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Synthesis of Helical Rod−Coil Multiblock Copolymers by Living Block Copolymerization of Isocyanide and 1,2-Diisocyanobenzene Using Arylnickel Initiators

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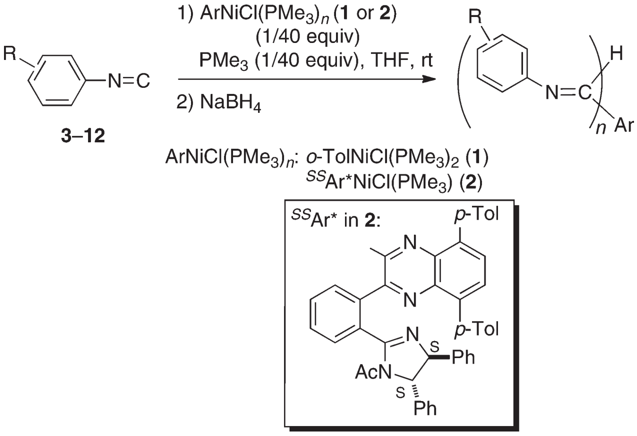
Block copolymers have attracted much attention in polymer sciences and technologies because of the highly ordered arrangement of blocks of functional groups along the polymer main chains and their ability for self-organization to form nanoscale architectures.[1] With the aim of efficient and practical synthesis of block copolymers, a variety of living polymerization systems on the basis of radical,[2] anionic,[3] cationic,[4] and coordination polymerizations[5] have been developed. Much effort is still being devoted to the development of new methods for the synthesis of block polymers featuring new unit structures, controlled polymerization degrees, and a combination of sharply different main chain structures, which would lead to a new horizon for block polymer chemistry.

Isocyanides are known to undergo polymerization in the presence of transition metal catalysts such as nickel, palladium, and rhodium complexes.[6] The poly(*N*-substituted iminomethylene)s thus formed are unique in that they adopt helical structures, which can be asymmetrically constructed using chiral initiators,[7] using optically active isocyanides as chiral monomers[8] or using chiral guests that interact with functional groups in the polymer side chains.[9] Among the transition metals, nickel complexes have most frequently been used as an initiator, in contrast to the limited use of palladium complexes as initiators. A major reason for the less common use of palladium complexes is their tendency to form a trimer intermediate involving intramolecular N−Pd coordination, which terminates the living polymerization,[10] although unique alkynylpalladium complexes have been developed as initiators for the polymerization of isocyanides.[6e,8e,f] In sharp contrast, nickel initiators exhibit high polymerization activity, leading to the synthesis of a variety of poly(isocyanide)s including block copolymers.[11]

On the other hand, polymerization of 1,2-diisocyanobenzenes has provided the only synthetic route to poly(quinoxaline-2,3-diyl)s, an ortho-linked aromatic polymer adopting a rigid helical structure.[12] The helical structure is assumed to be much more rigid than poly(iminomethylene)s, allowing the adoption of an optically active helical structure with one-handed helical sense.[13] The polymerization of diisocyanobenzene proceeds through a mechanism involving successive insertion of the isocyano group into the transition metal−carbon bond, which also is the key elementary step for the polymerization of isocyanides. In the polymerization of diisocyanobenzenes, successive insertion of the two neighboring isocyano groups led to aromatizing formation of a quinoxaline ring. In this polymerization, organopalladium initiators are mostly utilized, while the nickel initiators were also found to be effective.[14] In the course of our recent study on the asymmetric polymerization of 1,2-diisocyanobenzenes using chiral organonickel initiators,[15] we became interested in copolymerization of isocyanide and 1,2-diisocyanobenzenes using the same organonickel complexes as initiators. The copolymerization would allow us to obtain copolymers that consist of highly contrasting polymer main chains, i.e., poly(quinoxaline-2,3-diyl)s as a highly rigid rod and poly(*N*-aryliminomethylene)s as a relatively flexible, yet tense, coil. Although "change-of-mechanism" copolymerizations of isocyanide with 1,3-butadienes,[16] allenes,[17] and glutamate *N*-carboxyanhydride[18] have been reported using nickel initiators, the present copolymerization is likely to proceed with a single mechanism, i.e, insertion of the isocyano group into the M−C bond of the living polymer intermediates, despite the formation of two highly contrasting helical polymer backbones. In this report, we describe the copolymerization of isocyanide and 1,2-diisocyanobenzenes with organonickel initiators, which provides poly(*N*-substituted iminomethylene-*b*-quinoxaline-2,3-diyl)s featuring helical structures for both blocks. The polymerization allows not only polymerization of isocyanide after 1,2-diisocyanobenzenes but also "reverse block formation", which leads to the synthesis of multiblock copolymers.

Table 1. Polymerization of Monoisocyanides in the Presence of Arylnickel Complexes 1 and 2



entry	initiator	isocyanide	% yield	M_n	M_w/M_n	$\Delta\varepsilon$ [dm^3 cm^{-1} mol^{-1}][a]
1	**1**	**3**	87	5.2×10^3	1.12	
2	**1**	**4**	83	3.9×10^3	1.15	
3	**1**	**5**	0[b]			
4	**1**	**6**	0[b]			
5	**1**	(1*R*)-**7**	89	6.1×10^3	1.12	9.7
6	**2**	**4**	95	3.9×10^3	1.15	5.1×10^{-3}
7	**2**	**8**	81	5.2×10^3	1.12	7.9×10^{-2}
8	**2**	**9**	75	1.0×10^4	1.09	2.7×10^{-1}
9	**2**	**10**	84	8.4×10^3	1.07	3.4×10^{-1}
10	**2**	**11**	80	9.4×10^3	1.09	5.0×10^{-1}
11	**2**	**12**	84	1.1×10^4	1.10	6.4×10^{-1}
12	**2**	**3**	99	6.3×10^3	1.15	(2.7)[c]

[a] Molar circular dichroism ($\Delta\varepsilon$) at 366 nm. Conversion between $\Delta\varepsilon$ and molar ellipticity ([θ]) is made according to the following equation: $[\theta] = 3298\Delta\varepsilon$. [b] Incomplete consumption of the monomer. Only short oligomers below the permeation limit were formed. [c] The shape of the CD spectra was completely different from those obtained in entries 5−11, thus being unable to determine the degree of screw-sense induction directly from the $\Delta\varepsilon$ value.

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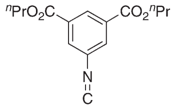
To test the feasibility of our assumption, polymerization of isocyanides in the presence of an achiral arylnickel complex, *o*-TolNiCl(PMe$_3$)$_2$ (**1**), was examined (Table 1). The polymerization was greatly affected by the structure of the isocyanides. Alkyl isocyanides such as cyclohexyl isocyanide and *tert*-butyl isocyanide did not undergo polymerization at all. Among the aromatic isocyanides tested, 3,5-di(propoxycarbonyl)phenyl isocyanide (**3**) and *p*-propoxycarbonylphenyl isocyanide (**4**) underwent polymerization, giving the corresponding poly(*N*-aryliminomethylene)s in good yields in the presence of achiral organonickel initiator **1** (Table 1, entries 1 and 2). In contrast, *p*-aminocarbonyl-substituted phenyl isocyanide **5** or *p*-*tert*-butylphenyl isocyanide (**6**) failed to give the corresponding poly(isocyanide)s (entries 3 and 4).



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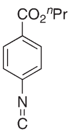

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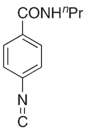

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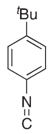

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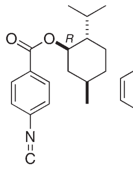
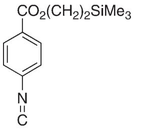


(1*R*)-**7**



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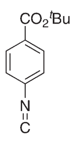

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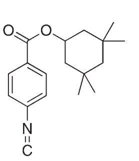

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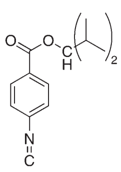

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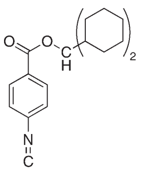

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We then checked the possibility of helical sense induction to the poly(*N*-aryliminomethylene) main chain by a chiral terminal group, which is introduced from the chiral initiator **2**. As a measure of the degree of screw-sense induction, poly(*p*-menthoxycarbonylphenyl isocyanide) poly(1*R*)-**7** was synthesized from chiral isocyanide (1*R*)-**7** with achiral initiator **1** (Table 1, entry 5), exhibiting a circular dichroism (CD) spectrum characteristic of optically active helical poly(*p*-menthoxycarbonylphenyl isocyanide), which was obtained in the palladium-initiated polymerization by Takahashi et al.[8f,19] The intensity ($\Delta\varepsilon$) of the CD spectrum (+9.7) at 366 nm was comparable with the value reported for the pure right-handed helical structure by Takahashi (+12.2),[8g] allowing us to use the CD intensity of our polymer poly(1*R*)-**7** as an approximate measure for the single-handed helical conformation. Several achiral *p*-alkoxycarbonylphenyl isocyanides have been polymerized in the presence of chiral organonickel initiator **2** (entries 6−11). The obtained polymers all showed CD spectra typical for optically active poly(*p*-alkoxycarbonylphenyl isocyanide)s. The intensities varied with the steric bulkiness of the alkoxy substituents: polyisocyanides bearing larger alkoxy groups exhibited higher screw-sense induction, although the estimated screw-sense inductions were less than 10% screw-sense excess (s.e.) in comparison with the standard poly(1*R*)-**7**. With these results, we concluded that the helical sense induction by the chiral terminal group was not effective for poly(isocyanide)s produced from *p*-alkoxycarbonylphenyl isocyanides. Note that 3,5-di(propoxycarbonyl)phenyl isocyanide (**3**) afforded optically active polymer poly-**3** showing a relatively intense CD spectrum (entry 12), although the degree of helical induction could not be estimated because of lack of a standard.

Although only a small screw-sense induction was observed, the successful polymerization of monoisocyanides with the quinoxalinylnickel initiator **2**, which can be regarded as a model of living intermediate carrying a quinoxaline−nickel bond at the living terminus, prompted us to examine block copolymerization of isocyanides with 1,2-diisocyanobenzene. 1,2-Diisocyanobenzene **13** (40 equiv) was subjected to polymerization with chiral initiator **2**, affording poly(quinoxaline-2,3-diyl) **14** as a living polymer that exhibited a narrow molecular weight distribution after complete consumption of **13** (Figure 1). To this reaction mixture, 20, 40, or 80 equiv of isocyanide **3** was added at room temperature. Polymerization proceeded quickly at room temperature and gave diblock copolymer **15a**−**c**, which still showed small polydispersity indexes. On addition of **13** (40 equiv) to the reaction mixture

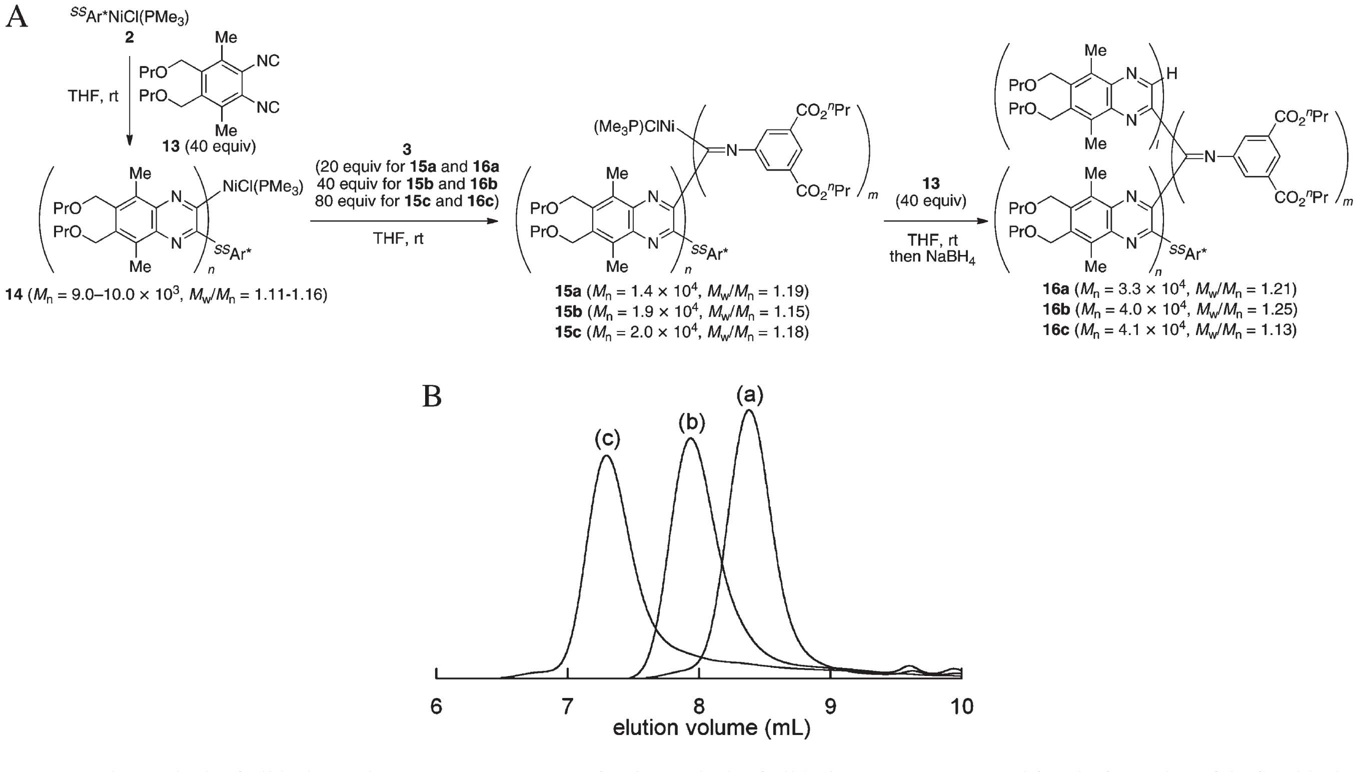


Figure 1. (A) Synthesis of triblock copolymer **16**. (B) GPC traces for the synthesis of triblock copolymer **16b**. (a) After the formation of the first block (**14**). (b) After the formation of the second block (**15b**). (c) GPC trace of **16b** (quenched with NaBH$_4$).

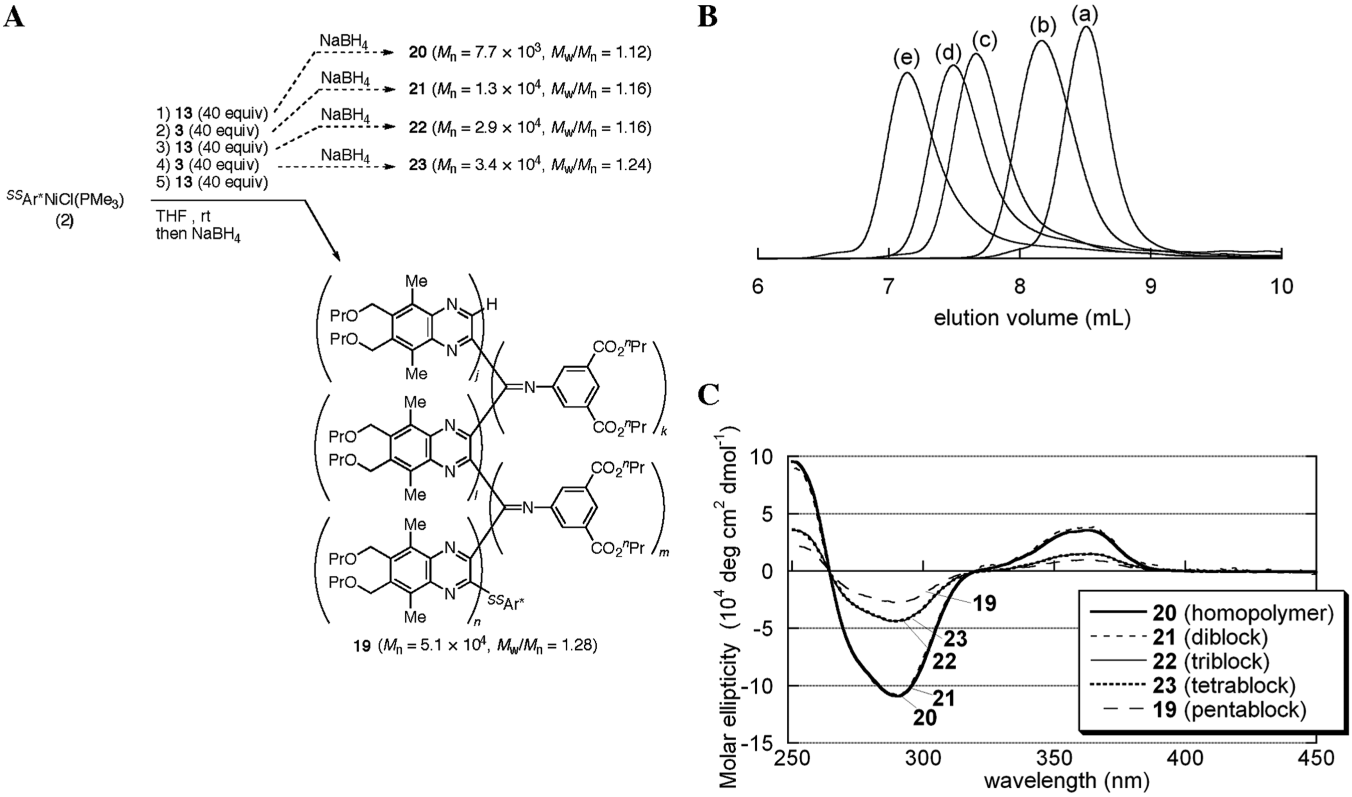
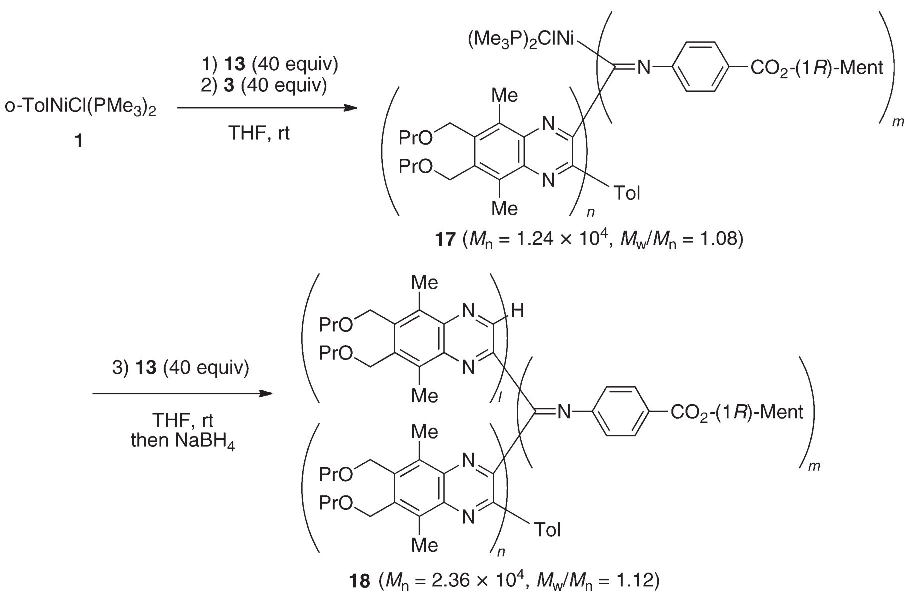


Figure 2. (A) Synthesis of pentablock copolymer **19**. (B) GPC traces for (a) **20**, (b) **21**, (c) **22**, (d) **23**, and (e) **19**. (C) CD spectra of **19**, **20**, **21**, **22**, and **23**.

Scheme 1. Synthesis of Triblock Copolymer 18



containing **15a**−**c**, further polymerization of **13** proceeded smoothly, giving triblock copolymer **16a**−**c** in good yields. The successful formation of the third block is in sharp contrast to the previously reported "change-of-mechanism" copolymerizations, in which no polymerization proceeded after polymerization of the isocyanides.[16,17] This successful triblock copolymer formation may be attributed to the involvement of a single mechanism, i.e., insertion of the isocyano group into the Ni−C bond, in the copolymerization sequence. The switch of the monomer was highly efficient, as shown by the GPC traces of each block copolymerization steps, in which no "dead" living polymer molecules could be found in the reaction mixtures (Figure 1B).

It would be interesting to discuss the transfer of the chirality between the chiral helical rod, i.e., the poly(quinoxaline) unit, and the chiral coil, i.e., the poly(iminomethylene) unit. We prepared di- (**17**) and triblock (**18**) copolymers of **13** and *p*-menthoxycarbonylphenyl isocyanide ((1*R*)-**7**) with achiral initiator **1** (Scheme 1). It was assumed that (1*R*)-**7** would provide a coil block with an almost pure right-handed structure.[8f] The helical rod blocks of **17** and **18** both showed optically active helical structures with 42 and 40% s. e. for the left-handed helix.[20] Although the efficiency of the helix sense transmission at the rod−coil interface is not very high (40−42%), we found that the right-handed helical poly((1*R*)-*p*-menthoxycarbonylphenyl isocyanide) unit induces the left-handed helical structure in the poly(quinoxaline) unit.

We finally carried out the synthesis of the pentablock copolymer of **3** and **13** in the presence of chiral initiator **2** (Figure 2). The profile of the copolymerization was monitored at each polymerization step by quenching a portion of the reaction mixture and analyzing with GPC and CD measurements (Figure 2B,C). The block copolymerization proceeded efficiently, providing pentablock copolymers in good yield. The GPC traces taken at each step clearly showed that no "dead" living polymer formed, even in the fourth and fifth steps (Figure 2B). Other important information obtained in these experiments was the degree of screw-sense induction at each stage. In the first step, as judged from the CD spectrum, ca. 80% screw-sense excess was induced to the poly(quinoxaline) unit (40-mer) by the chiral terminal group,[15] which was retained during the second polymerization stage, in which achiral monoisocyanide was used as the monomer (Figure 2C). Note that the intensity of the CD spectrum is discussed based on the molar concentration of a quinoxaline unit calculated from the UV spectrum, which can be separated from the absorption of the poly(iminomethylene) block.[20] This treatment allows us to focus on the estimation of s.e. solely for the poly(quinoxaline) block. After the third step, the averaged s.e. for the two poly(quinoxaline) blocks dropped to ca. 50% of the original screw-sense induction. It is assumed that the drop in s.e. is attributed to the formation of 1:1 *P*- and *M*-helices as the second poly(quinoxaline) block, while the first quinoxaline block kept its original right-handed helical conformation unchanged. In the fifth step, the averaged s.e. for the polyquinoxaline blocks dropped further to ca. 30% of the initial stage, suggesting again that almost no helical sense was induced in the third block.

In summary, living copolymerization of isocyanides and 1,2-diisocyanobenzenes has been demonstrated for the first time with use of achiral and chiral arylnickel complexes as initiators. The copolymerization system allows the synthesis of multiblock copolymers, up to pentablock copolymer, the formation of which involves both isocyanide-to-1,2-diisocyanobenzene and its reverse. The multiblock copolymers featuring combination of the two distinctive helical main chain structures may allow unique and highly ordered self-assembly on the surface or in the bulk of the materials, leading to the development of new functional materials. Although not being remarkably efficient, the right-handed helical poly((1*R*)-*p*-menthoxycarbonylphenyl isocyanide) block induced a left-handed helical structure in the poly(quinoxaline) block. Copolymerization with other isocyanides and 1,2-diisocyanobenzenes with functional groups, optimization of the polymerization protocol, and investigation of the properties of the formed copolymers are now being undertaken in this laboratory.

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Supporting Information Available: 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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(19) See the Supporting Information for the UV and CD spectra of poly(iminomethylene)s and poly(quinoxaline)s.

(20) The screw-sense excesses of the helical quinoxaline rods of the block copolymers were estimated on the assumption that their UV and CD spectra were the linear combinations of the spectra of polyquinoxaline and poly(iminomethylene) homopolymers. This treatment affords virtual CD and UV spectra of the polyquinoxaline blocks of the block copolymers, leading to virtual *g* value for the polyquinoxaline block, which corresponds to the screw-sense excess. This treatment, however, is *not* applicable to the estimation of the se of poly(iminomethylene) block because it is difficult to obtain virtual CD spectra of the poly(iminomethylene) block due to much weaker CD intensity of the poly(iminomethylene) structure than that of poly(quinoxaline) block. See the Supporting Information for details.