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Enhancement of Discrimination Ability for *cis*- and *trans*-Decalins through Side-chain Ordering in Comb-shaped Polymer

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We propose poly(octadecyl acrylate), ODA_n as a host polymer for discriminating *cis*- and *trans*-decalins. Liquid chromatographic method enabled to detect a thermally induced change in selectivity and enhanced selectivity was achieved at lower temperature, where the side chains in ODA_n formed an ordered structure. The thermodynamic analysis for temperature-varied elution behaviors was also described.

Hydrogen is promised to be one of the clean energy sources without any emission of greenhouse gases. Cyclic saturated hydrocarbons such as decalin, methylcyclohexane, and cyclohexane were proposed as new mobile hydrogen storage media for proton exchange membrane fuel cells.[1] Hydrogen can be obtained by catalytic dehydrogenation of the cyclic saturated hydrocarbons to the corresponding aromatic compounds such as naphthalene, toluene, and benzene. In the case of hydrogen production from decalin, *cis*-isomer is more preferable because dehydrogenation rate of *cis*-decalin is faster than that of *trans*-decalin.[2] Therefore, separation of *cis*- and *trans*-decalins and/or selective hydrogenation of naphthalene to *cis*-decalin is important for improving hydrogen fuel cells. Initial step for it would be to develop a host molecule discriminating *cis*- and *trans*-decalins because of discrimination difficulty due to the non-interaction groups and similar hydrophobicity in these decalins. In this study, we first propose poly(octadecyl acrylate), ODA_n, as host polymer for discriminating *cis*- and *trans*-decalins. ODA_n is simple comb-shaped polymer but can undergo a thermally induced phase transition between ordered and disordered states.[3,4] The ordered state of ODA_n is expected to bring an enhanced selectivity, which often achieved by well-organized binding units at air–water[5] and liquid–solid interfaces.[6]

We synthesized ODA_n having a trimethoxysilyl group at one side of polymer main chain according to the previously reported method,[7] and then ODA_n was covalently grafted onto porous silica particles. (Sil–ODA_n) The discrimination ability was evaluated by the elution times of decalins in liquid chromatography using a stainless-steel column packed with Sil–ODA_n. This method is on the basis of the fact that stronger interactions cause a longer elution time and thus normalized elution time, k[8] reflects the strength of host–guest interaction. The selectivity, α is given by the ratio of ks of *cis*- and *trans*-decalins. Figure 1 shows the plots of selectivity against temperatures with Sil–ODA_{21} (average of polymerization degree: 21; amount of immobilization: 13.1 wt %)[9] and octadecylated silica, ODS.[10] ODS recognizes hydrophobicities of decalins, and thus provided low selectivity ($\alpha = 1.00$–1.03) in the temperature range of 0–60 °C. On the other hand, we first observed a thermally induced change in the selectivity for decalins by using Sil–ODA_{21}: the selectivity was almost constant at 45–60 °C ($\alpha = 1.01$) similarly to that of ODS, but the remarkable selectivity-increase was observed at temperature below 45 °C. DSC thermogram obtained for Sil–ODA_{21} in the presence of a methanol–water mixture (80/20 v/v), which was corresponding to an eluent used in liquid chromatography, showed an endothermic peak at 36 °C as a peak-top temperature (T_c) in heating process. This peak can be assigned to an ordered-to-disordered phase transition of on the basis of the results of our previous investigation using suspension-state ^{1}H NMR and ^{13}C CP/MAS NMR spectroscopies: *trans*-to-*guache* conformational change and mobility change of octadecyl side-chains.[4] Since the selectivity increase occurred around T_c, it can be concluded that the increasing selectivity with decreasing temperature is closely related to the phase transition of ODA_{21} and higher selectivity at 0–30 °C is realized by the side-chain ordering.

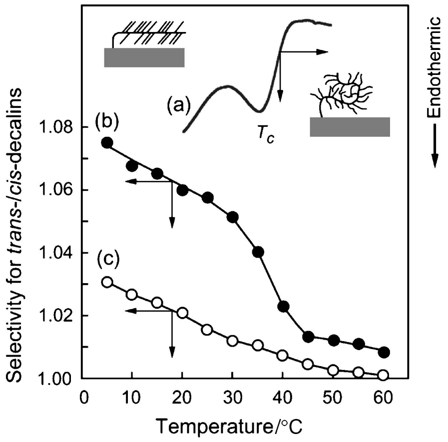

Figure 1. DSC thermogram of Sil–ODA_{21} dispersed in a mixture of methanol and water (80/20 v/v) (a) and temperature dependencies of the selectivity for *trans*-/*cis*-decalins with Sil–ODA_{21} (b) and ODS (c). The eluents were the methanol–water mixtures, 80/20 v/v for Sil–ODA_{21} and 70/30 v/v for ODS.

To understand the association between decalin and ODA_{21} at the molecular level, the temperature-varied elution behaviors were thermodynamically investigated by using van't Hoff analysis. As shown in Figure 2, no substantial change in van't Hoff plots was observed in ODS. This linear plots indicate that a change in heat capacity, ΔC_p caused by transfer of *trans*-decalin into or onto octadecyl groups is constant over that temperature range, and thus changes in enthalpy ΔH and entropy ΔS are also constant ($\Delta H = -22.0\,\mathrm{kJ\,mol^{-1}}$; $\Delta S = -51.5\,\mathrm{J\,mol^{-1}\,K^{-1}}$).[11] On the contrary, Sil–ODA_{21} provided nonlinear van't Hoff plots, which is indicative of a change in ΔC_p and is often explained by change in the association mechanism.[12] Curve-fitting of the plots in the range of 278–308 K, where the ordered-to-disordered phase transition of

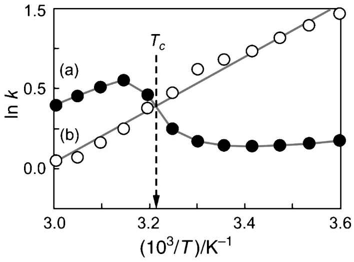

Figure 2. van't Hoff plots for *trans*-decalin with Sil–ODA_{21} (a) and ODS (b). The eluents were the methanol–water mixtures, 80/20 v/v for Sil–ODA_{21} and 70/30 v/v for ODS.

Table 1. Theromodynamic parameters for *trans*-decalin eluted with methanol–water mixture (80/20 v/v) in Sil–ODA_{21}

Temp/K	ΔH/kJ mol^{-1}	ΔS/J mol^{-1} K^{-1}	$-T\Delta S$/kJ mol^{-1}
278	−3.8	1.5	−0.4
283	−0.8	12.3	−3.5
288	−0.1	14.5	−4.2
293	0.9	18.2	−5.3
298	4.9	31.6	−9.4
303	13.6	60.4	−18.3
308	28.5	109.2	−33.6

ODA_{21} begins in the heating process, allowed to calculate the ΔH and ΔS values as summarized in Table 1.[13] The ΔH values changed from negative to positive and the positive ΔS values increased as temperature increased. This indicates that the entropic and enthalpic contributions become significant and less-significant as temperature increase, respectively. Such a tendency was also observed in the case of *cis*-decalin and can be explained by using an association model based on *interphase theory*[14] as follows. At low temperature, decalin have tight contact with side-chains in ODA_{21} (favorable ΔH) but this tight contact will be opposed by ΔS. At high temperature, decalin have a less-tight contact (less-favorable ΔH) but this process will be favored by ΔS. The result of the thermodynamic analysis leads to assume the association mechanism as shown in Figure 3. Decalins cannot rigidly incorporate into the ordered side-chains in ODA_{21} but can tightly contact on them at a temperature below T_c. A longer and planar molecule such as *trans*-decalin would provide larger contact area for the ordered side-chains than shorter and bending one such as *cis*-decalin (*shape-fit effect*), and thus substantial selectivity was observed.[15] At a temperature above T_c, decalins can incorporate into the disordered side-chains and be loosely solvated with alkyl chains. The solvations of whole molecules increase their elution times (Figure 2a) but decrease the selectivity.

In summary, we first reported the thermally induced change in selectivity for *cis*- and *trans*-decalins in the comb-shaped polymer. The substantial selectivity at lower temperature was observed and would be realized by side-chain ordering. These results should offer a useful concept for development of a host molecule not only discriminating *cis*- and *trans*-decalins but also other isomers of cyclic saturated hydrocarbons. Controlling stereoregularity of ODA_n might increase the selectivity, leading to improving a hydrogen fuel cell.

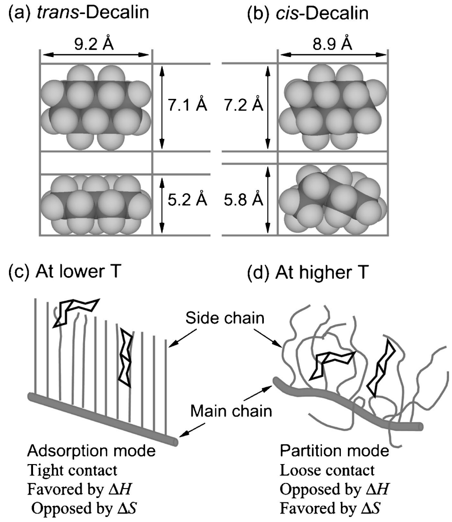

Figure 3. CPK models of *trans*- (a) and *cis*-decalins (b) estimated by HyperChem ver.5.1 with molecular mechanics and following semiempirical AM1 method. Schematic illustrations to explain the temperature dependence of the selectivity through side-chain ordering in ODA_n (c, d). If the octadecyl groups are ordered, the shape-fit effect is expected for *trans*-decalin than *cis*-decalin (c). However, such effect does not occur when ODA_n is in a disordered structure (d).

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7 ODA_n was prepared by one-step radical telomerization of octadecyl acrylate in the presence of trimethoxy(3-sulfanylpropyl)silane as a radical transfer reagent. See: H. Ihara, S. Nagaoka, H. Tanaka, S. Sakaki, C. Hirayama, *J. Liq. Chromatogr. Relat. Technol.* **1996**, *19*, 2967.

8 Liquid chromatography was carried out at a flow-rate of 0.5 mL min^{-1}. The *k* value was determined by $(t_e - t_0)/t_0$, where t_e and t_0 were elution times of decalin and void volume mark, respectively.

9 The average of polymerization degree was determined by the integral ratio between $-SiOCH_3$ and $-C(=O)OCH_2-$ peaks in ^1H NMR spectrum (in $CDCl_3$). The amount of immobilization on silica was calculated by using the C% value in elemental analysis.

10 ODS was prepared by the conventional method using chlorodimethyl-*n*-octadecylsilane (C% = 13.2%).

11 The ΔH and ΔS values were calculated from the slope and intercept in van't Hoff plot. Phase ratio of the column was determined to be 0.17 by using previously-reported method. See: ref. 12 and W. Cheng, *Anal. Chem.* **1985**, *57*, 2409.

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13 The thermodynamic parameters were calculated by curve-fitting based on a fourth degree polynomial ($r^2 = 0.9997$) using a phase ratio of 0.10, whose value was determined according to previous reported method. See: ref. 12.

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