Supplementary Material (ESI) for Chemical Communications

Supporting information

The Morphological Control of Anisotropic Polystyrene/Silica Hybrid Particles Prepared by Radiation Miniemulsion Polymerization

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Experimental

Materials

Styrene (Shanghai Chemical Reagents Co., China) was purified by passing through a basic alumina column to remove the inhibitor before use. Hexdecane (HD), sodium dodecyl sulfate (SDS), Tetraethoxysilane (TEOS), ammonia (25%), Methacryloxypropyltrimethoxysilane (MPS) and ethanol were all purchased from Shanghai Chemical Reagents Co. China in their reagent grade and used without further purification.

Synthesis of silica particles

Silica particles were synthesized according to the Stöber procedure.[9] 200ml of absolute ethanol and 15ml ammonia were introduced into a 250ml round flask. Then, 6ml of TEOS was added to the solution under stirring at 300 rpm. The mixture was stirred for 24h at room temperature. Silica particles were collected by centrifugation (12000rpm, 5min). After washed with ethanol three times, the silica particles were dried in vacuum oven at 50 ^{o}C for 24h. These silica particles are named as w-silica in this paper since the surface of the silica particles are covered with hydroxyl groups and have a good affinity with water.

Partial modification of silica particles by MPS

The method of partial modification of silica particles was reported in the previous literatures.[7,10] 0.4g of w-silica particles was introduced into a beaker first. Then 0.2ml deionized water was added to wet the w-silica. After that, 13ml of toluene containing 0.25ml of MPS was added. After the addition of 0.5ml of triethylamine, the mixture

was stirred for 3 days at room temperature. Then the solid was collected by centrifugation (12000rpm, 5min), and dried under vacuum for 24h after washed three times by ethanol. These silica particles which were partially modified by MPS are identified as w/o-silica since a part of the particle surface was covered with hydroxyl groups which had a good affinity with water, but the other part of the particle surface was modified by MPS groups instead of hydroxyl groups, which makes this part of the silica particle surface has a good affinity with oil.

Thorough modification of silica particles by MPS

The thorough modification of silica particles with MPS were carried out by almost the same procedure as the above partial modification of silica partices, but no water was added. Thus the surface of silica particles would be modified thoroughly with MPS groups, which makes the silica particles only have an affinity with oil phase, so they are identified as o-silica in this paper.

Preparation of anisotropic PS/silica particles by radiation miniemulsion polymerization in the presence of modified silica particles

The recipes of the miniemulsions were presented in Table S1. 0.025g of w/o-silica or o-silica, 0.1g of HD and a certain amount of styrene were introduced into a flask first. Then the mixture was ultrasonicated for 10 minutes in an ice bath in order to disperse the modified silica particles homogeneously. After that, 12.5ml aqueous solution of SDS (0.029g) was added into the above dispersion. Then the mixture was emulsified first under a magnetic stirring for 1h at room temperature, then

miniemusified by ultrasonication for 1h in an ice bath. Finally the resultant miniemulsion was irradiated by ^{60}Co γ-ray (located in USTC, China) at a dose rate of 50 Gy/min for a total absorbed dose of 45 KGy after purged with nitrogen for 10 min to remove the dissolved oxygen in the system. After polymerization was complete, the products were collected by centrifugation (12000rpm, 5min) and dispersed in ethanol for storage after washed with ethanol three times.

Characterization

Fourier transform infrared spectra were recorded on a Bruker VECTOR-22 IR spectrometer. The morphology of anisotropic PS/silica hybrid particles was studied by TEM and SEM. TEM analysis was taken by a transmission electron microscope (Japan H800) operated at 200 kV of accelerating voltage and a high-resolution transmission electron microscopy(H800, JEOL2010); SEM analysis was taken by a field emission scanning electron microscopy (FESEM, JEOL JSM6700). Samples for TEM and SEM analysis were prepared at room temperature by dispersing one drop of ethanol solution of the sample on copper grid coated with carbon and then drying in air.

Table S1. The recipes of radiation miniemulsion.

Sample number	**1**	**2**	**3**	**4**	**5**	**6**	**7**
Weight ratio[a)]	28	40	60	72	80	100	72
Styrene	0.7g	1.0g	1.5g	1.8g	2.0g	2.5g	1.8g
w/o-silica	0.025g	0.025g	0.025g	0.025g	0.025g	0.025g	/
o-silica	/	/	/	/	/	/	0.025
Water	12.5g	12.5g	12.5g	12.5g	12.5g	12.5g	12.5g
SDS	0.029g	0.029g	0.029g	0.029g	0.029g	0.029g	0.029g
Hexadecane	0.1g	0.1g	0.1g	0.1g	0.1g	0.1g	0.1g

a) Weight ratio of monomer/silica.

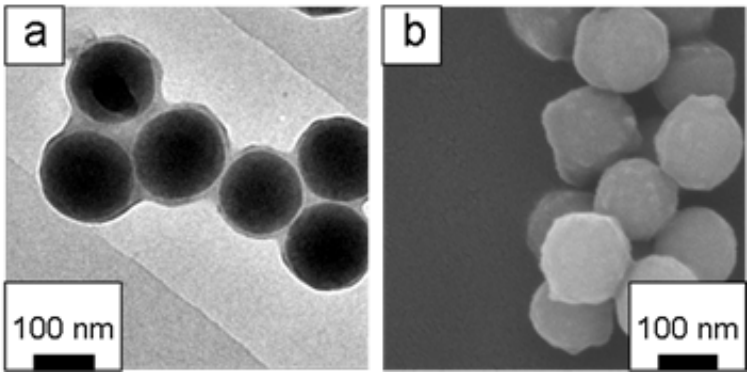

Figure S1. TEM and SEM images of PS/silica hybrid particles which were synthesized in the presence of o-silica. Weight ratio of monomer/silica was 72.

In order to further testify the reproducibility, the radiation miniemulsion polymerization was conducted repeatedly, as shown in the Figure S2 below.

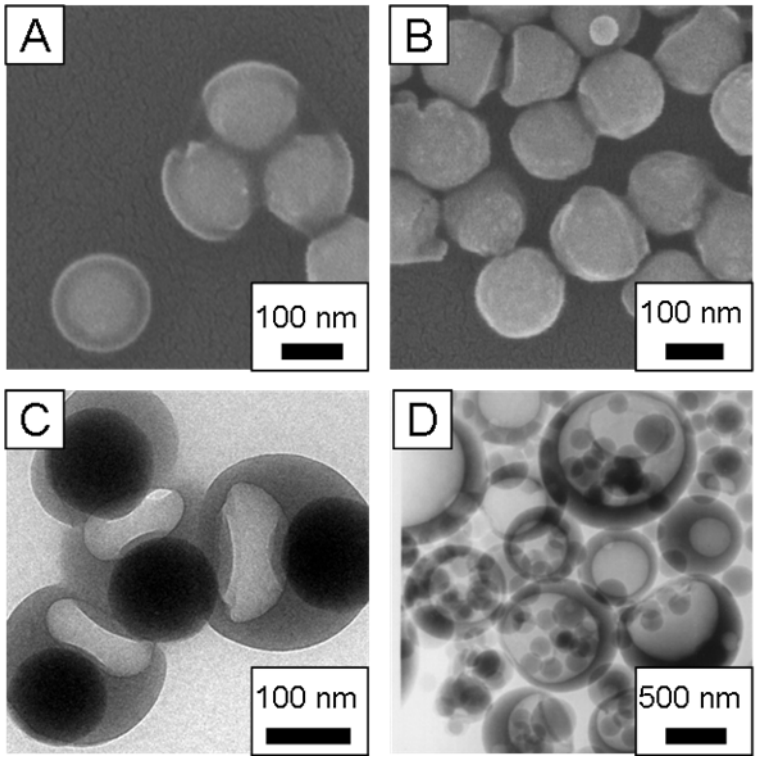

Figure S2. TEM (A-B) and SEM (C-D) images of anisotropic PS/silica hybrid particles synthesized in the presence of w/o-silica. The weight ratio of monomer/silica was increased from images of A-D. A: 28; B: 60; D: 100.