BUTTERWORTH
HEINEMANN

Polymer Vol. 36 No. 2, pp. 373–380, 1995

0032-3861/95/$10.00+0.00

Thermodynamic parameters relative to the melting of cellulose tributyrate

Umberto Piana and Maria Pizzoli*
Dipartimento di Chimica 'G. Ciamician' della Università di Bologna, and Centro di Studio per la Fisica delle Macromolecole del CNR, via Selmi 2, 40126 Bologna, Italy

and Charles M. Buchanan†
Department of Chemistry, East Tennessee State University, Johnson City, TN 37614, USA
(Received 10 May 1994)

Wide-angle X-ray scattering (WAXS) and differential scanning calorimetry (d.s.c.) measurements were made on cellulose tributyrate (CTB). In one case, CTB precipitated from solution in powdered form was annealed at different temperatures. In a second case, CTB was isothermally crystallized either from the melt or from the glass. Samples annealed from the powder showed higher crystallinity with respect to samples crystallized from the glassy or molten state. By applying the Hoffman–Weeks method to the melting temperatures of isothermally crystallized samples, a value of 192°C for the equilibrium melting temperature of CTB was obtained. From calorimetric results on samples with different crystalline/amorphous ratio, a linear dependence between ΔH_m and ΔC_p was found, whose extrapolation gave 34.5 J g^{-1} for the equilibrium heat of fusion ΔH_m°. A correlation between the experimental melting enthalpy arising from d.s.c. measurements and the percentage crystallinity estimated by WAXS measurements was attempted. In this manner a second, surprisingly high, value (67 J g^{-1}) for ΔH_m° was found. The difference between the values obtained from the two methods is believed to be due to the presence of macroscopic order in the amorphous phase, which influences the value of the WAXS crystallinity.

(Keywords: cellulose tributyrate; equilibrium melting parameters; X-ray crystallinity)

INTRODUCTION

Cellulose esters are thermoplastic materials having a wide range of properties depending on the type of substituents, the degree of substitution (*DS*) and the molecular weight[1]. Although they have been utilized commercially for a long time and their properties have been studied extensively, there are few reports concerning thermodynamic parameters such as the equilibrium enthalpy of fusion (ΔH_m°) and the equilibrium melting temperature (T_m°) of their crystal phase. For different molecular weights, isolation methods and acylation conditions, different crystallinity and enthalpy values are expected. Kamide *et al.*[2] studied the effect of *DS* and molecular weight on the glass transition and on the melting temperature of cellulose acetates. The three-dimensional crystalline structure of cellulose esters, prepared under homogeneous or heterogeneous acylation conditions, were investigated by X-ray and electron diffraction[3–8] and various polymorphic forms were observed.

With regard to the thermodynamic parameters of the melting process of cellulose esters, Sharma[9] carried out calorimetric measurements on melt-crystallized samples at different temperatures and derived a value of 301°C for the equilibrium melting point of cellulose tripropionate. Mandelkern and Flory[10] studied dilatometrically cellulose acetates and butyrates with different *DS* and, by measuring the depression of the melting temperature due to the presence of diluents, provided the only data available for ΔH_m° (33.8 J g^{-1}) and T_m° (206–207°C) of cellulose tributyrate. Finally, values of T_m° and ΔH_m° for cellulose acetate with $DS = 2.5$ were reported by Sun and Cabasso[11], who examined samples with different thermal histories.

Our interest revolves around the equilibrium melting parameters of cellulose tributyrate (CTB). This interest arises from the difficulties in the interpretation of the dynamic-mechanical behaviour of cellulose esters and polyhydroxybutyrate blends in which some esters were able to crystallize[12–14]. In this account we report calorimetric and X-ray measurements performed on CTB in the bulk. The calorimetric measurements were made in order to obtain a value of ΔH_m° and T_m° for CTB, and the X-ray measurements in order to correlate the percentage crystallinity with the corresponding experimental enthalpy of fusion of samples having a different degree of crystallinity. A comparison of the ΔH_m° value derived from calorimetric measurements with the value arising from X-ray data will be given. These measurements were performed on powders obtained by precipitation and on samples crystallized from the melt and from the glassy state.

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* To whom correspondence should be addressed

† Current address: Research Laboratories, Eastman Chemical Company, PO Box 1972, Kingsport, TN 37662, USA

EXPERIMENTAL

Cellulose tributyrate (CTB) was supplied by Eastman Chemical Co. (Kingsport, TN). The degree of substitution, determined by proton n.m.r., was found to be 3.0; the number- and weight-average molecular weights, determined via g.p.c. in $CHCl_3$, were found to be 1.33×10^4 and 3.01×10^4 respectively. As-supplied CTB is a partially crystalline powder with an experimental melting temperature $T_m = 173°C$ and enthalpy of fusion $\Delta H_m = 23.4\ J\ g^{-1}$. By rapid quenching from the melt it is possible to obtain CTB in a totally amorphous state characterized by a glass transition temperature $T_g = 81°C$ and an associated specific heat increment (ΔC_p) of $0.29\ J\ g^{-1}\ °C^{-1}$.

Calorimetric curves were recorded using a Du Pont 2100 differential scanning calorimeter at a heating rate of $20°C\ min^{-1}$ in the temperature range from -40 to 220°C. The values of ΔC_p were calculated from the vertical distance between the two extrapolated baselines at the glass transition. The melting points (T_m) were taken at the peak temperature of the endotherm curves. The peak area was taken as the heat of fusion (ΔH_m) of the crystalline domains.

Wide-angle X-ray scattering (WAXS) experiments were performed with a Scintag PAD VX diffractometer using Cu Kα radiation with a voltage of 45 kV and a current of 20 mA and a pressed graphite diffracted beam monochromator. The percentage crystallinity calculated from WAXS data may contain some errors because it depends on arbitrary choices, such as the manner in which the amorphous scattering is subtracted. Moreover, the spectra are influenced by the dimensions and the orientation of the crystals. In the present paper, the percentage crystallinity of CTB was calculated by using the Hermans–Weidinger method[15,16]. This method is based on the existence of proportionality between the experimentally measured crystalline intensity (I_c) and the crystalline fraction, and between the amorphous intensity (I_a) and the amorphous fraction[17]. In order to apply the method, the experimental spectrum of amorphous CTB was obtained by melting the powder on a metal plate suitable for X-ray analysis in an oven at 220°C and subsequently quenching it in dry ice. D.s.c. measurements carried out on this sample showed the absence of crystallinity. The crystallinity of the partially crystalline samples was calculated with reference to the amorphous sample, according to the following procedure:

(i) The background was separated from the experimental X-ray spectrum by selecting two points $I(2\theta_l)$ and $I(2\theta_h)$ at low and high 2θ values of the angular range examined and drawing a horizontal straight line between them (see *Figure 1*).

(ii) In *Figure 1a* the spectra of amorphous CTB and of the most crystalline sample examined are reported. The spectrum of amorphous CTB exhibits two broad maxima, the former centred at $2\theta = 6.5°$ and the latter centred near $2\theta = 20°$. The presence of crystallinity strongly increases the intensity in the first region, while the second region differs only in shape, and the corresponding scattering curve appears as the superposition of several peaks. This suggests that the amorphous component gives the largest contribution to the scattering in the latter region. By selecting the angle $2\theta_n = 21.8°$, where the difference between the intensity of the amorphous sample (I_a) and the intensity of the semicrystalline sample (I_{ex}) is the largest, it can be assumed that the scattering at this $2\theta_n$ value is due only to the diffraction of the amorphous fraction. After background subtraction, the ratio $r = I_{ex}(2\theta_n)/I_a(2\theta_n)$ was calculated for all experimental spectra and the scattering of the amorphous sample was normalized through r for every 2θ value in the range from $2\theta = 4$ to 32°. As an example, *Figure 1b* shows the spectra of *Figure 1a* after normalization of the amorphous spectrum. In order to obtain the intensities due to the crystalline phase, the normalized intensity of the amorphous component was subtracted from the experimental spectra. The crystallinity degree was then calculated from the ratio between the crystalline and experimental scattering area.

In order to study the phase behaviour of CTB, samples subjected to different heat treatments were examined.

Treatment A. Polymer plates were obtained by pressing the powder at $0.3\ ton/m^2$ ($\sim 3\ kPa$) at room temperature. D.s.c. measurements performed on these plates prior to annealing showed the same melting enthalpy of as-supplied CTB. Duplicate samples were annealed in an oven in the temperature range from 90 to 140°C for 18 h (unless otherwise specified) and were subsequently quenched in dry ice. Samples annealed for longer periods showed the same melting enthalpy and crystallinity with the exception of those samples annealed at 90 and 100°C. One sample was used for X-ray analysis and the other for d.s.c. measurements.

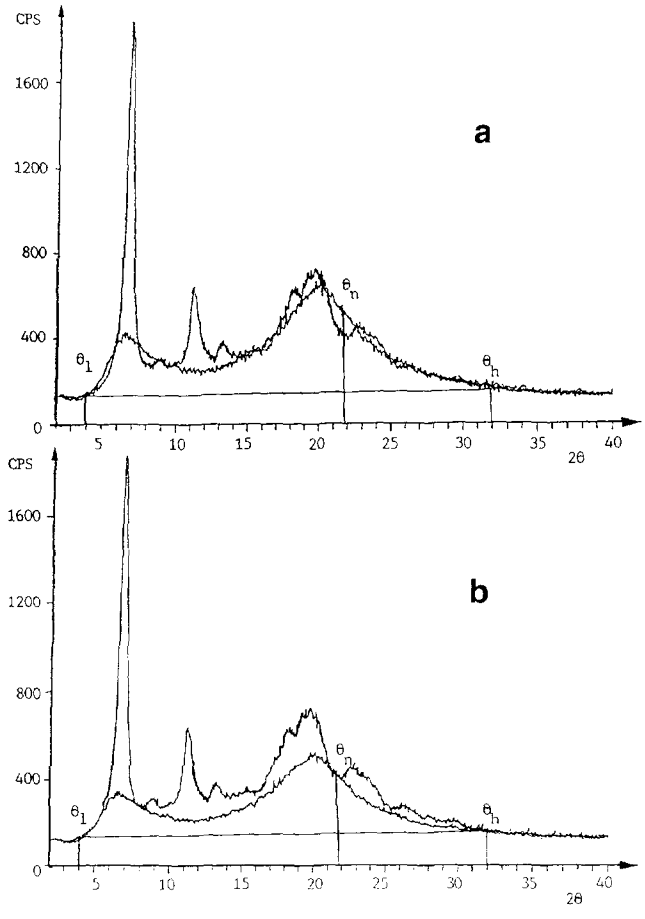

Figure 1 Application of the Hermans–Weidinger method to X-ray spectra of CTB

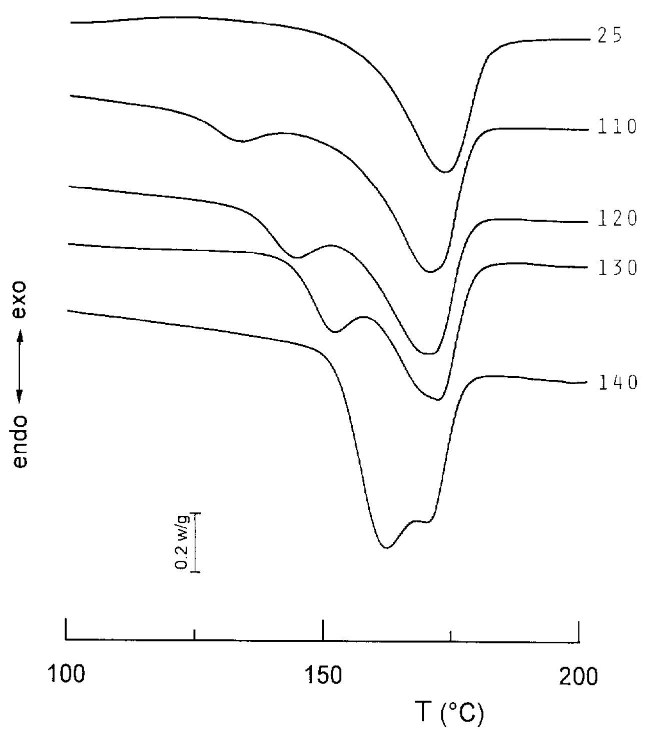

Figure 2 Calorimetric curves of CTB annealed at different temperatures (°C)

Treatment B. The CTB powder was melted at 220°C on a metal plate suitable for X-ray measurements, then either cooled from the melt to a fixed crystallization temperature or quenched in dry ice and subsequently heated from the glassy state to a selected crystallization temperature. The isothermal crystallization temperatures (T_c) were chosen between 100 and 140°C, and every isothermal treatment lasted 2 h. Owing to the impossibility of performing the thermal treatments directly in the X-ray diffractometer, they were carried out in the oven of a gas chromatograph (Hewlett Packard 5890 series II), where it was possible to heat and to cool the samples at tightly controlled rates.

Treatment C. CTB was melted in the d.s.c. cell at 220°C and quenched to -40°C, then heated to a fixed temperature T_c in the range from 113 to 157°C and allowed to crystallize for 2–3 h. As previously mentioned, rapid cooling from the melt hinders the crystallization process and CTB macromolecules are frozen in a glassy amorphous state at low temperature. When heated to constant temperature above T_g, isothermal crystallization from the rubbery state occurs and the nucleation rate is increased with respect to melt-crystallized samples[18].

Treatment D. CTB powder samples were partially melted in the d.s.c. by heating to various temperatures in the range from 160 to 220°C followed by rapid cooling to -40°C. Heat treatments at increasing temperature gradually destroy crystallinity and allow one to obtain samples with different crystalline/amorphous ratio.

RESULTS

Figure 2 shows some representative d.s.c. curves of CTB samples annealed at various temperatures (T_a) according to thermal treatment A. Two melting phenomena are observed: with increasing annealing temperature, the lower melting peak moves to higher temperature, while the second occurs at a temperature largely independent of T_a. The low-temperature endotherm shows the behaviour typical of the so-called 'annealing peak'[18] and can be associated with the melting of poorer crystals that grow at T_a between the pre-existing larger crystals. The second peak is related to earlier-developed, more-perfect crystals, which melt at constant temperature, very close to the value for the unannealed powder (top curve in *Figure 2*). The whole d.s.c. data for annealed CTB are collected in *Table 1* together with the corresponding X-ray results. *Figure 3* provides the X-ray spectra of samples annealed at 100 and 140°C together with those of the as-received powder ($T_a = 25$°C) and of quenched amorphous CTB. With increasing T_a, the development of new features and a general sharpening of the spectra are observed, in agreement with the literature[19]. The higher intensity of the first peak (at $2\theta = 6.5°$) at higher T_a reflects the increased crystallinity of CTB upon annealing, and nearly all of the changes in crystallinity degree can be associated with this peak. The region centred at $2\theta = 20°$ undergoes only a sharpening and a splitting into smaller peaks without any significant change in intensity.

The d.s.c. curves of samples crystallized from the glassy state and from the melt (following thermal treatment B)

Table 1 Calorimetric data and X-ray crystallinities of as-supplied CTB powder annealed at different temperatures (T_a) for 18 h in the oven

T_a (°C)	T_{m1} (°C)	T_{m2} (°C)	ΔH_m (J g^{-1})	Crystallinity (%)
25	–	173	23.4	36
90	118	172	27.1	40[a]
100	127	171	26.4	39[b]
110	133	170	29.3	41
120	145	170	29.7	43
125	151	171	29.2	–
130	152	172	29.6	43
135	157	170	28.7	–
140	162	170	32.6	45

[a] Sample annealed for 136 h
[b] Sample annealed for 72 h

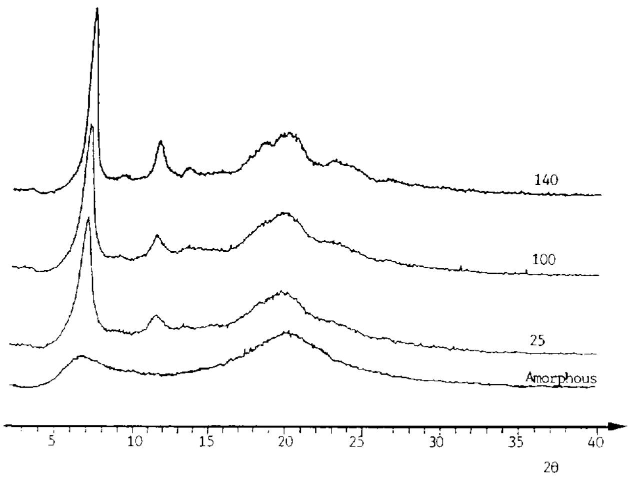

Figure 3 X-ray spectra of CTB annealed at different temperatures (°C)

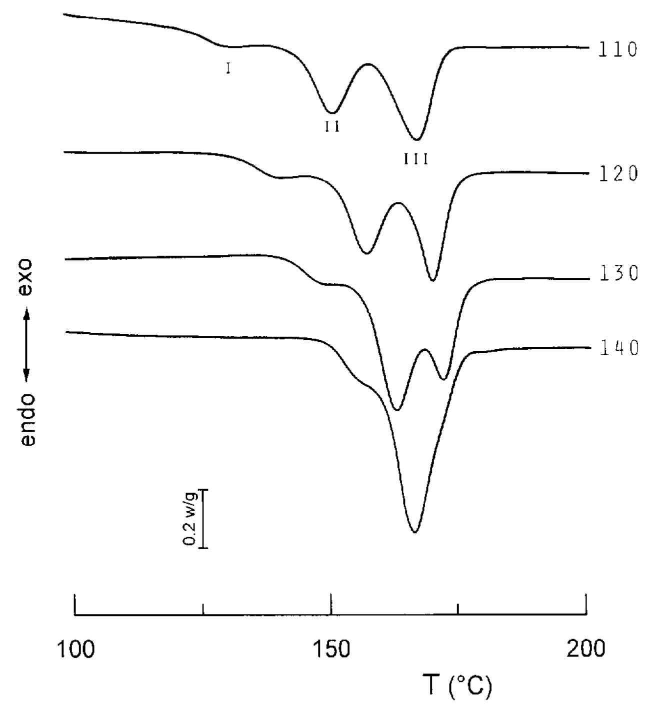

Figure 4 Calorimetric curves of CTB crystallized from the glass at different temperatures (°C)

are very similar, and some typical results are shown in *Figure 4*. At low crystallization temperatures, three melting endotherms are observed in both series. With increasing crystallization temperature, the melting endotherms evolve into one. Analogous behaviour is commonly observed for isothermally crystallized polymers[18], and the three endotherms (called I, II and III with increasing temperature) are usually attributed to: melting of crystals formed by a secondary crystallization process (endotherm I), melting of crystals grown by normal primary crystallization (endotherm II) and melting of crystals formed by recrystallization during the d.s.c. scan (endotherm III).

Figures 5 and *6* provide some X-ray spectra of CTB crystallized from the glassy and from the molten state respectively. The features of the scattering curves in both series are alike, with the exception of the spectra related to $T_c = 140°C$, in which the sample crystallized from the glassy state exhibits a higher intensity than that of the melt-crystallized sample. In addition, the peak centred at $2\theta = 6.5°$ is found to be much sharper and intense in isothermally crystallized CTB than the corresponding peak of the annealed powder (compare *Figures 5* and *6* with *Figure 3*). Pertinent d.s.c. and X-ray data are collected in *Table 2*.

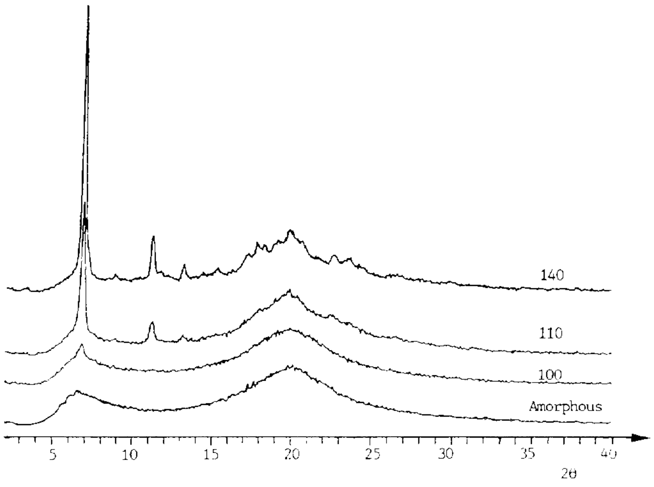

Figure 5 X-ray spectra of CTB crystallized from the glass at different temperatures (°C)

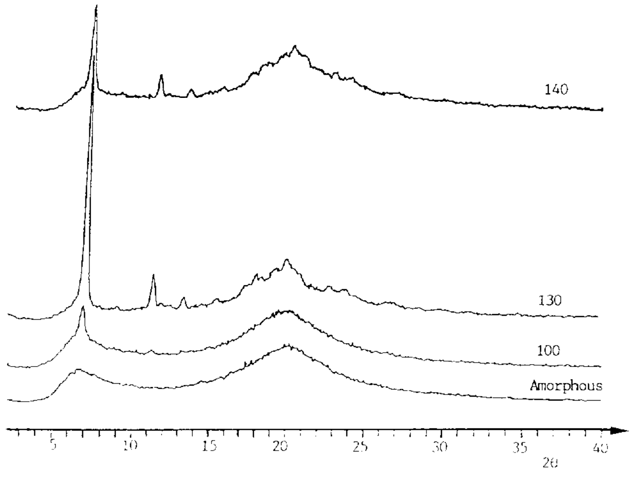

Figure 6 X-ray spectra of CTB crystallized from the melt at different temperatures (°C)

Table 2 Calorimetric and X-ray data of CTB samples crystallized at different temperatures T_c in the oven

T_c (°C)	100	110	115	120	125	130	135	140
Samples crystallized from the molten state								
T_{m1} (°C)	–	132	136	140	145	148	–	–
T_{m2} (°C)	–	153	157	159	160	162	164	166
T_{m3} (°C)	173	169	172	171	172	170	–	–
ΔH_m (J g^{-1})	8.3	16.4	20.1	21.7	21.5	21.1	19.3	17.0
Cryst. (%)	11	18	26	30	30	31	29	19
Samples crystallized from the glassy state								
T_{m1} (°C)	–	132	135	141	145	151	154	–
T_{m2} (°C)	–	151	153	158	160	163	167	167
T_{m3} (°C)	173	168	167	171	171	172	173	–
ΔH_m (J g^{-1})	5.4	14.0	17.1	19.0	20.9	21.8	22.1	21.7
Cryst. (%)	6	17	24	31	30	30	29	31

Table 3 Calorimetric data of CTB crystallized at different temperatures in the d.s.c.

T_c (°C)	T_{m1} (°C)	T_{m2} (°C)	T_{m3} (°C)	ΔH_m (J g^{-1})
113	134	154	169	17.7
118	138	157	171	17.2
123	143	159	171	17.6
128	148	160	170	17.3
133	150	163	170	17.6
138	156	167	–	17.8
143	158	168	–	16.7
147	–	172	–	14.9
152	–	172	–	13.7
157	–	175	–	11.4

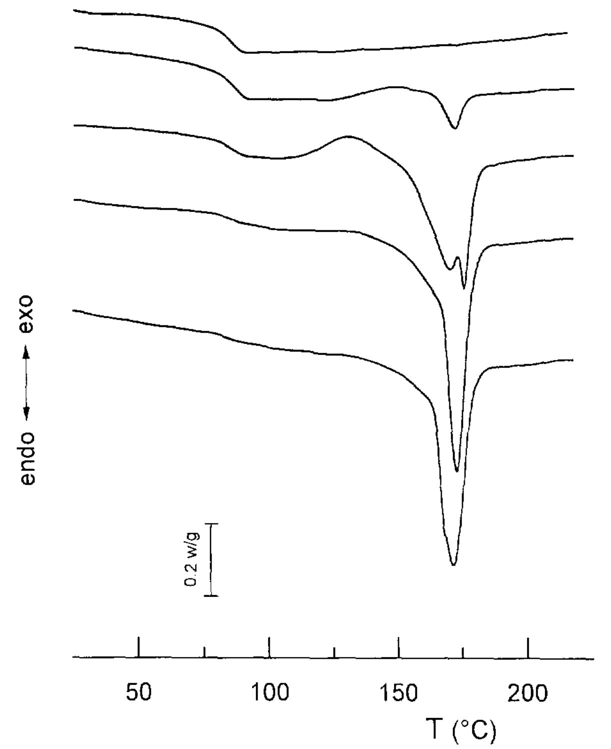

Figure 7 Calorimetric curves of CTB after partial melting (see text)

In order to explore the melting point *versus* T_c dependence over a wider range of crystallization temperatures, CTB samples were isothermally crystallized directly in the d.s.c. cell at T_c between 113 and 157°C according to procedure C described in the 'Experimental' section. Subsequent d.s.c. scans confirm the behaviour previously discussed in connection with *Figure 4*, and the corresponding results are reported in *Table 3*. No X-ray experiments were carried out on these samples.

Figure 7 shows the calorimetric curves of CTB powder partially melted in the d.s.c. pans by heating to different temperatures (heat treatment D). After heating to 160°C and rapid cooling to −40°C, the d.s.c. trace (bottom curve in *Figure 7*) exhibits a small step, in correspondence with the glass transition, and a large melting endotherm. Heating to progressively higher temperatures gradually destroys crystallinity, and subsequent d.s.c. curves show an increase in the specific-heat increment at T_g and a decrease of the melting area. Concomitantly, a cold-crystallization exotherm appears between glass transition and melting. For CTB quenched from 220°C to −40°C, only the glass-to-rubber transition is revealed by d.s.c. (top curve in *Figure 7*). Values of ΔC_p and ΔH_m pertaining to samples with different amorphous/crystalline ratio are collected in *Table 4*. The heat of fusion ΔH_m, representative of initial crystallinity, was calculated from the difference between the enthalpy associated with the whole melting endotherm and the crystallization exotherm.

DISCUSSION

The results collected in *Table 3* can be used to calculate the equilibrium melting point T_m° of CTB crystals. With this aim, the observed melting temperatures are plotted in *Figure 8* as a function of T_c. It can be noted that the

Table 4 Specific-heat increment at T_g and heat of melting of CTB with different amorphous/crystalline ratio

ΔC_p (J g^{-1} °C^{-1})	ΔH_m (J g^{-1})
0.084	25.0
0.113	20.4
0.126	19.8
0.150	17.4
0.185	12.0
0.200	10.0
0.205	9.0
0.221	8.4
0.224	6.8
0.230	7.0
0.249	4.6
0.250	4.0
0.267	3.8
0.285	0.6
0.290	0.0

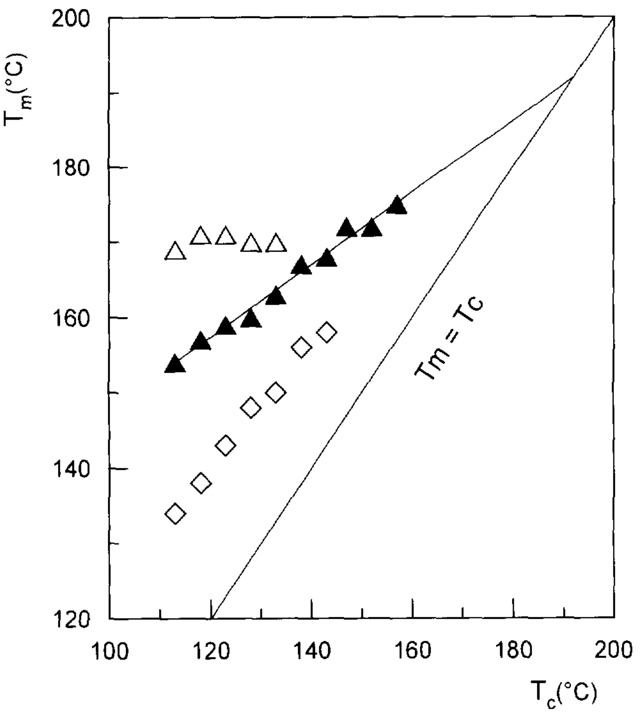

Figure 8 Melting temperatures of isothermally crystallized CTB as a function of crystallization temperature: (◇) endotherm II; (▲) endotherm II; (△) endotherm III

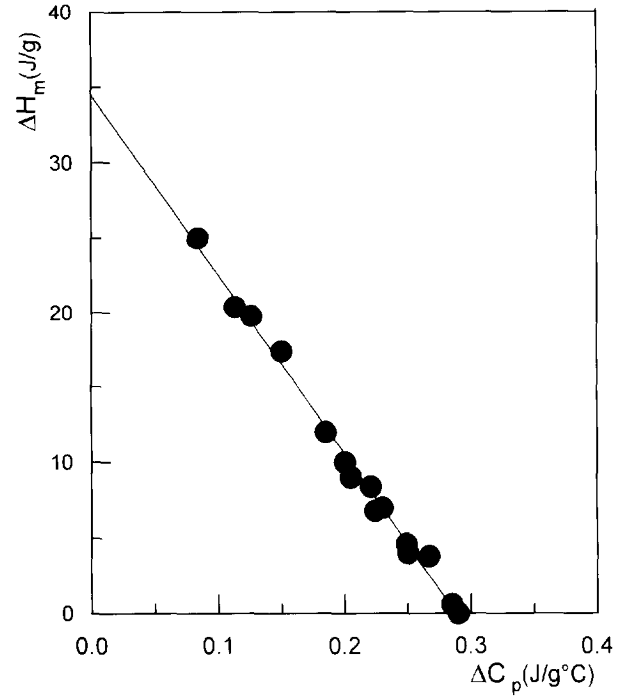

Figure 9 Heat of melting as a function of specific-heat increment of CTB with different crystallinity degree

difference between the peak temperature of endotherm I and T_c is approximately constant and amounts to about 20°C, in substantial agreement with the results obtained for samples crystallized in the oven (*Table 2*). Endotherm II is clearly related with the original main crystal population and its peak location increases with increasing T_c, reflecting the higher perfection of the crystals formed at higher temperature. Endotherm III is observed at a rather constant temperature only for T_c values up to 133°C and it can be taken as indicative of partially molten material that recrystallizes on heating into more perfect crystals. With increasing T_c, the originally grown material improves its degree of perfection up to a point where no further recrystallization occurs during the d.s.c. scan. It has been found that an increase in the d.s.c. heating rate reduces the recrystallization ability, drastically decreasing the area of the third melting peak.

By applying the Hoffman–Weeks extrapolation method[20] to the peak values of endotherm II, it is possible to evaluate the equilibrium melting temperature T_m° from the intersection of the experimental linear relationship with the reference line $T_m = T_c$. Such extrapolation yields a value of $T_m^\circ = 192$°C for CTB, slightly lower than that (206°C) obtained by Mandelkern and Flory[10] by measuring the melting-point depression in the presence of diluents. The apparent discrepancy can arise from differences either in molecular weight or in the experimental method employed. However, it has to be pointed out that close inspection of the data reported in table III of ref. 10 leads to values of T_m° ranging from 190 to 220°C depending on the diluent used.

In order to estimate the equilibrium melting enthalpy ΔH_m° of 100% crystalline CTB, the relationship between the specific-heat increment at T_g and the heat of fusion of CTB samples with different degree of crystallinity (*Table 4*) was examined. The experimental ΔH_m *versus* ΔC_p data, plotted in *Figure 9*, show a very good linear fit: ΔC_p steadily decreases as the melting enthalpy (proportional to the degree of crystallinity) increases. The extrapolation to $\Delta C_p = 0$ gives a value of 34.5 J g^{-1} for ΔH_m° of CTB, in very good agreement with the value obtained by Mandelkern and Flory[10] from dilatometric measurements.

Figure 10 shows the crystallinity of CTB obtained by X-ray analysis (*Tables 1* and *2*) as a function of the crystallization (T_c) or annealing temperature (T_a). It is clear that the crystallinity of the samples annealed from the powder increases slightly with increasing T_a and that the degree of crystallinity of the powder samples is higher than that arising from the other thermal treatments. This result can be accounted for by recalling that as-supplied CTB is obtained through precipitation from solution (in effect a 'solvent crystallization'), a procedure that allows crystallization of a larger fraction of the sample.

In *Figure 10*, a rapid increase in WAXS crystallinity is observed for samples isothermally crystallized between 100 and 120°C, then a fairly constant value is found from 120 to 135°C. The sample melt crystallized at $T_c = 140$°C has a lower crystallinity than the corresponding sample crystallized from the glassy state, while at the other crystallization temperatures the results for both series are very close irrespective of the type of thermal history. The different behaviour may be ascribed to differences in nucleation rate during crystallization from the melt or from the glass[18]. At temperatures between 100 and 135°C the nucleation rate of CTB is fast regardless of thermal history, and maximum crystallinity is reached between 120 and 135°C in the experimental conditions used (2 h isotherm). When T_c exceeds 135°C, crystallization of CTB from the glass allows formation of nuclei at low temperature, upon which large crystals can grow at high temperature. In CTB cooled from the melt to

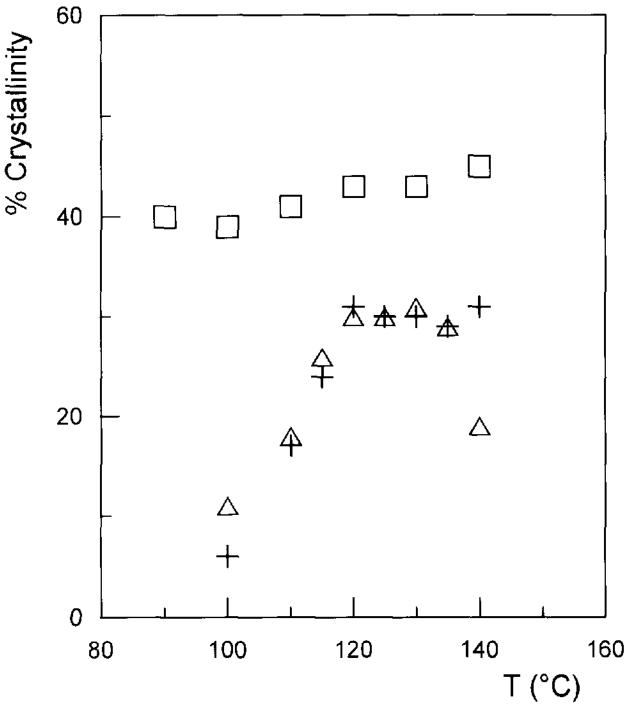

Figure 10 Percentage crystallinity of CTB as a function of crystallization or annealing temperature: (△) melt crystallized; (+) crystallized from the glassy state; (□) annealed powder

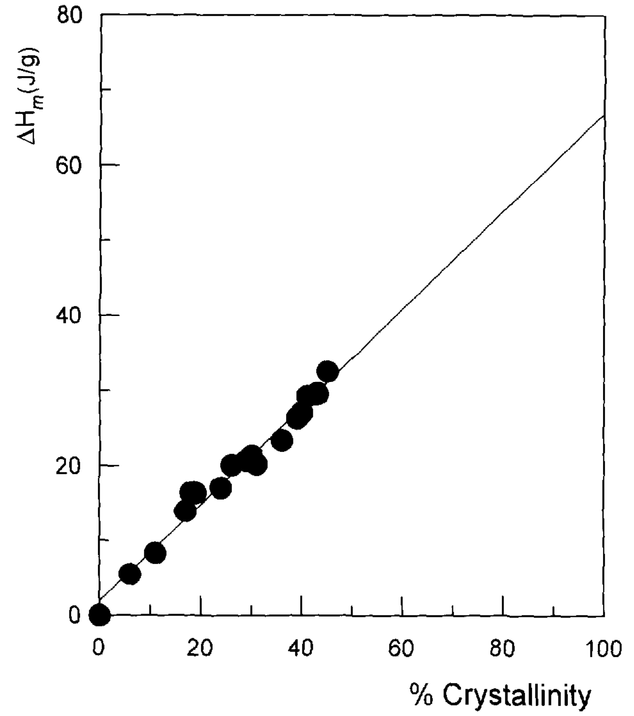

Figure 11 Enthalpy of melting as a function of X-ray crystallinity

140°C, the nucleation process is much slower, requiring large induction times and yielding lower crystallinity. Unfortunately, CTB does not crystallize in a spherulitic morphology and optical microscopy cannot be used to obtain information on the crystal growth rate as a function of T_c. On the other hand, the curve shown in *Figure 10* suggests that the overall crystallization rate has a maximum in the proximity of 130°C.

Isothermal crystallization experiments performed directly in the d.s.c. are not suitable to calculate the crystallization half-time because of difficulties in defining the initial baseline owing to exceedingly fast nucleation rate. Information on the crystallization process can be derived from the T_c dependence of the time corresponding to the isothermal crystallization peak. Although the peak time is usually smaller than the half-time of crystallization, it is also inversely proportional to the crystallization rate and in the present case shows a minimum at $T_c = 135°C$, in keeping with the conclusion derived from WAXS measurements.

The d.s.c. and X-ray results of CTB samples examined by the two techniques are summarized in *Figure 11*, where the heat of melting is plotted as a function of the corresponding WAXS crystallinity. Since both d.s.c. and X-ray measurements are more sensitive to the quantity of crystals than to the perfection of crystallites, the data fit on a linear relationship without respect to the thermal history of the samples. However, extrapolation to 100% crystallinity provides a value of $\Delta H_m^\circ = 67\,\mathrm{J\,g^{-1}}$, which is nearly twice that obtained from the ΔH_m vs. ΔC_p plot of *Figure 9* and is noticeably higher than all available literature data for tri-substituted cellulose derivatives[21]. A component that might possibly contribute to this abnormally high value of ΔH_m° is residual macroscopic ordering of the polymer chains in quenched CTB, taken as amorphous reference sample. In this connection, it is worth pointing out that many cellulose derivatives form lyotropic and thermotropic liquid-crystalline phases as a consequence of the relative stiffness of the cellulose chain[22]. Under certain conditions, solid films of amorphous cellulose triacetate were found to be relatively well ordered orientationally, indicating the presence of a glassy anisotropic phase at room temperature[23]. Moreover, Shiratsuchi *et al.*[24] showed that some cellulose triesters, including CTB, behave markedly differently from amorphous polymers in the molten state, owing to the presence of some orientation of the main chain at high temperature. Finally, Ioelovich *et al.*[25] observed an ordered mesomorphic state in the glassy state and suggested a model according to which the pyranose units form layers with an interlayer distance of 0.44 nm. Quite interestingly, this distance corresponds to the *d* value arising from the maximum centred at $2\theta = 20°$ in the present X-ray spectra. In line with these observations, the spectrum of quenched CTB, used to calculate the crystallinity according to the Hermans-Weidinger method, can contain scattering intensity contributed by some residual order, and therefore does not correspond to a truly 'amorphous' sample. Since no melting was detected in d.s.c. curves on quenched CTB, we conclude that the macroscopic ordering of the polymer chains is not destroyed upon heating at 220°C.

CONCLUSIONS

D.s.c. measurements provided a value of 192°C for T_m° and $34.5\,\mathrm{J\,g^{-1}}$ for ΔH_m° of CTB. Crystallinity measurements by WAXS on samples crystallized from the glassy and from the molten state at different temperatures for 2 h showed that the crystallization rate of CTB has a maximum at about 130°C. Calorimetric heat of melting and X-ray crystallinity degree fitted on a linear relationship, regardless of the thermal history. Extrapolation to 100% crystallinity yielded a value of ΔH_m° twice that obtained from the d.s.c. data. We suggest that this disagreement is due to an underestimation of WAXS crystallinity, resulting from the presence of macroscopic order in the quenched CTB sample taken as amorphous reference.

ACKNOWLEDGEMENTS

We would like to thank Dr Craig Sass for his help with X-ray measurements and Eddie Forbes for some d.s.c. measurements. We are particularly grateful to Eastman Chemical Co. and East Tennessee University for their cooperation. This work was partially supported by the Italian Ministero della Università e della Ricerca Scientifica e Tecnologica.

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