Preparation of Polysilsesquioxane $(CH_3SiO_{1.5})_8$ Crystals from Swollen PHEMA

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Polysilsesquioxane $(CH_3SiO_{1.5})_8$ crystals were prepared from $CH_3Si(OCH_2CH_3)_3$-trapped poly(2-hydroxyethylmethacrylate) (PHEMA) swollen in methanol in 23% yield under certain acidic or alkaline condition.

There has been a growing interest in the preparation of various functionalized silsesquioxanes $(RSiO_{1.5})_n$, such as ladder, cage, and partial cage frameworks.[1–3] Especially, spherosilicate silsesquioxane cages with octasilsesquioxanes (T_8) structures have been studied extensively for their promising applications in liquid crystals, biocompatible materials, catalysts, and so on.[4–6] However, in the preparation of these frameworks, most synthetic methods encountered the insurmountable disadvantage that alkyltriethoxysilane vigorously hydrolyzed and condensed to form undesirable crosslinked resins or gels by the facilitation of acidic or alkaline catalysts so that silsesquioxane cage crystals occurred as trace amount of byproducts because of silsesquioxane cages' stringent geometrical requirements, and more, it was difficult to isolate and purify these hydrolytic mixtures owing to their poor solubility in solvents.[2,7–9] Although Taylor recently introduced a new synthetic scheme for the preparation of T_8 using tetra-*n*-butylammonium fluoride as catalyst with the best yield of 95%, in this case, it was proven unsatisfactory that the yield of $(CH_3SiO_{1.5})_8$ from methyltriethoxysilane (MTES, $CH_3Si(OCH_2CH_3)_3$) was still less than 1%.[10] Therefore, a feasible route needs to be developed for the preparation of this species in high yield under mild synthetic conditions.

Here, we report a novel approach concerning the precursors predispersed in polymer matrix, and then the $(RSiO_{1.5})_8$ crystal product obtained outside the matrix. Namely, $(CH_3SiO_{1.5})_8$ crystals can be prepared using swollen poly(2-hydroxyethylmethacrylate) (PHEMA) as a "controller."[11] Habsuda reported that, in poly(silicic acid)s (PSA)/HEMA, MPTS/HEMA and PSA/MPTS/HEMA systems, HEMA components did not chemically link with alkyltriethoxysilanes because of the substitution reaction of alkyloxy (OR) groups with HEMA.[12] MTES trapped in PHEMA in advance could diffuse gradually and release slowly through swollen PHEMA matrix immerged in alcohol under certain pH condition. In this way, the concentration of MTES was controlled at a low level outside the polymer matrix over a 3 day period, where hydrolysis–condensation reaction proceeded completely to yield discrete, morphological octasilsesquioxanes $(CH_3SiO_{1.5})_8$ ("Me-T_8") crystals.

To a glass tube were added 2 mL of methyltriethoxysilane (MTES) ($d = 0.895\,g/cm^3$, Aldrich) and 18 mL of 2-hydroxyethylmethacrylate (HEMA, 0.1 wt % initiator AIBN) ($d = 1.073\,g/cm^3$, Aldrich). After ultrasonic shake, bulk-polymerization took place at certain temperature (50 °C for 24 h, 75 °C for 24 h, and 95 °C for 4 h) to produce a white opaque polymer rod. The rod was cut into several platelets and the platelets were immerged in methanol (anhydrous, 99.5%) under certain pH condition adjusted with hydrochloric acid (37 wt % in water) or aqueous ammonia (25 wt % in water), such as hydrochloric acid/methanol (v/v = 1/100) or aqueous ammonia/methanol (v/v = 1/20).

For example, a 16.44 g amount of platelets was immerged in aqueous ammonia/methanol (v/v = 1/20) at 40 °C for 3 d. Upon completion of swelling, the platelets were taken out and dried in air. A large number of cubic crystals were observed, and the platelets became translucent or even transparent. 0.12 g of $(CH_3SiO_{1.5})_8$ crystals was obtained from the platelet surface in 22.94% yield.

Two key steps to prepare these crystals were as follows: 1. Precursors MTES and HEMA were mixed at a ratio of HEMA:MTES = 9:1 (v/v). 2. Hydrolytic condensation reaction of MTES took place when polymer was swelling in hydrochloric acid/methanol = 1/100 (v/v) or in aqueous ammonia/methanol = 1/20 (v/v).

As shown in Figure 1a, MTES was dispersed homogeneously into the polymer networks when HEMA bulk polymerized into PHEMA, and the polymer chains separated MTES into microdroplets (<200 nm) within the polymer matrix. During PHEMA was swelling, methanol molecules could permeate into the polymer matrix, and MTES would diffuse outward in opposite directions. Physical blocking actions and molecular interactions coexisted within PHEMA hydrogels, and the diffusion coefficient of MTES would decrease with the decrease of its fraction in the gels.[13] The network of polymer chains was perceived as a "controller" for the diffusion of MTES through matrix in swollen state. As a result, MTES could be controlled to move calmly and slowly. It was convenient to keep the concentration of

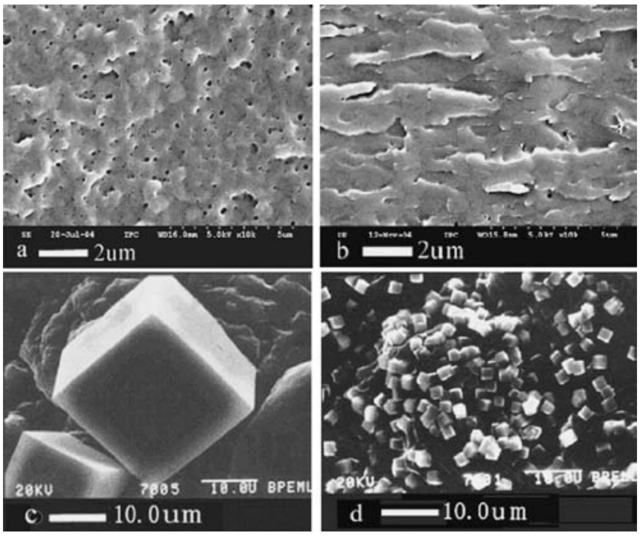

Figure 1. SEM of the interior of PHEMA before swelling (a) and after swelling (b), and SEM of $(CH_3SiO_{1.5})_8$ crystals on the surface of swollen PHEMA (c) and (d).

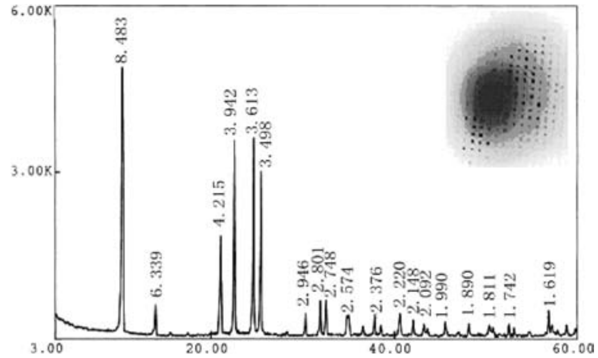

Figure 2. Electronic diffraction and powder X-ray diffraction image of the $(CH_3SiO_{1.5})_8$ crystal.

MTES outside the matrix at a low level. In addition, there was only a little water in this system so that hydrolysis–condensation of MTES could proceed gradually instead of vigorously. Under this condition, a large number of $(CH_3SiO_{1.5})_8$ crystals were obtained. Moreover, neither gels nor resins were observed. Cleanness and transparency of the solution could sustain throughout. Although the same hydrolysis–condensation reaction also occurred within the polymer matrix, it could be controlled to proceed mainly outside the matrix during PHEMA was swelling continuously. Just as seen in Figure 1b, after the polymer was completely swollen, it was difficult to find MTES or $(CH_3SiO_{1.5})_8$ crystals. The matrix became translucent or even transparent.

Figures 1c and 1d show that the crystals have cubic shape, clean surface. As seen in Figure 1c, some crystals are with dimensions of 20–30 um. The electron diffraction pattern and powder X-ray diffraction pattern were presented in Figure 2, and the XRD data were identical with the previous result.[1] The elemental analysis results (for $CH_3SiO_{1.5}$, calcd C, 17.91; H, 4.51%. found C, 17.98; H, 4.52; C/H molar ratio $= 1/3.00$) suggested that the crystal composition was in accordance with the formula $(CH_3SiO_{1.5})_n$. The GC-MS data indicated that the molecular weight was 536 and that this species was with high purity. Infrared spectra of the crystals was given in Figure 3, clearly indicating two distinctive features of the molecule: Si–CH_3 group (2972, 1270, and 774 cm^{-1})[14] and Si–O–Si silsesquioxane skeletal absorption (1117, 515, and 463 cm^{-1}).[15] In addition, there is almost no absorption at 3600 cm^{-1}, which is ascribed to Si–OH.[16,17] The crystals would sublime without melting when heating at 231–258 °C under atmospheric pressure (see Supporting Information). All these results highly prove that the product is $(CH_3SiO_{1.5})_8$ crystal. This is in accordance with Barry's conclusion[1] that the crystal belongs to the cage octamer $(CH_3SiO_{1.5})_8$ whose structure is shown in Figure 3.

In conclusion, we have developed a novel and efficient approach to the preparation of discrete and morphological polysilsesquioxane $(CH_3SiO_{1.5})_8$ crystals from MTES trapped in swollen polymer systems (such as PHEMA). It is noteworthy that swelling-based methods are being explored for preparing functional species.[18,19] We expect that the present findings will provide an important clue to prepare other organosilsesquioxane $(RSiO_{1.5})_n$ crystals. The further work is in progress.

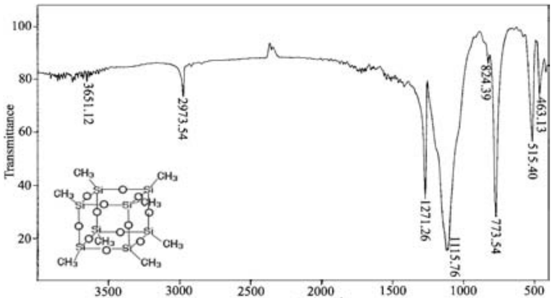

Figure 3. Structure and infrared spectra of the $(CH_3SiO_{1.5})_8$ crystal.

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