

Control of the macroscopic shape of assemblies formed from microparticles based on host–guest interaction

Takahiro Itami

Graduate School of Science, Osaka University

Akihito Hashidzume (✉ hashidzume@chem.sci.osaka-u.ac.jp)

Osaka University <https://orcid.org/0000-0003-0061-3432>

Yuri Kamon

Graduate School of Science, Osaka University

Hiroyasu Yamaguchi

Osaka University <https://orcid.org/0000-0002-4801-5071>

Akira Harada

Osaka University

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Abstract

Biological macroscopic assemblies have inspired researchers to utilize molecular recognition to develop smart materials in these decades. Recently, macroscopic self-assemblies based on molecular recognition have been realized using millimeter-scale hydrogel pieces possessing molecular recognition moieties. During the study on macroscopic self-assembly based on molecular recognition, we noticed that the shape of assemblies might be dependent on the host–guest pair. In this study, we were thus motivated to study the macroscopic shape of assemblies formed through host–guest interaction. We modified crosslinked poly(sodium acrylate) microparticles, i.e., superabsorbent polymer (SAP) microparticles, with β -cyclodextrin (β CD) and adamantyl (Ad) residues (β CD(x)-SAP and Ad(y)-SAP microparticles, respectively, where x and y denote the mol % contents of β CD and Ad residues). Then, we studied the self-assembly behavior of β CD(x)-SAP and Ad(y)-SAP microparticles through the complexation of β CD with Ad residues. There was a threshold of the β CD content in β CD(x)-SAP microparticles for assembly formation between $x = 22.3$ and 26.7 . On the other hand, the shape of assemblies was dependent on the Ad content, y ; More elongated assemblies were formed at a higher y . This may be because, at a higher y , small clusters formed in an early stage can stick together even upon collisions at a single contact point to form elongated aggregates, whereas, at a smaller y , small clusters stick together only upon collisions at multiple contact points to give rather circular assemblies. On the basis of these observations, the shape of assembly formed from microparticles can be controlled by varying y .

Introduction

Biological systems utilize macroscopic self-assemblies based on molecular recognition. In these decades, biological macroscopic assemblies have inspired researchers to utilize molecular recognition to develop smart materials, e.g., soft actuators¹⁻⁶ and self-healing materials⁷⁻²². Recently, macroscopic self-assemblies, which allow ones to see molecular recognition by naked eyes, have been realized using millimeter-scale hydrogel pieces possessing molecular recognition moieties²³⁻²⁷. Even if the difference in binding constants of molecular recognition moieties is small, the systems of mixture of gel pieces can exhibit perfect fidelity by controlling the contents of molecular recognition moieties²⁸⁻³⁰. During the study on macroscopic self-assembly based on molecular recognition, we noticed that the shape of assemblies might be dependent on the host–guest pair; For example, the pair of β -cyclodextrin (β CD) and adamantyl (Ad), which shows one of the highest binding constants, led to the formation of linear alternating assemblies, whereas β CD and *t*-butyl, which possesses a lower binding constant, might form planar checkered assemblies²³. We were thus motivated to study the macroscopic shape of assemblies formed through host–guest interaction. We have chosen crosslinked poly(sodium acrylate) microparticles, i.e., superabsorbent polymer (SAP) microparticles, because of the availability and ease of modification. We have employed a combination of β CD and Ad as host and guest residues, respectively, because this combination forms stable inclusion complexes. In the present article, we describe preparation of SAP microparticles modified with β CD and Ad residues (β CD(x)-SAP and Ad(y)-SAP microparticles,

respectively, where x and y denote the mol % contents of β CD and Ad residues), and the self-assembly behavior of β CD(x)-SAP and Ad(y)-SAP microparticles through the complexation of β CD with Ad residues, and discuss the effect of the contents of residues, i.e., x and y , on the self-assembly behavior.

Results

Preparation of Superabsorbent Polymer Microparticles Modified with β -Cyclodextrin and Adamantyl

Residues. SAP microparticles were modified with β CD and adamantyl (Ad) residues (β CD(x)-SAP and Ad(y)-SAP microparticles, respectively, where x and y denote the mol % contents of β CD and Ad residues) by coupling of mono-(6-amino-6-deoxy)- β -CD (β CD-NH₂) and 1-adamantanamine hydrochloride (Ad-NH₂•HCl) with carboxylic acid residues in SAP microparticles using 4-(4,6-dimethoxy-1,3,5-triazin-2-yl)-4-methylmorpholinium chloride *n*-hydrate (DMT-MM) as a coupling agent (Scheme 1). The β CD(x)-SAP and Ad(y)-SAP microparticles were purified by washing repeatedly with water for a few days. The β CD(x)-SAP and Ad(y)-SAP microparticles prepared were characterized by solid-state ¹H field gradient magic angle spinning (FGMAS) NMR and attenuated total reflectance (ATR) FT/IR spectroscopy (Figures S1 and S2 in Supporting Information, respectively). As can be seen in Figure S1, the ¹H FGMAS NMR spectra exhibited signals ascribable to β CD and Ad residues for β CD(x)-SAP and Ad(y)-SAP microparticles at 5.32 and 1.64 ppm, respectively. As shown in Figure S2, the ATR FT/IR spectra contain absorption bands ascribable to the stretching vibration of C=O of the amide bond at ca. 1650 cm⁻¹. These spectra are indicative of successful modification of SAP microparticles.

The contents of β CD and Ad residues in β CD(x)-SAP and Ad(y)-SAP microparticles, x and y , were roughly estimated by the weights of remaining β CD-NH₂ and Ad-NH₂•HCl recovered from the reaction mixtures, as listed in Tables 1 and 2. The β CD and Ad contents in β CD(x)-SAP and Ad(y)-SAP microparticles are markedly lower than those in feed. It should be noted here that the differences in contents are much larger for the Ad(y)-SAP microparticles than those for β CD(x)-SAP microparticles. This may be caused by the difference in reactivities of β CD-NH₂ and Ad-NH₂•HCl. β CD-NH₂ is a primary amine, whereas Ad-NH₂•HCl is a tertiary ammonium. The hydrochloride, Ad-NH₂•HCl, was used because of the low solubility of 1-adamantanamine in water. The pH values of reaction media were thus different for modification with β CD and Ad residues; pH = 8.1 and 6.3 for β CD and Ad residues, respectively. Since, in amide coupling reactions using DMT-MM, the 4,6-dimethoxy-1,3,5-triazine residue is attacked by a carboxylate ion, the coupling proceeds less efficiently at lower pH³¹. Therefore, the lower pH upon modification with Ad residues may be partly responsible for the reduced Ad contents in Ad(y)-SAP microparticles. It should be also noted that SAP microparticles exhibited different absorption properties for β CD-NH₂ and Ad-NH₂•HCl. The affinities of SAP microparticles for β CD-NH₂ and Ad-NH₂•HCl were compared by adsorption experiments. SAP microparticles fully swelled with water (2.0 g) were added to an aqueous solution of β CD-NH₂ or Ad-NH₂•HCl (5.0 mM, 10 mL). After equilibration, the concentration of solute, i.e., β CD-NH₂ or AdNH₂•HCl, and the volumes of aqueous solution and SAP microparticles were determined. Using these

data, the amounts of β CD-NH₂ and Ad-NH₂·HCl adsorbed were evaluated to be ca. 52 and 2.3 mg, respectively, per 1 g of SAP microparticles, indicating that β CD-NH₂ is adsorbed into SAP microparticles more strongly than Ad-NH₂·HCl. It is thus likely that β CD residues were introduced efficiently not only to carboxylate residues on the surface of SAP microparticles but also to those inside of SAP microparticles, whereas Ad residues were introduced dominantly to carboxylate residues on the outer layer of SAP microparticles.

Table 1 | Conditions and results of preparation of β CD(*x*)-SAP microparticles.

feed (mol%)	native-SAP / mg (COOH unit / mmol)	β CD-NH ₂ / mg (mmol)	DMT-MM / mg (mmol)	<i>x</i> (mol%)
30	10.1 (0.179)	60.7 (0.053)	22.3 (0.081)	16.2
40	10.2 (0.180)	81.2 (0.072)	30.0 (0.107)	22.3
100	10.1 (0.179)	203.6 (0.179)	74.5 (0.270)	26.7

Table 2 | Conditions and results of preparation of Ad(*y*)-SAP microparticles.

feed (mol%)	native-SAP / mg (COOH unit / mmol)	Ad-NH ₂ ·HCl / mg (mmol)	DMT-MM / mg (mmol)	<i>y</i> (mol%)
10	10.0 (0.178)	3.4 (0.018)	7.5 (0.027)	5.2
30	10.2 (0.180)	10.2 (0.053)	22.3 (0.081)	7.1
50	10.0 (0.180)	16.8 (0.090)	37.1 (0.13)	10.7
200	10.2 (0.180)	67.0 (0.36)	149 (0.54)	15.1

The average diameters (D_{av}) for a hundred of β CD(*x*)-SAP and Ad(*y*)-SAP microparticles were determined by observing on an optical microscope. Values of D_{av} were plotted in Figure 1 against the β CD or Ad content, i.e., *x* or *y*. The D_{av} values (ca. 100 μ m) for β CD(*x*)-SAP microparticles were significantly smaller than that for unmodified SAP microparticles, whereas the D_{av} values (ca. 190 μ m) for Ad(*y*)-SAP microparticles were almost the same as that for SAP microparticles independent of *y*. The smaller D_{av} values for β CD(*x*)-SAP microparticles indicate that β CD residues in β CD(*x*)-SAP microparticles interact with each other or with carboxylate residues presumably through hydrogen bonding formation, resulting in a reduced swelling ratio of microparticles. These observations may support the different fashions of modification for β CD and Ad residues.

For visual discrimination, dyeing of Ad(*y*)-SAP microparticles was tested using several dyes. The food pigments, which we had used for poly(acrylamide)-based gels in our previous studies^{23,24,28-30}, were not useful in this study because the pigment molecules quickly came out of Ad(*y*)-SAP microparticles. The results of dyeing test indicated that pararosaniline was a useful dye presumably because of electrostatic interaction between the ammonium in pararosaniline and carboxylate residues in Ad(*y*)-SAP microparticles (Figure S3 in Supporting Information). Under the dyeing conditions in this study, the size distributions of Ad(*y*)-SAP microparticles were almost the same before and after dyeing (data not shown). It is thus likely that pararosaniline has no effect on the properties of Ad(*y*)-SAP microparticles and on the interaction of β CD(*x*)-SAP and Ad(*y*)-SAP microparticles. In the following, Ad(*y*)-SAP microparticles dyed with pararosaniline were used; Colorless and red particles are β CD(*x*)-SAP and Ad(*y*)-SAP microparticles, respectively.

Interaction of β CD(*x*)-SAP and Ad(*y*)-SAP Microparticles. The interaction of β CD(*x*)-SAP and Ad(*y*)-SAP microparticles was investigated by observing on an optical microscope. A suspension containing ca. 50 β CD(*x*)-SAP microparticles in water (1 μ L) and a suspension containing ca. 50 Ad(*y*)-SAP microparticles in water (1 μ L) were mixed on a clean slide glass. Since the SAP microparticles used in this study did not undergo practically Brownian motion because of their larger size, the mixed suspension was agitated at 500 rpm using a mixer to investigate the interaction. Typical examples of assemblies formed are shown in Figure 2. The results of interaction are summarized in Table S1 in Supporting Information. In this table, “–” denotes no assembly formation from β CD(*x*)-SAP and Ad(*y*)-SAP microparticles, and “+” denotes the formation of assemblies from microparticles. β CD(*x*)-SAP microparticles of *x* = 16.2 or 22.3 did not adhere to any of the Ad(*y*)-SAP microparticles used in this study, indicating that the number of β CD residues on the surface of β CD(*x*)-SAP microparticles of *x* = 16.2 or 22.3 was not enough for assembly formation with the Ad(*y*)-SAP microparticles. On the other hand, β CD(26.7)-SAP microparticles interacted with all the Ad(*y*)-SAP microparticles examined to form assemblies. These observations indicate that there is a threshold of the β CD content in β CD(*x*)-SAP microparticles for assembly formation between *x* = 22.3 and 26.7.

The interaction of β CD(26.7)-SAP and Ad(*y*)-SAP microparticles was also investigated in the presence of competitors, i.e., β CD and sodium 1-adamantanecarboxylate (AdC). When β CD(26.7)-SAP and Ad(15.1)-SAP microparticles were agitated in water on a glass plate at 500 rpm for 1 min in the presence of 0.60 mM β CD or 0.20 mM AdC, no assemblies were formed. Since β CD molecules include Ad residues in Ad(15.1)-SAP microparticles, and AdC molecules are included in β CD residues in β CD(26.7)-SAP microparticles in these experiments, β CD or Ad residues on microparticles are masked, resulting in no assembly formation. These observations confirm that the formation of assemblies from β CD(26.7)-SAP and Ad(*y*)-SAP microparticles is based on the formation of inclusion complexes of β CD and Ad residues on the surface of SAP microparticles.

The interaction of β CD(26.7)-SAP and Ad(y)-SAP microparticles was also examined in the presence of varying concentrations of the competitors, i.e., β CD and AdC. In the presence of lower concentrations of the competitor, assemblies were formed from fewer β CD(26.7)-SAP and Ad(y)-SAP microparticles. The numbers (N) of microparticles forming assemblies were counted. The experiments were repeated three times under the same conditions to obtain the average N values. The N values were plotted in Figure 3 against the competitor concentration ($[\beta$ CD] or {AdC}). The dependencies of N on the competitor concentration are practically the same at a y independent of the species of competitor. As the competitor concentration increases, N decreases rapidly and reaches unity, i.e., no assembly formation, in the region of $10^{-1} - 10^0$ mM. It should be noted here that N values at lower competitor concentrations are larger at higher y . This observation indicates that the interaction of β CD(26.7)-SAP and Ad(y)-SAP microparticles is stronger at higher y ³².

As can be seen in Figure 2, the shape of assemblies seems to be dependent on the Ad content, y . The assembly formed at $y = 15.1$ (Figure 2b) shows a more elongated shape than does that formed at $y = 5.2$ (Figure 2a). Thus, the assemblies formed by agitating β CD(26.7)-SAP and Ad(y)-SAP microparticles of different y at 500 rpm were analyzed by ellipse fit using an ImageJ software³³ to evaluate the aspect ratio (a/b , where a and b are the longer and shorter axes, respectively). The same experiments were repeated three times, and the average value of a/b was calculated. Figure 4 demonstrates the aspect ratio, a/b , as a function of the Ad content, y . The aspect ratio, a/b , increases from ca. 1.5 to ca. 2.8 with increasing y from 5.2 to 15.1. These observations indicate that assemblies of a larger aspect ratio are formed at a higher y , i.e., upon stronger interaction.

Discussion

As can be seen in Figure 4, there is a remarkable correlation between the Ad content (y) in Ad(y)-SAP microparticles and the aspect ratio (a/b) of assemblies formed from β CD(26.7)-SAP and Ad(y)-SAP microparticles. In the assemblies, the interaction between β CD(26.7)-SAP and Ad(y)-SAP microparticles is stronger at higher y because of the larger number of inclusion complexes of β CD and Ad residues in a contact region. The correlation between y and a/b can be roughly explained as follows. Since the attractive interaction between β CD(26.7)-SAP and Ad(y)-SAP microparticles of a larger y is strong enough, small clusters formed in an early stage can stick together even upon collisions at a single contact point, resulting in the formation of elongated aggregates. On the other hand, at a smaller y , small clusters stick together only upon collisions at multiple contact points, leading to rather circular assemblies.

Although the β CD(x)-SAP and Ad(y)-SAP microparticles are non-Brownian particles, the formation of assemblies from the microparticles is similar to aggregation of colloidal particles which undergo Brownian motion. Colloidal particle aggregation has been studied in detail for a century or longer³⁴⁻³⁹. The aggregates of colloidal particles often take fractal structures which obey

$$M \propto R^D \quad (1)$$

where M and R are the mass and radius of colloidal aggregate, respectively, and D_f denotes the fractal dimension⁴⁰⁻⁴³. Colloidal aggregates of larger D_f are denser, whereas aggregates of smaller D_f are less dense. On the basis of simulation and experimental studies on colloidal aggregation, it is known that D_f is ca. 1.75 for aggregates formed through the diffusion-limited aggregation and D_f is ca. 2.05 for those formed through the reaction-limited aggregation^{44,45}. In the case of aggregates formed from a number of colloidal particles, the density of aggregates is dependent on D_f but the shape of aggregates is practically independent on D_f . Figure S4 in Supporting Information indicates colloidal aggregates of $D_f = 1.75$ and 2.05 formed from different numbers of particles (N_c) using a Tunable Diffusion Limited Aggregation software^{46,47}. As can be seen in this figure, aggregates of $D_f = 1.75$ are less dense than those of $D_f = 2.05$. It should be noted here that colloidal aggregates formed from 15 particles ($N_c = 15$) can be analyzed by the ellipse fit, whereas, in the cases of $N_c = 30, 100,$ and 200 , colloidal aggregates take star-shapes and may not be appropriate for the ellipse fit analysis. Using the two-dimensional projections of aggregates of $N_c = 15$ (Figures S4a and S4b in Supporting Information), the a/b values were estimated to be 1.75 and 1.45 for $D_f = 1.75$ and 2.05, respectively, with an ImageJ software. Thus, it can be concluded that the a/b ratio is dependent on D_f in the case of aggregates of smaller N_c .

Since in the present system of β CD(x)-SAP and Ad(y)-SAP microparticles, assemblies are formed through the formation of inclusion complexes of β CD and Ad residues, we should also discuss binary colloidal aggregation through attractive interactions, e.g., electrostatic interaction of oppositely-charged colloidal particles⁴⁸⁻⁵⁰. In the case of binary colloidal aggregation, it is known that the structure of aggregates is also dependent on the ratio of radii and the ratio of the numbers of colloidal particles of different types⁵¹⁻⁵⁶. In the present study, the ratio of average diameters, D_{av} , was approximately 2 and the ratio of the number of particles was set to almost unity. It should be noted here that the randomness of collision is also important. In the system of β CD(x)-SAP and Ad(y)-SAP microparticles, the collisions of microparticles, i.e., non-Brownian particles, may not be random because the mixtures of microparticles were agitated with a mixer. On the basis of these considerations, we can conclude that the assembly of β CD(x)-SAP and Ad(y)-SAP microparticles exhibited a strong correlation between y and a/b because of the limited conditions, e.g., the limited number of particles, the ratios of radii and the number of microparticles, and the mixing procedure. It may be possible to control the structure of assemblies of β CD(x)-SAP and Ad(y)-SAP microparticles in a different manner under other conditions.

Conclusions

In this study, the self-assembly behavior of β CD(x)-SAP and Ad(y)-SAP microparticles was investigated. SAP microparticles were modified with β CD and Ad residues by coupling of β CD-NH₂ and Ad-NH₂·HCl with carboxylic acid residues in SAP microparticles using DMT-MM as a coupling agent. The contents of β CD and Ad residues in β CD(x)-SAP and Ad(y)-SAP microparticles, x and y , were roughly estimated by the weights of remaining β CD-NH₂ and Ad-NH₂·HCl recovered from the reaction mixtures. The adsorption experiments indicated that β CD residues were introduced efficiently not only to carboxylate residues on

the surface of SAP microparticles but also to those inside of SAP microparticles, whereas Ad residues were introduced dominantly to carboxylate residues on the outer layer of SAP microparticles. For visual discrimination, Ad(y)-SAP microparticles were dyed with pararosaniline. The interaction of β CD(x)-SAP and Ad(y)-SAP microparticles was monitored with an optical microscope using aqueous suspension containing ca. 50 microparticles in each on a clean slide glass. Since the SAP microparticles used in this study did not undergo practically Brownian motion because of their larger size, the mixed suspension was agitated at 500 rpm using a mixer to investigate the interaction. β CD(x)-SAP microparticles of $x = 16.2$ or 22.3 did not adhere to any of the Ad(y)-SAP microparticles used in this study, whereas β CD(26.7)-SAP microparticles interacted with all the Ad(y)-SAP microparticles examined to form assemblies. These observations indicate that there is a threshold of the β CD content in β CD(x)-SAP microparticles for assembly formation between $x = 22.3$ and 26.7 . Competitive experiments using β CD and AdC as competitors indicated that the formation of assemblies of β CD(26.7)-SAP and Ad(y)-SAP microparticles was based on the inclusion complex formation between β CD and Ad residues on the surface of SAP microparticles, and the interaction of β CD(26.7)-SAP and Ad(y)-SAP microparticles was stronger at higher y . The observation with an optical microscope indicated that the shape of assemblies was dependent on the Ad content, y ; the aspect ratio (a/b) increased from ca. 1.5 to ca. 2.8 with increasing y from 5.2 to 15.1. Thus, it can be concluded that the shape of the assemblies is controlled by varying the strength of interaction of β CD(26.7)-SAP and Ad(y)-SAP microparticles.

Methods

Materials. Superabsorbent polymer 10SH-NF (SAP) microparticles were kindly supplied from Sumitomo Seika Chemicals Co., Ltd. (Osaka, Japan). Ad-NH₂·HCl was purchased from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan). DMT-MM and D₂O were purchased from FUJIFILM Wako Pure Chemical Corp. (Osaka, Japan). β CD was purchased from Junsei Chemical Co., Ltd. (Tokyo, Japan). Pararosaniline was purchased from Nacalai Tesque, Inc. (Kyoto, Japan). β CD-NH₂ was prepared by previously reported procedure with slight modification.⁵⁷ Other reagents were used without further purification.

Measurements. ¹H NMR spectra were recorded 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 D₂O, respectively). Solid-state ¹H FGMAS NMR spectra were obtained on a JEOL ECA400 spectrometer. Sample spinning rate was 7 kHz. ATR FT/IR spectra were measured on a JASCO FT/IR-6100 spectrometer equipped with a diamond ATR accessory. The FT/IR spectrometer was constantly purged with N₂ gas.

Preparation of β CD(x)-SAP and Ad(y)-SAP Microparticles. β CD(x)-SAP microparticles and Ad(y)-SAP microparticles were prepared by amide coupling of carboxylate residues in the SAP microparticles with β CD-NH₂ and Ad-NH₂·HCl, respectively, using DMT-MM as a coupling agent in water. Predetermined

amounts of SAP microparticles, β CD-NH₂ (or Ad-NH₂•HCl) and water were placed in a reaction vessel. After cooling the mixture at 5 °C, an aqueous solution (10 mL) of a predetermined amount of DMT-MM was added dropwise to the mixture. After agitating for 18 h at room temperature, the SAP microparticles were recovered by filtration with a glass filter, and the SAP microparticles were thoroughly washed with water to remove impurities soluble in water, i.e., unreacted DMT-MM and β CD-NH₂ (or Ad-NH₂•HCl) and by-products from DMT-MM. Portions of the β CD(*x*)-SAP and Ad(*y*)-SAP microparticles obtained were lyophilized for ¹H FGMAS NMR and ATR FT/IR spectroscopy.

For visual discrimination, the Ad(*y*)-SAP microparticles obtained were dyed by immersing in an aqueous solution of pararosaniline (0.05 M) for 1 h.

Adsorption Tests. SAP microparticles fully swollen with water (2.0 g) were added to an aqueous solution of β CD-NH₂ or Ad-NH₂•HCl (5.0 mM, 20 mL) and the mixture was stirred at room temperature (ca. 25 °C) for 18 h. After removing the SAP microparticles by filtration, the concentration of solution of β CD-NH₂ or Ad-NH₂•HCl was determined by an Anton-Paar DMA5000 density meter using the standard curve prepared separately. Using the volume and concentration of solution, the amount of β CD-NH₂ or Ad-NH₂•HCl adsorbed per gram of SAP microparticles swollen was estimated.

Interaction of β CD(*x*)-SAP and Ad(*y*)-SAP Microparticles. Suspensions of β CD(*x*)SAP and Ad(*y*)SAP microparticles (1 μ L each) were placed and mixed on a glass plate. The mixture was agitated at ca. 500 rpm using an EYELA CM-1000 cute mixer. The formation of assemblies was observed on an EVOS optical microscope.

Declarations

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Author Contributions

A. Harada supervised the project; T.I. A. Hashidzume, H.Y., and A. Harada designed the project; T.I. and A. Hashidzume, Y.K. performed the experiments; T.I., A. Hashidzume, Y.K. analyzed data; all the authors discussed the results; A. Hashidzume and A. Harada wrote the paper.

Additional Information

Competing Interests: The authors declare no competing interests.

Competing financial interests

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Scheme

Scheme 1 is available in the Supplementary Files

Figures

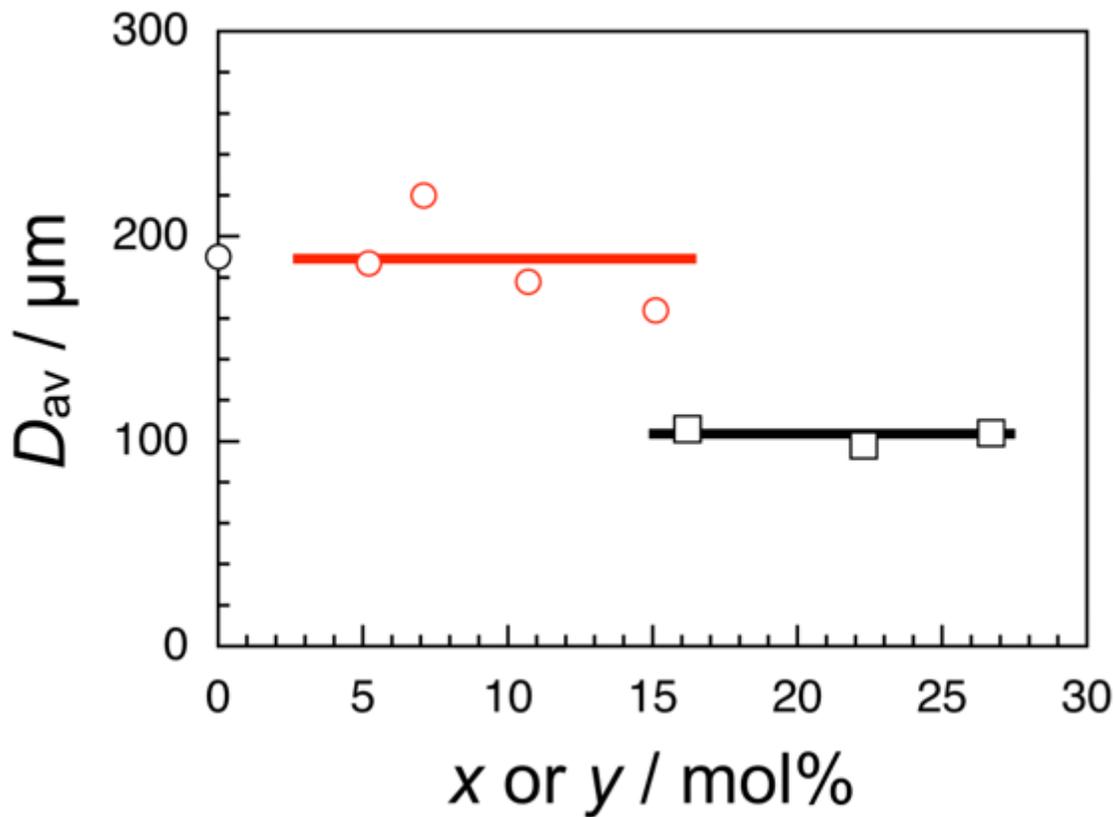


Figure 1

The average diameter (D_{av}) as a function of x or y for the unmodified SAP (black circle), $\beta\text{CD}(x)$ -SAP (black square) and Ad(y)-SAP microparticles (red circle).

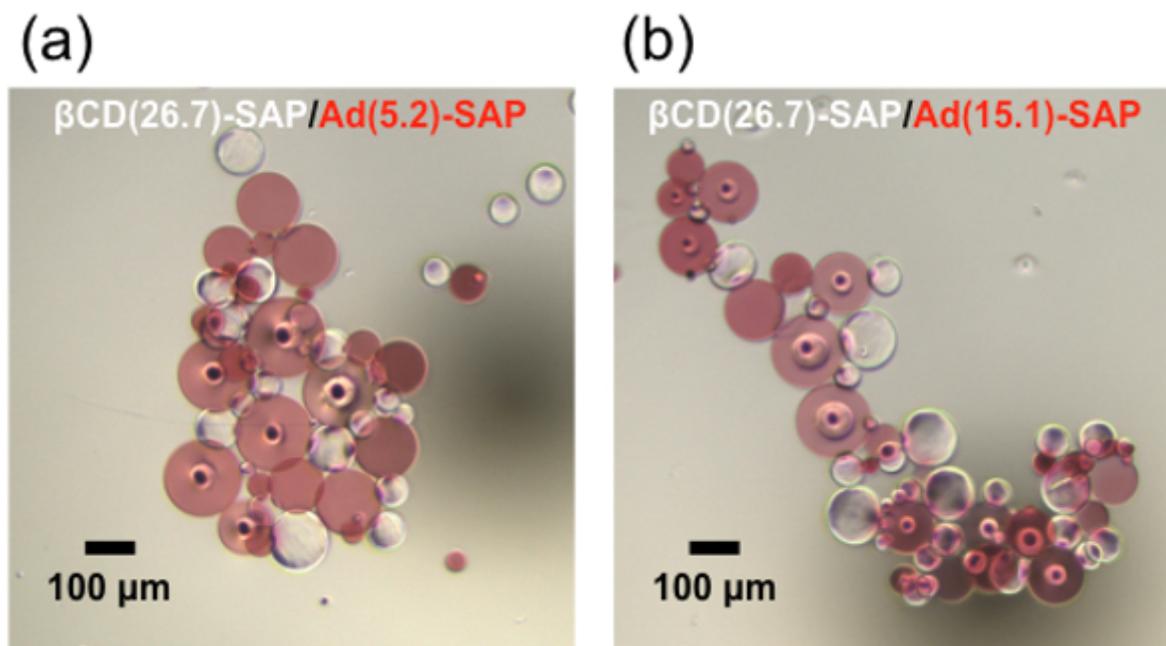


Figure 2

A typical example of optical micrograms for assemblies formed from β CD(27)-SAP and Ad(5)-SAP microparticles (a) and β CD(27)-SAP and Ad(15)-SAP microparticles (b).

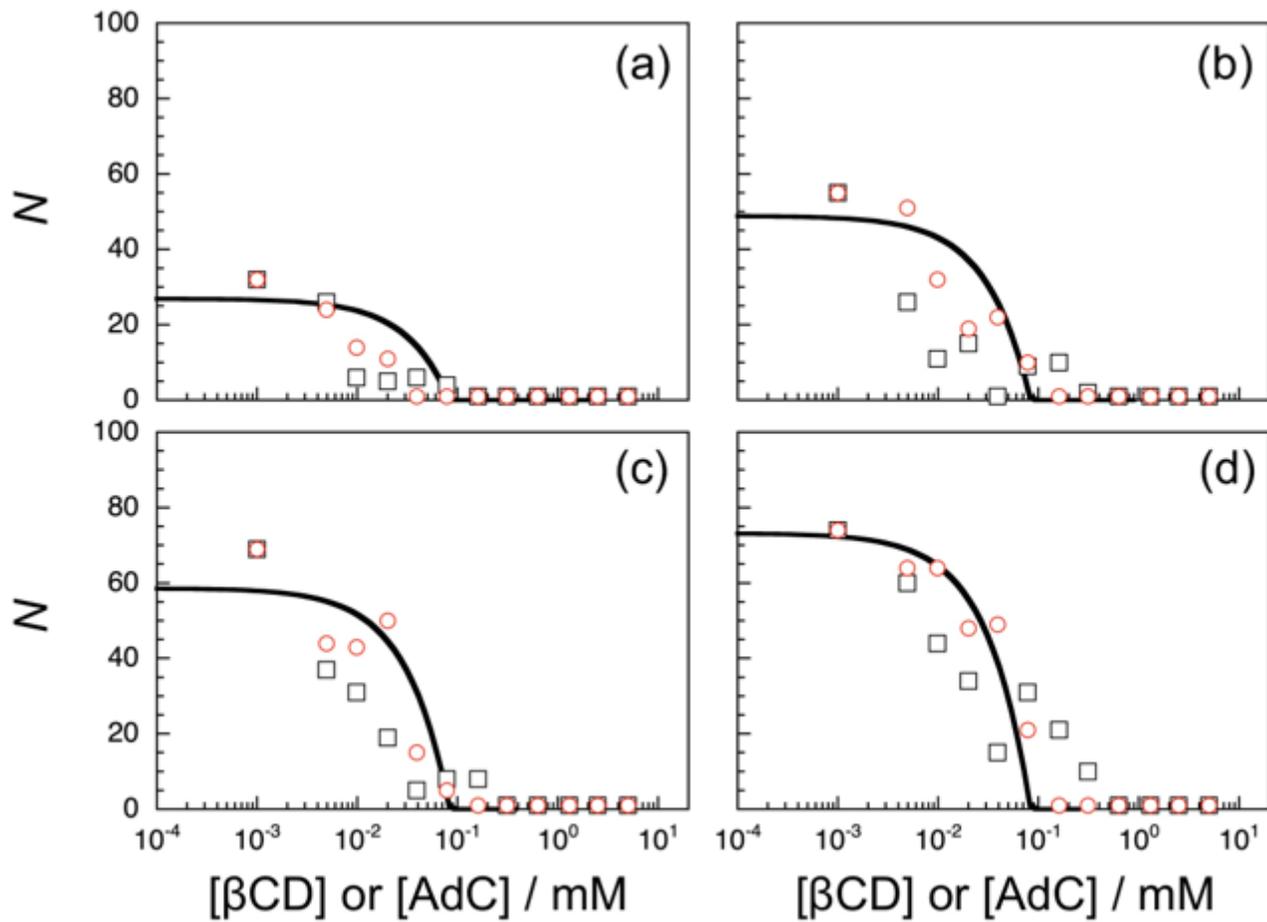


Figure 3

The number (N) of SAP particles in β CD(26.7)-SAP/Ad(y)-SAP assemblies in the presence of β CD (black square) and AdC (red circle); $y = 5.2$ (a), 7.1 (b), 10.7 (c), and 15.1 (d). The curves are drawn based on the simplified model we proposed previously³².

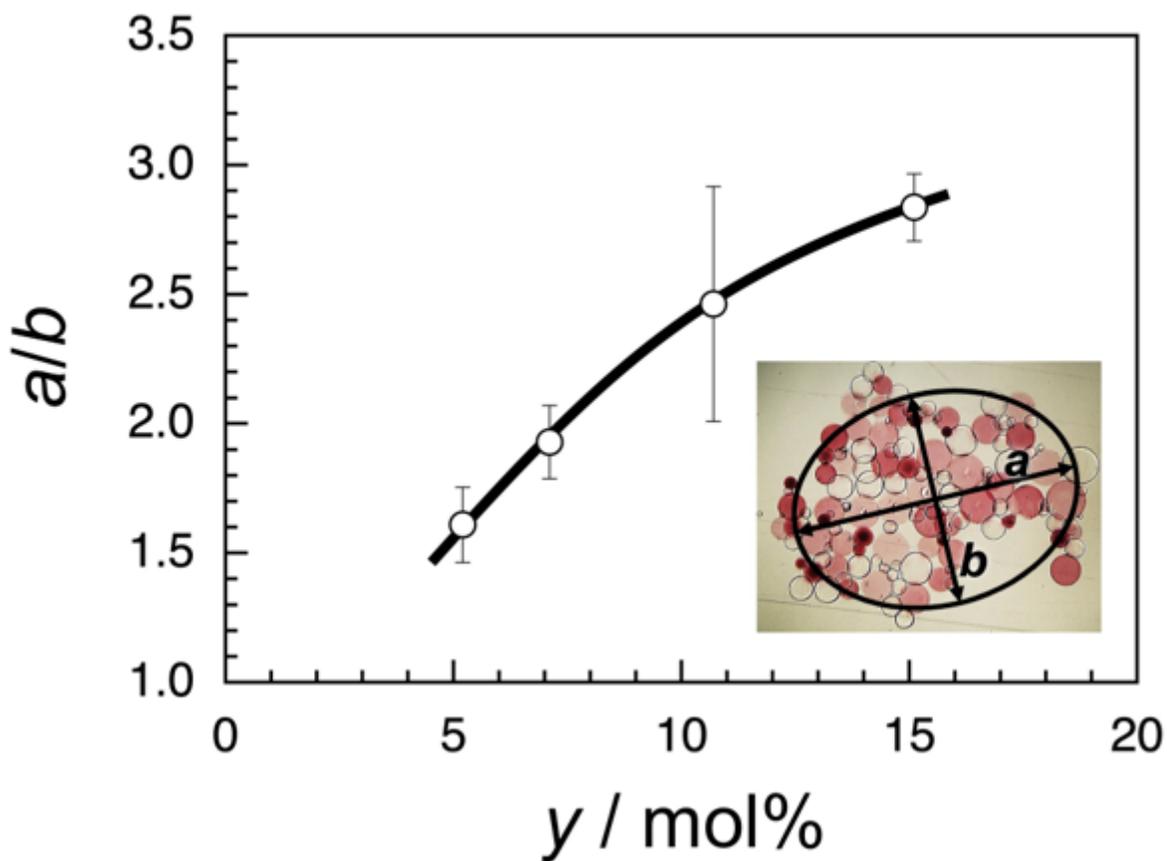


Figure 4

The aspect ratio, a/b , of assemblies as a function of y , and a typical example of estimation of a/b using an ImageJ software. The inset is an optical microgram for the assembly formed from β CD(26.7)-SAP and Ad(5.2)-SAP microparticles.

Supplementary Files

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- [Scheme1.png](#)
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