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Preparation and characterization of carbosilane dendrimer-bonded silica gel and its use in LC

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Abstract Divergently synthesized carbosilane dendrimers generations 1(G1) and 2 (G2) with allyl end groups were bonded onto silica gel. Reactions between the dendrimers and acid-processed silica gel took place, with toluene reflux and organic base as catalyst. Chemically bonded silica gel was characterized by transmission electron microscopy (TEM), infrared (IR), and other methods. The chemically modified silica gels were packed into high-pressure liquid chromatography (HPLC) column and their separation characters were evaluated. G2-bonded silica gel was effective in separating homologous compounds of alcohol, alkyl-substituted benzene, *N*-substituted benzene, metacrylic acid ester and phthalate.

Keywords carbosilane dendrimer, chemically modified silica-based stationary phases, new type of reversed phase, LC

1 Introduction

Silica gel is widely used as an inorganic porous material. It can be used solely as normal-phase material in the field of chromatography. Because of its excellent physical strength and plenty of silanol groups on the surface, chemically modified silica gel with a variety of chromatographic property was broadly studied [1].

Dendrimers are highly branched, three-dimensional regular and mono-polydispersed macromolecules. The large dendrimers take globular shape. Due to their large amount of functional groups on the surface, dendrimers have different properties compared with traditional polymers in

Translated from *Journal of Shandong University*, 2005, 40(6) (in Chinese)

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solubility, viscosity and thermal behaviors [2,3].

Organosilicone dendrimers were the first heteroatom dendrimers, and their synthesis can be traced up to 1993. There are three kinds of connecting points in their structures: Si—O, Si—C and Si—Si bonds [4].

Column efficiency is an important parameter for chromatography. Researches for new type of column packing materials have always been an effective way of achieving efficiency. Dendrimers are figured as bushy jungles while traditional linear C₈, C₁₈ groups as grassland when solutes runs through the surface and inner structure of bonded groups on silica gel and the former is expected to have higher column efficiency than the latter.

We attempted to bond carbosilane dendrimer onto silica gel to obtain a new type of packing materials for reversed-phase liquid chromatography.

2 Experiments

2.1 Chemicals

Allyl group-ended carbosilane dendrimers of generations 1 and 2 (G1 and G2) were synthesized in our laboratory by divergent synthesis method. Their structures are shown as Fig. 1.

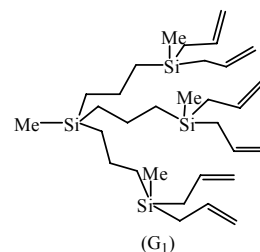


Fig. 1a Sketch Map of G1 of carbosilane dendrimer with allyl end groups

G1 data: ¹H nuclear magnetic resonance (NMR)

(CDCl₃, 300 MHz, δ): -0.145 (s, 3H, CH₃Si-G0), -0.082 (s, 9H, CH₃Si-G1), 0.509 (m, 12H, SiCH₂CH₂CH₂), 1.264 (m, 6H, SiCH₂CH₂CH₂), 1.492 (d, 12H, SiCH₂CH = CH₂), 4.816 (t, 12H, CH = CH₂), 5.724 (m, 6H, CH = CH₂). Infrared (IR): peaked at 1254 cm⁻¹ and is ascribed to SiCH₃ of CH₃Si-G1(Allyl)₆ and 1630, 1147 cm⁻¹ are ascribed to Si-CH₂CH = CH₂.

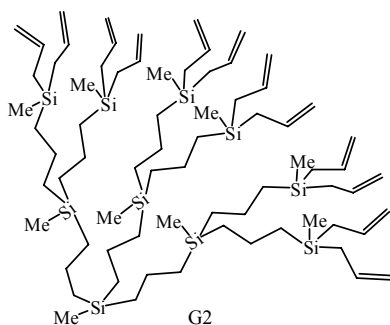


Fig. 1b Sketch map of G2 of carbosilane dendrimer with allyl end groups

G2 data: ¹H NMR (CDCl₃, 300 MHz, δ): -0.145 (s, 3H, CH₃Si-G0), -0.086 (s, 9H, CH₃Si-G1), -0.084 (s, 18H, CH₃Si-G1), 0.523 (m, 36H, SiCH₂CH₂CH₂), 1.210 (m, 18H, SiCH₂CH₂CH₂), 1.493 (d, 24H, SiCH₂CH = CH₂), 4.788 (t, 24H, CH = CH₂), 5.726 (m, 12H, CH = CH₂). IR: 1250 cm⁻¹ is ascribed to SiCH₃ and 1627, 1155 cm⁻¹ are ascribed to Si-CH₂CH = CH₂.

Spherical porous silica (the physical parameters are shown in Table 1) was purchased from Meigao Group Inc., China. All the chemicals were analytical grade. H₂PtCl₆·6H₂O was dissolved in isopropanol. All the reagents were dried and distilled before use.

2.2 Synthesis of organosilicane dendrimer-modified silica gel

(1) Hydrosilane additive reaction was continued with the Pt catalyst between G1 and G2 with MeHSiCl₂, respectively. $N(\text{dendrimer})/n(\text{MeHSiCl}_2) = 1/1.2$.

Table 1 Physical and chemical parameters of G1 and G2 of organosilicone dendrimer with allyl end groups

Parameters	Value
Diameter	5 μm
Specific area	135 m ² /g
Average pore size	14.8 nm
Pore volume	0.5 mL/g
pH	8.87

(2) Bonding procedure Silica gel was processed by 10% HCl, washed to neutral with distilled water. Dried at 100–110°C in an air oven; continued dried in a two-neck

flask at 150–180°C under vacuum of 5 mmHg for 4–10 hours. Cooled down to room temperature, the system was maintained at vacuum. Dried toluene solution of chlorinated dendrimer with triethylamine as catalyst was added by dropping into the vacuum system under the protection atmosphere of highly pure nitrogen. Ultrasonic device was used to uniquely stir the mixtures. The bonding reaction was carried out under reflux with the protection of nitrogen atmosphere for 24 hours. The product was filtered, washed with dried toluene, undried toluene, acetone and methanol in that order. Unreacted silanol groups were treated for 4–6 hours with di-trimethylsilazine in a process similar to the bonding procedure mentioned above. Final products were filtered, washed and dried in natural air.

2.3 Characterization

(1) IR analyses were performed on a Nicolet FT-IR 5DX; , sample template was prepared by KBr.

(2) TEM analysis: Hitachi H-800 TEM.

(3) Burning analysis : high-temperature stove 600°C \times 2 hours.

(4) Test of hydrophobicity: the bonded silica gel was suspended in water of certain volume. Methanol was added until all of the suspended silica gel precipitate. The volume of added methanol was recorded.

(5) Chromatographic test: the column was packed with slurry method. Waters Gel Permeation Chromatography with a differential refractive detector. (150 \times 4.6 mm column; 20 μmL syringe sampling; Column temperature: 30°C; flow rate: 1 mL/minute; mobil phase, $V(\text{methanol})/V(\text{water}) = 50/50.5$ mL each injection).

3 Results and discussion

3.1 IR spectrum comparison of silica gel before and after bonding process (Fig. 2, Fig. 3)

As can be seen from the two spectra,

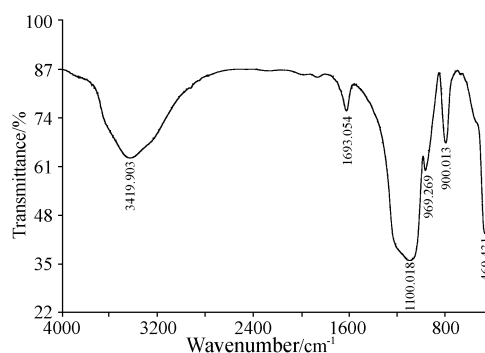


Fig. 2 IR spectrum of acid-processed silica gel

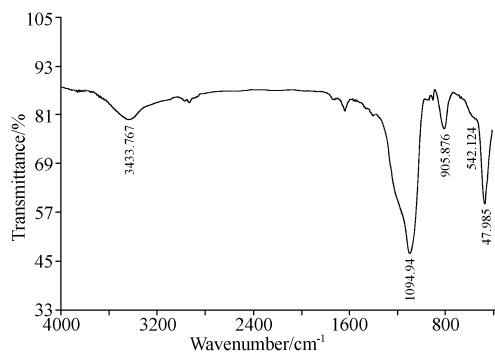


Fig. 3 IR spectrum of G1-bonded silica gel

(1) The peak at 3433 cm^{-1} of Si—OH was much smaller than that of before binding, which indicates most of the silanol groups were reacted during the bonding and the end-capping procedure.

(2) The peaks at 2938 cm^{-1} and 2918 cm^{-1} were ascribed to the stretching vibration of C—H(Si—CH₃).

(3) The peaks at 1400 cm^{-1} – 1464 cm^{-1} were ascribed to the flexural vibration of C—H(Si—CH₃ and Si—CH₂).

(4) The peak at 1645 cm^{-1} was ascribed to the stretching vibration of C=C, the peak of 907 cm^{-1} was ascribed to the flexural vibration of C=C—H.

It is clear that the binding reaction occurred successfully.

3.2 Morphology observation by TEM

The sample was chosen randomly after the bonding and washing processes as mentioned above. A translucent layer can be observed clearly on the outer surface of the silica gel while most of the dendrimer was bonded to the inner surface of the silica gel, which occupies the overwhelming majority of the surface of silica gel and plays an absolute chromatographic function. We can conclude from the morphology that dendrimer successfully bonded to the silica gel.

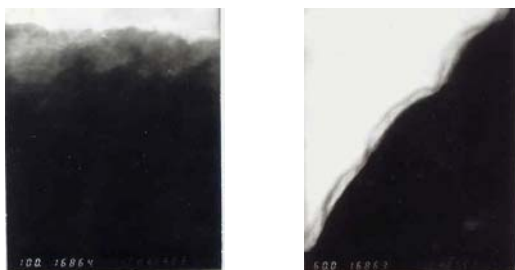


Fig. 4 TEM images of dendrimer-bonded silica gel

3.3 Burning experiments—a way to express the bonding density

The degree of surface covering is an expression of the bonding density. The silanol density of the silica gel after traditional procedure, i.e., drying and vacuuming as mentioned above is usually $8\text{--}9\text{ }\mu\text{mol/m}^2$ [5] and every silanol group occupies an area of 0.2 nm^2 ; the average distance between two silanol groups is 0.5 nm , which means there are four to five hydroxyl groups each nm^2 . Bonded Density % represents the ratio of the number of bonded organic groups to the number of hydroxyl groups that can potentially react. The burning experiments of G1-bonding and G2-bonding stationary phases were carried out in a stove of 600°C for 2 hours. The results were showed in Table 2. The lower density of G2-silica gel compared to G1-silica gel may result from the larger volume hindrance of the dendrimer of G2.

3.4 Test of hydrophobicity

The volume ratios of alcohol to water for immersing G1- and G2-bonding stationary phases are $51 : 49$ and $42 : 58$, respectively, which means that higher bonding density or higher organic component for G1 than that of G2. This is in accordance with the burning experiments.

3.5 Chromatography test

3.5.1 Separation behaviors of aromatics on the G1-bonded silica gel column

The separation behaviors of aromatics on the G1-bonded silica gel column are shown in Fig. 5.

G1-bonded silica gel has poor reversed-phase separation performance and the cause may be ascribed to the small molecule of G1, the shorter alkyl chains and the resulting poor hydrophobicity.

3.5.2 Separation behavior of G2-bonded silica gel stationary phase

The separation behaviors of G2-bonded silica gel stationary phase are shown in Fig. 6.

G2-bonded silica gel is suitable to separate alkyl-substituted benzene derivatives, *N*-substituted benzene, phthalic acid esters, metacrylic acid esters and alcohols and amines and unsuitable to separate neutral organic compounds such as benzene, naphthalene, phenanthrene and anthracene.

Table 2 Data of weight before and after combustion experiments

Sample	Weight before burning/g	Weight after burning/g	Weight loss/g	Surface covering density/ $(\mu\text{mol/m}^2)$
Blank experiment	33.9824	33.9802	0.002	0
G1—silica gel	0.023	0.016	0.007	4.5
G2—silica gel	0.026	0.022	0.004	2.8

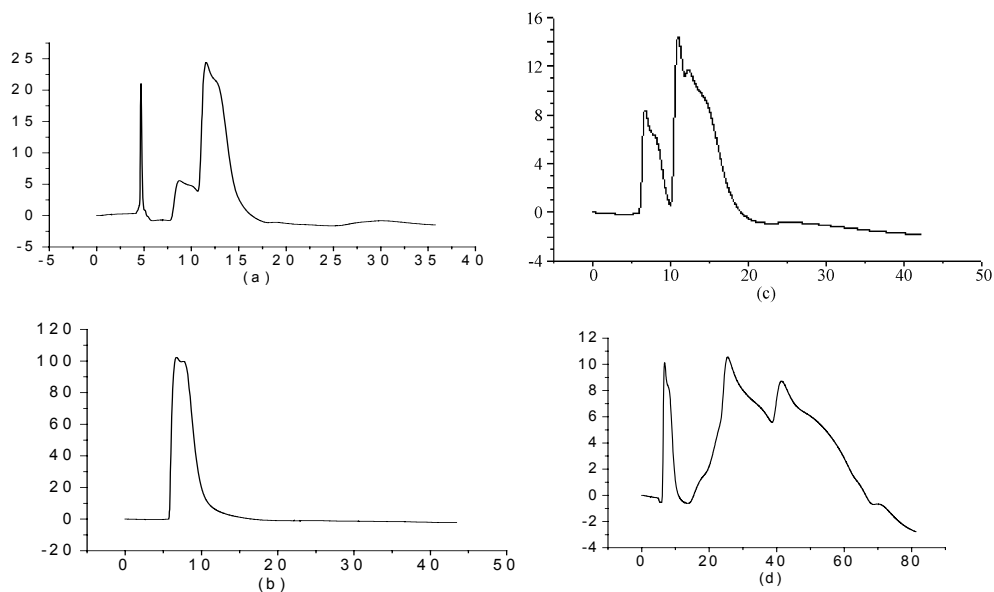


Fig. 5 Separations of several groups of compounds by G1-bonded silica gel

- (a) Separation of mixture of benzene, toluene and phenylethane (b) Separation of mixture of benzene, naphthalene, phenanthrene and anthracene
 (c) Separation of mixture of benzene, toluene and dimethylbenzene (d) Separation of mixture of aniline, phenol

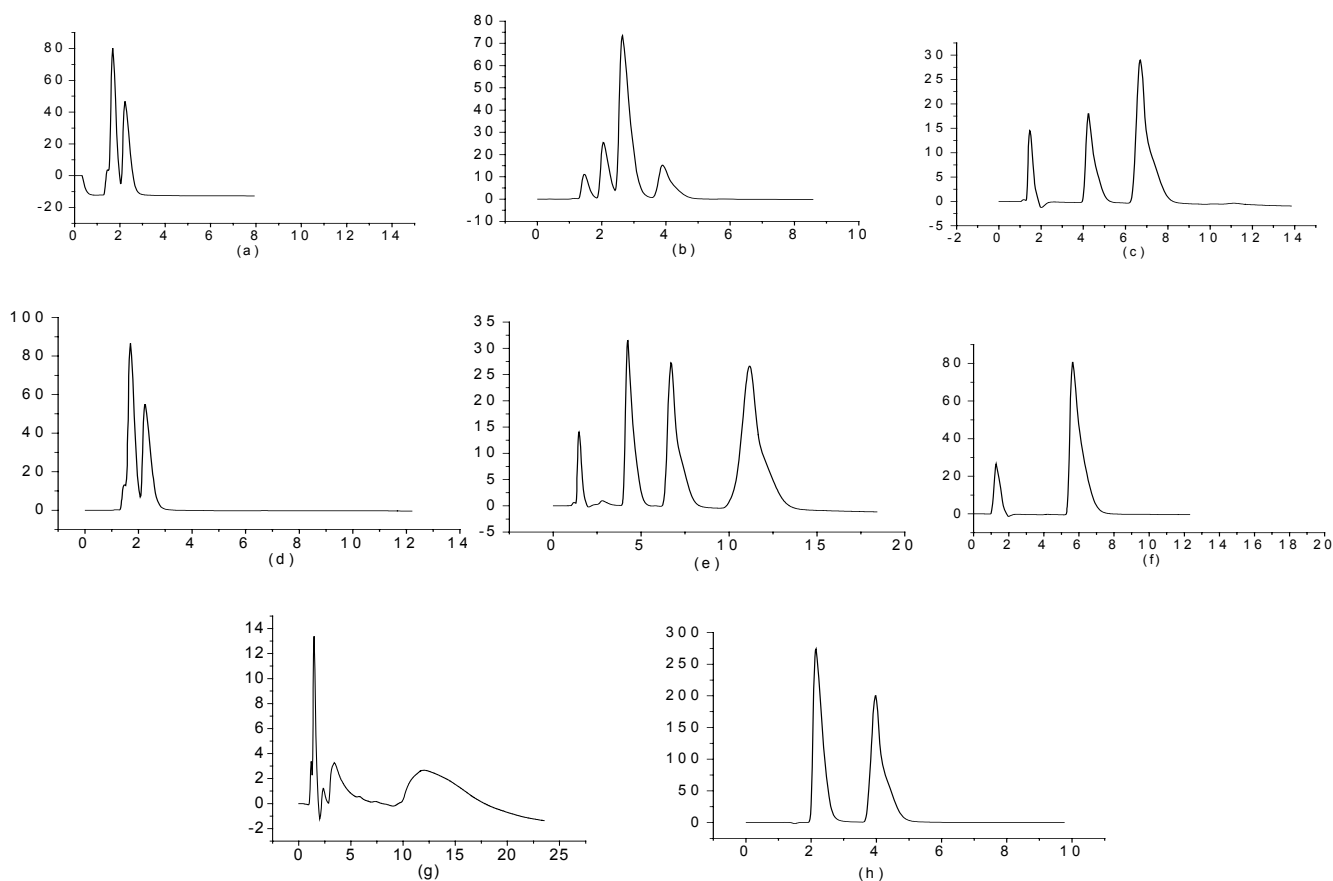


Fig. 6 Separations of several groups of compounds by G2-bonded silica gel

- (a) Separation of ethanol and *n*-propyl alcohol (b) Separation of *i*-propyl alcohol, *n*-butylalcohol, *n*-pentanol, *n*-hexanol
 (c) Separation of methyl methacrylate, methyl ethylacrylate and methyl butylacrylate
 (d) Separation of mixture of benzene, naphthalene, phenanthrene and anthracene
 (e) Separation of mixture of benzene, toluene, phenylethane and butylphenyl
 (f) Separation of diethyl phthalate and dibutyl phthalate (g) Separation of cyclohexamine, dimethylamine and trivinylamine
 (h) Separation of aniline and nitrobenzene

Although it has a lower bonding density than G1-bonded silica gel, G2-bonded silica gel has a better separation performance. We ascribed this phenomenon to the following reasons.

(1) The small space of G1, together with the small amount of its short allyl chains make G1-bonded silica gel not enough to give a positive reverse-phase property, although a comparative acceptable bonding density was obtained.

(2) The larger molecule volume of G2 compared with G1 G2-bonded silica gel can make better use of the space due to the larger molecule volume of G2 than G1. In the meantime, the large amount of allyl end groups of G2, which is four-folds of that of G1, together with the more inner branches of propyl chains make G2-bonded silica gel a very promising reverse phase in LC.

(3) While the bonding density remains the same, the increase in the length of the chains reflects an increase in the carbon content. This does not mean a necessary increase of hydrophobicity of the stationary phase [6]. The strength of the hydrophobicity is a function of the specific area of the packings. This provides a reasonable theoretical basis for the interpretation for the chromatographic difference of G1- and G2-bonded silica gel where G2 has a larger specific area than G1. We can predict that even with a lower bonding density, dendrimers will play an important role in the chromatography field due to the existence of multifunctional groups at the surface of the dendrimer having direct influence on the chromatographic behavior.

4 Conclusions

Dendrimer-bonded silica gel was synthesized and used as the stationary phase for HPLC. Several kinds of derivatives were separated with satisfactory results. Dendrimers will have an important influence in the separation area by its unique three-dimensional and its multifunctional-group structure.

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