

7원환 고리화합물의 개환중합 Ring-opening Polymerization of an aliphatic seven-membered Cyclic Acetal

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〈요약〉

기능성고분자재료 중의 하나인 7원환 고리아세탈 화합물인 1,3-dioxepan-2-one(1)을 합성하고 고온조건 하에서 중합반응을 조사한 결과 선택적인 개환중합이 일어났다. 그러나 낮은 농도에서 작은 분자량을 가지는 고분자가 얻어졌으며 넓은 분자량 분포와 낮은 수율이 얻어지며 이것은 중압반응 도중에 분자 내에서 상호반응을 일으킴을 보여준다.

Key words : ring-opening polymerization, cyclic oligomer, seven-membered cyclic acetal

1. Introduction

Cyclic acetals have been reported to be polymerized both by anionic and cationic initiators.¹ Anionic ring-opening polymerization of cyclic acetals effectively proceeds to yield the corresponding linear polyacetal unit with any side reactions. On the other hand, the cationic ring-opening polymerization of cyclic acetals is generally accompanied by partial elimination of CO₂ to yield polyacetals containing polyether units.

Recently, we have reported that cyclic carbonates undergo cationic polymerization without decarboxylation by allyl halide initiator such as methyl iodide and benzyl bromide, whose counter anions have higher nucleophilicity. Further, we have found that cyclic carbonates shows volume expansion on the polymerization. It may be suggested that this volume expansion can be accounted for by the difference in the

degree of intermolecular interaction between monomers and polymers. It shows that stronger interaction in polymers eventually cause the volume expansion.² As described above, cyclic carbonates seem to be one of attractive monomers from the view point of polymer synthesis. Although there are many reports on the ring-opening polymerization of cyclic acetals,³ few studies on the ring-opening polymerization of five- and seven-membered cyclic acetals have been reported.⁴ The polymerization behavior of cyclic acetals drastically influenced by the ring size. The polymerization of five-membered cyclic acetals is much lower than that of six-membered ones. A five-membered cyclic acetal is not converted by *sec*-BuLi (typical anionic initiator). In the cationic condition, no polymerization of carbonates takes place below 60° C, and poly(oxyethylene) is formed accompanying complete elimination of CO₂ at highly than 70° C. Meanwhile, the polymerization of seven-membered cyclic acetals is suggested to proceed smoothly

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similarly to that of six-membered ones.⁴ However, the detailed polymerization behavior of seven-membered cyclic acetals is still unclear. In this report the synthesis and anionic polymerization behavior of aliphatic seven-membered cyclic acetal are described.

2. Experimental

Measurement : ¹H- and ¹³C-NMR spectra were recorded on JEOL JNM-EX400 and JNM-EX90 spectrometers (90 MHz for ¹H- and 100 MHz for ¹³C-NMR), using tetramethylsilane (TMS) as an internal standard in deuteriochloroform (CDCl₃) at 27° C. IR spectra were obtained with JASCO FT/IR-5300 spectrometer at 27° C. Molecular weights and the distribution were estimated by gel permeation chromatography (GPC) on Tosoh HPLC CCP & 8000 system with data processor.

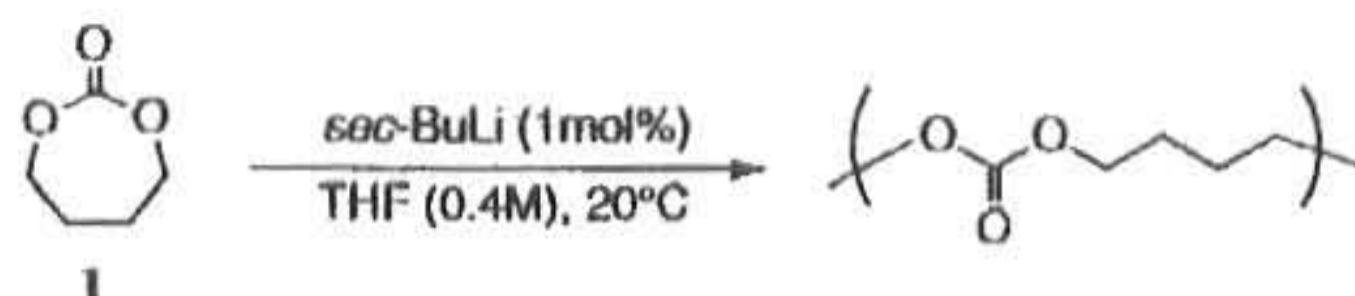
Materials : The THF was purified by distillation over sodium and benzophenone under nitrogen. Chloroform was purified by distillation over P₂O₅. 1,4-Butanediol was purified by distillation under reduced pressure. *Sec*-butyllithium (Kanto Chemical Co., Inc.) was used as received.

Synthesis of 1,3-dioxepan-2-one (1) : Synthesis of **1** was carried out referring to the reported method.⁵ A solution of triphosgen (16.8g, 0.056mol) in chloroform (90mL) was added dropwise to a solution of 1,4-butanediol (15g, 0.17mol) and pyridine (62.2g, 0.33mol) in chloroform (772mL) under stirring at 45-60° C. After being left overnight at room temperature, 600mL of 2.5% HCl aq. was added to the reaction mixture. The organic phase was separated and washed with aq. NaCl solution several times. The organic phase was dried over MgSO₄ and after removal of the solvent by evaporation, the residue was purified by silica gel column chromatography using ethyl acetate and *n*-hexane (ratio 1:1) as a eluent, and recrystallized from toluene-cyclohexane to afford a white crystal (6.1g). Yield 30%

Ring-opening Polymerization of 1 : All glass vessels were heated before use filled with nitrogen, and handled in a stream of dried nitrogen. To a solution of 0.2g (1.7mmol) of **1** in 2mL of THF was added 15 μL of 1.14M solution of *sec*-BuLi in cyclohexane. After the reaction, a solution of methanol/phosphoric acid (9:1) was added to the reaction mixture and it was poured into 120mL of methanol to isolate the polymer.

3. Result and Discussion

1 was prepared by the reaction of 1,4-butanediol and triphosgen in anhydrous chloroform in the presence of pyridine as a quencher for hydrochloric acid. The reaction gave **1** in 30% yield and the corresponding polycarbonate. Anionic ring-opening polymerization of **1** was carried out at 20° C for 5 min and 48 h in THF (0.4M) by *sec*-BuLi (1 mol%) as an initiator (Scheme 1).



Although the polymerization mixture after 5 min. showed a unimodal GPC curve.

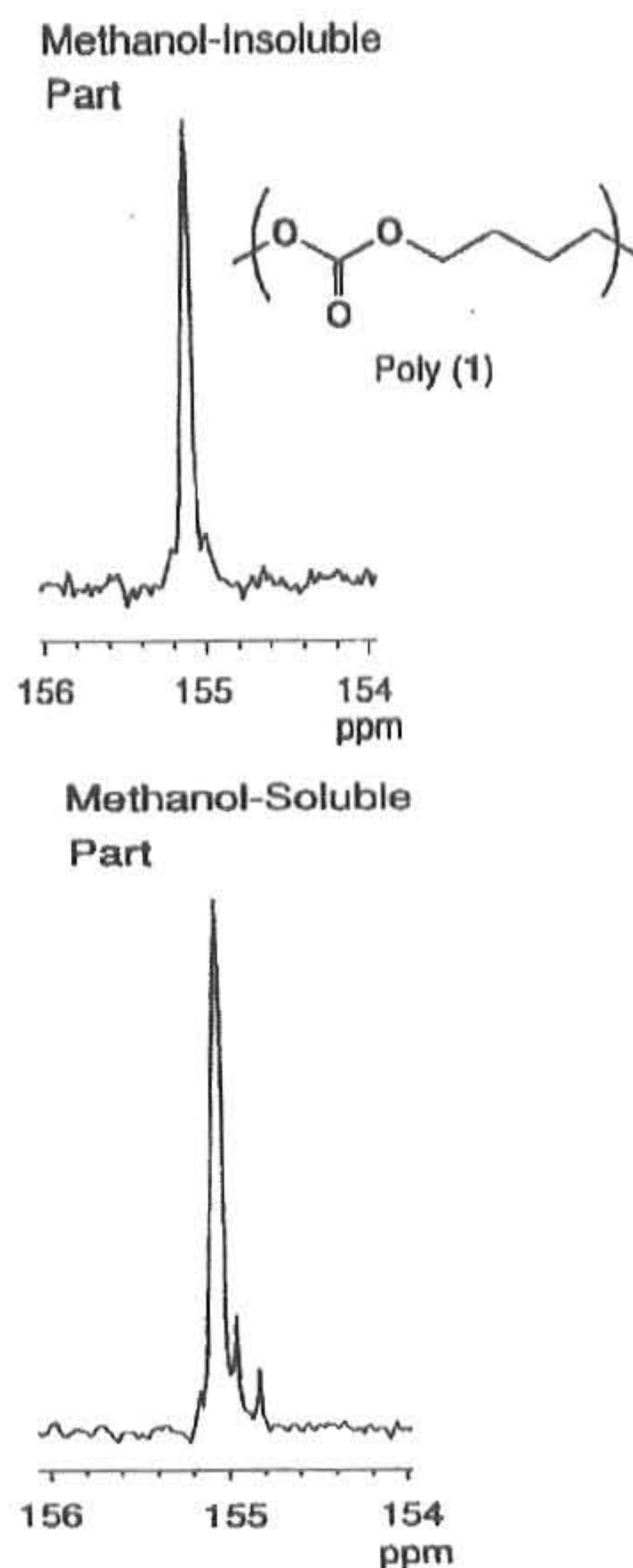


Figure 1. ¹³C-NMR spectra of the carbonate carbonyl regions of methanol-insoluble and soluble parts of poly(1)

The methanol-soluble part obtained in the polymerization at 20° C for 48 h was analyzed by ¹³C-NMR spectrum to confirm.

Next, the anionic ring-opening polymerization of **1** was carried out at 0, 20, 30, and 35° C for 1h in THF (0.9 M) by sec-BuLi (1 mol%) as an initiator to examine the effect of polymerization temperature on the polymerization. The results are summarized in Table 1. The higher polymerization temperature was, the lower yield and molecular weight of the polymer were obtained, similarly to usual equilibrium polymerizations.

Table 1. Anionic Polymerization of **1**

Entry	Temp °C	Yield ^a %	Mn ^{a,b}	Mw/Mn ^{a,b}
1	0	87	35,200	1.46
2	20	81	22,800	1.61
3	30	73	12,500	1.77
4	35	50	5,800	1.94

Conditions : initiator : sec-BuLi(1mol%), time : 1h, solvent : THF(0.9M)

^aMeOH-insoluble part.

^bEstimated by GPC based on polystyrene standard.

Table 2. Monomer Concentration of anionic polymerization of **1**

Entry	Conc. (M)	Yield ^a %	Mn ^{a,b}	Mw/Mn ^{a,b}
1	0.9	81	22,800	1.61
2	0.4	65	12,200	2.49
3	0.2	52	5,000	2.91

Conditions : initiator : sec-BuLi(1mol%), time : 1h, solvent : THF(0.9M)

^aMeOH-insoluble part.

^bEstimated by GPC based on polystyrene standard.

Anionic ring-opening polymerization of **1** was carried out at 20° C for 1h in THF by sec-BuLi (1 mol%) as an initiator with varying the monomer concentration (Table 2). The lower the initial monomer concentration in the polymerization of **1** was, the lower the yield and molecular weight of the polymer were obtained. This result seems to be attribute to the formation of a back-biting reaction. The intramolecular back-biting reaction might proceed besides the intermolecular propagation reaction in the lower initial monomer concentration although the structure is unclear, yet.

4. Conclusion

The anionic ring-opening polymerization of a seven membered cyclic acetal, 1,3-dioxepan-2-one (**1**), was carried out to observed that the higher the polymerization temperature and the lower the initial monomer concentration were, the lower the yield and molecular weight, and wider the molecular weight distribution of the obtained polymer were. These results might be explained by the formation of a back-biting reaction on the propagation.

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