Fluorinated Microgel Star Polymers as Fluorous Nanocapsules for Encapsulation and Release of Perfluorinated Compounds

Yuta Koda, Takaya Terashima,* and Mitsuo Sawamoto*

*Corresponding Author

Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University

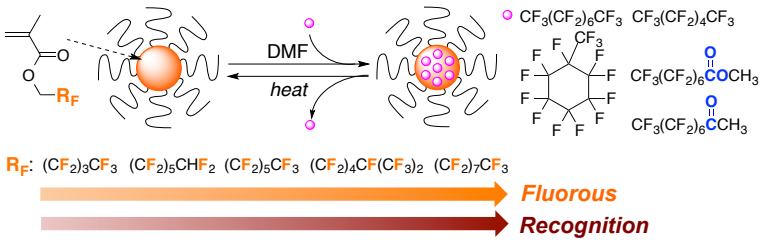
Katsura, Nishikyo-ku, Kyoto 615-8510, JAPAN

Tel: +81-75-383-2600, Fax: +81-75-383-2601

E-mail: terashima@living.polym.kyoto-u.ac.jp, sawamoto@star.polym.kyoto-u.ac.jp

Abstract

Fluorinated microgel star polymers were designed and synthesized as fluorous nanocapsules for the encapsulation and release of perfluorinated compounds. Five types of these fluorous star polymers were obtained by ruthenium-catalyzed linking reaction of chlorine-capped poly(methyl methacrylate) arms (macroinitiators) with a perfluorinated dimethacrylate linker and a perfluorinated methacrylate (R_FMA), so as to tune the in-core fluorous properties depending on the latter structure and fluorine content. ^{19}F nuclear magnetic resonance and ^{19}F spin-spin relaxation time (T_2) measurements revealed that the mobility of the in-core perfluorinated pendants derived from R_FMA decreased with increasing the number of fluorine and carbon atoms, or the pendant length. The cores effectively recognized and encapsulated perfluorinated guest compounds (e.g., perfluorooctane and perfluoromethylcyclohexane), and the encapsulation depended on the fluorous properties of the structures and fluorous nature of R_FMA and the guests. For example, encapsulation was promoted with increasing the number of in-core fluorine and CF_3 groups, and typically the core with perfluorodecyl pendants successfully captured perfluorinated esters and ketones. In addition, fluorinated star polymers could reversibly capture and thermo-responsively release a perfluorinated guest, indicating the encapsulation is selective but dynamic and stimuli-responsive.



Introduction

"Fluorophilicity" is a key character of perfluorinated compounds and related materials, which are generally immiscible with hydrophobic (lipophilic) and hydrophilic solvents and compounds.[1–15] Because of this unique feature, perfluorinated materials are widely employed in industry and academic research; e.g., as water/oil repellents, surfactants, and surface coating agents,[5,6] as well as key players in catalysis (for facile product separation, etc.),[2–4,7] molecular recognition,[8–10,12,13,14] and unique self-assembly.[11–13] In particular, the functionalization of perfluorinated polymers with hydrophobic and/or hydrophilic segments is promising in creating globular macromolecules with fluorous inner compartments that are fully solubilized and/or dispersed in common organic solvents and water.[8–13] Such fluorous compartments have been created within microgel-core star polymers,[8,9] micelles,[11-13] and the related self-assembly molecules,[10,14] typically applicable to molecular encapsulation vessels.

Microgel-core star polymers possess covalently crosslinked microgels in the center that are solubilized and covered with plenty of linear arm polymers (10 – 100),[16–22] in sharp contrast to micelles, vesicles, polymersomes, and nanogels that are based on the physical association of amphiphilic and/or functional polymers.[23] The microgel cores of star polymers have large free spaces and lots of cavities[22] to afford functional compartments that typically serve as nanocapsules for molecular capture and release and nanoreactors for catalysis.[8,9,16,17,24–29] In general, microgel star polymers are obtained from the cross-linking reaction of living linear polymers or macroinitiators (arm) with divinyl monomers (core-forming agent) in living polymerization.[30–34] Focusing on the high versatility and functionality tolerance, we have employed ruthenium-catalyzed living radical polymerization[30] for the arm-linking reaction with functional linking agents and monomers, to directly produce various core-functionalized star polymers with amide,[24] phosphine,[25–27] amine,[27] hydroxyl,[24,27] ionic,[28] and perfluorinated groups.[8,9] Importantly, the arm-linking method not only gives functionalized microgels but also affords the efficient and local accumulation of functional groups into microgel cores.

In particular, fluorinated microgel star polymers have been recently developed as fluorous compartments soluble in organic solvents[8] and aqueous media[9] to encapsulate and separate perfluorinated guest compounds. The fluorous microgels were created by the accumulation of a perfluorinated alkane methacrylate (13FOMA) and the solubility was controlled by the surrounding arm polymers: i.e., hydrophobic poly(methyl methacrylate) arm star polymers were soluble in organic solvents,[8] while amphiphilic and hydrophilic poly(ethylene glycol) arm counterparts were soluble in both organic solvents and aqueous media.[9] As a result, fluorinated microgel star polymers (host) efficiently and selectively encapsulated perfluorinated guest compounds (e.g., perfluorooctane: PFO, perfluorooctanoic acid: PFOA) into the cores in DMF or water via fluorous

host-guest interaction. Additionally, they released the guests from the core by reducing the fluorous interaction with $CHCl_3$ addition. ^{19}F nuclear magnetic resonance (NMR) measurements would allow us to evaluate a series of fluorous molecular recognition and the mobility of in-core perfluorinated alkyl pendants with ^{19}F spin-latice and/or spin-spin relaxation time (T_1, T_2). The dynamics characterization revealed that the accumulation of 13FOMA into microgel cores reduced the thermal mobility of the in-core perfluorinated pendants to result in stable fluorous compartments.[8] The fluorous microgels can thus efficiently recognize and tightly enclose perfluorinated guest compounds.

Herein, we report the synthesis of various fluorinated microgel star polymers (**S1** – **S5**) via living radical polymerization to create fluorous nanocapsules for the capture and stimuli-responsive release of perfluorinated compounds in organic media (Scheme 1). The in-core fluorous properties are effectively controlled with various perfluorinated alkyl methacrylates (R_FMA), affording the efficient recognition of various perfluorinated guest compounds.

S1 – **S5** were directly prepared by ruthenium-catalyzed linking reaction of a chlorine-capped poly(methyl methacrylate) (PMMA-Cl) with a perfluorinated alkyl spacer dimethacrylate (12FODMA) in the presence of R_FMA. The star polymers were characterized by size exclusion chromatography coupled with multi-angle laser light scattering (SEC-MALLS) and ^1H and ^{19}F NMR spectroscopy. Confirmed by ^{19}F T_2 measurements, the mobility of in-core perfluorinated pendants decreased with increasing the number of fluorine atom and CF_3 end-group in R_FMA. Fluorinated star polymers efficiently encapsulated perfluorinated alkanes and the derivatives with functional groups such as ester and ketone, where the fluorous recognition is dependent on in-core R_FMA species. The key was to increase fluorous interaction between the perfluorinated pendants and guest molecules.

Scheme 1

Experimental Section

Materials

For Monomer Synthesis and Perfluorinated Guests. 1*H*,1*H*,2*H*,2*H*-nonafluoro-1-hexanol (TCI, purity > 97%), 1*H*,1*H*,7*H*-dodecafluoro-1-heptanol (TCI, purity > 97%), 1*H*,1*H*,2*H*,2*H*-perfluoro-7-methyloctan-1-ol (Wako), 1*H*,1*H*,2*H*,2*H*-heptadecafluoro-1-decanol (TCI, purity > 96%), perfluoromethylcyclohexane (PFMCH: TCI, purity > 95%), perfluorooctane (PFO: Aldrich, purity > 98%), perfluorohexane (PFH: TCI, purity > 95%), methyl perfluorooctanoate (PFO-ester: TCI, purity > 97%), methyl perfluoroheptyl ketone (PFHp-ketone: TCI, purity > 95%), and 1*H*,1*H*-perfluoro-1-octanol (PFO-OH: Aldrich, purity > 98%) were used as received. Methacryloyl chloride (TCI, purity > 80.0%) and triethylamine (TCI, purity > 99.0%) were purified by distillation before use. Tetrahydrofuran (Wako, dyhydrated), dichloromethane (Wako, dehydrated), ethyl acetate (Wako, purity > 99.5%), and hexane (Wako, purity > 96%) were used as received.

For Star Polymer Synthesis. Methyl methacrylate (MMA: TCI, purity > 99%) was dried overnight over calcium chloride and purified by distillation from calcium hydride before use. 1*H*,1*H*,2*H*,2*H*-Perfluorooctyl methacrylate (13FOMA: Wako, purity > 95%) was purified by column chromatography charged with inhibitor remover (Aldrich) and purged by argon before use. 2,2,3,3,4,4,5,5,6,6,7,7-dodecafluoro-1,8,-octanediol dimethacrylate (12FODMA) was prepared according to the previous literature[8] and degassed before use. 1*H*,1*H*,2*H*,2*H*-Perfluorohexcyl methacrylate (9FHxMA), 1*H*,1*H*,7*H*-perfluoro-1-heptyl methacrylate (12FHpMA), 1*H*,1*H*,2*H*,2*H*-perfluoro-7-methyloctyl methacrylate (15FMOMA), and 1*H*,1*H*,2*H*,2*H*-perfluorodecyl methacrylate (17FDeMA) were prepared as shown below and degassed before use. Ethyl-2-chloro-2-phenylacetate (ECPA: Aldrich, purity > 97%) was purified by distillation under reduced pressure before use. $Ru(Ind)Cl(PPh_3)_2$ (Ind: indenyl, Aldrich) was handled in a grove box under a moisture- and oxygen-free argon atmosphere (H_2O < 1 ppm, O_2 < 1 ppm). *n*-Bu_3N (TCI, purity > 98%) was purged by argon before use. Tetralin (1,2,3,4-tetrahydronaphthalene: TCI, purity > 98%), as an internal standard for the conversion of 12FODMA and perfluorinated monomers determined by ^1H NMR, was dried over calcium chloride overnight and distilled from calcium hydride. Toluene (Kishida Chemical, purity > 99%) was purified by passing it through a purification column (Solvent Dispensing System, glass contour, HANSEN&CO., LTD) before use.

Characterization

Molecular weight distribution curves, number-average molecular weight (M_n), and dispersity (M_w/M_n) of the polymers were measured by SEC (shodex GPC-104) in THF at 40 ^oC (flow rate: 0.3 mL/min) on three polystyrene gel columns (shodex LF-404: exclusion limit = 2×10^6 g/mol; particle size = 6 μm; pore size = 3000 Å; 0.46 cm i.d. × 25 cm) that were connected to a shodex DU-H2000 pump, a shodex RI-74 refractive index detector, and a shodex UV-41 UV detector set at 250 nm. The columns were calibrated against 13 standard poly(MMA) samples (Polymer Laboratories; M_n = 620 –1200000; M_w/M_n = 1.02 – 1.30). ^1H and ^{19}F NMR spectra were recorded in $CDCl_3$, CD_2Cl_2, and DMF-d_7 at room temperature or 30 ^oC on a JEOL JNM-ECA500 spectrometer, operating at 500.16 (^1H) or 470.62 (^{19}F) MHz. For characterization and molecular encapsulation experiments, polymers were purified by preparative SEC in $CHCl_3$ at room temperature (flow rate: 10 mL/min) on a polystyrene gel column (K-5003: exclusion limit = 7×10^4 g/mol; particle size = 15 μm; 5.0 cm i.d. × 30 cm) that was connected to a Jasco PU-2086 precision pump, a Jasco RI-2031 refractive index detector, and a Jasco UV-2075 UV/vis detector set at 250 nm. Absolute weight-average molecular weight (M_w) and radius of gyration (R_g) of star polymers were determined by multi-angle laser light scattering (MALLS) equipped with SEC on a Dawn E instrument (Wyatt Technology, Ga-As laser, λ = 690 nm). The SEC was performed in DMF containing 10 mM LiBr at 40 ^oC (flow rate: 1 mL/min) on three linear-type polystyrene gel columns (shodex KF-805L: exclusion limit = 4×10^6 g/mol; particle size = 10 μm; pore size = 5000 Å; 0.8 cm i.d. × 30 cm) that were connected to a Jasco PU-2080 precision pump, a Jasco RI-1530 refractive index detector, and a Jasco UV-1570 UV/vis detector set at 270 nm. The refractive index increment (*dn/dc*) was measured in DMF at 40 ^oC on an Optilab DSP refractometer (Wyatt Technology, λ = 690 nm, c < 3.3 mg/mL).

Synthesis of Perfluorinated Monomers

***9FHxMA*.** In 200 mL round-bottomed flask filled with argon, methacryloyl chloride (143.3 mmol, 13.9 mL) was added to a solution of 1*H*,1*H*,2*H*,2*H*-nonafluoro-1-hexanol (95.5 mmol, 25.2 g) and trientylamine (143.3 mmol, 19.9 mL) in dry THF (50 mL) at 0 ^oC. The reaction mixture was stirred at 25 ^oC for 24 h. After the evaporation of the reaction solution, diethyl ether (150 mL) and distilled water (150 mL) were poured into the flask. The aqueous phase was separated and extracted by diethyl ether (150 mL), and the ether extracts were combined with the organic layer. The combined organic phase was washed with water three times. After the ether was removed by evaporation, the crude product was purified by silica gel column chromatography (the bottom and top layers were covered with sodium sulfate) with hexane/ethyl acetate (10/1, v/v) as an eluent. The solution was evaporated in vacuo to dryness to give colorless liquid of 9FHxMA. Yield: 21.9 g

(69%). δ_H (500 MHz; $CDCl_3$; chloroform) 6.13 (1H, m), 5.60 (1H, m), 4.45 (2H, t, J = 6.6 Hz), 2.51 (2H, tt, $^3J_{FH}$ = 18.3, $^3J_{HH}$ = 6.6 Hz) 1.94 (3H, t, J = 1.4 Hz). δ_C (125 MHz; $CDCl_3$; chloroform) 166.9 (C), 136.0 (C), 126.0 (CH_2), 117.6 (CH_2CF_2, tt, $^1J_{FC}$ = 255.5, $^2J_{FC}$ = 32.4 Hz), 117.1 (CF_3, qt, $^1J_{FC}$ = 287.9, $^2J_{FC}$ = 33.6 Hz), 112.9 – 106.7 (CF_2CF_2, m), 56.5 (CH_2), 30.5 (CH_2, t, $^2J_{FC}$ = 22.8 Hz), 17.9 (CH_3). δ_F (470 MHz; $CDCl_3$; CF_3COOH) -82.2 (3F, tt, $^3J_{FF}$ = 9.9, $^4J_{FF}$ = 3.6 Hz), -114.8 (2F, m), -125.6 (2F, m), -127.0 (2F, m).

***12FHpMA*.** In 300 mL round-bottomed flask filled with argon, methacryloyl chloride (222.7 mmol, 21.5 mL) was added to a solution of 1*H*,1*H*,7*H*-dodecafluoro-1-heptanol (148.4 mmol, 49.3 g) and trientylamine (222.7 mmol, 31.0 mL) in dry THF (75 mL) at 0 ^oC. The reaction mixture was stirred at 25 ^oC for 24 h. After the evaporation of the reaction solution, diethyl ether (150 mL) and distilled water (150 mL) were poured into the flask. The aqueous phase was separated and extracted by diethyl ether (150 mL), and the ether extracts were combined with the organic layer. The combined organic phase was washed with water three times. After the ether was removed by evaporation, the crude product was purified by silica gel column chromatography (the bottom and top layers were covered with sodium sulfate) with hexane/ethyl acetate (10/1, v/v) as an eluent. The solution was evaporated in vacuo to dryness to give colorless liquid of 12FHpMA. Yield: 20.1 g (34%). δ_H (500 MHz; $CDCl_3$; chloroform) 6.21 (1H, m), 6.04 (1H, tt, $^2J_{FH}$ = 51.8, $^3J_{FH}$ = 5.2 Hz), 5.70 (1H, m), 4.65 (2H, t, $^3J_{FH}$ = 13.5 Hz), 1.97 (3H, t, J = 1.2 Hz). δ_C (125 MHz; $CDCl_3$; chloroform) 166.8 (C), 135.0 (C), 127.7 (CH_2), 111.2 (CH_2CF_2, tt, $^1J_{FC}$ = 270.5, $^2J_{FC}$ = 32.4 Hz), 107.8 (CHF_2, tt, $^1J_{FC}$ = 254.9, $^2J_{FC}$ = 31.2 Hz), 60.1 (CH_2, t, $^2J_{FC}$ = 27.6 Hz), 18.0 (CH_3). δ_F (470 MHz; $CDCl_3$; CF_3COOH) -120.5 (2F, m), -123.2 (2F, m), -124.5 (4F, br s), -130.6 (2F, m), -138.2 (2F, dm, $^2J_{HF}$ = 51.7 Hz).

***15FMOMA*.** In 300 mL round-bottomed flask filled with argon, methacryloyl chloride (71.0 mmol, 6.9 mL) was added to a solution of 1*H*,1*H*,2*H*,2*H*-perfluoro-7-methyloctan-1-ol (47.3 mmol, 19.6 g) and trientylamine (71.0 mmol, 9.9 mL) in dry dichloromethane (50 mL) at 0 ^oC. The reaction mixture was stirred at 25 ^oC for 24 h. After the evaporation of the reaction solution, diethyl ether (150 mL) and distilled water (150 mL) were poured into the flask. The aqueous phase was separated and extracted by diethyl ether (150 mL), and the ether extracts were combined with the organic layer. The combined organic phase was washed with water three times. After the ether was removed by evaporation, the crude product was purified by silica gel column chromatography (the bottom and top layers were covered with sodium sulfate) with hexane/ethyl acetate (10/1, v/v) as an eluent. The solution was evaporated in vacuo to dryness to give colorless liquid of 15FMOMA. Yield: 20.8 g (91%). δ_H (500 MHz: $CDCl_3$; chloroform) 6.13 (1H, m), 5.61 (1H, m), 4.45 (2H, t, J = 6.3 Hz), 2.51 (2H, tt, $^3J_{FH}$ = 18.3, $^3J_{HH}$ = 6.3 Hz) 1.95 (3H, t, J = 1.2 Hz). δ_C (125 MHz; $CDCl_3$; chloroform) 167.0 (C), 136.0 (C), 126.3 (CH_2), 118.9 (CF_3, qd, $^1J_{FC}$ =

290, $^{2}J_{FC}$ = 26.4 Hz), 117.8 (CH_2CF_2, tt $^{1}J_{FC}$ = 256.7, $^{2}J_{FC}$ = 32.4 Hz), 115 – 108 (CF_2, m), 90.6 (CF, dsep, $^{1}J_{FC}$ = 226.7, $^{2}J_{FC}$ = 32.4 Hz), 56.7 (CH_2), 30.7 (CH_2, t, $^{2}J_{FC}$ = 21.6 Hz), 18.1 (CH_3). δ_F (470 MHz; $CDCl_3$; CF_3COOH) -72.9 (6F, m), -114.6 (2F, m), -116.1 (2F, br s), -121.7 (2F, br s), -124.2 (2F, br s), -187.1 (2F, br s).

***17FDeMA*.** In 300 mL round-bottomed flask filled with argon, methacryloyl chloride (80.9 mmol, 7.8 mL) was added to a solution of 1*H*,1*H*,2*H*,2*H*-heptadecafluoro-1-decanol (53.9 mmol, 25 g) and trientylamine (80.9 mmol, 11.2 mL) in dry THF (75 mL) at 0 ^{o}C. The reaction mixture was stirred at 25 ^{o}C for 24 h. After the evaporation of the reaction solution, diethyl ether (150 mL) and distilled water (150 mL) were poured into the flask. The aqueous phase was separated and extracted by diethyl ether (150 mL), and the ether extracts were combined with the organic layer. The combined organic phase was washed with water three times. After the ether was removed by evaporation, the crude product was purified by silica gel column chromatography (the bottom and top layers were covered with sodium sulfate) with hexane/ethyl acetate (10/1, v/v) as an eluent. The solution was evaporated in vacuo to dryness to give colorless liquid of 17FDeMA. Yield: 22.8 g (80%). δ_H (500 MHz; $CDCl_3$; chloroform) 6.14 (1H, br s), 5.61 (1H, m), 4.46 (2H, t, J = 6.2 Hz), 2.51 (2H, tt, $^{3}J_{FH}$ = 18.1, $^{3}J_{HH}$ = 6.7 Hz) 1.95 (^{3}H, t, J = 1.4). δ_C (125 MHz; $CDCl_3$; chloroform) 167.0 (C), 136.0 (C), 126.3 (CH_2), 117.8 (CH_2CF_2, tt, $^{1}J_{FC}$ = 256.7, $^{2}J_{FC}$ = 32.4 Hz), 117.4 (CF_3, qt, $^{1}J_{FC}$ = 297.9, $^{2}J_{FC}$ = 32.4 Hz), 114.2 – 106.1 (CF_2, m), 56.7 (CH_2), 30.7 (CH_2, t, $^{2}J_{FC}$ = 21.6 Hz), 18.1 (CH_3). δ_F (470 MHz; $CDCl_3$; CF_3COOH) -81.9 (3F, br s), -114.6 (2F, br s), -122.7 (2F, br s), -123.0 (4F, br s), -123.8 (2F, br s), -124.6 (2F, br s), -127.2 (2F, br s).

Synthesis of Fluorinated Microgel Star Polymers

The synthesis of star polymers (**S1**-**S5**) were carried out by syringe technique under argon in baked round-bottomed flasks equipped with a three-way stopcock.

S1: In a 200 mL round-bottomed flask, $Ru(Ind)Cl(PPh_3)_2$ (0.220 mmol, 171 mg) was placed. Into this flask, toluene (58.1 mL), tetralin (4.7 mL), a 400 mM toluene solution of *n*-Bu_3N (2.2 mmol, 5.5 mL), MMA (441 mmol, 47.2 mL), and ECPA (2.2 mmol, 0.38 mL) were added sequentially in this order at 25 ^{o}C under argon (total volume: 116 mL). The solution (25 mL) was distributed into four 100 mL round-bottomed flasks to prepare PMMA arms for star polymers (**S1**, **S2**, **S4**, **S5**). The flask with 25 mL polymerization solution was placed in an oil bath at 80 ^{o}C. After 14 h (48% conversion: by ^{1}H NMR), the solution was evaporated *in vacuo* at 25 ^{o}C to give PMMA-Cl (M_n = 12000, M_w/M_n = 1.13, 0.47 mmol) with non-volatile agents (tetralin, *n*-Bu_3N, and Ru catalyst). Into this flask, toluene (18.7 mL), a 1110 mM toluene solution of 12FODMA (2.5 mmol, 2.25 mL), and a 3290 mM toluene solution of 9FHxMA (5.0 mmol, 1.5 mL) were added at 25 ^{o}C, and the flask was placed in an oil bath at 80 ^{o}C. After 18 h, the reaction was terminated by

cooling the mixture to -78 °C (conversion of 12FODMA/9FHxMA: 90%/79% by ^{1}H NMR). The quenched reaction mixture was evaporated to dryness. The resulting crude was purified by preparative SEC in $CHCl_3$ (to remove catalysts and unreacted arm residue and monomers) and dried under vacuum to give **S1**. Star yield (SEC): 78%. *dn*/*dc* (DMF) = 0.029. SEC-MALLS (DMF, 0.01 M LiBr): M_w = 461000 g/mol; arm numbers = 23; R_g = 13 nm. δ_H (500 MHz; CD_2Cl_2; dichloromethane) 7.3 – 7.1 (aromatic), 6.2, 5.7 (olefin), 4.8 – 3.9 (-COC*H*$_2$CH$_2$CF$_2$-), 4.7 – 4.6 (-COCH$_2$CF$_2$-), 4.1 – 3.9 (-COC*H*$_2$CH$_3$), 3.8 – 3.4 (-OCH$_3$), 3.4 (-COC*H*PhCH$_2$-), 2.7 –2.3 (-COCH$_2$C*H*$_2$CF$_2$), 2.1 – 1.4 (-CH$_2$-), 1.2 – 0.6 (-CCH$_3$). δ_F (470 MHz; $CDCl_3$; CF_3COOH) -81.9 – -83.2 (-CF$_3$), -113.9 – -116.2 (-CH$_2$CH$_2$CF$_2$-), -119.9 – -121.2 (-COCH$_2$CF$_2$-), -121.4 – -125.1 (-COCH$_2$CF$_2$C*F*$_2$C*F*$_2$-), -125.1 – -126.6 (-C*F*$_2$CF$_2$CF$_3$), -126.6 – -128.1 (-C*F*$_2$CF$_3$).

S2: PMMA-Cl was prepared as shown in **S1**. Into the 100 mL round-bottomed flask containing PMMA-Cl (M_n = 12000, M_w/M_n = 1.13, 0.47 mmol) and non-volatile agents (tetralin, *n*-Bu$_3$N, and Ru catalyst), toluene (18.7 mL), a 1110 mM toluene solution of 12FODMA (2.5 mmol, 2.25 mL), and a 2690 mM toluene solution of 12FHpMA (5.0 mmol, 1.86 mL) were added at 25 °C, and the flask was placed in an oil bath at 80 °C. After 18 h, the reaction was terminated by cooling the mixture to -78 °C (total conversion: 85% by ^{1}H NMR). The quenched reaction mixture was evaporated to dryness. The resulting crude was purified by preparative SEC in $CHCl_3$ (to remove catalysts and unreacted arm residue and monomers) and dried under vacuum to give **S2**. Star yield (SEC): 77%. *dn*/*dc* (DMF) = 0.032. SEC-MALLS (DMF, 0.01 M LiBr): M_w = 399000 g/mol; arm numbers = 19; R_g = 23 nm. δ_H (500 MHz; CD_2Cl_2, dichloromethane) 7.3 – 7.1 (aromatic), 6.3 – 5.8 (-CHF$_2$), 6.2, 5.7 (olefin), 4.8 – 3.9 (-COC*H*$_2$CF$_2$-), 4.1 – 3.9 (-COC*H*$_2$CH$_3$), 3.8 – 3.4 (-OCH$_3$), 3.4 (-COC*H*PhCH$_2$-), 2.2 – 1.4 (-CH$_2$-), 1.2 – 0.4 (-CCH$_3$). δ_F (470 MHz; $CDCl_3$; CF_3COOH) -116.0 – -121.5 (-CH$_2$CF$_2$-), -122.0 – -127.2 (-CF$_2$-), -129.8 – -132.0 (-C*F*$_2$CHF$_2$), -137.4 – -139.6 (-CHF$_2$).

S4: PMMA-Cl was prepared as shown in **S1**. Into the 100 mL round-bottomed flask containing PMMA-Cl (M_n = 12000, M_w/M_n = 1.13, 0.47 mmol) and non-volatile agents (tetralin, *n*-Bu$_3$N, and Ru catalyst), toluene (18.7 mL), a 1111 mM toluene solution of 12FODMA (2.5 mmol, 2.25 mL), and a 1670 mM toluene solution of 15FMOMA (5.0 mmol, 3.0 mL) were added at 25 °C, and the flask was placed in an oil bath at 80 °C. After 19 h, the reaction was terminated by cooling the mixture to -78 °C (conversion of 12FODMA/15FMOMA: 89%/79% by ^{1}H NMR). The quenched reaction mixture was evaporated to dryness. The resulting crude was purified by preparative SEC in $CHCl_3$ (to remove catalysts and unreacted arm residue and monomers) and dried under vacuum to give **S4**. Star yield (SEC): 76%. *dn*/*dc* (DMF) = 0.026. SEC-MALLS (DMF, 0.01 M LiBr): M_w = 509000 g/mol; arm numbers = 25; R_g = 18 nm. δ_H (500 MHz; CD_2Cl_2; dichloromethane) 7.3 – 7.1 (aromatic), 6.2, 5.7 (olefin), 4.8 – 3.9 (-COC*H*$_2$CH$_2$CF$_2$-), 4.7 – 4.6

(-$COCH_2CF_2$-), 4.1 – 3.9 (-$COCH_2CH_3$), 3.8 – 3.4 (-OCH_3), 3.4 (-$COCH$PhCH$_2$-), 2.7 – 2.3 (-$COCH_2CH_2CF_2$), 2.1 – 1.4 (-CH_2-), 1.2 – 0.4 (-CCH_3). δ_F (470 MHz; $CDCl_3$; CF_3COOH) -72.7 – -74.4 (-CF_3), -113.7 – -115.7 (-$CH_2CH_2CF_2$-), -115.7 – -126.8 (-CF_2-), -186.8 – -188.1 [-$CF(CF_3)_2$].

S5: PMMA-Cl was prepared as shown in **S1**. Into the 100 mL round-bottomed flask containing PMMA-Cl (M_n = 12000, M_w/M_n = 1.13, 0.47 mmol) and non-volatile agents (tetralin, *n*-Bu_3N, and Ru catalyst), toluene (18.7 mL), a 1110 mM toluene solution of 12FODMA (2.5 mmol, 2.25 mL), and a 1490 mM toluene solution of 17FDeMA (5.0 mmol, 3.35 mL) were added at 25 ^oC, and the flask was placed in an oil bath at 80 ^oC. After 18 h, the reaction was terminated by cooling the mixture to -78 ^oC (conversion of 12FODMA/17FDeMA: 90%/82% by ^1H NMR). The quenched reaction mixture was evaporated to dryness. The resulting crude was purified by preparative SEC in $CHCl_3$ (to remove catalysts and unreacted arm residue and monomers) and dried under vacuum to give **S5**. Star yield (SEC): 73%. *dn*/*dc* (DMF) = 0.026. SEC-MALLS (DMF, 0.01 M LiBr): M_w = 954000 g/mol; arm numbers = 42; R_g = 21 nm. δ_H (500 MHz; CD_2Cl_2; dichloromethane) 7.3 – 7.1 (aromatic), 6.2, 5.7 (olefin), 4.8 – 3.9 (-$COCH_2CH_2CF_2$-), 4.7 – 4.6 (-$COCH_2CF_2$-), 4.1 – 3.9 (-$COCH_2CH_3$), 3.8 – 3.4 (-OCH_3), 3.4 (-$COCH$PhCH$_2$-), 2.7 – 2.3 (-$COCH_2CH_2CF_2$), 2.1 – 1.4 (-CH_2-), 1.2 – 0.4 (-CCH_3). δ_F (470 MHz, $CDCl_3$; CF_3COOH) -81.7 – -83.7 (-CF_3), -113.6 – -116.4 (-CH_2CF_2-), -119.7 – -126.5 (-CF_2-), -126.7 – -129.0 (-C_2CF_3).

^{19}F T_2 Measurements

Degassed solutions of star polymers (**S1**-**S5**: 50 mg) in DMF-d_7 (1 mL) were added into NMR tubes by syringe and the tubes were sealed under nitrogen before ^{19}F NMR analysis. ^{19}F T_2 values were determined by the Carr-Purcell-Meiboom-Gill (CPMG) pulse sequence using 32 values of τ, with a minimum value of 0.1 ms and the maximum value of 0.2 s. The NMR samples were not spun for the measurement. The number of scans was set at 128. Other parameters were as follows: spectral width = 30 ppm; 90° pulse width = 13.4 μs; relaxation delay = 1 s; data points = 32768.

Encapsulation of Perfluorinated Compounds

Encapsulation of perfluorinated compounds (PFMCH, PFO, PFH, PFO-ester, PFHp-ketone, PFO-OH) with **S1**-**S5** was evaluated with ^{19}F NMR.

PFMCH, PFO, and PFH: In a 6 mL vial, the guests (0.2 mL) were respectively added into the solution of a star polymer (**S1**-**S5**, 70 mg) in DMF-d_7 (1.4 mL). The mixture was vigorously stirred at room temperature for 24 h. After the emulsion mixture was kept calmly for a few days,

the solution was separated to two phases. The upper transparent layer containing a guest and a star polymer was analyzed by ^{19}F NMR.

PFO-ester and PFHp-ketone: In a 6 mL vial, the guests (0.2 mL) were respectively added into a solution of a star polymer (**S3** or **S5**: 50 mg) in DMF-d_7 (0.8 mL). The dispersed mixture was vigorously stirred at room temperature for 24 h. After the solution was kept calmly for a few hours, the solution was separated to two phases. The upper transparent layer containing a guest and a star polymer was analyzed by ^{19}F NMR.

PFO-OH: In a 6 mL vial, a DMF-d_7 solution of a star polymer (**S3** or **S5**, 50 mg/mL, 1.0 mL) was added to PFO-OH (17.2 mg). The homogeneous mixture was stirred at room temperature for 24 h. The solution was then analyzed by ^{19}F NMR.

Result and Discussion

Synthesis of Fluorinated Microgel Star Polymers

Five kinds of fluorinated microgel star polymers (**S1**-**S5**) were designed with methacrylates carrying different perfluorinated alkyl pendants (R_FMA) as core-fluorination groups: 1*H*,1*H*,2*H*,2*H*-perfluorohexcyl methacrylate (9FHxMA), 1*H*,1*H*,7*H*-perfluoroheptyl methacrylate (12FHpMA), 1*H*,1*H*,2*H*,2*H*-perfluorooctyl methacrylate (13FOMA), 1*H*,1*H*,2*H*,2*H*-perfluoro-7-methyloctyl methacrylate (15FMOMA), 1*H*,1*H*,2*H*,2*H*-perfluorodecyl methacrylate (17FDeMA). The fluorous nature of the monomers with CF_3 end group would increase with the fluorine numbers in the perfluorinated pendants, while 12FHpMA may have properties distinct from the others because of no CF_3 end group.

The star polymers were synthesized by Ru(Ind)Cl(PPh_3)$_2$/*n*-Bu_3N-catalyzed linking reaction of a chlorine-capped PMMA [PMMA-Cl: degree of polymerization (*DP*) = ~ 100] with 2,2,3,3,4,4,5,5,6,6,7,7-dodecafluoro-1,8-octanediol dimethacrylate (12FODMA) (*m* = [12FODMA]$_0$/[PMMA-Cl]$_0$ = 5) in the presence of R_FMA (*n* = [R_FMA]$_0$/[PMMA-Cl]$_0$ = 10). MMA was first polymerized with Ru(Ind)Cl(PPh_3)$_2$/*n*-Bu_3N (catalyst) and ethyl-2-chloro-2-phenylacetate (ECPA: chloride initiator) in toluene at 80 ^{o}C for 14 h (conversion: 48%) to give well-controlled PMMA-Cl with narrow molecular weight distribution (M_n = 12000, M_w/M_n = 1.13). After the removal of the residual MMA from the reaction vessel (by evaporation *in vacuo* at 25 ^{o}C), a toluene solution of 12FODMA and R_FMA was then added into the vessel containing the PMMA-Cl and non-volatile ruthenium catalyst under argon. In all cases, the linking reaction of PMMA-Cl efficiently and smoothly proceeded up to over 80% monomer conversion in 18 - 23 h at 80 ^{o}C to provide corresponding fluorinated microgel star polymers with

high molecular weight (**S1**-**S5**) in high yield (> 70%, by SEC in THF) (Figure 1). Importantly, 12FODMA and R_FMA were concurrently consumed during arm-linking process (Figure S1), resulting in random, virtually homogeneous, distribution of the perfluorinated alkyl pendants within microgel cores.

Figure 1

Figure S1

After purified by preparative SEC (removing the residues of unreacted arms, a ruthenium catalyst, and monomers), **S1**-**S5** were characterized by multi-angle laser light scattering coupled with SEC (SEC-MALLS) in DMF to determine absolute weight-average molecular weight (M_w), arm numbers (N_{arm}), and radius of gyration (R_g): M_w = 393000 – 954000 g/mol; N_{arm} = 19 – 42; R_g = 13 - 21 nm (Table 1). Uniquely, **S1**-**S4** have almost constant arm numbers (N_{arm} = ~20), whereas **S5** has N_{arm} (~ 40) about twice larger than **S1**-**S4**. The former corresponds to the fact that N_{arm}, i.e., the efficiency of intermolecular crosslinking, is generally determined by the molar ratio of a linking agent to an arm polymer chain (m = $[12FODMA]_0/[PMMA\text{-}Cl]_0$ = 5). The latter means that, beyond such a general feature, **S5** underwent the intermolecular linking of arm polymers more efficiently than the other star polymers. This is because the strong fluorous properties of the perfluorinated segment of 17FDeMA promote the intermolecular association of intermediates, i.e., block copolymers with dangling olefin and perfluorinated pendants and star polymers with small arm numbers therefrom, during microgel formation process.

Table 1

The numbers of in-core fluorine atoms (N_F), in-core CF_3 end groups (N_{CF3}), and in-core polyfluorinated groups (N_{RF}) were calculated form N_{arm}, the feed ratio of a linking reagent and R_FMA (m and n), and their conversion: $N_F = N_{arm} \times [12 \times m \times (conv./100) + (\text{the number of F in a monomer}) \times n \times (conv./100)]$, $N_{CF3} = N_{arm} \times (\text{the number of } CF_3 \text{ in a monomer}) \times n \times (conv./100)$, $N_{RF} = N_{arm} \times n \times (conv./100)$. As shown in Table 1, these were estimated as 2810 - 8070 (N_F), 0 - 388 (N_{CF3}), 150 - 343 (N_{RF}). Thus, lots of fluorine atoms and perfluorinated alkyl units were successfully accumulated within microgel cores by this simple arm-linking reaction.

S1-**S5** were analyzed by ^{1}H NMR in CD_2Cl_2 at 30 ^oC (Figure 2). **S1**-**S5** showed broad methylene proton signals of in-core 12FODMA (*g, g'*: 4.6 ppm) and corresponding R_FMA (*i*: 4.6 – 4.2 ppm, *j*: 2.6 – 2.4 ppm) and small olefin protons (*h*: 6.2, 5.7 ppm) in addition to the proton signals for PMMA arms (*e*: 1.3 – 0.7 ppm, *d*: 2.1 – 1.4 ppm, *f*: 3.7 – 3.4 ppm) and the *a*-end initiator

fragment (*a*: 4.1 – 4.0 ppm, *b*: 3.4 ppm, *c*: 7.4 – 7.2 ppm). The broad signals for the in-core R_FMA importantly support that R_FMA is placed within microgels crosslinked with 12FODMA. Calculated from the area ratio of olefin signal (*h*) to an initiator unit (*c*), the unreacted pendant olefin of 12FODMA was estimated as about 0.3 unit per a single arm chain: i.e., in all star polymers, over 94% of the pendant olefin was consumed by intra- and intermolecular crosslinking reaction. Additionally, **S2** quantitatively exhibited a tip proton signal (-CHF_2) of in-core 12FHpMA (*k*: 6.2 – 5.8 ppm); the area ratio is in good agreement with the content per a single arm chain (n = 10).

Figure 2

To evaluate the properties of the in-core perfluorinated alkyl pendants, **S1**-**S5** were further analyzed by ^{19}F NMR in $CDCl_3$ at 30 ^{o}C (Figure 3). All of the star polymers exhibited the ^{19}F signals of the in-core R_FMA pendants (*a-f*), whereas the ^{19}F signals of the 12FODMA perfluorinated spacer (*A*, *B*) were hardly detected. This indicates that R_FMA pendants are more thermally mobile than 12FODMA spacer unit. In particular, the tip CF_3 and CHF_2 groups of the perfluorinated pendants were the most clearly observed. They were thus used as a probe in analyzing the thermal mobility of in-core perfluorinated pendants below.

Figure 3

Core-Mobility Analysis by T_2 Measurements

Thermal mobility of the in-core perfluorinated pendants was evaluated with ^{19}F NMR spin-spin relaxation time (T_2) measurements of **S1**-**S5** in DMF-d_7. It has already found that the perfluorinated pendants in star polymers effectively aggregate within microgel cores via fluorous interaction in DMF. The mobility of the perfluorinated pendants would thus tend to decrease with increasing fluorous nature.

At 30 ^{o}C, ^{19}F T_2 values of the in-core CF_3 or CHF_2 groups in **S1**-**S5** were determined as 16 (**S1**), 20 (**S2**), 7.0 (**S3**), 5.4 (**S4**), and 2.6 (**S5**) ms (Table 2). The T_2 values decreased with increasing the fluorine atom numbers of in-core R_FMA unit (**S1** < **S3** < **S4**< **S5**). This indicates that perfluorinated pendants gradually aggregate each other within microgels to be less mobile as the fluorine numbers increase. **S5** comprising 12FODMA and 17FDeMA afforded the most stable fluorous compartment. Importantly, T_2 for **S2** was much larger than that for **S3** in spite of the almost identical fluorine atom numbers of R_FMA (12 - 13), meaning that CHF_2-capped pendants are not so fluorous to freely mobile within **S2** without aggregation.

Table 2

Temperature-dependent ^{19}F T_2 measurements of **S1**-**S5** were conducted in DMF-d_7 at the various temperatures of 30, 50, 70, 90, and 110 ^oC (Figure 4). Here, the effects of the in-core R_FMA species on the pendant mobility is quantitatively evaluated with the apparent activation energy (E_{ap}) for the molecular motion that is obtained from Arrhenius plots of T_2 (temperature-dependence of T_2). T_2 is proportional to reciprocal of correlation time of dynamics (τ_c) according to the following equation: $T_2 \propto \tau_c^{-1} = A \exp(- E_{ap} / RT)$ (1), where R and T means gas constant and temperature.

Figure 4

Figure 4 shows plots of logarithmic T_2 for **S1**-**S5** against inverse temperature ($1/T$) in DMF-d_7. All of ln T_2 values were inversely proportional to $1/T$, demonstrating that the mobility of their CF_3 or CHF_2 groups obeys Arrhenius equation (eq. 1). E_{ap} was estimated from the slope of the plots as follows: E_{ap} = 33 (**S1**), 26 (**S2**), 39 (**S3**), 44 (**S4**), and 44 (**S5**) kJ/mol (Table 2). This revealed that activation energy (E_{ap}) also increased with the physical association of perfluorinated pendants by fluorous interaction within the cores; **S5** had the largest E_{ap} to form most stable fluorous compartment.

Guest Encapsulation and Stimuli-Responsive Release

Encapsulation of perfluorinated guest molecules was investigated with fluorinated microgel star polymers (**S1**-**S5**) in DMF-d_7. Discussion was especially focused on encapsulation efficiency, fluorous interaction, and host/guest mobility, dependent on the in-core perfluorinated units. The guest encapsulation would be enhanced with increasing the fluorous interaction between the in-core perfluorinated pendants and a guest molecule.

PFMCH Encapsulation. Perfluoromethylcyclohexane (PFMCH) was first employed as a guest molecule that is fluorous, immiscible with common organic solvents (e.g., DMF) and water.[8,9] PFMCH was mixed and solubilized with **S1**-**S5** in DMF-d_7 at 25 ^oC for 24 h, resulting in emulsion mixtures. After the phase separation, the transparent supernatant was analyzed by ^{19}F NMR at 30 ^oC (Figure 5). The CF_3 multiplet signal of PFMCH alone (*a*: -70.25 ppm) turned broad and shifted to upfield in the presence of **S1** (*a'*: -70.35 ppm), **S3** (*a'*: -70.6 ppm), **S4** (*a'*: -70.7 ppm), and **S5** (*a'*: -70.95 ppm). This demonstrated that **S1**, **S3**-**S5** efficiently interacted with PFMCH to enclose the guest within their fluorous microgels. Particularly, **S5** with long perfluorinated alkyl units (1*H*,1*H*,2*H*,2*H*-perfluorodecyl) led to the broadest fluorine signal of PFMCH (Figure 5f). In the

presence of **S2**, the CF_3 signal of PFMCH was in turn still multiplet despite of the upfield shift (*a'*: -70.45 ppm). This indicates that **S2** actually solubilized PFMCH but does not so efficiently enclose it within the core owing to the less fluorous properties of the in-core 12FHpMA bearing a $-CHF_2$ end group.

Figure 5

The mobility of PFMCH enclosed within **S1**-**S5** was evaluated with ^{19}F T_2 measurements of the guest CF_3 group (Table 3). The T_2 values were dependent on the star polymer species: T_2 = 177 (**S1**), 472 (**S2**), 136 (**S3**), and 69 (**S4** and **S5**) ms. All of the values were much shorter than T_2 for PFMCH alone (3150 ms, in $CDCl_3$). In particular, **S4** and **S5** effectively shortened T_2 for PFMCH, i.e., reduced the guest mobility, indicating that **S4** and **S5** with long perfluorinated pendants tightly capture PFMCH within the cores. Among **S1**-**S5**, **S2** in turn gave relatively long T_2 for PFMCH. This clearly demonstrates that PFMCH is not so tightly bound with the 12FHpMA-based microgel owing to the less fluorous properties. The mobility for PFMCH (T_2: **S5** ~ **S4** < **S3** < **S1** < **S2**) decreased with increasing E_{ap} for the in-core perfluorinated pendants (E_{ap}: **S5** ~ **S4** > **S3** > **S1** > **S2**, Table 2). In contrast, the mobility of the in-core perfluorinated pendants in star polymers (T_2 values for the CF_3 or CHF_2 groups) was almost independent of a PFMCH guest molecule (Table 2 and 3).

Table 3

The encapsulation efficiency of PFMCH was quantitatively evaluated with the number of PFMCH solubilized in a single star polymer (N_{guest}). N_{guest} was calculated from the area ratio of the guest CF_3 signal (Figure 5) to the CF_3 or CF_2H signals of the in-core perfluorinated pendants by ^{19}F NMR, assuming that all of their ^{19}F signals were quantitatively observed: N_{guest} = 40 (**S1**), 80 (**S2**), 106 (**S3**), 250 (**S4**), and 260 (**S5**). The number of PFMCH bound by one R_FMA unit (N_{guest}/N_{RF}) was thus determined to be 0.24 (**S1**), 0.54 (**S2**), 0.64 (**S3**), 1.29 (**S4**), and 0.77 (**S5**) (Figure 6). This result reveals that the encapsulation efficiency is not only enhanced with the total fluorine atom numbers (**S1** < **S2** < **S3** < **S5**) but also with the tip CF_3 numbers (**S3** < **S4**). Actually, **S4** (1.29) was twice more effective per one R_FMA unit than **S3** (0.64), while the efficiency of **S4** per one CF_3 group was almost identical with that of **S3**. Thus, the accumulation of CF_3 group in microgels is also quite important for the encapsulation of large number of perfluorinated guests.

Figure 6

Various Guest Molecules. Next, **S3** and **S5** were applied to the encapsulation of various perfluorinated compounds including perflurooctane (PFO), perfluorohexane (PFH), methyl perfluorooctanoate (PFO-ester), methyl perfluoroheptyl ketone (PFHp-ketone), and 1*H*,1*H*-perfluoro-1-octanol (PFO-OH). These guests were mixed with **S3** or **S5** in DMF-d_7 for 24 h. PFO, PFH, PFO-ester, and PFO-ketone gave heterogeneous mixture (PFO and PFH: emulsion, PFO-ester, and PFO-ketone: dispersion), whereas PFO-OH did homogenous counterpart. The phase-separated, transparent supernatants or the homogenenous solution were analyzed by ^{19}F NMR (Figure 7).

Figure 7

In the presence of **S3**, the CF_3 peaks for PFO, PFH, and PFO-ester shifted to upfield and broadened, while those for PFHp-ketone and PFO-OH were still observed as triplet signals. This indicates that perfluorinated alkanes and the ester derivative are bound within **S3** core via fluorous interaction, whereas perfluorinated alkanes with ketone and alcohol functionality are freely mobile within and/or around **S3** because of their less fluorous properties originating from the polar functional groups (carbonyl, hydroxyl). In contrast, with the more fluorous core, **S5** made the CF_3 signal of PFHp-ketone broad, indicating the successful recognition of the guest (Figure 7d). Less recognition for PFO-OH with both **S3** and **S5** would be due to the originally high affinity of PFO-OH with DMF. These results reveal that fluorinated microgel star polymers can also encapsulate perfluorinated alkane derivatives with ester or ketone functional groups by enhancing the fluorous interaction.

Thermoresponsive Reversible Encapsulation and Release. We have already found that perfluorinated compounds can be released from perfluorinated microgel star polymers by the addition of good solvents for the guest compounds.[8,9] Here, we examined temperature-responsive, reversible encapsulation and release of PFMCH with **S3** in DMF-d_7 (Figure 8). PFMCH is known to have thermoresponsive solubility against organic solvents: i.e., the compound is miscible with them upon heating owing to reduced fluorous properties.[2] As already confirmed by ^{19}F NMR (up-field shift and broadening of CF_3: *a'* -70.6 ppm, Figure 8b), **S3** efficiently interacted with PFMCH in DMF-d_7 at 30 ^{o}C. Importantly, the correlation peak between PFMCH CF_3 group (*a*) and the CF_3 of the in-core perfluorinated unit (*b*) was clearly observed in ^{19}F nuclear Overhauser effect (NOE) difference spectrum (Figure 8c). This strongly supports that PFMCH is enclosed within **S3** core at 30 ^{o}C. Upon heating the solution to 60 ^{o}C, the CF_3 signal of PFMCH shifted to the original position (*a*: -70.3 ppm) and turned multiplet (Figure 8d); the NOE signal between PFMCH and in-core perfluorinated pendants also disappeared (Figure 8e). Thus, PFMCH was

released from the core at 60 °C. This is due to the reduced fluorophilicity of PFMCH upon heating. By cooling the solution to 30 °C, the released PFMCH was again encapsulated into **S3** core, as confirmed by ^{19}F NMR (Figure 8f). Similarly to **S3**, **S5** also showed such a thermoresponsive release of PFMCH upon heating. Thus, independently of the in-core fluorophilicity, fluorinated microgel star polymers, **S3** and **S5**, successfully realized the temperature-dependent, reversible encapsulation and release of PFMCH in DMF.

Figure 8

Conclusions

We successfully created fluorinated microgel star polymers as fluorous nanocapsules for the encapsulation and release of polyfluorinated guest compounds. Five kinds of star polymers with different fluorous cores were efficiently prepared in high yield via the ruthenium-catalyzed linking reaction of PMMA-Cl with a perfluorinated linking agent (12FODMA) in the presence of perfluorinated alkyl monomers (R_FMA); R_FMA consists of different perfluorinated pendants (the number of the carbon and fluorine atoms and CF_3 group, the tip structure of the pendants: CF_3 vs. CHF_2). ^{19}F T_2 measurements of star polymers revealed that the mobility of the in-core perfluorinated units decreased with increasing the fluorous properties: i.e., the number of fluorine substitution and CF_3 group in R_FMA unit. Core-fluorinated star polymers efficiently encapsulated perfluorinated alkanes and the derivatives with ester or ketone functionality in DMF. The efficiency increased with increasing the number of fluorine substitution and CF_3 group in the in-core R_FMA units. Additionally, a fluorinated star polymer successfully afforded the reversible encapsulation and release of a perfluorinated guest by changing temperature. Thus, star polymers developed herein would be useful as temperature-responsive fluorous nanocapsules for the encapsulation, separation, and delivery of various perfluorinated compounds.

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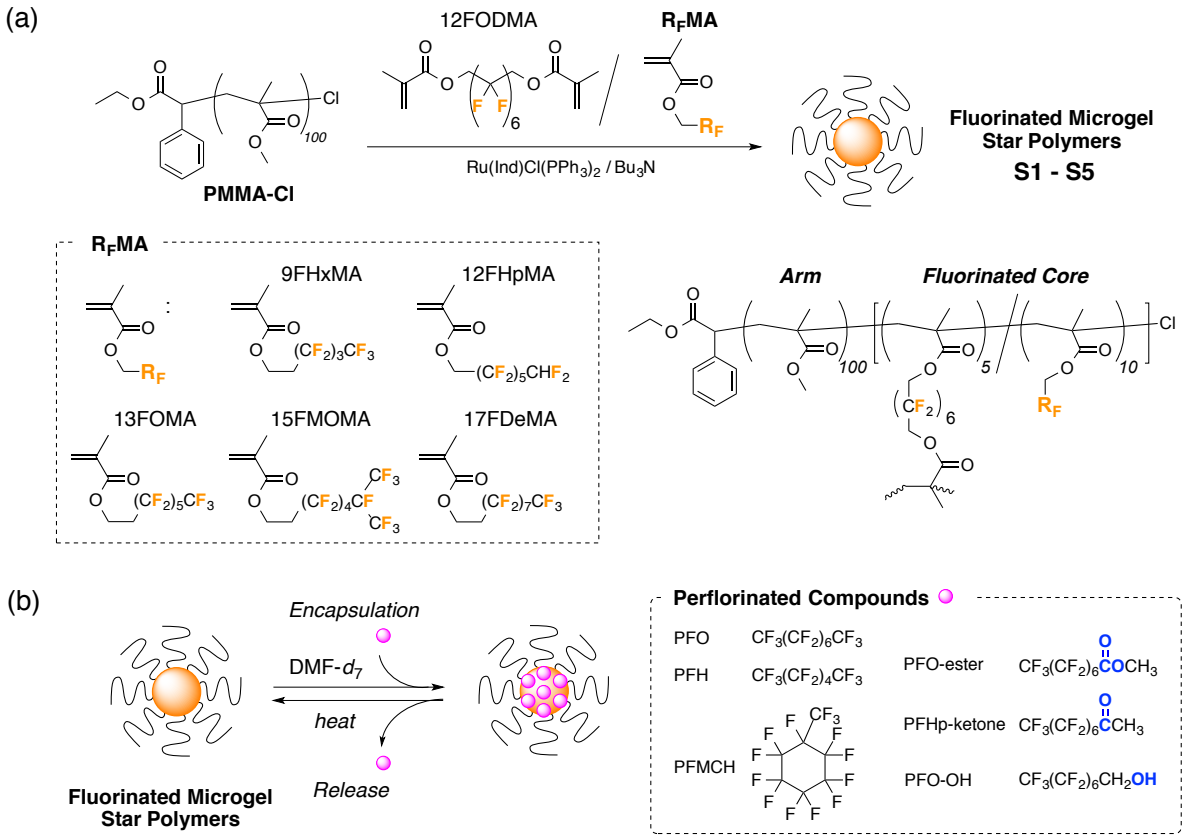

Scheme 1. (a) Synthesis of fluorinated microgel star polymers (**S1**-**S5**) via ruthenium-catalyzed living radical polymerization and (b) encapsulation and release of perfluorinated compounds with fluorinated star polymers.

Table 1. Characterization of Fluorinated Microgel Star Polymers[a]

Code	R_FMA	Time [h]	Conversion[b] (12FODMA/R_FMA) %	Yield[c] %	M_w[d] (SEC)	M_w/M_n[d] (SEC)	M_w[e] (MALLS)	N_{arm}[f]	N_F[g]	N_{CF3}[h]	N_{RF}[i]	R_g[e] [nm]
S1	9FHxMA	18	90/79	78	141000	1.24	461000	23	2970	177	177	13
S2	12FHpMA	18	85	77	141000	1.24	399000	19	2810	0	150	23
S3	13FOMA	23	89/79	71	155000	1.20	393000	21	3260	165	165	21
S4	15FMOMA	19	89/79	76	144000	1.22	509000	25	4220	388	194	18
S5	17FDeMA	18	90/82	73	200000	1.17	954000	42	8070	343	343	21

[a] **S1-S5** was prepared by ruthenium-catalyzed linking reaction of PMMA-Cl (**S1**, **S2**, **S4**, **S5**: M_n = 12000, M_w/M_n = 1.13; **S3**: M_n = 10500, M_w/M_n = 1.14) with 12FODMA and R_FMA: [PMMA-Cl]$_0$/[12FODMA]$_0$/[R_FMA]$_0$/[Ru(Ind)Cl(PPh_3)$_2$]$_0$/[*n*-Bu_3N]$_0$ = 17/85/170/1.7/17 mM in toluene at 80 °C; m = [12FODMA]$_0$/[PMMA-Cl]$_0$ = 5; n = [R_FMA]$_0$/[PMMA-Cl]$_0$ = 10.

[b] Monomer conversion determined by ^{1}H NMR with internal standard (tetralin). **S2**: total monomer conversion.

[c] Yield of star polymers in products, calculated from the SEC curve area ratio.

[d] Weight average molecular weight (M_w) and molecular weight distribution (M_w/M_n) determined by SEC in THF with PMMA calibration (**S1-S5**: purified by preparative SEC).

[e] Absolute weight average molecular weight [M_w (MALLS)] and radius of gyration (R_g) determined by SEC-MALLS in DMF (10 mM LiBr).

[f] Arm numbers per a star polymer: N_{arm} = (weight fraction of arm polymers) × M_w (MALLS)/$M_{w,arm}$ (SEC).

[g] Fluorine atom numbers in a polymer: $N_F = N_{arm} \times \{12 \times m \times (\text{conv.}/100) + (\text{the number of F in a monomer}) \times n \times (\text{conv.}/100)\}$.

[h] Pendant CF_3 group numbers in a polymer: $N_{CF3} = N_{arm} \times (\text{the number of } CF_3 \text{ in a monomer}) \times n \times (\text{conv.}/100)\}$.

[i] Pendant R_F group numbers in a polymer: $N_{RF} = N_{arm} \times n \times (\text{conv.}/100)\}$.

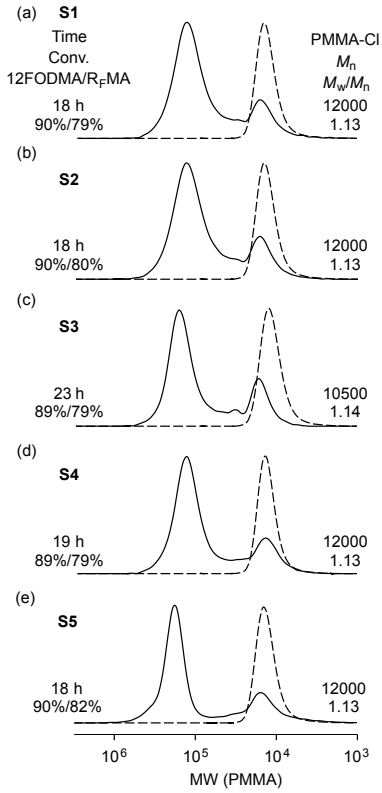

Figure 1. SEC curves of (a) **S1**, (b) **S2**, (c) **S3**, (d) **S4**, and (e) **S5** obtained from $Ru(Ind)Cl(PPh_3)_2/Bu_3N$-catalyzed linking reaction of PMMA-Cl with 12FODMA and R_FMA (a: 9FHxMA, b: 12FHpMA, c: 13FOMA, d: 15FMOMA, e: 17FDeMA) in toluene at 80 ^oC. Monomer feed ratio: $[PMMA\text{-}Cl]_0/[12FODMA]_0/[R_FMA]_0 = 1/5/10$.

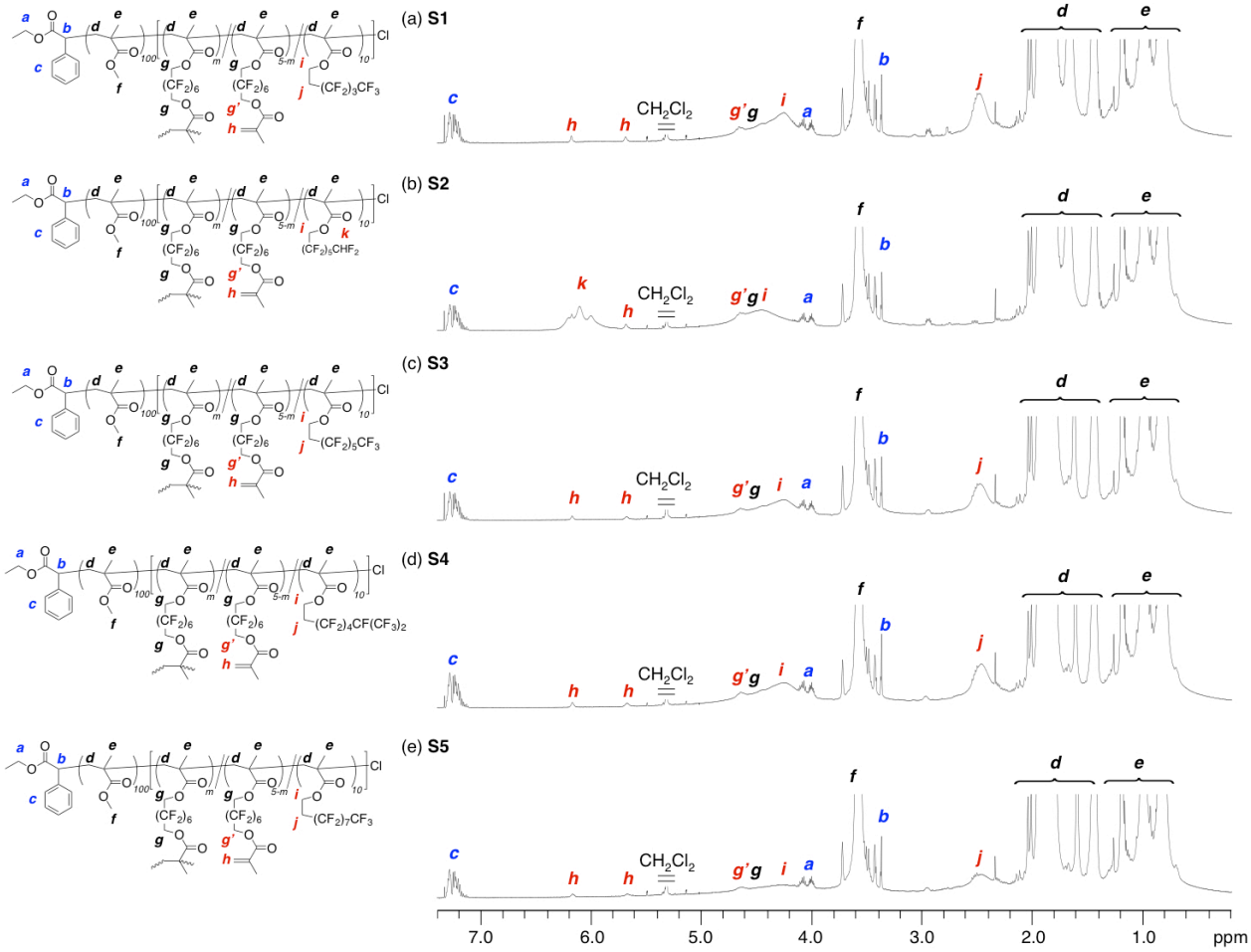

Figure 2. ^{1}H NMR (500 MHz) spectra of (a) **S1**, (b) **S2**, (c) **S3**, (d) **S4**, and (e) **S5** ([star] = 50 mg/mL) in CD_2Cl_2 at 30 ^{o}C.

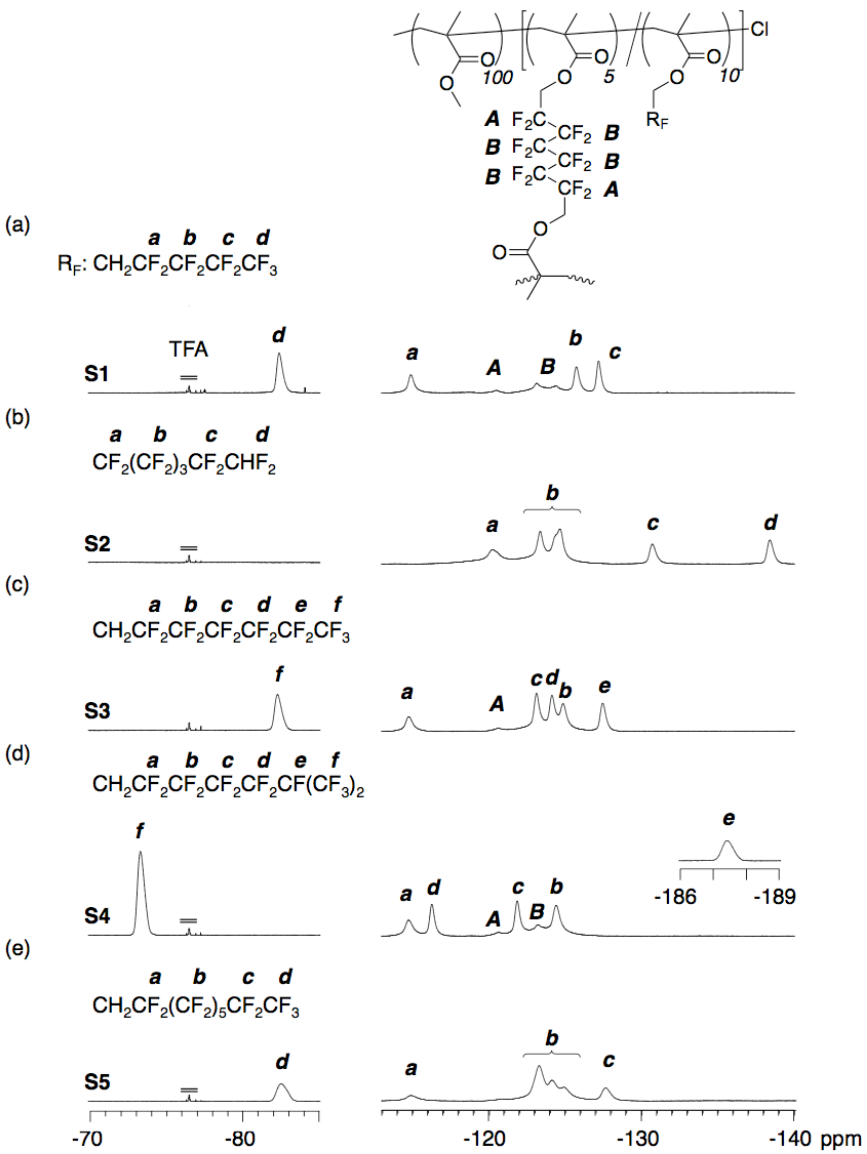

Figure 3. ^{19}F NMR (470 MHz) spectra of (a) **S1**, (b) **S2**, (c) **S3**, (d) **S4**, and (e) **S5** ([star] = 50 mg/mL) in $CDCl_3$ at 30 ^{o}C (TFA: trifluoroacetic acid, δ = -76.5 ppm).

Table 2. T_2 and E_{ap} of In-Core Perfluorinated Pendants in Star Polymers

Entry	Polymer	T_2 [ms] (30 °C)	E_{ap} [b] [kJ/mol]
1	**S1**	16	33
2	**S2**	20	26
3	**S3**	7.0	39
4	**S4**	5.4	44
5	**S5**	2.6	44

[a] ^{19}F T_2 values of the in-core CF_3 groups for **S1**-**S5** in DMF-d_7 at 30 °C.

[b] Apparent activation energy for molecular motion (E_{ap}): determined from the slope of Arrhenius plots of the ^{19}F T_2 values for the in-core CF_3 groups for **S1**-**S5** in DMF-d_7.

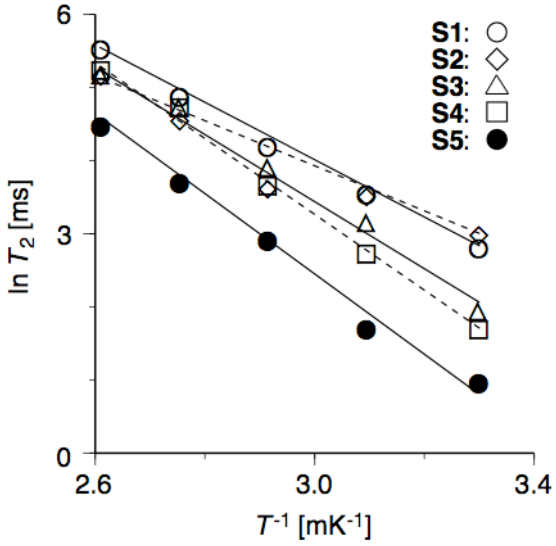

Figure 4. Arrhenius plots of ^{19}F T_2 values of the terminal CF_3 or CHF_2 groups for **S1** (open circle), **S2** (open rhombus), **S3** (open triangle), **S4** (open square), and **S5** (filled circle) determined in DMF-d_7 at 30, 50, 70, 90, and 110 ^{o}C.

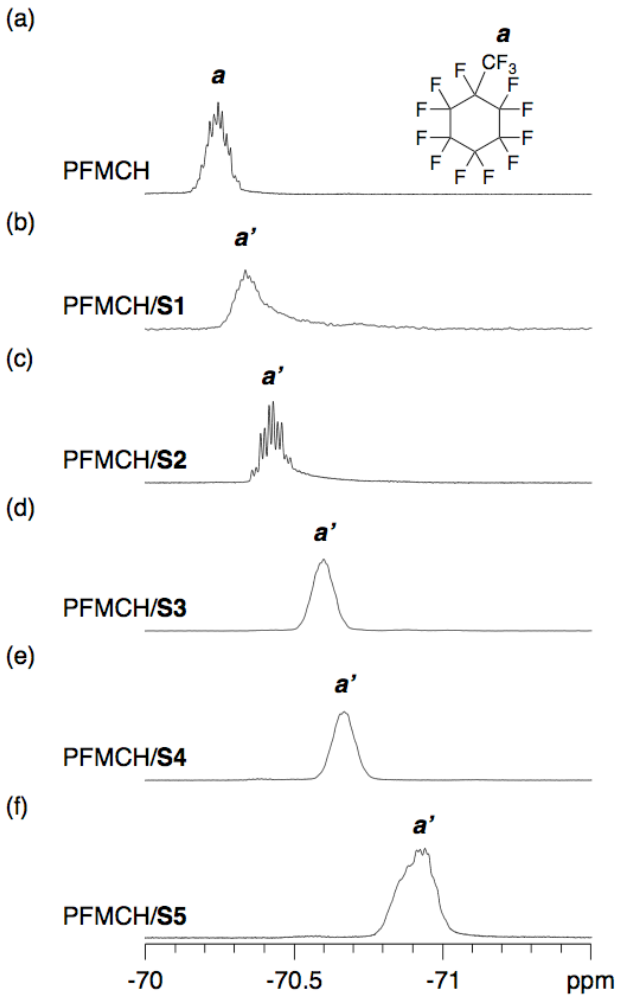

Figure 5. ^{19}F NMR (470 MHz) spectra of (a) PFMCH alone and (b-f) PFMCH with **S1**-**S5** (b: **S1**, c: **S2**, d: **S3**, e: **S4**, f: **S5**): [**S1**-**S5**] = 50 mg/mL in DMF-d_7 at 30 ^{o}C.

Table 3. Encapsulation of PFMCH into Fluorinated Microgel Star Polymers

Polymer	T_2 (PFMCH)[a] [ms]	T_2 (Core)[b] [ms]	N_{guest}[c]	Efficiency[d] (N_{guest}/N_{RF})
S1	177	15	40	0.24
S2	472	24	80	0.54
S3	136	8.2	106	0.64
S4	69	5.6	250	1.29
S5	69	7.4	260	0.77

[a] ^{19}F T_2 of the CF_3 groups for PFMCH with **S1**-**S5** in DMF-d_7 at 30 °C. PFMCH alone in $CDCl_3$ at 30 °C: T_2 = 3150 ms.

[b] ^{19}F T_2 of the in-core CF_3 groups for **S1**-**S5** with PFMCH in DMF-d_7 at 30 °C.

[c] The number of PFMCH encapsulated within a star polymer in DMF-d_7.

[d] Encapsulation efficiency of PFMCH per an in-core R_fMA unit: N_{guest}/N_{RF} (N_{RF}: see Table 1).

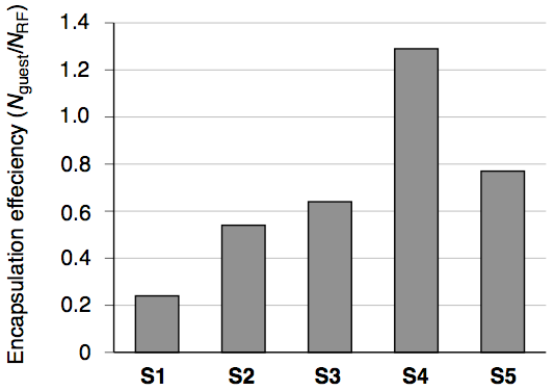

Figure 6. Encapsulation efficiency (N_{guest}/N_{RF}) of PFMCH into **S1**-**S5** per an in-core R_FMA unit in DMF-d_7 at 30 ^{o}C.

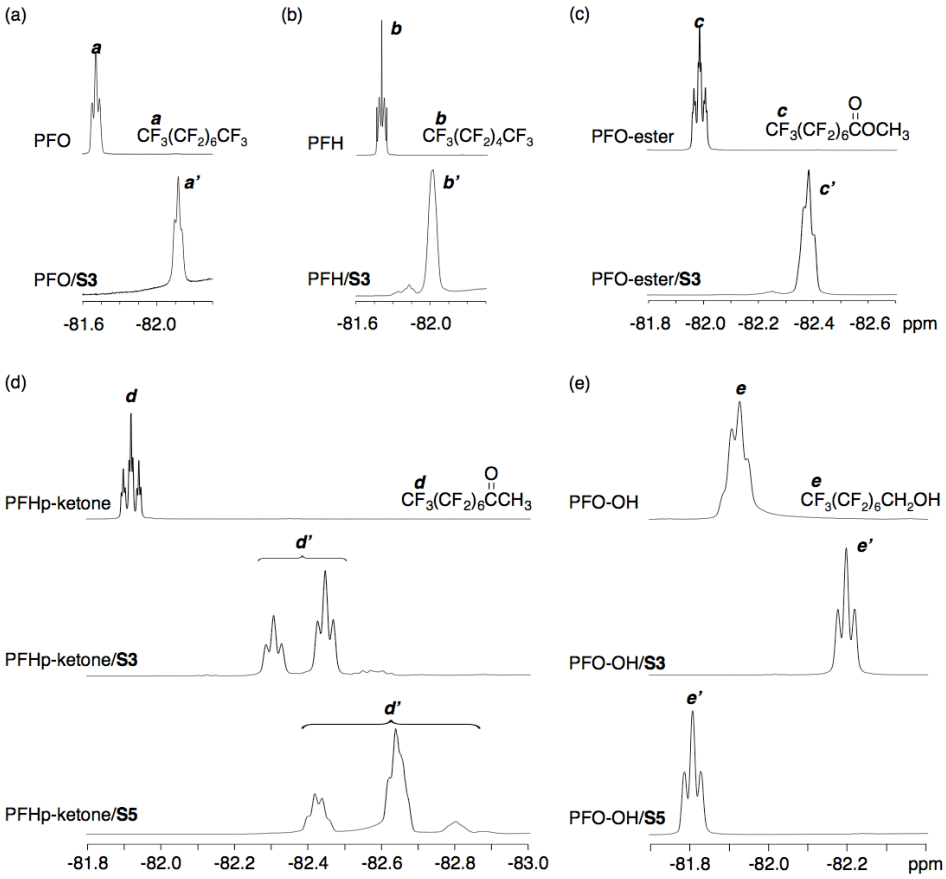

Figure 7. ^{19}F NMR (470 MHz) spectra of polyfluorinated guests (a: PFO, b: PFH, c: PFO-ester, d: PFHp-ketone, e: PFO-OH) with **S3** or **S5**: [**S3** or **S5**] = 50 mg/mL in DMF-d_7 at 30 ^{o}C.

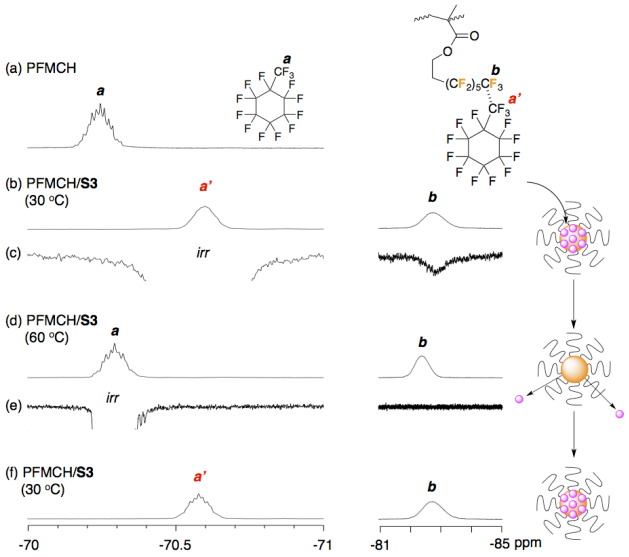

Figure 8. ^{19}F NMR (470 MHz) spectra of (a) PFMCH alone in DMF-d_7 at 30 °C and PFMCH with **S3** in DMF-d_7 at (b, f) 30 and (d) 60 °C. ^{19}F nuclear Overhauser effect (NOE) difference spectra of PFMCH with **S3** in DMF-d_7 at (c) 30 and (e) 60 °C.

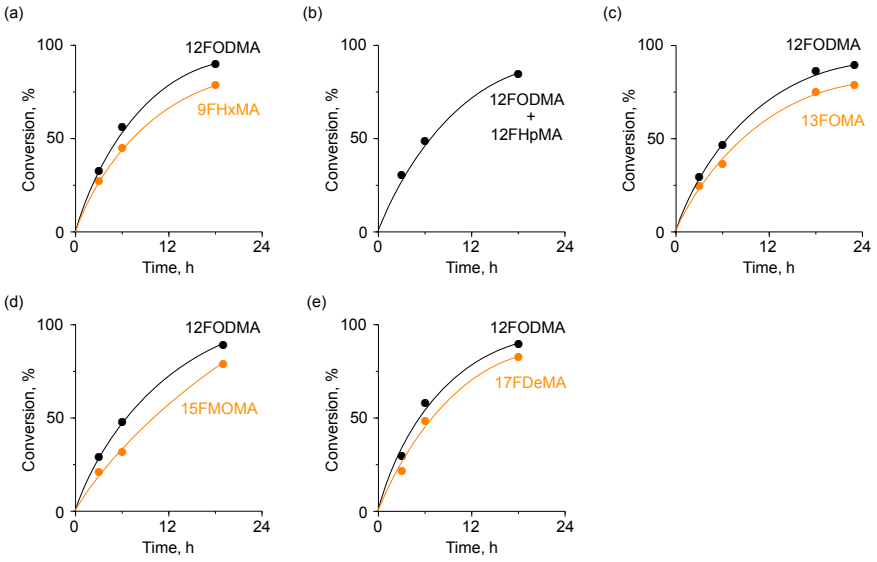

Figure S1. Time-conversion curves in the linking reaction of PMMA-Cl arms with 12FODMA (**1**) and R_fMA (a: 9FHxMA b: 12FHpMA c: 13FOMA, d: 15FMOMA, e: 17FDeMA) for (a) **S1**, (b) **S2**, (c) **S3**, (d) **S4**, and (e) **S5**.