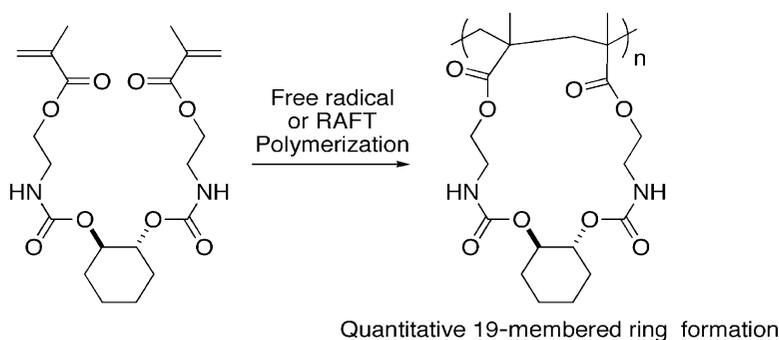


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## Controlled Cyclopolymerization through Quantitative 19-Membered Ring Formation

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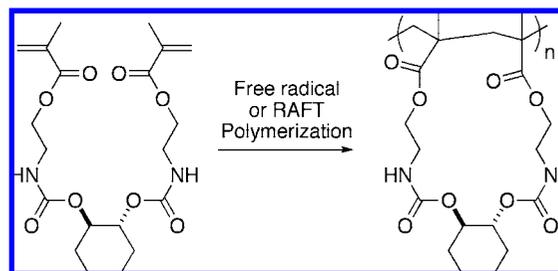
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Efficient cyclopolymerizations typically proceed via formation of thermodynamically stable five- or six-membered rings.<sup>1–3</sup> These very compact rings provide rigidity to the resulting polymers but are too small to capture molecules inside. Larger rings (e.g., larger than 12-membered rings such as 12-crown-4) can capture atoms or molecules inside depending on the ring size and the functional groups. Polymers with larger rings have specific affinities with ions or low-molecular weight compounds depending on the ring size, and their potential application involves stationary phases for chromatographic separation and metal scavengers.<sup>4,5</sup> In spite of the utility of these polymers with large rings, preparation of them must overcome the difficulty of forming the thermodynamically unfavorable large rings regardless of the preparation methods (i.e., cyclopolymerizations or polymerizations of monomers bearing large rings).<sup>4–7</sup>

We designed a bis-methacrylate (**1**) with conformations favorable for ring-closing owing to the two directing groups: the cyclohexane ring and the urethane groups straining with steric direction and hydrogen bonds, respectively. The cyclopolymerization of **1** potentially proceeds via a 19-membered ring formation. This bis-methacrylate could be easily prepared from 2-methacryloyloxyethyl isocyanate (MOI) and *trans*-1,2-hexanediol in a similar manner with other methacrylates prepared from MOI.<sup>8</sup> The difficulty of large-ring formation has limited the controlled cyclopolymerizations affording polymers bearing large rings, although many controlled cyclopolymerizations affording five- or six-membered rings have been developed.<sup>3</sup> The only example of a controlled cyclopolymerization with large-ring formation is cationic polymerization of a divinyl ether, whose double bond moieties are forced to stay in close proximity by steric regulation, affording a polymer with a 13-membered ring.<sup>7</sup> Its cyclization degree is very high (96%) but is not quantitative, resulting in broad polydispersity indexes at high conversions.

The polymerization of **1** was conducted in *N,N*-dimethyl formamide (DMF), dimethyl sulfoxide (DMSO), and 1,4-dioxane (DOX) (0.082 M) at 60 °C for 24 h in the presence of AIBN (3.3 mol% with respect to **1**) (Scheme 1, Table 1). The polymerization afforded soluble polymers in high yields without formation of observable amounts of insoluble products. The <sup>1</sup>H, <sup>13</sup>C, and 2D NMR spectra measured in CDCl<sub>3</sub> containing trifluoroacetic acid agreed well with the expected structure, and no signal assignable to the double bond moieties was observed (see Supporting Information). Although we tried the syntheses and polymerizations of the *N*-methylated monomer, these compounds were too unstable to be isolated. We postulated that the hydrogen bonding in **1** constraining the double bond moieties stabilizes **1**. The polymerization at a higher concen-

**Scheme 1.** Cyclopolymerization of Cyclohexane-*trans*-1,2-diyl-bis(2-methacryloyloxyethylcarbamate) (**1**)



**Table 1.** Cyclopolymerization of Cyclohexane-*trans*-1,2-diyl-bis(2-methacryloyloxyethylcarbamate) (**1**)<sup>a</sup>

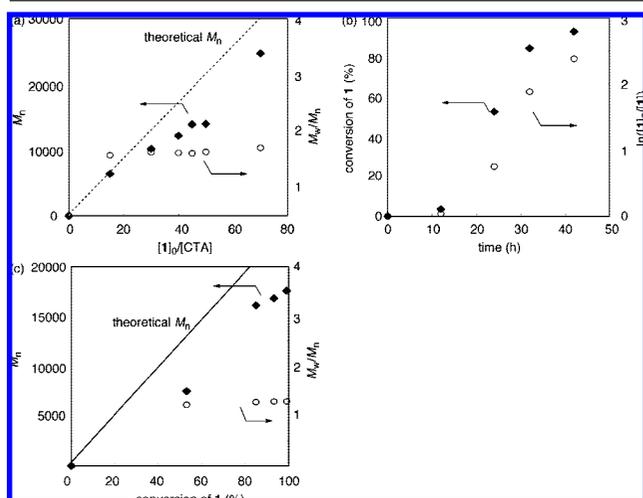
run	[AIBN]/[2]/[1]	solvent (M)	conv. (%) <sup>b</sup>	yield (%) <sup>c</sup>	<i>M<sub>w</sub></i> ( <i>M<sub>w</sub></i> / <i>M<sub>n</sub></i> ) <sup>d</sup>
1	1/0/100	DOX (0.200)			cross-linked polymer
2	1/0/100	DOX (0.082)	91	96	157 100 (2.31)
3	1/0/100	DMF (0.082)	92	97	39 300 (2.47)
4	1/0/100	DMSO (0.082)	>99	99	133 700 (3.62)
5	0.5/0/15	DOX (0.082)	>99	99	44 400 (3.85)
6	0.5/1/15	DOX (0.082)	>99	90	6400 (1.23)
7	0.2/1/15	DOX (0.082)	82	80	5000 (1.44)
8	0.5/1/15	DMF (0.082)	94	90	6700 (1.27)
9	0.2/1/15	DMF (0.082)	48	27	5200 (1.15)
10	0.5/1/15	DMSO (0.082)	97	98	6700 (1.27)
11	0.2/1/15	DMSO (0.082)	3	1	3000 (1.10)
12	0.5/1/15	DOX (0.164)	98	99	8900 (1.67)

<sup>a</sup> Conditions: 60 °C, 24 h, degassed sealed tube. <sup>b</sup> Determined by <sup>1</sup>H NMR spectroscopy. <sup>c</sup> Isolated yield after precipitation with diethyl ether. <sup>d</sup> Estimated by SEC (THF, polystyrene standard).

tration afforded an insoluble product, whose IR spectrum is identical to that of the soluble polymer, suggesting that the trace undesired cross-linking reaction is due to the increased probability of the intermolecular propagation. The polymerization of **1** was also conducted in the presence of cumyl dithiobenzoate (**2**) (runs 6–12),<sup>9</sup> which is a suitable RAFT<sup>9,10</sup> agent for methacrylates. The polymerization of **1** was conducted in DOX (0.082 M) using AIBN and **2** (runs 6 and 7). The higher concentration of **2** was not suitable due to the slow propagation, probably originating from the low concentration of **1**. The RAFT polymerization also afforded a soluble polymer whose *M<sub>w</sub>*/*M<sub>n</sub>* value is lower than that of the polymer obtained in the free radical polymerization (run 5). When the RAFT polymerization of **1** was conducted in DMF or DMSO, the conversions of **1** became lower when the amount of AIBN was lower. We ascribed the slower rates and the broader *M<sub>w</sub>*/*M<sub>n</sub>* to the weak intramolecular hydrogen bonds in **1** by <sup>1</sup>H NMR spectroscopy. Although polymerization at higher concentration, at which an insoluble polymer was obtained by the free radical polymerization,

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**Figure 1.** (a) Feed ratio– $M_n$  (conversion >91%), (b) time–conversion ( $[AIBN]/[2]/[1] = 0.5/1/45$ ), and (c) conversion– $M_n$  and  $M_w/M_n$  ( $[AIBN]/[2]/[1] = 0.5/1/45$ ) plots of the cyclopolymerization of **1** at 60 °C in 1,4-dioxane (0.082 M).

gave a soluble polymer, the SEC profile was bimodal (run 12), suggesting sufficient cyclization under appropriately diluted conditions.

The narrow  $M_w/M_n$  value and the quantitative yields of the polymerization in DOX imply the controlled nature of this RAFT cyclopolymerization. Accordingly, we polymerized **1** under conditions similar to those of run 7 at various feed ratios of **1** toward **2** ( $[2]/[AIBN] = 2$ ) (Figure 1a). Monomer **1** was consumed quantitatively in 48 h. The  $M_w/M_n$  values were narrow, and the  $M_n$  values increased linearly with the feed ratios. The consumption of **1** started after an induction period of 11 h, determined by extrapolating the pseudofirst-order kinetic plot (Figure 1b). The linear relationship between the  $\ln([1]_0/[1])$  value and time suggests this cyclopolymerization involves negligible irreversible termination reactions. The linear conversion versus  $M_n$  relationship also supports the controlled nature of this cyclopolymerization (Figure 1c). If the efficiency of the cyclization was low, the number of the propagating ends per one polymer chain should be increased by branching as polymerization progresses. The polymer obtained at lower conversion (29%) contained a very low amount of the double bond moieties (<2%), as confirmed by  $^1H$  NMR analysis, and it also supports the good selectivity of the cyclopolymerization. However, the slight shoulder in the SEC profiles implied the trace extent of branching at the latter stages.

In summary, the cyclopolymerization of a bifunctional methacrylate (**1**) proceeded through 19-membered ring formation and a controlled fashion via an RAFT process. The controlled nature of

the polymerization provides the possibility for block copolymerizations with other functional monomers. We are now evaluating the ability of poly(**1**) as a scavenger for specific metals or organic molecules originating from the large rings containing Lewis basic carbonyl groups and the protonic N–H groups in the repeating unit.

**Supporting Information Available:** Experimental procedures, and spectroscopic and SEC data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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