

Title	Circular Dichroism of Optically Active Poly(dialkylsilane) Aggregates in Microcapsules
Author(s)	Terao, Ken; Kikuchi, Noriaki; Sato, Takahiro et al.
Citation	Langmuir. 2006, 22(19), p. 7975-7980
Version Type	AM
URL	https://hdl.handle.net/11094/81828
rights	This document is the Accepted Manuscript version of a Published Work that appeared in final form in Langmuir, © American Chemical Society after peer review and technical editing by the publisher. To access the final edited and published work see https://doi.org/10.1021/la060810+ .
Note	

Osaka University Knowledge Archive : OUKA

<https://ir.library.osaka-u.ac.jp/>

Osaka University

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

Ken Terao,^{*,†,‡} Noriaki Kikuchi,[†] Takahiro Sato,[‡] Akio Teramoto,^{||} Michiya Fujiki,[§] and Toshiaki Dobashi[†]

Department of Biological and Chemical Engineering, Faculty of Engineering, Gunma University, 1-5-1 Tenjin-cho, Kiryu 376-8515, Japan; Department of Macromolecular Science, Graduate School of Science, Osaka University, 1-1 Machikaneyama-cho, Toyonaka 560-0043, Japan; Department of Applied Chemistry, Faculty of Engineering, Ritsumeikan University, 1-1-1 Nojihigashi, Kusatsu 525-8577, Japan; Graduate School of Materials Science, Nara Institute of Science and Technology, 8916-5 Takayama, Ikoma 630-0101, Japan.

* To whom correspondence should be addressed. E-mail: kterao@chem.sci.osaka-u.ac.jp (K. Terao)

† Gunma University.

‡ Osaka University.

|| Ritsumeikan University.

§ Nara Institute of Science and Technology.

Abstract: Poly(*n*-hexyl-(*S*)-3-methylpentylsilane) aggregates confined in microcapsules to keep the aggregation number and ranging in average polymer mass m_p in 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 M_w and the polydispersity index PDI (the ratio of M_w to the number-average molecular weight) of the polysilane sample were 6.6×10^4 and 1.07, respectively, and the average number of polymer molecule in each capsule was estimated to be 1.9×10^3 for $m_p = 2 \times 10^{-16}$ g and 1.7×10^5 for $m_p = 2 \times 10^{-14}$ g. The size of each aggregate did not affect the optical activity because the circular dichroism thus obtained was proportional to m_p at the same condition in the investigated m_p range; on the other hand, the peak height of the circular dichroism in tetrahydrofuran had a significant hysteresis between 0 and 25°C. Moreover, the circular dichroism appreciably reflected the prepared method, i.e. temperature and solvent; in other words, the aggregates memorized the initial condition in their stacking structures.

Introduction

The optical rotation and the circular dichroism (CD) are applied to determine the helical structure of polymer backbone for σ or π conjugate polymers, e.g. polyisocyanates^{1,2} and polysilanes^{3,4} because chiroptical effects are one of the local probes and usually insensitive to long range interactions. When two or more helical polymer chains overlap each other, that is, aggregates or thin films, it is expected that the circular dichroism is observed in terms of allocating polymer molecules anisotropically. Recently, Nakashima et al. and Koe et al.^{5,6} reported that aggregates of some poly[alkyl(alkylphenyl)]silanes bearing chiral side groups have much larger CD signal than those for molecularly dispersed system around the optical absorption band based on the Si-Si main chain, and the sign of the CD signal depends on the side chain, solvent, and/or temperature. Similar behavior was also found for chiral polythiophene aggregates.^{7,8,9}

To clarify these phenomena, the size of the aggregates should be observed for various conditions, however we have recognized only a few works reported for both the optical activity and the average size of aggregates,^{10,11,12} as some aggregates frequently grow up too quickly to control their dispersibility during measurements of optical properties. One of the representative methods to control the size of aggregates is to apply self-assembled micelles consisting of block copolymers. Indeed, optical activity of the chiral aggregates was investigated using origo-thiophenes having origo-ethyleneglycol chains on the both ends in selective solvents.^{9,13,14,15} Furthermore, Sommerdijk et al.¹⁶ and Sanji et al.^{17,18} synthesized amphiphilic block copolymers including polysilanes and showed that the local conformation observed by UV-absorption for the size-controlled polysilane aggregates in the micelle is

obviously different from the same polysilanes in molecularly dispersed systems; it is however laborious to apply the synthesis to polysilanes with chiral side chains. Recently, we developed a method to prepare size-controlled polysilane aggregates confined in poly(ethylene glycol)-grafted poly(urethane) (PUU) microcapsules as shown in Figure 1 and we reported our preliminary results that the aggregates composed of poly[*n*-hexyl-(*S*)-3-methylpentylsilane] (PH3MPS) or poly[*n*-decyl-(*S*)-2-methylbutylsilane] memorized the prepared temperature as CD signals.¹⁹ Similar behaviors were also found for thin films consisting of chiral polysilanes.²⁰ Incidentally, an advantage investigating polymer aggregates with microcapsules is that the maximum number of aggregates can be easily controlled by the polymer concentration of the solution confined in the microcapsules. However, there were few experimental evidences about the effects of the aggregation number and the wall membrane of the microcapsules, suggesting that different-sized aggregates should be investigated in the same condition. In this study, we therefore prepared PUU microcapsules confining PH3MPS solution with a variety of polymer concentrations and measured CD spectra for PH3MPS aggregates prepared in a non-solvent at different temperatures and in an associative solvent in a wide temperature range to characterize the chiroptical properties of aggregates and aggregate-dissolution behavior.

Experimental Section

Materials. The well-fractionated PH3MPS sample²¹ F62 with the weight-average molecular weight being 6.60×10^4 was dissolved in isooctane to prepare the solutions with the polymer mass concentration c_p being 2.0×10^{-4} , 6.0×10^{-4} , 2.0×10^{-3} , and 6.0×10^{-3} g cm⁻³. Takenate D120N (70-80% trimethylolpropane carbamate with hexahydroxylylene diisocyanate in ethyl acetate) gifted from Mitsui-Takeda Chemicals, Inc. was used as a wall-forming material. A poly(ethylene glycol) monomethyl ether (PEGME) sample with the molecular weight being 5000 was used as graft polymer chains on the microcapsules.

An adduct of Takenate D120N and PEGME was synthesized as follows; 40 g of Takenate D120 and 0.16 cm³ of tin(II)-2-ethylhexanoate as a catalyst were poured into PEGME solution of dried acetonitrile composed of 35 g of the polymer and 27 g of the solvent, and then the mixture was stirred for one hour at room temperature and for three hours at 50°C. To obtain microemulsion confining the polysilane solution, 1.0 g of the resultant mixture, 1.0 g of Takenate D120N, and 1 cm³ of the isooctane solution of PH3MPS F62 were added to 3.0 g of ethyl acetate, and then the resultant mixture was poured into 10 g of water and immersed vigorously for 10 min at 5000 or 15000 rpm with an emulsifier (Excel Auto, Nihon Seiki Co.) in an ice bath. Then, the interfacial polymerization of the Takenate D120N proceeded at the interface of each emulsion with stirring the suspension in a beaker at 40°C for four hours without wrapping to remove ethyl acetate and acetonitrile. The volume fraction of the polysilane-isooctane solution in the resultant aqueous suspension was estimated to be 0.081 from the feed ratio. Two series of microcapsule suspension emulsified at 5000 and 15000 rpm were designated as MC5k and MC15k, respectively.

To prepare polysilane aggregates in microcapsules, an appropriate amount (0.010 cm³ for MC15k and 0.025 cm³ for MC5k) of the microcapsule suspension which had been stored at room temperature (20°C) was poured into 10 cm³ of ethanol at the *prepared temperature* $T_p = 20^\circ\text{C}$ and $T_p = -78^\circ\text{C}$ or into tetrahydrofuran (THF) at $T_p = 20^\circ\text{C}$. It is known that the outer medium of PUU microcapsules replaces inner solvent when the inner and outer medium are miscible each other^{22,23,24,25,26,27,28} whereas polymer molecules stay in the capsule.¹⁹ The mass concentration c_{ps} of the polysilane sample per unit volume of the resulting suspension can be estimated to be $c_{ps} = 8.1 \times 10^{-5} c_p$ for MC15k and $c_{ps} = 2.03 \times 10^{-4} c_p$ for MC5k, and the contents of water and isooctane in the resulting suspension were quite small, that is about 0.08% and 0.008% for MC15k and 0.2% and 0.02% for MC5k, respectively.

Circular Dichroism (CD) Measurements. CD measurements for the microcapsules in ethanol at the *measured temperature* T_m between 10°C and 40°C and in THF at T_m between -10 and 40°C were made on a JASCO J720 spectropolarimeter combined with a Peltier temperature controller at a wavelength of the incident light between 250 and 400 nm. The scanning condition was as follows: A bandwidth of 1 nm, response of 1s, a scanning rate of 50 nm/min, and single or double accumulations.

A quartz cell with the optical pass length being 1.0 cm was used and the suspension in the cell was stirred with a magnetic stirrer during measurements. Cooling and heating rate of a cell holder was less than 10°C/min and each accumulation was begun about ten minutes after the temperature of the cell holder had stabilized. The optical shutter of the equipment was closed except during measurements to avoid decomposition of the Si-Si main chain of the polysilane sample.

Results and Discussions

Characteristics of Microcapsules Confining the Polysilane Sample. The number average outer diameter $d_{o,n}$ and the ratio d_i/d_o of inner to outer diameter for the microcapsule MC5k series were reported to be 2.0 μm and 0.9, respectively, in our previous paper.²² In addition, the $d_{o,n}$ value for the microcapsule MC15k series in water was determined to be 1.4 μm by a microscopic observation; we note that d_i/d_o is almost independent of d_o when the volume ratio of the core medium to the wall-forming material has a constant value.^{22,29} The number-average inner diameter $d_{i,n}$ was estimated to be 1.2₆ μm for MC15k and 1.8 μm for MC5k. The mass m_p and the average molecular number n_p for the polysilane sample in a microcapsule were therefore estimated to be $\pi d_{i,n}^3 c_p / 6$ and $m_p N_A / M_w$, respectively, where c_p , N_A and M_w are polysilane mass concentration of the confined isoctane solution, the Avogadro constant, and weight-average molecular weight for the polysilane sample, that is 6.6×10^4 .²¹ The obtained m_p and n_p values for each sample are summarized in Table 1.

Wavelength dependences of the differential absorption ΔA between microcapsule suspensions with and without polysilane in THF at 40°C are illustrated in Figure 2; we note that the polysilane sample is molecularly dispersed in THF at 40°C. UV spectra at other conditions we measured are fairly the same as the data shown in this figure, indicating that the dihedral angle of Si-Si main chain in aggregates molecule is not significantly different from that in solution. Whereas the extinction coefficient ϵ_{max} at the peak was determined to be 1.80×10^4 (Si-unit)⁻¹dm³cm⁻¹ for PH3MPS F62 in THF at 40°C, the apparent extinction coefficient $\epsilon_{\text{max,app}}$ of ϵ_{max} are determined from the peak height in Figure 2 to be 1.31×10^4 (Si-unit)⁻¹dm³cm⁻¹ and 3.48×10^3 (Si-unit)⁻¹dm³cm⁻¹ for MC15k and MC5k, respectively. Thus, the ratio of $\epsilon_{\text{max,app}}$ to ϵ_{max} are estimated to be 0.72₈ for MC15k and 0.19₃ for MC5k, suggesting that the MC15k sample is more suitable to obtain the absolute CD value; we note that the small $\epsilon_{\text{max,app}}/\epsilon_{\text{max}}$ value for MC5k is due to the higher turbidity of microcapsule suspension.

Aggregates in Ethanol. The CD spectra in ethanol at different concentrations c_p show a bisigned Cotton effect and are similar in shape as illustrated in Figure 3; note that the CD in this figure has been corrected with the ratio $\epsilon_{\text{max,app}}/\epsilon_{\text{max}}$. The intermediate wavelengths ≈ 320 nm of plus and minus peaks are fairly the same as those for the single peak in isoctane solution.³⁰ It is known that the bisignate CD is an aspect for chiral PH3MPS aggregates.¹⁹ Therefore, it was considered that the bisignate CD from aggregates is due to super-helical stacking of polysilane main chains,^{5,6} as the bisignate CD is a characteristic of exciton coupling between neighbor transition dipole moments in chiral configurations.³¹ While the peak height slightly decreased with rising temperature, the difference was only less than 10 % between 10 and 40°C.

To compare the strength of CD spectra on various conditions, the differential value ΔCD between the highest CD around $\lambda = 325$ nm and the lowest CD at about $\lambda = 310$ nm on each CD spectrum was introduced. The obtained ΔCD values plot against c_p and m_p in Figure 4 except for some samples with low c_p because of too small CD signals; we note that CD due to the helical structure of the main chain does not affect the total CD spectra because the peak height is calculated to be about only 0.08 mdeg for MC5k-6 and 0.03 mdeg for MC15k-6 in isoctane at 25°C.³⁰ ΔCD is almost proportional to m_p in the m_p range illustrated in Figure 4; indicating 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.

Figure 4 also shows that the differential circular dichroism ΔCD_{-78} at $T_p = -78^\circ\text{C}$ (the prepared temperature, see the experimental section) are obviously larger than that ΔCD_{20} at $T_p = 20^\circ\text{C}$ and the ratio of ΔCD_{-78} to ΔCD_{20} are estimated from the solid lines to be 3.9 and 3.1 for MC15k and MC5k,

respectively. The difference $\Delta\Delta\varepsilon$ of the molar circular dichroism, $\Delta\varepsilon$, defined by $\Delta\Delta\varepsilon = \Delta CD/33c_{ps}$ are calculated to be 335 and 85 (Si-unit) $^{-1}$ dm 3 cm $^{-1}$ for MC15k at $T_p = -78$ and 20°C , respectively. These $\Delta\Delta\varepsilon$ values are much larger than $\Delta\varepsilon = 17$ and 1.2 (Si-unit) $^{-1}$ dm 3 cm $^{-1}$ at the peak in a good solvent (isooctane) at -75 and 25°C ,³⁰ respectively; we note that the absolute ΔCD values for MC5k are about 30% smaller than those for MC15k because of difficulty to estimate $\varepsilon_{\text{app,max}}$ accurately due to the small value of $\varepsilon_{\text{max,app}}$ for MC5k. The proximity of the ratio $\Delta CD_{-78}/\Delta CD_{20}$ for the two microcapsules indicates that the ratio is not significantly affected by the difference in the size of the microcapsules. Therefore, the T_p dependence of ΔCD and the proportionality relation between ΔCD and m_p for each microcapsule suggest that T_p is memorized in the local structure in aggregates as $\Delta\Delta\varepsilon$. In addition, it seems reasonable to suppose that the larger ΔCD at lower T_p is associated with the enantiomer excess of each polymer backbone: The main chain of PH3MPS F62 at -78°C is composed of almost single-handed helix and the persistence length q of the polymer is 15 nm even at -27°C , whereas the same polymer chain at 20°C has about 13 helix reversals per molecule and lower q , that is, 6~7 nm.^{21,30} This suggestion is also supported by the following experimental results: T_p dependence of the poly[*n*-decyl-*(S)*-2-methylbutylsilane] aggregates having highly rigid main chain^{32,33} and almost single-handed screw³⁴ was appreciably weaker than that for PH3MPS.¹⁹

Aggregates in Tetrahydrofuran (THF). As CD spectra for MC15k-6 in THF illustrated in Figure 5a resemble those in ethanol, the same definition of ΔCD was introduced to discuss CD intensity in THF. The ΔCD value for MC15k in THF at 20°C has a small value, that is, 11.3 mdeg. The value of ΔCD increases gradually between 20 and 10°C with falling temperature, rapidly between 10 and 0°C , gently below 0°C , and reaches to 114 mdeg at -10°C as shown by open circles in Figure 5b. After annealed at 40°C , ΔCD illustrated in Figure 6b vanishes at the temperature higher than 10°C in the cooling process from 40°C due to dissociation of the polymer aggregate, increases extremely below 10°C , and reaches to about 240 mdeg at 0°C . The open circles for ΔCD measured every 5K from 20°C or 40°C almost corresponds to filled circles which was cooled directly from 20°C or 40°C to 0°C as shown in panels (a) and (b) in Figures 5 or 6, respectively; indicating that the cooling rate chosen for this study does not affect ΔCD of the polysilane aggregates. The difference of ΔCD at 0°C for Figures 5 and 6 will be described later.

Figure 7 shows c_p and m_p dependence of ΔCD for all samples in THF at typical temperatures on heating and cooling processes: Open and filled circles denote the data at 0°C on the first and second cooling, and filled triangles, open squares, and open triangles denote those at 20°C on first cooling (the initial condition), first heating, and second heating; we note that the temperature was changed as the following order: 20, -10, 40, 0, and 40°C . Straight lines illustrated in the figure represent the data points for each condition and have a slope of unity, indicating that $\Delta CD/m_p$ for each condition is independent of m_p . Indeed, the temperature variations of $\Delta\Delta\varepsilon$ for MC15k samples with different m_p in THF are fairly fitted by a universal curve as illustrated in Figure 8. Furthermore, from the solid lines in Figure 7a, the ratio $\Delta CD/\Delta CD_0$ of ΔCD for MC15k in THF at respective temperature to that for the initial condition (at 20°C) is determined to be 7.9 at 0°C on first cooling, 3.8 at 20°C on first heating, 20 at 0°C on second cooling, and 5.7 at 20°C on second heating. Solid lines in Figure 7b drawn to have the same $\Delta CD/\Delta CD_0$ as those for MC15k represent the data points almost quantitatively. These results confirm the above-mentioned suggestion; that is to say, the local structure in each aggregate is not influenced by the size of aggregates in the current m_p range.

Although fully temperature-reversible CD spectra was observed for molecularly dispersed PH3MPS in solution,³⁰ $\Delta\Delta\varepsilon$ in Figure 8 decreases gradually from 10°C and vanishes at about 30°C in heating process and then $\Delta\Delta\varepsilon$ vanishes even at 15°C in the second cooling process. This thermal hysteresis suggests that the aggregate-dissociation process is irreversible due to the formation of interchain structure. Similar hysteresis phenomena are also seen in some physical sol-gel transitions,^{35, 36} an aggregate-dissociation transition,³⁷ and a coil-globule transition of single molecule.^{38,39}

Each microcapsule confining F62 in THF has an unmistakable CD due to the aggregates even at the initial condition (20°C) as illustrated in Figures 5 and 8, indicating that the polymer chains are weakly aggregated. However, only a very small CD signal reflecting the helical structure of the main chain was observed for the PH3MPS F62 suspensions in THF; to prepare the suspensions, 0.01 cm³ or 0.3 cm³ of F62-isooctane solutions with the concentration being 0.001 g cm⁻³ had been added to 5 cm³ of THF at 20°C. Taking into account the no CD signal at 20°C for all investigated microcapsules annealed at 40°C, it seems that the wall membrane does not affect significantly the aggregation behavior; therefore, the following reason can be pointed out to explain the presence of ΔCD at the initial condition: The composition of water (a non solvent of PH3MPS) in microcapsule possibly became high enough to form aggregates of the polysilane during replacing solvents because the microcapsules were surrounded by water before addition to THF, and then the aggregates did not completely dissolve even in almost pure THF at 20°C. A further important point is that ΔCD at 0°C without annealing is about 0.4 times as large as that at the same temperature after annealing as shown in Figure 7. In addition, ΔCD at 0°C after annealing is much larger than that prepared in ethanol, indicating that the regularity of chiral structure in temperature-induced aggregates is higher than that induced by solvent replacement; indeed polymer-polymer interaction factors accompanying temperature variation changes usually much milder than that due to solvent exchange.

Conclusions

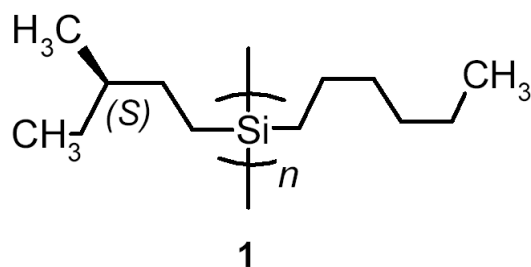
In the present study, we prepared different-sized microcapsules confining different mass of a poly(*n*-hexyl-(*S*)-3-methylpentylsilane) sample to control the aggregation number and we measured size dependence of circular dichroism for the aggregates in ethanol (a non-solvent) and in tetrahydrofuran (an associative solvent) at various temperatures. Temperature-induced aggregation-dissolution behavior shows a typical hysteresis whereas the local structure in aggregates is irrespective of polymer mass per microcapsule. Furthermore, the circular dichroism significantly depends on the prepared condition, i.e. temperature and solvent, unless the aggregates were molecularly dissolved at high temperature; in other words, the prepared condition was memorized as the local structure in aggregates and can be observed by the circular dichroism.

Acknowledgement. The authors are grateful to Dr. Kimio Ichikawa at Fuji Photo Film Co. for valuable discussions. This research was partially supported by Grant-in-Aid for Young Scientists (B) from Ministry of Education, Culture, Sports, Science, and Technology (MEXT) under grant number of 16750109.

References

- (1) Green, M. M. In *Circular Dichroism-Principles and Applications*, 2nd ed; N. Berova, K. Nakanishi, R. W. Woody Eds., Wiley-VCH: New York, 2000.
- (2) Teramoto, A. *Prog. Polym. Sci.* **2001**, *26*, 667-720.
- (3) Fujiki, M.; Koe, J. R.; Terao, K.; Sato, T.; Teramoto, A.; Watanabe, J. *Polym. J.* **2003**, *35*, 297-344.
- (4) Sato, T.; Terao, K.; Teramoto, A.; Fujiki, M. *Polymer* **2003**, *44*, 5477-5495.
- (5) Nakashima, H.; Koe, J. R.; Torimitsu, K.; Fujiki, M. *J. Am. Chem. Soc.* **2001**, *123*, 4847-4848.
- (6) Peng, W.; Motonaga, M.; Koe, J. R. *J. Am. Chem. Soc.* **2004**, *126*, 13822-13826.
- (7) Langeveld-Voss, B. M. W.; Christiaans, M. P. T.; Janssen, R. A. J.; Meijer, E. W. *Macromolecules* **1998**, *31*, 6702-6704.
- (8) Langeveld-Voss, B. M. W.; Waterval, R. J. M.; Janssen, R. A. J.; Meijer, E. W. *Macromolecules* **1999**, *32*, 227-230.
- (9) Leclere, P.; Surin, M.; Viville, P.; Lazzaroni, R.; Kilbinger, A. F. M.; Henze, O.; Feast, W. J.; Cavallini, M.; Biscarini, M.; Schenning, A. P. H. J.; Meijer, E. W. *Chem. Mater.* **2004**, *16*, 4452-4466.
- (10) Reidy, M. P.; Green, M. M. *Macromolecules* **1990**, *23*, 4225-4234.
- (11) Yue, S.; Berry, G. C.; Green, M. M. *Macromolecules* **1996**, *29*, 6175-6182.

-
- (12) Guenet, J.-M.; Jeon, H. S.; Khatri, C.; Jha, S. K.; Balsara, N. P.; Green, M. M.; Brulet, A.; Thierry, A. *Macromolecules* **1997**, *30*, 4590-4596.
- (13) Brustolin, F.; Goldoni, F.; Meijer, E. W.; Sommerdijk, N. A. J. M. *Macromolecules* **2002**, *35*, 1054-1059.
- (14) Schenning, A. P. H. J.; Kilbinger, A. F. M.; Biscarini, M.; Cavallini, M.; Cooper, H. J.; Derrick, P. J.; Feast, W. J.; Lazzaroni, R.; Leclere, Ph.; Mcdonell, L. A. J.; Meijer, E. W.; Meskers, S. C. *J. Am. Chem. Soc.* **2002**, *124*, 1269-1275.
- (15) Henze, O.; Feast, W. J.; Gardebien, F.; Jonkheijm, P.; Lazzaroni, R.; Leclere, Ph.; Meijer, E. W.; Schenning, A. P. H. J. *J. Am. Chem. Soc.* **2006**, *128*, 5923-5929.
- (16) Sommerdijk, N. A. J. M.; Holder, S. J.; Hiorns, R. C.; Jones, R. G.; Nolte, R. J. M. *Macromolecules* **2000**, *33*, 8289-8294.
- (17) Sanji, T.; Kitayama, F.; Sakurai, H. *Macromolecules* **1999**, *32*, 5718-5720.
- (18) Sanji, T.; Nakatsuka, Y.; Kitayama, F.; Sakurai, H. *Chem. Comm.* **1999**, 2201-2202.
- (19) Terao, K.; Mori, Y.; Dobashi, T.; Sato, T.; Teramoto, A.; Fujiki, M. *Langmuir* **2004**, *20*, 306-308.
- (20) Ohira, A.; Kunitake, M.; Fujiki, M.; Naito, M.; Saxena, M. *Chem. Mater.* **2004**, *16*, 3919-3923.
- (21) Terao, K.; Terao, Y.; Teramoto, A.; Nakamura, N.; Fujiki, M.; Sato, T. *Macromolecules* **2001**, *34*, 4519-4525.
- (22) Terao, K.; Ohsawa, A.; Mori, Y.; Narita, T.; Ichikawa, K.; Dobashi, T. *Colloids Surf., B* **2004**, *37*, 129-132.
- (23) Yamamoto, T.; Dobashi, T.; Kimura, M.; Chang, C. P. *Colloids Surf., B* **2002**, *25*, 305-311.
- (24) Sato, T.; Yamamoto, T.; Shibako, S.; Ichikawa, K.; Dobashi, T. *J. Membr. Sci.* **2003**, *213*, 25-31.
- (25) Chang, C. P.; Yamamoto, T.; Kimura, M.; Sato, T.; Ichikawa, K.; Dobashi, T. *J. Controlled Release* **2003**, *86*, 207-211.
- (26) Chang, C. P.; Kimura, M.; Yamamoto, T.; Nobe, M.; Dobashi, T. *Colloids Surf., B* **2003**, *30*, 123-127.
- (27) Furukawa, T.; Hung, S.; Yamamoto, T.; Terao, K.; Ichikawa, K.; Dobashi, T. *Trans. Mater. Res. Soc. Jpn.* **2003**, *28*, 989-992.
- (28) Chang, C. P.; Chang, J. C.; Ichikawa, K.; Dobashi, T. *Colloids Surf., B* **2005**, *44*, 183-186.
- (29) Dobashi, T.; Furukawa, T.; Narita, T.; Shimofure, S.; Ichikawa, K.; Chu, B. *Langmuir* **2001**, *17*, 4525-4528.
- (30) Terao, K.; Terao, Y.; Teramoto, A.; Nakamura, N.; Fujiki, M.; Sato, T. *Macromolecules* **2001**, *34*, 6519-6525.
- (31) Peeters, E.; Delmotte, A.; Janssen, R. A.; Meijer, E. W. *Adv. Mater.* **1997**, *9*, 493-496.
- (32) Fujiki, M. *J. Am. Chem. Soc.* **1996**, *118*, 7424-7425.
- (33) Natsume, T.; Wu, L.; Sato, T.; Terao, K.; Teramoto, A.; Fujiki, M. *Macromolecules* **2001**, *34*, 7899-7904.
- (34) Fujiki, M. *J. Am. Chem. Soc.* **1994**, *116*, 6017-6018.
- (35) Indovina, P. L.; Tettamanti, E.; Micciancio-Giammarinaro, M. S.; Palma, M. U. *J. Chem. Phys.* **1979**, *70*, 2841-2847.
- (36) Nishinari, K.; Koide, S.; Williams, P. A.; Phillips, G. O. *J. Phys. (Paris)* **1990**, *51*, 1759-1768.
- (37) Izumi, Y.; Takezawa, H.; Kikuta, N.; Uemura, S.; Tsutsumi, A. *Macromolecules* **1998**, *31*, 430-435.
- (38) Wu, C.; Wang, X. *Phys. Rev. Lett.* **1998**, *80*, 4092-4094.
- (39) Wang, X.; Qiu, X.; Wu, C. *Macromolecules* **1998**, *31*, 2972-2976.



Scheme 1. Chemical structure of poly[*n*-hexyl-(*S*)-3-methylpentylsilane] (PH3MPS)

Table 1. Prepared microcapsules confining PH3MPS

Series	MC15k			MC5k		
Immersed rotation / rpm	15000			5000		
Average outer diameter/ μm	1.4			2		
$c_p/10^{-3}\text{g cm}^{-3}$	Sample	$m_p/10^{-14}\text{g}$	$n_p/10^4$	Sample	$m_p/10^{-14}\text{g}$	$n_p/10^4$
0.20	MC15k-02	0.020 ₉	0.19 ₁	MC5k-02	0.061 ₁	0.55 ₇
0.60	MC15k-06	0.063 ₀	0.57 ₃	MC5k-06	0.18 ₃	1.6 ₇
2.0	MC15k-2	0.20 ₉	1.9 ₁	MC5k-2	0.61 ₁	5.5 ₇
6.0	MC15k-6	0.63 ₀	5.7 ₃	MC5k-6	1.8 ₃	16.7

Figure captions

Figure 1. Schematic representation to exchange the inner medium in microcapsules.

Figure 2. Differential UV absorption spectra for the indicated samples in tetrahydrofuran at 40°C.

Figure 3. CD spectra for MC15k prepared in ethanol at $T_p = -78^\circ\text{C}$ and measured at $T_m = 20^\circ\text{C}$. Open circles, MC15k-02; filled circles, MC15k-06; open triangles, MC15k-2; filled triangles, MC15k-6.

Figure 4. Plots of ΔCD vs polymer concentration c_p in microcapsules and average polymer mass m_p per microcapsule for (a) MC15k and (b) MC5k in ethanol at $T_m = 20^\circ\text{C}$. Open circles, $T_p = -78^\circ\text{C}$; filled circles, $T_p = 20^\circ\text{C}$.

Figure 5. Circular dichroism for MC15k-6 at $T_p = 20^\circ\text{C}$. (a) CD spectra at $T_m = 20^\circ\text{C}$ (triangles) and 0°C (stepwise cooling from 20°C , open circles; directly cooling from 20°C , filled circles). (b) ΔCD on cooling process from $T_m = 20^\circ\text{C}$ to -10°C ; the symbols are the same as those in panel (a). (c) ΔCD in multiple thermal cycles of cooling to 0°C and heating to 20°C .

Figure 6. Circular dichroism for MC15k-6 prepared at $T_p = 20^\circ\text{C}$ on cooling process from $T_m = 40$ to 0°C . (a) CD spectra at 40°C (triangles) and 0°C (stepwise cooling from 40°C , open circles; directly cooling from 40°C , filled circles). (b) Temperature dependence of ΔCD ; the symbols are the same as those in panel (a).

Figure 7. Plots of ΔCD vs average polymer concentration c_p in microcapsules and average polymer mass m_p per microcapsule for (a) MC15k and (b) MC5k in tetrahydrofuran at $T_m = 20^\circ\text{C}$ (open triangles, initial; filled triangles, first heating; open squares, second heating) and at $T_m = 0^\circ\text{C}$ (open circles, first cooling; filled circles, second cooling). Temperature was changed as the following sequences: 20, -10, 40, 0, 40°C.

Figure 8. Temperature dependence of $\Delta\Delta\varepsilon$ for MC15k-6 (filled triangles), MC15k-2 (open triangles), MC15k-06 (filled circles), and MC15k-02 (open circles) prepared at $T_p = 20^\circ\text{C}$ in tetrahydrofuran; (a) first cooling from 20°C and first heating, (b) second cooling from 40°C and heating.

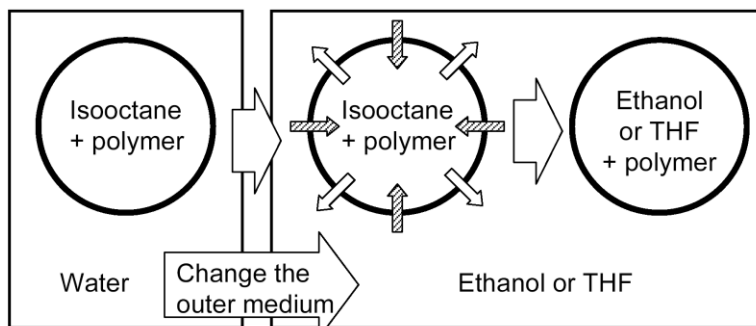


Figure 1

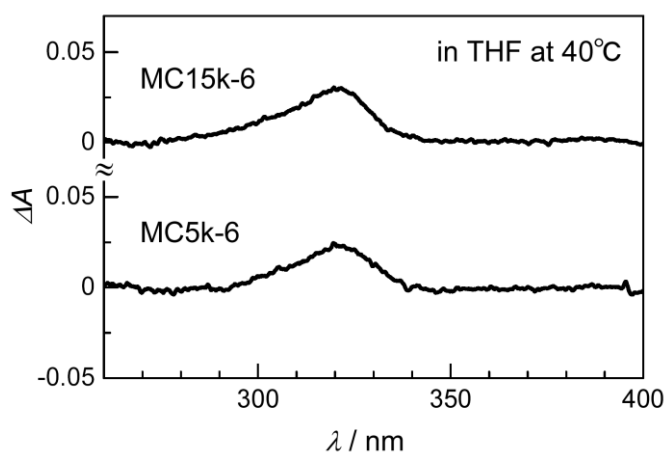


Figure 2

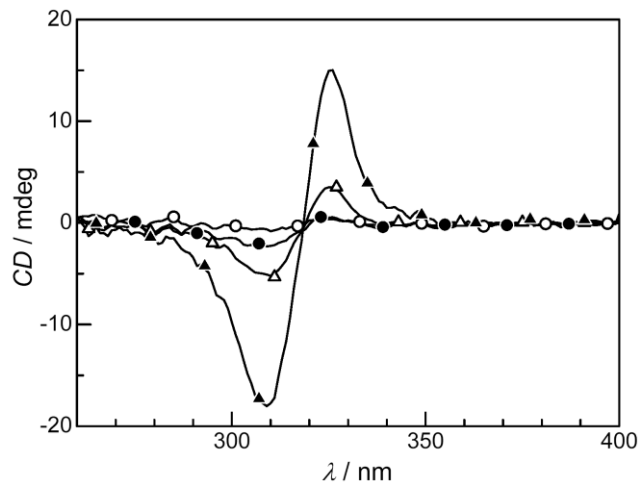


Figure 3

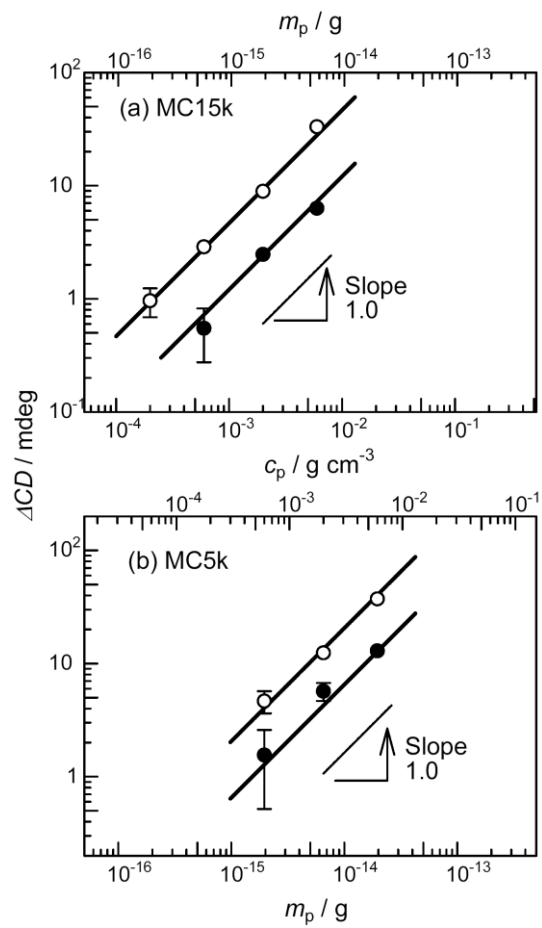


Figure 4

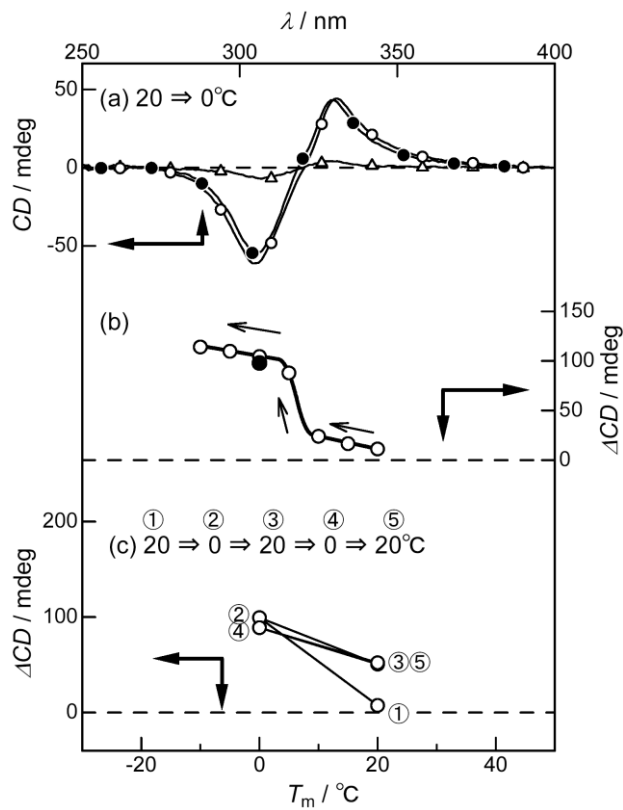


Figure 5

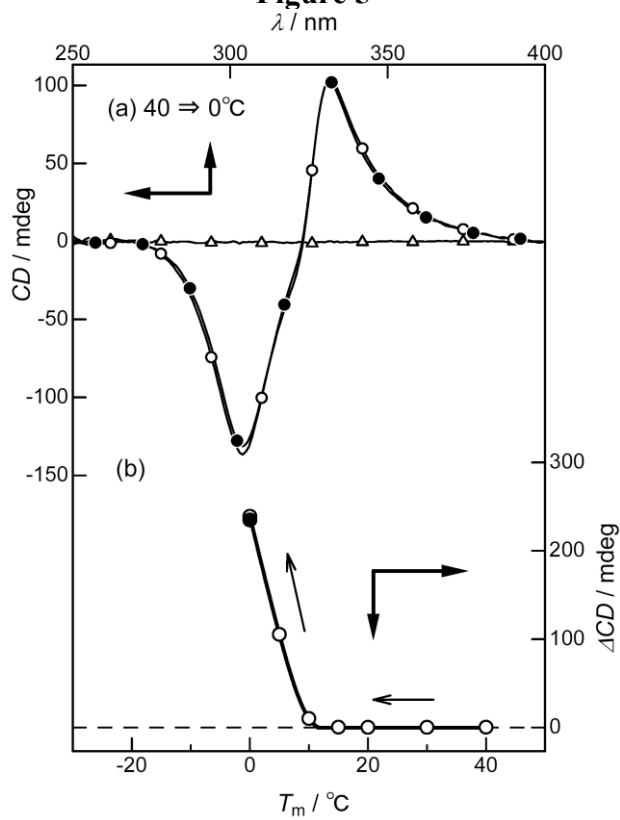


Figure 6

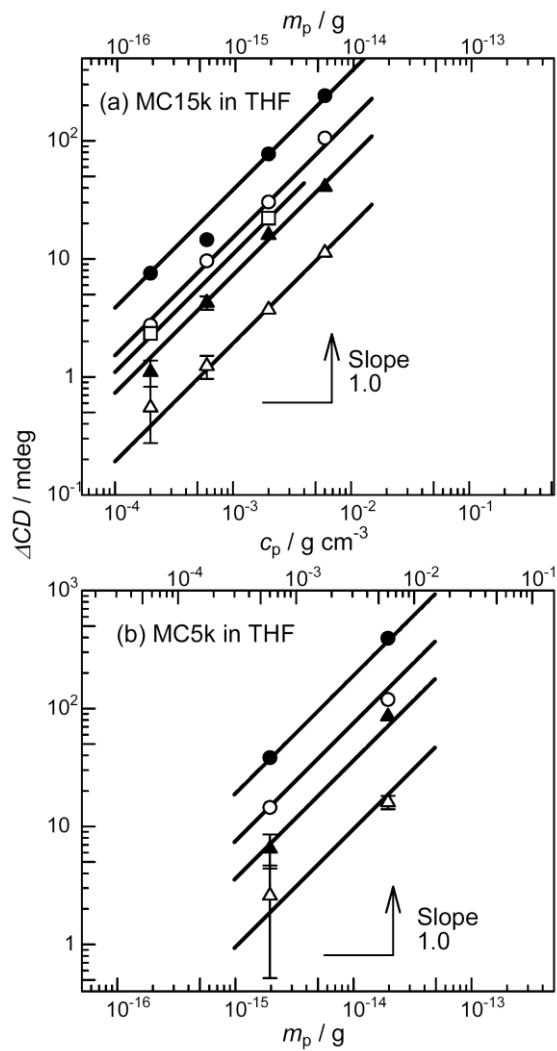


Figure 7

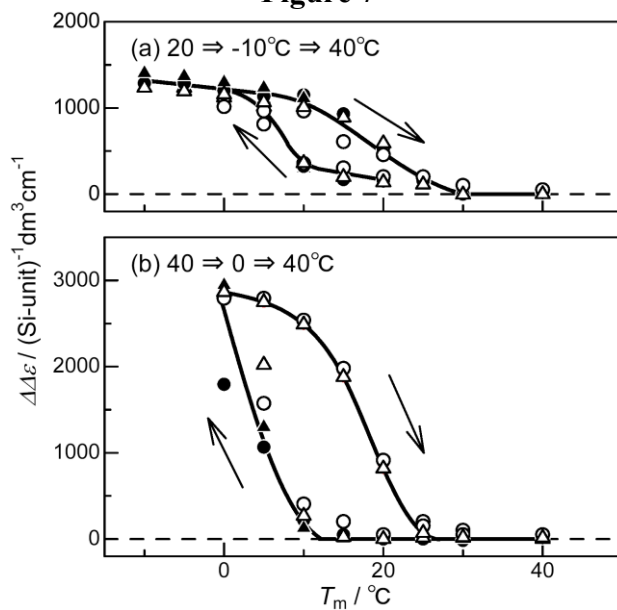


Figure 8

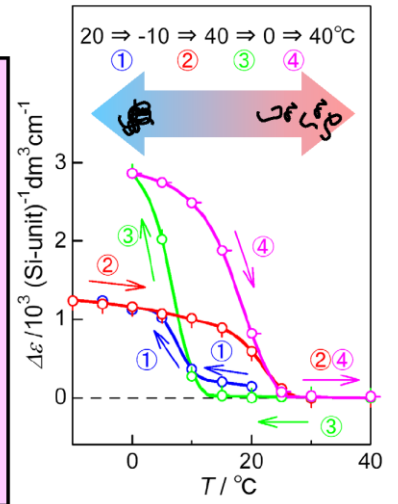
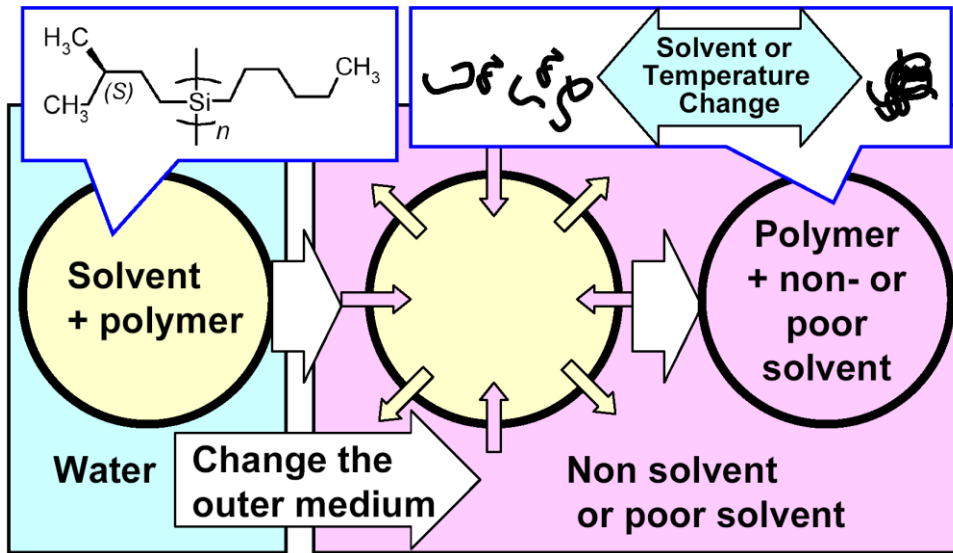


Table of Contents