Star-Shaped Polymers by Living Cationic Polymerization. 4. Selective Host–Guest Interaction of Small Molecules by Amphiphilic Star-Shaped Polymers of Vinyl Ethers

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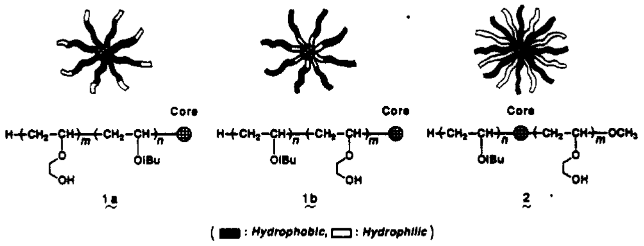
ABSTRACT: Amphiphilic star-shaped block polymers (1) of vinyl ethers, prepared by living cationic polymerization, were found to interact with small organic molecules (guests) with polar functional groups. The occurrence of the host–guest interaction was judged from reduction of the ^{13}C NMR spin–lattice relaxation time (T_1) of the guest molecules upon mixing with the host polymer 1 in $CDCl_3$ at 30 °C. With star polymer 1a, $\{H[-CH_2CH(OCH_2CH_2OH)]_m-[CH_2CH(OiBu)]_n\}_f-$(core) ($m = 10, n = 29, f = 8$ arms/molecule), for example, the T_1 of the aromatic carbons of benzoic acid (3) and methyl 3-hydroxybenzoate (5) decreased but those of ethyl benzoate (7) and *n*-pentylbenzene (8) remained unchanged. Thus, 1 could interact specifically with the guests carrying functional groups that are capable of forming hydrogen bonds with the hydroxyl groups of 1. Similar host–guest interactions were also observed for amphiphilic heteroarm star polymers, where two sets of homopolymer arm chains (hydrophilic and hydrophobic) were attached onto a single core. The host–guest interaction is also selective; when an equimolar mixture of 3 and 8 was brought into contact with 1a in $CDCl_3$, 3 interacted with 1a, whereas 8 was not complexed. The T_1 of 3 also decreased with the increasing mole ratio of the hydroxyl groups in 1 to the guest molecule.

Introduction

Molecular recognition has been eliciting considerable interest in recent years. To develop such functions of molecules, it is often important to control the three-dimensional shapes of hosts. In addition to crown ethers or cryptands, for instance, "multiarmed" compounds where several arms are attached to a single core moiety have been studied in the host–guest chemistry.[1,2] Other examples of topologically controlled molecules with similar properties may include "cascade" polymers, such as "dendrimers"[3] and "arborols",[4] which have been prepared by Tomalia and Newkome, respectively.

In addition polymerization, similar multiarmed polymers (star-shaped polymers) have been prepared primarily by living anionic polymerization in several ways,[5] most frequently by linking reactions of linear living polymers with divinyl compounds.[6] Most of the star-shaped polymers thus obtained, however, consist of nonpolar arms such as polystyrene, because of the difficulty in preparing living polymers with polar pendant groups. Quite recently, we have applied similar polymer-linking reactions to the synthesis of star-shaped polymers of vinyl ethers in living cationic polymerization.[7] We have also prepared two types of amphiphilic star-shaped polymers (1 and 2) with hydroxyl groups: star-shaped block copolymers 1 carrying, as arms, polyalcohol/poly(isobutyl vinyl ether) AB block copolymers [$(HOVE)_m-(IBVE)_n-$(core)];[8] and heteroarm star polymers 2 consisting of separate hydrophilic polyalcohol and hydrophobic poly(IBVE) arms that are independently attached to a single core [$(HOVE)_m-$(core)$-(IBVE)_n$].[9]



These amphiphilic star polymers 1 and 2 are characterized by the high accumulation of polar hydroxyl groups per molecule due to their highly branched structures. Noting these features, we herein examined the host–guest interaction of the amphiphilic star-shaped polymers with small organic molecules. In suitable aprotic solvents, the hydroxyl groups in 1 or 2 may interact with these guest molecules with polar functional groups through hydrogen bonds. Therefore, we examined the host–guest interaction of these amphiphiles (1 and 2, hosts) with substituted benzenes (guests), specifically in regard to the effects of the host polymer structure and the guest's functional groups on the selectivity and specificity, and relative to that of the corresponding linear polymers.

Results and Discussion

Host–Guest Interaction of Star Block Polymer 1a with Benzoic Acid. We first examined the host–guest interaction between benzoic acid (guest) and amphiphilic star block polymer 1a [with outer polyalcohol segments; *m* (OH) = 10; *n* (IBVE) = 29; *f* = 8 arms/molecule] in $CDCl_3$ at 30 °C. The occurrence of the host–guest interaction was evaluated from the changes in the ^{13}C spin–lattice relaxation time (T_1)[10,11] of the aromatic carbons of benzoic acid in the absence or presence of 1a ([benzoic acid] = 0.30 M; [benzoic acid]/[OH in 1a] = 2). When benzoic acid was mixed with 1a, the T_1 of the meta carbon was reduced by 50%, from 3.77 s for a pure benzoic acid solution to 1.92 s. This indicates that benzoic acid in fact interacts with 1a, and thereby its thermal motion is restricted.[10]

Such an interaction may be caused by the hydrogen bonds between the carboxyl group of benzoic acid and the pendant hydroxyl functions of 1a. The reduction of relaxation time T_1, however, turned out to be unattainable with a short-chain alcohol that would also capture the acid through hydrogen-bonding. For example, when ethanol ([benzoic acid]/[EtOH] = 2), instead of 1a, was mixed with benzoic acid, the T_1 slightly increased (from 3.77 to 3.93 s) rather than decreased. These results support that the reduction of the T_1 is due to a specific interaction with the added polymer.

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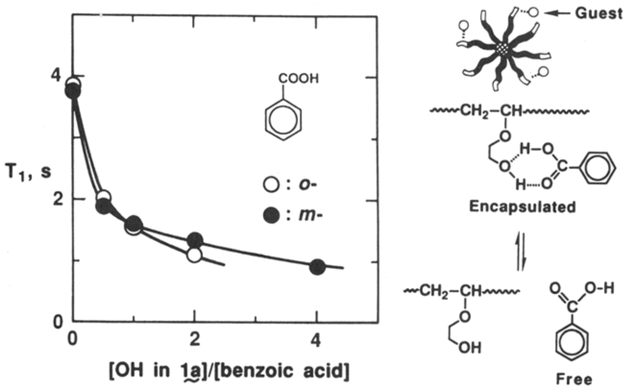


Figure 1. ^{13}C NMR spin–lattice relaxation times (T_1) for the ortho and meta carbons of benzoic acid as a function of [OH in **1a**]/[benzoic acid] in $CDCl_3$ at 30 °C: [OH in **1a**] = 0.15 M.

Figure 1 plots the T_1 values of the ortho and meta carbons as a function of the molar ratio of the hydroxyl groups in **1a** to the guest ([OH]/[guest]). The samples were prepared by the addition of varying doses of benzoic acid, while the concentration of the hydroxyl groups in the polymer was kept constant ([OH in **1a**] = 0.15 M). In the absence of **1a**, the T_1 of the acid remained unchanged independent of its concentration.

Figure 1 shows that the T_1 clearly depends on the concentration of the host/guest molar ratio. Even a low concentration of the hydroxyl groups ([OH in **1a**]/[guest] = 0.5) sharply shortened the T_1 of both ortho and meta carbons, which was reduced from ca. 3.8 s in polymer-free chloroform to ca. 2.0 s with **1a** and further decreased with decreasing guest concentration to a minimum of ca. 1.0 s when [OH]/[guest] = 4.

Such a concentration dependence indicates that benzoic acid molecules are most likely in an equilibrium, between free and complexed states, as schematically illustrated in Figure 1. Under such conditions, the observed T_1 would be taken as the weight average of the values for the free and the complexed states. The lower the benzoic acid concentration, the more the acid molecules are complexed, and thereby the more the T_1 is reduced. Accordingly, a decrease in the T_1 means an increase in the proportion of the complexed molecules.

Effects of Host and Guest Compounds. The primary factors that affect the host–guest interaction would include the structure and shape of the host polymers and the functional groups in the guests. This section concerns the effects of these factors.

Table I

T_1 Values of Benzoic Acid (3) in the Presence of Various Host Poly(vinyl ethers)[a]

code	shape[b]	polymer structure[c]	$\overline{DP}_n$(obsd)[d]		
			m/n	f[e]	T_1, s
		no polymer			3.77
A	linear	$(IBVE)_n$	0/38		3.07
B	star	$(IBVE)_n$–(core)	0/38	11	2.60
C	linear	$(HOVE)_m$–$(IBVE)_n$	10/29		2.18
D	star (**1a**)	$(HOVE)_m$–$(IBVE)_n$–(core)	10/29	8	1.92
E	star (**1b**)	$(IBVE)_n$–$(HOVE)_m$–(core)	9/30	8	1.67
F	star (**2**)	$(HOVE)_m$–(core)–$(IBVE)_n$	40/30	20	2.18
G	star (**2**)	$(HOVE)_m$–(core)–$(IBVE)_n$	21/30	20	2.06
H	star (**2**)	$(HOVE)_m$–(core)–$(IBVE)_n$	11/30	20	1.75

[a] The T_1 values for the meta carbon of benzoic acid in $CDCl_3$ at 30 °C; [benzoic acid]/[OH in polymer] = 2.0. [b] **1a** and **1b**, star block polymers; **2**, heteroarm polymers. [c] IBVE, isobutyl vinyl ether unit, $-CH_2-CH(OCH_2CHMe_2)$; HOVE, 2-hydroxyethyl vinyl ether unit, $-CH_2-CH(OCH_2CH_2OH)$; core, microgel derived from a bifunctional vinyl ether, $Me_2C[(C_6H_4)OCH_2CH_2OCH{=}CH_2\text{-}p]_2$; see refs 7–9 for detailed descriptions of the polymer syntheses and structures. [d] The observed degree of polymerization of segments, determined by ^{1}H NMR.[8,9] [e] The number of arms per molecule determined by light scattering.[7–9]

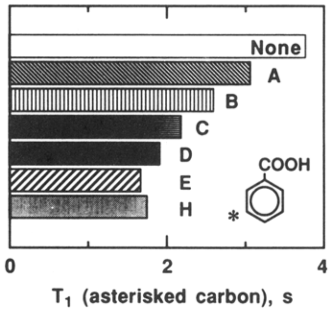


Figure 2. Relaxation time T_1 for the meta carbon of benzoic acid in the presence and absence of poly(vinyl ethers) A–E and H in $CDCl_3$ at 30 °C: [benzoic acid] = 0.30 M; [benzoic acid]/[OH in host polymer] = 2.0; (A) linear poly(IBVE) ($\overline{DP}_n$ = 38); (B) star-shaped poly(IBVE) [$\overline{DP}$(arm) = 38, f = 11]; (C) linear block polymer (HOVE/IBVE = 10/29); (D) star block polymer **1a** (HOVE/IBVE in arm = 10/29, f = 8); (E) star block polymer **1b** (IBVE/HOVE in arm = 30/9, f = 8); (H) heteroarm star polymer **2** (m/n = 11/30, f = 20).

(a) Structure and Shape of the Host Polymers. To examine the effects of the host structures, we employed a series of star and linear polymers (A–H) listed in Table I; namely, amphiphilic star block polymers with outer [D (**1a**)] or inner [E (**1b**)] polyalcohol arm segments, a linear AB block polymer (C) corresponding to each arm in D or E, hydrophobic linear (A) and star (B) poly(IBVE), and heteroarm amphiphilic star polyers **2** (F–H).[9] In the presence of these host polymers, the T_1 of the meta carbon of benzoic acid was measured in $CDCl_3$ at 30 °C, where the concentration of benzoic acid was invariably 0.30 M. For the amphiphilic linear and star polymers (C–H), their concentrations were set so as to give the hydroxyl groups 0.5 equiv to the acid ([benzoic acid]/[OH in the polymer] = 2.0); for the hydrophobic counterparts (A and B), the concentration of the IBVE units was as twice that of benzoic acid. Table I summarizes the T_1 values and the characterization data of the host polymers [the segment compositions (m/n) and the arm number (f) per molecule]; Figure 2 presents selected T_1 data in a bar chart form to visualize the results in Table I.

As Figure 2 shows, both the linear and star amphiphiles (C–E) proved to efficiently capture benzoic acid, shortening the T_1 value by 45–60% (1.67–2.18 s). Such an efficient interaction obviously stems from the hydroxyl groups of polymers C–E, because both linear (A) and star (B) poly(IBVE) induced less decrease in T_1 and are clearly inferior to the amphiphilic hosts C–E. The slight reduction of T_1 by the linear and the star-shaped poly(IBVE) is probably due to a weak hydrogen bonding between the carboxyl group of benzoic acid and the ether oxygen in the hydrophobic poly(vinyl ether)s.

Comparison of the T_1 values with the amphiphilic star polymers (D and E) and with the corresponding linear counterpart (C) shows that the host–guest interaction also depends on the spatial shape of the host polymers. The amphiphilic star polymers D and E gave the lower T_1 values (1.92 and 1.67 s, respectively) relative to that with the linear polymer C (2.18 s). Though to a smaller extent, similar results were obtained for the hydrophobic poly(IBVE) versions (A vs B). This trend demonstrates that, for efficient interactions, the host polymers need a branched or multiarmed structure which would lead to the higher accumulation of polar hydroxyl groups per

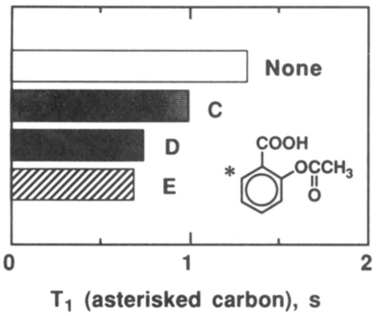


Figure 3. Relaxation time T_1 for the asterisked carbon (ortho to the carboxyl) of aspirin in the presence and absence of linear and star block amphiphilic polymers C–E in $CDCl_3$ at 30 °C: [aspirin] = 0.27 M; [aspirin]/[OH in host polymer] = 2.0. The structural data for the host polymers are shown in Table I.

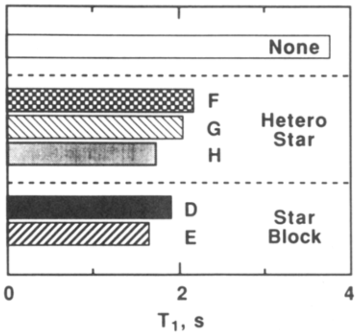


Figure 4. Relaxation time T_1 for the meta carbon of benzoic acid in the presence and absence of star block (D and E) and heteroarm (F–H) star amphiphilic polymers in $CDCl_3$ at 30 °C: [benzoic acid] = 0.30 M; [benzoic acid]/[OH in host polymer] = 2.0; (D) and (E) star block polymers **1a** and **1b**, respectively; (F–H) heteroarm star polymers **2**. m/n: (F) 40/30; (G) 21/30; (H) 11/30; see also Table I.

molecule. Thus, the larger amount of the hydroxyl groups may facilitate the interaction with the guest and capture more guest molecules.

A similar interaction was observed for aspirin (*o*-acetoxybenzoic acid) as a guest that could also interact with either the linear or the star amphiphilic block polymers (Figure 3). The T_1 of the aspirin's carbon adjacent to the carboxyl group (asterisked in Figure 3) was reduced by 50–60%, from 1.3 s in polymer-free chloroform to 0.6–0.7 s with **1a** (D) and **1b** (E), in contrast to the linear block polymers (C), for which the T_1 reduction was clearly minor (down to ca. 1.0 s). Under these conditions ([aspirin] = 0.27 M), this interaction affected not only T_1 but also the solubility of aspirin. For example, aspirin, which is hardly soluble in $CDCl_3$, became readily soluble in the presence of **1a** and **1b**.

Amphiphilic heteroarm star polymers **2** (F–H, Table I) are expected to interact with small organic molecules efficiently, because **2** is structurally similar to **1** and equally carries hydroxyl groups.[9] Thus, we also examined the interaction between **2** and benzoic acid in $CDCl_3$ at 30 °C, specifically relative to those with star block polymers **1** (D and E). For all these samples, the degree of polymerization for the hydrophobic chain [poly(IBVE)] was invariably ca. 30, while that for the hydrophilic polyalcohol chain was varied in the range from 10 to 40, so that all of them would be completely soluble in $CDCl_3$, and the number (f) of arms was also constant (f = 20). Figure 4 compares the T_1 values for the heteroarm star polymers (F–H) and for the star block polymers (D and E).

These amphiphilic star polymers all turned out to be similarly effective as host polymers and lowered the T_1 of benzoic acid from 3.77 s for the polymer-free state of ca. 2.0 s or below in the presence of the hosts (Figure 4; see Table I). Among the three samples of the hetero star polymers, interestingly, the T_1 decreased more for shorter hydrophilic arm chains (F > G > H). As seen from the $\overline{\mathrm{DP}}_n$ (m and n) values for F–H in Table I, sample F has a polyalcohol arm longer than the poly(IBVE) arm ($\overline{\mathrm{DP}}_n$ = 40 vs 30), whereas samples G and H have shorter polyalcohol arms, indicating that in G and H, the hydrophilic arms are probably buried inside the hydrophobic poly(IBVE) arms. A similar trend can be observed for the star block polymers, where the inner alcohol version E excels the outer alcohol counterpart D. Judging from these results, the position of the hydroxyl groups appears to be more important to the interaction than their total amount per molecule.

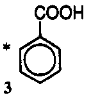
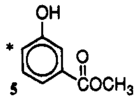
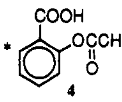
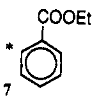
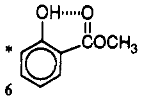
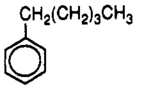
(b) Functional Groups of Guest Compounds. In addition to benzoic acid (**3**) and aspirin (**4**), we herein employed four substituted benzenes (**5**–**8**) as guests for the host–guest interaction with **1a** in $CDCl_3$ at 30 °C ([guest]/[OH in **1a**] = 2.0). The six guest compounds differ in the functional groups; **3** and **4** carry a carboxyl group, and methyl 3-hydroxybenzoate (**5**) and methyl salicylate (**6**) have a hydroxyl group, whereas ethyl benzoate (**7**) and n-pentylbenzene (**8**) have no hydrophilic groups. Table II summarizes the T_1 values of the six guests in the presence and absence of **1a**.

Among the six substituted benzenes (guests), interactions with star block polymers **1a** were found specifically for **3**–**5** but not for **6**–**8**. For **3**–**5**, the T_1 values of the hosts' carbons (asterisked in Table II) were reduced by 40–50% with **1a**, indicating efficient host–guest interactions. On the other hand, the T_1 of **6**–**8** remained unchanged upon treating with **1a**, irrespective of the guests' substituents. These results show that for efficient interactions with **1a**, guests need polar hydrophilic groups, such as carboxyl (**3** and **4**) or hydroxyl (**5**), that can be hydrogen-bonded to the hydroxyl groups in **1a**.

Particularly interesting is the result for methyl salicylate (**6**), which indeed has a hydroxyl group but does not interact with **1a**. The hydroxyl group in **6** is known to form an intramolecular hydrogen bond with the vicinal ester carbonyl, and this internal blocking apparently keeps the hydroxyl group from interacting with the pendant hydroxyl in **1a**. The absence of changes in the T_1 for **6**–**8** also supports that the reduction of the T_1 observed for the other guests (**3**–**5**) is in fact due to the interaction between the guest and the host polymer, not due to an increase of the medium's viscosity in the presence of the latter, which might also restrict the thermal motion of guest molecules (like **8**) even without polar substituents.

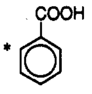
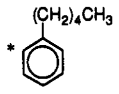
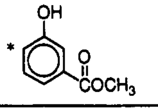
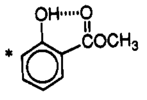
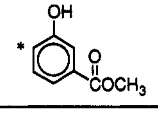
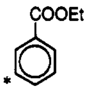
Selective Host–Guest Interaction. We thus found that six compounds listed in Table II fall into two groups; **3**–**5** (good guests) interact with **1a**, whereas **6**–**8** (poor guests) elude such an interaction. In addition to such a specificity toward the guest structures, the amphiphilic star-shaped polymers would thus selectively interact with guests carrying functional groups that are capable of forming hydrogen bonds with the hydroxyl groups in the arm chains. Thus, the host–guest interaction was also examined for an equimolar mixture of good and poor guests exposed to **1a** in $CDCl_3$ at 30 °C. We herein selected three pairs of guests; **3** and **8** (carboxyl vs alkyl), **5** and **6** (the meta and ortho isomers of methyl hydroxybenzoates), **5** and **7** (hydroxyl vs ester). All samples were prepared by the addition of two guest compounds to a solution of **1a** where each guest was 2 equiv to the hydroxyl groups in **1a**. The results are summarized in Table III.

Table II
Host-Guest Interaction between 1a and Small Organic Molecules[a]

		guest					
							
T_1,[b] s	none	3.84	1.88	1.32	5.63	6.15	5.26
	with 1a	2.01	0.83	0.74	5.64	6.01	5.20

[a] [guest] = 0.30 M, [guest]/[OH in 1a] = 2; in $CDCl_3$ at 30 °C. [b] The carbon-13 spin-lattice relaxation time for the asterisked carbon of the guest substrate.

Table III
Selective Host-Guest Interaction by Amphiphilic Star Block Polymer 1a[a]

combination		3 vs 8		5 vs 6		5 vs 7	
guest pair							
T_1,[b] s	none	3.56	4.49	2.06	5.95	1.76	4.24
	with 1a	2.02	4.30	0.78	4.96	0.83	3.94

[a] [guest] = 0.30 M, [guest I]/[guest II]/[OH in 1a] = 2/2/1; in $CDCl_3$ at 30 °C. [b] The carbon-13 relaxation time for the asterisked carbon of the guest substrate.

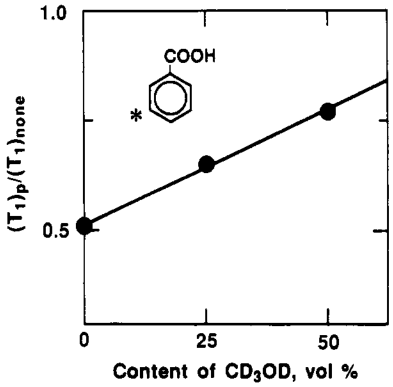


Figure 5. Effects of solvent polarity on the T_1 for the meta carbon of benzoic acid at 30 °C in $CDCl_3/CD_3OD$ mixtures: [benzoic acid] = 0.30 M; [benzoic acid]/[OH in 1a] = 2.0.

When **3** and **8** were employed, the T_1 of **3** alone sharply decreased, from 3.56 to 2.02 s, while that of **8** was almost unchanged. Similar results were obtained for the other two pairs of guests (Table III, **5** vs **6** or **7**). In both cases, host polymer **1a** led to the decrease of the T_1 for **5** alone, but not that for another guest (**6** or **7**). Thus, the amphiphilic star polymer **1a** could selectively interact with the good guests (**3** and **5**), regardless of their combination with the poor guests. The selective host-guest interaction of **5** in its isomer mixture with **6** is particularly interesting in that the amphiphilic star block polymer **1a** may be able to extract a particular compound from its isomeric mixtures. When two guest compounds were mixed, the T_1 slightly changed, and this may be simply due to the changes in the medium's polarity.

Hydrogen Bonds between Hydroxyl Groups of 1a and Guest. If the observed host-guest interaction stems from hydrogen bonds (cf. Figure 1), alcohols such as methanol, known as hydrogen bond breakers, may disturb the interaction. Thus, the effect of methanol (CD_3OD) on the host-guest interaction between benzoic acid and polymer **1a** in $CDCl_3$ was studied (Figure 5). Because T_1 is influenced by solvent polarity, we herein evaluated the interaction in a particular solvent mixture from the ratio $[(T_1)_p/(T_1)_{none}]$ of the relaxation time $[(T_1)_p]$ in the presence of **1a** to that $[(T_1)_{none}]$ in its absence. When the interaction is completely disturbed, therefore, the $(T_1)_p/(T_1)_{none}$ ratio should be unity.

In Figure 5, the $(T_1)_p/(T_1)_{none}$ values are plotted as a function of the content of CD_3OD. In pure $CDCl_3$, **1a** reduced the T_1 of benzoic acid (meta carbon) almost by half $[(T_1)_p/(T_1)_{none} = 0.53]$ whereas the T_1 reduction became less efficient with increasing the amount of CD_3OD, where the $(T_1)_p/(T_1)_{none}$ increased up to 0.77. This indicates that the hydrogen-bonding of excess CD_3OD with the hydroxyl groups of **1a** or the carboxyl group of benzoic acid effectively inhibits the interaction between **1a** and benzoic acid and thereby reduces the amount of benzoic acid molecules captured by **1a**.

^1H NMR analysis on a mixture of **1a** and benzoic acid also provided evidence for the interaction between the guest acid and the hydroxyl groups of **1a** via hydrogen-bonding. The absorption (c; 12.2 ppm, Figure 6A), assigned to the carboxylic proton of benzoic acid, progressively shifted upfield as the benzoic acid concentration decreased (peak c′, Figure 6B-E), whereas other signals (e.g., a and b, Figure 6) remained unchanged. These upfield shifts are due to the rapid exchange between the carboxylic and the hydroxyl protons, which gives a single coalesced peak whose position depends on the concentration of the exchanging protons.

As described above, we demonstrated that two types [star block (**1**) and heteroarmed (**2**)] of amphiphilic star-shaped polymers of vinyl ethers can interact with particular types of small organic molecules. To attain effective host-guest interactions, guests need polar hydrophilic groups, carboxyl or hydroxyl, that can be hydrogen-bonded to the hydroxyl groups in the added polymer. The amphiphilic star polymers can also selectively capture the guests carrying appropriate functional groups.

Experimental Section

Materials. All samples of the amphiphilic star polymers (**1** and **2**) were synthesized as reported previously.[8,9] The guest compounds (**3-8**) were of commercial source and used as received; solid guest compounds **3-5** were vacuum dried at least overnight just before use.

NMR Measurements. ^1H and ^{13}C NMR spectra were recorded on a JEOL GSX-270 spectrometer (270 and 67.8 MHz, respectively) in a 5-mm sample tube at 30 °C. The solvents were

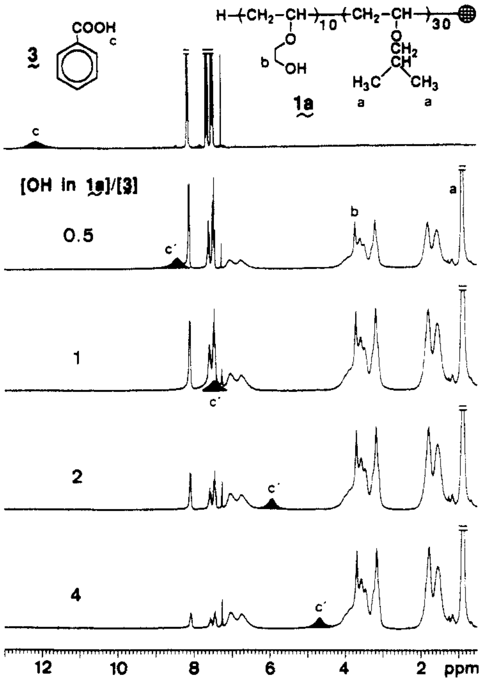


Figure 6. ^{1}H NMR spectra of benzoic acid (3) in the presence and absence of amphiphilic star block polymer 1a in CDCl$_3$ at 30 °C. [OH in 1a]/[benzoic acid] as indicated.

degassed by magnetic stirring under reduced pressure. The probe temperature was controlled on a JEOL NM-GVT3 temperature controller.

^{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° pulses). Other parameters were as follows: spectral width = 17 006.8 Hz (250 ppm), 180° pulse width = 16–17 μs, pulse-repetition delay time = 5T_1, FIDs for each point = 160–200 times/spectrum, data points = 32 768. The T_1 values were calculated using the linear-regression T_1 calculation package of the JEOL PLEXUS software.

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