Cationic Polymerizations of Dioxepane and Its 2-Alkyl Derivatives

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ABSTRACT: Equilibrium polymerizations of unsubstituted and 2-methyl- and 2-butyl-1,3-dioxepanes (DOP, 2-Me-DOP, and 2-Bu-DOP) in 1,2-dichloroethane have been investigated. The rate constants for propagation have been determined from −20 °C to 10 °C, with activation energies lying between 18 and 21 kcal mol^{-1}. ^{1}H and ^{13}C NMR spectra of the polymers are consistent with a regular microstructure for exclusive ring opening at the acetal C–O bond during polymerization. The MW is strongly dependent on conversion and M_w/M_n ranges from 1.4 to 1.54. Thermodynamic parameters have been obtained; the T_c values at 1 M monomer are 233, 222, and 305 K for poly(2-Me-DOP), poly(2-Bu-DOP), and poly(DOP), respectively. The similarities in the kinetics and thermodynamics of polymerizations of the three monomers suggest a commonality of linear alkoxycarbenium ions for the propagating species.

Introduction

The mechanism of the cationic polymerization of oxygen heterocyclic compounds has been much discussed. Cyclic oxonium ion is often thought to be the propagating species in the polymerization of tetrahydrofuran.[1] However, in the polymerization of cyclic acetals this ion is in equilibrium with an alkoxycarbenium ion stabilized by the α-oxygen atom. Chain propagation involving the oxonium ion is an S_N2 process, and therefore steric hindrance due to a substituent on the acetal carbon may be expected to retard the polymerization of 1,3-dioxacycloalkanes by this pathway. In the case of five-membered ring monomers, 1,3-dioxolane (DOL)[2] is reported to be polymerizable to linear high polymers but 2-Me-DOL[3] and 4-Me-DOL[4] formed only oligomers of DP 10 and 20, respectively. This difference was thought to be consistent with a steric effect of the alkyl substituent on the propagating oxonium ion.[1] It is, therefore, exciting to find that 2-butyl-1,3,6-trioxocane (2-Bu-TOC) and unsubstituted TOC polymerize at comparable rates.[5] The absence of a steric effect by the 2-butyl substituent suggests the possibility of the alkoxycarbenium ion being a propagating species.

It seems reasonable to hypothesize that alkoxycarbonium ion may be the dominant propagating species in the ring-opening polymerizations of other cyclic acetals such as the seven-membered 1,3-dioxepanes (DOP). Even though the polymerizations of DOP[6] and 2-Me-DOP[7] have been previously reported, they were performed by using different initiators and solvents. In this study the kinetics and thermodynamics of polymerizations of DOP, 2-Me-DOP, and 2-Bu-DOP were compared under identical experimental conditions.

Experimental Section

Materials. Valeraldehyde, paraformadelhyde, paraldehyde, 1,4-butanediol, Dowex 50-X8-100 ion exchange resin, boron trifluoride etherate, and tetralin were all obtained from Aldrich. Benzene, toluene, methanol, and 1,2-dichloroethane were Fischer Reagent materials. Tetralin and 1,2-dichloroethane were purified by distillation over calcium hydride. Boron trifluoride etherate was distilled immediately before use. Dowex resin was treated with 10% hydrochloric acid overnight, washed with water and then with methanol, and finally air dried.

Monomers. DOP was prepared by the reaction of 1,4-butanediol with paraformaldehyde at 150–180 °C in the presence of sulfuric acid. The reaction mixture was washed with aqueous KOH and dried over $MgSO_4$. The product was reacted with $LiAlH_4$ at 150–160 °C. Distillation gave 1,3-DOP analyzed 99.89% pure by gas chromatography. 2-Bu-DOP was prepared by the reaction of 1,4-butanediol and paraldehyde in the presence of Dowex 50-X8 ion exchange resin according to Astles method.[9] It was refluxed with $LiAlH_4$ and then distilled; bp 45–46 °C (0.5 Torr). 2-Me-DOP was similarly prepared from 1,4-butanediol and paraldehyde, purified by reflux with CaH_2 and distillation to give a colorless liquid, bp 63–64 °C (90 Torr). Anal. Calcd for $C_6H_{12}O_2$: C, 68.35; H, 11.40. Found: C, 68.14; H, 11.45. ^{1}H NMR spectra of both 2-Me-DOP and 2-Bu-DOP were in full accord with their structures. Both monomers were shown by GC to have >99.5% purity.

Polymerizations. Schlenk tube was flame-dried under vacuum and filled with N_2. A magnetic stir bar was added and the tube fitted with a rubber septum. The monomer solution in either methylene chloride or 1,2-dichloroethane was introduced by syringe and allowed to thermally equilibrate at the reaction temperature, and then the catalyst solution was injected. During the course of a polymerization samples were removed with a syringe and quenched with a precisely weighed excess triethylamine. A known amount of tetralin, according to conversion, was added as GC standard. After dilution with 1,2-dichloroethane, the mixture was GC analyzed for unreacted monomer. The monomer concentration was calculated by using calibration curves constructed from known mixtures of each monomer and tetralin in 1,2-dichloroethane.

The possibility of thermal decomposition of the dioxepane polymers to monomer in the GC injection port was examined. A sample of monomer-free polymer was dissolved in 1,2-dichloroethane to which tetralin and triethylamine were added. This mixture was injected into the gas chromatograph with conditions identical with those used for determination of unreacted monomer. Only the elution peaks of the solvent, tetralin, and triethylamine were observed, and no monomer was detected.

Polydioxepane was isolated by pouring the polymerization mixture into cold methanol containing triethylamine and allowing it to stand at room temperature for several hours. The filtered polymer was dissolved in dichloroethane, reprecipitated with aqueous methanol, and dried to constant weight.

Methods. Gas chromatography was carried out on a Hewlett-Packard 5790A chromatograph with an OV-101 silicone-packed column. Infrared spectra were recorded with a Perkin-Elmer Model 1420 spectrometer, calibrated by the 1601 cm^{-1} band of polystyrene. ^{1}H NMR spectra were obtained with a Varian XL-300 instrument. Deuteriochloroform was used as the solvent and tetramethylsilane as standard. GPC was performed on *N*-methylpyrrolidone solutions of the polymers with a Waters Associates Model 6000A instrument with 10^3 and 10^5 Å columns. Universal calibration curve constructed from monodisperse polystyrene were used to calculate $\bar{M}_n$, $\bar{M}_w$, and polydispersity $\bar{M}_w/\bar{M}_n$.

TGA measurements were made with a Perkin-Elmer TGS-2 instrument on 9–11-mg samples under N_2 and a heating rate of 2° min^{-1}. For acid catalysis of decomposition of polydioxepanes, 2% of toluenesulfonic acid in methylene chloride was added to the polymer and then vacuum dried before TGA measurement.

Results

Time–conversion curves for polymerizations of 2-Bu-DOP, 2-Me-DOP, and DOP are shown in Figures 1, 2, and 3, respectively. As temperature increases, the polymerization rate also increases but equilibrium conversion decreases. That these are equilibrium polymerizations is demonstrated by the results shown in Figure 4. A po-

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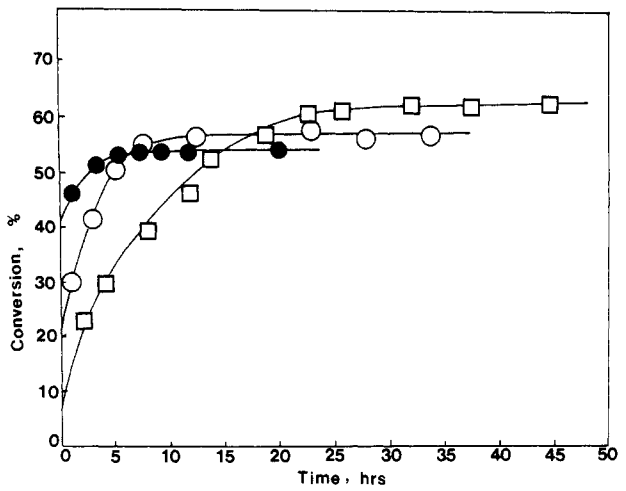


Figure 1. Time–conversion curves for polymerizations of 2-Bu-DOP: $[M]_0$ = 4.8 M; $[BF_3{\cdot}OEt_2]$ = 41 mM; solvent is dichloroethane. Temperatures: (●) 10 °C; (○) 0 °C; (□) −10 °C.

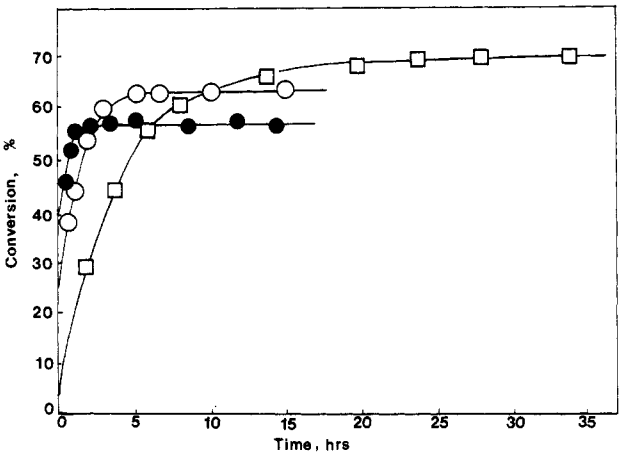


Figure 2. Time–conversion curves for polymerizations of 2-Me-DOP. Temperatures: (●) 0 °C; (○) −10 °C; (□) −20 °C. Other conditions are the same as in Figure 1.

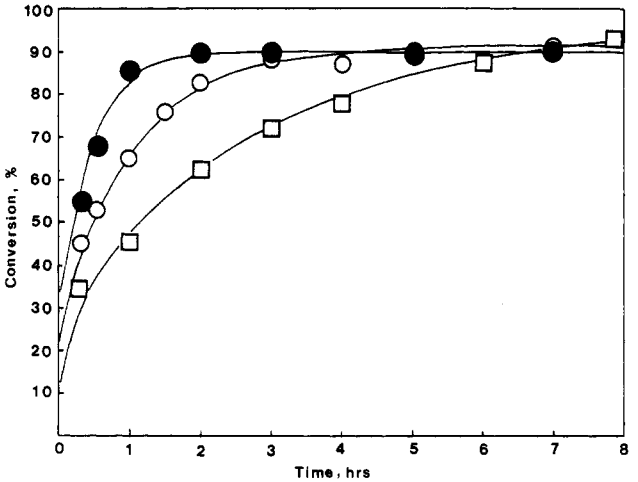


Figure 3. Time–conversion curves of polymerization of DOP. Conditions and symbols are the same as in Figure 1.

lymerization was first taken to equilibrium at 10 °C. Subsequent equilibration at progressively lower temperatures led to increasing degrees of conversion.

The kinetics of approach to equilibrium of a reversible polymerization is given by

$$\ln\left(\frac{[M]_t - [M]_e}{[M]_0 - [M]_e}\right) = k_p[C]t \qquad (1)$$

Table I
Rate Constants of Polymerization for dioxepanes[a]

temp, °C	10^3k_p, $(M\ s)^{-1}$ 2-Bu-DOP	2-Me-DOP	DOP
−20	0.23 ± 0.03	0.77 ± 0.04	
−10	0.71 ± 0.04	2.0 ± 0.4	3.8 ± 0.5
0	3.0 ± 0.04	0.64 ± 0.04	11.0 ± 2.0
10	67 ± 0.4		47.0 ± 5.0
ΔE, kcal mol^{-1}	18.7 ± 1.5	18.2 ± 1.2	20.6 ± 1.5

[a] $[M]_0$ = 4.8 M; solvent, dichloroethane; catalyst $[BF_3OEt_2]$ = 41 mM.

Table II
Molecular Weight of Poly(2-Bu-DOP)

temp, °C	time, h	convn, %	$\bar{M}_n$	$\bar{M}_w$	PD[a]
10	14	53.0	6000	9200	1.54
0	35	56.2	6200	9400	1.52
−10	61	60.9	7800	11000	1.41
−20	180	65.7	9600	12700	1.32

[a] Based on GPC in *N*-methylpyrrolidone and a universal calibration curve based upon monodisperse polystyrene samples of known molecular weight.

Table III
Equilibrium Polymerization of 2-Bu-DOP[a]

temp, °C	convn, %	$[M]_e$, M	$\bar{P}_n$	K_e, M^{-1}	$\Delta G_{ss}°$, kcal mol^{-1}
−20	65.7	1.65	61	0.60	0.26
−10	60.9	1.88	50	0.52	0.34
0	56.2	2.10	38	0.46	0.42
10	53.0	2.26	37	0.43	0.48

[a] $[M]_0$ = 4.8 M; $[BF_3{\cdot}OEt_2]$ = 41 mM; solvent, 1,2-dichloroethane.

Table IV
Equilibrium Polymerization of 2-Me-DOP[a]

temp, °C	convn, %	$[M]_e$, M	K_e, M^{-1}	$\Delta G_{ss}°$, kcal mol^{-1}
−20	69.0	1.54	0.65	0.22
−10	63.5	1.82	0.55	0.31
0	57.5	2.04	0.49	0.38

[a] $[M]_0$ = 4.98 M; $[BF_3{\cdot}OEt_2]$ = 41.2 mM; solvent, 1,2-dichloroethane.

where $[M]_0$, $[M]_t$, and $[M]_e$ are the monomer concentrations at times zero and t and at equilibrium, respectively. Here, k_p is the rate constant using catalyst concentration [C]. The polymerization data of Figures 1–3 were plotted according to eq 1 to give Figures 5–7 for short polymerization time, i.e., low conversion. Deviations from linearity at high conversion are due to approach to equilibrium. From the slopes one can calculate the values of k_p summarized in Table I. They are in the order of DOP > 2-Me-DOP > 4-Me-DOP. Arrhenius plots of k_p (Figure 8) gave experimentally equivalent activation energies: 18.7 ± 1.5 kcal mol^{-1} for 2-Bu-DOP, 18.2 ± 1.2 kcal mol^{-1} for 2-Me-DOP, and 20.6 ± 1.5 kcal mol^{-1} for DOP.

The molecular weights of poly(2-Bu-DOP) have been determined with GPC. Figure 9 shows the GPC curves; the values of $\bar{M}_n$, $\bar{M}_w$, and PD are summarized in Table II.

From the values of $[M]_e$ and the number-average degree of polymerization, $\bar{P}_n$, the equilibrium constants can be calculated.[10,11]

$$K_e = \frac{1}{[M]_e}\frac{\bar{P}_n - 1}{\bar{P}_n} \qquad (2)$$

The resulting values of K_e and $\Delta G_{ss}°$ are given in Tables III–V. Figure 10 shows that $\bar{P}_n$ is greater for poly(2-

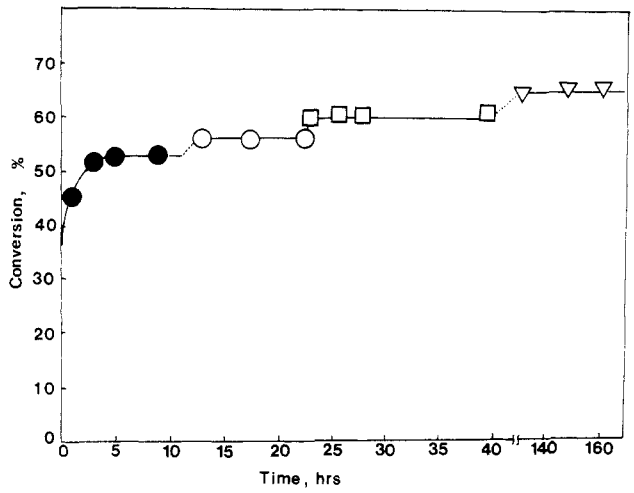


Figure 4. Variation of equilibrium conversion with temperature for 2-Bu-DOP polymerizations [(●) 10 °C; (○) 0 °C; (□) −10 °C; (▽) −20 °C] obtained by equilibrating the same sample at four decreasing temperatures.

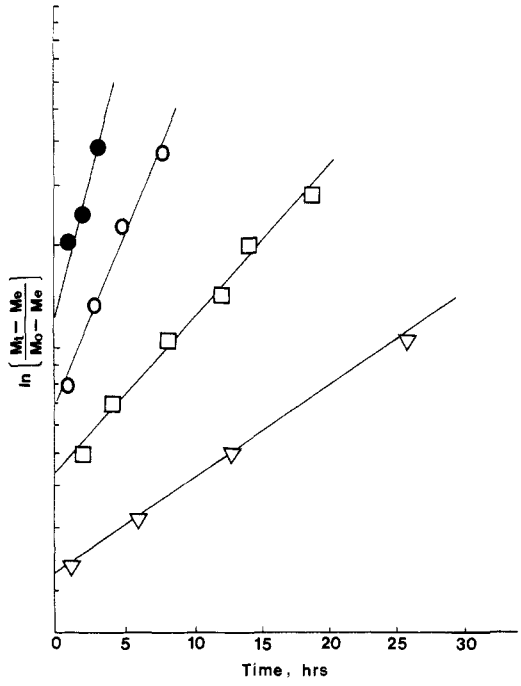


Figure 5. First-order kinetic plots for 2-Bu-DOP polymerization data of Figure 1 plus (▽) at −20 °C.

Table V
Equilibrium Polymerization of DOP[a]

temp, °C	convn, %	$[M]_e$, M	K_e, M^{-1}	$\Delta G_{ss}°$, kcal mol^{-1}
−10	93	0.30	3.33	−0.63
0	92	0.36	2.78	−0.54
10	90	0.47	2.13	−0.43

[a] Same conditions as in Table IV.

Me-DOP) than poly(2-Bu-DOP) both obtained at −10 °C, the $\bar{M}_n$ of other polymer samples are being determined. It is reasonable to assume that $\bar{P}_n \gg 1$ for poly(2-Me-DOP) and poly(DOP) and values of K_e may be simply approximated from $[M]_e^{-1}$ without significant errors. The results can be found in Tables IV and V.

The thermodynamic parameters were obtained from plots of $\Delta G_{ss}°/RT$ versus T^{-1} as illustrated by Figure 11 for DOP polymerizations. The values of $\Delta H_{ss}°$, $\Delta S_{ss}°$, and T_c are summarized in Table VI; the same value of T_c for

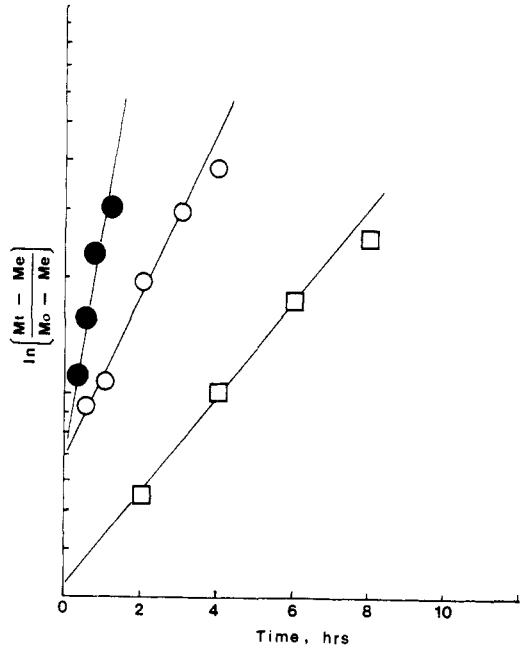


Figure 6. First-order kinetic plots for 2-Me-DOP polymerization data of Figure 2.

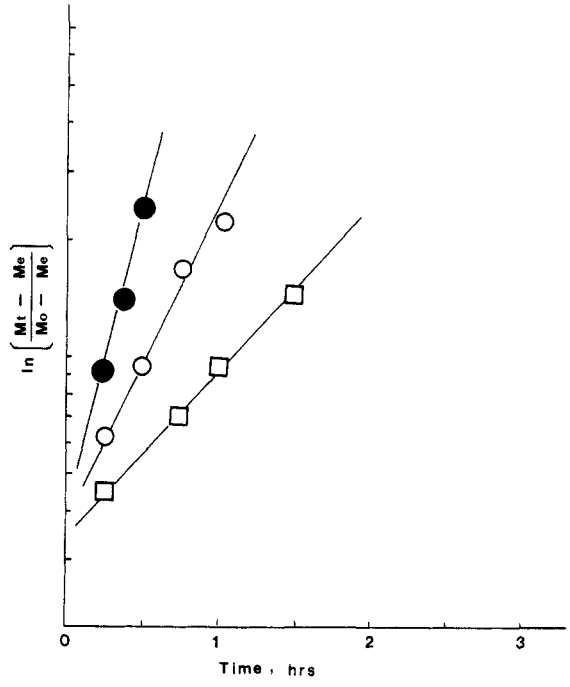


Figure 7. First-order kinetic plots for DOP polymerization data of Figure 3.

Table VI
Thermodynamic Parameters of Polymerization[1] of DOP's

monomer	$-\Delta H_{ss}°$, kcal mol^{-1}	$-\Delta S_{ss}°$, eu	T_c, K	ref
2-Bu-DOP	1.74 ± 0.29	7.9 ± 1.6	222 ± 6	this work
2-Me-DOP	2.10 ± 0.31	8.9 ± 1.3	236 ± 5	7
	2.17 ± 0.29	9.4 ± 1.5	233 ± 5	this work
4-Me-DOP	2.17 ± 0.31	9.3 ± 1.7	240 ± 6	7
DOP	3.32 ± 0.31	10.3 ± 1.5	305 ± 6	this work

[a] Conditions are the same as in Tables II–V.

each system was obtained either from the intercept of plot of $\Delta G_{ss}°/RT$ versus T^{-1} or from the values of ΔH_{ss} and $\Delta S_{ss}°$.

The thermal stabilities of poly(2-Me-DOP) and poly(2-Bu-DOP) have been studied. On the basis of the TGA

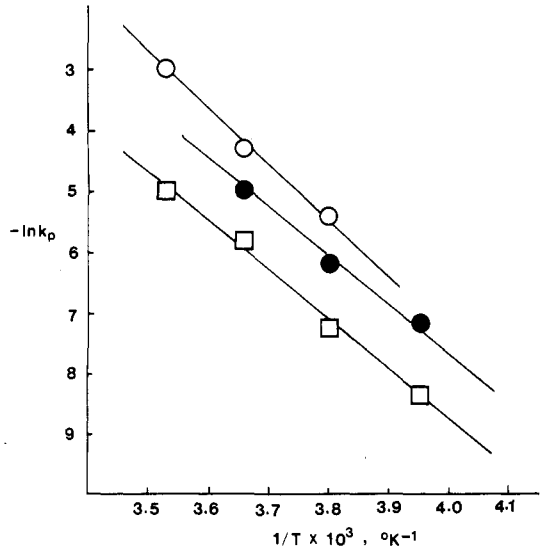


Figure 8. Arrhenius plots of ln k_p versus T^{-1} for polymerizations of DOP (○), 2-Me-DOP (●), and 2-Bu-DOP (□).

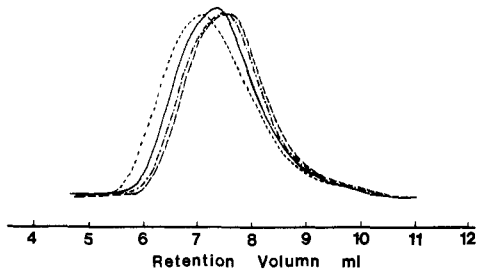


Figure 9. GPC curves for poly(2-Bu-DOP) at equilibrium: (--) 10 °C; (---) 0 °C; (—) - 10 °C; (---) -20 °C.

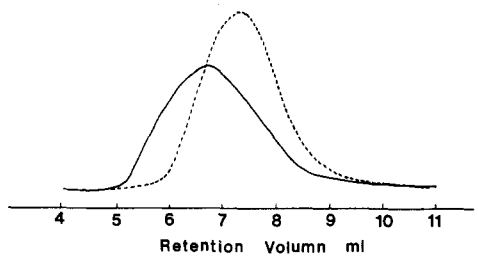


Figure 10. GPC curves for poly(2-Bu-DOP) (---) and poly(2-Me-DOP) obtained (—) at 10 °C polymerizations.

curves (Figure 12), they do not decompose below 250 °C. Two-stage pyrolysis ensued above that temperature.

Acids have a strong effect on the decomposition of polyacetals. Acid-catalyzed depolymerizations of poly(2-butyl-1,3,6-trioxocane)[12] and poly(4-methyl-1,3-dioxolane)[13] have been described previously. The data in Figure 13 demonstrate similar catalysis; the maximum decomposition temperature is lowered by more than 190 °C in the presence of 2% of toluene sulfonic acid. Acid-catalyzed depolymerization is a single-stage process in contrast to thermolysis.

Discussion of Results

The thermodynamic parameters for the polymerization of 2-Bu-DOP, 2-Me-DOP, and DOP have been obtained in this work. The results of the 2-Me-DOP in the same dichloroethane solvent[7] are in fair agreement with literature values.[6,7] The effect of substituent is to decrease the magnitude of the thermodynamic parameter. The change in the thermodynamic properties due to alkyl substituents in the equilibrium polymerization of ϵ-caprolactams has been explained[14] by the existence of rotational isomers. In this analysis the free energy of the macromolecule is given by the sum of contributions from N_i conformational isomers with i number of gauche interactions having a potential energy difference ΔE_i between the trans and gauche

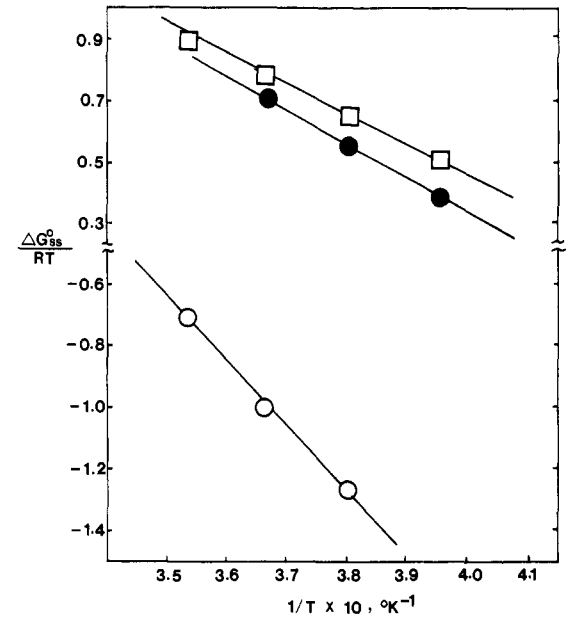


Figure 11. Variation of $\Delta G_{ss}/RT$ versus T^{-1} for polymerizations of DOP (○), 2-Me-DOP (●), and 2-Bu-DOP (□).

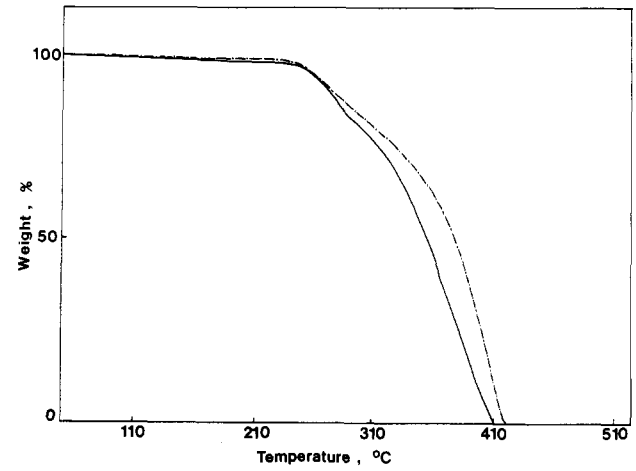


Figure 12. TGA curves for poly(2-Bu-DOP) (---) and poly(2-Me-DOP) (—).

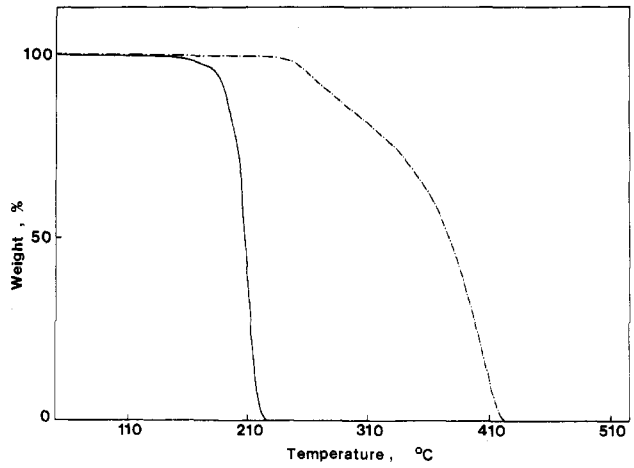


Figure 13. Effect of acid catalysis on the decomposition of poly(2-Bu-DOP): (---) no acid; (—) with 2% of toluenesulfonic acid.

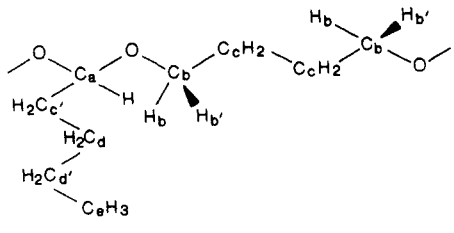
states. The free energy for the monomer has contribution from N_j number of conformational isomers having ring strain energy Δe_j which is the sum of the energies due to gauche interactions, bond opposition strain, and 1,3-nonbonded interaction. This analysis has been applied[8] to calculate the thermodynamic parameters of dioxolanes having 4-alkyl, 4,4-dialkyl, and 4,5-dialkyl substituents. According to this treatment, the number of rotational isomers and the gauche interactions involved are the same for poly(2-Me-DOL) and poly(4-Me-DOL) and, consequently, their thermodynamic parameters of polymerization should also be the same. Furthermore, if the ring strain of DOL is not altered by methyl substitution for one of the two hydrogen atoms in the 2-position of DOL, the thermodynamic parameters of 2-Me-DOL should be close to those of unsubstituted DOL. These predictions are inconsistent with the findings of Firat and Plesch[3] that 2-Me-DOL is even less polymerizable than 4-Me-DOL. The present results showed that 2-Me-DOP and 4-Me-DOP[7b] have the same thermodynamic parameters, in agreement with the expectation of the rotational isomer theory. Okada et al.[8] had suggested that the apparent lower polymerizability of 2-Me-DOL[3] may be due to depolymerization during workup.[8] It is worthy of note that the 4-Me-DOL has been polymerized to MW > 10000 in this laboratory,[13] contrary to the previous report[4] of low polymerizability.

2-Bu-DOP has a less negative $\Delta H_{ss}°$ than 2-Me-DOP by 0.4 kcal mol^{-1} which is comparable to the difference in $\Delta H_{ss}°$ of 0.3 kcal mol^{-1} between 4-*i*-Pr-DOL and 4-Me-DOL.[8]

The $-\Delta S_{ss}°$ of polymerization for DOP's decreases in the same order as $-\Delta H_{ss}°$ values, i.e., DOP > 2-Me-DOP = 4-Me-DOP > 2-Bu-DOP. This is different from the order found for DOL's[7b] which have $-\Delta S_{ss}°$ which decrease in the order of 4-*i*-Pr-DOL > 4-Et-DOL > 4-Me-DOL > DOL. However, the effect of substitution on the thermodynamic parameters of 1,3,6-trioxocane polymerizations[5] share the same trend as DOP's. 2-Bu-TOC has $\Delta H_{ss}°$ = −1.9 kcal mol^{-1} and $\Delta S_{ss}°$ = −3.9 eu as compared to $\Delta H_{ss}°$ = −3.1 kcal mol^{-1} and $\Delta S_{ss}°$ = −5.1 eu for TOC itself.

The results in Tables II and III reveal a steady increase of MW with conversion in the polymerizations of 2-Bu-DOP. Furthermore, these MW increases can be achieved by stepwise lowering of the equilibrium polymerization temperature as shown in Figure 3. At −20 °C, the value of $\bar{P}_n$ calculated from $\{[M]_0 - [M]_e\}[C]_0^{-1}$ is 77 as compared to the observed value of $\bar{P}_n$ = 61. The discrepancy increases with the increase of polymerization of temperature. The MW of polydioxepanes are controlled by chain-transfer processes. Of course, in monomer–polymer equilibria the polymer should have the most probable distribution, in contrast to ideal monodisperse products obtainable by irreversible living ionic polymerizations. The actual PD of poly(2-Bu-DOP) is between 1.4 and 1.54. The narrower than expected distribution may be the result of loss of oligomers in the polymer work up.

The ^{1}H and ^{13}C NMR spectra of 2-Bu-DOP are in accord with the regularly alternating sequence of tetrahydrofuran and valeraldehyde units shown.



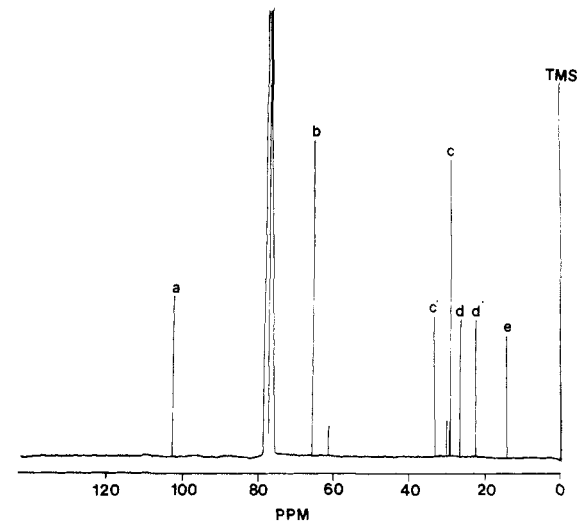


Figure 14. ^{13}C NMR spectrum of poly(2-Bu-DOP) (P_n = 55) (5% in $CDCl_3$; 3000 transients).

Table VII
Nuclear Magnetic Resonance Data of Poly(2-DOP)

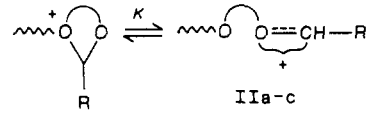
	chem shifts,[a] ppm		
	obsd	calcd[b]	obsd
C_a	102.8	122.7	H_a 4.48 (t)
C_b	65.6	67.4	H_b 3.60 (m)
C_c	29.3	27.3	H_b, 3.40 (m)
$C_{c'}$	34.0	35.4	H_c and $H_{c'}$, 1.61 (m)
C_d	27.0	22.9	H_d and $H_{d'}$, 1.32 (m)
$C_{d'}$	22.5	22.8	
C_e	14.0	13.7	H_e 0.90 (t)

[a] With respect to TMS. [b] Reference 15.

The ^{13}C NMR spectrum of poly(2-Bu-DOP) is shown in Figure 14. The observed chemical shift values, with peak assignments assisted by off-resonance technique,[14] are given in Table VI along with calculated shifts.[15] The fact that there is only one acetal carbon resonance is consistent with scission only at the acetal O–C bonds. In the case of polymerization of 4-Me-DOP polymerization, random scission of the two acetal bonds occurs which leads to a four diad structure having three nonequivalent acetal carbon resonances.[7b] The ^{1}H NMR data are also summarized in Table VII. H_a is a simple triplet corresponding to a single type of acetal carbon. Resonances belonging to the diastereotopic protons H_b and H_b' were not sufficiently resolved to allow coupling constants to be measured. But the line widths of ca. 25 Hz (Figure 15) could accommodate the expected $J_{bb'}$ of about 15 Hz.

The IR spectrum of neat poly(2-Bu-DOP) is lacking in bands attributed to either C=C or C—O vibrations.

In previous discussions of ring-opening polymerization of cyclic acetals[5] it was pointed out that cyclic oxonium ions, I, are in equilibrium with open-chain α-oxycarbenium ions, II. The well-known stabilization of carbocations by



(3)

Ia-c IIa-c

	R	monomer
a	H	DOP
b	CH_3	2-Me-DOP
c	n-C_4H_9	2-Bu-DOP

alkyl groups attached to the electron deficient center guarantees that $K_a \ll K_b \approx K_c$.

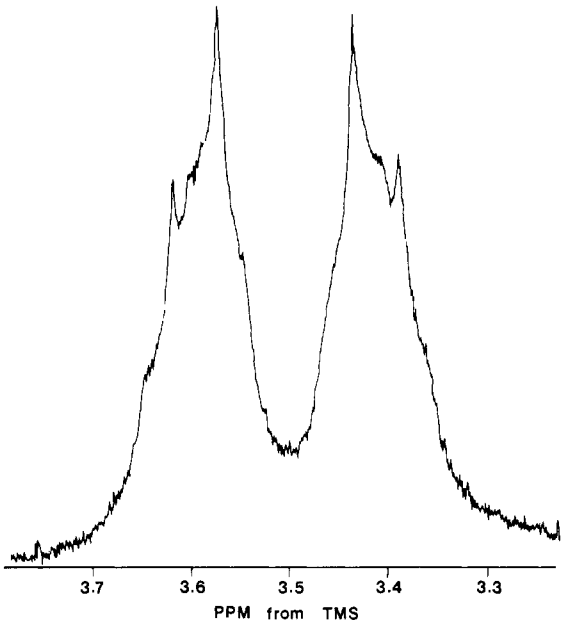


Figure 15. 200-MHz ^{1}H NMR spectrum of H_b and $H_{b'}$ in poly(2-Bu-DOP) in $CDCl_3$.

Propagation can occur either via I or II,[16] giving two possible propagation pathways, eq 4 and 5 where M = monomer. Neglecting possible depropagation and assuming that the I $\rightleftharpoons$ II equilibration is fast relative to propagation, the overall propagation rate is given by eq 6. The rate of S_N2 displacement at the acetal carbon by nucleophilic monomer, eq 4, will be sensitive to steric effects. The change from a primary to a secondary center as well as to a more bulky nucelophile should make k_{1b} and k_{1c} smaller than k_{1a} by 2 orders of magnitude or more. The rate of reaction of unsubstituted α-oxycarbenium ion IIa with nucleophilic monomer will be larger than that of its substituted analogues IIb and IIc owing to its lower stability and less steric crowding in the transition state: $k_{2a} > k_{2b}$ and k_{2c}. The above considerations suggest that for 2-alkyl DOP's k_{2b}[IIb] $\geq k_{2c}$[IIc] $\gg k_{1b}$[Ib] $\geq k_{1c}$[Ic]. In other words, the open-chain α-oxycarbenium ion is the major chain propagating species, as we have previously suggested in the case of 2-butyl-1,3,6-trioxocane polymerization.

$$\mathrm{I} + \mathrm{M} \xrightarrow{k_1} \mathrm{I} \quad (4)$$

$$\mathrm{II} + \mathrm{M} \xrightarrow{k_2} \mathrm{II} \quad (5)$$

$$R_p = -\mathrm{d[M]}/dt = k_1[\mathrm{I}][\mathrm{M}] + k_2[\mathrm{II}][\mathrm{M}] \quad (6)$$

Since k_p's for DOP and 2-Me-DOP are within a factor of 2 at 0 and −10 °C, we can write

$$k_{1a}[\mathrm{Ib}] + k_{2a}[\mathrm{IIa}] \approx k_{2b}[\mathrm{IIb}] \quad (7)$$

To evaluate the terms on the left side we have used the following considerations. Owing to the known high reactivity of carbenium ion intermediates toward nucleophiles, $k_{2a} > k_{1a}$, but for the unsubstituted acetal lower open-chain carbenium ion stability will probably mean that [Ia] > [IIa]. Therefore, we can exclude the possibility of k_{2a}[IIa] $\ll k_{1a}$[Ia], i.e., propagation of DOP polymerization via cyclic oxonium ion exclusively. The approximate equality of eq 7 is then attributable to k_{2a}[IIa] $\geq k_{1a}$[Ia]. Whether the alkoxycarbenium ion propagation predominates or both it and the cyclic oxonium ions are involved cannot be ascertained. In any case, owing to compensating effects on the rates of the two pathways caused by substitution, C_2-substituted cyclic acetals polymerize at nearly the same rates as their unsubstituted analogues.

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Registry No. DOP, 505-65-7; DOP (homopolymer), 25037-55-2; 2-methyl-DOP, 4469-25-4; 2-methyl-DOP (homopolymer), 40907-98-0; 2-butyl-DOP, 2243-66-2; 2-butyl-DOP (homopolymer), 113055-96-2; toluenesulfonic acid, 104-15-4.

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