Electronic Supplementary Material (ESI) for Polymer Chemistry.

Polymerization of α-(Holomethyl)acrylate through Sequential Nucleophilic Attacks of Dithiols by the Combination of Addition-Elimination and Click Reactions

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Electric Supplementary Information

Cyclization reaction as a side reaction of polymerization

Cyclization reaction was found as a side reaction in the polymerization of **A1** (0.750 mmol) and **C1** (1.00 equiv.). The polymerization was conducted in CH_3CN (0.50 mL) with DBU (1.20 equiv.) for 24 h under reflux (Run 5). Figure S1 shows the SEC curves of the resulting product. Apparently, it has a tail towards the lower molecular weight region, and the estimated M_n and M_w/M_n were 200 and 17.1, respectively. The ^{1}H NMR spectrum of the product (Figure S2) shows signals assignable to the end group (**a**,**b**, and **o**). From the intensity ratio of *O*-CH_2 signals to them, the M_n could be estimated 12000, which was much higher than that estimated by SEC. The overestimation can be explained by the formation of cyclic products, which decrease the intensity of end-group NMR signals as well as polymerization. The cyclized products also give the explanation to the broad M_w/M_n and the tailing of SEC curve.

Similar experiment was employed with **C2** instead of **C1** (Run S1). In this case, the SEC curve shows a broad peak in the polymeric region accompanying several sharp peaks at the oligomeric region (MW < 10^3) (Figure S3). In the ^{1}H NMR spectrum shows complete disappearance of end group signals (Figure S4). Therefore, it can be concluded that cyclization occurred, probably due to the more flexible oligo(ethylene glycol) linker of **C2** than alkyl linker of **C1**.

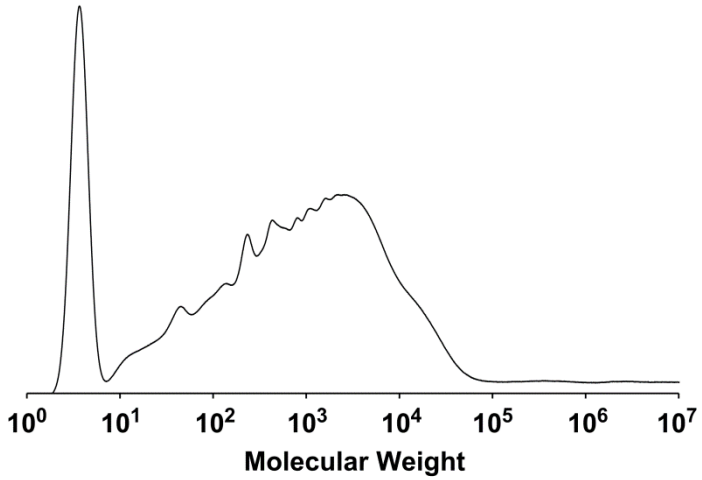

Figure S1. SEC curve of the product in Run 5 (THF, 40 °C, PS standards).

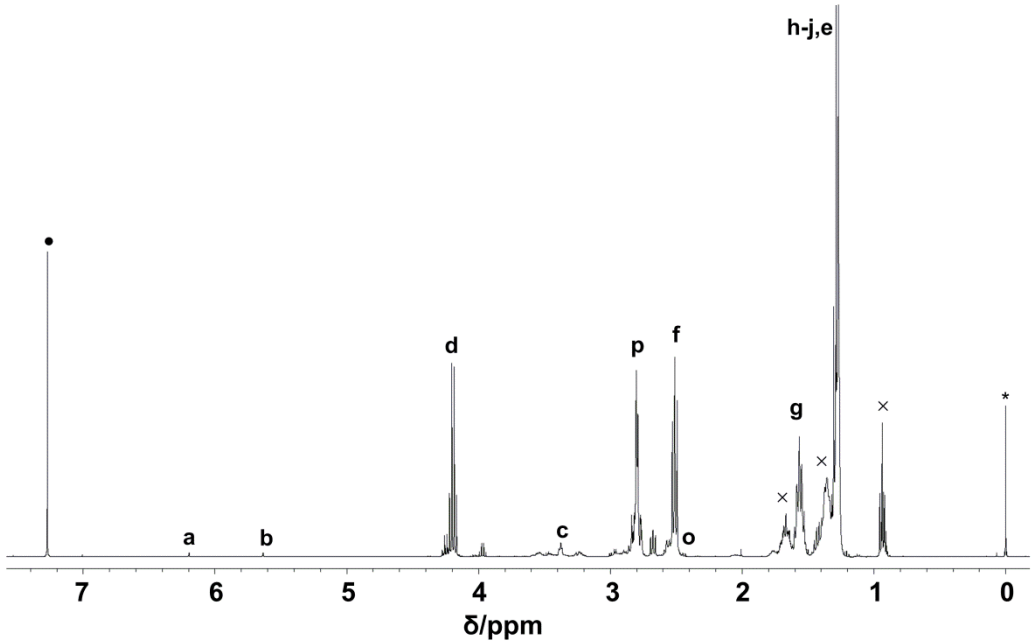

Figure S2. ^{1}H NMR spectrum of the product in Run 5 (400 MHz, $CDCl_3$, 30 °C). ●: $CHCl_3$,*: tetramethylsilane and ×: Bu_3P. The other labels correspond to those in Scheme 2.

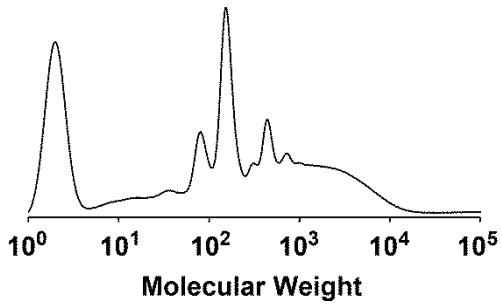

Figure S3. SEC curve of the product in Run S1 (THF, 40 °C, PS standards).

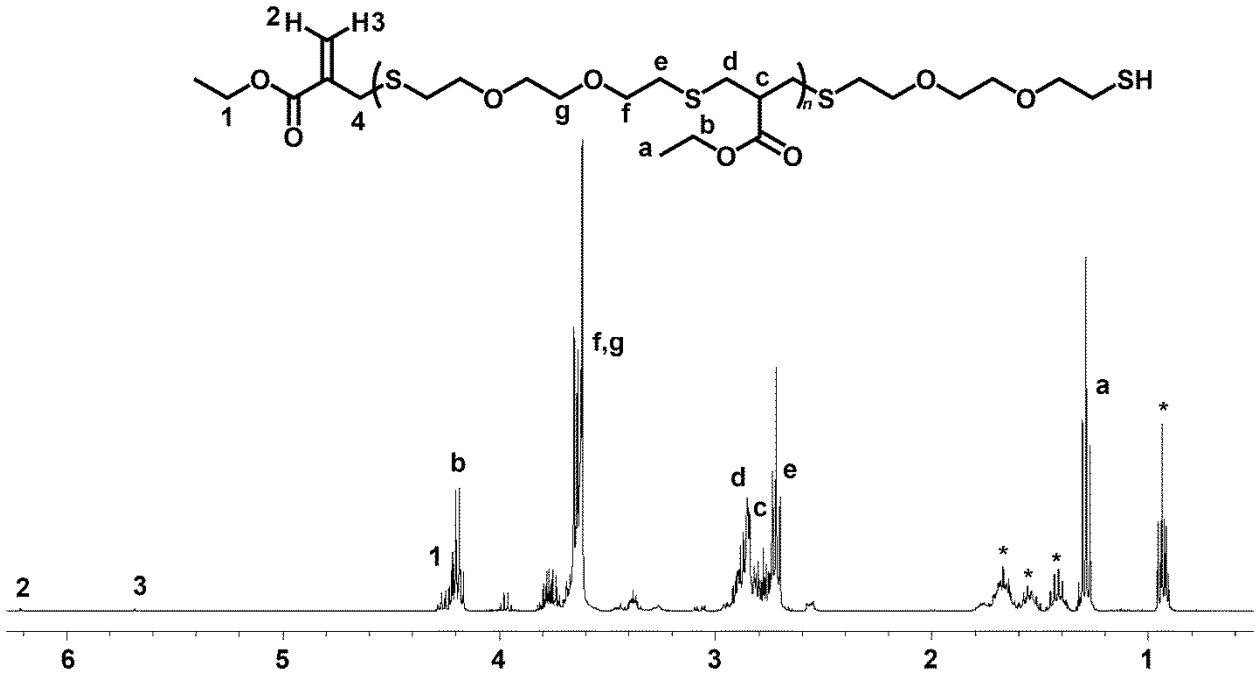

Figure S4. ^{1}H NMR spectrum of the product in Run S1 (400 MHz, $CDCl_3$, 30 °C). *: Bu_3P.

Effects of heating process on the cyclization and polymerization

In the all examples described in the main manuscript (Runs 1-11), **A1** was added to a mixture of **C1** and base at the set temperatures, and Bu_3P was added after 30 min. Consequently, the second reaction, *i.e.* the Michael addition started at the set temperatures. In order to know the effect of heating process on the cyclization and polymerization, the reaction mixture was prepared at 20 °C in a similar manner to Run 9 and stirred for 48 h, and the reaction mixture was heated at 80 °C for more 24 h (Run S2). Similar experiment was employed, where the initial temperature was changed to 50 °C (Run S3). In both case, the growth of M_n was monitored with SEC. Figure S5 shows the time vs. M_n plots in each experiment. After the elevation of temperature, M_ns were changed from 23000 to 26300 in Run S2 and from 14700 to 14200 in Run S3, respectively. In a sharp contrast to Run 10, M_ns were kept higher even under reflux conditions, and therefore, the cyclization seems to arise in the early stage of polymerization.

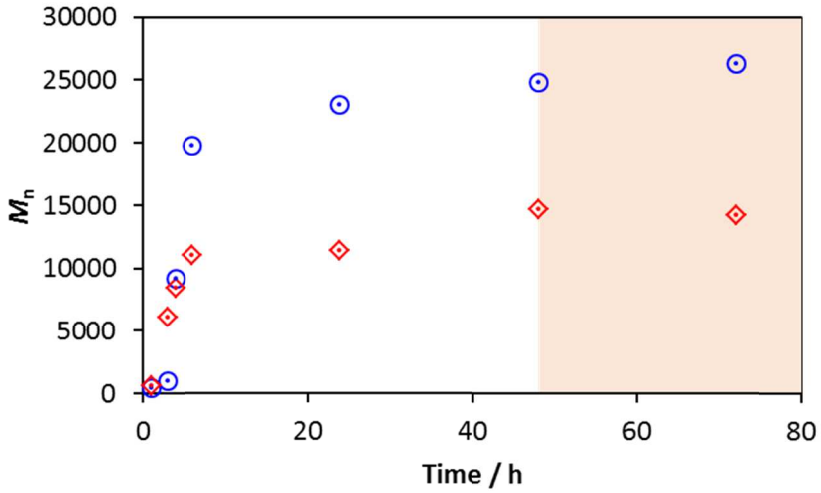

Figure S5. Plots of time vs. M_n in Runs S2 (blue circles) and S3 (red diamonds) determined by SEC (THF, 40 °C, PS standards). The orange highlighted area means after increasing temperature to 80 °C.