An investigation of the thermal properties of cellulose tricarbanilate–polystyrene graft copolymers

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The thermal properties of a cellulose tricarbanilate–polystyrene graft copolymer and also unirradiated and irradiated cellulose, converted to the tricarbanilate, have been studied. Samples heated to specified temperatures have been examined by scanning electron microscopy. Simultaneous heating and visual appraisal have provided an understanding of the physical changes which take place on heating the samples. Data relating to the decomposition of the samples are presented which indicate that the grafted polystyrene has a marked influence on the thermal stability of cellulose tricarbanilate. Heating produces significant differences in the surface characteristics of the samples studied. Evidence is presented which shows that irradiation of cellulose produces changes in chemical reactivity which have an influence on subsequent chemical modification.

INTRODUCTION

Many of the characteristics of cellulosic graft copolymers have been thoroughly investigated as indicated by reviews which deal with this subject[1,2]. Included in this work are such important aspects as the kinetics and mechanisms involved[3,4], and the effects of additives, solvents, and swelling agents[5]. Where the products appear to have commercial significance, interest has been shown in the physical properties of the resultant grafted products, especially with regard to wear and handling properties. Since the greater demand has centred on fibrous cellulosic substrates, it is understandable that interest in property modification has centred on cotton, rayon and the cellulose acetates. Recent advances in paints, inks and printing technology have meant that new avenues have opened up for those cellulose derivates which are less fibrous in character. This has led to interest being generated in the thermal properties of cellulose derivates. Our particular interests lie in cellulose graft copolymers and copolymers containing substituted celluloses.

Here we wish to report results obtained during the thermal characterization of a cellulose tricarbanilate–polystyrene (CTC–PS) graft copolymer and its constituent homopolymeric species (CTC and PS). The techniques used include differential thermal analysis (d.t.a.), thermogravimetric analysis (t.g.a.), hot stage optical microscopy (h.s.o.m.) and scanning electron microscopy (s.e.m.). We hope to demonstrate that a combination of these four techniques can provide a great deal of insight into the nature of this type of graft copolymer. The samples being studied here have been the subjects of extensive study in investigations aimed at understanding their dilute solution properties as seen in both single and mixed solvents through light scattering and differential refractometry[6]. We hope to compile data on cellulose graft copolymers which will lead to a deeper understanding of the nature of non-fibrous cellulosic copolymers.

Cellulose tricarbanilate has been studied extensively for its solution properties[7] and its proven chemical stability[8]. CTC is also of interest because of the significant level of protection afforded cellulose by the inclusion of carbanilate groups into the structure[9]. However, very little is known of the thermal properties of CTC, of the effect of PS on the thermal stability of CTC, of the mode of ultimate breakdown of CTC and equally of the effects of high energy radiation on the thermal properties of CTC and CTC–PS copolymers.

EXPERIMENTAL

General

Although specific details relating to the preparation of CTC and the CTC–PS copolymer have been given elsewhere[9] a brief summary is included for ease of reference.

Styrene was grafted onto deplasticized, tared regenerated cellulose film using gamma-radiation-induced techniques in the simultaneous, heterogeneous mode under vacuum. Features of the kinetics and mechanisms involved in grafting have been disclosed. Occluded homopolymer was removed from the grafted films by Soxhlet extraction with dioxane/water (98/2). Subsequent drying and weighing gave the level of apparent grafting. Ungrafted cellulose was removed from the copolymer by repeated extraction with Cadoxen (tris-ethylene diamine cadmium dihydroxide). This extraction provided relatively large quantities of cellulose which, although not grafted, had been subjected to exposure to high energy radiation. This cellulose is the intermediate in the formation of irradiated CTC which is referred to later.

The non-extracted product (essentially true cellulose–polystyrene graft copolymer) was then thoroughly dried and carbanilated from a pyridine–phenyl isocyanate mixture under initially heterogeneous conditions at 105°C. Reaction proceeded over 24 h. A sample of unmodified regenerated cellophane film was also carbanilated to be used for comparison purposes. This sample is later referred to as unirradiated CTC. All samples were thoroughly washed to ensure the complete removal of reagents and then dried at 40°C under vacuum.

Instrumentation

Differential thermal analysis measurements were taken on a Du Pont 900 thermal analyser using a nitrogen purge (0.2 l/min) and a heating rate of 10°C/min. After an initial through-scan of each sample, a modification of the standard procedures was adopted. This allowed features of interest to be scrutinized more closely. Using fresh batches of samples, reruns were undertaken until the temperature was reached at which a transition had been previously observed. Now heating was ceased and the sample isolated. The procedure was repeated to give the product after the first transition (endotherm, exotherm etc). This repetition was continued until a sample was obtained for each point of interest, noted in the thermograms of the irradiated CTC, the non-irradiated CTC and the CTC–PS copolymer samples, at various stages of their heating programme. The partly degraded or modified samples were then subjected to scanning electron microscopy.

Thermogravimetric analysis was used to provide information as to the nature of the decomposition processes and ultimately the composition of the CTC–PS copolymer. In addition we sought values for the activation energies of decomposition and information relating to the effects of high energy radiation on regenerated cellulose film. Measurements were taken on a Stanton Redcroft Thermobalance using a heating rate of 8°C/min and a nitrogen purge of 0.2 l/min.

Electron micrographs of irradiated CTC, unirradiated CTC and the CTC–PS copolymer, at various stages of their thermal decomposition, were taken. Samples were mounted with double-faced adhesive tape on specimen studs for the JEOL (JSM 15) s.e.m. and then coated under vacuum with a thin layer of gold to a depth of 200 Å using a Polaron s.e.m. coating unit, model E5000. Scans were made at reduced pressure, and an operating voltage of 15 kV. A preliminary survey indicated that beam damage was negligible. The micrographs shown are representative of each sample type investigated in this programme. Samples were scanned by oscilloscope viewing and ancillary T.V. monitoring before being photographically recorded.

As is always the case with photographic recording in electron microscopy, a measure of selectivity must occur in the sections chosen for recording. However, in each instance, sections were taken which were representative of the whole sample. Each sample was examined before heating and at each of the stages of decomposition as shown by d.t.a.

Hot stage optical microscopy concerns visual observations of the behaviour of solids or solutions over a range of temperatures. Depending on the particular facilities available, the range 0°–400°C can be studied in a controlled manner. In our work, this stage was considered adequate. The experimental set-up consists of three essential components: the hot stage cell, the microscope, and a heating/temperature controlling unit. The hot stage cell used here was designed for use on the stage of a Vickers M41 Photoplan microscope, though it can easily be accommodated on other microscopes. Details of the cell design and construction have been described elsewhere[10]; hence it will suffice to state that we were able to monitor visually changes which took place in the samples in the temperature range from 0° to 400°C. Although this approach carries the disadvantages inherent in optical microscopy, (lack of depth of field etc.) it was hoped that significant information would be obtained from its use.

A finely divided sample was presented to the microscope, encased between two microscope slides within the high temperature hot stage cell. A programmed heating rate (8° C/min) was used and any changes in sample form during heating were recorded photographically. Samples were photographed before heating, on completion of the heating cycle, and both prior to and after any significant physical or chemical changes. Such changes were identified by previously run differential thermal analyses. In our observations we have used a X200 overall magnification throughout. The microscope slides were of thickness within the limits of image deterioration for a low power objective and also within the desired strength characteristics, bearing in mind some of the possible pressure changes likely to take place on heating and subsequent decomposition of samples undergoing investigation. The temperature control unit provides high accuracy and easy setting to within ±0.2°C provided draughts are excluded. Samples were analysed under two modes: in natural light, and between crossed polars.

RESULTS

The thermograms shown in *Figure 1* relate to unirradiated cellulose converted to the tricarbanilate (A), irradiated cellulose extracted from the apparently grafted copolymer and subsequently converted to the tricarbanilate (B), and the cellulose–PS copolymer whose cellulose component has been converted to the tricarbanilate (C). Thus we have unirradiated CTC (A), irradiated CTC (B), and the CTC–PS copolymer (C).

From C the composition of the copolymer was calculated at 76% cellulose tricarbanilate and 24% polystyrene. This result is in reasonable agreement with those obtained by other methods of analysis: elemental analysis (70.6%:29.4%); differential refractometry (70%:30%); and gravimetric procedures (67.6%:32.4%). Hence we have another satisfactory means of obtaining the composition of cellulose copolymers. The observed differences between the thermograms A and B and the similarities between B and C in the 320°–420°C temperature range give an indication that high energy gamma radiation causes pronounced changes in the reactivity of cellulose which are maintained in subsequent carbanilation. Thus the CTC–PS copolymer has similarities with the ir-

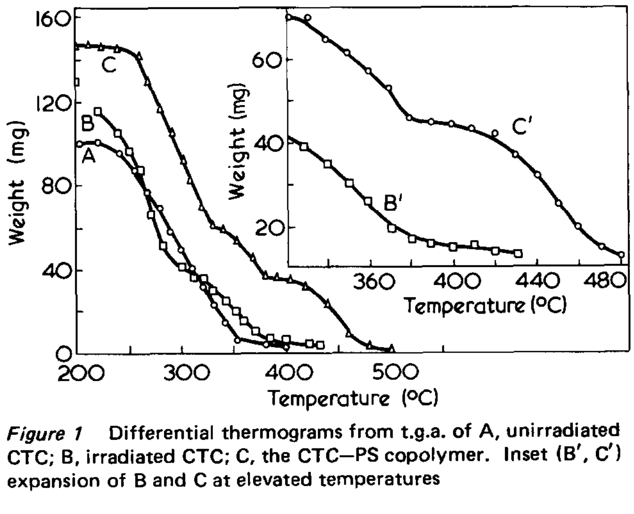

Figure 1 Differential thermograms from t.g.a. of A, unirradiated CTC; B, irradiated CTC; C, the CTC–PS copolymer. Inset (B', C') expansion of B and C at elevated temperatures

Table 1

Sample and temperature range	Method of analysis	Assumed reaction order	Activation energy of decomposition (kJ/mol)	Correlation coefficient
Non-irradiated CTC 160°–270°C	Reich and Levi[11]	0	59.2 ± 3.2	–
		1	64.8 ± 4.0	–
	Reich[12,13] (linear regression analysis – l.r.a.	0	57.2	0.96
		1	65.6	0.96
Irradiated CTC 160°–230°C	Reich and Levi[11]	0	40.0 ± 1.6	–
		1	44.0 ± 1.2	–
CTC–PS copolymer	Reich and Levi[11]	0	48.0	–
		1	49.2	
Section (a) (230°–330°C)	Reich (l.r.a.)[12,13]	0	26.4	0.86
		1	44.0	0.95
Section (b) (340°–400°C)	Reich (l.r.a.)[12,13]	0	81.2 ± 1.2	0.92
		1	112.0 ± 1.6	0.95
Section (c) (410°–480°C)	Reich (l.r.a.)[12,13]	0	No meaningful result	–
		1	166.0 ± 0.8	1.0

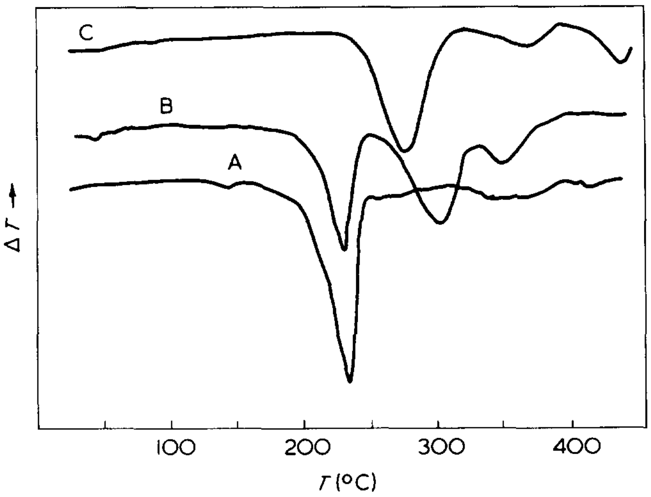

Figure 2 Differential thermograms from d.t.a. of A, unirradiated CTC; B, irradiated CTC; C, the CTC–PS copolymer

radiated CTC though it possesses the added stability afforded by the grafted polystyrene branches.

The thermograms differ considerably in construction. Non-irradiated CTC produces a monosigmoidal trace A while the irradiated CTC and the CTC–PS copolymer give multisigmoidal thermograms. In order to provide greater detail of the decomposition processes, the thermograms were thoroughly analysed.

Various methods have been developed for treatment of thermogravimetric analytical data. Each of these has its own problems and is more suited to certain types of decomposition process. The method of Reich and Levi[11] can be used with some confidence in decompositions where the following conditions apply:

(1) all measurements made under the same conditions;

(2) the t.g.a. curve does not possess more than one plateau:

(3) the t.g.a. curve is free from irregularities;

(4) extensive decomposition (up to 50%) takes place in the temperature range considered.

Here we have a means of obtaining the overall activation energy of decomposition of the unirradiated CTC sample. This method of analysis was also applied to the irradiated CTC despite the fact that condition (2) is not obeyed. Values for E_d, the activation energy of decomposition, are given in *Table 1.*

An alternative method of analysis is that proposed by Reich[11,12] which is more mathematically based and very sensitive to minor fluctuations in experimental traces. This procedure was applied to data from the thermogram of non-irradiated CTC. Details concerned with these methods of thermogram analysis have been fully documented by the authors and will not be repeated here.

In the thermogram from the CTC–PS copolymer three distinct types of decomposition are indicated. These sections are highlighted when the data are plotted in terms of the weight remaining on increasing the temperature. The first section accounts for 59% pyrolysis and was analysed by the methods of Reich[12] and Reich and Levi[11]. The second and third sections were analysed by the method of Reich[12] only. Values of the activation energy of decomposition together with incidental correlation coefficients are given in *Table 1.* Analyses were conducted assuming a value of the reaction order, *n*, of both unity and zero.

The thermograms obtained from d.t.a. studies, and subsequently used in preparing samples for electron microscopy‘ are shown in *Figure 2a* (unirradiated CTC), *Figure 2b* (irradiated CTC) and *Figure 2c* (CTC–PS copolymer). The relative simplicity of the trace produced by the unirradiated CTC is supported by observations reported elsewhere[14]. The slight endotherm seen at 132°C (non-irradiated CTC) is absent from the other thermograms. The endotherm commencing at 197°C and minimizing at 226°C is typical of cellulose tricarbanilate. It is clear that *Figures 2b* and *2c* show definite similarities of decomposition. However there is evidence of enhancement of thermal stability being imparted to the CTC by the presence of the grafted polystyrene. This is seen in the displacement, to a higher temperature, of the three endothermic troughs. It is worth noting that the primary endotherms correspond to the initial weight losses, observed in t.g.a. studies. with respect to the temperatures at which changes were noted. The initial endotherm appears at the same temperature for both the irradiated and non-irradiated varieties of CTC.

A visual appraisal, achieved by hot stage optical microscopy of changes observed in d.t.a. and t.g.a. studies, confirmed our suspicion that the decomposition processes are complex and differ for the three samples under investigation. *Figure 3* portrays the change in physical characteristics in non-irradiated CTC under the conditions observed in the Figure legend. On heating above 160°C, breakdown occurs to produce a vapour which immediately condenses on the coverslide of the microscope as very sharply defined needle-like crystals (*Figure 3b*). On holding the temperature at 185°–187°C these crystals are seen to grow at a relatively rapid rate, supplied by vapour from the decomposing CTC (*Figure 3c*). An increase in the temperature beyond 203°C

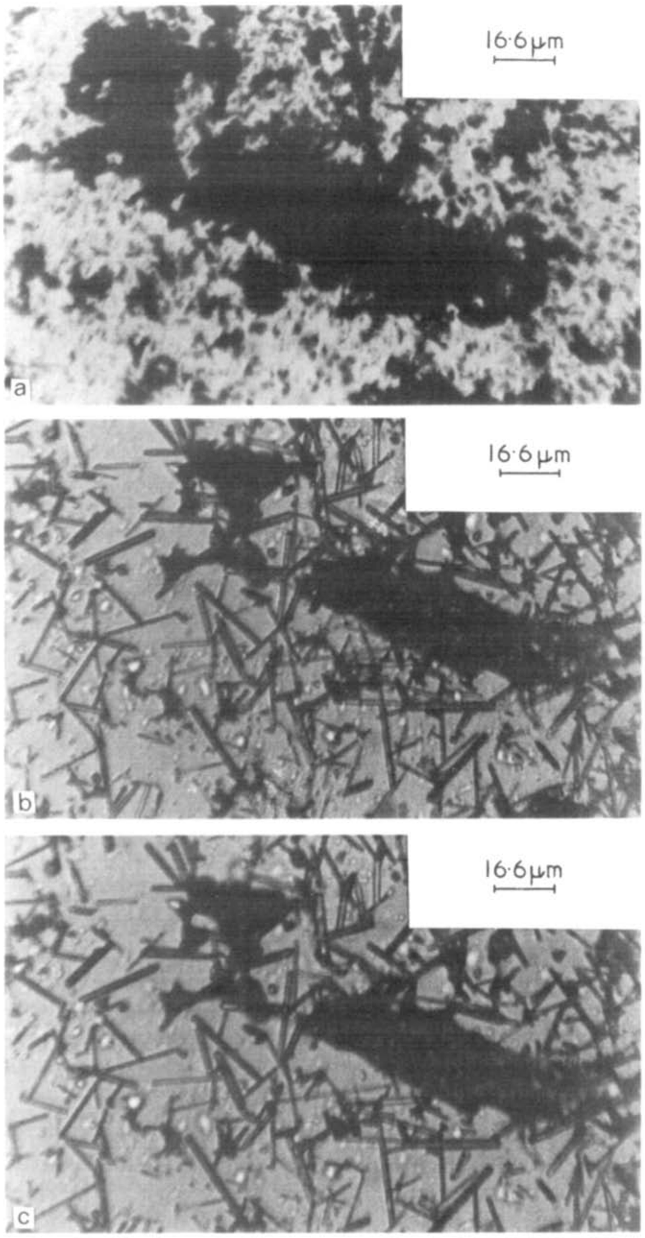

Figure 3 Hot stage optical microscopical examinations. Unirradiated CTC: (a) unheated; (b) at 164°C; (c) at 187°C. Prints 3X (X200)

leads to rapid melting of these crystals. At this point little of the original CTC remains, though this residue appears to undergo a decomposition process normally associated with unsubstituted cellulose. There are indications that the continued growth of the large crystals occurs at the expense of the smaller ones.

Similar observations were made with the irradiated CTC though here the extent of crystallization was reduced. The product as seen after the initial decomposition (165°C) is shown in *Figure 4a*, while *Figure 4b* shows the sample at 187°C, when crystal growth is taking place. The second and third endotherms shown in *Figure 2b* must be associated with changes taking place in the cellulosic residues. Such changes cannot be accounted for from evidence obtained by visual examination since no further changes were observed by optical microscopy.

Examination of the CTC–PS copolymer under these conditions showed no vaporization and crystallization in the temperature range studied (25°–425°C). A partial melt process was seen at 236°C which produced a swollen ash that underwent little change until 415°C when an ill-defined melting process occurred. This gives direct visual evidence (*Figure 5*) of the effect of polystyrene grafts on the thermal stability of CTC. Thus the composite is stable through melting and beyond the temperatures normally associated with the decomposition of styrene itself. Electron micrographs were taken of each of the three samples, the irradiated and non-irradiated CTC and the CTC–PS copolymer, after heating to the given temperature. The micrographs relate to residues unless otherwise specified. The details are given in the accompanying legends where the term exo or endo refers to the changes noted on the d.t.a. trace at the particular temperature.

Figure 6 deals with non-irradiated CTC at various temperatures. *Figure 6a* shows the sample before heating. Here

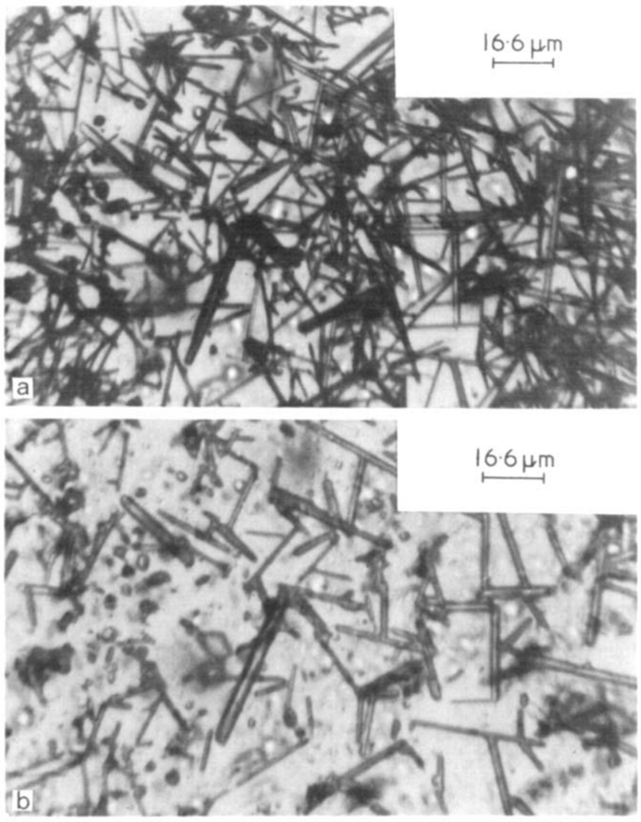

Figure 4 Hot stage optical microscopical examination. Irradiated CTC: (a) at 165°C; (b) at 187°C. Prints 3X (X200)

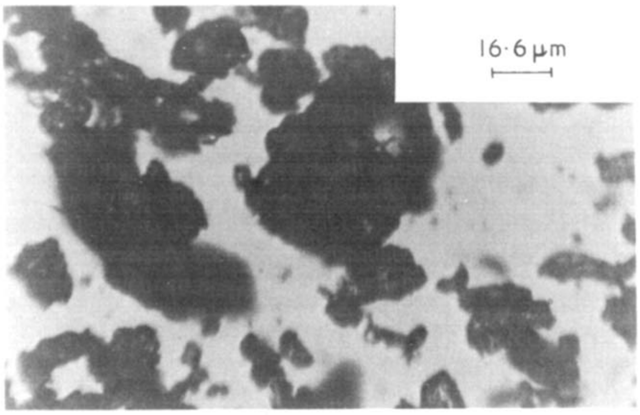

Figure 5 Hot stage optical microscopical examination. CTC–PS copolymer, 420°C. Prints 3X (X200)

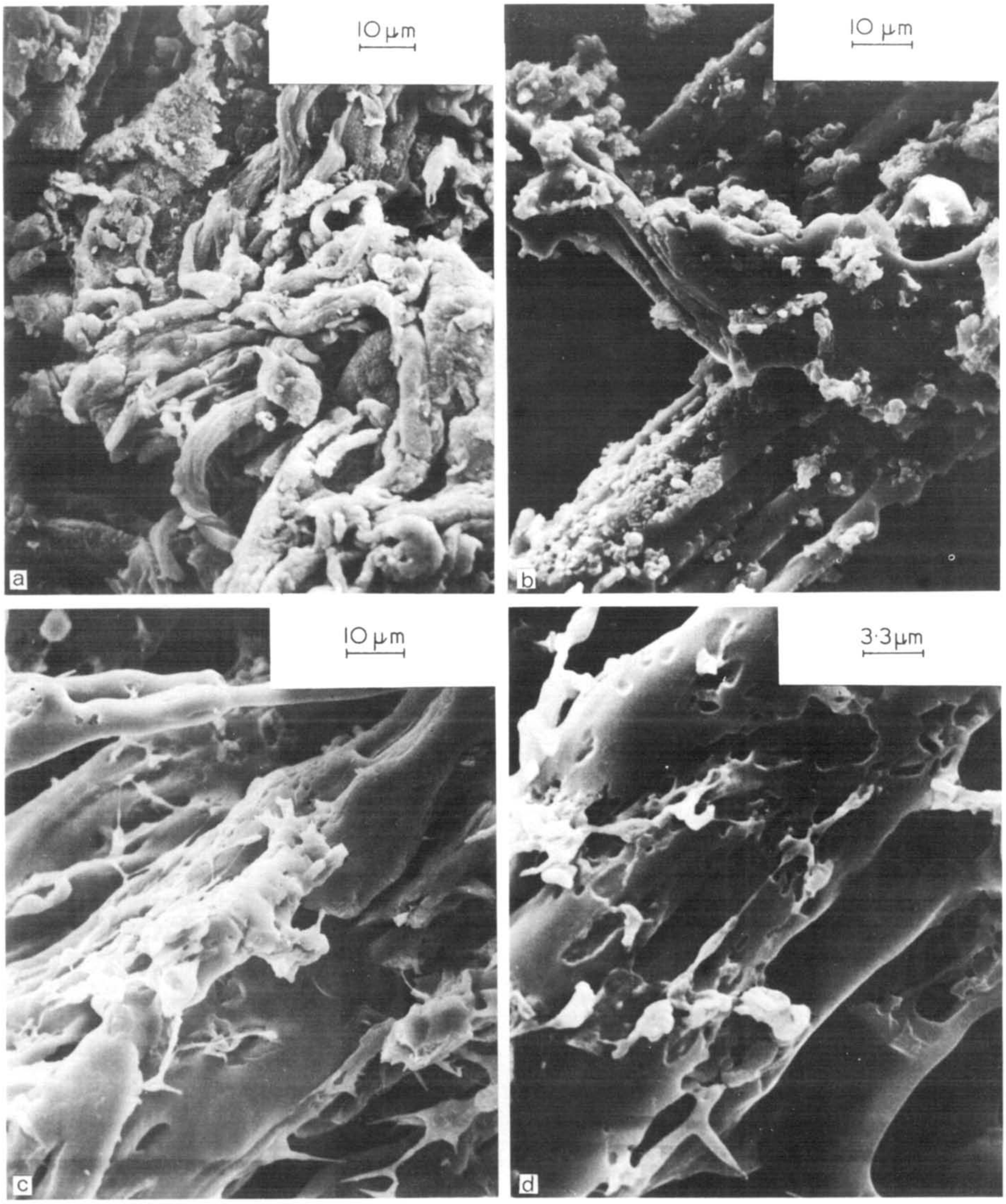

Figure 6 Electron micrographs. Non-irradiated CTC: (a) × 10^3, unheated; (b) × 10^3, after 132°C endo; (c) × 10^3 after 250°C endo; (d) × 3 × 10^3, after 250°C endo

we see the amorphous nature of the sample, each chain having a semi-independent existence. *Figure 6b* represents the sample after heating to 132°C (endo on d.t.a.) in which there is evidence of partial phase change during which the fibres are expanding and losing their separate identity. *Figures 6c* and *6d* show the residue after the 250°C endotherm. In these micrographs we see the smooth nature of the highly expanded sections which appear as a continuous melt residue. *Figure 7* shows the micrograph of a crystal corresponding to those shown in *Figures 3* and *4*. However, this crystal has grown on the surface of the residue during the cooling operation which follows from isolating the

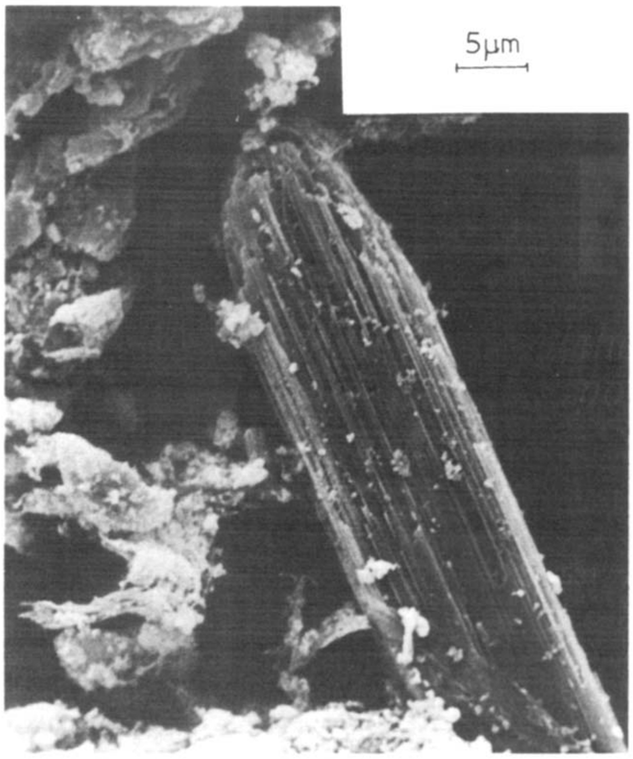

Figure 7 Electron micrograph. Non-irradiated CTC X 2 X 10^3 after heating to 185°C. Crystal growth

sample from the differential thermal analyser on achieving a temperature of 185°C. Clearly shown is the needle-like nature of the crystals and the form of growth on the surface from the inner core in layer-like fashion. In *Figure 8* are displayed the micrographs from the irradiated CTC sample, before and after heating. *Figure 8a* shows that the irradiated CTC exists in a less fibrous, more film-like state than its unirradiated CTC counterpart. Heating through the various changes noted in d.t.a. studies gives little evidence of any melt and flow characteristics in that the residues invariably have amorphous open structures which is in complete contrast to the unirradiated samples.

Figure 9 displays the micrographs from the CTC–PS copolymer. The unheated sample (*9a*) has a scaled-fibre appearance when seen on the T.V. monitor and shows similar evidence of film formation as does *Figure 8a*. Similar micrographs for cellulose copolymers have been recorded elsewhere[15]. Heating to 200°C produced the residue whose micrograph is given in *Figure 9b*. Again there is little evidence of any flow, through the fibrous nature of the granules is still evident. Heating to higher temperatures in excess of 325°C produces a melt and flow condition which leads to coverage of the inner pores. The initial conclusion is that we have reached the melting temperatures of the CTC–PS chains and the PS component serves as a surface coating for the enclosed amorphous network. These flow characteristics are in marked contrast to the irradiated CTC and the unirradiated CTC. Irradiated CTC shows no tendency for flow and the unirradiated CTC, although flow occurs at relatively low temperatures, maintains a degree of surface order. This order is lost in the CTC–PS copolymer.

DISCUSSION

The effects of high energy radiation on cellulose have been thoroughly investigated both in terms of primary events as seen by techniques such as electron spin resonance spectroscopy[16] and also in changes in physical properties[17]. It is known that the events following irradiation are complex. This complexity is increased on storage of the irradiated cellulose, especially when such storage takes place in air[18]. The thermal degradation of cellulose has also been covered and shown to be complex even in the absence of side effects arising from irradiation[19]. Madorsky *et al.*[20] surmised that a random-chain scission process operates during thermal decomposition accompanied by the formation of laevoglucosan. This finding was supported by Golova *et al.*[21] who claimed yields of laevoglucosan of the order of 60%. Patel *et al.*[22] have studied the pyrolysis of cellulose and also cellulose acetylated to various degrees of substitution. Their comprehensive investigation considers the mechanisms involved in the pyrolysis reactions and provides data for the essential kinetic parameters. Although these kinetic parameters are of little direct relevance to the present investigation, they indicate that the pyrolysis of cellulose and cellulose acetate is far more complex than is that of unirradiated CTC.

On heating to 185°C, unirradiated CTC undergoes decomposition though the exact mechanism is as yet uncertain. This decomposition is accompanied by simultaneous evaporation of the volatile decomposition products, which leads to an overall endotherm in the d.t.a. trace. Analysis of t.g.a. data shows the activation energy of this decomposition to be low (58.0 kJ/mol), so the heat evolved would be small relative to the heat required for the vaporization of volatile products.

Pyrolysis of the irradiated CTC leads to an even lower value of E_a for the 160°–230°C region of the thermogram (42.0 kJ/mol) which indicates the lesser stability of the irradiated CTC in this temperature range. Because of difficulties in analysis, values of E_a corresponding to the second stage of the decomposition are not available. However this change is absent from the unirradiated CTC sample and possesses a higher though unknown activation energy. It is feasible that this second endotherm arises from decomposition of the cellulose residues or more tightly bonded carbanilate groups.

The CTC–PS possesses significantly greater overall thermal stability than either CTC variety. This is seen in the high temperature endotherm for the primary decomposition. Here we have no evidence for vaporization and subsequent crystallization. The endotherms are associated with melt or swelling processes and weight losses which are difficult to specify. The final melting process (410–480°C) concerns polystyrene branches in the PS–CTC copolymer. The value of E_a for this process, at 166 kJ/mol, is in agreement with independently published data for polystyrene decomposition[23] for which a radical chain reaction is assumed to be the mechanism of degradation.

Explanation for the increase in thermal stability of the PS–CTC copolymer without any interference in the mechanism of the subsequent decomposition is not easily found. The possibility of negative catalysis arises, though the pathway could be indirect. Evidence from the literature suggests that the breakdown of cellulose[22] derivatives and polystyrene[23] is free radical in character. Hence the polystyrene must interfere with the pathway which is open to unmodified CTC. Such interference could originate in the radiation induced graft copolymerization reaction which preceded carbanilation. Evidence is available indicating that Trommsdorff effects operate during the preparation of graft copolymers which have cellulose as the substrate[24]. This leads to the production of high molecular weight branches. Further work has shown the occurrence of intramolecular crosslink-

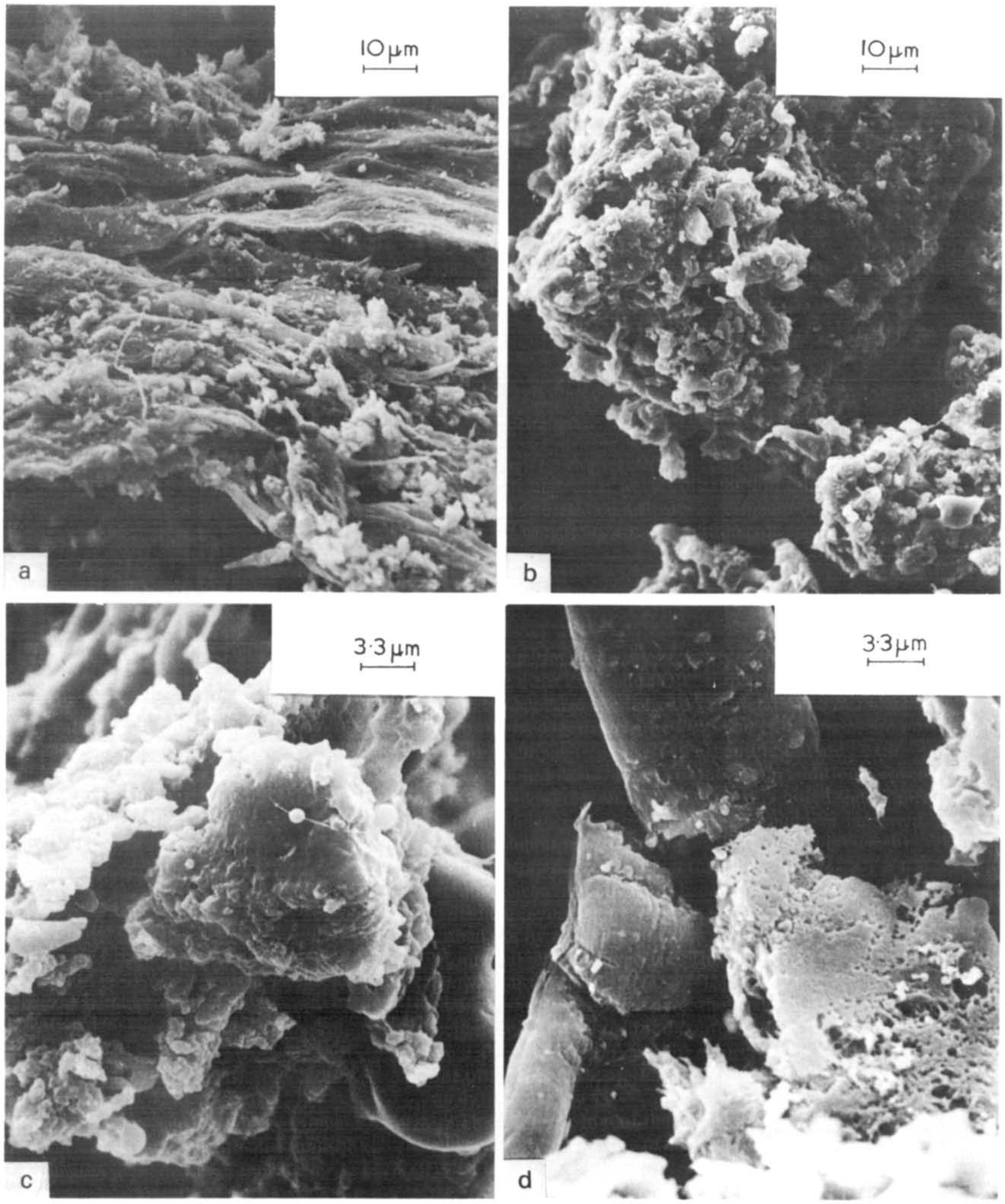

Figure 8 Electron micrographs. Irradiated CTC: (a) X 10^3 unheated; (b) X 10^3, 200°C endo; (c) X 3 X 10^3, 200°C endo; (d) X 3 X 10^3, heated to 325°C endo

ing within the graft copolymer[25]. Such crosslinks are maintained during carbanilation and would increase the thermal stability of the carbanilated celluloses relative to unmodified samples. These crosslinks could also explain the reluctance for release of volatile products on decompositon. On heating to the temperature at which polystyrene normally breaks down (300°C), little change is observed in the PS–CTC copolymer. Subsequent heating produces the examples of overall flow shown in the electron micrographs (*Figures 9c* and *9d*) which occur at a temperature in excess of 450°C. Again we have evidence for crosslinking having occurred during the preparation of the cellulose–polystyrene graft copolymer.

The nature of the crystalline species shown in *Figures 3* and *4* is being investigated and the information will be presented in due course. The electron micrographs shown in *Figures 6–8* relate to the residues at various temperatures. The amorphous nature of the residues from irradiated CTC suggest potential adsorption systems or catalyst supports. Such work would require information of the adsorption

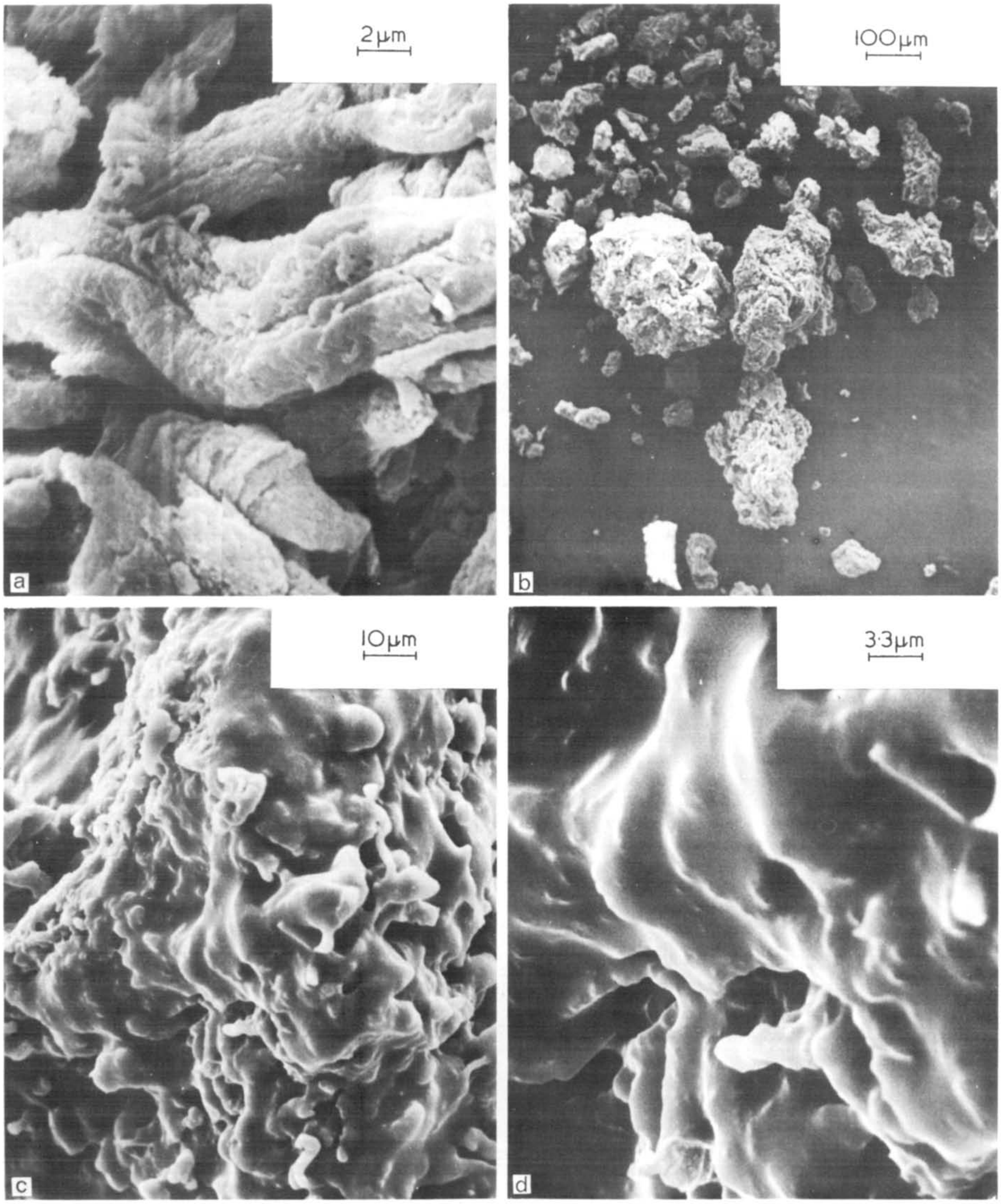

Figure 9 Electron micrographs. CTC–PS: (a) × 5 × 10^3 unheated; (b) × 10^2 at 200°C; (c) × 10^3 after 325°C and (d) × 3 × 10^3 after 325°C

characteristics. No such possibility exists for the non-irradiated CTC residues which appear as a frozen melt. The graft copolymer (PS–CTC), apart from having the advantages of any thermally and chemically stable cellulose derivative, presents an interesting problem. *Figure 9b* shows the copolymer to exist as a granular powder, while *9c* shows the surface to be completely covered in molten, frozen polystyrene when seen under high magnification. Two possibilities arise. Firstly, that the graft–substrate bond is cleaved and subsequent migration of the molten polystyrene to the surface takes place. The second possibility involves melting without decomposition; hence we may be seeing frozen melted grafts on the cellulose substrate.

It is obvious that various avenues have been opened in studies of the thermal properties of cellulose derivates. Much work remains to be carried out in this field, and the results will be available in due course. The use of the four techniques in a concerted investigation, as employed in this work, provides a convenient combination for use in the thermal characterization of materials when applied as suggested here.

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