

研 究 主 論 文 抄 録

論文題目：RP-HPLC 固定相用ポリマーグラフト化シリカにおけるカルボニル基の機能に関する研究

(Study on functionality of carbonyl groups in polymer-grafted silica for RP-HPLC stationary phases)

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主論文要旨

Poly (vinyl octadecanoate) grafted silica stationary phases (Sil-VOD₂₃ and Sil-from-VOD) were prepared by two different techniques namely “grafting to” and “grafting from” method. Short alkyl chain poly (vinyl acetate) Sil-VAc₂₅ was also synthesized by grafting to method. Sil-ODA₂₅, Sil-MA₃₀, monomeric and polymeric ODS were used as reference columns. All the polymer-grafted silica particles were elaborately characterized by elemental analysis, thermogravimetric analysis, DSC measurement, suspended-state ¹H NMR, solid state ²⁹Si and ¹³C CP-MAS NMR.

It has been found that Sil-VOD₂₃ had lower surface coverage than conventional monomeric and polymeric ODS and similar to Sil-ODA₂₅. Differential scanning calorimetry of VOD₂₃ demonstrated that octadecyl alkyl chains showed crystalline to isotropic phase transition with endothermic peak at 48.7°C which was similar to ODA₂₅. After grafting phase transition phenomenon was almost disappeared in Sil-VOD₂₃ whereas Sil-ODA₂₅ still exhibits phase transition although at lower endothermic peak top temperature. Normalized intensity of ¹H NMR peak of methylene groups was used to compare the type of mobility of alkyl chain on different stationary phases. The normalized intensity in Sil-VOD₂₃ was gradually increased with increasing temperature indicating flexibility of the phase. On the other hand, the normalized intensity in Sil-ODA₂₅ was lower than Sil-VOD₂₃ below phase transition temperature but distinct increase was observed close to the phase transition temperature. ¹³C CP-MAS NMR measurement showed that the alkyl chain orderness in Sil-VOD₂₃ dominant with *gauche* or disordered form with low field shoulder as *trans* at 20°C and this remain same even the temperature as high as 50°C. In contrast, Sil-ODA₂₅ showed dominant *trans* conformation at lower temperature and *gauche* conformation at higher temperature respectively. The detailed chromatographic behaviour of newly synthesized-phases were investigated for shape selective planar and non-planar poly aromatic hydrocarbons (PAHs). It has been shown that much higher selectivity was observed in Sil-VOD₂₃ as compared with monomeric and polymeric ODS. Thus

carbonyl groups in Sil-VOD₂₃ played an important role for selective separation of PAHs through multiple carbonyl $\pi - \pi$ interaction. However, Sil-ODA₂₅ showed better selectivity than Sil-VOD₂₃. The aligned carbonyl groups of Sil-ODA_n enhance molecular-shape selectivity for PAHs through multiple π - π interactions. Higher shape selectivity by Sil-VOD₂₃ compare to conventional ODS confirmed that carbonyl groups in Sil-VOD₂₃ are effective for molecular shape recognition of PAHs through carbonyl π -interactions even in the disordered state. Temperature dependent selectivity for PAHs were also carried out by Sil-VOD₂₃ and compared with Sil-ODA₂₅ and conventional ODS columns. Aspects of shape selectivity were also evaluated with standard reference materials (SRM 869a). Separation of EPA16 and vitamin-A mixture was carried out by Sil-VOD₂₃ as an application.

PAHs were examined by Sil-VAc₂₅ and Sil-MA₃₀ where both these phases have no long alkyl chain and they differ only in carbonyl group position likewise Sil-VOD₂₃ and Sil-ODA₂₅. It was evident that both Sil-VAc₂₅ and Sil-MA₃₀ showed similar results in PAHs separation. Exceptional separation was obtained for geometrical isomers in Sil-VAc₂₅. Planarity selectivity of Sil-VAc₂₅ is higher as compared with the same of Sil-MA₃₀.

High dense Poly (vinyl octadecanoate) grafted silica stationary phase (Sil-from-VOD) have been prepared by radical chain-transfer grafting from approach and compared with Sil-VOD₂₃ to examine the influence of synthetic route in polymeric and chromatographic properties. A combination of DRIFT-IR, ¹³C CP/MAS NMR and ²⁹Si CP/MAS NMR reveals that Sil-from-VOD have more *trans* conformation than Sil-VOD₂₃. Both phases along with a commercial polymeric ODS column (ODS-p) were applied to RP-HPLC and evaluated by PAHs as solutes. Sil-from-VOD, prepared by grafting from approach and having high density provided better retentivity and selectivity for PAHs compared to other reference columns.

A L-glutamic acid derived new HPLC stationary phase containing carbonyl group and pyrene moiety was also synthesized. This new phase was evaluated for RP-HPLC to examine the $\pi - \pi$ interaction in separation process. Here we try to develop different carbonyl functional group embedded stationary phases which will help the separation chemists to understand the role of functional group in HPLC application.