

Fabrication of Dendrimer-like PAMAM Based on Silica Nanoparticles[†]

LIU, Peng^{*,a,b}(刘鹏) TIAN, Jun^b(田军) LIU, Wei-Min^b(刘维民) XUE, Qun-Ji^b(薛群基)

^a Department of Chemistry, Lanzhou University, Lanzhou, Gansu 730000, China

^b State Key Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou, Gansu 730000, China

A G 4.0 dendrimer-like poly(amido amine) (PAMAM) based on silica nanoparticles was fabricated via a divergent approach. It was built from γ -aminopropyl silica nanoparticles (APSN) core via repetitive addition of acrylate (MA) and hexylenediamine (HDA). FT-IR and EA were used to monitor the progress of dendrimer during each step. The amino group content of the resulting product increased from 0.49 to 3.72 mmol/g after the 4th generation. In addition, the percentage of grafting increased with increasing generation and reached to 65.9% after 4th generation. It was found that the resulting silica nanoparticles could be dispersed in methanol with a mean hydrodynamic particle diameter of 152.7 nm although the silica nanoparticles had agglomerated during the storage period.

Keywords fabrication, dendrimer-like PAMAM, silica nanoparticle

Introduction

Dendrimer chemistry is a rapidly developing field of research.^{1,2} Dendrimers offer the prospect of novel materials with advantageous properties, allow them to serve as catalysts,³⁻⁵ medical materials,^{6,7} surfactant,⁸ light-harvesting materials,⁹ supports for organic synthesis,¹⁰ dendritic boxes¹¹ or other supramolecule dendritic arrangements.

Recently, self-assembly of dendritic molecules has been of great interest to create functional materials with nanoscale supramolecular structures.¹² The large size and globular shape of poly(amido amine) (PAMAM) dendrimers make them suitable building blocks for self-assembled monolayer or multiplayer ultrathin films. Watanabe and Regen¹³ used the procedure of repeated deposition of amine terminated PAMAM dendrimers onto a Pt²⁺ bearing surface, followed by reactivation with K₂PtCl₄, giving multiplayer films. Wells and Crook¹⁴ reported the first covalently bound dendrimer monolayer, which resulted from linking PAMAM dendrimers to a mercaptoundecanoic acid self-assembled monolayer via amide bond formation.

Tsukruk's group fabricated composite molecular films by self-assembly of dendritic molecules of two adjacent generations using electrostatic layer-by-layer deposition.¹⁵ All these examples showed the potential application of mono- or multi-layer films as chemical sensors,¹⁶ size selective heterogeneous catalysts or a basis for optical filters and optical devices.¹⁷⁻¹⁹ Cao and his coworkers²⁰ reported the formation of a stable ultrathin multiplayer film by converting hydrogen or ionic bonds to covalent bonds under ultraviolet irradiation. This conversion of the bonding increases the resistance of films to etching by polar solvents.

In the present work, a highly branched polymer, dendrimer-like PAMAM was fabricated onto silica nanoparticles surface via a divergent approach. The fabrication of dendrimer-like PAMAM onto the surface contained two processes: (1) Michael addition of methyl acrylate (MA) to amino groups as an initiator site introduced onto silica surface, and (2) terminal amidation of the resulting esters with hexylenediamine (HDA). The percentage of grafting was calculated from the elemental analysis. The resulting product was characterized with elemental analysis (EA), fourier transform infrared spectroscopy (FTIR), transmission electron microscope (TEM) and laser scattering system (LSS).

Experimental

Materials

Silica nanoparticles (MN1P) was obtained from Zhoushan Mingri Nano-materials Co. Ltd., Zhejiang, China. The surface area and particle size were 640 m²·g⁻¹ and 10 nm, respectively. It was dried *in vacuo* at 110 °C for 48 h before use.

γ -Aminopropyltriethoxysilane (APS) (Gaizhou Chemical Industrial Co. Ltd., Liaoning, China) was used without further purification. Methyl acrylate (MA) (Tian-

* E-mail: pliu@lzu.edu.cn

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jin Chemicals Co. Ltd., China) was dried over sodium sulfate and distilled just before use. Hexylenediamine (HDA) (Tianjin Chemicals Co. Ltd., China) was refluxed over sodium and distilled just before use. Anhydrous methanol (Tianjin Chemicals Co. Ltd., China) used as solvent was analytical grade reagent.

Grafting of dendrimer from silica surface

The initiator, γ -aminopropyl silica nanoparticles (APSN) was prepared by the self-assembly of APS on the silica nanoparticles.²¹

Michael addition (Scheme 1, Step A) was carried out as following: Into a 500 mL flask of that contained 3.0 g of APSN, 100 mL of methanol and MA (0.5 mL, about 5 mmol) were added. The flask was sealed and the mixture was stirred with a magnetic stirrer at 50 °C for 48 h after being dispersed with ultrasonic vibrations for 30 min. The resulting silica was dispersed-reprecipitated (centrifugation at 10^4 r·min⁻¹ for 0.5 h) for five times.

The amidation of terminal ester groups (Scheme 1, Step B) was carried out as followed: Into a 500 mL of flask that contained the silica, 100 mL of methanol and HDA (2.0 g, about 17 mmol) were added. The flask was sealed and the mixture was stirred with a magnetic stirrer at 50 °C for 48 h after being dispersed with ultrasonic vibrations for 30 min. The resulting silica was dispersed-reprecipitated (centrifugation at 10^4 r·min⁻¹ for 0.5 h) for five times.

To propagate the 2nd generation, the double amounts of MA and HDA were used. The preparation procedure of the dendrimer-like PAMAM-grafted silica nanoparticles could be summarized schematically as Scheme 1.

Characterizations

Elemental analysis (EA) of C and H was performed on an Elementar vario EL instrument. FT-IR spectrum was performed using a Bio-RAD FTS-165 Spectrometer by

pressing the samples as a potassium bromide (KBr) disk. TEM was used for the morphology analysis of the silica nanoparticles with a JEM-1200 EX/S transmission electron microscopy. The silica nanoparticles was dispersed in methanol in an ultrasonic bath for 10 min, and then deposited on a copper grid covered with a perforated carbon film. The dispersibility and the mean hydrodynamic particle diameter of the dendrimer-like PAMAM grafted silica were dispersed in methanol and investigated by a BI-200SM Laser Scattering System (LSS, Brookhaven Instrument Co., USA).

Determination of amino group content and percentage of grafting

The content of amino groups introduced onto the surface of silica and dendrimer-like PAMAM-grafted silica was determined by EA.

The percentage of grafting (PG) was determined by the following equation:

$$PG (\%) = A/B \times 100$$

where A = dendrimer (polymer) grafted (g) and B = silica nanoparticles charged (g). The weight of dendrimer (polymer) grafted onto the silica surface was calculated from the EA results or the TGA results.

Results and discussion

Fabrication of dendrimer-like polymer onto silica surface

The amino group contents and percentage of grafting of the dendrimer-like PAMAM-grafted silica nanoparticles were shown in Table 1, calculated from the elemental analysis results. In the first propagation procedure from initiator to G 1.0, more than 50% amino group had reacted with MA with a molecular ratio of 1:2, and the other part with a molecular ratio of 1:1. From G 1.0 to G 2.0,

Scheme 1 Ideal synthetic route to the dendrimer-like PAMAM grafted silica nanoparticles.

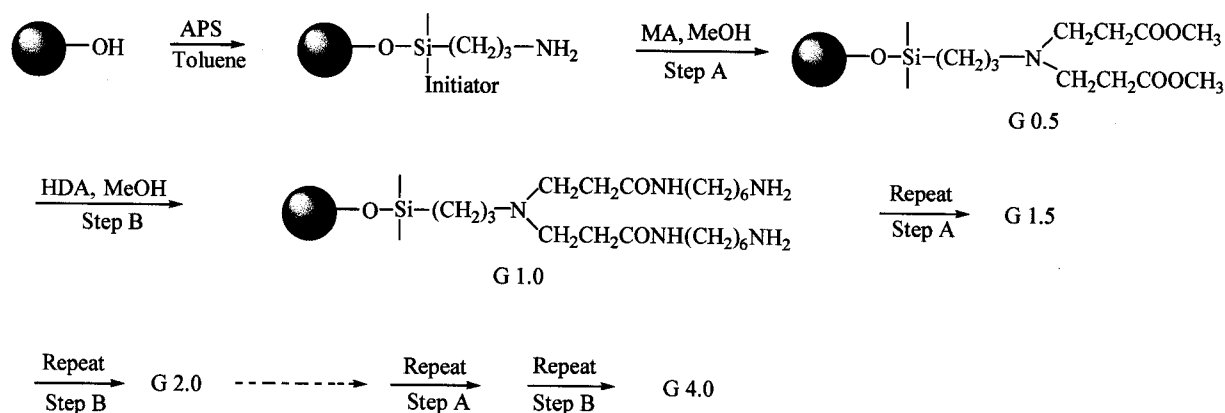


Table 1 Amino group contents and the PGs of the dendrimer-grafted silica nanoparticles

Generation	EA results (%)			Total amino groups (mmol/g)		PG (%)	
	N	C	H	Obsd. ^a	Theo. ^b	Obsd. ^c	Theo.
G 0	0.69	4.18	1.98	0.49	—	—	—
G 1.0	2.21	12.76	2.77	1.58	2.10	19.7	20.3
G 2.0	3.70	22.12	3.46	2.64	4.24	41.5	54.8
G 3.0	4.74	26.31	4.14	3.39	6.54	53.1	123.9
G 4.0	5.21	29.14	5.71	3.72	8.51	65.9	262.0

^a Calculated from the EA results. ^b Theoretical values. ^c Calculated from the TGA results.

only about 30% of the amino groups on the surface of G 1.0 had reacted with MA with a molecular ratio of 1:2, and the other part with a molecular ratio of 1:1. From G 2.0 to G 3.0, more than 90% of the amino groups on the surface of G 2.0 had reacted with MA with a molecular ratio of 1:1. From G 3.0 to G 4.0, only about 50% of the amino groups on the surface of G 3.0 had reacted with MA with a molecular ratio of 1:1. The theoretic C:N mass ratio, which was calculated from the repeating cell, was 5.14. However, the C:N mass ratios of the dendrimer-like PAMAM based on silica nanoparticles (all > 5.50), which were calculated from the EA results, were all bigger than it. It is shown that a lot of ester groups had not been amidated. Therefore, the incomplete propagation of dendrimer from amino groups on silica surface may be due to the fact that (1) complete Michael addition and the amidation with surface functional groups hardly proceed because of heterogeneous reaction system, and (2) the grafted chains on the silica surface interfere with the propagation of the dendrimer from the surface because of the space hindrance. So a PG more near the theoretic value could be achieved if an APSN has a smaller amino group content.

FT-IR characterization

Fig. 1 shows the FT-IR spectrum of the G 4.0 PAMAM dendrimer grafted silica nanoparticles. It became apparently that the absorption at 1645 cm^{-1} is characteristic of amide groups, while the absorption at 2936 cm^{-1} is characteristic of methylene groups. The absorption at 1705 cm^{-1} implied the presence of ester bonds, indicating the

incomplete amidation with HAD. It was also found that the IR absorption bands at the above-mentioned four wavenumbers increased with the increase of the number of generations from G 1.0 to G 4.0. The results were good agreement with the results of EA. It was concluded that the dendrimer-like PAMAM was grafted from amino groups on silica nanoparticles surface by repeating treatment with MA and HAD.

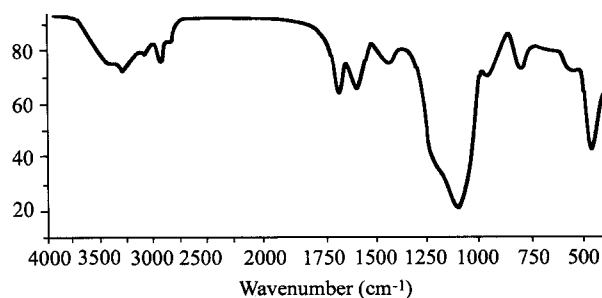


Fig. 1 FT-IR spectrum of G 4.0 dendrimer-like PAMAM grafted silica nanoparticles.

Morphological analysis

The TEM images of the silica nanoparticles, APSN and the G 4.0 PAMAM grafted silica nanoparticles were shown in Fig. 2. The mean hydrodynamic particle diameters of the dendrimer-like PAMAM grafted silica nanoparticles, from G 1.0 to G 4.0, investigated by LSS, were all about 150 nm. It maybe due to the smaller chain length of PAMAM compared with the dimension of the silica nano-

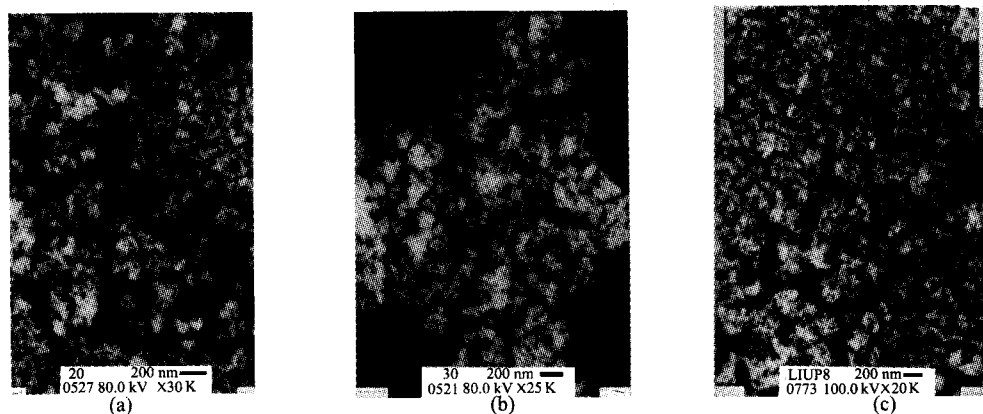


Fig. 2 TEM images of (a) silica nanoparticles, (b) APSN and (c) dendrimer-like PAMAM grafted silica nanoparticles.

particles. However, The mean hydrodynamic particle diameters of the silica nanoparticles and the APSN were 240 and 560 nm, dispersed in methanol, respectively. It also proved that the grafting of dendrimer-like PAMAM could improve the dispersibility of silica nanoparticles in methanol. The mean hydrodynamic particle diameters of the dendrimer-like PAMAM grafted silica nanoparticles were bigger than 10 nm because the silica nanoparticles had aggregated in the period of storage and the hard aggregation could not be broken up in the reaction conditions.

Conclusions

A G 4.0 dendrimer-like poly(amido amine) (PAMAM) grafted silica nanoparticles was fabricated from APSN via a divergent approach. It could be dispersed in methanol with a mean hydrodynamic particle diameter of 152.7 nm. It could be concluded that the fabrication of the dendrimer-like PAMAM onto silica nanoparticles could improve its dispersibility in organic solvents.

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