Supporting Information

Synthesis and morphology studies of a polystyrene-poly(arylene ether sulfone)-polystyrene coil-semirod-coil triblock copolymer

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Synthesis of the telechelic polymers

Synthesis of polystyrene end-functionalized with anhydride group (PS-anh). Polystyrene end-functionalized with anhydride group was synthesized by means of anionic living polymerization. The polymerizations and the subsequent reactions were performed in all-glass, sealed reactors with break-seals under high vacuum conditions. The anionic polymerization of styrene was carried out in *tert*-butyl benzene at 30 ^{o}C with s-BuLi for 2

h. After addition of an equal volume of THF at -78 ^{o}C to the polymerization mixture, a 1.5-fold excess of 6-bromo-3-metylene-1-hexene was added. The reaction was terminated with degassed methanol. This led to the polystyrene end-functionalized with butadienyl group. The polymer was precipitated twice in methanol and freeze-dried from benzene solution. In order to convert the butadiene terminus into anhydride group, the Diels-Alder reaction was carried out with maleic anhydride using a catalytic amount of Et_2AlCl in CH_2Cl_2 at room temperature for 24 h. After usual work up, polystyrene end-functionalized with anhydride group (PS-anh) was quantitatively obtained. Yield: 97%

Synthesis of poly(arylene ether sulfone) bifunctionalized with amine group (PAES-amn). Poly(arylene ether sulfone) was synthesized by the direct aromatic nucleophilic substitution polycondensation of F6-BPA and 4-FPS as illustrated in Scheme 1. Both F6-BPA (3 g, 1 equiv) and 4-FPS (2.52 g, 1.12 equiv) were dissolved in DMAc (30 mL) in a two-neck flask equipped with a magnetic stirrer, a nitrogen inlet, and Dean-Stark trap, and then the reaction mixture was vigorously stirred for 30 min. To the clear reaction mixture, K_2CO_3 (1.7 g, 1.30 equiv) was added followed by benzene (30 mL). The reaction bath was heated to 120 °C, and this temperature was maintained for 2 h to ensure complete dehydration by azeotropic distillation of benzene using Dean-Stark trap. After removing benzene, the reaction mixture was stirred at this temperature for a further period of 2 h. To introduce the amine group at the termini of the polymer, 3-aminophenol (3.24 g, 3.00 equiv) dissolved in benzene (30 mL) was added to the reaction mixture, and then reaction was continued for 3 h. The reaction mixture was cooled and then the desired polymer, (PAES-amn), was precipitated into 400 mL of methanol/water (1:1 solution).

The precipitated polymer was dissolved in THF (10 mL) and reprecipitated into excess methanol. The polymer was filtered, washed with methanol, and dried under vacuum at 60 °C for 3 days. Yield: 91 %

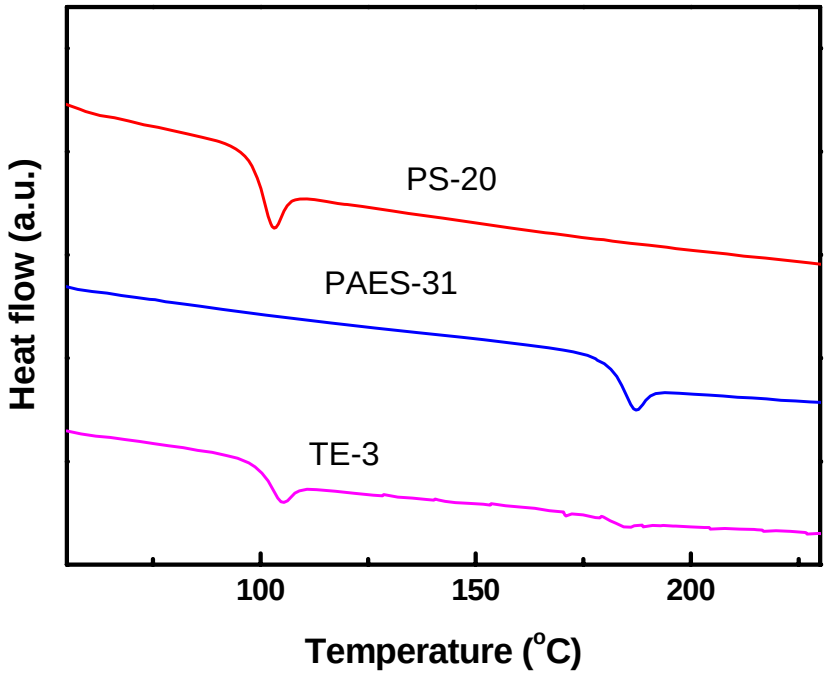

Figure S1 DSC traces of end-functionalized PS with anhydride group, end-functionalized PAES with amine group, and block copolymer TE-3.

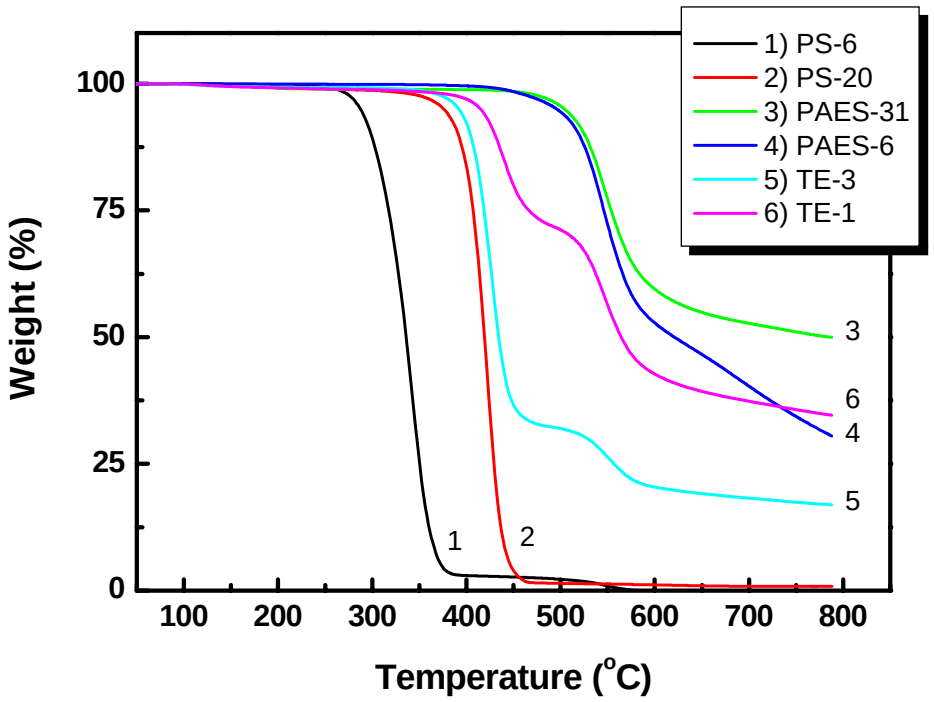

Figure S2 TGA traces of end-functionalized PS with anhydride group, end-functionalized PAES with amine group, and block copolymers TE-1 and TE-3.

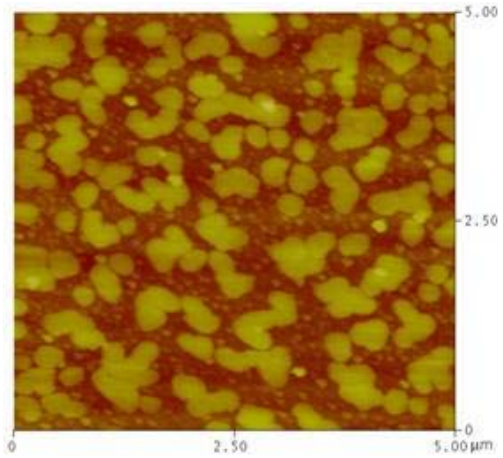

Figure S3 AFM image of (a) PAES-31 homopolymer showing random distribution of the particles due to aggregation.

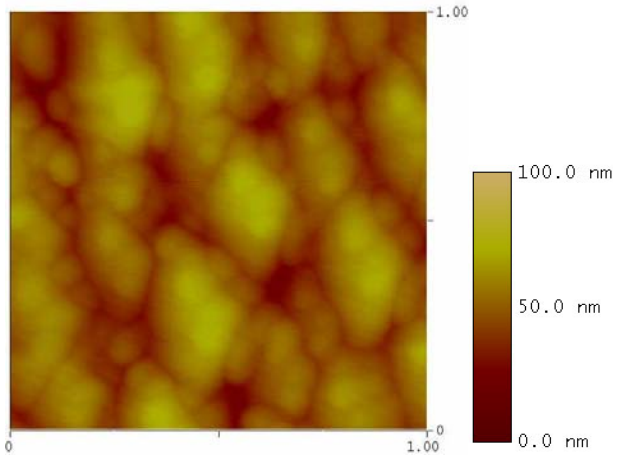

Figure S4 Magnified image of TE-2 block copolymer.

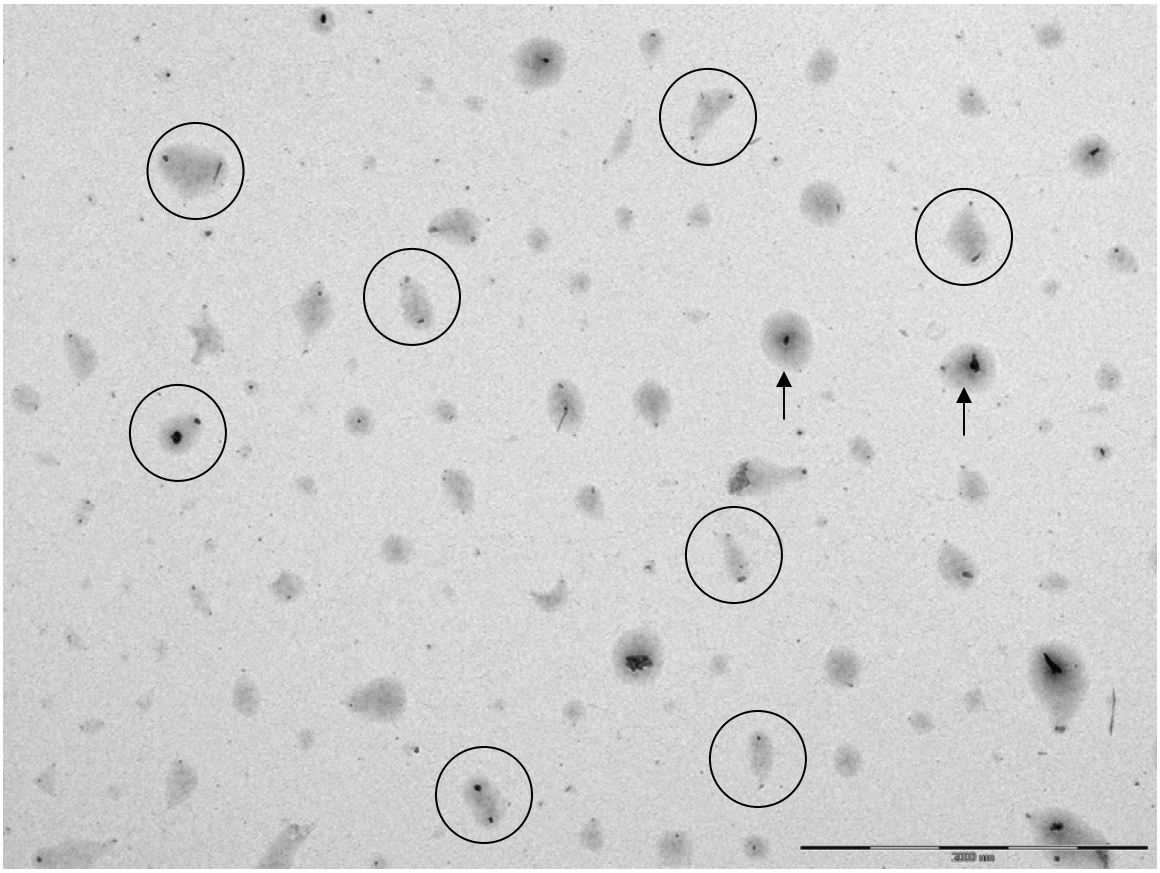

Figure S5 A low resolution TEM picture of TE-3 block copolymer (scale bar 2000 nm). Several elliptical micelles with two dark spots at the termini are encircled. Some of the micelles are of irregular shape. Micelles with one dark spot (marked by arrows) could be of the micelles oriented vertically to the substrate surface.