

Helical-Sense Programming through Polysilane-Poly(triphenylmethyl methacrylate) Block Copolymers

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We herein report the first example of helical-sense programming through synthetic block copolymers, polysilane-*b*-poly-(triphenylmethyl methacrylate). The block copolymer has a helical poly(triphenylmethyl methacrylate) of one particular type with a right-handed helix.¹ This system can lead to a reversible one-handed helical-sense induction of the polysilane chain in the block copolymer.

In nature, the helical screw sense plays an important role in the performance of a wide variety of functions, such as molecular recognition and information storage.² Some synthetic polymers can also adopt a helical-screw conformation even in solution.³ Recently, controlling the helical structure of macromolecules has attracted a great deal of interest in chiroptical materials. Interestingly, a few polymers exhibit a helix–helix transition under appropriate stimuli, such as temperature, pH, and solvent.⁴ Since polysilanes have strong UV absorptions due to the σ – σ^* transition, which are sensitive to the conformational changes,⁵ it should be interesting to investigate the optical properties of polysilanes with helical screw sense. Indeed, it has been reported that polysilanes with chiral alkyl substituents can adopt a one-handed helical-screw conformation.⁶ It is also reported that the terminal chiral substituents can induce helicity in oligosilanes.⁷ These findings indicate that polysilane can take a stable one-handed helix sense as a result of chiral stimuli.⁸

We imagined that the helical sense of one polymer chain could induce a helical sense in another polymer chain throughout block copolymer systems in response to an external stimulus (Figure 1). Such a model would be useful as a potential information storage system, and provide chiroptical materials for switch and

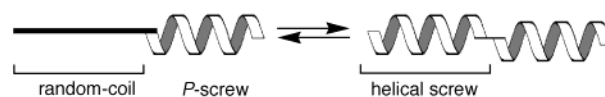
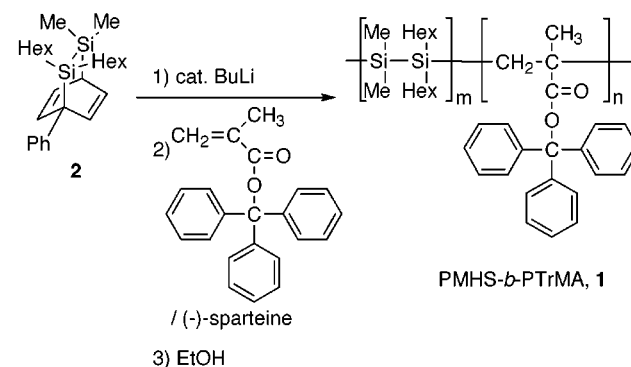


Figure 1. Schematic illustration of the helical-sense programming throughout the block copolymer with external stimuli.

Scheme 1



memory devices. Recently, several reports have addressed helical induction in copolymer systems.^{9,10} An example of helical superstructures of poly(styrene)-poly(isocyanodipeptide) block copolymers in a solvent selective for one block polymer has been reported.¹¹

Poly(1,1-dimethyl-2,2-dihexyldisilene)-*b*-poly(triphenylmethyl methacrylate) (PMHS-*b*-PTrMA, **1**) was prepared by the sequential anionic polymerization of a masked disilene **2**, as shown in Scheme 1.^{12,13} First, anionic polymerization of **2** was initiated by butyllithium in THF. After the polymerization, (–)-sparteine was added to the solution. Sparteine is well-known as a chiral amine to induce optical induction.¹ TrMA was added to the reaction mixture at -78 °C and then the polymerization was carried out for 4 h to give the block copolymer ($M_n = 1.0 \times 10^4$, $M_w/M_n = 1.5$).¹⁴ The ratio of PMHS to PTrMA, estimated by ¹H NMR, was 1/1.

Polysilanes with a long alkyl side chain exhibit unique electronic spectra depending upon their conformation, which changes with the environment, such as temperature.¹⁵ At low temperature, the polysilane main chain adopts either an *all-trans* planar conformation (dihedral angles of 180°) or a *transoid* helical

(9) An example is the screw-sense polymerization of an achiral isocyanide monomer initiated by a chiral isocyanide oligomer subsequently to give a helical polymer with the same sense as the small oligomer. Another example is that the one-handed helical sense of the polymer is determined by the major helix component. In these cases, however, the parent backbone is the same unit for the copolymers. See: (a) Takei, F.; Yanai, K.; Onitsuka, K.; Takahashi, S. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1554–1556. (b) Green, M. M.; Gareta, B. A.; Munoz, G. B.; Chang, H.; Hoke, S.; Cooks, R. G. *J. Am. Chem. Soc.* **1995**, *117*, 4181–4182. (c) Green, M. M.; Peterson, N. C.; Sato, T.; Teramoto, A.; Cook, R.; Lifson, S. *Science* **1995**, *268*, 1860–1866.

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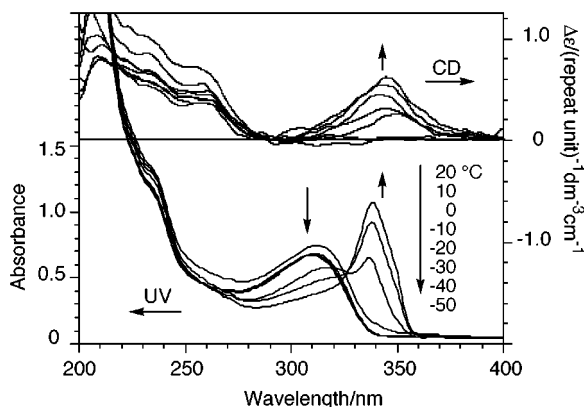


Figure 2. Temperature-dependent UV and circular dichroism (CD) spectra of the polysilane-poly(triphenylmethyl methacrylate) block copolymer **1** in THF.

conformation (dihedral angles of 165–170°).^{16,17} In the temperature-dependent UV spectra of the block copolymer, the spectroscopic features are almost the same as previously observed for PMHS homopolymer (Figure 2).^{12b} The block copolymer exhibited an absorption maximum at 310 nm at room temperature in THF, where the PMHS block adopts a random conformation. However, the block copolymer underwent an abrupt shift in the absorption maximum to 340 nm at temperatures below -20 °C, where the PMHS block adopts a *transoid* conformation.

Figure 2 also shows the temperature-dependent circular dichroism (CD) spectra¹⁸ of the block copolymer. At room temperature, the PTrMA block chain exhibited positive Cotton signals at about 210 nm, indicating that the PTrMA chain in the block copolymer adopts a one-handed helix chain.¹⁹ The PMHS of the block copolymer did not show CD signals at about 310 nm under these conditions, because the polysilane chain adopts a random-coil conformation. However, when temperatures decreased below -20 °C, a new positive Cotton signal was observed at about 340 nm and then the intensities of the signals increased with a decrease in temperature, where the PMHS chain adopts a *transoid* conformation. The screw sense of the PMHS of the block copolymer is identical with that of the PTrMA chain. In the UV spectra, no significant differences are evident. This clearly indicates that the PMHS block chain is induced to a one-handed helical sense at temperatures below -20 °C by the helix sense of the PTrMA chain of the block copolymer.²⁰

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(19) The intensity of the Cotton signals for the PTrMA units of the block copolymer is relatively low ($\Delta\epsilon/(\text{repeat unit})^{-1} \text{ dm}^3 \text{ cm}^{-1} = 0.72$ at 208 nm) compared with that of the PTrMA homopolymer prepared by the BuLi/(–)-sparteine system in toluene ($\Delta\epsilon/(\text{repeat unit})^{-1} \text{ dm}^3 \text{ cm}^{-1} = 7.5$ at 208 nm; $M_n = 6900$, $M_w/M_n = 1.09$). Under these polymerization conditions, (–)-sparteine might not coordinate effectively as a ligand to the propagation ends.

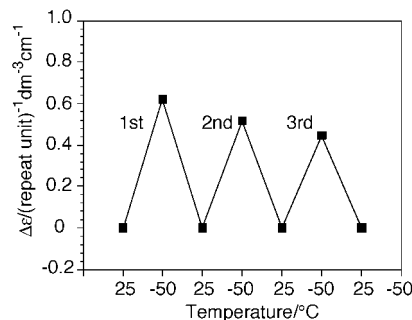


Figure 3. Temperature cycling experiment from 25 to -50 °C showing the CD spectrum intensity at 340 nm of the polysilane-poly(triphenylmethyl methacrylate) block copolymer **1** in THF.

Interestingly, this helical induction of the polysilane chain is reversible, as shown by a temperature cycling experiment (Figure 3). When the temperature changed from -50 to 25 °C, the positive Cotton signal at 340 nm disappeared, whereas the UV absorption shifted from 340 to 310 nm, identical with that previously observed. However, once the temperature was again decreased to -50 °C, the positive Cotton signal again appeared at 340 nm. Such a cycle could be repeated many times, although the intensities were reduced somewhat step by step with succeeding cycles. This indicates that the chiral information is encoded within the block copolymer.

All the features of the induced CD signals were observed independently for the solutions in concentration ranging from 10^{-4} to 10^{-3} M per Si unit,²¹ but in the absence of the chiral copolymers, the CD signals observed for the PMHS at low temperature disappeared completely. In addition, a sample of the block copolymer with a short sequence of PTrMA units ($m/n = 3$, $M_n = 1.0 \times 10^4$, $M_w/M_n = 1.5$) did not show CD signals, because at least 7 or 9 monomer units are required for forming the stable one-handed helical screw.^{1c}

Furthermore, this unique induction of the helix sense was also observed in a film of the block copolymer (see Supporting Information). The CD spectra of the film, even at room temperature, showed a positive Cotton signal at about 340 nm, where the PMHS chain adopts a *transoid* conformation probably due to the restriction of the conformational mobility.

The present system is a new approach in the field of helical expression in molecular and macromolecular systems, i.e., one-handed helical programming throughout the block copolymer.

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Supporting Information Available: Experimental procedure, thermal hysteresis of the CD signal at 340 nm, and UV and CD spectra of a film of the block copolymer (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(20) The transition at a temperature below about -20 °C for this block copolymer in solution is essentially induced by the conformational change of a single molecule, although the overall behavior of the transition is not obvious.

(21) This CD event was also observed for the toluene solutions in concentration ranging from 10^{-4} to 10^{-3} M per Si unit.