Effect of Guest Compounds on Template Polymerization of Multivinyl Monomer of Cyclodextrins

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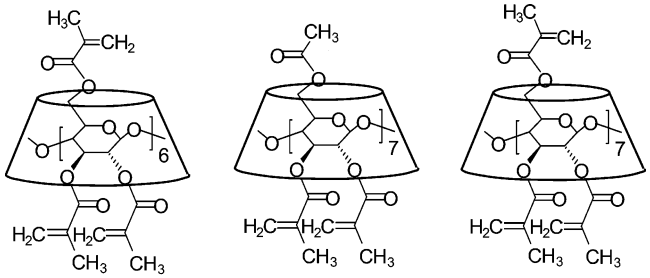
ABSTRACT: Copper-mediated atom transfer radical polymerization of the following three methacryloyl type multivinyl monomers was carried out with many guest compounds; the effect of the guest on degree of polymerization [DP] of methacryloyl group was investigated. The multivinyl monomers were α-MVM with 17.4 methacryloyl groups prepared from α-cyclodextrin [α-CD], *β*-MVM1 with 11.6 methacryloyl groups prepared from *β*-cyclodextrin [*β*-CD], and *β*-MVM2 with 20.4 methacryloyl groups prepared from *β*-CD. The arrangement of the methacryloyl groups in the multivinyl monomer by inclusion of the guest compound was simulated by MM2 and measured by 2D-NMR. Methacrylic acid oligomers [PMAA] were obtained by hydrolysis of the polymerized products. The DP of PMAA was determined by GPC measurements calibrated with MALDI−TOF−mass measurement. Molecular weight and molecular weight distribution of PMAA were varied by the guest compound. A long alkyl group in the guest enhanced the ordering of methacryloyl groups in the multivinyl monomer, and PMAA with DP = 6 and 7 with narrow molecular weight was obtained for multivinyl monomers with α-CD and *β*CD, respectively. A phenyl group in the guest disturbed the arrangement of the methacryloyl groups and resulted in the intermolecular polymerization.

Introduction

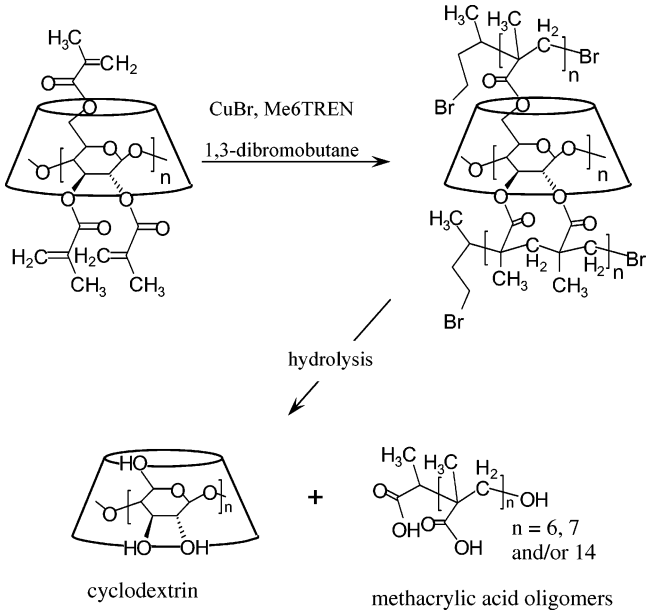
A template polymerization technique has been widely investigated to control molecular weight and molecular weight distribution of polymer synthesized by radical polymerization.[1−7] However, well-defined polymer with narrow molecular weight distribution has not been obtained by combination of template polymerization and traditional free radical polymerization.[8] It was due to bad control of radical concentration and high reaction rate of radical. Recently, the molecular weight and molecular weight distribution of polymers could be controlled by so-called living radical polymerization techniques, such as atom transfer radical polymerization [ATRP][9−18] and reversible addition−fragmentation chain transfer [RAFT] polymerization,[19−23] which are effective methods to reduce the reaction rate of radical. However, in the case of oligomer, it is still difficult to control molecular weight and molecular weight distribution by living radical polymerization because the polymerization should be halted at a very early stage of polymerization.

Authors have successfully obtained methacrylic acid oligomers [PMAA] with specific degree of polymerization [DP] with narrow molecular weight distribution by combining copper-mediated ATRP and the template polymerization technique with *β*-cyclodextrin [*β*-CD] as a template.[24,25] Two types of multivinyl monomers, *β*-MVM1[24] and *β*-MVM2[25] (Scheme 1), were synthesized from *β*-cyclodextrin by esterification of secondary and all hydroxyl groups with methacrylic anhydride, respectively. In such multivinyl monomers, copper-mediated ATRP of methacryloyl groups on each rim of *β*-CD ring provides polymerized methacrylate sequence with well-defined DP value and narrow molecular weight distribution (Scheme 2). For example, in the case of *β*-MVM1 with 10.9 methacryloyl groups, DP of polymerized methacryloyl sequence was 11; hydrolysis of polymerized products provided poly(methacrylic acid) oligomers

Scheme 1. Chemical Structures of Multivinyl Monomers, α-MVM, *β*-MVM1, and *β*-MVM2



Scheme 2. Template Polymerization of *β*-MVM2



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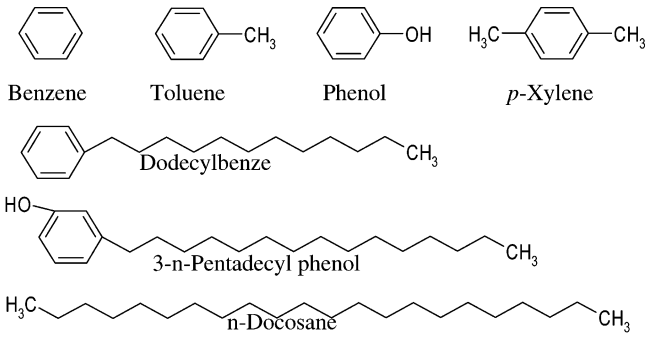
Scheme 3. Chemical Structures of Guest Compounds



[PMAA] with DP = 11, and their molecular weight distribution was narrow.[24] In the case of β-MVM2, which 7 and 13.4 of primary and secondary hydroxyl groups were methacryloyled (totally 20.4 methacryloyl group in a molecule), the two types of PMAA with DP = 7 and 14 were synthesized from the same multivinyl monomer molecule at the same time.[25] Kinetic analysis of polymerization of β-MVM1 and β-MVM2 indicated that polymerization proceeded in a living manner in the template polymerization system. However, it was impossible to synthesize PMAA with various DP, except for 7 and 14 from β-CD, because it is difficult to reduce the methacryloyl groups in the multivinyl monomers homogeneously. To synthesize PMAA with various DP, another template is required.

α-Cyclodextrin, α-CD, has 6 primary and 12 secondary hydroxyl groups. If α-CD is chosen as a template instead of β-CD, PMAA with DP = 6 and 12 will be obtained. To vary the DP of PMAA, α-CD is used as a template in this work.

From previous investigations, we have found that the addition of toluene, which was a guest compound for β-MVM1 and β-MVM2, improved the template effect on the template polymerization. Without toluene, the conversion of vinyl group was low and the molecular weight distribution of PMAA was wide. Thus, the guest compound was an important factor for the template polymerization of β-CD. However, the effect of other guest compound has not been investigated. The cavity size of α-CD, 4.5 Å, is narrower than that of β-CD, 7.0 Å; the optimum guest compound for the template polymerization of the multivinyl monomer of α-CD will be different from β-CD. Thus, in this work, the effect of guest compound on the template polymerization of the multivinyl monomers of α-CD and β-CD is also investigated.

For these investigations, three types of multivinyl monomers (Scheme 1), α-MVM with 17.4 methacryloyl groups, β-MVM1, and β-MVM2, were prepared and were polymerized by copper-mediated ATRP with the various guest compounds shown in Scheme 3. The inclusion complexes were experimentally and theoretically analyzed by 2D-NMR measurements and MM2 simulation, respectively. To investigate the proceeding of polymerization, the polymerized products, methacrylic acid oligomers, were separated from the cyclodextrin templates by hydrolysis, and their DP was measured by GPC calibrated by MALDI−TOF−Mass.

Experimental Section

Materials. α-Cyclodextrin (α-CD, Nihon Shokuhin Kako Co. Ltd., Celdex-A-100, 95%), β-cyclodextrin (β-CD, Kanto Chemical Co., Inc.), and 3,*n*-pentadexylphenol (PDP, ACROS, 90−95%) were dried at 100 °C overnight under vacuum. Methacrylic anhydride (Aldrich, 94%), pyridine (Tokyo Chemical Industry Co., Ltd., 99.5%), hydroquinone (Kanto Chemical Co., Inc., 99%), methanol (Tokyo Chemical Industry Co., Ltd., 99.8%), toluene (Tokyo Chemical Industry Co., Ltd., 99.5%), copper(I) bromide (CuBr, Wako Pure Chemical Industries, Ltd., 99.9%), 1,3-dibromobutane (Tokyo Chemical Industry Co., Ltd., 98%), benzene (Kanto Chemical Co., Inc., 99%), *n*-dodecylbenzene (Kanto Chemical Co., Inc., 98%), and docosane (Aldrich, 99%) were used without purification. Tris(2-(dimethylamino)ethyl)amine (Me_6TREN, 98%) was synthesized following the reported procedure.[26]

Table 1. Conditions and Results of Atom Transfer Radical Polymerization of α-MVM, β-MVM1, and β-MVM2[a]

code	monomer	guest	conversion of methacryloyl group (mol %)[b]	gel fraction (wt %)[c]
α-None	α-MVM	none	17.8	0
α-Bz		benzene	44.7	0
α-Tol		toluene	41.9	4.1
α-Xy		*p*-xylene	51.2	3.2
α-PhOH		phenol	42.2	61.0
α-DBz		dodecylbenzene	35.8	95.7
α-PDP		3-*n*-pentadecyl-phenol	35.9	100
α-Doc		*n*-docosane	43.5	0
β1-Doc	β-MVM1	*n*-docosane	31.6	0
β2-None	β-MVM2	none	22.7	0
β2-Tol		toluene	55.2	0
β2-Xy		*p*-xylene	57.6	87.8
β2-DBz		dodecylbenzene	61.8	29.0
β2-PDP		3-*n*-pentadecyl-phenol	31.6	62.5
β2-Doc		*n*-docosane	37.0	0

[a] [MVM]:[CuBr]:[1,3-dibromobutane]:[Me_6TREN]:[guest] = 1:2:2:3:5. Solvent: methanol/water mixture (water: 10 wt %). Temperature: 50 °C. Reaction time: 6 h. [MVM] = 3.96×10^{-3} mol/L. [b] Determined by GPC with double detected equipment of UV at 292 nm and RI. [c] Determined from GPC peak area detected by RI.

Synthesis of Multivinyl Monomers. β-MVM1 [(2,3-di-*O*-methacrylated)β-cyclodextrin][27] and β-MVM2 [(2,3-di-*O*-methacrylated-6-methacrylated)β-cyclodextrin][25] with 11.6 and 20.4 vinyl groups were previously synthesized and analyzed elsewhere. α-MVM [(2,3-di-*O*-methacrylated-6-methacrylated)α-cyclodextrin] was synthesized from α-CD by using a method similar to β-MVM2.[25,28] The average number of vinyl groups in α-MVM was 17.4. Yield: 43.6%. ^{1}H NMR (500 MHz, $CHCl_3$-d_6): δ [ppm] = 5.18 (6H, C(1)H of α-CD), 4.80 (6H, C(2)H of α-CD), 4.60 (6H, C(3)H of α-CD), 3.58 (6H, C(4)H of α-CD), 3.95−4.37 (6H, C(5)H and 12H, C(6)H of α-CD), 5.62 (17.7 H, CH_2=C in methacryloyl), 6.17 (17.1 H, CH_2=C of methacryloyl), 1.95 (52.0 H, CH_3 in methacryloyl).

Typical ATRP of the Template Monomer. The polymerization was carried out by ATRP at 50 °C for 6 h. The ATRP conditions are listed in Table 1. The concentration of multivinyl monomer and the molar ratio of guest to MVM were 3.96×10^{-3} mol/L and 5.0. The procedure of β2-Tol is shown as a typical case of ATRP. β-MVM2 (1.0 g, 0.396 mmol, 80.78 mmol of vinyl group), 1,3-dibromobutane (0.097 mL, 0.792 mmol), Me_6TREN (0.249 g, 1.18 mmol), CuBr (0.114 g, 0.792 mmol), and toluene (a guest compound: 0.2 mL, 1.98 mmol) were dissolved in methanol (90 mL) and water (10 mL) in a sealable Pyrex reactor. The solution in the reactor was degassed by using three freeze−pump−thaw cycles. The reactor was sealed under vacuum and heated at 50 °C for 6.0 h. To stop the polymerization, the solution was cooled to room temperature and was poured in water (200 mL). The precipitate was collected by filtration and purified by reprecipitation for two times with methanol (10 mL) and cold (0 °C) water (50 mL). The product was white powder. The conversion of reacted vinyl group was determined by GPC equipped with both RI and UV at 292 nm as well as the previous work.[25]

Hydrolysis of the Polymerized Products.[24] Polymerized product (0.1 g, 0.037 mmol) was dissolved in methanol (4.0 mL). Sodium hydroxide (0.04 g, 1.0 mmol) was added to the solution. The solution was stirred at room temperature for 4 h and then poured in acetone (20 mL). The precipitate, PMAA, was washed with 0.1 N−HNO_3 (20 mL), collected, and dried. The degree of hydrolysis was determined by ^{1}H NMR spectroscopy. Yield: 60−85 wt %. ^{1}H NMR (methanol-d_4): δ [ppm] = 0.8−1.2 (3H, CH_3), 1.9−2.0 (2.2H, CH_2).

Molecular Weight Measurements. Number-average molecular weight (M_n) and distribution of molecular weight (M_w/M_n) of the polymerized products and PMAA were measured with gel permeation chromatography (Tosoh, GPC-2010) double-detected with refractive index and ultraviolet at 292 nm. Column TSK-α-2500 (the optimum range of M_w: $<1 \times 10^4$ in THF and $200-5 \times 10^3$ in methanol). Eluent, flow rate, and temperature were THF, 0.6 mL/min, and 35 °C for polymerized products and methanol, 0.6 mL/min, and 30 °C for PMAA. The calibration curves[24] of PMAA previously prepared by combining GPC and matrix-assisted laser desorption ionization time-of-flight (MALDI−TOF) mass spectrometry were used.

2D-NMR Measurement. 2D-NMR measurement was carried out with a ^{1}H NMR spectrometer (JEOL, GSX-500 Hz) with deuterated chloroform ($CHCl_3$-d) as a solvent at room temperature using the signal of the deuterated solvent as lock and the internal standard for chemical shift data in the δ-scale relative to TMS.

MM2 Simulation. Before the inclusion process, the energy minimum of hosts, (α-MVM, β-MVM1, and β-MVM2) and guest compounds were fully optimized without restrictions. The host molecules were orientated with all the glycosidic atoms in the *XY* plane, the *Z*-axis in the geometric center of the hexagon and heptagon formed by the oxygen of α-cyclodextrin ring and β-cyclodextrin ring, respectively, and the wider half of the cyclodextrin cavity placed in the negative zone of the *Z*-axis. For the inclusion process, the guests were located in proper orientation at a *Z*-coordinate of −14 Å and were moved though the host cavity along the *Z*-axis to +14 Å in 2 Å steps. The systematic variation of transition and rotation along the *Z*-axis produces an energy surface. The different minima found on them were minimized along without restrictions for the guests.

Results and Discussion

Polymerization of MVMs. The copper-mediated ATRP of multivinyl monomers [MVMs] was carried out with and without guests. The conditions of copper-mediated ATRP and the conversion of methacryloyl group are listed in Table 1. The conversion of the methacryloyl group was determined by using the GPC peak areas detected by RI and UV at 292 nm. It was previously found that the conversion estimated by GPC double detected with RI and UV at 292 nm showed a good agreement with the conversion estimated from the titration method.[25] On the other hand, the conversion estimated by NMR was not quantitative because of the decrease of mobility of methacrylate remaining in the MVM molecule by surrounding the polymerized methacrylate. Thus, in this work, the conversion was estimated by GPC double detected with RI and UV at 292 nm as well as the previous work.[25] For all MVMs, the conversion of the methacryloyl group was drastically improved by addition of the guests. This agreed well with the previous results[25] that the conversions of methacryloyl group of β-MVM2 by ATRP with HMTETA increased by addition of toluene. It was found that not only toluene but also other guests were effective to increase the conversion of methacryloyl group for template polymerization of cyclodextrins.

The most important feature of the template polymerization is to limit polymerization in the MVM molecule. On the other hand, it is difficult for MVM

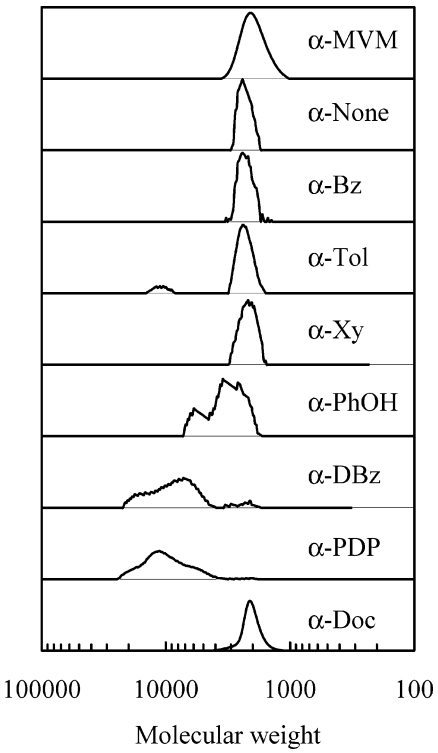


Figure 1. RI absorption of GPC polymerized products of α-MVM.

polymerization to hinder gelation, i.e., intermolecular polymerization, because the MVM contains many vinyl groups. Here, the intermolecular polymerization between MVM molecules was detected by GPC. Figure 1 shows the RI absorption of GPC profiles of α-MVM and its products. The GPC peaks of α-Bz and α-Doc synthesized with benzene and docosane, respectively, were very similar to that of α-MVM, indicating that the polymerization was limited in the α-MVM molecule. In contrast, in cases of α-PDP, α-DBz, and α-Tol, the new peaks appeared at higher molecular weight than that of α-MVM. Thus, PDP, dodecylbenzene, and toluene could not hinder the intermolecular polymerization. The gel fraction was calculated from the peak area and is shown in Table 1. It should be notice that toluene was a good guest for β-MVM1 and β-MVM2.[24,25] The good guest depended on the MVMs. The cavity size of α-CD is narrower than β-CD. The cavity of α-MVM would be too narrow for toluene. Figure 2 shows the GPC profiles of β-MVM1 and β-MVM2 series. It was found that polymerization was limited in the MVM molecules when toluene or docosane was added. Other guests could not hinder the intermolecular polymerization. Therefore, the addition of guest improved the conversion of methacryloyl group, and the suitable guest for the template polymerization with cyclodextrin template depended on the type of cyclodextrin.

To investigate the polymerization in the template molecules, the polymerized part was detached from the polymerized products as poly(methacrylic acid) oligomer [PMAA] by hydrolysis. Then, the degree of polymerization [DP] of PMAA was measured by GPC previously calibrated by MALDI−TOF−Mass. Figures 3 and 4 show the GPC profiles of the PMAA obtained from α-MVM series and β-MVM series, respectively. Theoretically, the template polymerization of α-MVM occurring on each hydroxyl group side provides PMAA with DP = 6 and 14. The expected DP values are 7 for

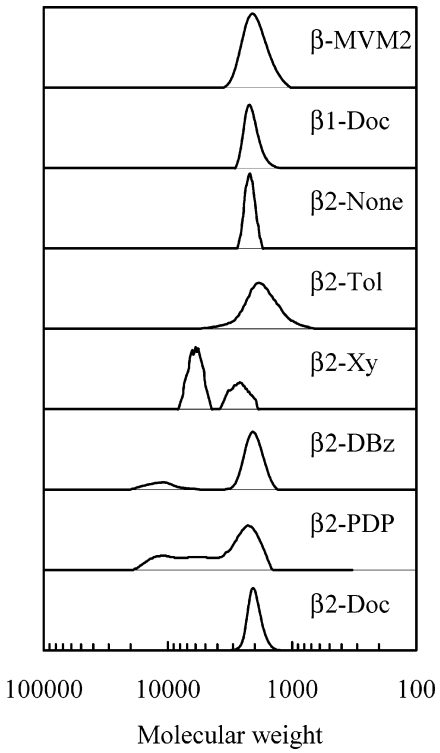


Figure 2. RI absorption of GPC of polymerized products of β-MVM1 and β-MVM2.

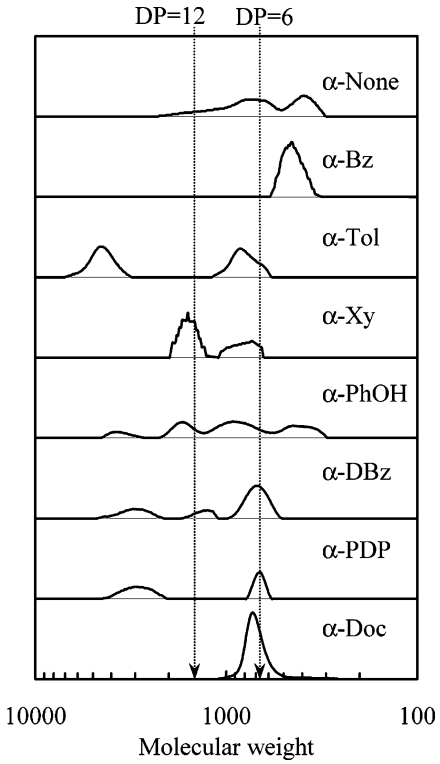


Figure 3. RI absorption of GPC of methacrylic acid oligomers obtained by hydrolysis of polymerized products of α-MVM.

β-MVM1 and 7 and 14 for β-MVM2. The peak positions of PMAA with DP = 6, 7, 12, and 14 previously calibrated by MALDI−TOF−Mass are shown in Figures 3 and 4. In the case of α-MVM series (Figure 3), the broad PMAA peaks at DP = 4 and 6.5 were observed for α-None. Since the conversion of methacryloyl of α-None was 17.8 mol %, the polymerization insignificantly proceeded. When benzene was added, the clear

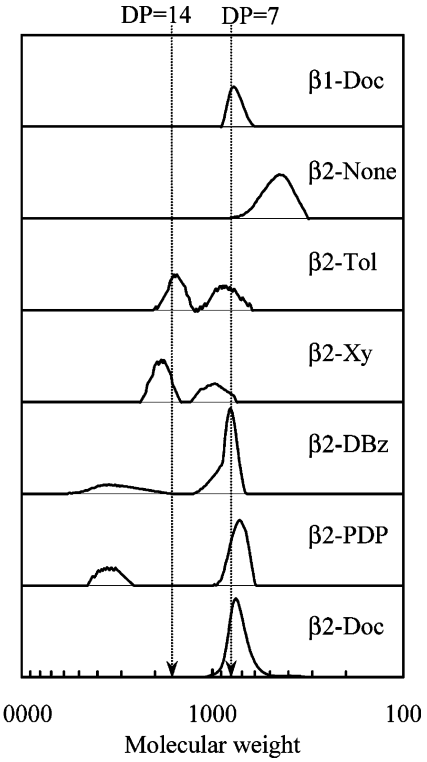


Figure 4. RI absorption of GPC of methacrylic acid oligomers obtained by hydrolysis of polymerized products of β-MVM1 and β-MVM2.

peak appeared at DP = 4. Thus, PMAA with low molecular weight was formed by addition of benzene.

Interestingly, in the case of α-DBz, α-PDP, and α-Doc, the PMAA with DP = 6 with narrow molecular weight distribution was obtained, indicating that the polymerization of six methacryloyl groups on the primary hydroxyl group side was succeed. Dodecylbenzene, PDP, and docosane were composed with long alkyl groups. Thus, the guests with long alkyl group were effective to control the polymerization on the primary hydroxyl group side of α-MVM. Generally, long alkyl group tends to be included in the α-cyclodextrin cavity. Thus, the specific inclusion behavior of long alkyl group in α-MVM would result in the ideal template polymerization of α-MVM on the primary hydroxyl group side. In the trans conformation, the length of docosane molecule is ca. 3 nm. It is possible to form inclusion complexes with a long narrow chain such as alkyl molecule and more than one cyclodextrin molecule.[29,30] On the other hand, Tabushi et al.[31] reported that the depth of hydrophobic cavity was increased by modification of primary hydroxyl group. In fact, the calculated depth of the cavity was increased from 0.65 nm for α-CD to 1.52 nm for α-MVM and β-MVM2 and to 1.07 nm for β-MVM1 by modification of the primary and secondary hydroxyl groups. Therefore, only one MVM molecule was threaded through a long alkyl group.

In contrast to PMAA with DP = 6, no PMAA with DP = 12 were obtained from any cases. The polymerization on the secondary hydroxyl group side of α-MVM was not controlled with any guests. Especially, the broad PMAA peaks indicating the intermolecular polymerization at larger than DP = 12 were observed for α-Tol, α-Xy, α-DBz, α-PhOH, and α-PDP. They contain phenyl groups. The phenyl group would disturb the template polymerization of α-CD. The details are discussed in a later section.

In the case of β-MVM2 (Figure 4), the addition of toluene provided PMAA with DP = 7 and 14 as well as the previous work.[25] Their molecular weight distribution was narrow. On the other hand, PMAA with DP = 14 was not obtained with other guests. Thus, the template polymerization of cyclodextrins did not depend on the initiator/complex system but the guest. In the cases of β2-Doc, β2-PDP, and β2-DBz, PMAA with DP = 7 was obtained. As well as the α-MVM series, polymerization on the primary hydroxyl group side was controlled with long alkyl compounds. When the guests contain a phenyl group, except for toluene, the broad PMAA peaks owing to the intermolecular polymerization were observed (β2-Xy, β2-DBz, and β2-PDP). The phenyl group disturbed the template polymerization of β-CD, except for typical case, i.e., toluene. Interestingly, the addition of docosane provided PMAA with DP = 7 from β-MVM1, which contains not 7 methacryloyl groups on the primary hydroxyl group side but 14 methacryloyl groups on the secondary hydroxyl group side. This indicates that docosane controlled the polymerization not only on the primary hydroxyl group side but also on the secondary hydroxyl group side. Additionally, only the half of methacryloyl groups on the secondary hydroxyl group side were polymerized with docosane. This well agreed with the results of α-Doc that the only PMAA with DP = 6 with narrow molecular weight distribution was obtained. Consequently, the long alkyl group in the guest controlled the template polymerization, while the phenyl group disturbed it, except the typical case. As a typical case, toluene was the most suitable guest for the template polymerization of β-MVM series; however, the most ideal guest for α-MVM was not found. Docosane controlled polymerization not only on primary but also on secondary hydroxyl group side of α-CD and β-CD.

Structure of Inclusion Complex Determined by NMR. In former section, it was found that the template polymerization was strongly affected on the guest. Thus, the structure of inclusion complex was investigated by NMR. Figures 5 and 6 show 2D-NMR measurement spectra of α-MVM and β-MVM2 series, respectively. In the case of α-MVM series (Figure 5), when toluene was added to α-MVM, the interaction peaks between methyl proton of methacryloyl group (CH_2=C(CH_3)−) at 1.95 ppm and phenyl proton of toluene at 7.12 and 7.27 ppm appeared. On the other hand, the interaction between the cyclodextrin ring proton (C_1−C_6H) from 3.58 to 5.18 ppm and the phenyl proton of toluene was not observed. Toluene did not exist in the α-MVM cavity but near methacryloyl groups. In the case of α-DBz and α-Doc, the interaction peaks appeared at cross points of methylene protons of long alkyl group (−CH_2−CH_2−CH_2−) at 1.2 ppm and the protons of cyclodextrin ring (C_1−C_6H) from 3.58 to 5.18 pm and vinyl protons (CH_2=C(CH_3)−) at 5.62 and 6.17 ppm. Thus, dodecylbenzene and docosane were included in the α-MVM cavity.

In the case of β-MVM2 series (Figure 6), the interactions of phenyl protons of toluene with vinyl and cyclodextrin ring protons appeared by addition of toluene. Toluene was included in the β-MVM2 cavity. As well as the α-MVM series, the interaction peaks of protons of long alkyl groups with the protons of cyclodextrin ring protons of β-MVM2 were observed by addition of dodecylbenzene and docosane. It has been reported that two molecules of long alkyl compound were included in a molecule of β-CD for the stable inclusion complex.[30] The molar ratio of docosane to

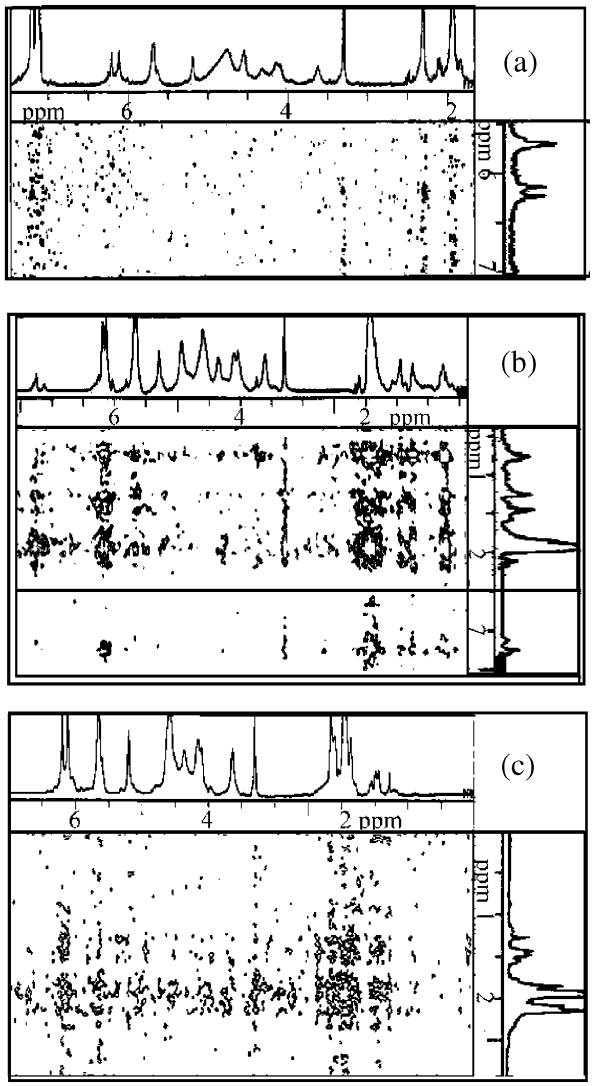


Figure 5. 2D ^{1}H NMR spectra of α-MVM with (a) toluene, (b) dodecylbenzene, and (c) docosane.

β-MVM1 and β-MVM2 is 5. It was possible to form the stable complex with docosane β-MVMs. Here, further complex structure was simulated in a later section. In the case of β2-DBz, another interaction peak appeared at the cross-point of phenyl proton and protons of cyclodextrin ring, indicating that the phenyl group of dodecylbenzene was included in the β-MVM2 cavity. As described above, the phenyl group was not included in α-MVM. The inclusion of a phenyl group in β-MVMs would be due to the larger cavity size of β-CD than that of α-CD. Since the structure of the secondary side of β-MVM1 would be similar to that of β-MVM2, the inclusion behavior of β-MVM1 will be similar to that of β-MVM2.

Simulation of Inclusion Structure by MM2. The 2D-NMR measurements suggested the inclusion of long alkyl group of the guests into α-MVM and β-MVM2. Here, the arrangement of methacryloyl group, which was an important factor of the template polymerization, was simulated by MM2. Figure 7 shows the view of primary and secondary hydroxyl group sides of the simulated arrangement of methacryloyl groups of α-MVM with and without guests. The clear color atoms corresponded to methacryloyl groups and the guests. Other atoms are shown in black and white. The left three figures summarize the arrangements of methacryloyl

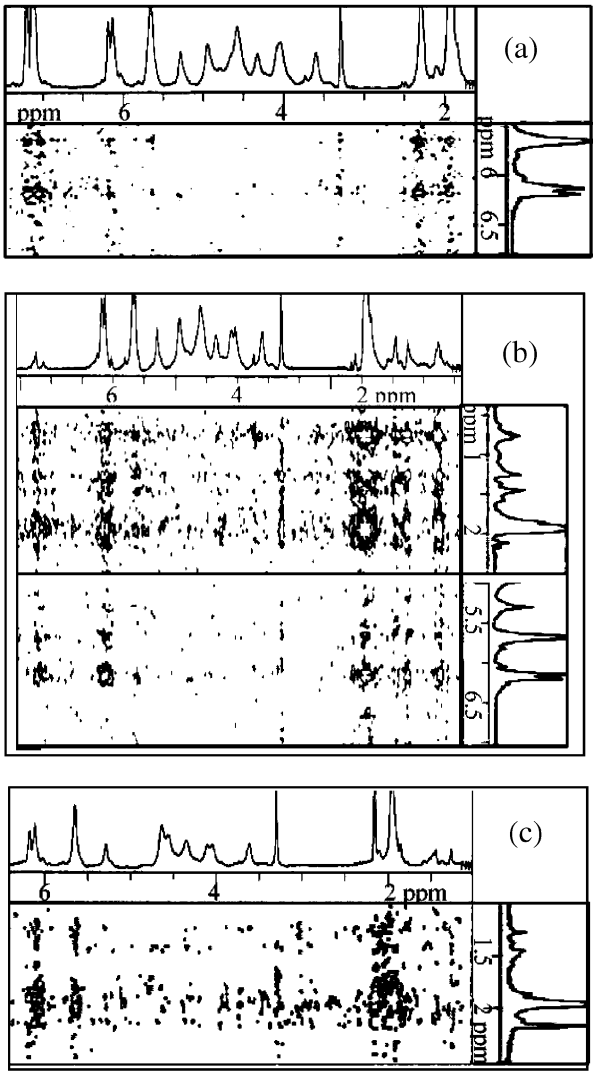


Figure 6. 2D ^{1}H NMR spectra of β-MVM2 with (a) toluene, (b) dodecylbenzene, and (c) docosane.

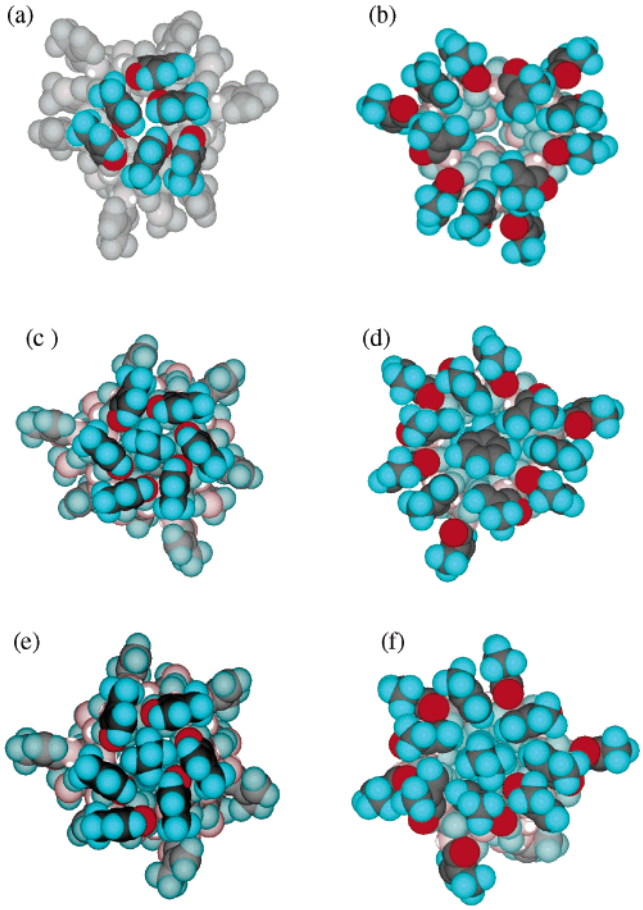


Figure 7. Calculated arrangement of methacryloyl groups of α-MVM by MM2: black particle: C; blue particle: H; red particle: O. (a) The primary hydroxyl group side without guest, (b) the secondary hydroxyl group side without guest, (c) the primary hydroxyl group side with dodecylbenzene, (d) the secondary hydroxyl group side with dodecylbenzene, (e) the primary hydroxyl group side with docosane, and (f) the secondary hydroxyl group side with docosane.

groups on the primary hydroxyl group side, and the right three figures summarize the arrangements of methacryloyl groups on the secondary hydroxyl group side. Without guest, methacryloyl groups on the primary and secondary hydroxyl group sides were segregated outside of the cavity. The distances between neighboring methacryloyl groups were widely dispersed in a range from 2.1 to 7.64 Å. The wide distance between methacryloyl groups would cause the low conversion and the wide PMAA peaks at low DP. In contrast, when dodecylbenzene and docosane were added, six methacryloyl groups on the primary hydroxyl group side were well arranged around the long alkyl chain. An average distances between neighboring methacryloyl groups with docosane and dodecylbenzene on the primary hydroxyl group side were the same, and they were 4.51 ± 0. 84 Å. On the other hand, the arrangements of methacryloyl groups on the secondary hydroxyl group side with docosane and dodecylbenzene were different. When docosane was added, six methacryloyl groups on the secondary hydroxyl group side homogeneously arranged near the alkyl group of docosane. The average distance between nearest methacryloyl groups was 3.83 ± 1.07 Å. The other six methacryloyl groups expanded into the solvent. Therefore, only PMAA with DP = 6 was obtained.

When dodecylbenzene was added, the phenyl group of dodecylbenzene was included in the cavity of α-CD. Because of the vertical threading of alkyl group to the cavity, the included phenyl group was tilted in the α-MVM cavity. The methacryloyl groups on the secondary hydroxyl group side near the tilted phenyl group were irregularly expanded into the solvent (Figure 7d). This suggests that PMAA with DP = 6 was prepared on the primary hydroxyl group side and gelation mainly occurred on the secondary hydroxyl group side. The arrangements of methacryloyl groups of α-PDP were very similar to the case of dodecylbenzene. However, the phenolic hydroxyl group of PDP enhanced the irregularity of methacryloyl groups on the secondary hydroxyl group side. We have previously reported that the expansion of methacryloyl groups to the solvent by increasing the solubility of methacryloyl groups to the solvent caused the gelation.[24] Thus, the irregular expansion of methacryloyl groups by phenyl groups of dodecylbenzene and PDP was the cause of the intermolecular polymerization.

Figure 8 shows the simulated views of primary and secondary hydroxyl group sides of β-MVM2. As well as Figure 7, the methacryloyl groups and the guest are shown in color. When the guest was not added, the methacryloyl groups were inhomogeneously segregated and some were included in the cavity of β-MVM2. In

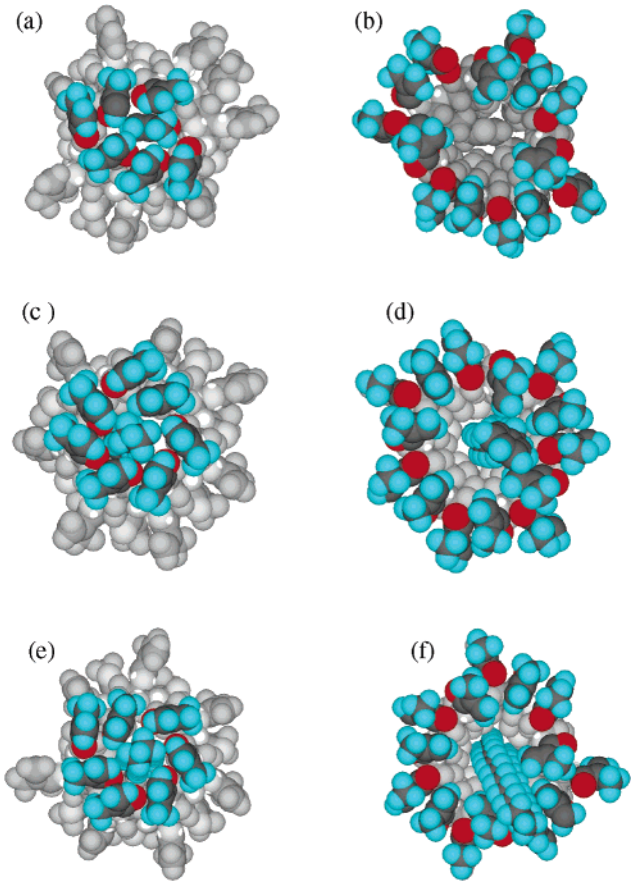


Figure 8. Calculated arrangement of methacryloyl groups of β-MVM2 by MM2: black particle: C; blue particle: H; red particle: O. (a) The primary hydroxyl group side without guest, (b) the secondary hydroxyl group side without guest, (c) the primary hydroxyl group side with dodecylbenzene, (d) the secondary hydroxyl group side with dodecylbenzene, (e) the primary hydroxyl group side with docosane, and (f) the secondary hydroxyl group side with docosane.

the case of α-MVM, the methacryloyl group was not included in the cavity. Therefore, the conversion of α-None was slightly larger than β-None. The inclusion of methacryloyl groups of β-MVM2 would be due to the larger cavity size than α-MVM.

The simulation indicated that, for β2-Tol, toluene existed at the center of β-MVM2 cavity, and the methacryloyl groups of β-MVM2 were well arranged on the both sides. This result shows a good arrangement with the GPC result that PMAA with DP = 7 and 14 was synthesized by addition of toluene. When dodecylbenzene was added to β-MVM2, the methacryloyl groups on the primary hydroxyl group side were well arranged with an average distance between neighboring methacryloyl groups = 4.036 Å. In contrast, on the secondary hydroxyl group side, the methacryloyl groups were drastically disordered as well as α-DBz. As well as the case of α-MVM, the polymerization on the primary hydroxyl group side was controlled with a long alkyl group while the gelation occurred on the secondary hydroxyl group side. The β2-PDP showed a very similar structure to β2-DBz.

For β2-Doc, the seven methacryloyl groups were well arranged on the primary hydroxyl group side around the long alkyl chain. On secondary hydroxyl group side, seven methacryloyl groups were selectively arranged around the long alkyl group of docosane. The arrangements of methacryloyl groups of β1-Doc and β2-Doc on the secondary hydroxyl group side were very similar. Since PMAA with DP = 7 was synthesized on the secondary hydroxyl group side of β1-Doc, PMAA with DP = 7 would be synthesized on both sides of β2-MVM. As well as β-MVM2, PMAA with DP = 6 would be synthesized on both primary and secondary hydroxyl group sides of α-MVM with docosane.

To form the stable inclusion complex with β-CD, not only one but also two molecules of long alkyl chain compound are generally included in a molecule of β-CD.[32] The feed molar ratio of docosane to β-MVM1 and β-MVM2 was 5. Thus, enough amount of docosane existed in the system, even if the 2:1 complex (= [guest]:[β-MVM2]) was formed. However, the molar ratio of docosane included to β-MVM2 was not confirmed in this work. Consequently, the inclusion of guest to cyclodextrin cavity of multivinyl monomer strongly affected the arrangement of methacryloyl groups, and when the methacryloyl groups were well ordered, the template polymerization ideally proceeded along the rims of the multivinyl monomers. The included long alkyl group enhanced the arrangements of methacryloyl groups, and the included phenyl group tended to disturb the arrangement of methacryloyl groups.

Conclusion

To control the degree of polymerization of methacrylic acid oligomer [PMAA], template polymerization of three types of multivinyl monomers, α-MVM with 17.4 methacryloyl groups, β-MVM1 with 11.4 methacryloyl groups, and β-MVM2 with 20.4 methacryloyl groups, synthesized from cyclodextrins was carried out with various guest compounds. Without guests, the conversion was very low because the methacryloyl groups were inhomogeneously segregated. The template polymerization of cyclodextrins with guests was categorized to the following three cases: (1) Gelation, i.e., intermolecular polymerization, was completely hindered, and PMAA with specific molecular weight was synthesized. (2) Gelation was not hindered, but PMAA with specific molecular weight was synthesized in the same batch. (3) Gelation was not hindered, and the molecular weight of PMAA could not be controlled. From NMR measurements and simulation, it was found that the arrangements of methacryloyl groups of multivinyl monomers were widely changed by the guests. For case 1, the methacryloyl groups on both primary and secondary hydroxyl group sides were well-arranged by the guest. Toluene for β-MVM1 and β-MVM2, and docosane, which enhanced the arrangement of methacryloyl groups, for three multivinyl monomers resulted in case 1. For case 2, the methacryloyl groups on the primary hydroxyl group side were ordered and those on secondary hydroxyl group side disordered by the guests. In such a case, the guests, dodecylbenzene and PDP, were composed with a long alkyl group, which enhanced the arrangement of methacryloyl groups on the primary hydroxyl group side, and phenyl group, which cause the irregular expansion of methacryloyl groups on the secondary hydroxyl group side. When all methacryloyl groups were disordered by the inclusion, the polymerization was gelated, and no PMAA with specific molecular weight was obtained (case 3). To order the methacryloyl groups, the inclusion of long alkyl group in the cavity of methacryloyl groups was strongly effective. Especially, when docosane was used, the PMAA with DP = 6 and 7 was selectively synthesized from α-MVM

and β-MVM1 and β-MVM2, respectively. It was due to the strong arrangement of the methacryloyl groups around the long alkyl groups of the guests.

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