Atom Transfer Radical Polymerization of Poly(2-methacryloyloxyethyl methacrylate)

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ABSTRACT: Template polymerization of poly(2-methacryloyloxyethyl methacrylate)s (number-average molecular weight: 3.47×10^4, an average number of vinyl group in molecule: 163.4) prepared from poly(2-hydroxyethyl methacrylate) was carried out by using a copper-mediated atom transfer radical polymerization (ATRP). When the concentration of poly(2-methacryloyloxyethyl methacrylate) was less than 0.31 wt %, the polymerization was limited in the molecule and proceeded in a living manner at 25 °C. An apparent polymerization rate, 5.0×10^{-5} s^{-1}, which was very close to that of the copper-mediated ATRP in bulk, indicates that the vinyl groups were highly concentrated in the molecule. The intensity of ethyl group detected by ^{1}H nuclear magnetic resonance spectroscopy drastically decreased by polymerization, the gel permeation chromatography peak shifted to lower molecular weight side, and the dependence of solution viscosity on share rate was increased. These suggested that the ladderlike molecule was formed by the template polymerization. Glass transition temperature of ladderlike molecule measured by differential scanning calorimetry was observed at 210 °C.

Introduction

Atom transfer radical polymerization (ATRP) is a convenient and useful method to synthesize polymer with well-controlled molecular weight and molecular weight distribution.[1−4] Not only linear homopolymers but also many polymers with interesting architectures, such block copolymers,[5−10] graft copolymers,[11−14] branched polymers,[15−17] and brush polymers,[18−20] have been synthesized by ATRP. Template polymerization has been investigated to control molecular weight and molecular weight distribution of polymers.[21−25] When the polymerization is limited in template polymer chain and proceeds along the template polymer chain, molecular weight and molecular weight distribution of the daughter part obey those of the template polymer chain.[26] Many types of multivinyl monomers in which vinyl groups are combined with the template polymer chain through covalent bonds have been synthesized and polymerized by free radical polymerization to control the molecular weight and molecular weight distribution.[21,27−29]

One of the interesting features of the template polymerization is that a ladder polymer is formed by template polymerization of multivinyl monomer. However, the hindrance of gelation during the polymerization is difficult because the multivinyl monomer act as a cross-linker. The possibilities of branching and gelation were increased by decreasing the molecular weight of multivinyl monomer.

Good control of radical concentration by ATRP would improve the template polymerization. We previously synthesized β-cyclodextrin [β-CD] multivinyl monomer by esterification of hydroxyl groups of β-CD with methacrylic anhydride and polymerized by copper-mediated ATRP.[30,31] The degree of polymerization [Dp] of poly(methacrylic acid) [PMAA] completely obeyed the degree of methacryloyl groups introduced to each side to β-CD scaffold. PMAA with Dp = 7 was formed on the primary hydroxyl group side of β-CD and PMAA with Dp = 14 on the secondary hydroxyl group side.[31] Cyclic PMAA oligomers were also obtained by the connection of initiated and propagating sites of the polymerization.[32] Template polymerization of multivinyl monomer with linear template chain by ATRP will provide better control of intramolecular polymerization.

The purpose of this work is to investigate the effect of ATRP on the polymerization of multivinyl monomer with linear template chain. It was difficult to hinder the gelation during the free-radical polymerization of poly(2-methacryloyloxyethyl methacrylate) than that during the free-radical polymerization of poly(2-acryloyloxyethyl methacrylate). Thus, poly(2-methacryloyloxyethyl methacrylate) was chosen as a multivinyl monomer. If the polymerization is limited in the molecule of poly(2-methacryloyloxyethyl methacrylate), ladderlike polymer will be obtained (Scheme 1). The polymerized products were characterized by gel permeation chromatography (GPC), Fourier transform infrared (FT-IR) spectroscopy, differential scanning calorimetry (DSC), and ^{1}H nuclear magnetic resonance (NMR) spectroscopy.

Experimental Section

Materials. 2-Hydroxyethyl methacrylate (HEMA: Tokyo Chemical Industry Co., Ltd., 95%) was purified by distillation under vacuum.

1,4-Dioxane (99%), 2,2′-dipyridyl (99%), methanol (99.5%), hydroquinone (99.0%), *n*-hexane (95%), tetrahydrofuran (THF, 99%), potassium hydroxide (85.5%), sodium sulfate (99.0%), dimethyl sulfoxide (DMSO, 98.0%), and lithium hydroxide monohydrate (95.0%) were purchased from Kanto Chemical, Co., Inc., and used as received.

α,α′-Dibromo-*p*-xylene (Aldrich, 97%), methacrylic anhydride (Aldrich, 94%), CuBr (Wako Pure Chemical Industries, Ltd., 99.9%), methacryloyl chloride (Tokyo Chemical Industry Co., Ltd., 80%), chloroform-d_1 with 1% TMS (ACROS ORGANICS, d = 99.8%), methanol-d_4, and dimethyl-d_6 sulfroxide (Aldrich, 99.9%) were used as received.

Tris(2-dimethylaminoethyl)amine (Me_6TREN, 99.5%) was prepared on the basis of the literature.[33]

Toluene (Kanto Chemical, Co., Inc., 99%) and pyridine (Kanto Chemical, Co., Inc., 99.5%) were dried over calcium hydride (Kanto

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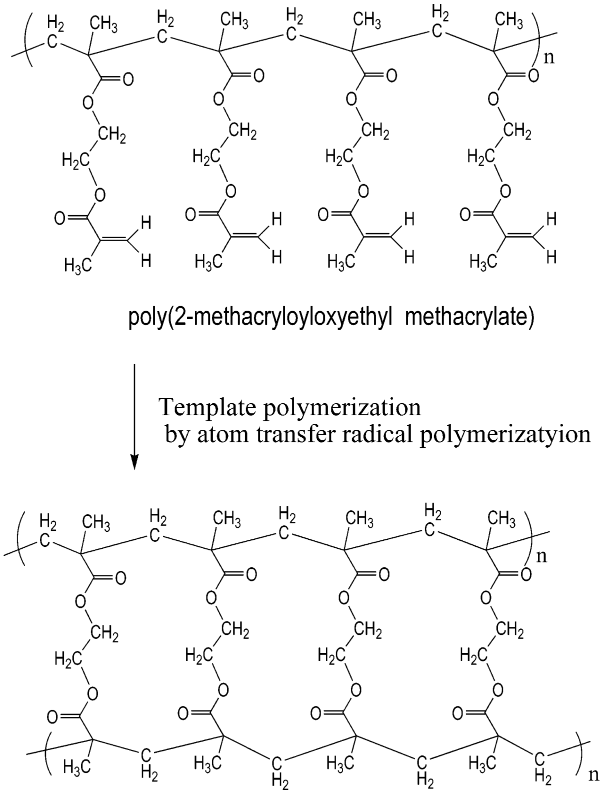
Scheme 1. Template Polymerization of Poly(2-methacryloyloxyethyl methacrylate)



Chemical, Co., Inc., 95%) for overnight and distilled under vacuum, immediately prior to use.

Synthesis of Poly(2-hydroxylethyl methacrylate) (PHEMA) Template Polymers. Polymerization of HEMA was carried out by ATRP at room temperature. The ATRP conditions are listed in Table 1. The procedure of PHEMA1 is as follows: HEMA (13.0 g, 99.8 mmol), α,α′-dibromo-*p*-xylene (0.257 mmol), 2,2′-dipyridyl (1.29 mmol), and CuBr (0.514 mmol) were dissolved in methanol (22.0 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 room temperature for 1 h. To stop the polymerization, the solution was cooled to −5 °C and was poured in cold (0 °C) water (200 mL). 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. Conversion of HEMA was about 50 wt %. The number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) were measured by GPC.

Synthesis of Poly(methacryloyloxyethyl methacrylate) (Multivinyl Monomer). Multivinyl monomers as template monomers were synthesized from PHEMA by two methods, i.e., the esterification with methacrylic anhydride and the Shotten−Baumann method.[29] The conditions are listed in Table 2. The procedure of esterification by methacrylic anhydride, MVM1, is as follows: PHEMA1 (0.0580 mmol, 10.6 mmol of hydroxyl group) was dissolved in dried pyridine (10.0 mL). Then, methacrylic anhydride (21.2 mmol) and hydroquinone (0.091 mmol) were added to the PHEMA solution. The mixture was stirred at room temperature for 2 days in a dark place. After the reaction, the product was precipitated into *n*-hexane (70.0 mL), purified by reprecipitation with THF (10.0 mL) and water (50.0 mL) three times, collected, and dried under vacuum. The typical procedure of the Shotten−Baumann method is as follows (MVM4-2): PHEMA1 (0.00134 mmol, 2.30 mmol of hydroxyl group) was dissolved in a THF/water mixture (10.0 mL) with 40 vol % of water. 3.0 N potassium hydroxide solution (10.0 mL) and THF (10.0 mL) were added to PHEMA solution. Methacryloyl chloride (2.90 mmol) and dried toluene (2.0 mL) were added to THF (11.0 mL). The methacryloyl chloride solution was added dropwise to the well-stirred PHEMA solution at −8 °C for 80 min. Then, the upper layer was separated from the mixture and dried with sodium sulfate overnight. After the reaction, sodium sulfate was removed by filtration, and the product was precipitated into *n*-hexane (200 mL), purified by reprecipitation with THF (10.0 mL) and water (50.0 mL) three times, collected, and dried under vacuum.

The number of vinyl groups introduced to PHEMA was characterized by ^{1}H NMR measurements with chloroform-d_1 by comparison with the resonances of 4.11−4.26 and 5.56−6.08 ppm owing to $-COO-CH_2-CH_2$ and $CH_2{=}C$.

Typical ATRP of Template Monomer. The polymerization was carried out with and without an initiator by ATRP from 25 to 40 °C for 2.0−48 h. The ATRP conditions are listed in Table 3. The procedure of PMVM4-5 is shown as a typical case of ATRP. MVM4 (0.0290 mmol, 4.66 mmol of vinyl group), α,α′-dibromo-*p*-xylene (0.0348 mmol), Me_6TREN (0.313 mmol), and CuBr (0.0870 mmol) were dissolved in a mixture of THF/water (223 mL) with 10 vol % of water in a sealable Pyrex reactor. The solution in the reactor was degassed by three freeze−pump−thaw cycles. The reactor was sealed under vacuum and heated at 30 °C for 16 h. To stop the polymerization, the solution was cooled to 0 °C and poured in water (1 L). The precipitate was collected by filtration and purified by reprecipitation for three times with THF (10.0 mL) and cold (0 °C) water (50.0 mL). The product was white powder. The reaction between template monomer molecules was determined by GPC. The conversion of reacted vinyl group was determined by FT-IR (Jasco, FT/IR-410) by the KBr method using the absorption at 1730 and 1636 cm^{-1} owing to carboxyl and vinyl groups, respectively.

Hydrolysis of Poly(2-hydroxyethyl methacrylate) and Poly merized Product of Multivinyl Monomer. PHEMA1 or polymerized multivinyl monomer, MVM4-5 (0.10 g), was dissolved in a mixture of DMSO (10 mL) and water (3 mL). Lithium hydroxide (10 mmol) was added to the solution. The solution was stirred at 40 °C for 180 h and then poured into 0.5 N HNO_3(aq) (30 mL). pH of the mixture was ca. 3. The precipitate, PMAA, was collected by centrifugation (KOKUSAN, H-103n, 400 rpm, 10 min), washed with water (20 mL) for three times, and dried under vacuum. The degree of hydrolysis was determined by ^{1}H NMR spectroscopy. ^{1}H NMR (methanol-d_4): δ [ppm] = 0.8−1.2 (3H, CH_3), 1.9−2.0 (2.2 H, CH_2).

Measurement of GPC. PHEMA, multivinyl monomers, polymerized multivinyl monomers: Polymer (0.010 g) was dispersed in THF (10 mL). In the case of PHEMA, phenyl isocyanate was added to the PHEMA solution to cap the hydroxyl group of PHEMA. The solution was stirred at room temperature for 24 h. For template monomers and polymerized products, polymer (0.010 g) was dissolved in THF (10 mL). M_n and M_w/M_n of PHEMA, multivinyl monomers, polymerized products were measured with a gel permeation chromatography (HITACHI, L-7100 series) double detected with a refractive index detector (HITACHI, L-2490) and a UV spectrometer (TOSOH, UV-8011) at 292 nm. The column was TSK-GEL G5000HHR (7.5 mm × 300 mm, 5 μm particle size, linear molecular weight range $3000-4 \times 10^6$). Eluent, flow rate, and temperature were THF, 0.6 mL/min, and 35 °C. The calibration curved were prepared using poly(methyl methacrylate) with various molecular weights.

Hydrolyzed product, PMAA (0.01 g), was dissolved in methanol (10 mL). M_n and M_w/M_n were measured with a GPC detected with a refractive index detector (TOSOH, GPC-8020). The column was TSK-GEK α-3000 (7.5 mm × 300 mm, 57 μm particle size, linear molecular weight range $1000-9 \times 10^4$). Eluent, flow rate, and temperature were methanol, 0.6 mL/min, and 35 °C. The calibration curves of PMAA previously prepared by combining GPC and matrix-assisted laser desorption ionization time-of-flight mass spectrometry were used.[31]

^{1}H NMR Measurement. ^{1}H NMR measurement was carried out with a ^{1}H NMR spectrometer (JEOL, GLX-400, 400 MHz) with deuterated dimethyl sulfoxide (DMSO-d_8) as a solvent for template monomers and polymerized products at room temperature using a

Table 1. Synthesis of Poly(2-hydroxyethyl methacrylate)

code	HEMA (mol/L)	dibromo-*p*-xylene (mol/L)	CuBr (mol/L)	2,2′-dipyridyl (mol/L)	solvent[a]	reaction temp (°C)	reaction time (h)	M_n[b]	M_w/M_n[b]
PHEMA1	4.54	0.0117	0.0234	0.0584	methanol	25.0	1.0	2.36×10^4	1.52
PHEMA2	1.60	0.0209	0.0417	0.105	diox/methanol	20.0	24	1.38×10^4	1.33

[a] Diox/methanol indicates a 1,4-dioxane/methanol mixture with 40 vol % of 1,4-dioxane. [b] M_n and M_w: number-average and weight-average molecular weights determined by gel permeation chromatography.

Table 2. Esterification of Poly(2-hydroxyethyl methacrylate)s[a]

code	method[b]	polymer weight (g)	solvent[c] (mL)	[MA]/[OH][d] (mol/mol)	[COCl]/[OH][e] (mol/mol)	reaction temp (°C)	reaction time (h)	conversion of esterification (mol %)[f]
MVM1	MA	1.375	10.0	2.0		30	58	88.6
MVM2	SB	0.315	10.0		1.2	-8	1.5	71.1
MVM3	SB	0.315	10.0		2.0	-8	1.5	52.8
MVM4	SB	0.650	10.0		1.2	-8	2.0	90.0
MVM5	SB	0.497	26.2	0.0	1.2	0	1.5	82.0

[a] Precursor polymer of MVMs except for MVM5 was poly(2-hydroxyethyl methcarylate), PHEMA1, with $M_n = 2.36 \times 10^4$ and $M_w/M_n = 1.52$. Precursor polymer of MVM5 was PHEMA2 with $M_n = 1.38 \times 10^4$ and $M_w/M_n = 1.33$. [b] SB and MA indicate the Shotten−Boumann method and direct esterification with methacrylic anhydride, respectively. [c] Pyridine and a water/THF mixture with 40 vol % of water were used in cases of SB and MA with methacrylic anhydride [MA] methods, respectively. [d] Molar ratio of methacrylic anhydride to a 2-hydroxyethyl methacrylate unit. [e] Molar ratio of methacryloyl chloride to a 2-hydroxyethyl methacrylate unit. [f] Determined by ^{1}H NMR resonances of 4.11−4.26 and 5.56−6.08 ppm.

Table 3. Atom Transfer Radical Polymerization of Poly(methacryloyloxyethyl methacrylate) Multivinyl Monomers

code	MVM type	MVM concn (wt %)	solvent type[a]	[initiator]/[MVM] (mol/mol)[b]	polymer system[c]	reaction temp (°C)	reaction time (h)	conversion of vinyl groups (mol %)[d]	remarks
PMVM1-1	MVM1	0.25	diox/water	0	A	40	48	33.1	gel
PMVM4-1	MVM4	0.25	diox/water	0	A	40	48	0.0	
PMVM4-2	MVM4	0.10	diox/water	1.0	A	25	40	56	
PMVM4-3	MVM4	0.30	diox/water	1.0	A	25	6.0	77.8	
PMVM4-4	MVM4	0.31	THF/water	1.2	B	30	2.0	48.1	
PMVM4-5	MVM4	0.31	THF/water	1.2	B	30	16.0	75.9	
PMVM4-6	MVM4	0.31	THF/water	0.8	C	30	16.0	68.1	gel
PMVM5-1	MVM5	0.30	diox/water	1.0	B	25	4.0	66.6	

[a] Diox/water and THF/water indicate a 1,4-dioxane/water mixture with 10 vol % of water and a tetrahydrofuran−water mixture with 11 vol % of water, respectively. [b] Molar ratio of an initiator to MVM. An initiator was α,α′-dibromo-*p*-xylene, except for PMVM4-6. An initiator system of PMVM4−6 was H_2O_2/Fe^{2+}. [c] System A: [initiation site]:[CuBr]:[tris(2-dimethylaminoethyl)amine (Me_6TREN)] = 1:2:4. System B: [α,α′-dibromo-*p*-xylene]:[CuBr]:[Me_6TREN] = 1:4:8. System C: [H_2O_2]:[Fe^{2+}] = 1:1. [d] Determined by FT-IR spectroscopy with the absorption at 1730 and 1636 cm^{-1}.

resonance of the deuterated solvent as lock and the internal standard for chemical shift date in the δ-scale relative to TMS. Deuterated methanol was used as a solvent for PMAA.

Measurement of Solution Viscosity. The solution viscosity of template monomer, polymerized product, and poly(methyl methacrylate) was measured using a cone/plate type Brookfield viscometer (Brookfield Engineering Laboratories, Inn., RVDV-II+) with a CP-40 cone at speed varying from 0.2 to 20 rpm. The sample solution (1.0 mL) was loaded between the cone and plate. The measurement was carried out at 35 °C.

Measurement of Differential Scanning Calorimetry (DSC). Polymer (acetylated PHEMA2 or polymerized product PMVM5-1, 12.1 mg) was sealed in an aluminum pan and measured with a differential scanning calorimeter (Perkin-Elmer, Pyris 1) in a temperature range from −30 to 300 °C with ramping and cooling rate 30 K min^{-1}.

Results and Discussion

Synthesis of PHEMA. First, PHEMA, the parent polymer, was synthesized by copper-mediated ATRP for the template. The narrow molecular weight distribution is important for the analysis of template polymerization. Thus, the ATRP, which is a convenient method to obtain well-defined PHEMA, was chosen. Conditions and results of synthesis of PHEMA1 and PHEMA2 are listed in Table 1. Conversions were about 50 mol %, which was a general value for copper-mediated ATRP. M_w/M_n values determined by GPC were 1.52 and 1.33 for PHEMA1 and PHEMA2, respectively (Table 1). Average degrees of polymerization were 181.5 and 106.2 for PHEMA1 and PHEMA2, respectively. The M_w/M_n value of PHEMA1 was slightly wide. It would be due to the fact that the polymerization solution became viscous at the latter stage of polymerization. However, it is narrow enough to distinguish intra- and intermolecular polymerization during the template polymerization. Thus, PHEMA1 and PHEMA2 were used for the synthesis of multivinyl monomer without further fractionation.

Synthesis of Multivinyl Monomer. Poly(methacryloyloxyethyl methacrylate)s, multivinyl monomers, were synthesized with PHEMA1 with two methods, which were the Shotten−Baumann method[29] and the esterification with methacrylic anhydride proposed by Bowen.[32] Jantas et al. synthesized poly(methacryloyl ethylene) and poly(methacryloyloxyethyl methacrylate) with good yield from poly(vinyl alcohol) and PHEMA, respectively, with methacrylic chloride by the Shotten−Baumann method.[28,29] Bowen succeeded the complete esterification of β-CD with methacrylic anhydride in pyridine.[34] Here, these two methods were compared. The advantage of esterification with methacrylic anhydride is higher polymer concentration than that of the Shotten−Baumann method. On the other hand, the advantage of Shotten−Baumann method is lower reaction temperature and shorter reaction time than those by the esterification with methacrylic anhydride. Lower reaction temperature and shorter reaction time will be more favorable to prevent the side reaction of vinyl group during the esterification.

The conditions and results are listed in Table 2. Figure 1 shows a GPC profile of acetylated PHEMA1 and MVM4 as a typical case. The peak top and width of the peak of MVM4 were close to those of acetylated PHEMA1. In all cases, the

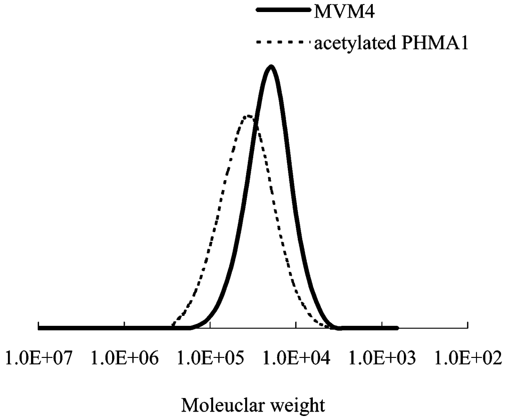


Figure 1. Profiles of gel permeation chromatography of acetylated poly(2-hydroxyethyl methacrylate), PHEMA1, and poly(2-metharyloyloxyethyl methacrylate) multivinyl monomer, MVM4, measured with tetrahydrofuran as an eluent. Molecular weight was calibrated with poly(methyl methacrylate).

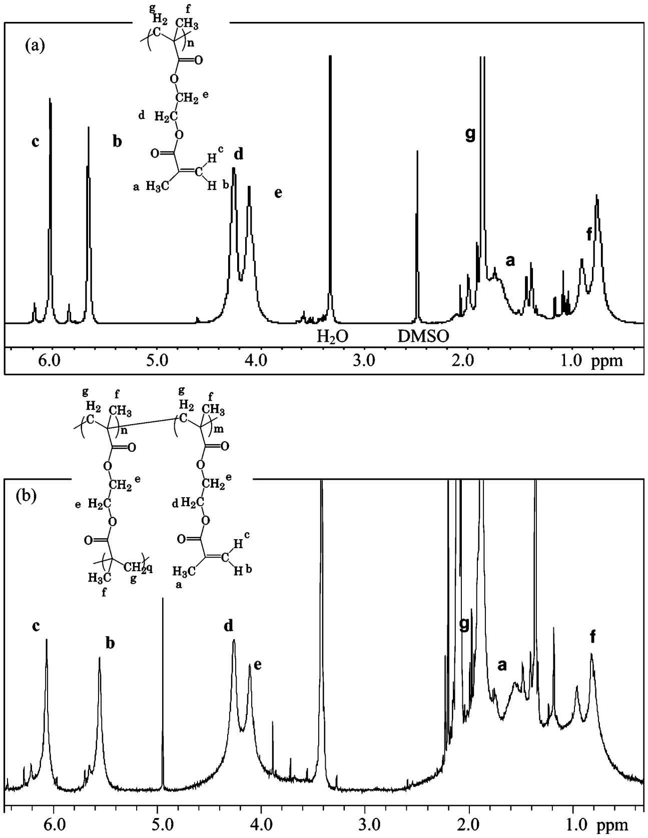


Figure 2. Proton nuclear magnetic resonance spectra of poly(2-metharyloyloxyethyl methacrylate) multivinyl monomer, MVM4, and the polymerized product of MVM4, PMVM4-5. (a) Multivinyl monomer MVM4. (b) Polymerized product, PMVM4-5.

peak top of multivinyl monomer did not shift to larger molecular weight side than that of acetylated template. Consequently, the hydroxyl groups were esterificated by those two methods without the side reaction of methacryloyl group. The number of vinyl groups in the multivinyl monomer was analyzed by ^{1}H NMR spectroscopy. To neglect the mobility of hydroxyl group and methacrylate group, DMSO-d_8, which was a good solvent for both hydroxyl and methacrylate groups, was used. Figure 2a shows the ^{1}H NMR spectra of MVM4. Resonances b and c corresponding to the vinyl group appeared at 6.5 and 5.56 ppm after esterification. The degree of esterification was calculated by comparison of the total area of resonances of vinyl group (resonances b and c in Figure 2a) to the total area of resonances of ethylene group in the HEMA unit (resonances d and e at 4.26 and 4.11 ppm in Figure 2a) (Table 2). The maximum degrees of esterification of both methods were about 90 mol %; from the viewpoint of degree of esterification, both methods were useful to introduce the vinyl group in PHEMA1. Consequently, the multivinyl monomers, MVM1 and MVM4, with Dp = 181.5 and number of vinyl group = 163.3 were obtained.

The multivinyl monomer of PHEMA2, MVM5, was also prepared by the Shotten–Baumann method as well as MVM4. The conversion of esterification, 82.0 mol %, was close to the cases of PHEMA1. The GPC profiles of acetylated PHEMA2 and MVM5 were very similar. The molecular weight dependence of PHEMA on the esterification by the Shotten–Baumann method was not observed in these polymers. Dp and number of vinyl group of MVM5 were 106.2 and 87.08, respectively.

Template Polymerization of Multivinyl Monomers. ATRP of multivinyl monomers was carried out. The conditions and results are listed in Table 3. Conversion of the vinyl group estimated by FT-IR is also listed in Table 3. First, the polymerization with Br groups existing at the chain ends of parent chain was investigated. The template polymer, PHEMA1, was synthesized with a bifunctional initiator, α,α′-dibromo-*p*-xylene, by ATRP. If the initiation starts at the ends of the template sequence of multivinyl monomer, a very regular ladderlike structure is expected. Banford proposed this idea but did not investigate experimentally.[35] Therefore, the template polymerization of multivinyl monomers was carried out without additional initiators (code PMVM1-1 and PMVM4-1). In the case of PMVM1-1 prepared with methacrylic anhydride, polymerization started without the additional initiator, indicating that the terminal Br groups in MVM1 were active. The solution gelled at 48 h with low conversion of vinyl group, 33.1 mol %. In this work, the distance between Br group at the end of template sequence and vinyl group in the next unit to Br group was too far to control the polymerization because the vinyl groups were attached to PMAA backbone via ethylene glycol esters. Again, the most important feature for the template polymerization is to limit the polymerization inside the molecule and to hinder the polymerization between template molecules. MVM1 with an active Br group at the end of template sequence was not suitable for this work. On the other hand, when MVM4 prepared by the Shotten–Baumann method was used, the conversion of vinyl group was zero. Br groups in MVM4 were probably hydrolyzed with potassium hydroxide by the Shotten–Baumann method.

Next, the polymerization with the additional initiator was investigated. To avoid the side reaction with Br groups in the template sequence, MVM4 which did not have Br group was chosen. To neglect the initiating position with the additional initiator, α,α′-dibromo-*p*-xylene, a bifunctional initiator, was used because polymerization proceeds toward both ends of the backbone at the same time from the initiator. To compare the ATRP, the redox polymerization of MVM4 at 0.31 wt % with H_2O_2/Fe^{2+} was carried out (MVM4-6). Figure 3 shows GPC profiles of the multivinyl monomer MVM4 and its products, PMVM4-4 and MVM4-5, polymerized at 0.31 wt % at 30 °C. The shape and the position of these peaks were very similar, indicating that polymerization was completely limited in the molecule of MVM4. When MVM4 was polymerized by ATRP, all GPC profiles agreed with that of MVM4. In contrast, when the redox initiator was used, the solution was gelated. Thus, polymerization was completely limited in the molecule of MVM4 by ATRP when the concentration of MVM4 was less

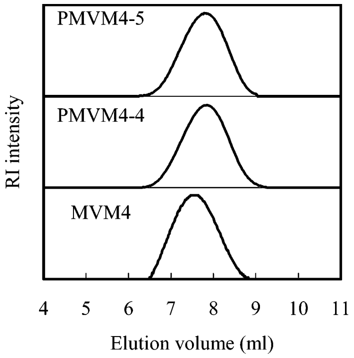


Figure 3. Profiles of gel permeation chromatography of poly(2-metharyloyloxyethyl methacrylate) multivinyl monomer, MVM4, and the polymerized products of MVM4, PMVM4-4 and PMVM4-5, in a tetrahydrofuran/water mixture (water content, 11 vol %) at 30 °C with [MVM4]:[α,α′-dibromo-*p*-xylene]:[CuBr]:[tris(2-dimethylaminoethyl)-amine] = 1:1:2:4.

than 0.31 wt %. Jantas et al. polymerized poly(2-methacryloyloxyethyl methacrylate) with $M_n = 2.69 \times 10^4$ with α,α′-azobis-(isobutyronitrile) at 75 °C at 1.2 wt % of concentration of poly(2-methacryloyloxyethyl methacrylate) and found that the intermolecular polymerization had started over 40% of conversion.[34] The maximum conversion of this work, 77.8%, was much larger than their value. The lower the concentration of multivinyl monomer, the lower the possibility of intermolecular polymerization. Additionally, the concentration of radical is well controlled by ATRP. Consequently, template polymerization proceeds successfully by decreasing the concentration of multivinyl monomer and using ATRP.

Figure 2b shows the ^{1}H NMR spectra of MVM4-5 with 75.9 mol % of conversion. The resonance corresponding to methylene group observed from 1.4 to 2.2 ppm for the template monomer broadened from 0.8 to 2.4 ppm by polymerization. After polymerization, however, the ratio of whole resonance area of vinyl group ($CH_2{=}$) at 6.08 and 5.56 ppm to that of ethylene ($-CH_2-CH_2-$) at 4.26 and 4.11 ppm increased from 0.42 to 1.44, indicating that the ^{1}H NMR spectra of the polymerized products were not quantitative. When the polymerization proceeds along the backbone, the product will be a ladderlike polymer. Hydrogen in the crosspiece sequence in the ladder polymer was not quantitatively detected by ^{1}H NMR spectroscopy in solution because of the drastic decrease of the mobility of crosspiece sequence. In this work, ethylene group exist in crosspiece sequence. The mobility of ethylene group would be drastically decreased by polymerization, and the quantitativity of resonance area of ^{1}H NMR spectroscopy was lost after polymerization.

Kinetic Study of Polymerization of MVM4. Next, the kinetics of the polymerization was analyzed. Figure 4 shows the kinetic plot of PMVM4-3 with 0.31 wt % of polymer concentration at 25 °C in the 1,4-dioxane/water mixture. The induction time of polymerization until 0.25 h was observed. In a range from 0.25 to 1.5 h, the first-order kinetic plots showed good linearity. Over 1.5 h, the conversion was saturated, indicating the polymerization was completed. Thus, the ATRP of MVM4 proceeded in a living manner. The slope from 0.25 to 1.5 h, an apparent polymerization rate constant, k_{app} (= k[M]), was 5.0×10^{-5} s^{-1}. Here k is the polymerization rate constant, and [M] is the concentration of vinyl group around radical. The k_{app} values of methyl methacrylate, which were calculated from the k values of methyl methacrylate on copper-mediated ATRP with Br groups, were 3.52×10^{-5} s^{-1} in bulk at 80 °C[36] and 3.78×10^{-5} s^{-1} in ethylene carbonate with 50 wt % of MMA at 60 °C.[37] The k_{app} of this work was close to those values. Here, it should be noticed that the concentration of MVM4 was only 0.3 wt %; the average concentration of methacryloyl group in the system was 1.46×10^{-2} mol/L. Theoretically, [M] is not an average concentration of vinyl group in the system, but a local concentration of vinyl group around radicals. The average concentration of vinyl group in the system generally agrees with the local concentration of vinyl group around the radicals in the conventional solution radical polymerization. In contrast, the average concentration of vinyl group in the system does not agree with the local concentration of vinyl group around radical. The agreement of the k_{app} value of MVM4 and the reference values indicates that the local concentration of vinyl group around radical in MVM4 was close to that in bulk even the average concentration of vinyl group in the system was only 1.46×10^{-2} mol/L. A similar phenomenon, which was the agreement of k_{app} value of multivinyl monomer and bulk solution, was observed in the case of template polymerization with *β*-CD for the template.[31] Thus, the vinyl groups were highly concentrated in the template molecules in the template polymerization.

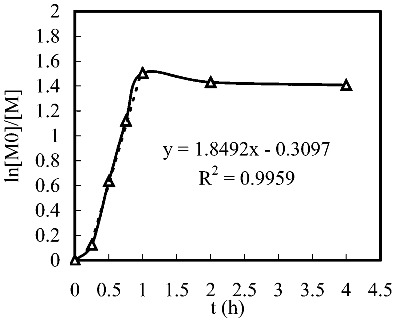


Figure 4. Kinetic plot for atom transfer radical polymerization of methacryloyl group in a 1,4-dioxane/water mixture (water 10 vol %); [poly(2-metharyloyloxyethyl methacrylate) multivinyl monomer, MVM4] = 0.31 wt % = 8.93×10^{-5} mol/L, [methacryloyl group] = 1.46×10^{-2} mol/L, [α,α′-dibromo-*p*-xylene] = 8.93×10^{-5} mol/L, [CuBr] = 1.79×10^{-4} mol/L, [tris(2-dimethylaminoethyl)amine] = 3.57 × 10-^{4} mol/L.

Structure of Polymerized Products. As described above, the GPC peak was not shifted to larger molecular weight side by polymerization but slightly shifted to lower molecular weight side. Two reasons can be proposed to explain the shift to lower molecular weight side. The first possibility is the homogeneous shrinkage of multivinyl monomer globule by cross-linking. The multivinyl monomer is expected to form a spherical random coil. If polymerization proceeds at random in the template, a spherical random coil will be cross-linked and the spherical microgel, which has smaller hydrodynamic diameter than the random coil, will be formed. The second possibility is the shape change of polymer chain from spherical to cylindrical by polymerization. If the polymerization proceeds along the backbone of template, the ladderlike polymer chain, which shape will be assumed the hard cylinder, will be obtained. To clarify this point, the shear dependence on the solution viscosity was measured.

Figure 5 shows the solution viscosity of the polymer/1,4-dioxane/water mixtures (polymer concentration: 0.3 wt %, water 10 vol %) of MVM4, PMVM4-5, and poly(methyl methacrylate) with $M_n = 5.3 \times 10^4$ synthesized by conventional radical polymerization with α,α′-azobis(isobutyronitrile) at 60 °C. The viscosity of MVM4 and poly(methyl methacrylate) decreased drastically at slow rotation rate and became stable over 2 rpm, indicating that these polymer chains were random coils. In contrast, the solution viscosity of PMVM4-5 decreased gradually

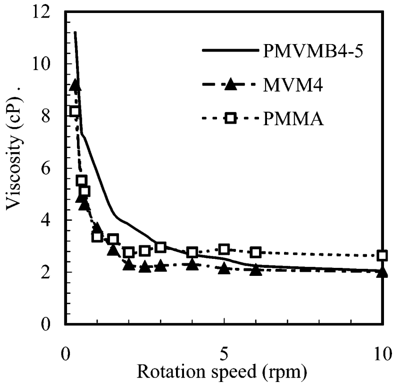


Figure 5. Solution viscosity of polymer/1,4-dioxane/water mixtures (polymer concentration = 0.3 wt %, water 11 vol %) of poly(2-metharyloyloxyethyl methacrylate), MVM4, polymerized product of MVM4, PMVM4-5, and poly(methyl methacrylate) at 25 °C.

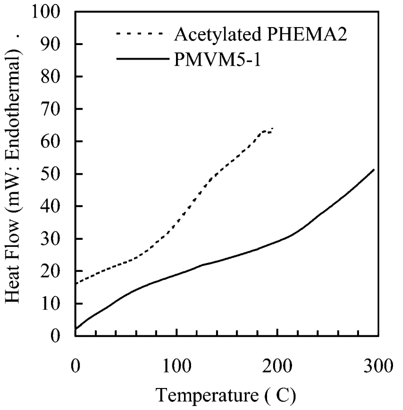


Figure 6. Profiles of differential scanning calorimetry of acetylated poly(2-hydroxyethyl methacrylate) PHEMA2 and the polymerized product of poly(2-metharyloyloxyethyl methacrylate) multivinyl monomer MVM5, PMVM5-1.

by increasing the rotation rate and was saturated over 6 rpm. The clear share rate dependence of PMVM4-5 on the viscosity indicates the shape of PMVM4-5 was not spherical but cylindrical. The M_w of PMVM4-5 calculated by universal calibration method well agreed with that of MVM4. Consequently, the peak shift of GPC to the lower molecular weight side by polymerization would be due to the conformation change of polymer chain from the random coil to cylinder, i.e., the ladderlike structure. Further detailed analysis of the conformation of product, such as light scattering measurements, etc., is under investigation.

Glass Transition Temperature (T_g) Measured by DSC. Highly thermal stability is expected for ladderlike polymers.[38,39] In fact, Jantas et al. reported that the T_g of polymerized product of poly(2-methacryloyloxyethyl methacrylate) with α,α′-azobis-(isobutyronitrile) was not observed below 270 °C by DSC.[40] The degree of ladder of polymerized products of poly(2-methacryloyloxyethyl methacrylate) in this work is lower than the literature. Thus, T_g of the polymerized product of MVM5, PMVM5-1, was measured by DSC. Figure 6 shows DSC profiles of first heating and first cooling of polymerized product MVM5-1. Since the multivinyl monomer was not suitable for reference because of the vinyl groups, acetylated PHEMA2, which was used for GPC measurement, was used for reference. Here, PHEMA2 is a precursor polymer of multivinyl monomer MVM5. In the case of polymerized product PMVM5-1, T_g was observed at 210 °C. It was clearly higher than the T_g of acetylated MVM5, 65 °C (line b), and poly(2-butyrylethyl methacrylate).[40] Thus, the ladderlike structure would be formed.

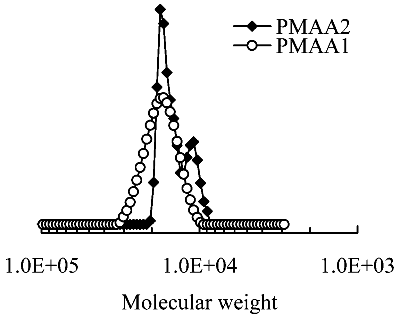


Figure 7. Profiles of gel permeation chromatography of poly-(methacrylic acid)s, PMAA1 and PMAA2, obtained from poly(2-hydroxyethyl methacrylate), PHEHA1, and polymerized product of poly(2-metharyloyloxyethyl methacrylate) multivinyl monomer MVM5, PMVM4-5, by hydrolysis.

However, it was lower than the literature value. The lower T_g of this work would be due to the lower degree of ladder than the literature. T_g and thermal decomposition behavior of polymerized product of multivinyl monomer as a function of degree of ladder are now under investigation and will be reported elsewhere.

Molecular Weight of Daughter Chain. Finally, the molecular weight of the daughter sequence was investigated. The daughter sequence was detached by hydrolysis. Figure 7 shows the GPC profiles of PMAAs, PMAA1, and PMAA2, which were the hydrolyzed products of PHEMA1 and PMVM4-5, respectively. For PMAA2, two peaks were observed at $M_n = 1.70 \times 10^4$ and 1.09×10^4 (Dp: 197.7 and 126.7). The Dp of PHEMA1 was 182. Taking account of the degree of esterification with methacryloyl group, 0.9, and the conversion of vinyl group by ATRP, 0.75, the theoretical Dp of daughter PMAA was 123 ($= 182 \times 0.9 \times 0.75$). The experimental Dp agreed well with the theoretical value. Therefore, the template polymerization proceeded in the multivinyl monomer when PHEMA and ATRP were chosen for the template and polymerization system.

Summary

Two types of multivinyl monomer, poly(2-methacryloyloxyethyl methacrylate), with 3.47×10^4 of an number-average molecular weight and 163.4 of an average number of vinyl group in the molecule were prepared with PHEMA by the direct esterification with methacrylic anhydride and by the Shotten−Baumann method. These multivinyl monomers were polymerized by ATRP in solution. The products were analyzed by GPC, FT-IR spectroscopy, and ^{1}H NMR spectroscopy. Because of the reactive Br groups existing at the ends of template sequence, it was impossible to hinder the intermolecular polymerization of the multivinyl monomer synthesized by the esterification with methacrylic anhydride. When the multivinyl monomer synthesized by the Shotten−Baumann was used, the polymerization was limited in the molecule by ATRP in the dilute solution (0.3 wt % ≥ polymer concentration). In the case of 25 °C, the ATRP of MVM4 proceeded in a living manner with the apparent polymerization rate, 5.0×10^{-5} s^{-1}, which was very close to that of the ATRP in bulk, indicating that the vinyl groups were highly concentrated in MVM4. The resonance of ethyl group detected by ^{1}H NMR spectroscopy drastically decreased by polymerization, the GPC peak shifted to lower molecular weight side, and the dependence of solution viscosity on share rate was increased. T_g of polymerized product of MVM5, PMVM5-1, measured by DCS was observed at 210 °C instead of the T_g of acetylated PHEMA2, ca. 65 °C. These suggest that the ladderlike molecule was formed by the intramolecular polymerization.

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