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Cationic Polymerizations of 1,3,6-Trioxocane and 2-Butyl-1,3,6-trioxocane

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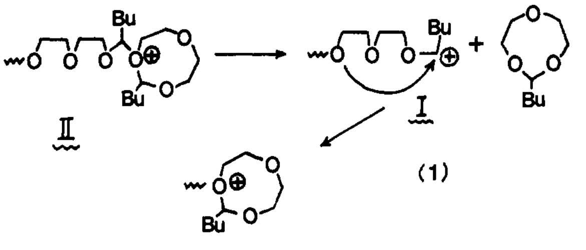
ABSTRACT: The polymerization of 1,3,6-trioxocane (TOC) has been reinvestigated. The reaction occurs without an induction period to give high MW linear polymers. The degree of polymerization is not independent of conversion. Polymers having $\bar{M}_n$ as high as 81 000, $\bar{M}_w/\bar{M}_n \sim 1.4$, and good mechanical strength can be obtained. These results contrast with earlier reports of long induction periods and products with $\bar{M}_n \sim 5000$. Substituents at the 2-position greatly reduce the polymerizability of dioxolane and dioxepanes. It is therefore a significant result that 2-butyl-1,3,6-trioxocane (2-Bu-TOC) is readily polymerized and at a slightly faster rate than polymerization of TOC under identical conditions. The $\bar{M}_n$ of poly(2-Bu-TOC) increases monotonically with conversion, reaching a value of 7700. The thermodynamic parameters for the polymerizations of both systems have been obtained. There is strong argument in favor of the open-chain alkoxycarbenium ion as the propagating species for trioxocane polymerizations over the cyclic oxonium ion.

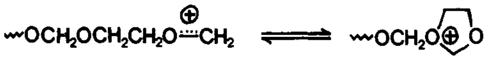
Introduction

In the course of our studies on acid-catalyzed degradation of polyacetals, we observed[1] that the eight-membered ring monomer 2-butyltrioxocane (2-Bu-TOC)[2] is the main acidolysis product of poly(2-Bu-TOC). The results suggested that the unzipping mechanism involves a linear alkoxycarbenium ion intermediate (I), eq 1. According to the principle of microscopic reversibility, the same alkoxycarbenium ion should be the propagating species in the polymerizations of 2-Bu-TOC.[1]



(1)

In the polymerization of oxygen heterocyclic compounds, the oxonium structure for the propagating species is thought to be indisputable in the case of tetrahydrofuran.[3] However, in the polymerization of dioxolane and other cyclic acetals, because of the strong stabilizing effect of the α-oxygen atom, alkoxycarbenium ions are in equilibrium with cyclic oxonium ions. This is illustrated for 1,3-dioxolane (DOL)[3] (eq 2). Both of these species can add to another monomer molecule for propagation. Penczek et al.[3] have argued that in the case of dioxolane the cyclic oxonium ion is responsible for the majority of propagation. Observations on the polymerizability of cyclic acetals having substituents on the 2- or 4-positions seem to support this mechanism. For instance, 2-Me-DOL[4] and 4-Me-DOL[5] were only oligomerized to $\overline{DP}$'s of 10 and 20, respectively, as compared to the polymerization of DOL to high molecular weight linear polymer together with macrocyclics.[6] Whereas 1,3-dioxepane (DOP) is readily converted to high MW linear polymer by cationic initiators,[6] the same process for 2-Me-DOP[7] and 4-Me-DOP[8] gave products with $\overline{DP}$ of ca. 75. Additional methyl substituents reduces polymerizability further. Thus, 2,4-Me_2-DOP yielded only oligomeric products even at high monomer concentration and 2,2-Me_2-DOP forms only a crystalline cyclic dimer.[7] These results can be rationalized in terms of the severe steric hindrance to approach a 2- and/or 4-substituted cyclic acetal monomer to a similarly substituted cyclic oxonium ion chain end.



(2)

On the basis of literature results, the prospect of polymerizing 2-Bu-TOC is not promising. Polymerization of unsubstituted TOC[9] in 1,2-dichloroethane using triethyloxonium tetrafluoroborate ($Et_3O^+BF_4^-$) as catalyst exhibits an induction period of 2–3 h. The polymer has $\overline{DP}$ of only about 30 which is independent of percent conversion. If the effect of a 2-Bu substituent on TOC is like that of the 2-Me substituent in the other cyclic acetals (vide supra), polymerizability of 2-Bu-TOC should be very low.

The central purpose of this work is to investigate the polymerization of 2-Bu-TOC and to deduce the probable

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mechanism of propagation. During the course of our study, polymerization of TOC was also investigated.

Experimental Section

Materials. Diethylene glycol, paraformaldehyde, boron trifluoride etherate, tetralin, and triethyloxonium tetrafluoroborate (1 M methylene chloride solution) were from Aldrich Chemical Company. Benzene, toluene, and methylene chloride were Fisher Reagent grade solvents.

Diethylene glycol and benzene were dried with molecular sieves and distilled prior to use. Tetralin and methylene chloride were purified by distillation over CaH_2. Boron trifluoride etherate was distilled immediately before use. Paraformaldehyde was used as received. Amberlite IR-120 was treated with 10% hydrochloric acid overnight and washed with water and then with methanol. The resin was oven dried at 100 °C.

Monomers. 1,3,6-Trioxocane was prepared by the condensation of diethylene glycol and paraformaldehyde in the presence of Amberlite IR-120 according to Astle's method.[10] It was purified by distillation from $LiAlH_4$ collecting the fraction boiling between 154 and 155 °C.

2-Butyl-1,3,6-trioxocane was prepared as described previously.[1] It was refluxed with CaH_2 and then distilled at 0.3 mmHg at 44–45 °C.

The monomers were analyzed by gas chromatography, showing purities in excess of 99%.

Polymerization. Polymerization was carried out in a Schlenk tube which had been flame dried under vacuum and filled with purified nitrogen. The tube was equipped with a magnetic stir bar and fitted with a rubber septum. Both the monomer solution and catalyst solution were injected by syringe. Either methylene chloride or toluene was used as solvent. The monomer solution was equilibrated at the reaction temperature in a thermostated bath prior to introduction of catalyst. Samples were taken with a stainless steel cannula at intervals during the course of polymerization. The sample was quenched with triethylamine, precisely weighed, and a known amount of tetralin according to conversion was added as GC standard. The mixture was analyzed with GC. Conversion was calculated, using a calibration curve, from the peak area ratio for the monomer and tetralin.

Poly(TOC) was isolated by pouring the reaction mixture into cold methanol and allowing it to stand at −20 °C for several hours. The precipitated poly(TOC) was collected by filtration while cold and dried at 120 °C in vacuo. The white waxy polymer has the known T_m of 36 °C by DSC.

It was not possible to precipitate poly(2-Bu-TOC). Instead, the polymerization mixture was washed with water several times. The organic phase was dried with anhydrous $MgSO_4$ overnight. After the solvent was removed by distillation, the residual solvent was removed from polymer at 120 °C in vacuo.

Equilibrium Monomer Concentration, $[M]_e$. To determine $[M]_e$ for TOC, the polymerization mixture at desired conversion was quenched, a weighed amount of tetralin was added, and the mixture was cooled to −196 °C and evacuated. With the stopcock to the vacuum pump closed, the polymerization mixture was heated to 120 °C while a receiver section was maintained at −196 °C to effect cryogenic distillation of unconsumed monomer and tetralin for GC analysis. In the case of polymerization of 2-Bu-TOC, the mixture was first diluted with 1,2-dichloroethane as the solvent to about 4 times the volume, followed by GC analysis. This choice of solvent is necessitated by the fact that CH_2Cl_2 is too volatile, whereas toluene in a poor solvent for the polymer and the polymerization mixture became a gel rendering cryogenic distillation inefficient. The above methods of $[M]_e$ determination were developed to avoid any possible depolymerization occurring in the GC injection port.

Analytical Methods. Gas chromatography was carried out on a Hewlett-Packard 5790A chromatograph using a Foxboro Super Pak II 6-ft × $^1/_8$-in.-o.d. column, temperature programmed (30 °C for 3 min, 30–200 °C at 20 deg/min, 200 °C for 5 min for analyzing 2-Bu-TOC; 30 °C for 3 min, 30–120 °C for 10 deg/min, 120 °C for 5 min for analyzing TOC).

^1H NMR spectra were obtained by using Perkin-Elmer R-12 and Varian Associates XL-300 instruments. $CDCl_3$ was used as the solvent, and tetramethylsilane (Me_4Si) was used as internal standard. In the case of low-temperature ^1H NMR, $CDCl_3$ and Me_4Si were sealed in the capillary which was put into the NMR tube with the sample.

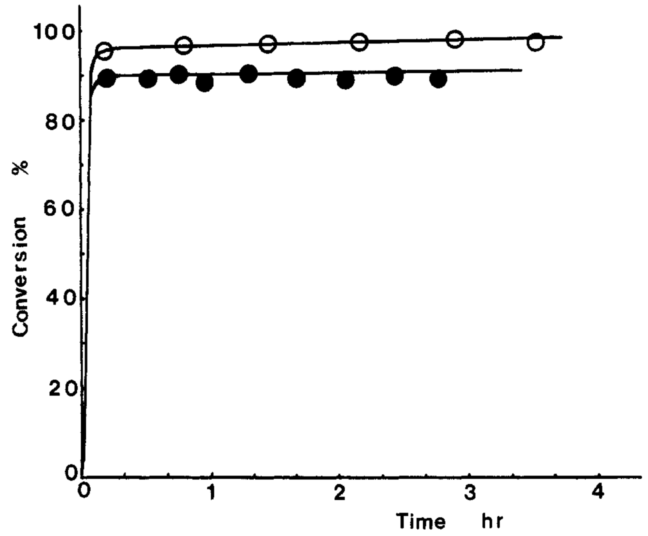


Figure 1. Polymerization time–conversion curves using 1 mol % $Et_3O{\cdot}BF_4$ as catalyst and CH_2Cl_2 as solvent at −10 °C; (○) 1,3,6-trioxocane, $[M]_0 = 2.56$ M; (●) 2-butyl-1,3,6-trioxocane, $[M]_0 = 2.53$ M.

GPC was carried out on a Waters Associates GPC instrument. Tetrahydrofuran was used as solvent (flow rate 0.8 mL/min); 10^5- and 10^3-Å columns were used. Number-average molecular weight ($\bar{M}_n$), weight-average molecular weight ($\bar{M}_w$), and polydispersity ($PD = \bar{M}_w/\bar{M}_n$) were calculated from the standard curve determined using monodispersed polystyrene samples.

DSC curves were obtained from Perkin-Elmer DSC-IV. The temperature was calibrated using indium and cyclohexane.

Results and Discussion

The polymerization of trioxocanes were performed with two different catalysts and solvents. Polymerizations initiated by triethyloxonium tetrafluoroborate ($Et_3O^+BF_4^-$) in methylene chloride at −10 °C have very fast rates reaching equilibrium within 15 min (Figure 1). It is worthy of note that the polymerizations commenced immediately upon mixing of monomer and catalyst. This is contrary to the long induction periods observed by Okada and co-workers for TOC[9] and 1,3-dioxolane in 1,2-dichloroethane initiated by $Et_3O^+BF_4^-$.[11] It seems that an inhibitor may be present in their system.

The rates of polymerization of TOC and 2-Bu-TOC in CH_2Cl_2 are too rapid to be monitored with accuracy. Since ionic polymerizations have reduced rates in nonpolar media, the kinetics were studied at −10 °C using toluene as the solvent. It can be seen in Figure 2 that 2-Bu-TOC actually approached $[M]_e$ faster than TOC. This result is contrary to expectations based on behavior of other 2- and/or 4-substituted cyclic acetals discussed above.

Polymerization of TOC. The rate constant of propagation in the case of polymerization without an induction period can be obtained by the relationship

$$\log\left\{\frac{[M]_t-[M]_e}{[M]_0-[M]_e}\right\} = k_p[C^*]_0 t/2.303 \qquad (3)$$

where $[M]_0$ and $[M]_t$ are the monomer concentrations at time zero and t, respectively, and $[C^*]_0$ is the concentration of propagating species. Since the value of $[C^*]_0$ is not known, one may use the slope of the first-order plots (Figure 3) to calculate $k'_p[C]_0$ where k'_p is the apparent rate constant and $[C]_0$ is the initiator concentration. If for living cationic polymerization, $k'_p = k_p$ and $[C^*]_0 = [C]_0$, then the values of k_p are $(2.4 \pm 0.4) \times 10^{-3}$ and (3.4 ± 0.7)

Table I
Molecular Weights of Poly(TOC)

	no.					
	6-3	6-5	6-6	6-7	6-8	K-6
reaction time,[a] h	3	7	9	11.5	12.5	30.5
conversion, %	40.7	74.0	84.3	87.9	91.1	94.0
$\bar{M}_n$	15 300	27 400	27 300	26 500	26 700	27 000
$\bar{M}_w$	23 400	38 000	38 200	39 300	39 000	38 500
PD	1.53	1.38	1.40	1.48	1.46	1.43

[a] Polymerization at −10 °C for $[TOC]_0 = 2.67$ M in toluene initiated by 26.7 mM $BF_3 \cdot Et_2O$.

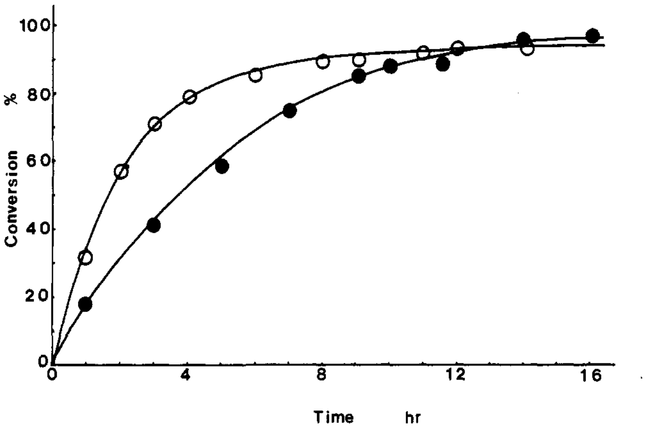


Figure 2. Polymerization time–conversion curves using 1 mol % $BF_3 \cdot Et_2O$ as catalyst and toluene as solvent at −10 °C: (○) 1,3,6-trioxocane, $[M]_0 = 2.67$ M; (●) 2-butyl-1,3,6-trioxocane, $[M]_0 = 2.56$ M.

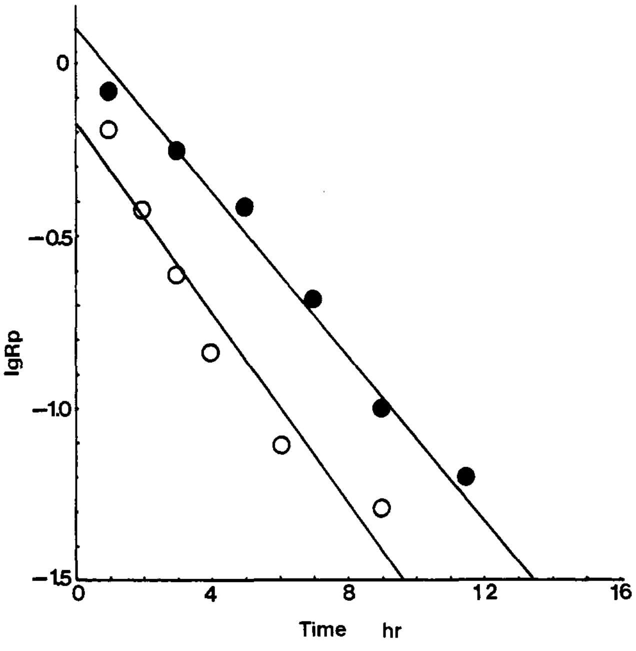


Figure 3. First-order plots of data in Figure 2.

$\times 10^{-3}$ M^{-1} s^{-1}, respectively, for TOC and 2-Bu-TOC at −10 °C.

In polymerization of cyclic acetals, sometimes both linear and macrocyclic polymers were produced. Okada et al.[9] reported $\bar{M}_n$ values of up to ~3000 only for their poly(TOC) using vapor-phase osmometry. In our work, the MW of a poly(TOC) is much greater than this. Furthermore, the GPC curves (Figure 4) showed the formation of both linear and macrocyclic polymers. The fraction eluted with smallest retention volume is assumed to be that of linear high MW poly(TOC). There is one small and one large peak at higher retention volumes which are probably the macrocyclics. Finally, there is a solvent peak the intensity of which is dependent on the particular sample and unknown variation on how the sample was injected into the GPC.

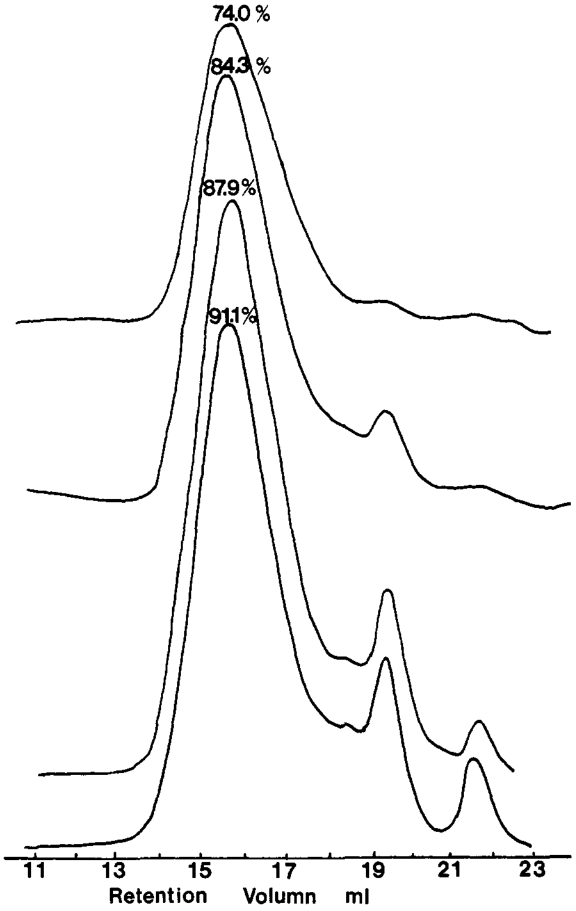


Figure 4. GPC curves of samples obtained during the polymerization of 1,3,6-trioxocane at 74.0%, 84.3%, 87.9%, and 91.1% conversion. Conditions are the same as in Figure 2.

If one calculates MW and PD including the entire trimodal distribution curve, the results are without much quantitative significance. Since the high MW linear fraction is by far the dominant one, we have resolved the trimodal GPC curves into three Gaussian components and report the MW values for the major GPC peak in Table I. It took several hours of polymerization for the MW to reach the maximum constant values of $\bar{M}_n = (2.70 \pm 0.04) \times 10^4$ and $\bar{M}_w = (3.86 \pm 0.05) \times 10^4$. The molecular weight distribution is quite narrow, having a constant PD value after 7 h of polymerization of 1.43 ± 0.04. These results are contrasted with those of Okada et al.[9] who found after ca. 3 h of induction period $\bar{M}_n \sim 3000$, which is the same at all conversions. The same unknown inhibitors which cause the induction period may also be limiting the chain growth.

In fact the polymerizations described in Table I may have been complicated by the sampling process. We have

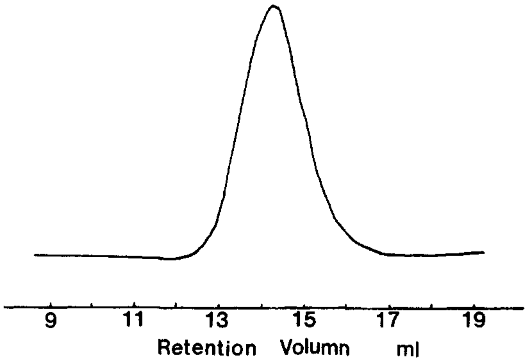


Figure 5. GPC curve of poly(1,3,6-trioxocane) obtained in a continuous run. See text for discussion conditions are the same as in Figure 2.

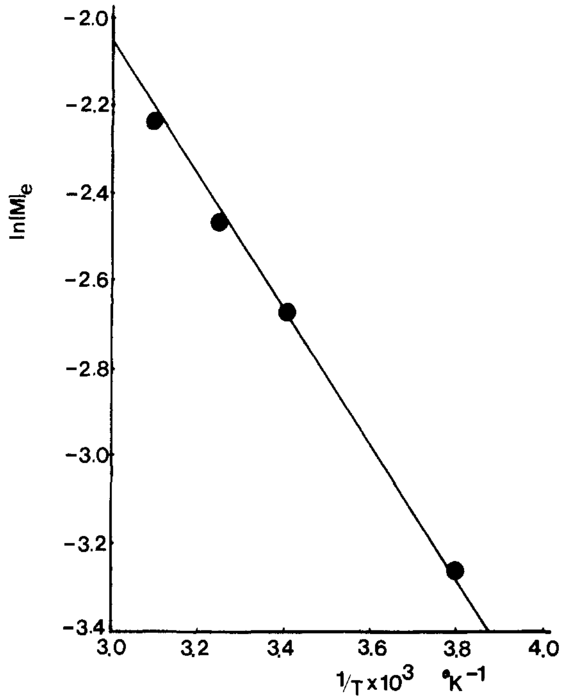


Figure 6. Relationship between ln $[M]_e$ and $1/T$ for TOC.

polymerized TOC at 0 °C ([TOC] = 2.5 M in toluene; $[BF_3{\cdot}Et_2O]$ = 25 mM) for 20 h without taking samples from it. Poly(TOC) isolated exhibits only one narrow GPC peak (Figure 5). The MW values are $\bar{M}_n = 8.1 \times 10^4$, $\bar{M}_w = 1.15 \times 10^5$, and PD = 1.43. This poly(TOC) is flexible, very tough, and appears opaque and slightly yellow. Therefore, poly(TOC) with interesting and useful mechanical and physical properties can be obtained.

The $[M]_e$ was determined by GC on the volatile components in the absence of polymer as described above. Results at various temperatures are plotted in Figure 6. Using Dainton's equation,[12]

$$\ln [M]_e = \frac{\Delta H^\circ}{RT} - \frac{\Delta S^\circ}{R} \qquad (4)$$

with $\Delta G^\circ_{eq} = 0$ for a 1 M solution in monomer, we obtained $\Delta H^\circ_{ss} = -3.1$ kcal mol^{-1}, $\Delta S^\circ_{ss} = 5.1$ cal (mol K)$^{-1}$, and T_c = 330 °C.

Polymerization of 2-Bu-TOC. Polymerization of 2-Bu-TOC was carried out under the same conditions described above for TOC. The results are summarized in Table II. The GPC curves of the poly(2-Bu-TOC) (Figure 7) showed similar trimodal distribution with a solvent peak as seen with poly(TOC). Therefore, linear and macrocyclic polymers were obtained in both cases and the $\bar{M}_n$ of the former increases monotonically with conversion (Figure 8).

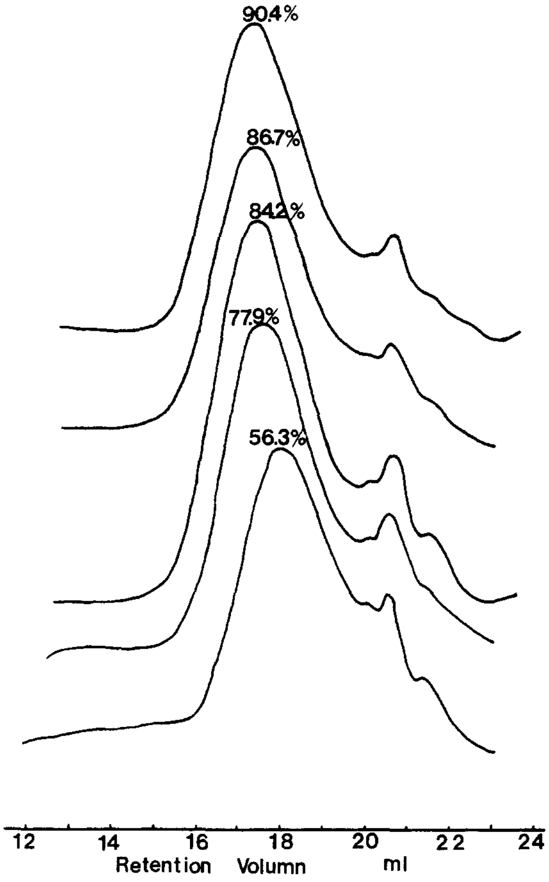


Figure 7. GPC curves of samples obtained during the polymerization of 2-butyl-1,3,6-trioxocane at 56.3%, 77.9%, 84.2%, 86.7%, and 90.4% conversion. Conditions are the same as in Figure 2.

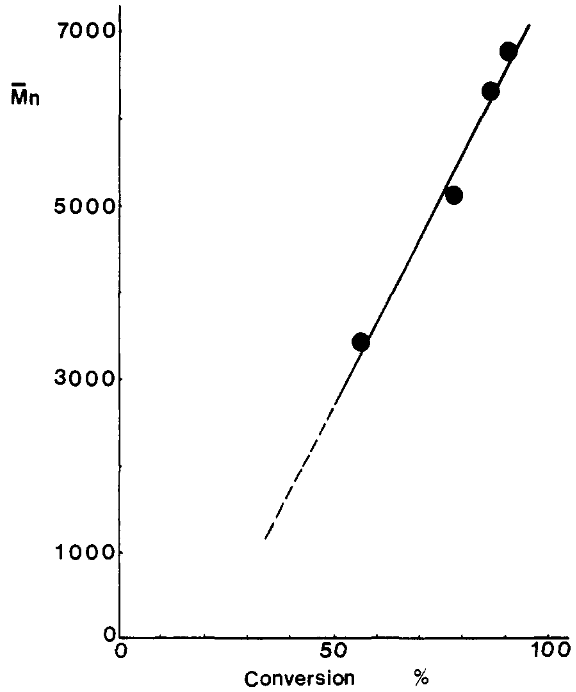


Figure 8. Variations number-average molecular weight with conversion during the polymerization of 2-butyl-1,3,6-trioxocane. Conditions are the same as in Figure 2.

We have also performed 2-Bu-TOC polymerization without sampling. Unlike in the case of TOC, the products

Table II
Molecular Weights of Poly(2-Bu-TOC)

	no.					
	5-3	5-5	5-7	5-10	5-13	K-5
reaction time,[a] h	2	4	6	9	12	24
conversion, %	56.3	77.9	84.2	86.7	90.4	91.2
$\bar{M}_n$	3450	5150	6330	6290	6780	7710
$\bar{M}_w$	5500	8210	9970	10000	10600	12200
PD	1.60	1.59	1.57	1.59	1.57	1.58

[a] Polymerization at −10 °C for $[\text{2-Bu-TOC}]_0$ = 2.56 M in toluene initiated by 25.6 mM of $BF_3{\cdot}Et_2O$.

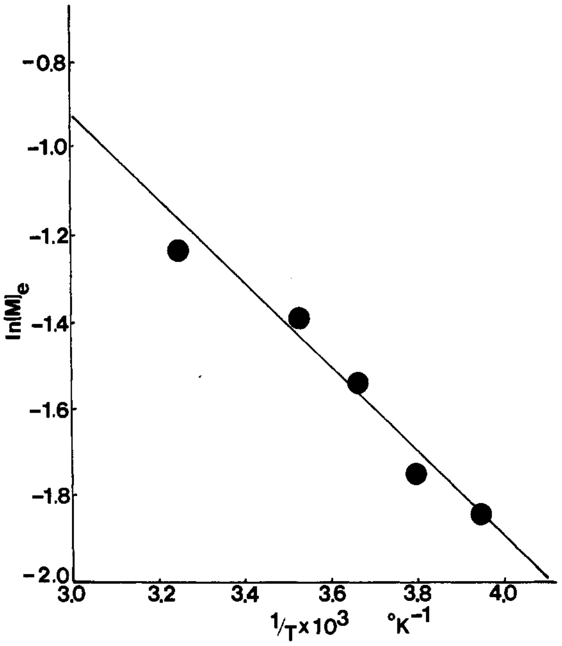
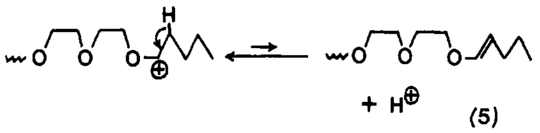


Figure 9. Plot of ln $[M]_e$ vs. T^{-1} for 2-butyl-1,3,6-trioxocane.

have the same $\bar{M}_n$ and PD as those polymers isolated from extracted samples at the same conversion.

The slow, monotonic increase of molecular weight throughout the course of polymerization can be understood as a consequence of the ability of alkoxycarbenium ion chain ends to equilibrate with unreactive vinyl ether chain ends by loss of β-protons (eq 5). Vinyl ether chain ends


(5)

can be reactivated by protonation (reverse of eq 5). This pathway is unavailable for polymerizing TOC itself, hence, poly(TOC) may attain higher molecular weights than poly(2-Bu-TOC) under identical conditions. Alternatively, the proton could initiate another chain.

Variation of $[\text{2-Bu-TOC}]_e$ with temperature is plotted in Figure 9. From the slope and intercept, we found ΔH°_{ss} = −1.9 kcal mol⁻¹, ΔS°_{ss} = −3.9 cal (mol K)⁻¹, and T_c = 220 °C. Experimental errors may be large owing to difficulties in separation of low MW polymer from unreacted monomer and related experimental difficulties which were not encountered in the case of poly(TOC).

Copolymerization of TOC and 2-Bu-TOC. Copolymerizations of TOC and 2-Bu-TOC were conducted at −10 °C in 1,2-dichloroethane for 24 h to ca. 90% conversion. The amount of $BF_3{\cdot}Et_2O$ was 1% of the total number of moles of the comonomers. Products were isolated by the procedure used for poly(2-Bu-TOC). GPC curves showed a single high MW peak (Figure 10); mixtures of homopolymers would give different GPC results.

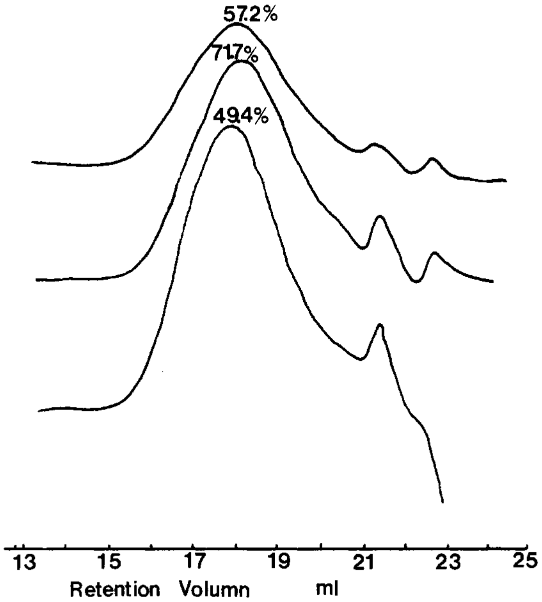


Figure 10. GPC curves of copolymers of 1,3,6-trioxocane and 2-butyl-1,3,6-trioxocane. 2-Butyl-1,3,6-trioxocane mol % in copolymers: 49.4%, 57.2%, and 71.7%. Conditions are the same as in Figure 2.

Table III
Copolymerizations of TOC and 2-Bu-TOC[a]

[2-Bu-TOC] in feed, mol %	47.0	56.5	71.8
[2-Bu-TOC] in copolymer, mol %	49.4	57.2	71.1
$\bar{M}_n$	3110	2910	2540
$\bar{M}_w/\bar{M}_n$	2.1	2.2	2.2

[a] Copolymerization in 1,2-dichloroethane at −10 °C initiated by 1 mol % $BF_3{\cdot}Et_2O$ for 24 h.

The MW's of the copolymers are given in Table III. A range of comonomer feed compositions was studied. The copolymer compositions were analyzed by NMR. The results in Table III show the copolymerization to be nearly ideal.

Thermodynamics. Owing to relief of ring strain, polymerization of most small and medium ring heterocycles is exothermic. Ring strain of the eight-membered cyclic 1,3-formal[13] is −3.94 kcal mol⁻¹ which lies between the values of −5.1 and −3.5 kcal mol⁻¹ for the five- and seven-membered analogues,[14,15] respectively. Any substituent tends to increase nonbonded repulsions in the polymer, resulting in lower exothermicity for the polymerization. For multiply substituted cyclic acetals, the free-energy change becomes positive and there is no polymerization (vide supra). The thermodynamic parameters for polymerizations of some cyclic acetals are compared in Table IV.

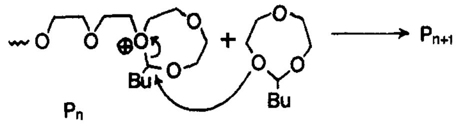
Methyl substitutions at the 4-position in DOL or DOP decrease $-\Delta H^\circ_{ss}$ by 1.0 and 1.4 kcal mol⁻¹, respectively. Substitution causes only small changes in ΔS°_{ss} for these compounds. The ΔH°_{ss} for 2-Me-DOP is 1.5 kcal mol⁻¹ smaller than for DOP. The degree of polymerization of 2-Me-DOL is too low[4] for the determination of thermo-

Table IV
Thermodynamic Parameters of Polymerization of Cyclic Acetals

monomer	solvent	$-\Delta H^\circ_{ss}$, kcal mol^{-1}	$-\Delta S^\circ_{ss}$, cal (mol K)$^{-1}$	T_c, °C	ref
TOC	1,2-dichloroethane	3.1 ± 0.1	5.1 ± 0.3	330	this work
2-Bu-TOC	1,2-dichloroethane	1.9 ± 0.2	3.9 ± 0.5	220	this work
DOP	methylene chloride	3.6	11.5	27	7, 8
2-Me-DOP	methylene chloride	2.1	8.9	−37	7, 8
4-Me-DOP	methylene chloride	2.2	9.3	−33	7, 8
DOL	methylene chloride	4.2	11.4	95	16
4-Me-DOL	methylene chloride	3.2	12.7	−21	16

dynamic parameters. Butyl substitution at C_2 in TOC causes a 1.2 kcal mol^{-1} decrease in $-\Delta H_{ss}$, comparable to the increments cited above.

Mechanism. The ^{1}H NMR spectrum of poly(2-Bu-TOC)[1] is consistent with a regular head-to-tail structure. The polymers prepared by condensation of diethylene glycol with pentanal and by polymerization of 2-Bu-TOC exhibit identical spectra. This arises from preferential ring opening at the more reactive acetal C–O bonds, the higher basicity of the 6-oxygen notwithstanding. The ambiguity of the propagating species in cyclic acetal polymerization has been discussed above. The nearly identical polymerization rates we have observed for TOC and 2-Bu-TOC in toluene are consistent only with an alkoxycarbenium ion propagating species in the case of 2-Bu-TOC. If the propagation step involved attack of 2-Bu-TOC monomer on a cyclic oxonium ion chain end, eq 7, steric hindrance involving butyl–butyl interactions should slow propagation drastically (eq 6). 2-Bu-TOC is able to avoid this by formation of the open-chain alkoxycarbenium ion (I in eq 1) and subsequent propagation by nucleophilic attack of I by 2-Bu-TOC. Formation of a secondary alkoxycarbenium ion in this case is far more favorable than formation of its primary counterpart in the case of TOC owing to the much greater stability of the secondary carbenium ion.



(6)

Our data do not permit identification of the propagating species in the case of TOC. Two possibilities exist. The first explanation for the nearly identical polymerization rates for TOC and 2-Bu-TOC is that they have different propagation mechanisms. We suggest that the extra steric hindrance in attack of the secondary oxocarbenium ion, I, would be insufficient to compensate for the lower rate of formation of the less stable primary ion from TOC chain ends. Alternatively, the two monomers may polymerize both via essentially the same open-chain alkoxycarbenium ions, I, but the propagation of I and cyclic oxonium ions, II, in their equilibrium is different in the two cases. Thus, the concentration of the propagating species, I, is lower but its reactivity is higher for TOC, and vice versa for 2-Bu-TOC. We have attempted to determine [I] in polymerization mixtures of both monomers by NMR but were unable to find resonances definitely attributable to the alkoxycarbenium ion.

Conclusion

The polymerization of TOC is more facile than earlier reported.[9] Not only is there no induction period, the MW of poly(TOC) is not independent of conversion. In fact very high MW ($\bar{M}_n = 81000$) of good mechanical properties can be obtained under certain conditions. A rather unexpected result of this work is the polymerizability of 2-Bu-TOC. The MW of poly(2-Bu-TOC) reached 7700, and the rates of polymerization of 2-Bu-TOC are slightly greater than that of TOC.

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