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Organocatalytic controlled/living ring-opening polymerization of cyclotrisiloxanes initiated by water with strong organic base catalysts

Ring-opening polymerization of cyclotrisiloxanes using water as an initiator and strong organic bases such as guanidines possessing an R–N=C(N)=NH–R’ unit as catalysts produced a variety of well-defined symmetric polysiloxanes with controlled number-average molecular weights ($M_n = 2.64–102.3$ kg mol$^{-1}$) and narrow polydispersity ($Đ = 1.03–1.16$). Controlled syntheses of statistical and triblock copolymers were also achieved. Various terminal functionalities were successfully introduced by the end-capping reaction of propagating polysiloxanes using functional chlorosilanes. In this system, even non-dehydrated solvents are usable for the polymerization.

As featured in:

Organocatalytic controlled/living ring-opening polymerization of cyclotrisiloxanes initiated by water with strong organic base catalysts†

Keita Fuchise,* Masayasu Igarashi, Kazuhiko Sato* and Shigeru Shimada*†

Organocatalytic controlled/living ring-opening polymerization of cyclotrisiloxanes, such as hexamethyldicyclotrisiloxane, 1,3,5-trimethyl-1,3,5-triphénylcyclotrisiloxane, 1,3,5-trimethyl-1,3,5-trivinylcyclotrisiloxane, and 1,3,5-trimethyl-1,3,5-tris(3,3,3-trifluoropropyl)cyclotrisiloxane, using water as an initiator and strong organic bases, such as amidines, guanidines, phosphazene bases, and proazaphosphatrane, as catalysts produced a variety of polysiloxanes with controlled number-average molecular weights ($M_n = 2.64–102.3 \text{ kg mol}^{-1}$), narrow polydispersity ($D = 1.03–1.16$), and well-defined symmetric structures. Controlled syntheses of statistical copolymers and triblock copolymers were achieved by copolymerizations of two cyclotrisiloxanes. Various terminal functionalities were successfully introduced by the end-capping reaction of propagating polysiloxanes using functional chlorosilanes. Kinetic investigations demonstrated that the polymerization proceeded through the initiator/chain-end activation mechanism, namely activations of water in the initiation reaction and of terminal silanols in propagating polysiloxanes in the propagation reaction. Catalytic activities of strong organic bases were revealed to depend on their Brønsted basicity and efficiency of the proton transfer in the initiation and propagation reactions. Guanidines possessing an $R-N=C(N)-NH-R'$ unit, in particular 1,3-trimethylene-2-propylguanidine, showed excellent performance as a catalyst. In this system, even non-dehydrated solvents are usable for the polymerization.

Introduction

Polysiloxanes are major components of organosilicon materials that have a wide range of applications including lubricants, insulating and coating materials, sealants, adhesives in the form of oil, rubber, gel, and resin due to their excellent chemical and physical properties.† Precise control of the linear, branched, and cross-linked structure of polysiloxanes is difficult, but would be essential for preparing the next generation of organosilicon materials with much superior properties. The linear polysiloxanes are industrially synthesized by (1) hydrolysis and simultaneous polycondensation of dichlorosilanes or dialkoxysilanes or (2) ring-opening polymerization (ROP) of cyclopolysiloxanes, in particular cyclopolysiloxanes, using acidic species as catalysts or hydroxide salts as initiators, although the molecular weight distribution of the products becomes broad and the formation of cyclic oligomers as by-products are unavoidable.‡ Anionic ROP of cyclotrisiloxanes initiated by lithium compounds, such as organolithiums and lithium silanolates, has been the sole method to synthesize polysiloxanes and their copolymers with narrow molecular weight distributions and well-defined structures. However, the biggest drawback of this method is that highly purified and dried starting materials must be used to avoid undesired side reactions, such as termination, backbiting, and chain-transfer reactions. The synthetic difficulty of polysiloxanes with a controlled structure has been a hurdle to actively employ them for developing organosilicon materials.

In the field of polymer science, there has been continuous motivation to develop controlled polymerization that can be conducted with simple starting materials and procedures. Organocatalytic polymerization has been studied over the last decades to realize it. In particular, organocatalytic ROP of cyclic monomers, such as lactones, cyclic carbonates, epoxides, and cyclic phosphoesters, has been studied using organic acids, such as sulfonic acids, bis(sulfonylimides), and phosphoric acids, as well as organic bases, such as amines, amidines, guanidines, phosphazene bases, proazaphosphatrane, cyclopropenimines, and $N$-heterocyclic carbenes (NHC), as catalysts. Many of them proceed in a controlled/living fashion...
and have been extensively applied to controlled synthesis of various well-defined polymers, including end-functionalized polymers, block copolymers, and star-shaped polymers. The success of the organocatalytic ROP inspired us to apply it to cyclooligosiloxanes and develop a convenient method to synthesize various polysiloxanes with well-defined structures.

ROP of cyclooligosiloxanes has been attempted with organic acids and bases as catalysts. Regarding acidic catalysts, HOSO₂CF₃, HB(C₆F₅)₃, and B(C₆F₅)₃ (ref. 27,28) have been used for ROP of hexamethylcyclotrisiloxane (D₃(Me₂)) using 1-tert-butyl-4,4,4-tris(dimethylamino)-2,2-bis[tris(dimethylamino)phosphoranylidenamino]-2α,4α,5,7α-tetramethyl-1,3,5,7-tetraphenylcyclotetrasiloxane (D₄(Me,Ph)). However, none of them produced poly(dimethylsiloxane) (PDMS) with a narrow molecular weight distribution. For the basic catalysts, only those with quite high Brønsted basicity, such as phosphazene bases, NHCs, and bicyclic guanidines, have been employed. Möller and coworkers were the first to employ an electronically neutral strong organic base. They reported a polymerization of octamethylcyclotetrasiloxane (D₄(Me₂)) using 1-tert-butyl-4,4,4-tris(dimethylamino)-2,2-bis[tris(dimethylamino)phosphoranylidenamino]-2α,4α,5,7α-tetramethyl-1,3,5,7-tetraphenylcyclotetrasiloxane (D₄(Me,Ph)) using tBu-P₄ as a catalyst and methanol as an initiator. The polymerization was very rapid and the resulting PDMS had a very high number-average molecular weight (Mₙ) up to 440 kg mol⁻¹, although polydispersity (D) was broad, 1.7–1.9. Hupfeld and Taylor also reported that a polymerization of D₄(Me₂) using tBu-P₄ as a catalyst almost immediately produced PDMS with Mₙ of up to 4 × 10⁶ kg mol⁻¹ with D of 1.5–1.9. However, only a few examples of controlled/living ROP of cyclooligosiloxanes have been reported. Baceiredo and colleagues reported ROP of D₃(Me₂) using NHCs, such as 1,3-dicyclohexylimidazol-2-ylidine and 1,3-di-tert-butyl-4,5-dimethylimidazol-2-ylidine, as catalysts and alcohols as initiators to give PDMS with high D of 1.5–1.7. Waymouth and Hedrick and coworkers reported the only example that succeeded in obtaining PDMS with narrow D (<1.2) by organocatalytic ROP of D₃(Me₂). They used 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) as a catalyst and 4-pyrenebutan-1-ol as an initiator, although spectral and chromatographic data of the products were not provided. Thus, controlled synthesis of polysiloxanes by organocatalytic polymerization has not been well established. We considered that an appropriate choice of a catalyst and an initiator is the key to develop a controlled/living ROP of cyclooligosiloxanes. The acidity/basicity of the catalyst should not be too high to avoid side reactions, such as main chain scission and condensation of propagating polysiloxanes, that affect Mₙ, D, and terminal structures of resulting polysiloxanes. Furthermore, an initiation reaction between a cyclooligosiloxane and an initiator should generate propagating polysiloxanes with a sufficiently stable terminal structure at a sufficiently fast rate in comparison with a propagation reaction.

We herein report a controlled/living ROP of cyclooligosiloxanes using water as an initiator, strong organic bases as catalysts, and organochlorosilanes as end-capping agents. As shown in Scheme 1, the developed system is capable of polymerizing various cyclooligosiloxanes in a controlled/living fashion and producing a variety of (telechelic) polysiloxanes with controlled Mₙ, narrow molecular weight distributions, and well-defined symmetric structure, which are difficult to obtain by the conventional anionic ROP using lithium compounds as initiators. This new polymerization method has a further advantage that non-dehydrated solvents can be used to give well-defined polysiloxanes.

Results and discussion
Optimization of catalyst for the polymerization of D₃(Me₂)

We found that water initiates a polymerization of D₃(Me₂) in the presence of strong organic bases acting as catalysts to give

Scheme 1 | Ring-opening polymerization (ROP) of cyclooligosiloxanes using water as an initiator and strong organic bases as catalysts.
PDMS with narrow molecular weight distributions. We first optimized the catalysts for the polymerization by testing the catalytic activity of various strong organic bases with different Bronsted basicity and structural classes. The strong organic bases tested in this study were classified into the following four categories. Amides/guanidines A are amides and guanidines with no hydrogen atoms on their amino groups, such as 1,1,3,3-tetramethylguanidine (TMGa),39 1,5-diazabicyclo[4.3.0]non-5-ene (DBN),39 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU),39 and 7-methyl-1,5,7-triazacyclo[4.4.0]dec-5-ene (MTBD).39,40 Guanidines B are guanidines with an R-N=C(N)-NH-R’ unit, such as 1,5,7-triazacyclo[4.3.0]-non-6-ene (TBN)39 and TBD.39,40 Phosphazene bases include 2-tert-butylylimino-2-diethylamino-1,3-dimethylperhydro-1,3,2-diazaphosphorine (BEMP),39 tert-butylylimino-tri(pyrroldino) phosphorane (tBu-P1(pyr)),39 and 1-ethyl-2,2,4,4,4-pentakais(di-methylamino)-2,5,5′,4′,4′-catenadi(phosphazene) (Et-P2).39 As proazaphosphoranes, only 2,8,9-trisobutyl-2,5,8,9-tetraaza-1-phosphacyclo[3.3.3]undecane (TIBP)39 was employed. The Bronsted basicity of the bases in MeCN (McCNpK_BH) are shown in Scheme 1 and Table 1.

The catalytic activity of the bases was determined from the apparent rate coefficients of propagation (k app, h⁻¹) observed in the polymerizations in tetrahydrofuran (THF) at 30 °C under the conditions of [D(Me2)3]0 = 1.80 mol L⁻¹ and [McCNpK_BH]0/[H2O]0/[C (catalyst)]0 = 10/1/0.005 for Et-P2 and TIBP, 10/1/0.007 for TBD, and 10/1/0.10 for other bases. The polymerization was initiated by adding a stock solution of water in THF and that of TBD, and 10/1/0.005 for Et-P2 and TIBP, 10/1/0.007 for TBD, and 10/1/0.10 for other bases. The polymerization was carried out under the conditions of [D(Me2)3]0 = 1.80 mol L⁻¹ and [McCNpK_BH]0/[H2O]0/[C (catalyst)]0 = 10/1/0.005 for Et-P2 and TIBP, 10/1/0.007 for TBD, and 10/1/0.10 for other bases. The polymerization was initiated by adding a stock solution of water in THF and that of the catalysts in dry THF to a solution of D3(Me2) in dry THF in this order. A linear relationship between the polymerization time, t (h), and −ln(1 − c), where c is monomer conversion, was observed in the first-order kinetic plot of each polymerization. According to the eqn (1), the k app values were determined from the slope observed in the plots.

\[-\ln(1 - c) = k_{app}t\]  

(1)

The observed k app values were normalized to k app [([H2O]0/[C (catalyst)]0), as listed in Table 1 to directly compare k app values observed in the polymerizations using different amounts of the catalysts. This conversion should be rational, since we confirmed an almost linear relationship of k app with the initial molar ratio of the catalyst and water, [C (catalyst)]0/[H2O]0, as discussed in the next section (see Fig. 5).

Fig. 1 shows the dependence of log(k app) values on McCNpK_BH of strong organic bases. McCNpK_BH instead of those in THF can be used for the discussion, since Leito’s group has reported that McCNpK_BH values in MeCN and THF have a good linear correlation.41–43 The catalytic activity of an organic base per its Bronsted basicity, k app/10 McCNpK_BH, increased in the following order: TBD < phosphazene bases < guanidines/amidines A < guanidines B, which indicated that McCNpK_BH values of the catalysts were not the only single factor that affected the rates of polymerization. Interestingly, the amidines/guanidines A and the phosphazene bases independently showed linear relationships between log(k app) and their McCNpK_BH.

Among the phosphazene bases and TBD with McCNpK_BH values of 27.5–33.5 (Table 1, entries 11–14), Et-P2 (1.1 × 10⁻¹ h⁻¹) and TBD (5.2 × 10⁻² h⁻¹) showed significantly higher catalytic activity than the other bases due to their very high Bronsted basicity. On the other hand, BEMP (0.14 h⁻¹) and tBu-P1(pyr) (0.60 h⁻¹) showed catalytic activities that were only comparable to MTBD (0.29 h⁻¹) and TBN (0.16 h⁻¹), which have more than 100 times weaker Bronsted basicity. The very high Bronsted basicity of the phosphazene bases and TBD caused the frequent occurrence of undesired side reactions (vide infra), in particular, in the polymerizations catalyzed by Et-P2 and tBu-P1(pyr), which made these bases unfavorable for controlling the polymerization as can be seen from the D of the products in each polymerization.

Regarding the amidines/guanidines A with McCNpK_BH values of 23–25.5 (Table 1, entries 1–4), TMGa (0.0026 h⁻¹), DBN

<table>
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<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>McCNpK_BH</th>
<th>k app, b (h⁻¹)</th>
<th>D of the product (Conv. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>TMGa</td>
<td>23.3</td>
<td>0.0026</td>
<td>1.08 (50.7)</td>
</tr>
<tr>
<td>2</td>
<td>DBN</td>
<td>23.79</td>
<td>0.019</td>
<td>1.10 (98.5)</td>
</tr>
<tr>
<td>3</td>
<td>DBU</td>
<td>24.34</td>
<td>0.039</td>
<td>1.11 (99.1)</td>
</tr>
<tr>
<td>4</td>
<td>MTBD</td>
<td>25.43</td>
<td>0.29</td>
<td>1.11 (99.6)</td>
</tr>
<tr>
<td>5</td>
<td>TBO</td>
<td></td>
<td>0.0036</td>
<td>n.d.</td>
</tr>
<tr>
<td>6</td>
<td>TMGb</td>
<td></td>
<td>0.093</td>
<td>1.13 (99.3)</td>
</tr>
<tr>
<td>7</td>
<td>TBN</td>
<td>24.55</td>
<td>0.16</td>
<td>1.11 (99.9)</td>
</tr>
<tr>
<td>8</td>
<td>TMIPG</td>
<td></td>
<td>0.17</td>
<td>1.11 (99.5)</td>
</tr>
<tr>
<td>9</td>
<td>TmnPg</td>
<td></td>
<td>0.26</td>
<td>1.11 (98.0)</td>
</tr>
<tr>
<td>10</td>
<td>TBD</td>
<td>25.96</td>
<td>6.3</td>
<td>1.12 (99.1)</td>
</tr>
<tr>
<td>11</td>
<td>BEMP</td>
<td>27.58</td>
<td>0.14</td>
<td>1.14 (99.2)</td>
</tr>
<tr>
<td>12</td>
<td>tBu-P1(pyr)</td>
<td>28.35</td>
<td>0.60</td>
<td>1.23 (99.5)</td>
</tr>
<tr>
<td>13</td>
<td>Et-P2</td>
<td>32.94</td>
<td>1.1 × 10⁻¹</td>
<td>1.22 (99.8)</td>
</tr>
<tr>
<td>14</td>
<td>TIBP</td>
<td>33.33</td>
<td>5.2 × 10⁻¹</td>
<td>1.13 (99.9)</td>
</tr>
</tbody>
</table>

* The polymerizations were carried out under the conditions of [D(Me2)3]0 = 1.80 mol L⁻¹ and [McCNpK_BH]0/[H2O]0/[C (catalyst)]0 = 10/1/0.005 for Et-P2 and TIBP, 10/1/0.007 for TBD, and 10/1/0.10 for other bases.
* Calculated with k app = k app [H2O]0/[C (catalyst)]0.  "D" of the obtained PDMS at the indicated conversion of monomer.  "Not reported." Not determined.
(0.019 h⁻¹), DBU (0.039 h⁻¹), and MTBD (0.29 h⁻¹), showed only low catalytic activity, although undesired side reactions almost never occurred within the observed time range. In contrast, the guanidines B with MeCN values of 24.5–26 (Table 1, entries 7 and 10), such as TBD (6.3 h⁻¹) and TBN (0.16 h⁻¹), showed much higher k_app/10^10(MeCN) than the amidines/guanidines A as shown in Fig. 1, even though their structures and Bronsted basicity were not very different. For example, TBD showed 22 times higher catalytic activity than MTBD, although its Bronsted basicity was only around 3.4 times stronger than TBD. This high catalytic activity of the guanidines B may have originated from the R–N=1(N)=NH–R' unit that enables high efficiency of the initiation and propagation reactions as described in the section regarding the mechanism (see Scheme 3).

We hence evaluated the catalytic activity of four more guanidines B of which \( k_{\text{BH}} \) values have not been reported, such as 1,4,6-triazabicyclo[3.3.0]oct-4-ene (TBO), 1,1,2,3-tetramethylguanidine (TMGb), 1,3-trimethylene-2-isopropylguanidine (TMiPG), and 1,3-trimethylene-2-propylguanidine (TMnPG), since undesired side reactions rather frequently occurred in the polymerizations catalyzed by TBD and TBN. TMGb and TMiPG were newly synthesized in this study. TBO (0.0036 h⁻¹), a bicyclic guanidine with two five-membered rings, showed much lower catalytic activity than TBD and TBN, presumably due to its much lower Bronsted basicity than TBD and TBN. 44 TMGb (0.093 h⁻¹), an acyclic tetramethylguanidine with an R–N=1(N)=NH–R' unit, showed 36 times higher catalytic activity than TMGa. The replacement of an H–N=1(N)=NMMe₂ unit of TMGa with an Me–N=1(N)=NH–Me unit certainly contributed to the increase in the catalytic activity. TMiPG (1.7 h⁻¹) and TMnPG (2.6 h⁻¹), monocyclic guanidines with a six-membered ring and the same number of carbon atoms as TBD, showed high catalytic activity next to TBD. The Bronsted basicity of TMnP was reported to be at least higher than TBN in CD3OD/D2O at 8/2 (w/w). 44 TMiPG showed a slightly lower catalytic activity than TMnP presumably because of the higher steric hindrance of the isopropyl group than that of the propyl group. It is noteworthy that the undesired side reactions were much less frequent in the polymerization catalyzed by TMiPG and TMnP in comparison with that catalyzed by other bases with comparable catalytic activity. Hence, we identified TMnP as the most suitable catalyst for the polymerization of cyclosiloxanes initiated by water.

**Characteristics of the polymerization of D₃(1-Me₂) using water and TMnP**

TmnPG catalyzed a polymerization of \( \text{D₃(1-Me₂)} \) in THF at 30 °C under the conditions of \([\text{D₃(1-Me₂)}]_0/[\text{H₂O}]_0/[\text{TMnP}]_0 = 10/1/0.10 \) and \([\text{D₃(1-Me₂)}]_0 = 1.80 \text{ mol L}^{-1} \) to give \( \text{PDMS-(OH)₂} \) \( \text{PDMS-(OH)₂} \) with \( M_n \) estimated by M NMR measurement \((M_n,\text{NMR}) \) of 2.64 kg mol⁻¹ and \( D \) of 1.14 (Table 2, entry 1). The observed \( M_n,\text{NMR} \) corresponded well to the \( M_n \) calculated from the polymerization conditions \((M_n,\text{calc}) \) of 2.20 kg mol⁻¹. The conversion of monomer reached 98.0% after 90 min of polymerization. The purification of the product was easily achieved by neutralizing TMnP with an excess amount of benzoic acid and by washing the concentrated oily crude product with acetone (MeCN). 44 Removal of the MeCN layer with a pipette and drying the residue under vacuum gave pure \( \text{PDMS-(OH)₂} \) as a colorless viscous liquid. End-capping of the propagating PDMS-(OH)₂ was achieved by directly adding pyridine (8 equiv.) and chloromethyl(phenyl)silane (Me₂PhSiCl, 5

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**Fig. 2** SEC chromatograms of the PDMS-(OH)₂ \((M_n,\text{NMR} = 2.64 \text{ kg mol}^{-1}, D = 1.14) \) and the PDMS-(OSiMe₂Ph)₂ \((M_n,\text{NMR} = 3.17 \text{ kg mol}^{-1}, D = 1.11) \) synthesized in THF at 30 °C under the conditions of \([\text{D₃(1-Me₂)}]_0/[\text{H₂O}]_0/[\text{TMnP}]_0 = 10/1/0.10 \) and \([\text{D₃(1-Me₂)}]_0 = 1.80 \text{ mol L}^{-1} \) (Table 2, entry 1).

**Fig. 3** ¹H and ²⁹Si{¹H} NMR spectra of the synthesized PDMSs (Table 2, entry 1) in CDCl₃: (a) ¹H NMR spectrum of PDMS-(OH)₂, (b) ¹H NMR spectrum of PDMS-(OSiMe₂Ph)₂, (c) ²⁹Si{¹H} NMR spectrum of PDMS-(OH)₂, (d) ²⁹Si{¹H} NMR spectrum of PDMS-(OSiMe₂Ph)₂.
Table 2: Polymerizations of D₃(Me₂) initiated by water and catalyzed by TMnPG at 30 °C

<table>
<thead>
<tr>
<th>Entry</th>
<th>[D₃(Me₂)]₀/[H₂O]₀/[C]₀</th>
<th>Solvent</th>
<th>End-capping agent</th>
<th>Time (h)</th>
<th>Conv (%)</th>
<th>Mₙ,NMR (kg mol⁻¹)</th>
<th>SEC</th>
<th>NMR</th>
<th>D</th>
<th>k_app (h⁻¹)</th>
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<td>1</td>
<td>10/1/0.10</td>
<td>THF</td>
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<td>98.0</td>
<td>2.20</td>
<td>1.66</td>
<td>2.64</td>
<td>1.14</td>
<td>2.6</td>
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<td>2</td>
<td>10/1/0.05</td>
<td>THF</td>
<td>Me₂PhSiCl</td>
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<td>98.1</td>
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<td>2.83</td>
<td>1.13</td>
<td>1.3</td>
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<tr>
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<td>10/1/0.01</td>
<td>DMAc/THF = 57/43</td>
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<td>98.6</td>
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<td>0.83</td>
<td>2.81</td>
<td>1.33</td>
<td>8.2</td>
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<td>10/1/0.10</td>
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<td>98.6</td>
<td>2.21</td>
<td>1.80</td>
<td>2.70</td>
<td>1.12</td>
<td>4.6</td>
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<td>CH₂Cl₂/THF = 84/16</td>
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<td>5.70</td>
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<td>50/1/0.50</td>
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<td>93.8</td>
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<td>100/1/1.0</td>
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<td>97.3</td>
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<td>15.6</td>
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<td>102.3</td>
<td>1.03</td>
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<td>2.95</td>
<td>1.15</td>
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<td>2.39</td>
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</tr>
<tr>
<td>12</td>
<td>10/1/0.10</td>
<td>CH₂Cl₂/THF = 57/43</td>
<td>AllylMe₃SiCl</td>
<td>1</td>
<td>99.5</td>
<td>2.42</td>
<td>1.67</td>
<td>2.77</td>
<td>1.13</td>
<td></td>
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<tr>
<td>13</td>
<td>10/1/0.10</td>
<td>CH₂Cl₂/THF = 57/43</td>
<td>(ClCH₂)₂Me₃SiCl</td>
<td>1</td>
<td>99.5</td>
<td>2.44</td>
<td>1.84</td>
<td>3.14</td>
<td>1.10</td>
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<tr>
<td>14</td>
<td>10/1/0.10</td>
<td>CH₂Cl₂/THF = 57/43</td>
<td>(BrCH₂)Me₃SiCl</td>
<td>1</td>
<td>98.8</td>
<td>2.52</td>
<td>1.71</td>
<td>3.18</td>
<td>1.13</td>
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<tr>
<td>15</td>
<td>10/1/0.10</td>
<td>CH₂Cl₂/THF = 57/43</td>
<td>Me₃(C₆F₅)₂SiCl</td>
<td>1</td>
<td>99.3</td>
<td>2.68</td>
<td>1.72</td>
<td>3.38</td>
<td>1.13</td>
<td></td>
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<tr>
<td>16</td>
<td>10/1/0.10</td>
<td>CH₂Cl₂/THF = 57/43</td>
<td>(EtO)₂Me₃SiCl</td>
<td>1</td>
<td>99.5</td>
<td>2.57</td>
<td>1.84</td>
<td>3.25</td>
<td>1.11</td>
<td></td>
</tr>
</tbody>
</table>

* [D₃(Me₂)]₀ = 1.80 mol L⁻¹. ² Volume ratios of two solvents are shown for the mixed solvents. ³ Determined by ¹H NMR. ⁴ Calculated from $M_{n,calcd} = \frac{[D₃(Me₂)]₀[H₂O]₀}[[TMnPG]₀] × Conv. × (MW. of $D₃(Me₂)$) = 222.46 + (MW. of terminal structures). ⁵ Determined by SEC measurements in THF using polystyrene standards.

equiv.) to the reaction mixture at 30 °C and continuing the reaction for 15 min. The purification of the end-capped product (PDMS-(OSiMe₂Ph)₂), was also easily achieved by washing the concentrated crude product with methanol or MeCN. The $M_{n,NMR}$ and $D$ of the obtained PDMS-(OSiMe₂Ph)₂ were determined to be 3.17 kg mol⁻¹ and 1.11, respectively. The end-capping reaction hence did not affect the $D$ of the original product. Fig. 2 shows the molecular weight distribution of the products measured by the size-exclusion chromatography (SEC) using THF as an eluent and polystyrene as calibration standards.

The well-defined structures of the obtained PDMS-(OH)₂ and PDMS-(OSiMe₂Ph)₂ were proven by ¹H and ²⁹Si{¹H} NMR analysis as shown in Fig. 3. In each spectrum, signals due to the terminal groups and several monomeric units from the termini were separately observed from that due to the inner repeating units. In both ¹H and ²⁹Si{¹H} NMR spectra of the PDMS-(OSiMe₂Ph)₂, the signals due to the PDMS-(OH)₂ were not observed, which evidenced the quantitative end-capping of the PDMS-(OH)₂.

Structures of the obtained PDMS-(OH)₂ and PDMS-(OSiMe₂Ph)₂ were further analyzed by positive ion matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) using trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) as a matrix and sodium trifluoroacetate as a cationization agent. Only one series of peaks was observed in both of the spectra shown in Fig. 4, which indicated that the obtained PDMS-(OH)₂ and PDMS-(OSiMe₂Ph)₂ consisted of only linear PDMS with two terminal hydroxy groups and two terminal dimethyl(phenyl)siloxy groups, respectively. The $m/z$ values of the observed molecular ion peaks corresponded to the calculated molar mass of PDMS-(OH)₂ and PDMS-(OSiMe₂Ph)₂ cationized by a sodium cation. Interestingly, the obtained PDMSs contained PDMSs of which the degree of polymerization was not a multiple of 3, although those PDMSs should not be produced if only a simple ring-opening reaction of D₃(Me₂) occurred in the polymerization. This point will be discussed in a later section regarding the mechanism of the polymerization.

As already mentioned in the previous section, a linear relationship was observed in the first-order kinetic plot of the polymerizations carried out with [D₃(Me₂)]₀/[H₂O]₀/[TMnPG]₀ = 10/1/0.10 and 10/1/0.05 (Table 2, entries 1 and 2) as shown in Fig. 5a. The $k_{app}$ for the former and the latter polymerizations were determined to be 2.6 and 1.3, which suggested that the $k_{app}$ varies linearly with the initial ratio of the catalyst and water, i.e., $[C]₀/[H₂O]₀$.

Fig. 5b shows the dependence of $M_{n,NMR}$ and $D$ on monomer conversion (c). In both of the polymerizations, $M_{n,NMR}$ increased linearly as $c$ increased, while $D$ remained in a range of 1.08–1.14 even until the late stage of polymerization. It was hence found that the propagation reaction was the dominant process in the polymerizations and undesired side reactions were not frequent.
controlled/living polymerizations of cyclotrisiloxanes other than D₃[Me₂] were also achieved using water as an initiator and TMnPG.
as a catalyst, 1,3,5-Trimethyl-1,3,5-triphenylcyclotrisiloxane (D(Me,Ph))
(D(Me,Ph)), cis/trans = 24/76), 1,3,5-trimethyl-1,3,5-trivinylcyclotrisiloxane (D(Me,Vi),
cis/trans = 23/77), and 1,3,5-trimethyl-1,3,5-tris(3,3,3-trifluoropropyl)cyclotrisiloxane
(D(Me,TFPr), cis/trans = 20/80) were polymerized in a mixed solvent of CH2Cl2 and THF at 30 °C
under the conditions of [M]0/[H2O]0 = 10/1 and [M]0 = 1.80 mol L−1. Chloro-
tritylethylsilane (Et3SiCl) was used as an end-capping agent for the polymerization of D(Me,Ph),
while Me2PhSiCl was used for the polymerizations of D(Me,Vi) and D(Me,TFPr) to give well-
defined PMPs, poly[methyl(vinyl)siloxane] (PMVS), and poly[
methylyl(3,3,3-trifluoropropyl)siloxane] (PMTFPS) with Mw,NMR (Đ) of 5.60 kg mol−1 (1.16),
3.64 kg mol−1 (1.11), and 6.00 kg mol−1 (1.12), respectively (Table 3, entries 1, 3, and 5).
Table 3
Water-initiated ROP of various cycloolsilosiloxanes catalyzed by TMnP in CH2Cl2/THF at 30 °C

<table>
<thead>
<tr>
<th>Entry</th>
<th>Monomer</th>
<th>[M]0/[H2O]0</th>
<th>CH2Cl2/THF (v/v)</th>
<th>End-capping</th>
<th>Time (min)</th>
<th>Conv.a,b (%)</th>
<th>Calc.e</th>
<th>SEC.d</th>
<th>NMR a</th>
<th>Đ d</th>
<th>k_p,app [ = k_p,app[H2O]0/(10[Ci]0)]</th>
<th>k_p,app [h−1]</th>
<th>k_p,app [h−1]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>D(Me,Ph)</td>
<td>10/1/0.01</td>
<td>57/43</td>
<td>Et3SiCl</td>
<td>219</td>
<td>92.4</td>
<td>4.02</td>
<td>4.39</td>
<td>5.60</td>
<td>1.16</td>
<td>1.2f</td>
<td>17</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>D(Me,Ph)</td>
<td>30/1/0.03</td>
<td>79/21</td>
<td>Et3SiCl</td>
<td>240</td>
<td>83.3</td>
<td>10.5</td>
<td>5.04</td>
<td>9.92</td>
<td>1.15</td>
<td>1.0f</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>D(Me,Vi)</td>
<td>10/1/0.01</td>
<td>57/43</td>
<td>Me2PhSiCl</td>
<td>72</td>
<td>95.5</td>
<td>2.76</td>
<td>2.73</td>
<td>3.64</td>
<td>1.11</td>
<td>3.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>D(Me,Vi)</td>
<td>30/1/0.03</td>
<td>79/21</td>
<td>Me2PhSiCl</td>
<td>51</td>
<td>80.6</td>
<td>2.76</td>
<td>2.73</td>
<td>3.64</td>
<td>1.11</td>
<td>3.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>D(Me,TFPr)</td>
<td>10/1/0.004</td>
<td>70/30</td>
<td>Me2PhSiCl</td>
<td>40</td>
<td>92.8</td>
<td>6.65</td>
<td>5.28</td>
<td>5.68</td>
<td>1.15</td>
<td>2.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>D(Me,TFPr)</td>
<td>30/1/0.012</td>
<td>88/12</td>
<td>Me2PhSiCl</td>
<td>100</td>
<td>94.2</td>
<td>4.63</td>
<td>2.94</td>
<td>6.00</td>
<td>1.12</td>
<td>3.9f</td>
<td>99</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>D(Me,Vi)</td>
<td>7.5/1/0.10</td>
<td>65/35</td>
<td>None</td>
<td>1500</td>
<td>10.6</td>
<td>0.16</td>
<td>n.d.</td>
<td>n.d.</td>
<td>1.13</td>
<td>1.7</td>
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<tr>
<td>8</td>
<td>D(Me,Vi)</td>
<td>7.5/1/0.01</td>
<td>57/43</td>
<td>None</td>
<td>1500</td>
<td>10.6</td>
<td>0.29</td>
<td>n.d.</td>
<td>n.d.</td>
<td>1.13</td>
<td>1.7</td>
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<tr>
<td>9</td>
<td>D(Me,Vi)</td>
<td>6/1/0.10</td>
<td>65/35</td>
<td>None</td>
<td>1500</td>
<td>1.5</td>
<td>0.031</td>
<td>n.d.</td>
<td>n.d.</td>
<td>1.13</td>
<td>1.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>D(Me,Vi) + D(Me,Vi)</td>
<td>25 + 8/1/0.05</td>
<td>70/30</td>
<td>Me2PhSiCl</td>
<td>540</td>
<td>64.9</td>
<td>6.02</td>
<td>4.68</td>
<td>6.34</td>
<td>1.13</td>
<td>1.13</td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>D(Me,Vi)</td>
<td>25/1/0.05</td>
<td>67/33</td>
<td>Me2PhSiCl</td>
<td>540</td>
<td>84.9</td>
<td>4.74</td>
<td>4.16</td>
<td>5.11</td>
<td>1.09</td>
<td>1.09</td>
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</tr>
<tr>
<td>12</td>
<td>D(Me,Vi)</td>
<td>25/1/0.25</td>
<td>84/16</td>
<td>Et3SiCl</td>
<td>60</td>
<td>92.7</td>
<td>5.17</td>
<td>4.48</td>
<td>5.89</td>
<td>1.08</td>
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</table>

Calculated from Mw,calcd = [M]0/[H2O]0 × (Conv. to polymer) × (MW. of monomer) + (MW. of terminal structures). Determined by SEC measurements in THF using polystyrene standards. Not determined. \( a \) Determined by 1H NMR. \( b \) Mol% of the monomer converted to the corresponding polysiloxanes and cyclotetrasiloxanes. \( c \) Determined by 29Si NMR. \( d \) Calculated from Equation (2). \( e \) Determined by 1H NMR. \( f \) Determined by NMR. \( g \) Calculated from Equation (2).
NMR analysis (Fig. S19) on D(Me2)D(Me2)D(Me2)/D(Me2)D(Me2)D(Me,Vi)/D(Me,Vi)D(Me2)D(Me,Vi) monomeric sequences in the obtained copolymer were determined to be 6.34 kg mol⁻¹ and 1.13, respectively. ²⁵Si¹H NMR analysis revealed that the molar ratios of the triad monomeric sequences in the obtained copolymer were D(Me2)D(Me2)D(Me2)/D(Me2)D(Me,Vi)/D(Me,Vi)D(Me2)D(Me,Vi) = 71/29/0 and D(Me,Vi)D(Me,Vi)D(Me,Vi)/D(Me,Vi)D(Me,Vi)D(Me,Vi) = 43/44/13, and the terminal monomeric unit of the product was D(Me2) as shown in Fig. S20.† The monomeric sequence of the obtained copolymer was visualized based on the population of the triad monomeric sequences, n(D(Me2))/n(D(Me,Vi)), and D as shown in Fig. S21,† which indicated the almost segregated presence of D(Me2)D(Me2) and D(Me,Vi)D(Me,Vi) units. In contrast, copolymerization of D(Me2) and D(Me,Vi) by adding TMnPG to a premixed solution of the two monomers resulted in a rapid and preferential polymerization of D(Me,Vi) followed by a slow polymerization of D(Me2) as previously observed in a copolymerization of D(Me2) and D(Me,Vi) using n-butyllithium as an initiator.† The difference of each monomer consumption and the time-dependent SEC chromatogram changes are shown in Fig. S4 and S5,† respectively. The product was almost segregated copolymers of PMVS and PDMS with a broad molecular weight distribution as determined from Fig. S19 and S20.† A terminal methyl(vinyl)siloxane unit, Si(Me,Vi)-OH, generated from D(Me,Vi) preferentially reacted with D(Me,Vi) rather than D(Me2) presumably due to higher electrophilicity of the former than the latter. Besides, side reactions involved by the Si(Me,Vi)-OH were more frequent than those of a dimethylsiloxane unit, Si(Me₂)-OH, and caused the broadening of the molecular weight distribution.

Consecutive copolymerizations of D(Me2) and D(Me,Vi) (ref. 52,53) as well as D(Me2) and hexaphenylcyclotrisiloxane (D(Ph₃)₃)²⁴ gave triblock copolymers of PDMS and PMVS (PMVS-b-PDMS-b-PMVS, Table 3, entry 11) as well as PDMS and poly(diphenylsiloxane) (PDPS) (PDPS-b-PDMS-b-PDPS, Table 3, entry 12). The syntheses were successful even though homopolymerization of D(Ph₃)₃ using water and TMnPG was hard to control because of very low solubility of PDPS in common organic solvents.³⁴–³⁶ The polymerizations of D(Me2) were first carried out in CH₂Cl₂/THF at 30 °C under the conditions of [D(Me₂)]₀/[H₂O]₀/[TMnPG]₀ = 25/1/0.05 for the former and 25/1/0.25 for the latter. The polymerizations were further continued by adding 25 equiv. (with respect to the initial amount of water) of D(Me₂) or 7.5 equiv. Of D(Ph₃)₃ after 540 min or 75 min from the initiation of the first polymerization. SEC chromatograms of the obtained PDMS-(OH)₂, PMVS-b-PDMS-b-PMVS, and PDPS-b-PDMS-b-PDPS indicated that PDMS-(OH)₂ generated in the first polymerization quantitatively initiated the second polymerization as shown in Fig. 7. The products did not have a gradient structure between the segments of PDMS and PMVS as well as PDMS and PDPS as observed in the ²⁵Si¹H NMR spectra shown in Fig. S20 (ref. 57) and S22,†²²,³³–³⁵ although the conversions of D(Me2) in the first polymerization were not quantitative in both of the syntheses. This result indicated that D(Me2) almost did not react in the second stage of the polymerization due to very low reactivity of the propagating end of PMVS and PDPS against D(Me2). The obtained PDPS-b-PDMS-b-PDPS had a much narrower molecular weight distribution (D = 1.06) than those synthesized by the conventional anionic ROP using dithiium diphenylsilanediolate as an initiator (D = 1.4–1.8).²⁴ These successful block copolymerizations demonstrated the controlled/living nature of the ROP of cyclosiloxanes using water and strong organic bases.

**Mechanism of the polymerization**

It is worth discussing the mechanism of the polymerization catalyzed by the strong organic bases, since it has different characteristics compared to that of the conventional anionic ROP of cyclooligosiloxanes using hydroxide salts, organolithiums, and lithium silanolate as initiators. The structure of the propagating end in the former is a silanol, while that of the latter is a silanolate. Scheme 2 shows the possible elementary reactions in the ROP of cyclosiloxanes using water as an initiator and strong organic bases as catalysts. The polymerization is considered to proceed through the initiator/chain-end activation mechanism. (a) In the initiation reaction (Scheme 2a), a strong organic base first activates a water molecule. The ring-opening reaction of a cyclosiloxane occurs through the nucleophilic attack of the activated water at a silicon atom of a cyclosiloxane, followed by a proton transfer from the water to the cyclosiloxane to form a 1,5-dihydroxytrisiloxane. (b) The propagation reaction (Scheme 2b) proceeds through the activation of a terminal silanol group of a propagating polysiloxane by the strong organic base. The degree of polymerization of a propagating polysiloxane, n, increases by three after one propagation reaction. Kᵥ and Kₚ can be defined as the equilibrium constants for the activation of water and a terminal silanol, and kᵥ and kₚ can be defined as the rate coefficients for the ring-opening reaction of a monomer with the activated water and terminal silanol. The high catalytic activity of the...
guanidines B may have originated from the high efficiency of the proton transfer in the initiation and propagation reactions. The R-N=C(N)-NH-R’ unit in the guanidines B would simultaneously activate water or a silanol on a propagating polymer by the imino group and transfer the hydrogen atom on the amino group to an incoming monomer based on the ‘proton shuttling mechanism’ as depicted in Scheme 3a. In contrast, the bases in the other categories are incapable of ‘proton shuttling’ and need to directly transfer the hydrogen atom as depicted in Scheme 3b. \( K_p \) would increase as the acidity of the terminal silanol increases and the steric hindrance of the silanol decreases. \( k_p \) would increase as nucleophilicity of the activated silanol increases, electrophilicity of the monomer increases, and the steric hindrance of the silanol and the monomer decrease. (c) ‘Intermolecular transfer’ of a terminal hydroxsilyl group from one propagating polymer to another one (disproportionation) can be considered to occur by a nucleophilic attack of the activated terminal silanol to another terminal silanol (Scheme 2c). This reaction increases and decreases the degree of polymerization of the two propagating polymers by one and causes the formation of polysiloxanes, of which degree of polymerization is not a multiple of 3, as observed in Fig. 4. A model reaction using 1,5-dihydroxy-
1,1,3,3,5,5-hexamethyltrisiloxane (D\( \text{Me}_2 \)\( \text{OH} \)) and TMnPG produced a mixture of \( \alpha,\omega \)-dihydroxy-terminated per-
methyloigosiloxanes with different numbers of siloxy units in 6 min in THF at 30 °C under the conditions of [D\( \text{Me}_2 \)\( \text{OH} \)]/ [TMnPG] = 1/0.1 (Fig. S6†). Similar reactions, ‘intermolecular transfer’ of terminal lithium silanolates on PDMS\(^{14,59}\) as well as ‘disproportionation’ of hydroxy-terminated oligodimethylsilox-
anes\(^{60-62}\) have also been reported to occur in the conventional anionic ROP of D\( \text{Me}_2 \)\( \text{OH} \) as well as in a transformation of oligo-
siloxanol in the presence of a strong base. The intermolecular transfer is an allowable side reaction since it does not largely affect \( M_n \) and \( D \) of the resulting polysiloxanes. (d) Condensation (dimerization, Scheme 2d) also occurs during the polymerization by a similar mechanism to (c) as an undesired side reaction. As already mentioned, the condensation of two propagating polysiloxanes becomes pronounced, in particular in the late stage of polymerization, and causes increasing of \( D \) of the resulting polysiloxanes. It occurs much less frequently than (c). The similar tendency was observed in the disproportion-
ation of oligosiloxanol using phosphazenium hydroxide.\(^{62}\) (e) Backbiting (depolymerization, Scheme 2e) occurs by intra-
molecular nucleophilic attack of the activated terminal silanol of a propagating polymer to a silox unit in its inner repeating units. The backbiting produces cyclooligosiloxanes, such as

![Scheme 2 Possible elementary reactions in the polymerization of cyclotrisiloxane using water as an initiator and strong organic bases as catalysts.](image1.png)

![Scheme 3 Proposed mechanism for the ring-opening reaction of cyclotrisiloxanes catalyzed by strong organic bases.](image2.png)
cycloptetrasiloxane and cyclopentasiloxane, and reduces the degree of polymerization and yield of propagating polymers. On the other hand, (f) the intermolecular chain-transfer reaction (Scheme 2f), which is known to occur in a conventional anionic ROP of cyclotrisiloxane, did not occur at least in the polymerization of D1(Me2)2 catalyzed by TMnPG in THF at 30 °C, although it is a possible undesired side reaction. Trimmethylsiloxy-terminated PDMS was not produced in a model polymerization of D1(Me2)2 in the presence of dodecamethylpentasiloxane (see ESL, Fig. S7†). The difference in the chances of side reactions (e) and (f) would be originated from the fact that the silanol and the silicon atom to be attacked always closely present for the former. The terminal silicon atom bearing a hydroxy group would be sterically and electronically more susceptible to a nucleophilic attack than the silicon atoms in the inner repeating units, since a hydroxy group is less bulky and a stronger electron withdrawing group than a dialkylsiloxy group. The frequency of the side reactions increased in the following order: (e) < (d) < (c).

Although only the intramolecular condensation of a propagating polysiloxane can be considered as a possible termination reaction, we did not observe this process in any polymerizations that we conducted. Hence, the polymerization is characterized by the absence of termination reactions, which ensures the controlled/living nature of the polymerization. The total numbers of reactive hydroxy groups in water, which has ‘two’ hydroxyl groups, and propagating polysiloxanes do not change throughout the polymerization even when side reactions (c), (d), and (e) occur. The polymerization can be terminated only by neutralization of the catalyst or end-capping of propagating polymers.

Another possible polymerization mechanism is the ‘nucleophilic monomer activation mechanism’ that is based on the activation of the monomer by the nucleophilic attack of the catalyst. However, if so, (1) catalytic activity of the strong organic bases would not be linear to their Bronsted basicity as shown in Fig. 1, since the nucleophilicity (‘siliconphilicity’) of the bases and their basicity are independent as it was demonstrated in a condensation of a silanol and an organosilanes with a leaving group catalyzed by an organic base.

Effects of reaction conditions on kinetics of the polymerization

The plausibility of the proposed polymerization mechanism was confirmed by comparing a rate equation derived from the kinetics of the elementary reactions, eqn (1), with the experimentally obtained rate equation, eqn (2). The rate of propagation, r, can be expressed by the product of the rate coefficient of propagation, kP (L mol⁻¹ h⁻¹), the concentration of hydroxy groups activated by catalyst, [P*] (mol L⁻¹), and the concentration of unreacted monomer, [M] (mol L⁻¹), when both Kc and kT are comparable to or greater than Kf and kP.

\[
\frac{d[M]}{dt} = k_p[P^*][M]
\]

[**] is expressed by the product of the concentration of hydroxy groups not being activated, [P] (mol L⁻¹), the concentration of catalyst not interacting with hydroxy groups, [C] (mol L⁻¹), and the equilibrium constant for the activation of silanol groups by the catalyst, Kc (L mol⁻¹), i.e., [P*] = Kc[P][C], since Kc is defined as Kc = [P*]/[P][C]. [P*] is hence expressed by eqn (3) using the initial concentration of hydroxy groups, [P]0 (mol L⁻¹), the initial concentration of the catalyst, [C]0 (mol L⁻¹), since [P] = [P]0 – [P*] and [C] = [C]0 – [P*].

\[
[P^*] = K_c([P]_0 - [P^*])([C]_0 - [P^*])
\]

From the quadratic formula, [P*] is expressed by eqn (4) as the function of three constants, i.e., [P]0, [C]0, and Kc that varies depending on the catalyst, the temperature, and the solvent employed for a polymerization:

\[
[P^*] = K_c\left(\frac{[P]_0[C]_0 - [P]_0[P^*] - [C]_0[P^*] + [P^*]^2}{4\frac{[P]_0[C]_0}{[P]_0 - [P^*]}}\right)
\]

\[
0 = [P]_0[C]_0 - \left(\frac{[P]_0 + [C]_0 + \frac{1}{K_c}}{2}\right)^2 - [P^*]^2
\]

\[
[P^*] = \frac{1}{2}\left(\frac{[P]_0 + [C]_0 + \frac{1}{K_c}}{2} - \sqrt{\left(\frac{[P]_0 + [C]_0 + \frac{1}{K_c}}{2}\right)^2 - 4\frac{[P]_0[C]_0}{[P]_0 - [P^*]}}\right)
\]

The integration of eqn (2) gives eqn (5):

\[
-\ln(1 - c) = k_p[P^*]t
\]

which corresponds well with eqn (1) when kP,app is regarded as:

\[
k_p,app = k_p[P^*]
\]

Hence, the proposed mechanism for the polymerization shown in Scheme 2 were proven to be reasonable. The polymerization is considered to proceed through the initiator/chain-end activation mechanism.

Effects of reaction conditions on the kinetics of polymerization can be expected with eqn (4)–(6). Fig. 8a shows the expected dependence of kP,app on Kc and [C]0/[P]0 under the conditions of [M]0 = 1.80 mol L⁻¹ and [M]0/[P]0 = 5. The calculated kP,app was normalized by dividing it by the kP,app on [M]0/[P]0 = 1. It was found that kP,app is almost proportional to [C]0/[P]0 when [C]0/[P]0 ≤ 1 regardless of Kc, which corresponded to the results shown in Fig. 5. In contrast, the increase in kP,app with increasing [C]0/[P]0 depends on Kc when [C]0/[P]0 > 1 and its rate of change decreases with increasing Kc. Fig. 8b shows the expected dependence of kP,app on Kc and [M]0/[P]0 under the conditions of [M]0 = 1.80 mol L⁻¹ and [M]0/[C]0 = 100. The calculated 1/kP,app was normalized by multiplying it by the kP,app on [M]0/[P]0 = 5. It was found that kP,app is almost inversely proportional to [M]0/[P]0 when Kc is small, while kP,app only gradually decreases with increasing [M]0/[P]0 when Kc is large. Considering the values of kP,app observed in the polymerizations...
moisture content of the solvent is taken into account, since it has been considered ‘common sense’ that intensive dehydra-
tion and purification of reagents and solvents is essential for
conventional anionic ROP initiated by lithium compounds.
This new convenient method to synthesize well-defined poly-
siloxanes will enable the synthesis of organosilicon and
organic/inorganic hybrid materials with diverse architectures
and may lead to the development of new advanced materials
with improved properties.

Conflicts of interest
There are no conflicts to declare.

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