Thermodynamics of Polymerization of Heterocyclic Compounds Part V. The heat capacity, entropy, enthalpy and free energy of 1,3-dioxolan and poly-1,3-dioxolan

G. A. CLEGG and T. P. MELIA

An adiabatic vacuum calorimeter and a differential scanning calorimeter have been used to measure the heat capacities of 1,3-dioxolan and poly-1,3-dioxolan from 80°K to 390°K. An estimate has been made of heat capacity values below 80°K for both monomer and polymer. Entropy, enthalpy, and free energy values have been derived and are listed at 10 °K intervals for the monomer and 58% crystalline polymer. For 1,3-dioxolan a crystal–crystal and a melting transition have been observed. The transition temperature, heat of transition, melting point, and heat of fusion were found to be 142·4 ± 1°K, 2·677 ± 0·011 kJ mole^{-1}*, 175·93 ± 0·05°K and 6·567 ± 0·026 kJ mole*$^{-1}$*, respectively. For poly-1,3-dioxolan the glass transition temperature, melting point, and heat of fusion were found to be 209°K, 325 ± 1°K and 16·698 ± 0·320 kJ mole*$^{-1}$*. Estimates have been made of the heat capacities of 100% crystalline and completely amorphous poly-1,3-dioxolan. The increase in heat capacity of the amorphous polymer at the glass transition temperature, 11·1 J°K*$^{-1}$ *mole bead*$^{-1}$*, is in agreement with that predicted on the basis of the hole theory of melting. The entropy of polymerization,* ΔS_{lc}*, has been calculated as −66·0 ± 4·6 J°K*$^{-1}$ *mole*$^{-1}$*. This compares with a value of −63 J°K*$^{-1}$ *mole*$^{-1}$ *obtained from equilibrium polymerization data.*

THIS paper is the fifth in a series[1-4] concerned with the thermodynamics of polymerization of oxygen-containing heterocyclic compounds. Heat capacity measurements on 1,3-dioxolan and poly-1,3-dioxolan over the temperature range 80°–390°K are described. The results have been used to estimate the entropy of the monomer and polymer and to derive the Third Law value of ΔS_{lc}. This is compared with previously published Second Law values[5-11].

EXPERIMENTAL

Calorimetry

Two calorimeters were employed. A precision, adiabatic, vacuum calorimeter, which has been described previously[1], and a Perkin-Elmer differential scanning calorimeter (D.S.C.)[12]. The weights of 1,3-dioxolan and poly-1,3-dioxolan used in the adiabaticv acuum calorimeter were 27·8409 g and 18·2183 g, respectively. The weights of polymer used in the D.S.C. varied between 35 and 45 mg. A heating rate of 4 degrees per minute was employed in the D.S.C. measurements.

Materials

1,3-Dioxolan—Prior to sealing in the adiabatic vacuum calorimeter, the laboratory reagent grade 1,3-dioxolan was refluxed over sodium and the fraction boiling at 348°K was collected. The reagent was then stood over lithium aluminium hydride under vacuo, before being distilled into the calorimeter.

Poly-1,3-dioxolan—The polymerization of 1,3-dioxolan was carried out in vacuo under anhydrous conditions. 26 ml of purified monomer and 64 ml of methylene dichloride were distilled into a 150 ml reaction vessel containing a phial of perchloric acid initiator in methylene dichloride solution. The initiator concentration was 10^{-4} molar. The phial was broken and the vessel was cooled to 228°K. The polymerization was allowed to proceed for 1 h. Termination was brought about by introducing dry ammonia into the reaction vessel. The methylene dichloride was removed from the polymer by evaporation on a water bath. The polymer was then heated in a vacuum oven at 320°K for about 16 h and finally allowed to cool to room temperature. The molecular weight of the polymer was determined on a Mecrolab Vapour Pressure Osmometer (Model 301A) and yielded a value of $\bar{M}_n = 2800$. The polymer is thought to be cyclic[5].

RESULTS

1,3-Dioxolan

The observed values of the heat capacity are presented in *Figure 1*. Smoothed values of the heat capacity, together with derived values of the entropy, enthalpy, and free energy are presented in *Table 1*. The heat capacity data below 80°K were obtained using the extrapolation procedure of Kelley, Parks and Huffmann[13]. Cycolopentane[14], for which reliable heat capacity data are available, was chosen as the standard substance for this extrapolation. Over the temperature range 80°K to 160°K the smoothed values of the heat capacity may be represented by the equation:

$$C = (1{\cdot}7033 \times 10^{-1} + 9{\cdot}0450 \times 10^{-3}T - 4{\cdot}2344 \times 10^{-5}T^2 + 1{\cdot}2032 \times 10^{-7}T^3)\ \mathrm{J\,{}^\circ K^{-1}g^{-1}} \quad (1)$$

Since a considerable amount of pre-melting occurs in the monomer at temperatures above 160°K the smoothed values of the heat capacity shown in *Table 1* were corrected for pre-melting by extrapolating the data for the solid from below 160°K to the melting point using equation (1). It is necessary to correct the measured heat capacity, C, to the quantity, C_{SAT}. This correction makes allowance for the fact that the measured heat capacity includes some heat of vaporization. The heat capacity of liquid 1,3-dioxolan (C_m) may be represented by

$$C_m = 1{\cdot}3094 + (9{\cdot}4550 \times 10^{-4}T)\ \ \mathrm{J\,{}^\circ K^{-1}g^{-1}}$$

Examination of *Figure 1* reveals the existence of two transitions in 1,3-dioxolan. The first, of unknown origin, occurs at 142·4°K. The second, which occurs at 175·9°K, is due to the melting of 1,3-dioxolan crystals. The transition heats are 2·677 ± 0·071 and 6·567 ± 0·026 kJ mole^{-1}, respectively.

The melting of 1,3-dioxolan has been studied under equilibrium conditions in order to determine its true melting temperature and to assess its purity. The melting point of the pure sample was determined by the method used by

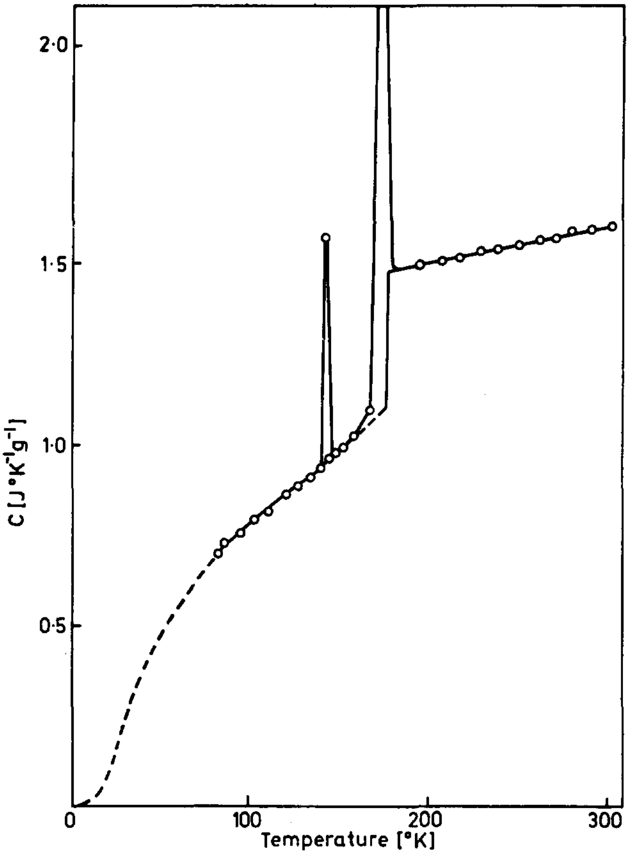

Figure 1—Observed heat capacities for 1,3-dioxolan

Douslin and Huffmann[16]. In this method the temperatures corresponding to given fractions of material in the liquid form are observed. The observed temperatures are then plotted against $1/F$, where F is the fraction melted, and the graph is extrapolated to $(1/F) = 0$ to obtain the melting point of the pure sample. The value obtained is 175·93° ± 0·05°K.

Mair, Glasgow and Rossini[17] have shown that if the impurity present in a sample is soluble in the liquid phase, but insoluble in the solid phase, the thermodynamic relation between the temperature of equilibrium and impurity present in the liquid phase is

$$N_2 = (\Delta H_f/RT_f^2)\Delta T = K\Delta T \tag{3}$$

when N_2 and ΔT are small. N_2 denotes the mole fraction of impurity corresponding to a given fraction melted, T_f is the melting point of the pure substance in °K, ΔH_f is the heat of fusion of the major component in the pure state, $\Delta T = T_f - T$, where T is the given equilibrium temperature and $K = \Delta H_f/RT_f^2$. The total impurity present (N_{TOTAL}) is 0·07 ± 0·05 mole %. This was obtained from the expression

$$N_{TOTAL} = K(\Delta T)F \tag{4}$$

Table 1. Smoothed values of the heat capacity, entropy, enthalpy and Gibbs free energy for 1,3-dioxolan

Temperature (°*K*)	C ($J°K^{-1}g^{-1}$)	$S^0_T - S^0_0$ ($J°K^{-1}g^{-1}$)	$H^0_T - H^0_0$ (Jg^{-1})	$-(G^0_T - G^0_0)$ (Jg^{-1})
Crystal II				
0	0	0	0	0
10	0·014	0·007	0·05	0·03
20	0·108	0·041	0·58	0·23
30	0·245	0·110	2·34	0·97
40	0·373	0·199	5·44	2·50
50	0·477	0·293	9·72	4·96
60	0·560	0·388	14·92	8·36
70	0·625	0·480	20·86	12·71
80	0·685	0·567	27·40	17·94
90	0·729	0·650	34·47	24·03
100	0·772	0·729	41·98	30·93
110	0·813	0·805	49·90	38·60
120	0·854	0·877	58·24	47·01
130	0·895	0·947	66·98	56·13
140	0·937	1·015	76·14	65·94
142·4	0·947	1·031	78·44	68·37
Crystal I				
142·4	0·947	1·285	114·6	68·37
150	0·980	1·335	121·8	78·36
160	1·026	1·400	131·8	92·20
Extrapolated Data for Solid Crystal I				
170	1·075	1·464	142·3	106·6
175·93	1·107	1·501	148·8	115·2
Liquid				
175·93	1·476	2·005	237·4	115·2
180	1·480	2·039	243·5	123·5
190	1·489	2·119	258·3	144·3
200	1·499	2·196	273·2	166·0
210	1·508	2·269	288·2	188·3
220	1·517	2·339	303·4	211·2
230	1·527	2·407	318·6	235·0
240	1·536	2·472	333·9	259·4
250	1·546	2·535	349·3	284·5
260	1·555	2·596	364·8	310·2
270	1·565	2·655	380·4	336·5
273·16	1·568	2·673	385·4	344·8
280	1·574	2·712	396·1	363·3
290	1·584	2·767	411·9	390·5
298·16	1·591	2·811	424·8	413·3
300	1·593	2·821	427·8	418·5

The results obtained in the present investigation together with previously published vapour pressure data for liquid 1,3-dioxolan[18] have been used to calculate the entropy of 1,3-dioxolan gas at one atmosphere pressure and

298·16°K. The equation of Fletcher, Mortimer and Springall[18] was used in this calculation

$$\log P\,(\text{cmHg}) = 7{\cdot}21 - (1\,854/T) \qquad (5)$$

where P is the vapour pressure and T is the temperature in °K. The results of this calculation are presented in *Table* 2.

Table 2. Entropy of 1,3-dioxolan gas at 1 atmosphere pressure and 298·16°K

Source of Data	*Entropy Contribution* ($J°K^{-1}$ mole^{-1})
$(S^0_{80} - S^0_0)$ (Kelley, Parks and Huffmann extrapolation)	42·0 ± 2·1
$\int_{80}^{142\cdot4} (C/T)\mathrm{d}T$	34·4 ± 0·1
ΔS crystal II → I	18·8 ± 0·1
$\int_{142\cdot4}^{175\cdot93} (C/T)\mathrm{d}T$	16·0 ± 0·1
ΔS (fusion)	37·3 ± 0·2
$\int_{175\cdot93}^{298\cdot16} (C/T)\mathrm{d}T$	59·7 ± 0·2
$\Delta S_{298\cdot16}$ (vaporization)	119·3 ± 1·4
$\Delta S = R \ln(9{\cdot}8/76)$	− 17·0 ± 0·1
Entropy of gas at 298·16°K	310·5 ± 4·1

Poly-1,3-dioxolan

The observed values of the heat capacity are presented in *Figures 2* and *3* and *Table 3*. Examination of *Figure 2* reveals the existence of a number of peaks in the heat capacity versus temperature plot for poly-1,3-dioxolan in the melting region. Such behaviour has been observed with other polymers[24, 25] and is known to depend on the thermal history of the sample and the heating rates employed in the experimental measurements. It is thought to be due to reorganisation in the polymer matrix prior to melting[25]. In run 6 only a single sharp peak was observed and these data were used to obtain the smoothed values of the heat capacity shown in *Figure 3* and *Table 4*. The entropy, enthalpy, and free energy functions for the 58 % crystalline polymer were derived from these data. These are presented in *Table 4*. The heat capacity data below 80°K were obtained using the Kelley, Parks and Huffmann[13] extrapolation procedure. Polyoxymethylene[19] (Delrin) was chosen as the standard substance for this extrapolation.

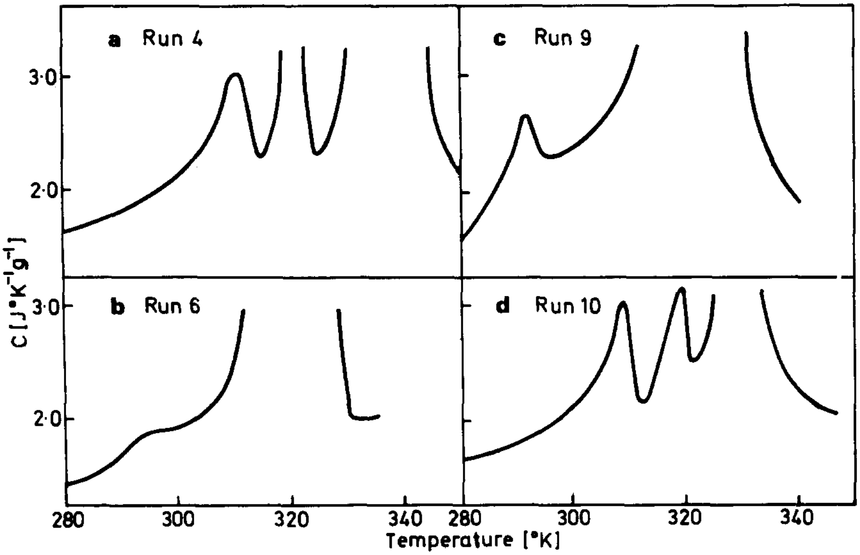

Figure 2—Observed heat capacities for poly-1,3-dioxolan obtained in runs 4, 6, 9 and 10

Table 3. Observed values of the heat capacity for poly-1,3-dioxolan obtained in the adiabatic vacuum calorimeter

Temperature (°*K*)	*C* ($J°K^{-1}g^{-1}$)	*Temperature* (°*K*)	*C* ($J°K^{-1}g^{-1}$)
Run 1		*Run 2*	
82·02	0·4783	199·92	0·9226
90·14	0·5106	207·98	1·112
100·19	0·5550	217·39	1·320
110·46	0·6008	226·97	1·369
121·01	0·6452	236·57	1·397
131·93	0·6779	246·36	1·479
142·37	0·7131	256·00	1·574
153·27	0·7548	265·74	1·676
167·13	0·8046	275·37	1·855
177·92	0·8562	284·41	2·099
188·33	0·8890	293·47	2·177
199·28	0·9380	301·71	3·333
210·22	1·205		

Below the glass transition temperature (T_g) the heat capacity is represented by equation (6)

$$C_c = 0{\cdot}189 + (3{\cdot}700 \times 10^{-3}\, T) \;\; \mathrm{J°K^{-1}g^{-1}} \qquad (6)$$

This equation has been used to obtain an estimate of the heat capacity of 100% crystalline polymer between T_g and the melting temperature (T_m). The basis of this type of extrapolation has been discussed previously[2, 20]. Above T_m the heat capacity is represented by equation (7) and this is used to estimate the heat capacity of the amorphous polymer (C_a) below T_m.

$$C_m = 1{\cdot}396 + (1{\cdot}472 \times 10^{-3}\, T) \;\; \mathrm{J°K^{-1}g^{-1}} \qquad (7)$$

Table 4. Smoothed values of the heat capacity, entropy, enthalpy and free energy of poly-1,3-dioxolan (58% crystalline)

Temperature (°*K*)	*C* ($J°K^{-1}g^{-1}$)	$S^0_T - S^0_0$ ($J°K^{-1}g^{-1}$)	$H^0_T - H^0_0$ (Jg^{-1})	$-(G^0_T - G^0_0)$ (Jg^{-1})
0	0	0	0	0
20	0·071	0·026	0·39	0·14
40	0·237	0·128	3·53	1·59
60	0·367	0·250	9·62	5·37
80	0·467	0·370	17·99	11·58
90	0·513	0·427	22·90	15·57
100	0·556	0·484	28·35	20·12
110	0·597	0·539	34·02	25·24
120	0·635	0·592	40·18	30·89
130	0·672	0·645	46·72	37·08
140	0·709	0·696	53·62	43·78
150	0·744	0·746	60·89	50·99
160	0·781	0·795	68·51	58·69
170	0·818	0·844	76·51	66·89
180	0·857	0·891	84·88	75·56
190	0·898	0·939	93·65	84·71
200	0·950	0·986	102·8	94·40
210	1·110	1·037	113·2	104·6
220	1·200	1·091	124·8	115·2
230	1·285	1·146	137·2	126·4
240	1·361	1·203	150·5	138·2
250	1·395	1·260	164·3	150·7
260	1·420	1·315	178·4	163·5
Extrapolated data for the solid				
270	1·447	1·369	192·7	176·9
273·16	1·456	1·386	197·3	181·3
280	1·475	1·422	207·3	190·9
290	1·504	1·475	222·2	205·4
298·16	1·527	1·517	234·6	217·7
300	1·532	1·526	237·4	220·4
310	1·560	1·577	252·9	235·9
320	1·588	1·627	268·6	251·9
325	1·602	1·651	276·6	259·9
Liquid				
325	1·874	2·053	407·3	259·9
330	1·882	2·082	416·7	270·4
340	1·896	2·138	435·6	291·3
350	1·911	2·193	454·6	313·0
360	1·926	2·247	473·8	335·1
370	1·941	2·300	493·1	357·9
380	1·955	2·352	512·6	381·2
390	1·970	2·403	532·2	405·0

In the temperature range 240° to 260°K the heat capacity of the semi-crystalline polymer may be presented by equation (8)

$$C = 0{\cdot}685 + (2{\cdot}822 \times 10^{-3}\,T)\ \mathrm{J°K^{-1}g^{-1}} \qquad (8)$$

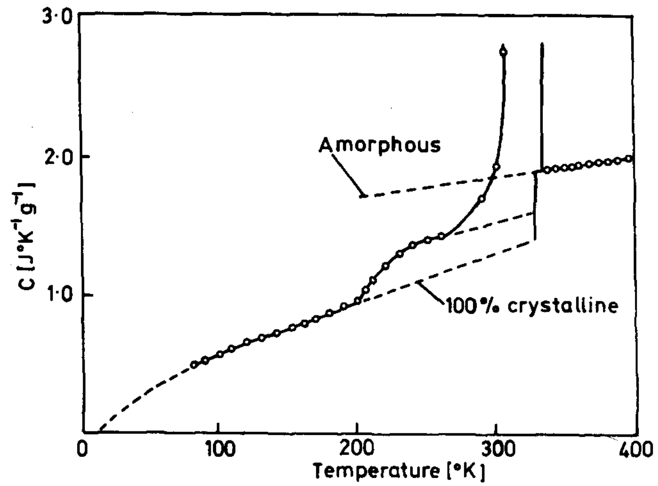

Figure 3—Observed heat capacities of 58% crystalline poly-1,3-dioxolan

The smoothed heat capacity values between 260° and 325°K were obtained by use of equation (8).

The increase in slope of the heat capacity versus temperature curve at about 209°K is probably associated with the onset of the glass transition in the material. The glass transition temperature was taken as the temperature corresponding to the half height of the upward sweep in the heat capacity versus temperature curve. For this purpose data obtained from measurements in the adiabatic vacuum calorimeter were used (runs 1 and 2).

The crystallinity of a semi-crystalline polymer may be estimated using heat capacity data for the crystalline, amorphous and semi-crystalline forms of the polymer[21]. The fraction of crystallinity may then be calculated from

$$X = (C_a' - C')/(C_a' - C_c') \qquad (9)$$

where C', C_a' and C_c' are the heat capacities of semi-crystalline, amorphous and crystalline polymers, respectively, at the glass transition temperature. The data of run 6 were used to estimate the crystallinity of the particular sample under investigation. The fraction of crystallinity obtained is 0·58. This method has been used successfully by Gianotti and Capizzi[21] to estimate the crystallinities of various olefin polymers.

The heat of fusion, ΔH_f^*, of the semi-crystalline polymer was calculated using equation (6) of reference 22. The heat of fusion of the 100% crystalline polymer, ΔH_f, was then estimated from[23]

$$\Delta H_f = \Delta H_f^*/X \qquad (10)$$

The value obtained is 225·4 ± 4·4 J g^{-1}. The fraction of crystallinity, X, for the samples used in runs 4, 9 and 10 were then calculated using the above equation and equation (6) of reference 22. The results of these calculations, together with the melting points obtained in the various runs, are presented in *Table 5*.

Table 5. Values of ΔH_f^* for poly-1,3-dioxolan samples subjected to various thermal treatments in the differential scanning calorimeter

Run no.	ΔH_f^* (Jg^{-1})	*X*	*Melting point* (°*K*)
4	175·5 ± 3·5	78	339
6	130·7 ± 2·6	58	325
9	164·5 ± 3·2	73	330
10	162·3 ± 3·2	72	331

DISCUSSION

Inspection of *Figure 1* reveals the existence of two transitions in 1,3-dioxolan. The first, which occurs at 142·4°K is probably associated with a change in crystal structure in the solid phase. The second, which occurs at 175·9°K is the melting transition.

The increase in heat capacity ($C_a - C_c$) for poly-1,3-dioxolan at the glass transition temperature, 11·1 J $°K^{-1}$ mole $bead^{-1}$, is in agreement with the predictions of Wunderlich[26].

In *Table 6* some thermodynamic data for poly-1,3-dioxolan, other polyethers, and polyethylene are compared. Poly-1,3-dioxolan appears to follow the same general trends as the other polyethers. The only exception is the value of ΔS_f, which is higher than expected.

Table 6. Thermal properties of polyethers and polyethylene

Polymer	ΔH_f (Jg^{-1})	ΔS_f ($J°K^{-1}g^{-1}$)	T_M (°*K*)	T_g (°*K*)	$C_{298\cdot16}$(Crystal) ($J°K^{-1}g^{-1}$)	*Refs.*
Polyoxymethylene	247	0·545	453	195	1·225	19, 27, 28
Poly-1,3-dioxolan	225	0·643	347	209	1·292	this work
Poly(ethylene oxide)	188	0·560	336	205	1·234	29, 30
Polytetrahydrofuran	172	0·548	314	185	1·647	2
Polyethylene	293	0·711	412	200	1·719	24, 31, 32, 33

Knox[34], in his studies of polyethylene, has found a linear relationship between melting point and crystallinity. Such a plot of the data in *Table 5* leads to a value of 347°K for the melting point of 100% crystalline poly-1,3-dioxolan.

The entropy changes associated with the transformation of gaseous (one atmosphere pressure and 298·16°K) and liquid (9·8 mmHg pressure and 298·16°K) 1,3-dioxolan to crystalline and amorphous polymer, respectively, are presented in *Table 7*. The entropy change, $\Delta S^o_{gc'}$ associated with the polymerization of one mole of gaseous 1,3-dioxolan at one atmosphere pressure and 298·16°K to crystalline poly-1,3-dioxolan (−205 ± 5 J $°K^{-1}$ $mole^{-1}$) compares with that obtained for the polymerization of cyclopentane[14] to polyethylene[35] (−178 J $°K^{-1}$ $mole^{-1}$).

Table 7. Entropies of polymerization of poly-1,3-dioxolan at 298·16°K

State of Monomer	*State of Polymer*	*Monomer entropy ($J°K^{-1}mole^{-1}$)*	*Polymer entropy ($J°K^{-1}mole^{-1}$)*	*Entropy of Polymerization ($J°K^{-1}mole^{-1}$)*
Gas (1 atm.)	crystalline	311 ± 4	106 ± 1	− 205 ± 5
	amorphous	311 ± 4	142 ± 2	− 169 ± 6
Liquid	crystalline	208 ± 3	106 ± 1	− 102 ± 4
(9·8 mmHg)	amorphous	208 ± 3	142 ± 2	− 66 ± 5

Published thermodynamic data for the 1,3-dioxolan system are summarized in *Table 8*. Most data refer to solution polymerization. The ΔS_{1c} value of −63 J °K^{-1} mole^{-1} estimated by Kyzub[10] *et al* compares with the present value of −66 ± 6 J °K^{-1} mole^{-1}.

Table 8. Heats and entropies of polymerization of 1,3-dioxolan

$-\Delta H_x$ (*kJ mole*$^{-1}$)	$-\Delta S_x$ ($J°K^{-1}$ *mole*$^{-1}$)	*X*	*Method used*	*Refs*
21·3 ± 0·8	77·8 ± 5·0	s s	equilibrium polymerization	5
21·8 ± 0·4		s s	reaction calorimetry	5
25·9		l c		6
25·9		g g	from combustion data on monomer and semi-empirical methods on the polymer	7
15·1 ± 2·5	58·8 ± 8·4	s s	equilibrium polymerization	8
27·2	93·7	s s	,, ,,	9
23·0	62·8	l c	,, ,,	10
17·6 ± 0·8		s s	,, ,,	11

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Dept. of Chemistry and Applied Chemistry,
University of Salford.

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