Living cationic ring-opening polymerization by water-stable initiator: synthesis of a well-defined optically active polythiourethane†

Atsushi Nagai, Bungo Ochiai and Takeshi Endo*

Department of Polymer Science and Engineering, Faculty of Engineering, Yamagata University, 4-3-16 Jonan, Yonezawa, Yamagata 992-8510, Japan. E-mail: tendo@poly.yz.yamagata-u.ac.jp
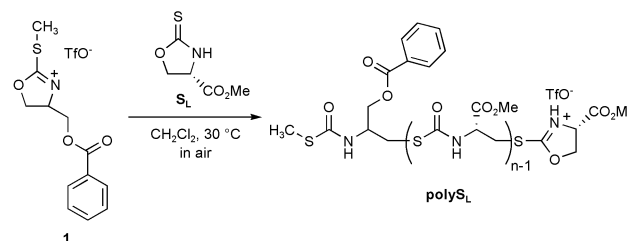
Living cationic ring-opening polymerization under air and water was achieved using a well-defined water-resistant cationic initiator in dichloromethane without purification at ambient temperature.

Living and controlled polymerizations will be the most advanced synthetic methods in the field of polymer synthesis. Advantages of these polymerizations include control of molecular weight, monodisperse polymers that have narrow molecular weight distribution, precise topology (*e.g.*, block, graft, and star polymers), and controlled architecture.[1–4] In spite of the remarkable aspects of these polymerizations, they generally require conditions without moisture and/or oxygen. That is, purification of solvents, an inert gas, or a sealed tube technique must be employed to avoid termination or chain transfer reaction. These complicating processes prompt many researchers to explore air- and moisture-tolerant initiators and catalysts. For instance, ruthenium carbene complexes for olefin metathesis and rare-earth metal triflates as water-tolerant Lewis acids realized efficient syntheses of varieties of chemical substances even in the presence of air and moisture.[5] However, their effectiveness is still remaining in the range of syntheses of low molecular weight compounds. Although living and controlled polymerizations in the presence of air or water are being currently developed using these catalysts, the molecular weight and their distribution in these polymerization systems (*i.e.*, $M_n < 10^4$, $M_w/M_n > 1.2$) were not competitive with those of polymerizations under severely purified conditions.[6]

Recently, we have developed a controlled cationic ring-opening polymerization of a 1,3-oxazolidine-2-thione derived from L-serine affording a chiral polythiourethane. The polymerization was carried out at 30 °C by methyl trifluoromethanesulfonate as a cationic initiator in purified dichloromethane under dry nitrogen atmosphere.[7] The controlled character depends on the highly stable nature of the propagation terminal (cyclic *endo*-iminothiocarbonate) in this polymerization system. With this point in mind, we synthesized a new cationic initiator (benzoic acid 2-methylsulfanyl-4,5-dihydro-oxazolinium-4-ylmethyl ester trifluoromethanesulfonate, **1**) by the reaction of a 1,3-oxazolidine-2-thione derivative and methyl trifluoromethanesulfonate (TfOMe). This initiator is insensitive toward air and water to the degree that the measurement of the ^{1}H NMR spectrum in D_2O is possible (see ESI). Herein, we describe the cationic ring-opening polymerization of a 1,3-oxazolidine-2-thione derived from L-serine (**S_L**) by **1** as an initiator under air and moisture (Scheme 1).

The cationic polymerization of **S_L** was carried out at 30 °C by **1** ([**S_L**]/[**1**] = 100) in CH_2Cl_2 without any purification under air whose humidity was as high as *e.g.*, 80–90%. The complete consumption of **S_L** was confirmed within 35 h and a white powdery polymer (poly(**S_L**)) was obtained in 99% yield. The SEC analysis of the crude mixture showed a unimodal peak (number-average molecular weight (M_n) was estimated to be 19600) whose distribution ($M_w/M_n = 1.09$) was narrow enough. Although this M_n was a little higher than the theoretical value

(16551) based on the feed ratio [*i.e.*, M_n (theoretical) = (formula weight of **S_L**; 161.18) × ([**S_L**]/[**1**]; 99) + (formula weights of end groups; the initiating group (284.38) and **S_L** at the terminal group (310.25))], the M_n value (17233) determined from the ^{1}H NMR spectrum (based on the integral ratio of the methyl ester protons in the repeating units and the *S*-Me protons of the initiating ends) was in good agreement with the theoretical one. The ^{1}H NMR spectrum of the polymer ($M_n = 19605$) obtained under air was almost equivalent to that ($M_n = 19540$) obtained under purified conditions reported previously, demonstrating their identical primary structures (see ESI). The specific rotations ($[\alpha]_D^{30}$) of these polymers were almost the same value ($[\alpha]_D^{30} = 165.9°$ and 163.3°). This result also indicates that these polymers consisted of comparable secondary structures. The controlled nature of the present aerial system was confirmed by polymerization with different ratios of [**S_L**]/[**1**] (Fig. 1). Regardless of the [**S_L**]/[**1**] ratios, polymers with narrow molecular weight distribution were obtained in quantitative yield and the SEC profiles exhibited unimodal peaks ($M_w/M_n = 1.17–1.05$). The molecular weight of the polymers had a linear relationship with [**S_L**]/[**1**] ratios. Although number average molecular weights of these polymers estimated by SEC analysis were a little higher than those expected from the ratios of [**S_L**]/[**1**], those determined by ^{1}H

**Scheme 1** Living cationic ring-opening polymerization of **S_L** with **1**.
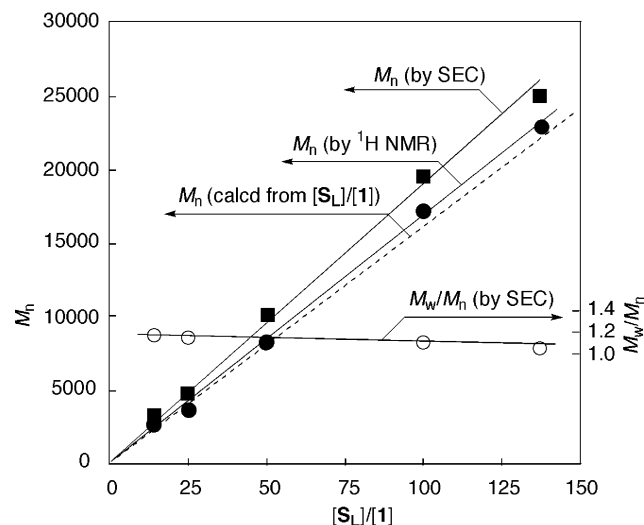


Fig. 1 M_n and M_w/M_n *vs.* feed ratio ([**S_L**]/[**1**]).

† Electronic supplementary information (ESI) available: experimental details. See http://www.rsc.org/suppdata/cc/b3/b310735c/

NMR spectroscopy agreed well with expected ones (*vide supra*). The present system therefore proceeds through the controlled nature and the initiation step occurs quantitatively as the polymerization under purified conditions. To confirm whether the cationic polymerization of S_L proceeds without termination, we examined the relationship between molecular weight and conversion, or reaction time in the polymerization of S_L at 30 °C under air. Fig. 2a shows a straight line of $\ln([S_L]_0/[S_L])$ *versus* time, supporting the constant concentration of active species during the polymerization until the conversion reached 99%. The SEC profiles of all obtained polymers showed that the M_ns increased linearly with the monomer conversion keeping the narrow unimodal peaks, and those studied by ^1H NMR spectroscopy also exhibited similar results (Fig. 2b). These data demonstrate that termination and chain transfer reactions are not detectable in the present polymerization. Furthermore, the cationic ring-opening polymerization of S_L in the presence of water was achieved by **1** ($[S_L]/[1] = 33.35$) in mixed solvent ($CH_2Cl_2 : H_2O = 2 : 1$) at 30 °C under air to give the corresponding polymer in 98% yield. The SEC profile also showed a unimodal peak with narrow distribution ($M_w/M_n = 1.14$), although the M_n (5720) is slightly higher than in the conditions without water. This finding indicates the stability of the active species toward water.

A post-polymerization experiment was also performed to elucidate the stability of the growing ends. When S_L ($[S_L]/[1] =$
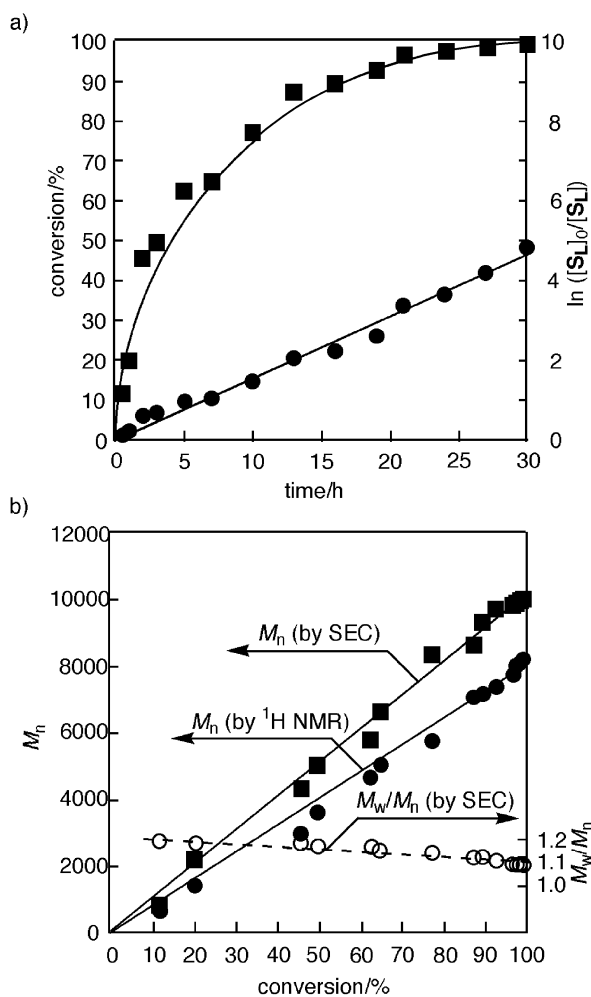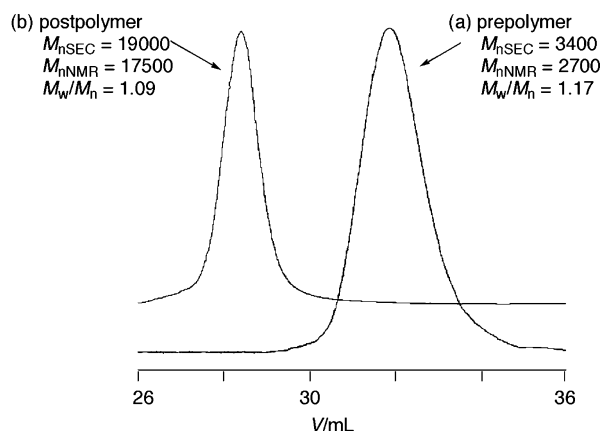
Fig. 3 SEC profiles before and after the post-polymerization experiment on S_L. PolyS_L: prepolymer obtained in the first-stage polymerization, $M_{n\,SEC} = 3400$, $M_{n\,NMR} = 2700$, $M_w/M_n = 1.17$. Poly(S_L-*p*-S_L): postpolymer obtained in the second stage polymerization, $M_{n\,SEC} = 19000$, $M_{n\,NMR} = 17500$, $M_w/M_n = 1.09$.

79.86) was recharged after the complete consumption of the monomer ($[S_L]/[1] = 14.29$) fed at the first stage and the post-polymerization was conducted, the recharged monomer was completely consumed to give a corresponding polymer in quantitative yield with respect to the total amounts of S_L. As shown in Fig. 3, the elution peak in the SEC profile shifted toward the higher molecular weight region after the post-polymerization keeping a unimodal distribution, which confirms that a growing end in the cationic polymerization of S_L is stable enough to re-initiate the further polymerization.

To the best of our knowledge, this report is the first example of a well-defined controlled cationic ring-opening polymerization ($M_n > 10^4$, $M_w/M_n < 1.18$) under air and water.

Notes and references

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Fig. 2 (a) Time–conversion and first-order time–conversion plots for the polymerization of S_L with **1** in CH_2Cl_2 at 30 °C under air. (b) Conversion–M_n and conversion–M_w/M_n plots in the polymerization of S_L with **1** in CH_2Cl_2 at 30 °C under air; $[1]_0 = 0.01$ M, $[S_L]_0/[1]_0 = 50$.