NOTES

# Immobilization of Highly-Oriented Perfluoroalkyl Polymers onto Porous Silica Gels for High Performance Liquid Chromatography

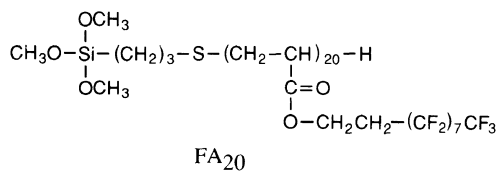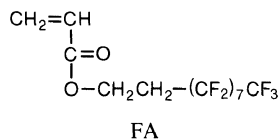Chuichi Hirayama, Hirotaka Ihara,* Shoji Nagaoka,
and Takeshi Wada

*Department of Applied Chemistry Faculty of Engineering, Kumamoto University,
2-39-1 Kurokami, Kumamoto 860, Japan*

Fluorine-containing stationary phases for liquid chromatography have been readily obtained by suspension copolymerization of perfluoroalkyl acrylate (FA) and ethylene glycol dimethacrylate as crosslinking agents.[1-3] These packings showed specific retention behavior for fluorine-containing substances due to the rigid and sorvophobic properties of perfluoroalkyl groups. It is known that perfluoroalkyl groups form highly-oriented structures and show limited miscibility with hydrocarbon substances. For example, amphiphilic compounds with perfluoroalkyl groups produce highly-oriented aggregates like lipid bilayer membranes in water[4] and organic solvents[5] and show specific incorporation behavior.[6] However, it is probably difficult to obtain highly-oriented fluorocarbon polymers by conventional suspension polymerization of FA. Direct introduction of fluorine-containing groups onto silica gels can be performed using perfluoroalkylsilane derivatives,[7-9] although this method cannot control the orientation of perfluoroalkyl groups on stationary phases either.

This paper reports a new and facile immobilization of highly-oriented perfluoroalkyl polymers onto silica gels for liquid chromatography. For this purpose, we prepared a comb-shaped polymer ($FA_{20}$) with a reactive terminal group using telomerization[10] of FA and 3-mercaptopropyltrimethoxysilane. The polymers ($FA_{20}$) were immobilized onto silica gels and showed crystal-to-isotropic phase transition on silica gels and specific retention behavior in liquid chromatography.

$$CH_2=CH$$
$$|$$
$$C=O$$
$$|$$
$$O-CH_2CH_2-(CF_2)_7CF_3$$

FA

$$OCH_3$$
$$|$$
$$CH_3O-Si-(CH_2)_3-S-(CH_2-CH)_{20}-H$$
$$|\qquad\qquad\qquad\qquad |$$
$$OCH_3\qquad\qquad\qquad C=O$$
$$|$$
$$O-CH_2CH_2-(CF_2)_7CF_3$$

$FA_{20}$

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* To whom all correspondence should be addressed.

## EXPERIMENTAL

### Materials

A comb-shaped telomer from FA was prepared as previously reported by us.[10] Heptadecafluoro-decylacrylate (10 g) and 3-mercapto-trimethoxysilane (0.12 ml) were dissolved in 100 ml of acetone. Azobisisobutyronitrile (0.01 g) was added to the solution at 60°C. The mixture was stirred for 6 h at 60°C under $N_2$ gas atmosphere. The mixture was concentrated to 30 ml *in vacuo*. White precipitates were obtained by the addition of methanol (100 ml) and washed successively with methanol. The chemical structure of the product ($FA_{20}$) was determined by elemental analysis, IR and NMR spectroscopies. The average degree of polymerization found by NMR was 20.

$FA_{20}$ (3 g) was mixed with 2 g of porous silica gels (YMC SIL-120-S5, pore sizes: 300 Å, specific surface area: $300 \, m^2 \, g^{-1}$) in acetone (200 ml) and stirred at 80°C for 12 h. Elemental analysis showed that 29.3 wt% (C, 10.5%) of $FA_{20}$ was immobilized on the silica gels. Successive washing of the resulting gels with acetone showed no change in weight.

### Measurements

Silica-supported $FA_{20}$ was packed into a stainless steel column (4.6 mm i.d. × 100 mm) and liquid chromatography was conducted using methanol or methanol-aqueous buffer as eluents. The chromatograph includes a JASCO 880 PU pump and a Shimadzu UV-visible photodiode array SPD-M6A. Five ml of the sample dissolved in methanol were injected through a Reodyne Model 7125 injector. Chromatography was carried out at flow-rate $0.5 \, ml \, min^{-1}$. DSC thermograms of $FA_{20}$ (5 mg) were obtained using a heating rate of $2°C \, min^{-1}$ with a Seiko I & E SSC-580 with a DSC-10 instrument.

## RESULTS AND DISCUSSION

Polymer $FA_{20}$ showed an endothermic peak at 60—80°C (peak-top temperatures, $T_c = 70°C$) in the differential scanning calorimetry. Microscopic observation with a polarizing microscope indicated that $T_c$ was derived from a crystal-to-isotropic phase transition. Homopolymers with long-chain perfluoroalkyl groups form oriented structures in their side chain groups.[11,12]

Silica-supported $FA_{20}$ (Sil-$FA_{20}$) also showed an endothermic peak in the presence and absence of 2-propanol–water (4 : 6) as an eluent used in the liquid chromatography process. The phase transition temperature almost agreed with that of original $FA_{20}$. This indicates that carrier silica gels have no effect on the orientation of $FA_{20}$ and the immobilized $FA_{20}$ is in a crystal state in the eluent even at room temperature.

The column packed with Sil-$FA_{20}$ showed complete separation of the 1-alcohol mixture. The elution order agreed with the order observed in conventional octadecylated silica gels (Inertsil ODS, GL Science Co., Ltd.). The relationship between $\log k'$[13] and the number of carbon atoms ($C_4$–$C_{14}$) in the solutes provided a good linear correlation as shown in Figure 1. These results indicate that the separation in the $FA_{20}$ column obeys a usual reversed phase liquid chromatography (RPLC) mode based on hydrophobic interaction
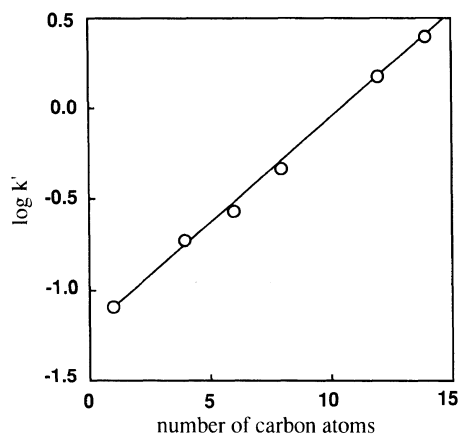


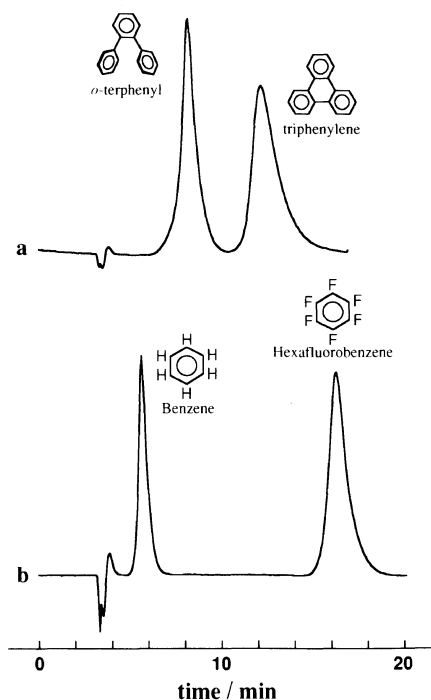**Figure 1.** Relationship between $\log k'$ and carbon number of 1-alcohol.

o-terphenyl

triphenylene

a

F
F F
F   F
F
Hexafluorobenzene

H
H   H
H   H
H
Benzene

b

0                10               20
time / min

**Figure 2.** Separation of aromatic compounds with a Sil-FA$_{20}$ column. Eluent, 2-propanol (4)–water (6); temperature, 25°C.



**Figure 3.** Temperature dependency on capacity facors for hexafluorobenzene (●) and benzene (○) with Sil-FA$_{20}$ column.

between immobilized organic phase and solutes.

Specific retention behavior was observed for aromatic or fluorine-containing compounds. For example, Figure 2a shows complete separation of triphenylene and o-terphenyl using the Sil-FA$_{20}$ column. The separation factor ($\alpha$)[14] is 1.9, although the peaks are broadened. Such broadening is often observed in usual polymer packings and is related to rigidity of the polymer main chain and sample solute.[15–17] Complete separation with the same elution order was also observed in the ODS column, although $\alpha$ was only 1.2. ODS shows longer retention for triphenylene as a planar compound than for o-terphenyl as a non-planar compound.[10,18] This elution order does not obey a usual RPLC mode because of the reversed order in their solubility parameters[19,20] which are often used as those for retention capacities. To explain this specific
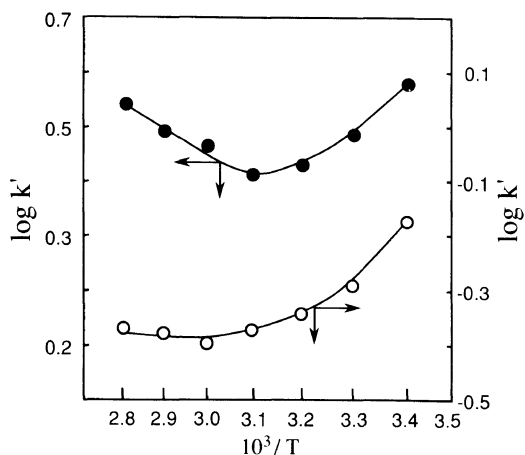
retention mechanism, Kimata et al.[18] indicated that bonded phases recognize molecular planarity of solutes, and Sanders and Wise[21] proposed a "slot model" for recognition sites. These assumptions suggest that Sil-FA$_{20}$ provides effective retention sites for molecular-shape recognition. These assumptions indicate that Sil-FA$_{20}$ provides good "slots" for molecular recognition.

The Sil-FA$_{20}$ column showed good separation ($\alpha = 6.0$) for a mixture of benzene and hexafluorobenzene (Figure 2b). This $\alpha$ was much higher than that of the ODS column ($\alpha = 2.2$). As shown in Figure 3, the temperature dependence on the $k'$ of hexafluorobenzene suggested an unusual retention mechanism. $k'$ increased with temperature at temperatures above 50°C, but decreased at temperature range between 20 and 50°C. No similar increase of $k'$ was observed for benzene with the Sil-FA$_{20}$ column (Figure 3) or hexafluorobenzene with the ODS column (Figure 4). $k'$ is related to thermodynamics parameters as follows:[22]

$$\log k' = \log f + \frac{\Delta H^{\circ}_{s-m}}{2.3RT} + \frac{\Delta S^{\circ}_{s-m}}{2.3R}$$

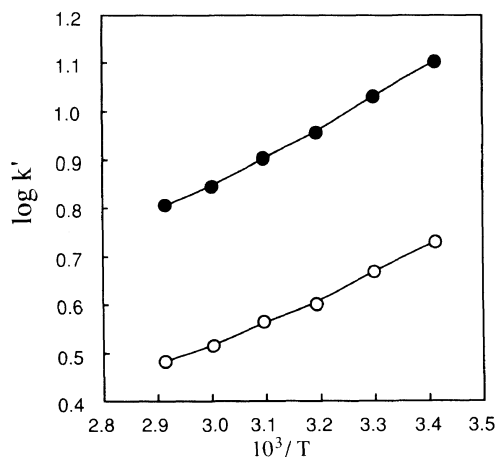where $f$ is the ratio of the volumes of stationary

**Figure 4.** Temperature dependency on capacity facors for hexafluorobenzene (●) and benzene (○) with ODS column.



**Figure 5.** Temerature dependency on separation facors (α) of hexafluorobenzene to benzene with Sil-FA$_{20}$ (○) and ODS columns (●).

to mobile phases, $\Delta H^\circ_{s-m}$ is the heat of transfer from the stationary to mobile phases, $\Delta S^\circ_{s-m}$ is the standard entropy of transfer assuming that the standard state is unit molar concentration in either phase. Plots of $\log k'$ against $1/T$ in the ODS column provide a positive slope. Similar positive slopes are commonly observed in usual RPLC packings.[22,23] These can be explained by increase of the solubility of the solutes from stationary to mobile phase with temperature.[22,23] The Sil-FA$_{20}$ column provides a negative slope at temperatures above 50°C. However, the Sil-FA$_{20}$ column showed a positive slope for benzene. Therefore, α also increases with temperature as shown in Figure 5, but decreases in the ODS column. Such unusual increases of $k'$ and α can not be explained only by hydrophobic interactions between stationary phases and solutes. As an exceptional case, we found that $k'$ increased remarkably with temperature in poly(γ-methyl L-glutamate) spherical particles whose conformation of the main chain was composed of rigid α-helices.[24] In this case, α-helices produce "molecular slits". Therefore, we assumes that Sil-FA$_{20}$ also possesses specific retention sites like "molecular slits", which have temperature-dependent affinity for fluorine atoms. This is
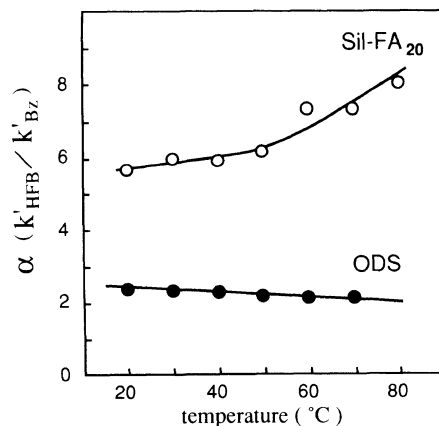
based on the crystal-to-isotropic phase transition of FA$_{20}$. As reported previously,[2] fluorine-containing compounds have much smaller solubility parameters than the corresponding hydrocarbons. This shows that fluorine-containing compounds are extremely sorvophobic, and that perfluoroalkyl groups have limited miscibility for hydrocarbons, although they are easily misicible for fluorocarbons. Therefore, FA$_{20}$ moieties are strongly aggregated and are highly oriented in the crystal state. The disordered state is induced by the phase transition. However, disordering is remarkable only in the hydrocarbon main chain, because the fluorocarbon side chain is still very rigid and sorvophobic because of the bulkiness of its fluorine atoms. Perhaps immobilized FA$_{20}$ can produce suitable incorporation sites for fluorine-containing compounds by disordering the main chain.

In conclusion, perfluoroalkyl acrylate polymer with a reactive terminal group (FA$_{20}$) was prepared and immobilized onto porous silica gels. The immobilized FA$_{20}$ moieties produce highly-oriented structures on silica gels. The column showed specific retention behavior for aromatic and fluorine-containing compounds. We assume that the silica-supported FA$_{20}$ possesses two retention sites as schematically
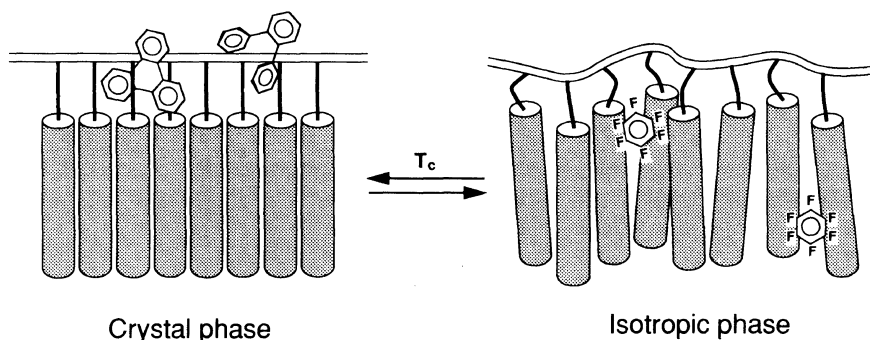
**Figure 6.** Schematic illustration of retention sites of Sil-FA$_{20}$.

illustrated in Figure 6: the hydrocarbon main chain is comparably ordered at crystal-state temperatures by the orientation of the fluorocarbon side chain. A planar hydrocarbon is more strongly retained in the main chain and the neighborhood than a non-planar hydrocarbon. The main chain of Sil-FA$_{20}$ is disordered at temperatures above $T_c$. At these temperatures, perfluoroalkyl side chains are still rigid but orientation is lowered. Perfluorobenzene is retained in the perfluoroalkyl side-chain moieties.

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