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On the Composition-Driven Helical Screw-Sense Inversion of Chiral−Achiral Random Copolymers

Takahiro Sato*

Department of Macromolecular Science, Osaka University,
and CREST of Japan Science and Technology,
1-1 Machikaneyama-cho, Toyonaka, Osaka 560-0043, Japan

Ken Terao† and Akio Teramoto

Research Organization of Science and Engineering and
Faculty of Science and Engineering, Ritsumeikan
University, and CREST of Japan Science and Technology,
Nojihigashi 1-1-1, Kusatsu, Siga 525-8577, Japan

Michiya Fujiki‡

NTT Basic Laboratories, NTT Corporation, and CREST of
Japan Science and Technology, 3-1 Wakamiya, Morinosato,
Atsugi, Kanagawa 243-0198, Japan

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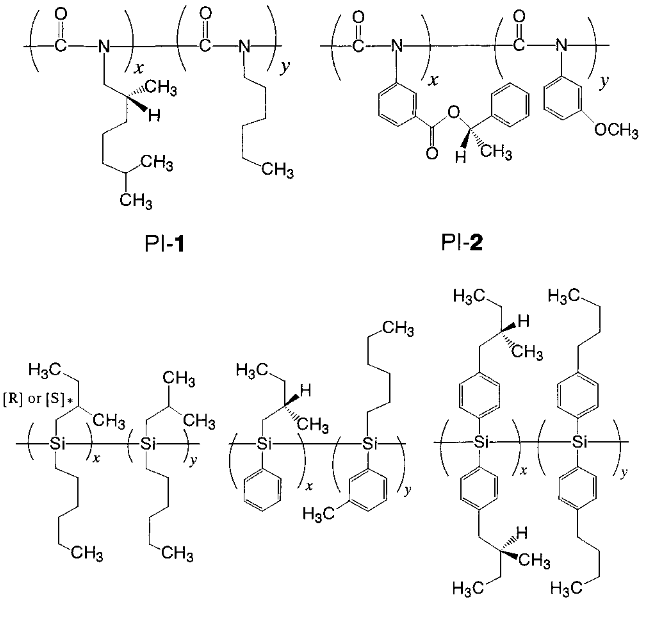
Chiral−achiral random copolymers often exhibit optical activity of varying degrees. In the sergeants-and-soldiers experiment of Green et al.,[1,2] a random copolymer of achiral (soldiers) and chiral (sergeants) isocyanate comonomers tends to take selectively the same helical sense of the chiral isocyanate comonomer. This tendency makes the copolymers optically active as strongly as the pure chiral polymer, even at a small chiral monomer content. The sergeants-and-soldiers experiment was also reported with polysilylene[3] and polyacetylene[4] copolymers, where optical activity changes monotonically with copolymer composition. Quantitatively, it has been explained in terms of the Ising model.[5−7]

However, there are some random copolymers which change their helical screw sense while changing the chiral monomer content, where the soldier may not be obedient to his sergeant.[8,9] This composition-driven helical sense inversion cannot be explained by the conventional Ising model theory applied so far to helical copolymers. In the present communication, we propose a modification of the Ising model, which is applicable to such copolymers as well, and present an analysis of the existing data.

In Scheme 1, PI-**1** is the polyisocyanate used by Green et al.[1] for the sergeants-and-soldiers experiment. We may expect that the asymmetric center on the side chain chirally interacts with the main-chain carbonyl group, which discriminates the right-handed (P) and left-handed (M) helical state to make the polyisocyanate chain to take one screw sense. On the other hand, if the chiral center on the side chain is apart from the main chain, and the chiral interaction occurs between neighboring side chains, like PI-**2** (a polyisocyanate studied by Maeda and Okamoto[8]) or PS-**3** (a polysilylene studied by Koe et al.[9]) in Scheme 1, the chiral discrimination should depend on types of the pair of interacting side chains. For chiral−achiral random copolymers, there are three different types of interacting pairs: chiral−chiral (CC), chiral−achiral (CA), and achiral−achiral (AA) pairs. Only the CC and CA pairs can contribute to the chiral discrimination in different manners. The difference in the chiral interaction between the CC and CA pairs was not considered by the conventional Ising model theory.

Scheme 1



We denote the free energy difference (per monomer unit) between the M and P helical states of a *chiral* monomer unit in the copolymer chain as $2\Delta G_{\mathrm{h,CC}}$ when the unit interacts with the preceding *chiral* monomer unit along the chain, and as $2\Delta G_{\mathrm{h,CA}}$ when it interacts with the preceding *achiral* one. On the other hand, the corresponding quantity of an *achiral* monomer unit interacting with the preceding *chiral* one is denoted as $2\Delta G_{\mathrm{h,AC}}$. The effect of the chiral interaction between the chiral monomer unit and main chain may be also included in $\Delta G_{\mathrm{h,CC}}$ and $\Delta G_{\mathrm{h,CA}}$. When $\Delta G_{\mathrm{h,CC}} = \Delta G_{\mathrm{h,CA}}$ and $\Delta G_{\mathrm{h,AC}} = \Delta G_{\mathrm{h,AA}} = 0$, our model is reduced to the conventional Ising model. If the chiral center on the side chain of the chiral monomer unit interacts only with the side chain of the preceding monomer unit, and also the head and tail of the main chain are indistinguishable, we may identify $\Delta G_{\mathrm{h,CA}}$ with $\Delta G_{\mathrm{h,AC}}$ from symmetry.

The helical-conformational partition function Z_N for our copolymer model with the degree of polymerization N can be formulated by the matrix method as employed previously.[6] The only difference is the statistical weights of the P- and M-helical states, which are written as

$$\begin{cases} u_{\mathrm{P},i(k)i(k+\nu)} = \exp(\Delta G_{\mathrm{h},i(k)i(k+\nu)}/RT) \\ u_{\mathrm{M},i(k)i(k+\nu)} = \exp(-\Delta G_{\mathrm{h},i(k)i(k+\nu)}/RT) \end{cases} \qquad (1)$$

where $i(k)$ $(1 \le k \le N)$ specifies the copolymer sequence with $i(k)$ being the chiral (C) or achiral (A) monomer units, RT is the gas constant multiplied by the absolute temperature, and we have assumed that the monomer

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† Present address: Department of Biological and Chemical Engineering, Faculty of Engineering, Gunma University, Kiryu, Gunma 376-8515, Japan.

‡ Present address: Graduate School of Materials Science, Nara Institute of Science and Technology (NAIST), 8916-5 Takayama, Ikoma, Nara 630-0101, Japan.

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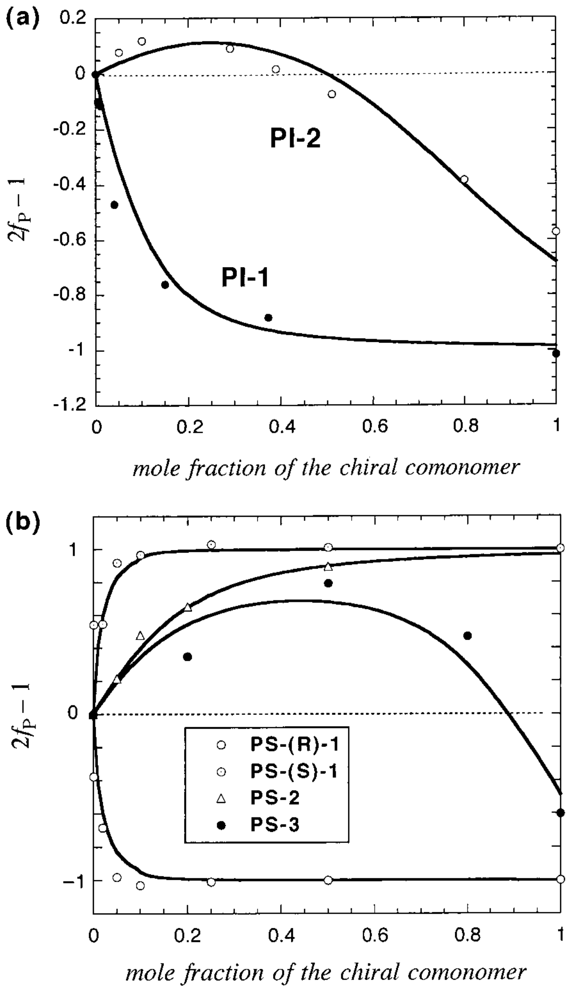

Figure 1. Composition dependence of the enantiomer excess $2f_{\mathrm{P}} - 1$ of the P state of polyisocyanate copolymers PI-**1** (in 20 °C chloroform)[1] and PI-**2** (in 25 °C tetrahydrofuran)[8] and of polysilylene copolymers PS-**1** (in −5 °C isooctane),[3] PS-**2** (in 23 °C tetrahydrofuran),[10] and PS-**3** (in −10 °C isooctane).[9] Solid curves: calculated by the modified Ising model theory.

unit k interacts with the preceding monomer unit $k - \nu$ along the copolymer chain. [If the polyisocyanate chain takes a near cis−transoid conformation, or the polysilylene chain takes a near all-trans conformation, the unit k may interact with the unit $k - 2$, i.e., $\nu = 2$.] Generating a large number of sequences of chiral−achiral random copolymers with a given N and mole fraction x of the chiral unit on a computer, we can calculate the average partition function $\langle Z_N \rangle$ numerically to obtain the fraction f_{P} of monomer units taking the P state, or the enantiomer excess $2f_{\mathrm{P}} - 1$ in the routine procedure.[6]

Figure 1 shows composition dependencies of $2f_{\mathrm{P}} - 1$ for sergeants-and-soldiers and non-sergeants-and-soldiers copolymers by circles and triangles. Here $2f_{\mathrm{P}} - 1$ was calculated from the molar rotation subtracting the contribution of the chiral side-chain molar rotation for polyisocyanate copolymers,[1,8] and from the dissymmetry ratio for polysilylene copolymers;[3,9,10] for PS-**1**, the maximum dissymmetry ratio was assumed to slightly depend on the composition. The weight-average degree of polymerization N of each copolymer (averaged over samples with different compositions) is listed in Table 1.

To compare the experimental results shown in Figure 1 with our model, we have to choose four free energy parameters, $\Delta G_{\mathrm{h,CC}}$, $\Delta G_{\mathrm{h,CA}}$, $\Delta G_{\mathrm{h,AC}}$, and ΔG_{r} for each copolymer system. We may assume that ΔG_{r} of each copolymer is identical with that of a homopolymer of the same family,[11] which was previously reported.[6,12,13] For PI-**2** and PS-**3** with the asymmetric carbon apart from the main chain, we may expect that the chiral interaction takes place only between neighboring side chains, so that we assume $\Delta G_{\mathrm{h,CA}} = \Delta G_{\mathrm{h,AC}}$. Solid curves for PI-**2** and PS-**3** in Figure 1 indicate theoretical values calculated using the modified Ising model with the free energy parameters listed in Table 1. They closely fit the experimental data exhibiting the composition-driven helical screw-sense inversion. It is noted that the inversion cannot be explained by the conventional Ising model.

Table 1. Free Energy Parameters of Polyisocyanate and Polysilylene Copolymers

copolymer	N	$\Delta G_{\mathrm{h,CC}}$^{a}	$\Delta G_{\mathrm{h,CA}} = \Delta G_{\mathrm{h,AC}}$^{a}	ΔG_{r}^{a}
PI-**1**	5000^{b}	−130	−84	11500^{6}
PI-**2**	130^{8}	−50	33	9200^{6}
PS-(*S*)-**1**	1000^{c}	330	330	12000^{13}
PS-**2**	450^{d}	330	210	8400^{12}
PS-**3**	600^{d}	−42	170	8400^{12}

[a] In units of J/mol. [b] Estimated from the viscosity-average molecular weight.[1] [c] Value of a homopolymer sample polymerized with the chiral monomer in the same procedure.[14] [d] Estimated from reported apparent molecular weights[9,10] ($M'_{\mathrm{w,PS}}$) estimated by SEC calibrated with polystyrene standard samples, using the $N - M'_{\mathrm{w,PS}}$ relation for poly[*n*-decyl-((*S*)-2-methylbutyl)silylene].[15]

On the other hand, the optical rotation behavior of PI-**1**, PS-**1**, and PS-**2**, bearing the chiral center near the main chain, may be explained by the conventional Ising model, but can be also satisfactorily described using the modified one, as shown by solid curves in Figure 1. The chiroptical data of PI-**1**, PS-**1**, and PS-**2** are not enough to uniquely determine the ΔG_{h} parameters. We can say, however, that $\Delta G_{\mathrm{h,CC}}$ and $\Delta G_{\mathrm{h,CA}}$ ($=\Delta G_{\mathrm{h,AC}}$) induce the same sense of the helical state in PI-**1**, PS-**1**, and PS-**2** copolymers, while those induce the opposite sense in PI-**2** and PS-**3** copolymers, as indicated by the signs of $\Delta G_{\mathrm{h,CC}}$ and $\Delta G_{\mathrm{h,CA}}$ (cf. Table 1). Although it is not easy to predict signs of the ΔG_{h} parameters from the side-chain chemical structures, the remoteness of the asymmetric center from the main chain may be necessary for the composition-driven helical screw-sense inversion.

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