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Complete List of Authors:	Takashima, Rikito; Tokyo Institute of Technology, Aoki, Daisuke; Chiba University, Department of Applied Chemistry and Biotechnology, Faculty of Engineering Kuwata, Shigeki; Ritsumeikan University College of Life Sciences Graduate School of Life Sciences, Department of Applied Chemistry Otsuka, Hideyuki; Tokyo Institute of Technology, Department of Chemical Science and Engineering

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Ring–Chain Equilibria of Dynamic Macrocycles with a Bis(hindered amino)disulfide Linker

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Rikito Takashima,[a] Daisuke Aoki,*[b] Shigeki Kuwata,[c] and Hideyuki Otsuka*[a]

Entropy-driven ring-opening polymerization (ED-ROP) of macrocyclic monomers (MMs) facilitates simple and green processes derived from ring–chain equilibria; however, the preparation of MMs typically requires highly diluted conditions and catalysts, preventing a detailed investigation of equilibrium reactions and application potentials based on the dynamic nature of equilibrium reactions. We have previously reported simple ROP of macrocycles containing one bis(2,2,6,6-tetramethylpiperidin-1-yl)disulfide (BiTEMPS) structure as a dynamic unit. In this report, we investigate the effect of chain length on ring–chain equilibria to both reveal their dynamic equilibrium reactions and expand the availability of BiTEMPS-based MMs. Equilibrium reactions based on BiTEMPS are ideal for studying the dynamic nature of cyclic topology because 1) the radicals generated by BiTEMPS upon heating exhibit high tolerance to oxygen-based moieties and olefins and high reactivity in exchange reactions, and 2) catalysts and/or additives are not required to induce the dynamic state. We prepared linear precursors (LPs) with various chain lengths (*N*) between each BiTEMPS unit and characterized the cyclodepolymerization, i.e., ring–chain equilibria. We found that the yield of MMs clearly depends on *N* and the presence of distortions in some ring structures. This study provides important insights into ring–chain equilibria for entropy-driven ROP systems because our MMs are characterized by a well-defined structure, good stability at room temperature, high reactivity in high-temperature exchange reactions, and reversibility.

Introduction

The polymerization of cyclic and macrocyclic compounds with reactive sites *via* ring-opening polymerization (ROP)[1–6] has great potential for the synthesis of polymeric materials, having numerous benefits, such as recyclability, structural versatility, an absence of byproducts in the polymerization system, excellent processability, and easy operativity. Consequently, many libraries of polymerization chemistries in ROP have been developed.[7–21] Recently, the industrial value of ROP has become increasingly important from the sustainability viewpoint.

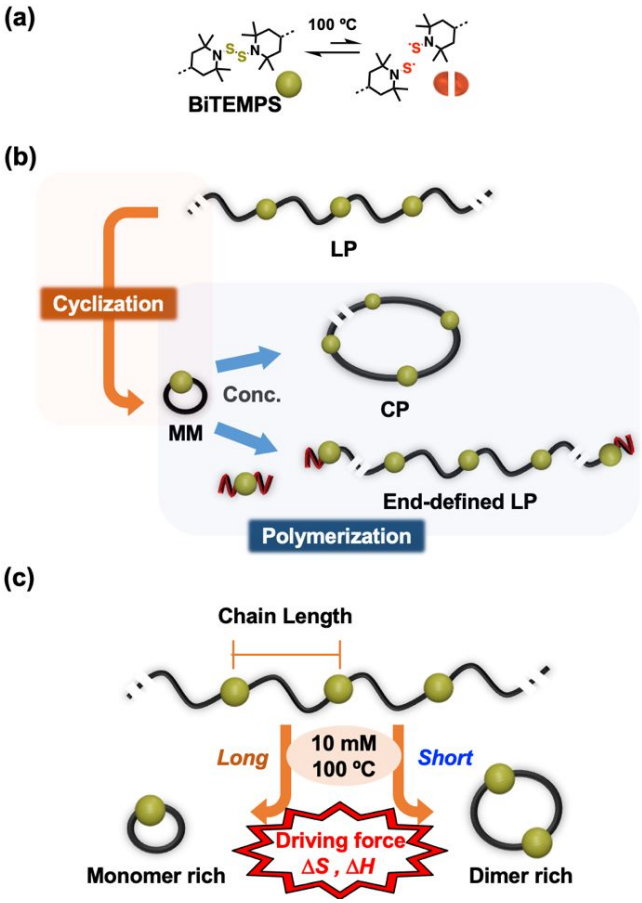
Ring strain is among the most important factors when designing ROP systems. The ROP of strained cyclic compounds is generally triggered by the release of ring-strain energy (RSE). Polymerization of strained lactone and cyclic alkenes is perhaps the best example of monomers for ROP. In contrast, many recent reports have described polymerization methods with unstrained large macrocycles, termed entropy-driven ROP (ED-ROP); such methods have significant advantages over conventional ROP due to their ring–chain equilibria:[22–26] (i) ED-ROP is characterized by polymerization and depolymerization processes that are facile because they can be controlled by thermodynamic equilibria, and (ii) ED-ROP can reduce byproducts during the polymerization process due to its low amount of eliminated products. For example, Zhu et al. isolated a macrocycle (above 35 ring member numbers) with olefins and conducted ED-ROP *via* metathesis polymerization.[27] The thermodynamic equilibria of ROP can be represented by equation (1) below. ΔH and ΔS imply enthalpy and entropy, respectively, *R* is the gas constant, *T* is the temperature, $[M]_{eq}$ is an equilibrium monomer concentration, and $[M]_{ss}$ is a standard state monomer concentration. In the particular case of ED-ROP, the equation is controlled by entropy ($\Delta H \approx 0$); thus, the polymerization or cyclodepolymerization depends only on the concentration and structure of a monomer. However, no systematic investigation of ED-ROP has been achieved so far because synthetic methods of reactive macrocycles with targeted structures are limited.

$$\ln \frac{[\mathbf{M}]_{\mathbf{eq}}}{[\mathbf{M}]_{\mathbf{ss}}} = \frac{\boldsymbol{\Delta H}}{\boldsymbol{RT}} - \frac{\boldsymbol{\Delta S}}{\boldsymbol{R}} \quad \ldots(\mathbf{1})$$

[a] Department of Chemical Science and Engineering, Tokyo Institute of Technology, 2-12-1 Ookayama, Meguro-ku, Tokyo 152-8550, Japan. [b] Department of Applied Chemistry and Biotechnology, Graduate School of Engineering, Chiba University, 1-33 Yayoi-cho, Inage-ku, Chiba-shi, Chiba 263-8522, Japan. [c] Department of Applied Chemistry, College of Life Sciences, Ritsumeikan University, 1-1-1 Noji-higashi, Kusatsu, Shiga 525-8577, Japan
*D. Aoki. E-mail: daoki@chiba-u.jp
*H. Otsuka. E-mail: otsuka@mac.titech.ac.jp

We previously developed a ROP system utilizing the dynamic covalent chemistry[28–30] of bis(2,2,6,6-tetramethylpiperidin-1-yl) disulfide (BiTEMPS). [31–35] The BiTEMPS structure can exchange its disulfide bonds above 80 °C *via* the generation of relatively stable sulfide radicals (**Scheme 1a**), providing a dynamic polymer system.[36–39] Macrocyclic monomers (MMs) with desired structures and one BiTEMPS unit can be synthesized *via* selective and efficient cyclodepolymerization[31] of linear polymers containing BiTEMPS units in their repeating units, i.e., ring–chain equilibria with low concentrations. Isolated MMs can be polymerized by heating in highly concentrated conditions, whereupon they are converted to cyclic polymers (CPs),[32] mechanically interlocked CPs (MICPs),[33] or end-defined LPs[34] (**Scheme 1b**). The resulting polymers may be recycled by heating without any catalysts because they contain a dynamic amino disulfide bond in their repeating units.

The proposed ROP method using BiTEMPS is easy to manage and can be applied to the synthesis of polymers with various structures. This enables us to investigate, in detail, the structural dependencies of ring–chain equilibria. In this work, we investigate the effects of MM ring size for the cyclodepolymerization (**Scheme 1c**), which serves as a benchmark for the synthetic library of MMs. This provides the first example demonstrating the detailed effects of entropy and enthalpy in ring–chain equilibria of macrocycles and may contribute to the discovery of highly useful materials obtained by ROP.



Scheme 1. (a) Dynamic behaviour of the BiTEMPS structure. (b) Previously reported ROP system for MMs containing the BiTEMPS structure. (c) Chain length dependency for the cyclodepolymerization.

Experiment

Materials

All reagents and solvents were purchased from Tokyo Chemical Industry (Tokyo, Japan), Kanto Chemical (Tokyo, Japan), FUJIFILM Wako Pure Chemical Corporation (Tokyo, Japan), and Sigma-Aldrich (MO, USA). All reagents were used without further purification. Some BiTEMPS derivatives were synthesized according to previous studies.[31,35]

Instruments

^{1}H spectra were recorded on a Bruker AVANCE III HD500 spectrometer. ^{13}C{^{1}H} NMR spectra were recorded on a JEOL JNM-ECZ400S/L1 spectrometer. Analytical GPC measurements were carried out at 40 °C on TOSOH HLC-8320 SEC system equipped with a guard column (TOSOH TSK guard column Super H-L), three columns (TOSOH TSK gel SuperH 6000, 4000, and 2500) and a UV-vis detector. Tetrahydrofuran (THF) was used as the eluent at a flow rate of 0.6 mL/min. Polystyrene (PS) standards (M_n = 4430–3142000; M_w/M_n = 1.03–1.08) were used to calibrate the SEC system. Electrospray ionization mass spectrometry (ESI-TOF-MS) measurements were carried out on Bruker micrOTOF II.

Synthesis of linear precursors (LPs)

Two kinds of LPs for macrocyclic monomers were synthesized *via* a Michael addition between diacrylate derivatives of BiTEMPS and **DT(R)**s, for which a typical procedure is presented below. **BiTEMPS-diacrylate-S** (658 mg, 1.00 mmol) and **DT(C_4)** (915 mg, 1.00 mmol) were dissolved in THF (5.0 mL), after which dimethylphenylphosphine (DMPP) (10.0 µL, 70.0 µmol) was added and the mixture was stirred for 15 minutes at room temperature. The mixture was poured into hexane (50 mL) and the precipitate formed was separated by decantation and dried under reduced pressure to obtain **LP(C_4)-S** as a yellow solid. We also obtained other LPs as white solids as a result of changing the combination of diacrylate and dithiol. In addition, we prepared **LP(C_4)-L** with different molecular weight by changing the molar balance of diacrylate and dithiol monomers (**1a**; 1.1/1, **1b**; 1.01/1, **1c**; 1/1) to investigate the effects of the molecular weight of LPs for cyclodepolymerization. Yields and properties are summarized in **Table 1**.

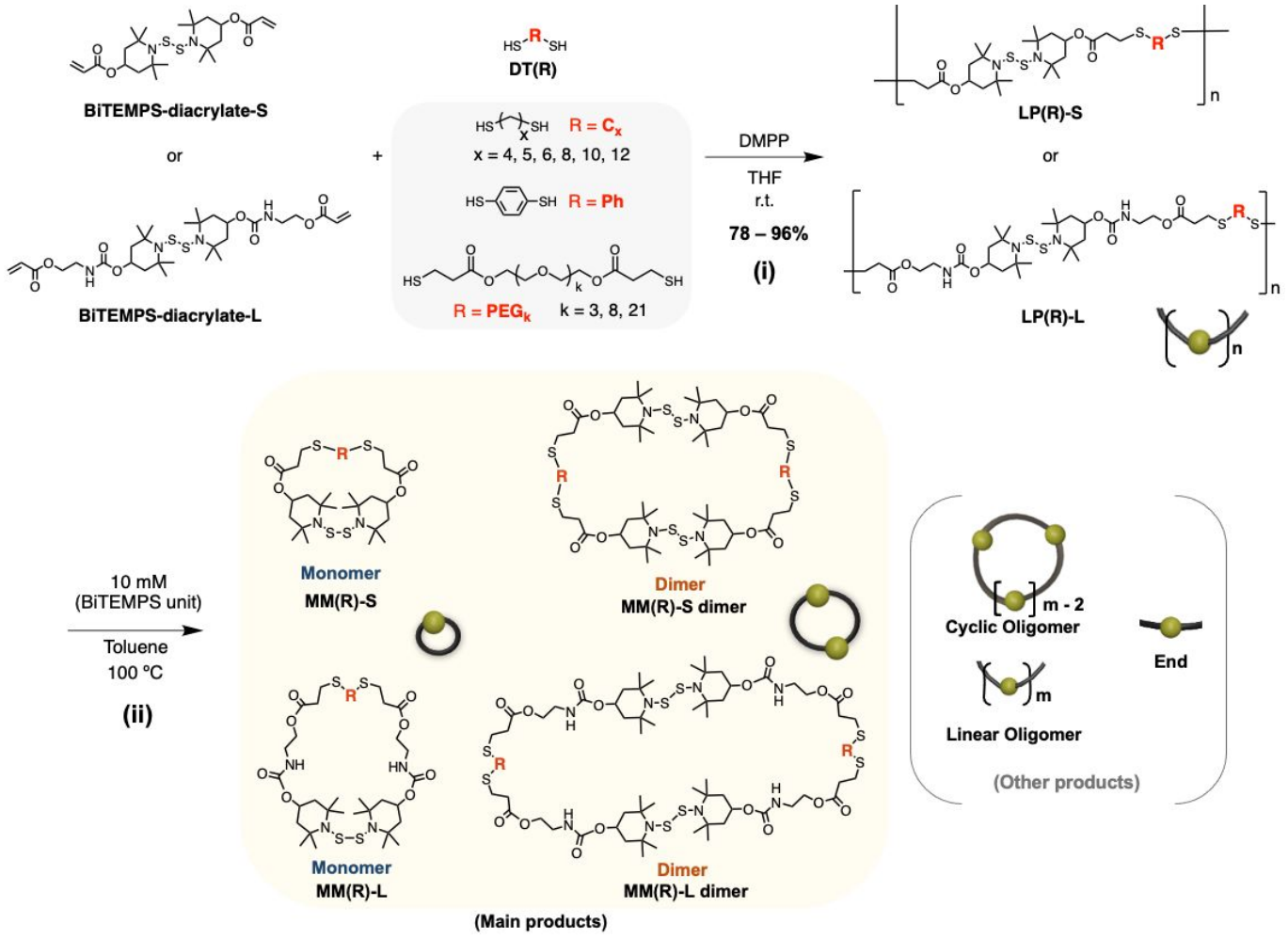
Reaction tracking of cyclodepolymerization

A typical procedure is presented below. In a test tube, **LP(R)-S** or **LP(R)-L** (in toluene, 10.0 mM BiTEMPS unit concentration) was added and stirred at 100 °C for 48 hours. The upper side of the test tube was kept at a temperature below 10 °C in order to prevent solvent removal outside during this experiment. The reaction was tracked by gel permeation chromatography (GPC). Generation ratio of monomer and dimer were calculated according to the area ratio of the corresponding peaks. The ratio represents how many repeating units are containing in the component, not the molar ratio of monomer and dimer. Assuming that all UV absorption is derived from the structure of repeating units, the GPC area ratio was

corresponded to the number of repeating units, and absorption derived from end components was ignored.

Isolation of macrocyclic compounds

A typical procedure for the isolation of macrocyclic compounds is as follows: In a 300 mL flask, **LP(C$_8$)-S** (1.12 g) was dissolved in toluene (112 mL) and stirred at 100 °C for 9 hours. Then, the solvent was evaporated *in vacuo*. The residue was purified by silica gel column chromatography using a dichloromethane/ethyl acetate (v/v = 98/2) mixture. The elute obtained was evaporated *in vacuo* to afford **MM(C$_8$)-S** as a white solid. (361 mg, 32% by weight) MS (ESI): 685.3156 $[M+Na]^+$, calculated for $C_{32}H_{58}N_2O_4S_4Na$ $[M+Na]^+$: 685.3171. **MM(C$_6$)-S**; **LP(C$_6$)-S** (932 mg) was used instead of **LP(C$_8$)-S** and was purified by column chromatography with a dichloromethane/hexane (v/v = 9/1) mixture (white solid, 353 mg, 38%). MS (ESI): 657.2846 $[M+Na]^+$, calculated for $C_{30}H_{54}N_2O_4S_4Na$ $[M+Na]^+$: 657.2859. **MM(C$_5$)-S**; **LP(C$_5$)-S** (2.36 g) was used after purification using preparative GPC with chloroform as the eluent. (**MM(C$_5$)-S**: white solid, 573 mg, 24% by weight, MS (ESI): 643.2684 $[M+Na]^+$, calculated for $C_{29}H_{52}N_2O_4S_4Na$ $[M+Na]^+$: 643.2702) (**MM(C$_5$)-S dimer**: white solid, 457 mg, 19% by weight, MS (ESI): 1263.5507 $[M+Na]^+$, calculated for $C_{58}H_{104}N_4O_8S_8Na$ $[M+Na]^+$: 1263.5512)



Scheme 2. Synthesis of (i) LPs from diacrylate derivatives of BiTEMPS (**BiTEMPS-diacrylate-S** and **BiTEMPS-diacrylate-L**) and various dithiols (**DT(R)**). *k* values (average values) of PEG$_k$ estimated by ^{1}H NMR (ii) Cyclodepolymerization of LPs to form MMs. **LP(R)-S** or **L** denotes LPs synthesized from **BiTEMPS-diacrylate-S** or **L** and **DT(R)**.

Result and discussion

Synthesis of LPs and reaction tracking their cyclodepolymerization

As shown in **Scheme 2** (**reaction i**), we prepared LPs as precursors for cyclodepolymerization by polyaddition between diacrylate derivatives of BiTEMPS and dithiol compounds with various chain lengths (**DT(R)**s); these were characterized using proton nuclear magnetic resonance (^{1}H NMR) measurements and GPC (**Figures S1–S5**). Two kinds of diacrylates, **BiTEMPS-diacrylate-S** and **BiTEMPS-diacrylate-L**, were synthesized from the diol derivative of BiTEMPS as reported previously.[29] As dithiol monomers **DT(R)**s, we used various compounds with different spacers as shown in **Scheme 2** (**reaction i**). Using the same manner as a previous study,[31] polyaddition under phosphine catalyst proceeded successfully as shown in **Table 1**. LPs had different chain lengths (*N*), enabling us to

investigate the structural dependency for cyclodepolymerization in detail. We first synthesized samples **1a** to **1c** to investigate the effects of the molecular weight of LPs for cyclodepolymerization. We also prepared samples **2**–**7** to confirm how relatively short alkylene chains influence the reaction, and samples **8** to **10** for comparison in the cases of longer chains. In addition, samples **11** and **12** have a phenylene structure in place of the alkylene chain. In our previous report, we mentioned that LPs synthesized by polyaddition may contain cyclic as well as linear components[32], but the effect of the terminal components of LPs was minor and ignored in this study. After determining the LPs, we investigated their heat-induced cyclodepolymerization behaviour (**Scheme 2, reaction ii**). Taking into consideration their cyclization efficiencies, side reactions, and polymer solubility, we determined the conditions for the cyclodepolymerization in toluene at 100 °C for 48 hours. First, we investigated the dependency of LP molar mass for producing the MM ratio. The concentration of BiTEMPS was adjusted to 10 mM according to the molecular weight of the repeating unit, ignoring the end structure, and the cyclodepolymerization was performed. Our results revealed that the effect of LP molecular weight can be ignored in ring–chain equilibria provided that LP has a sufficient value of M_n (around 5,000) (**Figure 1**).

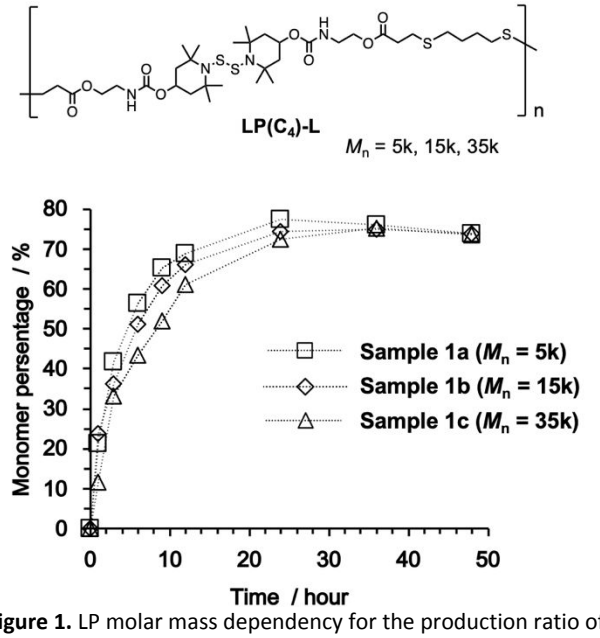


Figure 1. LP molar mass dependency for the production ratio of monomer at cyclodepolymerization in toluene at 10 mM at 100 °C.

Table 1. The properties of LPs

Sample	Name	Chain length (*N*) [a]	Molecular weight per one repeating unit	Yield[c] (%)	$M_{n,\ GPC}$[d]	M_w/M_n [d]
1a	**LP(C_4)-L**	34	781	95	5,100	2.13
1b	**LP(C_4)-L**	34	781	92	15,100	2.03
1c	**LP(C_4)-L**	34	781	96	34,700	1.72
2	**LP(C_4)-S**	24	607	95	6,800	2.20
3	**LP(C_5)-S**	25	621	95	17,500	1.80
4	**LP(C_6)-S**	26	635	96	17,600	1.75
5	**LP(C_8)-S**	28	663	91	21,600	1.76
6	**LP(C_{10})-S**	30	690	92	16,700	1.91
7	**LP(C_{12})-S**	32	718	84	11,500	1.52
8	**LP(PEG_3)-L**	49	1, 029[b]	81	21,500	1.65
9	**LP(PEG_8)-L**	64	1, 249[b]	95	18,700	1.47
10	**LP(PEG_{21})-L**	103	1, 821[b]	95	13,300	1.31
11	**LP(Ph)-S**	24	627	78	3,600	1.64
12	**LP(Ph)-L**	34	801	92	8,100	2.24

[*a*] *N;* chain length of a repeating unit. [*b*] Molecular weight of PEG_k were estimated by ^1H NMR. [*c*] Yields of polyaddition. [*d*] Polystyrene standard used.

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We then investigated the effect of chain length on cyclodepolymerization. All LPs in **Table 1** were cyclodepolymerized at 10 mM concentration and the yields of macrocyclic monomers and macrocyclic dimers from GPC data at predetermined times (0–48 hours) were calculated (**Figures S8–S9**). **Figure S9** shows the productivities of macrocyclic monomers and dimers in samples **2–7**, indicating that they reached thermodynamic equilibria within 48 h. Note that productivity indicates how many repeating units are containing for each component, not the mol ratio of each molecule, i.e., this value indicates the weight ratio of the product molecules. **Figure 2a** shows the final productivities of monomers and dimers when using **BiTEMPS-diacrylate-S** and alkyl dithiols **DT(C_x)** as monomers. With increasing chain length of the alkyl chain in **LP(C_x)-S**, the total yields and the ratios of monomer formation increased. In this case, the main product changed from a dimer to a monomer with 26 ring members (N = 26); thus, N can be used as an important indicator for determining whether monomers or dimers are preferred. **Figure 2b** also shows the productivities of cyclodepolymerization when using LPs with long chains, e.g., samples **8**–**10**. Contrary to the results of samples **2**–**7**, the result revealed that the productivities of monomers decreased with increasing chain length. **LP(Ph)-S** (sample **11**) exhibited a remarkably low monomer yield compared with the other samples studied and smaller than sample **2** (**Figure 2c**). On the other hand, the yield of **LP(Ph)-L** (sample **12**) was higher than sample **1b**. These results were due to the structural difference between rigid phenylene and flexible butylene chain. Thus, ring chain equilibria might be impacted by not only the number of ring members, but also the structure of the chain.

According to equation (1), productivity can be determined using entropy ΔS (i.e., the negative entropy change arising from conformation loss during cyclodepolymerization $\Delta S_{conf.}$ and the positive change from increasing free movements of molecules $\Delta S_{trans.}$) and ΔH (i.e., RSE). In this study, the smallest value of N is 24, which is much larger than the corresponding values of strained cyclic monomers, such as δ-valerolactone, ε-caprolactone, and cyclooctene. Thus, the productivities of monomers were mainly determined by $\Delta S_{trans.}$ and $\Delta S_{conf.}$ when monomers have large-size macrocycles.[1] Smaller molecules have larger values of $\Delta S_{trans.}$; however, their negative value of $\Delta S_{conf.}$ also becomes larger. Hence, our results suggest that short chains restrict the conformation of monomers, strongly enhancing the negative entropy effects of $\Delta S_{conf.}$ to reduce their yields. In contrast, although the negative effects of $\Delta S_{conf.}$ decrease when using precursors with much larger chain lengths, the positive entropy effect $\Delta S_{trans.}$ for cyclodepolymerization was also reduced. In this case, the effect of the positive $\Delta S_{trans.}$ became too small, resulting in low productivities of monomers with much longer chains at 10 mM condition. In addition, the rigid structure of the phenyl group has more conformational restrictions than the butyl group when the chain length is short, thereby reducing its monomer productivity (13% in sample **2** vs. 7% in sample **11**). Conversely, when the chain is large enough (N = 34), we estimate that the compact phenyl structure enhances the positive effect of $\Delta S_{trans.}$ and slightly increases monomer productivity (74% in sample **1b** vs. 77% in sample **12**).

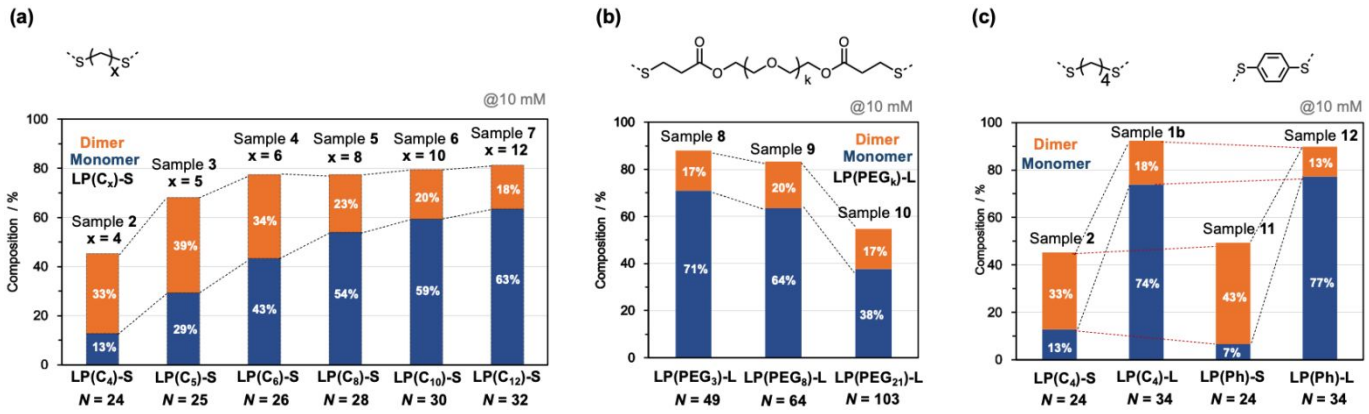

Figure 2. Productivities of macrocyclic monomers and dimers in samples **1–12** at 10 mM. (a) Final composition when using **LP(C_x)-S**, (b) **LP(PEG_k)-L**, and (c) LPs with butyl or phenyl structure.

Furthermore, to investigate these entropy effects, we conducted further cyclodepolymerization under diluted conditions. **Figure 3a** shows the relationships between the concentration and yield of monomers in samples **1b** and **2** (N = 34 and 24, respectively). High dilution conditions significantly enhance the productivity of monomers in sample **2** as the value of $\Delta S_{trans.}$ became larger under

extremely diluted conditions; however, the yield of sample **2** was still less than half that of sample **1b**, even at 0.1 mM, suggesting that a strong negative effect of $\Delta S_{conf.}$ influenced sample **2**. Similarly, the cyclodepolymerization under 10 times higher dilution conditions (1 mM) enhanced the productivities of monomers in samples **8–10** (**Figure S11–S12**), because the value of $\Delta S_{trans.}$ became larger. Overall, these results indicate that the balance of $\Delta S_{trans.}$ and $\Delta S_{conf.}$ determines cyclodepolymerization efficiency (**Figure 3b**). These results are consisted with other ED-ROP and confirm that the chemistry of BiTEMPS-containing macrocyclic molecules follows equation (1).

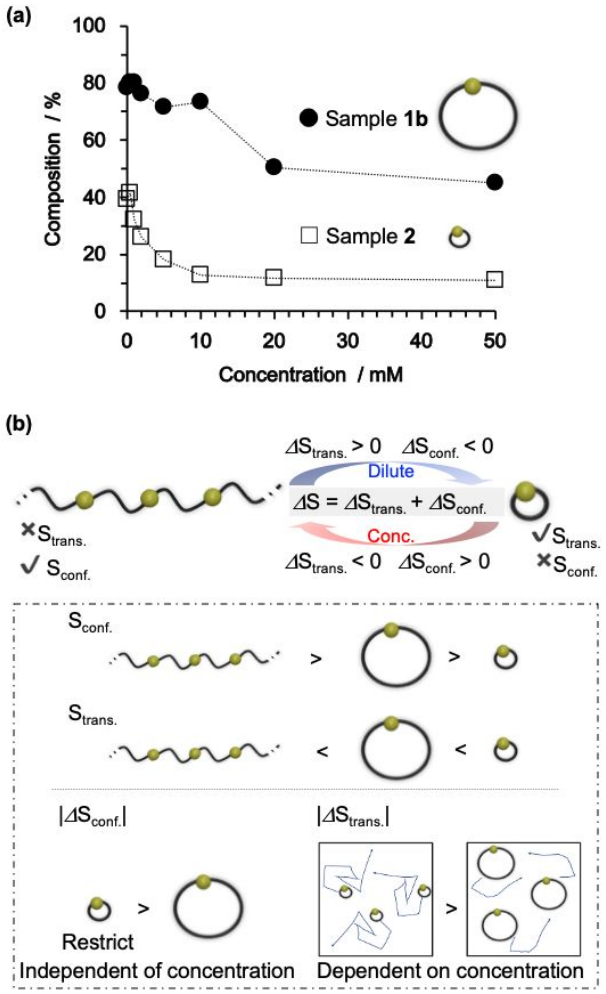

Figure 3. (a) Concentration dependences on the yields of monomers at sample **1b** and **2**. (b) Ring-chain equilibria in this study.

Herein, we characterized cyclic products to understand the effects of entropy in terms of the macrocyclic structure. Some macrocycles (monomer or dimer products from the cyclodepolymerization of samples **3**, **4**, and **5**) were successfully isolated by column chromatography to characterize their structures. We also successfully prepared crystals of **MM(C_5)-S** and **MM(C_8)-S** for X-ray crystallography (**Figures S18–S19**). These X-ray analyses confirmed macrocyclic monomer structures without the oligomers and linear precursor. Although the other samples were not obtained as a crystal amenable to characterization by X-ray analysis, their GPC curves indicated successful isolation (**Figure S15**). The ^{1}H NMR spectra of the purified **MM(C_8)-S**, **MM(C_6)-S**, **MM(C_5)-S**, and **MM(C_5)-S dimer** are shown in **Figure 4**. Signals **a** and **b** in a grey area of the spectrum in **MM(C_6)-S** and **MM(C_5)-S** are clearly different from those in the **MM(C_8)-S** and **MM(C_5)-S dimer**. For example, signal **a** was observed as two singlet peaks in the **MM(C_8)-S** and **MM(C_5)-S dimer**, whereas two broader peaks and two doublet peaks were observed in **MM(C_6)-S** and **MM(C_5)-S**. Small-size macrocycles restrained the rotation of the six-membered piperidine ring in the BiTEMPS structure and influenced the signals of **a** and **b** in short chain length macrocycles. In addition, the ^{13}C{^{1}H} NMR spectra of the purified **MM(C_8)-S**, **MM(C_6)-S**, **MM(C_5)-S**, and **MM(C_5)-S dimer** are shown in **Figure S17**. The signals of carbons adjacent to the proton **a** and **b** similarly changed according to the number of ring members. Moreover, the ^{1}H NMR spectra of **MM(C_5)-S** were different from those of its precursor **LP(C_5)-S (Figure S16)**. This conformational restriction enhanced the negative effect of $\Delta S_{conf.}$ in the cyclodepolymerization, resulting in low monomer yields. This result is consistent with the observation that the monomer productivities were remarkably low at chain length *N* below 26.

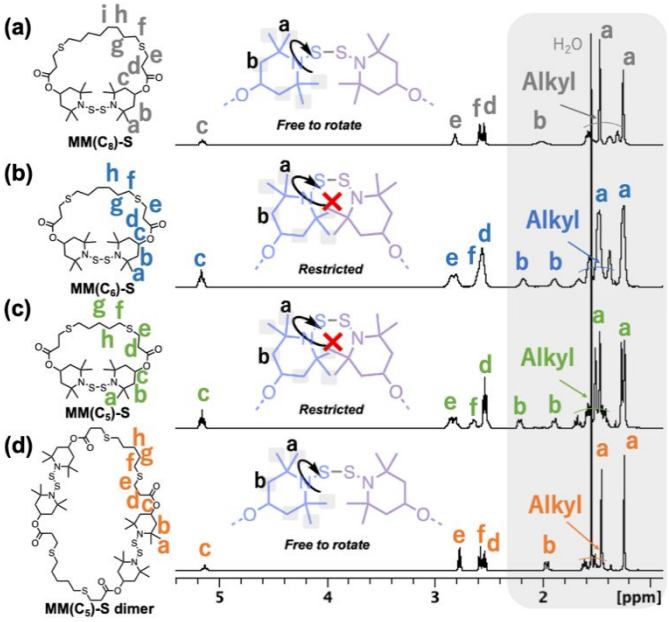

Figure 4. ^{1}H NMR spectra of isolated macrocyclic compounds: (a) **MM(C_8)-S**, (b) **MM(C_6)-S**, (c) **MM(C_5)-S**, and (d) **MM(C_5)-S dimer** (500 MHz, 25 °C, $CDCl_3$).

Estimation of enthalpy of ring–chain equilibria

Thus far, we have found that cyclodepolymerization efficiency is low when *N* is too small or too large due to the effect of entropy ΔS. Here, we explore the effects of enthalpy ΔH in equation (1). To demonstrate the presence of ΔH, we investigated the temperature dependence of the oligomerization of an isolated MM. We chose **MM(C_5)-S** as a small-size macrocycle because it had the smallest size of the MMs investigated while having a sufficient monomer yield. **Figure S13** shows the residual ratio of the monomer during the oligomerization process at 10 mM and 80–100 °C and the final composition of both the monomer and dimer. Although oligomerization occurred more rapidly under high temperatures, the

final productivities were similar. Thus, ΔH in equation (1) was approximately zero and can be ignored.

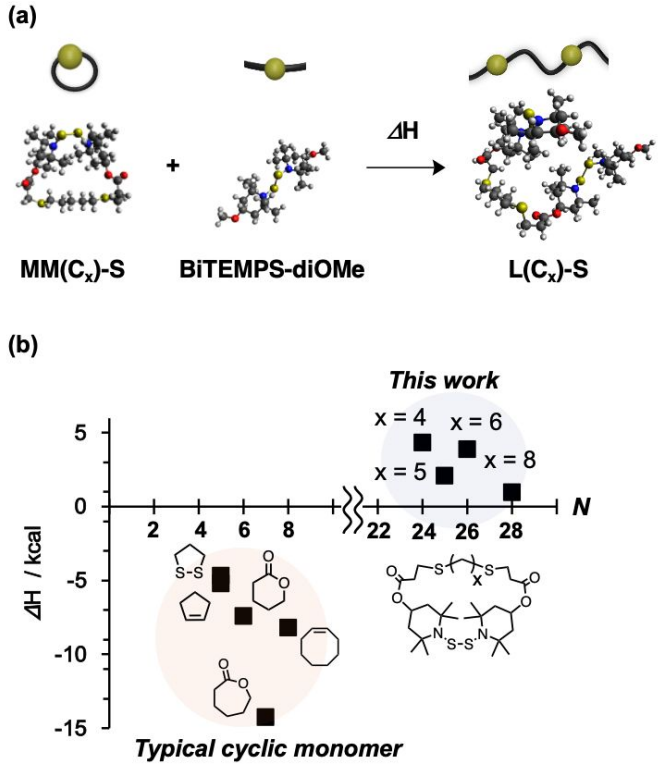

Figure 5. (a) Reaction required to calculate the RSEs of MMs. (b) Calculated RSEs.

Additionally, we estimated ΔH using density functional theory (DFT) calculations. The enthalpy of ring strain was calculated by comparing the enthalpy of macrocycles with that of the linear counterpart (**Figure S21**). **Figure 5a** shows a comparison between the enthalpy of the formation of **MM(C_x)-S** and linear counterparts (**L(C_x)-S**) and an elimination component with a terminal structure (**BiTEMPS-diOMe**). Calculations for ΔH were conducted using DFT at the UB3LYP/6-31G(d,p) at almost the same level as B3LYP/6-31G(d,p), which provides a reasonable estimation for the ΔH of cyclic monomers, such as cyclic olefins.[7,40] **Figure 5b** compares the the ΔH values of **MM(C_x)-S** (x = 4, 5, 6, and 8) and those of typical strained cyclic monomers. The ΔH values of **MM(C_x)-S** were significantly lower than those of other typical cyclic monomers and have negative values. The ΔH values were not related to the chain length of **MM(C_x)-S** (x = 4, 5, 6, and 8). These results also support that the ΔH in equation (1) is approximately zero and can be ignored. Thus, the ring–chain equilibria of MMs depend on the ΔS and are almost the same as other ED-ROP systems.

Conclusions

In conclusion, we have systematically and successfully synthesized LPs with various chain lengths and studied their cyclodepolymerization in detail. The productivities of macrocyclic product with one dynamic unit decreased significantly when macrocyclic chain lengths exhibited less than N = 26 in their ring. Conversely, it increased over N = 26 and reached a peak at N = 49 and then decreased as the value of N increased (N > 49). The results of experiments and DFT calculations reveal that MM ring–chain equilibria are controlled by a balance between $\Delta S_{conf.}$ and $\Delta S_{trans.}$, suggesting that it is possible to ignore the effects of ΔH. These results help to establish a guideline for the preparation of macrocycles containing BiTEMPS for ROP. We have also revealed that LPs with short chain lengths result in conformational restriction for the produced MMs. This restriction enhances their activities for ROP, and is expected to control polymerization kinetics. Because ring–chain equilibria based on the dynamic nature of the BiTEMPS unit facilitate the introduction of the desired structure into the resulting linear polymers and macrocyclic compounds, studies of ring–chain equilibria were systematically and successfully undertaken. The results of this study provide not only important insights into the preparation of MMs for ED-ROP but also demonstrated an effective way by which functional polymers may be obtained and decomposed in reverse.

Acknowledgements

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