# Enhanced Molecular-Shape Selectivity for Polyaromatic Hydrocarbons through Isotropic-to-Crystalline Phase Transition of Poly(octadecyl acrylate)

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We report temperature-triggered enhancement of molecular-shape selectivity by poly(octadecyl acrylate) which undergoes isotropic-to-crystalline phase transition. In this communication, it is also proposed that π–π interaction is included in this selective interaction and is enhanced through orientation of the carbonyl groups which are in a crystalline state.

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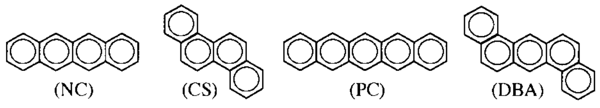
Macrocyclic structures often yield supramolecular function in host–guest chemistry. Crown ethers, cyclodextrins and calixarenes are their typical examples. Especially, it should be noted that weak interactions can be enhanced by conformational effect through the rigid structures and thus extremely large binding constants have been often realized beyond their corresponding non-cyclic compounds. However, the rigidity of cyclic structures prevents to control the function. To overcome this dilemma, many modified macrocyclic compounds have been synthesized. One of the most succeeded examples is shown in photo-sensitive crown ethers such as azobenzene-capped derivatives.[1] The binding constants against metal ions are critically changed through photo-induced trans–cis transformation of an azobenzene moiety.[1] On the other hand, we know that supramolecular functions in biosystems can be realized by inter- or intramolecular orientations of functional groups in non-cyclic polymers and this is easily controllable by external factors. From these viewpoints, we have had an interest in poly(long-chain alkyl acrylate) as a non-cyclic linear polymer because their carbonyl groups can work as π–π interaction sources to aromatic guest molecules and the polymers undergo temperature-dependent crystalline-to-isotropic phase transition.[2] In this communication, we describe that poly(octadecyl acrylate) in a crystalline state shows unique molecular-shape selectivity for polycyclic aromatic hydrocarbons and this selectivity can be controlled through the phase transition.

To evaluate the molecular recognition ability, we synthesized poly(octadecyl acrylate) with a reactive trimethoxysilyl group at one side of the terminal group according to the previously reported telomerization method.[2,3] And the polymer was grafted onto porous silica[4] and then packed into a stainless-steel column. The selectivity was evaluated by the retention time of guest molecules in the column liquid chromatography.[5]

**Table 1.** Typical retention factors (k') and separation factors (α) for aromatic hydrocarbons with Sil-ODA$_{23}$ and ODS in ethanol as a mobile phase at 5 °C



| Aromatic hydrocarbons | | Sil-ODA$_{23}$ | | | ODS | | |
|---|---|---|---|---|---|---|---|
| | | k' | α | | k' | α | |
| Naphathalene (NL) | $C_{10}H_8$ | 0.28 | | | 0.20 | | |
| | | | 1.8 | | | 2.0 | |
| Anthracene (AC) | $C_{14}H_{10}$ | 0.51 | | | 0.40 | | |
| | | | 4.6 | | | 1.6 | |
| Naphthacene (NC) | $C_{18}H_{12}$ | 2.35 | | | 0.65 | | |
| | | | | 1.8 | | | 1.03 |
| Crysene (CS) | $C_{18}H_{12}$ | 1.30 | 17.6 | | 0.63 | 1.6 | |
| Pentacene (PC) | $C_{22}H_{14}$ | 41.4 | | | 1.03 | | |
| | | | | 9.4 | | | 1.06 |
| Dibenzo[*a*,*h*]-anthracene (DBA) | $C_{22}H_{14}$ | 4.40 | | | 0.97 | | |

Table 1 summarized the retention factors (k')[5] and separation factors (α)[5] for various polyaromatic hydrocarbons with silica-supported poly(octadecyl acrylate), Sil-ODA$_{23}$ (average degree of polymerization, 23; immobilization, 19.9 wt%). All the guest molecules used are planar compounds. As a result, the slender and longer molecules such as pentacene (PC) and naphthacene (NC) show much larger retentions (k') than the corresponding bending molecules such as dibenzo[*a*,*h*]anthracene (DBA) and chrysene (CS). In general, k'-increase with increase of the number of carbon atoms is understandable by hydrophobic effect when a polar solvent is used as a mobile phase,[6,7] but it cannot explain both the extremely long retention (k' = 41.4) in pentacene and the large separation factors (α = 17.6 in $k'_{PC}$ / $k'_{NC}$ and 9.4 in $k'_{PC}$ / $k'_{DBA}$) because of the small values in simply-hydrophobized silica, ODS.[8] These abnormalities of ODA$_{23}$ can be furthermore emphasized by examining the temperature dependence. As shown in Figure 1, the α–temperature plots showed distinct bending points at temperature around 35–40 °C. For example, remarkable increase of α in $k'_{PC}$ / $k'_{DBA}$ is observed at temperature below 35 °C (α = 9.4 at 5 °C), but small and almost constant at temperature above 40 °C (α = 1.6 at 60 °C). The bending point almost agreed with the phase transition temperature between crystalline and isotropic states (a peak-top temperature, $T_c$ = 32 °C in ethanol) measured by differential scanning calorimetry. The crystallization of ODA$_n$ at temperature below $T_c$ was also confirmed by following results: (1) $\nu_{C-H}$ was detected at 2920 cm$^{-1}$ by an FTIR measurement and (2) remarkable broadening of long-chain alkyl H-signal was observed by $^1$H NMR spectroscopy with a Nanoprobe from Varian, Inc. These results indicate that the abnormal behaviors are detected only at temperature which the immobilized ODA$_{23}$ is in a highly-oriented state. As supported by this, ODS which is always in an isotropic state showed very small k' and α independent of temperature: α = 1.1–1.0 at 5–60 °C. These small values in ODS indicate that the ocatadecyl group provides small contribution to the selectivity and that the crystalline ODA$_{23}$ provides a specific binding site against long and slender compounds such as pentacene. As supported by this, the similar molecular-slenderness selectivity showing larger than those in ODS were observed in the other structural isomers between naphthacene and chrysene (dibenzo[*a*,*h*]naphthalene) and between *p*- and *m*-terphenyls: at 5 °C, $\alpha$ = 1.81 and 2.5 in Sil-ODA$_{23}$; 1.12 and 1.15 in ODS.

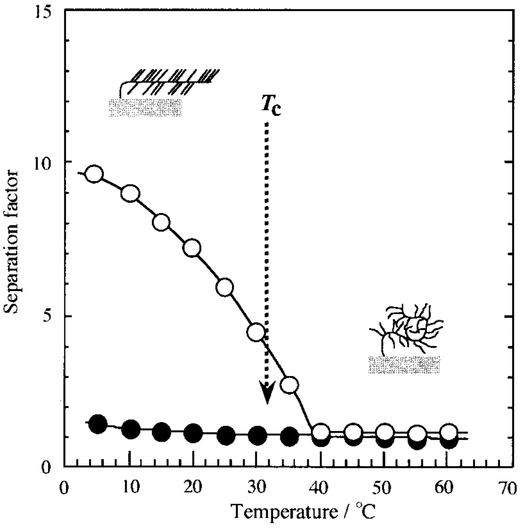


**Figure 1**. Temperature dependencies on the separation factor (the ratio of the retention factors) between pentacene (PC) and dibenzo[*a*,*h*]anthracene (DBA) with Sil-ODA$_{23}$ ( ○ ) and ODS ( ● ) column. Mobile phase: ethanol. $T_c$ shows the peak-top temperature of the immobilized ODA$_{23}$ in ethanol.

The structural difference of the organic phases between Sil-ODA$_{23}$ and ODS can be characterized by carbonyl groups in ODA$_{23}$. Therefore, the interaction between the carbonyl groups and the aromatic rings of guest molecules should be discussed. As supported by this, it was confirmed that use of acetone as a carbonyl group-including solvent reduced both the retention factor and the selectivity while 2-propanol did not effect. In addition, theoretical discussion has been done in a model system of formaldehyde–benzene complex by ab initio MO calculation optimized with the MP2/6-31G* method.[9,10] The binding energy was calculated to be 2.83 kcal mol$^{-1}$ (2.80 Å) without correction of basis set superposition error (BSSE) and 1.86 kcal mol$^{-1}$ (2.90 Å) with BSSE correction. This binding energies are significant to consider because it is greater than the CH–$\pi$ interaction in the methane-benzene complex (0.57 kcal mol$^{-1}$) [10] and in a similar extent to the $\pi$–$\pi$ interaction in the benzene–benzene complex (0.49 and 1.78 kcal mol$^{-1}$ in the plane-to-plane and plane-to-edge stackings, respectively).[10]

In conclusion, we have shown a distinct molecular-shape recognition against polyaromatic hydrocarbons by crystalline polymer. Also we have described that this is through a carbonyl–$\pi$ interaction and that the recognition ability is extremely enhanced by the molecular orientation of the polymer. The carbonyl–$\pi$ interaction is not yet directly detected although we have tried to do it with NMR spectroscopies. However, it is supported by the facts that the selectivity reduced remarkably by addition of a carbonyl group-containing solvent such as acetone and that the theoretical calculation of a carbonyl–benzene $\pi$ interaction shows comparably large binding energy compared to a benzene $\pi$–benzene $\pi$ interaction. On the basis of these results and estimations, we wish to propose the multiple carbonyl–$\pi$ interactions to understand the molecular-slenderness recognition. This is explained with Figure 2: (1) ODA$_n$ includes a crystalline phase at temperature below $T_c$ to be rigid and compact. (2) A guest molecule cannot be incorporated into the crystalline ODA$_n$ but interacts at the surface. This is like an adsorption phenomenon and supported by the fact that the remarkable decrease of k' was observed below $T_c$. (3) Probably, the crystallization of ODA$_n$ is accompanied by the orientation of some of the carbonyl groups. These carbonyl groups can interact more effectively with aromatic $\pi$-electrons in linear and planar compounds (Figure 2a) than in cubic or bending compounds (Figure 2b) because the interaction ability would be dominated by the contact area between host–guest molecules. (4) On the other hand, ODA$_n$ should be in an isotropic state and the carbonyl groups are not oriented. A guest molecule can be incorporated into the polymer as shown in Figure 2c. This causes an increase of the retention but a decrease of the selectivity.

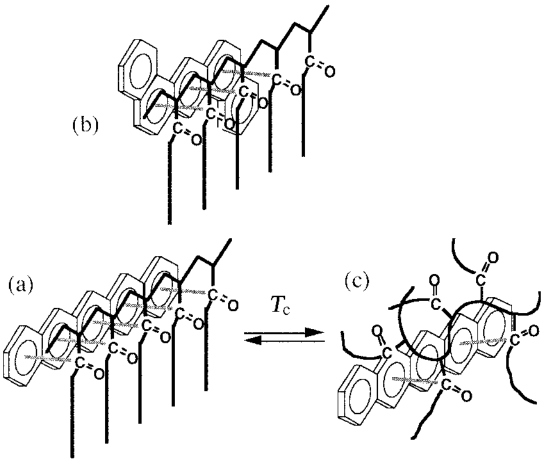


**Figure 2**. Schematic illustration to explain the temperature dependence of moleular-linearity recognition through carbonyl–$\pi$ interaction. If the carbonyl groups are linearly-aligned on highly-oriented structure (a), multiple interaction effect will be expected for a linear and planar substance such as pentacene (a) than dibenzo[*a*,*h*]anthracene (b). Howewrver, no such effect occurs when ODA$_n$ is disordered (c).

### References and Notes

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4 YMC 120-S5 (diameter 5 µm, pore size 120 Å, specific surface area 300 cm$^2$ g$^{-1}$) were used as porous silica.
5 The chromatograph included a JASCO 880 PU pump, a Waters 996 UV–visible photodiode array detector. Five µL of the sample dissolved in methanol was injected through a Reodyne Model 7125 injector. Chromatography was carried out at flow-rate 0.5 or 1.0 mL min$^{-1}$. The retention factor (k') was determined by (t$_e$ – t$_o$) / t$_o$, where t$_e$ and t$_o$ are retention time of samples and methanol, respectively. The separation factor ($\alpha$) was given by the ratio of retention factor.
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