Journal of Chromatography A, 1216 (2009) 7440–7445

Contents lists available at ScienceDirect

Journal of Chromatography A

journal homepage: www.elsevier.com/locate/chroma

Effect of the direction of ester linkage on molecular shape selectivity through multiple carbonyl–π interaction with octadecyl chain branched polymers as organic phases in reversed-phase high-performance liquid chromatography

Ashequl A. Rana, Makoto Takafuji, Hirotaka Ihara*

Department of Applied Chemistry and Biochemistry, Kumamoto University, 2-39-1 Kurokami, Kumamoto 860-8555, Japan

ARTICLE INFO

Article history:
Available online 3 June 2009

Keywords:
Poly(vinyl octadecanoate)
Poly(octadecylacrylate)
Phase transition temperature
Enhanced selectivity
Highly oriented structure
Polycyclic aromatic hydrocarbons

ABSTRACT

Poly(vinyl octadecanoate)-grafted porous silica (Sil-VOD$_n$, $n = 23$) was newly prepared to investigate the efficiencies of the carbonyl groups in the polymer chain for recognition of polycyclic aromatic hydrocarbons (PAHs) in RP-HPLC. In Sil-VOD$_{23}$, the octadecyl side chains were connected to the polymer main chain through ester linkage in opposite direction to that in poly(octadecylacrylate)-grafted silica (Sil-ODA$_n$, $n = 25$) which has been reported by us. Sil-ODA$_n$ performs enhanced molecular shape selectivity of PAHs in RP-HPLC through multiple carbonyl–π interaction of aligned carbonyl groups which are induced by the formation of highly oriented structure of side chains. Differential scanning calorimetry of VOD$_{23}$ demonstrated that octadecyl alkyl chains showed crystalline to isotropic phase transition with endothermic peak at 48.7 °C which was similar to ODA$_{25}$ (at 47.8 °C). After grafting of both polymers, phase transition phenomenon was completely disappeared in Sil-VOD$_{23}$ whereas Sil-ODA$_{25}$ still exhibits phase transition although at lower endothermic peak top temperature (38.5 °C). This indicates that the slight structural change in Sil-VOD$_n$ and Sil-ODA$_n$ influence the ordered structure of side alkyl chains. Moreover, solid-state ^{13}C NMR revealed that the long alkyl chain in Sil-VOD$_{23}$ is highly disordered as compared with that of Sil-ODA$_{25}$. Sil-VOD$_{23}$ was applied to RP-HPLC stationary phase using PAHs as π-electron containing elutes, and compared with Sil-ODA$_{25}$ and conventional monomeric octadecylated silica (ODS). Results confirmed that Sil-VOD$_{23}$ showed much higher selectivity for PAH isomers than ODS, but lower than Sil-ODA$_{25}$. For example, the separation factors for *trans-/cis*-stilbene were 1.47 (Sil-VOD$_{23}$), 1.70 (Sil-ODA$_{25}$) and 1.07 (ODS), respectively. These results indicate that carbonyl groups in Sil-VOD$_{23}$ are effective for molecular shape recognition of PAHs through carbonyl–π interactions even in the disordered state.

1. Introduction

Specific behaviours of many polymers are based on their configuration and conformation. The chemical structure of monomer units and their arrangements influence on the conformational structures of polymer chain and then closely relate to their functions which are carried out by multiple interactions through accumulation and orientation of their functional groups. Synthetic polymers are used as many industrial materials such as fiber, film and adhesion. Our group have interested in the hybridization of synthetic polymer and porous silica particles [1–7] which were applied for stationary phases in the reversed-phase high-performance liquid chromatography (RP-HPLC). Though octadecylated silica (ODS) has been widely used as a stationary phase in RP-HPLC, it is not always useful for the separation of the solutes with similar hydrophobicity such as structural and geometrical isomers. Alternatively hybrid RP-type phase providing additional interaction sites and properties due to embedded functional groups become widely expected and gained increased importance. So far, various RP-polymeric stationary phases with different functionalized groups were prepared and applied for the packing materials for HPLC separation [8–11]. It is well known that rigidity, surface density and polymerization degree influence the separation behaviours of silica–polymer hybrid in HPLC use [12–14]. The position of functional group in the polymer chain is also an important structural factor with regard to conformation and configuration [15]. We have reported that the poly(octadecyacrylate)-grafted silica (Sil-ODA$_n$) showed extremely large selectivity for polyaromatic hydrocarbons (PAHs) including biomolecules and drugs. It was also found that the oriented carbonyl groups of the polymer work as a subsidiary interaction source for π-electron containing compounds and the selectivity is extremely enhanced by ordering of the carbonyl groups which is induced by the formation of highly oriented structure of the long-chain alkyl groups [1,16]. Vinyl octadecanoate

---

* Corresponding author. Tel.: +81 96 342 3661; fax: +81 96 342 3662.
E-mail address: ihara@kumamoto-u.ac.jp (H. Ihara).

0021-9673/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.chroma.2009.05.079

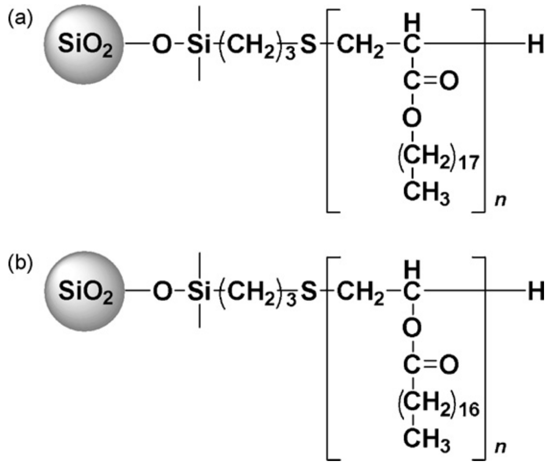


Fig. 1. Structures of the polymer-grafted silica: Sil-ODA$_n$ (a) and Sil-VOD$_n$ (b).

(VOD) and octadecylacrylate (ODA) both have similar molecular structure with similar physical properties. The polymer of VOD contrasts to that of ODA in a sense that the bond direction of the ester group in the repeating unit of VOD is reversed as compared with the ester group in ODA, i.e. VOD has the chemical structure of the R-O-CO-Ŕ whereas ODA has the chemical structure of the R-CO-O-Ŕ, where R and Ŕ represent the vinyl group and long alkyl chain, respectively. This structural difference may cause difference in not only polymeric properties but also molecular shape and size recognition in RP-HPLC. Thus their polymeric stationary phase in RP-HPLC is a subject matter of interest. Chemical structure of these two mentioned polymeric phases are shown in Fig. 1. In order to understand better the functionality of the carbonyl group and conformation of the long alkyl chain, poly(vinyl octadecanoate)-grafted silica stationary phase (Sil-VOD$_n$) was newly prepared. The Sil-VOD$_n$ is then compared elaborately with Sil-ODA$_n$ by a combination of suspension-state ^{1}H NMR and solid-state ^{13}C Cross Polarization/Magic Angle Spinning (CP/MAS) NMR and differential scanning calorimetry (DSC). The liquid chromatographic behaviours of Sil-VOD$_{23}$ were evaluated by using PAHs as solute and compared with that of Sil-ODA$_{25}$ in a wide range of temperature.

2. Experimental

2.1. Reagents and materials

Vinyl octadecanoate (VOD) and octadecylacrylate (ODA) were purchased from Tokyo Kasei (Tokyo, Japan) and used after removal of polymerization inhibitor. 3-Mercaptopropyltrimethoxysilane (MPS) was purchased from Azmax (Chiba, Japan) and used without further purification. Azobisisobutyronitrile (AIBN) as an initiator was purified by recrystallization from methanol. Silica particles 120-S5 (diameter 5 μm, pore size 120 Å, specific surface area 300 m^2 g^{-1}) were obtained from YMC (Kyoto, Japan). All other materials and reagents were purchased from Sigma–Aldrich (Tokyo, Japan), Wako (Osaka, Japan) and Nakalai Tesque (Kyoto, Japan). A monomeric ODS column (ODS) (Intersil ODS, GL Science, Tokyo, Japan) was used as reference for chromatographic analysis.

2.2. Synthesis of polymeric stationary phase

2.2.1. Synthesis of Sil-VOD$_n$ [poly(vinyl octadecanoate) grafted on porous silica]

Sil-VOD$_{23}$ was prepared by one step radical telomerization of vinyl octadecanoate with 3-mercaptopropyltrimethoxysilane and following immobilization onto silica mostly according to our previously reported method [3]. Preparation procedure was as follow: VOD and MPS (10:1 molar ratio) were dissolved in methanol. AIBN (1 wt.% of the monomer) in methanol solution was added to the solution mixture at 60 °C. The mixture was stirred for 24 h at 60 °C under the atmosphere of N_2 gas. After the reaction, the solution was cooled to room temperature and the resulting white precipitates were gathered by filtration. The precipitate was then dissolved in $CHCl_3$ and reprecipitate in ethanol for further purification. After purification, the precipitate was washed successively with ethanol, methanol, acetone and dried in *vacuo*. The average polymerization degree of VOD$_n$ was determined by ^{1}H NMR spectrum by the integration ratio at 3.57 and 2.25.

VOD$_{23}$ was then readily immobilized onto porous silica by mixing in toluene at reflux temperature for 72 h. The product was gathered after filtration and washed several times with toluene, chloroform and ether consecutively. After 72 h vacuum drying the amount of carbon and hydrogen were determined to be 10.06 and 2.15% by elemental analysis. Successive washing with chloroform as a good solvent for VOD$_{23}$ showed no significant change in elemental analysis results.

2.2.2. Synthesis of Sil-ODA$_n$ [poly(octadecylacrylate) grafted on porous silica]

Sil-ODA$_n$ was prepared exactly by our previously published literature [16]. The average degree of polymerization was determined by the proton ratio at 3.6 and 4.0 ppm. After immobilization on to silica, the amount of carbon and hydrogen were determined to be 8.50 and 2.01% by elemental analysis. Similarly successive washing with chloroform as a good solvent for ODA$_{25}$ showed no significant change in elemental analysis results.

2.3. Instrumentation

2.3.1. Differential scanning calorimetry (DSC)

Differential scanning calorimetry was determined at a heating rate of 2 °C min^{-1} using a Seiko Exstar 6000 with a DSC6200 instrument. For the measurement in a methanol/water (80/20) mixture, 20 mg of sample and 50 μl of solvent mixture were sealed in a silver pan and a silver pan filled with 50 μl of the solvent mixture was used as a reference.

2.3.2. Thermogravimetric analysis (TGA)

TGA was performed on a Seiko Exstar 6000 TG/DTA 6300 thermobalance in static air from 30 to 800 °C at a heating rate of 10 °C min^{-1}.

2.3.3. NMR spectroscopy

All NMR spectra were measured by using Varian Unity$^{\mathrm{Inova}}$AS400 at static magnetic field of 9.4 T using GHX Varian AS400 nanoprobe for suspension-state ^{1}H NMR and Varian 7mm VT CP/MAS probe for solid-state ^{13}C CP/MAS NMR. Spin rate of 2000–3500 Hz for suspension-state ^{1}H NMR measurements and 4000–4500 Hz for solid-state ^{13}C NMR measurements were used, respectively.

2.3.4. Chromatography

Sil-VOD$_{23}$ and Sil-ODA$_{25}$ was packed into a stainless steel column (150 mm × 4.6 mm). The chromatographic system consists of a JASCO Gulliver PU-1580 intelligent HPLC pump with a Rheodyne sample injector having 20 μl loop. A JASCO multi-wavelength UV detector MD 1510 plus was used. The column temperature was maintained by using a column jacket with a circulator having a heating and cooling system. A personal computer connected to the detector with JASCO-Borwin (Ver. 1.5) software was used for system control and data analysis. As the sensitivity of UV detector is high, 5 μl of sample solution was used for each injection. Separations were performed using HPLC grade methanol and water mixture (80:20) as mobile phase at a flow rate of 1.0 ml min^{-1}. The retention factor (k) measurement was done under isocratic elution conditions. The separation factor (α) is the ratio of the retention factor of two solutes that are being analyzed. The retention time of D_2O was used as the void volume (t_0) marker (the adsorption for D_2O was measured at 400 nm, which actually considered as injection shock). A water/1-octanol partition coefficient ($\log P$) was measured by the retention studies with octadecylated silica, C_{18} (monomeric) (Intersil ODS, 250 mm × 4.6 mm I.D., GL Science).

3. Results and discussion

3.1. Surface coverage of octadecyl-branched polymer-grafted silica

Poly(vinyl octadecanoate) with terminal reactive group was prepared by one-step telomerization method with 3-mercaptopropyltrimethoxysilane. The polymerization degree was determined by ^{1}H NMR spectrum to be 23. Then the telomer was grafted onto the surface of porous silica particles (Sil-VOD_{23}) to evaluate their molecular shape selectivity as a stationary phase for HPLC. Poly(octadecylacrylate) with trimethoxysilyl terminal group was prepared and grafted onto porous silica particles according to our previous report [16]. Average polymerization degree was determined to be 25 (Sil-ODA_{25}). In Sil-VOD_{23}, the octadecyl side chain was connected with polymer main chain by ester group in opposite direction to that in Sil-ODA_{25}. The grafting densities are calculated from the C% in elemental analysis result according to our previously reported formula [17]. The grafting densities of Sil-VOD_{23} and Sil-ODA_{25} are 1.57 and 1.25 μmol m^{-2}, respectively. Thermogravimetric analysis (TGA) results of both Sil-VOD_{23} and Sil-ODA_{25} showed good agreement with elemental analysis results. These results are summarized in Table 1.

3.2. Phase transition behaviour

DSC measurement for VOD_{23} provided a sharp endothermic peak with peak top at 48.7 °C (T_C) in the heating process. A polarization microscopic observation of VOD_{23} showed that a crystalline to isotropic phase transition was induced around T_C. Similar phase transitions were also observed in methanol/water (80/20) dispersions and accompanied by a slight decrease in temperature of about 3 °C. DSC measurement of ODA_{25} was also done in similar fashion and gives T_C at 47.8 and 46 °C without and with methanol/water (80/20) mixture, respectively. These results indicate that VOD_{23} and ODA_{25} polymer can form highly oriented structures even in the presence of organic media used in the column chromatography process. In the case of ODA_{25} in a methanol/water (80/20) mixture, the peak top temperature (T_C) was decreased from 47.8 to 38.5 °C with broadening after grafting onto silica surface. The lowering of this peak top temperature indicates that the orientation of bound ODA_{25} is slightly influenced but the bonded phase can still maintain oriented structure and undergo crystalline-to-isotropic phase transition on silica surface [17]. Compare with ODA_{25}, the phase transition behaviour of VOD_{23} was almost disappeared after grafting onto silica. This may be explained by the fact that disturbance caused by the silica particle and organic media which actually effect the alkyl chain ordering is much high in case of Sil-VOD_{23} than Sil-ODA_{25}. This observation clearly suggests that, orientation of long chain alkyl group of Sil-VOD_{23} is much more disordered as compared with Sil-ODA_{25}. All the DSC thermograms were shown in supporting Fig. 1.

Table 1
Elemental analysis and TGA result of Sil-VOD_{23} and Sil-ODA_{25}.

	C%	H%	N%	Grafting density (μmol m^{-2})	Mass loss% (TGA)
Sil-VOD_{23}	10.07	2.15	0	1.57	12.0
Sil-ODA_{25}	8.50	2.01	0	1.25	10.8

Experimental condition: Elemental analyses were carried out on a Yanaco CHN Corder MT-6 apparatus and TGA was performed on a Seiko Exstar 6000 TG/DTA 6300 thermobalance in static air from 30 to 800 °C at a heating rate of 10 °C min^{-1}. Grafting density was measured according to our previous reported formula [17].

3.3. Mobility and conformation of octadecyl group

Suspension-state ^{1}H NMR spectra for Sil-VOD_{23} and Sil-ODA_{25} were obtained in d4-methanol at variable temperatures from 20 to 50 °C. Normalization of the peak for long alkyl chain methylene groups in ODA_{25} and VOD_{23} moieties appeared around 1.25 ppm. This was carried out with methyl groups of methanol in deuterated solvent and the normalized intensities were plotted against measurement temperatures according to our previously reported formula [17]. The normalized intensity in Sil-VOD_{23} was gradually increased with increasing temperature. On the other hand, the normalized intensity in Sil-ODA_{25} was lower than that in Sil-VOD_{23} at 20 °C and distinct increase was observed around 40 °C which is close to the phase transition temperature (38.5 °C) observed in methanol/water (80/20) mixture.

It is well known that ^{13}C signals for methylene carbons in alkyl chains are observed at two resonances, one at 32.6 ppm due to *trans* conformation indicating rigid and ordered chains while the other at 30.0 ppm due to *gauche* form describing mobile and amorphous region [18]. Sil-VOD_{23} showed a dominance of *gauche* form (30.2 ppm) at 20 °C that remains almost same even at high temperature as high as 50 °C On the other hand, the octadecyl groups on the Sil-ODA_{25} formed *trans* conformation predominantly at 20 °C, but eventually converted to *gauche* form with increasing temperature.

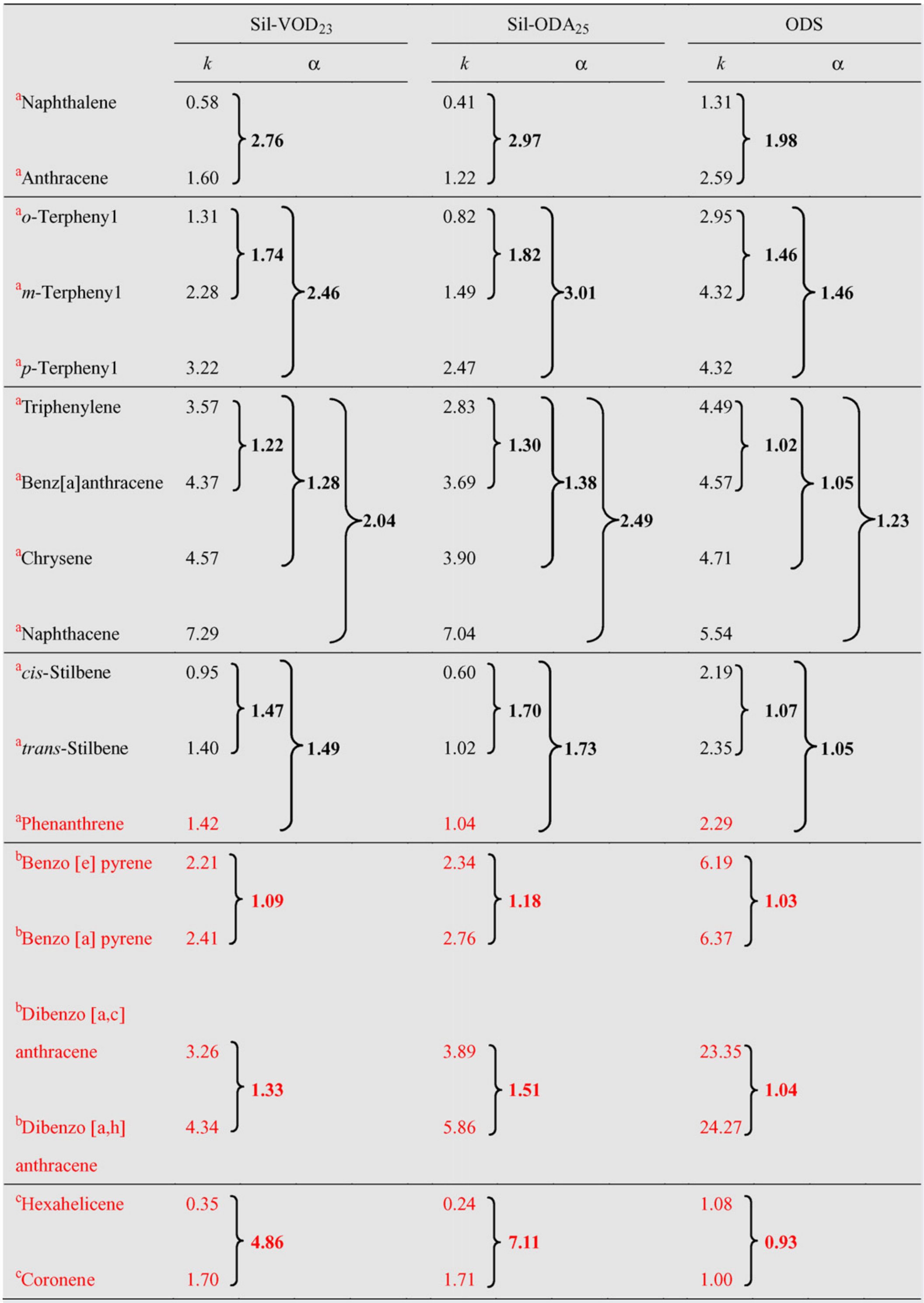
These results indicate that octadecyl group on the Sil-ODA_{25} formed highly oriented structures in the crystalline state with *trans* conformation, however it transform to disordered structures in isotropic state with *gauche* form. Compared with Sil-ODA_{25}, Sil-VOD_{23} formed *gauche* form in isotropic state at a wide range of temperatures.

3.4. Chromatographic studies

The retention mode of the packing materials in HPLC can be estimated by retention studies of alkylbenzenes as elutes [19,20]. When alkylbenzenes were used as solutes in HPLC with methanol/water (80/20) mixture as a mobile phase, Sil-VOD_{23} and Sil-ODA_{25} showed the same elution order as octadecylated silica (ODS). It was also confirmed that the retention factors (k) increased with increase of water content in the mobile phase. These results indicate that both Sil-VOD_{23} and Sil-ODA_{25} have the retention mode similar to RP-HPLC. According to our previous report, Sil-ODA_n recognizes aromaticity through multiple carbonyl–π interaction instead [21,22]. Furthermore, we have clarified that the alkyl chains of Sil-ODA_n form highly oriented structures in the crystalline state. Thus the aligned carbonyl groups enhance molecular shape selectivity for PAHs through multiple π–π interactions. Even though Sil-VOD_{23} showed no phase transition and *trans* conformation, it showed much better selectivity than ODS. Moreover, Sil-VOD_{23} showed higher retention for PAHs than alkylbenzenes compared with ODS. For instance, the $\log P$ of naphthacene (5.71) is much smaller than that of octylbenzene (6.30) but the logarithm of retention factor (k) of naphthacene (0.86) is higher than octylbenzene (0.50). The $\log k$ value of naphthacene and octylbenzene in ODS is 0.74 and 0.95, respectively. This increase of $\log k$ for PAHs was

Table 2

Retention (k) and separation (α) factors of PAHs for Sil-VOD$_{23}$, Sil-ODA$_{25}$ and octadecylated silica (ODS) stationary phases in RP-HPLC.



	Sil-VOD$_{23}$		Sil-ODA$_{25}$		ODS	
	k	α	k	α	k	α
[a]Naphthalene	0.58		0.41		1.31	
[a]Anthracene	1.60	**2.76**	1.22	**2.97**	2.59	**1.98**
[a]*o*-Terpheny1	1.31		0.82		2.95	
[a]*m*-Terpheny1	2.28	**1.74**	1.49	**1.82**	4.32	**1.46**
[a]*p*-Terpheny1	3.22	**2.46**	2.47	**3.01**	4.32	**1.46**
[a]Triphenylene	3.57		2.83		4.49	
[a]Benz[a]anthracene	4.37	**1.22**	3.69	**1.30**	4.57	**1.02**
[a]Chrysene	4.57	**1.28**	3.90	**1.38**	4.71	**1.05**
[a]Naphthacene	7.29	**2.04**	7.04	**2.49**	5.54	**1.23**
[a]*cis*-Stilbene	0.95		0.60		2.19	
[a]*trans*-Stilbene	1.40	**1.47**	1.02	**1.70**	2.35	**1.07**
[a]Phenanthrene	1.42	**1.49**	1.04	**1.73**	2.29	**1.05**
[b]Benzo [e] pyrene	2.21		2.34		6.19	
[b]Benzo [a] pyrene	2.41	**1.09**	2.76	**1.18**	6.37	**1.03**
[b]Dibenzo [a,c] anthracene	3.26		3.89		23.35	
[b]Dibenzo [a,h] anthracene	4.34	**1.33**	5.86	**1.51**	24.27	**1.04**
[c]Hexahelicene	0.35		0.24		1.08	
[c]Coronene	1.70	**4.86**	1.71	**7.11**	1.00	**0.93**

Experimental condition: Mobile phase: methanol/water (80/20) for PAHs (a), methanol/water (90:10) for PAHs (b) and ethanol (100%) for PAHs (c); temperature: 25 °C; flow rate: 1.0 ml min^{-1}; injection volume: 5 µl; UV detection: 254 nm.

accompanied by selectivity enhancement which provides specific interaction sites for PAHs that can recognize aromaticity besides molecular hydrophobicity. For instance $\alpha_{\text{anthracene/benzene}}$ for Sil-VOD$_{23}$ is 5.91 while the same for ODS is 3.53. As shown in Table 2, selectivity enhancements for each elute sets were observed in Sil-VOD$_{23}$ stationary phase compared with the ODS column. For the isomeric aromatic pair, benz[*a*]anthracene/triphenylene Sil-VOD$_{23}$ yielded a selectivity factor of $\alpha_{\text{benz}[a]\text{anthracene/triphenylene}} = 1.23$ while ODS showed 1.02 provided evidence that Sil-VOD$_{23}$ recognize not only molecular planarity but also the geometry of the solutes. Separation factor of higher polycyclic aromatic hydrocarbons (e.g. 5-ring and 6-ring PAHs) were also examined to evaluate the column efficiency and the results were also given in Table 2. Interestingly Sil-VOD$_{23}$ showed better compactness selectivity of the equal

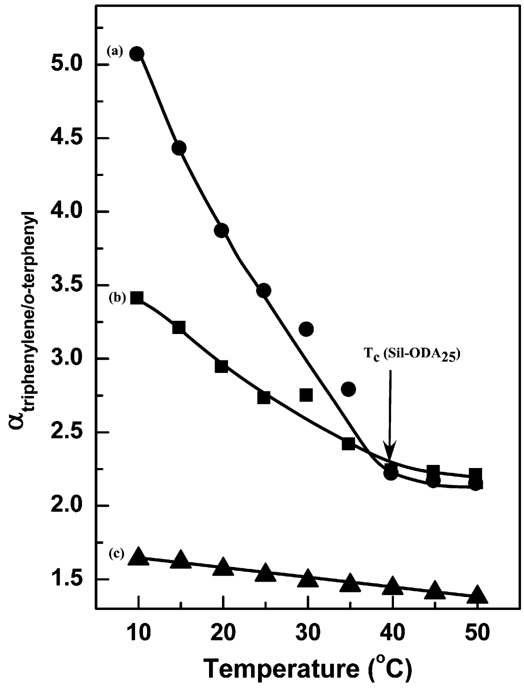


Fig. 2. Temperature dependencies of the separation factors between triphenylene and *o*-terphenyl with Sil-ODA$_{25}$ (a), Sil-VOD$_{23}$ (b) and ODS (c). Mobile phase: methanol/water (80/20); flow rate: 1.0 ml min^{-1}; temperature range: 10–50 °C.

Table 3
Retention (k) and separation (α) factors of PAHs for Sil-VOD23 and Sil-ODA25 in NP-HPLC.

	Sil-VOD$_{23}$		Sil-ODA$_{25}$	
	k	α	k	α
o-Terphenyl	0.25		0.24	
m-Terphenyl	0.28	1.12	0.25	1.04
p-Terphenyl	0.43	1.72	0.39	1.63
Triphenylene	0.49	1.96	0.45	1.87
Benz[a]anthracene	0.47		0.43	
Chrysene	0.49	1.04	0.44	1.03
Naphthacene	0.48	1.02	0.44	1.03
Fullerene (C$_{60}$)	0.98		0.86	
Fullerene (C$_{70}$)	1.53	1.56	1.28	1.49

Experimental condition: Mobile phase: *n*-hexane/2-propanol (80/20); temperature: 25 °C; flow rate: 1.0 ml min^{-1}; injection volume: 5 µl; UV detection: 254 nm.

numbered ring molecules over Sil-ODA$_{25}$. For instance, anthracene and isomeric terphenyls contain equal number of aromatic rings. Anthracene is condensed and comparatively more compact while isomeric terphenyls are less compact PAHs molecules. So selectivity between anthracene and *o*-/*m*-terphenyl may be considered as compactness selectivity. The $\alpha_{m\text{-terphenyl/anthracene}}$ for Sil-VOD$_{23}$ (1.43) is much higher than Sil-ODA$_{25}$ (1.23). Therefore it seems that carbonyl–π interactions are very effective for the recognition of molecular shape of PAHs in Sil-VOD$_{23}$ even though the phase remain in isotropic state at a wide range of temperatures. To know the relevance between the separation behaviour and the conformation of alkyl chains, HPLC analyses for planar triphenylene and non-planar *o*-terphenyl were examined with Sil-VOD$_{23}$, Sil-ODA$_{25}$ and ODS stationary phases in a wide range temperature from 10 to 50 °C. As shown in Fig. 2, the $\alpha_{triphenylene/o\text{-}terphenyl}$ with Sil-VOD$_{23}$ and Sil-ODA$_{25}$ at 10 °C were 3.4 and 5.06 respectively and decreased with increasing temperature. Sil-ODA$_{25}$ showed distinct bending

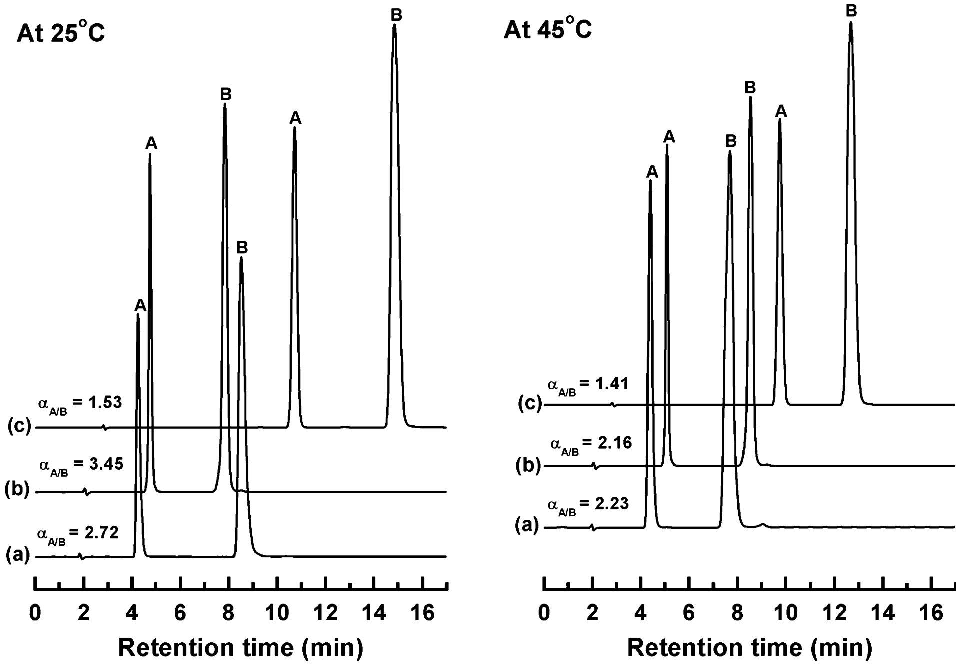


Fig. 3. Separation of *o*-terphenyl (A) and triphenylene (B) at 25 °C and 45 °C respectively in Sil-VOD$_{23}$ (a), Sil-ODA$_{25}$ (b) and ODS (c). Mobile phase: methanol/water (80/20); flow rate: 1.0 ml min^{-1}; UV detection: 254 nm.

in the plots of temperature vs. α value in HPLC around 40 °C which agreed with phase transition temperature, but no such bending was observed in the plots with Sil-VOD$_{23}$. These results indicate that the selectivity was strongly affected by the physical state of side alkyl chains. However alkyl chains were disordered in both Sil-VOD$_{23}$ and ODS stationary phases but Sil-VOD$_{23}$ showed much better separation in all temperature range. These results confirmed that multiple carbonyl π–π interaction plays an important role in PAHs separation in RP-HPLC even in the disordered state. Moreover, at higher temperature Sil-VOD$_{23}$ showed comparatively good result than Sil-ODA$_{25}$ suggesting that carbonyl groups may have stronger interaction in vinyl ester linkage position rather than acrylate linkage position (Fig. 3). Supporting this observation we investigated both phases in NP-HPLC where hydrophobic effect is negligible and the separation is mainly due to dipolar carbonyl groups. All the results were presented in Table 3. It is evident from Table 3 that, dipolar interaction of carbonyl group is intense in case of Sil-VOD$_{23}$ rather than Sil-ODA$_{25}$. It was also revealed that planarity selectivity of Sil-VOD$_{23}$ is higher than Sil-ODA$_{25}$ while linearity selectivity is almost same under normal phase mode (Table 3). Moreover being a strong hydrophobic phase, Sil-VOD$_{23}$ can effectively separate fullerene isomers in NP-HPLC. We may predict from these observations that the carbonyl groups in Sil-VOD$_{23}$ was in a favourable position to interact more frequently with PAHs as compared with that of Sil-ODA$_{25}$. However due to disorderness of the long alkyl chain, the selectivity of Sil-VOD$_{23}$ was eventually reduced in RP-HPLC

4. Conclusion

Several attempts were made to investigate the physical states and separation behaviours for PAHs of two octadecyl chain-branched polymer-grafted silica (Sil-VOD$_{23}$ and Sil-ODA$_{25}$) in which the side alkyl chains were connected to the main chain through ester bonds with opposite direction. The carbonyl groups of Sil-VOD$_{23}$ and Sil-ODA$_{25}$ play an important role for molecular shape selectivity of PAHs through carbonyl–π interactions. The separation factors for PAHs in Sil-ODA$_{25}$ are higher than those in Sil-VOD$_{23}$ below phase transition temperature of Sil-ODA$_{25}$. This would be due to the aligned carbonyl groups which can be induced by the highly oriented structures of octadecyl groups in Sil-ODA$_{25}$. Further investigation is necessary to clarify the disappearance of highly oriented structures of octadecyl chains in Sil-VOD$_{23}$ after immobilizing onto silica surface. However, it can be emphasized that the carbonyl groups of disordered state in Sil-VOD$_{23}$ recognize molecular shape of π-electron containing PAHs.

Acknowledgement

This research was partially supported by Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.chroma.2009.05.079.

References

[1] C. Hirayama, H. Ihara, T. Mukai, Macromolecules 25 (1992) 6375.
[2] H. Ihara, T. Fukamoto, C. Hirayama, Anal. Sci. 9 (1993) 711.
[3] H. Ihara, H. Tanaka, S. Nagaoka, K. Sasaki, C. Hirayama, J. Liq. Chromatogr. 19 (1996) 2967.
[4] H. Ihara, S. Okazaki, K. Ohmori, S. Uemera, C. Hirayama, S. Nagaoka, Anal Sci. 14 (1998) 349.
[5] H. Ihara, H. Tanaka, M. Shibata, S. Sasaki, C. Hirayama, Chem. Lett. 26 (1997) 113.
[6] H. Ihara, S. Uemura, S. Okazaki, C. Hirayama, Polym. J. 30 (1998) 394.
[7] H. Ihara, T. Nakanishi, T. Sagawa, C. Hirayama, T. Sakurai, T. Kinoshita, Y. Tsujita, Chem. Lett. 27 (1998) 963.
[8] J. Layne, J. Chromatogr. A 957 (2002) 149.
[9] T. Czajkowska, M. Jaroniec, J. Chromatogr. A 762 (1997) 147.
[10] H. Engelhardt, R. Gruner, M. Scherer, Chromatographia 53 (2001) 154.
[11] C.R. Silva, I.C.S.F. Jardim, C. Airlodi, J. Chromatogr. A 987 (2003) 127.
[12] S. Chen, J.C. Fetzer, M.E. Meyerhoff, Fresenius J. Anal. Chem. 369 (2001) 385.
[13] A. Catabay, Y. Saito, C. Okumura, K. Jinno, J.J. Pesek, E. Williamsen, J. Microcol. Sep. 9 (1997) 81.
[14] L.C. Sander, M. Pursch, S.A. Wise, Anal. Chem. 71 (1999) 4821.
[15] M.M. Béar, S. Randriamahefa, V. Langlois, Ph. Guérin, Polymer 41 (2000) 3705.
[16] H. Ihara, T. Sagawa, Y. Goto, S. Nagaoka, Polymer 40 (1999) 2555.
[17] H.R. Ansarian, M. Derekshan, M.M. Rahman, T. Sakurai, M. Takafuji, I. Taniguchi, H. Ihara, Anal. Chim. Acta 547 (2005) 179.
[18] M. Pursch, S. Strohschein, H. Handel, k. Albert, Anal. Chem. 68 (1996) 386.
[19] A.K. Mallik, M.M. Rahman, M. Czaun, M. Takafuji, H. Ihara, J. Chromatogr. A 1187 (2008) 119.
[20] A. Shundo, T. Sakurai, M. Takafuji, S. Nagaoka, H. Ihara, J. Chromatogr. A 1073 (2005) 169.
[21] H. Ihara, Y. Goto, T. Sakurai, M. Takafuji, T. Sagawa, S. Nagaoka, Chem. Lett. 30 (2001) 1252.
[22] M.A.J. Chowdhury, H. Ihara, T. Sagawa, C. Hirayama, J. Chromatogr. A 877 (2000) 71.