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Abstract (Doctor)

Title of Thesis	Retention Behavior of Polycyclic Aromatic Hydrocarbons on Novel Polymer-Based Stationary Phases in High Performance Liquid Chromatography
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Approx. 800 words

Liquid Chromatography (LC) is a powerful and convenient technique in the field of analytical chemistry for the separation and determination of complex sample mixtures. The stationary phase in LC plays an important role, especially, octadecylsilica (ODS) stationary phases have been widely used in LC because of its high versatility, separation performance and reasonable cost. However, ODS stationary phases still have a several problems to be solved, such as less heat/chemical resistance. In addition, it is necessary for the development of a new stationary phase which has a different selectivity from conventional ODS phases. On the basis of the above background, the several types of synthetic polymeric materials, which has a high heat/chemical resistance, have been applied as a stationary phase in LC as well as in gas chromatography (GC). In this thesis, novel polymer-based particles have been introduced as the stationary phase in high performance LC, and the retention behaviors on these stationary phases have been examined by using polycyclic aromatic hydrocarbons (PAHs) as the sample analytes.

In Chapter 1, general introduction of this thesis is described along with the background of this work.

In Chapter 2, spherical particles of copolymers, polyimide (PI), was introduced as the stationary phase in LC, and the retention behavior of PAHs was compared with that of typical ODS stationary phases. In addition, the heat-resistance of the PI stationary phase was examined by elevating the column temperature up to 100°C. The PI is prepared with the starting materials of pyromellitic dianhydride (PMDA) and 4,4'-diaminodiphenyl ether (4,4'-oxydianiline, ODA), resulting the spherical PI (PMDA-ODA type) particles with an average diameter of about 5 μm. The chromatographic results of the PI stationary phase showed the significantly larger retentivity of PAHs than that of ODS stationary phases, while the retention tendency of PI phase for PAHs was similar to ODS phases. From the experiments of the column temperature up to 100°C, it was confirmed a good high-temperature stability of the PI phase. A larger retention on the PI phase could be attributed to the surface structure of the PI particles, because a number of aromatic functionalities are existed in the chemical structure of the polymer backbone.

In Chapter 3, another type of polymeric material, poly(benzoguanamine-*co*-formaldehyde) (BF) was applied to the stationary phase in LC. The BF has a good heat/chemical resistance which can be applied as matting agent, car paint, and toner additive. The spherical BF particle has an average diameter of about 5 μm. The retention behavior of PAHs on the BF stationary phase was systematically compared with that of a commercially-available ODS and phenylbutylsilica (PBS) stationary phases. The PBS phase shows similar retention behavior to the ODS phase. In contrast, the retention behavior study for the BF phase shows its different selectivity from that of the ODS and the PBS phases. The results suggest that the BF phase has the retentivity mainly on the basis of hydrophobic interaction between the stationary phase ligands and the solute molecule. On the basis of the comparison with the PBS phase which has a retentivity by these phenyl ligands, the unique selectivity of the BF phase could be attributed to the restricted movement of the phenyl ligands.

In Chapter 4, poly(benzoguanamine-*co*-melamine-*co*-formaldehyde) (BMF), where melamine is additionally introduced as one of the starting materials of the copolymer along with benzoguanamine and formaldehyde, was applied to the LC stationary phase, and the retention behavior of PAHs on BMF stationary phase was compared with typical ODS and the BF stationary phases. The BMF is a co-polymer of BF and melamine, which has a good heat/chemical resistance that can be applied as matting agent, car paint, and toner additive as well as BF. The spherical BMF particle has an average diameter is about 9.5

µm. The retention behavior of PAHs on the BMF stationary phase was systematically compared with that of a commercially-available ODS and the BF phase. Although a similar retention behavior on the BF phase was observed on the BMF phase, at the same time, the BMF phase shows different retention behavior from that of ODS phase. A smaller retentivity for some PAHs was found on the BMF phase when comparing with the BF phase. The results suggest that the BMF phase has a retentivity on the basis of hydrophobic interaction between the stationary phase ligands and the solute molecule as found on the BF phase. It is considered that distance of phenyl ligands of the BMF phase are further apart from each other than those of the BF phase, inducing a more interaction with analyte compounds with a certain molecular length.

Finally, the over-all conclusion of this thesis is summarized in Chapter 5. These novel polymer-based stationary phases showed a characteristic selectivity, which is somewhat different from the selectivity on typical ODS phases. These results suggest that novel polymer-based stationary phase could be developed on the basis of a systematic consideration of the retention behavior. Taking advantage of the unique retentivity of these novel polymer-based stationary phases, the development of new sample preparation device is also expected.