Thermodynamic Studies of Solid Polyethers.

I. Poly(Oxacyclobutane), $[-(\text{CH}_2)_3\text{O}-]_n$ and Its Hydrate

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ABSTRACT: Specific heat of semicrystalline and glassy poly(oxacyclobutane) was measured from 90 to 320 °K by using an adiabatic calorimeter and the following thermodynamic values were determined: $T_g = 195$ °K, ΔC_p (at T_g) = 0.895 J/g°K, $T_2 = 155$ °K, $S_0 = 0.189$ J/g°K, $T_m = 305$ °K, $\Delta H_m = 162.5$ J/g°K and $\Delta S_m = 0.533$ J/g°K.

As for the hydrated poly(oxacyclobutane), isotherms and dissociation pressures were measured from -25 to 20°C. The result confirmed that water molecules in the hydrated poly(oxacyclobutane) exist as stoichiometric water in the crystalline part of the solid polymer. The temperature dependence of the dehydration pressures was also represented by the following equation; $\log P = 10.82 - 2.93 \times 10^3 T^{-1}$, and the dissociation heat was evaluated to be 3.25×10^3 J/mol.

KEY WORDS Solid Poly(Oxacyclobutane) / Specific Heat / Glass Transition / Residual Entropy / Melting / Crystalline Hydrate / Isotherm / Dissociation Pressure / Dissociation Heat /

Poly(oxacyclobutane) (abbreviated as POCB) is a member of a polyether series $\{(\text{CH}_2)_m\text{O}\}_n$ with $m = 3$. Every member of this series exhibits interesting properties in structure, in the thermodynamic quantities of melting and in its interaction with water.

Recently, it has been found from X-ray diffraction studies¹ that there are three modifications in the crystalline part of POCB. The modification I, which is formed by crystallization of POCB-melt under direct contact with ice water, is not a modification of this polymer in the literal sense but a crystalline hydrate of the polymer. In this paper, "the modification I" is hence replaced with "hydrate". This hydrate is also formed from the modifications II and III, when the samples in these modifications are immersed in water at ordinary temperature. The crystal structure of the hydrate is monoclinic; $C2/m-C_{2h}^3$, $Z = 4$ with $4\text{H}_2\text{O}$. The modification II is formed when the polymer melt is quenched in liquid nitrogen and subsequently stretched. As the modification II transforms gradually into the modification III at ordinary temperature, the latter seems to be

more stable than the former under this condition. The modification II is also made when either the hydrate is stretched and subsequently dehydrated or the modification III stretched. This modification II is trigonal; $R3c-C_{3v}^6$, $Z = 9$, while the modification III is orthorhombic; $C222_1-D_2^5$, $Z = 2$.

Besides the crystalline state mentioned above, the existence of a glassy state should not be ruled out. In the present investigation, we have found this is to be the case. The relationship

Figure 1. Interrelation of available forms in POCB.

among all these states is shown schematically in Figure 1.

In order to clarify the thermodynamic properties of these states, we have studied the specific heat of the semicrystalline state in which the crystalline part belongs to the modification III. We have also studied the specific heat of the glassy state, the supercooled liquid state and the liquid state. The modification II is not amenable to specific heat measurements because of the difficulty of preparing the sample in this modification in the calorimeter cell.

As to the modification I, *i. e.*, the hydrated POCB, its crystal structure has been determined by the X-ray method of Tadokoro, *et al.*¹ According to their results, the water molecules play the role of a constituent unit in the crystalline part. That is to say, the water molecules penetrate into the crystalline lattice. In order to confirm this fact from other side of the investigation, we measured the isotherms and the dissociation pressures at various temperatures.

EXPERIMENTAL

Preparation of POCB

POCB was synthesized after the method of Rose.² Oxetane (monomer) synthesized from trimethylene glycol (Nakarai Chemicals) was polymerized in methyl chloride (Matheson) by using BF_3 (Hashimoto Kasei) as a catalyst at about -70°C . POCB thus obtained was purified from methanol by precipitation with water and dried in vacuum (10^{-4} mmHg) at ordinary temperature for a week. In one run of the preparation, the number average molecular weight of the product was estimated to be 6000 from the data of viscosity measurement. Molecular weight distribution was found to extend over the range 2500 to 20000 by means of gel permeation chromatography. This sample was used for the specific-heat measurement. In another run, the polymer with $M_n = 2000$ was prepared and was used for the preparation of the polymer hydrate.

Determination of Crystallinity

The crystallinity of the semicrystalline POCB sample subjected to the specific-heat measurement was determined at 0°C by means of the

density method by using a Gay—Lussac type picnometer. In fact, this sample was subjected to the same heat treatment as that in the calorimeter cell. The density of the amorphous part was evaluated by the extrapolation of the density vs. temperature curve to the lower temperature. The density of the liquid polymer was measured by use of a Lipkin—Davidson type picnometer. The density of the crystalline part was calculated from the unit cell dimension determined from X-ray diffraction studies.¹

Specific-Heat Measurement

Prior to the precise specific-heat measurement, a preliminary experiment was carried out by using a Differential Scanning Calorimeter (DSC-1B) (Perkin-Elmer) in order to determine approximate values of temperatures of glass transition, crystallization and of melting.

The calorimeter used in this study was an adiabatic calorimeter which is designed to measure specific heat of solid or liquid samples for temperature ranges 80 to 550°K . The details of the calorimeter have already been reported.³ Because of the limited amount of the polymer sample, a container for small samples was specially designed and constructed, and made of chromium-plated copper. The weight and the volume of the container was found to be 45 g and 21 cm^3 , respectively. Before the measurement, a POCB sample (M_n , 6000) of 13.0935 g was put into the container and then sealed by Wood's alloy under a dried nitrogen atmosphere and evacuated for about 24 hours, finally helium gas being introduced into the container up to 200 mmHg.

Specific heat was measured for the annealed and the quenched samples. Both samples were prepared by different heat treatments in the container of the calorimeter. In the preparation of the annealed sample, the sample container was kept at 310°K for about half an hour, chilled down to 80°K at the rate of $5\text{--}10^\circ\text{K/hr}$, heated again to 260°K and then kept at $260 \pm 5^\circ\text{K}$ for about 60 hours. In the case of preparation of the quenched sample, the sample container was kept at 315°K for an hour, while all the other parts of the calorimeter system were kept at 80°K . The sample container was then quickly chilled by interruption of the

heating current with the simultaneous introduction of helium gas up to 760 mmHg in the calorimeter system in order to facilitate rapid cooling of the whole sample. During this procedure, the temperature of the sample was read with a resistance recorder (Lead & Northrup). The cooling rate was more than $10^{\circ}\text{K}/\text{min}$ and there was no indication of a crystallization effect in the resistance vs. time curve. The measurement was performed over a temperature range 90 to 320°K . The heating rate was 6 to $8^{\circ}\text{K}/\text{hr}$ during the measurement. An intermittent heating technique was undertaken with the temperature intervals ranging from 3 to 6°K . Time for equilibration was found to be about 15 to 20 minutes, but it increased greatly in the vicinity of the transition temperatures.

Preparation of POCB Hydrate

Hydrated POCB was prepared by repeating the quenching procedures of dipping POCB into water at 0°C . The number-average molecular weight of the sample subjected to hydration was *ca.* 2000 which is lower than that for the specific-heat measurement.

Measurement of Dissociation Pressure of the Hydrate

Dissociation pressures were measured by use of an apparatus similar to that reported previously.⁴ Several hundred milligrams of the hydrated sample were used in a series of the isotherm measurements at -5.1 , 0 and 9.7°C . Temperature dependence of the dissociation pressure for the crystalline hydrate was studied in the temperature range from -25 to 20°C . It was found that about 26 hours were necessary for the crystalline hydrate to come into equilibrium with the water vapor above it after the temperature of the hydrate was increased and stopped at the predetermined temperature. Therefore, the pressures attained after the standing for 40 hours at -24 and -21°C and those after 24 hours at temperatures higher than -21°C were taken as the equilibrium pressures for safety purposes.

RESULTS AND DISCUSSIONS

Analysis of Specific-Heat Data

The DSC curve obtained in the preliminary

Figure 2. DSC thermogram of POCB crystallized by slow cooling (cooling rate, $10^{\circ}\text{K}/\text{min}$). The heating rate is $10^{\circ}\text{K}/\text{min}$.

experiment is shown in Figure 2. In these results, the temperatures of the glass transition and of the crystallization are a little higher than those in the results of the specific-heat measurement of the quenched sample as will be described below. This is due to the difference between the heating rates in the two methods of measurement and/or the different thermal histories of the samples.

The specific-heat data are shown in Figure 3. and recorded in Table I and II. The quenched sample showed a glass transition temperature, T_g , at 195°K where the increment of the specific heat amounted to $0.895 \text{ J/g}^{\circ}\text{K}$. This sample started to crystallize at 204°K . In the case of the annealed sample, T_g was found to be 199.5°K where the increment of the specific

Figure 3. Specific heat of POCB: Δ , annealed sample; $\circ$, quenched sample; —, completely crystalline POCB; ---, semi-crystalline POCB with fixed crystallinity; $\cdots$, POCB in supercooled liquid state.

Table I. Specific heat of annealed POCB

$T, ^\circ\text{K}$	$C_p, \text{J/g}^\circ\text{K}$	$T, ^\circ\text{K}$	$C_p, \text{J/g}^\circ\text{K}$
93.43	0.609	215.28	1.316
96.95	0.621	220.71	1.362
107.06	0.652	224.38	1.393
110.94	0.666	228.12	1.424
115.24	0.685	232.39	1.465
119.45	0.702	237.28	1.511
132.02	0.750	244.57	1.562
135.87	0.780	250.70	1.647
139.65	0.806	256.30	1.690
143.67	0.816	261.49	1.725
148.16	0.834	276.98	1.887
156.32	0.868	281.07	2.666
160.40	0.887	285.20	3.189
165.42	0.901	288.88	4.592
171.35	0.927	292.01	6.712
177.15	0.953	302.13	2.170
182.85	0.973	303.00	2.155
188.60	1.024	304.24	2.138
193.35	1.025	307.60	2.124
197.49	1.061	308.96	2.125
201.83	1.178	311.06	2.132
206.04	1.234	313.16	2.138
209.27	1.276	315.25	2.194

Table II. Specific heat of quenched POCB

$T, ^\circ\text{K}$	$C_p, \text{J/g}^\circ\text{K}$	$T, ^\circ\text{K}$	$C_p, \text{J/g}^\circ\text{K}$
94.50	0.616	151.84	0.857
98.22	0.625	154.65	0.865
101.35	0.634	157.79	0.874
104.39	0.646	167.17	0.918
107.37	0.660	170.17	0.930
110.28	0.681	173.14	0.946
113.13	0.687	184.27	0.984
115.95	0.698	187.77	1.046
118.71	0.726	190.84	1.099
121.44	0.729	193.70	1.344
124.93	0.738	196.11	1.887
129.37	0.757	198.26	1.899
131.95	0.768	200.75	1.911
134.50	0.780	203.24	1.917
137.02	0.787	205.44	1.867
149.34	0.830		

heat was $0.211 \text{ J/g}^\circ\text{K}$. From the ratio of these two increments of the specific heat at T_g , the crystallinity of the annealed sample was estimated to be 76.4%, with the assumption of the complete amorphous state for the quenched

sample.

The melting region extended from 200 to 300°K . The melting point in this work was defined as the temperature where the temperature drift no longer showed an abnormal drift such as 0.003°K/min due to the melting process. Accordingly this definition may be looked upon as a calorimetric one which corresponds to Flory's viewpoint.⁵ The melting temperature, T_m , was found to be 305°K .

The differences between the extrapolated values of the specific heats of the melt and the observed specific heat of the supercooled liquid just above T_g were negligible within the experimental errors. Therefore, it was considered that a completely glassy state was realized below T_g for this substance. Consequently the linearly interpolated values between the observed specific heat of the supercooled liquid and the normal liquid were regarded as the specific heat of the supercooled liquid in the temperature region $203\text{--}305^\circ\text{K}$. Since the specific heat of the glassy state was almost consistent with that of the partially crystalline sample below 180°K , it may be assumed that the specific heat of the completely crystalline sample below this temperature is equal to that of the partially crystalline sample. The specific heat of the completely crystalline sample between T_g and T_m may be obtained by a linear extrapolation

Figure 4. Enthalpy of POCB: Δ , annealed sample; $\circ$, quenched sample; —, completely crystalline POCB; - - -, semi crystalline POCB with fixed crystallinity; - · - · -, POCB in supercooled liquid state.

Table III. Enthalpy of annealed POCB
(referred to T_m)

T , °K	H , J/g	T , °K	H , J/g
90	-366.3	202	-275.1
95	-363.3	204	-271.5
100	-360.2	206	-269.1
105	-353.7	208	-264.5
110	-350.3	210	-262.0
120	-346.5	215	-255.5
130	-343.3	220	-249.0
135	-335.6	245	-212.4
140	-331.7	250	-204.0
145	-327.7	255	-196.0
150	-323.5	260	-187.3
155	-319.3	265	-178.2
160	-315.0	270	-168.4
165	-310.5	275	-157.7
170	-306.0	280	-145.7
175	-301.3	285	-131.6
180	-296.6	290	-111.6
185	-291.7	292	-109.6
190	-286.8	303	-4.777
192	-284.8	305	0
194	-282.7	310	10.69
196	-280.6	315	21.44
198	-278.4	320	32.19
200	-276.3	325	42.99

Table IV. Enthalpy of quenched POCB
(referred to T_m)

T , °K	H , J/g	T , °K	H , J/g
90	-307.5	188	-229.7
95	-304.5	190	-227.6
100	-301.4	192	-225.4
105	-298.2	194	-222.9
110	-294.9	196	-219.5
115	-291.5	200	-211.9
120	-288.0	205	-202.3
125	-284.4	210	-192.7
130	-280.6	215	-183.1
135	-276.8	220	-173.4
140	-272.9	225	-163.6
145	-268.9	230	-153.8
150	-264.8	240	-128.7
155	-260.5	250	-112.2
160	-256.2	260	-87.18
165	-251.7	270	-73.35
170	-247.2	290	-31.74
175	-242.4	295	-21.23
180	-237.6	300	-10.64
185	-232.7	305	0
186	-231.7		

of the specific heat below T_g .

In calculating the thermodynamic quantities below T_m from the results of the specific-heat data, it is necessary to establish a numerical value of the heat of fusion. To calculate this quantity, an estimate is required of the base line which represents the specific heat of the quasi-equilibrium mixture of the amorphous and the crystalline POCB in the melting region. Discussions of this problem have been already made by E. Passaglia, *et al.*,⁶ and F. E. Karasz, *et al.*⁷ In the present study, we have estimated this straight base line by connecting the specific-heat value just above T_g with the expected one just above T_m , assuming the invariance of the crystallinity in this temperature. The estimated specific-heat curves were also given in Figure 3. The heat of fusion was thus evaluated to be 124.34 J/g for the annealed sample with 76.4 %

Table V. Excess entropy of supercooled liquid
and glassy state relative to that of the 100 %
crystalline state of POCB

T , °K	ΔS_{ex} , J/g°K	T , °K	ΔS_{ex} , J/g°K
305	0.533	191	0.191
300	0.526	190	0.191
295	0.515	189	0.190
290	0.504	188	0.190
285	0.492	187	0.190
280	0.480	186	0.190
275	0.468	185	0.189
270	0.455	184	0.189
265	0.442	180	0.189
260	0.428	175	0.189
255	0.413	170	0.189
250	0.398	165	0.189
245	0.383	160	0.189
240	0.367	155	0.189
235	0.351	150	0.189
230	0.334	145	0.189
225	0.316	140	0.189
220	0.298	135	0.189
215	0.279	130	0.189
210	0.260	125	0.189
205	0.240	120	0.189
200	0.219	115	0.189
196	0.202	110	0.189
195	0.198	105	0.189
194	0.195	100	0.189
193	0.193	95	0.189
192	0.192	90	0.189

Figure 5. Excess entropy of supercooled liquid and glassy state relative to that of the 100% crystalline state of PO CB.

crystallinity and 162.59 J/g for the completely crystalline one. Figure 4 shows the temperature dependence of enthalpy referred to T_m for the annealed and the quenched samples as well as the estimated ones for the completely crystalline sample and the semicrystalline sample with fixed crystallinity, which have been calculated by use of the heat of fusion described above. Enthalpies for the annealed and the quenched samples are also given in Table III and IV, respectively. Also the excess entropies of the supercooled liquid and the glassy state were calculated for the completely crystalline state as given in Table V and shown in Figure 5.

Crystallinity

The crystallinity determined by the density method was 72.7% at 273°K. As was described above, the crystallinity was also estimated to be 76.4% with the calorimetric method from the specific-heat value at 210°K. The difference between these two values determined independently may be due either to the partial melting over the temperature range from 210 to 273°K or to the difference in these two methods of estimation. The crystallinity is also able to be evaluated in a calorimetric way by the following equation;⁸ $X = (H_a - H)/(H_c - H)$, where X is the crystallinity, H the enthalpy of the annealed sample, H_a the enthalpy of the amorphous part and H_c the enthalpy of the crystalline part. The crystallinity obtained by this method was found to be 71.0% at 273°K. This value is also less than the crystallinity given above at

210°K. It may be reasonable to assume that the semicrystalline sample is regarded as partially melted in the temperature range of 210–273°K. A further discussion of these results may require knowledge of the dependency of the premelting phenomenon upon the molecular-weight distribution.

Glassy State and Excess Entropy

As is shown in Figure 5, the excess entropy ($\Delta S_{ex}(T)$) of the supercooled liquid relative to that of the completely crystalline material is 0.533 J/g°K at T_m (305°K). This value also corresponds to the entropy of fusion of the completely crystalline sample. This excess entropy gradually decreases in the lower temperature region of 210–273°K and reaches the value of 0.198 J/g°K at T_g (195°K). Below this temperature the excess entropy of the glassy state decreases slightly further to 165°K and shows an almost constant value of 0.189 J/g°K down to 90°K. Provided the specific heat of the glassy state is equal to that of the crystalline state further below 90°K, this excess entropy is regarded as a residual entropy, S_0 , of the glassy state of PO CB.

Furthermore, as shown in Figure 5, the extrapolation of the $\Delta S_{ex}(T)$ curve between T_g and T_m down to the temperature where $\Delta S_{ex}(T) = 0$ yields the so-called thermodynamic equilibrium glass transition temperature ($T_2 = 155^\circ\text{K}$), which was proposed first by Gibbs and Dimarzio.⁹ Also the magnitudes of $(T_g - T_2)$ and (T_g/T_2) are evaluated to be 40°K and 1.32 respectively. These results are in good agreement with the predictions by Gibbs, *et al.*⁹

According to Wunderlich,¹⁰ the increment of the specific heat at T_g shows a constant value of 2.7 ± 0.5 cal per motional unit (bead) regardless of various kinds of sample. In the case of PO CB, three $-\text{CH}_2-$ and one $-\text{O}-$ groups may be regarded as the constituent beads. Thus, the increment of the specific heat per bead is evaluated to be 3.1 cal/bead °K. This result is also in agreement with Wunderlich's proposition.¹⁰

Comparison with Other Polyethers

The variation of the melting point of each member in the polyether series has already been reported by Lal, *et al.*¹¹ In the present study,

Figure 6. Temperature, enthalpy and entropy of fusion in polyether series: ●, temperature of fusion; ○, enthalpy of fusion; △, entropy of fusion; ----, enthalpy curve estimated by Miki.

the relation of temperature, entropy and enthalpy of melting in polyether series are compared and inspected by utilizing the present results together with some other data.^{12,13} These quantities are summarized in Figure 6. As an extreme case the thermodynamic values¹⁴ of polyethylene are also quoted here for reference. The melting-temperature curve in polyethers has a minimum in the neighborhood of POCB. In passing, the thermodynamic data of the members with higher m -values than that of PTHF have never been reported. The enthalpy of melting of POCB is very small in comparison with the others in this series, while entropies of melting show almost the same values. Therefore the principal reason why the melting temperature of POCB is lower than those of the others may be due to its small value of the enthalpy of melting. This result is in qualitative agreement with the statistical mechanical evaluation by Miki.¹⁵

Isotherms and Dissociation Pressures of Hydrate

In general, it has been known that water molecules are exclusively accessible to the amorphous part of the solid high polymer. On the other hand, cellulose^{16,17}, poly(vinyl alcohol)¹⁸ and some others are reported to form their hydrates. These results are, however, mainly based on the X-ray method. If we want to use the term "hydrate" in a strict sense, we should also carry out thermodynamic studies to confirm

Figure 7. Schematic diagram of dehydration isotherms: —, stoichiometric hydrate; ----, zeolitic hydrate.

whether these hydrates have stoichiometric hydration water in their crystalline parts or not. From the shape of the dehydration isotherm as is shown in Figure 7, the state of the aggregation of water molecules in the crystalline hydrates may be classified into two classes; *i. e.*, the stoichiometric water of crystallization and the so-called zeolitic (non-stoichiometric) water. The former exhibits a stepwise decrease of the dissociation pressure with the progress of dehydration, while the latter a continuous decrease. So far as the authors are aware, only the examples of the latter have ever been found in hydrated polymers but examples of stoichiometric hydration water have not yet been found.

Our results of the isotherms on POCB at 9.7, 0 and -5.1°C are shown in Figure 8. Each

Figure 8. Dehydration isotherms of the hydrated POCB.

observed initial dissociation pressure at 9.7 and -5.1°C was in agreement with vapor pressures of water or ice at these temperatures. It is supposed that these pressures were those exhibited by the remaining free water or ice phases at surfaces. At 0°C , however, the measurement was made for the partially dehydrated sample and the initial pressure corresponded to that of the partially dehydrated one. In all cases after free water, if any, was removed, the dissociation pressure decreased gradually with an increasing amount of water extracted and then again showed a constant value characteristic of temperature in the definite range of amount of dehydrated water. At the stage where the final water involved was completely removed, the pressure dropped down rather sharply as shown in Figure 8. The gradual dropping down of the dissociation pressure is due to the zeolitic type dehydration and it seems to represent the dehydration of water from the amorphous part in the sample. The region of constant pressure is characteristic of the stoichiometric crystallization water and it is confirmed that water in the hydrated POCB exists really as stoichiometric water in the crystalline part. Because of rather difficult conditions for preparing the sample, the length of duration of constant pressure relative to the

whole region investigated depends on the relative ratio of the amounts of crystalline and amorphous parts. Based on this consideration we can evaluate the crystallinity of the hydrated samples employed by utilizing information on structural analysis. The crystallinity thus determined was found to be 43, 52 and 40% for the samples subjected to the measurement at 9.7, 0 and -5.1°C , respectively. The temperature dependence of the dissociation pressure determined for the crystalline part of the hydrated sample is also shown in Figure 9, which is represented with the following expression; $\log P = 10.82 - 2.93 \times 10^3 T^{-1}$, where P is the dissociation pressure in mmHg and T the absolute temperature. By putting this equation into the Clausius—Clapeyron equation, we can obtain the heat of dissociation amounting to 3.25×10^3 J/mol.

In conclusion, it is confirmed that water molecules in the hydrated POCB exist stoichiometrically in the crystalline part of the solid polymer. Further, the dissociation heat was evaluated. This kind of thermodynamical investigation on the behavior of water molecules in hydrated solid high polymer may be the first case ever known.

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Figure 9. Clausius—Clapeyron plot of the dehydration pressure of the hydrated POCB.

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