Synthesis of Polymers by Template Polymerization. 2. Effects of Solvent and Polymerization Temperature

Reiko Saito* and Hiroaki Kobayashi

Department of Organic and Polymeric Materials, Tokyo Institute of Technology, 2-12 Ookayama, Meguro-ku, Tokyo 152-8552, Japan

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ABSTRACT: Copper-based atom-transfer radical polymerization for a template monomer with 10.9 methacryloyl groups, which was synthesized with β-cyclodextrin by the esterification of secondary hydroxyl groups with methacrylic acid anhydride, was carried out with 1,3-dibromobutane, 1,1,4,7,10,10-hexamethyltriethylenetetramine, and CuBr as an initiator, a ligand, and a catalyst, respectively. The effects of solvent, polymerization temperature, and molar ratio of the initiator to the template monomer on polymerization were investigated. The progress of polymerization was investigated by kinetic analysis of conversion and the molecular weight of methacrylic acid oligomers (PMAA) obtained by hydrolysis of the polymerized products by gel permeation chromatrography and matrix-assisted laser desorption/ionization time-of-flight mass spectrometry. Increasing the polymerization temperature and tetrahydrofuran caused an increase of the polydispersity of PMAA.

Introduction

Strict control of the architecture of a polymer is a very important technique in the development of polymers. By many approaches, it is possible to synthesize polymers with high molecular weight and low polydispersity. Anionic and cationic living polymerization is one of the well-known techniques to control the polymerization.[1] However, anionic living polymerization is technically difficult, and available monomers are limited. In recent years, controlled/living radical polymerization has been investigated from the viewpoints of the high ability of control of the polymerization and the convenience of the polymerization technique.[2−11] Several well-controlled radical polymerization systems have been developed. In such systems, one of the most successful controlled/radical polymerizations is atom-transfer radical polymerization (ATRP).[7,8,10,11] By ATRP, the concentration of the radical can be controlled and irreversible radical−radical termination, which causes an increase of the molecular weight distribution, is prevented. A macrocyclic compound with a rigid ring will be obtained by connection of both ends of the oligomers. The size of the ring is drastically controlled by changing the degree of polymerization of the oligomer. By optimization of the size of the ring of the macrocyclic compound synthesized from the oligomer, inclusion of many types of low molecules in the macrocyclic compounds is expected. However, it is still difficult to synthesize oligomers with low polydispersity.

Template polymerization is another approach to control the polymerization.[12−18] However, even if a linear polymer with a narrow molecular weight distribution is used as a template polymer, strict control of the free radical polymerization has not been successful. This was due to the facts that the free radical polymerization was initiated at random in the template and that the arrangement of the vinyl groups in the template was insufficient.

* To whom correspondence should be addressed. Phone: +81-3-5734-2937. Fax: +81-3-5734-2937. E-mail: rsaito@polymer.titech.ac.jp.

If the vinyl group is completely arranged in the template, the template polymerization will be improved. β-Cyclodextrin is a macrocyclic compound with 7 primary hydroxyl groups and 14 secondary hydroxyl groups on both sides of a ring. If 14 vinyl groups are introduced to 14 secondary hydroxyl groups of β-cyclodextrin, the vinyl groups will exist along one side of the ring of β-cyclodextrin. The arrangement of vinyl groups in the template monomer of β-cyclodextrin is stricter than that in a template synthesized with a linear polymer. Thus, stricter control of polymerization was expected for the template polymerization with the template monomer of β-cyclodextrin. Since the maximum number of vinyl groups in the template monomer of β-cyclodextrin is 14, this template monomer of β-cyclodextrin will be suitable for the synthesis of origomers. This concept of the template polymerization is shown in Scheme 1.

On the basis of this concept, we synthesized a novel template monomer with multiple methacryloyl groups with β-cyclodextrin by the acetylation of primary hydroxyl groups and the esterification of secondary hydroxyl groups with methacrylic acid anhydride.[19] When the monomer concentration was lower than 4.12×10^{-3} M, radical polymerization was limited in the molecule of the template monomer with any initiator. As well as radical polymerization of a linear polymer, for the template polymerization, controlled/living radical polymerization was expected to be preferable. Since the local concentration of vinyl groups in the template monomer is as high as that of the bulk polymerization, control of the radical concentration in the system and prevention of irreversible radical−radical termination are required. In fact, when α,α′-azodiisobutyronitrile (AIBN), which is one of the common free radical initiators, was used, the degree of polymerization (DP) of the methacryloyl group in the template monomer was polydispersed. When *p*-xylyl *N*,*N*-dimethyldithiocarbamate (XDC) or α-bromo-*p*-xylyl *N*,*N*-dimethyldithiocarbamate (BXDC), which are controlled/living radical initiators, were used at 25 °C, the values of DP of the methacryloyl group were 13 and 14, despite the fact that

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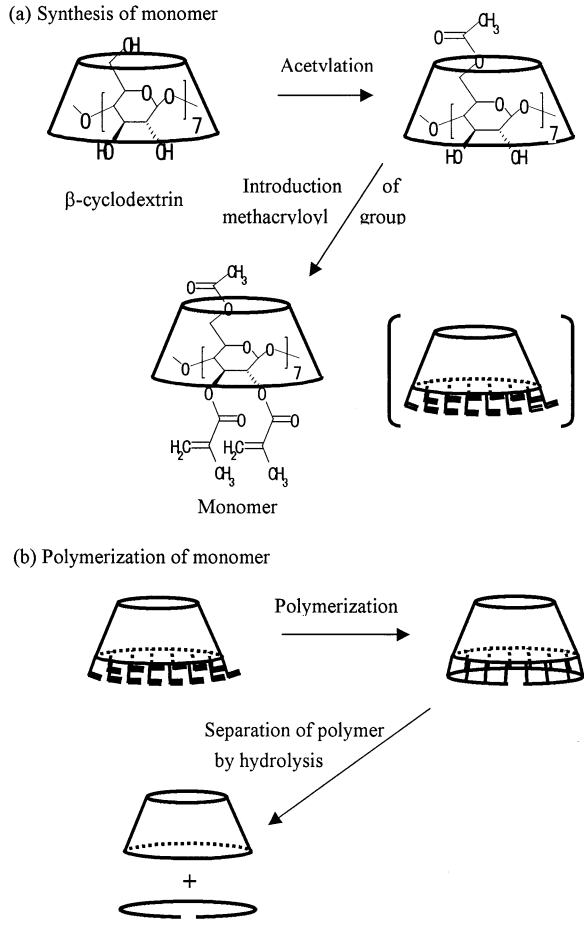
Scheme 1. Schematic Concept of Copper-Based Atom-Transfer Radical Polymerization of the *β*-Cyclodextrin Template Monomer



the average number of methacryloyl groups in the template monomer was 10.9.[19] However, XDC and BXDC are improper for the template monomer of *β*-cyclodextrin. Aromatic compounds tend to be included in *β*-cyclodextrin. XDC and BXDC are aromatic compounds. XDC and BXDC would be included in the template monomer. Thus, it was unclear whether the controlled/living radical polymerization is effective for the template polymerization. Additionally, it is impossible for XDC and BXDC to change polymerization temperature and solvent. They do not dissolve in methanol, and are not controlled/living radical initiators but traditional radical initiators at high temperature.[2,3] On the other hand, in the case of the 1,3-dibromobutane/1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTEMA)/CuBr system, which is an initiator system of ATRP of methacrylate, the polymerization temperature and solvent can be widely changed.[20]

The main purpose of this study is to investigate the effects of the solvent and polymerization temperature with the 1,3-dibromobutane/HMTEMA/CuBr ATRP initiator system on the template monomer. Methanol and tetrahydrofuran (THF) were used as the solvents. The polymerization temperature was changed in a range from 35 to 65 °C. The changes in the conversion of the methacryloyl group and the DP of methacrylic acid oligomers (PMAA) were investigated by gel permeation chromatography (GPC) and matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry.

Table 1. Conditions and Results of Atom-Transfer Radical Polymerization of the *β*-Cyclodextrin Monomer

sample code[a]	solvent	temp (°C)	[initiator]/[monomer]	yield[b] (wt %)	concn of reacted vinyl groups[b] (mol %)
T-35-1.0	THF	35	1.0	73.2	30.6 (28.7[c])
T-35-2.0	THF	35	2.0		58
T-50-1.0	THF	50	1.0	82.9	56.5
T-50-2.0	THF	50	2.0	67.5	52.7
T-65-1.0	THF	65	1.0	70.4	54.4
M-35-1.0	methanol	35	1.0	55.7	
M-50-1.0	methanol	50	1.0	43.3	

[a] T and M of the sample code indicate THF and methanol, respectively, used as a solvent. The middle and last numbers correspond to the polymerization temperature and molar ratio of the initiator to the template monomer, respectively. [b] Estimated by GPC with double detectors of RI and UV light at 292 nm. [c] Estimated by Volhart's titration.

Experimental Section

Materials. The synthesis of the template monomer of *β*-cyclodextrin was described elsewhere.[19] The template monomer was characterized by ^{1}H NMR. Average numbers of acetyl groups and methacryloyl groups introduced to primary and secondary hydroxyl groups of *β*-cyclodextrin determined were 7.0 and 10.9, respectively.[19]

Number average molecular weight (M_n) calculated from ^{1}H NMR: 2451. ^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) = 4.97 (7H, C(1)H of *β*-CD), 1.81 (21H, CH_3 of acetyl), 5.5 (10.8H, CH_2=C of methacryloyl), 6.1 (11H, CH_2=C of methacryloyl), 1.4 (33H, CH_3 of methacryloyl).

ATRP of the Template Monomer. Methanol (Tokyo Chemical Industry Co., Ltd., 99.8%), THF (Tokyo Chemical Industry Co., Ltd., 99%), *n*-hexane (Tokyo Chemical Industry Co., Ltd., 96%), copper(I) bromide (CuBr; Wako Pure Chemical Industries, Ltd., 99.9%), 1,3-dibromobutane (Tokyo Chemical Industry Co., Ltd., 98%), and HMTETA (Aldrich, 98%) were used without purification.

The products were prepared by ATRP in 43.3−82.9 wt % yields as in the following example. For T-35-1.0, template monomer (0.50 g, 0.204 mmol), THF (50 mL), 1,3-dibromobutane (0.045 mL, 0.204 mmol), HMTETA (0.048 mL, 0.204 mmol), and CuBr (0.030 g, 0.204 mmol) were added to a sealable Pyrex reactor. The solution in the reactor was degassed using three freeze−pump−thaw cycles. The reactor was sealed under vacuum and heated at 35 °C for 3.0 h. To stop the polymerization, the product was precipitated in *n*-hexane (200 mL), collected, and purified by reprecipitation two times from THF (10 mL) into cold (0 °C) *n*-hexane (50 mL). The product was a white powder.

Other detailed conditions are listed in Table 1. When methanol was used as a solvent, the solution was evaporated under vacuum after the polymerization. Then, the product was purified and dried as above. Conversion of the reacted methacryloyl group was determined by ^{1}H NMR and Volhart's titration with aqueous $AgNO_3$.

Yield: 73.2 wt %. ^{1}H NMR (DMSO-d_6): δ (ppm) = 4.97 (7H, C(1)H of *β*-CD), 1.81 (21H, CH_3 of acetyl), 5.5 (7.5H, CH_2=C of methacryloyl), 6.1 (7.6H, CH_2=C of methacryloyl), 0.8−1.4 (33H, CH_3 of methacryloyl), 1.9−2.1 (6.7H, CH_2 of methacryloyl).

Hydrolysis of the Polymerized Products.[19] 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 for 4 h at room temperature. Then, the solution was poured into acetone (20 mL). The product was washed with 0.1 N HNO_3 (20 mL), collected, and dried. The degree of hydrolysis in the product was determined with ^{1}H NMR. Yield: 62 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. The number-average molecular weight (M_n) and distribution of molecular weight (M_w/M_n) of the polymerized products and PMAA were mea-

sured with gel permeation chromatography (Tosoh, GPC-2010) double detected with the refractive index (RI) and ultraviolet light at 292 nm. The column was TSK-α-3000 (the range of M_w 400 to 9×10^4). The eluent, flow rate, and temperature were THF, 0.8 mL min^{-1}, and 35 °C for polymerized products and methanol, 0.8 mL min^{-1}, and 30 °C for PMAA, respectively. Measurement of the molecular weight of PMAA was also carried out with MALDI-TOF mass spectrometry (Shimazu, Kraros Kompact MALDI 2) incorporating a 337 nm nitrogen laser with a 5 ns pulse duration (30 μm spot size). The instrument was operated at positive state in a linear mode with an accelerating potential of 20 kV. The accumulation number of the laser shot was 30. The sample of analysis was prepared by mixing PMAA (1 mL/mL) and dihydroxybenzoic acid (10 mg/mL) in methanol. Then, the solution was loaded onto a stainless steel sample plate (about 100 μm spot size of the sample), and methanol was evaporated. Since the PMAA obtained by hydrolysis contained a small amount of $NaNO_3$ as an impurity, no extra salt was added.

^{1}H NMR Measurement. ^{1}H NMR measurement was carried out with a ^{1}H NMR spectrometer (JEOL, GSX-500 Hz) with deuterized dimethyl sulfoxide (DMSO-d_6) as solvent at room temperature using the signal of the deuterated solvent as lock and the internal standard for chemical shift data on the δ-scale relative to TMS.

Results and Discussion

The conditions and results of ATRP of the template monomer are listed in Table 1. In the sample code, the first character and middle and final numbers indicate the solvent (T = THF and M = methanol), reaction temperature, and molar ratio of the initiator to the template monomer, respectively. 1,3-Dibromobutane containing primary and secondary bromine groups is a monofunctional initiator of copper-mediated ATRP. Not the primary but the secondary bromide group of 1,3-dibromobutane is an initiation site of the ATRP in this system.

According to the previous investigation,[19] a template monomer concentration higher than 4.12×10^{-3} M caused the macrogelation of the system with any initiators. Thus, ATRP was carried out at a 4.12×10^{-3} M concentration of the template monomer. As in previous work, the gelation was macroscopically not observed for all cases.

The polymerization between the template monomer was investigated by GPC. Figure 1 shows GPC profiles of the template monomer and polymerized products. The shape and position of the peaks of the polymerized products agreed well with those of the template monomer. It was found that the polymerization between the template monomers was prohibited at 4.12×10^{-3} M in both THF and methanol.

Then, the time dependence of the conversion of the methacryloyl group was measured by GPC double detected by the RI and UV light at 292 nm. Figure 2 shows time conversion curves of the methacryloyl group of T-35-1.0 and T-50-1.0. It was found that the conversions of the methacryloyl group were drastically increased in the early stage, and saturated at 30.6 and 56.6 mol % at 3.0 h for T-35-1.0 and at 0.5 h for T-50-1.0, respectively. For ATRP, the conversion of ATRP is not saturated at such a low conversion, because ATRP shows a living manner. The low efficiency of the initiation was considered as a reason. The macroscopic concentration of vinyl groups in the solution in this work, 4.49×10^{-2} M (= the concentration of the template monomer times the average number of methacryloyl groups in the template monomer = 4.12×10^{-3} M × 10.9), was lower than the vinyl concentration of general ATRP (>4.0 M).

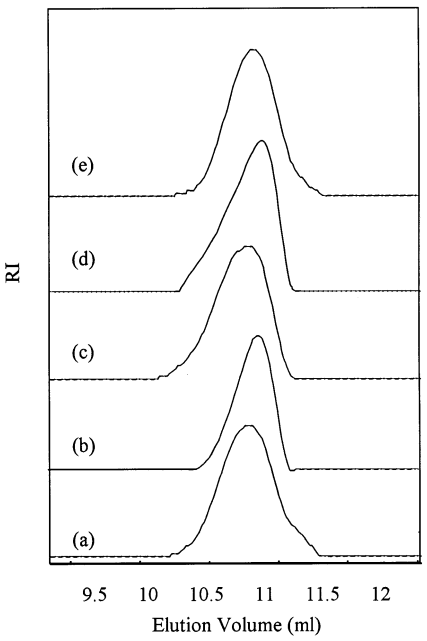


Figure 1. GPC profiles of the template monomer and polymerized products: a, monomer; b, M-50-1.0; c, T-35-1.0; d, T-50-1.0; e, T-65-1.0.

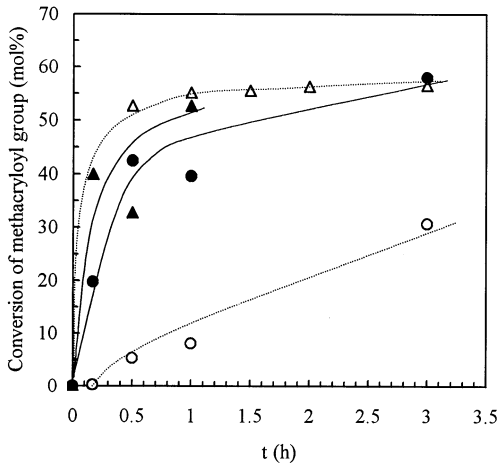


Figure 2. Time conversion curved for ATRP of the template monomer: open circles, T-35-1.0; closed circles, T-35-2.0; open triangles, T-50-1.0; closed triangles, T-50-2.0.

To increase the conversion, the molar ratio of the initiator to the monomer was increased from 1.0 to 2.0. For both T-35-2.0 and T-50-2.0, the rate of polymerization was increased with increasing molar ratio of the initiator to the monomer. However, the saturated conversions were not increased. From these results, it was concluded that the ATRP of the template monomer was completed within 3.0 h. Kinetic details are discussed in a later section.

Next, to investigate the DP of methacryloyl groups in the template monomer, the products were hydrolyzed after ATRP, and the DP of PMAA obtained by hydrolysis was measured by GPC. Figure 3 shows GPC profiles of PMAA. Here, it should be noticed that the elution volume of GPC profiles was converted to the molecular weight of PMAA by combining the results of GPC and MALDI-TOF-MS measurements shown in Figures 3 and 4, respectively. The results of MALDI-TOF-MS measurements of T-50-1.0 are also listed in Table 2.

For PMAA of T-35-1.0 and M-35-1.0, one clear peak was observed, indicating that monodispersed PMAA was

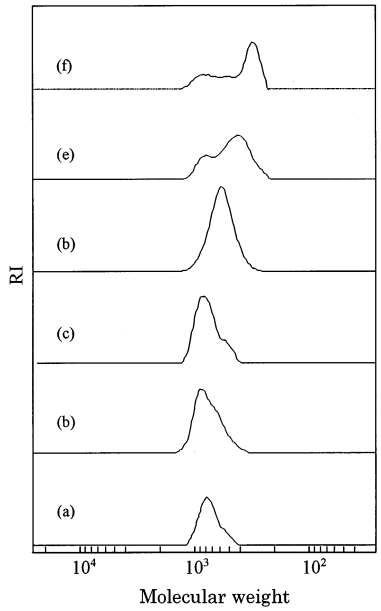


Figure 3. GPC profiles of hydrolyzed products polymerized at 180 min: a, M-35-1.0; b, M-50-1.0; c, T-35-1.0; d, T-35-2.0; e, T-50-1.0; f, T-65-1.0.

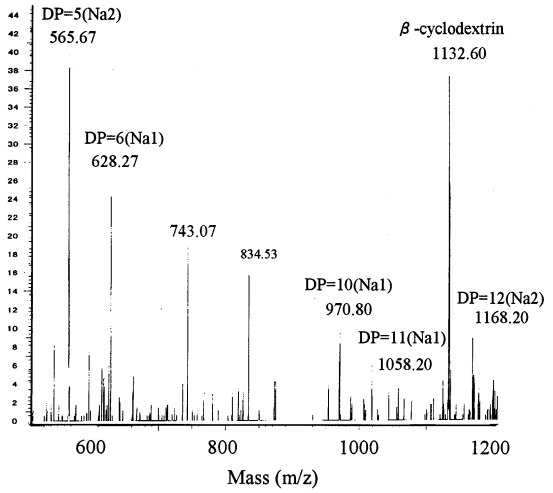


Figure 4. MALDI-TOF-MS spectra of the hydrolyzed product of T-50-1.0.

Table 2. Molecular Weight of PMAA[a]

m/z	DP of MAA	no. of sodium salts	*m/z*	DP of MAA	no. of sodium salts
565.67	5	2	1058.2	11	1
628.27	6	1	1168.2	12	2
970.8	10	1			

[a] Molecular weight = m/z + 1 = 90.12 + (86.09(DP of PMAA)) + (23(no. of sodium salts)).

synthesized. A DP of 10.9 for T-35-1.0 and M-35-1.0 calculated from the number average molecular weights, 832, of T-35-1.0 and M-35-1.0 agreed well with the number of methacryloyl groups in the template monomer. Thus, it was found that the template polymerization was controlled in both THF and methanol by the ATRP technique, when the molar ratios of the initiator to the monomer were equal.

The peaks except for those of PMAA of T-35-1.0 and M-35-1.0 were bimodal. Additionally, the peak of T-35-2.0 was drastically broadened. Both in THF and methanol, new peaks appeared at a molecular weight lower than 830 by increasing the temperature from 35 to 65 °C and the molar ratio of the initiator to the template monomer (Figure 3). A higher temperature increased the amount of PMAA with a molecular weight lower than 830 and decreased the molecular weight of PMAA. The temperature effect on the distribution of the molecular weight of PMAA in THF was clearer than that in methanol. The effect of solvent on the polymerization is discussed in a later section.

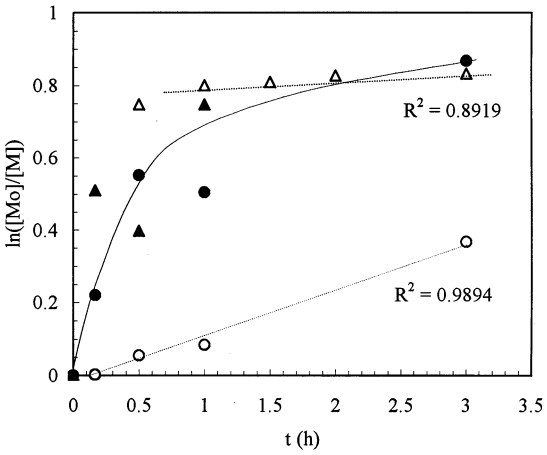


Figure 5. Kinetic plots, $\ln([M]_0/[M])$ vs t, for ATRP of the template monomer: open circles, T-35-1.0; closed circles, T-35-2.0; open triangles, T-50-1.0; closed triangles, T-50-2.0.

First, the architecture of the template monomer was considered. The distribution of the number of methacryloyl groups in the template monomer was not narrow. The lack of a methacryloyl group on the ring of β-cyclodextrin would inhibit the polymerization if the mobility of the methacrylate group were low. As a result, the template polymerization occurred in the template monomer without a lack of methacryloyl groups, in other words, in the template monomer with a DP higher than 10.9. Increasing the temperature would increase the mobility of the methacryloyl group in the template monomer. The methacryloyl groups in the template monomer with a low number of methacryloyl groups would be reacted at high temperature. As a result, PMAA with a lower DP was synthesized. Another possibility is radical hopping in the template monomer. As described above, the mobility of the methacryloyl group increases by increasing the temperature. Thus, radical hopping may occur in the template monomer. This also would lead to the synthesis of PMAA with a lower DP.

To clarify these points, kinetic investigation of the ATRP of the template monomer was carried out. The kinetics of ATRP in the homogeneous system is described by the following equations:

$$\ln\left(\frac{[M]_0}{[M]}\right) = k_p K_{eq}\frac{[RX][Cu^I]}{[Cu^{II}]}t = K_{app}t \qquad (1)^{21}$$

$$\ln\left(\frac{[M]_0}{[M]}\right) = \frac{3}{2}k_p([RX]_0[Cu^I]_0)^{1/3}\left(\frac{K_{eq}}{3k_t}\right)t^{2/3} = K_{Fischer}t^{2/3} \qquad (2)^{22}$$

Here, t, k_p, and K_{app} are the reaction time, rate constant of propagation, and observed rate constant of polymerization. Here, it should be noticed that $[M]_0$ and $[M]$ are molar concentrations of methacryloyl groups at the initial state and at time t, respectively. Figure 5 shows

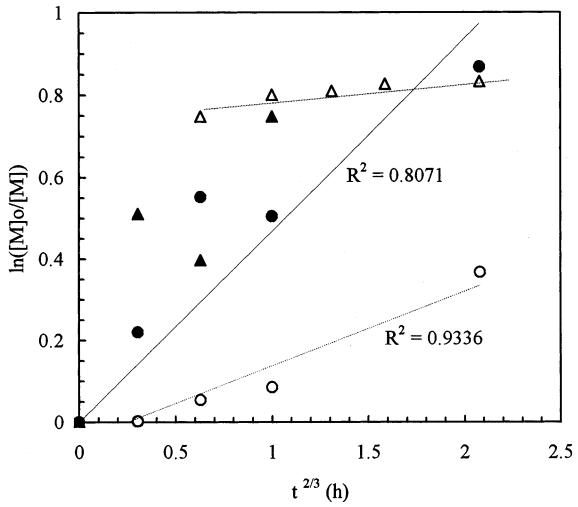


Figure 6. Kinetic plots, $\ln([M]_0/[M])$ vs $t^{2/3}$, for ATRP of the template monomer: open circles, T-35-1.0; closed circles, T-35-2.0; open triangles, T-50-1.0; closed triangles, T-50-2.0.

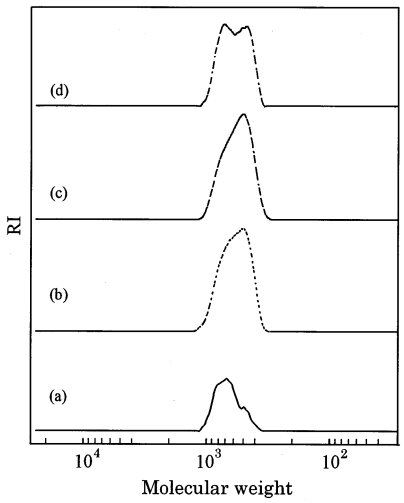


Figure 7. GPC profiles of T-35-2.0 with [initiator]/[template monomer] = 2.0: a, t = 0.168 h; b, t = 0.5 h; c, t = 1.0 h; d, t = 3.0 h.

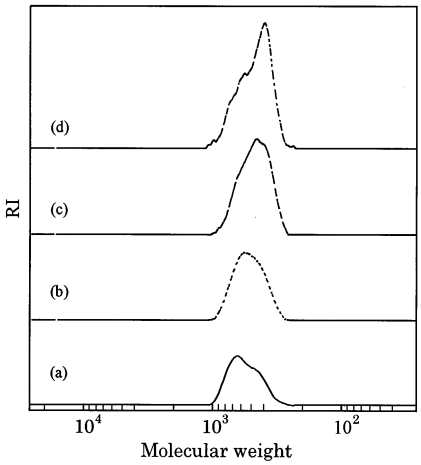


Figure 8. GPC profiles of T-50-1.0 with [initiator]/[template monomer] = 1.0: a, t = 0.168 h; b, t = 0.5 h; c, t = 1.0 h; d, t = 3.0 h.

the kinetic plots for ATRP of the template monomer. The $\ln([M]_0/[M])$ vs t plot of T-35-1.0, in which monodispersed PMAA was synthesized, based on eq 1, was linear, indicating first-order kinetics with respect to the monomer and the constant radical concentrations throughout the polymerization. The plots of $\ln([M]_0/[M])$ vs t, except that for T-35-1.0, were not linear. For T-35-2.0, T-50-1.0, and T-50-2.0, not only PMAA with a DP of 11 but also PMAA with a DP lower than 11 was synthesized. Drastically increasing $\ln([M]/[M])$ in the early stage of T-35-2.0, T-50-1.0, and T-50-2.0 suggested the preferential polymerization of the template monomer with a number of methacrylic groups higher than 10.

Figure 6 shows the kinetic plot of $\ln([M]_0/[M])$ vs $t^{2/3}$ for ATRP of the template monomer based on Fishers's eq 2. Similarly to the $\ln([M]_0/[M])$ vs t plot, the kinetic plots of Fischers's equation of T-35-2.0, T-50-1.0, and T-50-2.0 were not linear in the early stage. It should be noticed that the T-35-1.0, which showed linearity in the $\ln([M]_0/[M])$ vs t plot, was not linear. Linearity regression coefficients (R^2) were smaller than 0.94, suggesting that these systems cannot be filled by eq 2. It was found that the kinetics of ATRP of the template monomer was described with eq 1.

From the kinetic plots, $\ln([M]_0/[M])$ vs t (Figure 5), it was suggested that the polymerization of the template monomer with a number of methacrylic groups higher than 10 was preferable than that of the template monomer with a number of methacrylic groups lower than 10. The rate of polymerization was described as follows:

$$R_p = k_p K_{eq}[\text{initiator}]\frac{[Cu^I]}{[Cu^{II}X]}[M] \qquad (3)^{23}$$

The linear relationship of $\ln([M]_0/[M])$ vs t in each region suggests that polymerization was first order with respect to monomer concentration and that the concentration of the radical during the polymerization was constant in each region. Since the polymerization conditions in each system were constant, the values in eq 3, except for [M], were constant. Thus, the existence of two slopes in each plot suggests the existence of two concentrations of methacryloyl groups. Here, it should be noticed that [M] of the $\ln([M]_0/[M])$ vs t plots was the overall concentration of methacryloyl groups in the system. In this work, the overall concentration and the local concentration of methacryloyl groups did not agree. Strictly, [M] and $[M]_0$ should be the local concentrations of methacryloyl groups in the template around the activated radical. The local concentration of methacryloyl groups in the template was dependent on the number of methacryloyl groups introduced into the template monomer. Thus, the changing of the slope suggests the difference in the number of methacryloyl groups in the template monomer. Thus, it is expected that PMAA with a high molecular weight was polymerized in the early stage, and then PMAA with a low molecular weight was continuously synthesized.

To confirm this consideration, the time dependence of the DP of PMAA was investigated. Figures 7−9 show the GPC profiles of PMAA of T-35-2.0, T-50-1.0, and T-50-2.0, respectively. It was found that PMAA with a DP = 11 was synthesized in the early stage. Then, PMAA with a low DP was continuously synthesized. Consequently, it was concluded that the formation of bimodal products of PMAA was due to the inhomogeneity of the number of methacryloyl groups in the template monomer.

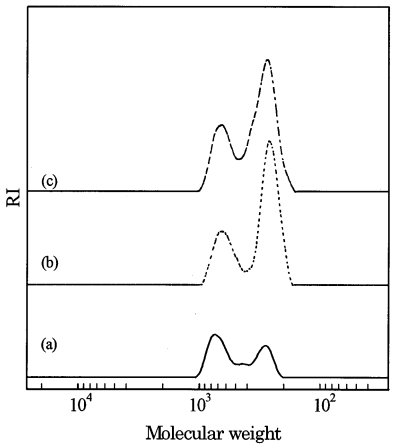


Figure 9. GPC profiles of T-50-2.0 with [initiator]/[template monomer] = 2.0: a, t = 0.168 h; b, t = 0.5 h; c, t = 1.0 h.

The molecular weight distribution of PMAA was decreased by decreasing the temperature. This was due to the increase in the difference in polymerization rate between the template monomers with high and low numbers of methacryloyl groups, because the value of k_pK_{eq} at 35 °C is expected to be lower than that at 50 °C.

Here, it should be noticed that the molecular weight of PMAA of T-35-2.0 was polydispersed (Figure 3). The rate of polymerization of T-35-2.0 was larger than that of T-35-1.0. Thus, the polymerization of methacryloyl groups in the template monomer with a low number of methacryloyl groups was accelerated. It was concluded that the increasing deference of the rate of polymerization between the template monomers is one of the important factors for the ATRP of the template polymerization. However, all PMAA with a DP lower than 5 was not experimentally recovered in this work. Therefore, here, the kinetic analysis for the template monomer with each DP is not discussed.

Next, the effect of solvent is discussed. In contrast to THF, the molecular weight distribution of PMAA synthesized in methanol was not increased with increasing temperature. A hydroxyl group drastically increases the polymerization rate of methyl methacrylate.[24,25] The polymerization rate in methanol is larger than that in THF. K_{app} is generally increased with increasing temperature in any solvent. Thus, the molecular weight distribution of PMAA of M-50-1.0 should be larger than that of T-50-1.0. In contrast to this consideration, the molecular weight distribution of PMAA of M-50-1.0 was narrower than that of T-50-1.0. This is explained from the viewpoint of the solubility of the methacryloyl group in methanol and THF. The solubility of the methacryloyl group in THF is higher than that in methanol. The mobility of the methacryloyl group increases by increasing the solubility of the methacryloyl groups in the solvent. Thus, the mobility of the methacryloyl group in the template monomer with a DP less than 10 in THF is larger than that in methanol. Collision between the methacryloyl group and radical is increased with increasing mobility of the methacryloyl group. As a result, the molecular weight distribution of PMAA in THF was larger than that in methanol at 50 °C. Consequently, it was found that decreasing the solubility of the methacryloyl group and decreasing the polymerization rate decreased the distribution of the DP of the methacryloyl group in the template.

Conclusions

To strictly control template polymerization, atom-transfer radical polymerization of methacryloyl groups in the template monomer synthesized from β-cyclodextrin was carried out with varying polymerization temperature, solvent, and molar ratio of the initiator to the template monomer. As well as free radical polymerization, when the monomer concentration was lower than 4.12×10^{-3} M, the polymerization between the molecules of the template monomer was completely hindered at any conditions. PMAA a DP within a range of 5−12 of were obtained by hydrolysis of polymerized products. Monodispersed PMAA with a DP = 11 was obtained by polymerization at 35 °C in both THF and methanol. By analysis of PMAA, it was found that the polymerization of methacryloyl groups in the template monomer with a high number of methacryloyl groups in a template monomer, 11, preferentially occurred over that in a template monomer with a low number of methacryloyl groups. Increasing the reaction temperature and the molar ratio of the initiator to the template monomer increased the dispersity of the DP of PMAA. Even though the polymerization rate in methanol should be higher than that in THF, the amount of PMAA with a low DP synthesized in methanol was less than that synthesized in THF. Therefore, it was found that the increasing polydispersity of PMAA by increasing the reaction temperature and the molar ratio of initiator to the template monomer was due to not only an increase of the polymerization rate but also an increase of the mobility of the methacryloyl group in the template monomer.

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References and Notes

(1) Swarc, M. *Carbanions, Living Polymers and Electron-Transfer Processes*; Interscience Publishers: New York, 1968.
(2) Otsu, T.; Yoshida, M. *Makromol. Chem. Rapid Commun.* **1982**, *3*, 127−132.
(3) Otsu, T.; Kuriyama, A. *Polym. Bull.* **1984,** *11*, 135−142.
(4) Golubev, V. B.; Zaremski, M. Yu.; Mel'nikov, S. M.; Olenin, A. V.; Kabanov, V. A. *Vysokmol. Soedin., Ser. A* **1994**, *36*, 320−326.
(5) Kannurpatti, A. R.; Lu, S.; Bunker, G. M.; Bowman, C. N. *Macromolecules* **1996**, *29*, 7310−7315.
(6) Otsu, T. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 2121−2136.
(7) Percec, V.; Barboiu, B.; Bera, T. K.; van der Sluis, M.; Grubbs, R. B.; Fréchet, J. M. J. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 4776−4791.
(8) Tokuchi, K.; Ando, T.; Kamigaito, M.; Sawamoto, M. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 4735−4748.
(9) Boutevin, B. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 3235−3243.
(10) Rodlert, M.; Harth, E.; Rees, I.; Hawker, C. J. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 4749−4763.
(11) Davis, K. A.; Charleux, B.; Matyjaszewski, K. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 2274−2283.
(12) Jantas, R. *J. Polym. Sci., Part A: Polym. Chem.* **1990**, *28*, 1973−1982.
(13) Frisch, H. L.; Xu, Q. *Macromolecules* **1992**, *25*, 5145−5149.
(14) Baranovsky, V. Yu.; Kotlyarsky, I. V.; Etlis, V. S.; Kabanov, V. A. *Eur. Polym. J.* **1992**, *28*, 1427−1432.
(15) Jantas, R. *Polym. Int.* **1993**, *32*, 357−360.
(16) Jantas, R.; Szumilewicz, J.; Strobin, G.; Polowinski, S. *J. Polym. Sci., Part A: Polym. Chem.* **1994**, *32*, 295−300.

(17) Tanjima, K.; Ogawa, G.; Aida, T. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 4821−4825.
(18) Yoshida, M.; Hatate, Y.; Uezu, K.; Goto, M.; Furuwaki, S. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 689−696.
(19) Saito, R.; Okuno, Y.; Kobayashi, H. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 3539−3576.
(20) Zhang, X.; Xia, J.; Matyjaszewski, K. *Macromolecules* **1998**, *31*, 5167−5169.
(21) Matyjasewski, K.; Pattern, T. E.; Xia, J. *J. Am. Chem. Soc.* **1997**, *119*, 674.
(22) Fischer, H. *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 1885−1901.
(23) Matyjaszewski, K.; Wang, J. L.; Grimaud, T.; Shipp, D. A. *Macromolecules* **1988**, *31*, 1527−1534.
(24) Haddleton, D. M.; Shooter, A. J.; Heming, A. M.; Crossman, M. C.; Duncalf, D. J.; Morsley, S. R. In *Controlled Radical Polymerization*; Matyjaszewski, K., Ed.; ACS Symposium Series No. 685; American Chemical Society: Washington, DC, 1997; p 284.
(25) Chambard, G.; De Man, P. A. P.; Klumperman, B. *Macromol. Symp.* **2000**, *150*, 45−51.

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