**Supporting Information for**

**Confinement effect of blocks on morphology of composite particles in co-assembly of block copolymers/homopolymers**

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S1. Materials

Styrene and methyl acrylate (St, DaeJung, 99%, MA; Sigma-Aldrich, 99%) were passed through a basic alumina column to remove the polymerization inhibitor before use. 2,2'-Azobis(2-methylpropionitrile) (AIBN, Sigma-Aldrich ,99%) was recrystallized in cold methanol before use and dried at room temperature under vacuum. Tetrahydrofuran (THF, Merck, 99%) was dried by heating under reflux over sodium wire in presence of benzophenone as indicator and stored in the 3Å activated molecular sieves. Methanol (Merck, 99.9%), 1-dodecanethiol (Sigma-Aldrich, 98%), carbon disulfide (CS2, Sigma-Aldrich, 99%), sodium hydride (Sigma-Aldrich, 60% in oil), diethyl ether (Sigma-Aldrich, 99%), iodine (Sigma-Aldrich, 99.8%), sodium thiosulfate (Sigma-Aldrich, 99.9%), ethyl acetate (Sigma-Aldrich, 99.8%), *n*-hexane (Sigma-Aldrich, 99.8%), aluminum oxide (Al2O3, Merck), aniline (ANI,CDH, 99.5%), ammonium persulfate (APS, Sigma-Aldrich), and *N*,*N*-dimethylformamide (DMF, DaeJung, 99.5%) were used as received.

S2. Instrumentation

1H NMR (500 MHz) spectra were recorded on a Varian Unity Inova 500 MHz using deuterated chloroform (CDCl3) as solvent and tetramethylsilane (TMS) as an internal standard. Gel permeation chromatography (GPC) was carried out using THF solvent at 30 °C and 1 mL/min flow rate by Shimadzu apparatus. The output solution was measured by the refractive index (RI). The device was calibrated using standard polystyrene with a molecular weight of 650 to 30,000 g.mol−1. The morphology of self-assembled structures was observed by MIRA3 TESCAN FE-SEM. The samples were freeze-dried and coated with gold before FE-SEM characterization. Fourier transform infrared (FT‐IR) spectroscopy was performed by means of a Bruker Tensor 27 FT‐IR spectrophotometer, in the range between 500 and 4000 cm−1 with a resolution of 4 cm−1. Size and size distribution of self-assembled hydrophobic polymers were measured by a DLS instrument (Malvern Nano Zetasizer ZS 90, UK) with a scattering angle of 176.1°.

S3. Synthesis of cyanomethyl dodecyl trithiocarbonate (CMDTTC)

Dodecane-1-thiol (7.69 g, 38 mmol) was added to a suspension of NaOH (60% *wt*. % in oil, 1.575 g, 39.4 mmol) in diethyl ether (75 mL) under stirring in the ice water bath. A potent evolution of hydrogen gas was observed and the gray suspension was converted to thick white grout of sodium thiododecylate. Afterward, CS2 (3.0 g, 39.4 mmol) was added to the mixture and reaction was continued for 4 h. The resulting sodium dodecyl trithiocarbonate was collected by filtration and a yellow solid product was obtained. Then, iodine (4.82 g, 38 mmol) was added dropwise to suspension of sodium dodecyl trithiocarbonate in diethyl ether (75 mL). Afterward, mixture was stirred at room temperature for 2 h and white sodium iodide was removed by filtration. Yellow filtrate product was washed with aqueous sodium thiosulfate to remove excess iodine, then diethyl ether phase was dried over sodium thiosulfate and evaporated to leave a residue of bis(dodecylsulfanylthiocarbonyl) disulfide in qualitative yield. In the next step, AIBN (9.35 g, 56.9 mmol) was added to the solution of bis(dodecylsulfanylthiocarbonyl) disulfide in ethyl acetate (150 mL) and heated at reflux for 20 h. After removal of vaporizable in vacuum, the final product was purified by flash column chromatography to obtain cyanomethyl dodecyl trithiocarbonate (CMDTTC)as a pale-yellow oil (8.4 g, 65% yield) [S1].

**FT-IR of CMDTTC (KBr, cm-1, Figure S1):** (2250 str. (**CN**)CH2S), (2850, 3000 assym. str. **CH3**, **CH2**).

**1H NMR of CMDTTC** **(500 MHz, CDCl3, δ/ppm, Figure S2):** 0.86 (t, 3H, CH3CH2); 1.28 (s, 18H, (CH2)6); 1.71 (m, 2H. CH2CH2S); 3.40 (t, 2H, CH2CH2S); 4.15 (s, 2H, (CN)CH2S).

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**Figure S1. FT-IR spectra of CMDTTC**

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**Figure S2.** (A) 1H NMR and (B) 13C NMR spectra of CMDTTC.

S4. Contact angle results

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**Figure S3.** Contact angle between (a, b, c) PANI, PS and, PAM and distilled water, (d, e, f) PANI, PS, and, PMA and diiodomethane.

**Table S1.** Liquids and surface tension data (mN/m).

|  |  |  |  |
| --- | --- | --- | --- |
| **γL** | **γLp** | **γLd** | **Liquids** |
| 72.8 | 51 | 21.8 | **Distilled water** |
| 50.8 | 0.0 | 50.8 | **Diiodomethane** |

**References**

[S1] Chong K, Moad G, Rizzardo E, Thang H (2007) Thiocarbonylthio end group removal from RAFT-synthesized polymers by radical-induced reduction. Macromolecules 40: 4446-4455 <https://doi.org/10.1021/ma062919u>.