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(*n*-hexyl-(S)-3-methyl-pentylsilane) (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.

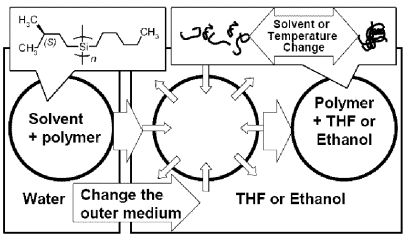

Figure 1. Schematic representation of the process to prepare aggregates in a microcapsule and chemical structures of poly(*n*-hexyl-(*S*)-3-methylpentyl silane).

Experimental

PH3MPS aggregates confined in poly(urea-urethane) microcapsules grafted with poly-ethyleneglycol to disperse in various solvents without surfactants and ranging in the polymer mass m_p per a microcapsule from 2×10^{-16} to 2×10^{-14} 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-average molecular weight and polydispersity index of the PH3MPS sample were 6.6×10^4 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_p= 20°C and T_p= -78°C or into tetrahydrofuran (THF) at T_p = 20°C. CD measurements in ethanol and THF at the *measured temperature* T_m were made on a JASCO J720 spectropolarimeter at a wavelength of the incident light between 250 and 400 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 ΔCD between the highest CD around λ = 325 nm and the lowest CD at about λ = 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 ΔCD 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 ΔCD is about 1000 times larger than the peak height of CD spectra in isooctane 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 $\Delta\Delta\varepsilon$ of the molar circular dichroism calculated by $\Delta\Delta\varepsilon = 370(\Delta CD/\mathrm{deg})/c_p$. The temperature dependencies of $\Delta\Delta\varepsilon$ 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, $\Delta\Delta\varepsilon$ in THF at 0°C is much larger than that prepared in ethanol, that is calculated to be about 500 and 1500 $(\text{Si-unit})^{-1}\text{dm}^3\text{cm}^{-1}$ at T_p = 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.

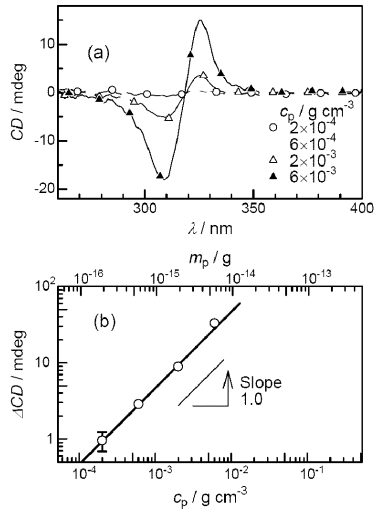

Figure 2. (a) CD spectra for PH3MPS aggregates with indicated c_p at T_p = -78°C and T_m = 20°C. (b) Plots of ΔCD vs polymer concentration c_p in microcapsules and average polymer mass m_p per microcapsule for the same microcapsules shown in panel (a).

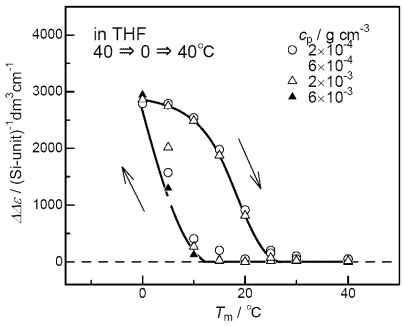

Figure 3. Temperature dependence of $\Delta\Delta\varepsilon$ for in tetrahydrofuran (an associative solvent for the polysilane at low temperature).

References

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