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at the same time they are too short to display the general scaling laws discussed here. What is needed is a systematic effort based on block copolymers.

Acknowledgment. The author has greatly benefited from discussions with R. Audebert, R. Cantor, C. Taupin, and C. Quivoron.

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Ring–Chain Equilibrium of Macrocyclic Formals[1]

Yuya Yamashita, Jyunji Mayumi, Yuhsuke Kawakami,* and Koichi Ito

Department of Synthetic Chemistry, Faculty of Engineering, Nagoya University, Nagoya 464, Japan. *Received February 7, 1980*

ABSTRACT: Equilibrium polymerizations of 1,3,6-trioxacyclooctane (TOC), 1,3,6,9-tetraoxacycloundecane (11-CF-4), 1,3,6,9,12-pentaoxacyclotetradecane (14-CF-5), and 1,3,6,9,12,15-hexaoxacycloheptadecane (17-CF-6) were studied in dichloromethane by using boron trifluoride ethyl etherate ($BF_3{\cdot}OEt_2$) as a catalyst. Thermodynamic parameters of the polymerization of these macrocyclic formals and their oligomers were evaluated from the dependence of their equilibrium concentrations on polymerization temperature. Although the enthalpy changes for polymerization, ΔH_p, are observed to be finite even for the 34-membered ring (dimer of 17-CF-6), those for the cyclic oligomers having rings with more than 40 members are virtually equal to 0. The polymerizability of these macrocyclic oligomers is controlled only by the entropy term. The molar cyclization equilibrium constant decreases in proportion to the −2.5 power of the ring size x, in accordance with the Jacobson–Stockmayer theory, when ΔH_p is negligibly small.

The polymerizability of cyclic monomers has been extensively investigated for the cyclics having rings with less than 10 members, but little attention has been devoted to macrocyclics. The recent development of GPC has made it posible to isolate, identify, and quantify high molecular weight compounds, and formation of cyclic oligomers has become a matter of increasing interest, particularly in the field of cationic polymerization of heterocyclic monomers.

We investigated the polymerization behavior of macrocyclic formals having ether oxygens along with acetal oxygens and found that the cationic polymerization of these monomers was accompanied by the formation of considerable amounts of cyclic oligomers,[2-5] a fact which seems very interesting from a thermodynamic point of view. Recently, we reported[6] that the polymerization of 17-CF-6 could be described essentially as a thermodynamically controlled ring–chain equilibrium system and suggested that its dimer (34-membered ring) might have some ring strain because a negative enthalpy value (−0.76 kcal/mol) was determined from a plot of Dainton's equation. In order to clarify the nature of the ring-opening polymerizability of these macrocyclic formals, we have carried out an investigation on the thermodynamics of the cationic polymerizations of TOC, 11-CF-4, 14-CF-5, and 17-CF-6 by $BF_3{\cdot}OEt_2$.

Experimental Section

Materials. TOC, 11-CF-4, 14-CF-5, and 17-CF-6 were prepared from the corresponding glycols and paraformaldehyde according to the method described in the literature.[2,5] These formals were purified by fractional distillation over lithium aluminum hydride. They were redistilled from lithium aluminum hydride under a nitrogen atomosphere just before use: TOC, bp 66.0 °C (50 mm); 11-CF-4, bp 60.0 °C (0.5 mm); 14-CF-5, bp 98 °C (1.8 mm); 17-CF-6, bp 127 °C (0.1 mm). These monomers proved to be pure (>99.98%) by gas chromatography. Commercial dichloromethane was refluxed over phosphorus pentoxide and fractionally distilled under a nitrogen atmosphere. Commercial *n*-decane and *n*-tetradecane were used as internal standards in gas chromatography.

Polymerization and Depolymerization Products. Under a nitrogen atmosphere the dichloromethane solutions of a monomer, an internal standard, and an initiator were mixed in a 30-mL volumetric flask to which was attached a three-way stopcock, and the flask was immediately immersed in a thermostated bath. At specified intervals, a small portion of the reaction mixture was taken out with a syringe through the

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three-way stopcock, the reaction was quenched by excess diethylamine, and the mixture was subjected to gas chromatography and GPC analyses to determine the amount of unreacted monomer and the product distribution.

The polymers were isolated from the reaction mixture by evaporating off the solvent after quenching by diethylamine. They were purified by reprecipitation from benzene into hexane three times and were finally freeze-dried. Depolymerization was carried out in a manner similar to the polymerization. The polymerization temperature was varied from −30 to +30 °C for TOC and 14-CF-5, from −20 to +30 °C for 11-CF-4, and from −30 to +25.5 °C for 17-CF-6.

Isolation and Identification of Cyclic Oligomers. Cyclic oligomers were isolated from the hexane-soluble fraction by preparative GPC. Dimers, tetramers, and hexamers were purified by recrystallization from a benzene–hexane (1:1 v/v) mixture. The isolated cyclic oligomers were identified by elemental, NMR, and IR analyses. NMR and IR spectra of each fraction were fully consistent with the cyclic structure, and there was no indication of the existence of end groups which might exist in the linear chains. The melting points and elemental analyses of the isolated oligomers are summarized in Table I. For the unseparated higher oligomers, these values were assumed to be equal to that of the highest oligomer isolated.

Determination of Product Distribution. Unreacted monomer concentration was determined by gas chromatography by using *n*-decane or *n*-tetradecane as an internal standard. Gas chromatographs used were a Yanagimoto gas chromatograph G 180 for TOC and 14-CF-5 and a Hitachi K-23 for 11-CF-4 fitted with 2-m silicone GE-SE30-packed columns. Product distribution was determined in THF (chloroform for 17-CF-6) by a Toyo Soda HLC 802UR GPC equipped with 4-ft G 2000 H8 (exclusion limit 2.5 × 10^2 Å) columns. The flow rate was 1 mL/min. The peak intensity was calibrated by authentic samples. The peak areas per unit weight, relative to that of the dimer or monomer, were as follows: $a_3/a_2 = 1.05$, $a_4/a_2 = 1.06$, $a_5/a_2 = 1.08$, $a_6/a_2 = 1.10$, $a_p/a_2 = 1.13$ for TOC; $a_3/a_2 = 1.01$, $a_4/a_2 = 1.02$, $a_5/a_2 = 1.04$, $a_6/a_2 = 1.06$, $a_p/a_2 = 1.06$ for 11-CF-4; $a_3/a_2 = 1.02$, $a_4/a_2 = 1.04$, $a_5/a_2 = 1.05$, $a_p/a_2 = 1.10$ for 14-CF-5; $a_2/a_1 = 1.03$, $a_3/a_1 = a_4/a_1 = a_5/a_1 = 1.07$, $a_p/a_1 = 1.18$ for 17-CF-6. a is the peak area per unit weight of cyclic x-mer, and a_p is the peak area of the polymer. For the unseparated higher oligomers, these values were assumed to be equal to that of the highest oligomer isolated. These values were used in the following equations to determine the concentration of each product:

$$C_x = \frac{b_x a_1/a_x}{\sum\limits_{x=1} b_x a_1/a_x}[\mathrm{M}]_0$$

for 17-CF-6 and

$$C_x = \frac{b_x a_2/a_x}{\sum\limits_{x=2} b_x a_2/a_x}([\mathrm{M}]_0 - [\mathrm{M}]_e)$$

for TOC, 11-CF-4, and 14-CF-5 (the equilibrium monomer concentration $[\mathrm{M}]_e$ was determined separately by gas chromatography). b_x is the peak area of the x-mer in GPC, $[\mathrm{M}]_0$ is the initial monomer concentration in mol/L, and C_x is in mol/L. The initial monomer concentration was calibrated by taking the volume change of the solvent on temperature change ($\partial d/\partial t = 0.00180$ for CH_2Cl_2[7]) into account.

Results and Discussion

Equilibrium Product Distribution. The typical change of product distribution was shown as a function of time for 11-CF-4 in the GPC chromatograms (Figure 1). The GPC chromatogram after 3 h was identical with that after 24 h and the concentration of each product did not change during this period. The equilibrium was considered to be reached at the point when no change of product distribution was seen.

Table I
Analyses of Cyclic Oligomers of TOC, 11-CF-4, 14-CF-5, and 17-CF-6

oligomers	mp, °C	elemental anal. % C	elemental anal. % H
	TOC		
$(TOC)_2$	59.9–60.3	50.67	8.60
$(TOC)_3$	liquid	49.81	8.04
$(TOC)_4$	34.7–35.2	50.76	8.18
$(TOC)_5$	liquid	50.95	8.29
$(TOC)_6$	39.7–40.1	49.88	8.32
	calcd for $(TOC)_x$	50.84	8.53
	11-CF-4		
$(11\text{-CF-}4)_2$	88.0–88.6	51.90	8.61
$(11\text{-CF-}4)_3$	liquid	51.78	8.78
$(11\text{-CF-}4)_4$	54.1–54.5	51.80	8.23
$(11\text{-CF-}4)_5$	liquid	51.77	8.74
$(11\text{-CF-}4)_6$	38.3–39.5	52.50	8.42
	calcd for $(11\text{-CF-}4)_x$	51.85	8.70
	14-CF-5		
$(14\text{-CF-}5)_2$	44.0–44.6	52.71	8.64
$(14\text{-CF-}5)_3$	liquid	52.60	8.61
$(14\text{-CF-}5)_4$	61.0–61.7	52.66	8.63
	calcd for $(14\text{-CF-}5)_x$	52.41	8.80
	17-CF-6		
$(17\text{-CF-}6)_2$	79.1–79.5	52.64	8.48
$(17\text{-CF-}6)_3$	~28	52.85	7.84
$(17\text{-CF-}6)_4$	54–58		
	calcd for $(17\text{-CF-}6)_x$	52.74	8.86

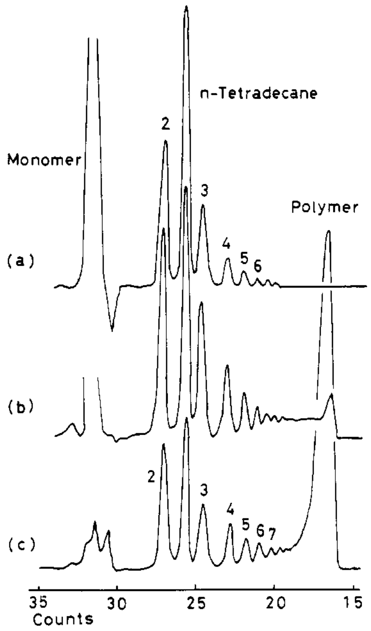

Figure 1. Change in GPC chromatogram in the course of polymerization of 11-CF-4. Polymerization time: (a) 1 h; (b) 2 h; (c) 3 and 24 h. The number of each peak indicates the degree of polymerization of the cyclic oligomers. $[\mathrm{M}]_0 = 2.21 \times 10^{-1}$ mol/L, $[\mathrm{I}]_0 = 1.53 \times 10^{-2}$ mol/L in dichloromethane at 0 °C.

After equilibrium was confirmed by gas chromatography and GPC, equilibrium concentrations of monomer, cyclic oligomers, and polymers were determined. The quantitative data are summarized in Tables II–IV. Those of 17-CF-6 were reported previously. As expected from the Jacobson–Stockmayer theory,[8] the concentration of each product at equilibrium at 0 °C was influenced exclusively by the concentration of total monomer present. This situation is clearly shown for 17-CF-6 in Figure 2. In the figure, a critical monomer concentration is found at about 0.06 mol/L, below which the polymers are effectively absent and above which the polymers appear in proportion to the monomer concentration and the concentrations of the cyclic oligomers level off. Similar situations were also observed for all of the other monomers (TOC, 11-CF-4,

Table II
Equilibrium Concentration of Cyclic Oligomers of TOC

					concentration of cyclic oligomers, M × 10²									
run	[M]$_0$, M	10³[I]$_0$, M	temp, °C	time, h	$x = 1$	$x = 2$	$x = 3$	$x = 4$	$x = 5$	$x = 6$	$x = 7$	$x = 8$	$x = 9$	polymers
1	0.394	6.65	+30	22	7.21	5.78	3.29	2.39	1.43	1.13	0.844	0.610	0.469	15.75
2	0.493	5.21	+30	4	6.95	6.27	4.31	2.55	1.77	1.26	0.950	0.792	0.712	23.74
3	0.616	7.28	+30	2.5	7.02	7.45	4.78	2.52	1.90	1.52	1.02	0.848	0.508	34.29
4	0.118	29.0	0	22	3.61	3.16	1.96	1.11	0.467	0.326	0.234			0.955
5	0.238	39.7	0	22	4.72	4.88	3.51	2.22	1.27	0.940	0.714	0.488	0.414	4.65
6	0.257	1.00	0	23	3.75	5.55	3.70	1.69	1.36	0.972	0.729	0.608		7.33
7	0.387	25.2	0	49.5	3.76	5.46	4.18	2.55	1.70	1.28	1.08	0.786		17.91
8[a]	0.480	17.1	0	72	3.77	5.65	2.68	1.97	1.28	0.953	0.852	0.601		30.25
9	0.513	9.09	0	23	3.71	5.19	3.66	2.17	1.70	1.31	1.05	0.874		31.63
10	0.517	25.2	0	20.5	3.77	5.67	3.66	2.48	1.75	1.27	0.971	0.896		31.26
11	0.591	55.5	0	23.5	3.85	6.60	4.48	3.21	2.09	1.89	1.38	1.20		34.40
12	0.399	21.8	−30	108	1.35	4.41	3.72	2.20	1.39	1.16	0.957	0.753	0.616	23.63
13	0.533	20.8	−30	108	1.33	3.96	3.11	1.55	1.39	1.24	0.991	0.867		38.87

[a] Depolymerization.

Table III
Equilibrium Concentration of Cyclic Oligomers of 11-CF-4

					concentration of cyclic oligomers, M × 10²								
run	[M]$_0$, M	10³[I]$_0$, M	temp, °C	time, h	$x = 1$	$x = 2$	$x = 3$	$x = 4$	$x = 5$	$x = 6$	$x = 7$	$x = 8$	polymers
1	0.182	11.8	+30	2	2.08	4.56	2.25	1.27	0.825	0.603	0.511		6.10
2	0.254	11.8	+30	3.3	2.09	4.31	2.20	1.37	1.02	0.762	0.691	0.501	12.40
3	0.0978	8.57	0	45	1.34	3.28	1.69	0.877	0.595	0.380	0.279	0.228	1.14
4	0.131	8.57	0	25.5	1.33	3.17	1.58	1.14	0.856	0.616	0.476		3.90
5	0.163	8.57	0	25	1.57	3.37	1.57	1.42	1.00	0.534			6.84
6	0.189	12.20	0	69	1.21	3.81	1.93	1.27	0.938	0.669	0.563	0.456	8.06
7	0.196	8.57	0	24	1.27	3.61	1.81	1.28	0.983	0.737	0.737	0.595	9.31
8	0.327	8.57	0	24.5	1.44	3.38	2.12	1.59	1.13				24.16
9	0.192	24.8	−10	20	1.00	3.77	1.91	1.25	0.928	0.677	0.554	0.422	8.69
10	0.195	25.0	−20	60	0.678	3.18	1.63	1.12	0.879	0.768	0.537		10.7
11	0.242	6.93	−20	70.5	0.715	3.31	1.50	1.26	0.926	0.722	0.588	0.455	15.3
12	0.250	25.0	−20	43.5	0.840	3.22	1.79	1.19	0.903	0.681	0.579		17.9

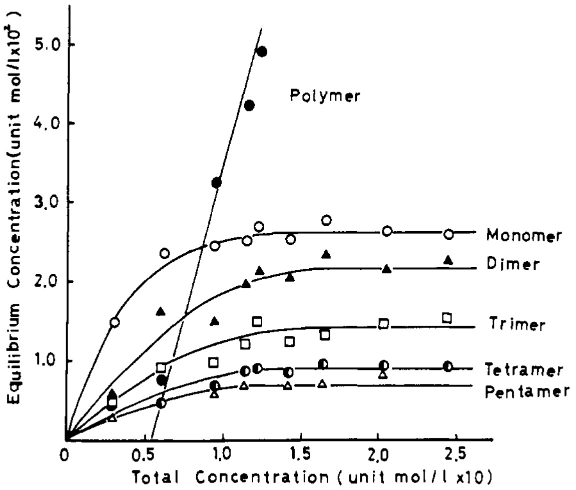

Figure 2. Equilibrium concentrations of monomer (○), cyclic dimer (▲), trimer (□), tetramer (◐), pentamer (△), and linear polymer (●) as a function of total monomer unit concentration in the polymerization of 17-CF-6 at 0 °C in dichloromethane.

14-CF-5). The molar cyclization equilibrium constant is defined[8,9] by

$$-\mathrm{M}_n- \underset{K_p}{\overset{K_x}{\rightleftarrows}} -\mathrm{M}_{n-x}- + \text{c-M}_x \tag{1}$$

$$K_x = \frac{[-\mathrm{M}_{n-x}-][\text{c-M}_x]}{[-\mathrm{M}_n-]} = \frac{[\text{c-M}_x]}{p^x} \tag{2}$$

where $-\mathrm{M}_n-$ and $-\mathrm{M}_{n-x}-$ are the linear n- and $(n-x)$-mers, c-M_x is the cyclic x-mer, and p is the ratio of the concentration of the chain ends of linear n-mer to that of $(n-1)$-mer at the condition $n \gg 1$. Since p should approach unity at the condition $n \gg 1$, K_x should be given directly by the equilibrium concentration of corresponding cyclic x-mer at an initial monomer concentration sufficiently greater than 0.06 mol/L (critical monomer concentration) where the condition $n \gg 1$ was satisified.

$$K_x \simeq [\text{c-M}_x] \qquad n \gg 1 \tag{3}$$

A more elaborate analysis of the Jacobson–Stockmayer theory is given by Semlyen and Flory on the basis of a Gaussian chain:[10]

$$K_x = \left(\frac{3}{2\pi}\langle r_x^2\rangle\right)^{3/2} N^{-1}\sigma_{\mathrm{RX}} \tag{4}$$

N is Avogadro's number and σ_{RX} is the number of skeletal bonds of an x-meric ring that can be open in the reverse reaction of eq 1. σ_{RX} is $2x$ for the cyclic oligomers of the present macrocyclic formals. The characteristic ratio is defined as

$$C_x = \frac{\langle r_x^2\rangle}{nl^2} \qquad C_\infty = \left(\frac{\langle r^2\rangle_0}{nl^2}\right)_{n\to\infty} \qquad n = \nu x \tag{5}$$

where $\langle r_x^2\rangle$ is the mean-square end-to-end length, $\langle r^2\rangle_0$ is the unperturbed mean-square end-to-end length, n is the number of skeletal bonds of length l, and ν is the number of bonds per repeated unit. By substituting (4) into (3), we get

$$K_x = \left(\frac{3}{2\pi}\right)^{3/2}\frac{1}{2Nx}(C_x n l^2)^{-3/2} = \left(\frac{3}{2\pi}\right)^{3/2}\frac{1}{2N}(C_x \nu l^2)^{-3/2}x^{-5/2} \tag{6}$$

and by taking the logarithm of eq 6

$$\log K_x = \log\left\{\left(\frac{3}{2\pi}\right)^{3/2}\frac{1}{2N}(C_x \nu l^2)^{-3/2}\right\} - \frac{5}{2}\log x \tag{7}$$

Table IV
Equilibrium Concentration of Cyclic Oligomers of 14-CF-5

run	$[\mathrm{M}]_0$, M	$10^3[\mathrm{I}]_0$, M	temp, °C	time, h	concentration of cyclic oligomers, M × 10^2							
					$x = 1$	$x = 2$	$x = 3$	$x = 4$	$x = 5$	$x = 6$	$x = 7$	polymers
1	0.145	6.10	+30	3.5	3.08	2.95	1.55	0.905	0.638	0.495	0.377	4.51
2	0.172	6.13	+30	3	2.82	3.09	1.71	1.01	0.665	0.545	0.428	6.93
3	0.231	6.51	+30	1.7	3.26	3.02	1.68	1.06	0.785	0.598	0.524	12.17
4	0.151	6.36	0	10	2.16	2.16	1.53	0.953	0.685	0.542	0.449	6.62
5	0.171	6.76	0	2	2.12	2.34	1.57	1.05	0.698	0.528	0.453	8.35
6	0.212	6.73	0	17.5	2.07	2.26	1.59	0.977	0.704	0.566	0.446	12.58
7	0.256	6.76	0	3.5	2.34	2.27	1.70	1.06	0.764	0.562	0.483	16.42
8	0.297	6.73	0	17.5	2.14	2.02	1.57	1.16	0.741	0.645	0.544	20.87
9	0.155	6.53	−20	9	1.16	1.68	1.59	0.962	0.708	0.524	0.429	8.44
10	0.157	6.61	−30	17	0.879	1.45	1.98	1.12	0.811	0.571	0.420	8.47
11	0.185	6.61	−30	24	1.05	1.45	1.78	0.970	0.707	0.530	0.378	11.63
12	0.232	6.61	−30	47	1.37	1.46	1.84	1.00	0.697	0.509	0.376	15.94

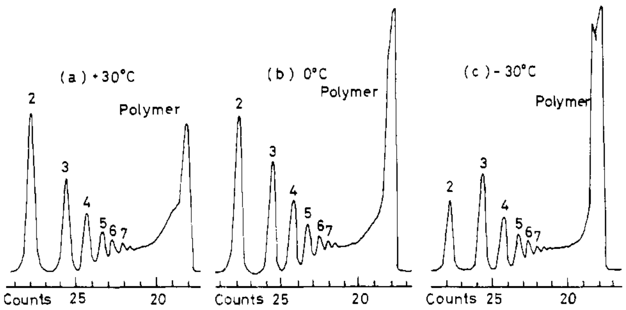

Figure 3. Change in GPC chromatogram of the polymerization products of 14-CF-5 with reaction temperature: (a) +30 °C, $[M]_0 = 1.71 \times 10^{-1}$ mol/L; (b) 0 °C, $[M]_0 = 1.72 \times 10^{-1}$ mol/L; (c) -30 °C, $[M]_0 = 1.85 \times 10^{-1}$ mol/L.

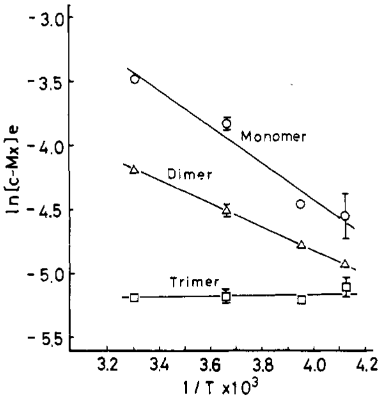

Figure 4. Plots of Dainton's equation in the polymerization of 14-CF-5: (○) monomer; (△) dimer; (□) trimer.

can be obtained. A plot of eq 7 should give a slope of −2.5, and the intercept will yield the C_∞ value, which is a measure of the chain flexibility of the polymer as can be seen in eq 5.

As eq 1 or 2 also stands for the equilibrium from right to left for the polymerization of the respective cyclic x-mer, the reciprocal of K_x is the equilibrium constant for polymerization (K_p)

$$K_p = 1/K_x \tag{8}$$

Therefore, the free energy change for polymerization, $\Delta G_p°$, can be obtained as follows:

$$-RT \ln K_p = \Delta G_p° = \Delta H_p - K_p - T\Delta S_p° \tag{9}$$

If the enthalpy change, ΔH_p, is equal to 0, the entropy change, $\Delta S_p°$, can be directly calculated from the K_p value.

Plots of Dainton's Equation. The monomers were polymerized at various reaction temperatures in order to examine the change of product distribution with polymerization temperature. The result for 14-CF-5 is shown in Figure 3 as an example. With increasing temperature, the dimer peak grows faster than peaks of oligomers with $x \geq 3$. This indicates that the equilibrium has been shifted to the smaller rings at higher temperature.

Dainton and Ivin related the equilibrium monomer concentration $[M]_e$ to temperature by the equation[11]

$$\ln [M]_e = \frac{1}{T}\frac{\Delta H_p}{R} - \frac{\Delta S_p°}{R} \tag{10}$$

where ΔH_p is the heat of polymerization and $\Delta S_p°$ is the entropy change for $[M]_e = 1$ mol/L. Assuming a similar relation for dimer and higher oligomers, the equilibrium concentrations of each oligomer were plotted against reciprocal temperatures in Figure 4 for 14-CF-5. TOC, 11-CF-4, and 17-CF-6 gave similar straight lines.

Table V
Thermodynamic Parameters in Equilibrium Polymerization of TOC

x	$10^2 K_x$, M	$\Delta G_p°$ at 0 °C, kcal/mol	ΔH_p, kcal/mol	$\Delta S_p°$, cal/(mol·deg)
1^a	3.90	−1.8 ± 0.4	−4.0 ± 0.2	−8.2 ± 0.8
2^a	2.79	−2.0 ± 0.4	−1.1 ± 0.2	+3.0 ± 0.8
3^b	1.25	−2.4 ± 0.1	0	+8.7 ± 0.3
4^b	0.573	−2.8 ± 0.1	0	+10.3 ± 0.3
5^b	0.317	−3.1 ± 0.1	0	+11.4 ± 0.3
6^b	0.207	−3.4 ± 0.1	0	+12.3 ± 0.4
7^b	0.137	−3.6 ± 0.1	0	+13.1 ± 0.3
8^b	0.0971	−3.8 ± 0.1	0	+13.8 ± 0.4

[a] ΔH_p and $\Delta S_p°$ were determined from the plots of Dainton's equation (eq 10) by the linear least-squares method, and $\Delta G_p°$ was calculated from the ΔH_p and $\Delta S_p°$ thus obtained. The errors indicated are standard deviations. [b] $\Delta G_p°$ and $\Delta S_p°$ were determined from the mean of K_x values by using eq 8 and 9, assuming $\Delta H_p = 0$. The errors indicated are standard deviations.

Table VI
Thermodynamic Parameters in Equilibrium Polymerization of 11-CF-4

x	$10^2 K_x$, M	$\Delta G_p°$ at 0 °C, kcal/mol	ΔH_p, kcal/mol	$\Delta S_p°$, cal/(mol·deg)
1^a	1.36	−2.4 ± 0.6	−3.2 ± 0.3	−3.1 ± 1.1
2^a	1.72	−2.2 ± 0.4	−0.9 ± 0.2	+4.8 ± 0.7
3^a	0.594	−2.8 ± 0.6	−0.9 ± 0.3	+6.9 ± 1.0
4^b	0.313	−3.1 ± 0.1	0	+11.5 ± 0.3
5^b	0.183	−3.4 ± 0.1	0	+12.5 ± 0.3
6^b	0.108	−3.7 ± 0.1	0	+13.6 ± 0.3
7^b	0.0768	−3.9 ± 0.1	0	+14.3 ± 0.3
8^b	0.0516	−4.1 ± 0.1	0	+15.0 ± 0.4

[a] ΔH_p and $\Delta S_p°$ were determined from the plots of Dainton's equation (eq 10) by the linear least-squares method, and $\Delta G_p°$ was calculated from the ΔH_p and $\Delta S_p°$ thus obtained. The errors indicated are standard deviations. [b] $\Delta G_p°$ and $\Delta S_p°$ were determined from the mean of K_x values by using eq 8 and 9, assuming $\Delta H_p = 0$. The errors indicated are standard deviations.

Table VII
Thermodynamic Parameters in Equilibrium Polymerization of 14-CF-5

x	$10^2 K_x$, M	$\Delta G_p°$ at 0 °C, kcal/mol	ΔH_p, kcal/mol	$\Delta S_p°$, cal/(mol·deg)
1^a	2.17	−2.1 ± 0.5	−2.7 ± 0.3	−2.0 ± 0.9
2^a	1.11	−2.5 ± 0.1	−1.8 ± 0.1	+2.4 ± 0.3
3^b	0.558	−2.8 ± 0.1	0	+10.3 ± 0.2
4^b	0.255	−3.2 ± 0.1	0	+11.9 ± 0.1
5^b	0.143	−3.6 ± 0.1	0	+13.0 ± 0.1
6^b	0.0933	−3.8 ± 0.1	0	+13.9 ± 0.2
7^b	0.0632	−4.0 ± 0.1	0	+14.6 ± 0.2

[a] ΔH_p and $\Delta S_p°$ were determined from the plots of Dainton's equation (eq 10) by the linear least-squares method and $\Delta G_p°$ was calculated from the ΔH_p and $\Delta S_p°$ thus obtained. The errors indicated are standard deviations. [b] $\Delta G_p°$ and $\Delta S_p°$ were determined from the mean of K_x values by using eq 8 and 9, assuming $\Delta H_p = 0$. The errors indicated are standard deviations.

Thermodynamic Parameters. Thermodynamic parameters obtained from Dainton's equation and molar cyclization equilibrium constants are summarized in Tables V–VIII. It is clear that the polymerizability of these four monomers is controlled primarily by the ΔH_p term. The absolute values of ΔH_p decrease when ring size increases from 8 to 17. For TOC and 11-CF-4, the large negative values of ΔH_p, −4.0 and −3.2, were obtained, respectively, in fair accordance with the reported ones,[2,12] and these values may be ascribed to the ring strain due to the repulsion between hydrogen atoms across the ring. It is

Table VIII
Thermodynamic Parameters in Equilibrium Polymerization of 17-CF-6

x	10^2K_x, M	$\Delta G_p°$ at 0 °C, kcal/mol	ΔH_p, kcal/mol	$\Delta S_p°$ cal/(mol·deg)
1[a]	2.62	-2.0 ± 0.2	-2.5 ± 0.1	-2.0 ± 0.4
2[a]	1.03	-2.5 ± 0.6	-0.7 ± 0.3	$+6.7 \pm 1.1$
3[b]	0.454	-2.9 ± 0.1	0	$+10.7 \pm 0.2$
4[b]	0.231	-3.3 ± 0.1	0	$+12.1 \pm 0.2$
5[b]	0.142	-3.4 ± 0.1	0	$+13.1 \pm 0.2$

[a] ΔH_p and $\Delta S_p°$ were determined from the plots of Dainton's equation (eq 10) by the linear least-squares method, and $\Delta G_p°$ was calculated from the ΔH_p and $\Delta S_p°$ thus obtained. The errors indicated are standard deviations. [b] $\Delta G_p°$ and $\Delta S_p°$ were determined from the mean of K_x values by using eq 8 and 9, assuming $\Delta H_p = 0$. The errors indicated are standard deviations.

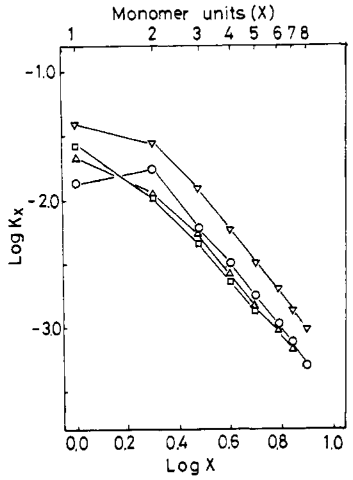

Figure 5. log–log plots of molar cyclization equilibrium constants (K_x) against x: (▽) TOC; (○) 11-CF-4; (△) 14-CF-5; (□) 17-CF-6.

interesting to point out that the negative ΔH_p value (ring strain) was observed in macrocycles with 14-membered (14-CF-5) and even 17-membered (17-CF-6) rings, which had been believed to be free from strain. Furthermore, the larger rings, dimers of TOC (16-membered ring), 11-CF-4 (22), 14-CF-5 (28), and 17-CF-6 (34) and the trimer of 11-CF-4 (33), also show some negative ΔH_p values. The reason for this fact is not clear at present but may be ascribed to the different conformation of the oligo(oxyethylene) unit in cyclic oligomers compared with the linear poly(oxyethylene) unit whose most favorable conformation is GTT. For the rings larger than 40, ΔH_p tends to 0, and the polymerizability is determined only by the entropy term; i.e., the driving force of polymerization is completely attributable to the increase in the degrees of freedom which result when chain ends are released by ring opening.

The molar cyclization constants are plotted against the number of monomer units x in cyclic oligomers. The log–log plot in Figure 5 shows that log K_x decreases in proportion to the −2.5 power of x in the region where ΔH_p can be taken as 0, in accordance with Jacobson–Stockmayer theory[8] (eq 7). All the monomers and dimers deviate from linearity, indicating that the enthalpy term cannot be neglected even for the medium-size (10–30) rings. The calculated values of $C_\infty = (\langle r^2\rangle_0/nl^2)_{n\to\infty}$ in eq 5 were between 7 and 9 for the macrocyclic formals examined (TOC, 8.1; 11-CF-4, 8.3; 14-CF-5, 7.6; 17-CF-6, 7.2), in good agreement with Schulz's[13] value for 11-CF-4 (7.8). A little smaller value was reported for 1,3-dioxolane (4.8).[9] The flexibility of the polyether chain is considered to be similar to that of polysiloxanes (C_∞ ranging from 5 to 10).[9]

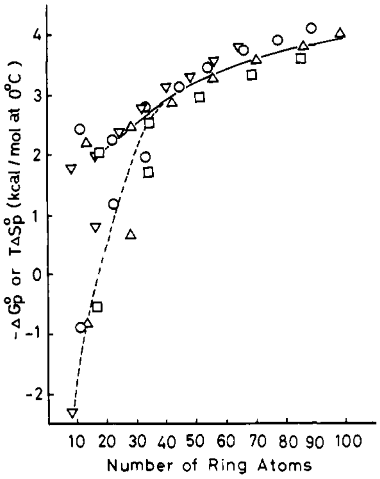

Figure 6. Change in $-\Delta G_p°$ (solid line) and $T\Delta S_p°$ (broken line) at 0 °C with ring size of macrocyclic formals: (▽) TOC; (○) 11-CF-4; (△) 14-CF-5; (□) 17-CF-6.

A value of 10.2 was reported for polystyrene.[14]

The change of $T\Delta S_p°$ and $-\Delta G_p°$ at 0 °C with the number of ring atoms is shown in Figure 6. In this figure, $-\Delta G_p°$ is shown by a solid line and $T\Delta S_p°$ by a broken line. The longitudinal difference corresponds to ΔH_p. For rings larger than 40, which are free from strain, both lines coalesce into one line, indicating negligible ΔH_p. The increment of $T\Delta S_p°$ and $-\Delta G_p°$ with increasing number of ring atoms gradually becomes small; consequently, the polymerizability of a macrocyclic per unit weight decreases with increasing number of ring atoms, although the value should continuously increase according to the Jacobson–Stockmayer theory. This means that the free energy difference between cyclic polymer and linear polymer increases gradually and infinitely with an increasing number of ring atoms. In the polymerization of macrocyclic formals, it was shown that an equilibrium exists between macrocyclics and the polymers. If the polymers were cyclic, the free energy of formation of the polymers should be identical with that of macrocyclics having the same degree of polymerization. Accordingly, there should not be any free energy difference between macrocyclics and polymers; thus, contrary to the suggestion of Plesch,[15] the polymers formed in the polymerization of cyclic formals cannot be cyclic. The ring-expansion mechanism of the cationic polymerization of cyclic formals, based on the absence of end groups in the polymer, seems very unlikely.

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