Circular Dichroism of Optically Active Poly(dialkylsilane) Aggregates in Microcapsules

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Introduction
Aggregates of some chiroptical polysilanes have significant circular dichroism (CD) and some of the CD signals are much stronger than those for fully dispersed polymers. However, it is difficult to obtain aggregates with an appropriate size for many systems. Therefore, the aggregates should be wrapped before aggregation in order not to generate too big aggregates while we investigate their optical properties, e.g. the absorption or the CD spectra. In this study, to control the size of poly(3-hexyl-1-(S)-3-methylpentylsilane) (PH3MPS) aggregates dispersed in solvent and to measure their CD spectra quantitatively, the aggregates were prepared in microcapsules after the polysilane solution were confined in the microcapsules as shown in Figure 1.

Figure 1. Schematic representation of the process to prepare aggregates in a microcapsule and chemical structures of poly(3-hexyl-1-(S)-3-methylpentylsilane).

Experimental
PH3MPS aggregates confined in poly(vinylurea-urethane) microcapsules grafted with poly-ethylene glycol to disperse in various solvents without surfactants and ranging in the polymer mass $m_p$ per a microcapsule from $2 \times 10^{-16}$ to $2 \times 10^{-15}$ g were studied by circular dichroism measurements in ethanol (a non solvent) and tetrahydrofuran (an associative solvent at low temperature) at various temperatures. The weight-averaged molecular weight and polydispersity index of the PH3MPS sample were 6.6 x 10^4 and 1.07, respectively, and the average number of polymer molecule in each capsule was estimated to be between 2,000 and 200,000. To prepare polysilane aggregates in microcapsules, an appropriate amount of the microcapsule suspension was poured into ethanol at the prepared temperature $T_0 = 20{\text{C}}$ and $T_0 = -78{\text{C}}$ or into tetrahydrofuran (THF) at $T_0 = 20{\text{C}}$. CD measurements in ethanol and THF at the measured temperature $T_{\text{m}}$ were made on a JASCO J720 spectropolarimeter at a wavelength of the incident light between 250 and 450 nm.

Results and discussion
The CD spectra of the aggregates in ethanol at different concentrations $c_p$ are shown in Figure 2. All CD spectra are similar in shape, and the differential value $\Delta CD$ between the highest CD around $\lambda = 325$ nm and the lowest CD at about $\lambda = 310$ nm are almost proportional to $c_p$ (or average polymer mass $m_p$ per microcapsule) as shown in panel (b). This result indicates that the $\Delta CD$ reflects only the average of local structures in the aggregates and the local structure is insensitive to the wall membrane of microcapsules. The value of $\Delta CD$ is about 1000 times larger than the peak height of CD spectra in isocanone solution. Moreover, the CD strength appreciably reflected the prepared temperature; in other words, the prepared condition was memorized as the local structure in aggregates and can be observed by the circular dichroism.

Figure 3 illustrates the temperature-induced aggregation-dissolution behavior in the difference $\Delta \alpha$ of the molar circular dichroism calculated by $\Delta \alpha = 370(\Delta CD/\text{deg})/c_p$. The temperature dependencies of $\Delta \alpha$ with different $c_p$ in THF are fairly fitted by a universal curve, indicating that the local structure in each aggregate is not influenced by its own size. On the other hand, it can be seen a significant hysteresis in THF between 0 and 25°C. This phenomenon suggests that the aggregate-dissociation behavior is irreversible due to the formation of interchain structure. Furthermore, $\Delta \alpha$ in THF at 0°C is much larger than that prepared in ethanol, that is calculated to be about 500 and 1500 (Si-unit) dm³ cm⁻¹ at $T_0 = 25$ and -78°C, respectively, indicating that the regularity of chiral structure in temperature-induced aggregates is obviously higher than that induced by solvent replacement.

Figure 2. (a) CD spectra for PH3MPS aggregates with indicated $c_p$ at $T_0 = -78°C$ and $T_0 = 20°C$. (b) Plots of $\Delta CD$ vs polymer concentration $c_p$ in microcapsules and average polymer mass $m_p$ per microcapsule for the same microcapsules shown in panel (a).

Figure 3. Temperature dependence of $\Delta \alpha$ for in tetrahydrofuran (an associative solvent for the polysilane at low temperature).

References