

Corner-Opened Cage-Silsesquioxane as a Directional Template for Tripodal Poly(methyl methacrylate)

Ryota TANAKA¹, Amato IGARASHI¹, Taihei HAYASHI¹, Hideaki TAKAGI², Nobutaka SHIMIZU²,
Noriyuki IGARASHI², Shinichi SAKURAI¹, Hiroaki IMOTO¹, and Kensuke NAKA¹

¹ Graduate School of Kyoto Institute of Technology, Matsugasaki, Sakyo-ku, Kyoto 606-8585, Japan

² Photon Factory, Institute of Materials Structure Science,
High Energy Research Organization, 1-1 Oho, Tsukuba, Ibaraki 305-0801, Japan

1 Introduction

The branched structures of polymers, such as stars, brushes, hyperbranches, and dendrimers, exhibit properties that are different from those of linear polymers.[1,2] Among them, star polymers have attracted significant attention because of the diversity in their synthetic methods and structures. In this study, the structure and properties of the incompletely condensed polyhedral oligomeric silsesquioxanes (IC-POSS) containing three poly(methyl methacrylate) chains at the open corners of the cubic siloxane core have been studied.

2 Experiment

The small-angle X-ray scattering (SAXS) measurements were performed at BL-10C beamline of photon factory (PF) of high-energy research organization (KEK), Japan, with the wavelength of 0.10 nm and the size of the incident X-ray beam being 182 μ m (H) \times 346 μ m (V). The distance between the specimen and the 2-dimensional detector (PILATUS3 2M, DECTRIS, Switzerland) was set at 2.5 m. The exposure time of the one-shot measurement was 30s.

3 Results and Discussion

To obtain clear evidence of the aggregation of the POSS moieties, we performed SAXS, as shown in Figure 1. The measured SAXS profiles [I(q), the scattering intensity I as a function of q] for 1a and 1b indicate a power-law behavior as $I(q) \sim q^{-4}$, which is well known as Porod's law. On the contrary, those for 3a and 3b exhibit a shoulder and a peak around $q = 0.77 \text{ nm}^{-1}$, respectively, providing a clear indication of aggregation of corner-opened POSS moieties. We conducted the fitting by assuming a spherical particle scattering function for the SAXS profile to evaluate the particle size distribution in the specimen. The resulting particle size distributions are shown in Figure 2 for 3a and 3b (as-cast and annealed), which were annealed at 110 °C for 12 h. The particle size is monodisperse for almost all the specimens studied herein, except for the annealed 3b. In particular, the diameter of the particles in as-cast 3b was the lowest at 3 nm. Considering the 1-nm diameter of the corner-opened POSS moiety, approximately 27 (= 33) moieties were included in this aggregation of the POSS moieties. For this specimen, peak fitting (see Supporting Information) revealed 7.24 nm as the distance between two neighbouring particles. Owing to the phase separation between the POSS and PMMA moieties, a core-shell

structure can be assumed. Then, from the value of 7.24 nm, the thickness of the outer PMMA layer (shell) can be estimated as 2.12 nm (= (7.24-3)/2) if we consider the direct contact between the two neighbouring particles. Thus, the structure of the core-shell particle is deduced from the SAXS results for the as-cast 3b; the core diameter of 3.0 nm and the PMMA layer thickness of 2.1 nm are reasonable from the chemical structure of the molecule.

By contrast, as-cast 3a exhibits monodisperse features with a diameter of 6 nm, which is twice as large as that of as-cast 3b. It is interesting to find this contrasting result even though the difference between 3a and 3b exists in the numbers of PMMA chains attached to the corner-opened POSS and its molecular weight while maintaining the same volume percentage of the composition (for a more detailed discussion on the particle size, see the supporting information). Furthermore, the particles of 3a do not exhibit a lattice peak, as shown in Figure 1. This implies that the particles of 3a do not have direct contact with each other and, which in turn, implies the existence of a homogeneous dispersion of the molecules without aggregation. The fact that the size distribution of the particles for 3a (Figure 2) did not change significantly upon thermal annealing confirms the robustness of the aggregation. This is in contrast to 3b 1b, which exhibited a broadening of the particle size distribution upon thermal annealing. However, notably, the average diameter is 5.5 nm for both specimens (3a and 3b). Therefore, larger particles are formed upon annealing for 3b, suggesting the coalescence and merging of particles. As the lattice peak for annealed 3b is still clearly observed in Figure 1, the original particles with a diameter of 3 nm, which are in direct contact with neighbouring particles, remained upon annealing.

* shin@kit.ac.jp

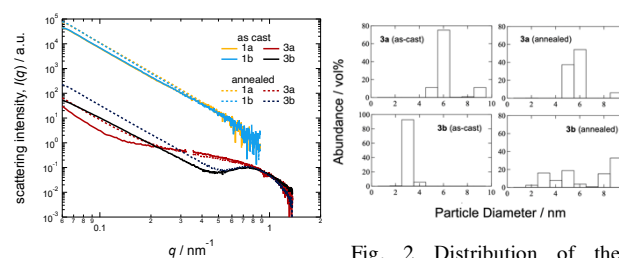


Fig. 1 SAXS profiles of 1a, 1b, 3a, and 3b (as-cast and annealed). Annealing was conducted at 110 °C for 12 h.

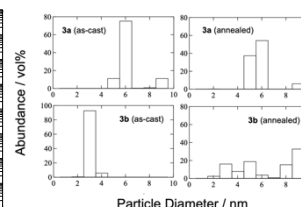


Fig. 2 Distribution of the particle size in 3a and 3b (as-cast and annealed). Annealing was conducted at 110 °C for 12 h.