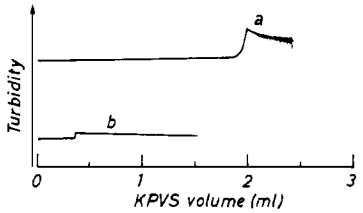

Figure 3. Turbidimetric titration data of KPVS–Hb–PDDA complex with 0.002 49 N KPVS at (a) pH 3.1 and (b) pH 6.1. The sample solution (52.63 mL) contains the three-component complex prepared by the titration of 8.74 mg of KPVS–Hb complex with 0.005 13 N PDDA solution (2.63 mL) at pH 12.3. The titration curve was not represented by absolute turbidity because the change in turbidity was measured with an automatic recording titrator.

boxyl group and PDDA ion.

The increase of M_s in the pH range above the inflection point can be related to the salt linkage of PDDA ion with the phenolic OH and mercapto groups which are ionized in the basic region. However, the M_s value (1.51 mmol/g) observed at pHs above 12 is larger than the total contents (0.99 mmol/g) of the acidic groups in the KPVS–Hb complex. This contradiction might be avoided if we assume that the salt linkage between the $^-OSO_3$ and basic groups in the KPVS–Hb complex is severed during the course of the complexation with PDDA ion in the basic region and that the isolated $^-OSO_3$ group in the KPVS component forms a new salt linkage with PDDA ion. In order to confirm this assumption, the colloid titration with KPVS titrant was carried out for the KPVS–Hb–PDDA complex prepared at pH 12.3. From the turbidimetric titration curve shown in Figure 3, it is observed that the titrant volume at pH 3.1 is larger than that at pH 6.1. This could indicate the existence of a free basic group[11] in the KPVS–Hb–PDDA complex which results from the cleavage of the salt linkage between the KPVS and Hb components during the complexation with PDDA ion.

On the basis of the results obtained here and reported previously,[3] it is found that a three-component polyion complex can be prepared by the salt linkage formations of the acidic and basic groups in Hb with KPVS and PDDA ions if the complexation is carried at an appropriate pH. In the basic region, however, the cleavage of the salt linkage between the $^-OSO_3$ and basic groups in the KPVS–Hb complex is observed in the process of the complexation with PDDA ions. Thus the salt linkage in the KPVS–Hb (or KPVS–Hb–PDDA) complex can be regarded as relatively loose. This could be due to the fact that the Hb component is polyampholite and also the ionizable groups are irregularly located in the α- and β-globin chains.

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(10) The KPVS–Hb complex (1 g) formed stoichiometrically is composed of 0.838 g of Hb and 0.162 g of KPVS ion.
(11) The amount of basic groups isolated from 1 g of KPVS–Hb complex is 0.57 and 0.52 mmol, as estimated by KPVS volume at pH 3.1 (Figure 3) and from the difference between the M_s value at pH >12 and the total acidic group content of KPVS–Hb complex (Figure 2), respectively. These results seem to agree approximately with the content (0.49 mmol) of imidazolyl group in 1 g of KPVS–Hb complex.

Mechanistic Aspects of Selective Formation of 10-, 20-, and 25-Membered Macrocyclic Oligoesters in the Cationic Polymerization of 6,8-Dioxabicyclo[3.2.1]octan-7-one

Ichiro Tajima, Masahiko Okada,* and Hiroshi Sumitomo

Faculty of Agriculture, Nagoya University, Chikusa, Nagoya 464, Japan.
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ABSTRACT: Mechanisms of the selective formation of 10-, 20-, and 25-membered macrocyclic oligoesters (cyclic dimer, tetramer, and pentamer, respectively) from 6,8-dioxabicyclo[3.2.1]octan-7-one (**1**) are discussed on the basis of product distributions in the oligomerization of racemic monomer **1**, optically active (+)-(1*R*,5*R*)-6,8-dioxabicyclo[3.2.1]octan-7-one (**1R**), and enantiomerically unbalanced monomer mixtures. Optically active cyclic tetramer (**4R**) and cyclic pentamer (**5R**) of **1R** are predominantly formed by a tail-biting reaction of a growing oligomer chain, while racemic cyclic tetramer (**4**) and cyclic pentamer (**5**) are mainly produced by a back-biting reaction of an initially formed polymer of **1**. Cyclic dimer (**2**) is formed primarily by intramolecular reaction of unsymmetrical oligomers which are formed from **4** and **5** by the reaction with monomer. All these macrocyclic oligomers are formed via an S_N2-type mechanism involving the exclusive alkyl-oxygen fission of **1**. The selective formation of **2**, **4**, **5**, **4R**, and **5R** is remarkably dependent upon the reaction conditions, especially temperature, time, solvent, and optical purity of the monomer. Solubility and molecular symmetry of cyclic oligomers, interactions between a cyclic oligomer and its opposite enantiomer or a solvent molecule, and conformation of a growing chain are important factors controlling the selective formation of the cyclic oligomers of specific ring sizes.

It is not an unusual but rather common phenomenon that cyclic oligomers of various ring sizes are formed in the cationic ring-opening polymerization of a variety of cyclic monomers.[1] These cyclic oligomers are often in equilib-

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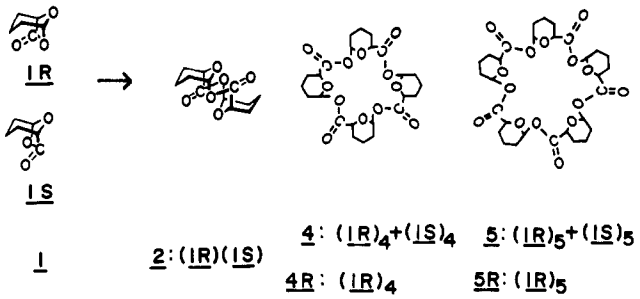
rium with their linear polymers, and the cyclic populations of some polymeric equilibrates were satisfactorily described by the Jacobson–Stockmayer equation derived on the basis of statistical treatment[2-5] or by the modified expressions proposed by Flory et al.[6-9] On the other hand, a kinetic treatment has been recently proposed by Penczek and co-workers[10] to interpret time and conversion dependence of the formation of cyclic oligomers. In some cases, however, cyclic oligomers of specific ring sizes are predominantly or selectively formed, for example, cyclic tetramer from 1-benzyl-2-ethylaziridine,[11] cyclic tetramer from (*R*)-*tert*-butylethylene oxide,[12] and cyclic trimer and tetramer from oxetanes.[13] Furthermore, attempts have been made to synthesize crown ethers by the ring-opening polymerization of ethylene oxide, using various metal salts as templates.[14-16] These macrocyclic oligomers, containing heteroatoms arranged regularly in the ring structure, are expected to act as complexing agents or synthetic ionophores. Therefore, selective formation of cyclic oligomers of specific ring sizes by the ring-opening polymerization of cyclic monomers is not only interesting from the standpoint of reaction mechanism but also valuable from the standpoint of synthetic chemistry.



Recently, we found that in the cationic polymerization of racemic 6,8-dioxabicyclo[3.2.1]octan-7-one (1), 10-, 20-, and 25- membered cyclic oligoesters (cyclic dimer **2**, tetramer 4, and pentamer **5**) were highly selectively formed in acetonitrile, chloroform, and 1-nitropropane, respectively, by proper selection of the reaction conditions.[17-19] In a similar manner, optically active cyclic tetramer (**4R**) and pentamer (**5R**) of (+)-(1*R*,5*R*)-6,8-dioxabicyclo-[3.2.1]octan-7-one (**1R**) were preferentially formed in acetonitile and 1-nitropropane, respectively.[20-22] (Hereafter, **1R** denotes the enantiomer having the **R** configuration of the asymmetric carbon bearing a carbonyl group and, therefore, **1S** denotes the enantiomer having the *S* configuration of the corresponding carbon.) The macrocyclic oligoesters consist of alternating tetrahydropyran and ester moieties, and they bear structural resemblance to the naturally occurring antibiotic nonactin (a 32-membered tetrolide), which includes penetration of potassium ion, but not sodium ion, into mitochondria.[23] The present paper is chiefly concerned with mechanisms for the selective formation of these macrocyclic oligoesters from racemic monomer 1 and optically active monomer **1R**.

Experimental Section

Both the racemic monomer 1 and optically active monomer **1R** were synthesized from sodium 3,4-dihydro-2*H*-pyran-2-carboxylate.[18,20] The polymerization procedure was described in a previous paper.[18] The composition of the reaction products was determined from the relative peak areas corrected for the differences in the refractive indices of the different compounds by a JASCO TRIROTAR gel permeation chromatograph (column, JASCO JSP101, 50 cm; eluent, chloroform). IR spectra were measured on a JASCO A-3 spectrophotometer. NMR spectra were taken with JEOL JNM-MH-100 and JNM-FX-100 Fourier transform NMR spectrometers in deuteriochloroform or deuterioacetonitrile with tetramethylsilane as internal reference. Optical rotations were measured in chloroform at 25 °C by using a JASCO DIP-4 automatic polarimeter and a 1-dm cell. The properties of the pure oligomers have been reported previously (**2**,[18] 4,[18] **5**,[18] **4R**,[21] and **5R**[20]).

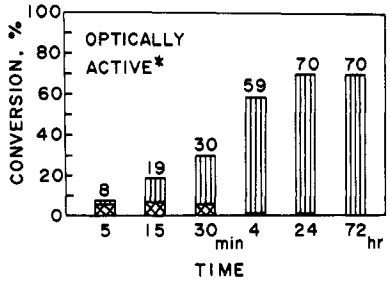


Figure 1. Time–conversion diagram for the oligomerization of (+)-(1*R*,5*R*)-6,8-dioxabicyclo[3.2.1]octan-7-one (**1R**) in 1-nitropropane. Monomer, 1 g; 1-nitropropane, 2 mL; BF_3·OEt_2, 1 mol % to monomer; temperature, −40 °C; vertical bars, cyclic pentamer (**5R**); cross-hatched, cyclic tetramer (**4R**).

Results and Discussion

Selective Formation of Optically Active Cyclic Tetramer 4R and Pentamer 5R from (+)-(1*R*,5*R*)-6,8-Dioxabicyclo[3.2.1]octan-7-one (1R). Figure 1 shows the time–conversion diagram for the oligomerization of **1R** in 1-nitropropane at −40 °C, using boron trifluoride etherate as initiator. It is clearly demonstrated that the cyclic tetramer **4R** was preferentially formed in the early stage of the polymerization and that as the reaction proceeded, it was gradually converted to the cyclic pentamer **5R**, which was the sole product in the final stage. A similar trend was observed also in the oligomerization in chloroform and in acetonitrile, except that in the latter solvent, **4R** was obtained as a major product in a yield of nearly 30% in the middle stage of the reaction, and that even in the final stage, it was still obtained in a yield of about 20% along with the main product **5R**.[21] Figure 2 illustrates a tail-biting mechanism for the formation of **4R** and **5R** from **1R**. The expression of configuration and conformation of the monomer and oligomers used throughout this paper is exemplified in the caption to Figure 2. For example, an ester oxygen on the extrapolated line connecting the acetal carbon and its neighboring methylene carbon signifies that the oxygen is in the axial position of the tetrahydropyran ring, while a carbonyl carbon on the line at right angles to the line connecting the carbonyl bearing methine carbon and its neighboring methylene carbon signifies that the carbonyl carbon is in the equatorial position. A main chain consisting of alternating ester and ether linkages is placed on a nearly flat plane, and the four C–C bonds connecting the carbons of a tetrahydropyran ring come either above the plane (a bold line) or below the plane (a dotted line). Taking such a spatial orientation of atoms into consideration, the absolute configuration (*R* or *S*) of the two asymmetric carbons of each monomeric unit can be determined as shown in the caption. An ester linkage connecting two tetrahydropyran rings takes the trans conformation because of steric hindrance between them.

As Figure 2 shows, a monomer (2) attacks the partially positively charged acetal carbon of the terminal oxonium ion (1) to invert its configuration (an alkyl-oxygen fission, as proved by the X-ray analysis of a **4R**–acetonitrile (1:1) complex[24]), and simultaneously the flipping of the tetra-

Table I
Solubilities of Cyclic Oligomers of 6,8-Dioxabicyclo[3.2.1]octan-7-one[a]

solvent	solubility, g/100 mL				
	2	4	5	4R	5R
CH_3CN	0.10	0.71	1.1	1.6	1.2
$C_3H_7NO_2$	0.17	5.1	1.7	(8)	1.4
$CHCl_3$	1.9	0.88	22	(45)	(9)

[a] Temperature, −40 °C and (26 °C).

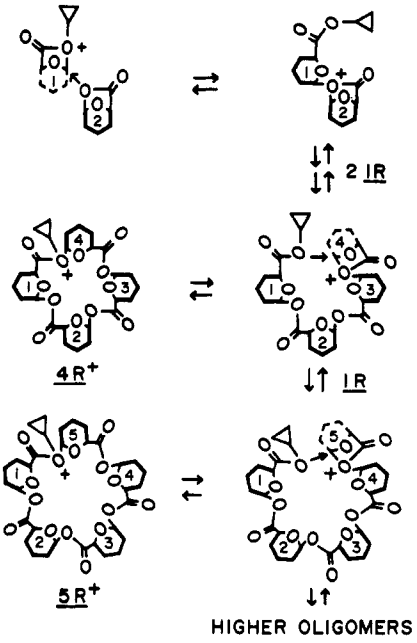
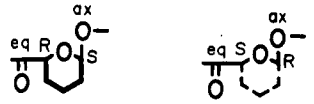


Figure 2. Mechanism of the formation of optically active cyclic tetramer (**4R**) and pentamer (**5R**) of (+)-(1*R*,5*R*)-6,8-dioxabicyclo[3.2.1]octan-7-one (**1R**) by tail-biting.



R, *S*: configuration of asymmetric atoms
ax, eq: conformation of substituent groups
Δ: initiator fragment

hydropyran ring of the ring-opened monomeric unit (1) occurs to give a conformation with its ester oxygen in the axial position and its carbonyl carbon in the equatorial position. As the middle formula on the right side in Figure 2 shows, the ester oxygen of the inactive terminal unit (1) attacks the partially positively charged acetal carbon of the active terminal unit (4) to form a cyclic tetramer oxonium ion (**4R**$^+$) from which an initiator fragment is removed to provide **4R** (tail-biting).

In a similar manner the cyclic pentamer **5R** is also produced. One of the driving forces for these processes seems to be the crystallization of these cyclic oligomers due to their high molecular symmetry: **4R** and **5R** are chiral but not asymmetric molecules ("gyrochiral" molecules according to the definition proposed by Nakazaki et al.[25]). These oligomers have C_4 and C_5 symmetry axes, respectively, and they are readily crystallized as expected. In contrast, conformationally highly strained gyrochiral dimer and trimer seem to be extremely unstable and, even if formed, would exist only transiently.

The transformation of once-formed **4R** to **5R** with reaction time and the predominant formation of **5R** in the

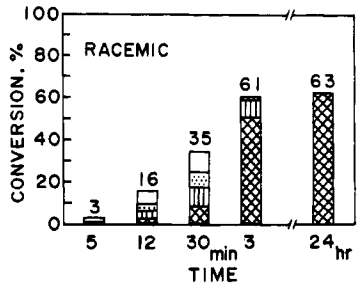


Figure 3. Time–conversion diagram for the oligomerization of racemic 6,8-dioxabicyclo[3.2.1]octan-7-one (1) in chloroform. Monomer, 1 g; chloroform, 1 mL; BF_3·OEt_2, 5 mol % to monomer; temperature, −40 °C; unshaded, polymer; dots, other oligomers; vertical bars, cyclic pentamer (5); cross-hatched, cyclic tetramer (4); shaded, cyclic dimer (2).

final stage of the reaction presumably arise from the lower solubility of **5R** than that of **4R** in the reaction media as shown in Table I and also from the lower conformational strain of **5R**. In the oligomerization in acetonitrile, as described above, the formation of a 1:1 **4R**–acetonitrile complex seems to be responsible for the preferential formation of **4R**, at least up to the middle stage of the reaction.

In the tail-biting mechanism shown in Figure 2, the transformation of **4R** to **5R** occurs via ring–chain equilibrium (cyclic oligomer–linear oligomer): **4R**$^+$ is ring-opened intramolecularly to give a linear tetramer oxonium ion, which in turn reacts with a monomer **1R**, and subsequent ring closure by tail-biting leads to **5R**$^+$. Direct attack of **1R** on **4R**$^+$ would give, via a linear pentamer oxonium ion and its tail-biting, an unsymmetrical cyclic pentamer. Actually, however, such a cyclic pentamer was not detected at all in the reaction mixture, and hence the reaction process involving direct attack of **1R** on **4R**$^+$ can be excluded.

One might think that a ring-expansion mechanism proposed by Plesch and colleagues[26,27] for the polymerization of cyclic acetals such as 1,3-dioxolane and 1,3-dioxepane can satisfactorily interpret the exclusive formation of cyclic oligomers in the present case. However, the mechanism cannot fully account for the selective formation of gyrochiral **4R** and **5R** and is also incompatible with the oligomerization behavior of racemic monomer which will be discussed in a later section.

Selective Formation of Cyclic Tetramer 4 and Cyclic Pentamer 5 from Racemic Monomer 1. In the cationic oligomerization of racemic monomer 1, there are two characteristic products which cannot be detected at all in the oligomerization of optically active monomer **1R** under similar reaction conditions. One is a relatively high molecular weight polymer ($\bar{M}_n \sim 10000$ by GPC) formed in the initial stage of the reaction at temperatures below −40 °C, and the other is cyclic dimer **2**, which is formed predominantly or nearly quantitatively in the final stage of reaction in acetonitrile and 1-nitropropane. The formaion of **2** will be discussed separately in a later section.

Figure 3 shows the time–conversion diagram for the oligomerization of racemic monomer 1 in chloroform at −40 °C. In the early stage of the reaction, a polymer rather than oligomers was preferentially formed, and as the reaction proceeded, cyclic tetramer **4**, cyclic pentamer **5**, and other higher oligomers gradually accumulated. After 3 h most of the polymer and other higher oligomers were transformed to **4** and **5**, and eventually the latter was completely converted to **4**. Throughout the reaction, the formation of cyclic dimer **2** was negligible. Such an ex-

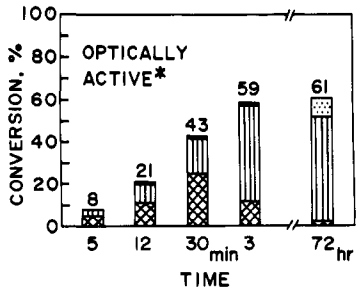


Figure 4. Time–conversion diagram for the oligomerization of optically active (+)-(1*R*,5*R*)-6,8-dioxabicyclo[3.2.1]octan-7-one (**1R**) in chloroform. Monomer, 1 g; chloroform, 1 mL; $BF_3{\cdot}OEt_2$, 7 mol % to monomer; temperature, −40 °C; dots, other oligomers; vertical bars, cyclic pentamer (**5R**); cross-hatched, cyclic tetramer (**4R**).

Table II
Depolymerization of Cyclic Pentamer 5 and Polymer of 6,8-Dioxabicyclo[3.2.1]octan-7-one[a]

	initial	
	5,[b] 1 g; $CHCl_3$, 1 mL	polymer,[c] 0.9 g; $CHCl_3$, 1.8 mL
final		
% polymer	0	6
% other oligomers	0	5
% 5	29	3
% 4	39	53
% 2	2	2
% 1	30	31
% total	100	100

[a] Temperature, −40 °C; time, 3 days; $BF_3{\cdot}OEt_2$, 10 mol % to monomer. [b] 5 fractionated by GPC from the oligomers obtained in the oligomerization of racemic 1 at −40 °C in 1-nitropropane. [c] Polymer fractionated by GPC from the products obtained in the oligomerization of racemic 1 at −60 °C in chloroform.

clusive formation of 4 is in remarkable contrast to the predominant formation of optically active cyclic pentamer **5R** in the oligomerization of optically active monomer **1R** under similar conditions.

The time–conversion diagram for the oligomerization of **1R** in chloroform at −40 °C is presented in Figure 4. Contrary to the oligomerization of racemic monomer **1**, no polymer was formed even in the initial stage of the reaction. The optically active cyclic tetramer **4R** once formed in the relatively early stage was transformed to the cyclic pentamer **5R**, and after 3 days, **5R** was obtained as the main product along with a small amount of other oligomers. The conversion from **4R** to **5R** in this case is indeed in the reverse direction to the conversion from **5** to **4** observed in the oligomerization of racemic monomer **1**. Such peculiar and intriguing phenomena will be discussed later.

Table II presents the results of depolymerization of **5** at −40 °C in 1-nitropropane and of a polymer obtained at −60 °C in chloroform. It was confirmed that **5** and the polymer were transformed mainly to **4** and monomer **1** in chloroform at −40 °C in the presence of boron trifluoride etherate, although the reaction was rather slow. This finding proves that **4** is formed also by the degradation of **5** and polymer.

Inspection of molecular models reveals that a growing chain entirely consisting of syndiotactic dyads (–R–S–) tends to form a linear polymer, while a growing chain entirely consisting of isotactic dyads (–R–R– and –S–S–) can readily form a cyclic structure because of steric repulsion of the tetrahydropyran rings. (R and S denote **1R** and **1S** monomeric units, respectively.) Actually, X-ray

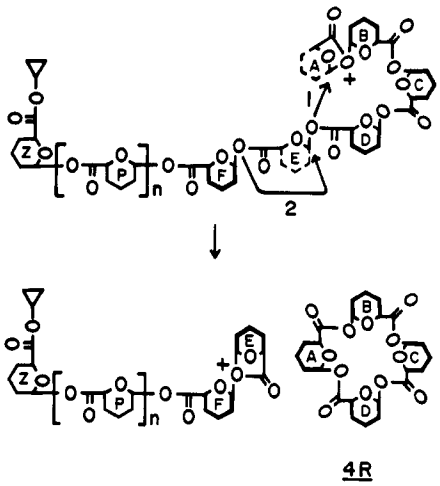


Figure 5. Mechanism of the formation of cyclic tetramer (**4**) of 6,8-dioxabicyclo[3.2.1]octan-7-one (**1**) by back-biting.

analysis of the crystals of the optically inactive cyclic tetramer **4** disclosed that it was not a meso compound (R–S–R–S) but a racemic mixture of **4R** (R–R–R–R) and **4S** (S–S–S–S).[28]

Figure 5 shows a back-biting mechanism for the formation of **4** from the polymer. In the upper formula, A–B–C–D is an isotactic sequence of **1R** (R–R–R–R), and D–E–F is a syndiotactic sequence of **1R**–**1S**–**1R** (R–S–R). The ester oxygen of the monomer unit (D) attacks the activated acetal carbon of the terminal monomer unit (A) (arrow 1) to form a macrocyclic oxonium ion. Subsequently, the ester oxygen of the monomer unit (E) attacks its own acetal carbon (arrow 2) to liberate **4** (**4R** in this case). Depolymerization of the polymer to **1** also occurs. Such depolymerization of a growing chain or depolymerization followed by polymerization continues until an isotactic sequence of at least four identical enantiomeric units appears at the active chain end, from which **4** and **5** can be produced by back-biting.

The transformation from **5** to **4** in the oligomerization or racemic monomer in chloroform (Figure 3) is in the reverse direction to the transformation from **4R** to **5R** in the oligomerizaion of optically active monomer in the same solvent (Figure 4). Such a remarkable difference in the oligomerization behavior, which at first glance seems very strange, arises at least partly from the difference in the cyclization mechanism between the two systems; namely, **4R** and **5R** are produced by tail-biting, while **4** and **5** are produced chiefly by back-biting.

In the oligomerization of **1R**, it is conceivable that a linear tetramer growing ion cyclizes by tail-binting to **4R** faster than it propagates to a linear pentamer growing ion, which in turn cyclizes by tail-biting to **5R** more readily than it propagates further. Thus, **4R** is preferentially formed in the early stage of the reaction, but it is gradually converted to **5R** by the mechanism depicted in Figure 2, since **5R** is conformationally more stable than **4R**.

In the oligomerization of racemic monomer, tail-biting cyclization to **4** and **5** is less likely to take place because there is a relatively small probability for a linear growing chain to consist of four or five identical enantiomeric units $X\text{–}R_{n-1}\text{–}R^+$ or $X\text{–}S_{n-1}\text{–}S^+$ (n = 4 or 5; X = initiator fragment). After the polymerization has proceeded to middle or later stages, where polymerization–depolymerization equilibrium becomes significant, sequences of the same enantiomeric units would be formed at a growing chain end, from which **4** or **5** is produced by back-biting. In view of the finding that comparable amounts of **4** and **5** are

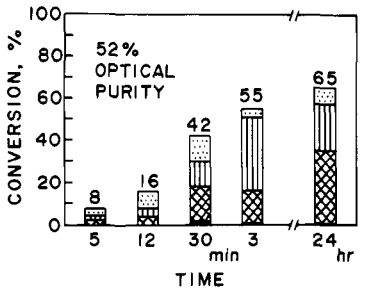


Figure 6. Time–conversion diagram for the oligomerization of optically active 6,8-dioxabicyclo[3.2.1]octan-7-one of 52% optical purity in chloroform. Monomer, 2 g; chloroform, 2 mL; BF_3·OEt_2, 5 mol % to monomer; temperature −40 °C; dots, other oligomers; vertical bars, cyclic pentamer; cross-hatched, cyclic tetramer; shaded, cyclic dimer.

Table III
Variation of Specific Rotation of Residual Monomer, Cyclic Tetramer, and Cyclic Pentamer in the Oligomerization of 6,8-Dioxabicyclo[3.2.1]octan-7-one of 52% Optical Purity[a]

time	conversion, %	$[\alpha]_D$[b], deg monomer	tetramer	pentamer
5 min	8	+68 (3.2)[c]		
12 min	16	+62 (2.7)[c]	−144	−56
30 min	42	+51 (2.3)[c]	−145	−64
3 h	55	+44 (2.1)[c]	−59	−105
24 h	65	+72 (3.4)[c]	−9	−108

[a] Monomer ([1R]/[1S] = 3.2), 2 g; chloroform, 2 mL; BF_3·OEt_2, 5 mol % to monomer; temperature, −40 °C. [b] $[\alpha]_D$(chloroform, 1%): 1R, +130°; 4R, −168°; 5R, −112°. [c] Figures in parentheses denote the enantiomer ratio [1R]/[1S].

produced up to the middle stage of the polymerization, the rate of back-biting of a growing chain end having four consecutive same enantiomeric units to 4 may be lower than, or at most nearly equal to, the rate of propagation.

The difference in the reactivity of a growing chain end between tail-biting and back-biting seems to arise from the fact that the former involves the attack of an active chain end at the ester oxygen of a carboxyl or ethoxycarbonyl end group, while the latter involves the attack of an active chain end at the ester oxygen of an inner chain unit: Because of steric crowding, such a back-biting reaction undoubtedly requires a higher activation energy than tail-biting.

In order to further clarify the cause for the remarkable difference in the oligomerization behavior between racemic monomer 1 and optically active monomer **1R** as described above, the oligomerization of enantiometrically unbalanced monomer mixtures was undertaken under similar reaction conditions. Figure 6 shows the time–conversion diagram of the oligomerization of a monomer mixture of 52% optical purity (**1R**/**1S** = 3.2). Table III summarizes the variation of specific rotation of residual monomer, cyclic tetramer, and cyclic pentamer with conversion. In the early and middle stages of the reation, the specific rotation of the cyclic tetramer was close to that of pure **4R** (−168°) obtained from **1R**. Therefore, it is highly probable that this cyclic tetramer was formed by a tail-biting reaction as the formation of **4R** in the oligomerization of **1R** (Figure 2). However, the specific rotation of cyclic tetramer became significantly less negative with increasing reaction time, and after 1 day it was as low as −9°. The formation of the practically optically inactive cyclic tetramer in the later stage of the reaction seems to indicate that it was formed primarily by a back-biting reaction from **5** or other oligomers as the formation of **4** in the oligomerization of racemic monomer 1 (Figure 5). On the contrary, the specific rotation of cyclic pentamer changed from −56 to −108° with reaction time. The latter value was very close to that of pure **5R** (−112°) obtained from **1R**, suggesting that the cyclic pentamer in the later stage of the reaction was formed mainly from **4R** through the process proposed in the previous section for the selective formation of **5R** in the oligomerization of **1R** (Figure 2).

The specific rotation of residual monomer, on the other hand, decreased with reaction time and it became +44° ([**1R**]/[**1S**] = 2.1) after 3 h. This means that the **1R** enantiomer, being in excess, was preferentially converted to cyclic oligomers; in other words, the preferential selection of the monomer of the same chirality as that of the terminal unit of the growing chain occurred in this reaction. Such stereoregulation was found in the cationic polymerization of 6,8-dioxabicyclo[3.2.1]octane at low temperatures.[29] After 24 h, however, the specific rotation of the residual monomer increased to nearly the same value as that of the starting monomer ([**1R**]/[**1S**] = 3.2), although the total conversion to cyclic oligomers did not increase appreciably. This is probably due to a thermodynamic equilibrium between monomer and cyclic oligomers. In the final stage, and therefore presumably in an equilibrium state, nearly half of the total products was optically inactive cyclic tetramer **4** and the other half was optically active cyclic pentamer **5R** plus some other oligomers. Furthermore, a similar phenomenon was observed in the oligomerization of a monomer mixture of 35% optical purity ([**1R**]/[**1S**] = 2.1): In the later stage of the reaction, about two-thirds of the total products was **4** and the remaining third was mainly **5R**. These results are closely related to the selective formation of **5R** from **1R** of 100% optical purity and of **4** from **1** of 0% optical purity in chloroform at −40 °C. Such a characteristic product distribution depending on the optical purity of monomer can be interpreted as follows: In view of the fact that **4** is an equimolar mixture of **4R** and **4S** which form a racemate crystal as proved by X-ray analaysis,[28] it seems very likely that in the oligomerization of **1** in chloroform, **4R** is stabilized only when it can intereact with its counterpart **4S** to precipitate out of the solution. On the contrary, in the absence of **4S** or in the presence of a smaller amount of **4S**, **4R**, being in excess, is transformed to more stable **5R**. This is supported by the facts that the solubility of **4** in chloroform is much lower than that of **4R** in the same solvent (Table I) and that **4** is readily crystallizable in chloroform, while **4R** is not. The preferential formation of **5**, instead of **4**, in the oligomerization of **1** in 1-nitropropane suggests that such stabilization of **4** by an interaction between its enantiomer pair is not strong enough to suppress the transformation of **4** to **5** in solvents of higher polarity, such as 1-nitropropane.

Formation of Cyclic Dimer 2 from Racemic Monomer 1. The cyclic dimer **2** consists of a pair of different enantiomers of **1**, and all four substituents attached to the two tetrahydropyran rings are axially oriented.[24] Therefore, the fact that no cyclic dimer is formed in the oligomerization of optically active **1R** is quite reasonable. Furthermore, the possibility that the cyclic dimer **2** polymerizes to afford selectively the cyclic oligomer **4** is definitely excluded because **2**, consisting of a pair of **1R** and **1S** monomeric units, cannot be converted, by any simple mechanism, directly to **4**, which is a racemic mixture of **4R** and **4S**. In addition, the fact that the ester oxygen and carbonyl carbon of each monomeric unit in **4**

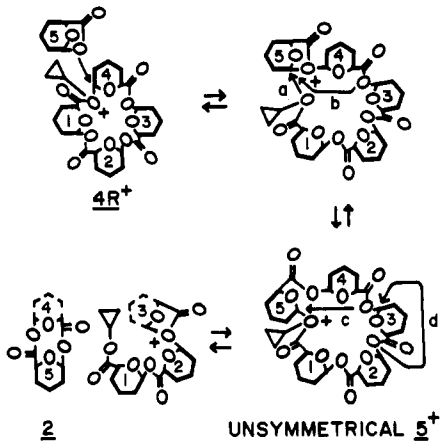


Figure 7. Mechanism of the formation of cyclic dimer (**2**) of 6,8-dioxabicyclo[3.2.1]octan-7-one (**1**) by the reaction of cyclic tetramer with monomer.

are located in axial and equatorial positions of the tetrahydropyran ring, respectively, is further evidence against the possibility described above.

There are at least two experimental findings which would provide useful information on the mechanism of the formation of **2**. First, **2** was hardly produced in the initial stage of the oligomerization of **1**, where **4** and **5** were preferentially formed, but it was produced highly selectively in the final stage of reaction, except in chloroform. Second, as revealed by X-ray analysis,[24] the configuration of all the acetal carbons of **4R** is inverted compared with that of the acetal carbon of **1R**; in other words, the oligomerization proceeds via an S_N2-type mechanism with an exclusive alkyl-oxygen bond fission of **1R**. In view of these facts, it seems reasonable that **2** is formed by the reaction of cyclic oligomer with monomer.

Figure 7 illustrates a possible mechanism for the formation of **2** by intramolecular reaction of unsymmetrical oligomer 5^+, which is formed by the reaction of $4R^+$ with **1S**: The activated acetal carbon of the monomeric unit (4) of $4R^+$ is attacked by the ester oxygen of **1S** (5) to give a linear oxonium ion with the inversion of the configuration of the acetal carbon of the monomeric unit (4) from *S* to *R*. Then the acetal carbon of the terminal oxonium ion (5) is attacked by the ester oxygen of monomeric unit (1) (arrow a) to give unsymmetrical cyclic pentamer oxonium ion (unsymmetrical 5^+). This oxonium ion seems to exist only transiently because of its unstability due to the unsymmetrical structure. Thus, intramolecular reaction of the ester oxygen of the monomeric unit (4) with the partially positively charged acetal carbon of the monomeric unit (5) (arrow c) takes place to give a linear pentamer having a cyclic dimer oxonium ion at its end. It seems likely that this reaction is accompanied by flipping of the tetrahydropyran ring (4) since it allows its ester oxygen to come near the acetal carbon of the monomeric unit (5). Subsequent attack of the ester oxygen of the monomeric unit (3) to its partially positively charged acetal carbon (arrow d) occurs to liberate 2, which consists of a pair of different enantiomers (**1R** (4) and **1S** (5)) and has all four substituents in the axial positions of the tetrahydropyran ring.

Direct back-biting from a linear oxonium ion can be ruled out. For example, in the upper formula on the right side, intramolecular reaction of the ester oxygen of the monomeric unit (4) with the acetal carbon of the linear pentamer oxonium ion (5) (arrow b) would lead to a cyclic dimer in which three substituents are equatorially oriented and one substituent is axially oriented (or vice versa). However, cyclic dimer having such a configuration was not detected at all in the present oligomerization.

In comparison with **4R** and **5R**, which are chiral but not asymmetric molecules (gyrochiral molecules), the cyclic dimer (**2**) is a symmetric molecule having a center of symmetry and it is more readily crystallized. In fact, among the three cyclic oligomers (**2**, **4**, and **5**), **2** has the lowest solubility in acetonitrile and 1-nitropropane, as shown in Table II. Therefore, as in the selective formation of cyclic tetramer and pentamer, solubility and molecular symmetry also play an important role in the formation of **2**.

Conclusion

The aforementioned results and discussion lead us to the following conclusions as to the mechanisms of the selective formation of the 10-, 20-, and 25-membered macrocyclic oligoesters.

(1) In the oligomerization of optically active monomer **1R**, the optically active cyclic tetramer **4R** and cyclic pentamer **5R** are formed by a tail-biting reaction of a growing oligomer chain.

(2) In the oligomerization of racemic monomer **1**, on the other hand, the racemic cyclic tetramer **4** and cyclic pentamer **5** are produced mainly by a back-biting reaction of a growing polymer chain.

(3) The cyclic dimer **2**, which is obtained only in the oligomerization of racemic monomer **1** in acetonitrile and 1-nitropropane, is formed primarily by intramolecular reaction of unsymmetrical cyclic oligomers which are formed by the reaction between cyclic oligomers and monomer.

(4) All these macrocyclic oligoesters are formed via an S_N2-type mechanism involving the exclusive alkyl-oxygen fission of **1**.

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Nonionic Diblock Copolymers as Surfactants between Immiscible Solvents

Robert Cantor*

Physique de la Matière Condensée, Collège de France, 75231 Paris Cedex 05, France.
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ABSTRACT: A theoretical study is done to investigate nonionic diblock copolymers used as amphiphilic surfactants for a pair of otherwise immiscible solvents. It is assumed that the block junction points rest on the interfaces, with no chain adsorption, each chain staying in its preferred solvent. First the properties of a single flat interface saturated with polymer chains are obtained; then its curvature properties are calculated. We examine also the properties of a multilamellar arrangement, both in equilibrium with excess solvent and in the absence of either or both bulk solvent phases. The calculations are all done in mean field approximation for chains in at least moderately good solvent in semidilute solution. A phase diagram is obtained, under the constraint of multilamellar geometry.

I. Introduction

There exist a wide variety of amphiphilic surfactants (and combinations of surfactants) used to lower the effective surface tension at the interface between otherwise immiscible solvents.[1] There has been much recent interest in using nonionic diblock copolymers as surfactants, particularly for oil/water systems, where the two blocks strongly prefer different solvents.[2] In principle, these can lead to a variety of geometrical arrangements, depending on the properties of the three components.[3,4] In the current study, we will attempt to analyze such systems for a few simple cases; that is, we restrict ourselves to a simple lamellar geometry to obtain the characteristic equilibrium properties of the system, except to consider local slight curvature to determine the elasticity and curvature properties of the interface.

We consider first a single interface saturated by the chains. By "saturated" is meant the state for which the concentration of chains at the interface is such as to force the chains to stretch perpendicular to the interface and thus to generate a lateral pressure equal and opposite to the "bare" surface tension, γ_0, such that the effective surface tension, $\gamma = \gamma_0 - \pi$, vanishes. This is done by assuming first a flat interface; this restriction is then relaxed somewhat to allow slight, spherically symmetric curvature in order to obtain the equilibrium radius of curvature and the coefficient of elasticity.

In the next part, we consider a concentration of chains many times that needed to saturate one interface. We consider the formation of a multilamellar "middle-phase"[2,5] geometry; that is, between the two bulk solvent phases is formed a phase consisting of many alternating layers of the two solvents stabilized at their interfaces by the chains. The conditions for which this geometry is most likely are calculated by analyzing the spontaneous radius of curvature obtained earlier. It will be shown that to good approximation, these layers will have the same properties as the single saturated layer described in the first part; they will neither compress nor swell, assuming that there remains enough of each solvent to form a three-phase system. We will then consider the case for which one or both of the bulk solvent phases is exhausted, determining the equilibrium properties of the resulting two-phase and one-phase systems. Finally, these results will be summarized in a phase diagram for the three-component system.

II. Single Saturated Interface

1. Flat Interface. We consider a system consisting of uncharged homogeneous diblock copolymers A/B of arbitrary but uniform number of monomers n_A and n_B, and two immiscible solvents labeled a and b. We assume that the two solvents are sufficiently incompatible so that the density profile going from one bulk solvent to the other can be replaced to good approximation by a sharp dividing plane. It is assumed that a is a good, although not necessarily athermal, solvent for block A monomers, and likewise for B in b, and that a is a poor solvent for monomers B, and likewise for A in b. That is, we assume that both χ_{Aa} and $\chi_{Bb} < {}^1/_2$, but not necessarily zero (χ_{Ik} is the Flory interaction parameter[6] for block I in solvent k), and χ_{Ab} and $\chi_{Ba} > {}^1/_2$; there is no adsorption of chains at the interface.

We consider the case where to good approximation we can assume that the A chains rest entirely on the a side and likewise for B in b, and thus where the distribution of block junction points is sufficiently narrowly peaked at

* Current address: Department of Chemistry, University of Florida, Gainesville, Fla. 32611.

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