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Phase change behavior of single component optically transparent film of star-shaped cage silsesquioxane derivative

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1 Introduction

Modularly synthesized giant molecular clusters containing rigid spherical molecules as element-blocks are regarded as a new class of unconventional macromolecules. Among various candidates for rigid spherical molecules, cage octasilsesquioxane (T8) frameworks have been demonstrated to be an efficient building block for designing well-defined 3D solid materials due to flexible designability of their organic substituents. Here, we studied the crystalline phase and phase transition behavior of the optically transparent film of star-shaped (heptaisobutyl-T8-silsesquioxy)propyl-substituted octadimethylsiloxy-Q8-silsesquioxane (star-POSS) by DSC and wide-angle X-ray scattering (WAXS) measurement. The present star-POSS exhibited the crystalline phase with the hexagonal system at room temperature and underwent melting above the melting temperature (Tm). Furthermore, the specimens underwent re-crystallization even at high temperature above Tm to have the same hexagonal system with slightly larger a and c axis lengths. Amorphous state of the surrounding isobutyl substituents on the T8-cage framework provides the optically transparent film of star-POSS.

2 Experiment

Wide-angle X-ray scattering (WAXS) measurements using synchrotron X-rays were performed on the BL-10C beamline at the Photon Factory of the High Energy Accelerator Research Organization, Tsukuba, Japan. PILATUS3-300K (DECTRIS Ltd., Baden, Switzerland) was used as a two-dimensional detector. The wavelength of the X-ray was set at 0.15 nm, and the sample-to-detector distance was 250 mm. The typical exposure time was in the range of 10 s. A polyethylene crystal was used as the standard sample to calibrate the magnitude of the scattering vector, q, as defined by $q = (4\pi/\lambda) \sin(\theta/2)$, with λ and θ being the wavelength of X-ray and the scattering angle, respectively. The two-dimensional WAXS patterns were further converted to one-dimensional profiles by conducting a circular average. Time-resolved WAXS measurements were performed in the heating process with 1.55 ˚C/min. up to 160˚C and then in the cooling process down to 45˚C without precisely controlling the cooling rate. The measuring time for each WAXS pattern was 10 sec and the interval time between the measurements was 0.01 sec. After the completion of the time-resolved measurements, the specimen was cooled in a refrigerator at -37˚C for 10 min, and then a shot of WAXS pattern for thus-cooled specimen was immediately measured at room temperature for 10 sec.

3 Results and Discussion

To determine the crystalline structures of star-POSS, the wide-angle X-ray scattering (WAXS) measurements were performed for the cast film of star-POSS. The resulted changes in the one-dimensional WAXS profiles (gray scale of the scattering intensity) as a function of temperature in the heating process with the heating rate of 1.55 ˚C/min and the subsequent cooling process without precisely controlled cooling rate are shown in Figure 6a. Note here that the changes are shown in a series of the time elapsed and thereby the temperature axis is not proportionally scaled for the cooling process. The panels (b) and (c) in Figure 6 highlight the WAXS profiles in the heating and subsequent cooling processes. It was found that the present star-shaped POSS derivative exhibited the crystalline phase at 40˚C, the crystalline character weakened at 80 ˚C, and underwent melting above 95 ˚C.

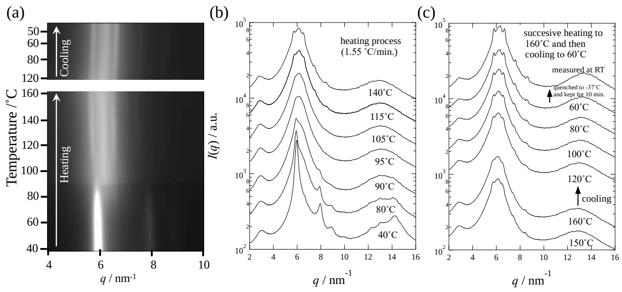

Fig. 1: (a) Changes in the one-dimensional WAXS profiles in the heating process and the subsequent cooling process. The panels (b) and (c) highlight the WAXS profiles in the heating and subsequent cooling processes.

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