

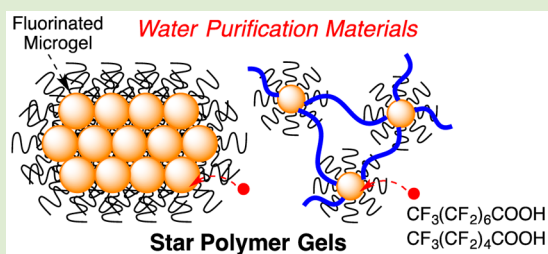
Star Polymer Gels with Fluorinated Microgels via Star–Star Coupling and Cross-Linking for Water Purification

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S Supporting Information

ABSTRACT: Two types of star polymer gels containing perfluorinated microgels were created as purification materials to separate polyfluorinated surfactants (e.g., perfluorooctanoic acid) from water. One macrogel is prepared by the radical coupling of fluorine and/or amine-functionalized microgel star polymers alone, while another is done by the radical cross-linking of the star polymers with poly(ethylene glycol) methyl ether methacrylate. Importantly, the reactive olefin remaining within the microgel cores was directly employed for both coupling and cross-linking reactions. Swelling properties of star polymer gels were effectively controlled by the latter cross-linking technique. Analyzed by small-angle X-ray scattering, a star–star coupling gel typically consists of a three-dimensional network where star polymers are sequentially connected with the microgels at the constant interval of about 20 nm. Owing to the fluororous and acid/base cooperative interaction, star polymer gels carrying fluorine/amine-functionalized microgels efficiently captured polyfluorinated surfactants in water and successfully afforded the removal from water via simple mixing and filtration.



Perfluorinated alkanes bearing polar functional groups such as carboxylic acid (e.g., perfluorooctanoic acid: PFOA)¹ possess unique amphiphilic properties based on fluorophilicity and hydrophilicity.^{1–3} Thus, they efficiently work as surfactants in water to be typically often employed for the industrial production of fluorinated polymers. Owing to the high chemical and physical stability, such perfluorinated surfactants are bioaccumulated and may be possibly toxic.¹ In industrial processes, they are often removed from water via physical adsorption with activated carbon or ion exchange resins. However, the development of novel purification materials and technologies against perfluorinated compounds are yet required so as to enhance the removal efficiency and selectivity toward a sustainable society without environmental problems therefrom.

From this viewpoint, microgel-core star polymers are promising as nanocapsules to efficiently capture, stimuli-responsively release, and separate various molecules.^{4–10} The key is to accumulate functional groups into microgel cores in high local concentration. Such core-functionalized star polymers are efficiently obtained from the linking reaction of linear arm polymers with functional linking agents and monomers via living radical polymerization.^{4–12} With this methodology, we have recently produced core-fluorinated star polymers with hydrophilic poly(ethylene glycol) (PEG) arms for the removal of perfluorinated compounds and surfactants from water.¹⁰ The star polymers homogeneously provide fluororous microgel spaces in aqueous media and thereby efficiently encapsulate perfluorinated surfactants via fluororous interaction in water. However, homogeneous solubility of star polymers results in the requirement of a bothersome separation process of surfactant-bearing star polymers via dialysis.

Given these backgrounds, we herein developed star polymer gels with perfluorinated microgel spaces for the efficient and convenient separation of perfluorinated surfactants from water (Scheme 1). As perfluorinated domains, fluorine-functionalized (S1) or fluorine/amine-functionalized (S2) microgel star polymers were synthesized by the linking reaction of a chlorine-capped PEG macroinitiator (PEG-Cl) with ethylene glycol dimethacrylate (EGDMA), 1*H*,1*H*,2*H*,2*H*-perfluorooctyl methacrylate (13FOMA), and 2-(dimethylamino)ethyl methacrylate (DMAEMA). Intriguingly, with the pendant olefin remaining in the microgel cores, these star polymers were directly coupled and cross-linked with a free radical initiator (2,2'-azobisisobutyronitrile: AIBN). Thus, this synthetic process is quite simple and convenient without any special modification of star polymers.

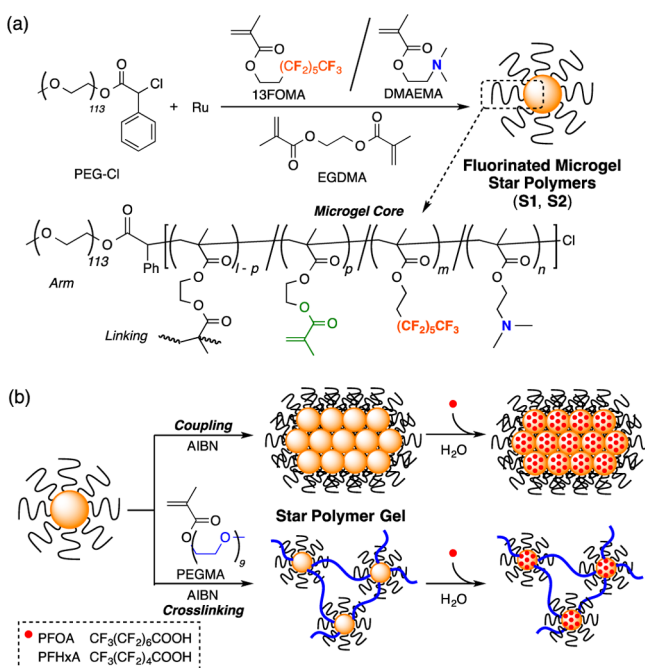
The resulting star polymer gels comprise core-fluorinated microgel star polymers that are sequentially and three-dimensionally connected to macroscopic level. The star polymer gels are thus regarded as a new class of precision macrogels,¹³ in sharp contrast to conventional macroscopic gels heterogeneously containing microgel domain within cross-linked network.^{4b,14} Owing to the perfluorinated microgels, fluorinated star polymer gels are much more effective for the separation of perfluorinated surfactants than a conventional fluorinated macrogel. It should be also noted that, to our best knowledge, this work first revealed the structure of star–star coupling products.¹²

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Scheme 1. (a) Synthesis of Fluorinated Microgel Star Polymers via Living Radical Polymerization and (b) Star Polymer Gels Obtained from the Radical Coupling or Cross-Linking of Fluorinated Star Polymers for the Separation of Perfluorinated Surfactants from Water



First, two kinds of fluorinated microgel star polymers were prepared by the linking reaction of PEG-Cl ($M_n = 4900$, $M_w/M_n = 1.03$) with EGDMA, 13FOMA, and DMAEMA via ruthenium-catalyzed living radical polymerization: a fluorous-core star polymer (S1) with 13FOMA and a fluorous/amine-core counterpart (S2) with 13FOMA and DMAEMA. For them, a ruthenium catalytic system, $\text{RuCp}^*\text{Cl}[\text{P}(m\text{-tol})_3]_2/4$ -dimethylamino-1-butanol (4-DMAB),¹⁵ was employed in ethanol at 40 °C. The feed ratio of monomers to initiator was set as 10 equiv.: $l = [\text{EGDMA}]/[\text{PEG-Cl}] = 10$, $m = [13\text{FOMA}]/[\text{PEG-Cl}] = 10$, and $n = [\text{DMAEMA}]/[\text{PEG-Cl}] = 10$. In both cases, the linking agent and their monomers were smoothly and almost simultaneously consumed up to 50–77% conversion in 14–17 h (Figure 1a) to yield star polymers (S1 and S2) with high molecular weight. The conversion for S1 was 75% (EGDMA) and 60% (13FOMA) and that for S2 was 77% (EGDMA), 57% (13FOMA), and 47% (DMAEMA). Importantly, the cross-linking reaction was terminated at the middle stage in order to leave unreacted olefin within microgels.

After purification by dialysis against methanol, these star polymers were characterized by multiangle laser light scattering coupled with size exclusion chromatography: The absolute weight-average molecular weight (M_w) was 527000 (S1) and 256000 (S2). Thus, S1 and S2 had 58 and 26 PEG arms (N_{arm}), 4520 and 1960 fluorine atoms (N_F), 350 and 150 perfluorinated alkyl pendants (N_{CF_3}), and 0 and 125 amino group (N_N), respectively, where $N_F = N_{\text{arm}} \times (13m \times \text{conv}_{13\text{FOMA}}/100)$; $N_{\text{CF}_3} = N_{\text{arm}} \times (m \times \text{conv}_{13\text{FOMA}}/100)$; and $N_N = N_{\text{arm}} \times [n \times \text{conv}_{\text{DMAEMA}}/100]$.¹⁰

Analyzed by ¹H NMR spectroscopy, S1 and S2 showed olefinic protons (g), pendant methylene and methyl protons (f, h, i, j, k, l), and polymethacrylate backbone (d, e) within their cores, in addition to PEG arm protons (a, b, c; Figures 1b and S1). Calculated from the area ratio of the olefin signal (g) and

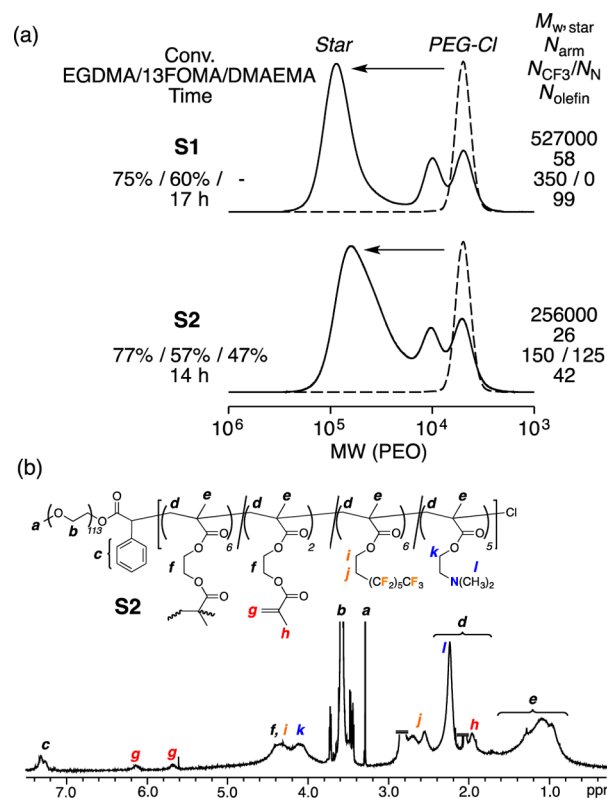


Figure 1. (a) SEC curves of star polymers (S1, S2) obtained from the cross-linking of PEG-Cl with EGDMA, 13FOMA, and DMAEMA in ethanol at 40 °C: $[\text{EGDMA}]/[13\text{FOMA}]/[\text{DMAEMA}]/[\text{PEG-Cl}]/[\text{RuCp}^*\text{Cl}(\text{P}(m\text{-tol})_3)_2]/[4\text{-DMAB}] = 100/100/0$ or $100/10/2.0/100$ mM. (b) A ¹H NMR spectrum of S2 in acetone-d₆ at rt: [S2] = 30 mg/mL. M_w^{star} : Absolute weight-average molecular weight. N_{arm} : The number of arm polymers. N_{CF_3} , N_N , and N_{olefin} : The number of fluorinated pendants, amino groups, and olefin in microgel cores.

the aromatic signal (c), the core-bound olefins for S1 and S2 were estimated as 1.7 and 1.6 unit per their single arms; the number of olefin per a star (N_{olefin}) were thus 99 (S1) and 42 (S2).

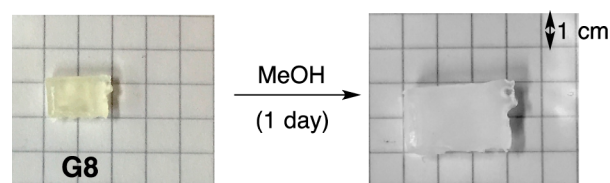
For star polymer gels, star–star coupling of S1 or S2 was then examined with AIBN in methanol at 60 °C (Scheme 1). The polymer concentration was set as 400 mg/mL: for example, S1 (800 mg) was solubilized with AIBN in methanol (2 mL; Table 1); S1-olefin/AIBN = 75/40 mM. In 3 h, gelation proceeded but the behavior was dependent on their star polymers. S1 induced phase-separation to give the mixture of dispersed, small macrogels and precipitated macrogels (G1), while S2 in turn totally led to jellylike macrogels (G2).

To control the swelling properties of star polymer gels, S1 or S2 was further cross-linked with PEGMA and AIBN in methanol at 60 °C for 19 h (Table 1). The concentration of star polymers was fixed to 200 mg/mL, but the weight ratio of the stars and PEGMA was changed as follows: star/PEGMA = 80/20, 45/55, and 30/70, w/w. All conditions efficiently led to jellylike gels (G3–G8). Quantitative consumption of the star polymers and PEGMA was confirmed by ¹H NMR. The resulting gels tended to swell well in methanol with increasing PEGMA content: for example, dry G8 swelled to approximately 5× larger volume after soaking in methanol for 1 day (Figure 2). Gels containing over 50 wt % PEGMA were self-supporting. As a control sample, a conventional macrogel (G9) was also prepared by free radical copolymerization of PEGMA,

Table 1. Synthesis of Star Polymer Gels with Fluorine and Amine-Functionalized Microgels^a

gel	star	star/PEGMA in gel (w/w, %)	13FOMA/DMAEMA in gel (w/w, %)
G1	S1	100/0	29/0
G2	S2	100/0	25/7.6
G3	S1	80/20	23/0
G4	S1	45/55	13/0
G5	S1	30/70	8.7/0
G6	S2	80/20	20/6.0
G7	S2	45/55	11/3.4
G8	S2	30/70	7.5/2.2

^aStar polymer gels were prepared by the radical coupling or cross-linking of S1 or S2 with AIBN in the absence or presence of PEGMA in methanol at 60 °C. G1 and G2: [star]/[AIBN] = 400/6.6 mg/mL. G3–G8: [star]/[PEGMA]/[AIBN] = 200/50, 250 or 500/3.3 mg/mL.

**Figure 2.** Swelling properties of G8: (a) dry G8; (b) G8 soaked in MeOH for 1 day.

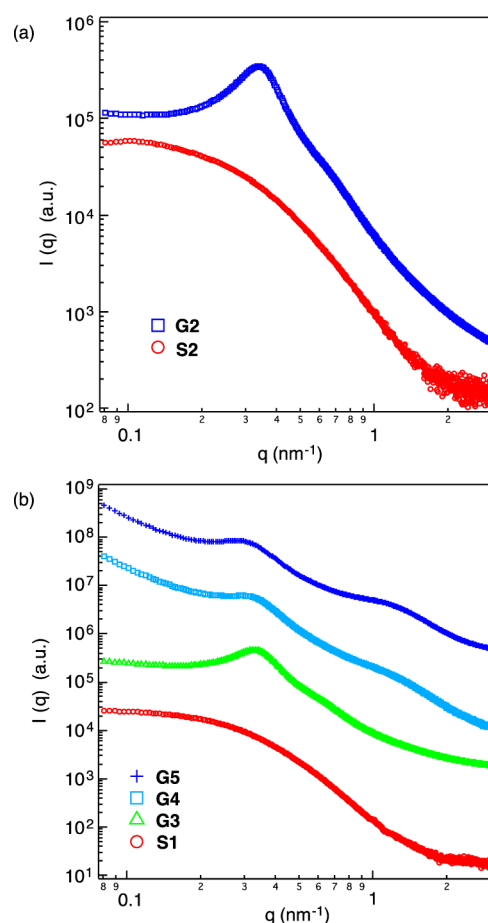
EGDMA, and 13FOMA (PEGMA/EGDMA/13FOMA = 100/10/10, molar ratio) with AIBN in methanol.

The structure of star polymers (S1 and S2), their gels (G1–G5), and a conventional gel (G9) were analyzed by small-angle X-ray scattering (SAXS) in methanol (Figures 3 and S2). The SAXS profiles of the star polymers originate from their isolate molecules. By their Guinier plots (Figure S3), radii of gyration (R_g) were determined as 6.1 (S1) and 6.2 (S2) nm.

Star–star coupling gels (G1, G2) exhibited SAXS profiles different from their original star polymers (S1, S2) and G9. In particular, G2 clearly demonstrated a scattering intensity maximum (q_m) derived from the interparticle distance of S2 at 0.34 nm^{-1} (Figure 3a). This importantly demonstrates that G2 consists of the three-dimensional network where multiple S2 is sequentially connected with the microgel at the average interval ($D = 2\pi/q_m$) of 18.5 nm (Scheme 1b). It should be noted that this is the first elucidation of the structure of star–star coupling. In contrast, owing to the lower efficiency of star–star coupling, G1 did not so clearly exhibit q_m (Figure S2).

Similarly to G2, G3–G5 showed q_m , while the q_m shifted from 0.34 to 0.30 nm^{-1} with increasing the PEGMA content. This importantly means that the interparticle distance of S1 incorporated within the gels gradually increased with the PEGMA content: $D = 18.8$ (G3), 19.5 (G4), and 20.9 (G5) nm (Figure 3b). The scattering intensity for G4 and G5 increased with decreasing q , suggesting that PEGMA-cross-linked star polymer domain is heterogeneously incorporated in poly-(PEGMA)-rich network in high concentration of PEGMA over 50 wt %.

Finally, the removal of polyfluorinated surfactants (perfluorohexanoic acid: PFHxA; perfluorooctanoic acid: PFOA) from water was investigated with G1–G9. The gels (125–625 mg) were mixed with aqueous solutions of PFHxA or PFOA ($[\text{surfactant}]_0 = 10 \text{ ppm}$, 25 mL) for 12 h (Table 2). After the removal of the gels via simple filtration, the aqueous filtrates

**Figure 3.** SAXS profiles of (a) S2 and G2, and (b) S1 and G3–G5 in methanol. [star] = 5.0 mg/mL in methanol.**Table 2. Separation of Polyfluorinated Surfactants from Water^a**

entry	surfactant	gel	gel (mg/mL)	star content (mg/mL)	surfactant ^b (ppm)	removal efficiency ^c (%)
1	PFHxA	G1	5.0	5.0	6.7	33
2	PFHxA	G2	5.0	5.0	2.4	76
3	PFHxA	G3	5.0	4.0	8.4	16
4	PFHxA	G4	5.0	2.3	7.8	22
5	PFHxA	G5	5.0	1.5	9.3	7
6	PFHxA	G6	5.0	4.0	2.8	72
7	PFHxA	G7	5.0	2.3	4.2	58
8	PFHxA	G8	5.0	1.5	5.9	41
9	PFHxA	G8	25	7.5	0.9	91
10	PFHxA	G9	5.0		10	0
11	PFOA	G1	5.0	5.0	2.6	74
12	PFOA	G2	5.0	5.0	0.6	94
13	PFOA	G4	11.2	5.0	2.4	76
14	PFOA	G9	5.0		5.1	50

^aCondition: [G1–G9] = 5, 11.2, and 25 mg/mL (mg gel per mL solution), [surfactant]₀ = 10 ppm. ^bSurfactants in water after filtration: determined by LC-MS/MS. ^cRemoval efficiency of polyfluorinated surfactants from water, calculated by the following equation: $100 \times [1 - ([\text{surfactant}]/[\text{surfactant}]_0)]$.

were analyzed by tandem mass spectroscopy coupled with liquid chromatography (LC-MS/MS) to determine the residue of their polyfluorinated surfactants in their solutions

([surfactant]). The removal efficiency was evaluated with the following equation: $100 \times (1 - [\text{surfactant}]/[\text{surfactant}]_0)$.

Both PFHxA and PFOA were removed with **G1** and **G2** from water more effectively than a conventional gel (**G9**) at 5 mg/mL of their gels (Table 2, entries 1, 2, 10–12, and 14), indicating that fluorinated microgels within the star polymer gels efficiently entrap their surfactants. In particular, **G2** comprising fluorine/amine-functionalized **S2** was quite effective even for relatively hydrophilic PFHxA. This is because **S2** microgels in **G2** can cooperatively bind PFHxA via both the fluororous interaction between the in-core 13FOMA pendants and the surfactant and the acid/base interaction between the in-core amine and the surfactant carboxylic acid.¹⁰

With star polymer gels containing PEGMA network (**G3**–**G8**), the removal efficiency for PFHxA decreased with decreasing star polymer (**S1** or **S2**) content in constant total concentration (5 mg/mL, Table 2, entries 3–8). This indicates that the separation of PFHxA is actually triggered by the encapsulation of the surfactant into star polymer microgels. Owing to the fluororous and acid/base cooperative interaction, **S2**/PEGMA-based gels (**G6**–**G8**) were more effective than **S1**/PEGMA counterparts (**G3**–**G5**). PFHxA was successfully removed with **G8** up to 91% with increasing the gel feed to 25 mg/mL (Table 2, entry 9).

Additionally, in the constant concentration of **S1** (5 mg/mL), **G1** (entry 11), and **G4** (entry 13) showed almost identical removal efficiency for PFOA. This indicates that the star polymer microgels in PEGMA/star-based gels also have the same capacity and efficiency for surfactant separation as those in star–star coupling gels.

In conclusion, star polymer gels were successfully synthesized as water purification materials by free radical coupling or cross-linking of fluorinated (or fluorine/amine-functionalized) microgel star polymers. Conveniently, star polymers were directly linked with the in-core olefins for macroscopic gelation. As a result, the star polymer gels consist of fluorinated star polymers that are sequentially connected at the constant interval of approximately 20 nm. Thus, the gels are regarded as novel precision network macrogels containing fluorinated microgels. Owing to the fluororous microgels, star polymer gels efficiently entrapped polyfluorinated surfactants (PFHxA and PFOA) and afforded the separation from water via simple mixing and filtration. Therefore, this work would open new vistas for various research fields including functional gel materials, water purification technology, and the related environmental engineering.

■ ASSOCIATED CONTENT

● Supporting Information

Experimental details, ¹H NMR spectra, SAXS profiles, and Guinier plots. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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