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Synthesis of ester-capped carbosilane dendrimers *via* a hybrid divergent–convergent method

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ABSTRACT

A series of novel ester-capped carbosilane dendrimers (**G0**-$COOCH_3$–**G2**-$COOCH_3$) were designed and successfully synthesized *via* a hybrid divergent–convergent method through a facile hydrosilylation reaction. The structures of these dendrimers were confirmed by FTIR, ^{1}H NMR, and HRMS analyses.

1. Introduction

Dendrimers are highly branched macromolecules with well-defined architectures and surface functionality that are obtained from iterative stepwise procedures. They have been one of the most extensively studied materials during the last decade because of their controllable nanosize, unique topological structure, and versatile physicochemical properties, and were widely used in the fields of catalysis, medicinal chemistry, and nanotechnologies [1–3]. In recent years, there has been a rapid growth in the discovery and application of new dendrimers. Carbosilane dendrimers are among the most widely used because of their high flexibility, catalytic inertness, and accessibility [4]. These dendrimers typically possess low glass transition temperatures and relatively low viscosities. They are kinetically and thermodynamically stable owing to the low polarity of the Si–C bond and its high bond strength (306 kJ/mol), which is very similar to that of C–C bond (345 kJ/mol) [5]. In addition, the availability and versatility of many synthetic reactions in organosilicon chemistry enable the facile synthesis of these dendrimers. As a result, the synthesis, characterization, and application of different types of carbosilane dendrimers have attracted wide attention [6–8].

Carbosilane dendrimers are generally synthesized by the divergent method. They are built stepwise from the central core that possesses alkenyl groups through the reiteration of sequential hydrosilylations with chlorosilanes and alkenylations with Grignard reagents, which allow the construction of dendrimers with various generations [9]. The synthetic route of carbosilane dendrimers offers high flexibility and versatility as the hydrosilylation and alkenylations reagents can be varied accordingly. Especially, the hydrosilylation reaction, an addition of a hydrosilane unit (Si–H) to a double bond, has been proved to be high yielding and selective and represents a powerful tool for the rapid and efficient synthesis of carbonsilane dendrimers [10]. In our previous studies, a series of acetyl, *N*,*N*-dimethylaniline, and platinum-capped carbosilane dendrimers were synthesized [11–13]. However, the main drawback of these dendrimers is that such functional groups exhibit relative low reactivity, which may limit further functionalization and application of the carbosilane dendrimers. The synthesis of carbosilane dendrimers with reactive functional groups at periphery is still a great challenge.

In the present study, a series of ester-capped carbosilane dendrimers were synthesized *via* a hybrid divergent–convergent method and their structures were confirmed by FTIR, ^{1}H NMR, and HRMS analyses. The peripheral reactive ester functional groups can

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be further functionalized using appropriate synthetic procedures to expand the application of carbosilane dendrimers.

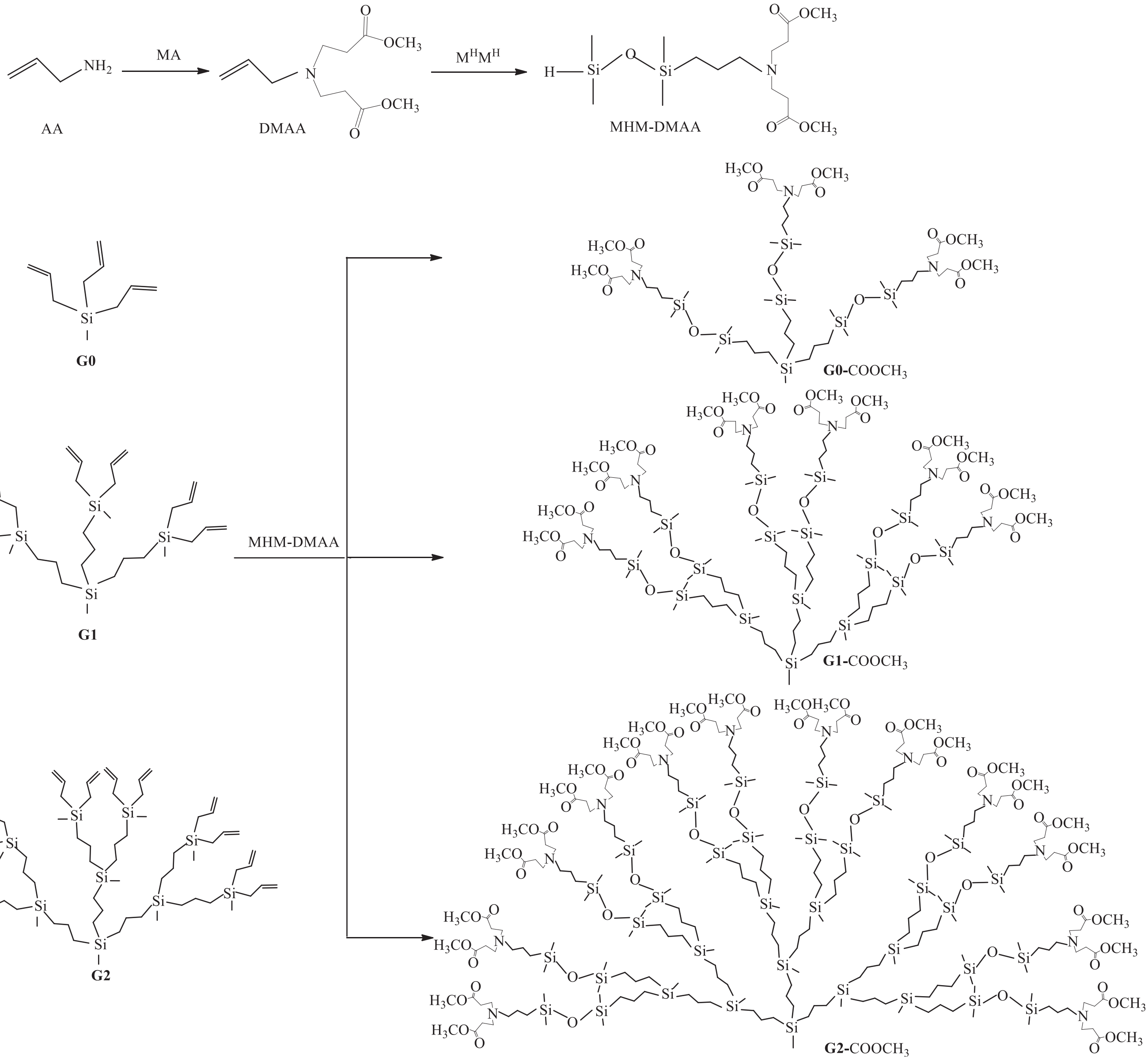
2. Experimental

Fourier transform infrared spectra (FTIR) were recorded on a Bruker Tensor 27 spectrophotometer (Bruker, Switzerland) in the range of 400–4000 cm^{-1} with a resolution of 4 cm^{-1} by accumulating 32 scans. The data were treated with an OPUS spectroscopy software of version 6. ^1H NMR was measured in chloroform on a Bruker AVANCE-400 NMR Spectrometer, and chemical shifts were recorded in parts per million (ppm) without an internal reference. Molecular weights were determined by an Agilent Technologies 6510 Q-TOF LC–MS (HRMS). Methyl acrylate (MA), ethylenediamine (EDA), allylamine (AA), 1,1,3,3-tetramethyldisiloxane (M^HM^H) and tetrahydrofuran (THF) were redistilled just before use. All other reagents used were of analytical-reagent grade. The starting materials carbosilane dendrimers **G0**, **G1**, and **G2** were prepared according to the method described in Ref. [13]. DMAA was prepared by a Michael addition reaction of MA with AA according to the procedure described in our previous work [14]. The synthetic routes of ester-capped carbosilane dendrimers are illustrated in Scheme 1.

2.1. Synthesis of MHM-DMAA

MHM-DMAA was prepared according to a similar method described in Ref. [14]. A suspension of 2.68 g (0.020 mol) of M^HM^H and three drops of the Karstedt catalyst were added into the flask and the mixture was heated slowly at 70 °C under argon atmosphere. Then 1.15 g (0.0050 mol) of DMAA was added drop wise with stirring and the reaction mixture was allowed to stir for 12 h. After the reaction completed, the excess M^HM^H was removed under reduced pressure and 1.70 g (0.0047 mol) of MHM-DMAA was obtained. Yield: 94.10%.

FTIR (KBr, cm^{-1}): υ 2969, 2863 (CH_3, CH_2), 2110 (SiH), 1738 ($COOCH_3$), 1251 (Si–CH_3), 1041 (Si–O–Si); ^1H NMR ($CDCl_3$): δ −0.07 to 0.02 (m, 12H, SiCH_3), 0.30–0.35 (t, 2H, Si$CH_2CH_2CH_2N$),



Scheme 1. The hybrid divergent–convergent synthesis routes of ester-capped carbosilane dendrimers.