Molecular-shape selectivity tuned by donor–acceptor type copolymers as organic phase in reversed-phase high-performance liquid chromatography

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A B S T R A C T

The copolymer with a terminal reactive group (copoly-VP$_{17}$MA$_{12}$) was newly designed and prepared by selecting 4-vinylpyridine (VP) as an electron-donating monomer and methyl acrylate (MA) as an electron-accepting monomer. Copoly-VP$_{17}$MA$_{12}$ was grafted onto porous silica particles by a silanol coupling reaction with the terminal group. Individually, poly-VP$_{15}$ and poly-MA$_{20}$ with a terminal reactive group were also synthesized and co-grafted onto silica (Sil-cograft-VP$_{15}$MA$_{20}$) to compare the effect of the copolymer-grafted (Sil-copoly-VP$_{17}$MA$_{12}$) and polymer co-grafted stationary phases in HPLC separation. All the polymers were characterized by ^{1}H NMR and FT-IR analysis before grafting on silica. Polymer grafting was confirmed by diffuse reflectance infrared Fourier transform (DRIFT), elemental analysis and thermogravimetric analysis (TGA). The intra- and intermolecular interaction between monomer units in copolymer-grafted and polymer co-grafted systems, respectively was observed by DRIFT measurement. The detailed chromatographic study revealed using PAHs as solutes that remarkably higher selectivity for planar/non-planar discrimination was observed with the copolymer-grafted phase than with the co-grafted stationary phase. In this paper, it is also discussed that the selectivity enhancement by copolymer-grafting in the Sil-copoly-VP$_{17}$MA$_{12}$ phase can be brought through intramolecular interaction between VP and MA.

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1. Introduction

Copolymerization is the most powerful method for the preparation of materials with tailor-made properties, due to the incorporation, in the same structure, of two different monomers having diverse chemical and/or physical properties [1]. It is possible to modulate both the intramolecular and intermolecular forces exerted upon like and unlike polymer segments, and thus properties such a glass transition temperature, melting point, solubility, crystallinity, permeability, dyeability, adhesion, elasticity and chemical reactivity may be varied within wide limits [2].

In the field of liquid chromatography, separation of polycyclic aromatic hydrocarbons (PAHs) demonstrates as a separation challenge, and the investigation of PAHs has been the subject of abundant interest [3–10]. Generally, better separations of PAHs can be achieved by polymeric stationary phases than monomeric one [11,12]. The development of new chemically bonded stationary phases for RP-HPLC, engineered for solving specific separation problems, has led to improved analyses for a broad range of compounds. Refinements in approaches used to characterize chemically modified surfaces have resulted in increased understanding of

stationary-phase morphology, which in turn has permitted development of novel stationary phases with properties tailored for specific applications. We and many other groups have developed various special ligands and immobilized onto silica [13–24].

On the other hand, poly(4-vinylpyridine) (VP$_m$) as a synthetic adsorbent is emerging as a new promising adsorbent for RP-HPLC because of its non-sensitivity for molecular hydrophobicity but high sensitivity for molecular shape of π-electron-containing substances [22]. Since this unique selectivity is based on multiple electrostatic interaction, this uniqueness is available even in normal-phase HPLC [25,26]. The other advantage of VP$_m$ is masking effect against remaining silanol groups on silica surface [27] while in the case of basic compounds analysis with ODS phase serious problem has been noted during separation specifically peak-tailing and poor reproducibility through residual silanol groups on silica surfaces.

In this paper, we wish to describe the easy and effective synthesis of copolymer from two important monomers (4-vinylpyridine and methyl acrylate) those can work as electron-donating and electron-accepting moieties, respectively. This copolymer was synthesized with 3-mercaptopropyltrimethoxysilane (MPS) and grafted onto silica (Fig. 1) for its application as an HPLC packing material. The aim was to prepare new material with tailor-made properties, due to the incorporation, in the same structure, of two different monomers having different chemical and/or physical properties. At the same
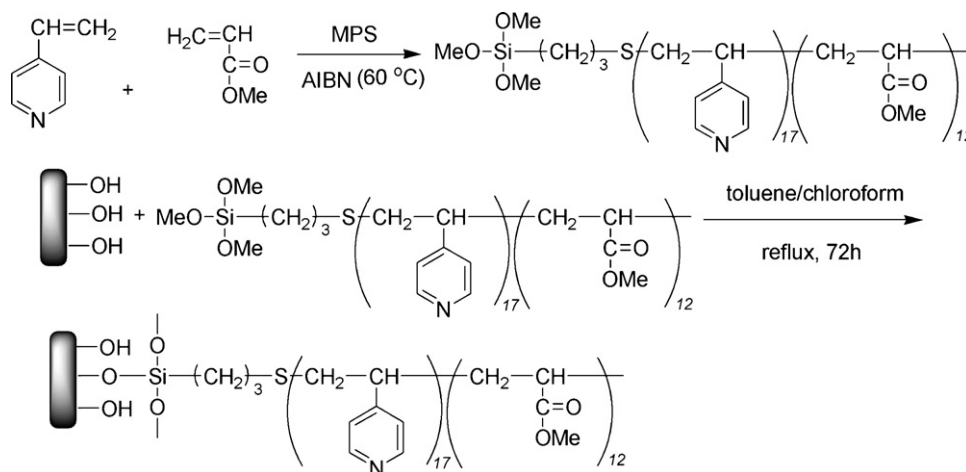

Fig. 1. Synthesis scheme of copolymer with terminal reactive group followed by immobilization onto silica.

time, individually poly(4-vinylpyridine) and poly(methyl acrylate) were synthesized and co-grafted onto silica particles and packed as HPLC column. Molecular recognizability of both the stationary phases will be evaluated from retention studies of different sized and shaped PAHs and aromatic positional isomers. The selectivity results of copolymer-grafted silica and polymer co-grafted onto silica packing materials will be compared and discussed in the following sections.

2. Experimental

2.1. Materials and methods

4-Vinyl pyridine monomer was obtained from Aldrich (Tokyo, Japan) and used after distillation. Methyl acrylate monomer was purchased from Nacalai tesque (Kyoto, Japan) and used after removing polymerization inhibitor. 3-Mercaptopropyltrimethoxysilane was purchased from Azmax (Chiba, Japan). A YMC silica (YMC SIL-120-S5) having diameter 5 μm, pore size, 12 nm, and surface area 300 $m^2\,g^{-1}$ (YMC-gel, Kyoto, Japan) was used in all cases. HPLC grade methanol was obtained from Wako (Osaka, Japan). All PAHs were commercially available and used without further purification.

FT-IR measurements were conducted on a JASCO (Japan) FT/IR-4100 plus instrument in KBr. For DRIFT measurement accessory DR PRO410-M (Jasco, Japan) was used. Thermogravimetric analyses (TGA) were 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}. For characterization of synthesis ^{1}H NMR spectra were recorded on a JEOL JNM-LA400 (Japan) instrument was used. Chemical shifts (δ) of ^{1}H were expressed in parts per million (ppm) with use of the internal standards Me$_4$Si.

2.2. HPLC measurement

The chromatographic system included a JASCO 1580 pump and a JASCO MD-1510 UV–vis photodiode array detector. As the sensitivity of UV detector is high, 5 μL sample was injected through a Reodyne Model 7125 injector. The column temperature was maintained by using a column jacket with a circulator having 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. Chromatographic grade solvent was used to prepare mobile phase solutions. Methanol–water mixture (80:20) was used as a mobile phase at flow rate 1.00 mL min^{-1}. The retention factor (k) measurement was done under isocratic elution conditions. The separation factor (α) was given by the ratio of retention factors.

The chromatography was done under isocratic elution conditions. The retention time of D$_2$O was used as the void volume (t_0) marker (the absorption for D$_2$O was measured at 400 nm, which actually considered as injection shock).

2.3. Synthesis of Sil-copoly-VP$_m$MA$_n$

The copolymer of 4-vinylpyridine and methyl acrylate with terminal reactive group was synthesized followed by immobilization onto silica. The typical synthetic procedure is as follows: 4-vinylpyridine (12 g, 0.11 mol), methyl acrylate (8.6 g, 0.10 mol), mercaptopropyltrimethoxysilane (1.96 g, 0.01 mol), and 100 mg AIBN initiator was taken in a round bottomed flask. The solution was degassed with three freeze-pump-thaw cycle and then heated for 6 h at 60 °C to complete the polymerization. After the formation of the polymer, the copolymer was dissolved in minimum amount of chloroform and re-precipitated from diethyl ether. Similar precipitation was repeated three times and the collected powders were successively washed with diethyl ether and dried under vacuum to obtain copoly-VP$_m$MA$_n$. The resultant copoly-VP$_m$MA$_n$ was grafted onto silica by using the terminal trimethoxysilyl group: 4.0 g of porous silica and 4.0 g of copoly-VP$_m$MA$_n$ were taken in a 100 mL three-necked flask and mixed in 40 mL of chloroform and then was stirred gently at 60 °C for 3 days. The silica was collected and washed successively with chloroform and methanol. To remove non-grafted polymer soxhlet extraction was carried out with chloroform for 24 h and again washed with methanol and finally with diethyl ether to obtain copolymer-grafted silica (Sil-copoly-VP$_m$MA$_n$).

2.4. Synthesis of Sil-cograft-VP$_m$MA$_n$

The homopolymers of 4-vinylpyridine (VP$_m$) and methyl acrylate (MA$_n$) with terminal reactive groups were synthesized according to previously reported methods [13,27] and then co-grafted onto silica. Co-grafting of the polymers was done as follows: 3.0 g of porous silica, 1.5 g of VP$_m$ and 3.0 g of MA$_n$ were mixed in 30 mL of toluene and then stirred gently at reflux temperature for 3 days. Toluene was used as grafting solvent because of higher solubility of MA$_n$ in chloroform and consequently lower grafting amount of MA$_n$ compared with VP$_m$. The silica was collected and washed successively with toluene, chloroform and methanol. To remove non-grafted polymer soxhlet extraction was carried out with chloroform for 24 h and again washed with methanol and finally with diethyl ether to obtain polymer co-grafted silica (Sil-cograft-VP$_m$MA$_n$).

Table 1
Elemental analysis and TGA data of Sil-copoly-VP$_{17}$MA$_{12}$ and Sil-cograft-VP$_{15}$MA$_{20}$.

	C (%)	H (%)	N (%)	C/N	Grafting (%) (elemental analysis)	Grafting (%) (TGA)
Sil-copoly-VP$_{17}$MA$_{12}$	14.38	1.94	1.81	7.94	20.01	19.94
Sil-cograft-VP$_{15}$MA$_{20}$	19.25	2.71	2.61	7.38	28.78	28.84

3. Results and discussion

3.1. Synthesis of poly(4-vinyl pyridine-co-methyl acrylate)

Poly(4-vinylpyridine-co-methyl acrylate), copoly-VP$_m$MA$_n$, where m and n are the average degrees of polymerization, with a terminal reactive group at the one side was prepared by modification of the telomerization method [13,17] of 4-vinylpyridine and methyl acrylate with 3-mercaptopropyltrimethoxysilane. The reaction scheme for the telomerization and followed by grafting processes are given in Fig. 1. The obtained copoly-VP$_m$MA$_n$ showed specific adsorptions at ν = 2949, 2854, 1733, 1599, 1416, 1374 and 821 cm^{-1} in IR (KBr). The average degree of polymerization was estimated by ^{1}H NMR spectroscopy (shown in supporting information as Fig. S1) to be 17 for m and 12 for n, respectively.

3.2. Immobilization of copolymer onto silica

The resultant copoly-VP$_{17}$MA$_{12}$ was grafted onto silica by using the terminal trimethoxysilyl group to get the copolymer-grafted silica (Sil-copoly-VP$_{17}$MA$_{12}$). The grafting was confirmed with the appearance of the characteristic hetero aromatic ring stretching (1599 cm^{-1}) of 4-vinylpyridine and ester carbonyl stretching (1733 cm^{-1}) of methyl acrylate measured by DRIFT spectroscopy is shown in supporting information as Fig. S2. The amount of immobilization was determined to be 20.01 and 19.94 wt.% by elemental and TGA, respectively (Table 1).

3.3. Synthesis of poly(4-vinylpyridine) and poly(methyl acrylate) and co-grafted onto silica

Poly(4-vinylpyridine), VP$_m$, and poly(methyl acrylate), MA$_n$, where m and n are the average degree of polymerization, were synthesized by telomerization of 4-vinylpyridine and methyl acrylate,

respectively according to the literature methods [13,27]. The degree of polymerizations was determined by ^{1}H NMR spectroscopy to be 15 and 20 for m and n, respectively. The reaction scheme for the telomerization and co-grafting processes is shown in Fig. 2 to obtain the polymer co-grafted silica (Sil-cograft-VP$_{15}$MA$_{20}$). The grafting of both the polymer was confirmed with the appearance of the characteristic hetero aromatic ring stretching (1599 cm^{-1}) of 4-vinylpyridine and ester carbonyl stretching (1736 cm^{-1}) of methyl acrylate measured by DRIFT spectroscopy (supporting information, Fig. S2). The co-grafting amount was determined to be 28.78 and 28.84 wt.% by elemental and TGA, respectively (Table 1).

3.4. Diffuse reflectance infrared Fourier transform (DRIFT) analysis

Fourier transform infrared spectroscopy is extensively used in the study of polymer blends. This method is valuable for determining the presence of interactions between various groups due to the sensitivity of the force constants to inter- and intramolecular interactions [28].

Fig. 3 shows typical DRIFT spectra of poly(methyl acrylate)-grafted silica (Sil-MA$_{20}$), polymer co-grafted silica (Sil-cograft-VP$_{15}$MA$_{20}$), and copolymer-grafted silica (Sil-copoly-VP$_{17}$MA$_{12}$) in the carbonyl stretching region, which is a region of interest because of the involvement of carbonyl groups in electrostatic interaction. In the spectrum of Sil-MA$_{20}$, the absorption band at around 1741 cm^{-1} is attributed to that of a non-interacted carbonyl group based on an MA unit. The slight absorption shifts to 1336 and 1333 cm^{-1} were observed in Sil-cograft-VP$_{15}$MA$_{20}$ and Sil-copoly-VP$_{17}$MA$_{12}$, respectively. These shifts can be explained by inter- (Fig. 4a) and mostly intramolecular (Fig. 4b) interactions between a pyridine group based on a VP unit and a carbonyl group based on an MA unit. Therefore, it is estimated that the copolymer-grafting method promotes a more effective VP-to-MA interaction than the polymer
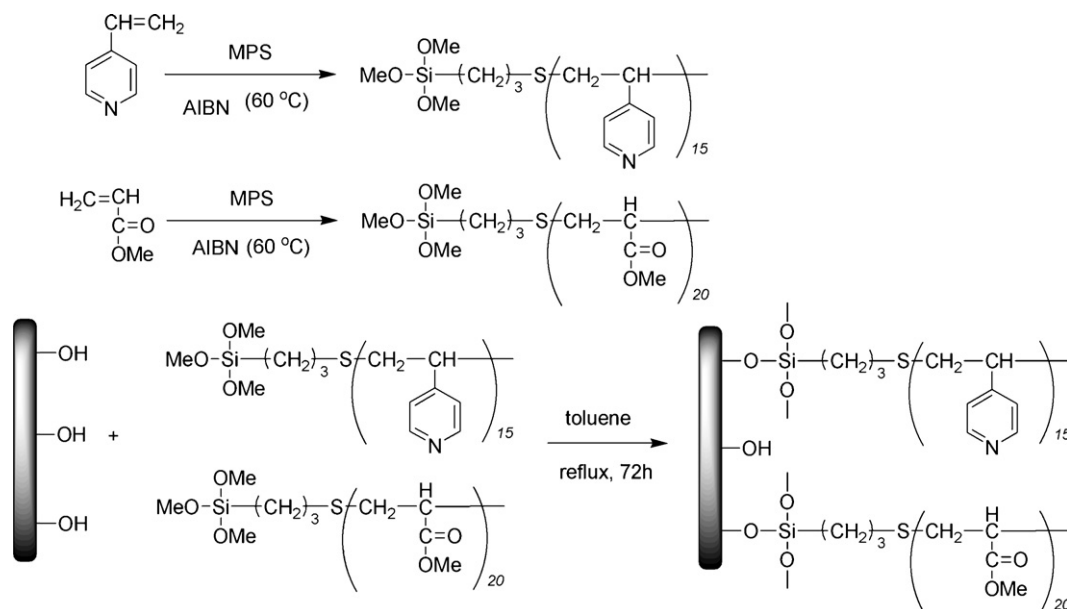

Fig. 2. Synthesis scheme of poly(4-vinylpyridine) and poly(methyl acrylate) with terminal reactive groups followed by co-grafting onto silica.
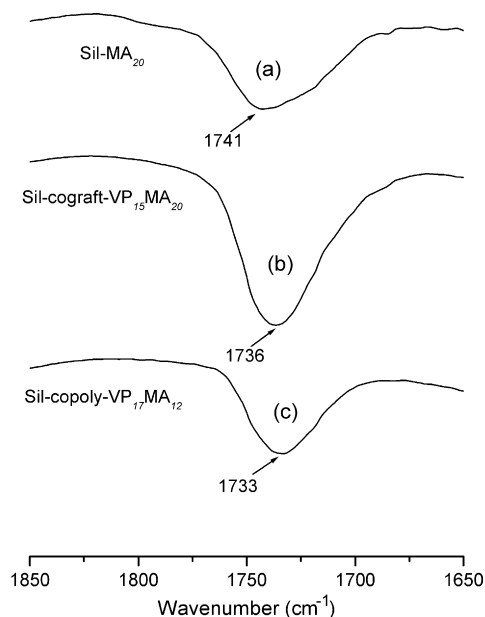
Fig. 3. Partial DRIFT spectra of (a) Sil-MA$_{20}$, (b) Sil-cograft-VP$_{15}$MA$_{20}$ and (c) Sil-copoly-VP$_{17}$MA$_{12}$.

co-grafting method. This finding agrees with the chromatographic evaluation of the organic phases, which will be described in the following sections.

3.5. Molecular-shape selectivity for PAHs in RP-HPLC

For the separation of structurally similar compounds, including natural products and polycyclic aromatic hydrocarbons (PAHs), to enhance the molecular-shape selectivity is essentially powerful. Several size and shape parameters for PAHs were introduced for systematic investigations on retention behavior. The F number is a molecular size descriptor proposed by Hurtubise and co-workers [29], which is defined as follows: F = (number of double bonds) + (number of primary and secondary carbons) − 0.5(number of nonaromatic rings). The selectivity for the two-dimensional shape has been further studied with a molecular shape descriptor, length-to-breadth (L/B) ratio. The parameter was proposed by Wise et al. [30] and Kaliszan et al. [31] and has been defined as the length-to-breadth ratio of the two-dimensional shape of a molecule, and it

quantitatively classifies *rodlike* molecules and *squarelike* molecules. The combination of these size and shape parameters, F and L/B, has been successfully introduced for the characterization of octadecylsilylated silica (ODS) phases [32]. Tanaka and co-workers [33] established a commonly used method to determine molecular-shape selectivity.

In this study, two compounds containing the same number of carbon atoms but having different molecular shapes (non-planar and planar), *o*-terphenyl (F = 9, L/B = 1.11) and triphenylene (F = 9, L/B = 1.12) were used as probes. In a typical monomeric ODS phase, the selectivity $\alpha_{\text{triphenylene}/o\text{-terphenyl}}$ ranges from 1.0 to 1.7, while the value on a polymeric ODS phase lies between 2.0 and 2.7. However, a selectivity $\alpha_{\text{triphenylene}/o\text{-terphenyl}} \geq 2.0$ is an indication of significant solute planarity recognition suggested by Jinno et al. [34,35].

On the other hand, Sil-copoly-VP$_{17}$MA$_{12}$ demonstrated remarkably higher selectivity ($\alpha_{\text{triphenylene}/o\text{-terphenyl}}$ = 8.42) than conventional ODSs, while Sil-cograft-VP$_{15}$MA$_{20}$ also showed good selectivity ($\alpha_{\text{triphenylene}/o\text{-terphenyl}}$ = 5.22). The typical chromatogram for the separation of *o*-terphenyl and triphenylene on Sil-copoly-VP$_{17}$MA$_{12}$ and Sil-cograft-VP$_{15}$MA$_{20}$ is shown in Fig. 5a. Similarly, better selectivities for planar/non-planar discrimination were observed in the other sample sets such as *trans-/cis*-stilbenes and coronene/hexahelicene as planar/non-planar elutes, those were 2.01 and 5.53 with Sil-copoly-VP$_{17}$MA$_{12}$ but 1.78 and 4.87 with Sil-cograft-VP$_{15}$MA$_{20}$, respectively (Table 2).

Table 2 and Fig. 5b include the significant results for the other sample sets. For example, the selectivity of naphthacene to triphenylene and chrysene, those are all planar compounds but their L/B values are very different, are only 1.33 and 1.08 in Sil-copoly-VP$_{17}$MA$_{12}$, although further smaller values are observed in Sil-cograft-VP$_{15}$MA$_{20}$. These results indicate that both the organic phases are sensitive for the molecular planarity but not so significantly sensitive for the molecular aspect ratio.

3.6. Molecular-recognition mechanism

In our previous works, it has been clarified that the selectivity with π-electron-containing polymer-grafted silicas increases with increase of the immobilization amount of polymeric phase and this is due to an entropic effect for promoting multiple π–π interaction with high density polymer packing on silica [25,36,37]. Interestingly, Sil-copoly-VP$_{17}$MA$_{12}$ exhibited higher selectivity than Sil-cograft-VP$_{15}$MA$_{20}$ in all the cases, despite it having lower immobilization amount (Table 1). These results revealed that the intramolecular interaction with copolymer is more effective for
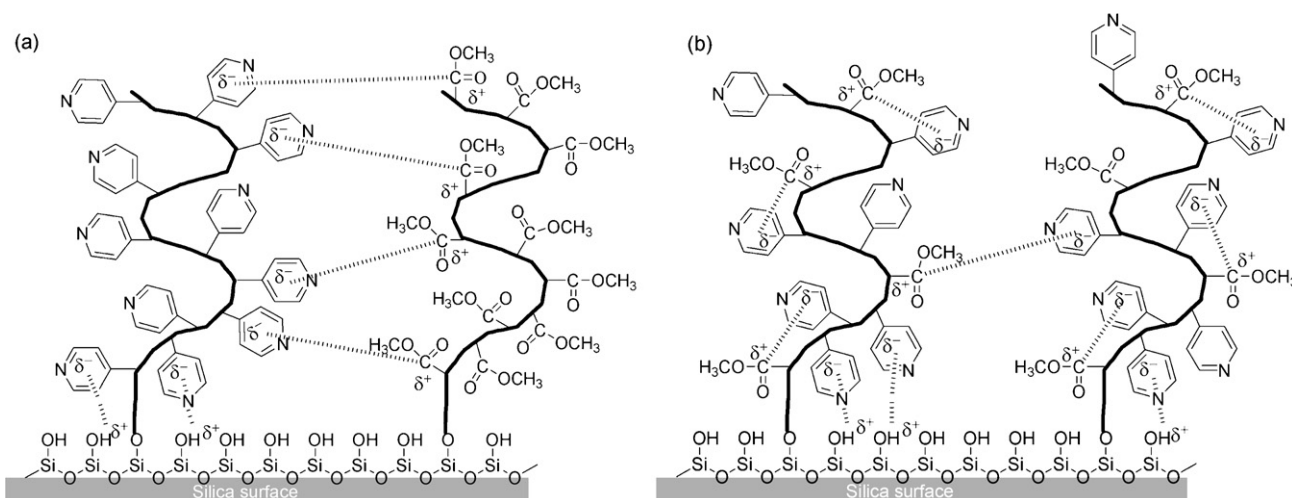

Fig. 4. Schematic illustrations of (a) inter- and (b) intramolecular interactions between VA and MA in Sil-cograft-VP$_{15}$MA$_{20}$ and Sil-copoly-VP$_{17}$MA$_{12}$, respectively.
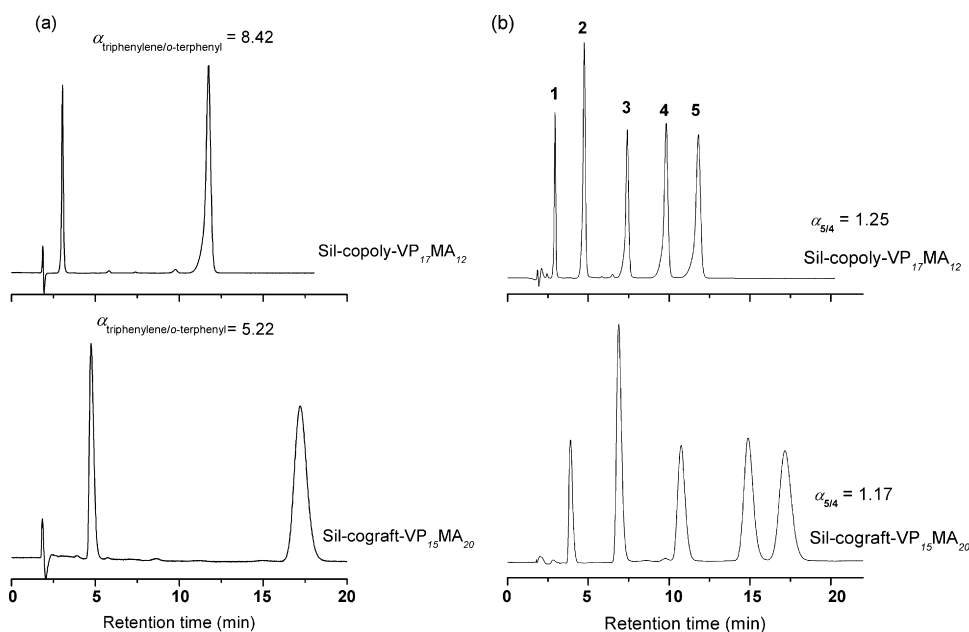
Fig. 5. (a) Chromatogram for a mixture of *o*-terphenyl and triphenylene with Sil-copoly-VP$_{17}$MA$_{12}$ and Sil-cograft-VP$_{15}$MA$_{20}$. Mobile phase: methanol–water (80:20), column temperature 30 °C, and flow rate: 1.00 mL min^{-1}. (b) Chromatogram for a mixture of PAHs with Sil-copoly-VP$_{17}$MA$_{12}$ and Sil-cograft-VP$_{15}$-MA$_{20}$. Elutes: 1, naphthalene; 2, anthracene; 3, pyrene; 4, benz[a]anthracene; 5, triphenylene. Mobile phase: methanol–water (80:20), column temperature 30 °C, and flow rate: 1.00 mL min^{-1}.

selectivity enhancement than intermolecular interaction with co-grafting.

To understand the selectivity enhancement for Sil-copoly-VP$_m$MA$_n$ phase, we propose the following concert effect. Fig. 6 includes two possibilities on the concert effects but both are based on a VP–MA interaction as an electron donor–acceptor interaction. It has been confirmed theoretically [38,39] and with experiments [40] that a carbonyl group can work as an electron-accepting group towards benzene π-electrons in HPLC. Therefore, it is reasonably acceptable that a benzene–carbonyl interaction can be expanded to a VP–MA interaction.

In Fig. 6, the mechanism (a) indicates that a VP as an electron-donating moiety interacts with hydrogen atoms of PAHs while the mechanism (b) indicates that an MA moiety interacts with π-electrons of PAHs. However, we adopt the mechanism (a) because our previous calculation study [38] indicated that in a benzene–benzene interaction, a hydrogen-to-plain interaction was almost three times stronger than a plane-to-plain interaction (Fig. 7) [39]. In addition, the selectivity mode of VP$_m$MA$_n$ is similar to a pure VP$_m$ phase than a pure MA$_n$ phase: for example, it shows less sensitivity for molecular aspect ratio alike to that of pure VP$_m$ [22].

Table 2
Retention and separation factors of PAHs for Sil-copoly-VP$_{17}$MA$_{12}$ and Sil-cograft-VP$_{15}$MA$_{20}$ stationary phases.

Solute	Planar or non-planar	L/B or slenderness or linearity	Sil-copoly-VP$_{17}$MA$_{12}$		Sil-cograft-VP$_{15}$MA$_{20}$	
			k	α	k	α
Benzene	Planar	1.109	0.22		0.48	
				2.68		2.32
Naphthalene	Planar	1.24	0.60		1.12	
				2.65		2.45
Anthracene	Planar	1.57	1.58		2.74	
				2.56		2.51
Chrysene	Planar	1.73	4.37		7.26	
				1.08		1.05
Naphthacene	Planar	1.90	4.05		6.89	
				1.33		1.20
Triphenylene	Planar	1.12	5.38		8.28	
				8.36		5.22
o-Terphenyl	Non-planar	1.11	0.64		1.59	
				2.77		2.21
m-Terphenyl	Non-planar	1.47	1.78		3.59	
				1.11		1.02
p-Terphenyl	Almost planar	2.34	1.61		3.51	
trans-Stilbene	Planar	–	1.02		3.01	
				2.01		1.78
cis-Stilbene	Non-planar	–	0.51		1.18	
Coronene	Planar	1.00	34.33		48.93	
				5.53		4.87
Hexahelicene	Non-planar	–	6.18		10.04	

Mobile phase: methanol–water (80:20). Column temperature: 30 °C; flow rate: 1.00 mL min^{-1}.
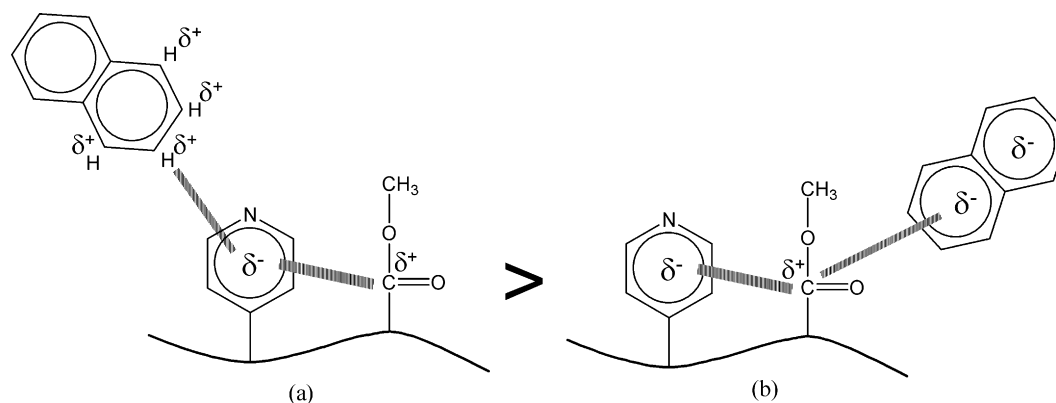
Fig. 6. Proposed illustrations of concert effects of host–guest molecules on copolymeric stationary phase.
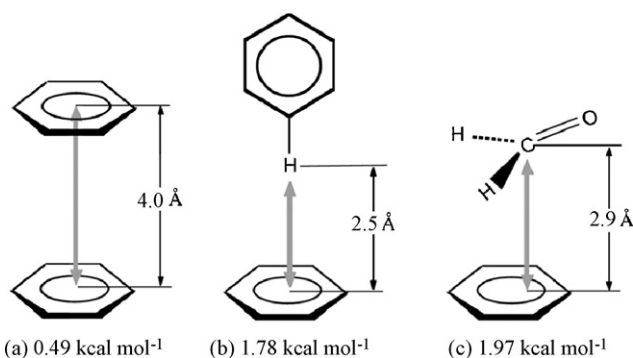

Fig. 7. Proposed structures and energies of (a) and (b) benzene–benzene (c) formaldehyde–benzene complexes estimated by *ab initio* study.

A molecular slit model should be removed in the present mechanism. This mechanism has been often adopted for understanding high selectivity in high density ODS [11,41]. However, the VP_mMA_n phase has no ordered structure showing a slit effect and only amorphous VP_mMA_n polymer network provides micropores for guest molecules. Therefore, compact and planar molecules such as triphenyrene and *trans*-stilbene can be incorporated into micropores to promote multiple interactions but not suitable for bulky molecules such as *o*-terphenyl and *cis*-stilbene. In addition, the VP_mMA_n phase is not sensitive for molecular slenderness, *L/B*.

The more significant discussion point is a distinct difference of the selectivity between the Sil-copoly-VP_mMA_n and Sil-cograft-VP_mMA_n phases. This indicates that a concert effect between VP and MA can be effectively performed by intramolecular system. This finding encourages us that the selectivity enhancement can be promoted by precise control of primary structures in a copolymeric system as well as highly ordered structures.

4. Conclusion

In the present paper, the application of copolymer-based stationary phase for selectivity enhancement towards PAHs has been discussed. Higher molecular recognition was obtained by using copolymer-grafted than polymer co-grafted silica stationary phases, which is induced by electrostatic interactions among the monomer units. Therefore, copolymer-grafted stationary phases would be a good candidate for better molecular recognition in HPLC because a driving force for molecular interaction can be tuned by using kinds of monomers and their composition ratio. These results indicate that preparation of copolymer-grafted silica stationary phases is promising for future applications. Combinations of appropriate monomers, as well as more detailed study on the mechanism of molecular recognition by copolymers, are currently under way in our laboratory.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.chroma.2009.05.053.

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