JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
Article
pubs.acs.org/JACS

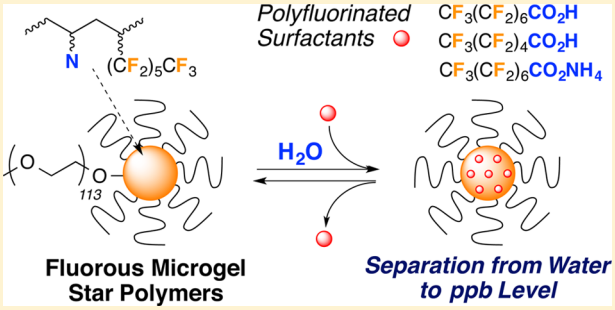
Fluorous Microgel Star Polymers: Selective Recognition and Separation of Polyfluorinated Surfactants and Compounds in Water

Yuta Koda, Takaya Terashima,* and Mitsuo Sawamoto*

Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Katsura, Nishikyo-ku, Kyoto 615-8510, Japan

Supporting Information

ABSTRACT: Immiscible with either hydrophobic or hydrophilic solvents, polyfluorinated compounds (PFCs) are generally "fluorous", some of which have widely been employed as surfactants and water/oil repellents. Given the prevailing concern about the environmental pollution and the biocontamination by PFCs, their efficient removal and recycle from industrial wastewater and products are critically required. This paper demonstrates that fluorous-core star polymers consisting of a polyfluorinated microgel core and hydrophilic PEG-functionalized arms efficiently and selectively capture PFCs in water into the cores by fluorous interaction. For example, with over 10 000 fluorine atoms in the core and approximately 100 hydrophilic arms, the fluorous stars remove perfluorooctanoic acid (PFOA) and related PFCs in water from 10 ppm to as low as a parts per billion (ppb) level, or an over 98% removal. Dually functionalized microgel-core star polymers with perfluorinated alkanes and additional amino (or ammonium) groups cooperatively recognize PFOA or its ammonium salt and, in addition, release the guests upon external stimuli. The "smart" performance shows that the fluorous-core star polymers are promising PFC separation, recovery, and recycle materials for water purification toward sustainable society.



INTRODUCTION

Globular and/or branched macromolecules comprising nanocompartments potentially encapsulate guest molecules and thus act as functional capsules and delivery vessels.[1−5] Within this family, microgel-core star polymers[4−18] are a class of soluble, compartmentalized macromolecules; the star polymers have a cross-linked microgel core that is covered by linear arm chains. These star polymers are readily synthesized in high yield in living radical and any other living polymerizations[19−23] via the linking reaction of linear living polymers or macroinitiators (arms) with a small amount of a bifunctional monomer (linking agent), in which arm polymers are locally cross-linked (core formation) after block copolymerization from the active end. Importantly, despite the cross-linked network in the core, the star polymers are totally soluble in good solvents for the arm chains. The synthesis is straightforward, efficient, versatile, and in one-pot, differing from that for cross-linked micelles and related nanogels.

The microgel core is unique in that it not only is a solubilized gel totally different from an insoluble macro-scale gel but it also provides a nanoscale network space where hundreds and thousands of heteroatoms and/or functional groups can be embedded within the core, to result in a functionalized microgel.[5] These "core-functionalized" star polymers[10−18] can be directly obtained from the arm-linking with a divinyl compound (e.g., ethylene glycol dimethacrylate) in the presence of a functional monomer that typically carries amide,[10] hydroxyl group,[10] phosphine,[11−13] poly(ethylene glycol),[14] quaternary ammonium,[15] and perfluorinated alkane,[16] thus generating densely functionalized compartments to induce active catalysis[11a,12,13,17,18] and selective molecular recognition.[10,15,16]

Owing to the unique phase-separation and/or selective interaction originating from fluorous nature, polyfluorination of (macro)molecules[16,24−32] is now a powerful strategy for easy catalyst separation in catalysis,[26−29] the construction of designed nano-objects,[30] and molecular encapsulation into perfluorinated compartments.[16,30b,31] For instance, we have recently reported that polyfluorinated microgel star polymers with poly(methyl methacrylate) (PMMA) arms provide fluorous compartments soluble in dimethylformamide (DMF) and a variety of common organic solvents.[16] These "fluorous-core" star polymers selectively encapsulate polyfluorinated alkanes (e.g., perfluorooctane C_8F_{18}) into the core and thus solubilize them in DMF, where they are originally insoluble. Equally important, the molecular recognition driven by fluorous interaction is quite selective for PFCs even in the presence of hydrophobic and hydrophilic fluorine compounds (e.g., C_8F_{18} versus trifluorotoluene and trifluoroethanol). These PMMA-armed fluorous stars are, however, of a hydrophobic exterior and thus insoluble in water and effective specifically for water-insoluble PFCs.

Received: September 2, 2014
Published: October 10, 2014

   dx.doi.org/10.1021/ja508818j | J. Am. Chem. Soc. 2014, 136, 15742−15748

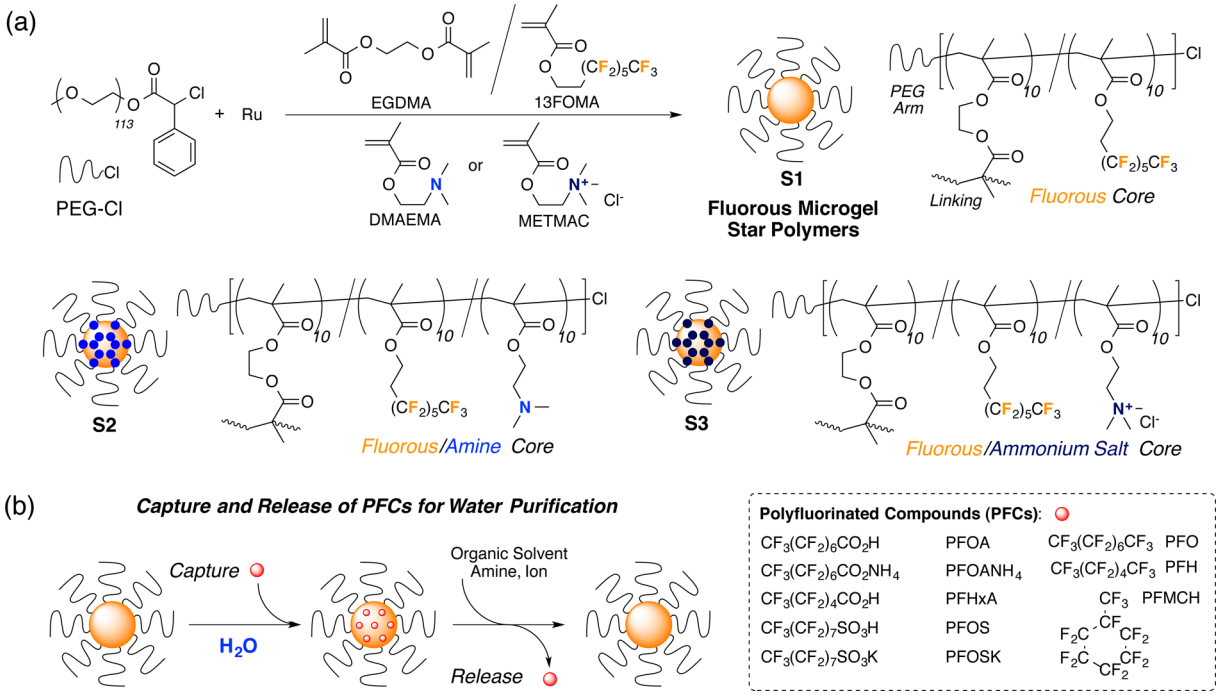


Figure 1. Fluorous microgel star polymers for recognition and separation of polyfluorinated compounds (PFCs) from water. (a) Fluorous microgel star polymers with hydrophilic PEG arms (**S1**–**S3**) were synthesized by the linking reaction of PEG-Cl with ethylene glycol dimethacrylate (EGDMA), perfluoroalkyl methacrylate (13FOMA), and amine or ammonium salt-bearing methacrylate (DMAEMA or METMAC) in ruthenium-catalyzed living radical polymerization. (b) Capture of PFCs with fluorous microgel star polymers in water and stimuli-responsive release of the core-bound PFCs toward water purification.

Polyfluoroalkanes capped with acidic or ionic groups, such as perfluorooctanoic acid (PFOA), are water-soluble but amphiphilic, and thus excellently work as surfactants that have widely been used in industry, typically in the production of fluoropolymers.[25,33a] However, it is now increasingly recognized that very stable and potentially biohazardous PFCs would cause water pollution, unintentional exposure to animal and human bodies, and bioaccumulation,[33] though their toxicity and biohazardous effects have not yet been fully demonstrated. Therefore, the PFC residues in industrial wastewater, however low in concentration, should be removed and preferably recovered. The current PFC removal/recovery processes are mostly established via solid phase extraction with activated carbons and/or ion exchange membranes, whereas they still need improvement in efficiency and selectivity. For example, the former activated carbons are not so effective for less fluorous, i.e., more hydrophilic, perfluoroalkane surfactants [e.g., perfluorohexanoic acid (PFHxA)]. The latter ion exchange membranes in turn easily lose the absorption ability of surfactants by other salts included in wastewater.

Given these issues, in this work we developed fluorinated microgel-core star polymers with hydrophilic arms (**S1**–**S3**) as conceptually new materials that selectively recognize and separate PFCs in water (Figure 1). Poly(ethylene glycol) methyl ether (PEG) was introduced into arm units for better solubility in aqueous media. The microgel cores were designed for the efficient recognition of PFCs: i.e., **S1** carries a perfluoroalkane-functionalized core to capture PFCs via fluorous interaction, whereas **S2** and **S3** have dually functionalized cores (**S2**, perfluoroalkane/amine, fluorous and acid–base interaction; **S3**, perfluoroalkane/ammonium, fluorous and ionic interaction) to more strongly bind fluorous and amphiphilic PFCs bearing acidic or ionic groups, respectively, via cooperative interactions. In addition, **S1**–**S3** allowed the stimuli-responsive release of core-bound PFCs, where their dually functionalized cores released two kinds of PFCs stepwise one by one upon sequential change of external solvents, thus opening a way toward the reuse and separable recovery of PFCs.

RESULTS AND DISCUSSION

Synthesis of Fluorous-Core Star Polymers. Star polymers **S1**–**S3** were synthesized by the linking reaction of a chlorine-capped PEG macroinitiator (PEG-Cl: M_n = 4900; M_w/M_n = 1.03) with ethylene glycol dimethacrylate (EGDMA), functional methacrylates, and a ruthenium catalytic system [RuCp*Cl[P(*m*-tol)$_3$]$_2$ (Cp*, pentamethylcyclopentadienyl; P(*m*-Tol)$_3$, tri(*m*-tolyl)phosphine)/4-(dimethylamino)-1-butanol (4-DMAB)][15,34] in ethanol at 40 °C. The functional methacrylates include 1*H*,1*H*,2*H*,2*H*-perfluorooctyl methacrylate (13FOMA),[16] 2-(dimethylamino)ethyl methacrylate (DMAEMA), and [2-(methacryloyloxy)ethyl]-trimethylammonium chloride (METMAC) for core functionalization: 13FOMA for **S1**; 13FOMA and DMAEMA for **S2**; 13FOMA and METMAC for **S3** (Figure 1).

The feed ratio of monomers relative to the initiator (arm) was all set to 10, defined as l = [EGDMA]$_0$/[PEG-Cl]$_0$; m = [13FOMA]$_0$/[PEG-Cl]$_0$; n = [DMAEMA]$_0$/[PEG-Cl]$_0$] or [METMAC]$_0$/[PEG-Cl]$_0$. The core-forming reactions, i.e., the copolymerization of the linking agent and their functional monomers, smoothly and homogeneously proceeded up to 78 to 100% conversion each, even for the combinations of components with completely different polarity and properties (e.g., 13FOMA and METMAC for **S3**). As a result, the star polymers **S1**–**S3** were invariably obtained in high yield (>80%) with a high molecular weight and a narrow molecular weight

dx.doi.org/10.1021/ja508818j | J. Am. Chem. Soc. 2014, 136, 15742–15748

distribution [M_w/M_n = 1.1−1.5; by size-exclusion chromatography (SEC) in DMF, Figure 2a, Table 1, see Supporting Information Figure S1]. Importantly, the simultaneous consumption of 13FOMA, DMAEMA (or METMAC), and EGDMA during arm-linking reaction (time−conversion curves, Supporting Information Figure S1) supports the random distribution of perfluorinated pendants and amine or quaternary ammonium groups within the microgel cores of **S2** and **S3**. Similarly, amine-functionalized star (**S4**, core function: DMAEMA alone) and nonfunctionalized star (**S5**) polymers were also prepared in high yield as control host polymers for the encapsulation and separation of perfluorinated guests in water (Supporting Information Figure S1, Table 1).

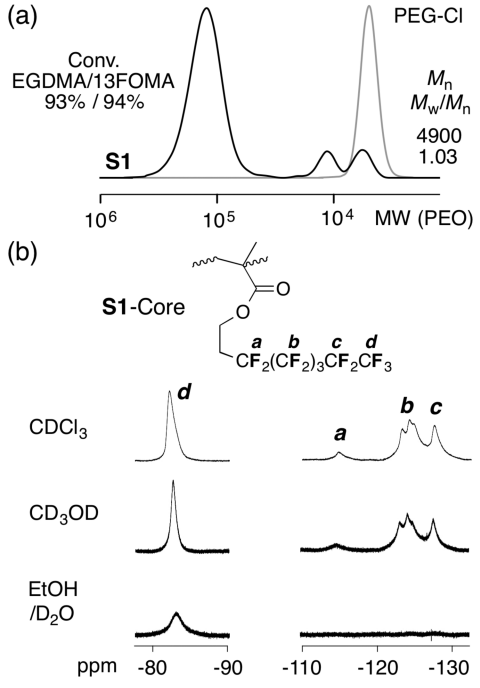


Figure 2. (a) SEC curves of **S1** (black line) obtained from the linking reaction of PEG-Cl (gray line) with EGDMA and 13FOMA: $[EGDMA]_0/[13FOMA]_0/[PEG\text{-}Cl]_0/[RuCp^*Cl(P(m\text{-}Tol)_3)_2]_0/[4\text{-}DMAB]_0$ = 100/100/10/2.0/100 mM in ethanol at 40 °C. (b) ^{19}F NMR spectra of **S1** in $CDCl_3$, CD_3OD, and EtOH/D_2O (1/1, v/v) at 30 °C.

After the purification by dialysis against methanol, these star polymers were characterized by proton and fluorine nuclear magnetic resonance (^1H, ^{19}F NMR), multiangle laser light scattering coupled with SEC (SEC-MALLS), and dynamic light scattering (DLS) (Table 1). Determined by SEC-MALLS, **S1**−**S3** had absolute weight-average molecular weight (M_w) of 939 000−1 960 000, arm number (N_{arm}) of 77−155 arm/core, and hydrodynamic radius (R_H) of 24−37 nm. Importantly, large numbers of fluorine atoms (N_F), trifluoromethyl groups (N_{CF3}), and nitrogen atoms (N_N) can be incorporated directly into the cores: e.g., **S1** had N_F of 10 570 and N_{CF3} of 810, where $N_F = N_{arm} \times (13m \times conv_{13FOMA}/100)$; $N_{CF3} = N_{arm} \times (m \times conv_{13FOMA}/100)$; and $N_N = N_{arm} \times [n \times (conv_{DMAEMA}$ or $conv_{METMAC})/100]$.[15,16]

The fluorous properties of the perfluorinated pendants in **S1**−**S3** were analyzed by ^{19}F NMR. In $CDCl_3$ and MeOH-d_4 at 30 °C, **S1**−**S3** clearly exhibited ^{19}F signals originating from the pendent perfluoroalkyl groups [$-(CF_2)_5CF_3$] of the in-core 13FOMA units (Figure 2b, peaks *a*−*d*; Supporting Information Figure S2). In the presence of water (in EtOH/D_2O, 1/1 v/v), however, the signal of the tip CF_3 (*d*; −83 ppm) clearly broadened and the other CF_2 signals (*a*−*c*) disappeared (Figure 2b). Therefore, while the PEG-armed **S1** itself was fully soluble in the aqueous solvent, the fluorous core shrinks and the pendent perfluoalkyl moieties therein are forced to tightly aggregate and thus to hardly move, effectively providing a fluorous compartment. Additionally, the proton signals of the in-core amine and quaternary ammonium salt in **S2** and **S3** were not observed even in D_2O by ^1H NMR, which indicates that their functional groups are placed within their microgel cores.

Encapsulation of Perfluorinated Compounds in Water. The capture of perfluorooctanoic acid (PFOA), a typical polyfluorinated surfactant abundantly employed in industry,[33] was first examined with **S1** in aqueous media (Figure 3). PFOA was mixed with **S1** in EtOH/D_2O (1/1, v/v) at 30 °C for 12 h ([PFOA] = 10 mM; [**S1**] = 25 mg/mL; [core-CF_3] = 22 mM), and the homogeneous mixture was analyzed by ^{19}F NMR. The ^{19}F signal of the CF_3 on PFOA (*a*)

Table 1. Characterization of Star Polymers[a]

code	core functionality[a]	time (h)	conversion EGDMA/13FOMA/R_NMA (%)[b]	yield (%)[c]	$M_{w,star}$ (SEC)[d]	$M_w/M_{n,star}$ (SEC)[d]	$M_{w,star}$ (MALLS)[e]	N_{arm}[f]	N_F[g]	N_{CF3}[g]	N_N[g]	R_H (nm)[h]
S1	13FOMA	46	93/94/-	85	124000	1.13	939000	87	10570	810	-	24
S2	13FOMA/DMAEMA	23	98/100/78	77	103800	1.21	957000	77	10000	770	600	26
S3	13FOMA/METMAC	20	98/94/85	82	133300	1.51	1960000	155	18870	1450	1310	37
S4	DMAEMA	21	98/-/77	85	79700	1.21	335000	41	-	-	320	19
S5	-	21	100/-/-	82	82500	1.10	324000	46	-	-	-	21

[a]Star polymers (**S1**−**S5**) are synthesized by the ruthenium-mediated linking reaction of PEG-Cl with ethylene glycol dimethacrylate (EGDMA), 1*H*,1*H*,2*H*,2*H*-perfluorooctyl methacrtlate (13FOMA), and 2-(dimethylamino)ethyl methacrylate (DMAEMA) or [2-(methacryloyloxy)ethyl]-trimethylammonium chloride (METMAC). **S1**, **S2**, **S4**, **S5**: $[EGDMA]_0/[13FOMA]_0/[DMAEMA]_0/[PEG\text{-}Cl]_0/[RuCp^*Cl(P(m\text{-}Tol)_3)_2]_0/[4\text{-}DMAB]_0$ = 100/100 (**S1**, **S2**) or 0 (**S4**, **S5**)/100 (**S2**, **S4**) or 0 (**S1**, **S5**)/10/2.0/100 mM in ethanol at 40 °C. **S3**: $[EGDMA]_0/[13FOMA]_0/[METMAC]_0/[PEG\text{-}Cl]_0/[RuCp^*Cl(P(m\text{-}Tol)_3)_2]_0/[4\text{-}DMAB]_0$ = 150/150/150/15/2.0/100 mM in ethanol at 40 °C. [b]Monomer conversion: determined by ^1H NMR with tetralin as an internal standard. [c]Star polymer yield: estimated from the SEC curve area ratio of star polymers to products. [d]Weight-average molecular weight ($M_{w,star}$) and molecular weight distribution ($M_w/M_{n,star}$) of star polymers: determined by SEC in DMF (10 mM LiBr). [e]Absolute weight-average molecular weight of star polymers: determined by SEC-MALLS in DMF (10 mM LiBr). [f]Arm numbers: [(weight fraction of arm) × $M_{w,star}$ (MALLS)]/$M_{w,arm}$; $M_{w,arm}$ = 5050. [g]The number of fluorine atoms (N_F), CF_3 groups (N_{CF3}), and nitrogen atoms (N_N) per a star polymer: $N_F = N_{arm} \times (13m \times conv_{13FOMA}/100)$; $N_{CF3} = N_{arm} \times (m \times conv_{13FOMA}/100)$; $N_N = N_{arm} \times [n \times (conv_{DMAEMA}$ or $conv_{METMAC})/100]$. [h]Hydrodynamic radius: determined by dynamic light scattering in DMF ([polymer]$_0$ = 2.5 mg/mL).

dx.doi.org/10.1021/ja508818j | J. Am. Chem. Soc. 2014, 136, 15742−15748

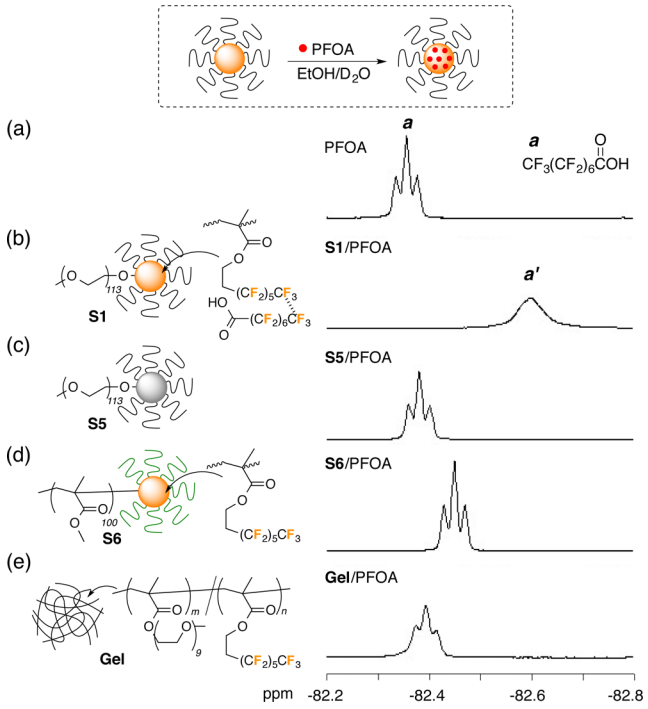


Figure 3. Capture of PFOA with host polymers in water. ^{19}F NMR spectra of (a) PFOA alone and PFOA in the presence of various host polymers (b) **S1**, (c) **S5**, (d) **S6**, (e) **Gel**): $[host]_0$ = 25 mg/mL; $[PFOA]_0$ = 10 mM in EtOH/D_2O (1/1, v/v) at 30 °C.

turned broad and shifted to upfield [PFOA alone: −82.4 ppm (Figure 3a); PFOA/**S1** (*a*′): −82.6 ppm (Figure 3b)], indicating that it was recognized and captured by the perfluorinated core.[16] Such recognition was actually achieved immediately after the mixing of **S1** and PFOA (at least less than 10 min). The fluorous recognition was further confirmed by the absence of such spectral changes in PFOA with a non-fluorinated star polymer (**S5**: $M_{w,star}$ = 324 000; M_w/M_n = 1.10; N_{arm} = 46); the CF_3 signal of PFOA with **S5** was almost identical to that of PFOA alone (Figure 3c). Similarly, a fluorous-core star polymer with PMMA arms (**S6**) [$M_{w,star}$ = 1 190 000; M_w/M_n = 1.57; N_{arm} = 52; N_F = 5900; N_{CF3} = 450; M_n (arm) = 13 000], i.e., a hydrophobic arm version of **S1**,[16] was ineffective for PFOA recognition in water, where the host was hardly soluble (Figure 3d).

The observed recognition (encapsulation) of PFOA is most likely caused by fluorous interaction within the densely fluorine-enriched microgel nanospace and not by a simple cavity or gel-network entrapment with the perfluoroalkyl pendent groups of 13FOMA units. As seen in Figure 3e, PFOA in water hardly interacted with a conventional macroscopic gel comprising short PEG chains and perfluorooctyl pendants (**Gel**; no ^{19}F-NMR signal changes), synthesized by the free radical copolymerization of 13FOMA, EGDMA, and poly(ethylene glycol) methyl ether methacrylate [PEGMA: CH_2═C (CH_3)$MeCO_2(CH_2CH_2O)_nCH_3$; n = 9; M_n = 500] ($[PEGMA]_0/[13FOMA]_0/[EGDMA]_0$ = 90/10/10 mM) (see Supporting Information). In water, either with or without PFOA, the fine-powdered gel indeed swelled and was dispersed but did not impose any spectral changes on the guest. This is probably because the polyfluorinated pendants were randomly placed in the gel network without forming fluorine-condensed micro domains. Thus, the key for the efficient PFOA recognition is to create a highly fluorinated and totally solubilized nanoscopic gel space in water by condensing perfluoroalkyl groups into the microgel cores of a star polymer. Additionally, **S1** selectively captures PFOA even in the presence of octanoic acid (OA), a nonfluorinated but hydrophobic carboxylic acid that might potentially competes with it in penetrating into the microgel core (Supporting Information Figure S3).

Recognition of other perfluorinated compounds was then investigated with **S1** in water. **S1** efficiently interacted not only with PFOA but also with various water-soluble polyfluorinated surfactants including ammonium perfluorooctanoate ($PFOANH_4$), perfluorohexanoic acid (PFHxA), perfluorooctanesulfonic acid (PFOS), and its potassium salt (PFOSK), as similarly confirmed by the broad ^{19}F signals of their guests CF_3 in the presence of **S1** in ^{19}F NMR spectra (*a*′, *b*′, *c*′, Figure 4a–c; *a*′, Figure 5b).

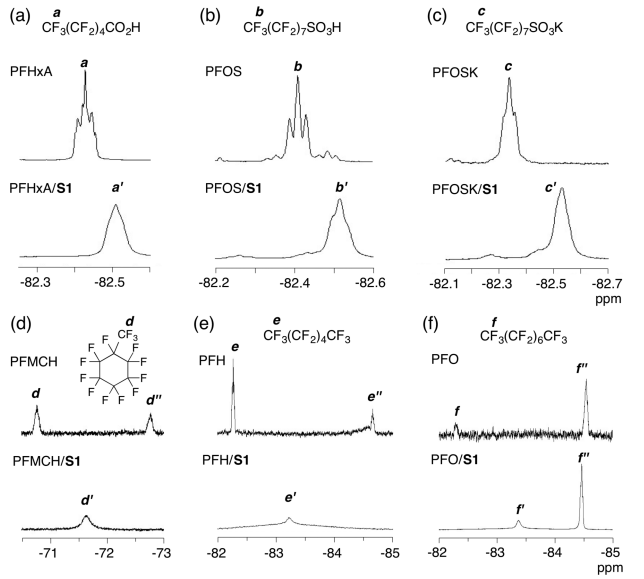


Figure 4. ^{19}F NMR spectra (470 MHz) of perfluorinated guests ((a) PFHxA; (b) PFOS; (c) PFOSK; (d) PFMCH; (e) PFH; (f) PFO) in the presence of **S1**: $[S1]_0$ = 25 mg/mL, $[guest]_0$ = 10 (a–c), 100 (d–f) mM in EtOH/D_2O (1/1, v/v) at 30 °C.

In contrast to such perfluorinated surfactants with acidic or ionic groups, perfluoroalkanes [perfluorooctane (PFO), perfluorohexane (PFH), and perfluoromethylcyclohexane (PFMCH)] are hardly soluble in water. As a result, these perfluorinated guests respectively showed the two signals of homogeneously soluble molecules (*d*, *e*, *f*) and aggregated and/or insoluble (dispersed) counterparts (*d*″, *e*″, *f*″) in EtOH/D_2O (1/1, v/v) (Figure 4d–f). However, even in relatively high concentration ([guest] = 100 mM), a fluorous star **S1** efficiently solubilized and/or interacted with the guests (Figure 4d–f, see peaks *d*′, *e*′, *f*′). In contrast to PFH, PFO still showed the aggregated form (peak *f*″) in the presence of **S1** probably owing to the less affinity of the fluorinated core to the guest. The maximum encapsulation capacity of **S1** for PFMCH was determined to 5600 molecules/star (or up to 150 mM) by ^{19}F NMR titration in EtOH/D_2O (1/1, v/v) (Supporting Information Figure S4). The efficient encapsulation of PFMCH within the perfluorinated core was also confirmed by nuclear Overhauser effect (NOE) difference spectroscopy.

dx.doi.org/10.1021/ja508818j | J. Am. Chem. Soc. 2014, 136, 15742–15748

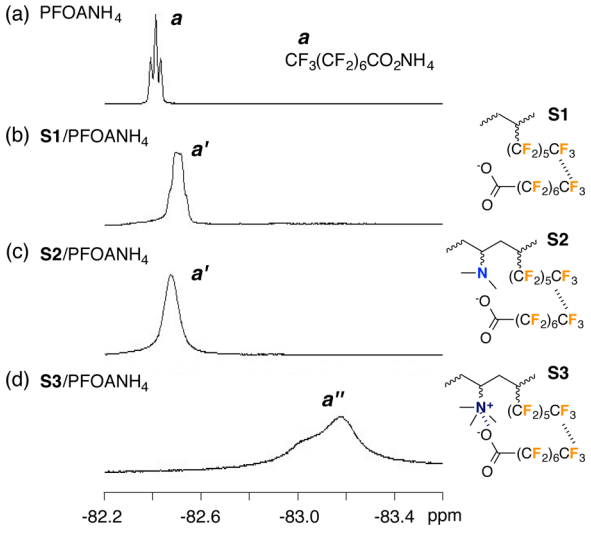


Figure 5. Cooperative recognition of $PFOANH_4$ with **S3** in water. ^{19}F NMR spectra of (a) $PFOANH_4$ alone and $PFOANH_4$ in the presence of host star polymers ((b) **S1**, (c) **S2**, (d) **S3**): $[host]_0$ = 25 mg/mL; $[PFOANH_4]_0$ = 10 mM in $EtOH/D_2O$ (1/1, v/v) at 30 °C.

Cooperative interaction between a host and a guest via multiple functional groups would enhance the efficiency and selectivity in molecular recognition. Thus, recognition of water-soluble polyfluorinated surfactants was examined with dually core-functionalized star polymers (**S2**, **S3**) in water (Figure 5). As expected, a perfluoroalkane/ammonium dually functionalized star polymer (**S3**: N_F = 18 870; N_{CF3} = 1450; N_N = 1310) recognized $PFOANH_4$ in $EtOH/D_2O$ (1/1, v/v) more efficiently than **S1** (Figure 4b,d). Typically, the CF_3 peak of $PFOANH_4$ broadened and shifted to upfield more extensively with **S3** than with **S1** [−83.2 (*b″*) versus −82.5 (*b′*) ppm], indicating a more efficient cooperative capture through the fluorous interaction by perfluoroalkanes and the salt formation ($-N^+Me_3O^-COR$) between the guest ($RCOO^-$) and the host ($-N^+Me_3$). Such a cooperative binding is dependent on the compatibility of the functional groups in a host and a guest. For instance, in recognition of the same ammonium guest, a perfluoroalkane/amine dually core-functionalized star (**S2**: M_w = 957 000; N_{arm} = 77; N_F = 10 000; N_{CF3} = 770; N_N = 600) was less effective than **S3** and more or less equivalent to **S1** (all the three hosts with similar fluorous functionality N_F and N_{CF3}), because of no interaction between the in-core amine and the ammonium guest (Figure 5c). Alternatively, **S2** captured PFOA more efficiently than **S1** by the cooperative recognition through fluorous and acid−base interaction: the CF_3 peak of PFOA broadened and shifted to upfield more extensively with **S2** than with **S1** (Supporting Information Figure S5).

Selective and Stepwise Release of Guests from Star Polymers. As a result of the cooperative interaction, **S2** and **S3** further realized a selective and stepwise release of multiple polyfluorinated guests from the cores where these guests had been simultaneously encapsulated (Figure 6).

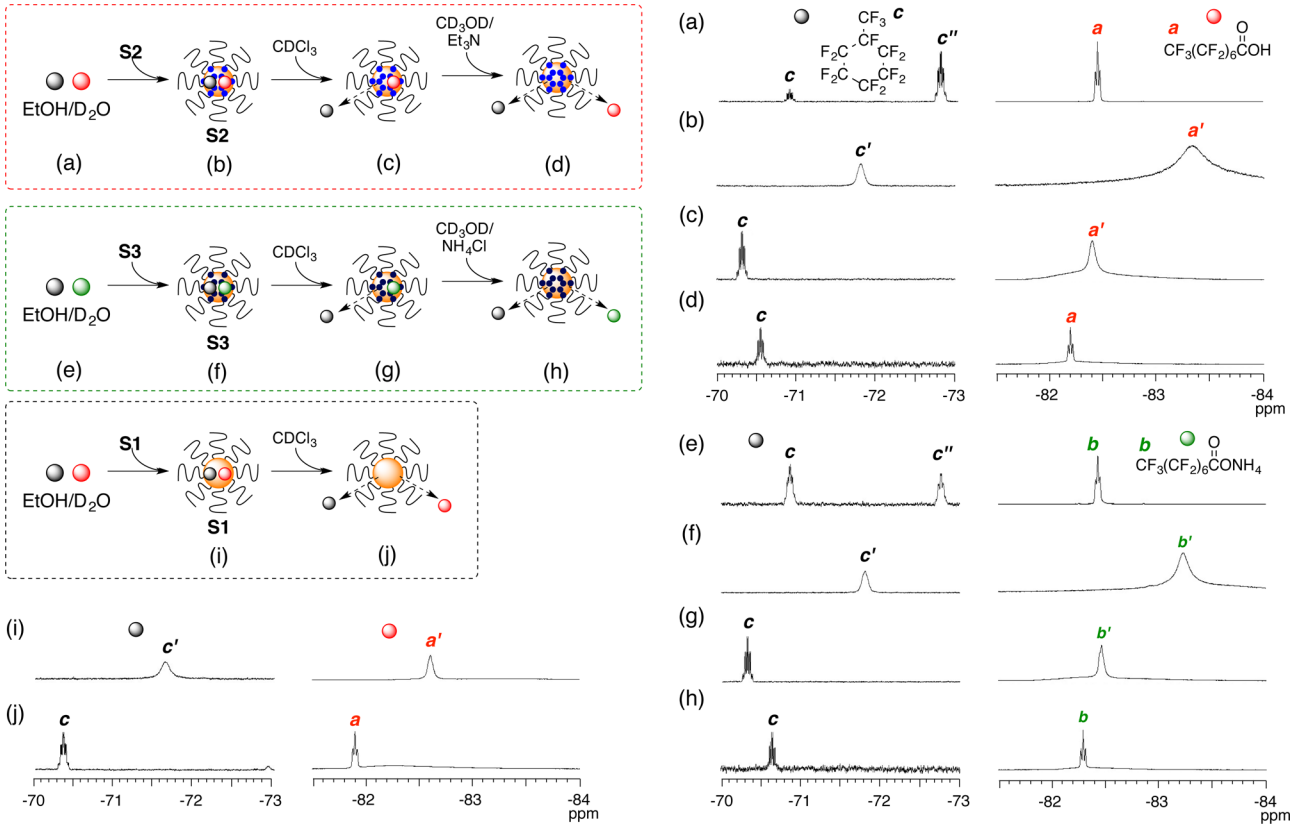


Figure 6. ^{19}F NMR spectra of perfluorinated compounds released from star polymers ((a−d) **S2**, (e−h) **S3**, (i and j) **S1**) in water at 30 °C. **S2** encapsulating PFMCH and PFOA in $EtOH/D_2O$ (1/1, v/v) (b) initially releases the core-bound PFMCH via $CDCl_3$ addition (c) and subsequently does the PFOA via an Et_3N/CD_3OD solution (d). Similarly to **S2**, **S3** containing PFMCH and $PFOANH_4$ (f) first releases the core-bound PFMCH via $CDCl_3$ addition (g) and subsequently does the $PFOANH_4$ via a NH_4Cl/CD_3OD solution (h). In contrast, **S1** carrying both PFMCH and PFOA in $EtOH/D_2O$ (1/1, v/v) (i) simultaneously releases both of the guests via $CDCl_3$ addition (j).

dx.doi.org/10.1021/ja508818j | J. Am. Chem. Soc. 2014, 136, 15742−15748

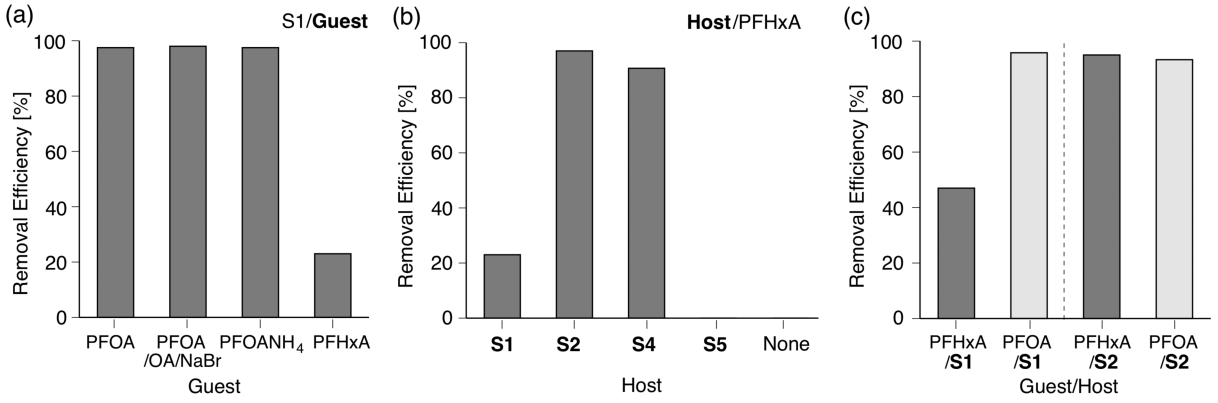


Figure 7. Separation of perfluorinated surfactants from water with fluorinated microgel star polymers. (a) Removal of PFOA, PFOA [in the presence of octanoic acid (OA: ~10 ppm) and NaBr (~10 ppm)], $PFOANH_4$, and PFHxA (~10 ppm) from water with **S1**: $[host]_0$ = 25 mg/mL; $[guest]_0$ = 8.7 (PFOA), 10 ($PFOANH_4$), 8.2 (PFHxA) ppm in water. (b) Effects of host polymers (**S1**, **S2**, **S4**, **S5**, none) on the separation of PFHxA from water: $[host]_0$ = 25 mg/mL; $[PFHxA]_0$ = 8.2 ppm in water. (c) Concurrent removal of two guests (PFHxA, PFOA) with **S1** or **S2** from water: $[host]_0$ = 25 mg/mL; $[guest]_0$ = 10 (PFHxA), 12 (PFOA) ppm in water.

As shown in Figure 6a,b, **S2** simultaneously encapsulated PFMCH and PFOA into the core in EtOH/D_2O (1/1, v/v) ([**S2**] = 25 mg/mL; [PFMCH]/[PFOA] = 102/10 mM). On addition of $CDCl_3$ (5 mL), this aqueous solution (5 mL) turned phase-separated, with an upper aqueous layer (D_2O/EtOH) and a lower organic layer ($CDCl_3$/EtOH). Most of the **S2**-guests complexes moved to the organic phase where only PFMCH was released from the core owing to the weakened fluorous interaction in $CDCl_3$, as confirmed by the appearance of CF_3 multiplets at −70.3 ppm (*c*, Figure 5c).[16] Note that PFOA still remained in the core owing to the acid−base interaction enhanced in the less polar phase, in which the guest's CF_3 signal (*a*′; −82.4 ppm) remained as broad as in the aqueous solution. Subsequent addition of an Et_3N/CD_3OD solution (652 mM) into the $CDCl_3$/EtOH layer induced the secondary release of PFOA (*a*; −82.2 ppm, triplet) where its acid−base interaction with the in-core amine was now overridden by the externally added amine in excess (Figure 6d).

Similarly, **S3** with PFMCH and $PFOANH_4$ in EtOH/D_2O first released PFMCH alone upon $CDCl_3$ addition and subsequently did $PFOANH_4$ upon NH_4Cl/CD_3OD addition (166 mM) via ion exchange (Figure 6e−h). On the contrary, **S1** simultaneously released PFMCH and PFOA from the core by an initial $CDCl_3$ treatment, because the encapsulation is just driven by fluorous interaction (Figure 6i,j).

Separation of Polyfluorinated Surfactants from Water. Finally, the removal of polyfluorinated surfactants (PFOA, $PFOANH_4$, PFHxA) from water was investigated with star polymers (fluorinated core, **S1**−**S3**; amine-functionalized core, **S4**; nonfunctionalized core, **S5**, Figure 7, Supporting Information Table S1). Star polymers were mixed with the surfactants in water for 12 h ($[star]_0$ = 25 mg/mL, $[surfactant]_0$ = ~10 000 ppb) and the aqueous mixture (1 mL) was then dialyzed against water (99 mL) for 12 h. Here, free surfactants pass through the dialysis tube (molecular weight cutoff: 1000) to spread in the whole water, whereas the surfactants-bearing star polymers are placed in the tube. Thus, the outer dialysis water was analyzed by tandem mass spectroscopy coupled with liquid chromatography (LC−MS/MS) to determine the concentration of free polyfluorinated surfactants in water ([surfactant]). The removal efficiency of surfactants was estimated from the following equation: $100[1 - ([surfactant]/0.01 \times [surfactant]_0)]$.

PFOA and $PFOANH_4$ were efficiently separated from water with **S1** up to 98% via fluorous interaction (Figure 7a). The efficiency was close to that with dually functionalized star polymers (**S2**: fluorous/amine; **S3**: fluorous/ammonium cation), indicating the sufficient fluorous interaction of **S1** to guests (Supporting Information Table S1). On the contrary, cooperative recognition was remarkably effective for PFHxA, a less fluorous guest (Figure 7b). The removal efficiency with **S2** reached over 97% much better than that with **S1** (~23%) or **S4** carrying an amine-functionalized core (~90%). Separation of polyfluorinated surfactants (PFOA, $PFOANH_4$, PFHxA) was also effectively achieved with **S1**−**S3** (removal efficiency >98%) even in the presence of hydrophobic and other ionic compounds (OA, hexanoic acid, NaBr) (Figure 7a, Supporting Information Table S1). The successful removal of PFHxA and the related surfactants in the presence of salts is particularly important for **S1**−**S3** as novel and promising water purification materials because the removal under such conditions is typically difficult with conventional solid absorbent.

S2 was further effective for the concurrent removal of both PFOA and PFHxA from water (PFOA, 93%; PFHxA, 95%, Figure 7c), while **S1** uniquely induced the selective separation of PFOA over PFHxA from water (PFOA, 96%; PFHxA, 47%) owing to the preferential affinity to PFOA; **S1** serves as a selective scavenger of a surfactant from water. Therefore, the tuning of microgel cores in star polymers realized efficient and/or selective removal of polyfluorinated surfactants from water on demand.

■ CONCLUSION

In summary, core-fluorinated star polymers efficiently and selectively recognized PFCs in water to be effective for the separation of PFCs from water. The key is to design microgel cores of star polymers, directed to condensation of a perfluorinated alkane for efficient fluorous recognition; dual-functionalization with a perfluorinated alkane; and an amine or an ammonium salt for cooperative recognition (fluorous/acid−base, fluorous/ionic). Their star polymers further realized the selective and stepwise release of encapsulated PFCs from the cores via external stimuli, which could be thus reused for water purification from perfluorinated surfactants (PFOA, $PFOANH_4$, PFHxA). Further tuning of arm polymers and core functionality in fluorinated microgel star polymers would

dx.doi.org/10.1021/ja508818j | J. Am. Chem. Soc. 2014, 136, 15742−15748

not only provide robust films and swelled macroscopic gels with the fluorous microgel domain for practical water purification but also afford biocompatible nanocapsules for the *in vivo* separation of toxic and carcinogenic polyfluorinated surfactants from human blood and/or bodies. Thus, fluorous star polymers would be one of the best candidates to solve environmental problems such as water pollution and bioaccumulations by PFCs to provide us safe and sustainable society.

■ ASSOCIATED CONTENT

Supporting Information

Synthesis and characterization of polymers, the encapsulation, release, and separation of PFCs, experimental details, SEC curves, and ^{1}H and ^{19}F NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Authors

terashima@living.polym.kyoto-u.ac.jp
sawamoto@star.polym.kyoto-u.ac.jp

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This research was supported by the Ministry of Education, Science, Sports and Culture through a Grant-in-Aid for Scientific Research (A: 24245026) and Young Scientist (B: 20750091; B: 24750104), for which T.T. is grateful. Y.K. is grateful to the Japan Society for the Promotion of Sciences (JSPS) for a Grant-in-Aid for JSPS Research Fellows (DC1:24-6140). We also thank Mr. Yuuji Tanaka (Daikin Industries, Ltd.) for LC−MS/MS analysis and Daikin Industries, Ltd. for kind supply of PFHxA.

■ REFERENCES

(1) (a) Nishiyama, N.; Kataoka, K. *Adv. Polym. Sci.* **2006**, *193*, 67−101. (b) van Dongen, S. F. M.; de Hoog, H.-P. M.; Peters, R. J. R. W.; Nallani, M.; Nolte, R. J. M.; van Hest, J. C. M. *Chem. Rev.* **2009**, *109*, 6212−6274. (c) Kabanov, A. V.; Vinogradov, S. V. *Angew. Chem., Int. Ed.* **2009**, *48*, 5418−5429. (d) Elsabahy, M.; Wooley, K. L. *J. Polym. Sci., Part A: Polym. Chem.* **2012**, *50*, 1869−1880. (e) Walther, A.; Müller, A. H. E. *Chem. Rev.* **2013**, *113*, 5019−5261.

(2) Jansen, J. F. G. A.; de Brabander-van den Berg, E. M. M.; Meijer, E. W. *Science* **1994**, *266*, 1226−1229.

(3) Cooper, A. I.; Londono, J. D.; Wignall, G.; McClain, J. B.; Samulski, E. T.; Lin, J. S.; Dobrynin, A.; Rubinstein, M.; Burke, A. L. C.; Fréchet, J. M. J.; DeSimone, J. M. *Nature* **1997**, *389*, 368−371.

(4) (a) Blencowe, A.; Tan, J. F.; Goh, T. K.; Qiao, G. G. *Polymer* **2009**, *50*, 5−32. (b) Gao, H.; Matyjaszewski, K. *Prog. Polym. Sci.* **2009**, *34*, 317−350. (c) Gao, H. *Macromol. Rapid Commun.* **2012**, *33*, 722−734.

(5) (a) Terashima, T.; Sawamoto, M. *ACS Symp. Ser.* **2012**, *1101*, 65−80. (b) Terashima, T. *Kobunshi Ronbunshu* **2013**, *70*, 432−448. (c) Terashima, T. *Polym. J.* **2014**, *46*, 664−673.

(6) Baek, K.-Y.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **2001**, *34*, 215−221.

(7) Gao, H.; Matyjaszewski, K. *Macromolecules* **2006**, *39*, 7216−7223.

(8) Terashima, T.; Motokawa, R.; Koizumi, S.; Sawamoto, M.; Kamigaito, M.; Ando, T.; Hashimoto, T. *Macromolecules* **2010**, *43*, 8218−8232.

(9) Shibata, T.; Kanaoka, S.; Aoshima, S. *J. Am. Chem. Soc.* **2006**, *128*, 7497−7504.

(10) (a) Baek, K.-Y.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **2001**, *34*, 7629−7635. (b) Baek, K.-Y.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **2002**, *35*, 1493−1498.

(11) (a) Terashima, T.; Kamigaito, M.; Baek, K.-Y.; Ando, T.; Sawamoto, M. *J. Am. Chem. Soc.* **2003**, *125*, 5288−5289. (b) Terashima, T.; Ouchi, M.; Ando, T.; Kamigaito, M.; Sawamoto, M. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 4966−4980. (c) Terashima, T.; Ouchi, M.; Ando, T.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **2007**, *40*, 3581−3588.

(12) (a) Terashima, T.; Ouchi, M.; Ando, T.; Sawamoto, M. *J. Polym. Sci., Part A: Polym. Chem.* **2010**, *48*, 373−379. (b) Terashima, T.; Ouchi, M.; Ando, T.; Sawamoto, M. *J. Polym. Sci., Part A: Polym. Chem.* **2011**, *49*, 1061−1069. (c) Terashima, T.; Ouchi, M.; Ando, T.; Sawamoto, M. *Polym. J.* **2011**, *43*, 770−777.

(13) (a) Terashima, T.; Nomura, A.; Ito, M.; Ouchi, M.; Sawamoto, M. *Angew. Chem., Int. Ed.* **2011**, *50*, 7892−7895. (b) Terashima, T.; Nomura, A.; Ouchi, M.; Sawamoto, M. *Macromol. Rapid Commun.* **2012**, *33*, 833−841.

(14) Terashima, T.; Nishioka, S.; Koda, Y.; Takenaka, M.; Sawamoto, M. *J. Am. Chem. Soc.* **2014**, *136*, 10254−10257.

(15) Fukae, K.; Terashima, T.; Sawamoto, M. *Macromolecules* **2012**, *45*, 3377−3386.

(16) Koda, Y.; Terashima, T.; Nomura, A.; Ouchi, M.; Sawamoto, M. *Macromolecules* **2011**, *44*, 4574−4578.

(17) (a) Helms, B.; Guillaudeu, S. J.; Xie, Y.; McMurdo, M.; Hawker, C. J.; Fréchet, J. M. J. *Angew. Chem., Int. Ed.* **2005**, *44*, 6384−6387. (b) Chi, Y.; Scroggins, S. T.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **2008**, *130*, 6322−6323.

(18) Kanaoka, S.; Yagi, N.; Fukuyama, Y.; Aoshima, S.; Tsunoyama, H.; Tsukuda, T.; Sakurai, H. *J. Am. Chem. Soc.* **2007**, *129*, 12060−12061.

(19) (a) Ouchi, M.; Terashima, T.; Sawamoto, M. *Acc. Chem. Res.* **2008**, *41*, 1120−1132. (b) Ouchi, M.; Terashima, T.; Sawamoto, M. *Chem. Rev.* **2009**, *109*, 4963−5050.

(20) (a) Tsarevsky, N.; Matyjaszewski, K. *Chem. Rev.* **2007**, *107*, 2270−2299. (b) Matyjaszewski, K.; Tsarevsky, N. V. *Nat. Chem.* **2009**, *1*, 276−288. (c) Matyjaszewski, K. *Macromolecules* **2012**, *45*, 4015−4039. (d) Matyjaszewski, K.; Tsarevsky, N. V. *J. Am. Chem. Soc.* **2014**, *136*, 6513−6533.

(21) Hawker, C. J.; Bosman, A. W.; Harth, E. *Chem. Rev.* **2001**, *101*, 3661−3688.

(22) Aoshima, S.; Kanaoka, S. *Chem. Rev.* **2009**, *109*, 5245−5287.

(23) Hsieh, H. L.; Quirk, R. P. *Anionic Polymerization: Principles and Practical Applications*; Marcel Dekker, Inc.: New York, 1996.

(24) (a) Riess, J. G. *Tetrahedron* **2002**, *58*, 4113−4131. (b) Kraff, M. P. *Adv. Drug Delivery Rev.* **2007**, *47*, 209−228. (c) Kraff, M. P.; Riess, J. G. *Chem. Rev.* **2009**, *109*, 1714−1792.

(25) Bruno, A. *Macromolecules* **2010**, *43*, 10163−10184.

(26) Horváth, I. T.; Rábai, J. *Science* **1994**, *266*, 72−75.

(27) Studer, A.; Hadida, S.; Ferritto, R.; Kim, S.-Y.; Jeger, P.; Wipf, P.; Curran, D. P. *Science* **1997**, *275*, 823−826.

(28) Yoshida, J.; Itami, K. *Chem. Rev.* **2002**, *102*, 3693−3716.

(29) Curran, D. P.; Sinha, M. K.; Zhang, K.; Sabatini, J. J.; Cho, D.-H. *Nat. Chem.* **2012**, *4*, 124−129.

(30) (a) Li, Z.; Kesselman, E.; Talmon, Y.; Hillmyer, M. A.; Lodge, T. P. *Science* **2004**, *306*, 98−101. (b) Lodge, T. P.; Rasdai, A.; Li, Z.; Hillmyer, M. A. *J. Am. Chem. Soc.* **2005**, *127*, 17608−17609.

(31) Sato, S.; Iida, J.; Suzuki, K.; Kawano, M.; Ozeki, T.; Fujita, M. *Science* **2006**, *313*, 1273−1276.

(32) Honda, K.; Morita, M.; Sakata, O.; Sasaki, S.; Takahara, A. *Macromolecules* **2010**, *43*, 454−460.

(33) (a) Lindstrom, A. B.; Strynar, M. J.; Libelo, E. L. *Environ. Sci. Technol.* **2011**, *45*, 7954−7961. (b) Houde, M.; De Silva, A. O.; Muir, D. C. G.; Letcher, R. J. *Environ. Sci. Technol.* **2011**, *45*, 7962−7973. (c) D'eon, J. C.; Mabury, S. A. *Environ. Sci. Technol.* **2011**, *45*, 7974−7984.

(34) Yoda, H.; Nakatani, K.; Terashima, T.; Ouchi, M.; Sawamoto, M. *Macromolecules* **2010**, *43*, 5595−5601.