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Template Polymerization with Noria as a Template

Yoichi Saito,[†] Reiko Saito,*,[†] Hiroto Kudo,[‡] and Tadatomi Nishikubo[‡]

Department of Organic and Polymeric Materials, Tokyo Institute of Technology, 2-12, Ookayama, Meguro, Tokyo 152-8552, Japan, and Department of Material and Life Chemistry, Faculty of Engineering, Kanagawa University, 3-27-1, Rokkakubashi, Kanagawa-ku, Yokohama 221-8686, Japan

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Introduction. Template polymerization is a useful technique to synthesize polymer with a strictly controlled degree of polymerization (DP).[1–13] In the case of template polymerization, the DP and molecular weight distribution depend on the architecture of the template molecule. For strict control of DP, the arrangement of vinyl groups in the template molecule and the fine adjustment of radical concentration are required. We previously synthesized 7-mer and 14-mer of methacrylic acid oligomers (PMAA) by template polymerization with β-cyclodextrin (β-CD) as a template.[14–17] The arrangement of vinyl groups was influenced by the architecture of template molecule. Noria is a cyclic oligomer developed by Kudo et al.[18] Twenty-four OH groups are arranged with a zigzag structure on the side of the Noria ring. A multivinyl monomer of Noria (Noria-MVM) was obtaind by introducing methacrylic groups to 24 OH groups of Noria. This communication reports the template polymerization of Noria-MVM by copper-mediated atom transfer radical polymerization (ATRP) and redox polymerization. By intramolecular template polymerization with Noria-MVM, a 24-mer of PMAA will be synthesized.

Results and Discussion. Table 1 lists the polymerization conditions and results of atom transfer radical polymerization (ATRP) and redox polymerization of multivinyl monomer of Noria (Noria-MVM). Polymerization solutions did not gel by polymerization; polymerization would be limited in Noria-MVM molecules. Conversion of the vinyl group was determined by proton nuclear magnetic resonance (^{1}H NMR) spectroscopy by comparison of resonance areas of $\rangle C{=}CH_2$ and $\rangle CH-$ of the Noria frame. In both cases, the conversions of vinyl groups in crude product were less than 38 mol %. It should be noticed that the conversion indicates of all the Noria-MVM monomers. Generally, the polymerization rate of template polymerization of ATRP was similar to that of free radical polymerization in the bulk state.[14,19,20] Five hours was enough to complete the polymerization of 24 vinyl groups of Noria-MVM. Therefore, polymerization time was not increased. For the low conversion, two reasons are considered. First, polymerization proceeded in all Noria-MVM molecules, but the conversion was uniformly low. In another case, two types of products, which were completely polymerized Noria-MVM and unpolymerized Noria-MVM, existed in solution. When template polymerization was carried out with β-CD,[14–17] polymerization was completed in the MVM molecule, but unpolymerized MVM molecules remained in solution.

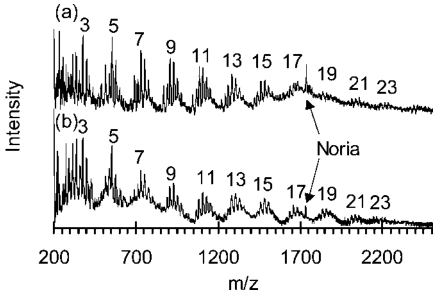

Figure 1. MALDI-TOF MASS spectra of poly(methacrylic acid) (PMAA) obtained by hydrolysis of polymerized product of multivinyl monomer of Noria (Noria-MVM). Mode: positive at 20 kV; laser: 337 nm nitrogen laser with 5 ns pulse duration (30 μm spot size); accumulation number: 100; matrix: 2,5-dihydroxybenzoic acid. (a) Product polymerized by atom transfer radical polymerization of Noria-MVM in methanol ([Noria-MVM] = 3.00 mM) at 50 °C for 5 h. [Noria-MVM]:[methyl 2-bromopropionate]:[CuBr]:[tris[2-(dimethylamino)-ethyl]amine] = 1:1:1:1.5. (b) Product polymerized by redox polymerization of Noria-MVM in methanol ([Noria-MVM] = 3.02 mM) at 50 °C for 5 h. [Noria-MVM]:[benzoyl peroxide]:[*N*,*N*-dimethylaniline] = 1:1:1. The value on peaks corresponds to degree of polymerization of PMAA derived from Noria-MVM.

To clarify this point, the DP value of polymerized sequence was investigated. First, polymerized products were hydrolyzed to Noria and poly(methacrylic acid) (PMAA) with NaOH ([−COOC−]:[NaOH] = 1:10) in methanol for 48 h. After hydrolysis, red solutions containing precipitate were obtained. Taking account of solubility of products, the precipitate was Noria. Next, matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass measurement was carried out for the hydrolyzed solution. To prevent losing compounds in the solution, the hydrolyzed solution was not purified. Figure 1 shows the MALDI-TOF mass spectra of hydrolyzed product. The peaks owing to Noria were observed at m/z = 1726.84, 1735.76, 1759.67, and 1751.18 in the spectra of product by ATRP and at 1703.67, 1726.09, and 1736.49 in the spectra of product by redox polymerization. The peak of Noria-MVM was not observed in either case.

The maximum m/z peaks in the spectra were 2235.94 and 2193.62 in the cases of ATRP and redox polymerization, respectively. In the case of ATRP, the calculated m/z value of 23-mer of PMAA with four sodium atoms, methyl propionate as an initiator fragment, and bromide as an end group is 2236.61 (= 87.04 [methyl propionate] + 23 × 86.03 [methacrylic acid] + 4 × 22.99 [sodium] + 78.92 [bromide]). In the case of redox polymerization, the calculated m/z value of 23-mer of PMAA with six sodium atoms, phenyl group as an initiator fragment, and a proton as an end group is 2194.20 (= 77.10 [phenyl] + 23 × 86.03 [methacrylic acid] + 6 × 22.99 [sodium] + 1.01 [proton]). The maximum m/z peaks in the spectra correspond to the calculated m/z values of 23-mer of PMAA. Twenty-four vinyl groups existed in Noria-MVM. Therefore, not all of vinyl groups in each Noria-MVM molecule were polymerized in both cases. Table 1 in the Supporting Information shows the obtained m/z. In both cases, the DP of PMAA were one in the range of 3−23. Addition polymerization of vinyl monomer propagates one by one. But in these systems, all DP values were odd numbers. This phenomenon was observed in both cases. This was common for Noria-MVM in this work. This unusual phenomenon can be explained from the viewpoint of architecture of Noria. Again, for the template polymerization of multivinyl

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* Corresponding author: Ph +81-3-5734-2937; Fax +81-3-5737-2888; e-mail rsaito@polymer.titech.ac.jp.

[†] Tokyo Institute of Technology.

[‡] Kanagawa University.

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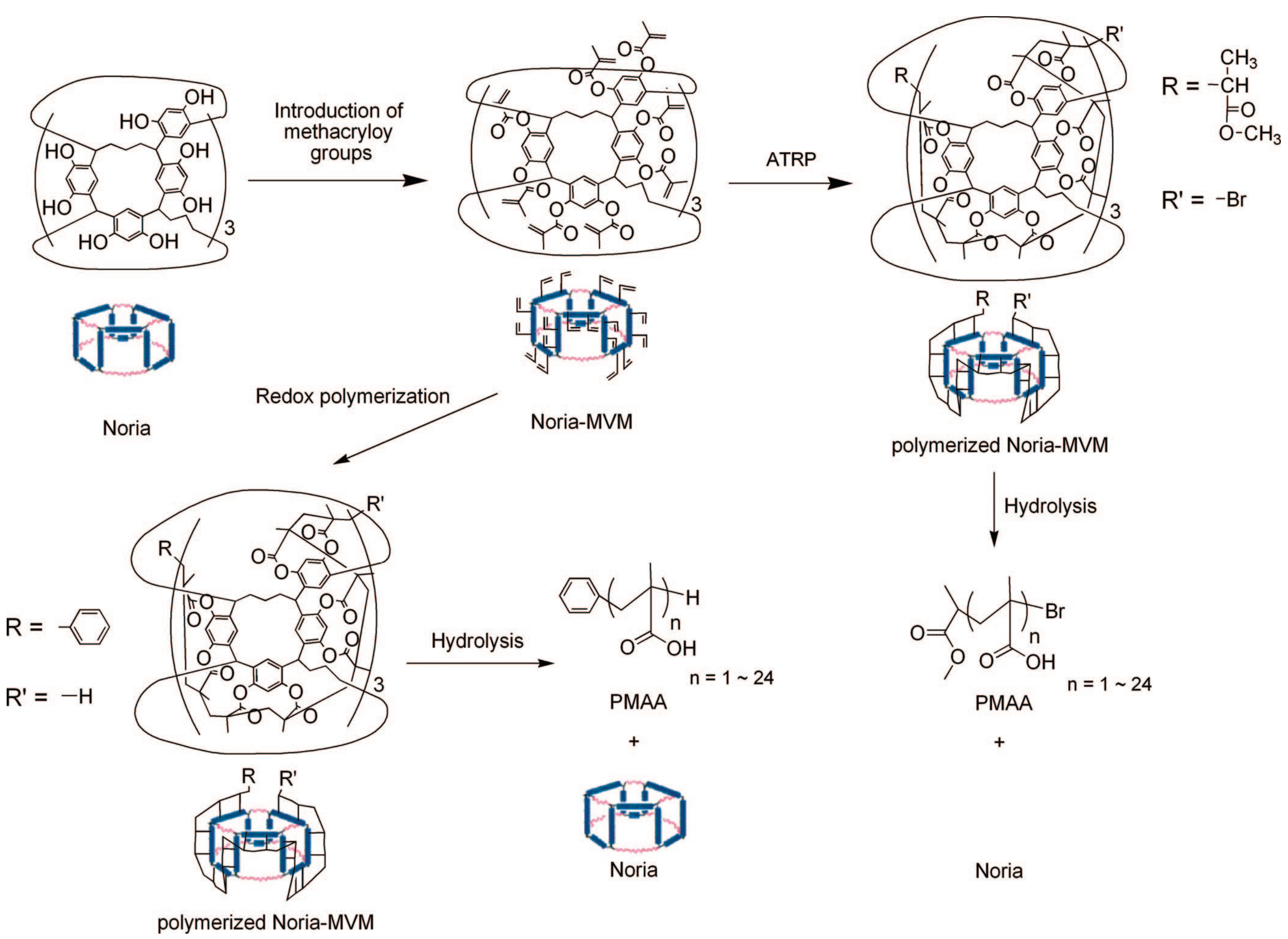
Table 1. Conditions and Results of Polymerization of Multivinyl Monomer of Noria[a]

code	method	Noria-MVM[b] [mmol/L]	initiator [mmol/L]	catalyst [mmol/L]	ligand [mmol/L]	yield[c] [wt %]	conversion[d] [mol %]
1	ATRP[e]	3.00	4.80	2.95	4.50	40	38
2	redox[f]	3.02	2.48	2.97		98	25

[a] Solvent: methanol; reaction temperature: 50 °C; reaction time: 5 h. [b] Multivinyl monomer of Noria. [c] Yield [wt %] of crude product to initial Noria-MVM. [d] Conversion of vinyl groups to the crude product determined by proton nuclear magnetic resonance by comparison of resonance areas of ⟩C=CH$_2$ (5.43−6.35 ppm) and ⟩C*H*− (4.16−4.19) of Noria frame. [e] Atom transfer radical polymerization. Initiator: methyl 2-bromopropionate; catalyst: CuBr; ligand: tris[2-(dimethylamino)ethyl]amine. [f] Redox polymerization. Initiator: benzoyl peroxide; catalyst: *N*,*N*-dimethylaniline.

Scheme 1. Synthetic Concept of Polymerization of the Multivinyl Monomer of Noria (Noria-MVM)



monomer, the architecture of template strongly influences on DP. When β-CD was used as a template, polymerization proceeded along the rim of β-CD.[14–17] Radical did not skip the vinyl group because vinyl groups did not move freely on the rim of the β-CD scaffold. In the case of Noria, OH groups, at which vinyl groups were introduced, arranged with a zigzag structure on the side of the Noria ring. The long and short distances between neighboring OH groups appeared alternately. The arrangement of vinyl groups in Noria-MVM would be similar to that of OH groups. When the distance is long, radical tends to terminated. On the other hand, when the distance is short, polymerization proceeds rather than terminates. Therefore, the unusual polymerization phenomenon would be observed for the template polymerization with Noria. However, architectural details of Noria-MVM are unclear. Further investigations from viewpoint of Noria-MVM architecture are being carried out.

Experimental Section. Polymerization of Noria-MVM. Polymerization conditions are listed in Table 1. In the case of ATRP, Noria-MVM (0.31 g, 0.090 mmol, 2.2 mmol of vinyl group), methanol (30 mL), methyl 2-bromopropionate (0.024 g, 0.14 mmol), tris[2-(dimethylamino)ethyl]amine (0.031 g, 0.14 mmol), and CuBr (0.013 g, 0.089 mmol) were added to a sealable Pyrex reactor. The reactor was sealed under vacuum and heated at 50 °C for 5.0 h. To stop polymerization, hydroquinone (0.050 g) was added to the solution, and then the solution was concentrated by evaporation until the solution volume became 5 mL. The product was precipitated in water (30 mL), collected, and purified by reprecipitation for two times from methanol (10 mL) and cold (0 °C) water (50 mL). The product was white powder. Yield was 84 wt % for Noria-MVM. In the case of redox polymerization, Noria-MVM (0.31 g, 0.090 mmol, 2.2 mmol of vinyl group), methanol (30 mL), benzoyl peroxide (0.024 g, 0.074 mmol), and *N*,*N*-dimethylaniline (0.011 g, 0.090 mmol) were added to a sealable Pyrex reactor. The reactor was heated 50 °C for 5.0 h under a N_2 gas atmosphere. To stop polymerization, hydroquinone (0.050 g) was added to the solution, and then the solution was concentrated by evaporation until the solution volume became 5 mL. The product was precipitated in water (30 mL), collected, and purified by reprecipitation for two times from methanol (10 mL) and cold (0 °C) water (50 mL). The product was gray powder. Yield was 98% for Noria-MVM.

MALDI-TOF Mass Measurement. To hydrolyze product, polymerized product (0.10 g, 0.030 mmol, 0.72 mmol of ester groups) and sodium hydroxide (0.29 g, 7.2 mmol) were dissolved in methanol (2.0 mL). The solution was stirred at room temperature for 48 h and then used as a sample for MALDI-TOF mass measurement without purification. Molecular weight of hydrolyzed products was measured with (MALDI-TOF) mass spectrometer (Shimazu, Kraros Kompact MALDI2) incorporating a 337 nm nitrogen laser with 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 laser spot was 100. For matrix solution, 2,5-dihydroxybenzoic acid (300 mg, 1.8 mmol) was dissolved in acetone (3 mL), and then sodium trifluoroacetate (3 mg, 0.022 mmol) was added to the solution. Sample solution (1 μL) was added to matrix solution (100 μL). Then, the solution was loaded onto a stainless steel sample plate (about 100 μm spot size of simple), and the solvents were evaporated.

^{1}H NMR Measurement. ^{1}H NMR measurement was carried out with a ^{1}H NMR spectrometer (JEOL, GLX, 400 MHz) with methanol-d_6 as a solvent, except for polymerized product by redox polymerization (DMSO-d_6), at room temperature using a resonance of the deuterated solvent as lock and the internal standard for chemical shift data in the δ-scale relative to TMS.

Supporting Information Available: Text giving the experimental part including description of all materials and their purification, synthesis of Noria-MVM, and the table of obtained *m/z* value. This material is available free of charge via the Internet at http://pubs.acs.org.

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