however, characteristic induced CD (ICD) signals appeared in the wavelength region where the polymer absorbs. A mirror image of the spectrum was obtained in the presence of an antipode saccharide, ***β*-L-Glc**, demonstrating that the emerging ICD signals of $\mathbf{1}_{\mathbf{poly}}$ resulted from the chirality of the saccharides added (Figure 6A). While **α-D-Glc** gave a rather small but similar negative ICD band at 355−325 nm, other biologically important monosaccharide (hexose) derivatives of D-series showed very weak (***β*-D-Gal**, **α-D-Gal**)

(21) In *Circular Dichroism*: *Principles and Applications*, 2nd ed.; Berova, N., Nakanishi, K., Woody, R. W., Eds.; Wiley-VCH: New York, 2000.

Chart 1. *n*-Octyl Glycosides Subjected as a Guest Saccharide



or opposite (***β*-D-Man**, **α-D-Man**, ***β*-D-Fru**) ICD signals at the same wavelength range (Figure 6A). Guidance from the unfolded conformation to the helical one was driven by hydrogen-bonding interactions between the pyridine nitrogen atoms in $\mathbf{1}_{\mathbf{poly}}$ and saccharide-OH groups. This was unambiguously confirmed by a silent CD spectrum of $\mathbf{1}_{\mathbf{poly}}$ upon addition of **Me-*β*-D-Glc**, a nonhydrogen-bonding analogue of ***β*-D-Glc**. Furthermore, upon addition of MeOH to $\mathbf{1}_{\mathbf{poly}}$ with ***β*-D-Glc** in CH_2Cl_2, quenching of the ICD signals was observed (Figure S2 in Supporting Information). From these CD experiments we inferred that the spatial arrangement of 2,3,4,6-OH groups of β-glucoside strongly caused the polymer to bias a single-handed (right-handed or left-handed) helix (Figure 1)[22,23] and those of other saccharides had little effect on it or biased another-handed helix. Our previous macrocyclic terpyridine host also associated with octyl β-glucoside more strongly than octyl β-galactoside.[15] Thus, induction of chiral helicity in the synthetic polymer was found to be driven by *hydrogen-bonding interaction within the central pore of the helix*.[24] Poly(*m*-ethynylpyridine) was also prepared from "true" monomer **1** in the usual polymer synthesis sense. The polymer thus prepared ($M_n = 1100$, $M_w = 3200$) showed relatively weak but apparent ICDs in the presence of the saccharides, and noteworthy is that the signs of the ICDs are the same as those observed for $\mathbf{1}_{\mathbf{poly}}$.

To obtain quantitative information for the complexation, we investigated the interactions between oligomers **2**−**24** with the saccharides. Treatment of 2-mer to 12-mer **2**−**12** with the saccharides revealed no ICD signals, while similar ICDs were observed in the cases of 18-mer **18** and 24-mer **24** under the same conditions conducted for $\mathbf{1}_{\mathbf{poly}}$ (Figure 6B). As mentioned above, the fluorescence and UV−vis spectra suggested that the oligomers longer than 12-mer may have a partial contribution of intramolecular π-stacking structures in their ground state, so the correlation of the stacking with the CD activity possibly

(22) For an example of a small molecule which associates with saccharides by hydrogen-bonding to induce CD, see: Tamaru, S.; Shinkai, S.; Khasanov, A. B.; Bell, T. W. *Proc. Natl. Acad. Sci. U.S.A.* **2002**, *99*, 4972−4976.
(23) For an example of a self-assembled complex which associates with saccharides by hydrogen-bonding to induce CD, see: Ishi-i, T.; Mateos-Timoneda, M. A.; Timmerman, P.; Crego-Calama, M.; Reinhoudt, D. N.; Shinkai, S. *Angew. Chem., Int. Ed.* **2003**, *42*, 2300−2305.
(24) Solvophobically driven binding of pre-folded oligomers with chiral hydrocarbons was reported. Prince, R. B.; Barnes, S. A.; Moore, J. S. *J. Am. Chem. Soc.* **2000**, *122*, 2758−2762.

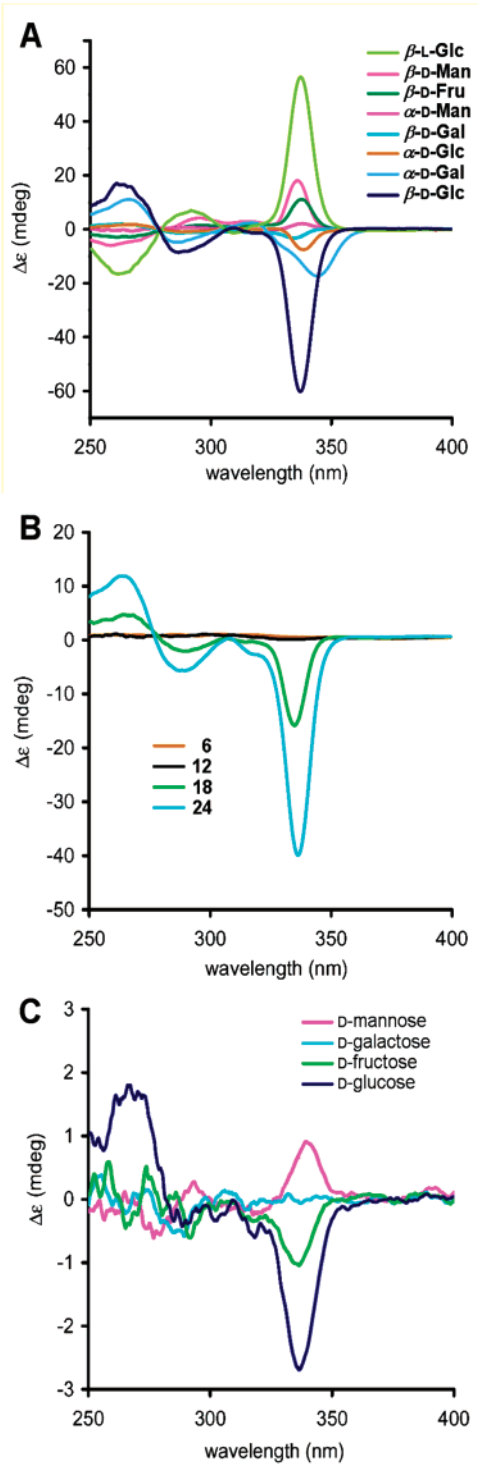


Figure 6. (A) Induced circular dichroism on complexes of $\mathbf{1}_{poly}$ with *n*-octyl pyranosides. Conditions: $\mathbf{1}_{poly}$ (1.0×10^{-3} M, monomer unit concentration), pyranoside (2.0×10^{-3} M), CH_2Cl_2, 25 °C. Light-path length was 1 mm. (B) Induced circular dichroism on complexes of **6**, **12**, **18**, and **24** with ***β*-D-Glc**. Conditions: **6** (1.0×10^{-4} M), **12** (7.8×10^{-5} M), **18** (5.3×10^{-5} M), or **24** (4.0×10^{-5} M), ***β*-D-Glc** (2.0×10^{-3} M), CH_2Cl_2, 25 °C. Light-path length was 1 mm. (C) Induced circular dichroism on complexes of $\mathbf{1}_{poly}$ with native saccharides in CH_2Cl_2.

exists.[25] Considering the angle connecting each pyridine ring, one turn necessitates six ethynylpyridine units when the molecules adopt a helical conformation. Thus, the helices from the 18-mer **18** and 24-mer **24** consist of three and four turns, respectively. The cavity made from at least three turns of the helices may be enough to surround the molecular surface of monosaccharides. This situation allows the convergent hydrogen-bonding interactions from the pyridine nitrogen atoms of the oligomers to saccharide-OH groups in the helix inside.

The stoichiometry and association constants for the complexation were assessed on the basis of CD titrations.[26] When ***β*-D-Glc** was added incrementally to a CH_2Cl_2 solution of **24** (4.0×10^{-5} M), several characteristic changes were observed in the CD spectra with isodichroic points (279 and 307 nm) at 0 mdeg (Figure S3 in Supporting Information). The intensities at 337 nm were monitored as a function of the concentrations of **24** and the saccharides at 298 K. A Job's plot of the complex concentration vs mole fraction of **24** gave a maximum at a mole ratio of 0.5, confirming the formation of the 1:1 complex (Figure S4 in Supporting Information). The strict 1:1 stoichiometry and the presence of the isodichroic points ruled out nonspecific associations for the complexation. The association constant (K_a) between **24** and ***β*-D-Glc** ($1.2 \pm 0.4 \times 10^3$ M^{-1}) was determined by using an iterative least-squares curve-fitting method. As free energy changes (ΔG) can be calculated from association constants using $\Delta G = -RT \ln K_a$, the binding of **24** and ***β*-D-Glc** yielded a stabilization energy ($-\Delta G_{298}$) of 18 kJ mol^{-1}. This value must be a sum of the enthalpic gain and the entropic loss during the complexation. The former will result from the hydrogen bonding and, if any, inter- and intramolecular van der Waals interactions, while the latter is mainly derived from the transition of the disordered structure to the well-ordered structure in the oligomer.[27]

Native saccharides are essentially insoluble in less polar solvents such as CH_2Cl_2 and $CHCl_3$, in which the polymer and the oligomers dissolve. Surprisingly, polymer $\mathbf{1}_{poly}$ and 24-mer **24** showed ICDs in the presence of even native glucose in such solvents. A CH_2Cl_2 suspension of $\mathbf{1}_{poly}$ or **24** containing solid D-glucose was shaken and filtered, and the filtrate was analyzed directly by CD spectroscopy. The sign of the ICDs is same to those observed for ***β*-D-Glc** and **α-D-Glc**, while D-mannose showed opposite signs (Figure 6C). Interestingly, D-fructose revealed the reversed ICDs compared with that of its *n*-octyl derivative, ***β*-D-Fru**, implying contribution of the furanoside structure for the interaction. Native saccharides possess plural hydroxy groups that tightly interact with each other intermolecularly, so that only protic solvents, usually water, can dissolve them. When the polymer adopts the helical conformation, the resulting cavity must be surrounded with a number of lone-pair electrons of the pyridine nitrogens. This makes the cavity a highly polar microenvironment, resulting in the solubilization of the saccharides into the inside. The findings obtained from these extraction experiments have a significantly important effect in that the present system may be applied to simple and nondestructive detection of native glucose[28] in connection with diagnosis of diabetes.[29]

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Conclusion

Poly- and oligo(*m*-ethynylpyridine)s mainly exist in a disordered conformation in less polar solvents such as $CHCl_3$ and CH_2Cl_2. The transition from the disordered state to the ordered helical state was driven by hydrogen-bonding interactions with saccharides, and the chiral sense of the helices was transferred from the bound saccharides. Furthermore, ICD signs of the chiral helices can distinguish glucosides and even native glucose from other monosaccharides and/or their derivatives, illustrating the glucose-specific detection. By modifying side chains of the polymers and oligomers, this recognition event may be read out even in more practically useful media.

Acknowledgment. We are grateful to the Inamori Foundation (M.I.) and the Foundation Advanced Technology Institute (H.A.) for financial support.

Supporting Information Available: The entire Experimental Section, Figure S1, S2, S3, and S4, and ^{1}H NMR spectra for compounds **1**, **1b**−**d**, **2**, **2b**, **2e**, **3**, **3b**, **3e**−**g**, **4**, **4h**, **5**, **5h**, **6**, **6h**, **12**, **12h**, **18**, **18h**, **24**, and **24h**. This material is available free of charge via the Internet at http://pubs.acs.org. See any current masthead page for ordering information and Web access instructions.

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