Articles

Core-Functionalized Star Polymers by Transition Metal-Catalyzed Living Radical Polymerization. 2. Selective Interaction with Protic Guests via Core Functionalities[1]

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ABSTRACT: Core-functionalized star-shaped polymers consisting of linear poly(methyl methacrylate) arms and a microgel core with functional groups were found to act as efficient hosts for selective interaction with small organic molecules as guests. For example, star polymer **1** with an amide-functionalized core ($M_w = 1.21 \times 10^3$; DP(arm) = 100; 71 arms/molecule; −NH−CO− in the core) could interact with benzoic acid, benzyl alcohol, and benzylamine, whereas such interaction was absent with acetophenone, ethyl benzoate, and amylbenzene, indicating that the interaction stems from hydrogen bonding between the host's amide core and the guest. Thus, polymer **1** specifically interacts with benzoic acid in an equimolar mixture of the acid and its ethyl ester. The host−guest interaction is inhibited by polar solvents such as DMF and by acids like CF_3CO_2H.

Introduction

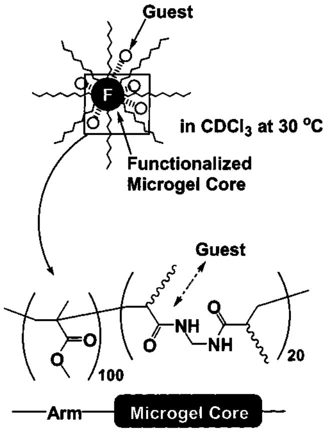
Quite recently, we have reported the synthesis of "core-functionalized" star polymers via our ruthenium-mediated living radical polymerization.[2] This is based on the microgel or polymer-linking method in which linear living polymers are allowed to react with a small amount of a bifunctional monomer (divinyl compound; linking agent) to form star-shaped polymers. Those polymers consist of a microgel "core" from the linking agent and "arms" from the living chains that are radially attached to the core.

In addition to other living polymerizations,[3] we have already shown that our metal-catalyzed living radical polymerization, with selected linking agents, provides efficient methods for such star polymer synthesis.[4]

The "core-functionalized" star polymers are, in our view, an interesting family of stars via a microgel methodology, where the linking agent is a functionalized divinyl compound such as bis(acrylamide). These linking agents therefore give a microgel core in which a large number of polar functionalities, like amides, hydroxyl, etc., are concentrated in a relatively small nanoscale gel network; a fairly large number of linear arms are attached to the functional core.

The high concentration and confinement of functional groups are features that differentiate the core-functionalized star polymers from other stars where functionalities are mostly placed within the linear arms and/or the arm's terminals. In particular, we expect that these polar groups might exhibit unique functions such as host−guest interaction and molecular recognition via core functionalities.

Scheme 1. Host−Guest Interaction between Core-Functionalized Star Polymer and Low Molecular Weight Compounds



Herein we report that the amide−core star polymer **1** undergoes selective host−guest interaction with such guest compounds as benzoic acid which carry a polar functional group for hydrogen bonding with the core−amide groups. Similar interactions by star polymers have been reported, but mostly those are via functionalities in the arm chains.[5]

Results and Discussion

Host−Guest Interaction with Benzoic Acid. (a) Samples and Analysis Conditions. Possible host−guest interaction by star polymers was first examined with benzoic acid (**A**) as the guest. As potential hosts were employed, a series of star and linear polymers **1**−**6** are shown in Figure 1.

Table 1 shows their characterization data. The three star polymers (**1**−**3**) are all core-functionalized versions[2]

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Table 1. Characterization of Host Polymers[a]

code	shape	structure[b]	M_w (SEC)[c] ($\times 10^{-3}$)	M_w (MALLS)[d] ($\times 10^{-3}$)	M_w/M_n (SEC)	f[e]
1	star	$[(MMA)_{100}]_{arm}-[(MBAA)_{20}]_{core}$	243	1210	1.46	71
2	star	$[(MMA)_{100}]_{arm}-[(EGDMA)_{20}]_{core}$	233	2650	1.22	141
3	star	$[(MMA)_{100}]_{arm}-[(EGDMA)_{20}]_{core}$	148	434	1.34	24
4	linear	$(MMA)_{100}$	11.5		1.28	
5	linear	$(MMA)_{100}-(DMAA)_{20}$	15.9		1.44	
6	linear	$(NIPAM)_{100}$	24.4		1.44	

[a] See also Figure 1 for polymer structures. [b] MMA = methyl methacrylate; MBAA = *N*,*N*′-methylenebis(acrylamide); GDMA = glycerol dimethacrylate; EGDMA = ethylene glycol dimethacrylate; DMAA = *N*,*N*-dimethylacrylamide; NIPAM =*N*-isopropylacrylamide. [c] SEC = size exclusion chromatography. [d] MALLS = multiangle laser light scattering. [e] The number of arms per molecule.

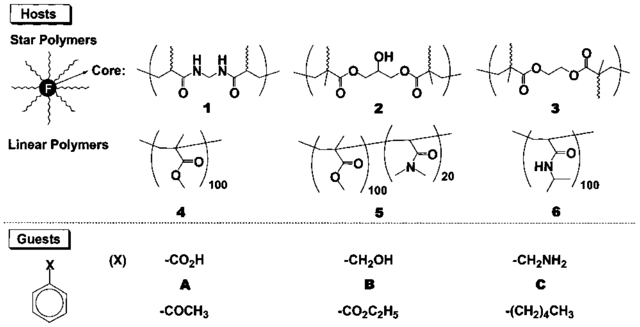


Figure 1. Host and guest molecules employed in this work. Hosts: (**1**−**3**) star polymers with PMMA arms and different cores as shown; (**4**) linear PMMA; (**5**) MMA−DMAA block copolymer. Guests (substituted benzene): (**A**−**C**) protic compounds; (**D**−**F**) aprotic compounds.

with the identical poly(MMA) arm chains (DP = 100), prepared under the same conditions, [arm chain]$_0$/[linking agent]$_0$ = 1/20 mole ratio, as designated in Table 1 as, for example, $[(MMA)_{100}]_{arm}-[(MBAA)_{20}]_{core}$ (MBAA: *N*,*N*′-methylenebis(acrylamide)). However, their core functions (**1**, amide; **2**, hydroxyl + ester; **3**, ester), total molecular weights [M_w(MALLS)], and the arm number (*f*) vary from one to another.

Polymers **4** and **5** mimic respectively the single arm chain $[(MMA)_{100}]$ and the arm core unit for **1** $[(MMA)_{100}]_{arm}-[(MBAA)_{20}]_{core}$, though the amide functions in **5** differ from those in **1**. Polymer **6** is a linear polymer with amide function and a free hydrogen, which mimics the core functions in **1**. Throughout this work, these samples were employed for the analysis of host−guest interactions to be described herein.

The interaction between benzoic acid (guest **A**) and these host polymers was examined by two methods: ^{1}H NMR spectroscopy on the guest's aromatic protons and ^{13}C NMR on the spin−lattice relaxation time (T_1) by the ortho carbon of **A**. Unless otherwise specified, the forthcoming condition held: [guest] = 0.60 M; [guest]/[core functional group in the host] = 4 (mole ratio); in $CDCl_3$ solvent at 30 °C. Thus, the host polymer concentration was determined so as to keep the [guest]/[core function] ratio the same for all the guest−host mixtures. [**1**] = 49.42 g/L, and the same polymer concentration was used for its linear mimics **4**, **5**, and **6**.

The expected host−guest interaction will reduce the thermal movement of the guest, hereby broadening its ^{1}H NMR signals and also decreasing its ^{13}C NMR T_1 values.[5]

(b) Star 1 vs Linear Polymers. To examine the effects of the host structures, the star (**1**) and linear polymers (**4**−**6**) were utilized (Figure 2). In the absence of hosts, **A** showed three sets of sharp absorptions (7.5−8.3 ppm) in the aromatic protons region (Figure 2A), whereas in the presence of **1**, all of them clearly broadened (Figure 2E). However, such changes were absent for the mixtures with the linear poly(MMA) (**4**) (Figure 2B) and the linear MMA−DMAA block copolymer (**5**) (Figure 2C) and the linear poly(NIPAM) (**6**) (Figure 2D).[7]

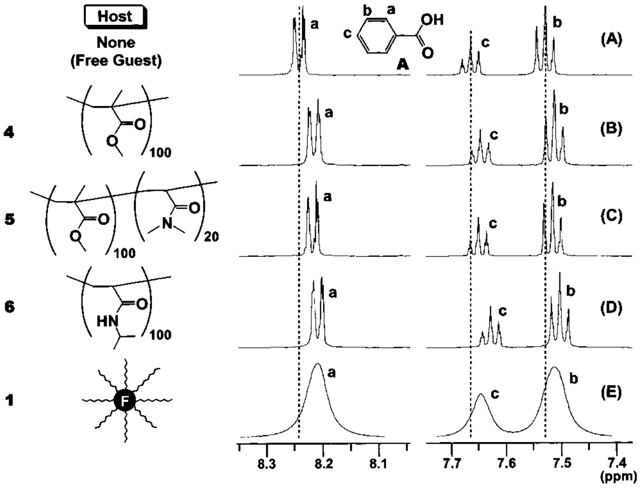


Figure 2. Interaction of benzoic acid (**A**) with varying guests: ^{1}H NMR spectra in the absence or presence of guest polymers in $CDCl_3$ at 30 °C: [**A**] = 0.6 M; [polymer] = 49.42 g/L; [**A**]/[−NHCO− in **1**] = 4. (A) **A** alone; (B) **A** with linear poly(MMA) **4**; (C) **A** with linear MMA−DMAA block copolymer **5**; (D) **A** with linear poly(NIPAM) **6**; (E) **A** with core amide-functionalized star polymer **1**.

Table 2. ^{13}C NMR Spin−Lattice Relaxation Time (T_1) of the Ortho Carbon for Benzoic Acid (A) in the Presence and the Absence of Host Polymers[a]

host	(code)	T_1, s
none		3.01
star	**1**	2.23
	2	2.40
	3	2.78
linear	**4**	3.09
	5	2.72

[a] The T_1 values for the ortho carbon of benzene-substituted guests in $CDCl_3$ at 30 °C: [**A**] = 0.60 M; [polymer] = 49.42 g/L; [**A**]/[−NHCO− in **1**] = 4. See Figure 1 and Table 1 for the structures of the host polymers.

These trends were also observed in the T_1 values of benzoic acid (**A**) (Table 2). Thus, T_1 was 3.01 s in the absence of the hosts, whereas it clearly decreased in the mixture with the core-functionalized star polymer (**1**) or the linear block copolymer (**5**) (2.23 and 2.72 s, respectively). In contrast, with the linear poly(MMA)s (**4**) T_1 remained nearly unchanged.

These results demonstrated that the amide-core star **1** effectively capture benzoic acid. Such interaction is absent with the arm PMMA alone (**4**) and is nearly absent or very weak with the block polymer (**5**), indicat-

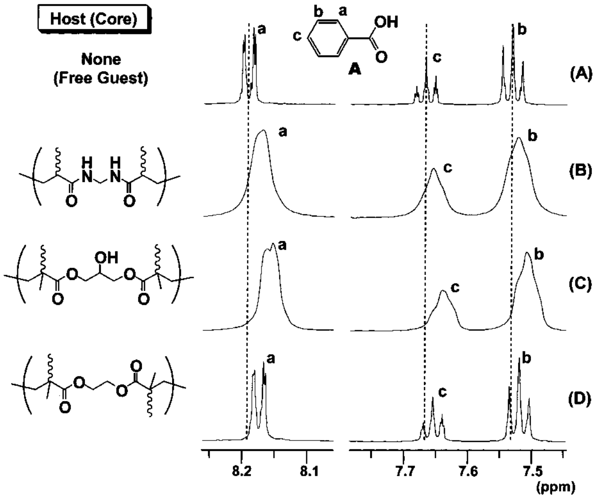


Figure 3. Effects of core functionalities on guest recognition: ^{1}H NMR spectra of benzoic acid (**A**) in the absence or presence of various core-functionalized star polymers (**1**−**3**) in $CDCl_3$ at 30 °C: [**A**] = 0.60 M; [**1**] = 49.42 g/L; [**2**] = 111.5 g/L; [**3**] = 53.3 g/L; [**A**]/[functional group in the core] = 4. (A) **A** alone; (B) **A** with amide-core star **1**; (C) **A** with hydroxyl-core star **2**; (D) **A** with ester-core star polymer **3**.

ing the concentrated amide functions in the core are critically important.

Effects of the Core Functions. Figure 3 shows ^{1}H NMR spectra of **A** in the presence of the three star polymers with various core-functional groups (**1**−**3**). The sharp aromatic peaks of **A** (Figure 3A) clearly broadened with **1** and **2** (Figure 3B,C), whereas such changes were absent with **3** (Figure 3D).

As seen in Table 2, the star polymers **1**−**3** decreased the T_1 of **A** in the order (none) > **3** > **2** > **1**, again indicating that as the core-function amides are the best among the three, followed by hydroxyl, and that the methacrylate esters are much less effective, either in the core (as in **3**) or in the linear chains (arms).

The above-described results demonstrated (i) that the core-functionalized star polymers **1** and **2** undergo effective interaction with benzoic acid; (ii) that the interaction occurs through the amide (or hydroxyl) functionality in the core, i.e., the core-functionalized star polymers are more effective than the linear counterparts (**4** and **5**); and (iii) that, as core function, amides are most effective: amide > hydroxyl ≫ ester.

Effects of Functional Groups of Guest Compounds. In addition to benzoic acid (**A**), related benzene derivatives (**B**−**F**) were employed as potential guests to examine the guest specificity of the interactions with the amide-core star polymer **1**. The six guests consisted of two class: benzoic acid (**A**), benzyl alcohol (**B**), and benzylamine (**C**), with protic groups; acetophenone (**D**), ethyl benzoate (**E**), and amylbenzene (**F**), with aprotic groups. Figures 4 and 5 show their ^{1}H NMR spectra (the aromatic regions) in the presence and absence of the host **1**, and Table 3 shows relevant T_1 data.

For **A**−**C** (with protic groups) the ^{1}H NMR absorptions clearly broadened with **1** (e.g., Figure 4, A vs B), and the ortho carbon T_1 was considerably reduced in the presence of **1**. For **D**−**F** with aprotic groups, on the other hand, such changes in ^{1}H NMR, and the T_1 values were absent (Figure 5 and Table 3).

These results indicate that for the efficient interactions with the core amide star polymer, guests have such protic groups as carbonyl (**A**), alcohol (**B**), or amine (**C**), which can form hydrogen bonding with the amide groups in the core.

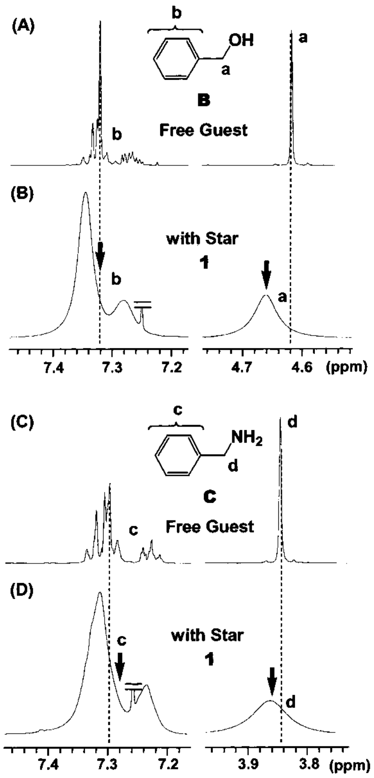


Figure 4. Interaction of benzyl alcohol (**B**) and benzylamine (**C**): ^{1}H NMR spectra of guests in the absence or presence of amide-core star polymer **1** in $CDCl_3$ at 30 °C: [guest] = 0.60 M; [**1**] = 49.42 g/L; [guest]/[−NHCO− in **1**] = 4. (A) **B** alone; (B) **B** with star **1**; (C) **C** alone; (D) **C** with star **1**.

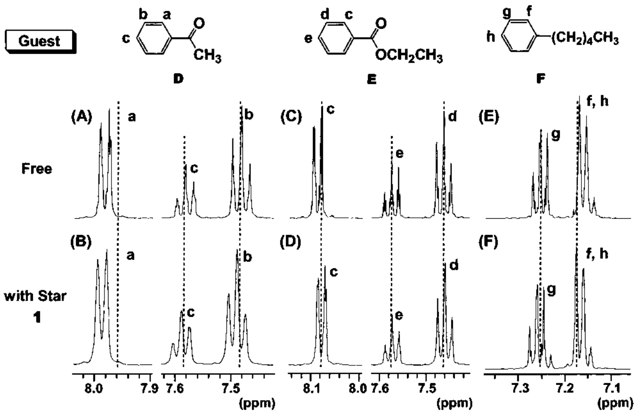
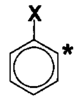


Figure 5. ^{1}H NMR spectra of various aprotic guests (**D**−**F**) in the absence or presence of amide-core star polymer **1** in $CDCl_3$ at 30 °C: [guest] = 0.60 M; [**1**] = 49.42 g/L; [guest]/[−NHCO− in **1**] = 4. (A, C, E) guest alone; (B, D, F) guests with star **1**.

Selective Host−Guest Interaction. Core amide-functionalized star polymer was found to strongly interact only with protic polar guests **A**−**C**. This specificity further suggests that the polymer **1** could recognize a protic polar guest over structurally similar but aprotic compounds. Thus, an equimolar mixture of benzoic acid (**A**) and its ester, ethyl benzoate (**E**), was examined (Figure 6 and Table 4).

In the absence of **1**, the mixture showed sharp and well-resolved six sets of absorptions, a−c for benzoic acid (**A**) and d−f for the ethyl ester (**E**) (Figure 6A). Upon

Table 3. ^{13}C NMR Spin–Lattice Relaxation Time (T_1) of the Ortho Carbons for Monosubstituted Benzenes in the Presence and the Absence of Star Polymer 1[a]

Compound (Guest)	–X (Code)	T_1, sec	
		Free Guest	With 1
	–CO$_2$H (**A**)	3.01	2.23
	–CH$_2$OH (**B**)	9.21	4.63
	–CH$_2$NH$_2$ (**C**)	10.2	4.05
	–COCH$_3$ (**D**)	7.47	6.38
	–CO$_2$C$_2$H$_5$ (**E**)	4.98	4.74
	–(CH$_2$)$_4$CH$_3$ (**F**)	6.38	6.48

[a] The T_1 values in CDCl$_3$ at 30 °C: [guest] = 0.60 M; [**1**] = 49.42 g/L; [guest]/[–NHCO– in **1**] = 4.

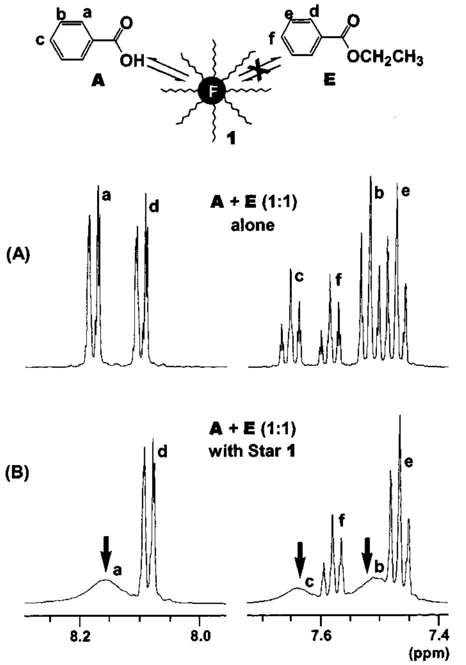
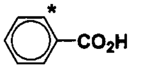
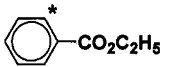


Figure 6. Molecular recognition of benzoic acid (**A**) over ethyl benzoate (**E**) by amide-core star **1**: ^{1}H NMR spectra of an equimolar mixture of **A** and **E** in the absence and the presence of **1** in CDCl$_3$ at 30 °C: [**A**] = [**E**] = 0.60 M; [**1**] = 49.42 g/L; [**A**]/[**E**]/[–NHCO– in **1**] = 4/4/1.

Table 4. Selective Host–Guest Interaction by Star Polymer 1 in an Equimolar Mixture of Benzoic Acid (A) and Ethyl Benzoate (E)[a]

Host	T_1 for Guest Pair, sec	
	 (A)	 (B)
none	3.04	4.56
with 1	1.90	4.85

[a] The T_1 values for the ortho carbon of benzene-substituted guests in CDCl$_3$ at 30 °C: [**A**] = [**E**] = 0.60 M; [**1**] = 49.42 g/L; [guest]/[–NHCO– in **1**] = 4/4/1.

addition of the host, only the three signals of **A** broadened, while those of **E** remained almost as sharp and well-resolved as in the absence of **1** (Figure 6B). Similarly, the T_1 of **A** was shortened by **1** but not for ester version **E** (Table 4).

Thus, even in a homogeneous mixture of guests, the amide-core star **1** apparently recognizes a polar hydrogen-bonding compound over a nonpolar counterpart with a similar shape and structure.

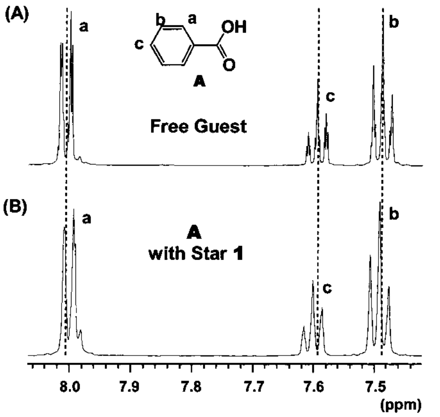


Figure 7. Effects of DMF-d_7 on the host–guest interaction: ^{1}H NMR spectra of benzoic acid **A** in the absence or presence of amide-core star polymer **1** in DMF-d_7 at 30 °C: [**A**] = 0.60 M, [**1**] = 49.42 g/L; [**A**]/[–NHCO– in **1**] = 4.

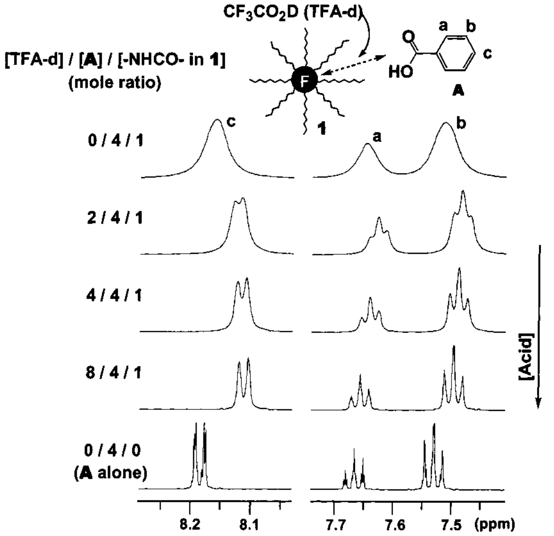


Figure 8. ^{1}H NMR spectra of benzoic acid **A** with amide-core star **1** in the absence or presence of TFA-*d* in CDCl$_3$ at 30 °C: [**A**] = 0.60 M; [**1**] = 49.42 g/L; [**A**]/[–NHCO– in **1**] = 4; [TFA-*d*] as indicated.

Nature of the Host–Guest Interaction: Hydrogen Bonding. The selective interaction induced by star **1** seems to involve hydrogen-bonding interaction, because of the effectiveness of amides in the core and carboxylic acid and amine as the guest. To verify this, two sets of experiments were performed.

(A) Effects of DMF. Polar solvents such as DMF and DMSO are known to break hydrogen bonds. As shown in Figure 7, the interaction between **1** and benzoic acid is indeed interfered by adding DMF-d_7 into their mixture. No broadening of the guest aromatic signals was detected by ^{1}H NMR under the conditions where a clear broadening with **1** occurred (cf. Figure 3B).

(B) Effects of Trifluoroacetic Acid. As another hydrogen bond breaker, deuterium trifluoroacetic acid (TFA-*d*) was utilized to examine the host–guest interaction at various pH in the mixture of **1** and **A** (Figure 8). ^{1}H NMR spectra showed that as the amounts of the TFA-*d* increased, the peak shapes of **A** were increasingly sharpened from the broad peaks without the acid added and with excess acid the signals are very similar to those of **A** free from both **1** and TFA-*d*.

Additionally, as the concentration of TFA-*d* increased, the T_1 values also increased from 2.23 to 4.34 s, which finally exceed the T_1 (3.01 s) for alone.

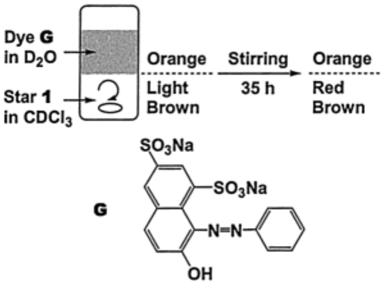


Figure 9. Extraction of a hydrophilic dye (**G**) in D_2O by amide-core star **1** in $CDCl_3$ at 80 °C: $[\mathbf{G}]_0 = 0.10$ M; [**1**] = 33 g/L; [−NHCO− in **1**] = 0.10 M.

These results indicate that the hydrogen bond interaction between the amide groups of **1** and benzoic acid (and also that among the latter molecules) is effectively broken.

Extraction of a Hydrophilic Dye. The star polymer **1** consisted of hydrophobic poly(MMA) arms and the microgel core with hydrophilic amide groups. Therefore, star polymer **1** is soluble only in organic solvents such as toluene, chloroform, DMF, etc., and insoluble in water and related aqueous media, but its structure indicates that the polymer would be amphiphilic in nature, given the hydrophilic amide core. This further suggests that **1** could extract hydrophilic substances in an aqueous phase into an organic phase by the host−guest interaction between the amide groups and the substances in aqueous phase.

We thus examined possible liquid−liquid extraction of orange G (**G**, an hydrophilic dye) from water into $CDCl_3$ containing polymer **1** as an extractant (Figure 9). For control runs, extraction with pure $CDCl_3$ and with a $CDCl_3$ solution of linear poly(MMA) was also carried out.

A dark orange solution of **G** (0.10 M) in D_2O was brought into contact with a solution of **1** in $CDCl_3$ ([−NHCO− in **1**] = 0.10 M; 33 g/L; colored light brown due to some catalyst residue in **1**). The two-phase system was then mixed vigorously for 35 h at 80 °C and was allowed to stand at room temperature so as to phase-separate once again. The organic phase turned intense red, showing a part of **G** in the aqueous phase was transferred into the organic phase. ^{1}H NMR analysis indicated 12.5% of dye was extracted.

Such a liquid−liquid extraction did not occur with pure $CDCl_3$ or with the solution of the linear PMMA with similar molecular weight of **1** ($M_w = 1.2 \times 10^6$; $M_w/M_n = 1.04$; 33 g/L). These results indicate that the extraction is via the amide core in polymer **1**.

Conclusions

Functionalized star poly(MMA)s (**1** and **2**) with amide or hydroxyl groups in their microgel core were found to serve efficient host molecules that interact with benzoic acid and other polar guest molecules. The interaction is selective and specific for organic molecules that carry hydrogen-bonding substituent such as carboxylic acid, and **1** could recognize benzoic acid from its ester in their equimolar mixture.

Experimental Section

Materials. All samples of the core-functionalized star poly(MMA)s (**1**−**3**), the linear poly(MMA) (**4**), and the MMA−DMAA block copolymer (**5**) were synthesized as described in previous literature.[2,4,6] This linear poly(NIPAM) was prepared via iron-catalyzed living radical polymerization.[8] The guest compounds (**A**: Aldrich, purity >99.5%; **B**: Aldrich, purity >99.5%; **C**: Aldrich, purity >99.8%; **D**: Aldrich, purity >99%; **E**: Aldrich, purity >99%; **F**: Aldrich, purity >99%) were used as received. Hydrophilic dye (orange G, **G**: Wako) was used as received. The solvents ($CDCl_3$: Aldrich, 99.8 atom % D; DMF-d_7: Aldrich, 99.5 atom % D; D_2O: Aldrich, 100.0 atom % D) were used as received. Hydrogen bond breaker (TFA-d: Aldrich, 99.5 atom % D) was used as received.

Polymer Characterization. The MWD, M_n, and M_w/M_n ratios of the polymers were measured by SEC in DMF containing 10 mM LiBr at 40 °C (flow rate: 1 mL/min) on three linear-type polystyrene gel columns (Shodex KF-805L; exclusion limit = 5×10^6; pore size = 20−1000 Å; 0.8 cm i.d. × 30 cm) that were connected to a Jasco PU-980 precision pump, a Jasco RI-930 refractive index detector, and a Jasco UV-970 UV/vis detector set at 256 nm. The columns were calibrated against 13 standard poly(MMA) samples (Polymer Laboratories; M_n = 200−1 200 000; M_w/M_n = 1.06−1.22) as well as MMA monomer.

The weight-average molecular weight (M_w) of the polymers was determined by multiangle laser light scattering (MALLS) in DMF at 40 °C on a Dawn E instrument (Wyatt Technology; Ga−As laser, $\lambda = 690$ nm) accompanying ASTRA software (version 4.73.01 for Windows). The refractive index increment (dn/dc) was measured in DMF at 40 °C on a Photal DRM-1020 refractometer ($\lambda = 690$ nm, $c < 8.0$ mg/mL). The dn/dc values were 0.067 mL/g for **1**, 0.028 mL/g for **2**, 0.063 mL/g for **3**, and 0.119 mL/g for **4**.

^{1}H and ^{13}C NMR Spectroscopies. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ at 30 °C on a JEOL JNM-LA500 spectrometer, operating at 500.16 and 125.78 MHz, respectively. The probe temperature was regulated with a variable temperature apparatus (temperature fluctuation ≤0.1 deg). Polymer samples were fractionated by preparative SEC (column: Shodex K-5003). The solvents were degassed by freezing−thawing or magnetic stirring under reduced pressure.

^{1}H NMR spectra were obtained by following parameters: spectral width = 12 500 (25.0 ppm), pulse width = 6.20 μs, (45° pulse), pulse-repetition delay time = 27.3786 s, FIDs for each point = 8 times/spectrum, data points = 32 768.

^{13}C NMR spin−lattice relaxation times (T_1) were obtained by the inversion−recovery method. Typically, 10 different τ values were used to determine T_1 (where τ is the interval between 180° and 90° pulse). Other parameters were as follows: spectral width = 33 898.3 Hz (269 ppm), 180° pulse width = 27 μs, pulse-repetition delay time = 5T_1, FIDs for each point = 32−128 times/spectrum, data points = 65 536.

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References and Notes

(1) This work was presented in part at the following meetings: (a) The 49th Annual Meeting on the Society of Polymer Science, Nagoya, Japan, May 2000; paper IPc013: Baek, K.-Y.; Kamigaito, M.; Sawamoto, M. *Polym. Prepr. Jpn.* **2000**, *49* (2), 277. (b) The 49th Symposium on Macromolecules, the Society of Polymer Science, Sendai, Japan, Sept 2000; paper IB17: Baek, K.-Y.; Kamigaito, M.; Sawamoto, M. *Polym. Prepr. Jpn.* **2000**, *49* (7), 1215.

(2) Baek, K.-Y.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **2001**, *34*, 7629.

(3) For reviews on synthesis of star-shaped polymers, see: (a) Morton, M. *Anionic Polymerization: Principle and Practice*; Academic Press: New York, 1983; pp 221−232. (b) Hsieh, H. L.; Quirk, R. P. *Anionic Polymerization*; Marcel Dekker: New York, 1996; pp 333−368. (c) Simms, J. A.; Spinelli, H. J. In *Macromolecular Design of Polymeric Materials*; Hatada, K., Kitayama, T., Vogl, O., Eds.; Marcel Dekker: New York, 1997; pp 379−391. (d) Sawamoto, M. In *Cationic Polymerization*; Matyjaszewski, K., Ed.; Marcel Dekker: New York,

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

(5) Kanaoka, S.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1992**, *25*, 6414.

(6) Senoo, M.; Kotani, Y.; Kamigaito, M.; Sawamoto, M. *Macromol. Symp.* **2000**, *157*, 193.

(7) All peaks of **A** in the presence of the three polymers with carboxyl groups shifted upfield in comparison to those in the absence. This is probably due to disruption of the acid−acid dimmer formation of **A** in the more polar environment where these polymers are present. A similar shift was also observed in the presence of ethyl acetate.

(8) Higashi, T.; Ando, T.; Kamigaito, M.; Sawamoto, M. *Polym. Prep. Jpn.*, in press.

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