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Acid-Promoted Living Ring-Opening Polymerization of Cyclic Carbonates with $B(OR)_3$

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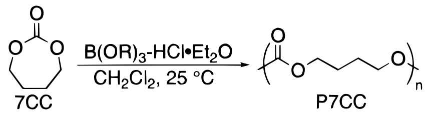
ABSTRACT: Ring-opening polymerization of cyclic carbonates (1,3-dioxepan-2-one and 5,5-dimethyl-1,3-dioxan-2-one) with triethyl and triisopropyl borates as initiators promoted by hydrogen chloride was carried out. The molecular weights of the obtained polymers could be controlled by the amount of alkylborates, and their polydispersity ratios were small (∼1.15). The polymerization obeyed good first-order kinetics throughout the reaction. After the monomers were completely consumed, the polymerization proceeded again quantitatively when the same amount of monomers were introduced into the polymerization mixtures. ^{1}H and ^{13}C NMR spectroscopic studies suggested that the polymerization proceeded in a living manner via insertion of the monomer to the boron−oxygen bond.

Introduction

Lewis acids play an important roll in cationic ring-opening polymerization of cyclic monomers as well as of vinyl monomers. Though versatile, these catalysts generally cause back biting reaction forming cyclic oligomers which makes it difficult to control the molecular weights (M_n) and polydispersity ratios (M_w/M_n) of the polymers.[1] The stoichiometric reaction between lactones with various Lewis acids has been studied, where ω-halogenatedcarboxylic acids are formed in all cases.[2] Especially in the cases of Lewis acids with energetically favorable d-orbitals such as $SnBr_4$ and $ZnBr_2$, metal−oxygen bonds form to produce high M_n polymers (∼70 000) via an insertion mechanism at 60 °C, although their polydispersities of the formed polymers are large (∼1.7). This insertion mechanism has been also demonstrated in the ring-opening polymerization of six-membered cyclic carbonates with $TiCl_4$[3] and alkyltin(IV) chloride initiators[4] to give the corresponding polycarbonates without decarboxylation reaction, but M_n cannot be precisely controlled by changing the feed ratios, and the polydispersities are large (∼1.7). Aluminum alkoxides can also produce polycarbonate via an insertion mechanism in the polymerization of nonsubstituted six-membered cyclic carbonate (6CC) at 80 °C. Although the polymerization is not “living”, the molecular weight is controllable by adjusting the initiator-to-monomer ratio.[5]

Organo borons are also useful compounds showing wide variety of catalytic activities in organic synthesis, but their use for polymer synthesis has been rather limited. Our preliminary work on BX_3 (X = Cl or Br) in the polymerization of a seven-membered cyclic carbonate (7CC) has revealed that the propagating species is stabilized with boron atom to afford a living polymer.[6] We describe here a novel method for ring-opening polymerization of cyclic carbonates with boron alkoxides in the presence of HCl under mild conditions to give polymers with controlled M_n and M_w/M_n in high yields suppressing side reactions such as decarboxylation and back-biting.

Scheme 1



Experimental Section

Materials. CH_2Cl_2 and $CDCl_3$ were distilled sequentially over P_2O_5 and CaH_2 under nitrogen. The monomers, 1,3-dioxepan-2-one (7CC)[7] and 5,5-dimethyl-1,3-dioxan-2-one (DM6CC),[8] were prepared according to the literature and stored at −20 °C under nitrogen. Triethyl borate [$B(OEt)_3$] and triisopropyl borate [$B(O\text{-}i\text{-}Pr)_3$] were purchased from Aldrich and distilled under nitrogen before use. A 2.0 M HCl solution in diethyl ether (Et_2O) was purchased from Aldrich and used without further purification.

Measurements. ^{1}H and ^{13}C NMR spectra were recorded with a JEOL Lambda-300 spectrometer. Number and weight-average molecular weights (M_n and M_w) were measured by gel permeation chromatography (GPC) on a Tosoh HLC-8120 system equipped with two consecutive polystyrene gel columns eluted with tetrahydrofuran (THF) at a flow rate of 1.0 $mL\cdot min^{-1}$ calibrated by standard polystyrenes.

Polymerization. All manipulations were carried out under dry nitrogen. A typical procedure was following: Into a 30 mL baked glass flask equipped with a three-way stopcock was placed a solution of 0.116 g (1.0 mmol) of 7CC and 20 μL (0.010 mmol) of $B(OEt)_3$ in 0.9 mL of CH_2Cl_2. The polymerization was initiated by the addition of 50 μL (0.10 mmol) of a HCl solution (2 M) in Et_2O at 25 °C. After a set time the reaction mixture was poured into 100 mL of methanol/*n*-hexane (1/1 volume ratio) to precipitate a polymer.[9] The precipitate was filtered, washed sequentially with methanol (5 mL), *n*-hexane (5 mL), and dried at 25 °C for 5 h in vacuo.

Results and Discussion

Scheme 1 and Table 1 summarize the results of the ring-opening polymerization of a nonsubstituted seven-membered cyclic carbonate (7CC) with $B(OEt)_3{-}HCl\cdot Et_2O$ and $B(O\text{-}i\text{-}Pr)_3{-}HCl\cdot Et_2O$ initiator systems in CH_2Cl_2 at 25 °C. In our previous report, we have examined $HCl\cdot Et_2O$ as an initiator for the polymerization of 7CC in CH_2Cl_2 at 25 °C, but it did not work effectively.[10]

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Table 1. Polymerization of 7CC Initiated with Trialkyl Borates[a]

run	initiator system	$[M]_0/[B^{3+}]_0$	$[HCl]_0/[B^{3+}]_0$	conv[b] (%)	yield[c] (%)	M_n[d]	M_w/M_n[d]
1	$B(OEt)_3$	40	0	1	*e*	*e*	*e*
2	$B(OEt)_3$/$HCl{\cdot}Et_2O$	40	20	98	90	1900	1.19
3	$B(OEt)_3$/$HCl{\cdot}Et_2O$	38	10	98	91	1800	1.16
4	$B(OEt)_3$/$HCl{\cdot}Et_2O$	90	10	98	85	3500	1.17
5	$B(OEt)_3$/$HCl{\cdot}Et_2O$	135	10	98	92	6500	1.14
6	B(O-*i*-Pr)$_3$	40	0	0	*e*	*e*	*e*
7	B(O-*i*-Pr)$_3$/$HCl{\cdot}Et_2O$	40	10	99	90	1700	1.15
8	B(O-*i*-Pr)$_3$/$HCl{\cdot}Et_2O$	55	10	99	92	2100	1.15

[a] Conditions; $[M]_0 = 1$ mol/L in CH_2Cl_2 at 25 °C for 24 h. [b] Determined by ^1H NMR. [c] Methanol/*n*-hexane (1/1 volume ratio)—insoluble part. [d] Determined by GPC (THF, polystyrene standards). [e] Not determined.

Table 2. Polymerization of DM6CC Initiated with Triethyl Borate[a]

run	initiator	$[M]_0/[B^{3+}]_0$	$[HCl]_0/[B^{3+}]_0$	time (h)	conv[b] (%)	yield (%)	M_n[c]	M_w/M_n[c]
1	$B(OEt)_3$	30	0	48	0	*d*	*d*	*d*
2	$B(OEt)_3$/$HCl{\cdot}Et_2O$	60	10	48	15	*d*	*d*	*d*
3	$B(OEt)_3$/$HCl{\cdot}Et_2O$	30	20	48	86	81	1570	1.12
4	$B(OEt)_3$/$HCl{\cdot}Et_2O$	60	30	96	82	75	2200	1.11
5	$B(OEt)_3$/$HCl{\cdot}Et_2O$	90	30	96	91	83	2700	1.16
6	$B(OEt)_3$/$HCl{\cdot}Et_2O$	120	30	96	90	83	3100	1.11

[a] Conditions; $[M]_0 = 1$ mol/L in CH_2Cl_2 at 25 °C. [b] Determined by ^1H NMR. [c] Determined by GPC (THF, polystyrene standards). [d] Not determined.

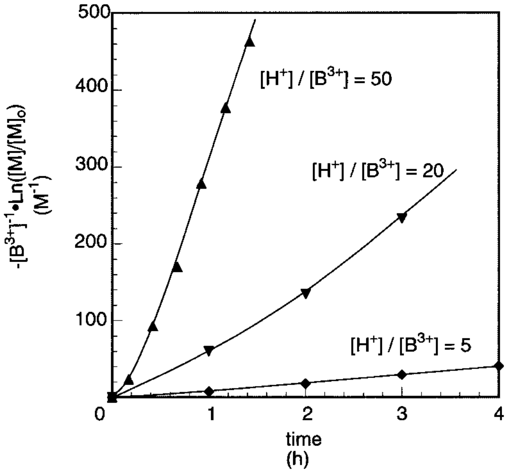


Figure 1. First-order kinetic plots for the polymerization of 7CC. Conditions: in CH_2Cl_2 at 25 °C, $[M]_0 = 1$ M, and $[HCl{\cdot}Et_2O]_0/[B(OEt)_3]_0 = 5$, 20, and 50.

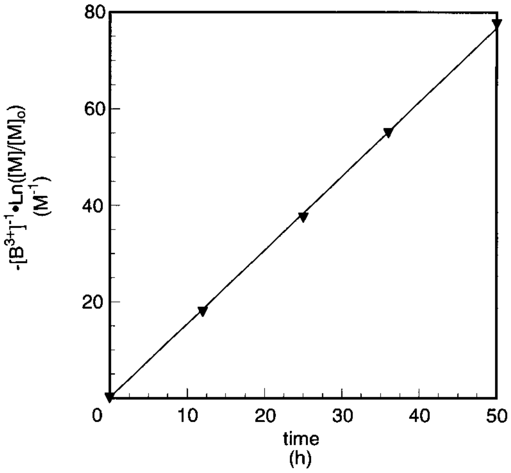
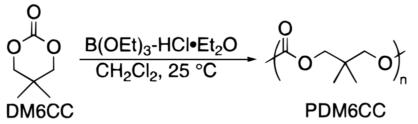


Figure 2. First-order kinetic plot for the polymerization of DM6CC. Conditions: in CH_2Cl_2 at 25 °C, $[M]_0 = 1$ M, and $[HCl{\cdot}Et_2O]_0/[B(OEt)_3]_0 = 20$.

Scheme 2



Use of $B(OEt)_3$ alone did not produce the polymer as well (run 1). The combination of $B(OEt)_3$ and $HCl{\cdot}Et_2O$ provided the polymer of 7CC quantitatively (runs 2–5). The M_n varied with the ratio of the borate to the monomer, but did not with the amount of $HCl{\cdot}Et_2O$ (runs 2 and 3). Although B(O-*i*-Pr)$_3$ also did not work as an initiator by itself (run 6), it initiated the polymerization smoothly in the presence of 10 equiv of $HCl{\cdot}Et_2O$, where the M_n and M_w/M_n could be controlled (runs 7 and 8). Thus, in these polymerizations, it was confirmed that $HCl{\cdot}Et_2O$ only served as a promoter for the polymerization of 7CC.

Scheme 2 and Table 2 summarize the results of the polymerization of trimethylene carbonate containing dimethyl group as the substituent (DM6CC) with $B(OEt)_3$–$HCl{\cdot}Et_2O$ initiator system in CH_2Cl_2 at 25 °C. Although $B(OEt)_3$ showed no polymerizability (run 1), in the presence of more than 20 equiv of $HCl{\cdot}Et_2O$ to $B(OEt)_3$ the corresponding polymers were obtained in high yield where the molecular weights could be tailored varying with the monomer/initiator ratios keeping small polydispersity ratios (runs 3–6). The decrease of the $HCl{\cdot}Et_2O$ amount (10 equiv to $B(OEt)_3$) resulted in significant decrease of monomer conversion (run 2). These results might suggest that $HCl{\cdot}Et_2O$ acted a promoter in this system.

Figure 1 illustrates the first-order kinetic plots for the polymerization of 7CC with $B(OEt)_3$–$HCl{\cdot}Et_2O$ initiator system in CH_2Cl_2 at 25 °C varying the amount of $HCl{\cdot}Et_2O$; $[HCl{\cdot}Et_2O]_0/[B(OEt)_3]_0 = 5$, 20, and 50. They showed some acceleration in early stage becoming a linear variation to indicate that the absence of termination reaction, but slow initiation in the polymerization. The rate constants (k_p) of the 7CC polymerization were estimated as 10, 87, and 340 $M^{-1}{\cdot}h^{-1}$ (in CH_2Cl_2 at 25 °C), respectively. Figure 2 illustrates the first-order kinetic plots for the DM6CC polymerization with $B(OEt)_3$–$HCl{\cdot}Et_2O$ initiator system in CH_2Cl_2 at 25 °C, showing a linear variation to indicate the absence of termination. The rate constant (k_p) of the DM6CC polymerization at 25 °C ($[HCl{\cdot}Et_2O]_0/[B(OEt)_3]_0 = 20$) was estimated as 1.6 $M^{-1}{\cdot}h^{-1}$, much smaller than those

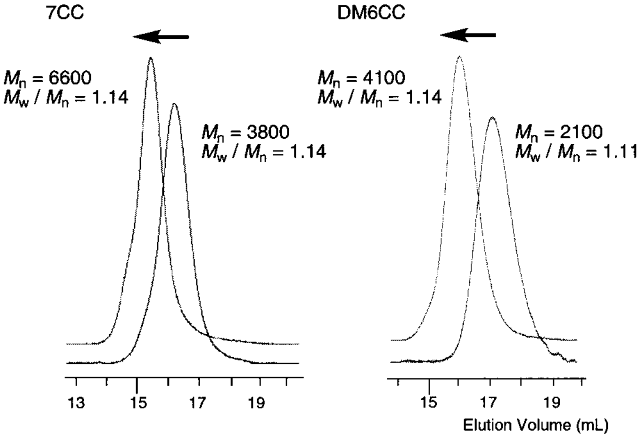


Figure 3. GPC profiles of the prepolymers obtained by the polymerization of 90 equiv of 7CC and 60 equiv of DM6CC with $B(OEt)_3$ in the presence of $HCl{\cdot}Et_2O$ (10 and 30 equiv vs $B(OEt)_3$), and the postpolymers obtained by the addition of the same amounts of the monomers.

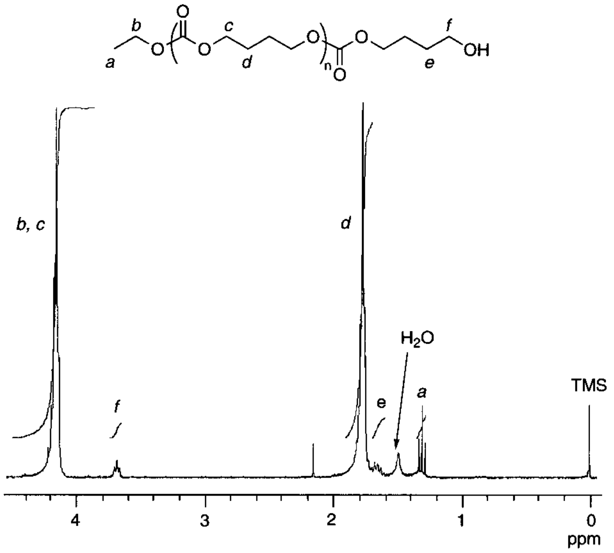


Figure 4. ^1H NMR spectrum (300 MHz, $CDCl_3$) of P7CC obtained by the polymerization in run 3 in Table 1.

of 7CC. To verify the living nature, the second feed experiments were carried out in the polymerization of 7CC and DM6CC. 90 and 60 equiv of 7CC and DM6CC were polymerized with $B(OEt)_3-HCl{\cdot}Et_2O$ initiator system in CH_2Cl_2 to obtain the prepolymers, respectively. After the quantitative consumption of the first monomers, the same amounts of the monomers were recharged into the polymerization mixtures to conduct the post polymerization, respectively. In both cases, the elution peaks in GPC shifted to the higher M_n region maintaining the small M_w/M_n as shown in Figure 3.

Table 3. Polymerization of 7CC[a]

run	$[M]_0/[B(OEt)_3]_0$	conv[b] (%)	$x_{(NMR)}$[c]	$x_{(GPC)}$[d]	M_w/M_n[d]
1	9	99	3.7	3.8	1.37
2	18	99	5.2	9.8	1.20
3	27	99	7.3	13	1.15
4	45	91	14	18	1.14
5	50	99	17	21	1.14

[a] Conditions: in CH_2Cl_2 at 25 °C for 24 h, $[M]_0$ = 1 M, and $[HCl]_0/[B(OEt)_3]_0$ = 10. [b] Determined by ^1H NMR. [c] Average unit number calculated by ^1H NMR. [d] Average unit number calculated by GPC (THF, polystyrene standards).

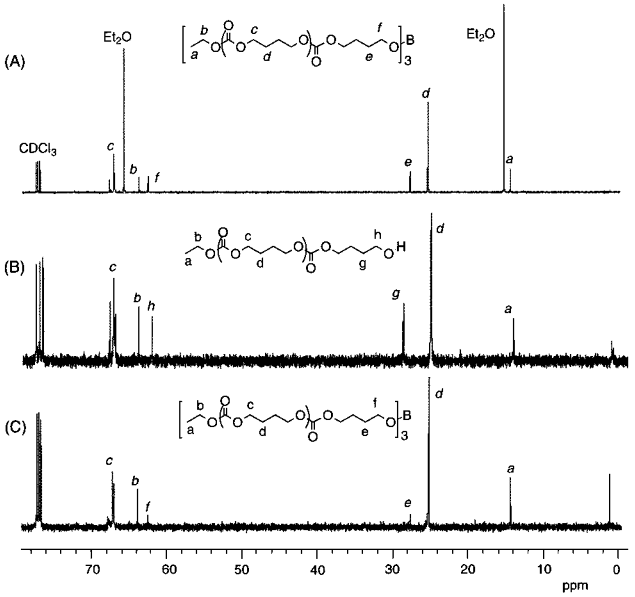


Figure 5. ^{13}C NMR spectra (75 MHz, $CDCl_3$) of (a) living P7CC obtained by the polymerization of 7CC (9 equiv) with $B(OEt)_3-HCl{\cdot}Et_2O$ (1/10 molar ratio) in $CDCl_3$ at 25 °C for 12 h, (b) P7CC obtained by quenching the living P7CC with pyridine, followed by washing with HCl(aq) and subsequent extraction with toluene, (c) and P7CC treated with BH_3 in THF at 0 °C for 30 min, and then 25 °C for 1 h.

Scheme 3

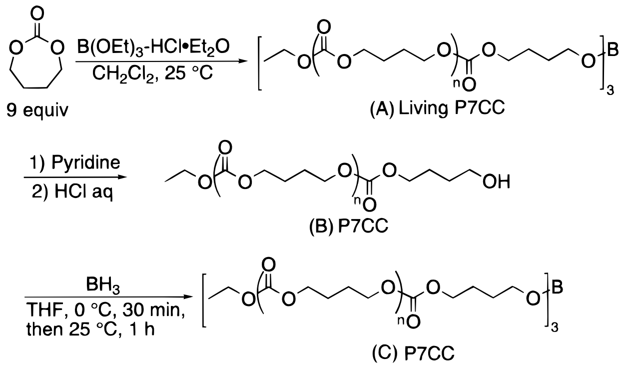
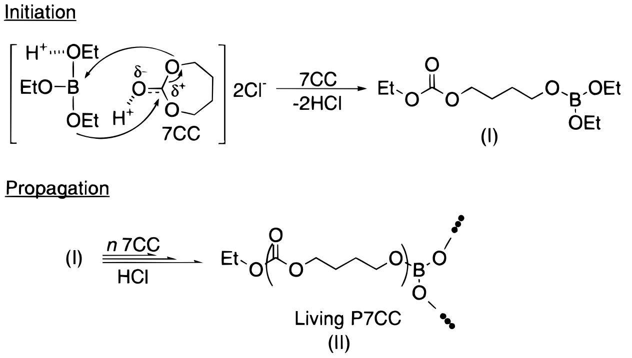


Figure 4 illustrates the ^1H NMR spectrum of P7CC obtained by the polymerization in run 3 in Table 1. In addition to signals *c* and *d* assignable to α- and *β*-methylene protons of the carbonate moiety at 4.17 and 1.75 ppm, signals *a* and *f* assignable to terminal methyl and α-methylene proton signals of a hydroxyl group were observed at 1.30 and 3.68 ppm, respectively. The integration ratio of the signals *a* to *f* was 3/2, which agreed well with the theoretical value. Table 3 summarizes the dependence of the average unit number of the oligo 7CC estimated by ^1H NMR (*x*(NMR)) and GPC (*x*(GPC)) on the feed ratio of the monomer to initiator. Both values almost agreed with one-third of the $[M]_0/[B(OEt)_3]_0$, suggesting that all the three ethoxide moieties on the boron initiated the polymerization.

Figure 5 illustrates the ^{13}C NMR spectra of (A) living polymer obtained by the living polymerization of 7CC with $B(OEt)_3-HCl{\cdot}Et_2O$ initiator system, (B) P7CC obtained by quenching the living P7CC with pyridine, followed by washing with HCl(aq) and subsequent extraction with toluene, and (C) and P7CC treated with BH_3 in THF at 0 °C for 30 min, then 25 °C for 1 h (Scheme 3). Signals *a*−*d* assignable to terminal ethyl group and α- and *β*-methylenes of the carbonate moiety were observed in all the samples. In Figure 5A, signals

Scheme 4



e and *f* adjacent to a borate moiety were observed at 27.3 and 62.3 ppm, respectively. In Figure 5B, the two signals disappeared while signals *g* and *h* assignable to β- and α-methylenes of a hydroxyl group appeared at 28.8 and 62.1 ppm, respectively. In Figure 5C, signals *e* and *f* assignable to the β- and α-methylens of the terminal borate moiety appeared again at 27.5 and 62.5 ppm, respectively. These results might suggest that the propagating polymer end should be a stable borate structure. The formation of a hydroxyl chain end by protonation of the terminal borate with HCl was negligible by these results.

Scheme 4 depicts the possible mechanism of the polymerization of 7CC with $B(OEt)_3$–HCl·Et_2O initiator system. The monomer activated with HCl·Et_2O coordinates the borate, followed by the attack of ethoxy group to the carbonyl carbon of the monomer reproducing the borate structure (I). The propagation may proceed via a monomer insertion to the B–O bond. Consequently, the polymer isolated after hydrolysis by HCl(aq) has ethyl carbonate and hydroxyl groups as the initial and terminal units, respectively.

Summary

In this article, we demonstrated the novel HCl promoted living ring-opening polymerization of a nonsubstituted seven-membered (7CC) and dimethyl substituted six-membered cyclic carbonates (DM6CC) with $B(OR)_3$ (R = Et and *i*-Pr) as the initiator. The addition of HCl·Et_2O promoted the monomer insertion to the B–O bond at ambient temperature to produce the corresponding polymers with controlled M_n and small M_w/M_n values.

References and Notes

(1) (a) Dale, J.; Daasvatn, K.; Grønneberg, T. *Makromol. Chem.* **1977**, *178*, 873. (b) Bucquoye, M. R.; Goethals, E. J. *Makromol. Chem.* **1981**, *182*, 3379.

(2) (a) Olah, C. A.; Karpeles, R.; Narang, S. C. *Synthesis* **1982**, 963. (b) Kricheldorf, H. R.; Sumbel, M. V. *Makromol. Chem.* **1988**, *189*, 317.

(3) Kricheldorf, H. R.; Weegen-Schulz, B. *J. Macromol. Chem: Pure Appl. Chem.* **1995**, *A32*, 1847.

(4) (a) Kricheldorf, H. R.; Mahler, A. *J. Macromol. Chem: Pure Appl. Chem.* **1996**, *A33*, 821. (b) Kricheldorf, H. R.; Weegen-Schulz, B. *Polymer* **1995**, *36*, 4997. (c) Kricheldorf, H. R.; Weegen-Schulz, B. *J. Polym. Sci., Part A: Polym. Chem.* **1995**, *33*, 2193. (d) Kricheldorf, H. R.; Jenssen, J.; Kreiser-Saunders: I. *Makromol. Chem.* **1991**, *192*, 2391. (e) Kricheldorf, H. R.; Mahler, A. *J. Polym. Sci., Part A: Polym. Chem.* **1996**, *34*, 2399. (f) Kricheldorf, H. R.; Lossin, M.; Mahler, A. *Macromol. Chem. Phys.* **1997**, *198*, 3559.

(5) (a) Carter, K. R.; Richter, R.; Kricheldorf, H. R.; Hedrick, J. L. *Macromolecules* **1997**, *30*, 6074. (b) Kühling, S.; Keul, H.; Höcker, H. *Makromol. Chem.* **1992**, *193*, 1207.

(6) Shibasaki, Y.; Sanda, F. Endo, T. *Macromol. Rapid Commun.* submitted for publication.

(7) Matsuo, J.; Sanda, F.; Endo, T. *Macromol. Chem. Phys.* **1998**, *199*, 97.

(8) Matsuo, J.; Aoki, K.; Sanda, F.; Endo, T. *Macromolecules* **1998**, *31*, 4432.

(9) In the polymerization of DM6CC, the reaction mixture was diluted with CH_2Cl_2, washed with Na_2CO_3(aq), and dried at 25 °C for 5 h under reduced pressure.

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