

Synthesis and Characterization of Dendritic Poly(amidoamine)-Silica Gel Hybrids

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ABSTRACT: Novel dendrimer-silica gel hybrids were prepared from amino-terminated poly(amidoamine) generation 3 (32 cascade) and its partly ester-terminated derivatives with tetraethoxysilane in the presence of a coupling agent 3-glycidoxypropyltrimethoxysilane by *in situ* sol-gel process. The scanning electron micrograph spectra showed that these transparent hybrids have the nanocomposite structure. Their transparent and thermal properties were characterized by ultraviolet, thermogravimetric analysis. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 2186–2190, 2000

Key words: PAMAM; organic–inorganic hybrid; GOTMS; nanocomposite materials; sol-gel process

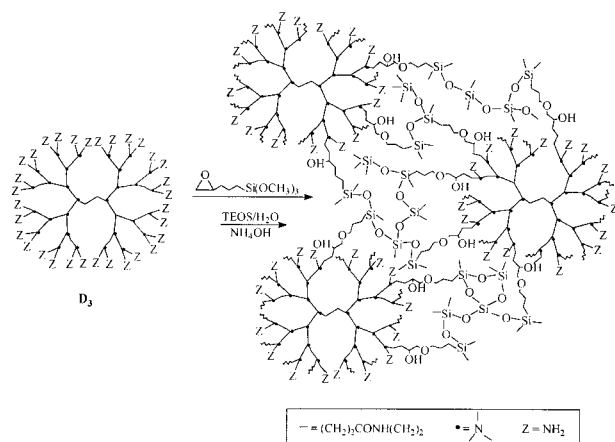
INTRODUCTION

The synthesis of organic–inorganic nanocomposite hybrid materials by sol-gel process is an expanding field of investigation.^{1–6} Hybrid organic–inorganic materials are intimate combinations of these dissimilar materials that are not constrained by the classical material compromises. The quantum leap in behavior often arises with hybrids from two sources: the reduction of the domain size of the inorganic phase to 100 nm or much less, and generation of enormous interfacial areas, which enable numerous covalent bonds or other compatibilization between the phases. The application areas for hybrid materials have expanded from their original base of enhanced mechanical properties and abrasion resistance. The current generation of materials is providing examples of novel fiber optics, wave guides and nonlinear optical materials, and ion-conduction behavior, etc.^{7–13}

Recently, dendritic polymers have attracted considerable research interest because of their unique molecular architecture and unusual properties.¹⁴ The construction of hybrid materials from dendrimers will be possible to incorporate their fascinating structure features, including the nanoscopic size, spherical structure, and cavernous interior, into the hybrid systems which might provide an interesting approach for the preparation of novel functional hybrid materials. However, such hybrid materials based on the dendritic polymers have not been studied in any great detail and only a few articles are found.^{15–18} Among them, Saegusa¹⁶ reported a hybrid material prepared by the sol-gel reaction of ethyl orthosilicate in the presence of the organic dendrimer poly(amidoamine) (PAMAM) without coupling agent for the preparation of highly porous silica gel. In this case, the PAMAM was dispersed in the framework of silica gel. Liu et al.¹⁷ reported another kind of hybrid material—multilayers of Gantrez [poly(maleic anhydride)-*c*-poly(methyl vinyl ether) lightly crosslinked with 1% ethylenediamine] and a PAMAM dendrimer beginning with an amino-functionalized silica/silicon-wafer surface. In the present work, novel organic–inor-

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Scheme 1 The hybrid structure from PAMAM and TEOS with 3-glycidoxypropyltrimethoxysilane as coupling agent by *in situ* sol-gel process.

ganic hybrid materials containing highly functionalized nanomolecules PAMAM are synthesized by using 3-glycidoxypropyltrimethoxysilane as a coupling agent. When polycondensation takes place between trialkoxysilyl groups on the PAMAM and tetraethoxysilane (TEOS), the covalent bonds between two phases can be formed by an *in situ* sol-gel process, and the process was expected, as shown in Scheme 1.

Besides, a modified PAMAM with methylacrylate was prepared in which most of the terminal —NH_2 groups was replaced by the ester groups, and about 25% of the —NH_2 groups remained. Its hybrid behavior was also described.

EXPERIMENTAL

Materials

Dendritic PAMAM (generation 3) (D_3) was prepared according to the literature.¹⁹ TEOS and 3-glycidoxypropyltrimethoxysilane (GOTMS) were domestic products, purified by distillation before use. The solvents used were purified by common methods.

Preparation of Modified PAMAM (Generation 3) with Methylacrylate (MD_3)

A 50-mL three-neck flask equipped with a stirrer was added with 1 g D_3 (0.1447 mmol) and 20 mL of methanol under nitrogen; after the PAMAM was dissolved in the solution, 20 mL of methanol with 0.79 mL of methylacrylate was dropped into the flask by dropping funnel at ambient temper-

ature. Then the mixture was stirred for 24 h. The solvent was distilled under vacuum pressure and a transparent solid (1.58 g) was obtained and then dissolved and stored in THF solution. According to the yield, it might be estimated that about 25% of the —NH_2 group was remaining in this ester-terminated PAMAM. This modified PAMAM was abbreviated as MD_3 .

Preparation of D_3 Hybrid Materials

To a 25-mL flask equipped with a stirrer was added 4 mL of methanol solution of D_3 (0.2 g) under nitrogen, then 0.19 mL GOTMS (molar ratio of GOTMS over —NH_2 of $\text{D}_3 = 1$) was added by a syringe. After stirring for 12 h at room temperature, 0.2 g of TEOS, 0.069 mL of water, 0.02 mL of NH_4OH (4*N*), and another 1 mL of methanol were added by syringe. The mixture was stirred rapidly at room temperature for 30 min, then the solution was transferred into a 25-mL flat-bottom cup and covered with parafilm. One week later, several pinholes were made in it. To evaporate the solvent and small molecules produced in the hydrolysis, the solution was left to dry for 1 month and then cured at 50°C under vacuum for 24 h.

Preparation of MD_3 Hybrid Materials

To a 50-mL flask equipped with a stirrer was added 2.1 mL of THF solution of MD_3 (0.2 g) under nitrogen, then 0.059 mL of GOTMS (molar ratio of GOTMS over —NH_2 of $\text{MD}_3 = 2$); 10 mL of THF was added by a syringe. After stirring for 6 h at room temperature, 0.2 g of TEOS, 0.069 mL of water, 0.02 mL of NH_4OH (4*N*), and another 5 mL of THF were added by syringe. The mixture was stirred rapidly at room temperature for 2 h, then the same procedure as the preparation of D_3 hybrid was followed.

MEASUREMENTS

Fourier transform infrared (FTIR) spectra were recorded on an IFT-113V Bruker spectrometer. Thermogravimetric (TG) analysis spectrum was performed on a Perkin-Elmer TGA7 Thermogravimetric Analyzer at a heating rate of 20°C/min⁻¹. Differential scanning calorimetry scan was conducted under a nitrogen atmosphere using a Perkin-Elmer DSC7 Differential Scanning Calorimeter at a heating rate of 20°C/

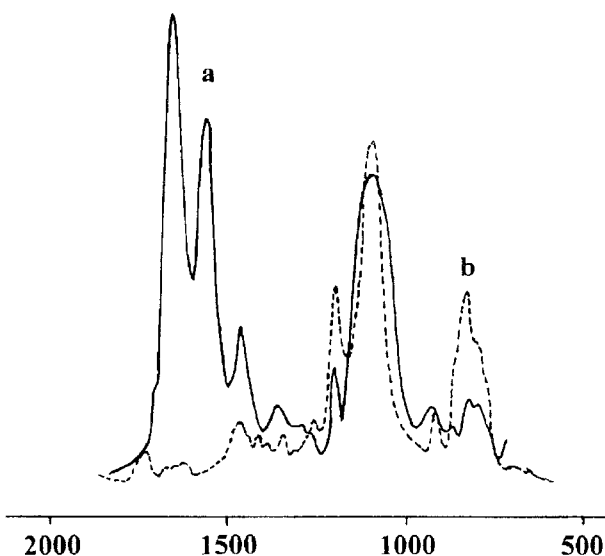


Figure 1 FTIR spectra of coupling product (a, solid line) and GOTMS (b, dashed line).

min^{-1} . Transmittance was measured by a Shimadzu UV-250 spectrometer. The fracture surfaces of hybrid materials were observed by Scanning Electron Microscopy (SEM) on a Hitachi S-530 electron microscope.

RESULTS AND DISCUSSION

The Proof of a New Bond Forming Between D_3 and GOTMS

To rectify the existence of a chemical bond formed between PAMAM and the couple agent GOTMS, the coupling product of PAMAM and GOTMS (the ratio of GOTMS over $-\text{NH}_2$ group was 1) was taken for infrared measurement. Figure 1 shows the FTIR spectra of the coupling product (curve a) and pure GOTMS (curve b).

Figure 1 shows that the peak at 818 cm^{-1} for the epoxy skeleton vibration apparently decreases in curve a and the height ratio of the Si—O peak (1090 cm^{-1}) to the epoxy peak in curve a is much higher than that in curve b. Because the amounts of the Si—O group in both cases are the same, the higher height ratio of the Si—O peak to epoxy peak in the coupling product can only be attributed to the disappearance of the epoxy group, which implies that the ring opening addition reaction takes place between the epoxy in GOTMS and $-\text{NH}_2$ in PAMAM, and the new bond should be formed between D_3 and GOTMS.

Effect of Molar Ratios of GOTMS over PAMAM Amine Group on Gel Time and Gel Fraction

Only seen from appearance, the samples with the coupling agent GOTMS are transparent, whereas the samples without GOTMS are opaque (Table I). With the fraction of GOTMS decreasing, the gel time of hybrid samples were becoming longer and longer. It was 12 h for Hd-01, then it gradually prolonged to 286 h for Hd-04.

In the MD_3 hybrid cases, the gel time becomes much longer because of their low content of $-\text{NH}_2$ in the dendrimer molecules. For Hd-05 and Hd-08, without coupling agent, a serious phase separation occurred during the sol-gel process, and the determination of the gel time was very difficult.

To measure the sol fractions, all samples were extracted thoroughly with methanol for D_3 hybrid materials and THF for MD_3 hybrid materials for 48 h. The results show that the higher the ratio of coupling agent GOTMS to $-\text{NH}_2$, the better the results of coupling reactions will be. From Table II, in the cases of D_3 , it is found that when the molar ratio of coupling agent GOTMS to $-\text{NH}_2$ decreases from 1 to 0.3, the sol fraction of the hybrid samples Hd-01, Hd-02, Hd-03, and Hd-04 gradually increases and the content of residual organic phase, i.e., the content of the dendrimer, which is incorporated in hybrid by covalent bond, decreases. That is also the case with MD_3 ; for example, the residual organic phase of sample Hd-06 (GOTMS: $-\text{NH}_2 = 2$, sol fraction 5.8) is more than that of sample Hd-07 (GOTMS: $-\text{NH}_2$

Table I Effect of Molar Ratios of GOTMS over PAMAM End Group on Gel Time^a

Sample ^b	Molar Ratio of GOTMS to $-\text{NH}_2$	Gel Time (h)	Appearance
Hd-01	1	12	Transparent
Hd-02	0.8	22	Transparent
Hd-03	0.5	46	Transparent
Hd-04	0.3	286	Transparent
Hd-05	0	—	Opaque
Hd-06	2	312	Transparent
Hd-07	1	552	Transparent
Hd-08	0	—	Opaque

^a The feeding ratios were as follows: $[\text{TEOS}]/([\text{TEOS}] + [\text{PAMAM}]) = 50\text{ wt } \%$; $[\text{NH}_4\text{OH}]/[\text{TEOS}] = 0.07$ (molar ratio), $[\text{TEOS}]/[\text{H}_2\text{O}] = 4$ (molar ratio).

^b Hd-01–05 were samples of D_3 hybrid materials; Hd-06–08 were samples of MD_3 hybrid materials.

Table II Effect of Molar Ratios of GOTMS over PAMAM Amine Group on Sol Fraction^a

Sample	Molar Ratio of GOTMS to —NH ₂	Sol Fraction (%)	Residual Organic Phase Weight (%)
Hd-01	1	2.41	95.50
Hd-02	0.8	3.50	93.87
Hd-03	0.5	6.53	89.70
Hd-04	0.3	11.79	82.76
Hd-05	0	77.7	0
Hd-06	2	5.8	91.45
Hd-07	1	17.54	75.78
Hd-08	0	77.6	0

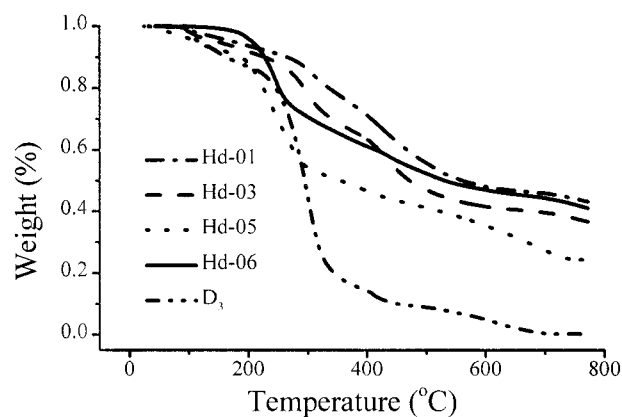
^a Sol fraction = $(W_a - W_b)/W_a$.

^b W_a , the sample weight before extracting; W_b , the sample weight after extracting.

= 1, sol fraction 17.54). Because the coupling reaction of GOTMS with —NH₂ would not be completed by performing under the present experimental condition, i.e., room temperature and 12 h, it is considered that only part of the —NH₂ groups in dendrimers could take part in the coupling reaction. In the Hd-06 case, more amounts of GOTMS were added which would be favorable to the coupling reaction processing fully and resulting in the lower sol fraction. Besides, for the modified PAMAM dendrimer samples, only about 25% of —NH₂ groups remained which means the amount of the reaction points (—NH₂) of MD₃ is obviously less than that of D₃. As a result, the modified sample Hd-07 (sol fraction 17.54) loses more organic composition compared with the Hd-01 (sol fraction 2.41), though they are in the same molar ratio of GOTMS to —NH₂. The samples Hd-05 and Hd-08, which are without coupling agent, lose their dendrimers completely after extraction, as expected.

The Thermal Stability of the Hybrid Materials

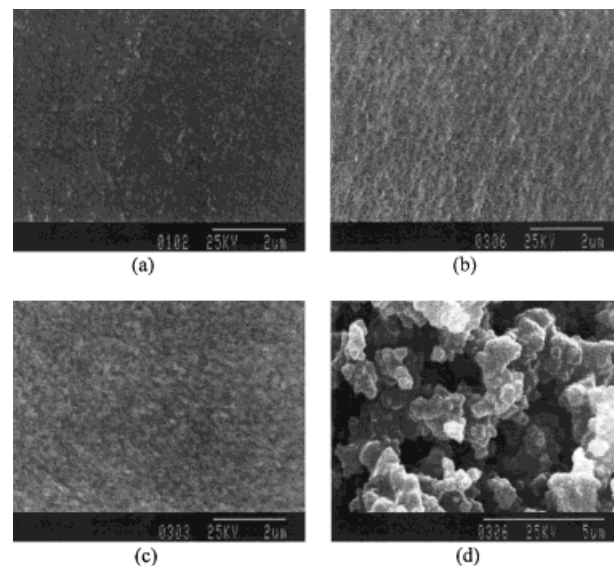
The TG measurements of these new hybrid materials are showed in Figure 2. The onset temperature for D₃ was 264.48°C and at this point the weight remaining was about 80%; then its weight decreased sharply afterward and was lost completely at 700°C. In the case of Hd-01, the onset temperature occurred at 280.24°C, at which point the residual weight was about 90%, and then the weight decreased gradually and finally it kept its weight in ca. 40% at 800°C. From Hd-01 to Hd-05 the onset temperatures slowed down with the mo-

**Figure 2** The TG curves of Hd-01 (dash dot), Hd-03 (dash), Hd-05 (dot), Hd-06 (solid), and D₃ (dash dot dot).

lar ratio of GOTMS to —NH₂ group of PAMAM decreasing. The modified, ester-terminated PAMAM silica gel hybrid (Hd-06) exhibited similar thermal behavior as Hd-01 and Hd-03.

The Morphology of Hybrid Materials

These hybrid materials are transparent except Hd-05 and Hd-08, which are opaque for absence of coupling agent. Hd-01, Hd-03, Hd-05, and Hd-06 are selected as samples for SEM photographs (Fig. 3). With the aid of the coupling agent, Hd-01, Hd-03, and Hd-06 exhibit an excellent dispersion and uniformity. Unlike the linear polymer-silica

**Figure 3** SEM of the surface of Hd-01 (a), Hd-03 (b), Hd-06 (c), and Hd-05 (d).

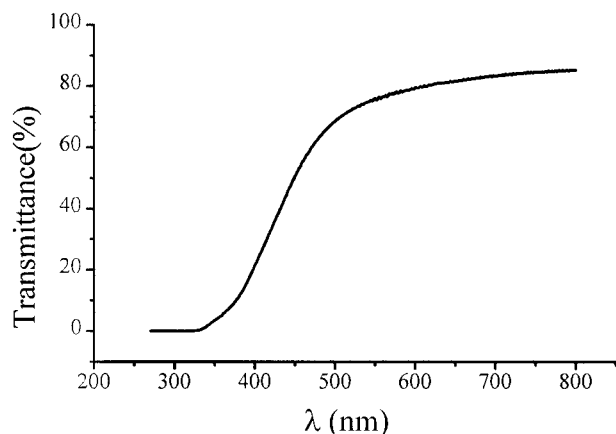


Figure 4 Transparency of Hd-06.

hybrid materials in which the organic phase composed of long linear chains is possible to be the continuous phase, in the dendrimer-silica hybrid case, the organic phases composed of the monodispersed global molecules results in the indistinguishable interface in the SEM. The inorganic corpuscles are very difficult to identify in these novel hybrid materials. Though the size of particles is not recognized by estimation according to the SEM photograph, it is in nanoscale. The Hd-05 sample is opaque and has a distinct phase separation and the inorganic particles are not in nanoscale as shown in its SEM photograph clearly.

The Transparency of the Samples

Figure 4 shows the transmittance of Hd-06 as a typical example for coupled hybrid materials. Its transmittance reaches over 80% in the range of visible light (600–700 nm). The higher transparency is owing to the coupling agent which links the organic and inorganic phases by chemical bond and hence the prevention of macrophase separation which occurs in sample Hd-05 without coupling agent.

CONCLUSION

The novel dendrimer-silica gel hybrids prepared from amino-terminated PAMAM generation 3 (32

cascade) in the presence of a coupling agent GOTMS by *in situ* sol-gel process were transparent nanometer materials. The thermostability of the PAMAM hybrid materials was better than that of their organic precursors. Their partly ester-terminated derivatives also formed transparent hybrids with silica gel, and exhibited similar properties as amino-terminated PAMAM-silica gel hybrids. It is expected that other functional groups can be incorporated into the dendrimer-silicon gel hybrids, and exhibit their potential application to fields such as nonlinear optical materials, catalytic, and separation.

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