

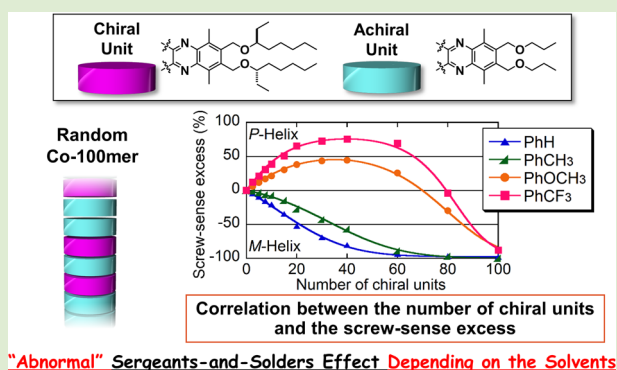
# Solvent Effect on the Sergeants-and-Soldiers Effect Leading to Bidirectional Induction of Single-Handed Helical Sense of Poly(quinoxaline-2,3-diyl)s Copolymers in Aromatic Solvents

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## S Supporting Information

**ABSTRACT:** Random poly(quinoxaline-2,3-diyl) copolymers, containing chiral (S)-3-octyloxymethyl and achiral propoxymethyl side chain units, experience an abnormal sergeants-and-soldiers effect, that is, they adopt, depending on the chiral monomer mole fraction, either *P*- or *M*-helical conformations in anisole (PhOCH<sub>3</sub>) and benzonitrile (PhCN). In benzene (PhH) and toluene (PhCH<sub>3</sub>), these copolymers exclusively adopt an *M*-helical conformation, regardless of the chiral monomer mole fraction. For a co-300mer, with a 40% mole fraction of chiral units, the selective induction of an *M*-helix (>99%) was observed in PhH, while in PhCN, a *P*-helical conformation was induced selectively (>99%). This helix inversion of the polymer backbone is thus able to control the chirality of a chiral polymer ligand in aromatic solvents. The incorporation of a small amount of coordinating PPh<sub>2</sub> groups into the copolymer resulted in a chiral macromolecular ligand, which allowed the enantioselective synthesis of both enantiomeric products in an asymmetric Suzuki–Miyaura coupling reaction (*R*-product: 91% ee in PhH; *S*-product: 95% ee in PhCN) from a single catalyst.



The sergeants-and-soldiers effect is the most important principle to control macromolecular and supramolecular helical chirality.<sup>1–3</sup> Green and co-workers reported the sergeants-and-soldiers effect in the context of the nonlinear induction of nonracemic helical conformations, which arise from the introduction of chiral and achiral side chains in copolymers. This effect is based on the accumulation of small energy differences from each chiral unit, resulting in the induction of an overall helical sense according to the Ising model.<sup>4</sup> The sergeants-and-soldiers effect could be extended to supramolecular chemistry by using the helical columnar stacks of chiral and achiral disk-shaped molecules.<sup>5</sup>

In contrast to the conventional sergeants-and-soldiers systems, some helical copolymers exhibit an “abnormal” effect of the sergeant monomer mole fraction on the induction of the helical sense.<sup>6</sup> Specifically, one of the two helical senses can be induced at low mole fractions of the chiral unit, while the other can be induced at higher mole fractions. In 2002, Sato and co-workers explained the abnormal sergeants-and-soldiers effect by using a model, in which the preference of screw-sense induction arising from a certain monomer unit depends on the monomer units in its immediate vicinity.<sup>7</sup>

Recently, we have reported that poly(quinoxaline-2,3-diyl) (PQX) can serve as a new helical macromolecular scaffold, which exhibits solvent-induced switches of its helical chirality.<sup>8</sup> We have also reported that helically chiral PQXs with

diarylphosphino pendants<sup>9</sup> can serve as effective chiral ligands in various asymmetric reactions.<sup>10,11</sup> The helical PQX scaffold could also be used to generate circularly polarized light (CPL) in the visible region, and the handedness of the CPL could be switched via a solvent-dependent helix inversion.<sup>12</sup> In one of our previous papers,<sup>13</sup> we demonstrated that random PQX copolymers, containing chiral (S)-3-octyloxymethyl and achiral *n*-butoxy groups, adopt *M*- or *P*-helical conformations in chloroform upon changing the molar ratio of chiral and achiral units. However, details of the abnormal sergeants-and-soldiers effect still remains unexploited.

In this paper, we describe the impact of the solvent on the sergeants-and-soldiers effect of helical PQX copolymers. It was found that a PQX copolymer with a particular combination of chiral and achiral units exhibited a solvent-dependent abnormal sergeants-and-soldiers effect in aromatic solvents. We also demonstrate the synthetic utility of this solvent-dependent abnormal sergeants-and-soldiers effect in a chirality-switchable asymmetric catalyst, which allows the controlled formation of both enantiomeric products with high enantioselectivity from a single catalyst.

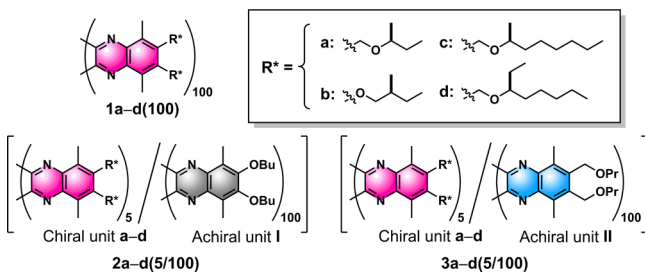
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Initially, we prepared homopolymers **1a(100)**–**1d(100)** with a degree of polymerization (DP) of 100, bearing various chiral side chains. We then measured the CD spectra of **1a(100)**–**1d(100)** in the aromatic solvents benzene (PhH), toluene (PhCH<sub>3</sub>), anisole (PhOCH<sub>3</sub>), and benzotrifluoride (PhCF<sub>3</sub>; Table 1, entries 1–4).<sup>14</sup> While **1a(100)**, **1c(100)**, and **1d(100)**

**Table 1. Structures and Screw-Sense Induction Properties for Homopolymers **1a(100)**–**1d(100)**, as Well as for Random Copolymers **2a(5/100)**–**2d(5/100)** and **3a(5/100)**–**3d(5/100)** Based on Kuhn's CD-Derived Dissymmetry Factor  $g_{\text{abs}}$**



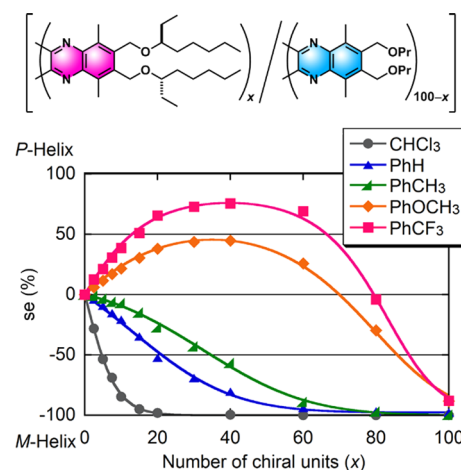
entry	polymer	relative CD intensity <sup>a</sup>			
		PhH	PhCH <sub>3</sub>	PhOCH <sub>3</sub>	PhCF <sub>3</sub>
1	<b>1a(100)</b>	−0.93 (M)	−1 (M)	−1.03 (M)	−1.01 (M)
2	<b>1b(100)</b>	+0.68 (P)	+0.69 (P)	+0.66 (P)	+0.67 (P)
3	<b>1c(100)</b>	−0.72 (M)	−0.81 (M)	−0.81 (M)	−0.78 (M)
4	<b>1d(100)</b>	−0.74 (M)	−0.85 (M)	−0.73 (M)	−0.79 (M)
5	<b>2a(5/100)</b>	−0.17 (M)	−0.10 (M)	−0.16 (M)	−0.14 (M)
6	<b>2b(5/100)</b>	+0.11 (P)	+0.11 (P)	+0.08 (P)	+0.09 (P)
7	<b>2c(5/100)</b>	−0.24 (M)	−0.17 (M)	−0.09 (M)	+0.01 (P)
8	<b>2d(5/100)</b>	+0.05 (P)	+0.07 (P)	+0.14 (P)	+0.24 (P)
9	<b>3a(5/100)</b>	−0.27 (M)	−0.22 (M)	−0.33 (M)	−0.22 (M)
10	<b>3b(5/100)</b>	+0.13 (P)	+0.11 (P)	+0.08 (P)	+0.10 (P)
11	<b>3c(5/100)</b>	−0.33 (M)	−0.27 (M)	−0.24 (M)	−0.08 (M)
12	<b>3d(5/100)</b>	−0.07 (M)	−0.04 (M)	+0.07 (P)	+0.18 (P)

<sup>a</sup>  $g_{\text{abs}}$  values ( $\Delta\epsilon/\epsilon$  at 366.0 nm,  $T = 293$  K) were normalized by the  $g_{\text{abs}}$  value of **1a(100)** (entry 1) in PhCH<sub>3</sub>, whose  $se$  was determined to be >99% in our previous report.<sup>8b</sup>

adopted *M*-helical conformations in these aromatic solvents, **1b(100)** with (*S*)-2-methylbutoxy groups adopted a *P*-helical conformation. However, none of these homopolymers exhibited a solvent-dependent helix inversion. Subsequently, we prepared random copolymers **2a(5/100)**–**2d(5/100)**, which contained achiral *n*-butoxy side chains (achiral unit I) in combination with various chiral side chains (entries 5–8). The screw-sense excess ( $se$ ) of these copolymers was relatively low on account of the low proportion of chiral units. A similar screw-sense induction behavior was observed for **2a(5/100)** and **2b(5/100)** relative to that of the corresponding homopolymers, resulting in the induction of *M*- and *P*-helical conformations, respectively. For **2d(5/100)**, a *P*-helical conformation was observed, that is, the opposite helix sense of the corresponding homopolymer **1d(100)**, which can be explained by the abnormal sergeants-and-soldiers effect caused by the mismatched structures of the chiral and achiral monomer units.<sup>7</sup> It should be noted that **2c(5/100)** adopted an *M*-helical conformation in PhH, PhCH<sub>3</sub>, and PhOCH<sub>3</sub>. The random copolymers **3a(5/100)**–**3c(5/100)**, containing various chiral and achiral propoxymethyl side chains (achiral unit II, entries 9–11), exhibited the same screw-sense induction as the

corresponding homopolymers. In contrast, **3d(5/100)** with (*S*)-3-octyloxymethyl side chains clearly displayed a solvent-dependent helix inversion in these aromatic solvents. For **3d(5/100)**, an *M*-helical conformation was observed in PhH and PhCH<sub>3</sub>, whereas an inversion of the helical sense to a *P*-helical conformation was induced in PhOCH<sub>3</sub> and PhCF<sub>3</sub>.

Subsequently, the effect of the chiral monomer mole fraction on the screw-sense induction in the random **3d** copolymers was investigated in aromatic solvents. A series of random co-100mers **3d(x/100–x)** were prepared and subjected to CD measurements (Figure 1, see SI for each spectra). The  $se$  of



**Figure 1.** Correlation between the number of chiral units  $x$  and the  $se$  of **3d(x/100–x)** (DP = 100) in aromatic solvents. All data points were calculated from experimental  $g_{\text{abs}}$  values at 366.0 nm, while the regression lines were generated from  $g_{\text{max}}$ ,  $\Delta G_{\text{h,CC}}$ ,  $\Delta G_{\text{h,CA}}$ , and  $x$  (see eqs 1 and 2). The results for CHCl<sub>3</sub> were obtained from a previous report and are added for comparison.<sup>13</sup>

these copolymers was evaluated on the basis of their CD intensities (Kuhn's dissymmetry factor  $g_{\text{abs}}$ ). As previously reported,<sup>13</sup> **3d(x/100–x)** exhibited a conventional sergeants-and-soldiers effect<sup>8</sup> and adopted *M*-helical structures in CHCl<sub>3</sub>. In PhH, however, **3d(x/100–x)** displayed a nonlinear, monotonic increase of the *M*-helical structure as a function of the increase in mole fraction of the sergeant monomer (Figure 1, blue curve), which is not in exact agreement with Green's theory.<sup>8</sup> As a result of the change in mole fraction of the chiral units, **3d(x/100–x)** exhibited a more moderate change in helix induction in PhCH<sub>3</sub> relative to PhH (Figure 1, green curve). In contrast to these solvents, abnormal relationships between the chiral monomer mole fraction and the screw sense induction were observed in PhOCH<sub>3</sub> and PhCF<sub>3</sub> (Figure 1, orange and pink curves).<sup>6</sup> There, a bidirectional induction of *P*- or *M*-helical structures was observed for sergeant unit contents below and above 70–80%.

The observed abnormal sergeants-and-soldiers effect for **3d(x/100–x)** in aromatic solvents agrees well with Sato's model<sup>7</sup> in which both the degree and the direction of the helical induction depend on the structure of the neighboring monomer units. There, different energy preferences ( $\Delta G_{\text{h}}$ ) have to be considered for the two cases, where a chiral sergeant unit is either adjacent to another chiral sergeant unit ( $\Delta G_{\text{h,CC}}$ ) or to an achiral soldier unit ( $\Delta G_{\text{h,CA}}$ ). The plot of  $se$  as a function of the number of the chiral monomer ( $x$ ) in a polymer chain with a degree of polymerization ( $n$ ) was subjected to a

nonlinear, least-squares fitting of the parameters  $\Delta G_{CC}$ ,  $\Delta G_{CA}$ , and  $g_{\max}$  using the following equations:

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

$$\Delta G_h = x \times \{x \times \Delta G_{h,CC} + (n - x) \times \Delta G_{h,CA}\}/n \quad (2)$$

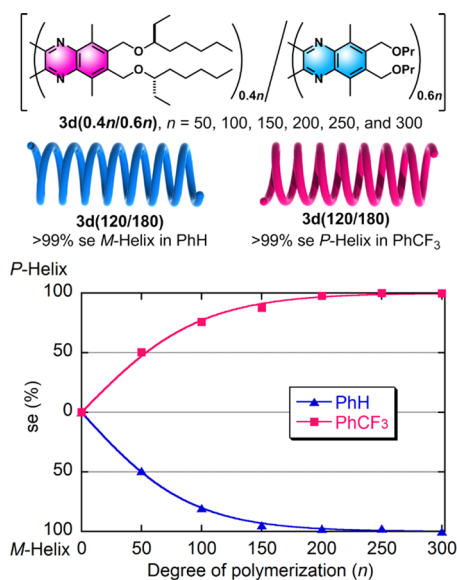
where  $R$ ,  $T$ , and  $g_{\max}$  refer to the universal gas constant ( $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ ), the operating temperature (293 K), and the  $g_{\text{abs}}$  value of the purely single-handed PQXs. The parameters could be converged successfully, affording solvent-dependent  $\Delta G_{h,CC}$  and  $\Delta G_{h,CA}$  values (Table 2). In PhH,  $3d(x/100-x)$  showed

**Table 2.**  $\Delta G_{h,CA}$  and  $\Delta G_{h,CC}$  Values for  $3d(x/100-x)$  in Aromatic Solvents

	$\Delta G_{h,CA}$ and $\Delta G_{h,CC}$ (kJ/mol)			
	PhH	PhCH <sub>3</sub>	PhOCH <sub>3</sub>	PhCF <sub>3</sub>
$\Delta G_{h,CA}$	+0.11 (M)	+0.032 (M)	−0.14 (P)	−0.25 (P)
$\Delta G_{h,CC}$	+0.22 (M)	+0.16 (M)	+0.059 (M)	+0.065 (M)

relatively large positive  $\Delta G_{h,CC}$  and  $\Delta G_{h,CA}$  values for the induction of an *M*-helix. In PhCH<sub>3</sub>, the  $\Delta G_{h,CA}$  values were found to be very small, thus, offering an explanation for the moderately changing curve described above. It should also be noted that  $3d(x/100-x)$  exhibited  $\Delta G_{h,CC}$  and  $\Delta G_{h,CA}$  values with opposite signs in PhOCH<sub>3</sub> and PhCF<sub>3</sub>.

In order to gain insight into the relationship between *se* and the degree of polymerization, copolymers with different degrees of polymerization (50–300mer) were prepared (Figure 2),



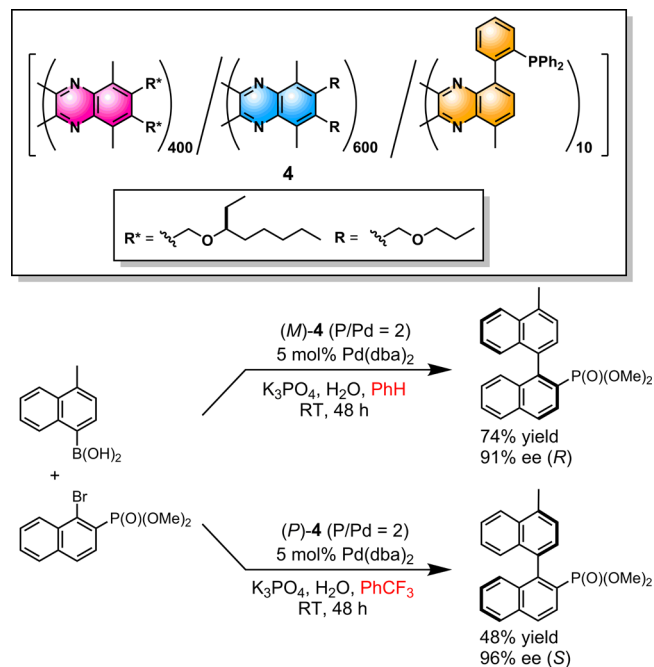
**Figure 2.** Structures for  $3d(0.4n/0.6n)$  and the correlation between their degree of polymerization and their *se* in PhH and PhCF<sub>3</sub>.

while the ratio between sergeant and soldier units was kept constant (40:60). For the corresponding 300mer  $3d(120/180)$ , *se* values of >99% were observed, resulting in the formation of selective *M*- and *P*-helical structures in PhH or PhCF<sub>3</sub>, respectively.

The switch between *P*- and *M*-helical macromolecular scaffolds, which is induced by either PhH or PhCF<sub>3</sub> can be exploited in asymmetric Suzuki–Miyaura cross coupling reactions for the generation of axially chiral biaryls.<sup>15</sup> For that

purpose, a random copolymer (**4**), bearing 2-diphenylphosphinophenyl, (*S*)-3-octyloxymethyl, and propoxymethyl side chains was prepared. Here, the smallest amount of the achiral unit bearing 2-diphenylphosphinophenyl group as possible was added to avoid its effect on the screw-sense induction. This PQX-based chiral ligand was able to afford the (*R*)-enantiomer with 91% *ee* in PhH and the (*S*)-enantiomer with 95% *ee* in PhCF<sub>3</sub> (Scheme 1). This result clearly demonstrates that single-handed *P*- or *M*-helical structures were induced in **4** in reaction mixtures containing PhH or PhCF<sub>3</sub> as a solvent.

**Scheme 1.** Asymmetric Suzuki–Miyaura Cross-Coupling Reaction in PhH or PhCF<sub>3</sub> Using **4** as a Chiral Ligand



In summary, we have demonstrated a bidirectional screw sense induction for PQX copolymers in aromatic solvents, arising from a solvent-dependent abnormal “Sergeant and Soldiers” effect. The preference of the chiral sergeant units for the formation of *P*- or *M*-helices thereby depends on their adjacent monomer units in the polymer chain. We were able to reveal that a random PQX copolymer, containing chiral (*S*)-3-octyloxymethyl and achiral propoxymethyl side chains, exhibits an abnormal “Sergeant and Soldiers” effect in anisole (PhOCH<sub>3</sub>) and benzotrifluoride (PhCF<sub>3</sub>). Based on these results, we found that a 300mer, consisting of 120 chiral and 180 achiral units, exhibited an almost perfect solvent-dependent helix inversion between benzene (PhH) and PhCF<sub>3</sub>. A random PQX copolymer, bearing 2-diphenylphosphinophenyl, (*S*)-3-octyloxymethyl, and propoxymethyl side chains could be employed as a highly enantioselective chiral ligand in an asymmetric Suzuki–Miyaura cross coupling reaction in PhH or PhCF<sub>3</sub>. The terpolymer ligand underwent solvent-dependent helix inversion between PhH and PhCF<sub>3</sub>, leading to a highly enantioselective solvent-dependent generation of both enantiomeric products. To the best of our knowledge, this represents the first example that demonstrates how the solvent-dependent sergeants-and-soldiers effect is able to induce a perfect switch of the helical chirality. Further applications of such chirality-switchable PQX polymers as novel chiral materials are currently



under investigation in our laboratory, together with mechanistic studies of the abnormal sergeants-and-soldiers effect.

## ■ ASSOCIATED CONTENT

### ■ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsmacrolett.6b00191.

Experimental procedures and spectral data for the new compounds (PDF).

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### Notes

The authors declare no competing financial interest.

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(14) In Table 1, the CD intensities are shown by relative  $g_{\text{abs}}$  values, where the  $g$  value of **1b(100)** in toluene (>99% ee) was taken arbitrarily as the standard. It should be noted that the relative  $g$  value can be viewed not as a quantitative, but as a qualitative indication of their degree of screw-sense induction, because the  $g_{\text{max}}$  values are relied with the structures of side chains and the solvent used in the measurement.

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