ON THE THERMAL TRANSITIONS OF THE AMYLOSE–CETYLTRIMETHYLAMMONIUM BROMIDE COMPLEX

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ABSTRACT

Thermal transitions of the amylose–cetyltrimethylammonium bromide (CTAB) complex have been studied by differential scanning calorimetry (d.s.c.). The complex crystallised from solution gave a single endotherm, whereas, at the second heating, a double endotherm was observed. Rheological measurements showed that the initial complex was more elastic than the heated complex. The appearance of the endotherms was not affected by changing the procedure for the formation of the complex or the thermal treatment. The thermal transitions are discussed in relation to the concept of chain-folding.

INTRODUCTION

Of the great variety of polar organic substances that form helical inclusion complexes with amylose[1], the polar lipids are of special interest due to their occurrence and function in starch-containing food products. The structure of the complex, determined from X-ray diffraction measurements[2–4] and from Raman spectroscopy[5] and referred to as V-amylose, appears to be the same for all types of monoacyl lipids, but helices with seven or eight glucosyl residues per helical turn, instead of the usual six, have been suggested for complexes with other more bulky, complexing agents[6]. Although the structure of the V-amylose might be the same, different polar lipids differ greatly in their effects on starch[7], an observation which has not yet been satisfactorily explained.

Recently, the thermal behaviour of several types of amylose–lipid complexes has been studied[8–17] by d.s.c. The complex exhibits an endothermic transition at temperatures above the range of temperatures for the gelatinisation of starch, which depends on the water content[8,14,15,18], on the chain length[10,12,13,17] and type of polar head[11,13] of the fatty acid, and on the environment of the complex[19]. The thermal behaviour of the amylose–lipid complex also seems to be affected by certain processes which a starch-rich food item might undergo, such as extrusion cooking[17] and drum drying[20].

The transition is reversible to a certain degree, and the endotherms observed

on first and second heatings might be similar[15,16] or different depending on the nature of the complexing agent[8,9,15]. Usually, the transition temperature is shifted towards higher temperatures during re-heating, and the differences could be indicative[8,13,15] of different polymorphic forms of the amylose–lipid complexes. Non-ionic complexing agents such as alcohols give rise[13] to two complexes differing in transition temperatures by ~25°. The thermal transitions of complexes with monopalmitin and lauric acid, respectively, were complex at low contents of water, whereas complexes with lysolecithin gave rise to a much simpler thermal behaviour[15]. The thermal behaviour was explained on the basis of melting–recrystallisation phenomena occurring during d.s.c. The transition might result also from a dissociation of the complex into amylose and free lipid[21]. The more complex appearance of the endotherm, especially during a second scan, might be due variously to melting, recrystallisation, and helix→coil transformations. Further, the chain folding during crystallisation of the complex[4,22,23] might also complicate the overall thermal behaviour.

The thermal behaviour of the complex formed between amylose and cetyltrimethylammonium (CTAB) is now described. This complex gives rise to a double peak on a second heating in the d.s.c. even at high contents of water, and, due to the solubility of the surfactant, the procedure for the formation of the complex is simple.

EXPERIMENTAL

Materials. — The amylose (from potato starch) and the cetyltrimethylammonium bromide (CTAB) were commercial products, and the wheat starch was A-starch prepared[24] from the Swedish spring wheat Amy. Distilled-deionised water was used throughout and other chemicals were of analytical grade.

Precipitation of the complex. — A solution of amylose (500 mg) in M NaOH (5 mL) was neutralised with M HCl (to pH 6.5–7.5), and then diluted to 10 mg amylose/mL. This solution (50 mL) was used immediately and aqueous CTAB (5 mL, 20 mg/mL) was added followed by water (5 mL). In one experiment, the concentration of CTAB was 40 mg/mL. The sample was stirred for 30 min and then centrifuged at 1000g for 30 min, and the precipitate was stored at +4°. In one experiment, the amylose solution was added to the CTAB solution. Further, the duration of stirring was varied, as were the pH and ionic strength (5 mL of mM NaCl was added instead of water after the addition of CTAB).

Amylose remaining in the supernatant solution after centrifugation, determined according to the "blue value" method[25], was always <1% but never zero.

D.s.c. — Aliquots (5–10 mg) of the wet precipitated complex were sealed in DuPont coated sample-pans, which were introduced into a Perkin–Elmer 2 instrument at 23°. In a typical run, the sample was heated to 117° at 10°/min, kept for 2 min at 117°, cooled to 23° at 10°/min, and then re-heated under the same conditions. Other scanning rates investigated were 2.5, 5, 20, and 40°/min. The conditions

during the scans were also varied to give different time–temperature protocols (Fig. 5).

The amylose–CTAB complex was also allowed to form in the sample pan. Thus, amylose, CTAB solution, and water were mixed to give a CTAB–amylose ratio of 0.1:1 or 0.2:1 and a water–amylose ratio of 3:1. Wheat starch was also used with a CTAB–starch ratio of 0.1:1 and a water–starch ratio of 3:1.

The thermograms were evaluated as described[11] and the results presented are the mean and standard deviations of the temperature at peak maximum (T) and the transition enthalpy (ΔH) for at least three samples. When double peaks appeared on the thermogram, they were separated into two peaks by approximating the peaks with triangles (see Fig. 2).

The water content of each sample was determined after the scan by puncturing and drying the pan for 16 h at 105°.

Rheological measurements. — The Bohlin Rheometer V.O.R. (Bohlin Rheology, Lund) was used in the oscillation mode. A cone-plate system with a plate diameter of 30 mm and a cone angle of 5.4° was used. The shear amplitude was 0.176° and a frequency sweep was performed in the range 0.02–2 Hz. Measurements were carried out on the precipitated amylose–CTAB complex, and after that the complex was heated for 5 min at ~100°. After cooling, this sample was centrifuged for 30 min at 1000g. An unheated and centrifuged sample was used as the control and measurements were carried out at +25°.

X-Ray diffraction studies. — These were performed in the low-angle region and in the wide-angle region[26].

RESULTS

On heating of the precipitated amylose–CTAB complex, a single endotherm at 98.0° was obtained on the d.s.c. thermogram (Fig. 1 and Table I). Heating up to 140° did not reveal any further transitions and, on cooling, an exothermic transition at 85.8° was observed. On second heating, the temperature of the endotherm was elevated slightly and showed a shoulder at the low temperature side. A second cooling followed by a third heating did not change the appearance of the endotherm. The ΔH and T values are given in Table I, where also the ΔH value for the double peak has been separated according to Fig. 2. X-Ray diffraction of the precipitated amylose–CTAB complex gave diffraction lines at 12.8, 6.9, 4.5, 3.5, and 3.1 Å in good agreement with the values reported for the V-hydrate[27]. When the same sample was heated to 98.4° and then allowed to cool, the diffraction pattern was not affected significantly (d-spacings at 12.6, 6.4, 4.5, 3.6, and 3.1 Å). No diffraction lines were obtained in the low-angle region; only diffuse low-angle scattering was observed.

The thermal behaviour of the amylose–CTAB complex was similar to that observed when the complex was formed by heating amylose and CTAB or starch and CTAB in the calorimeter (Fig. 3). Some typical ΔH and T values are given in
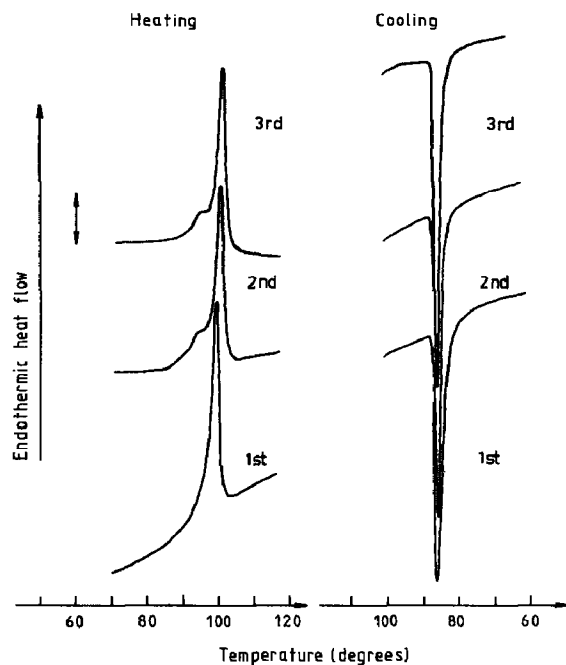
Fig. 1. D.s.c.-thermograms of the heating and cooling of the amylose–CTAB complex at a scanning rate of 10°/min. The content of dry matter was 0.54 mg and the arrow indicates 0.1 mJ/s.
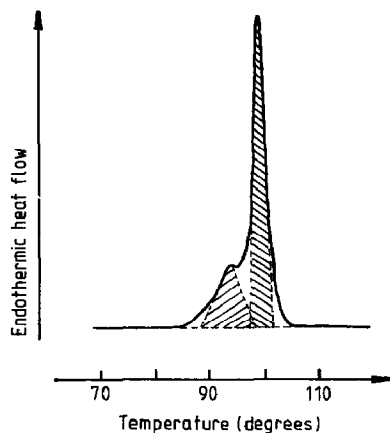

Fig. 2. The separation of a double peak into two peaks by approximating the peaks with triangles. There has to be a maximum point in each peak for the computer to recognise two peaks.

TABLE I

TRANSITION TEMPERATURE (T) AND ENTHALPIES (ΔH) DURING REPEATED HEATING AND COOLING CYCLES IN THE D.S.C. OF AMYLOSE–CTAB COMPLEX

Thermal treatment	T (degrees)	ΔH (J/g of dry matter)	Separation of the double peak into two peaks[a]	
			T (degrees)	ΔH (J/g of dry matter)
First heating (n = 58)	98.0 ±0.4	17.9 ±1.9	[b]	
First cooling (n = 20)	85.8 ±0.6	16.1 ±1.6	[b]	
Second heating (n = 9)		17.4 ±1.5	94.0 ±0.8	5.9 ±1.3
			99.4 ±0.7	10.5 ±2.0
Second cooling (n = 4)	85.0 ±0.9	17.6 ±2.1	[b]	
Third heating (n = 3)		18.4 ±1.1	93.8	7.3
			99.0 ±1.3	10.0 ±3.3

[a]The separation of the double peak was performed according to Fig. 2. [b]Only a single peak was obtained.

Table II, although the double peak obtained on a second heating was not separated into two peaks.

Thus, the qualitative behaviour of the amylose–CTAB complex is independent of the method used for its formation. Moreover, the appearance of a double peak after the first heating was not due to the conditions during the d.s.c. scan. When the first heating was performed simply in a test tube, the white, solid precipitate was transformed into a clear solution.

Conditions during the complex precipitation procedure. — (a) *Moisture con-*
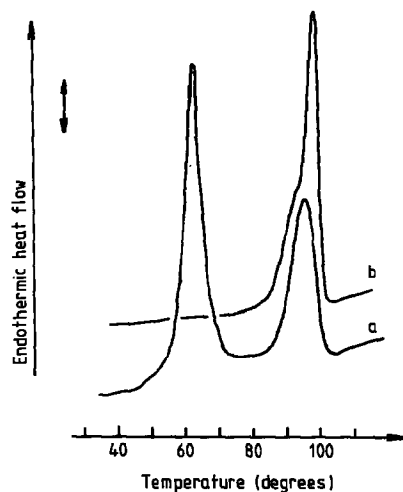

Fig. 3. D.s.c.-thermograms of heating (a) and re-heating (b) wheat starch in CTAB (0.1 g of CTAB/g of starch) at a water-to-starch ratio of 3:1. Arrow indicates 0.1 mJ/s.

TABLE II

A COMPARISON BETWEEN TRANSITION TEMPERATURE (T) AND ENTHALPY (ΔH) OF AMYLOSE-CTAB COMPLEXES FORMED IN DIFFERENT WAYS

Complex	Thermal treatment	Appearance of endotherm (peaks)	T^a (degrees)	ΔH^b (J/g of dry matter)
Precipitated from solution	1st	single	98.0 ±0.4	17.9 ±1.9
	2nd	double	99.4 ±0.7	17.4 ±1.5
	3rd	double	99.0 ±1.3	18.4 ±1.1
Complexes formed during d.s.c.^{c}				
0.1 g of CTAB/g of amylose	1st	single	Not calculated	
	2nd	double	96.1 ±0.3	16.0 ±0.1
	3rd	double	96.3 ±0.0	17.2 ±0.9
0.2 g of CTAB/g of amylose	1st	single	Not calculated	
	2nd	double	96.4 ±0.8	12.9 ±0.5
	3rd	double	97.3 ±0.4	13.6 ±0.4
0.1 g of CTAB/g of wheat starch	1st	single	94.7 ±1.9	4.2 ±0.3
	2nd	double	98.1 ±1.3	6.8 ±0.2

^{a}The temperature for the second peak in the double endotherm is given. ^{b}Calculated for the total endotherm. ^{c}Water-to-amylose (starch) ratio was 3:1.

tent. When the amylose–CTAB complex was formed by precipitation from solution, the ΔH value for the collected complex varied considerably, whereas the T value could be determined accurately (see Table I). The variation in ΔH is not surprising since the precipitation procedure involves helix formation, nucleation, and crystal growth. Moreover, the water content of the precipitated complex can vary, and, for the samples investigated, the content of dry matter was in the range 5.2–6.3%. However, in this range, no correlation between transition enthalpy and water content was observed. At lower moisture contents, the T value increased (Table III). A single endotherm was obtained on the first heating, independent of the water content in the range investigated. Moreover, ΔH did not vary significantly. Thus, the T value of the amylose–CTAB complex was more sensitive to the water content than the complexes (lysolecithin, lauric acid, and monopalmitin) described by Biliaderis et al.[15], the transition temperature of which did not change until the dry matter content was >30%.

TABLE III

INFLUENCE OF WATER CONTENT ON THE TRANSITION TEMPERATURE (T) AND ENTHALPY (ΔH) OF THE AMYLOSE–CTAB COMPLEX

Dry-matter content (weight %)	T (degrees)	ΔH (J/g of dry matter)
5.2–6.3	98.0 ±0.4	17.0 ±1.9
9.3	99.0	21.6
16.6	102.0	18.2

TABLE IV

INFLUENCE OF SOME PARAMETERS ON THE TRANSITION TEMPERATURE (T) AND ENTHALPY (ΔH) DURING THE PREPARATION OF THE AMYLOSE–CTAB COMPLEX

Conditions	T (degrees)	ΔH (J/g of dry matter)
Standard	98.0 ±0.4	17.9 ±1.9
Without stirring	98.2 ±0.5	15.4 ±0.8
heavy stirring	98.5 ±0.4	19.3 ±2.9
pH 8.3	98.1 ±0.0	17.2 ±0.3
pH 5.9	98.1 ±0.4	16.1 ±1.0
+ added NaCl at pH 6.9	97.9 ±0.2	17.2 ±0.6

(b) *pH, ionic strength, and stirring*. The results in Table IV show that none of these parameters affected the T or ΔH values. Further, the endotherm observed on the first heating was always a single endotherm, independent of the conditions in the procedure for the formation of the complex.

(c) *Temperature*. Complexes were prepared at 23, 85, and 100°, and the subsequent thermograms for the first heating are shown in Fig. 4; the corresponding ΔH and T values are given in Table V. The thermal behaviour of the amylose–CTAB complex was not affected by its preparation at 23° and 85°, whereas a temperature above the T value of the complex resulted in a double endotherm on the first heating similar to that obtained on a second heating of the other complexes.

Kowblansky[13] observed two different endotherms when the temperature at which the complex was formed was varied. However, this was not observed for ionic complexing agents, a finding which was supported in the present work.

(d) *CTAB–amylose ratio*. Although the weight ratio for CTAB and amylose

TABLE V

INFLUENCE OF THE TEMPERATURE (T_F) OF THE FORMATION OF THE COMPLEX ON THE TRANSITION TEMPERATURE (T) AND ENTHALPY (ΔH) OF THE AMYLOSE–CTAB COMPLEX

T_F (degrees)	First heating in the d.s.c.		Second heating in the d.s.c.	
	T (degrees)	ΔH[a] (J/g of dry matter)	T (degrees)	ΔH[a] (J/g of dry matter)
23	98.0 ±0.4	17.9 ±1.9	94.0 ±0.8	5.9 ±1.3
			99.4 ±0.7	10.5 ±2.0
				17.4 ±1.5
85	99.6 ±0.7	21.9 ±2.1	93.6	5.1
			99.6	7.7
				17.1
100	95.1 ±0.5	5.3 ±0.4	[b]	[b]
	101.1 ±0.5	11.5 ±0.2	100.9	10.8
		18.3 ±1.1		16.8

[a]When three ΔH values are given, the first values correspond to the separation of a double peak according to Fig. 2, whereas the third value is the enthalpy calculated from the total area. [b]The low-temperature peak was not possible to calculate separately.
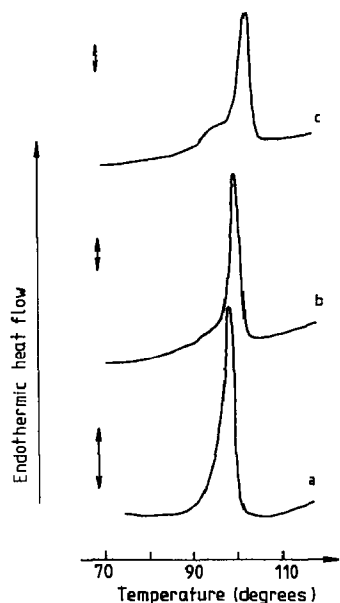
Fig. 4. D.s.c.-thermograms of heating of the amylose–CTAB complex prepared at (a) 23°, (b) 85°, and (c) 100°. The amount of dry complex was 0.51, 0.61 and 0.86 mg, respectively. The arrows indicate 0.1 mJ/s.

was 0.2 in all the experiments, this is not necessarily the ratio in the precipitated complex. However, no endotherm due to the Krafft point of uncomplexed CTAB was detected down to 5°. An increase in the weight ratio to 0.4 did not significantly change the T and ΔH values of the complex (Table VI). When the CTAB–amylose ratio was increased during complex formation in the calorimeter, ΔH decreased (Table II), probably due to a dilution of the amount of complex by uncomplexed CTAB. Further, when the amylose solution was added to the CTAB solution instead of the reverse (standard) procedure, the thermal behaviour was not affected (Table VI). For all the complexes shown in Table VI, a single endotherm was obtained during the first heating. Thus, it might be concluded that the amylose is saturated with CTAB, and that the upper limit for the composition of the complex is 0.2 g of CTAB/g of amylose.

TABLE VI

INFLUENCE OF THE CTAB/AMYLOSE RATIO ON THE TRANSITION TEMPERATURE (T) AND ENTHALPY (ΔH) OF THE AMYLOSE–CTAB COMPLEX

Sample	T (degrees)	ΔH (J/g of dry matter)
Standard conditions	98.0 ±0.4	17.9 ±1.9
40 mg of CTAB/100 mg of amylose	97.4 ±0.3	17.8 ±1.2
Amylose solution added to CTAB solution	98.7 ±0.4	20.7 ±2.3

Conditions during d.s.c. — (*a*) *Rate of heating.* When the rate of heating was changed, a dependence of T on scanning rate was observed (Table VII and Fig. 5) for the endotherm obtained on the first and second heatings, probably due to limitations in the transfer of heat at the very high scanning rates. The cooling rate was always 10°/min. The rate of heating was varied in order to facilitate recrystallisation and annealing. The appearance of the double endotherm during the second heating was not affected by the rate of heating (Fig. 5), whereas the complexes[15] between amylose and monopalmitin or lauric acid tend to recrystallise during d.s.c. Even exothermic transitions were observed for these complexes which, however, had much lower contents of water than those studied here. The data in Table VII also indicate that the high-temperature part of the endotherm increased in size with increasing rate of heating.

(*b*) *Thermal treatments.* — The effects of various heating–cooling cycles with holding periods up to 60 min are illustrated in Fig. 6.

Holding periods just below the endotherm during the first heating (Fig. 6,1), at 117° after the first heating (Fig. 6,2), after the exothermic transition during cooling (Fig. 6,3), and just before (Fig. 6,4) and in the middle of (Fig. 6,5) the endotherm on the second heating had no effect on T or ΔH values, or the appearance of the endotherms on the following scans. Thus, it might be concluded that the appearance of a double peak during re-heating is not due to melting and recrystallisation during the d.s.c. Only the heating above the transition temperature of the complex resulted in a double peak in d.s.c.

Rheological behaviour. — When rheological measurements are performed in the oscillation mode, it is possible to obtain information on viscosity and elasticity. The storage or elastic modulus (G') during a frequency sweep was used to characterise the complex, together with the phase shift (δ), and the result is shown in Fig. 7. The measurements were made before and after the solid→liquid transition. The

TABLE VII

INFLUENCE OF THE RATE OF HEATING ON THE TRANSITION TEMPERATURE (T) OF THE AMYLOSE–CTAB COMPLEX DURING THE FIRST AND SECOND HEATING, AND ON THE PROPORTION OF THE HIGH-TEMPERATURE ENDOTHERM DURING THE SECOND HEATING

Heating rate (degrees/min)	First heating T (degrees)	Second heating	
		High-temperature endotherm	
		T (degrees)	% of ΔH value[a]
2.5	96.6	97.7	50
5	97.4	99.3	47
10	98.0	99.4	60
20	99.9	102.1	63
40	103.0	106.3	77

[a]The ΔH value obtained for the high-temperature part of the endotherm according to Fig. 2 as a percentage of the ΔH value obtained for the total endotherm.
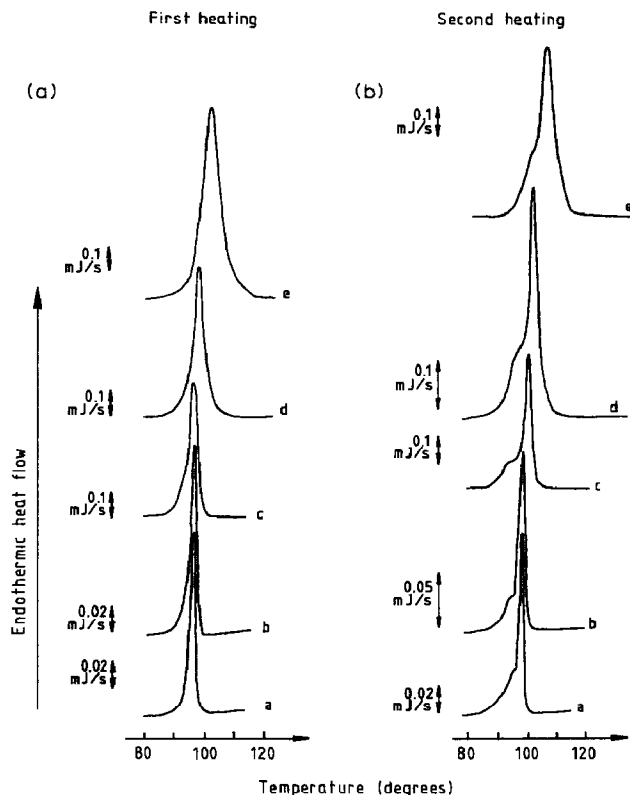
Fig. 5. D.s.c.-thermograms of heating and re-heating of the amylose–CTAB complex. The heating rate was (a) 2.5°, (b) 5°, (c) 10°, (d) 20°, and (e) 40°/min. The amount of dry sample was 0.66, 0.42, 0.81, 0.52, and 0.50 mg, respectively. The cooling was always carried out at 10°/min. The curves are those recalculated after the evaluation.
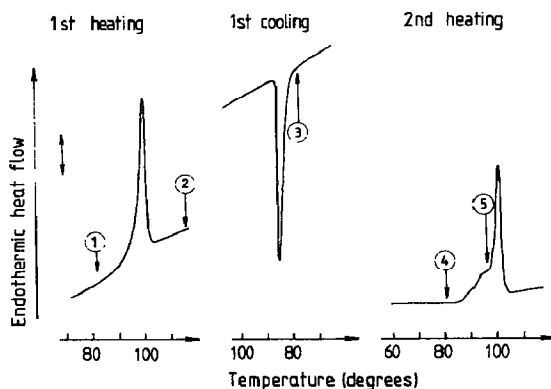

Fig. 6. Heating–cooling cycles for the amylose–CTAB complex: 1, →82° at 10°/min, 82° for 0–60 min, →22° at 320°/min, →117° at 10°/min; 2, →117° at 10°/min, 117° for 0–60 min, →22° at 10°/min, →117° at 10°/min; 3, →117° at 10°/min, →77° at 10°/min, 77° for 0–60 min, →22° at 320°/min, →117° at 10°/min; 4, →117° at 10°/min, →22° at 320°/min, →82° at 10°/min, 82° for 0–60 min, →22° at 320°/min, →117° at 10°/min; 5, →117° at 10°/min, →22° at 320°/min, →96° at 10°/min, 96° for 0–60 min, →22° at 320°/min, →117° at 10°/min.

water-holding capacity was decreased after heating and therefore the heated sample was centrifuged again. The increase in G' after heating is probably due to the changes in moisture content. The increase in loss angle, especially at low frequencies, indicated the heated sample to be more viscous than the unheated sample, as the increase in δ is not due to the centrifugation.

DISCUSSION

Two types of crystallisation conditions have been recognised, namely, the complex initially separated from solution and on cooling after heating to >98°. The same type of endotherm was always obtained when the complex had been heated above its transition temperature and also when CTAB was added to a solution of amylose at this high temperature. Thus, it is tempting to suggest that the helical inclusion complex formed in solution at this high temperature crystallises when the temperature is decreased. The structure of the complex in the X-ray wide-angle region seems to be independent of the way in which the complex crystallises. However, the macroscopic behaviour of the two types of complexes was different. Rapid precipitation of the complex at room temperature gave imperfect crystals with a fairly extensive net-work structure (low δ values in Fig. 7) and good water-holding capacity. When these crystals are melted and then recrystallised or when the complex was formed above the transition temperature and then crystallised, the crystal packing was improved, resulting in a higher melting temperature, less extensive net-work structure (δ increases, Fig. 7), and, thus, less water-holding capacity. This latter complex was stable, since further heating did not change the transition temp-
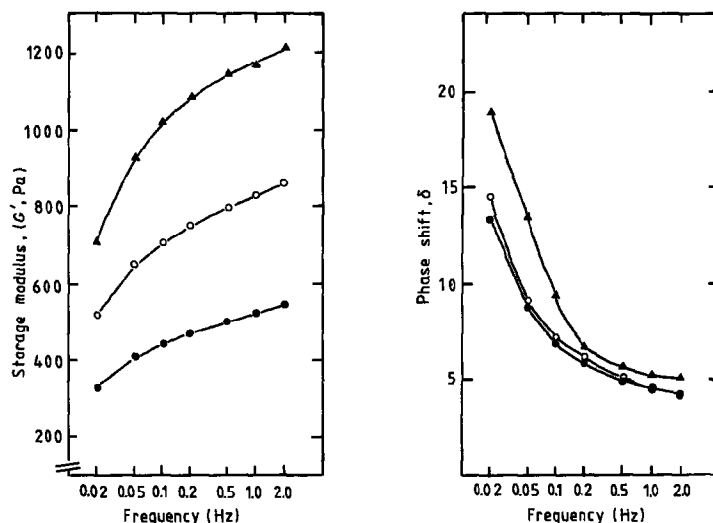
Fig. 7. Storage modulus (G') and loss angle (δ) of the amylose–CTAB complex during a frequency sweep: —●—, immediately after the preparation; —○—, after a second centrifugation; —▲—, after heating to 100° before centrifugation.

eratures or the proportions of the two endotherms. The amylose–CTAB complex was not prone to melting–recrystallisation or annealing during calorimetry since none of the thermal treatments applied changed the appearance of the endotherms. Further, increasing the heating rate increased the high-temperature endotherm, which is contrary to what would be expected from melting and recrystallisation[28]. Multiple endotherms might also arise from different crystal sizes, although this seemed not to be so for the amylose–CTAB complex since treatments during the formation of the complex thought to influence crystal growth[29] did not change the thermal behaviour.

Instead, the concept of chain-folding, which is commonly used to explain the crystallisation of flexible polymers at low concentrations[28,29], might be used to explain the thermal behaviour of the amylose–CTAB complex. Chain-folding has been suggested for V-amylose[4,22,23], and thicknesses of the lamellae of amylose crystals in the range 75–98 Å have been reported. Also enzymic hydrolysis of amylose–lipid complexes has been discussed from the point of view of chain-folding[30]. Initial hydrolysis is then due to folds at the surface and is rapid, whereas the rate of hydrolysis decreases when the stable crystal is reached. Thus, it is tempting to suggest that the double endotherm obtained for the more perfect crystals of the amylose–CTAB complex resulted from different melting temperatures, depending on whether the complexes were located in folds at the surface of the crystals (lower melting temperature) or inside the crystals (higher melting temperature). The higher co-operativity observed for the high-temperature part of the endotherm is also consistent with such an interpretation.

However, when the solution crystallised or the melted and recrystallised amylose–CTAB complex was analysed in the X-ray low-angle region, no diffraction line that could support the above hypothesis concerning the chain-folding was observed. The amylose sample used was not fractionated into different molecular sizes, and the polydispersity might result in crystals of various thicknesses. Thus, there will not be a preferred thickness of lamellae which results in a diffraction line. The hypothesis of chain-folding is worth further exploration for other types of complex-forming substances and at other concentration ranges, in order to explain the discrepancies in thermal behaviour between the different types of complexes.

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