Supporting Information

Morphology of Polypropylene/Polystyrene Composite Particles Prepared by Seeded Emulsion Polymerization: Influence of Azo Initiator Intrinsic Charge

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Liquid chromatography–mass spectrometry analysis

Liquid chromatography–mass spectrometry (LC–MS) analysis was performed on an Agilent 6100 LC/MS system of single-quadrupole MS (Agilent Technologies, Waldbronn, Germany) with an electrospray ionization source. A Cadenza CD-C18 (2.0 mm inner diameter × 150 mm, 3 μm) column was used for separation. Each sample for analysis was dissolved in methanol, and 1 μL of the resulting sample solution was injected into the instrument. The instrument operated at a flow rate of 0.2 mL/min using methanol and 10 mM ammonium acetate in water as the mobile phase.

Swelling degree of polypropylene with styrene

A polypropylene (PP) aqueous emulsion was heated to 65°C to completely remove the medium. The dried emulsion was melt-pressed at 165°C to produce PP films with a thickness of approximately 0.8 mm. The obtained PP film (0.07 g) was soaked in styrene (3.5 g) and heated to 40°C, 70°C, or 90°C for a set duration. Thereafter, the PP film was removed from the styrene, wiped with paper towel, and weighed. Based on the weight of the PP film before (W_1) and after (W_2) soaking in styrene, the swelling degree of styrene in PP was calculated as

$$\text{Swelling degree of styrene in PP (wt\%)} = \frac{W2 - W1}{W1} \times 100$$

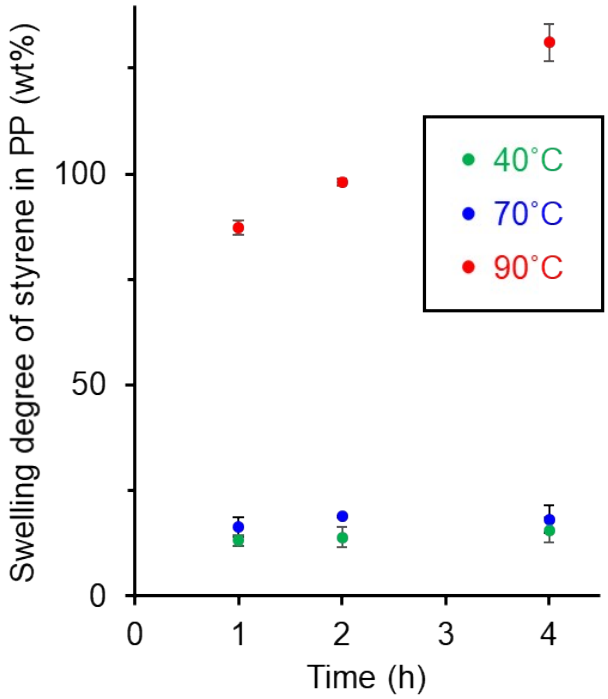

Fig. S1 Swelling degree of polypropylene (PP) with styrene at 40°C, 70°C, or 90°C over time. Results represent mean ± standard deviation of two replicates for each treatment.

Scanning electron microscopy observation of the composite particles obtained by seeded emulsion polymerization with increasing styrene concentration

PP/PS composite particles were prepared by seeded emulsion polymerization as follows. Styrene (1 g or 2 g), seed PP aqueous emulsion (2 g, giving 25% solid in water), and VA-086 were added to water (10.5 g). The ratio of [styrene]/[VA-086] was 533 in all experiments. Polymerization was performed in a closed glass tube purged with nitrogen gas for 24 h by shaking at 100 cycles per minute (3-cm strokes). After polymerization, the obtained emulsions contain a large amount of byproduct particles. The composite particles and byproduct particles could not be separated by centrifugation due to increase in the density of composite particle.

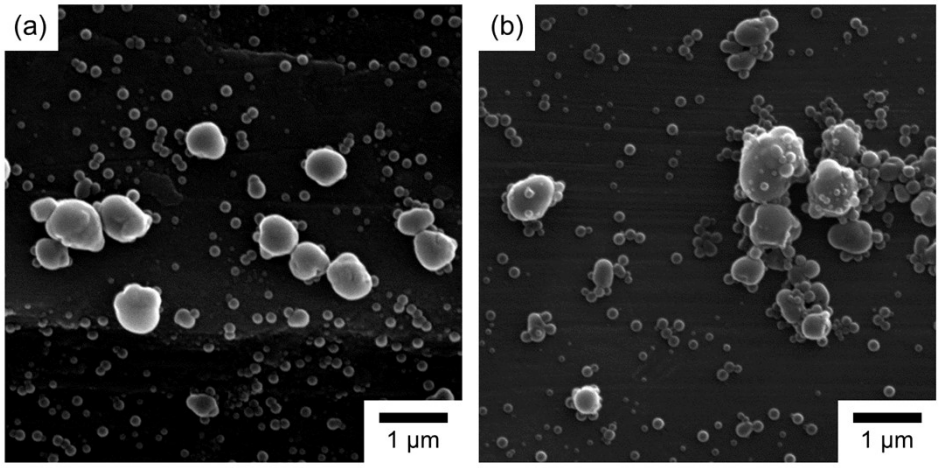

Fig. S2 Scanning electron microscopy images of the composite particles obtained by seeded emulsion polymerization with (a) 2 and (b) 4 times the amount of styrene per seed PP particle.

Field-emission scanning electron microscopy observation of cross sections of seed polypropylene particles

Freeze-dried seed polypropylene (PP) particles were ion-beam-milled (Gatan Ilion model 693) at an accelerating potential of 4 kV, coated with platinum, and subsequently observed using field-emission scanning electron microscopy (FE-SEM; SU8020, Hitachi High-Tech, Tokyo, Japan) operated at an accelerating potential of 2 kV.

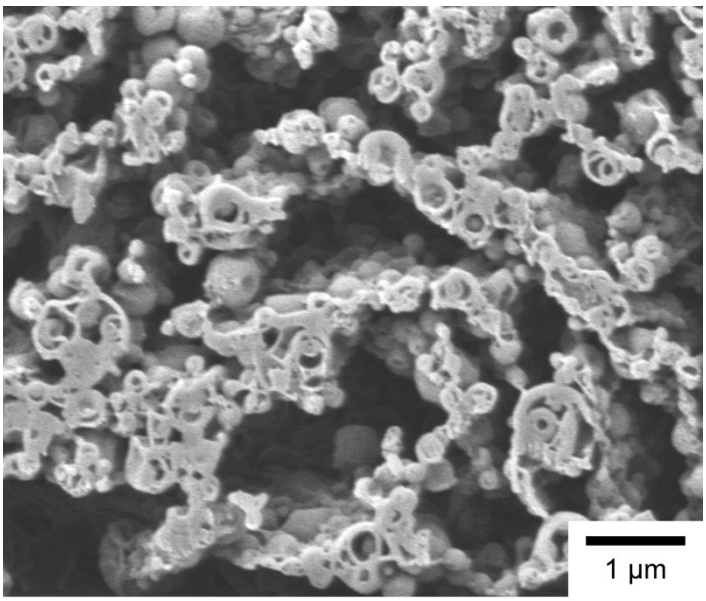

Fig. S3 Field-emission scanning electron microscopy image of ion-beam-milled polypropylene seed particles.

Gel permeable chromatography analysis

Molecular weights and polydispersity index (PDI) of PS extracted from the composite particles were analyzed by gel permeable chromatography (GPC) using PS standard and eluted in THF flow rate of 1 mL/min on a Shimadzu LC-20AD GPC instrument fitted with RID-20A refractive index detector and Shodex columns (KF-803 and two KF-804). PS was extracted from the composite particles prepared with VA-044, V-501, or VA-086 by reflux with THF, which can dissolve PS but not PP. The resulting PS solution was heated to 70°C for 1 hour to evaporate the THF, followed by standing under reduced pressure for 12 hours to dry completely. 10 mg of the dried solid was dissolved in 5 mL of THF, and 10 μL of the resulting sample solution was injected into the instrument.

Table S1 Molecular weight and polydispersity index of PS extracted from the composite particles prepared with each initiator

System*	M_n	M_w	PDI
VA-044	136,000	588,000	4.3
V-501	640,000	1,440,000	2.3
VA-086	486,000	1,021,000	2.1

* The PP/PS composite particles prepared under the conditions described in *Experimental Section* were analyzed. In the VA-044 system, the polymerization temperature was 40°C.