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Combination of template polymerization and atom transfer radical polymerization: Strategy for synthesis of specifically structural polymers

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ABSTRACT

Design and control of architecture of polymer are important keys to develop novel polymers. Combination of classic template polymerization and recent controlled/living radical polymerization has enabled the simple and convenient synthesis of well-defined methacrylate type ladder-like polymer and cyclic electrolytic oligomer. In this manuscript, the basic concept and specific features of template polymerization with atom transfer radical polymerization are described from the viewpoint of synthesis of ladder-like polymer and oligomer.

1. Introduction

Template polymerization of vinyl monomer is known as a classic approach to control molecular weight and molecular weight distribution. Its concept was firstly introduced by Szwarc with the term of "replica polymerization" [1]. By this method, the product is expected to be "a replica" of the template molecule. In other words, shape, molecular weight and molecular weight distribution of the product should be similar to those of the template molecule. Actually, in Mother Nature, many organic compounds, such as DNA, RNA, etc., are finely synthesized by template methods.

Radical polymerization is one of the major methods to synthesize vinyl polymers. The advantage of radical polymerization is its convenience. The disadvantage is bad control of the molecular weight and molecular weight distribution. The combination of the concepts of template polymerization and radical polymerization was expected for easy and fine control of polymer architecture. Based on this concept, vinyl monomers were polymerized with many templates by radical polymerization [2–11]. Generally, template polymerization of vinyl group is classified into two mechanisms, pick-up mechanism and zip mechanism [2]. In the case of "pick-up mechanism", monomer freely exists in whole system before polymerization. Polymerization starts with free monomer in solution. When oligomer is formed in solution, it is strongly connected to the template, then polymerization proceeds on the template. Not only organic polymer, but also inorganic and metallic nanoparticles and nanowires can be used as the templates. Polymer

capsules [12] and polymer nanotubes [13] were finely synthesized by pick-up mechanism with gold nanoparticles and silicon/silica core/shell nanowires, respectively, as the templates. In the case of "zip mechanism", monomer is connected to the template in advance of polymerization by strong bonds such as covalent bond, ionic bond, hydrogen bond, etc. The template molecule, in which many vinyl units are connected, is called "multivinyl monomer (MVM)". Fig. 1 shows the synthetic concept of template polymerization of vinyl polymer with zip mechanism. The connected vinyl groups are polymerized on template. When linear polymer is used as the template, the product will be a ladder-like polymer.

Kammerer and Jung polymerized the MVM, in which acrylic groups were attached to p-cresol oligomer, with azobisisobutylonitrile (AIBN), and obtained ladder-like oligomer. Interestingly, the degree of polymerization of a daughter sequence (an acrylate sequence) completely agreed to that of a parent sequence (a template sequence) [8]. Jantas et al. have successfully polymerized acrylic type and methacrylic type MVMs with poly(vinyl alcohol) (PVA) and poly(2-hydroxyethyl methacrylate) (PHEMA) as the templates, and found that the dilution of concentration of MVM reduced the possibility of intermolecular polymerization (crosslinking) [9–11]. They also observed high glass transition temperature (T_g), which was a clear evidence of ladder-like structure, for polymerized MVM [14]. However, the bad control of radical concentration and random initiation in the MVM owing to the radical polymerization hindered the formation of a very regular ladder-like polymer. In other words, the product is a mixture of ladder-like polymer and its precursor MVM. Since the molecular weight of ladder-like polymer and its precursor MVM was very similar, it is difficult to purify the product. Additionally, gelation during polymerization was hardly hindered.

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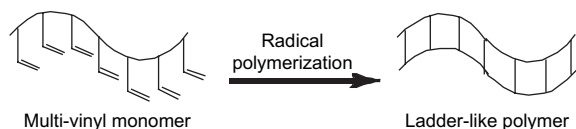 E-mail address: rsaito@polymer.titech.ac.jp

Fig. 1. Concept of template polymerization of multivinyl monomer with linear polymer as a template.

Recently, progress in control/living radical polymerization enabled easy control of architecture, molecular weight and molecular weight distribution of polymer [15–33]. The most important features of controlled/radical polymerization are livingness of radical and the strict control of radical concentration during polymerization. Again, bad control of radical concentration on template polymerization was a major problem of template polymerization. In the case of pick-up mechanism for polymer capsules and polymer nanowires, the thicknesses of polymer layer were finely controlled by atom transfer radical polymerization (ATRP) [12,13]. An introduction of controlled/living radical polymerization technique to template polymerization of MVM improved the template polymerization. Additionally, homogeneous propagation of polymerization simplifies the purification of product.

Taking account of the concept of template polymerization, low molecular weight molecules can be used as the templates. Novel product having unique architecture will be finely synthesized by template polymerization with low molecular weight molecules. For example, cyclodextrins [CDs] are cyclic compounds having many hydroxyl groups. It is easy to obtain MVM from CD. The number of hydroxyl group of α- and β-CD is 18 and 24, the products should be oligomers. Fig. 2 shows the concept of oligomer synthesis by template polymerization with CD. Template polymerization will be a fine approach to synthesize oligomers. In this manuscript, the template polymerization of two types of template, PHEMA and CD, by copper-mediated ATRP, which is a type of controlled/living radical polymerization, is described.

2. Template polymerization with linear polymer as a template and its product, ladder-like polymer

As described above, the template polymerization of MVM with long linear polymer as the template provides ladder-like polymer (Fig. 1). In this section, the general strategy of template polymerization on ATRP, kinetics of polymerization and thermal properties of polymerized products are described.
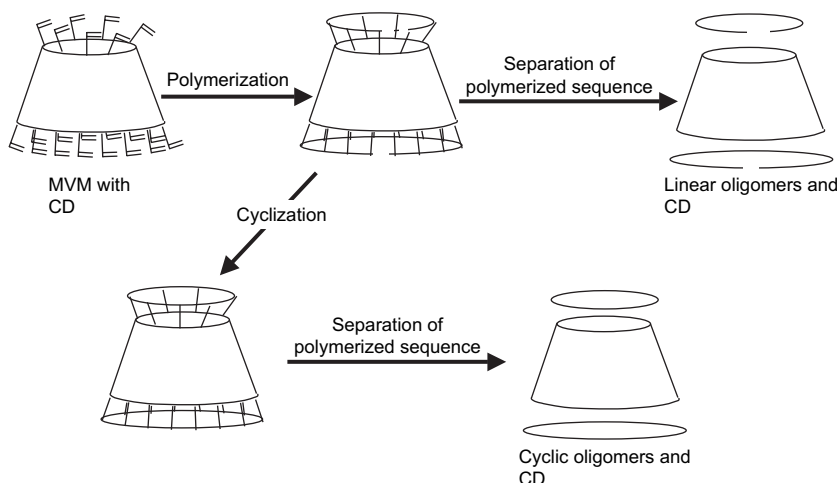
2.1. Template polymerization and kinetics

There are three categories for controlled/living radical polymerization, which are ATRP [15–22], stable free radical polymerization (SFRP) [23–28] and reversible addition–fragmentation transfer (RAFT) polymerization [29–33]. These three polymerization techniques are theoretically available for template polymerization. The suitable polymerization method depends on the vinyl group of MVM. In the case of methacryloyl type MVM, ATRP is the suitable polymerization method. Fig. 3 shows chemical structures of MVM with PHEMA (poly(2-methacryloyloxyethyl methacrylate)
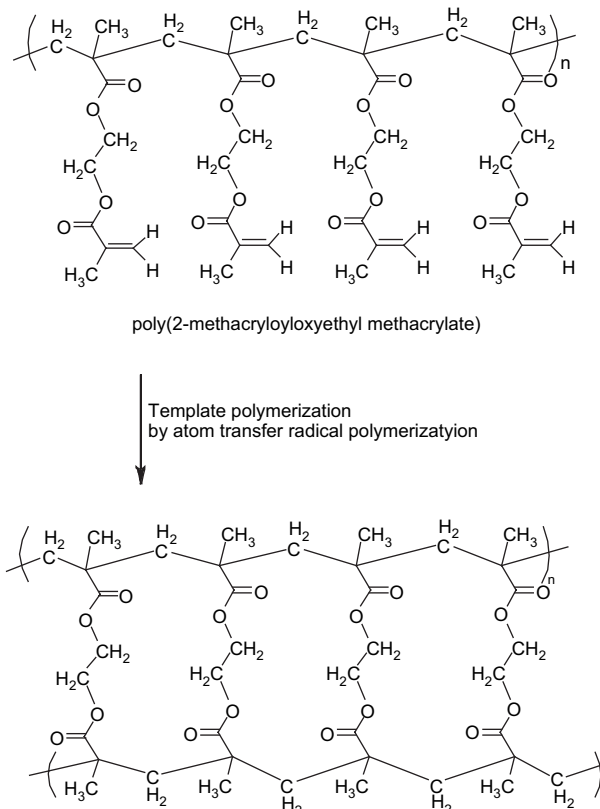

poly(2-methacryloyloxyethyl methacrylate)

Template polymerization
by atom transfer radical polymerizatyion

Fig. 3. Template polymerization of poly(2-methacryloyloxyethyl methacrylate) (MVM$_{PHEMA}$).

Fig. 2. Concept of template polymerization of multivinyl monomer with cyclodextrin as a template.

template, MVM$_{PHEMA}$) and its polymerized product. Methacryloyl type monomers, such as methyl methacrylate, etc., are polymerized by copper-mediated ATRP under mild conditions [23–25]. Elevation of polymerization temperature drastically increases the possibility of gelation because the mobility of vinyl group attached to template is increased. Low polymerization temperature is more preferable for template polymerization.

Again, the most important advantage of controlled/living radical polymerization for template polymerization is the fine control of radical concentration in polymerization system. The vinyl groups in the MVMs should be connected to one sequence by template polymerization. Thus, the theoretical molar ratio of an initiator to MVM is 1:1. The position, where the initiator initially reacts, in the MVM and the polymerization direction cannot be controlled. To neglect the initiating position, a bifunctional initiator is useful. Polymerization proceeds toward both ends of the backbone at the same time from the bifunctional initiator. For example, α,α'-dibromo-p-xylene (DBX) was an available initiator for the template polymerization of MVM$_{PHEMA}$ by copper-mediated ATRP [34].

When the template polymerization successfully proceeds, hydrodynamic diameters of MVM and its products should agree. In other words, GPC profiles of MVM and its products should agree. Fig. 4 shows GPC profiles of MVM$_{PHEMA}$ with $M_n = 2.34 \times 10^4$ and its products polymerized at 0.31 wt% at 30 °C [34]. The shape and the position of these peaks were very similar, indicating that polymerization was completely limited in the molecule of MVM$_{PHEMA}$. The maximum conversion by ATRP, 77.8%, was much larger than that for the product of MVM$_{PHEMA}$ with $M_n = 2.69 \times 10^4$ polymerized with AIBN at 75 °C, 40% [35]. Here, it should be noted that the concentration of MVM for ATRP was 0.31 wt%. The lower the concentration of MVM, the lower the possibility of intermolecular polymerization. Consequently, template polymerization proceeds successfully in dilute solution by ATRP.

The conversion of vinyl group was determined by FT-IR, instead of ^{1}H NMR in solution. The quantitativity of resonance area of ^{1}H NMR spectroscopy was lost after polymerization. When the polymerization proceeds along the backbone, the product will be a ladder-like 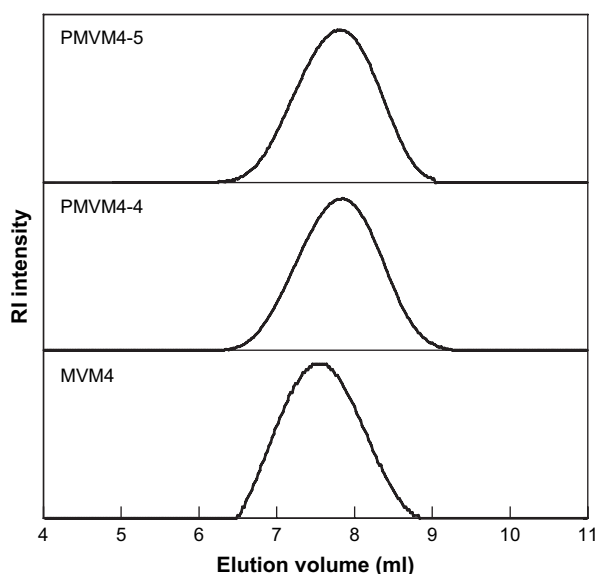polymer. Hydrogen in the crosspiece sequence in the ladder polymer was not quantitatively detected by ^{1}H NMR spectroscopy in solution because of the drastic decrease in the mobility of crosspiece sequence. In fact, after polymerization, the ratio of whole resonance area of vinyl group ($CH_2=$) at 6.08 and 5.56 ppm to that of ethylene ($-CH_2-CH_2-$) at 4.26 and 4.11 ppm in backbone of template increased from 0.42 to 1.44, indicating that the ^{1}H NMR spectra of the polymerized products were not quantitative [34]. Therefore, FT-IR measurement was an important method to determine the conversion of vinyl group.

2.2. Propagation of polymerization in molecule and kinetics of template polymerization

In the case of template polymerization, vinyl groups heterogeneously exist in whole system. In other words, vinyl groups are highly concentrated around the template molecule. The heterogeneity of vinyl group does not disturb the livingness of ATRP but enhanced the polymerization rate. Fig. 5 shows the first order kinetic plot of polymerization of MVM$_{PHEMA}$ with 0.31 wt% of polymer concentration at 25 °C in the 1,4-dioxane/water mixture [34,36]. The induction time of 0.25 h was observed before the proceeding of polymerization. In a range from 0.25 to 1.5 h, the plots showed good linearity, indicating that the livingness of ATRP was kept. Over 1.5 h, the conversion was saturated, and the polymerization was completed. An apparent polymerization rate constant, k_{app} ($= k[M] = 5.0 \times 10^{-5}$ s^{-1}), obtained from the slope from 0.25 to 1.5 h, was very close to those of methyl methacrylate on copper-mediated ATRP with Br groups (3.52×10^{-5} and 3.78×10^{-5} s^{-1}) in bulk at 80 °C [37] and in ethylene carbonate with 50 wt% of MMA at 60 °C [38], respectively. Here k is the polymerization rate constant, and [M] is the concentration of vinyl group around radical. The coincide of k_{app} value of template polymerization and ATRP of MMA indicates that the vinyl groups were highly concentrated in MVM.

There is a big question for template polymerization, which is whether the polymerization proceeds along backbone of template molecule. When the template is a linear polymer chain with soft sequence, the backbone forms globule. It may be possible to propagate polymerization at random in globule. The answer is "polymerization proceeded along the backbone of template". This can be explained from conversion of vinyl group and kinetic analysis. The first order kinetic plots of α,ω-styryl terminated poly(2-methacryloyloxyethyl methacrylate) (St–MVM$_{PHEMA}$–St) is also shown in Fig. 5. Fig. 6 shows the chemical structure of St–MVM$_{PHEMA}$–St.

Fig. 4. The profiles of gel permeation chromatography (GPC) of poly(2-methacryloyloxyethyl methacrylate) (MVM$_{PHEMA}$) with $M_n = 2.34 \times 10^4$ and the polymerized products, PMVM4-4 and PMVM4-5, in a tetrahydrofurane/water mixture (water content, 11 vol%) at 30 °C with [MVM$_{PHEMA}$]:[α,α'-dibromo-p-xylene]:[CuBr]:[tris(2-dimethylaminoethyl)amine] = 1:1.2:2.4:4.8. Reaction time of PMVM4-4 and PMVM4-5 was 2.0 and 16 h, respectively [34].
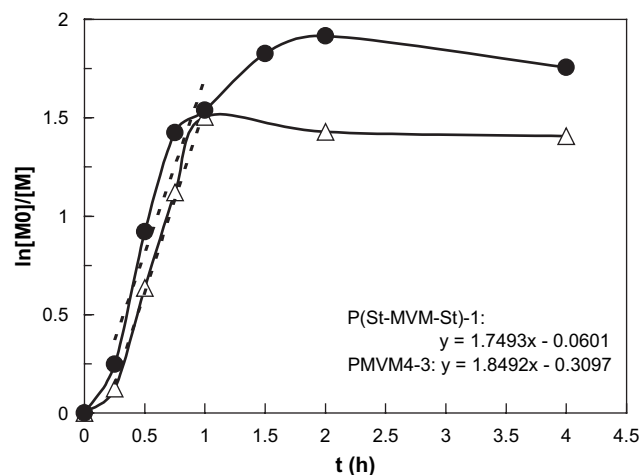

Fig. 5. The first order kinetic plot for copper-mediated atom transfer radical polymerization of poly(2-methacryloyloxyethyl methacrylate) (MVM$_{PHEMA}$ with $M_n = 2.34 \times 10^4$, triangle) and α,ω-styryl terminated poly(2-methacryloyloxyethyl methacrylate) (St–MVM$_{PHEMA}$–St, circle) [36].
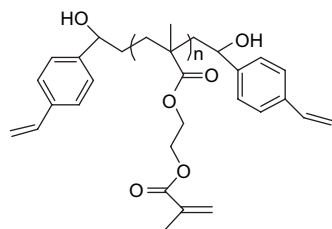
Fig. 6. Chemical structure of α,ω-styryl terminated poly(2-methacryloyloxyethyl methacrylate) (St–MVM$_{PHEMA}$–St).

Since the cleavage temperature of Br–styryl bond, >90 °C, is much higher than that of Br–methacrylate bond by copper-mediated ATRP, polymerization of methacrylate is terminated with styryl group when the polymerization is carried out at lower than 30 °C. If the polymerization proceeds along the backbone, the conversions of vinyl group and kinetic plots of MVM$_{PHEMA}$ and St–MVM$_{PHEMA}$–St containing styryl groups will be similar. If the polymerization proceeds at random in the globule, the polymerization of St–MVM$_{PHEMA}$–St will terminate earlier than that of MVM$_{PHEMA}$. The conversions of vinyl group of MVM$_{PHEMA}$ and St–MVM$_{PHEMA}$–St were 77.8 and 85.3 mol%, the radical in St–MVM$_{PHEMA}$–St did not attack styryl groups until the late stage of polymerization. The slops in a range from 0.25 to 1.0 h, which correspond to apparent polymerization rate constants, were very similar. Both plots were saturated at similar time (from 1.0 to 1.5 h), the polymerization in both MVMs was terminated around 1.0–1.5 h. Polymerization with styryl group did not occur until the late stage of polymerization. In conclusion, the polymerization proceeded along the backbone of template molecule.

2.3. Properties of polymerized product

The unique property of ladder-like polymer is that its T_g is much higher than its linear analogue. Theoretically and experimentally, the dense connection between sequences in the molecule results in high thermal stability [39,40]. When MVM$_{PHEMA}$ was polymerized by free radical polymerization with AIBN, T_g of product was not detected below 270 °C [14]. Fig. 7 shows differential scanning calorimetry profiles of the polymerized product of MVM$_{PHEMA}$ by ATRP. T_g of product polymerized with ATRP reached 210 °C [34]. These values are remarkably higher than other poly(methacrylate)s. In general, the T_g values of poly(methacrylate)s are mostly in a range from ca. 20 to 120 °C; T_g of poly(4-cyanophenyl methacrylate) is 155 °C. MVM$_{PHEMA}$ used for ATRP had lower degree of esterification with methacryloyl group than that used for free radical polymerization. The lower T_g of the product polymerized by ATRP would be due to the lower degree of crosspiece. Therefore, T_g of the product will be controlled by varying the conversion of vinyl group. Since the ladder-like polymers synthesized by template polymerization of MVM$_{PHEMA}$ were soluble in organic solvents, such as toluene, tetrahydrofurane, acetone, chloroform, etc., they will be applied to coating technology, etc.

3. Template polymerization with cyclodextrins

CDs are stereochemically pure macrocyclic compounds. Since they contain many hydroxyl groups, it is easy to introduce methacryloyl groups into CD. In other words, MVMs are easily obtained from CDs. As described above, well-defined methacrylic acid oligomers were finely synthesized by using CDs as templates. In this section, the specific features of template polymerization of MVM with CD templates are described.
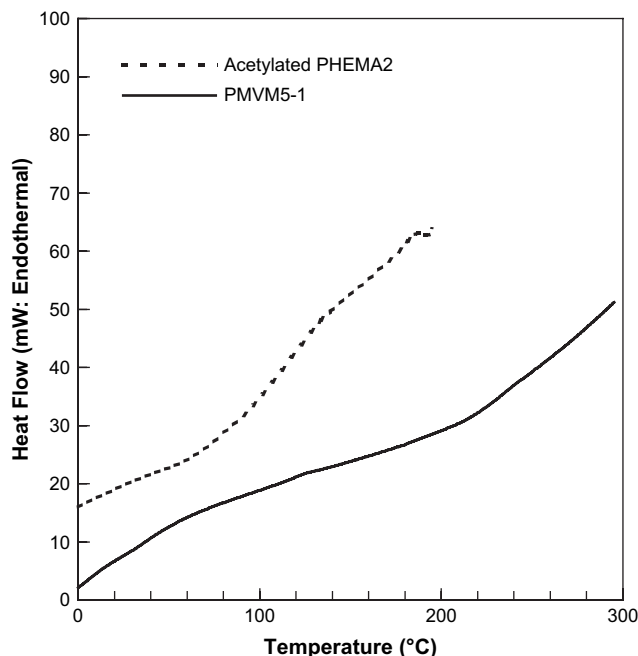

Fig. 7. The profiles of differential scanning calorimetry of acetylated poly(2-hydroxyethyl methacrylate) and the polymerized product of poly(2-methacryloyloxyethyl methacrylate) (MVM$_{PHEMA}$) [34].

3.1. Template polymerization and kinetics

Methacrylate type MVMs with β-CD, β-MVM1 and β-MVM2 (Fig. 8) are easily synthesized by esterification of hydroxyl groups of β-CD with methacrylic anhydride [41,42]. To complete pre-esterification of β-CD, carbonic anhydrides, instead of carbonic chlorides, were generally used [42,43]. Fig. 9 shows the concept of template polymerization of MVM with CD as the template. In β-CD, 7 and 14 hydroxyl groups exist on the primary and secondary hydroxyl group sides, respectively. When the template polymerization is carried out for MVM with β-CD, two types of polymerized sequence with 7 and 14 degrees of polymerization (DP), which correspond to the number of hydroxyl group on the primary and secondary hydroxyl group sides, respectively, are expected. Then, well-defined methacrylic acid (MAA) oligomers with finely controlled DP will be obtained by hydrolysis of polymerized product. Free radical polymerization of β-MVM1 and β-MVM2 with AIBN and a redox initiator caused the gelation of the polymerization solution on late stage of polymerization [44]. The DP of MAA oligomer detached from the product was larger than the number of vinyl group on the secondary hydroxyl group side, and widely dispersed.
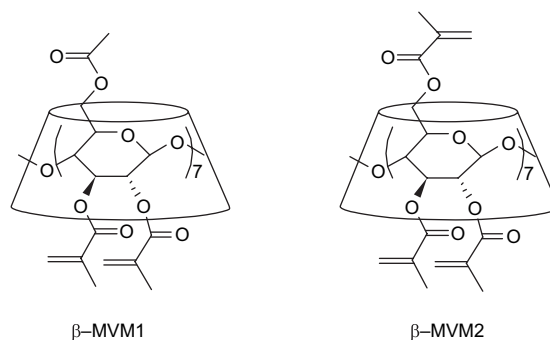

Fig. 8. Chemical structures of methacrylate type multivinyl monomer with β-cyclodextrin, β-MVM1 and β-MVM2.
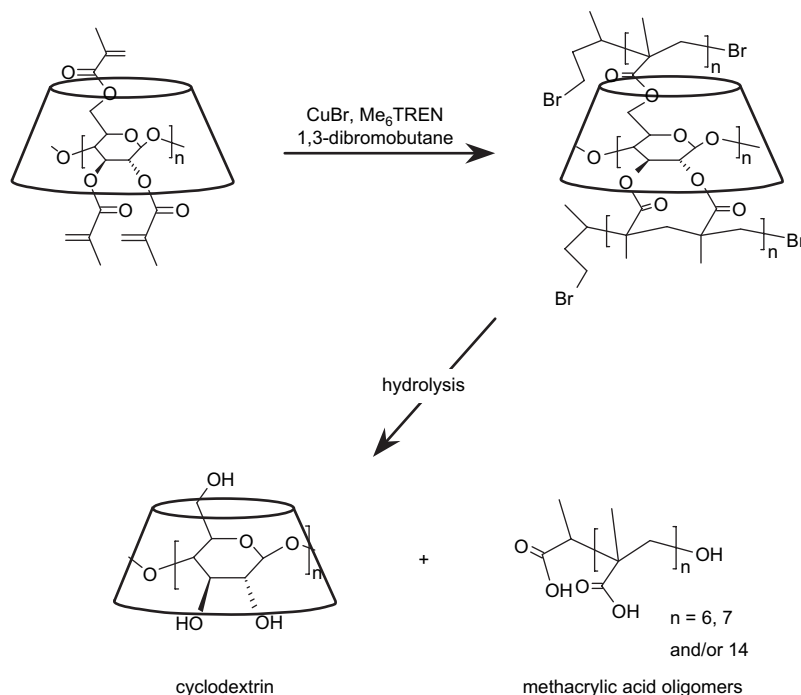
Fig. 9. Atom transfer radical polymerization of β-MVM2 and synthesis of methacrylic acid oligomers.

Consequently, polymerization was not limited in the MVM molecule by free radical polymerization. In contrast, by copper-mediated ATRP of β-MVM1, which contained vinyl groups on only secondary hydroxyl group side, with methyl 2-bromopropionate, which was a single functional initiator, the solution did not gel. By hydrolysis, single MAA oligomer was obtained. The DP of oligomer and the number of vinyl group on the secondary hydroxyl group side agreed well. Template polymerization was well controlled by ATRP in the case of MVMs with β-CD [44].

In β-MVM2, vinyl groups on the primary and secondary hydroxyl group sides are separated by CD scaffold. Thus, two independent reaction fields exist in the same molecule. When the molar ratio of initiator to β-MVM2 was 2:1, template polymerization individually proceeded in two fields in the same molecule. As a result, two types of MAA oligomer with DP = 7 and 14 were obtained from the same molecule [45]. Fig. 10 shows the GPC profile of hydrolyzed product obtained from the polymerized product of β-MVM2 [45]. As can be seen, the GPC profile was bimodal, the peaks corresponded to MAA oligomers with DP = 7 and 14. Therefore, in the case of CD template, it is possible to form the plural template fields in the same molecule.

Copper-mediated ATRP of template polymerization with CD template was living, as well as the polymerization with linear polymer as the template. Fig. 11 shows the first order kinetic plots of template polymerization of β-MVM2 at 25 and 50 °C. At 50 °C, polymerization proceeded in a living manner until 1.0 h, then conversion was saturated, indicating that the polymerization was completed. The slope corresponding k_{app} was very close to those of bulk and the template polymerization with linear polymer. Thus, the livingness of ATRP on the template polymerization was kept even in the small molecule as the template. At 25 °C, the slope of kinetic plot was changed at 1.0 h. The change at 1.0 h indicated the completion of polymerization on the primary hydroxyl group side and the propagation of polymerization on the secondary hydroxyl group side. The polymerization at 50 °C was too fast to detect the change of slope. In conclusion, the template polymerization proceeded in each template field, even when the plural template fields existed in the same molecule.

Since the shape of template field is cyclic, the radical proceeded along the cyclic CD rim and came back to the initiated position. When the initiator had the functional group, which may react with activated radical or deactivated state, it is possible to form cyclic the polymerized sequence by connection of initiated and initiating groups [46,47]. Radical transfer by using 1,3-dibromobutane as the initiator was investigated. ^{1}H NMR and MALDI-TOF mass spectrometric analysis indicated that the closing ring reaction
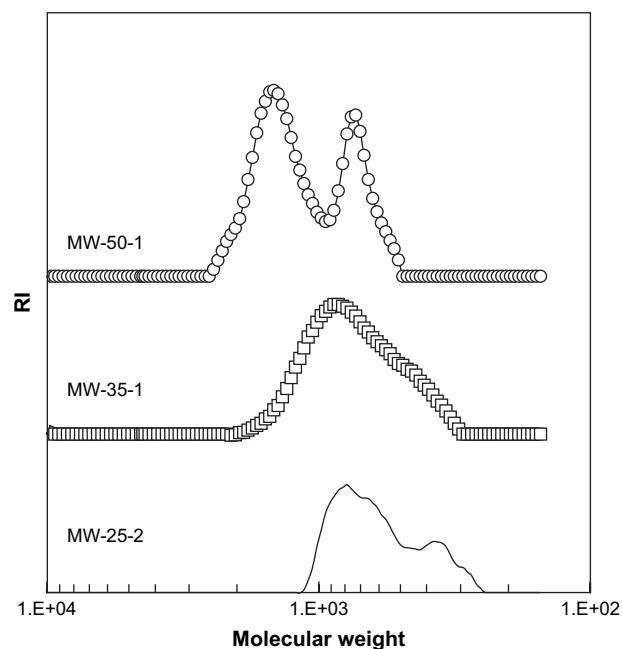

Fig. 10. The profiles of gel permeation chromatography of methacrylic acid oligomers obtained by hydrolysis of products polymerized in a methanol/water mixture (water content, 10 vol%) for 4 h with [β-MVM2] = 3.96 mM, [Initiator] = [CuBr] = 7.92 mM, [bipyridyl] = [toluene] = 19.81 mM. MW-25-2: 25 °C; MW-35-1: 35 °C; MW-50-1: 50 °C [45].
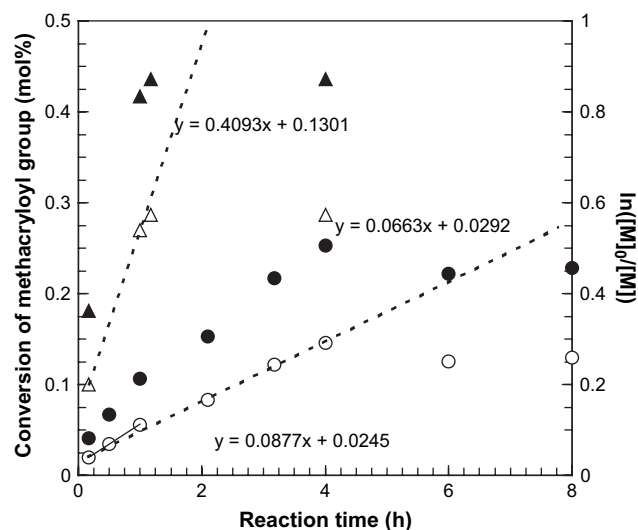
Fig. 11. First order kinetic plots for the copper-mediate atom transfer radical polymerization of methacryloyl group in a methanol/water mixture (water content, 10 vol%). [β-MVM2] = 3.96 mM; [Initiator] = [CuBr] = 7.92 mM; [bipyridyl] = [toluene] = 19.81 mM. Closed circle: conversion at 25 °C; open circle: −ln[M]$_0$/[M] at 25 °C; closed triangle: conversion at 50 °C; open triangle: −ln[M]$_0$/[M] at 50 °C [45].

preferentially occurred on the secondary hydroxyl group side than on the primary hydroxyl group side [47]. Though the reaction mechanism is unclear, the major advantage of using radical transfer is no reagent was required for the closing ring. Further investigation on mechanism of radical transfer is required. Cyclic MAA oligomer with DP = 14 showed an inclusion ability of methylene blue in methanol [48] as well as CDs. Cyclic MAA oligomer was a polyelectrolyte, therefore it will be a novel pH sensitive host compound.

3.2. Effect of guest on template polymerization

The most important factor of template polymerization is the arrangement of vinyl group in the template molecule. In the case of template polymerization with CD, guest molecule to CD strongly influences the arrangement of vinyl group. In other words, DP of MAA oligomer is controlled by guest [49]. Fig. 12 shows the MM2 images of primary and secondary hydroxyl group sides of β-MVM2 with and without guests. When no guest was added, the arrangement of vinyl group was disordered. Lack of guest resulted in the inclusion of methacryloyl groups into hydrophobic CD cavity. Fig. 13 shows GPC profiles of MMA oligomers obtained from the product of β-MVM2 polymerized with and without the guests [49]. Without guest, template polymerization did not proceed; MAA oligomer was not obtained. When toluene was the guest, vinyl groups on both sides were well arranged along the rim of CD ring. As a result, two types of MMA oligomer with DP = 7 and 14 were obtained. When long alkyl compound, docosane, was the guest, all vinyl groups on the primary hydroxyl group side and half of vinyl groups on the secondary hydroxyl group side were well arranged around docosane; single type of MAA oligomer with DP = 7 was selectively obtained from both β-MVM1 and β-MVM2. Therefore, the arrangement of vinyl groups in the template is one of the important factors to control template polymerization.

4. Conclusion

Combination of ATRP, which is one method of controlled/living radical polymerization, and template polymerization of multivinyl monomer was described. The important features of ATRP, which
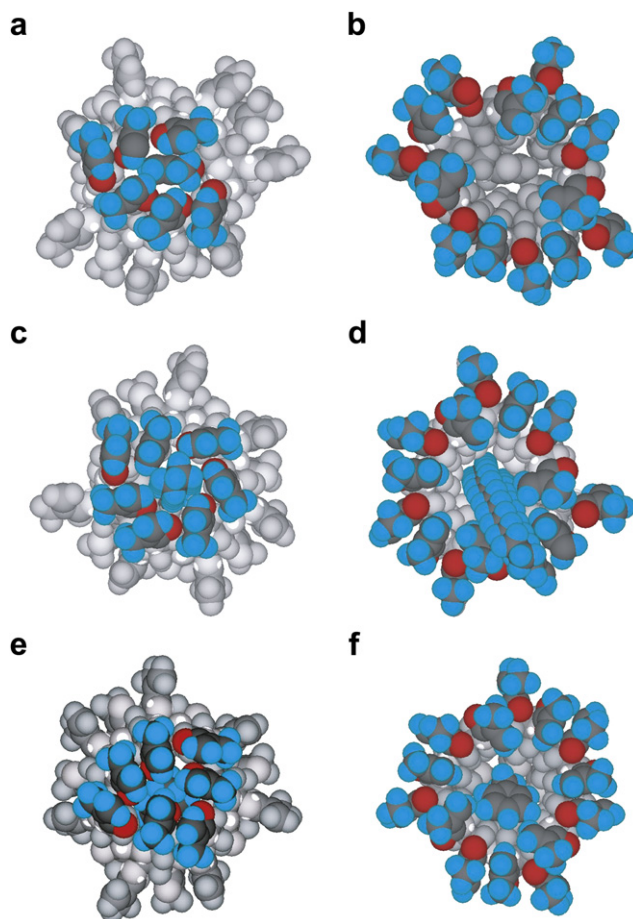

Fig. 12. Calculated arrangements of methacryloyl group of β-MVM2 by MM2. Black particle: C; blue particle: H; red particle: O. (a) The primary hydroxyl group side without guest, (b) the secondary hydroxyl group side without guest, (c) the primary hydroxyl group side with docosane, (d) the secondary hydroxyl group side with docosane [47], (e) the primary hydroxyl group side with toluene, and (f) the secondary hydroxyl group side with toluene.

are a good control of radical concentration and the livingness of radical, resulted in (1) higher conversion of vinyl group without gelation and (2) homogeneous structure of the products. In the case of template polymerization, ATRP proceeded in a living manner; the apparent polymerization rates of ATRP were very close to that of the ATRP in bulk. These indicated that the vinyl groups were highly concentrated in template molecules. The architecture of product is highly governed by the architecture of template molecule. When linear polymer was used as a template of multivinyl monomer, the ladder-like polymers were synthesized with the bifunctional initiator. Styryl group, which acts as an inhibitor in this work, introduced into the ends of polymer chain did not influence the kinetics for ATRP of multivinyl monomer. Template polymerization proceeded toward the chain ends along the backbone of multivinyl monomer. When cyclodextrins were used as the templates, well-defined oligomers were selectively synthesized. Since the template field was divided into two fields by cyclodextrin ring, two types of oligomer were individually synthesized in the same molecule. Additionally, guest molecule included into cyclodextrin ring during polymerization controlled the arrangement of vinyl group in the polymerization fields. As a result, the degree of polymerization of oligomer was finely controlled by the guest. The macrocyclic structure of cyclodextrin had enabled the easy synthesis of cyclic oligomer with controlled degree of polymerization. Ladder-like polymers and well-defined oligomers will be useful highly
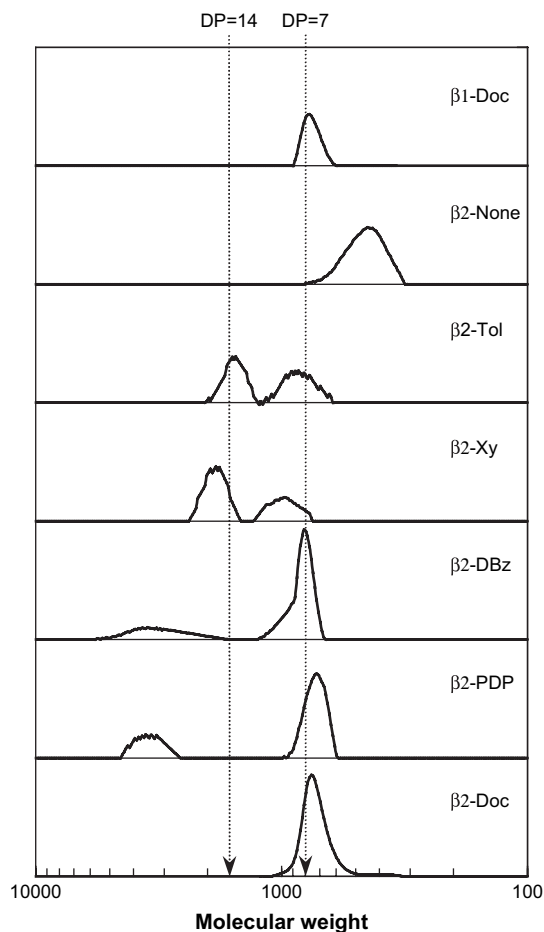
Fig. 13. RI absorption of gel permeation chromatography of methacrylic acid oligomers obtained by hydrolysis of polymerized products of β-MVM1 and β-MVM2 with guests. β1 and β2 correspond to multivinyl monomers, β-MVM1 and β-MVM2, respectively. None indicates no guest was used. Doc, Tol, Xy, DBz and PDP correspond the guests: docosane, toluene, *p*-xylene, dodecylbenzene and pentadecyl phenol, respectively [49].

functional materials. There are many molecules which have interesting architectures. The polymers having useful and interesting architecture will be synthesized from other molecules by the combination of template polymerization and controlled/living radical polymerization.

Acknowledgment

References

[1] Szwarc M. J Polym Sci 1954;13:317–8.
[2] Challa G, Tan TT. Pure Appl Chem 1981;53:627–41.
[3] Bamford CH, Haward RN, editors. Developments in polymerization. London: Appl Sci Pub; 1979. p. 215.
[4] Ferguson J, McLeod C. Eur Polym J 1974;10:1083–91.
[5] Papisov IM, Nekrasova NA, Pautov VD, Kabanov VA. Dokl Akad Nauk SSSR 1974;214:861–4.
[6] Buter R, Tan TT, Challa G. J Polym Sci A-1 1972;10:1031–49.
[7] Polowinski S. Prog Polym Sci 2002;27:537–77.
[8] Kammerer H, Jung A. Makromol Chem 1966;101:284–95.
[9] Jantas R, Polowinski S. J Polym Sci Part A Polym Chem 1986;24:1819–27.
[10] Jantas R. J Polym Sci Part A Polym Chem 1990;28:1973–82.
[11] Jantas R, Szumilewicz J, Strobin G, Polowinski S. J Polym Sci Part A Polym Chem 1994;32:295–300.
[12] Duan H, Kuang M, Zhang G, Wang D, Kurth DG, Mohwald H. Langmuir 2005; 21:11495–9.
[13] Mulvihill MJ, Rupert BL, He R, Hochbaum A, Arnold J, Yang P. J Am Chem Soc 2005;127:16040–1.
[14] Jantas R, Janowska G, Szocik H, Polowinski S. J Therm Anal 2000;60:371–6.
[15] Mardare D, Matyjaszewski K. Macromolecules 1994;27:645–9.
[16] Matyjaszewski K. J Macromol Sci Pure Appl Chem 1994;A31:989–1000.
[17] Kato M, Kamigaito M, Sawamoto M, Higashimura T. Macromolecules 1995;28: 1721–3.
[18] Matsuyama M, Kamigaito M, Sawamoto M. J Polym Sci Part A Polym Chem 1996;34:3585–9.
[19] Matyjaszewski K, Shigemoto T, Frechet JMJ, Leduc M. Macromolecules 1996; 29:4167–71.
[20] Patten TE, Xia J, Abernathy T, Matyjaszewski K. Science 1996;272:866–8.
[21] Kotani Y, Kato M, Kamigaito M, Sawamoto M. Macromolecules 1996;29:6979–82.
[22] Shemper BS, Acar AE, Mathias LJ. J Polym Sci Part A Polym Chem 2002;40: 334–43.
[23] Hawker CJ, Hedrick JL. Macromolecules 1995;28:2993–5.
[24] Chang C, Pugh C. Macromolecules 2001;34:2027–39.
[25] Hawker CJ, Elce E, Dao J, Volksen W, Russell TP, Barclay GG. Macromolecules 1996;29:2686–8.
[26] Greszta D, Matyjaszewski K. Macromolecules 1996;29:7661–70.
[27] Paik HJ, Matyjaszewski K. Polym Prepr (Am Chem Soc Div Polym Chem) 1996; 37:274–5.
[28] Hawker CJ, Barclay GG, Orellana A, Dao J, Devonport W. Macromolecules 1996; 29:5245–54.
[29] Chiefari J, Chong YK, Ercole F, Krstina J, Jeffery J, Le TPT, et al. Macromolecules 1998;31:5559–62.
[30] de Brouwer H, Tsavalas JG, Schork FJ, Monteiro MJ. Macromolecules 2000;33: 9239–46.
[31] Goto A, Sato K, Tsujii Y, Fukuda T, Moad G, Rizzardo E, et al. Macromolecules 2001;34:402–8.
[32] Mayadunne RTA, Jeffery J, Moad G, Rizzardo E. Macromolecules 2003;36: 1505–13.
[33] Stenzel MH, Cummins L, Roberts GE, Davis TP, Vana P, Barner-Kowollik C. Macromol Chem Phys 2003;204:1160–8.
[34] Saito R, Iijima Y, Yokoi K. Macromolecules 2006;39:6838–44.
[35] Jantas R, Polowinski S, Strobin G. Polym Int 1995;37:315–8.
[36] Saito R, Yokoi K, Iijima Y. Macromol Symp 2007;249–250:398–405.
[37] Wang JS, Matyjaszewski K. Macromolecules 1995;25:7901–10.
[38] Wang JS, Luo N, Yunn SK. J Polym Sci Part A Polym Chem 2001;159:77–83.
[39] Tessler MM. J Polym Sci A-1 1966:2521–32.
[40] Arnord Jr C. J Polym Sci Macromol Rev 1979;14:263–378.
[41] Saito R, Okuno T, Kobayashi H. J Polym Sci Part A Polym Chem 2001;39:3539–46.
[42] Bowen RL, Farahani M, Dickens SH, Guttman CM. J Dent Res 2000;79:905.
[43] Stenzel MH, Davis TP. J Polym Sci Part A Polym Chem 2002;40:4498–512.
[44] Saito R, Kobayashi H. Macromolecules 2002;35:7207–13.
[45] Saito R, Yamaguchi K. Macromolecules 2003;36:9005–13.
[46] Saito R, Kobayashi H. J Inclusion Phenom Macrocycl Chem 2002;44:303–6.
[47] Saito R, Yamaguchi K. J Polym Sci Part A Polym Chem 2005;43:6262–71.
[48] Saito R, Yamaguchi K, Hara T, Saegusa C. Macromolecules 2007;40:4621–5.
[49] Saito R, Yamaguchi K. Macromolecules 2005;38:2085–92.

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