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Novel Ring-Opening Polymerization and Its Application to Polymeric Materials

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SUMMARY: Ring-opening polymerization of cyclic carbonates was studied. Volume expansion during polymerization of cyclic carbonates could be explained by the difference between intermolecular interaction of monomers and polymers, which was evaluated by dipole moment. A seven-membered cyclic carbonate polymerized much faster than a six-membered one. Bulky substituents of six-membered cyclic carbonates increased the equilibrium monomer concentration. A novel initiator system, combination of alcohol and trifluoroacetic acid, efficiently polymerized cyclic carbonates.

Introduction

Chemistry of ring-opening polymerization was established in 1950s. The history of ring-opening polymerization is relatively shorter compared with vinyl polymerization and polycondensation, which have been widely developed both from scientific and industrial points of view.1) Nowadays, ring-opening polymerization plays an important role in industry such as production of nylon-6. Ring-opening polymerization can introduce functional groups like ether, ester, amide, and carbonate into the polymer main chain, which cannot be attained by vinyl polymerization affording polymers only with C-C main chain. Polymers obtained by ring-opening polymerization can be also prepared by polycondensation in most cases, but following control is possible in ring-opening polymerization, which is difficult in polycondensation.

- Equivalency of two functional groups is important to obtain a high molecular weight polymer in polycondensation. This is automatically achieved in ring-opening polymerization.
- Living polymerization can be expected in ring-opening polymerization. Molecular weight and polydispersity ratio can be controlled.
- Copolymerization with controlled unit sequence (block polymerization) is possible.

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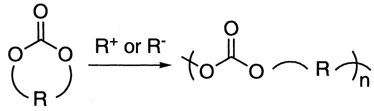
- Control of stereo regularity is possible.

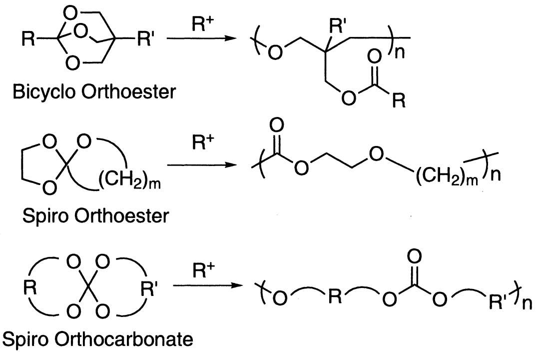
Recently, development of novel monomers and catalysts has enabled us to control molecular weights, structure, and configuration of the polymers more precisely than ever before. Cyclic carbonates undergo both cationic and anionic polymerizations to afford the corresponding polycarbonates (Scheme 1),[2] which are expected as biocompatible and biodegradable polymers.[3] Recently, ultra high molecular weight bisphenol A polycarbonate (> Mw 2,000,000) has been synthesized by the ring-opening polymerization a large-membered bisphenol A-based cyclic carbonate.[4] The obtained polymer is expected as engineering plastics with high impact resistance and thermal stability. As described above, polymerization of cyclic carbonates attracts much attention both from polymerization behavior and function. This article deals with controlled ring-opening polymerization of cyclic carbonates.



Scheme 1

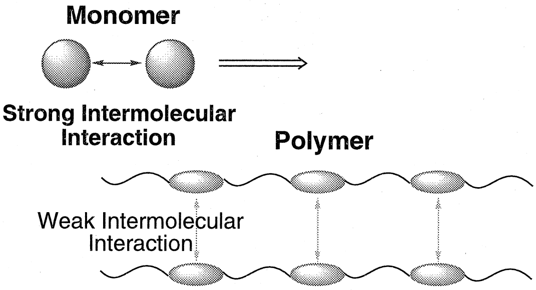
Volume expansion during ring-opening polymerization of cyclic carbonates

Polymerization of vinyl monomers such as styrene and methyl methacrylate, and cyclic monomers such as epoxides is accompanied by volume shrinkage as large as ~ 20%. The reason can be readily understood from the decrease of intermolecular distance of monomer molecules located at a van der Waals distance to a covalent distance by polymerization. Occurrence of volume shrinkage exhibits serious problems in many industrial applications of polymeric materials, and thereby development of monomers and materials showing volume expansion or zero-shrinkage is one of the most essential subjects in materials science.[2] Several attempts have been made to reduce volume shrinkage like improvement of adhesion method and addition of fillers. However, the problems of lowering of material properties caused by curing shrinkage have not been completely solved yet. We have previously reported that some bicyclic and spiro cyclic monomers such as bicyclo orthoesters, spiro orthoesters, and spiro orthocarbonates undergo cationic double ring-opening polymerization accompanying volume expansion (Scheme 2). Copolymerization of these expandable monomers with thermosetting resins is effective to reduce volume shrinkage during curing process and enhance the product property. These monomers exhibit volume expansion according to principle as follows. Free volume decreases by polymerization, because the distance between monomer molecules becomes close from van der Waals distance to covalent distance. Meanwhile, the covalent distance of the monomer transforms into near van der Waals distance by double ring-opening polymerization, which compensates the free volume decrease by polymerization.



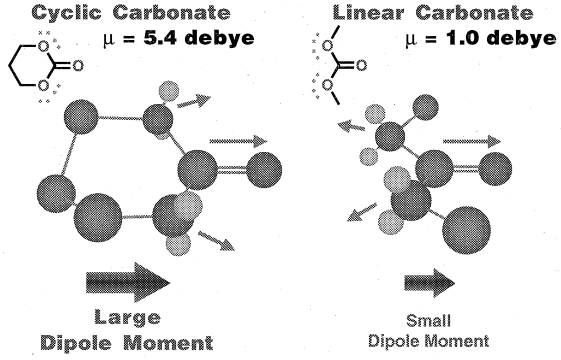
Scheme 2

Recently, we have found that cyclic carbonates show volume expansion on polymerization.[2)] This is very interesting and significant, because they only undergo single ring-opening polymerization, and therefore cannot be explained by the concept applicable to the expandable bicyclic and spirocyclic monomers described above. We have noticed that change in intermolecular interaction before and after polymerization can explain the volume expansion of cyclic carbonates, i. e., density decrease by decrease in intermolecular interaction during polymerization is more than density increase resulted by conversion of monomer molecules to the polymer (Scheme 3). It can be demonstrated that difference in dipole moment between monomer and polymer is available to evaluate the intermolecular interaction.



Scheme 3

We calculated the dipole moment of the monomer and the polymer model, dimethyl carbonate. The cyclic carbonate showed a large value (5.4 debye), while dimethyl carbonate showed a small value (1.0 debye) (Scheme 4). It was suggested that cyclic carbonates show volume expansion due to the large intermolecular interaction by the large dipole moment, and small interaction by the small dipole moment of the polymer.[5)] This mechanism of volume expansion of cyclic carbonates is completely different from that of bicyclic and spiro cyclic monomers.

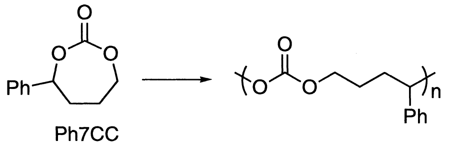


Scheme 4

Cationic and anionic ring-opening polymerizations of seven-membered cyclic carbonates

Many researches on ring-opening polymerization of six-membered cyclic carbonates have been reported concerning substituent effect, control of molecular weight and tacticity, depolymerization, and copolymerization with other monomers. On the contrary, only a few reports of ring-opening polymerization of cyclic carbonates have been reported so far. We examined the ring-opening polymerization of a seven-membered cyclic carbonate to find that the rates of anionic and cationic polymerizations of the seven-membered one were 36 and 100 times faster compared with those of a six-membered one, respectively.[6,7)] We further studied the anionic and cationic ring-opening polymerizations of a seven-membered cyclic carbonate

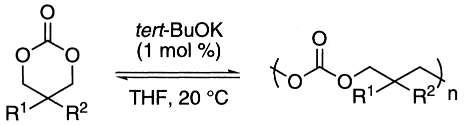
(Ph7CC) substituted with a phenyl group.[8)] The anionic polymerization of Ph7CC was carried out with *sec*-BuLi or *tert*-BuOK (1 mol %) as an initiator in tetrahydrofuran (0.8 M) at 20 °C for 1 h to afford the corresponding polycarbonate with M_n of 11,700 ~ 13,400 in 79 ~ 88% yield (Scheme 5). The cationic polymerization of Ph7CC was carried out with TfOMe, TfOEt, or BF_3•OEt_2 as an initiator (1 mol %) in CH_2Cl_2 (1 M) at 20 °C for 4 h to obtain the corresponding polycarbonate with M_n of 3,000-5,600 in 35-63% yield (Scheme 5). The ^{13}C-NMR spectrum of the polymer obtained by anionic polymerization showed three carbonyl carbon signals, while that by cationic polymerization showed one signal, suggesting the selective cleavage of the benzyl carbon-ether oxygen bond due to formation of stable benzyl cation.



Scheme 5

Anionic equilibrium polymerization of six-membered cyclic carbonates

Substituent effect on anionic equilibrium polymerization was examined. A cyclic carbonate substituted with aromatic groups showed a higher equilibrium monomer concentration, i. e., low polymerizability. Calculated thermodynamic parameters agreed well with the polymerizability (Scheme 6, Table 1).[9)] Introduction of aromatic substituents seemed to distort the carbonate moiety of the polymer main chain, resulting in destabilization of the polymer. The monomer with two phenyl groups at the 5-position did not polymerize at all. It was suggested from the molecular orbital calculation that back-biting reaction was predominate compared with propagation reaction.[10)] The copolymerization of this monomer with dimethyl substituted monomer could afford the copolymer.



Scheme 6

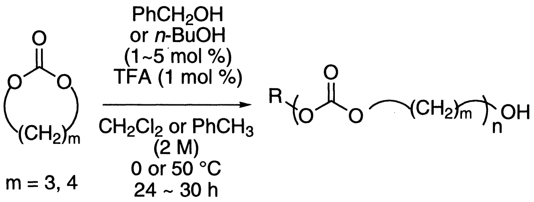
Table 1. Equilibrium monomer concentration and thermodynamic parameters in the anionic polymerization of six-membered cyclic carbonates [a)]

monomer		equilibrium monomer			
R^1	R^2	conc (M)	ΔH_p (kcal/mol)	ΔS_p (cal/K•mol)	ΔG_p (kcal/mol)
H	H	0.02 [b)]	-6.3	-10.7	-3.1
Me	Me	0.03	-5.1	-10.5	-2.0
Et	Et	0.08	-4.4	-10.9	-1.2
Me	Ph	0.11	-4.0	-9.7	-1.2
Et	Ph	0.41	-1.2	-2.4	-0.5
Ph	Ph	- [c)]	- [c)]	- [c)]	- [c)]

a) Conditions: initiator *tert*-BuOK (1 mol %), solvent THF (initial monomer conc. 0.6 M), temperature 20 °C. b) Initial monomer conc. 0.05 M. c) No polymerization.

Ring-opening polymerization of cyclic carbonates with alcohol-acid catalyst

Cyclic carbonates react with several nucleophiles to afford the corresponding ring-opened adducts. Reaction of cyclic carbonates with amines has been extensively studied, while that with alcohols has not. We examined the ring-opening polymerization of cyclic carbonates based on the reaction with alcohols in the presence of acid catalysts. The polymerization of six- and seven-membered cyclic carbonates was carried out with benzyl alcohol or *n*-butanol (1-5 mol %) in the presence of trifluoroacetic acid (1 mol %) in CH_2Cl_2 or toluene (2 M) at 0 or 50 °C. The polymers with M_n of 2,500-6,800 (M_w/M_n 1.16-1.24) were obtained in 75-93% yield (Scheme 7).[11)] The molecular weight of the polymer increased as the amount of the used alcohol decreased. No reaction of cyclic carbonates took place with alcohols in the absence of catalysts, but it efficiently proceeded in the presence of acids. It was suggested that the acids activated the cyclic carbonates by coordination. For confirmation, we examined the change of chemical shifts of the cyclic carbonates by the addition of trifluoroacetic acid by ^1H and ^{13}C NMR spectroscopy to find the lower field shift of the α and β-methylene protons, and also carbonyl carbon signal.



Scheme 7

Conclusion

In this article, we reviewed our recent study on controlled ring-opening polymerization of cyclic carbonates. Further development of novel monomers and initiators is expected, based on the previous information and molecular design utilizing computational chemistry.

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