

研 究 主 論 文 抄 録

論文題目 Development of High-Selective Polymeric HPLC Stationary Phases with Precise Arrangement of Weak Interaction Sites on Silica)

(シリカ界面での微弱相互作用の精密集積による高選択性 HPLC ポリマー固定相の開発)

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主論文要旨

High selective high-performance liquid chromatographic (HPLC) stationary phases are needed to separate certain classes of isomers that are important in the disciplines of environmental, pharmaceutical, clinical, and food sciences. We have demonstrated that the integration with ordered arrangement of functional groups in an organic phase on silica is a very useful strategy to enhance the selectivity in HPLC: well-oriented subsidiary weak interaction sites are the driving force for the separation of very complex component mixtures. Polymer-grafted silica stationary phase is one of the best ways to realize these requirements. In the present work, novel stationary phases have been developed by changing polymerization techniques, spacer lengths, monomer sets for copolymerization to solve these separation challenges.

To introduce high-density polymeric organic phase onto silica, initiator (obtained from undecyl ester)-modified silica was prepared and then surface-initiated atom transfer radical polymerization (ATRP) (“grafting-from” method) was carried out with octadecyl acrylate. The resultant polymer-grafted silica was characterized by diffuse reflectance infrared Fourier transform (DRIFT), differential scanning calorimetry (DSC), suspended-state ^1H NMR, solid-state ^{13}C cross-polarization magic angle spinning nuclear magnetic resonance (CP MAS/NMR), solid-state ^{29}Si (CP MAS/NMR) spectroscopies, and elemental analyses. ATRP-based poly(octadecyl acrylate)-grafted silica (Sil-ODA_n-1 or Sil-C₁₁-ODA_n), was used as a stationary phase in HPLC and the chromatographic behavior was evaluated by the retention studies of polycyclic aromatic hydrocarbons (PAHs) and aromatic positional isomers. Compared with previous

poly(octadecyl acrylate)-grafted silica (Sil-ODA_n), which was prepared by the “grafting-to” method, we have observed longer retention and greater selectivity for Sil-ODA_n-1 towards PAHs even at higher temperature.

At the same time, to examine the initiator chain length in ATRP based ODA_n-grafted silica; we prepared Sil-C₃-ODA_n (originated from allyl ester). Suspended-state ¹H NMR, solid-state ¹³C CP/MAS NMR and DSC analyses suggest that Sil-ODA_n-1 or Sil-C₁₁-ODA_n demonstrated more ordered structure than Sil-C₃-ODA_n and consequently better selectivity towards PAHs.

On the other hand, 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. To get the benefit of both of the monomers or synergistic effect of the monomers as well as functional groups, the copolymer with a terminal reactive group (copoly-VP₁₇MA₁₂) 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-VP₁₇MA₁₂ was grafted onto porous silica particles by a silanol coupling reaction with the terminal group. Individually, poly-VP₁₅ and poly-MA₂₀ with a terminal reactive group were also synthesized and co-grafted onto silica (Sil-cograft-VP₁₅MA₂₀) to compare the effect of the copolymer-grafted (Sil-copoly-VP₁₇MA₁₂) and polymer co-grafted stationary phases in HPLC separation. All the polymers were characterized by ¹H NMR and FT-IR analysis before grafting on silica. Polymer grafting was confirmed by 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. The selectivity enhancement by copolymer-grafting in the Sil-copoly-VP₁₇MA₁₂ phase can be brought through intramolecular interaction between VP and MA.

From the above knowledge of copolymer-grafted silica stationary phase, we prepared another novel packing material for high selective reversed-phase HPLC using alternating copolymer-grafted silica. This is the first application of alternating copolymer-grafted silica as a stationary phase in HPLC separation. The organic phase on silica was chemically designed in a way that the weak interaction sites are integrated with high orientation along the polymer main chain and high selectivity could be realized by multiple interactions with solutes. For the above purpose, we synthesized poly(octadecyl acrylate-*alt*-*N*-octadecylmaleimide)-grafted silica (Sil-poly(ODA-*alt*-OMI)) stationary phase. The alternating copolymerization was

carried out from 3-mercaptopropyltrimethoxysilane (MPS)-modified silica via surface-initiated radical-chain transfer reaction. Elemental analysis, DRIFT, ^1H NMR, solid-state ^{13}C CP/MAS NMR, and suspended-state ^1H NMR were used to characterize the new organic phase. Aspects of shape selectivity was evaluated with Standard Reference Material (SRM 869b), Column Selectivity Test Mixture for Liquid Chromatography. Enhanced molecular shape selectivity was observed, that lead to the separation of SRM 1647e (16 PAHs) in an isocratic elution. The effectiveness of this phase was also demonstrated by the separation of several β -carotene and tocopherol isomers. To the best of our knowledge, the complete baseline separation of the tocopherol isomers was achieved for the first time using the Sil-poly(ODA-*alt*-OMI) phase. Chromatographic study revealed that Sil-poly(ODA-*alt*-OMI) has extremely high separation ability compared to the conventional monomeric and polymeric ODS or C_{18} columns. Higher shape selectivity of the new RP material can be explained by a π - π and dipole-dipole interaction mechanism, which brought from the precise arrangement of weak interaction sites on silica. Application of alternating copolymers in the science of separation will open the way to the solution of many of its challenges in environmental, pharmaceutical, clinical, and food science, which can be accelerated by research into the system of cooperation between monomers.