# Interaction between Methylene Blue and Cyclic Methacrylic Acid Oligomer

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ABSTRACT: p$K_a$ values of linear and cyclic methacrylic acid oligomers with 14 of degree of polymerization were measured in aqueous solution by pH titration and compared with that of poly(methacrylic acid), PMAA, prepared by radical polymerization. p$K_a$ of cyclic methacrylic acid oligomer, 4.83, was between those of linear methacrylic acid oligomer and PMAA, 4.69 and 5.05, respectively, suggesting that the hydrophobic field was formed with methyl groups in cyclic methacrylic acid oligomer in aqueous solution. In order to investigate the inclusion ability of cyclic methacrylic acid oligomer in aqueous solution, methylene blue was added to the solution of cyclic methacrylic acid oligomer. Interaction between methylene blue and cyclic methacrylic acid oligomer was investigated by UV−vis spectrometry at pH = 7.2 and 2D-NMR with nuclear Overhauser enhancement spectroscopy. Cyclic methacrylic acid oligomer enhanced the dimer formation of methylene blue. The size of hydrophobic field in cyclic methacrylic acid oligomer was estimated by MM2.

## Introduction

Cyclodextrins have been well investigated because of their high inclusion ability from the viewpoints of supramolecular chemistry.[1−7] The formation of hydrophobic and hydrophilic fields in the same host molecule, the size of cavity, and the size of guest molecule are the most important factors to control the inclusion. α-, *β*-, and *γ*-cyclodextrins are composed of hydrophobic cavities with in a range from 4.5 to 8.5 Å in diameter,[8] which were suitable for inclusion of hydrophobic molecules, such as benzene, toluene, adamantane, etc. Poly(methacrylic acid) [PMAA] has a hydrophobic methyl group and a hydrophilic carboxylic acid group in the same monomer unit. Hydrophobic field is formed by aggregation of methyl groups under a hydrophilic atmosphere. Though, the hydrophobic field has little ability to include specific guest molecule because the size of the field is not unity. This suggests that if the size of the hydrophobic field is unity and controlled, in other words, if the length of methacrylic acid sequence, which forms the field, is unity and controlled, the molecule will be a good host molecule. Taking into account the size of guest molecules, oligomer of cyclic methacrylic acid, instead of long-chain poly(methacrylic acid), will be suitable for the host molecule.

The expected conformation of cyclic oligomer of methacrylic acid [MMA] is schematically shown in Scheme 1. In hydrophilic solvent at high pH, the carboxyl group will be ionized and expand to outside. The hydrophobic cavity, where the hydrophobic molecule will be included, will be formed with methyl groups at the center of the molecule. The hydrophobic cavity will break in the hydrophilic solvent at low pH or in a hydrophobic solvent; the hydrophobic molecules will not be included.

Authors have synthesized linear and cyclic MAA oligomers with 6, 7, and 14 of degrees of polymerization [dp] with narrow molecular weight distribution by template polymerization with α- and *β*-cyclodextrins for templates.[9−13] First, the hydroxyl groups in cyclodextrin were modified with methacrylic acid.

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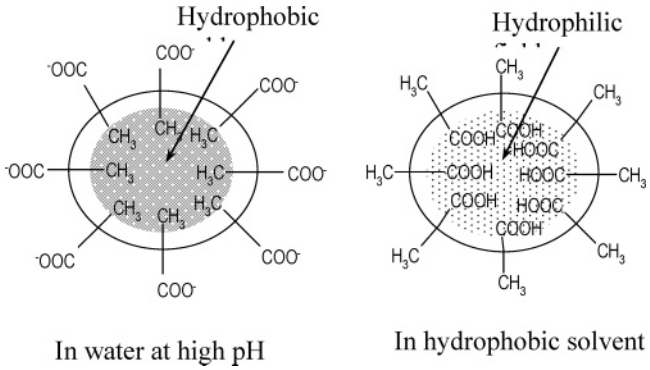
**Scheme 1. Schematic Arrangement of Groups and the Structure of Cyclic Methacrylic Acid Oligomers, *C*-MAA**




Next, methacryloyl groups were polymerized along the rims of cyclodextrin ring. By detachment of polymerized sequence from modified cyclodextrin by hydrolysis, linear MAA oligomer with narrow molecular weight distribution was obtained. When the initiated and propagating sites were connected by radical transfer before the hydrolysis, cyclic MAA oligomer was obtained by hydrolysis.[13] The dp values of MAA oligomers were in fair agreement with the numbers of methacryloyl groups introduced in each rim of cyclodextrin ring. As a result, dp values of MAA oligomers synthesized on the primary and the secondary hydroxyl group sides of *β*-cyclodextrin were 7 and 14, respectively.[9,12,13] The dp value of MAA oligomer synthesized on the primary hydroxyl group side of α-cyclodextrin was 6.[12]

Cyclodextrins were the templates for cyclic MAA oligomer, so that the cavity sizes of the oligomers will be similar to those of cyclodextrins. The purpose of this work is to investigate the inclusion ability of cyclic MAA oligomer. Here, linear and cyclic MAA oligomers with dp = 14, *L*-MAA and *C*-MAA, respectively, synthesized on the secondary hydroxyl group side of *β*-cyclodextrin were chosen. Scheme 2 shows the chemical structures of *L*-MAA, *C*-MAA, and methylene blue, a guest compound. Strictly, *C*-MAA is a mixture of *C*-MAA1 and *C*-MAA2 due to the two different radical transfer sites for closing the ring. The cavity sizes of *C*-MAA1 and *C*-MAA2

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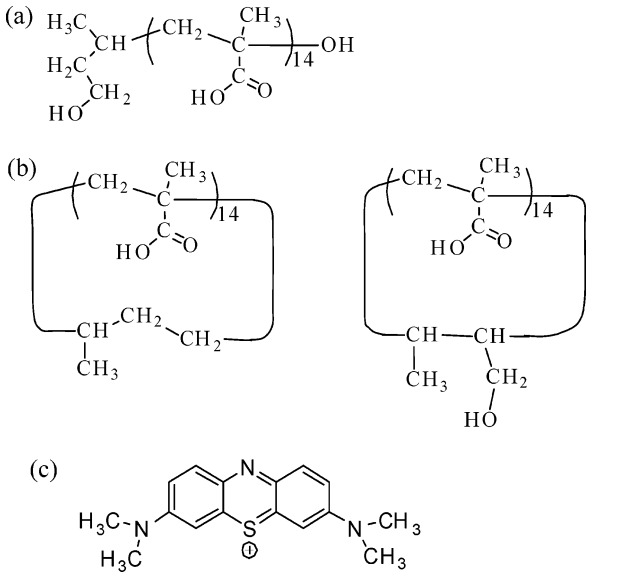
**Scheme 2. Chemical Structures of Linear and Cyclic Methacrylic Acid Oligomers with 14 of Degree of Polymerization and Methylene Blue: (a) Linear Methacrylic Acid Oligomer, *L*-MAA; (b) Cyclic Methacrylic Acid Oligomer, *C*-MAA; (c) Methylene Blue**



are similar; the effect of difference of chemical structure on the inclusion behavior will be neglected. Therefore, in this work, the mixture of cyclic oligomer, *C*-MAA, was used. First, in order to investigate the formation of hydrophobic field of *C*-MAA in water, p$K_a$ values of long chain PMAA, *L*-MAA, and *C*-MAA were determined by neutralization titration. For the investigation of inclusion in water, methylene blue (Scheme 2c), which has been well investigated as the guest molecule to $\beta$- and $\gamma$-cyclodextrin,[14−18] was chosen. The inclusion of methylene blue was investigated by UV−vis spectrometry in water and NMR with nuclear overhouser enhancement spectroscopy [NOESY] analysis.

## Experimental Section

**Materials.** Methacrylic acid oligomers: linear methacrylic acid oligomer, *L*-MAA, cyclic methacrylic acid oligomer, *C*-MAA, were previously synthesized and characterized.[12,13] Degree of polymerization: 14 for *L*-MAA and *C*-MAA. Molecular weight was determined by MALDI-Tof-Mass. Molecular weight of *L*-MAA: 1297.4 ($+H^+$), 1386.8 ($+4Na^+$). Molecular weight of *C*-MAA: 1261.4 ($+H^+$), 1300.6 ($+Na^+$). Conversion of cyclization of *C*-MAA determined by gel permeation chromatography with methanol: 91.7 wt %.

Methylene blue (Tokyo Chemical Industry, 98.5%), sodium hydroxide (Kanto Chemical, 95.0%), nitric acid 1.38 (Kanto Chemical, 60−61%), and methanol (Kanto Chemical, 99.5%) were used as received. Methacrylic acid (MAA, Kanto Chemical, 98%) was purified by distillation under vacuum.

**Neutralization Titration.** 0.05 g of specimen was dissolved in 4.0 mL of methanol. 150 mL of aqueous sodium hydroxide ($7.67 \times 10^{-3}$ mol/L) was added. A solution was stirred for 5 h and then was neutralized by titration with aqueous nitric acid ($7.80 \times 10^{-2}$ mol/L). The pH values of the solution were recorded with a pH meter (TOA PH meter, HM30S) with electrode GST-5311C.

**UV−vis Spectrometry.** The UV−vis measurement of mixtures of methylene blue and long-chain PMAA, *L*-MAA, or *C*-MAA was carried out based on the literature[18] as follows: 1 mL aliquot of methylene blue solution ($1.0 \times 10^{-5}$ mol/L) and an appropriate amount of 0.01 mol/L long-chain PMAA, *L*-MAA, or *C*-MAA solution was mixed in a 10 mL volumetric flask. The pH value was adjusted to 7.2 with aqueous sodium hydroxide ($7.67 \times 10^{-3}$ mol/L). The mixed solution was diluted to final volume with distilled water and shaken thoroughly, following equilibrated for 30 min at 20 °C. Absorption spectra were recorded on a Jasco V-530 spectrophotometer in a range from 400 to 900 nm with 200 nm/min in scan speed at 23.5 ± 0.9 °C.

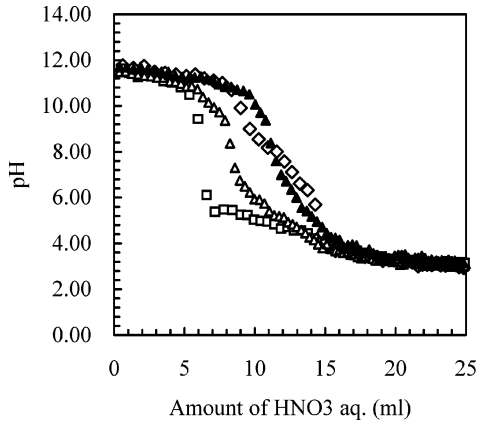



**Figure 1.** Neutralization curves of methacrylic acid monomer (MAA: open square), linear methacrylic acid oligomer, (*L*-MAA: open triangle), cyclic methacrylic acid oligomer, (*C*-MAA: closed triangle), and poly(methacrylic acid) (PMAA: open diamond).

**NMR Measurement.** NMR spectra of the mixture of *C*-MAA and methylene blue in $D_2O$ were measured on a GSX-NMR spectrometer (400 MHz, JEOL) at probe temperature of 298.3 K. The pH of solution was adjusted to 7.0 with NaOD/$D_2O$ solution. 2D-NOESY spectra were recorded with a mixing time of 500 ms.

**MM2 Simulation.** The energy minimum of *C*-MAA1, with dp = 14, with and without fully ionized carboxylic acid groups were fully optimized without restrictions. The molecule was orientated with all the backbone atoms in the *XY* plane. The systematic variation of transition and rotation along the *Z*-axis produces an energy surface. The different minima found on them were minimized.

## Results and Discussion

**pH Back-Titration of Linear and Cyclic MAA Oligomers.** In order to clarify the properties of *C*-MAA as an electrolyte and the formation of hydrophobic field in *C*-MAA molecule, pH back-titration was carried out in an aqueous solution. The carboxyl concentration was adjusted to $3.7 \times 10^{-3}$ mol/L, carboxyl acid was neutralized with NaOH, and pH value of solutions was adjusted to 12.0. Figure 1 shows back-titration curves of *C*-MAA and *L*-MAA with aqueous $HNO_3$. The curves of MAA monomer and long-chain PMAA prepared by conventional radical polymerization with $\alpha,\alpha'$-azobis(isobutyronitrile) in methanol at 60 °C are also shown. The titration curve of MAA solution showed a typical feature of the back-titration of weak acid−strong base solution with strong acid. The pH value of MAA solution drastically decreased from 10.5 to 5.5 at 6.0 mL of aqueous $HNO_3$. Then, the solution buffered in a range from pH 5.0 to 3.5. From the titration curve, the p$K_a$ value of MAA was calculated to 4.56. The solutions of PMAA and oligomers showed the buffer region as well as MAA solution. In the case of PMAA solution, the buffer region (from 5.0 to 6.5) shifted to higher pH region than that of MAA solution. The calculated p$K_a$ of PMAA at degree of dissociation $\alpha = 0$ was 5.05. The higher p$K_a$ of PMAA than MAA is due to the stabilization of compact coil structure of PMAA chain by formation of hydrophobic field with methyl groups in the chain.[19−24] Here, it should be notice that PMAA and oligomers of this work were atactic because they were synthesized by radical polymerization in solution. Thus, the tacticity effect on the p$K_a$ was neglected.

In the case of *L*-MAA, the titration curve appeared between those of MAA and PMAA. The calculated p$K_a$ of *L*-MAA at $\alpha$

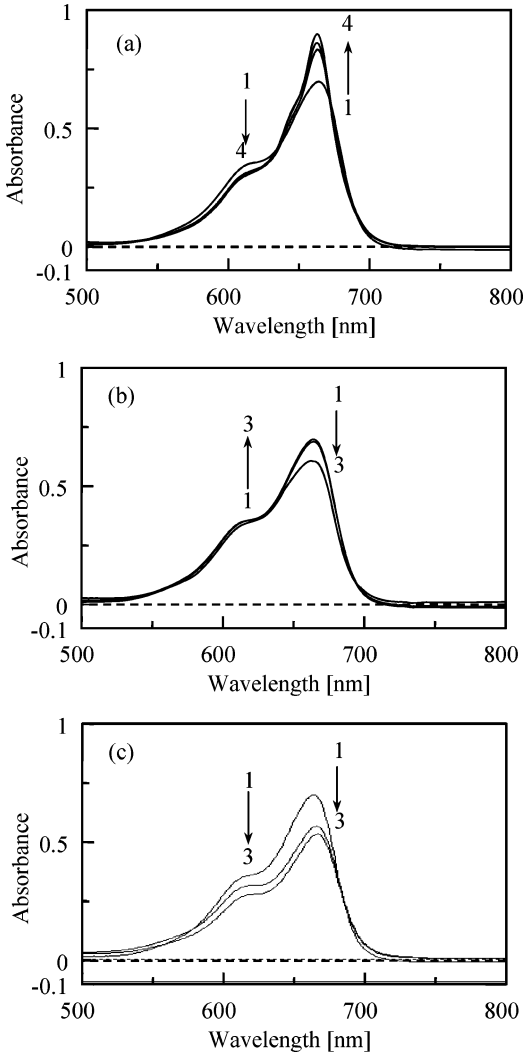



**Figure 2.** Absorption spectra of methylene blue ($1.0 \times 10^{-5}$ mo/L) in aqueous solution at pH = 7.2 containing various concentrations of long-chain poly(methacrylic acid), PMAA, cyclic methacrylic acid oligomer, *C*-MAA, and linear methacrylic acid oligomer, *L*-MAA. (a) With long-chain PMAA. Concentration of PMAA (mol/L); 1, 0.00; 2, $2.07 \times 10^{-4}$; 3, $4.65 \times 10^{-4}$; 4, $1.47 \times 10^{-3}$. (b) With *C*-MAA. Concentration of *C*-MAA (mol/L); 1, 0.00; 2, $2.50 \times 10^{-4}$; 3, $9.70 \times 10^{-4}$. (c) With *L*-MAA. Concentration of *L*-MAA (mol/L); 1, 0.00; 2, $2.75 \times 10^{-4}$; 3, $5.50 \times 10^{-4}$.

= 0 was 4.69, which was slightly larger than that of MAA. According to Bendnar et al., not only hydrophobic interaction between methyl groups but also intramolecular hydrogen bonds between the ionized and unionized carboxyl group causes the increase of p$K_a$.[21,22] An *L*-MAA molecule contained 14 carboxyl groups. Thus, the slightly larger p$K_a$ of *L*-MAA than MAA would be due to the formation of hydrogen bonds between carboxyl groups in the *L*-MAA molecule. In contrast to *L*-MAA, the calculated p$K_a$ value of *C*-MAA at $\alpha = 0$ was 4.83. Again, the dp values of *L*-MAA and *C*-MAA were the same (14). The differences of p$K_a$ and titration behaviors were due to the topology of chains, i.e., linear or cyclic. The larger p$K_a$ value of *C*-MAA than that of *L*-MAA indicates the increase of hydrophobic interaction in the molecule. Consequently. the formation of hydrophobic field in *C*-MAA was suggested.

**Interaction between Methylene Blue and *C*-MAA.** It has been reported that methylene blue and carboxylic acid group form ionic bonding at in a pH range from 6 to 14. *C*-MAA contains carboxylic groups. Methylene blue may not be included in but bonded with *C*-MAA by ionic bonding. To clarify this point, UV−vis measurement and NMR measurement with NOESY technique were carried out. As described in the Introducion, the inclusion of methylene blue into $\beta$- and $\gamma$-cyclodextrins has been well investigated by UV−vis spectrometry. First, UV−vis measurement was carried out. It has been reported that $\beta$-cyclodextrin and methylene blue formed a 1:1 host−guest inclusion compound in water;[25] the absorbance of the unimer at 666 nm was increased, and the absorbance of the dimer at 612 nm was decreased. In contrast, in the case of $\gamma$-cyclodextrin, the larger cavity size than $\beta$-CD induced the 1:2 host−guest inclusion compound with methylene blue in water; the absorbance of the unimer at 666 nm was decreased, and the absorbance of the dimer at 612 nm was increased.[25]

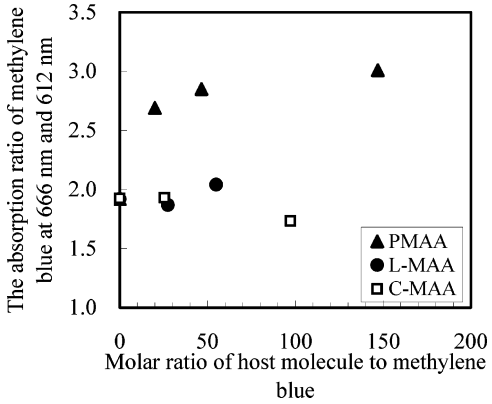



**Figure 3.** Plot of absorption ratio of methylene blue at 666 and 612 nm vs the molar ratio of cyclic methacrylic acid oligomer, *C*-MAA (open square), poly(methacrylic acid), PMAA (closed triangle), and linear methacrylic acid oligomer, *L*-MAA (closed circle), to methylene blue.

*C*-MAA, *L*-MAA, and long-chain PMAA were polyelectrolytes. If the ionic bonding were formed between methylene blue and *C*-MAA as well as PMAA, a similar absorption change of methylene blue solutions with *C*-MAA and PMAA would be observed. Figure 2 shows the absorption spectra of methylene blue with *C*-MAA, *L*-MAA, and long-chain PMAA. The pH of all solution was adjusted to 7.2, which was in the ionized region of *C*-MAA, *L*-MAA, and long-chain PMAA. In the case of lack of host molecules, two peaks owing to the unimer and dimer of methylene blue were observed at 666 and 612 nm, respectively. The dimerization constant *K* of the unimer/dimer equilibrium of methylene blue was reported to be $(6.2 \pm 1.1) \times 10^4$ L/mol.[18] The absorbance of methylene blue solution without host molecules agreed well with the literature.[18]

When long-chain PMAA was added, the absorbance of the unimer at 666 nm was increased and the absorbance of the dimer at 612 nm was decreased. The ionic bonding formation between methylene blue and carboxylic groups of polymer enhanced the unimer formation of methylene blue, which resulted in the increasing of absorption around 660 nm.[26,27] Thus, the increase of absorbance at 666 nm by addition of long-chain PMAA was due to the increase of methylene blue unimer by formation of ionic bonding between methylene blue and long-chain PMAA. In contrast, the addition of *C*-MAA led to the decrease of the absorbance of unimer at 666 nm and slight increase of the absorbance of dimer at 612 nm. This indicates that the formation of methylene blue dimer was enhanced by addition of *C*-MAA. The addition of *L*-MAA reduced the absorption at 612 and 666 nm. Again, the p$K_a$ values were similar; the different tendency of dimer formation of methylene blue with *C*-MAA, *L*-MAA, and PMAA suggests that the ionic bonding of methylene blue depends on the polyelectrolyte.

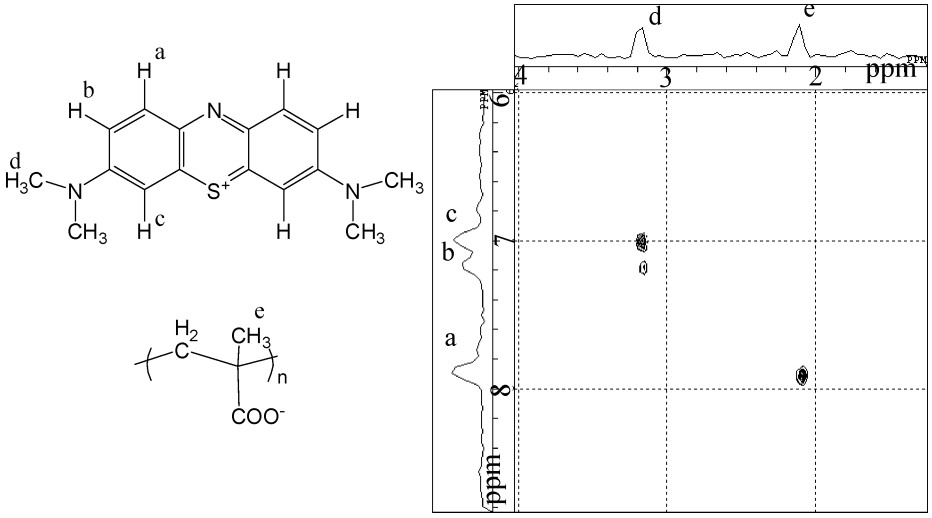



**Figure 4.** 2D-NOESY spectrum of mixture of methylene blue and cyclic methacrylic acid oligomer, *C*-MAA, in $D_2O$ at pH = 7.0.

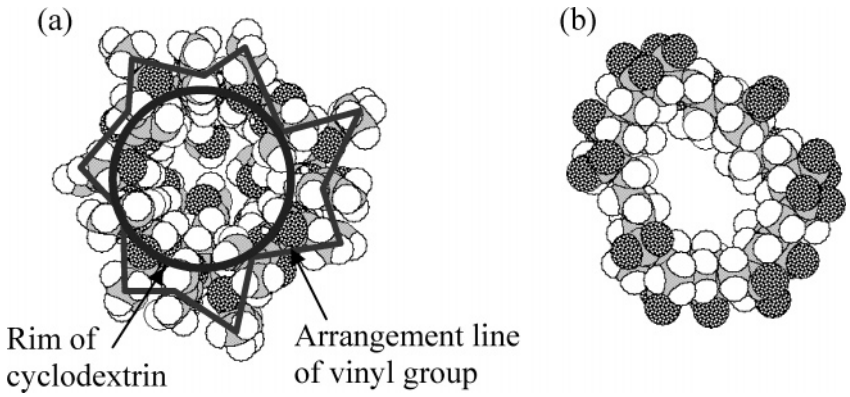



**Figure 5.** Simulated structures of template monomer and cyclic methacrylic acid oligomer, *C*-MAA, in aqueous solution: white particle, hydrogen atom; light gray particle, carbon atom; dark gray particle, oxygen atom. (a) View of template monomer from the secondary hydroxyl group side. (b) *C*-MAA with the degree of dissociation of *C*-MAA = 1.0.

To clarify the effect of concentration of host molecule on the dimer or unimer formation of methylene blue, the ratio of absorbance of unimer (666 nm) to that of dimer (612 nm) of methylene blue (D/M ratio) was calculated (Figure 3). When the host−guest compound is quantitatively formed, the M/D ratio linearly changes with the molar ratio of host molecule to guest molecule. In the case of PMAA, M/D ratio was increased then was saturated by increasing the molar ratio of long-chain PMAA to methylene blue. The formation of unimer of methylene blue by ionic bonding between PMAA and methylene blue was not quantitative but qualitative under the conditions of this work. This would be due to the inhomogeneous conformation in the random coil of PMAA. In contrast, M/D ratio of *C*-MAA quantitatively decreased by molar ratio of *C*-MAA to methylene blue, indicating the dimer was quantitatively formed by interaction with *C*-MAA. The structure of compound with *C*-MAA and methylene blue was 1:2 at pH = 7.2. When *L*-MAA was added, the M/D ratios remained constant. No interaction between methylene blue and *L*-MAA, such as inclusion of methylene blue to *L*-MAA, was observed. Here, it should be noticed that *C*-MAA and *L*-MAA were cyclic and linear oligomers, respectively, with the same dp values. Consequently, the cyclic structure of *C*-MAA resulted in the interaction to methylene blue.

**NOESY Analysis.** To investigate the interaction between methylene blue and *C*-MAA, the NOESY spectrum of a mixture of methylene blue and *C*-MAA was measured in $D_2O$. Figure 4 shows a contour plot of a section of the NOESY spectrum of a mixture of methylene blue and *C*-MAA. On the F1 axis, the resonances observed at 7.0, 7.2, and 7.9 ppm originated from the protons of heteroaromatic ring of methylene blue. The resonances at 7.0 and 7.2 ppm were shifted from 7.3 and 7.0 ppm by addition of *C*-MAA, respectively. A similar shift of resonances of methylene blue owing to the inclusion was reported in the case of the mixture of methylene blue and carlixarenes.[28] On the F2 axis, the resonance originating from protons of methylene groups of *C*-MAA was observed at 2.1 ppm. The resonance at 3.2 ppm was originated from the methyl group of methylene blue. The strong NOE between the protons of methylene group of *C*-MAA (2.1 ppm on F2 axis) and heteroaromatic ring of methylene blue at (7.9 ppm on F1 axis) was found. The methylene group of *C*-MAA and heteroaromatic ring of methylene blue strongly interacted. Since the methylene groups of *C*-MAA formed a backbone of the hydrophobic cavity in *C*-MAA, methylene blue was included in the cavity of *C*-MAA.

**Cavity Size of *C*-MAA and PMAA.** The state of methylene blue in host depends on the size of hydrophobic cavity. Inclusion of methylene blue in unimer and dimer states indicates the cavity sizes are similar to $\beta$-cyclodextrin and $\gamma$-cyclodextrin, respectively. Since methylene blue was included into PMAA in the unimer state and into *C*-MAA in the dimer state, the cavity sizes of PMAA and *C*-MAA were similar to $\beta$-cyclodextrin and $\gamma$-cyclodextrin, respectively. In the template of *C*-MAA, though, the cavity size of *C*-MAA was not similar to $\beta$-cyclodextrin but to $\gamma$-cyclodextrin. Thus, the cavity size of *C*-MAA was

estimated by MM2 simulation. When the carboxylic acid was not ionized, $\alpha = 0$, the clear cavity was not observed. In contrast, when all carboxylic acid groups were ionized, $\alpha = 1$, the strong aggregation of methyl groups and the expansion of charged carboxyl groups formed a clear cavity. The cavity was slightly oval. It would be due to the introduction of ethyl group to close the ring. The calculated average diameters were 11.2 and 9.2 Å in long and minor axes, respectively, which were clearly larger than the cavity diameters of $\beta$- and $\gamma$-cyclodextrins (6.4 and 8.3 Å, respectively).[8] This can be explained by the zigzag arrangement of secondary hydroxyl groups, 2- and 3-hydroxyl groups, on the rim of $\beta$-cyclodextrin ring. Figure 5a shows the simulated arrangement of methacryloyl group on the rim of $\beta$-cyclodextrin by MM2. Methacryloyl groups were not arranged on the line but arranged on a zigzag line along the rim. The diameter of cyclodextrin rim is smaller than that of arrangement line of methacryloyl groups. It is possible to expand the cavity of *C*-MAA larger than that of $\beta$-cyclodextrin by separation of polymerized sequence from the template. As a result, methylene blue dimer was stabilized with *C*-MAA.

On the other hand, the cavity size in PMAA was smaller than that of *C*-MAA instead of fact that the dp value of PMAA was larger than that of *C*-MAA. The larger cavity size of *C*-MAA is explained from the viewpoints of conformation of backbone and ionic atmospheres around the cavity. The driving force to form the hydrophobic cavity is not only the aggregation of methyl groups but also repulsion of ionized carboxylic acid groups. The backbone of *C*-MAA was cyclic, and the cyclic backbone is expanded due to the repulsion of carboxylic acid groups. The freedom of backbone of PMAA is higher than that of *C*-MAA. Thus, the shape of cavity in PMAA is more flexible than that of *C*-MAA. Additionally, many hydrophobic cavities were formed in the same molecule of PMAA, instead of only one cavity was formed in *C*-MAA molecule. Many hydrophobic cavities in PMAA would weaken the ionic atmosphere around the cavity in the molecule. Therefore, the cavity size in PMAA was smaller than that in *C*-MAA. This also suggests that smaller cyclic methacrylic acid oligomer than *C*-MAA may include methylene blue in the unimer state.

## Conclusions

In order to investigate the properties of methacrylic acid oligomers with dp = 14 for the electrolytes, pH titration of was carried out to cyclic and linear methacrylic acid oligomers, methacrylic acid monomer (MAA), and long-chain poly(methacrylic acid) (PMAA). The order of p$K_a$ calculated from titration curves was MAA (4.56) < linear methacrylic acid oligomer [*L*-MAA] (4.69) < cyclic methacrylic acid oligomer [*C*-MAA] (4.83) < PMAA (5.05). A larger p$K_a$ value of *C*-MAA than that of *L*-MAA was due to the formation of hydrophobic field in *C*-MAA, which was provided by the cyclic structure of *C*-MAA.

To investigate the interaction between methylene blue and oligomers, the dependence of UV−vis absorption of methylene blue solution on the concentration of *C*-MAA, *L*-MAA, and long-chain PMAA was measured at pH = 7.2. The presence of *L*-MAA did not affect the dimer formation of methylene blue. The presence of *C*-MAA enhanced the dimer formation of methylene blue; however, the presence of PMAA enhanced the unimer formation. The interaction between methylene groups of *C*-MAA and aromatic ring of methylene blue was observed by NMR−NOESY; it was concluded that the aromatic ring of methylene blue would be included in the hydrophobic cavity of *C*-MAA. Therefore, the hydrophobic field formed with methyl groups of *C*-MAA will be an inclusion field as well as the cavity of cyclodextrins. The MM2 simulation indicated that the cavity of *C*-MAA was oval with 11.2 and 9.2 Å in long and minor diameters, respectively. The disagreement of ring size of *C*-MAA with that of $\beta$-cyclodextrin (6.4 Å), which was the template of *C*-MAA, was due to the zigzag arrangement of methacrylate groups in the $\beta$-cyclodextrin template.

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