Specific Formation of a Polymer Containing Five-Membered Oxalactone Rings in the Main Chain in the Cationic Ring-Opening Polymerization of 6,8-Dioxabicyclo[3.2.1]octan-7-one

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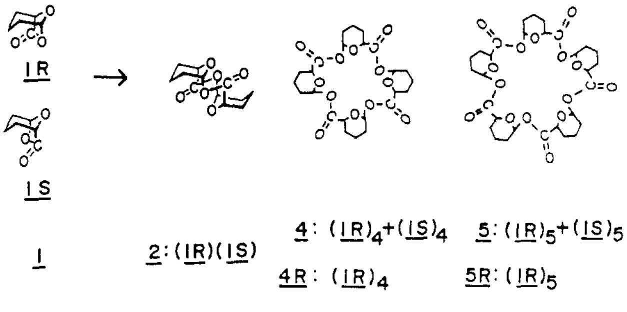
ABSTRACT: A polymer (polymer A) containing five-membered oxalactone (1,3-dioxolan-4-one) rings in the backbone chain was obtained in the polymerization of 6,8-dioxabicyclo[3.2.1]octan-7-one initiated with boron trifluoride etherate in chloroform at 0 °C, in sharp contrast to the formation of polyester (polymer B) and cyclic oligoesters consisting of alternating tetrahydropyran ring and ester moieties at or below -40 °C. The comparison of the spectroscopic data (IR, ^{1}H NMR, and ^{13}C NMR) of polymer A with those of polymer B and a model compound, 2,5-dimethyl-1,3-dioxolan-4-one (a mixture of trans and cis stereoisomers), revealed that polymer A was composed of 1,3-dioxolan-4-one rings linked at the 2- and 5-positions with trimethylene chains, the trans:cis ratio of the disubstituted ring structures being approximately 70:30. An optically active polymer of the same structure was obtained in the polymerization of (+)-(1*R*,5*R*)-6,8-dioxabicyclo[3.2.1]octan-7-one of 90% optical purity under similar reaction conditions. Polymer A is not formed directly by the ring-opening polymerization of the bicyclic monomer but by the isomerization of the once-formed polyester or oligoester chains. A mechanism for the isomerization induced with cationic species is proposed and discussed.

Cationic polymerization of a bicyclic oxalactone, 6,8-dioxabicyclo[3.2.1]octan-7-one, is unique in that the racemic monomer (1) gives highly selectively 10-, 20-, and 25-membered macrocyclic oligoesters (dimer (2), tetramer (4), and pentamer (5)) in acetonitrile, chloroform, and 1-nitropropane, respectively, at -40 °C,[1-3] while one of the enantiomers of 1, (+)-(1*R*,5*R*)-6,8-dioxabicyclo[3.2.1]octan-7-one (1***R***) affords preferentially the optically active cyclic tetramer (4***R***) in acetonitrile and the optically active cyclic pentamer (5***R***) in 1-nitropropane.[3-5] Furthermore, each cyclic oligoester derived from the racemic monomer 1 is not a mixture of cyclic oligomers of different structures but it is a single compound: The cyclic dimer 2 consists of a pair of enantiomeric monomeric units (1***R*** and 1***S***), and in contrast, the cyclic tetramer 4 and pentamer 5 are structurally identical with the optically active cyclic tetramer 4***R*** and pentamer 5***R***, respectively, derived from the optically active monomer 1***R***.[6-8] In other words, 4 is an equimolar mixture of 4***R*** and its enantiomer 4***S***, and 5 is an equimolar mixture of 5***R*** and its enantiomer 5***S***.


1R
1S
1
2: (1R)(1S)
4: $(1R)_4+(1S)_4$
4R: $(1R)_4$
5: $(1R)_5+(1S)_5$
5R: $(1R)_5$

When the polymerization of 1 was carried out in chloroform at -60 °C, a polymer of a regular polyester structure was predominantly produced along with some oligomers in reactions of shorter time (0.5-4 h).[9] In a prolonged reaction (24 h), however, the polymer was mostly converted into the cyclic oligomers 4 and 5. In the polymerization of 1 at -40 °C, a smaller amount of polymer was formed only in the initial stage of the reaction, and it was relatively rapidly transformed into the cyclic tetramer 4.[3] In remarkable contrast to the polymerization behavior of 1, no polymer was formed from the optically active monomer 1***R*** even at -60 °C.[9]

In the course of further studies on the specific behaviors of the cationic polymerization of the bicyclic oxalactone, we found that a polymer consisting of structural units completely differing from the regular polyester structure as expected from simple ring-opening polymerization of 1 was produced at higher temperatures. The present paper is concerned with the spectroscopic analysis of the polymer and mechanism for its formation.

Experimental Section

Materials. The racemic and optically active monomers 1 and 1***R*** were synthesized from sodium 3,4-dihydro-2*H*-pyran-2-carboxylate according to the procedures reported previously.[4,10] They were purified by drying over calcium hydride followed by distillation under reduced pressure. Chloroform was washed with 5% aqueous sodium carbonate and subsequently with water. It was refluxed over calcium hydride and fractionally distilled.

Polymerization. Polymerization of 1 and 1***R*** was carried out in chloroform at 0 °C with boron trifluoride etherate as an initiator. The polymerization and work-up procedures were the same as those described in the previous paper.[1]

Characterization. ^{1}H and ^{13}C NMR spectra were recorded on JEOL FX-200 and JEOL FX-100 spectrometers operating at 200 and 25 MHz, respectively. Deuteriochloroform and tetramethylsilane were used as the solvent and internal reference. IR spectra were measured with a Jasco A-3 spectrophotometer on solutions in chloroform. Molecular weights of polymers were estimated by gel permeation chromatography (column, Shodex 80M, 1 m; solvent, chloroform; polystyrene standard).

Preparation of 2,5-Dimethyl-1,3-dioxolan-4-one. A mixture of commercial lactic acid (25 mL, ca. 90% purity) and benzene (300 mL) was refluxed in a 500-mL flask equipped with a water separator (Dean-Stark trap) to remove water contained in the lactic acid. Subsequently paraldehyde (15 mL) and Amberlite IR 120B (1.68 g) were added to the benzene solution, and the mixture was refluxed for 5 h. Removal of the solvent followed by distillation under reduced pressure gave 2,5-dimethyl-1,3-dioxolan-4-one as a mixture of trans and cis stereoisomers (70:30 by ^{1}H NMR): yield 41%; bp 68-72 °C (40 mmHg).

Results and Discussion

Polymerization of the racemic monomer 1 was carried out in chloroform at 0 °C with boron trifluoride etherate as the initiator. The results are summarized in Table I.

The conversions of 1 into oligomers and polymer were estimated from gel permeation chromatogram of the reaction mixture after the reaction was terminated by the addition of a small amount of pyridine. At lower overall conversions (the first two runs in Table I), the products were mostly oligomeric materials with molecular weights

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Table I
Polymerization of *rac*-6,8-Dioxabicyclo[3.2.1]octan-7-one (1) at 0 °C[a]

monomer, g	solvent, mL	time, h	convrsn,[b] % lower MW	higher MW	yield,[c] %	$M_n \times 10^{-3}$ [c]	$M_w \times 10^{-3}$ [c]
1[d]	2	2	14	5	1.6	5.3	7.0
1	2	0.5	18	4	1.9	5.2	6.4
1	2	1	35	34	24	5.2	6.7
2	4	2	32	50	29	3.7	5.0

[a] Solvent, chloroform; initiator, $BF_3 \cdot OEt_2$, 5 mol % to monomer. [b] By gel permeation chromatography. Lower MW and higher MW refer to the polymers whose molecular weights are lower and higher, respectively, than 1.7×10^3 based on the calibration with standard polystyrene. [c] Methanol-insoluble polymer. [d] Initiator, $BF_3 \cdot Et_2O$, 1 mol % to monomer.

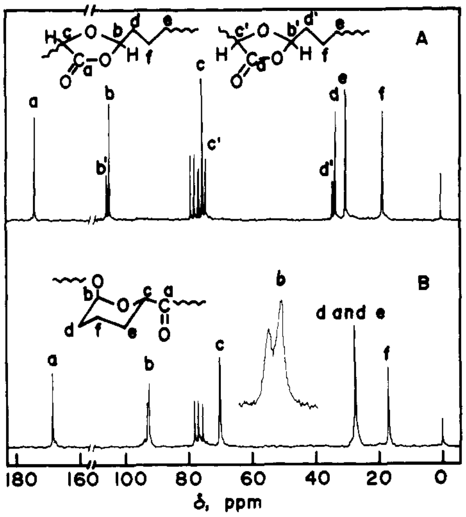


Figure 1. ^{13}C NMR spectra of the polymers of *rac*-6,8-dioxabicyclo[3.2.1]octan-7-one prepared in chloroform at 0 °C (A) and at -60 °C (B). Solvent, $CDCl_3$; temperature, 22 °C; 25 MHz; internal reference, tetramethylsilane. The inserted spectrum in (B) is the expanded spectrum of the signal b.

of less than 1000. Although a small amount of the cyclic dimer was detected, there was, if any, a very minor amount of other cyclic oligomers in the products. With increasing overall conversions, the fraction of higher molecular weight materials increased gradually. The reaction mixture dissolved in chloroform was poured into a large amount of methanol to precipitate methanol-insoluble polymer. (Hereafter, the polymer thus obtained is referred to as polymer A.) Polymer A is of relatively low molecular weight and soluble in dichloromethane, chloroform, dimethyl sulfoxide, and acetonitrile. It softened at 47-60 °C and began to decompose at about 115 °C.

The infrared spectrum of polymer A showed a strong carbonyl absorption at 1795 cm^{-1}, in contrast to the carbonyl absorption at 1755 cm^{-1} of a polymer prepared at -60 °C. (The latter polymer is referred to as polymer B.) Since γ-lactones with electronegative substituents in the γ-position exhibit the carbonyl absorption near 1800 cm^{-1},[11] the characteristic frequency of the carbonyl absorption of polymer A is indicative of the presence of five-membered lactone rings in the polymer chain instead of acyclic ester linkages as in polymer B.[12]

Figure 1 shows the ^{13}C NMR spectra of polymer A and polymer B. It has been established that polymer B consists of alternating tetrahydropyran and ester moieties, the carbonyl carbon and ester oxygen orienting equatorially and axially to the tetrahydropyran ring, respectively.[10] As the expanded spectrum clearly shows, the signal b in the spectrum of polymer B consists of a pair of peaks of different intensities. This is conceivably ascribed to the different dyad placements of the D,L-enantiomeric units along the polymer chain, as proved for the polymers of *rac*-6,8-dioxabicyclo[3.2.1]octane and its 4(e)-bromo derivative having a skeleton similar to that of **1**.[13,14]

Table II
Polymerization of Optically Active 6,8-Dioxabicyclo[3.2.1]octan-7-one (1*R*) at 0 °C[a]

monomer,[b] g	solvent, mL	time, h	convrsn,[c] % lower MW	higher MW	yield,[d] %	$M_n \times 10^{-3}$ [c,d]	$M_w \times 10^{-3}$ [c,d]
1.6	3.2	2	34	50	32[e]	4.4	6.0

[a] Solvent, chloroform; initiator, $BF_3 \cdot OEt_2$, 5 mol % to monomer. [b] $[\alpha]^{25}_D$ +128°(chloroform; optical purity, 90%). [c] By gel permeation chromatography. See footnote *b* of Table I. [d] Methanol-insoluble polymer; $[\alpha]^{25}_D$ +11.1° (chloroform). [e] Anal. Calcd for $(C_6H_8O_3)_n$: C, 56.25; H, 6.29. Found: C, 56.15; H, 6.23.

The spectrum of polymer A differs from that of polymer B not only in the chemical shifts of the signals but also in the splitting pattern. The differences in chemical shifts between the signals of each pair (b and b′, c and c′, and d and d′) in the spectrum of polymer A are 0.8-1.2 ppm, which are appreciably larger than that for the split signal b (0.3 ppm) in the spectrum of polymer B. Therefore, it would appear that the signal pairs of different intensities in the spectrum of polymer A do not arise from the different dyad placements of the D,L-enantiomeric monomeric units along the polymer chain but from the presence of two sterically different structural units. In order to clarify this point, the polymerization of the optically active monomer **1*R*** was undertaken in chloroform at 0 °C with boron trifluoride etherate as the initiator. The results are presented in Table II.

In contrast to the observation that no polymer was formed from **1*R*** at -60 °C, a polymer with a molecular weight of 4.4×10^3 was produced from **1*R*** at 0 °C. Its specific rotation was $[\alpha]^{25}_D$ +11.1° (cf. the specific rotations of the optically active cyclic tetramer and pentamer of **1*R***: **4*R***, $[\alpha]^{25}_D$ -189°; **5*R***, $[\alpha]^{25}_D$ -136°). The ^{13}C NMR spectrum of the polymer was practically identical with that of the polymer derived from the racemic monomer **1**. This is a clear indication that the signal pairs in the spectrum of polymer A are not ascribable to the different dyad placements of the D,L-enantiomeric units along the polymer chain but to the coexistence of two different structural units.

These ^{13}C NMR data in combination with the aforementioned infrared data strongly suggest that polymer A is composed of five-membered oxalactone rings linked with trimethylene chains as shown in Figure 1A. Therefore, as a model compound for the structural unit of polymer A, 2,5-dimethyl-1,3-dioxolan-4-one (a mixture of trans and cis stereoisomers) was prepared from lactic acid and paraldehyde, and its spectral data were compared with those of polymer A.

The model compound showed the infrared carbonyl absorption at 1796 cm^{-1} in good accordance with that of polymer A. Furthermore, it exhibited a ^{13}C NMR pattern similar to that of polymer A (Figure 2): The chemical shifts of the signals a, b (b′), and c (c′) due to the carbonyl carbon, acetal carbon, and methine carbon bearing the carbonyl carbon, respectively, are in good agreement with those of the corresponding signals of polymer A. The signal pairs b and b′, c and c′, d and d′, and e and e′ obviously arise from the presence of the trans and cis stereoisomers. From the comparison with the ^1H NMR spectrum, the signal of the stronger intensity of each signal pair was assigned to the trans isomer and that of the

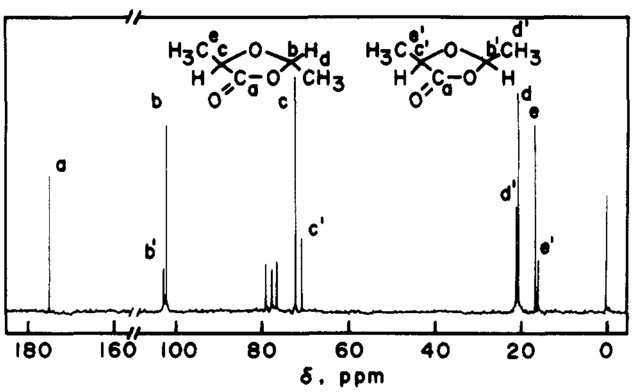


Figure 2. ^{13}C NMR spectrum of 2,5-dimethyl-1,3-dioxolan-4-one. Solvent, $CDCl_3$; temperature, 22 °C; 25 MHz; internal reference, tetramethylsilane.

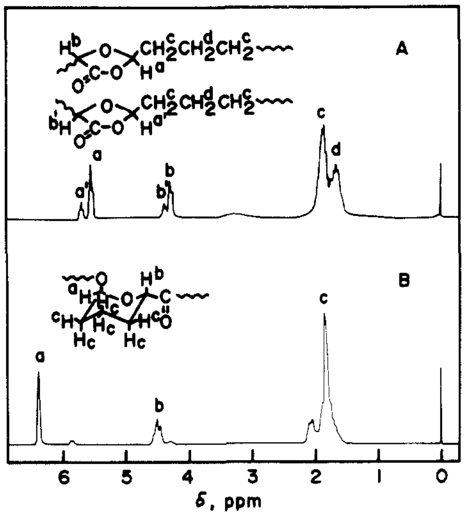


Figure 3. ^1H NMR spectra of the polymers of *rac*-6,8-dioxabicyclo[3.2.1]octan-7-one prepared in chloroform at 0 °C (A) and −60 °C (B). Solvent, $CDCl_3$; temperature, 22 °C; 200 MHz; internal reference, tetramethylsilane.

weaker intensity was assigned to the cis isomer.

Figure 3 presents the ^1H NMR spectra of polymer A (A) and polymer B (B). Their chemical shift data are listed along with those for 2,5-dimethyl-1,3-dioxolan-4-one and the cyclic pentamer 5 in Table III for comparison.

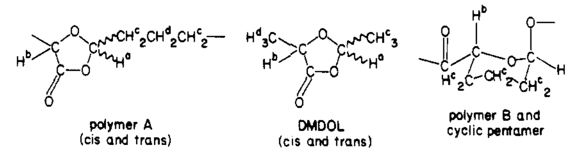
The chemical shifts of the acetal proton signals a and a′ and of the methine signals b and b′ of polymer A are very close to those of the corresponding signals of *trans* and *cis*-2,5-dimethyl-1,3-dioxolan-4-one. On the other hand, the chemical shifts of the signals a, b, and c of polymer B are similar to those of the cyclic pentamer consisting of alternating tetrahydropyran ring and ester moieties.

On the basis of the foregoing spectroscopic data, it is reasonably concluded that polymer A is composed of 1,3-dioxolan-4-one rings linked at the 2- and 5-positions with trimethylene chains. However, any simple ring-opening polymerization of the monomer does not lead directly to the polymer containing five-membered oxalactone rings in the main chain as illustrated in Scheme I: The acyl-oxygen fission (a) of the ester linkage affords a diequatorially substituted tetrahydropyran unit in the polymer chain, while the alkyl-oxygen fission (b) gives a tetrahydropyran unit with an equatorially oriented carbonyl group and an axially oriented oxygen atom (an S_N2-type reaction) or its mixture with the diequatorially substituted tetrahydropyran unit (an S_N1-type reaction). The C–O bond fission (c) of the tetrahydropyran ring in the monomer produces a seven-membered lactone unit.

Table III
^1H NMR Chemical Shift Data for the Polymers of 6,8-Dioxabicyclo[3.2.1]octan-7-one and Their Model Compounds[a]

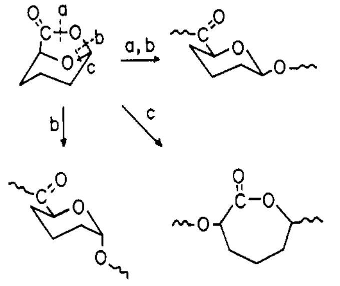
compd		assignment[b] a	b	c	d
polymer A	cis	5.68	4.37	1.85	1.66
	trans	5.53	4.28	1.85	1.66
DMDOL[c]	cis	5.82	4.49	1.53	1.46
	trans	5.62	4.34	1.57	1.50
polymer B		6.34	4.48	1.82[d]	
cyclic pentamer		6.50	4.60	1.85[d]	

[a] Solvent, $CDCl_3$; room temperature; 200 MHz; internal reference, tetramethylsilane. [b] Assignments on the basis of the following:



[c] 2,5-Dimethyl-1,3-dioxolan-4-one. [d] Chemical shift at the maximum of the broad peak.

Scheme I
Ring-Opening Modes of 6,8-Dioxabicyclo[3.2.1]octan-7-one in the Cationic Polymerization

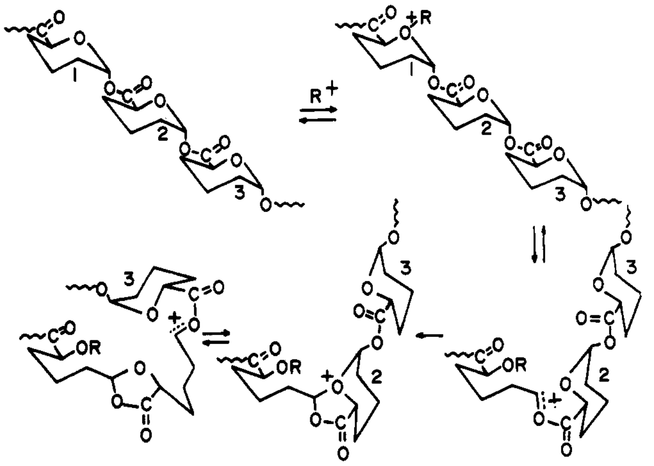


With regard to the mechanism of the formation of polymer A, it is to be noted here that a polymer obtained in the initial stage of the polymerization at 0 °C contained the structural unit of polymer B as the minor component. This finding implies that polymer A is formed by the isomerization of backbone chains possessing acyclic ester linkages. In fact, this is substantiated by the experimental result that when a solution of polymer B in chloroform containing a catalytic amount of boron trifluoride etherate was allowed to stand at 0 °C, polymer B was gradually transformed to polymer A with concomitant lowering of the molecular weight and broadening of the molecular weight distribution.

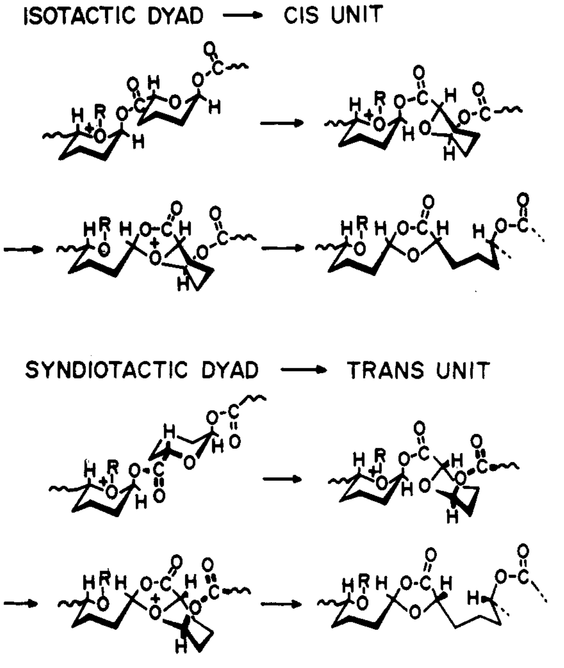
A possible isomerization mechanism is proposed in Scheme II: The isomerization is initiated by the addition of a cationic species R^+ onto the oxygen atom of a tetrahydropyran ring (1) (upper right). The C–O^+ bond of the tetrahydropyran ring is cleaved unimolecularly to give an oxacarbenium ion (lower right), to which the oxygen atom of the neighboring tetrahydropyran ring (2) attacks to form the oxonium ion of a five-membered oxalactone ring (1,3-dioxolan-4-one) structure (lower middle). Subsequent cleavage of the C–O^+ bond yields an oxacarbenium ion (lower left), which in turn produces another oxalactone ring. Thus, once the reaction is initiated, the isomerization proceeds along the polymer chain to afford a polymer consisting of the oxalactone rings linked with trimethylene chains (polymer A).

If the oxalactone ring is formed via an S_N2-type mechanism, that is, the direct attack of the oxygen atom of the

Scheme II
Mechanism for the Isomerization of the Structure Consisting of Alternating Tetrahydropyran Ring and Ester Moieties to the Structure Containing 1,3-Dioxolan-4-one Rings Linked with Trimethylene Groups



Scheme III
Formation of Cis- and Trans-Disubstituted Oxalactone Rings in the Polymer Chain by an S_N2-Type Mechanism Involving the Oxonium Ion of the Tetrahydropyran Ring and the Oxygen Atom of the Neighboring Tetrahydropyran Ring



tetrahydropyan ring to the positively charged acetal carbon atom of the trialkyloxonium ion, a cis-disubstituted oxalactone ring would be formed when the neighboring unit is of the same chirality as that of the preceding unit (isotactic dyad), while a trans counterpart would be produced when the neighboring unit is of the opposite chirality to that of the preceding unit (syndiotactic dyad) as illustrated in Scheme III. Therefore, a polymer exclusively composed of cis-disubstituted oxalactone rings would be obtained in the polymerization of the optically active monomer **1*R***. Actually, however, the polymer derived from **1*R*** consisted of both trans- and cis-disubstituted oxalactone rings, their ratio (trans:cis = 70:30) being nearly equal to that for the polymer obtained from the racemic monomer **1**. The result definitely shows that the isomerization proceeds through the oxacarbenium ion produced by the unimolecular cleavage of the C–O$^+$ bond of the oxonium ion of the tetrahydropyran ring, namely, by an S_N1-type mechanism.

Since polymer B is regarded as a polyester acetal, it is readily susceptible to the acid-catalyzed cleavage reaction of the ester acetal linkages.[15] Thus, in addition to the isomerization of polymer B to polymer A, the attack of a cationic species to the ester oxygen instead of the ring oxygen of polymer B would lead to the chain cleavage, followed by depolymerization from the resulting oxacarbenium ion of the terminal tetrahydropyran ring. Such a cleavage reaction accounts for the lowering of the molecular weight and the broadening of the molecular weight distribution of the polymer chains when polymer B was allowed to react with a catalytic amount of boron trifluoride etherate in chloroform at 0 °C.

In summary, a polymer (polymer A) containing five-membered oxalactone (1,3-dioxolan-4-one) rings in the main chain was obtained in the cationic polymerization of both racemic and optically active 6,8-dioxabicyclo[3.2.1]octan-7-one at 0 °C. This is in marked contrast to the formation of polyester (polymer B) and cyclic oligoesters consisting of alternating tetrahydropyran ring and ester moieties in the cationic polymerization of the bicyclic oxalactone at or below −40 °C. The specific formation of polymer A is reasonably interpreted in terms of the isomerization of the polyester or oligoester chains induced with cationic species.

Registry No. 2,5-Dimethyl-1,3-dioxolan-4-one, 4744-00-7; lactic acid, 50-21-5; paraldehyde, 123-63-7; (±)-6,8-dioxabicyclo-[3.2.1]octan-7-one (homopolymer), 91738-59-9; (+)-(1*R*,5*R*)-6,8-dioxabicyclo[3.2.1]octan-7-one (homopolymer), 76648-51-6.

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