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Helical Polymer Command Surface: Thermodriven Chiroptical Transfer and Amplification in Binary Polysilane Film System

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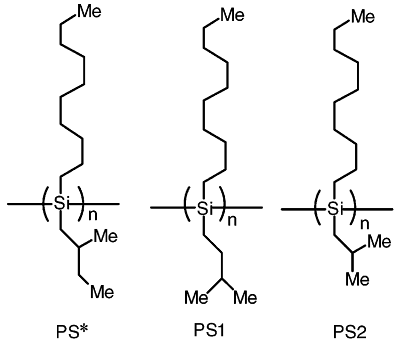
Supramolecular chirality is ubiquitous in nature, for example in DNA double helix, the triple helix of collagen, and α-helical structures of proteins. This knowledge has inspired many research groups to design well-ordered synthetic molecules, supramolecules, and polymers, which have widespread applications in the fields of molecular recognition and self-assembly,[1] asymmetric catalysis and autocatalysis,[2] chiral sensors,[3] molecular devices,[4] and polymer and material science.[5]

Helicity in synthetic polymers is induced by chiral centers present either in the backbone or in the side chains. Polymers having sterically bulky substituents with no chiral centers can adopt helical conformation with equal population of right- and left-handed screw senses.[6] However, one handedness in such polymers with a preferential screw sense is known to be achieved by the "sergeants-and-soldiers" principle, in which a very small amount of chiral monomer (ca. 1%) is randomly added during polymerization.[5b,7] The chiral monomers behave like "sergeants" which control the handedness of the "soldiers" achiral monomers. Molecular chirality into achiral polymers can also be transferred in the presence of small amount of chiral initiator/catalyst, or chiral additives.[6,8]

Scheme 1. Structures of Poly(*n*-decyl-(*S*)-2-methylbutylsilane) (PS*), Poly(*n*-decyl-3-methylbutylsilane) (PS1), and Poly(*n*-decylisobutylsilane) (PS2)



Recently, chirality transfer and amplification in polymer systems have been widely studied in aggregates and complexation of achiral polymers with chiral additives in solution.[3] However, amplification and transfer of chiral information have not been exploited in polymer solid films, which may have potential applications in chiroptical switch and memory, nonlinear optics, and data storage. Here we report a command surface type, thermodriven chiroptical transfer and amplification in optically inactive polysilane film from grafted (or spin-coated) optically active helical polysilane onto quartz substrate.

We have chosen optically active poly(n-decyl-(S)-2-methylbutylsilane) (PS*) with an almost pure P- (or M-) 7_3 helix and optically inactive poly(n-decyl-3-methylbutylsilane) (PS1) and poly(n-decylisobutylsilane) (PS2) for this study (Scheme 1). Although PS1 and PS2 have an equal population of P- and M-7_3 helices, the rigidities of PS*, PS1, and PS2 are much different. PS* and PS2, with β-branching methyl groups in the side chains, are classified into rigid rodlike polymers with a persistent length of about 70 nm, while PS1 belongs to the

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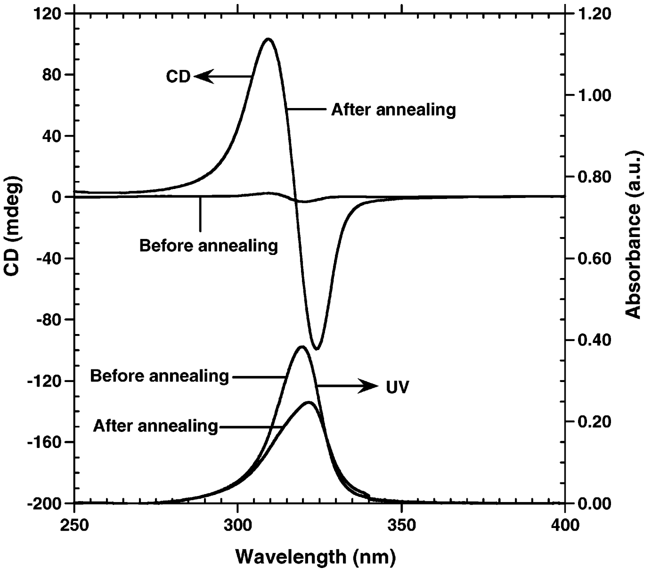

Figure 1. CD and UV spectra of PS*(g)−PS1(sc) onto quartz surface before and after annealing. The initial UV absorbance of PS* was 0.04, and the total UV absorbance of PS*(g)−PS1(sc) was 0.39.

semirigid polymer class with a persistent length of only 6 nm.[9]

All these polysilanes were prepared by conventional Wurtz condensation from their corresponding dichlorosilane monomers with sodium in the presence of 18-crown-6 catalyst and isolated by fractional precipitation from toluene solution with ethanol and/or methanol as the poor solvents.[10,11] The double layer of polysilane samples were prepared by chemically grafting or spin-coating of PS* ($M_w = 2.11 \times 10^5$, $M_w/M_n = 1.77$) onto the quartz substrate[11] (an initial intensity of UV absorbance at 320 nm was about 0.04), followed by spin-coating of PS1 ($M_w = 1.11 \times 10^5$, $M_w/M_n = 1.75$) or PS2 ($M_w = 3.36 \times 10^4$, $M_w/M_n = 1.17$) onto the PS* surface (total UV absorbance at 320 nm was adjusted between 0.39 and 1.50). We will use the terms "g" and "sc" for "chemically grafted at the surface" and "a spin-coated film onto the surface" respectively, in the following discussion. UV, circular dichroism (CD), and linear dichroism (LD) spectra were recorded simultaneously on a JASCO J-820 spectropolarimeter.

The melting point (mp) of PS1 was measured by differential scanning calorimetery (DSC). The PS1 showed a clear mp at about 40 °C in both heating and cooling cycle. However, no mp was observed for PS2 in the range −50 to +150 °C, presumably due to rigid rodlike architecture.

The CD spectra of PS*(g)−PS1(sc) and PS*(g) (which means that only PS* was grafted onto quartz surface) films were recorded before annealing (Figure 1). The spectra did not significantly affect the spectral intensity with rotation of the solid films at different angles. The samples were then annealed in a vacuum at 80 °C for 1 h and were cooled gradually to room temperature. CD and LD spectra of these samples were measured again after the thermal treatment at same angles as were before annealing.

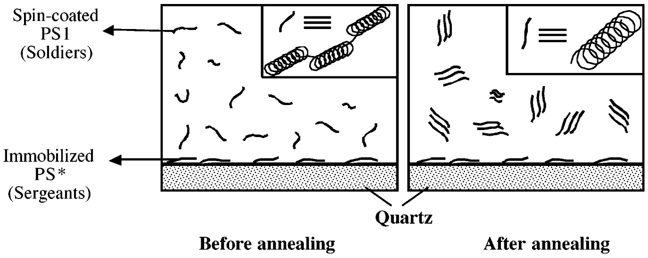

Figure 2. Schematic presentation of thermodriven chiroptical transfer and amplification in "soldier" optically inactive polysilane (PS1) from "sergeant" optically active helical polysilane on quartz.

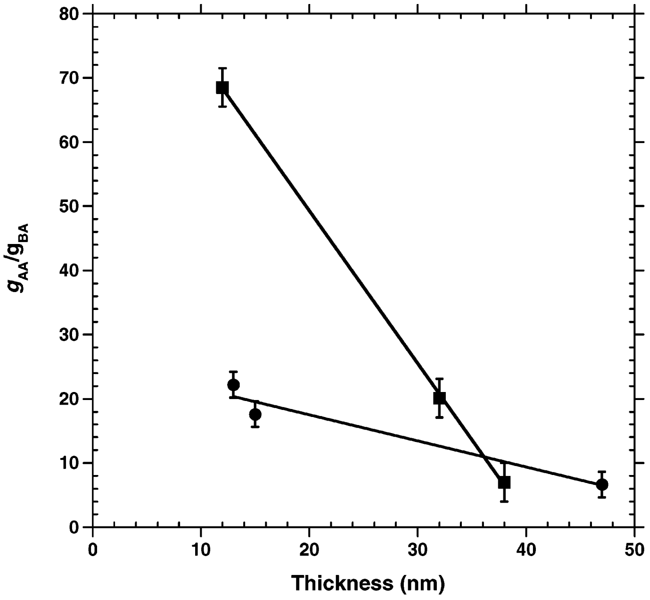

Figure 3. Relative Kuhn dissymmetry ratios of PS*(g)−PS1(sc) (filled square) and PS*(sc)−PS1(sc) (filled circle) on the quartz surface before (g_{BA}) and after annealing (g_{AA}) as a function of film thickness.

The CD spectra of PS*(g)−PS1(sc) and PS*(g) showed a bisignate CD signal with a positive-Cotton band at about 309 nm and a negative-Cotton band at about 324 nm (Figure 1), which are characteristics of the polysilane $\sigma-\sigma^*$ transition.[12] For PS*(g)−PS1(sc), both positive-Cotton CD and negative-Cotton CD intensities were greatly increased after thermal annealing. The enhancement in the CD signal intensities is believed to arise as a result of chirality transfer to PS1 either from the chiral side chain of PS* or polymer helical backbone itself and was drastically amplified after annealing. However, no significant changes of CD signal intensities were observed for only immobilized PS*(g) after annealing.

It is noted that the UV absorbance of PS*(g)−PS1(sc) sample decreased after the annealing treatment (Figure 1). Presumably, most polysilane chains may lie down before annealing in the quartz substrate plane, as the film was prepared by spin-coating technique. However, thermal annealing treatment of semirigid PS1 chains may partially orient some of the polymer chain segments perpendicularly and/or tilt to the substrate plane, leading to the decrease of the apparent UV absorbance at 321 nm, as illustrated in Figure 2.[13]

We have examined the effect of thickness of optically inactive PS1 (ranging from 10 to 50 nm) on uniformly formed thick optically active PS*(g) and/or PS*(sc) films (1−2 nm). The thickness of polysilane films was measured by atomic force microscopy. Figure 3 shows the change in relative Kuhn dissymmetry ratios ($g_{solid} = \Delta OD/OD$), after (g_{AA}) and before (g_{BA}) annealing with the film thickness. As evident, the ratios increase with the decrease in the thickness of PS1. However, the magnitude of g_{AA}/g_{BA} value was found to be much more in PS*(g) (filled square) than PS*(sc) (filled circle), presumably due to partial penetration of PS*(sc) polymer chains into the surface during spin-coating process of PS1 owing to similar solvent solubility behavior of PS* and PS1.

A tiny amount of immobilized optically active PS* could induce and amplify the optical activity in optically inactive PS1 layer by thermal treatment. Presumably, weak van der Waals interaction at the surface between these two polymers may result from the transfer and amplification of optical activity in PS1.The positional segmental movement of polymer chains in PS1 (mp = 40 °C) would easily occur, which may be responsible for the helical transfer from PS* to PS1 in the solid film state. This would be regarded as a certain "sergeants-and-soldiers" system at the solid surface.

A comparison between CD and LD spectra at different angles indicates that LD signals do not have significant influence on CD signals in PS*(sc)−PS1(sc) or PS*(g)−PS1(sc) systems (see Supporting Information). Presumably, LD signals responsible for the preferential in-plane orientation might be greatly reduced by a randomly oriented segmental movement of semirigid PS1 during the thermal annealing process.

In the case of PS*(sc)−PS2(sc) system, the optical activity transfer phenomenon was not observed. The CD signals of PS*(sc)−PS2(sc) sample were markedly influenced by LD signals (see Supporting Information). Even after a prolonged annealing time (overnight) and increased annealing temperature (as high as 150 °C), the LD influence was not reduced and could not be eliminated.

In conclusion, an optical activity of rigid rodlike polysilane, PS*(g) and PS*(sc), with a preferential helical sense, was transferred and greatly amplified to optically inactive semirigid helical PS1(sc) layer at the solid surface by thermal annealing. The choice of a proper rigidity of optically inactive helical polysilane was important for the emergence of a helical polymer command surface—"sergeants-and-soldiers" type—chiroptical amplification system in the solid film state.

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Supporting Information Available: Figures showing a comparison of CD and LD signal intensity of PS*(sc)−PS1(sc) at different angles, a comparison of CD and LD signal intensity of PS*(sc)−PS2(sc) at different angles, CD and UV spectra of PS2 and PS* spin-coated onto quartz surface before and after annealing, and a calibration plot between thickness and absorbance. This material is available free of charge via the Internet at http://pubs.acs.org.

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