Polymerization–depolymerization of 1,3-dioxolane

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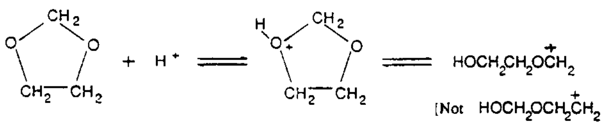
Poly(1,3-dioxolane) can be cleanly depolymerized to the monomer. As such, the 1,3-dioxolane system is a good one to study to learn about microscopic reversibility. Besides describing how to perform the reversible polymerization reaction, this paper also presents data on the pyrolysis-field ionization mass spectrometry (Py-f.i.m.s.) and g.p.c. of the polymer and n.m.r. characterization of the monomer and polymer. The Py-f.i.m.s. data indicate that unhydrolysed polymer fragments in a manner similar to the reverse of the polymerization sequence, i.e. the carbonium ion portion of the oxymethylene end group bites back on oxygen atoms in the backbone. Base-terminated polymer, on the other hand, appears to undergo mid-chain cleavage. A dominant peak in the Py-f.i.m.s. spectrum of either, however, corresponds to the protonated cyclic dimer, a 10-crown-4 ether. A sequestered proton structure is proposed for this protonated species.

(Keywords: polymerization; depolymerization; 1,3-dioxolane)

INTRODUCTION

Reversing polymerization processes to produce monomers is theoretically possible, but it is not easily accomplished. The principal problem resides in the fact that few polymers can be thermally degraded cleanly[1]. Poly(1,3-dioxolane) is an exception to this behaviour as it degrades cleanly to monomer in the presence of acid. The mechanism for polymer formation [equations (1)–(4)] has been well studied[2–10] and is first order in dioxolane[7]. The reaction is an excellent example wherein cation stability can be used to predict the preferred manner of ring opening. The reversibility of the polymerization reaction has also been demonstrated[3–5] and the pK_A (7.45) of protonated 1,3-dioxolane (shown to be present by u.v. spectroscopy) has been reported[6]. Steric hindrance effects have been illustrated with substituted dioxolanes[3]. Cyclic products ($\sim 2\%$) involving two to nine dioxolane units have been observed to form when the carbonium ion bites its own alcoholic tail[2,10,11]. Most of the literature revolves around the use of Lewis acid catalysts in aprotic solvents. The simplest catalyst, however, is H_2SO_4 as described in the 1946 patent of Gresham[12]. Since the polymerization and depolymerization reactions of 1,3-dioxolane are so simple, they can easily be carried out in the laboratory. Each stage requires 3 h to perform.



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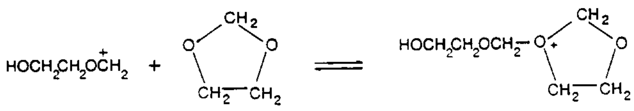

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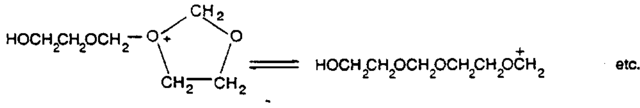

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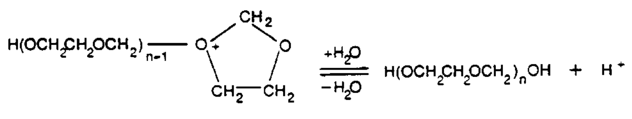

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Poly(1,3-dioxolane) has been characterized by a variety of techniques. These include viscosity[3,11], ^{1}H n.m.r.[13], ^{13}C n.m.r.[13], thermodynamic data (enthalpy, entropy, heat capacity)[4,14], and conformation analyses[15–17]. Because the polymer has three crystalline phases near room temperature, it has been subjected to microscopic[18], X-ray[3,15,18], and d.s.c.[18,19] analyses. I.r. data are available for both liquid and solid materials[15,20,21]. Comparisons with other oxyalkene polymers and polyethylene are available. The thermodynamic properties[14] of poly(1,3-dioxolane), which contains alternating OCH_2 and OCH_2CH_2 units, are intermediate between those of polyoxymethylene $[(OCH_2)_n]$ and those of polyoxyethylene $[(OCH_2CH_2)_n]$. Its dipole moment, however, is more like that of polyoxymethylene than that of polyoxyethylene[22]. Pyrolysis-mass spectrometric, g.p.c. and n.m.r. analyses of poly(1,3-dioxolane) are presented herein.

EXPERIMENTAL

Polymerization–depolymerization reaction

1,3-Dioxolane (100 ml) was placed in a 200 ml round bottom flask. A magnetic stirring bar was inserted, a condenser connected for reflux, and the assembly clamped in an oil bath which sat on the stirrer/heater. The condenser was raised and concentrated H_2SO_4 (0.5 ml) was added to the flask. While the reaction mixture was stirring, the oil bath temperature was raised rapidly to 85–90°C. After this temperature was reached, it was held for 30 min. During this heating period the reaction mixture became very viscous and difficult to stir. After the 30 min heating period, the condenser was removed. [If the polymer was to be isolated (see below), 25 ml of the reaction mixture was quickly transferred with a 25 ml pipette to a 100 ml round bottom flask which was stoppered and set aside.] The condenser was replaced with a distillation head and the condenser reattached to cool the distillate. The oil bath temperature was raised to ~135°C and the distillate (b.p. of 1,3-dioxolane = 74–75°C) was collected in a 100 ml graduated cylinder. After the distillate (95 ml) was collected (70 ml, if 25 ml of the polymer had been removed), the assembly was removed from the oil bath. Some polymer mixture (5 ml) was left to minimize clean-up problems. The flask was rinsed with acetone and cleaned with soap and water. This procedure can be completed in 3 h.

Polymer isolation

The 100 ml round bottom flask set aside from the reaction above was supplied with a magnetic stirring bar, fitted with a condenser for reflux, and clamped in an oil bath. The oil bath temperature was raised rapidly to ~85°C. During this time the contents of the flask melted. The condenser was lifted long enough to add concentrated NH_4OH (1 ml) and then aqueous NaOH (1 ml) to the stirred mixture. The bath temperature was raised to 100°C and held for 30 min. After the reflux period, the flask was removed from the oil bath and the pH of the mixture lowered to 8 with approximately four drops of concentrated H_2SO_4. The clear, colourless, hot mixture could be filtered through Whatman no. 42 paper to remove the salt that formed. Some loss of product occurred as the mixture was very viscous. (An optional approach involves adding 100 ml of acetone to the warm mixture, filtering the dilute mixture, and stripping the acetone with a rotary evaporator. This approach gives a better yield, but takes longer to accomplish.) On cooling, the polymer solidified to a milky wax. This procedure can also be completed in 3 h.

Gel permeation chromatography

Molecular weight data were obtained with a Waters model 440 high pressure liquid chromatograph using Waters' g.p.c. columns. Operating conditions were ambient temperature and tetrahydrofuran was used as the solvent.

Solution n.m.r.

^{1}H and ^{13}C spectra were obtained with a Jeol Fourier transform nuclear magnetic resonance model FX-90. The fully deuterated solvents used were: acetone, benzene and dimethyl sulphoxide (DMSO). The data were taken at ambient temperature and referenced to tetramethylsilane.

Pyrolysis-field ionization mass spectrometry (Py-f.i.m.s.)

Pyrolysis-f.i.m.s. data were obtained with a Finnigan MAT 731 double-focusing mass spectrometer. Typical operating conditions and applications of this technique to other polymeric systems can be found in references 23–27.

Thermal gas evolution analysis

This information is derived from plotting the total ion mass signals from Py-f.i.m.s. as a function of temperature[23–27].

RESULTS AND DISCUSSION

The reversibility of the reactions depicted in equations (1)–(4) is clearly demonstrated by the results of the polymerization–depolymerization experiment. The build-up in viscosity is slow as the polymerization begins. The polymer chains are short at first and even cyclic units containing several dioxolane moieties are likely. As the polymerization continues, both the molecular weight and the viscosity increase. A typical polymer product with a molecular weight of 1500 (20 dioxolane units) still has some short units as the gel permeation chromatogram in *Figure 1* demonstrates.

During the isolation of the polymer, the mixture is treated with base. The hydrolytically unstable hydroxymethylene terminal group is removed [as illustrated by equation (5)] to leave a stable hydroxyethylene group. At a molecular weight of 1500, the product is a milky wax. The ^{1}H n.m.r. spectra of the neat and acetone extracted products are the same. The proton peaks are singlets; so are the carbon peaks, if decoupling is applied. A summary of the n.m.r. data is given in *Table 1*.

$$HOCH_2OCH_2CH_2O\sim\!\sim\!\sim \xrightarrow{OH^-} O{=}CH_2 + HOCH_2CH_2O\sim\!\sim\!\sim \qquad (5)$$

The base-treated polymer is much more stable than the polymer in the acidic polymerization mixture. This is readily seen in the thermogravimetric curves of *Figure 2*. Thus, the acidic reaction mixture polymer decomposes in the low temperature range of 100–200°C (*Figure 2a*), whereas the base-treated polymer decomposes in two higher temperature events of 150–300°C and 330–400°C.

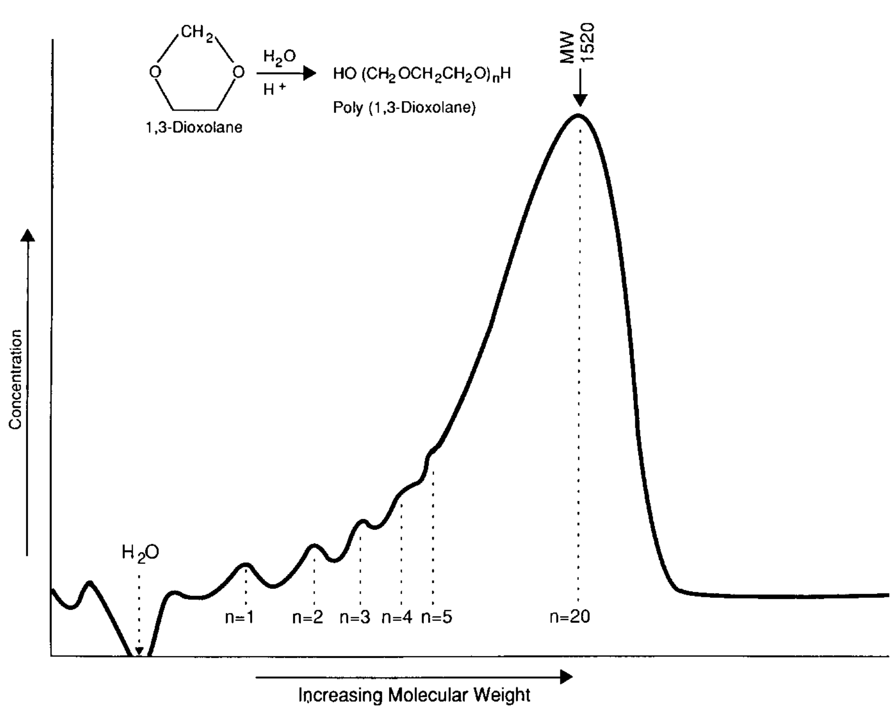


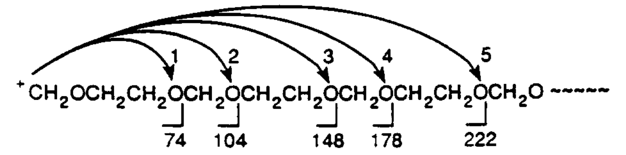
Figure 1 High pressure liquid chromatogram of the reaction mixture at the end of the polymerization of 1,3-dioxolane

Table 1 Summary of n.m.r. results[a]

Sample	OCH_2O	OCH_2CH_2O	Solvent
^1H *n.m.r.*			
1,3-Dioxolane	4.78 (2H)	3.78 (4H)	Acetone-d_6
Poly(1,3-dioxolane)	4.70	3.69	Acetone-d_6
	4.64	3.61	DMSO-d_6
	4.61	3.60	Benzene-d_6
	4.77[b]	3.75[b]	$CDCl_3$[b]
1,3-Dioxolane(spike)	4.70	3.39	Benzene-d_6
^{13}C *n.m.r.*			
1,3-Dioxolane	94.90	64.40	Benzene-d_6
Poly(1,3-dioxolane)	95.70	67.20	Benzene-d_6
	95.42[b]	66.71[b]	$CDCl_3$

[a] Peak positions (in ppm) relative to tetramethylsilane
[b] Reference 13

The Py-f.i.m.s. data of each polymeric material are shown in *Figure 3*. The assignment of ionized polymer fragments to the major peaks is shown in *Table 2*. All the peaks are attributable to some combination of either the dioxolane unit (A) or its two major fragments [oxymethylene (B) and oxyethylene (C)]. Four series, delineated in *Table 2*, appear to be present in the mass spectra. The dominant series (I) is an $[M + 1]^+$ series and is essentially the same for both materials. The formation of this series (except for mass 119) is easily visualized by protonating the cyclic species produced when the cationic methylene group attaches to oxygens 1–5 in the following diagram:



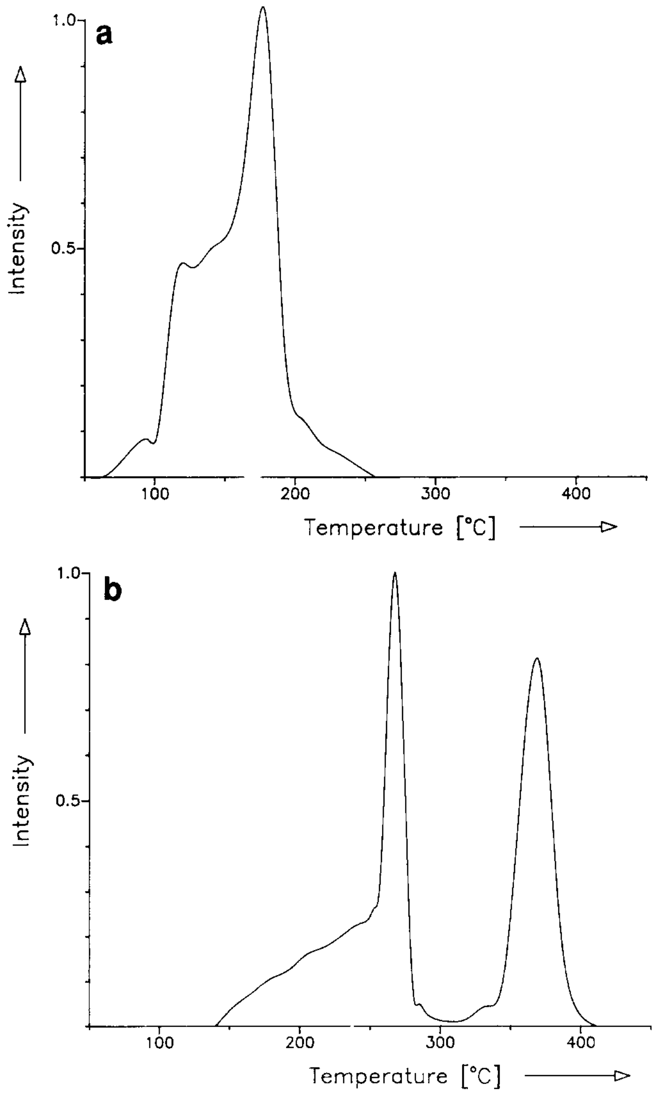


Figure 2 Thermal gas evolution profiles of sample submitted to f.i.m.s.: (a) unhydrolysed reaction material; (b) base-hydrolysed product

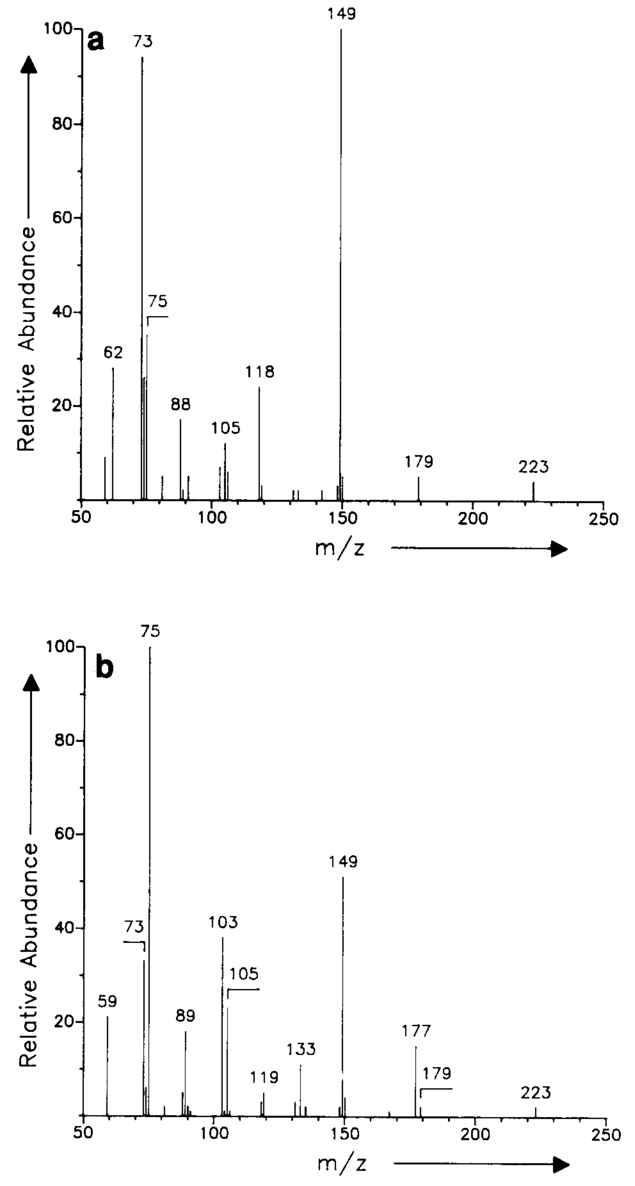
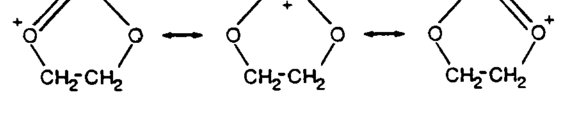


Figure 3 Mass spectrometric data of samples subjected to f.i.m.s.: (a) unhydrolysed reaction material; (b) base-hydrolysed product

Penczek[2] and others[10,11] have discussed this 'back-biting' during the polymerization process. The weak 119 mass is best explained by the following fragmentation:

$$----CH_2O\text{-/-}CH_2CH_2OCH_2OCH_2CH_2O\text{-/-}CH_2OCH_2CH_2OCH_2O-----$$

The second most prominent series is the $[M-1]^+$ series. This series occurs because the CH^+ between two oxygen atoms is very stable. The formation of the CH^+ requires the loss of an electron and a hydrogen atom or a hydride ion, however. The only $[M-1]^+$ species of significance derived from the acidic reaction mixture is the resonance-stabilized dioxolane cation:

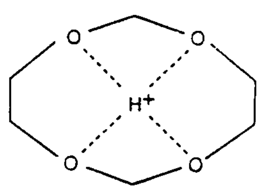


Although in lesser amounts than the above species, there are more $[M-1]^+$ series members from the base-hydrolysed material than from the acidic reaction mixture. The fragments could come from breakdowns such as the following for mass 73:

$$----O\text{-/-}CH_2OCH_2CH_2OCH_2O\text{-/-}CH_2CH_2O----$$

The presence of mass 133 suggests that multiple $CH_2{=}O$ units might be reacting with the cyclic species of series I to generate the members of this series. The presence of multiple $CH_2{=}O$ units is verified by series IV. Free or multiple $CH_2{=}O$ units are expected since the base-catalysed hydrolysis was performed to remove them from the polymer termini.

The absence of the 147 peak is most interesting. Its absence and the strong presence of mass 149 (the protonated 10-crown-4 ether) attest to greater stability for the latter and hence the absence of any unprotonated 10-crown-4 ether. A sequestered proton structure is proposed to account for the enhanced stability.



This structure is based on similar sequestering observed between alkali metal ions and crown ethers. The latter show optimum sequestering when the metal ionic radius and the inner ring of the sequestering crown ether are matched and the oxygens provide proper co-ordination[28]. Thus the 12-crown-4 ether provides the proper nest for the unsolvated Li^+ ion[29]. The 10-crown-4 ether would be expected to provide the smaller nest needed for the unsolvated proton. It is not clear that four oxygens are optimal, but the correspondence to the tetrahydrated form of the proton ($H_9O_4^+$) for which there is mass spectral evidence[30] is striking.

The third series is an $[M]^+$ series and is formed by the removal of an electron from the oxygen atom of a fragment. It is practically absent from the hydrolysed material and weak for the acidic reaction mixture. The 74 mass corresponds to dioxolane. The other masses evolve from the CH_2CH_2O unit. The possible source of this unit is the partial hydrolysis of dioxolane to glycol in the acidic media. Ethylene oxide could also be involved.

The predominance of the mass 73–75 peaks in the spectra is related to the cyclic dioxolane monomer unit and is as expected. The more stable, base-hydrolysed material would be expected to fragment more randomly than the $^+CH_2O$-terminated, acidic reaction mixture material, since the chance of 'tailing-biting' is reduced. A more varied cleavage behaviour is evidenced by the additional spectral series (II) for the base-hydrolysed material. The most amazing feature in the mass spectral data, however, is the magnitude, and hence the stability, of the protonated dioxolane dimer.

Table 2 Ionized polymer fragment assignments for Py-f.i.m.s. spectra[a]

	Units/fragment[b]				Spectral intensity[c]	
Series	A	B	C	Mass	Unhydrolysed polymer	Hydrolysed polymer
I	1			75	35	100
[M+1]	1	1		105	12	23
	1		1	119	3	5
	2			149	100	51
	2	1		179	5	2
	3			223	4	2
II	1			73	94	33
[M - 1]	1	1		103	7	38
	1	2		133	2	11
	2			147	(Missing!)	(Missing!)
	2	1		177		15
III			1+H_2O	62	28	
[M]	1			74	26	6
			2	88	17	5
	1	1		104		1
	1		1	118	24	3
	2			148	3	2
	2	1		178		
	3			222		
IV		2		59	9	21
[M - 1]		3		89	2	18

[a] See the dissociation diagram in the text for the 74, 104, 148, 178, 222, ... fragment series. A blank intensity is <1%
[b] Unit A = $CH_2OCH_2CH_2O$ (M = 74); B = CH_2O (M = 30); C = CH_2CH_2O (M = 44)
[c] The length of the line and the number at its end indicate the relative abundance of the mass

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