

Solvent-Dependent Switch of Helical Main-Chain Chirality in Sergeants-and-Soldiers-Type Poly(quinoxaline-2,3-diyl)s: Effect of the Position and Structures of the “Sergeant” Chiral Units on the Screw-Sense Induction

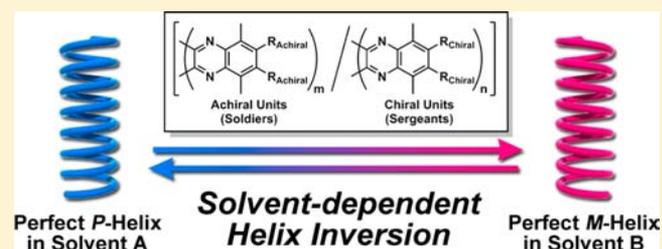
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S Supporting Information

ABSTRACT: Poly(quinoxaline-2,3-diyl) copolymers bearing various “sergeant” chiral units with common “soldier” achiral units have been synthesized to investigate the efficiency of screw-sense induction and its dependence on the nature of the solvents. Optically active 2-alkoxymethyl side chains located at the 6- and 7-positions of the quinoxaline ring induced a single-handed helical conformation more efficiently than 3-methylpentyl or 2-methylbutoxy chiral side chains. Among the 2-alkoxymethyl side chains, those bearing higher 2-alkoxy groups induced a single-handed screw sense more efficiently. For instance, a monomer unit bearing (*R*)-2-octyloxymethyl groups stabilized the *P*-helix by 1.01 kJ/mol, whereas the monomer bearing (*S*)-2-butoxymethyl groups stabilized the *M*-helix by 0.59 kJ/mol. The effect of the position of the sergeant units in the polymer main chain on the screw-sense induction was also investigated using copolymers in which the positions of the sergeant units were carefully controlled by their synthesis via living polymerization. Chiral units placed sparsely could induce single-handed helical structure efficiently. Chiral units bearing 2-alkoxymethyl, 3-methylpentyl, and 2-methylbutoxy groups showed solvent-dependent helix inversion in CHCl₃ and 1,1,2-trichloroethane. No helix inversion was observed in those solvents with chiral units bearing 2-butoxy or (2-methylbutoxy)methyl side chains. The 40-mer of the (*R*)-2-octyloxymethyl units showed *P*-helical structures in THF, *t*-BuOMe, and *c*-C₃H₁₁OMe, toluene, pyridine, Et₃N, 1-BuOH, CHCl₃, CH₂Cl₂, 1,4-dichlorobutane, 1,1-dichloroethane, and 1,1,1-trichloroethane, whereas *M*-helical structures were induced in 1-BuCN, 1-PrCN, 1,2-dichloroethane, 1,3-dichloropropane, and 2-BuOH.



INTRODUCTION

Much attention has been paid to the synthesis, structures, properties, and applications of helical macromolecules,¹ whose helical main chains are potentially interconvertible to the mirror image helical structure. In addition to the helical macromolecules supported by chiral stereogenic centers in their main chains, such as triphenylmethyl methacrylates² and polysilanes,³ those devoid of stereogenic centers, such as polyacetylenes,⁴ polyisocyanates,⁵ and polyisocyanides,⁶ are known and have attracted increasing attention. A major characteristic of such helical macromolecules is the reversible, i.e., thermodynamic, formation of right- and left-handed helical structures by introduction of chiral groups at the side chains or termini⁷ of the polymers or by interaction with guest chiral molecules.⁸ Introduction of chiral side chains to those dynamic helical polymers has been the most reliable strategy to obtain nonracemic helical structures. Since the 1980s, Green established the majority-rule effect^{5g} and the sergeants-and-soldiers effect^{5h} for the induction of nonracemic helical

structures by introduction of chiral side chains. Both effects are based on the accumulation of small energy differences in the helical macromolecules for the induction of a nonracemic macromolecular helical conformation. For instance, these macromolecular effects enabled induction of nonracemic helical structure even by an enantioenriched α -monodeuterated primary alkyl group attached to the nitrogen atoms of polyisocyanates.^{5b}

Remarkably, the dynamic helical polymers are able to undergo a switch of the helical chirality by external stimuli, such as temperature,⁹ light,¹⁰ metal ion,¹¹ pH,¹² and solvent.¹³ Because switchable helical structures would lead to the development of new functional materials, much effort has been directed to the exploration of macromolecular systems that exhibit highly efficient induction of both helical senses reversibly, depending on the external circumstances. However,

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it should be noted here that determination of the purity of the single-handed screw sense has not been an easy task. Although the nonracemic nature of the macromolecules is readily indicated by circular dichroism (CD) spectrometry, the degree of the purity of the helical sense cannot be estimated unless the maximum CD intensity for the purely single-handed helical structure is determined. It is therefore important to establish a macromolecular system in which the main chains adopt "pure" single-handed helical structure and undergo a "perfect" switch of helical structure to the other helical sense by some external stimulus.

We have developed aromatizing polymerization of 1,2-diisocyanobenzenes promoted by transition-metal complexes. The polymerization affords poly(quinoxaline-2,3-diyl)s, which possess a helical main chain because of steric repulsion of the two substituents at the 5- and 8-positions of the quinoxaline rings. The rigidity of the helical main chain is largely dependent on the bulkiness of the substituents at the 5,8-positions. For example, poly(quinoxaline-2,3-diyl)s having small alkyl substituents, such as methyl groups, at the 5,8-positions behaved as dynamic helical polymers, where the preference for the helical sense is determined by the thermodynamic stabilities. We have already reported that the single-handed screw sense of the poly(quinoxaline-2,3-diyl)s could be efficiently induced by chiral end groups.¹⁴

In our preliminary Communication,¹⁵ we reported that a single-handed screw sense was induced also by introduction of "sergeant" monomers bearing chiral side chains and inverted by the effect of solvent (Figure 1). For instance, poly(quinoxaline-

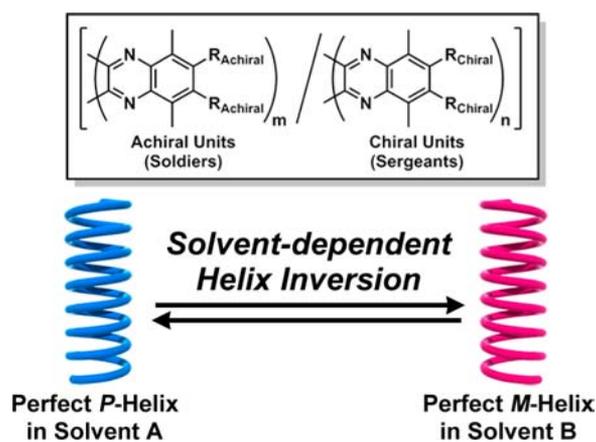


Figure 1. Solvent-dependent helix inversion of sergeants-and-soldiers-type poly(quinoxaline-2,3-diyl)s bearing achiral and chiral side chains.

2,3-diyl)s bearing (*R*)-2-butoxymethyl side chains adopt a pure right-handed helical structure in chloroform, while they adopt a pure left-handed helix in 1,1,2-trichloroethane (1,1,2-TCE).

We also reported that the single-handed helical poly(quinoxaline-2,3-diyl) bearing chiral 2-butoxymethyl side chains can serve as a highly effective scaffold to which a diarylphosphino pendant is attached covalently as the metal-binding site.¹⁶ They served as highly effective chiral catalysts in which the solvent-dependent switch of helical chirality enables highly enantioselective production of both enantiomers from a single chiral catalyst in various asymmetric reactions.¹⁷ To gain more insight into the origin and mechanism of the helix inversion and to find more applications, it is crucial to examine in detail the effect of chiral side chains on the induction of helical sense. In

particular, it should be useful to find chiral side chains that induce helically chiral backbones more efficiently in a chirality-switchable manner. We herein report the synthesis of a series of poly(quinoxaline-2,3-diyl)s bearing various chiral side chains to evaluate their screw-sense induction in various organic solvents, such as chloroform, 1,1,2-TCE, toluene, and THF. While the detailed mechanism was still not clear, an efficient "sergeant" chiral unit has been established for the solvent-dependent helix inversion.

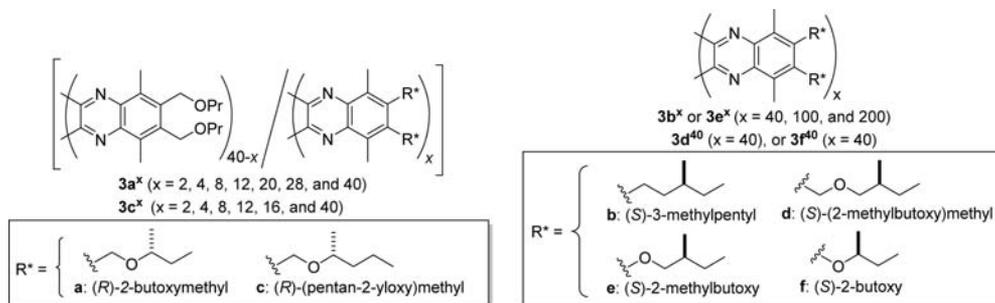
RESULTS AND DISCUSSION

In our preliminary report, we discussed degrees of screw sense induction of poly(quinoxaline-2,3-diyl)s bearing chiral side chains prepared by random copolymerizations of achiral monomer **1** and chiral monomer **2a**. In the random polymer, the chiral units are randomly dispersed throughout the polymer main chain. We were interested in knowing if the position and the sequence of the sergeant chiral monomer units change the degree of screw-sense induction. Because this polymerization proceeded in a living fashion, copolymers in which the positions and sequence of chiral monomer units are known can be readily obtained by controlling the addition of chiral and achiral monomers. As shown in Table 1, copolymers **3a⁴-S1** to **3a⁴-S6**, in which the positions of the sergeant monomer were regulated, were synthesized by virtue of the living nature of the polymerization, and their CD and UV-vis absorption spectra were measured in CHCl₃. Copolymers **3a⁴-S1**, **3a⁴-S3**, and

Table 1. Synthesis and Properties of Random Copolymer **3a⁴** and Sequence-Regulated Copolymers **3a⁴-S1** to **3a⁴-S6**

Polymer	Illustrations of polymer sequence ^a	x	M _n /10 ³ ^b	M _w /M _n ^b	g _{abs} /10 ⁻³ in CHCl ₃ ^c
3a⁴	random	40	7.7	1.07	+1.07
3a⁴-S1	●●●●	40	6.1	1.12	+0.51
3a⁴-S2	●●●●	40	6.0	1.12	+1.01
3a⁴-S3	●●●●	40	5.8	1.12	+0.60
3a⁴-S4	●●●●	40	6.4	1.12	+0.49
3a⁴-S5	●●●●	40	8.7	1.11	+0.99
3a⁴-S6	●●●●	40	8.5	1.12	+1.17
3a⁴-20	random	20	3.8	1.07	+0.93
3a⁴-80	random	80	16.7	1.19	+1.04
3a⁴-120	random	120	33.2	1.05	+1.09
3a⁴-160	random	160	48.1	1.05	+1.07
3a⁴-200	random	200	60.7	1.04	+1.08

^aA polymer main chain is shown as an arrowed line, whose start and end points mean initiating and terminating end groups, respectively. The red circles schematically represent positions of chiral units in the polymer chain. ^bMolecular weights were determined by gel permeation chromatography (GPC) with polystyrene standards. ^cg_{abs} values (Kuhn's dissymmetry factor) were measured at 366.0 nm.

Table 2. Structures and Dissymmetry Factors g_{abs} in CHCl_3 and 1,1,2-TCE of 40-, 100-, and 200-mers $3a^x$ – c^x , $3d^{40}$, $3e^x$, and $3f^{40}$ 

polymer	position ^a	confign. ^b	$M_n / 10^{3c}$	M_w / M_n^c	$g_{\text{abs}} / 10^{-3}$ (screw sense) ^d	
					CHCl_3	1,1,2-TCE
$3a^2$	3	R	7.5	1.07	+0.56 (P)	−0.39 (M)
$3a^4$	3	R	7.7	1.07	+1.07 (P)	−0.67 (M)
$3a^8$	3	R	7.7	1.08	+1.76 (P)	−1.49 (M)
$3a^{12}$	3	R	8.2	1.08	+2.13 (P)	−1.81 (M)
$3a^{20}$	3	R	7.9	1.08	+2.38 (P)	−2.49 (M)
$3a^{28}$	3	R	7.9	1.08	+2.34 (P)	−2.78 (M)
$3a^{40}$	3	R	7.9	1.07	+2.36 (P)	−2.81 (M)
$3b^{40}$	3	S	12.0	1.25	−0.53 (M)	+1.15 (P)
$3b^{100}$	3	S	35.1	1.31	−1.00 (M)	− ^e
$3b^{200}$	3	S	55.7	1.93	−1.23 (M)	− ^e
$3c^2$	3	R	4.5	1.22	+0.50 (P)	−0.37 (M)
$3c^4$	3	R	4.3	1.25	+1.21 (P)	−1.08 (M)
$3c^8$	3	R	5.0	1.20	+1.86 (P)	−1.87 (M)
$3c^{12}$	3	R	5.2	1.18	+2.07 (P)	−2.28 (M)
$3c^{16}$	3	R	4.8	1.27	+2.14 (P)	−2.53 (M)
$3c^{28}$	3	R	5.5	1.19	+2.24 (P)	−2.80 (M)
$3c^{40}$	3	R	4.7	1.43	+2.27 (P)	−2.90 (M)
$3d^{40}$	4	S	5.2	1.24	−0.99 (M)	−0.91 (M)
$3e^{40}$	3	S	11.1	1.08	−1.60 (M)	+1.22 (P)
$3e^{100}$	3	S	36.5	1.14	−2.35 (M)	− ^e
$3e^{200}$	3	S	117.6	1.09	−2.38 (M)	− ^e
$3f^{40}$	2	S	9.6	1.20	+1.39 (P)	+1.25 (P)

^aPosition of the chiral center in the side chains. ^bAbsolute configuration of the chiral side chain. ^cMolecular weights were determined by GPC with polystyrene standards. ^d g_{abs} values were measured at the following wavelengths; $3a^x$: 366.0 nm, $3b^x$: 366.0 nm, $3c^x$: 366.0 nm, $3d^{40}$: 365.0 nm, $3e^x$: 370.5 nm, and $3f^{40}$: 370.5 nm. ^eThese samples could not be measured because of their low solubility.

$3a^4$ –**S4**, which have chiral units at polymer termini, showed relatively small g_{abs} values, i.e., Kuhn's dissymmetry factor. This suggested that chiral helix induction by chiral units placed at polymer termini was not efficient. Comparison of $3a^4$ –**S2** with $3a^4$ –**S6** suggested that chiral units introduced sparsely could induce single-handed helices more efficiently. Although copolymer $3a^4$ –**S5** had chiral units introduced sparsely, its g_{abs} value was slightly smaller than that of $3a^4$ –**S6**. This can be attributed to the presence of the chiral unit at the terminus. Note that random copolymer $3a^4$ exhibited a similar g_{abs} value to $3a^4$ –**S6**. Therefore, in the following studies, all poly-(quinoxaline-2,3-diyl)s were synthesized by random copolymerization, taking advantage of the easy preparation.

We then examined the effect of the degree of polymerization (DP) on the single-handed screw-sense induction, while keeping the same number of chiral units in a single polymer main chain. This examination was carried out to estimate the

cooperative length,¹⁸ which was defined as the number of units that take a single helical sense without a helical reversal, because the degree of helix induction increases with the increase in DP, if the DP is within the cooperative length. Polymers $3a^4$ and $3a^4$ –**20** to $3a^4$ –**200** having four chiral units with varied degrees of polymerization were synthesized, and their g_{abs} values were determined. Polymer $3a^4$ –**20** showed a smaller g_{abs} than polymer $3a^4$, because of the high probability of having the chiral unit at the termini of the polymer main chain. Polymers $3a^4$ –**80** to $3a^4$ –**200** having larger DP showed identical g_{abs} values to polymer $3a^4$. We therefore concluded that the cooperative length of poly(quinoxaline-2,3-diyl)s is larger than 200 repeat units, which means that the helix reversal energy is larger than 12.9 kJ/mol according to the reported theory.^{5c}

The most striking aspect of the helical structures of poly(quinoxaline-2,3-diyl)s is its highly solvent-dependent nature. Homopolymer $3a^{40}$ bearing (R)-2-butoxymethyl side

chains adopts perfect right-handed helical structure in CHCl_3 , whereas the same $3\mathbf{a}^{40}$ adopts perfect left-handed structure in 1,1,2-TCE. To evaluate the solvent-dependent induction of single-handed helical conformations in chloroform and 1,1,2-TCE on the structures of the side chains, polymers $3\mathbf{b}^{40}$ – \mathbf{f}^{40} were prepared by aromatizing polymerizations of the corresponding 1,2-diisocyanobenzenes in the presence of an organonickel complex. The polymerization was evaluated by the measurements of molecular weights and polydispersity index (PDI) using polystyrene standards. Although the values based on polystyrene serve as a good measure of polymerization outcome, the values can be deviated from the exact values because poly(quinoxaline-2,3-diyl)s should be stiffer than polystyrene. Therefore the DP values for following theoretical calculations were estimated from the loading ratios of the monomers to the initiator.

No significant difference in UV–vis absorption spectra of polymers $3\mathbf{a}^{40}$ – \mathbf{f}^{40} was observed in CHCl_3 and 1,1,2-TCE. Absorption peaks at wavelengths below 400 nm were generally observed because of π – π^* transitions of the quinoxaline ring. CD spectra were measured to determine the degree of screw-sense induction of polymers $3\mathbf{a}^{40}$ – \mathbf{f}^{40} in CHCl_3 and 1,1,2-TCE. As reported before, the *P*-helical poly(quinoxaline-2,3-diyl) showed a positive CD signal around 370 nm and a negative CD signal at 290 nm, while the *M*-helical poly(quinoxaline-2,3-diyl) gave its mirror image. Polymer $3\mathbf{a}^{40}$ showed a solvent-dependent helix inversion between CHCl_3 and 1,1,2-TCE. Polymer $3\mathbf{b}^{40}$ showed a helix inversion, indicating that oxygen atoms in the side chain were not essential for the helix inversion. Polymer $3\mathbf{c}^{40}$ also exhibited the helix inversion. Polymers $3\mathbf{d}^{40}$ and $3\mathbf{e}^{40}$ were synthesized using (*S*)-2-methylbutanol as an inexpensive chiral source, which is easily available as a byproduct of an alcoholic fermentation. Although polymer $3\mathbf{d}^{40}$ bearing the (*S*)-2-methylbutoxymethyl group did not show helix inversion, polymer $3\mathbf{e}^{40}$ bearing the (*S*)-2-methylbutoxy group showed helix inversion. Polymer $3\mathbf{f}^{40}$, which possesses the (*S*)-2-butoxy group, did not show helix inversion. Here, chirality-switchable polymers $3\mathbf{a}^{40}$ – \mathbf{c}^{40} and $3\mathbf{e}^{40}$ commonly have the chiral center at the third position in the chiral side chains on the quinoxaline ring. It is suggested that the position of the chiral center in the side chain may be important to produce the solvent-dependent helix inversion.

The results obtained thus far indicate that polymers that have an *S* or *R* chiral center at the third atom in the side chain form *P*- or *M*-helices, respectively, and undergo the solvent-dependent helix inversion.

According to the previous report by Lifson and Green,^{5c} we determined the gained energy difference between *P* and *M*-helices per a chiral unit. On the basis of the supposition that the helix persistence length is sufficiently long, the total energy difference between *P* and *M* helical polymers is expressed as

$$\Delta G = -RT \ln([P]/[M]) \quad (1)$$

where R , T , $[P]$, and $[M]$ are the gas constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$), operating temperature (293.15 K), and molar concentration of *P* and *M* helical polymers ($[P] > [M]$). In the case where the polymer has no conformations containing helix reversal, ΔG is proportional to the number of chiral units N and E_h , i.e., the gained energy difference between *P* and *M*-helices per a chiral unit.

$$\Delta G = E_h N \quad (2)$$

The screw-sense excess (se) is defined as

$$se = ([P] - [M]) / ([P] + [M]) \quad (3)$$

Here, se is represented using E_h , N , R , and T as

$$se = \{\exp(-E_h N / RT) - 1\} / \{\exp(-E_h N / RT) + 1\} \\ = \tanh(-E_h N / 2RT) \quad (4)$$

where hyperbolic tangent function (\tanh) is involved. The observed dissymmetry factor g_{abs} is proportional to the screw-sense excess, namely

$$se = g_{\text{abs}} / g_{\text{max}} \quad (5)$$

where g_{max} is the g value for the purely single-handed poly(quinoxaline-2,3-diyl)s. Equation 4 can be expressed using g_{abs} and g_{max} as

$$g_{\text{abs}} = \tanh(-E_h N / 2RT) \times g_{\text{max}} \quad (6)$$

Nonlinear least-squares fitting of g_{abs} versus N was performed by using the Solver Function in Microsoft Office Excel 2007. Sums of the squares of the deviation were minimized by varying two parameters, g_{max} and E_h .

To determine the gained energy difference per monomer unit, E_h , a series of poly(quinoxaline-2,3-diyl)s having varied numbers of chiral monomers N was synthesized (Table 2). The parameters E_h and g_{max} were successfully converged and the final values are summarized in Table 3. The gained energy

Table 3. Calculated E_h and g_{max} Values of Polymers $3\mathbf{a}$ – \mathbf{c} and $3\mathbf{e}$

polymer	CHCl_3		1,1,2-TCE	
	E_h (kJ mol^{-1})	$g_{\text{max}} / 10^{-3}$	E_h (kJ mol^{-1})	$g_{\text{max}} / 10^{-3}$
3a	−0.59	+2.37	−0.32	−2.87
3c	−0.70	+2.23	−0.46	−2.81
3b	−0.05	+1.26	– ^a	– ^a
3e	−0.10	+2.40	– ^a	– ^a

^aCollected data were not sufficient for the nonlinear least-squares fitting.

differences per monomer unit of polymer $3\mathbf{a}$ were determined as 0.59 kJ mol^{-1} in CHCl_3 and 0.32 kJ mol^{-1} in 1,1,2-TCE. On the other hand, a monomer unit of polymer $3\mathbf{c}$ gained more energy (0.70 kJ mol^{-1} in CHCl_3 and 0.46 kJ mol^{-1} in 1,1,2-TCE). This increment can be explained by enhanced differences of the bulkiness of the substituents on the chiral center (polymer $3\mathbf{a}$: methyl and ethyl groups, polymer $3\mathbf{c}$: methyl and propyl groups). Because polymers $3\mathbf{b}$ and $3\mathbf{e}$ showed smaller E_h , benzyl ether moieties contained in $3\mathbf{a}$ and $3\mathbf{c}$ seemed to be essential for effective chiral helix inductions.

On the basis of the calculated g_{max} , the relationships between se and N are plotted in Figure 2. The observed se values (shown by circles and rhombuses) are in good agreement with the fitted curves in every polymer. The relationships between ΔG and N are shown in Figure 3. The values of ΔG (shown by circles and rhombuses) based on the observed g_{abs} are in good agreement with the fitted lines. These good agreements of the observed and calculated plots indicate that the least-squares fitting was performed correctly and efficiently. Figures 2 and 3 also show that helix induction was achieved very efficiently in polymers $3\mathbf{a}$ and $3\mathbf{c}$, while many chiral units are required to maintain a single-handed helical main chain in polymers $3\mathbf{b}$ and $3\mathbf{e}$.

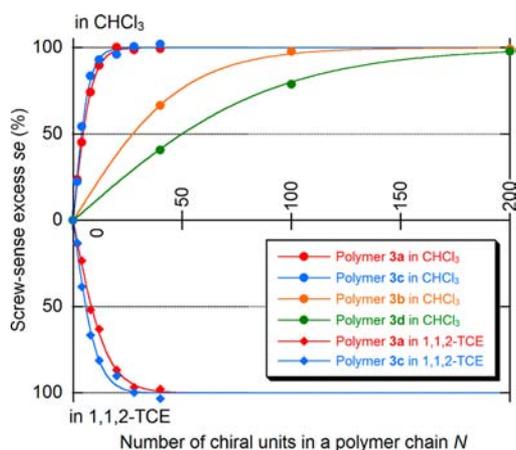


Figure 2. Relationships between number of chiral units N and se of polymers 3a–c and 3e in CHCl_3 or 1,1,2-TCE. The circles and the rhombuses were calculated from observed g_{abs} and g_{max} according to eq 5. The lines were generated from E_{h} and N according to eq 4.

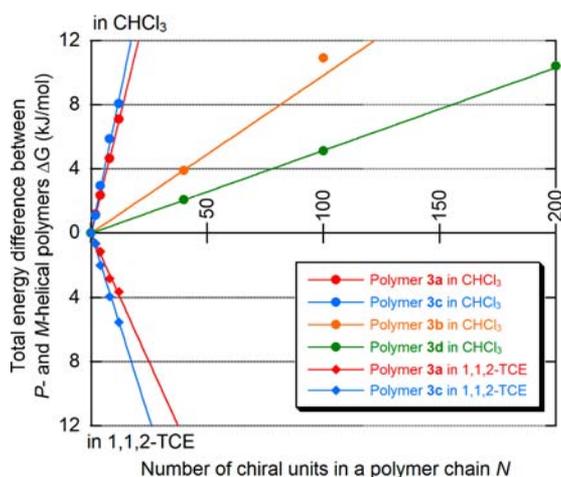
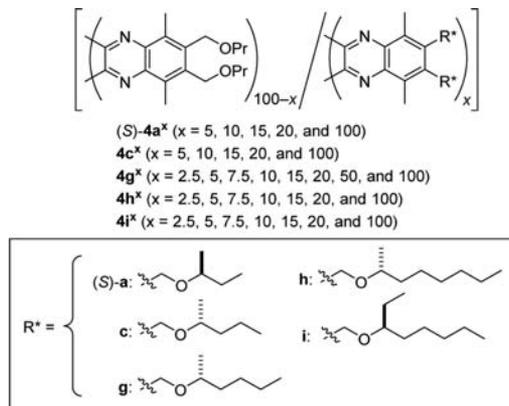


Figure 3. Relationships between number of chiral units N and the total energy difference between P - and M -helical polymers ΔG (kJ/mol) of polymers 3a–c and 3e in CHCl_3 or 1,1,2-TCE. The circles and the rhombuses were calculated from observed g_{abs} and g_{max} according to eq 6. The lines were generated from E_{h} and N according to eq 2.

We then synthesized additional homopolymers and copolymers having various benzyl–ether-type chiral side chains from diisocyanobenzenes (*S*)-2a, 2c, 2g, 2h, and 2i, as shown in Table 4. Note that (*S*)-4a x , in which x indicates the number of chiral units, is derived from monomer (*S*)-2a, which is the enantiomer of monomer 2a used thus far. Using (*S*)-4a x , we could confirm induction of the opposite helix, compared with the polymer obtained from 2a. Note that all of the polymerizations proceeded in a living fashion, giving the corresponding polymers with narrow PDI despite the presence of higher side chains. In Table 4, the observed values of g_{abs} in various solvents, including THF and toluene along with CHCl_3 and 1,1,2-TCE, are shown.

The parameters E_{h} and g_{max} of 100-mers (*S*)-4a, 4c, 4g–i in several solvents, which were determined by nonlinear least-squares fitting using eq 6 with the g_{abs} values in Table 4, are summarized in Table 5. The calculated parameters E_{h} and g_{max} of 100-mers (*S*)-4a and 4c showed good agreement with the values calculated for 40-mers. While the E_{h} values were slightly larger, this could be explained by the influence of the chiral

Table 4. Structures and Dissymmetry Factors g_{abs} of 100-mers (*S*)-4a x , 4c x , 4g x , 4h x , and 4i x in CHCl_3 , 1,1,2-TCE, THF, and Toluene



polymer	$M_n / 10^3$	M_w / M_n	$g_{\text{abs}} / 10^{-3}$			
			CHCl_3	1,1,2-TCE	THF	toluene
(<i>S</i>)-4a 5	25.3	1.08	−1.45	+1.15	−0.83	−0.56
(<i>S</i>)-4a 10	23.7	1.08	−2.04	+2.01	−1.44	−1.04
(<i>S</i>)-4a 15	23.0	1.09	−2.25	+2.51	−1.79	−1.40
(<i>S</i>)-4a 20	21.8	1.10	−2.25	+2.67	−1.87	−1.58
(<i>S</i>)-4a 100	27.9	1.07	−2.41	− ^a	−2.24	−2.23
4c 5	27.7	1.10	+1.64	−1.57	+0.96	+0.81
4c 10	27.5	1.10	+2.11	−2.41	+1.51	+1.38
4c 15	27.6	1.10	+2.27	−2.68	+1.72	+1.64
4c 20	28.0	1.08	+2.30	−2.78	+1.92	+1.83
4c 100	29.5	1.08	+2.42	− ^a	+2.22	+2.16
4g $^{2.5}$	28.9	1.11	+1.04	− ^b	− ^b	− ^b
4g 5	30.3	1.08	+1.69	−1.68	+0.93	+0.76
4g $^{7.5}$	29.8	1.08	+1.99	− ^b	− ^b	− ^b
4g 10	30.2	1.08	+2.21	−2.60	+1.53	+1.39
4g 15	30.8	1.07	+2.27	−2.91	+1.83	+1.69
4g 20	30.2	1.07	+2.32	−2.96	+1.92	+1.90
4g 50	28.9	1.08	+2.39	− ^b	− ^b	− ^b
4g 100	30.9	1.07	+2.41	− ^a	+2.16	+2.10
4h $^{2.5}$	27.4	1.07	+1.13	−0.95	− ^b	− ^b
4h 5	27.7	1.08	+1.78	−1.74	+0.90	+0.83
4h $^{7.5}$	27.4	1.07	+2.03	−2.20	− ^b	− ^b
4h 10	29.0	1.08	+2.21	−2.47	+1.45	+1.40
4h 15	28.5	1.08	+2.25	−2.69	+1.72	+1.67
4h 20	28.3	1.08	+2.25	−2.80	+1.89	+1.87
4h 100	28.4	1.11	+2.39	− ^a	+2.06	+1.94
4i $^{2.5}$	20.5	1.07	−0.63	− ^b	− ^b	− ^b
4i 5	20.5	1.09	−1.20	+1.22	+0.15	−0.07
4i $^{7.5}$	20.7	1.10	−1.55	− ^b	− ^b	− ^b
4i 10	19.7	1.11	−1.91	+1.90	+0.23	−0.16
4i 15	18.6	1.10	−2.16	+2.26	+0.30	−0.36
4i 20	19.9	1.11	−2.24	+2.41	+0.33	−0.57
4i 100	21.6	1.08	−2.63	− ^a	−2.14	−1.99

^aThese samples could not be measured because of their low solubility.
^bNot measured.

groups located at the termini. The E_{h} values increased with increase in the difference in bulkiness of the substituents on the chiral centers. Polymer 4h showed the largest E_{h} (1.01 kJ mol $^{-1}$), which was 1.7 times larger than the original structure (polymers 3a and (*S*)-4a). On the other hand, polymer 4i bearing 3-octyloxymethyl groups showed a smaller E_{h} compared with polymer 4h bearing 2-octyloxymethyl groups.

Table 5. Calculated E_h and g_{\max} Values of Polymers (S)-4a, 4c, 4g–i

polymer	CHCl ₃		1,1,2-TCE	
	E_h (kJ mol ⁻¹)	$g_{\max}/10^{-3}$	E_h (kJ mol ⁻¹)	$g_{\max}/10^{-3}$
(S)-4a	-0.59	-2.37	-0.42	+2.87
4c	-0.82	+2.33	-0.62	-2.81
4g	-0.88	+2.35	-0.62	-3.02
4h	-1.01	+2.29	-0.70	-2.79
4i	-0.50	-2.44	-0.49	+2.46

polymer	THF		toluene	
	E_h (kJ mol ⁻¹)	$g_{\max}/10^{-3}$	E_h (kJ mol ⁻¹)	$g_{\max}/10^{-3}$
(S)-4a	-0.37	-2.18	-0.24	-2.21
4c	-0.42	+2.13	-0.36	+2.10
4g	-0.44	+2.10	-0.39	+2.06
4h	-0.44	+2.02	-0.44	+1.95
4i	- ^a	- ^a	- ^a	- ^a

^aThe nonlinear least-squares fitting did not converge.

This can be explained by the smaller differences in bulkiness of the substituents on the chiral center (polymer 4h: methyl and hexyl groups, polymer 4i: ethyl and pentyl groups). It should be noted that parameters E_h and g_{\max} of polymer 4i in THF or toluene were not in accordance with eq 6. In particular, while polymer 4i in THF gave positive g_{abs} values when the number of chiral units N was small ($N = 2.5$ – 20), the g_{abs} value became negative when N was large ($N = 100$) (Table 4). Although the reason for this phenomenon is not clear at this moment, we assume that the chirality induction by the chiral unit is susceptible to the influence of neighboring monomer units in the case where the chiral group becomes bulkier.

The relationships between the number of chiral units N and the se in CHCl₃ or 1,1,2-TCE calculated with the parameters E_h and g_{\max} are plotted in Figure 4. Polymer 4h shows steeper

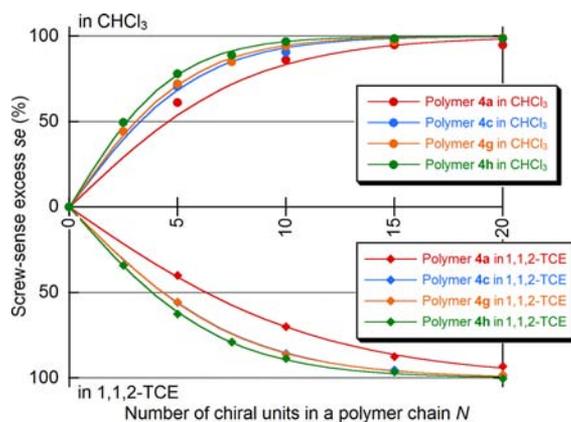


Figure 4. Relationships between number of chiral units N and se of polymers 4a, 4c, 4g, and 4h in CHCl₃ or 1,1,2-TCE. The circles and the rhombuses were calculated from observed g_{abs} and g_{\max} according to eq 5. The lines were generated from E_h and N according to eq 4.

curves than the other polymers, suggesting that the chiral unit in polymer 4h induced an asymmetric helix in the main chain more efficiently than the other polymers. In general, according to the relationship between the Gibbs free energy and the equilibrium constant, helix induction to the level of 99.0% se requires 12.9 kJ mol⁻¹ at 20 °C. Therefore, polymer 4h requires only 13 chiral units derived from chiral monomer 2h to gain 13.1 kJ mol⁻¹ for the formation of a single-handed helical

structure. Helix induction by the chiral units derived from 2h was found to be more efficient than the chiral units derived from 2a not only in CHCl₃ but also in other solvents, such as 1,1,2-TCE, THF, and toluene.

Next, we carried out CD and UV measurements of polymers 3a⁴⁰ and 3h⁴⁰ (40-mers) in 1,1,2-TCE/CHCl₃ with varied ratios (Figure 5). The observed g value was plotted against the

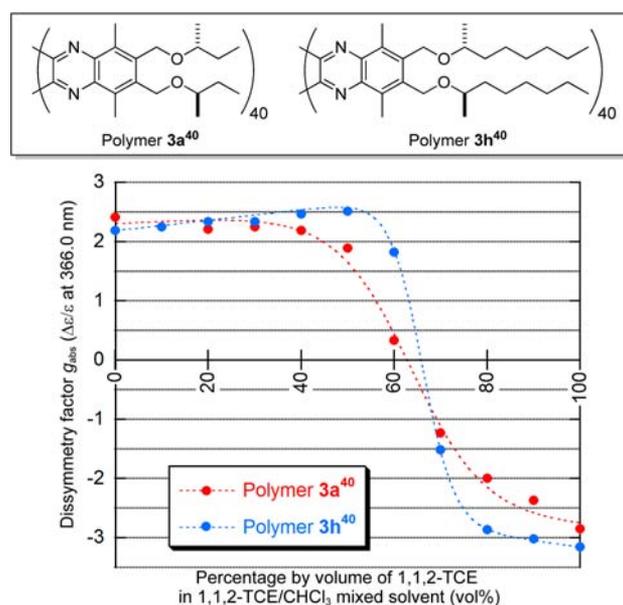


Figure 5. Relationships between percentage by volume of 1,1,2-TCE in 1,1,2-TCE/CHCl₃ mixed solvent and dissymmetry factor g at 366.0 nm of polymers 3a⁴⁰ and 3h⁴⁰.

ratio of the solvents. The polymers both adopted *P*-helical structures in pure CHCl₃. Polymer 3a⁴⁰ started to invert the helical sense at the 1,1,2-TCE/CHCl₃ ratio of ca. 40/60 and became racemic at a ratio around 60/40. Polymer 3h⁴⁰ exhibited sharper inversion of its helical sense as indicated by the steeper curve, which starts to descend at a 55:45 ratio. By virtue of the larger E_h value, 3h⁴⁰ can complete the inversion within the narrower range of the 1,1,2-TCE/CHCl₃ ratio.

Finally, we measured the dissymmetry factors g of polymer 3h⁴⁰ in various solvents to explore solvents for helix inversion (Figure 6; the abbreviations of solvents are summarized in the

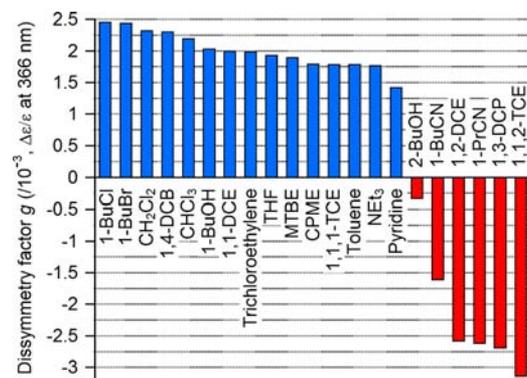


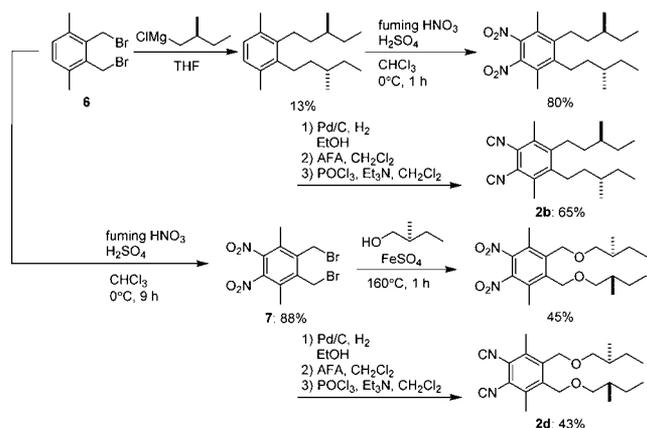
Figure 6. Dissymmetry factors g at 366.0 nm of polymer 3h⁴⁰ in various solvents. DCE: dichloroethane, DCP: dichloropropane, DCB: dichlorobutane, TCE: trichloroethane, MTBE: methyl *tert*-butyl ether, and CPME: cyclopentyl methyl ether.

with water and brine and dried over MgSO_4 . After evaporation of the solvent, the residue was purified by silica gel column chromatography (hexane:Et₂O = 20:1) to give **2h-Me** as pale-yellow oil (8.70 g, 87% yield). ¹H NMR (CDCl₃) δ 4.81 (2H, d, J = 10.0 Hz), 4.65 (2H, d, J = 10.0 Hz), 3.68–3.54 (2H, m), 2.79 (6H, s), 1.96–1.54 (4H, m), 1.53–1.37 (4H, m), 1.37–1.18 (18H, m), 0.88 (6H, t, J = 6.4 Hz); ¹³C NMR (CDCl₃) δ 155.4, 136.3, 128.6, 76.0, 64.4, 36.8, 31.9, 29.4, 25.8, 22.6, 19.8, 14.3, 14.1; IR (ATR, neat) 2957, 2926, 2854, 1456, 1373, 1337, 1119, 1074, 1051, 910, 878, 835, 723 cm⁻¹; HRMS (ESI⁺) m/z calcd for C₂₆H₄₄N₂O₂S + H⁺ (M + H⁺): 450.3230, found: 450.3218.

Synthesis of 2h. To a solution of **2h-Me** (8.70 g, 19.4 mmol) in EtOH (110 mL) and toluene (92.3 mg, 0.39 mmol) at room temperature. The mixture was heated gradually to 50 °C, stirred for 1 h, and passed through a pad of Celite. The resultant solution was evaporated in vacuo. Extraction with AcOEt followed by column chromatography on silica gel (hexane:AcOEt = 2:1) afforded diamine compound (7.25 g, 89% yield). To a CH₂Cl₂ (100 mL) solution of the diamine compound (7.25 g, 17.2 mmol) was added AFA (6.07 g, 68.9 mmol) at 0 °C. The mixture was stirred for 1 h with gradual warming up to room temperature. The mixture containing a diformamide compound was subjected to evaporation of volatile materials in vacuo and used for the next step without further purification. To a CH₂Cl₂ (40 mL) suspension of the diformamide compound (2.60 g, 5.45 mmol) and Et₃N (7.60 mL, 54.5 mmol) cooled to 0 °C, POCl₃ (1.53 mL, 2.51 g, 16.4 mmol) was added. After stirring for 45 min at 0 °C, saturated NaHCO₃ aq was added to the reaction mixture. Extraction with CH₂Cl₂ followed by column chromatography on silica gel (hexane:Et₂O = 10:1) gave **2h** as yellow oil (1.10 g, 2.50 mmol, 46% yield). ¹H NMR (C₆D₆) δ 4.32 (2H, d, J = 10.4 Hz), 4.10 (2H, d, J = 10.4 Hz), 3.38–3.20 (2H, m), 2.13 (6H, s), 1.60–1.45 (2H, m), 1.44–1.17 (18H, m), 1.10 (6H, d, J = 6.4 Hz), 0.91 (6H, t, J = 7.0 Hz); ¹³C NMR (C₆D₆) δ 175.6, 138.4, 133.9, 76.1, 64.2, 37.2, 32.3, 29.8, 26.0, 23.1, 19.7, 15.3, 14.3; IR (ATR, neat) 2957, 2928, 2856, 2114, 1456, 1373, 1337, 1227, 1198, 1136, 1119, 1084, 1049, 970, 922, 891, 723, 631, 623 cm⁻¹; HRMS (ESI⁺) m/z calcd for C₂₈H₄₄N₂O₂ + H⁺ (M + H⁺): 442.3509, found: 442.3501; [α]_D²⁹ 41.2 (c 0.54, CHCl₃).

Monomers **2b** and **2d** were synthesized from compound **6** as shown in Scheme 2. We adopted this route for the synthesis of monomer **2b**,

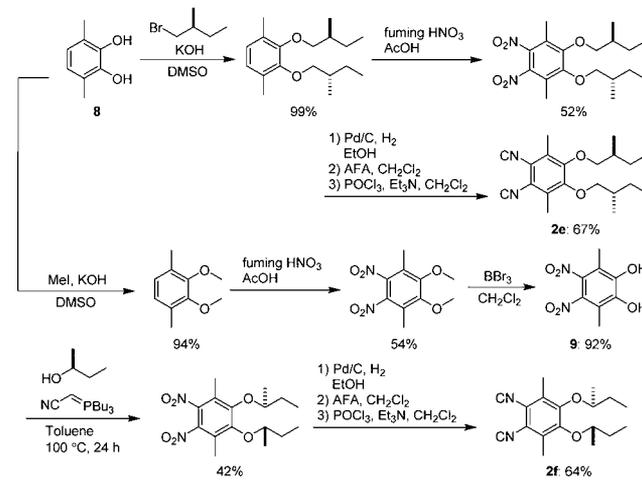
Scheme 2. Synthesis of Monomers 2b and 2d



because the Grignard reagent was too reactive to modify compound **5** and caused undesired side reactions. Monomer **2d** was synthesized via compound **7** by using Williamson ether synthesis mediated by anhydrous FeSO₄.²⁶

Monomers **2e** and **2f** were synthesized from compound **8** as shown in Scheme 3. Williamson ether synthesis with compound **8** and (*S*)-1-bromo-2-methylbutane successfully proceeded in the presence of KOH in dimethylsulfoxide (DMSO). It should be noted that this reaction was unsuccessful under other conditions using NaH/dimethylformamide (DMF) or K₂CO₃/acetone. Hydroxy groups of **8** were protected by methyl groups. The dimethoxy compound was

Scheme 3. Synthesis of Monomers 2e and 2f



nitrated under acidic conditions and then deprotected by treatment with BBr₃ to give compound **9**. Monomer **2f** was prepared from **9** by Mitsunobu reaction mediated by a phosphorane reagent.^{23,27}

A typical procedure for synthesis of sequence-regulated copolymers: Synthesis of 3a⁴-S6. THF solutions of **1** (0.10 M) and **2a** (0.011 M) were prepared. A THF solution of *o*-TolNiCl(PMe₃)₂ (0.050 M, 50 mL, 2.5 mmol) was diluted with THF (3.9 mL). To the solution was added a solution of PMe₃ in THF (1.0 M, 2.5 mL, 2.5 mmol). After stirring for 15 min, the solution of **1** (0.18 mL, 18 mmol) was added at room temperature. After stirring for 15 min, the solution of **2a** (0.23 mL, 2.5 mmol) was added at room temperature. The additions of the solutions of **1** and **2a** were repeated four times in the same manner. After 15 min from fourth addition of **2a**, the solution of **1** (0.18 mL, 18 mmol) was added at room temperature. After 15 min, a THF solution of *o*-TolMgBr (1.0 M, 50 mL, 50 mmol) was added to the reaction mixture at room temperature. After stirring for 15 min at room temperature, water was added. Extraction with CHCl₃ followed by preparative GPC gave **3a⁴-S6** as orange solid (25.9 mg, 85%). ¹H NMR (CDCl₃) δ 5.36–4.03 (40 × 4H, m), 3.46 ((4 × 2 + 36 × 4)H, br s), 2.57–1.92 (40 × 6H, m), 1.85–1.12 ((4 × 10 + 36 × 4)H, m), 1.05–0.63 (40 × 6H, m); GPC (CHCl₃, g/mol): M_n = 8.5 × 10³, M_w/M_n = 1.12.

Synthesis of 3h⁴⁰. A THF solution of *o*-TolNiCl(PMe₃)₂ (10.0 mM, 250 μ L, 2.5 μ mol) was diluted with THF (3.0 mL). A THF solution of **2h** (44.1 mg, 100.0 mmol) was diluted with THF (2 mL). The solution of the monomer **2h** was added to the solution of *o*-TolNiCl(PMe₃)₂. After stirring for 3 h at room temperature, NaBH₄ (33.3 mg, 0.88 mmol) was added to the reaction mixture and stirred for an additional 1 h. The mixture was diluted with water (10 mL) and extracted with CH₂Cl₂ (15 mL). The organic extract was washed with brine (10 mL), dried over MgSO₄, and evaporated under vacuum. The residue was subjected to preparative GPC to give **3h⁴⁰** as a beige solid (40.0 mg, 90 mmol, 90%). ¹H NMR (CDCl₃) δ 4.61 (40 × 2H, br s), 4.50 (40 × 2H, br s), 3.47 (40 × 2H, br s), 2.28 (40 × 6H, br s), 1.88–1.04 (40 × 26H, m), 0.84 (40 × 6H, br s); GPC (CHCl₃, g/mol): M_n = 9.7 × 10³, M_w/M_n = 1.11.

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures and spectral data for the new compounds. 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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