

Supporting Information

Polystyrenes with both hydrophilic and hydrophobic moieties: synthesis and self-assembly behaviors

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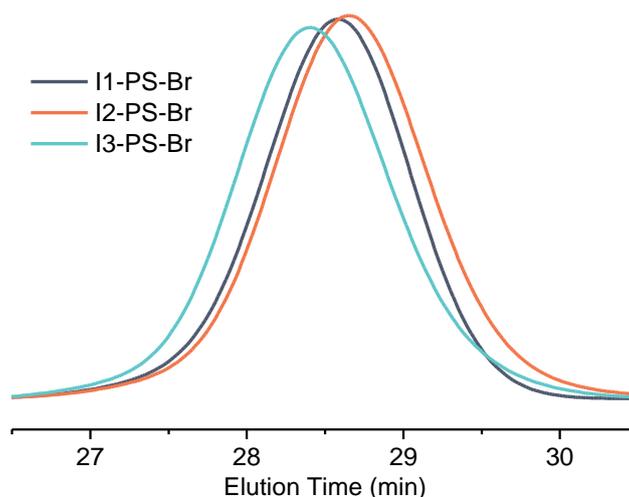


Fig. S1 GPC curves of I1/2/3-initiated polystyrenes ended with bromine (In-PS-Br).

Table S1 Results of polystyrenes prepared via ATRP using different difunctional initiators.

| Sample | Initiator | Reaction Time (min) | Conv. (%) ^a | Yield (%) ^b | $M_{n,GPC}$ ^c | PDI ^c |
|----------|-----------|---------------------|------------------------|------------------------|--------------------------|------------------|
| I1-PS-Br | I1 | 11 | 6.98 | 7.77% | 3600 | 1.09 |
| I2-PS-Br | I2 | 14 | 6.21 | 7.10% | 3400 | 1.11 |
| I3-PS-Br | I3 | 15 | 6.61 | 7.60% | 3800 | 1.11 |

^aRefer to the conversion rates of monomers and were calculated through the equation of Conv.% = $(W_p - W_I)/W_{St}$, where W_p , W_I , and W_{St} refer to the weight/mass of resultant polymer product, initiators in feed, and styrene monomers in feed, respectively. ^bCalculated by the equation of yield (%) = $W_p/(W_{St} + W_I)$. ^cResults obtained from GPC measurements.

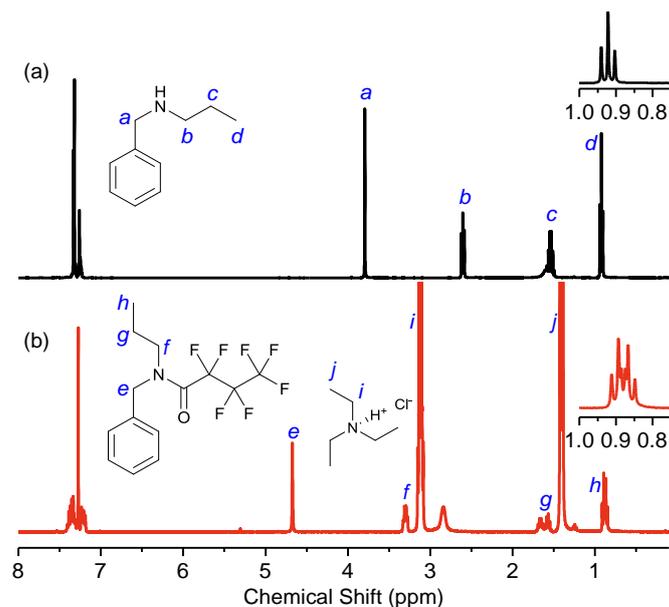


Fig. S2 ^1H NMR curves of (a) *N*-propylbenzylamine and (b) its product mixture after reacting with $\text{C}_3\text{F}_7\text{COCl}$ with triethylamine as the deacid agent. Insets are molecular structures of the reactants and product, and the spectra of peak *d* or *h*.

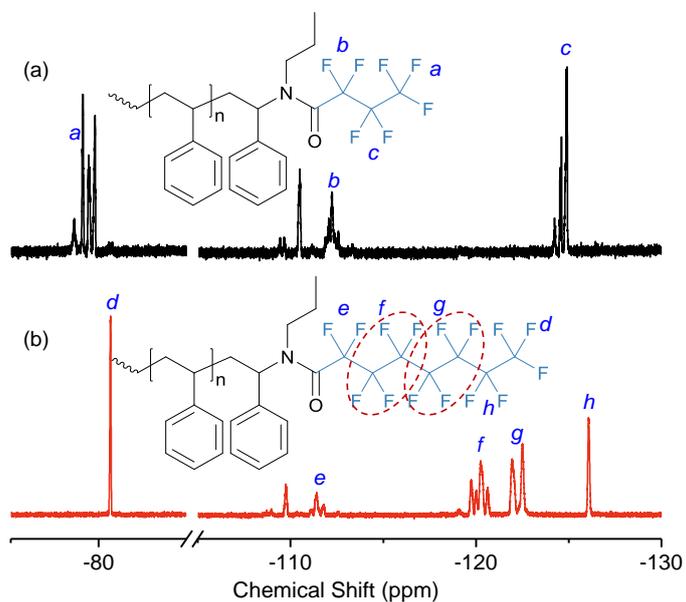


Fig. S3 ^{19}F NMR spectra of (a) I1-PS-7F and (b) I1-PS-15F. The low signal-to-noise ratio is ascribed to the relatively low content of fluorine atoms in the polymer chains.

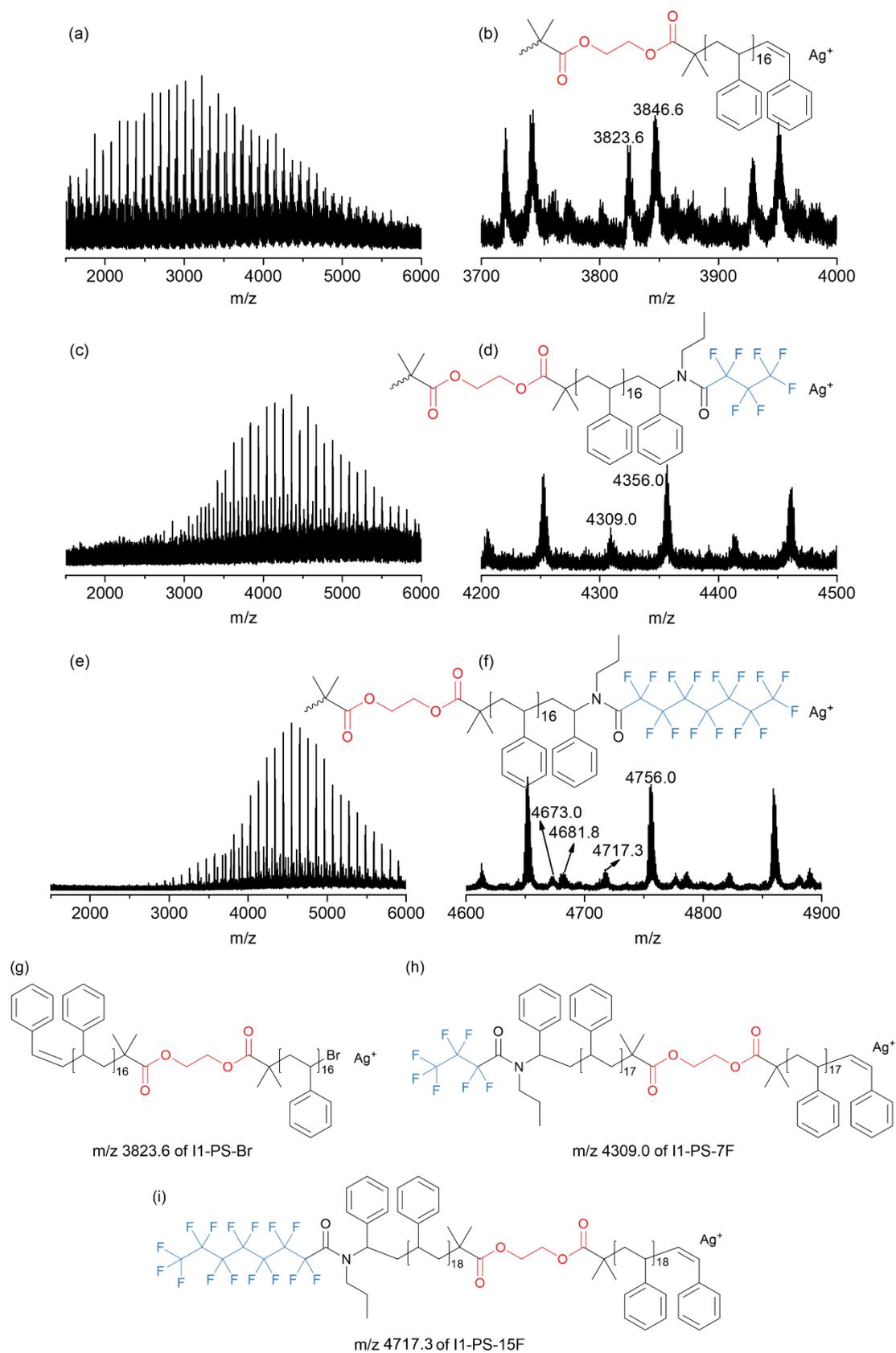


Fig. S4 MALDI-TOF MS spectra of (a, b) I1-PS-Br, (c, d) I1-PS-7F, and (e, f) I1-PS-15F. Insets show the molecular structures that correlate to the main peaks. (g–h) Possible molecular structures that correlate to the side peaks in (b), (d), and (h), respectively.

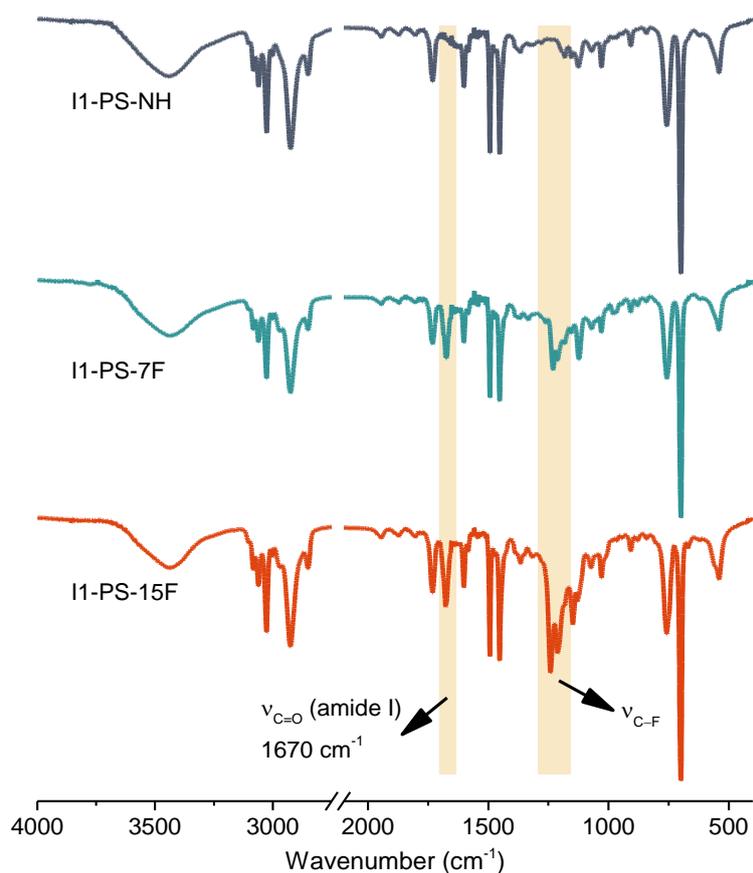


Fig. S5 FTIR spectra of I1-PS-NH, I1-PS-7F, and I1-PS-15F.

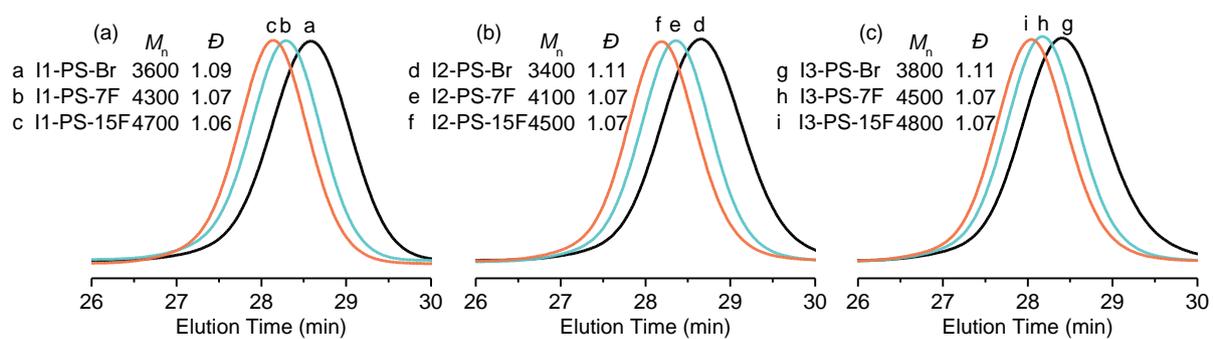


Fig. S6 GPC curves of (a) I1, (b) I2, and (c) I3-initiated polystyrenes with bromine (In-PS-Br), heptafluorobutyryl (In-PS-7F), or pentadecafluorooctanoyl (In-PS-15F) end groups. Insets show the number-average molecular weight (M_n) and the polydispersity index (\mathcal{D}) of each polymer.

Method for the calculation of surface free energies:

After obtaining the static contact angles of water and CH₂I₂ on the flat films, the surface free energies can be calculated using Owens method:¹

$$(1 + \cos\theta)\gamma_l = 2(\gamma_s^d \gamma_l^d)^{1/2} + 2(\gamma_s^p \gamma_l^p)^{1/2}$$

$$\gamma_s = \gamma_s^d + \gamma_s^p$$

$$\gamma_l = \gamma_l^d + \gamma_l^p$$

where γ_l and γ_s are the surface free energies of the liquids and the solid substrates, respectively. The superscripts of d and p indicate the dispersion and polar force component of surface free energies, respectively; the sum of which denotes the apparent surface free energies. Normally, the strong-polar H₂O and low-polar CH₂I₂ are used as testing liquids. $\gamma_{\text{H}_2\text{O}}^d$, $\gamma_{\text{H}_2\text{O}}^p$, $\gamma_{\text{CH}_2\text{I}_2}^d$, and $\gamma_{\text{CH}_2\text{I}_2}^p$ are known as 21.8, 51.0, 48.5, and 2.3 mJ m⁻², respectively.¹ By measuring the static contact angles (θ) of H₂O and CH₂I₂ on a solid substrate, two equations are obtained which can be solved for $(\gamma_s^d)^{1/2}$ and $(\gamma_s^p)^{1/2}$. Thus the γ_s is obtained.

Table S2 Calculation of surface free energies of flat films prepared from polystyrenes with various functional groups.

| Sample | Contact Angle (°) | | $(\gamma_s^d)^{1/2}$ (mJ ^{1/2} m ⁻¹) | $(\gamma_s^p)^{1/2}$ (mJ ^{1/2} m ⁻¹) ^a | γ_s (mJ m ⁻²) ^a |
|-----------|-------------------|--------------------------------|--|---|---|
| | H ₂ O | CH ₂ I ₂ | | | |
| I1-PS-Br | 99.1±1.9 | 20.4±1.2 | 7.04 | -0.31 | 49.62 |
| I1-PS-7F | 100.2±1.4 | 28.0±0.6 | 6.84 | -0.28 | 46.85 |
| I1-PS-15F | 102.3±1.8 | 37.9±0.4 | 6.49 | -0.23 | 42.18 |
| I2-PS-Br | 97.9±1.0 | 21.0±0.4 | 7.01 | -0.19 | 49.15 |
| I2-PS-7F | 93.4±1.9 | 23.6±1.1 | 6.87 | 0.31 | 47.27 |
| I2-PS-15F | 101.5±1.2 | 36.6±1.3 | 6.54 | -0.19 | 42.78 |
| I3-PS-Br | 101.5±1.9 | 17.7±0.9 | 7.14 | -0.59 | 51.04 |
| I3-PS-7F | 96.3±1.9 | 22.5±0.6 | 6.95 | 0.00 | 48.24 |
| I3-PS-15F | 102.7±1.3 | 36.0±0.8 | 6.58 | -0.33 | 43.35 |

^aThe negative values of $(\gamma_s^p)^{1/2}$ are obtained for some samples which is meaningless mathematically. Same phenomena have been observed in other works and the reasons were discussed.² In that case, γ_s^p is regarded as zero and $\gamma_s = \gamma_s^d$.

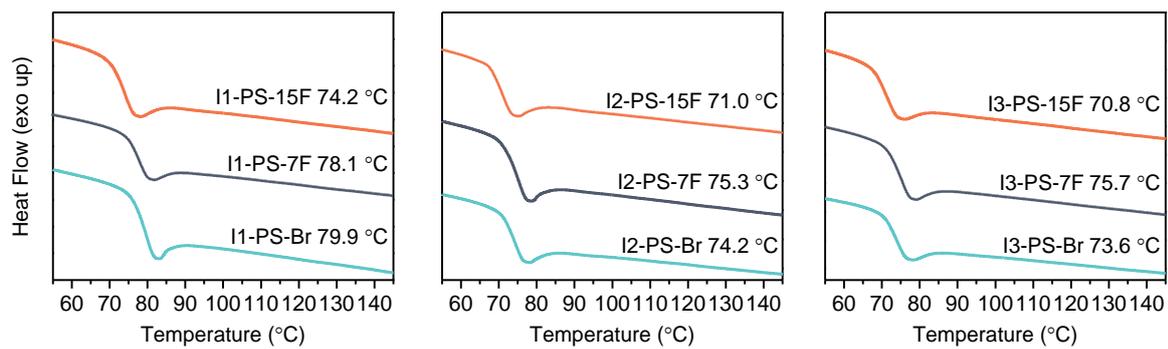


Fig. S7 DSC curves of the polymers with T_g values marked correspondingly.

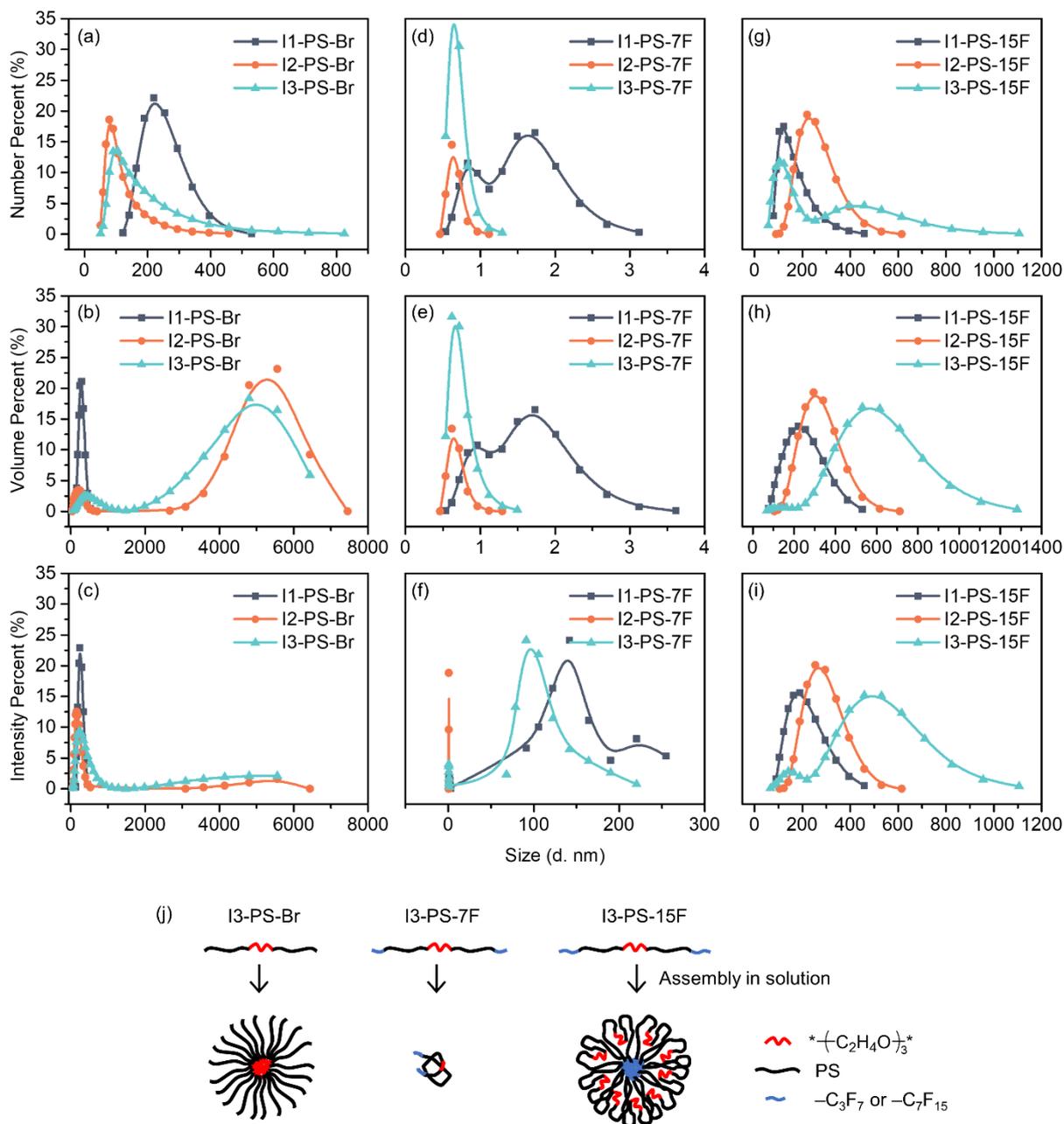


Fig. S8 (a–i) Size distributions of the aggregates of the polymers in CS_2 (10 mg mL^{-1}) by (a–c) number, (d–f) volume, and (g–i) intensity. (j) Cartoon schematics of the possible self-assembly of I3-initiated polystyrenes with different end groups. Figure a–i share the same vertical axis.

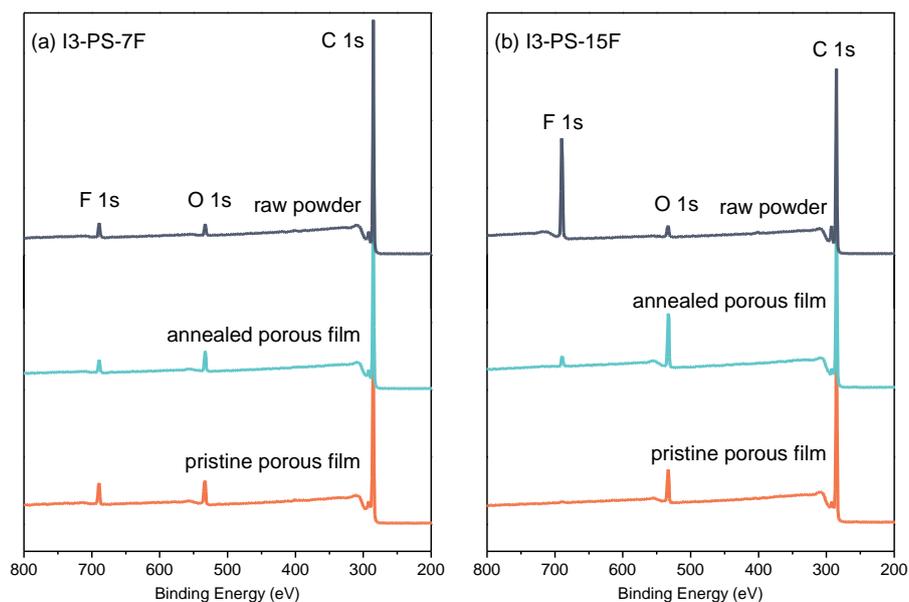


Fig. S9 XPS wide scan spectra of (a) I3-PS-7F and (b) I3-PS-15F, including results of the pristine porous films prepared by the breath figure method, films after annealing, and powders of the raw polymers.

Table S3 C/O/F atomic ratios of I3-PS-7F/15F materials in forms of pristine porous film prepared by the breath figure method, annealed porous film, and raw powder. XPS results and stoichiometry values are shown for comparison.

| Sample | C/O/F (at%) | | |
|-----------|----------------------|-------------------|--------------|
| | XPS | stoichiometry | |
| I3-PS-7F | pristine porous film | 88.6/7.1/4.3 | |
| | annealed porous film | 91.3/5.4/3.3 | 93.7/2.3/4.0 |
| | raw powder | 93.8/2.8/3.4 | |
| I3-PS-15F | pristine porous film | 91.5/8.5/0 | |
| | annealed porous film | 84.8/12.6/2.6 | 89.6/2.2/8.2 |
| | raw powder | 78.6/3.6/17.8 | |

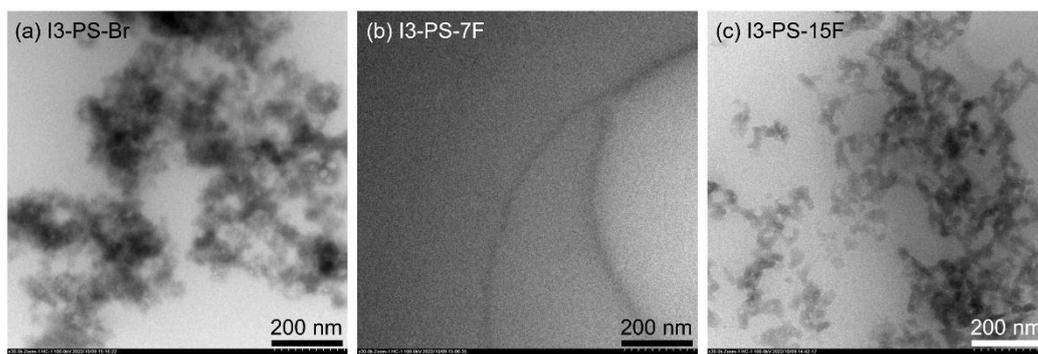


Fig. S10 TEM images of (a) I3-PS-Br, (b) I3-PS-7F, and (c) I3-PS-15F aggregates in CS₂ under a concentration of 10 mg mL⁻¹.

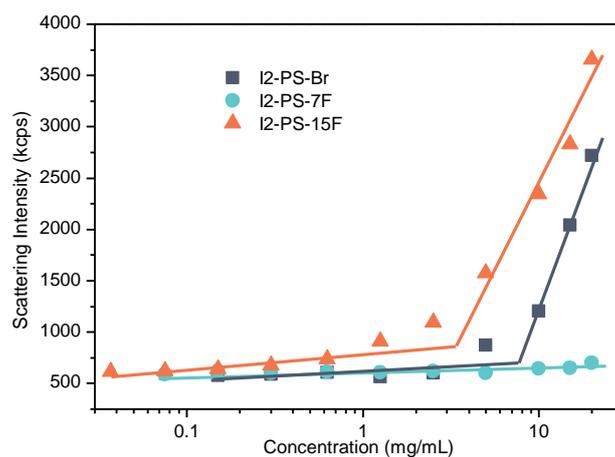


Fig. S11 Concentration-dependent static scattering intensity of I2-initiated polystyrenes in CS₂.

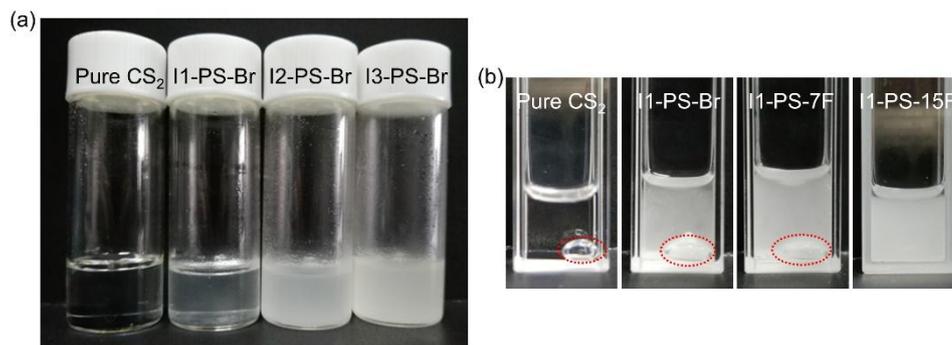


Fig. S12 Digital photographs of polymer-in-CS₂ solutions after the addition of (a) water (5 μ L) or (b) perfluorohexane (200 μ L) and successive ultrasonication (5 min). Isolated perfluorohexane droplets which are not fully dispersed in CS₂ are marked with red dotted circle.

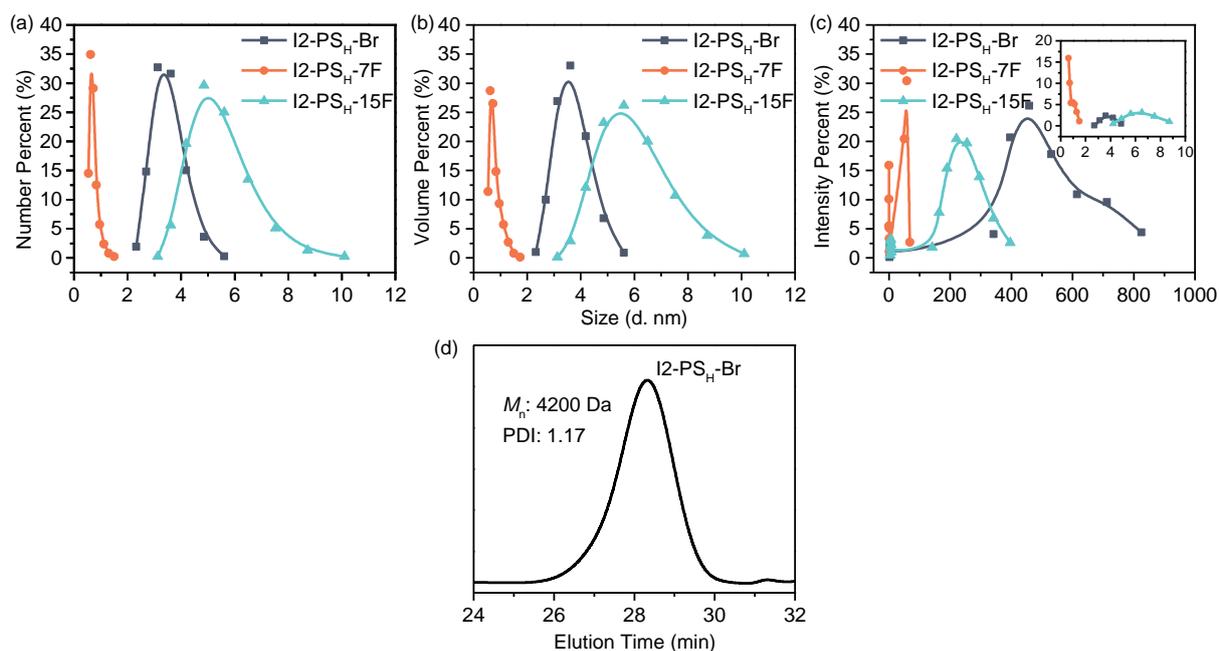


Fig. S13 Size distributions of the aggregates of the I2-initiated polystyrenes with various end groups in CS₂ (10 mg mL⁻¹) by (a) number, (b) volume, and (c) intensity. (d) GPC curves of I2-PS_H-Br. The subscript H of I2-PS_H-Br/7F/15F indicate the molecular weight is higher compared with I2-PS-Br. Inset in (c) shows the detailed signals correspondingly.

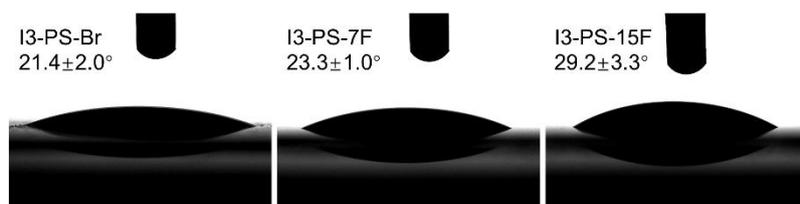


Fig. S14 Optical images of CS₂ drops (3 μL) dissolved with various polymers (10 mg mL⁻¹) on PET substrates. Insets show the averaged contact angles.

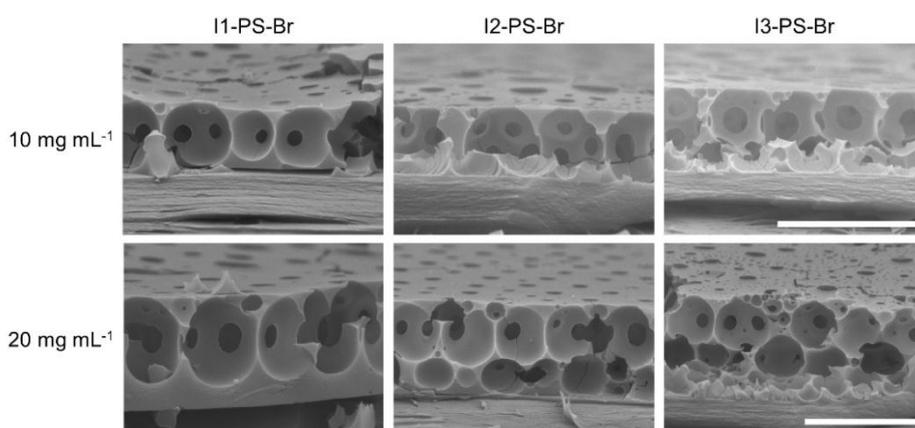


Fig. S15 Cross-sectional SEM images of porous films of bromine-terminated polystyrenes fabricated under the concentrations of 10 and 20 mg mL⁻¹. Scale bars are 10 μm.

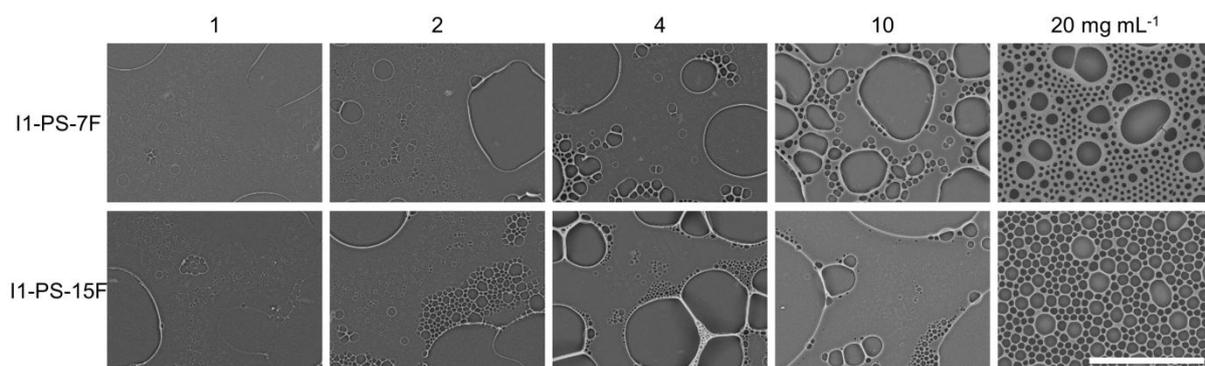


Fig. S16 SEM images of porous films of I1-PS-7F/15F fabricated under various concentrations. The scale bar is 100 μm .

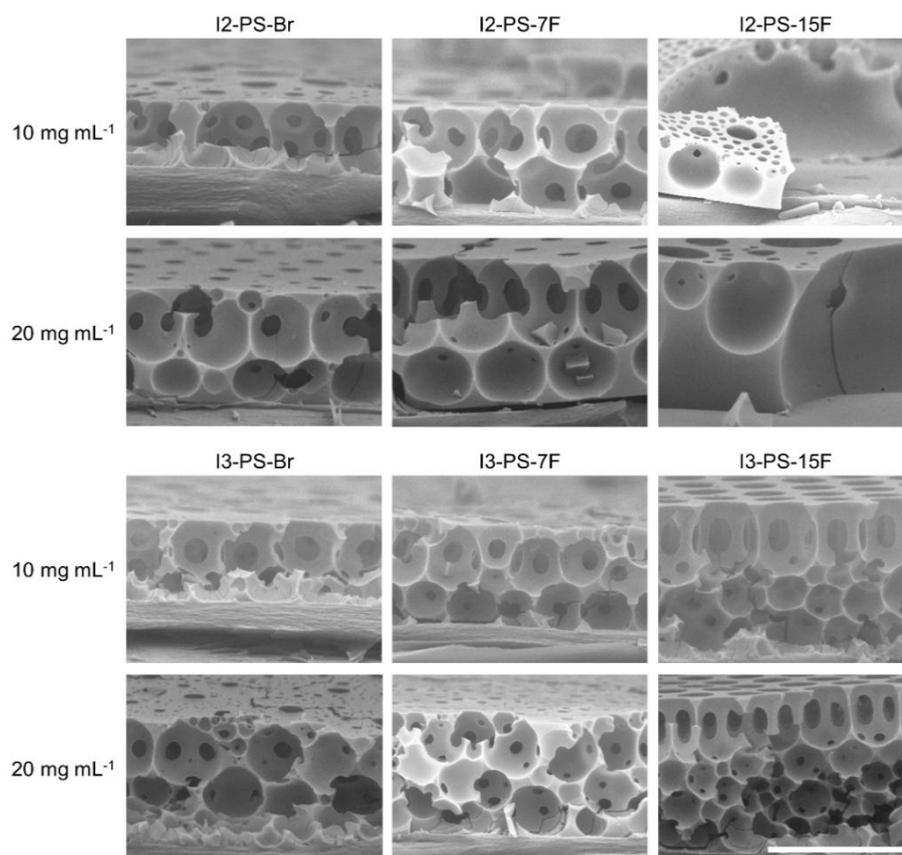


Fig. S17 Cross-sectional SEM images of porous films of I2- and I3-initiated polystyrenes with various end groups fabricated under concentrations of 10 and 20 mg mL⁻¹. Scale bar is 10 μm .

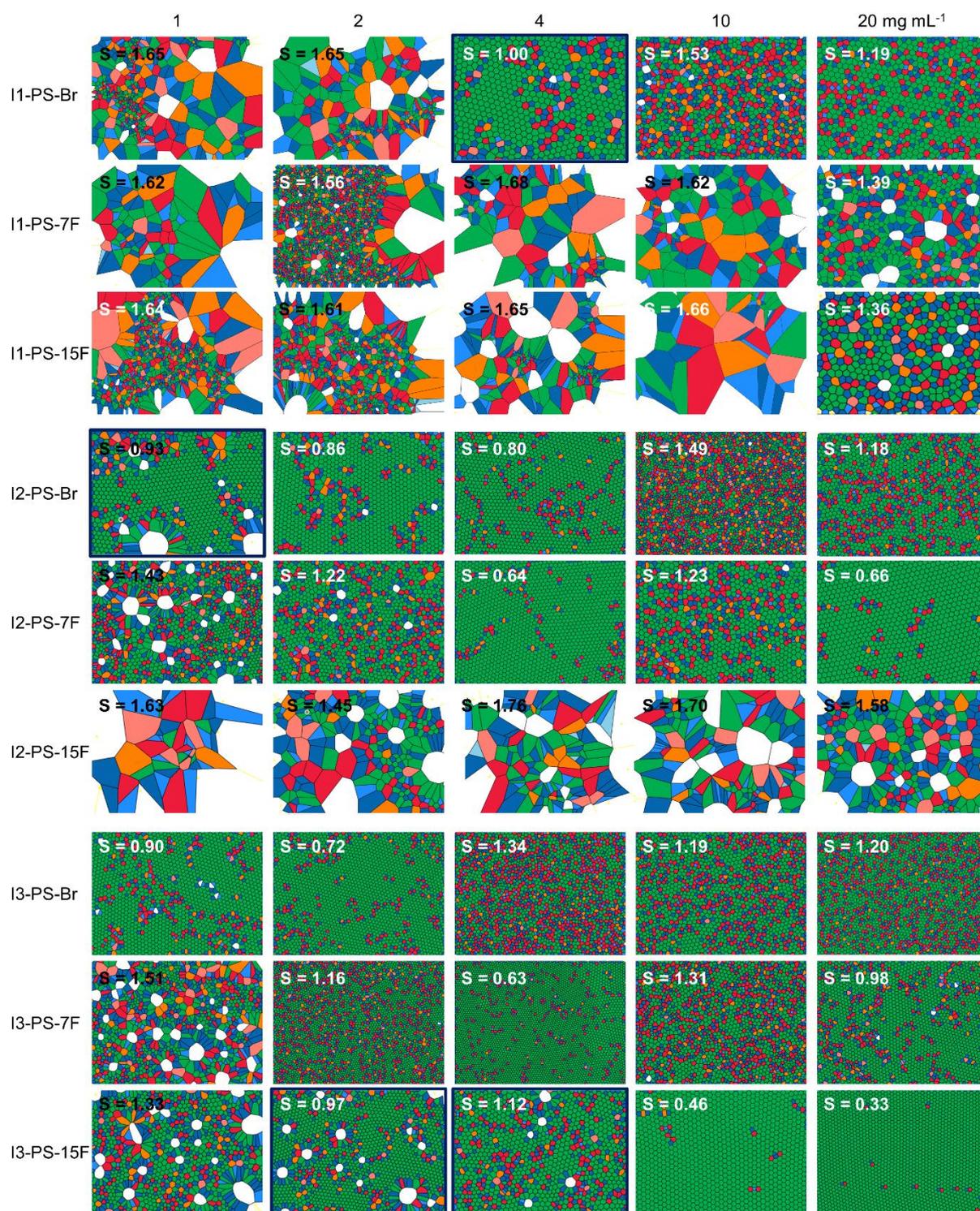


Fig. S18 Voronoi diagrams of SEM images of porous films prepared from different polymers at various concentrations. The corresponding conformational entropy (S) values are shown. Pictures highlighted with blue border emphasize patterns coexisted with hexagonally-packed pores (green) and much larger pores (white) whose S are smaller than 1.2, still, we consider them as irregular pattern.

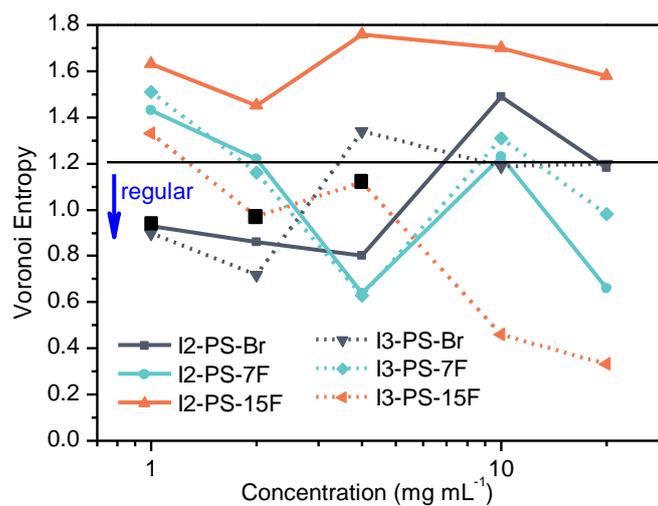


Fig. S19 Summarized conformational entropy values of porous films prepared from different polymers at various concentrations. Solid and dashed lines represent I2- and I3-initiated polystyrenes, respectively. S of 1.2 is set as a critical condition for the differentiation of regular and irregular pattern. Samples with S smaller than 1.2 but are irregular in practice are marked with black cubes.

References:

- 1 D. K. Owens and R. C. Wendt, *J. Appl. Polym. Sci.*, 1969, **13**, 1741-1747.
- 2 T. Białopiotrowicz, *J. Adhes. Sci. Technol.*, 2007, **21**, 1557-1573.