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Ring-opening polymerization of six-membered 1,3-dioxa-2-silacycloalkanes by an organobase catalyst: precision polymerization and monomer regeneration by polymer degradation†

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Exploring monomers that undergo polymerization–depolymerization processes is of great importance for constructing closed-loop chemical recycling systems. In this study, six-membered 1,3-dioxa-2-silacycloalkanes were demonstrated to undergo ring-opening polymerization with 1,5,7-triazabicyclo[4.4.0]dec-5-ene as a catalyst. Moreover, monomer regeneration via polymer degradation was achieved by a distillation-combined reaction with an acid catalyst.

Ring-opening polymerization (ROP) of various cyclic monomers proceeds *via* the propagation reactions consisting of bond cleavage in a monomer and subsequent formation of the same bond as that existing in a monomer. Such propagation reactions can be catalyzed by different mechanisms in many cases. For example, oxiranes undergo cationic and anionic ROP by acid and base catalysts, respectively, *via* the cleavage and formation of C–O bonds.^{1,2} The difference of the mechanisms is also related to side reactions that occur during ROP, such as proton abstraction by an oxyanionic species in anionic ROP of oxiranes and cyclic oligomer formation in cationic ROP.

Cyclosiloxanes are valuable cyclic monomers that are used for the synthesis of polysiloxanes (silicones) by ROP.^{3–5} Polysiloxanes are widely synthesized and used in industry due to the characteristics associated with Si–O bonds in the main chain. Both cationic and anionic ROP are applicable for cyclosiloxanes, while side reactions such as backbiting reactions and intermolecular exchange reactions often occur, which makes the control of polymer molecular weights (MWs) difficult. Fuchise and coworkers reported that organobase catalysts, such as guanidine bases and phosphazene bases, are

effective for controlled/living ROP of cyclosiloxanes.⁶ Polymerization accompanying negligible side reactions was achieved in their system, resulting in polysiloxanes with controlled MWs and narrow molecular weight distributions (MWDs).

Recently, we focused on 1,3-dioxa-2-silacycloalkanes as promising silicon-containing cyclic monomers for ROP.^{7–9} These silyl compounds are synthesized from dialkyldichlorosilanes or dialkoxydialkylsilanes with a diol. 1,3-Dioxa-2-silacycloalkanes were reported to undergo unintended polymerization during storage after synthesis.⁹ 1,3-Dioxa-2-silacycloalkanes correspond to silicon counterparts of cyclic acetals. Cyclic acetals undergo cationic ROP;¹⁰ hence, we recently examined cationic ROP of 1,3-dioxa-2-silacycloalkanes. In our previous study, we demonstrated that cationic terpolymerization of six-membered 1,3-dioxa-2-silacycloalkanes with vinyl ethers and aliphatic aldehydes successfully proceeded to yield polymers with high MWs and controlled monomer sequences.¹¹ Moreover, the obtained terpolymers exhibit acid-, alkaline-, or fluoride anion-triggered degradability due to the O–Si–O bonds in the main chain. Unlike successful terpolymerization, however, cationic homopolymerization did not proceed, resulting in very low monomer conversion and/or low-MW products.

In this study, we aimed to examine homopolymerization of 1,3-dioxa-2-silacycloalkanes. In particular, we focused on various organocatalysts that are suitable for the ROP of cyclosiloxanes.^{6,12} Both 1,3-dioxa-2-silacycloalkanes and cyclosiloxanes have O–Si–O bonds; hence, organocatalysts potentially catalyze ROP of 1,3-dioxa-2-silacycloalkanes (Scheme 1). When we were preparing this manuscript,¹³ very recently, Coates, Balsara, and coworkers reported that the anionic ROP of eight-membered 1,3-dioxa-2-silacycloalkanes successfully proceeds in a controlled manner with a suitable anionic initiator.¹⁴ Unlike their study, an organobase catalyst was demonstrated to catalyze the ROP of a six-membered 1,3-dioxa-2-silacycloalkane in this study. Moreover, the product polymer was successfully transformed into the original monomer by an acid-catalyzed reaction and isolated with a distillation apparatus.

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Scheme 1 Polymerization of 1,3-dioxo-2-silacycloalkanes.

First, we examined cationic ROP of 2,2,5,5-tetramethyl-1,3-dioxo-2-silacyclohexane (Si6M). However, only oligomers were obtained in the reactions with various Lewis acids or cationizing agents at different temperatures (Table S1†). Analyses of the products by ESI-MS and ^1H NMR suggested that cyclic oligomers were mainly produced by the cationic reactions (Fig. S1 and S2†).

Considering the effective organobase-catalyzed ROP of cyclosiloxanes,^{6,12} we conducted polymerization of Si6M with 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD), 1,8-diazabicyclo[5.4.0]-7-undecene (DBU), or phosphazene base (*tert*-butylimino-tri(pyrrolidino)phosphorane; BTTP) as an organocatalyst (Table S2† and Scheme 1). As a result, TBD exhibited excellent catalytic activity. A polymer with a number-average molecular weight (M_n) of over 20×10^3 was obtained when combined with ethanol as an initiator at 25 °C. DBU and BTTP were not effective for the Si6M polymerization under the examined conditions.

The polymerization of Si6M with TBD as a catalyst was next examined in more detail. Triethylene glycol (TEG) was used as a bifunctional initiator.† The polymerization smoothly proceeded to reach conversion of 69% in 60 h (Fig. 1A), resulting in polymers with very narrow MWDs (entry 1 in Table 1). The M_n values increased linearly with an increase in monomer conversion (Fig. 1B), suggesting that living propagating species were generated. When the initial concentrations of the initiator (TEG) were varied, the M_n values of the products changed depending on the concentrations (Fig. S4†), which indicates that TEG functioned as an initiator for polymerization.

^1H NMR analysis of the product polymer exhibited peaks assigned to the TEG moiety (Fig. 1C; see Fig. S5† for the ^{13}C NMR spectrum). The M_n values determined by gel permeation chromatography (GPC) with polystyrene calibration were lower than the theoretical values based on the initial monomer and TEG concentrations (Fig. 1B). Unintended initiation reactions from adventitious water and/or the residual alcohol (2,2-dimethyl-1,3-propanediol) used in monomer synthesis are most likely responsible for the lower values. Indeed, peaks whose m/z are consistent with those of polymer chains



Fig. 1 (A) Time-conversion and first-order plots for the polymerization of Si6M, (B) the M_n (open) and M_w/M_n (filled) values of poly(Si6M)s, and (C) ^1H NMR spectrum of poly(Si6M) (entry 1 in Table 1; in CDCl_3 at 30 °C; * Me_4Si , water, or CHCl_3 ; # ^{13}C satellite; † very minor peaks observed near peaks *b* and *c* are not assigned yet). The data correspond to entry 1 in Table 1 (see Table 1 for the polymerization conditions).

Table 1 Polymerization of 1,3-dioxo-2-silacycloalkanes by TBD^a

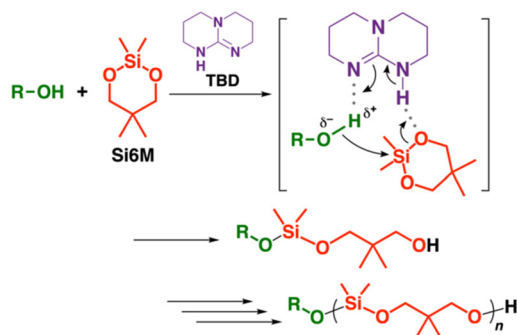
Entry	Monomer	Time (h)	Conv. (%)	$M_n \times 10^{-3}^b$	M_w/M_n^b
1	Si6M	60	69	24.9	1.06
2	Si6mM	8	86	27.8	1.12
3	Si6	2	77	2.2 ^c	1.71 ^c
4	Si5M	24	40 ^d	—	—
5	Si7	72	6 ^d	—	—
6	Si8O	24	<1	—	—

^a $[\text{Monomer}]_0 = 2.4$ (except for entry 4) or 2.0 (entry 4) M, $[\text{TEG}]_0 = 5.0$ mM, $[\text{TBD}]_0 = 5.0$ mM, in toluene at −30 °C. ^b By GPC (polystyrene calibration). ^c For a main peak. ^d A polymer was not obtained.

initiated from TEG, water, or the residual alcohol were detected by the matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS) analysis of the polymer (Fig. S6†).

TBD is considered to catalyze the ROP of Si6M by the dual activation of both the hydroxy group at the propagating end and a Si6M monomer (Scheme 2). The dual activation mechanism was suggested for the ROP of cyclic esters by TBD in several studies.^{15–17} This mechanism was also applied to ROP of cyclosiloxanes.⁶ The interaction between an alcohol and TBD was indicated by ^1H NMR analysis in a past study.¹⁸ DBU and BTTP were ineffective for polymerization; hence, the dual activation mechanism concerning TBD, hydroxy group, and monomer, which is characteristic to TBD, is likely of impor-





Scheme 2 Plausible polymerization mechanism.

tance for smooth propagation reactions. A detailed study is required to elucidate the polymerization mechanism.

To confirm livingness of the polymerization, a monomer addition experiment was conducted. After a fresh feed of Si6M was added at monomer conversion of 75%, the polymerization smoothly proceeded with a consumption of the added monomer (Fig. 2A). Moreover, the M_n values of the polymers linearly increased even after the monomer addition (Fig. 2B). The MWD curve also shifted to the higher-MW region without tailing peaks (Fig. 2C). The results indicate that the polymerization of Si6M with TBD proceeded in a living manner.

When the polymerization time was prolonged to 140 h, the monomer conversion ceased at approximately 80% (red symbols in Fig. 2D). We hypothesized that the ceiling temperature (T_c) of the Si6M polymerization is not high. To examine the effect of the ceiling temperature, which is also related to the equilibrium concentration, we conducted polymerization at different monomer concentrations or at higher temperatures. The concentrations of remaining monomers were found to be almost constant (approximately 0.4 M; the first-order plot shown in Fig. 1A is based on this concentration) when polymerization was conducted at a monomer concentration of 2.4, 1.2, or 0.60 M at -30°C (Fig. S7†). Moreover, the polymerization ceased at lower monomer conversion at 40, 20, or 0°C than that at -30°C (Fig. 2D). From the polymerization results

at different temperatures, the T_c was determined to be 46°C (Fig. S8†). In addition, the heat of polymerization (ΔH) and the entropy change of polymerization (ΔS°) were calculated to be -5.5 kJ mol^{-1} and $-17\text{ J mol}^{-1}\text{ K}^{-1}$, respectively.

The Si6M monomer was synthesized from dimethoxydimethylsilane and 2,2-dimethyl-1,3-propanediol with indium trifluoromethanesulfonate [$\text{In}(\text{OTf})_3$] as a catalyst by a distillation method. In the monomer synthesis, reactions among various compounds, such as the silane substrate, diol, methanol, Si6M, and oligomer/polymer, are likely in an equilibrium. The removal of methanol by distillation promotes the generation of Si6M and oligomers/polymers. After almost complete removal of methanol, Si6M is distilled, which also facilitates the conversion of oligomers/polymers to a Si6M monomer. Therefore, a Si6M polymer is potentially converted to a Si6M monomer by an acid catalyst. This kind of monomer regeneration from a polymer is attracting much attention as exemplified by the polymerization–depolymerization cycles of five-membered lactones and cyclic acetals.^{19,20} Depolymerization of polysiloxanes has also been extensively studied.²¹

We conducted polymer degradation into a monomer with a distillation apparatus shown in Fig. 3A. When a solution containing poly(Si6M) (5.0 g, $M_n = 37.0 \times 10^3$), $\text{In}(\text{OTf})_3$, and dichloromethane was heated at 80°C under reduced pressure (30 kPa), dichloromethane was first distilled off. Subsequently, after temperature was raised (130°C) and pressure was lowered (10 kPa), colorless, transparent liquid (4.0 g; yield = 80%) was distilled. This liquid was a Si6M monomer, as confirmed by ^1H NMR analysis (Fig. 3B, lower). The collected monomer was successfully used for repolymerization, resulting in a high-MW polymer (Fig. S9†). This experiment demonstrated that the polymerization–depolymerization cycle was constructed for this silyl monomer (Scheme 1).

We also examined polymerization of six-membered 1,3-dioxane-2-silacycloalkanes with the smaller number of methyl groups (Scheme 1). A six-membered monomer with one methyl group in the diol-derived unit (Si6mM) underwent smooth polymerization, resulting in polymers with high MWs and narrow MWDs (entry 2 in Table 1; Fig. S10, S11†). The

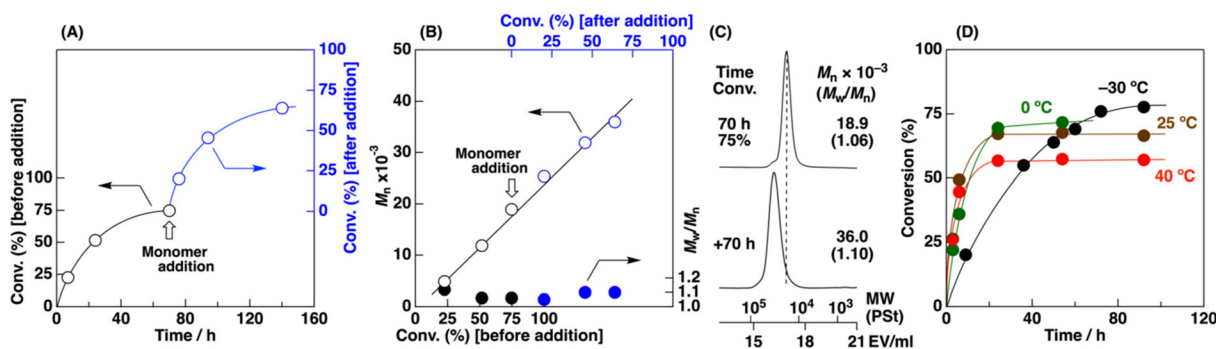


Fig. 2 Monomer addition experiments: (A) time–conversion plots for the polymerization of Si6M, (B) M_n and M_w/M_n values (black: before monomer addition, blue: after monomer addition), and (C) MWD curves for poly(Si6M)s ($[\text{Si6M}]_0 = 2.4\text{ M}$, $[\text{Si6M}]_{\text{added}} = 2.4\text{ M}$, $[\text{TEG}]_0 = 5.0\text{ mM}$, $[\text{TBD}]_0 = 5.0\text{ mM}$, in toluene at -30°C). (D) Polymerization of Si6M at -30°C (black), 0°C (green), 25°C (brown), or 40°C ($[\text{Si6M}]_0 = 2.4\text{ M}$, $[\text{TEG}]_0 = 5.0\text{ mM}$, $[\text{TBD}]_0 = 5.0\text{ mM}$, in toluene; the first four data at -30°C are the same as those in Fig. 1A).



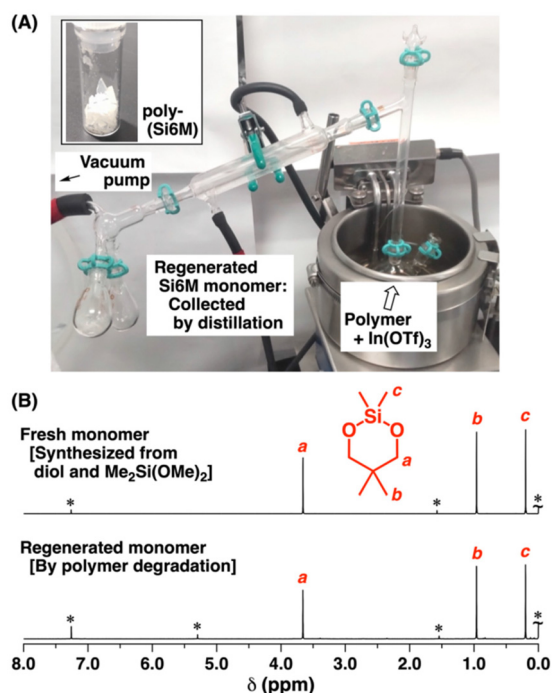


Fig. 3 (A) Photographs of poly(Si6M) and the apparatus used for monomer regeneration by polymer degradation. (B) ¹H NMR spectra of a fresh Si6M monomer [upper; synthesized from 2,2-dimethyl-1,3-propanediol and Me₂Si(OMe)₂] and the regenerated Si6M monomer [lower; by polymer degradation with In(OTf)₃] (in CDCl₃ at 30 °C; * water, Me₄Si, CHCl₃, or CH₂Cl₂).

polymerization was faster than that of Si6M. Unlike Si6M and Si6mM, polymers with high MWs were not obtained from a six-membered monomer that does not have methyl groups in the diol-derived unit (Si6) (entry 3 in Table 1; Fig. S12, S13[†]). The products had bimodal MWDs consisting of a broad polymer peak and a sharp oligomer peak. Side reactions, such as backbiting cyclization, likely occurred during the polymerization of Si6.

Other 1,3-dioxo-2-silacycloalkane monomers with different ring members (Scheme 1) were subjected to polymerization under the conditions suitable for the Si6M polymerization. However, polymers were not obtained from five- (Si5M), seven- (Si7), and eight-membered (Si8O) monomers (entries 4–6 in Table 1). The use of BTTP instead of TBD also resulted in ineffective reactions (Table S3[†]). Si8O was reported to yield a polymer with an anionic initiator by Coates, Balsara, and co-workers,¹⁴ while Si8O did not undergo polymerization with the organocatalysts.

We examined the thermal properties of the Si6M polymer by differential scanning calorimetry (DSC) analysis. The glass-transition temperature (*T_g*) and melting point (*T_m*) were detected at −69 °C and 33 °C, respectively (Fig. S14[†]). The *T_g* and *T_m* are higher than those of polydimethylsiloxane²² (*T_g* = −120 °C, *T_m* = −50 °C). Thermogravimetric analysis (TGA) indicated that poly(Si6M) started to degrade at approximately 200 °C on heating (Fig. S15[†]).

In conclusion, six-membered 1,3-dioxo-2-silacycloalkanes were demonstrated to undergo ROP with TBD as an organo-base catalyst. Si6M exhibited equilibrium polymerization behavior; hence, the polymerization at a low temperature at a high monomer concentration was suitable for effective polymerization. Moreover, the Si6M polymer was successfully converted to the original monomer by an acid catalyst. The polymerization–depolymerization cycle is very promising for a closed-loop chemical recycling system of silicon-containing cyclic monomers. The results obtained in this study contribute to the development of silicon-containing polymers, Si–O group related-organocatalyzed ROP, and closed-loop chemical recycling systems.

Data availability

The data supporting this article have been included as part of the ESI.[†]

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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References

[†] We first used ethanol as an initiator; however, polymers with bimodal MWDs were obtained (Fig. S3[†]) likely due to simultaneous initiation from adventitious water and/or 2,2-dimethyl-1,3-propanediol, which remained in a monomer. Water and the diol function as bifunctional initiators.

- 1 J. Herzberger, K. Niederer, H. Pohlitz, J. Seiwert, M. Worm, F. Wurm and H. Frey, *Chem. Rev.*, 2016, **116**, 2170–2243.
- 2 S. Hu, J. Zhao, G. Zhang and H. Schlaad, *Prog. Polym. Sci.*, 2017, **74**, 34–77.
- 3 J. E. McGrath, J. S. Riffle, A. K. Banthia, I. Yilgor and G. L. Wilkes, *ACS Symp. Ser.*, 1983, **212**, 145–172.
- 4 P. Sigwalt, *Polym. J.*, 1987, **19**, 567–580.
- 5 T. Köhler, A. Gutacker and E. Mejía, *Org. Chem. Front.*, 2020, **7**, 4108–4120.
- 6 K. Fuchise, M. Igarashi, K. Sato and S. Shimada, *Chem. Sci.*, 2018, **9**, 2879–2891.
- 7 R. H. Krieble and C. A. Burkhard, *J. Am. Chem. Soc.*, 1947, **69**, 2689–2692.
- 8 R. H. Cragg and R. D. Lane, *J. Organomet. Chem.*, 1984, **267**, 1–71.
- 9 R. H. Cragg and R. D. Lane, *J. Organomet. Chem.*, 1984, **268**, 1–3.



- 10 P. Kubisa and J. P. Vairon, in *Polymer Science: A Comprehensive Reference*, K. Matyjaszewski and M. Möller, Elsevier B.V., Amsterdam, 2012; Vol. 4.10.
- 11 R. Hada, A. Kanazawa and S. Aoshima, *Macromolecules*, 2022, **55**, 5474–5484.
- 12 J. Shi, N. Zhao, S. Xia, S. Liu and Z. Li, *Polym. Chem.*, 2019, **10**, 2126–2133.
- 13 I. Tanaka, A. Kanazawa and S. Aoshima, *Polym. Prepr., Jpn.*, 2024, **73**(1), 1C11.
- 14 H. J. Rugh, J. Lee, C. Sun, E. E. Abdo, J. N. Bem, N. P. Balsara and G. W. Coates, *Angew. Chem., Int. Ed.*, 2024, e202415069.
- 15 A. Chuma, H. W. Hom, W. C. Swope, R. C. Pratt, L. Zhang, B. G. G. Lohmeijer, C. G. Wade, R. M. Waymouth, J. L. Hedrick and J. E. Rice, *J. Am. Chem. Soc.*, 2008, **130**, 6749–6754.
- 16 L. Simón and J. M. Goodman, *J. Org. Chem.*, 2007, **72**, 9656–9662.
- 17 A. Pascual, H. Sardón, F. Ruipérez, R. Gracia, P. Sudam, A. Velose and D. Mecerreyes, *J. Polym. Sci., Part A: Polym. Chem.*, 2015, **53**, 552–561.
- 18 X. Wang and N. Hadjichristidis, *ACS Macro Lett.*, 2020, **9**, 464–470.
- 19 M. Hong and E. Y.-X. Chen, *Nat. Chem.*, 2016, **8**, 42–49.
- 20 B. A. Abel, R. L. Snyder and G. W. Coates, *Science*, 2021, **373**, 783–789.
- 21 S. Salahudeen, T. A. Thiel and E. Mejía, *RSC Sustainability*, 2024, **2**, 1904–1929.
- 22 E. Yilgör and I. Yilgör, *Prog. Polym. Sci.*, 2014, **39**, 1165–1195.

