Stabilization of Polystyrene Thin Films against Dewetting by Silsesquioxane-terminated Polystyrene Additives

Kyota Miyamoto,[1] Nao Hosaka,[1] Hideyuki Otsuka,[1,2] and Atsushi Takahara*[1,2]
[1]*Graduate School of Engineering, Kyushu University, Higashi-ku, Fukuoka 812-8581*
[2]*Institute for Materials Chemistry and Engineering, Kyushu University, Higashi-ku, Fukuoka 812-8581*

(Received June 26, 2006; CL-060713; E-mail: takahara@cstf.kyushu-u.ac.jp)

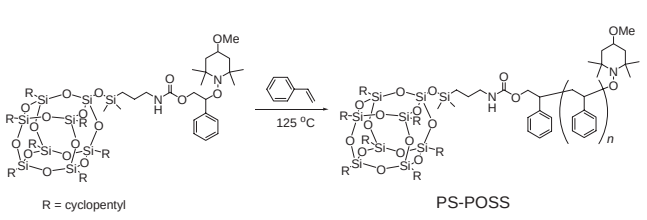
A polyhedral oligomeric silsesquioxane (POSS)-containing initiator for nitroxide-mediated radical polymerization was synthesized to prepare organic–inorganic hybrid polymers (PS-POSS), which are polystyrene (PS) with a POSS end group. PS-POSS were well dispersed in PS thin films and provided thermal stability to films against dewetting.

Polymer thin films have numerous technological applications which require the presence of a homogeneous film. However, producing stable films is problematic since the polymer thin films tend to dewet from the substrates.[1] Various approaches have been adopted to stabilize these films against dewetting.[2–4]

Polyhedral oligomeric silsesquioxanes (POSS) have gained considerable attention due to their organic–inorganic hybrid structure which consists of a silica cage with organic groups. The salient feature of this nanosized building block is the ability to functionalize the silicon corners with a variety of organic substituents. POSS cages can be incorporated into polymer systems via polymerization, grafting, and blending by introducing the specific functionalities. By such hybridization, properties superior to the organic material alone are realized, offering exciting possibilities for the development of new materials.[5–7]

Our previous study showed that the addition of octacyclopentyl-POSS (CpPOSS) to the polystyrene (PS) thin films led to an inhibition of dewetting in the films.[8] However, because of the low affinity of POSS with PS, the film surface was roughened by the aggregation of CpPOSS in the films after annealing treatment. In this paper, the authors report that nitroxide-mediated radical polymerization (NMRP)[9] can be applied to the synthesis of POSS-terminated polystyrene (PS-POSS), which improve the dispersibility of POSS units in PS thin films as well as the stability against dewetting.

The synthesis of POSS-containing initiator was carried out by the addition reaction of POSS with an isocyanate pendant group to the 2,2,6,6-tetramethylpiperidine-1-oxy (TEMPO)-based alkoxyamine with a hydroxy group.[10] PS-POSS were prepared by NMRP using this initiator (Scheme 1).[11] The number average molecular weight (M_n) and polydispersity (M_w/M_n) of the polymers were determined by gel permeation chromatography with PS standards.



Scheme 1. Synthesis of well-defined PS-POSS by nitroxide-mediated radical polymerization.

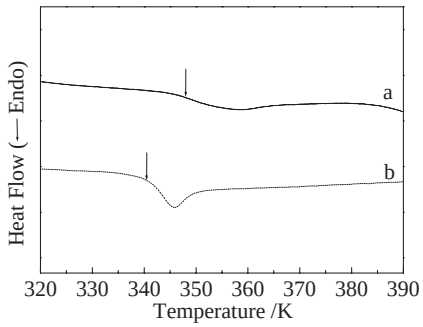


Figure 1. DSC curves of (a) PS-POSS2.5k ($M_n = 2500$, $M_w/M_n = 1.11$) and (b) PS2.1k ($M_n = 2100$, $M_w/M_n = 1.06$).

The formation of POSS-containing initiator and PS-POSS was confirmed by comparison of the Fourier transform infrared spectra of the two starting materials and the final product. After the addition reaction, the isocyanate absorption band at 2270 cm^{-1} of the starting material disappeared and the absorption corresponding to the stretching vibration of urethane carbonyl groups was observed at 1728 cm^{-1}. The synthesized PS-POSS showed the characteristic PS absorbance.

Differential scanning calorimetry (DSC) was carried out to estimate the glass transition temperature (T_g) of PS-POSS ($M_n = 2500$, $M_w/M_n = 1.11$; PS-POSS2.5k). PS ($M_n = 2100$, $M_w/M_n = 1.06$; PS2.1k) was used as the reference sample. Figure 1 represents the DSC thermograms of PS-POSS2.5k and PS2.1k. Data from the second heating run were recorded for a heating rate of 10 K/min under a nitrogen atmosphere. T_g (average value) of PS-POSS2.5k was 348.1 K, which means a noticeable increase from that of the pure PS2.1k, 339.8 K. The result suggested that interactions among the massive POSS inorganic groups inhibited thermal molecular motion of PS.

Blend thin films composed of PS-POSS2.5k and matrix PS ($M_n = 44$k, $M_w/M_n = 1.04$; PS44k) were prepared by spin-coating the mixture dissolved in toluene, which had been passed through a PTFE filter (pore size = 0.20 μm), onto acid-cleaned silicon wafers at 2000 rpm for 30 s. The concentration of the polymer solution was 3 wt %. The resulting films were approximately 120 nm in thickness as determined by ellipsometry. After annealing at various temperatures for 3 h, the film morphology was observed with optical microscopy and atomic force microscopy (AFM).

Figure 2 shows the AFM height images and line profiles of (a) PS-POSS2.5k/PS44k (28/72 w/w) and (b) CpPOSS/PS44k (10/90 w/w) blend thin films. The relative weight fractions of the POSS moiety to PS in these two films are almost the same. It was observed that PS-POSS2.5k/PS44k blend film possessed the small surface roughness, compared with CpPOSS/PS44k

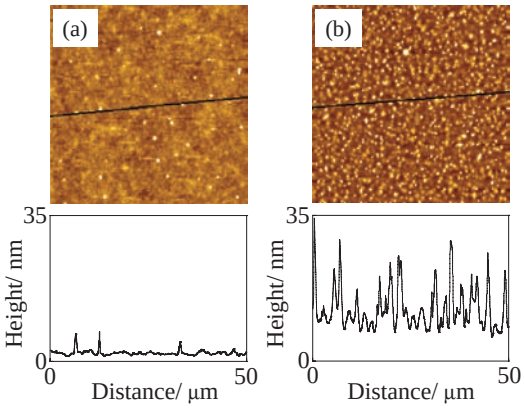


Figure 2. AFM height images and line profiles of (a) 124-nm thick PS-POSS2.5k/PS44k (28/72 w/w) blend film and (b) 124-nm thick CpPOSS/PS44k (10/90 w/w) blend film annealed at 393 K for 3 h.

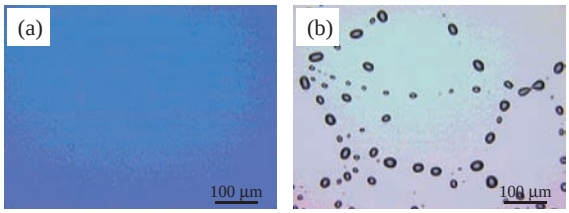


Figure 3. Optical micrographs of (a) 124-nm thick PS-POSS2.5k/PS44k (28/72 w/w) blend film and (b) 120-nm thick PS2.1k/PS44k (28/72 w/w) blend film annealed at 423 K for 3 h.

blend film. This result is indicative of the improvement in the dispersibility of POSS in PS thin films by the introduction of PS.

Figure 3 shows the optical micrographs of (a) PS-POSS2.5k/PS44k (28/72 w/w) and (b) PS2.1k/PS44k (28/72 w/w) blend thin films annealed at 423 K for 3 h. PS-POSS2.5k/PS44k blend film did not dewet at all, in contrast, the bare substrate was observed as a consequence of the complete dewetting of PS2.1k/PS44k blend film. This difference suggested that the film was stabilized against dewetting on this time scale by the presence of PS-POSS.

From the DSC results mentioned above, POSS-POSS interaction might be responsible for the film stabilization. The preliminary DSC study of PS-POSS2.5k/PS44k (28/72 w/w) and PS2.1k/PS44k (28/72 w/w) bulk blends showed no appreciable change in the T_g of the two blends. Further measurements are required to understand the dewetting inhibition mechanism. Several researchers reported that surface or interface segregation of nanofillers seemed to be important factors in the stabilization effect of the PS thin film.[2,12,13] In the case of (fluorinated-POSS end capped poly(methyl methacrylate) (PMMA)/PMMA) blend, Fukuda et al. revealed the enrichment of fluorinated-POSS at the surface region by neutron reflectivity (NR).[7] Similar enrichment of CpPOSS at the surface of PS film was also observed by the authors.[14] NR studies are currently underway to check this possibility.

In summary, organic–inorganic hybrid polymers, PS-POSS, which were PS with POSS end group, were prepared by nitroxide-mediated radical polymerization. AFM study for annealed films composed of PS-POSS and matrix PS showed that the POSS moieties in the films were well dispersed compared with CpPOSS/PS blend films. The addition of PS-POSS to a spin-coated polymer thin film can actually stabilize the film against dewetting as well as CpPOSS.

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10 Synthesis of POSS-containing initiator: 1 drop of dibutyltin dilaurate was added to the solution of the POSS with an isocyanate pendant group (4.0 g, 3.8 mmol) and TEMPO-based alcohol (1.2 g, 3.8 mmol) in dry toluene (3.5 mL). The reaction mixture was stirred at room temperature under nitrogen for 24 h. The crude product was purified by flash chromatography, eluting with 1:3:12 ethyl acetate/hexane/chloroform (v/v) and dried under vacuum to give the POSS-containing initiator as a white powder (3.2 g, 62% yield). ^{1}H NMR: δ/ppm 0.11 (s, 6H), 0.51 (m, 2H), 0.67 (s, 3H), 1.01 (m, 7H), 1.08 (s, 3H), 1.23 (s, 3H), 1.38 (s, 3H), 1.30–2.00 (m, 60H), 3.09 (m, 2H), 3.30 (s, 3H), 3.40 (m, 1H), 4.20 (dd, J = 6 Hz, 11 Hz, 1H), 4.56 (m, 1H), 4.63 (dd, J = 6 Hz, 11 Hz, 1H), 4.88 (t, J = 6 Hz, 1H), 7.20–7.40 (m, aromatic). FT-IR (KBr, cm^{-1}): 3100–2810, 1728 (C=O), 1522, 1452, 1252, 1200–1000, 913, 838, 757, 698, 505. Mass spectrum (FAB) 1365.
11 Polymerization: A mixture of the POSS-containing initiator (700 mg, 0.51 mmol) and styrene (1.5 mL, 13.1 mmol) was charged in a polymerization tube, degassed, and sealed off under vacuum. The mixture was incubated at 125 °C for 24 h, and after dilution with chloroform the solution was poured into methanol. The precipitate was further purified by reprecipitation with a chloroform/methanol system and dried under vacuum to give the PS-POSS as a white powder (1.3 g, 63% yield). M_n = 2500, M_w/M_n = 1.11. ^{1}H NMR: δ/ppm 0.01–0.60 (br), 0.80–2.60 (br, aliphatic H), 3.03 (br), 3.2–4.5 (br), 6.20–7.40 (br, aromatic H). FT-IR (NaCl, cm^{-1}): 3100–2810, 1728 (C=O), 1602 (C=C), 1493, 1453, 1252, 1200–1000, 908, 838, 757, 698, 505.
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