

Exerting Control over the Helical Chirality in the Main Chain of Sergeants-and-Soldiers-Type Poly(quinoxaline-2,3-diyl)s by Changing from Random to Block Copolymerization Protocols

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S Supporting Information

ABSTRACT: Chiral random poly(quinoxaline-2,3-diyl) polymers of the sergeants-and-soldiers-type (sergeant units bearing (S)-3-octyloxymethyl groups) adopt an *M*- or *P*-helical conformation in the presence of achiral units bearing propoxymethyl or butoxy groups (soldier units), respectively. Unusual bidirectional induction of the helical sense can be observed for a copolymer with butoxy soldier units upon changing the mole fraction of the sergeant units. In the presence of 16–20% of sergeant units, the selective induction of a *P*-helix was observed, while the selective induction of an *M*-helix was observed for a mole fraction of sergeant units of more than 60%. This phenomenon could be successfully employed to control the helical chirality of copolymers by applying either random or block copolymerization protocols. Random or block copolymerization of sergeant and soldier monomers in a 18:82 ratio resulted in the formation of 250mers with almost absolute *P*- or *M*-helical conformation, respectively (>99% ee). Incorporation of a small amount of coordination sites into the random and block copolymers resulted in chiral macromolecular ligands, which allowed the enantioselective synthesis of both enantiomers in the Pd-catalyzed asymmetric hydrosilylation of β -methylstyrene.

Strategies to control the screw sense in helical chiral macromolecules are receiving ever-increasing attention, due to their applications¹ in chiral separation, chiral recognition, chiroptical materials, and asymmetric synthesis.² The most simple and reliable approach is to introduce chiral substituents into the polymer side chains,³ resulting in *P*- or *M*-helical main chains, which can then be discriminated on the basis of their diastereomeric relationship. For the induction of nonracemic helical structures resulting from the introduction of chiral side chains, Green et al. reported the sergeants-and-soldiers effect.⁴ This effect is based on the accumulation of small local energy preferences for one helical structure in entire helical macromolecules⁴ or supramolecules,⁵ resulting in the induction of an overall helical sense according to the Ising model.⁶ The original Ising model predicts a nonlinear, but nevertheless monotonous increase in the screw-sense excess (se) for either right- or left-

handed helices as a result of an increase of the mole fraction of the chiral sergeant monomers.

In contrast to such conventional sergeants-and-soldiers systems, some helical sergeants-and-soldiers polymers were recently shown to exhibit an “abnormal” effect of the sergeant monomer mole fraction with respect to the induction of a helical sense.⁷ While one of the two helical senses was induced for low mole fractions of the sergeant monomer, the other helical sense was induced for higher mole fractions of the sergeant monomer. It was indeed suggested that both *P*- and *M*- helical structures could be induced arbitrarily through a single sergeant unit, depending on its mole fraction. Accordingly, Sato et al. proposed a modified Ising model, in which the preference of screw-sense induction of a monomer unit depends on the monomer units in its immediate vicinity.⁸ This finding clearly suggests that even a single chiral source can induce either *P*- or *M*-helical sense. However, it should be noted here that for the reported sergeants-and-soldiers polymers, this abnormal screw-sense induction has never been achieved in high se for both helical senses, particularly for low molecular fractions of sergeant monomers.

Here, we describe our results on a new sergeants-and-soldiers polymer that forms, depending on the mole fraction of the sergeant monomers, highly enriched right- and left-handed helical structures. The judicious choice of the soldier monomer is thereby of critical importance in order to obtain both helical configurations in high se. And even when keeping the mole fraction of the sergeant monomer constant, it was possible to successfully invert the helical sense of the polymer scaffold by switching between random or block copolymerization protocols.

For the exploration of this unprecedentedly high induction of helical chirality by the sergeants-and-soldiers effect, we chose poly(quinoxaline-2,3-diyl) as the helical scaffold,⁹ because it allows a highly efficient induction of enantiomerically pure helical structures, which is synthetically easily implemented via living polymerizations, and moreover, the resulting chiral macromolecules can be applied in chiral catalysis.¹⁰ Various sergeant monomers, in which chiral secondary alkoxy groups were attached to the quinoxaline rings through benzyl ether linkers, were explored. As soldier monomers, two isomeric achiral monomer units, namely propoxymethyl- (I) and butoxy-substituted (II) quinoxaline-2,3-diyl units, were employed.

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Achiral monomer unit **I** exhibits a close structural resemblance to the sergeant monomer units, as it hosts a benzyl ether-type linker in the side chain, while monomer unit **II** contains an aryl ether-type linker in the side chain. Using an organonickel initiator, random sergeants-and-soldiers-type copolymers (**1a–m**) containing 100 equiv of soldier monomer **I** with 5 equiv of the sergeant monomer were synthesized. The determination of the helical sense of copolymers **1a–m** containing soldier monomer unit **I** established that the *M*-helical conformation was generally formed from chiral, *S*-configured secondary alkoxy groups (Table 1, column 3, entries 1–13). The screw-sense induction

Table 1. Structures and Screw-Sense Induction Properties of Random Copolymers 1a–m(5/100) and 2a–m(5/100) Based on Kuhn's CD-Derived Dissymmetry Factor g_{abs}^a

Entry	Structure of the chiral unit (CH ₂ OR*)	se [%] ^b	
		1a–m (5/100)	2a–m (5/100)
1	a	51 (<i>M</i>)	19 (<i>M</i>)
2	b	38 (<i>P</i>)	7 (<i>P</i>)
3	c	82 (<i>M</i>)	17 (<i>M</i>)
4	d	59 (<i>P</i>)	12 (<i>P</i>)
5	e	65 (<i>M</i>)	3 (<i>M</i>)
6	f	54 (<i>M</i>)	4 (<i>M</i>)
7	g	54 (<i>M</i>)	19 (<i>P</i>)
8	h	43 (<i>M</i>)	28 (<i>P</i>)
9	i	58 (<i>M</i>)	29 (<i>P</i>)
10	j	56 (<i>M</i>)	36 (<i>P</i>)
11	k	67 (<i>M</i>)	65 (<i>P</i>)
12	l	72 (<i>P</i>)	37 (<i>M</i>)
13	m	44 (<i>M</i>)	74 (<i>P</i>)

^a $\Delta\epsilon/\epsilon$ at 366.0 nm in CHCl₃ ($T = 293$ K). ^bThe g_{abs} value of a single-handed helical polymer (100% se, *P*-helix) was set at 2.23×10^{-3} . ^cThe g_{abs} value of a single-handed polymer (100% se, *P*-helix) was set at 2.11×10^{-3} . Both these g_{abs} values were based on the curve fittings shown in Figure 1.

was subsequently examined for the same sergeant monomers (5 equiv) with aryl ether-type soldier monomers **II** (100 equiv; Table 1, column 4, entries 1–13). Several sergeant monomers induced the same screw-sense as that induced by the benzyl ether-type soldier monomer **I**, although the degree of chirality induced was consistently lower than that for the corresponding copolymers **1a–f** (entries 1–6). Interestingly, some other sergeant monomers (**2g–m**) induced a helical sense opposite to that induced by benzyl ether-type soldier monomer **I**, whereby

the se varied (entries 7–13). These results indicate that *S*-configured sergeants, surrounded by structurally matched soldiers (**I**), generally induce an *M*-helical conformation in the main chain, while the same sergeants, when paired with structurally mismatched soldiers (**II**), induce less preference for the formation of an *M*-helix or might even initiate the formation of a *P*-helix.

Subsequently, the effect of the sergeant monomer mole fraction in random copolymers on the screw-sense induction was investigated. For that purpose, a sergeant unit **m**, bearing (*S*)-3-octyloxymethyl groups, was chosen, due to its high screw-sense induction observed in copolymer **2** with an aryl ether-type soldier monomer **II** (Table 1, entry 13). Although the use of chiral monomer **k** was also considered, the prohibitively low solubility of the resulting copolymers inhibited any further investigations. Therefore, a series of random co-100mers **1m(x/y)** and **2m(x/y)** bearing (*S*)-3-octyloxymethyl groups were prepared and subjected to CD measurements. The se of those copolymers was evaluated on the basis of their CD intensities (Kuhn's dissymmetry factor g_{abs}). A series of copolymers **1m**, consisting of structurally matched sergeants and soldier monomers, exhibited a nonlinear, monotonic increase of the *M*-helical structure for increasing mole fraction of the sergeant monomer (Figure 1, blue

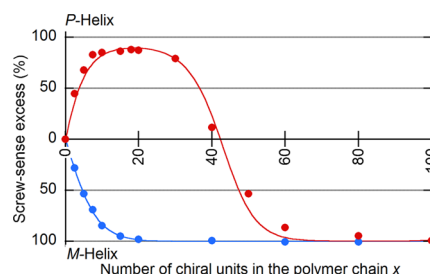


Figure 1. Correlation between the number of chiral units x and the se of polymers **1m(x/y)** and **2m(x/y)** ($x + y = 100$) in CHCl₃. Red and blue data points were calculated from observed g_{abs} and g_{max} values, while the regression lines were generated from ΔG_{h} , $\Delta G_{\text{h,CC}}$, $\Delta G_{\text{h,CA}}$, x , and y (see eqs 1 and 2).

curve), which is in good agreement with Green's original theory.⁸ In contrast, an "abnormal" relationship between the sergeant monomer mole fraction and the screw sense induction was observed for a series of copolymer **2m** (Figure 1, red curve),⁷ which adopted a predominantly *P*- or *M*-helical structure for contents of sergeant units below or above 40%, respectively. It should be noted that the maximum induction for a *P*-helical structure was achieved for 16–20 sergeant units in the polymer backbone of the 100mer.

This nonmonotonic sergeants-and-soldiers effect can be well explained by Sato's model, in which both the degree and the direction of the helical induction depend on the structure of the neighboring monomer units.⁸ There, two different energy preferences (ΔG_{h}) have to be considered for the cases, where a chiral unit is either adjacent to another chiral sergeant unit ($\Delta G_{\text{h,CC}}$) or next to an achiral soldier unit ($\Delta G_{\text{h,CA}}$). This model is superior to Green's original model, as the latter considers these two energy preferences to be equal, and hence only allows the use of ΔG_{h} in order to express the nonlinear, monotonic plots. The se plot against the mole fraction of the sergeant monomer was subjected to a nonlinear, least-squares fitting of the parameters ΔG_{CC} , ΔG_{CA} , and g_{max} using the following equations:

$$g_{\text{abs}} = \tanh(-\Delta G_{\text{h}}/2RT) \times g_{\text{max}} \quad (1)$$

$$\Delta G_{\text{h}} = x \times (x \times \Delta G_{\text{h,CC}} + y \times \Delta G_{\text{h,CA}})/(x + y) \quad (2)$$

The parameters can be converged successfully, affording $\Delta G_{\text{h,CC}}$ and $\Delta G_{\text{h,CA}}$ values of +0.89 and -0.65 kJ/mol, respectively.¹¹ This result clearly indicates that in polymer **2**, the *M*-helical structure is by 0.89 kJ/mol more preferable for a chiral unit, when adjoined by another chiral unit. However, the formation of a *P*-helical structure is by 0.65 kJ/mol more preferable for the same chiral unit, when its closest neighbor is an achiral soldier unit **II**. It is noteworthy that these $\Delta G_{\text{h,CC}}$ and $\Delta G_{\text{h,CA}}$ values are significantly larger than those of previously reported copolymers, including the polysilane originally used by Sato,⁸ which showed $\Delta G_{\text{h,CC}}$ and $\Delta G_{\text{h,CA}}$ values of -0.084 and +0.34 kJ/mol, respectively.

Subsequently, this strategy was further developed with the aim to induce higher *se* values. For that purpose, copolymers with different degrees of polymerization (50–250mer) were prepared, while the ratio between sergeant and soldier units was kept constant (18:82). Higher *se* values were observed for higher copolymers, i.e., *se* values of 94%, 97%, and >99% were found for 150, 200, and 250mers, respectively (Figure 2). It

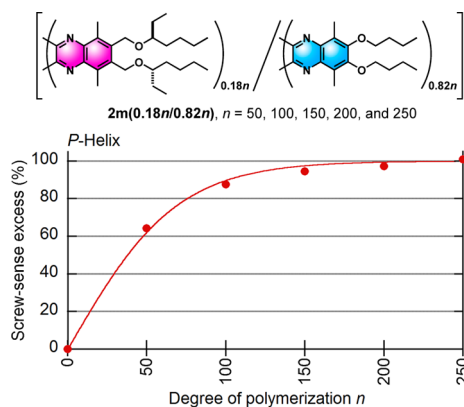


Figure 2. Correlation between the degree of polymerization *n* and the *se* of **2m(0.18*n*/0.82*n*)** (*n* = 50, 100, 150, 200, and 250) in CHCl_3 . Data points were calculated from observed g_{abs} and g_{max} values. The regression line was obtained from ΔG_{h} and *n*.

should be noted here that the reactivity ratio between the chiral and achiral monomers was determined to be 1.4, with which their copolymers can actually be regarded as a random copolymer (see SI).

So far, it has been demonstrated that the screw sense can be inverted by changing the ratio between the chiral–chiral (CC) and the chiral–achiral (CA) dyads, each of which makes the formation of an opposite helical conformation preferable. This example, as well as several previous ones, shows that the ratio of dyads can be controlled by changing the mole fraction of the sergeant monomers. However, another possibility to control the dyad ratio without changing the composition or structure of monomer units is conceivable, provided that the helical polymer has a sufficiently long persistent length of the helical conformation. Random and block copolymers of the sergeants-and-soldiers type with identical monomer composition should have different CC/CA ratios. For example, a random copolymer containing 18% sergeant units should exhibit a CC/CA ratio of 18:82, while in the corresponding block copolymer, the CC/CA ratio should be 100:0 in the block of the sergeant units. If the

forementioned theory is valid, random and block copolymers should be subjected to a diametral induction of the helical sense. Indeed, both block copolymer **block-2m(45/205)** and random copolymer **2m(45/205)** showed a highly enriched *M*- and *P*-helical conformation (>99% *se*), respectively (Figure 3). To the

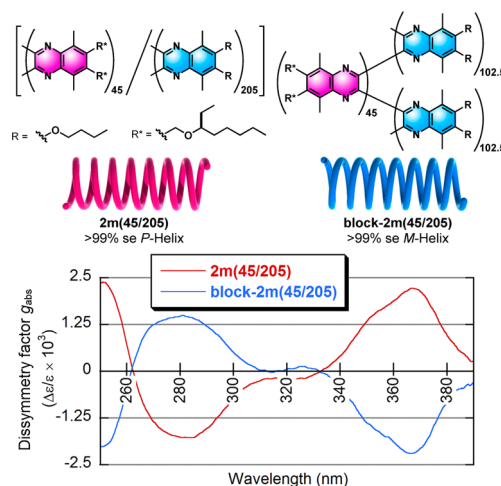


Figure 3. Structures and CD spectra of **2m(45/205)** and **block-2m(45/205)** in CHCl_3 .

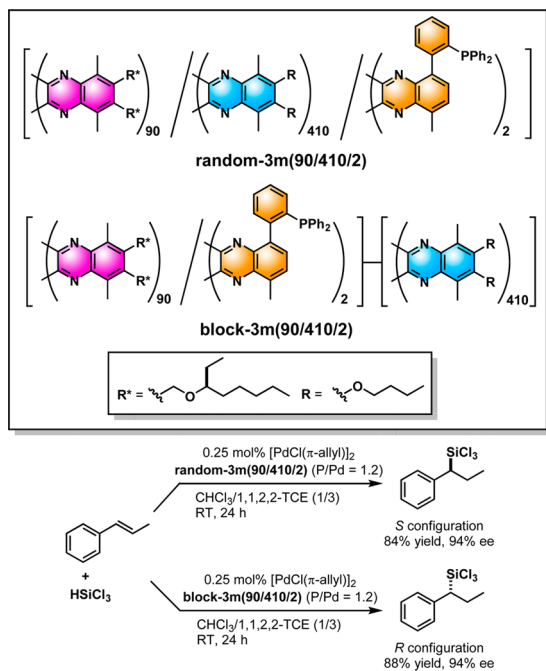
best of our knowledge, this is the first demonstration of control over the screw sense of a helical structure by way of the polymerization protocol, i.e., by using random or block copolymerization techniques.

The obtained *P*- or *M*-helical structures can furthermore be employed as chiral catalysts in, e.g., asymmetric hydrosilylation reactions. In order to demonstrate the chirality switch by the polymerization protocol, two isomeric copolymers, random copolymer **random-3m(90/410/2)** and block copolymer **block-3m(90/410/2)**, bearing 2-diphenylphosphinophenyl and (*S*)-3-octyloxymethyl groups as well as butoxy side chains were synthesized. Both copolymers were used as chiral macromolecular ligands for the Pd-catalyzed asymmetric hydrosilylation of β -methylstyrene (Scheme 1).^{10a} It should be pointed out here that in **block-3m(90/410/2)**, the coordination units are embedded in the block of the chiral monomer units.

In CHCl_3 , **random-3m(90/410/2)** and **block-3m(90/410/2)** furnished (*S*) and (*R*) enantiomers in 94% and 87% ee, respectively. Remarkably, the rather moderate enantioselectivity (87% ee) of **block-3m(90/410/2)** could be improved to 94% ee, merely by using a solvent mixture of CHCl_3 and 1,1,2,2-trichloroethane (1,1,2,2-TCE; $\text{CHCl}_3/1,1,2,2\text{-TCE} = 1/3$), while the enantioselectivity of **random-3m(90/410/2)** remained high (94% ee) in the same solvent mixture. This result, combined with CD-based solvent screenings (see SI) indicated that 1,1,2,2-TCE induces an *M*-helical conformation more efficiently in **block-3m(90/410/2)** relative to CHCl_3 . These results clearly demonstrate that almost absolute *P*- or *M*-helical structures of **random-3m(90/410/2)** and **block-3m(90/410/2)** were induced in the reaction mixture.

In summary, we have investigated the induction of a single-handed screw-sense by an “abnormal” sergeant-and-soldiers effect, where the preference for the formation of *P*- or *M*-helices by the chiral sergeant units critically depends on their immediate environment. A chirality switch of the main chain can be induced by either changing the structure of the achiral soldier units or by arranging the sergeant units through random or block polymer-

Scheme 1. Pd-Catalyzed Asymmetric Hydrosilylation of β -Methylstyrene Using random-3m(90/410/2) and block-3m(90/410/2) As Chiral Macromolecular Ligands



ization protocols, while the structure and mole fraction of the sergeant units may remain unchanged. Specifically, this system is the first example of exerting control over the helical chirality of a macromolecule by changing from random to block copolymerization protocols. Once catalytically active sites are incorporated in the copolymers, enantiomerically highly enriched products ((*S*)-product from *P*-configured random copolymer; (*R*)-product from *M*-configured block copolymer) could be obtained from the Pd-catalyzed hydrosilylation of β -methylstyrene. Again, it should be noted that the *P*-configured random copolymer-based catalyst and the *M*-configured block copolymer-based catalyst only differ in the arrangement of the chiral sergeant monomers, sharing the same composition of monomers and the same absolute configuration of the chiral sergeant unit. Further applications of these single-handed helical poly(quinoxaline-2,3-diyl)s as a new class of chiral materials are currently investigated in our laboratory, together with mechanistic studies regarding the single-handed screw-sense induction from chiral side chains.

■ 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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- (11) We supposed that chiral and achiral homopolymers have different g_{\max} values, and the copolymers have mean g_{\max} values of them depended on the composition, namely

$$g_{\max} = (x \times g_{\max}^x + y \times g_{\max}^y) / (x + y)$$
 where g_{\max}^x and g_{\max}^y are g_{\max} values of chiral and achiral homopolymers, and x and y are the number of chiral and achiral units, respectively. g_{\max}^x was converged to 2.51×10^{-3} . g_{\max}^y of **1m(x/y)** and **2m(x/y)** were converged to 2.23×10^{-3} and 2.11×10^{-3} , respectively.
- (12) Here, ΔG_h was defined as the energy difference between pure *P*- and *M*-helical structures. Because ΔG_h was defined as the energy difference between racemic and purely single-handed structures in the Sato's paper,⁵ the doubled values were shown here for clear comparison.