Polymer Bulletin 58, 963–968 (2007)
DOI 10.1007/s00289-006-0722-0

Polymer Bulletin

Morphology Study of Carbosilane Dendrimer-Platinum Complex

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Received: 7 October 2006 / Revised version: 10 December 2006 / Accepted: 13 December 2006
Published online: 23 December 2006 –

Summary

Amino-terminated carbosilane dendrimer-platinum complex was synthesized and their crystal and morphology were investigated with transmission electronic microscopy (TEM) and scanning electronic microscopy (SEM). Mono-dispersed complex molecule in DMSO solvent showed a size of about 3 nm. Microcrystal flake of the complex was found with a lattice of hexagonal symmetry. Furthermore, the aggregate of such complex appeared to be spherical particles and fractal dendritic patterns.

Introduction

During the past years, research on crystallography and morphology of polymer has advanced tremendously [1, 2]. Compared with linear polymer, dendrimer can form well-ordered spatial configuration due to its regular structure; researches on structure of dendritic liquid crystal [3, 4] and crystal [5-7] have been reported. The nano-sized metallodendrimers used as catalysts could meet the requirement of effective recovery by nanofiltration membrane techniques. G. van Koten and co-workers studied the crystal structure of platinum-dendritic carbosilanes with X-ray diffraction (XRD). [8] G. Friedmann and S. Harder and co-workers reported crystal structures of dendritic carbosilane complexes, respectively. [9, 10]

Previously, we reported the synthesis, characterization and catalytic activity of low-generation carbosilane dendrimer-transition metal (platinum and palladium) complex. [11, 12] Herein, high generation dendritic carbosilane-platinum complex was synthesized and we worked over the dispersed state, crystal and aggregation of the complex with electronic microscopy in order to investigate physical property of the dendrimer-metal complex.

Experimental

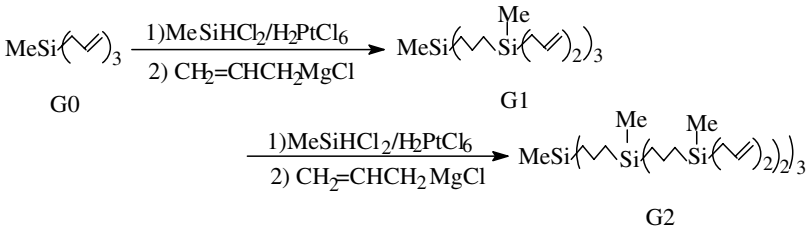
Synthesis of carbosilane dendrimer

The carbosilane dendrimer was synthesized according to the literature method [11] and the reaction route is present in Scheme 1. The synthesis started from

triallylmethylsilane as the core molecule which was prepared from allylation of trichloromethylsilane with allylmagnesium chloride. The core molecule was hydrosilylation with dichloromethylsilane and allylation with allylmagnesium chloride as the growth step. The final product with 12 allyl end groups was obtained by repetition of hydrosilylation-allylation cycles. Pure oily product was obtained by column chromatogram. (Yield 58%)

^{1}H NMR (ppm): -0.20-0.10 (d, 30H, SiCH_3), 0.40-0.80 (m, 36H, SiCH_2CH$_2$), 1.20-1.70(m, 42H, SiCH$_2$CH_2CH$_2$Si, SiCH_2CH=CH$_2$), 4.60-5.00 (m, 24H, CH_2=), 5.60-6.00 (m, 12H, CH$_2$=CH-CH$_2$-).

Elemental analysis: Calc (%) for $C_{73}H_{144}Si_{10}$: C, 67.38; H, 11.08. Found (%): C, 69.62; H, 11.10.



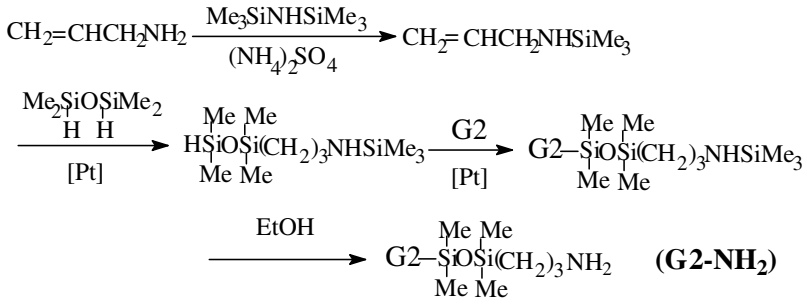
Scheme 1. Synthesis of carbosilane dendrimer

Synthesis of amino-terminated carbosilane dendrimer

The synthesis of amino-terminated carbosilane dendrimer according to the literature [11] was described in Scheme 2. The amino groups were protected by trimethylsilyl groups. Hydrosilylation reaction was used to link aminopropyl groups to the parent dendrimer. The product was obtained as yellow oil. (Yield 75%)

^{1}H NMR (ppm): -0.20-0.10 (m, 174H, SiCH_3), 0.40-0.70 (m, 108H, SiCH_2CH$_2$), 1.20-1.60(m, 66H, SiCH$_2$CH_2CH$_2$Si), 2.50-2.70 (m, 24H, NH$_2$CH_2-).

Elemental analysis: Calc (%) for $C_{157}H_{396}Si_{34}O_{12}N_{12}$: C, 52.45; H, 11.02; N, 4.68. Found (%): C, 50.97; H, 9.74; N, 4.67.



Scheme 2. Synthesis of amino-terminated carbosilane dendrimer

Preparation of dendrimer-platinum complex

Into a 100 ml flask were added 0.4g of G2-NH$_2$, 0.22g of H_2PtCl_6●6H_2O and 40 ml of anhydrous ethanol. The reaction mixture was brought to refluxing temperature, and

a yellow suspension was obtained after 1.5 h, the solid was isolated by centrifugation, and dried in vacuum to give the product as a yellow solid (0.38g, 60% yield).
^{1}H NMR(DMSO, ppm): −0.10–0.10 (m, Si–CH_3), 0.40–0.70(m, Si–CH_2CH$_2$–), 1.30–1.70 (m, Si–CH$_2$CH_2CH$_2$Si–), 2.60–2.90 (m, –CH_2NH–),7.40–7.80 (m, Pt ← NH<).
IR(cm−1, neat): 3211(m, –CH$_2$NH–), 2918 (m), 1577 (s, Pt ← NH<),1475 (s, –CH$_2$ – NH–), 1254 (s, Si–(CH$_3$)$_3$), 1076(m, Si–O–Si), 838 (s), 788 (s).
EDX analysis(normalized): Pt, 41.86%; Si, 23.41%; Cl, 34.70%.

Measurements
Transmission electron micrograph (TEM) images were obtained with a JEOL-2010 (Japan, Electron Company) at 200 KV. Dispersed and aggregated samples were prepared by dropping 100ppm complex solution in DMSO onto carbon-coated grids and vaporized in vacuum. Scanning electron microscopy (SEM) measurement was performed on Hitachi S4300 Microscope operating at 15 KV. Aggregated samples were prepared by dropping the DMSO solution of complex (about 1% in mass) onto silicon substrates that had been freshly treated with piranha solution (3:1 v/v mixture of concentrated H_2SO_4 and 30% H_2O_2) and vaporized in vacuum with infrared light heating. Crystal flakes of complex were obtained by slow diffusion of ethanol into thick DMSO solution, and crystal was separated out. Electronic diffraction (ED) pattern was obtained with JEOL-2010.

Results and Discussion

The carbosilane dendrimer-platinum complex was separated out of the ethanol solvent during the preparation, showing its low solubility in ethanol. The complex could be dissolved in DMSO but not in *n*-hexane, THF and $CHCl_3$. TEM images (Figure 1) of the dilute DMSO solution of the complex showed that the complex particles are nearly mono-dispersed and their shapes are roughly spherical with a diameter of about 3.0 nm. The mono-dispersed complex in certain solvent gives a perfect catalytic performance that has been proved in our experiment.
Microcrystal flakes visualized with SEM have a size about 1-2μm in diameter as shown in Figure 2a with a thickness of 50 nm. Figure 2b shows a large crystal aggregate with about 20μm size. Smaller typical lamellar particles can also be found

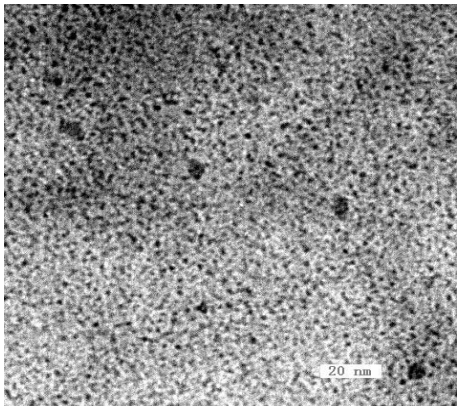


Figure 1. TEM micrograph of dispersed Complex. Scale bar: 20 nm

in TEM image (Figure 2c) with a size of 200-400 nm, ED pattern (Figure 2d) shows the crystal lattice is hexagonal symmetry. These results indicate that the dendritic carbosilane-platinum complexes are facilely crystallized and the transformation of crystal is maybe ascribed to their regular structure of dendritic molecule in which the peripheral platinum-chloride structure might induce the crystallization by inter-molecular interaction.

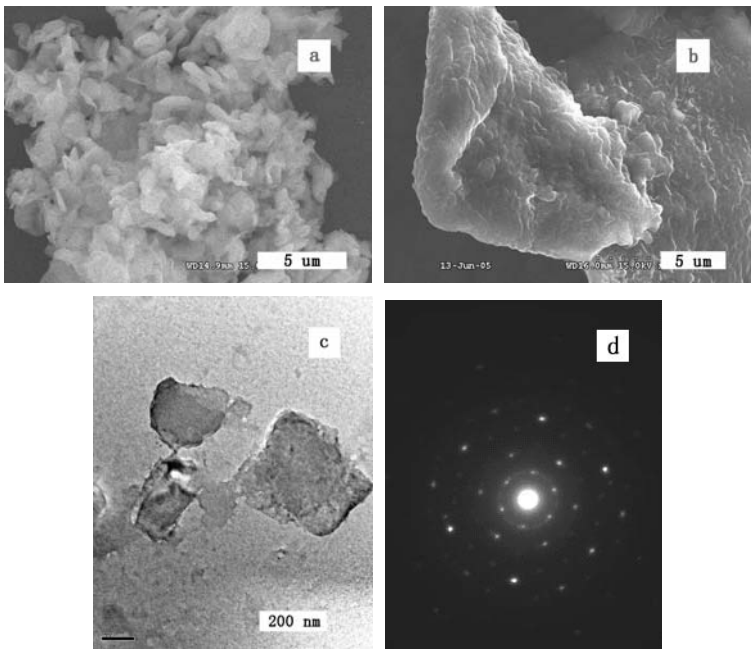


Figure 2. SEM images of microcrystal in disorder (a), and regularly assembly (b) and TEM micrograph (c) and ED pattern (d) of dendrimer-platinum complexes. Scale bar in a/b: 5μm; c: 200 nm

Two kinds of aggregated dendrimer-platinum particles are visible in electronic microscopy images: one is spherical pattern (Figure 3a); the other is typical dendritic particle (Figure 3b, 3d). In some regions, two kinds of aggregates can be observed simultaneously (Figure 3c, 3e), which demonstrates the aggregation patterns in the course of crystallization are formed optionally, relating to the thickness and the forming process.

It was pointed out in the literature that such crystallization was an unstable process, and the instabilities of diffusion were typical of growth from a solution. [13] The growth pattern in far-from-equilibrium crystallization was usually dendritic or ramified and sometimes fractal. The diffusion-limited aggregation (DLA) is the most well known model of fractal growth mechanism. [14] Molecules are assumed to be independent in fluid phase in the model; they diffuse randomly from a very large distance and stop moving as soon as they meet the solid, which will give rise to very irregular shapes. It was interesting that the pattern in Figure 3d resembled the two-dimensional DLA pattern from the computer. [13] It denotes that Crystallite aggregation of the carbosilane dendrimer-platinum complex in DMSO solvent shoud

be in accordance with the DLA model, showing that such complex behaves like a small molecule in the course of aggregating despite of its high molecular weight.

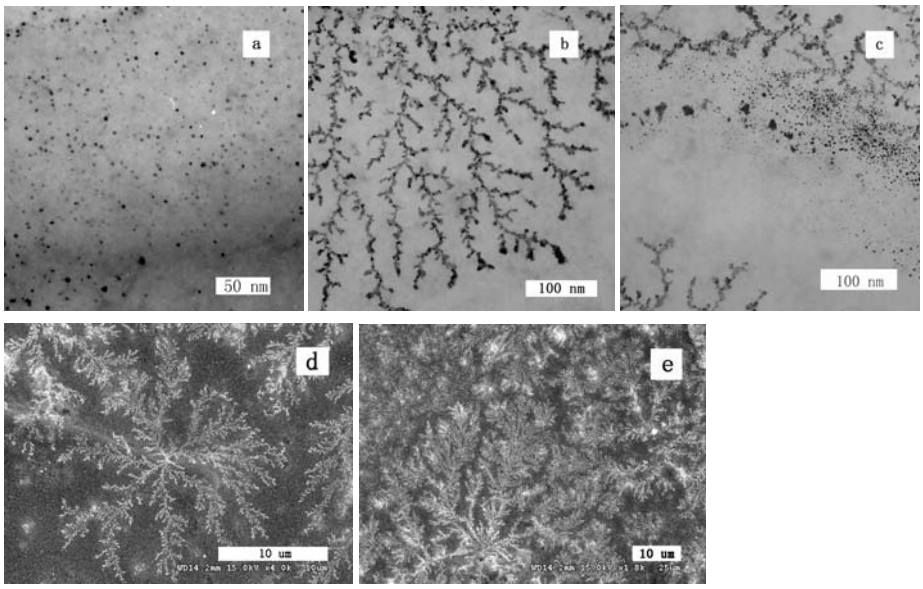


Figure 3. TEM micrograph (a, b, c) and SEM micrograph (d, e) of crystallite aggregation of complex. a: spherical aggregation; b/d: fractal pattern aggregation; c/e: simultaneous presence of both aggregation (middle in c and top left corner in e). Scale bar in a: 50 nm; b: 100 nm; c: 100 nm; d: 10μm and e: 10μm

Conclusion

In summary, the carbosilane dendrimer-platinum complex can form microcrystal with hexagonal symmetry. Their aggregate fractal patterns in crystallization from DMSO solvent demonstrates that the crystallite aggregation accords with DLA model like a small molecule. The work in this article will be significant for studying the character of the metallodendrimer complex and exploiting new application field.

Acknowledgment. We are grateful to the Shandong Natural Science Foundation of China for financial support of this work (Project No. Q 2003 B01 and Project No. Y 2003 B01).

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