ACS Macro Letters

Letter

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Temperature-Sensitive Macroscopic Assembly Based on Molecular Recognition

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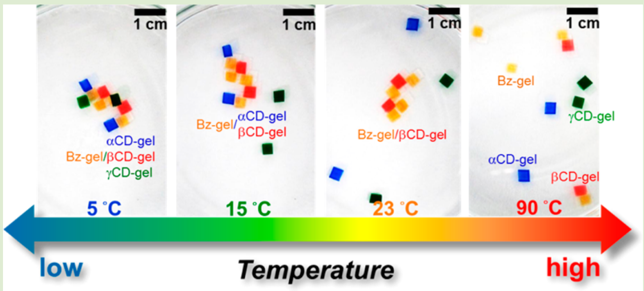
Supporting Information

ABSTRACT: The interaction of polyacrylamide(pAAm)-based gel modified with benzyl (Bz) moiety (Bz(*x*)-gel, where *x* denotes the mol % content of Bz moiety) with a pAAm-based gel possessing cyclodextrin (CD) moieties (αCD-gel, βCD-gel, and γCD-gel) was investigated at various temperatures to elucidate the effect of temperature on the formation of macroscopic assembly. The interaction of Bz(*x*)-gel with CD-gels was stronger at a lower temperature, consistent with the binding constants for the model system of pAAm modified with 1 mol % Bz moiety and native CDs. Bz(15)-gel interacted only with βCD-gel at a higher temperature (<ca. 90 °C), with αCD-gel at a temperature ≤15 °C, and with γCD-gel at 5 °C to form gel assemblies. The formation of gel assemblies depending on temperature showed a good reversibility. On the basis of these observations, it is concluded that temperature is also an important stimulus for macroscopic assembly based on molecular recognition.



Macroscopic assemblies based on molecular recognition play vital roles for living things in biological systems. In artificial systems, macroscopic assemblies based on molecular recognition also promise as highly functional materials, for example, self-healing and stimuli-responsive materials,[1] but construction of such artificial macroscopic assemblies has still been a great challenge. Recently, we have demonstrated macroscopic molecular recognition using polyacrylamide-(pAAm)-based hydrogels possessing cyclodextrin (CD) and guest moieties.[2] According to their binding affinities, gels possessing αCD, βCD, and γCD moieties recognize gels possessing their respective counterparts.[2−4] More recently, we have also realized macroscopic assemblies responsive to light[5] and chemical stimuli.[6] Among a variety of stimuli, temperature is one of the most important and utilized stimuli.[7] The formation of inclusion complexes of CDs with guest compounds is also strongly dependent on temperature.[8] In this study, we thus study the effect of temperature on the formation of macroscopic assemblies using pAAm-based gel modified with a benzyl (Bz) moiety and a pAAm-based gel possessing CD moieties (αCD-gel, βCD-gel, and γCD-gel).

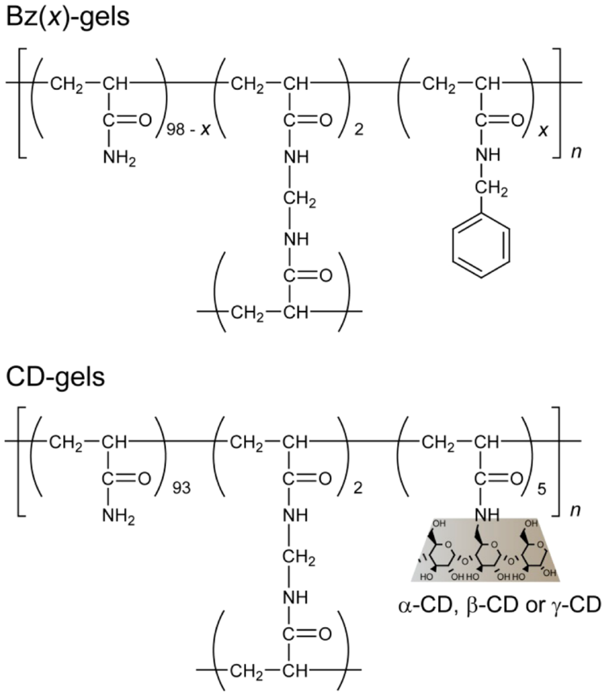
The host gels (CD-gels) and guest gels (Bz(*x*)-gels, where *x* denotes the mol % of the Bz monomer) used in this study were prepared by conventional radical copolymerization, as we reported previously (Scheme 1 and Supporting Information).[2−4] The mol % content of the CD monomer in the CD gels were fixed at 5 mol % in this study. Three Bz(*x*)-gel samples (Bz(5)-gel, Bz(10)-gel, and Bz(15)-gel) were prepared by adjusting the feed ratio of the Bz monomer. The basic characteristics of the Bz(*x*)-gel samples are listed in Table S1 in Supporting Information. It is noteworthy that the swelling ratio is smaller for Bz(*x*)-gel of a larger *x* because the Bz moiety is rather hydrophobic. Thus, Bz(15)-gel contains much more concentrated Bz moieties.

The formation of the gel assembly of Bz(15)-gel with αCD-gel, βCD-gel, and γCD-gel was first examined in a Petri dish containing water with shaking at different temperatures, as can be seen in Figure 1. Bz(15)-gel pieces do not form any assembly with αCD-gel pieces at 23 ± 1 °C, whereas these gel pieces interact to form an alternating assembly at 15 ± 1 °C (Figure 1a). Bz(15)-gel pieces interact rather strongly with βCD-gel pieces even at 23 ± 1 °C (Figure 1b). These observations are consistent with the binding constants (*K*) estimated by ^{1}H NMR for the model system of pAAm modified with 1 mol % Bz moieties (pAAm/Bz) (Table S2 and Scheme S1 in Supporting Information). The *K* values for αCD and βCD range $(1.3{-}2.2) \times 10^1$ and $(0.84{-}1.0) \times 10^2$ M^{-1}, respectively, and *K* decreases with increasing temperature, indicating that the interaction of the Bz moiety with αCD and βCD is more favorable at a lower temperature. Bz(15)-gel pieces do not interact with γCD-gel pieces at either 23 ± 1 or 15 ± 1 °C, but these gel pieces unexpectedly assemble at 5 ± 1

Received: July 3, 2012
Accepted: August 6, 2012
Published: August 8, 2012

dx.doi.org/10.1021/mz300338d | *ACS Macro Lett.* 2012, 1, 1083−1085

Scheme 1. Chemical Structures of Bz(*x*)-gels and CD-gels (*α*CD-gel, *β*CD-gel, and *γ*CD-gel)



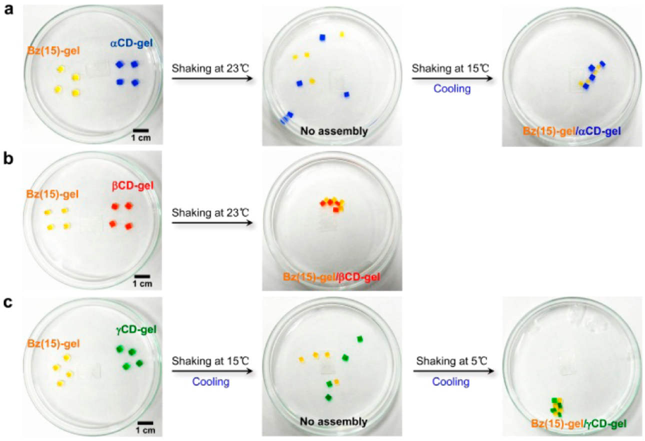


Figure 1. Photographs of the interaction of Bz(15)-gel with *α*CD-gel (a), *β*CD-gel (b), and *γ*CD-gel (c) at different temperatures.

°C despite almost no interaction for the model system (Figure 1c and Table S2). This may be because *γ*CD moieties in *γ*CD-gel include aggregated Bz moieties (e.g., dimers or trimers) on the surface of the Bz(15)-gel which possesses concentrated Bz moieties. These observations indicate that Bz(15)-gel adheres to all the CD-gels used in this study. On the basis of the temperatures at which gel assemblies are formed, the strength of adhesion of the Bz(15)-gel is considered to decrease in the order of *β*CD-gel > *α*CD-gel > *γ*CD-gel, consistent with the *K* values for the interaction of pAAm/Bz with native CDs.

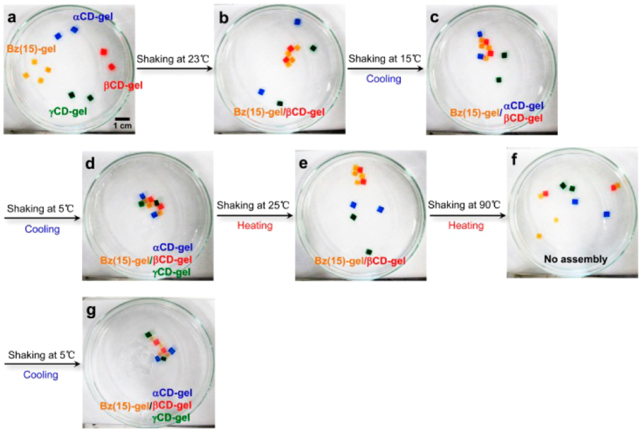


Figure 2. Photographs of the interaction of Bz(15)-gel with *α*CD-gel, *β*CD-gel, and *γ*CD-gel at different temperatures: before (a) and after mixing at 23 ± 1 °C (b), cooled down to 15 ± 1 °C (c), cooled down to 5 ± 1 °C (d), warmed to 25 ± 2 °C (e), heated up to 90 ± 3 °C (f), cooled down to 5 ± 1 °C (g).

It is noteworthy that the formation of gel assemblies depending on temperature demonstrates a good reversibility (Figure 2). A mixture of pieces of Bz(15)-gel, *α*CD-gel, *β*CD-gel, and *γ*CD-gel were located and shaken in a Petri dish containing water with changing temperature. At 23 ± 1 °C, Bz(15)-gel pieces interact only with *β*CD-gel pieces to form an assembly (Figure 2b). When temperature is decreased down to 15 ± 1 °C, Bz(15)-gel pieces form an assembly with both *α*CD-gel and *β*CD-gel pieces (Figure 2c). When the temperature is further decreased, all the gel pieces form a large assembly at 5 ± 1 °C (Figure 2d). When the temperature is increased from 5 ± 1 to 25 ± 2 °C with shaking, *α*CD-gel and *γ*CD-gel pieces are separated from the large assembly, whereas *β*CD-gel pieces still form an assembly with Bz(15)-gel pieces (Figure 2e). When temperature is further increased, the gel assembly composed of Bz(15)-gel and *β*CD-gel pieces dissociates at 90 ± 3 °C (Figure 2f), indicative of a strong interaction of Bz(15)-gel with *β*CD-gel presumably because of multisite interaction. When the system is cooled down to 5 ± 1 °C, all the gel pieces reassemble to form a large assembly (Figure 2g). These observations indicate that Bz(15)-gel associates with and dissociates from CD-gel at a certain temperature depending on the CD moiety. The association and dissociation are repeated at least several times, indicative of a good reversibility (Figure 3).

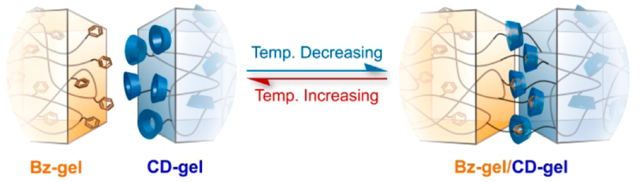


Figure 3. Conceptual illustration for thermally controlled assembly by Bz-gel and CD-gel.

As we reported previously,[4] the interaction of guest-gels with CD-gels depends on the guest content in guest gels. The effect of the Bz content, that is, *x*, on the interaction of Bz(*x*)-gel with CD-gels was thus investigated by shaking in a Petri dish containing water. The results are summarized in Table S3 in Supporting Information. Bz(5)-gel pieces do not interact with any CD-gel pieces at 23 ± 1 °C, but Bz(5)-gel pieces form an assembly only with *β*CD-gel pieces at 5 ± 1 °C. Bz(10)-gel pieces interact only with *β*CD-gel to form an assembly at 23 ± 1 °C, whereas Bz(10)-gel pieces assemble not only with *β*CD-gel pieces, but also with *α*CD-gel pieces at 5 ± 1 °C. On the other hand, neither the Bz(5)-gel nor the Bz(10)-gel interact with the *γ*CD-gel in the temperature range examined (5−23

°C). The concentrations of Bz moiety in Bz(5)-gel and Bz(10)-gel are much lower than that in Bz(15)-gel because of a larger swelling ratio. It is thus likely that γCD moieties in γCD-gel include associated Bz moieties on the surface of the Bz(15)-gel.

To estimate the strength of interaction of gels, the adhesion strengths for gel assemblies of Bz(x)-gels with αCD-gel, βCD-gel, and γCD-gel were evaluated by rupture stress−strain measurements. Because the gel samples for these rupture stress−strain measurements were prepared in a 1 cm quartz cuvette, all the gel samples were equally smooth. Thus, the differences in roughness (i.e., smoothness) of the gel surfaces had a negligible effect on these measurements. Figure 4 compares the stresses at rupture determined for pairs of Bz(x)-gel/CD-gel at different temperatures. For all the pairs of Bz(x)-gel/CD-gel, the stress at rupture increases with decreasing temperature, consistent with the K values for the model system composed of pAAm/Bz and native CDs. It is noteworthy that the Bz(15)-gel/βCD-gel system exhibits a rather weak tendency of an increase in the stress at rupture with a saturation at about 7×10^3 Pa, which is close to the stress at rupture of Bz(15)-gel ($(7.2 \pm 0.8) \times 10^3$ Pa). At a constant x and temperature, the stress at rupture for Bz(x)-gel/CD-gel decreases in the order of βCD-gel > αCD-gel > γCD-gel; Bz(x)-gel interacts most strongly with βCD-gel, showing a good agreement with the K values for the model system. In all cases of the CD-gels, the stress at rupture also increases with x. Compared with the results of the gel interaction (Table S3), gel assemblies are formed for a pair of Bz(x)-gel/CD-gel, which exhibits the stress at rupture > about 1×10^3 Pa.

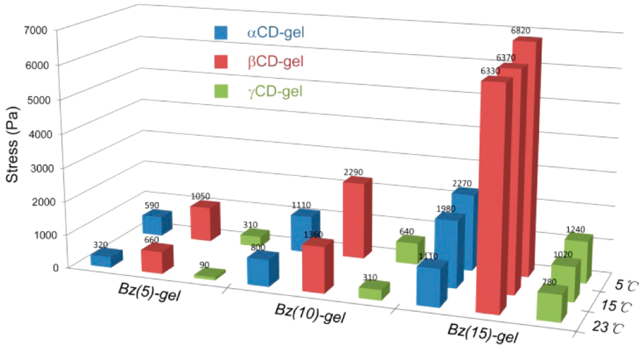


Figure 4. Stresses at rupture for assemblies of Bz(x)-gels with αCD-gel (blue), βCD-gel (red), and γCD-gel (green) at 5 ± 1, 15 ± 1, and 23 ± 1 °C, respectively.

In conclusion, macroscopic assembly of Bz(x)-gel with αCD-gel, βCD-gel, and γCD-gel was investigated at different temperatures. At 23 ± 1 °C, Bz(15)-gel interacted only with βCD-gel. When the temperature was decreased down to 15 ± 1 °C, the Bz(15)-gel interacted with both αCD-gel and βCD-gel. When the temperature was further decreased, the Bz(15)-gel interacted with all αCD-gel, βCD-gel, and γCD-gel to form a large assembly at 5 ± 1 °C. The formation of gel assemblies depending on temperature indicated a good reversibility. The strength of interaction of Bz(x)-gel with CD-gels decreased in the order of βCD-gel > αCD-gel > γCD-gel, consistent with the K values for the model system of pAAm/Bz and native CDs. This study has proved that temperature is also a critical stimulus for macroscopic assembly based on molecular recognition.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental section, determination of binding constants for the model system, and additional experimental data are included. 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 interests.

■ ACKNOWLEDGMENTS

The authors thank Mr. Ken-ichi Iijima and Ms. Tomomi Hirai, Osaka University, for elemental analysis. 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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