Detection of Potential Molecular Recognition Ability in Linear Poly(methyl acylate)

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Linear poly(methyl acrylate) was immobilized onto silica gels at the one side of the terminal group. The silica-supported polymer showed good selective retention for polycyclic compounds and seems to recognize the π-electron and molecular shape. Comparison with long-chain alkyl acrylate polymer is also described.

We have been recognizing that not only strong interactions such as ionic and hydrogen bonding interactions, but also weak interactions such as π-π* interaction are very important factors for selective binding. Therefore many compounds having π-electronic groups seem to be able to act as host molecules in host-guest chemistry, but they have been often neglected in this field. The reason is that it is difficult to detect affinity for selective binding because the interaction force is very small. For example, nobody expects a simple polymer such as poly(methyl acrylate) to behave as a host molecule, in spite of the fact that it is a π-electron-rich compound. In this communication, we report that unique selectivity can be produced between poly(methyl acrylate) and polycyclic compounds with π-electrons and can be detected by investigating liquid chromatographic retention behavior.

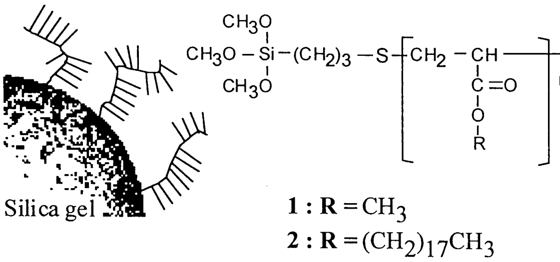


Figure 1. Schematic illustration of silica-supported poly (alkyl acrylate)s and their chemical structures.

Poly(methyl acrylate), **1** with a trimethoxysilyl group at the one side of the terminal group was prepared by telomerization of methyl acrylate with 3-mercaptopropyl-trimethoxysilane in ethanol according to previously reported method.[1-3] Similarly, poly(octadecyl acrylate), **2** was prepared using octadecyl acrylate. The degrees of polymerization (DP) were determined by ^{1}H-NMR and confirmed by size exclusion chromatography in tetrahydrofurane. ^{1}H-NMR spectroscopy[4] showed that the DPs of the polymers **1** and **2** were estimated to be 21 and 27, respectively. The polymers were readily immobilized onto porous silica gels (YMC 120-S5, diameter 5 μm, pore size 120 Å, specific surface area 300 cm^2g^{-1}, bonded phase 14.0 wt-%) by mixing in tetrachloromethane at reflux temperature (12 h). Successive washing of the resulting gels with chloroform showed no change in weight. The amount of **1** and **2** introduced were determined as 21.3 wt-% and 20.6 wt-%, respectively, by elemental analysis.

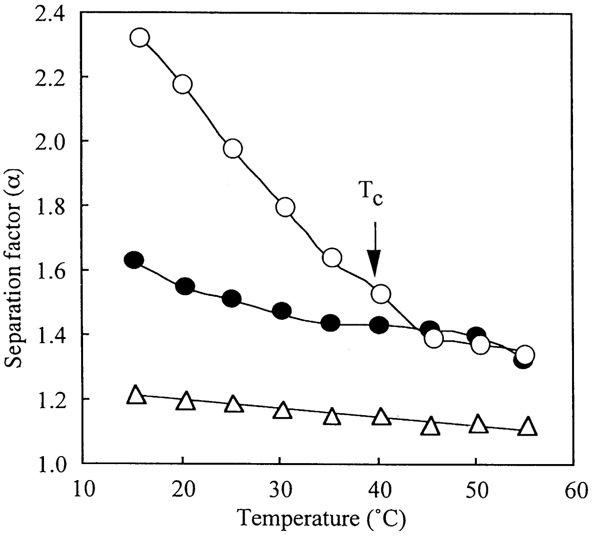


Figure 2. Temperature dependencies of separation factor (α) between *cis*- and *trans*-stilbenes with Sil-**2** (○), Sil-**1** (●) and ODS (△) columns. Mobile phase: methanol-water (7 : 3).

The polymer-immobilized silica gels (abbreviated as Sil-**1** and Sil-**2**, respectively) were packed into stainless-steel columns (4.6 mm I.D. x 250 mm) and retention behaviors for various aromatic compounds using aqueous solutions as mobile phases were investigated. Figure 2 shows the temperature dependency of separation factor (α) between *cis*- and *trans*-stilbenes on the columns packed with Sil-**1**, Sil-**2** and simply-hydrophobized silica (ODS[5]) gels. As shown in Figure 2, ODS provided a very small separation factor (below 1.2) regardless of temperature. On the contrary, Sil-**2** showed both a high separation factor and remarkable temperature dependence (α values lie in about 2.4 - 1.4 at temperature 15 - 55 °C). Similar specific retention behaviors were observed in the chromatographic separation for the geometrical isomers of 1,2-bis(phenylsulphonyl)ethylene. These differences can be explained by the fact that the immobilized polymer **2** undergoes phase transition and can form highly-oriented structures like crystal on silica gels.[6] Therefore, in the case of Sil-**2** the separation factor increases with the transition from isotropic to crystal states, but ODS does not provide such highly-oriented structure. However, it should be noted that Sil-**2** provides an even higher separation factor at isotropic state temperature (α = 1.38 at 55 °C) than that of ODS (α = 1.14 at 55 °C). This indicates that the good separation factor observed in Sil-**2** is reinforced by complementary interaction. This answer is clearly supposed by following results: (1) the Sil-**1** without highly-oriented groups shows higher separation factor at all measurement temperatures than ODS. (2) The separation factor for Sil-**1** at 55 °C is very closed to that for Sil-**2**. (3) When acetone was added to a mobile phase, the separation factor for Sil-**1** decreased with increase of the

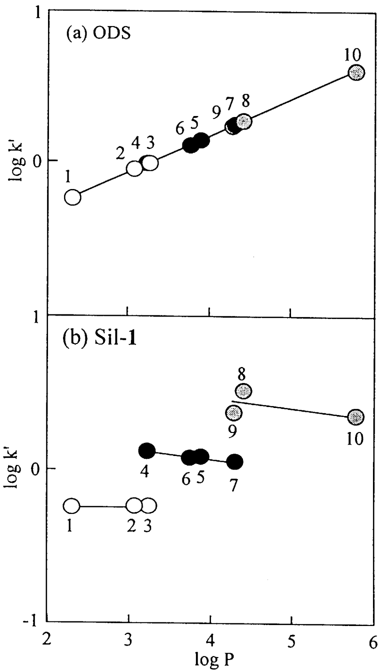
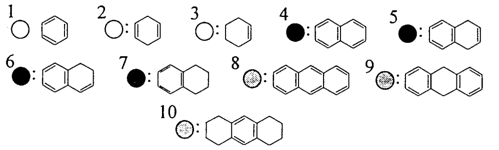


Figure 3. Relationship between log k' and log P with ODS (a) and Sil-**1** (b). Mobile phases: methanol-water (a, 9 : 1). methanol-water (b, 7 : 3).



content of acetone (α = 1.61, 1.49, 1.41 and 1.31 at 0, 5, 10 and 20 vol-%, respectively). When 2-propanol was used instead of acetone, no such decrease was observed. These results show that a good separation factor for stilbene isomers is induced by carbonyl groups included in polymers **1** and **2**. According to calculation of the energy level of the HOMO,[7,8] the *trans*-isomer is more electron-donating (-8.63 eV) than the *cis*-isomer (-9.06 eV). Therefore, it is estimated that the carbonyl carbon acts as an electron-accepting group. A similar interaction between benzene and formic acid was calculated by Bredás and Street.[9] Supporting this, geometrical isomers of 1,4-dichlorobutene and 2-hexenol having non-conjugating substituent group provide no significant difference in the energy level of the HOMO and in these cases Sil-**1** and -**2** showed a small selectivity for retention of these isomers independent of temperature.

The unique retention behavior of Sil-**1** is emphasized when compared with the retention behavior for polycyclic compounds. As shown in Figure 3-a, the retention capacity in ODS shows good linearity in the log k' - log P plots.[10] Sil-**2** provided a similar linearity with some deviation. These results indicate that long-chain alkyl groups in Sil-**2** and ODS play an important role for recognition of molecular hydrophobicity of samples. On the other hand, Sil-**1** showed many unique results in the plots: although we would expect the retention capacity to be related to π-electron density because of the small hydrophobicity, Figure 3-b seems to show that Sil-**1** instead recognizes the molecular size (the number of the ring). However, this specificity is unpredictable, and its mechanism is not yet specified. It may be necessary to consider the steric factor derived from the main chain.

In conclusion, we have described that specific selectivity is detectable in a simple polymer such as poly(methyl acrylate). This success was brought both by immobilizing polymer onto carrier with few perturbation and evaluating interaction as retention behavior.

References and Notes

1 C. Hirayama, H. Ihara, and T. Mukai, *Macromol.*, **25**, 6357 (1992).
2 H. Ihara, T. Fukumoto, and C. Hirayama, *Anal. Sci.*, **9**, 711 (1993).
3 T. Fukumoto, H. Ihara, S. Sakaki, H. Shosenji, and C. Hirayama, *J. Chromatogr.*, **672**, 237 (1994).
4 ^{1}H-NMR chemical shifts of 1 and 2 in $CDCl_3$ were follows: δ = 0.75 ppm ($SiCH_2$), δ = 2.35 ppm ($CHCO$), δ = 3.58 ppm ($SiOCH_3$), and δ = 4.15 ppm ($C(=O)OCH_2$).
5 Octadecylated silica gels from G. L. Sciences, Co. Ltd., (4.6 mm I.D. x 300 mm) was used.
6 DSC showed that silica-supported **2** provided an endothermic peak at temperature between about 28 and 46 °C (the peak-top temperature, T_c is near 40 °C) in a methanol-water (7 : 3) suspension. Porlarization microscopic observation indicated that the phase transition included that from crystalline to isotropic states. No similar phase transition was observed in silica-supported **1** and ODS.
7 Calculation of energy level of HOMO was carried out with a MATERIA (MOPAC 6.00 with PM3 option)[8] of Teijin System Technology (Japan).
8 J. J. P. Stewart, *J. Comp. Chem.*, **10**, 221 (1989).
9 J. L. Bredás and G. B. Street, *J. Chem. Phys.*, **90**, 7291 (1989).
10 log k' and log P values correspond to the retention capacity and the 1-ocatanol-water partition coefficient, respectively.