Macromolecules

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Macroscopic Self-Assembly Based on Molecular Recognition: Effect of Linkage between Aromatics and the Polyacrylamide Gel Scaffold, Amide versus Ester

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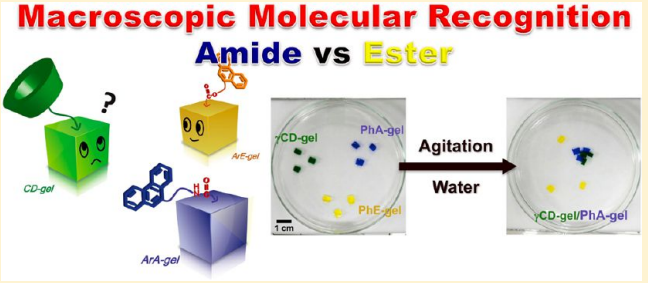
Supporting Information

ABSTRACT: The interactions of polyacrylamide- (pAAm-) based gels possessing cyclodextrin (CD) residues (CD-gels) with pAAm-based gels modified with aromatic residues through amide and ester linkages (ArA-gels and ArE-gels, respectively) were investigated to examine the effect of linkage (i.e., amide and ester) between aromatic residues and the pAAm gel scaffold. In the present study, benzyl (Bz), 2-naphthylmethyl (Np), 9-phenanthrylmethyl (Ph), and 1-pyrenylmethyl (Py) residues were chosen as a series of aromatic residues. αCD-gel did not interact notably with the ArA-gels and ArE-gels in water. βCD-gel interacted with the ArA-gels and ArE-gels possessing smaller aromatic residues (i.e., Bz and Np residues) in water to form gel assemblies. γCD-gel showed different tendencies of its interactions with the ArA-gels and with the ArE-gels; γCD-gel interacted with the ArA-gels carrying larger aromatic residues (i.e., Ph and Py residues), while γCD-gel formed stable gel assemblies only with NpE-gel among the ArE-gels examined. This is because γCD residues in γCD-gel included favorably dimeric aromatic residues in the ArA-gels and ArE-gels. Reflection fluorescence spectra for the ArA-gels and ArE-gels possessing fluorescent aromatic residues (i.e., Np, Ph, and Py residues) in the presence of 10 mM γCD were indicative of weak selectivities of γCD toward NpE, PhA, and PyA residues. Such weak selectivities may be largely enhanced in the macroscopic observation of interaction of CD-gels with the ArA-gels and ArE-gels presumably because of multivalency.



INTRODUCTION

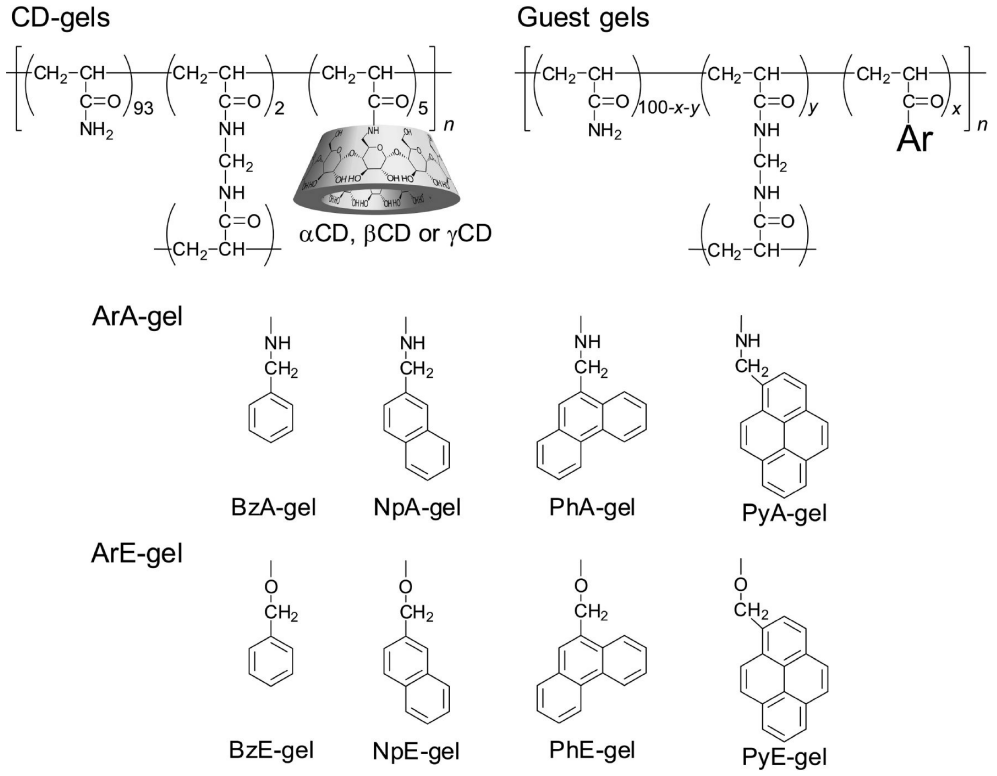
Macroscopic self-assemblies based on noncovalent interactions have been of increasing importance as smart materials which possess stimuli-responsiveness and self-healing ability.[1−3] Macroscopic self-assemblies have been reported based on magnetic interaction,[4−6] electrostatic interaction,[7,8] hydrophile−lipophile balance,[9−12] and capillary effect.[13−16] In biological systems, macroscopic self-assemblies based on molecular recognition are ubiquitous and sustain living activities.[17−19] In artificial systems, on the other hand, it has been still a great challenge to construct macroscopic self-assemblies based on molecular recognition.

Recently, we have first demonstrated macroscopic self-assemblies based on molecular recognition using polyacrylamide(pAAm)-based hydrogels possessing cyclodextrin (CD) and guest moieties.[20] Gels carrying αCD, βCD, and γCD moieties (αCD-gel, βCD-gel, and γCD-gel, respectively) recognized gels carrying their respective counterparts.[20−22] More recently, we have also realized macroscopic self-assemblies responsive to external stimuli, i.e., temperature,[23] chemical,[24] and light stimuli.[25] These previous studies have demonstrated that the formation of gel assemblies is dependent on the binding constant for CD and guest residues and on the concentration of CD and guest residues in gels.

Since the mobility of CD and guest residues should be also important for the interaction on the gel interface, the linkage between CD or guest residues and the pAAm gel scaffold may be a considerable structural factor. The linkage between hydrophobic residues and the polymer backbone can be critical in the self-organization behavior of hydrophobically modified water-soluble polymers.[26−31] For example, amide and ester linkages between hydrophobic residues and the polymer backbone can demonstrate different properties in self-organization of hydrophobically modified water-soluble polymers, although amide and ester seem to be similar. Hydrophobically modified polyanions of amide linkage, i.e., statistical

Received: November 14, 2012
Revised: January 24, 2013
Published: February 19, 2013

Chart 1. Chemical Structures for CD-Gels (αCD-Gel, βCD-Gel, and γCD-Gel) and Guest Gels (ArA-Gels and ArE-Gels)



copolymers of sodium 2-acrylamido-2-methylpropanesulfonate (NaAMPS) and *N*-dodecylmethacrylamide, show a strong tendency of intrapolymer hydrophobic interaction to form compact polymer micelles, in which the polymer main chain is highly folded.[32−35] Whereas, hydrophobically modified polyanions of ester linkage, i.e., statistical copolymers of NaAMPS and dodecyl methacrylate, indicate a tendency of interpolymer hydrophobic interaction to form larger polymer micelles.[36] Furthermore, the linkage between guest residues and CD residues in modified CDs can be also important in the formation of supramolecular assemblies.[37−40] Ueno et al.[37] modified γCD with a 3-(1-pyrenyl)propyl residue on the primary hydroxy side through amide and ester linkages, and reported that the equilibrium constant of the formation of dimeric inclusion complex for the modified γCD of amide linkage (1.74×10^5 M^{-1}) was an order of magnitude higher than that for the modified γCD of ester linkage (1.53×10^4 M^{-1}). Harada et al.[38−40] modified αCD with a cinnamoyl residue on the primary hydroxy side through amide and ester linkages, and reported the supramolecular structure depending on the linkage. The modified αCD of amide linkage forms a supramolecular cyclic dimer in aqueous media,[38,39] whereas the modified αCD of ester linkage forms supramolecular oligomers in aqueous media.[40]

These previous studies motivated us to investigate the effect of linkage on the macroscopic self-assemblies of CD-gels and guest gels. Hence, we investigate the effect of linkage on the formation of gel assemblies of CD-gels with gels modified with aromatic residues through amide and ester linkages (ArA-gels and ArE-gels, respectively). We first describe the interactions of CD-gels with the ArA-gels and with the ArE-gels, and then compare these interactions.

RESULTS AND DISCUSSION

Preparation of the Guest Gels Carrying Aromatic Amide and Aromatic Ester Residues (ArA-Gels and ArE-Gels) and CD-Gels Used in This Study. In the present study, benzyl (Bz), 2-naphthylmethyl (Np), 9-phenanthrylmethyl (Ph), and 1-pyrenylmethyl (Py) residues have been chosen as a series of aromatic residues because of ease of preparation of the monomers and gels. The guest gels (ArA-gels and ArE-gels in Chart 1) were prepared by radical terpolymerization of acrylamide (AAm), *N*,*N*′-methylenebis(acrylamide) (MBA) (a cross-linker), and an aromatic monomer in dimethyl sulfoxide (DMSO) using ammonium peroxodisulfate (APS) as an initiator at 60 °C. The feed ratios for the ArA-gels and ArE-gels are listed in Table S1 in the Supporting Information. The gels were soaked in water for several days before use. The CD-gels were also prepared by radical terpolymerization of AAm, MBA, and a CD monomer {5 mol % of mono(6-deoxyacrylamido)-α-cyclodextrin (Aα CD), mono(6-deoxyacrylamido)-β-cyclodextrin (Aβ CD), or mono(6-deoxyacrylamido)-γ-cyclodextrin (Aγ CD)} in water initiated by a redox pair of APS and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) at room temperature according to the procedure reported previously (Chart 1).[22−24] The gels obtained were washed with water to remove the unreacted monomers and initiators. The ArA-gels, ArE-gels, and CD-gels were dyed with different color dyes for visual identification.

Macroscopic Observation of the Interaction of CD-Gels with ArA-Gels. The interaction of CD-gels with the ArA-gels was investigated by shaking in water with a glass Petri dish of 9 cm in diameter, as can be seen in Figure 1. When αCD-gel pieces were shaken with BzA-gel, NpA-gel, PhA-gel, and PyA-gel pieces in water, no gel assemblies were formed, indicative of no significant interaction of αCD-gel pieces with any pieces of the ArA-gels (Figure 1a). As reported in our previous study,

dx.doi.org/10.1021/ma302344x | *Macromolecules* 2013, 46, 1939−1947

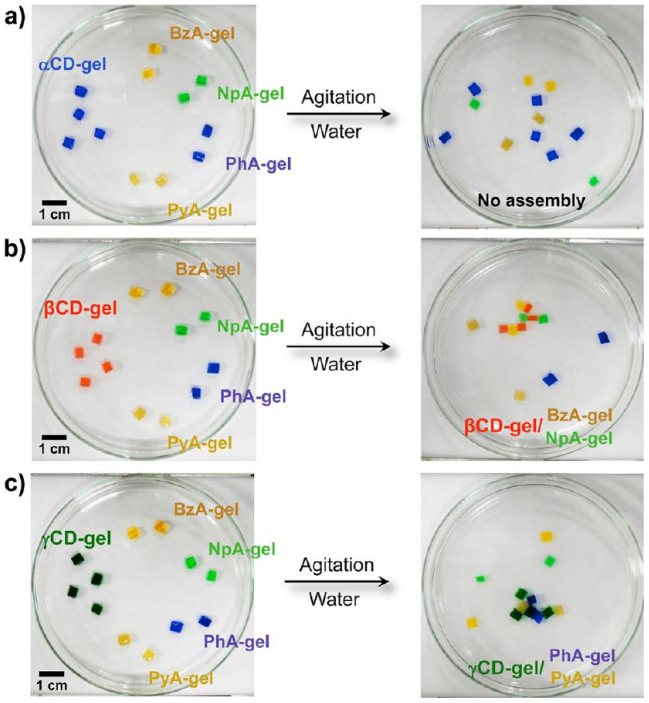


Figure 1. Pictures of the interaction of αCD-gel (gentian blue) (a), βCD-gel (red) (b), and γCD-gel (bottle green) with the ArA-gels {BzA-gel (orange), NpA-gel (green), PhA-gel (purple), and PyA-gel (yellow)} (c).

αCD-gel interacted favorably with gels possessing a linear aliphatic guest, but it did not with gels possessing a cyclic or branched aliphatic guest.[20,21] More recently, it was demonstrated that αCD-gel interacted with BzA-gel carrying 10 or 15 mol % Bz moieties only at lower temperatures.[23] The formation of no gel assemblies was ascribable to the lower binding constants for the model systems composed of native αCD and pAAm modified with aromatic residues through an amide linkage (Table S2 in the Supporting Information). When βCD-gel pieces were shaken with pieces of the four ArA-gels in water, βCD-gel pieces interacted with BzA-gel and NpA-gel pieces to form a gel assembly, whereas they did not interact with PhA-gel or PyA-gel pieces (Figure 1b). These observations are consistent with the binding constants for the model systems (Table S2 in the Supporting Information); βCD interacted preferably with BzA and NpA residues (8.4×10^1 and 2.7×10^2 M^{-1}, respectively). When γCD-gel pieces were shaken in water with pieces of the four ArA-gels, γCD-gel pieces did not interact considerably with BzA-gel or NpA-gel pieces while they interacted with PhA-gel and PyA-gel pieces to form a gel assembly (Figure 1c). These observations are also in a good agreement with the binding constants for the model systems; γCD did not interact notably with the smaller aromatic residues, i.e., BzA and NpA residues, whereas it interacted with the larger aromatic residues, i.e., PhA and PyA residues (Table S2 in the Supporting Information).

To investigate semiquantitavely the strength of interaction of the CD-gels with the ArA-gels, stress−strain measurements were carried out to evaluate the stress at rupture. The values obtained are listed in Table 1. All the pairs of αCD-gel/ArA-gels exhibited relatively small stresses of $(6.3-8.0) \times 10^2$ Pa. βCD-gel showed the largest stress at rupture with NpA-gel (1.6×10^3 Pa), and the stress decreased in the order of βCD-gel/NpA-gel > βCD-gel/BzA-gel (1.4×10^3 Pa) > βCD-gel/PhA-gel (7.6×10^2 Pa) > βCD-gel/PyA-gel (5.3×10^2 Pa). γCD-gel indicated the largest stress at rupture with PyA-gel (2.9×10^3 Pa), and the stress decreased in the order of γCD-gel/PyA-gel > γCD-gel/PhA-gel (2.0×10^3 Pa) > γCD-gel/NpA-gel (5.8×10^2 Pa) > γCD-gel/BzA-gel (3.1×10^2 Pa). On the basis of these data, it is likely that the stress at rupture of ca. 10^3 Pa is the lower limit for the formation of gel assemblies in water in the cases of CD-gels/ArA-gels.[23]

Table 1. Interaction of CD-Gels with ArA-Gels

CD-gel	ArA-gel	assembly[a]	stress at rupture/Pa
αCD-gel[b]	BzA-gel	N	800 ± 110
αCD-gel	NpA-gel	N	720 ± 30
αCD-gel	PhA-gel	N	630 ± 70
αCD-gel	PyA-gel	N	740 ± 90
βCD-gel[b]	BzA-gel	A	1360 ± 330
βCD-gel	NpA-gel	A	1600 ± 90
βCD-gel	PhA-gel	N	760 ± 110
βCD-gel[c]	PyA-gel	N	530 ± 200
γCD-gel[b]	BzA-gel	N	310 ± 20
γCD-gel	NpA-gel	N	580 ± 80
γCD-gel	PhA-gel	A	1970 ± 240
γCD-gel[c]	PyA-gel	A	2930 ± 310

[a]A and N denote assembly and no assembly, respectively. [b]Date from ref 23. [c]Data from ref 24.

Macroscopic Observation of the Interaction of CD-Gels with ArE-Gels. The interaction of CD-gels with the ArE-gels was also investigated, as can be seen in Figure 2. When αCD-gel pieces were shaken with BzE-gel, NpE-gel, PhE-gel, and PyE-gel pieces in water, no gel assemblies were formed, indicative of no considerable interaction of αCD-gel pieces with any pieces of the ArE-gels (Figure 2a).

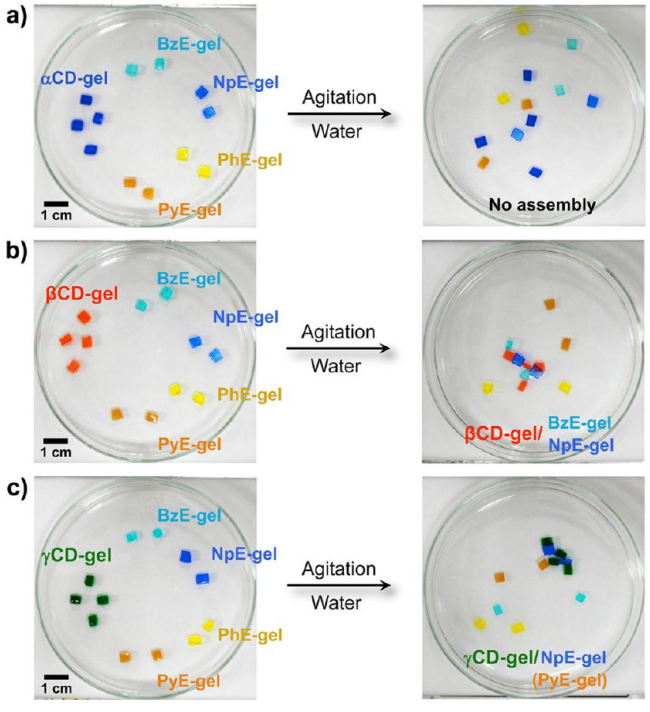


Figure 2. Pictures of the interaction of αCD-gel (gentian blue) (a), βCD-gel (red) (b), and γCD-gel (bottle green) with the ArE-gels {BzE-gel (sky blue), NpE-gel (blue), PhE-gel (yellow), and PyE-gel (orange)} (c).

dx.doi.org/10.1021/ma302344x | Macromolecules 2013, 46, 1939−1947

The formation of no gel assemblies was also caused by the lower binding constants for the model systems composed of native αCD and pAAm modified with aromatic residues through an ester linkage (Table S3 in the Supporting Information). When βCD-gel pieces were shaken with pieces of the four ArE-gels, βCD-gel pieces interacted with BzE-gel and NpE-gel pieces to form a gel assembly, whereas they did not interact with PhE-gel or PyE-gel pieces (Figure 2b). These observations also agree with the binding constants for the model systems (Table S3 in the Supporting Information). When γCD-gel pieces were shaken with pieces of the four ArE-gels, γCD-gel pieces did not interact notably with BzE-gel, PhE-gel, or PyE-gel pieces while they interacted strongly only with NpE-gel pieces to form a gel assembly (Figure 2c). (Only a PyE-gel piece attached to a γCD-gel piece in the gel assembly at an agitation speed of ca. 400 rpm, but the interaction was very weak.) These observations are not consistent with the binding constants for the model systems; γCD did not interact considerably with BzE or NpE residues because of the poor matching of size and shape, whereas it interacted preferably with PhE and PyE residues (Table S3 in the Supporting Information).

To investigate semiquantitatively the strength of interaction of the CD-gels with the ArE-gels, stress−strain measurements were also performed to estimate the stress at rupture, as listed in Table 2. All the pairs of αCD-gel indicated smaller stresses at rupture of (6.7−9.6) × 10^2 Pa. βCD-gel indicated larger stresses with BzE-gel and NpE-gel {(2.5−2.6) × 10^3 Pa}, with which βCD-gel formed gel assemblies in water. βCD-gel indicated a smaller stress with PhE-gel. Although βCD-gel did not form any gel assemblies with PyE-gel, βCD-gel/PyE-gel exhibited a larger stress at rupture of 1.6 × 10^3 Pa. The stress−strain measurements were carried out in air, while the formation of gel assemblies was examined in water. Since PyE-gel was sticky in air, the stress at rupture evaluated by the stress−strain measurements might be overestimated presumably because of the stickiness of PyE-gel. γCD-gel indicated smaller stresses at rupture with BzE-gel (9.1 × 10^2 Pa) and PhE-gel (1.2 × 10^3 Pa), with which γCD-gel did not form any gel assemblies in water. Whereas γCD-gel indicated a larger stress at rupture with NpE-gel (1.4 × 10^3 Pa), with which γCD-gel interacted significantly. Although γCD-gel/PyE-gel did not interact significantly in water, the pair showed a larger stress at rupture (2.2 × 10^3 Pa). It is likely that the stress at rupture for the γCD-gel/PyE-gel was also overestimated presumably because of the stickiness of PyE-gel in air.

Table 2. Interaction of CD-Gels with ArE-Gels

CD-gel	ArE-gel	assembly[a]	stress at rupture/Pa
αCD-gel	BzE-gel	N	780 ± 140
αCD-gel	NpE-gel	N	670 ± 130
αCD-gel	PhE-gel	N	720 ± 10
αCD-gel	PyE-gel	N	960 ± 180
βCD-gel	BzE-gel	A	2510 ± 170
βCD-gel	NpE-gel	A	2580 ± 150
βCD-gel	PhE-gel	N	820 ± 170
βCD-gel	PyE-gel	N	1630 ± 420
γCD-gel	BzE-gel	N	910 ± 70
γCD-gel	NpE-gel	A	1430 ± 50
γCD-gel	PhE-gel	N	1200 ± 290
γCD-gel	PyE-gel	N	2170 ± 420

[a]A and N denote assembly and no assembly, respectively.

Comparison between the Interactions of CD-Gels with the ArA-Gels and with the ArE-Gels. Here we compare the interactions of CD-gels with the ArA-gels and with the ArE-gels. αCD-gel and βCD-gel exhibited the same tendencies of their interactions with the ArA-gels and with the ArE-gels. αCD-gel did not form any gel assemblies with the ArA-gels and ArE-gels presumably because of the smaller cavity size of αCD residue. βCD-gel interacted with the ArA-gels and ArE-gels possessing smaller aromatic residues (i.e., Bz and Np residues) in water to form gel assemblies because of the middle cavity size of βCD residue. On the other hand, γCD-gel showed different tendencies of its interactions with the ArA-gels and with the ArE-gels. γCD-gel interacted with the ArA-gels carrying larger aromatic residues (i.e., Ph and Py residues). Whereas, γCD-gel formed stable gel assemblies only with NpE-gel among the ArE-gels examined, but did not interact notably with BzE-gel, PhE-gel, or PyE-gel. To confirm these differences, additional examinations of the formation of gel assemblies were carried out, as can be seen in Figure 3. When γCD-gel pieces were shaken with NpA-gel and NpE-gel pieces in water, γCD-gel pieces formed a gel assembly only with NpE-gel pieces (Figure 3a). When γCD-gel pieces were shaken with PhA-gel and PhE-gel pieces in water, γCD-gel pieces formed a gel assembly only with PhA-gel pieces (Figure 3b). In the case of γCD-gel with PyA-gel and PyE-gel pieces, γCD-gel pieces formed a gel assembly only with PyA-gel pieces at a higher agitation speed (ca. 500 rpm) (Figure 3c). These observations indicate that γCD-gel can discriminate the linkage between aromatic residues and the pAAm gel scaffold.

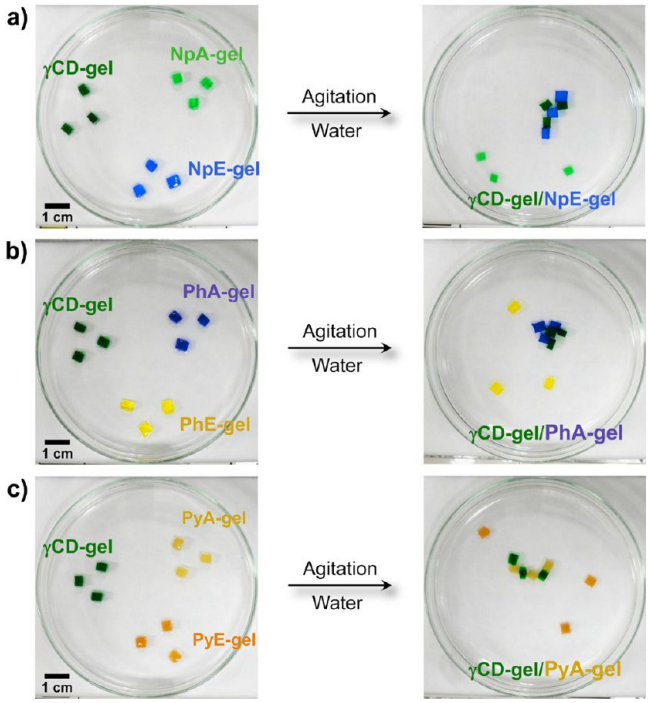


Figure 3. Pictures of the interaction of γCD-gel (bottle green) with NpA-gel (green) and NpE-gel (blue) (a), with PhA-gel (purple) and PhE-gel (yellow) (b), and with PyA-gel (yellow) and PyE-gel (orange) (c).

To understand the mechanism of the different tendencies of gel interactions of γCD-gel with the ArA-gels and with the ArE-

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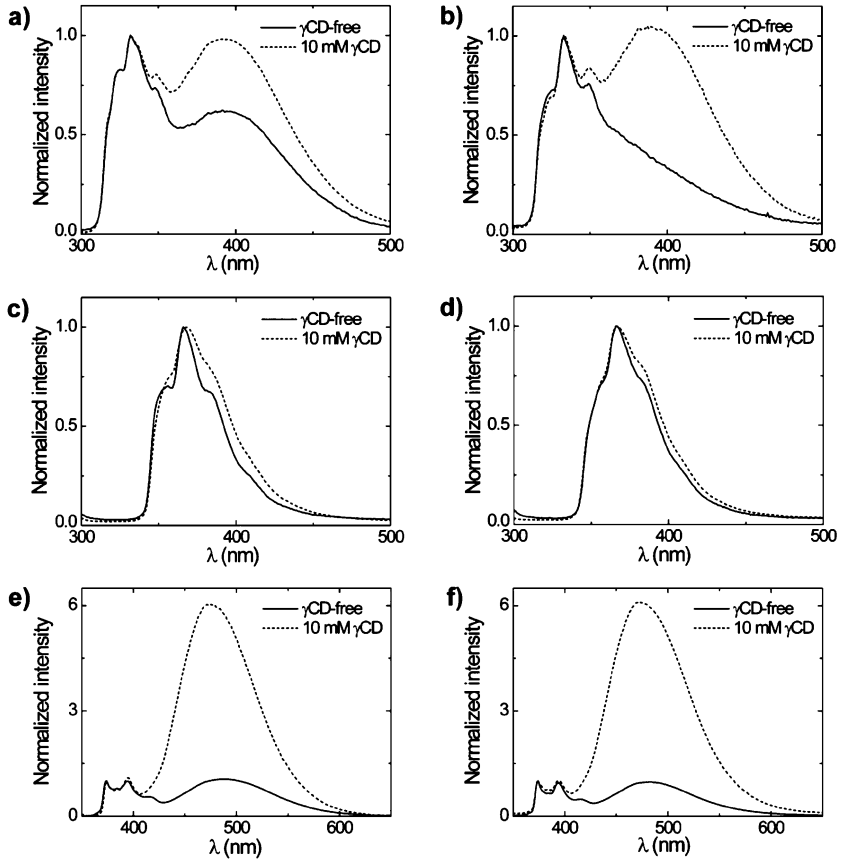

Figure 4. Reflection fluorescence spectra for NpA-gel (a), NpE-gel (b), PhA-gel (c), PhE-gel (d), PyA-gel (e), and PyE-gel (f) in the absence (solid line) and presence of 10 mM γCD (dotted line) excited at 280 (a and b), 295 (c and d), and 335 nm (e and f), respectively.

gels, reflection fluorescence spectra were recorded for the ArA-gels and ArE-gels possessing fluorescent aromatic residues (i.e, Np, Ph, and Py residues) as can be seen in Figure 4. The fluorescence spectrum for NpA-gel contained a marked band ascribable to Np excimer around 400 nm in the absence of γCD (Figure 4a). In the presence of 10 mM γCD, the spectrum exhibited a modest increase in the intensity of excimer fluorescence (Figure 4a), indicative of only a weak interaction of γCD with NpA residues in NpA-gel. On the other hand, the fluorescence spectrum of NpE-gel indicated a broad shoulder ascribable to Np excimer in the absence of γCD (Figure 4b). In the presence of 10 mM γCD, the spectrum indicated a band assignable to Np excimer enhanced remarkably (Figure 4b), indicating that γCD molecules added induced the formation of dimer of NpE residues. These observations are thus indicative of a marked interaction of γCD with NpE residues in NpE-gel. In the fluorescence spectra of PhA-gel and PhE-gel (Figure 4, parts c and d), there were no bands assignable to excimer fluorescence in the absence and presence of 10 mM γCD because it is known that phenanthrene and most of its derivatives do not emit excimer fluorescence.[41,42] In both cases, there were no remarkable differences between the spectra in the absence and presence of 10 mM γCD. However, it should be noted here that the fluorescence spectrum of PhA-gel in the presence of 10 mM γCD indicated a slight broadening and a small red shift (Figure 4c). This observation is suggestive of a weak selectivity of γCD toward PhA residues. Both the fluorescence spectra for PyA-gel and PyE-gel indicated comparable bands of monomer and excimer fluorescence in the absence of γCD, and exhibited a markedly enhanced excimer fluorescence in the presence of 10 mM γCD (Figures 4e and 4f). It is noteworthy that the maxima of excimer fluorescence indicated blue shifts and the blue shift for PyA-gel (16 nm) was larger than that for PyE-gel (8 nm) presumably because of the less polar environment inside the cavity of γCD residues.[43,44] This observation also indicates a weak selectivity of γCD toward PyA residues. All the cases examined here showed small differences in fluorescence spectra, indicative of weak selectivities of γCD. However, such weak selectivities may be largely enhanced in the macroscopic observation of interaction of CD-gels with guest gels presumably because of multivalency.

As reported in our previous paper, the formation of gel assemblies based on molecular recognition depends not only on the binding constant of CD residues with guest residues but also on the concentrations of CD and guest residues in gels.[22] In addition, in the gel interaction of γCD-gel, the aggregation properties of guest moieties are also important because γCD residues on the γCD-gel surface prefer dimeric aromatic residues.[24]

Here we compare the basic characteristics of the ArA-gels and ArE-gels used in this study (Table 3). The ArA-gels and ArE-gels were prepared by radical terpolymerization of AAm, MBA, and an aromatic monomer in DMSO using APS as an initiator. After polymerization, the solvent was replaced with water. Upon the replacement of the solvent, the ArA-gels and ArE-gels indicated different swelling properties depending on their hydrophobicity. Table 3 contains the swelling ratio (V/V_0, where V_0 and V denote the volumes of gel before and after replacement of the solvent, respectively) for the ArA-gels and

dx.doi.org/10.1021/ma302344x | Macromolecules 2013, 46, 1939−1947

Table 3. Properties for pAAm-Gel, ArA-Gels, and ArE-Gels

ArA-gel or ArE-gel	mol % content of Ara or ArE	swelling ratio[a] (V/V_0)	concn/M	stress at rupture/kPa	strain at rupture/%
pAAm-gel	–	4.9	0	1.7	320
BzA-gel	10	2.2	0.091	4.7	160
BzE-gel	10	0.7	0.286	15	310
NpA-gel	2.5	3.0	0.017	3.6	250
NpE-gel	2.5	2.0	0.025	5.1	140
PhA-gel	2.5	1.7	0.029	6.2	210
PhE-gel	2.5	1.2	0.042	17.6	500
PyA-gel	2.0	2.0	0.020	6.3	220
PyE-gel	2.0	1.2	0.033	16.5	110

[a]Swelling ratios were recorded after soaking gels in water for one week at room temperature (23 °C).

ArE-gels. For each aromatic residue, the V/V_0 value of an ArA-gel was larger than that of the corresponding ArE-gel, although the contents of AAm, MBA, and an aromatic guest were the same; 2.2 and 0.7 for BzA-gel and BzE-gel, 3.0 and 2.0 for NpA-gel and NpE-gel, 1.7 and 1.2 for PhA-gel and PhE-gel, and 2.0 and 1.2 for PyA-gel and PyE-gel, respectively. These observations indicate that the ArE-gels were more hydrophobic than the ArA-gels. In the present study, the content of cross-linker (i.e., MBA) was fixed at 2 mol % for the ArA-gels and ArE-gels carrying Bz, Np, and Ph residues and at 3 mol % for the PyA-gel and PyE-gel (see Table S1 in the Supporting Information). The stress at rupture of the ArA-gels and ArE-gels would depend on V/V_0 because an ArA-gel or ArE-gel of a larger V/V_0 contained a lower density of cross-links. It is noteworthy that PhE-gel and PyE-gel exhibited higher stresses at rupture although these V/V_0 values were modest (=1.2). This observation indicates that aggregates of PhE and PyE residues by hydrophobic or $\pi-\pi$ interactions acted as pseudocross-links in PhE-gel and PyE-gel. Furthermore, the morphologies of the ArA-gels and ArE-gels freeze-dried were observed by scanning electron microscopy (SEM). Figure 5 demonstrates a typical example of SEM images of the ArA-gels and ArE-gels. This figure also contains an image of SEM for a pAAm gel sample for comparison. All the images show network structures. Similar to previous reports on SEM observation of gels,[45−49] white parts seem to correspond to the polymer networks. These images indicate that a gel of a lower V/V_0 tends to have a network structure with smaller pores. Thus, the network structure in SEM images may depend on the hydrophobicity of gel.

The differences of properties of the ArA-gels and ArE-gels may be caused by differences of amide and ester linkages, which may be not only the difference in the hydrophobicity and rigidity of amide and ester but also the difference in the radical polymerization behavior of acrylamides and acrylates. Since the propagation rate constants of acrylates in radical polymerization are usually larger than those of the corresponding acrylamides,[50] the distributions of aromatic residues inside the gel may be different for the ArA-gels and ArE-gels. The difference in the distribution of aromatic residues may be responsible partly for the difference in hydrophobicity of the ArA-gels and ArE-gels. However, it is very difficult to investigate the distribution of aromatic residues inside the gels at present.

Since αCD and βCD residues on the gel surface prefer monomeric aromatic guest residues, the formation of gel assemblies of αCD-gel and βCD-gel is dependent dominantly on the binding constant for the model systems and on the concentrations of the CD and guest residues on the gel surfaces. In the present study, the difference in the concentration of aromatic guest residues was not critical, and αCD-gel and βCD-gel thus demonstrated the same tendencies in their interactions with the ArA-gels and with the ArE-gels. On the other hand, since γCD residues on the gel surface prefer dimeric aromatic residues, the formation of gel assemblies may depend on the aggregation behavior of aromatic residues on the gel surface, as well as on the binding constant for the model systems and the concentrations of the residues. Since the ArE-gels possessed a higher concentration of aromatic residues than did the ArA-gels because of their smaller swelling ratios (i.e., V/V_0), it is likely that the ArE-gels contained higher degrees of aggregation of aromatic residues. This may be responsible for the different tendencies of the formation of gel assemblies of γCD-gels with the ArA-gels and with the ArE-gels. γCD residues of γCD-gel may prefer aggregated NpE residues whereas they may not interact favorably with aggregated PhE or PyE residues presumably because of the size and stability of aggregates. As can be seen in Figure 4b, the fluorescence spectrum of NpE-gel exhibited only a broad shoulder assignable

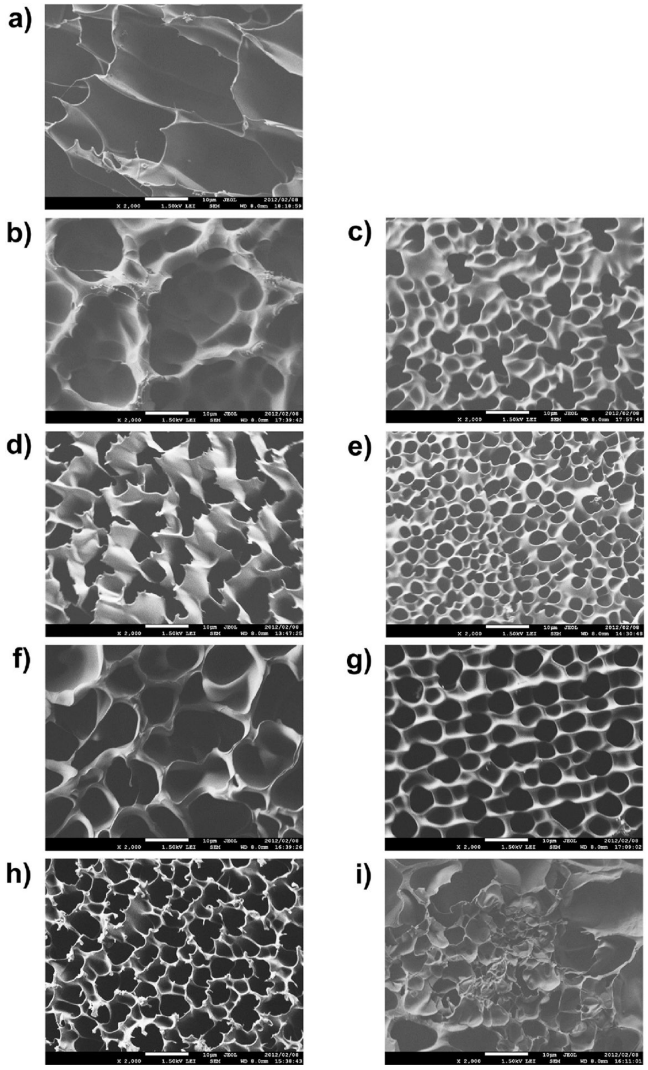

Figure 5. SEM images for freeze-dried samples of pAAm-gel (a), BzA-gel (b), BzE-gel (c), NpA-gel (d), NpE-gel (e), PhA-gel (f), PhE-gel (g), PyA-gel (h), and PyE-gel (i) at a magnification of 2×10^3. The bars correspond to 10 μm.

dx.doi.org/10.1021/ma302344x | Macromolecules 2013, 46, 1939−1947

to excimer of NpE residues even though NpE-gel contained more concentrated NpE residues. This observation is suggestive of the formation of nonfluorescent aggregates of NpE residues (larger than dimer). We are thus investigating the aggregated state of aromatic residues on the gel surface.

On the basis of the data described above, the linkage between guest residues and the pAAm gel scaffold can be an important structural factor in macroscopic observation of gel interaction, especially for γCD-gel. This is because the selectivity of macroscopic interaction can be largely enhanced by multisite interaction even though the difference between linkages is small.

CONCLUSION

The interactions of CD-gels with the ArA-gels and with the ArE-gels were investigated to examine the effect of linkage (i.e., amide and ester) between aromatic residues and the pAAm gel scaffold. The examinations of the formation of gel assemblies by shaking in water indicated that αCD-gel and βCD-gel exhibited the same tendencies of interactions with the ArA-gels and with the ArE-gels whereas γCD-gel showed different tendencies. αCD-gel did not form any gel assemblies with the ArA-gels and ArE-gels. βCD-gel interacted with the ArA-gels and ArE-gels possessing Bz and Np residues. γCD-gel formed gel assemblies with NpE-gel, PhA-gel, and PyA-gel. Reflection fluorescence spectra for the ArA-gels and ArE-gels possessing Np, Ph, and Py residues confirmed the weak selectivities of γCD toward NpE, PhA, and PyA residues. Since γCD residues in γCD-gel preferred dimeric aromatic residues, aggregation properties of the aromatic residues in the ArA-gels and ArE-gels might be important for the interaction of γCD-gel. On the basis of the data described above, the linkage between guest residues and the pAAm gel scaffold can be an important structural factor in macroscopic observation of gel interaction, because that the selectivity of macroscopic interaction can be largely enhanced by multisite interaction even though the difference between linkages is small.

EXPERIMENTAL SECTION

Measurements. ^{1}H NMR spectra were measured on a JEOL JNM-ECA500 spectrometer. Chemical shifts were referenced to the solvent values (2.49 and 4.79 ppm for DMSO-d_6 and D_2O, respectively). Positive-ion matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI−TOF−MS) experiments were performed using a Bruker autoflex speed mass spectrometer using 2,5-dihydroxy-benzoic acid as a matrix. Mass number was calibrated by four peptides, i.e., Angiotensin II ($[M + H]^+$ 1046.5418), Angiotensin I ($[M + H]^+$ 1296.6848), Substance P ($[M + H]^+$ 1347.7354), and Bombesin ($[M + H]^+$ 1619.8223). Gel assembly tests were carried out using an EYELA CM-1000 cute mixer. The agitation speed was fixed at ca. 400 rpm unless otherwise indicated. Stress−strain curves for gel assemblies were recorded using a Yamaden RE-33005 Rheoner creep meter. Each sample was prepared in a quartz mold of 5 × 3 mm^2 in cross sectional area and measured at a rate of 0.1 mm s^{-1} at room temperature. Fluorescence spectra for solutions of the model systems were obtained on a HITACHI F-2500 spectrophotometer using a 1 cm quartz cuvette. The slit widths for both excitation and emission sides were kept at 2.5 nm during measurement. Reflection fluorescence spectra for gel samples were obtained using a HORIBA FluoroMax-4 spectrofluorometer. A quartz plate with a thin gel film was fixed on the holder of the fluorometer to obtain spectra. SEM images were obtained on a JEOL-7600F scanning electron microscope. A piece of freeze-dried gel sample was set on the holder using a double-sided adhesive and conductive tape. The morphology of gel surface was scanned at an accelerating voltage of 1.50 kV with the LEI mode.

Materials. 1-Pyrenemethylamine hydrochloride was purchased from Sigma-Aldrich Co., Ltd. 2-Naphthalenemethanol, 2-naphthylmethylamine hydrochloride, 9-phenanthrenecarbaldehyde, carbon tetrabromide (CBr_4), and sodium azide (NaN_3) were purchased from Wako Pure Chemical Industries, Ltd. Benzyl alcohol, benzylamine, 1-pyrenemethanol, and acryloyl chloride were obtained from Tokyo Chemical Industry Co., Ltd. Triethylamine (Et_3N), sodium borohydride ($NaBH_4$), triphenylphosphine (PPh_3), magnesium sulfate, AAm, APS, TMEDA, MBA, DMSO, acetone, methanol, 2-propanol, ethyl acetate, diethyl ether, sodium bicarbonate, and sodium hydroxide were purchased from Nacalai Tesque Inc. *N*,*N*-Dimethylformamide, dichloromethane (DCM), and tetrahydrofuran (THF) were purified by utilizing a Glass Contour solvent dispending system. Water was purified by a Millipore Milli-Q system. αCD, βCD, and γCD were purchased from Junsei Chemical Co., Ltd. and recrystallized twice from water prior to use. Other reagents were reagent grade and used without further purification.

9-Phenanthrenemethanol was prepared from phenanthrylmethyl-9-carboxyaldehyde with $NaBH_4$ according to the procedure of Forrester et al.[51] 9-Bromomethylphenanthrene was prepared from 9-phenanthrenemethanol using CBr_4 in the presence of PPh_3 by a slight modification of the procedure of Drouet et al.[52] 9-Azidomethylphenanthrene was prepared from 9-bromomethylphenanthrene and NaN_3, and then 9-phenanthrylmethylamine was prepared from 9-azidomethylphenanthrene with PPh_3 by a slight modification of the procedure of Ahlford et al.[53]

AαCD, Aβ CD, and Aγ CD were prepared as reported previously.[54]

Preparation of Aromatic Acylamides (ArA). *N*-Benzylacrylamide (BzA),[23] *N*-(2-naphthyl)methylacrylamide (NpA),[22] and *N*-(1-pyrenyl)methylacrylamide (PyA)[24] were prepared as reported previously.

N-9-Phenanthrylmethylacrylamide (PhA). To a solution of 9-phenanthrylmethylamine (622 mg, 3.0 mmol) and Et_3N (622 μL, 4.5 mmol) in THF (15 mL), a solution of acryloyl chloride (354 μL, 4.5 mmol) in THF (5 mL) was added dropwise at 0 °C under an argon atmosphere with stirring. The reaction was allowed to run at room temperature overnight. The precipitate formed was removed by filtration. After evaporation of the solvent, the product was purified by silica gel column chromatography using a mixed solvent of ethyl acetate and hexane (1/2, v/v) as eluent to give the product in 41% yield. ^{1}H NMR (500 MHz, DMSO-d_6, 30 °C) δ 8.901−8.850 (m, 1H, phenanthryl), 8.809 (d, *J* = 8.2 Hz, 1H, phenanthryl), 8.643 (d, *J* = 5.3 Hz, 1H, NH), 8.126 (dd, *J* = 8.0 and 1.4 Hz, 1H, phenanthryl), 7.949 (dd, *J* = 7.7 and 1.4 Hz, 1H, phenanthryl), 7.771 (s, 1H, phenanthryl), 7.744−7.607 (m, 4H, phenanthryl), 6.320 (dd, *J* = 17.1 and 10.2 Hz, 1H, vinyl), 6.178 (dd, *J* = 17.0 and 2.3 Hz, 1H, vinyl), 5.632 (dd, *J* = 10.1 and 2.3 Hz, 1H, vinyl), 4.863 (d, *J* = 5.7 Hz, 2H, methylene). Positive ion MALDI−TOF−MS: *m*/*z* = 261.3, $[M]^+$ 261.3, $[M + Na]^+$ 283.9, $[M + K]^+$ 299.9.

Preparation of Aromatic Acrylates (ArE). To a solution of aromatic methanol (10 mmol) and Et_3N (15 mmol) in THF (40 mL), a solution of acryloyl chloride (15 mmol) in THF (5 mL) was added dropwise at 0 °C under an argon atmosphere with stirring. The reaction was allowed to run at room temperature overnight. The precipitate formed was removed by filtration. After evaporation of the solvent, the mixture was purified by silica gel column chromatography to give aromatic acrylate monomer.

Benzyl Acrylate (BzE). BzE was obtained as an oil after purifying by silica gel column chromatography using a mixed solvent of diethyl ether and hexane (1/20, v/v) in 40% yield. ^{1}H NMR (500 MHz, DMSO-d_6, 30 °C) δ 7.394−7.309 (m, 5H, phenyl), 6.359 (dd, *J* = 17.3 and 1.6 Hz, 1H, vinyl), 6.219 (dd, *J* = 17.3 and 10.3 Hz, 1H, vinyl), 5.961 (dd, *J* = 10.31 and 1.6 Hz, 1H, vinyl), 5.175 (s, *J* = 2H, methylene).

2-Naphthylmethyl Acrylate (NpE). NpE was obtained as an oil after purifying by silica gel column chromatography using a mixed solvent of DCM and hexane (1/10, v/v) in 48% yield. ^{1}H NMR (500 MHz, DMSO-d_6, 30 °C) δ 7.939−7.893 (m, 4H, naphthyl), 7.545−7.497 (m,

dx.doi.org/10.1021/ma302344x | Macromolecules 2013, 46, 1939−1947

3H, naphthyl), 6.390 (dd, J = 17.3 and 1.6 Hz, 1H, vinyl), 6.253 (dd, J = 17.3 and 10.3 Hz, 1H, vinyl), 5.978 (dd, J = 10.3 and 1.6 Hz, 1H, vinyl), 5.346 (s, 2H, methylene). Positive ion MALDI−TOF−MS: m/z = 212.2, $[M]^+$ 212.7, $[M + Na]^+$ 235.7, $[M + K]^+$ 251.7.

9-Phenanthrylmethyl Acrylate (PhE). PhE was obtained as a colorless crystalline product after purifying by silica gel column chromatography using a mixed solvent of DCM and hexane (1/6, v/v) in 65% yield. ^{1}H NMR (500 MHz, DMSO-d_6, 30 °C) δ 8.863 (dd, J = 29.7 and J = 8.3 Hz, 2H, phenanthryl), 8.040 (dd, J = 43.7 and J = 7.3 Hz, 2H, phenanthryl), 7.952 (s, 1H, phenanthryl), 7.762−7.639 (m, 4H, phenanthryl), 6.377 (dd, J = 17.2 and 1.4 Hz, 1H, vinyl), 6.246 (dd, J = 17.3 and 10.3 Hz, 1H, vinyl), 5.969 (dd, J = 10.3 and 1.4 Hz, 1H, vinyl), 5.700 (S, 2H, methylene). Positive ion MALDI−TOF−MS: m/z = 262.3, $[M]^+$ 262.7, $[M + Na]^+$ 285.7, $[M + K]^+$ 301.7.

1-Pyrenylmethyl Acrylate (PyE). PyE was obtained as colorless powder after purifying by silica gel column chromatography using a mixed solvent of DCM and hexane (1/10, v/v) in 40% yield. ^{1}H NMR (500 MHz, DMSO-d_6, 30 °C) δ 8.367−8.268 (m, 5H, pyrenyl), 8.221−8.132 (m, 3H, pyrenyl), 8.098 (t, J = 7.6 Hz, 1H, pyrenyl), 6.373 (dd, J = 17.3 and 1.6 Hz, 1H, vinyl), 6.237 (dd, J = 17.3 and 10.3 Hz, 1H, vinyl), 5.954 (dd, J = 10.3 and 1.6 Hz, 1H, vinyl), 5.927 (s, 2H, methylene). Positive ion MALDI−TOF−MS: m/z = 286.3, $[M]^+$ 286.3, $[M + Na]^+$ 309.3, $[M + K]^+$ 325.3.

Preparation of the Guest Gels (ArA-Gels and ArE-Gels). The ArA-gels (i.e., BzA-gel, NpA-gel, PhA-gel, and PyA-gel) and ArE-gels (i.e., BzE-gel, NpE-gel, PhE-gel, and PyE-gel) were prepared by radical terpolymerization of AAm, MBA, and an aromatic acrylamide or acrylate. A predetermined amount of AAm, MBA, and an aromatic monomer were dissolved in DMSO (1.5 mL). After purging with dry argon for 30 min, APS (3 mg, 13 μmol) was added to the monomer solution. The reaction mixture was placed into a 1 cm quartz cuvette and sealed. The cuvette was set in an oven thermostated at 60 °C for 6 h. The resulting gel was soaked in water for several days to remove the solvent and the unreacted monomers and initiators. For visual identification, the ArA-gels and ArE-gels obtained were dyed by immersing into solutions of the different dyes.

Preparation of the Host Gels (CD-Gels). The CD-gels used in this study were prepared as reported previously.[22−24] αCD-gel, βCD-gel, and γCD-gel were dyed with blue, red, and green color, respectively, by immersing into a solution of the corresponding dye.

■ ASSOCIATED CONTENT

Supporting Information

Preparation of the model polymers and the interaction of the model systems composed of native CDs and the model polymers, tables for conditions of the gel preparation and binding constants of the model systems, and a chart showing chemical structures for the model polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors thank Dr. Akihiro Ito, Department of Chemistry, Graduate School of Science, Osaka University, for SEM experiments. The authors appreciate the technical assistants from Mrs. Miyuki Otsubo, Mr. Takahiro Kakuta, and Mr. Masaki Nakahata, Department of Macromolecular Science, Graduate School of Science, Osaka University. This work was financially supported by the Japan Science and Technology Agency (JST), the Core Research for Evolutional Science and Technology (CREST).

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