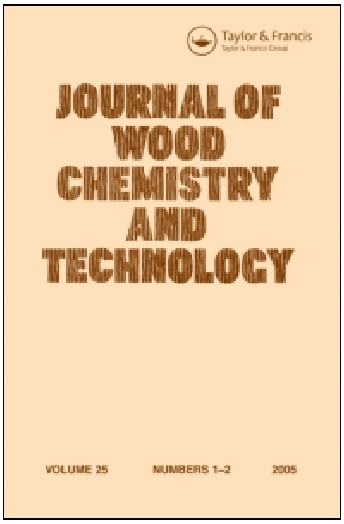

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SOME EFFECTS OF ELEVATED TEMPERATURES ON THE STRUCTURE OF CELLULOSE AND ITS TRANSFORMATION

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ABSTRACT

In many commercial processes cellulose is exposed to elevated temperatures in the 100 to 200°C range. Though this range is below the glass transition temperature (T_g) of dry cellulose, in the presence of polar media T_g is depressed, and molecular mobility is sufficient to allow structural reorganization. In the present study, a number of regenerated celluloses, some amorphous and some semicrystalline, were heat treated at elevated temperatures in water under pressure, as well as in other polar media. Two groups of factors were found to influence the type and amount of structural change. The first were the characteristics of the cellulose, that is, the degree of polymerization (DP) and the structure of the cellulose prior to treatment. The other group were the nature of the medium and the time and temperature of the treatment. The amorphous high DP celluloses were found to aggregate as cellulose IV, with the time and temperature determining the extent of ordering rather than resulting in qualitative reorganization. The low DP celluloses, which were of low enough molecular weight to reduce the constraints on molecular mobility imposed by molecular entanglements, had a more diverse pattern of responses. At ambient temperatures the aggregation was into high crystallinity cellulose II; at intermediate temperatures, a variety of forms fitting into the category of cellulose IV were produced; and finally, at high enough temperatures, a cellulose I of very high crystallinity was produced in low yield.

INTRODUCTION

In two earlier studies in our laboratory[1,2] it was established that heat treatment of cellulosic fibers at elevated temperatures

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led to an increase in crystallinity not unlike the annealing effect which is a well-recognized phenomenon among synthetic semicrystalline thermoplastic polymers.[3] In separate studies it was also observed that elevated temperatures of regeneration influence the polymorphic character of the resulting cellulose.[4,5] Taken together the studies suggested that exposure to elevated temperatures activates complex transformations of molecular form which result in both qualitative and quantitative alterations in the states of aggregation of the cellulosic chains. The studies reported here represent further exploratory investigations of these phenomena.

BACKGROUND

The response of cellulose to elevated temperatures has been the subject of a number of recent investigations which, however, focused on other aspects of behavior. One series of reports centered on the kinetic aspects of the initial stages in the ordering of amorphous celluloses.[6-10] Others have concentrated on a number of transitions in the mechanical response of cellulosics, which appear to be similar to second order transitions. The highest among these, at 220°C, has been characterized as the glass transition temperature.[11-12]

Perhaps more closely related to our work are the studies of cellulose IV reviewed in the earlier literature.[13-15] These, however, involved heat treatment in the range between 180 and 250°C in glycerol. Our purpose was to explore a number of variables other than temperature, and to extend the range of temperatures well below 180°C. Our primary objective was not so much to accomplish a particular transformation as to explore the inherent tendencies of cellulose to aggregation in different forms under different conditions. The investigation focused on samples of cellulose in two categories. The first, consisting of materials ranging in DP from about 300 to 3300 were taken as representative of the broad range of cellulosics of general interest. The second group were celluloses with a DP in the 15 to 20 range which perhaps could be regarded as the high end of the cello-oligosaccharides, more commonly referred as the cellodextrins. These were included because we believe they can reveal more clearly the inherent tendencies of the molecular chains to aggregate or undergo transformation. The movements of the relatively short oligosaccharide chains are less likely to be constrained by molecular entanglements which can restrict molecular mobility.

For both categories of samples the primary experiments involved regenerating the samples in amorphous form and then exploring their response to elevated temperatures in different media and under different conditions. The program for the low DP cellulose was extended to include the response of samples initially regenerated as cellulose II of high crystallinity. In addition some regeneration studies, complementary to those reported earlier,[4,5] were carried out on the low DP cellulose.

EXPERIMENTAL PROGRAM

Materials and Preparation

The celluloses used as the starting materials were all derived from cotton linters. The higher DP samples, received in fibrous form, had number average DPs of 3300 and 1700. The third, available in microcrystalline form, had a number average DP of 333.

The low DP cellulose was prepared by hydrolysis for six weeks in 85% phosphoric acid. More specifically, 85 grams of microcrystalline cellulose was wetted with 62 mL of distilled water and then added to 1590 mL of 85% phosphoric acid with continuous stirring. The solution became clear after standing over night. It was filtered through coarse fritted glass and allowed to stand for six weeks. It was then filtered through a fine glass filter (pore size 4 to 5.5 μ) and added to three times its volume of distilled water. The precipitated cellulose was washed till neutral and freeze dried. X-ray diffractograms indicate a high crystallinity cellulose II. This material was the starting material in a number of the heat treatment studies.

The amorphous celluloses were prepared by regeneration from the DMSO-PF solvent system[16] under anhydrous conditions. The most effective procedure involved regeneration in a solution of sodium isopropoxide in isopropyl alcohol, and washing in isopropyl alcohol, anhydrous ethyl ether, and cylcohexane, followed by drying from the cyclohexane. X-ray diffractograms indicated a completely amorphous character.

Heat Treatments

The heat treatments were carried out in small cylindrical stainless steel pressure vessels (5 cm high, 2 cm diameter) immersed in an oil bath wherein temperature was controlled within ± 2°C. The response time was such that the contents of the vessels attained bath temperature within about 5 minutes. Careful attention was given to degassing water and water-immersed samples prior to heat treatment. In some exploratory studies DMSO was used as a medium for heat treatment as well.

In the course of the investigation it became clear that when amorphous low DP cellulose was immersed in water prior to raising its temperature for heat treatment, it would crystallize in the cellulose II lattice form. Thus, an alternate procedure was developed wherein two vessels were connected with stainless steel tubing containing a valve so that the cellulose, under nitrogen in one vessel, could be exposed to the vapor from water in the other vessel, after both were brought up to the temperature of heat treatment. This technique was later also applied to some of the high DP amorphous celluloses.

Characterization

The ordering responses of the high DP celluloses were qualitatively similar, varying primarily in the degree of progress of crystallization. The response was therefore characterized in terms of changes in the X-ray diffractogram. Three parameters were used: the width at half height of the 002 peak; the crystallinity index based on the intensity of the 002 peak and the intensity at 18°, assumed representative of the amorphous content; and the ratio of the intensity at the position of the $10\bar{1}$ peak of cellulose II to the intensity of the 002 peak. None of these was assigned absolute significance; rather they were taken as complementary measures of progress in ordering, and in some respects as providing for internal consistency.

For the low DP celluloses the primary characterization relied on qualitative differences in the diffractograms which reflect polymorphic forms, although these also are reflected in the values of the parameters noted above. In addition to the diffractometric characterization, the Raman spectra of many samples were recorded. These provided valuable additional characterization, particularly for the amorphous samples.

RESULTS

High DP Celluloses

The diffractogram shown in Fig. 1 is representative of the response of the high DP celluloses to heat treatment. It is rather difficult to classify in terms of a pure polymorphic form. When compared with the diffractograms in Fig. 2, which are for highly crystalline representatives of polymorphs I, II, and IV, the diffractogram of Fig. 1 appears to be predominantly of the IV form, although hints of features of I and II occur.

The initial explorations were for the effect of time and temperature. The effect of time is depicted in Table 1, which shows that much of the ordering occurs in the early phases and is reflected in rapid development of the 002 peak, and the rise in the crystallinity index. Later phases of the heat treatment lead to growth or greater perfection of the order, with very little change in the type of order. Thus the narrowing of the width at half-height of the 002 peak, the decline in the $I(10\bar{1})/I(002)$ ratio, and the slow rise in the crystallinity index.

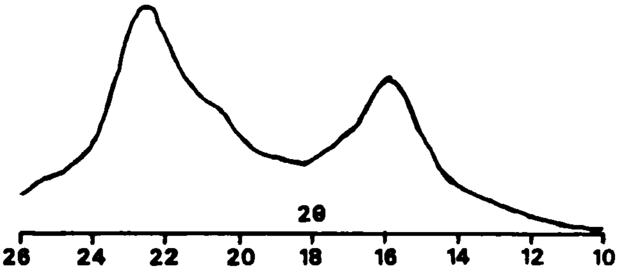

Figure 1. Diffractogram of DP 3300 cellulose after heat treatment in water at 190°C for 6 hours. The starting material was amorphous.

The effect of temperature is shown in Table 2 where it is seen that the higher temperatures result in a greater degree of order. Here it is clear, however, that some of the cellulose is lost during heat treatment at the higher temperatures. It may be that the lost cellulose arises primarily from the amorphous component; thus, the degree of ordering may appear exaggerated. Nevertheless, the pattern of response to higher temperature is consistent with expectation on the basis of earlier experience.

A number of experiments were carried out in which amorphorous cellulose regenerated from the samples having DPs of 333, 1700, and 3300 were compared with respect to their response at different times and temperatures. The general pattern was that the responses were relatively similar, although the rates of increase in crystallinity declined with increase in DP.

Finally, in another series of experiments the higher DP celluloses were heat treated in steam. In every instance the indices pointed to more rapid ordering when the heat treatment was in steam.

Low DP Cellulose

The earliest experiments with the low DP cellulose established that it crystallized very rapidly to cellulose II upon immersion in water. Indeed, exposure to atmospheric moisture is sufficient to cause some crystallization. The investigation of the low DP

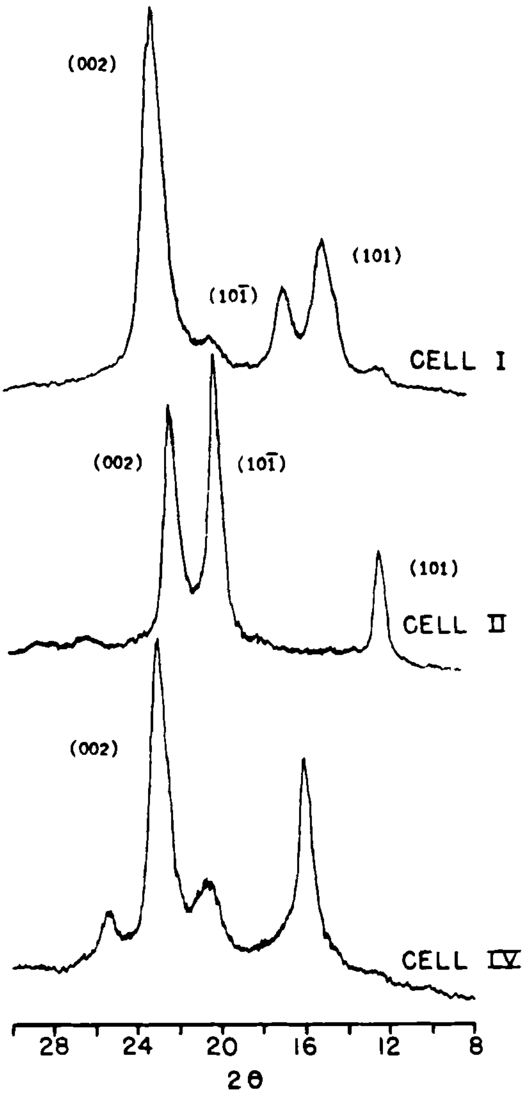

Figure 2. Diffractograms of high crystallinity samples of cellulose I, II, and IV. The cellulose I sample has a small residue of cellulose II in it. All the samples are low DP cellulose.

TABLE 1
Effect of time at 180°C; DP 3300

Time, hr	Whh[a] (002)	$\frac{I(10\bar{1})}{I(002)}$[b]	CI[c]
--	—	1.494	0
1.5	3.33	0.748	44.9
6.0	2.66	0.635	54.7
24.0	2.35	0.487	58.7

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[a] Width at half-height 002 peak in degrees.
[b] Ratio:intensity ($10\bar{1}$) peak/intensity (002) peak; the ($10\bar{1}$) taken at its position for II.
[c] Crystallinity index.

TABLE 2
Effect of temperature held for 6 hr; DP 3300

Temp., °C	Whh (002)	$\frac{I(10\bar{1})}{I(002)}$	CI	Loss, %
130	3.98	0.891	44.8	7.5
150	3.59	0.801	46.9	4.4
180	2.66	0.635	54.7	19.3
190	2.10	0.478	70.7	24.3
200	1.67	0.313	79.5	43.1
210	1.55	0.352	77.8	51.5

TABLE 3
Effect of temperature held for 2 hr; DP 15-20

Temp., °C	Whh (002)	$\frac{I(10\bar{1})}{I(002)}$	CI	Loss, %
130	1.46	1.093	88.5	14.3
150	1.34	1.093	91.2	21.2
170	1.46	0.913	89.2	33.7
180	1.33	0.476	87.3	61.0
190	1.30	0.326	87.2	62.1
200	1.31	0.245	89.8	86.1
210	1.28	0.054	94.4	96.7

cellulose was, therefore, modified to bypass this stage when heat treatment was to be in water as the medium. Thus, the starting material was the high crystallinity cellulose II regenerated from phosphoric acid.

To explore its response to temperature, the low DP cellulose was heat treated at temperatures ranging from 130 to 210°C for two hours. The results are summarized in Table 3 and Fig. 3. The results show that, beginning at 170°C, the cellulose II lattice seems to be perturbed in a manner that leads to transformation first to cellulose IV and eventually to cellulose I. The transformation to cellulose IV is not entirely unexpected in light of prior reports in the literature. The eventual appearance of a small residue of cellulose I was entirely unexpected. Yet it was not inconsistent with our prior encounters with cellulose I in small yield in celluloses regenerated from phosphoric acid.[4]

A question arises with respect to the formation of cellulose I. Because of the low yield, can it be a residue that had never been dissolved in phosphoric acid in the first instance? A number of tests have ruled this out. SEM micrographs reveal a particle size larger than the pore size of the filter. An effort to determine the DP using the tricarbanilate method[17] revealed that the DP was too low to be resolved by the column, thus likely below 20. Finally a small amount of the sample was redispersed in phosphoric acid and did in fact go into solution. The solution was examined under a polarizing microscope but showed no sign of birefringence.

In light of the low yield, a second question arose. Was the cellulose I formed during the regeneration, or the heat treatment? A partial answer was provided by subjecting a sample of the regenerated cellulose II to acid hydrolysis; it was reasoned that if the cellulose I resisted hydrolytic action at 210°C, it might, at the least, be enriched by hydrolysis in acid. After 48 hours of boiling in 4N HCl, a residue of cellulose I was found in yield approximately similar to that from the heat treatment in water at 210°C. Clearly, at least the nuclei for this cellulose I were present in the cellulose II regenerated from phosphoric acid.

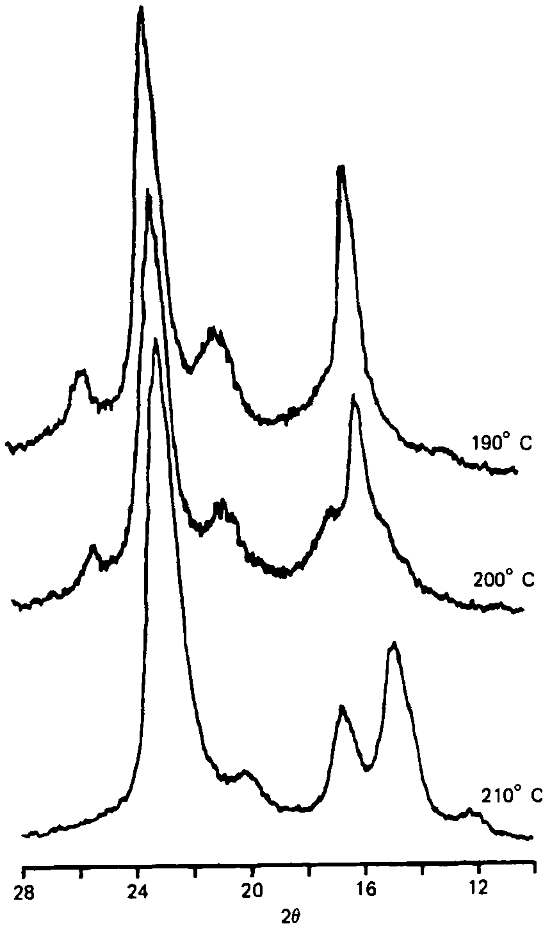

Figure 3. Diffractograms of samples of low DP cellulose after heat treatment in water at 190°C, 200°C, and 210°C, for 2 hours. The starting material was high crystallinity cellulose II.

Whether 24 hours of boiling in 4N HCl are equivalent to two hours in water at 210°C remains an open question.

The next series of experiments involved comparison of the response of the amorphous low DP cellulose to heat treatment in different media at 130°C. The comparison included DMSO, water, and steam. The results, shown in Fig. 4, are quite remarkable, for although the treatment in water produced a cellulose II as

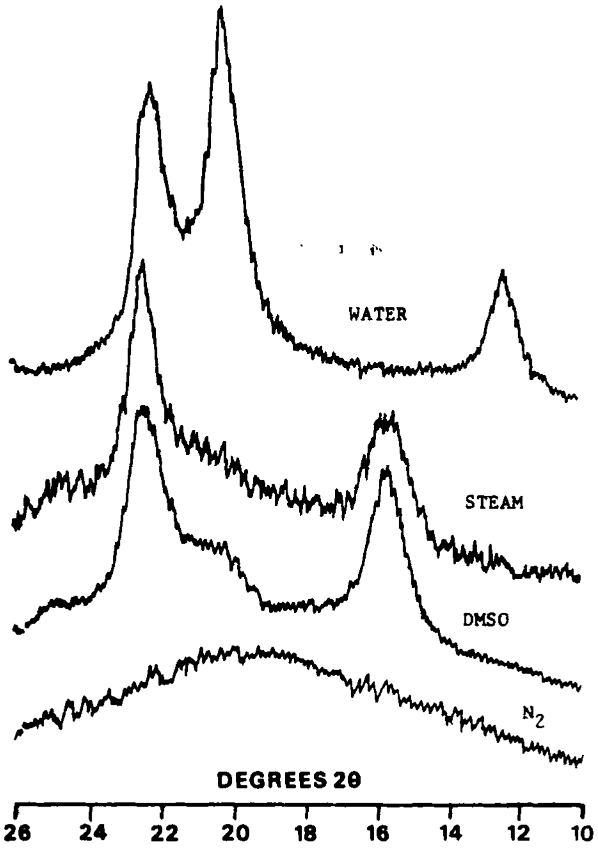

Figure 4. Diffractograms of low DP cellulose heat treated at 130°C for two hours in the media indicated. The starting material was amorphous.

expected, the treatment with steam produced a cellulose IV. The treatment in DMSO also produced a cellulose IV, but with a slightly different diffraction profile.

Regeneration Experiments

In our previous study it was found that DP and temperature of regeneration were key factors in determining the polymorphic form of the cellulose recovered. In particular it was found that elevating the temperature of regeneration resulted in recovery of cellulose IV. To complement these earlier results, an effort was made, in the present program, to regenerate the low DP cellulose in the IV polymorph. It was found possible to do so by allowing the DMSO-PF solution to stand at 75°C. The diffractogram of this sample is shown in Fig. 5. The most remarkable characteristic of this sample is its Raman spectrum, which is essentially identical to that of the amorphous material recovered when the low DP cellulose is regenerated from the DMSO-PF system using the anhydrous procedure described above. The Raman spectra are shown in Fig. 6 together with the spectra of high crystallinity samples of celluloses I and II.

DISCUSSION

The results described above represent an interesting set of observations revealing a pattern not unlike that found in the studies of regeneration. In those studies it was also observed that lower temperatures favored the cellulose II form, whereas the intermediate and elevated temperatures (80 to 160°C) favored cellulose IV. Furthermore, it was also found that in the special circumstance of low DP and temperatures at the upper extreme of the range studied, a high crystallinity cellulose I was recovered in small yield.

Though our observations are very much in keeping with the enigmatic character of cellulose IV, we believe the results, particularly when taken in conjunction with the Raman spectra, point to a plausible mechanistic interpretation based on our general model of cellulose structure. The model, which has been presented in greater detail elsewhere,[18] is based on the hypothesis that two stable ordered conformations of the cellulose molecule coexist in different proportions in most celluloses. These conformations have been identified as k_I and k_{II} based on their dominance in celluloses I and II, respectively; the less ordered state has been identified as k_0.

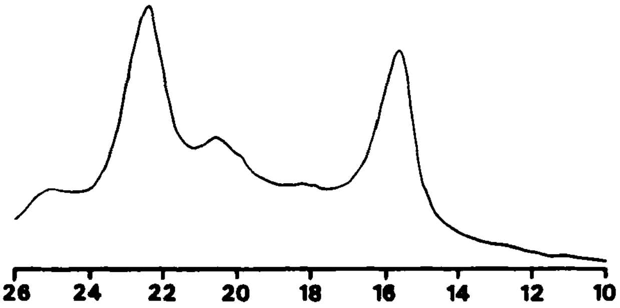

Figure 5. Diffractogram of the low DP cellulose IV sample regenerated from DMSO-PF at 75°C.

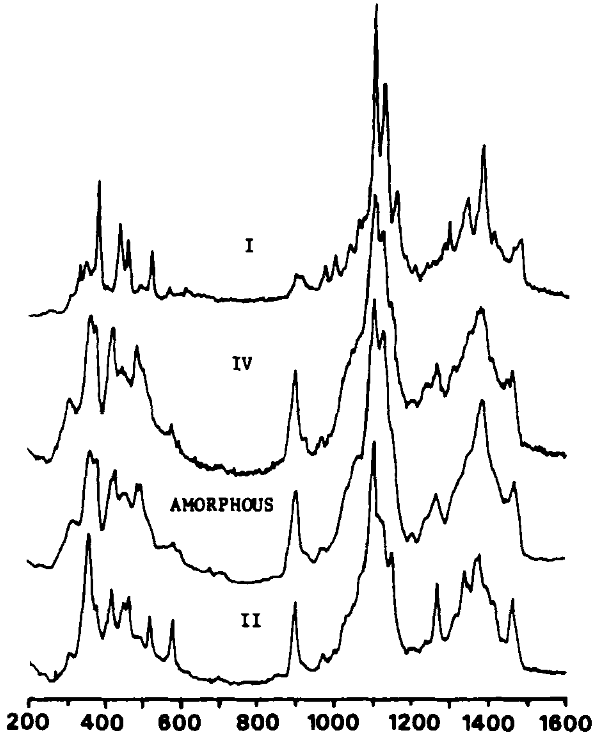

Figure 6. Raman spectra of highly crystalline samples of cellulose I, II, and IV, and of an amorphous low DP cellulose.

The relevance of the model is suggested in Fig. 5, where the spectra of cellulose IV and an amorphous cellulose are compared with the spectra of cellulose I and cellulose II. The first point to be noted is that the spectrum of cellulose IV is quite close to a superposition of the spectra of I and II. This observation, typical of many cellulose IV samples, has led to our proposal that the cellulose IV lattice is a mixed lattice in which k_I and k_{II} coexist.[5] Another point to be noted with respect to Fig. 5 is that the spectra of cellulose IV and the amorphous cellulose are nearly identical. This leads to the conclusion that the amorphous cellulose contains a large fraction of molecules linearly ordered in the k_I and k_{II} conformations, which nevertheless have not aggregated into crystalline domains. Further, it is noted that the relative proportions of k_I and k_{II} revealed in the spectra of cellulose IV regenerated at 75°C are similar to those in amorphous cellulose, suggesting that this proportion, which appears in the range of 30% k_I, may approximate an equilibrium distribution in the DMSO-PF solution.

Low DP Cellulose

In Fig. 4 it is seen that treatment at 130°C in steam or DMSO results in aggregation as cellulose IV. Thus the indication is that the balance between k_I and k_{II} is approximately retained. The treatment media thus provide the requisite molecular mobility without drastically altering the balance between k_I and k_{II}.

The treatment in water, however, appears to bring about a drastic transformation in the balance, resulting in a high crystallinity cellulose II. A preliminary conclusion, therefore, is that an excess of water at ambient temperature results in the transformation of k_I to k_{II} resulting in crystallization of pure polymorphic II. Based on earlier experiments, it must be concluded that the sample depicted in Fig. 4 as heat treated in water must have crystallized as II immediately after immersion in water at ambient temperature, with the exposure to 130°C for two hours serving primarily to promote higher crystallinity.

There are a number of indications that the balance between k_I and k_{II} is shifted toward k_I as temperature is increased. In the earlier study of regeneration it was found that cellulose II was recovered at ambient temperatures, but that cellulose IV, with increasing proportions of k_I, was recovered at higher temperatures. In the present study it would seem that the treatment with steam would have shifted the form toward cellulose II if a certain proportion of k_I were not inherently part of the most stable state of the system.

The most difficult to interpret are the transformations of the low DP celluloses at the higher end of the temperature range. Though many aspects of the transformations remain obscure, a plausible mechanism can be suggested. Thus, it is proposed that at high enough temperatures the driving force for the transition from k_{II} to k_I becomes large enough to disrupt the cellulose II lattice, resulting in a simultaneous conversion of some molecules from k_{II} to k_I and the loss of k_{II} by dissolution and hydroylsis; the rationale for greater susceptibility of k_{II} to hydrolysis has been presented elsewhere.[19] The disruption of the II lattice and conversion of some k_{II} to k_I make possible reaggregation of some k_I and k_{II} together to give the more stable IV lattice. The Raman spectra suggest that at the higher temperatures the loss of k_{II} is greater so that the proportion of k_I in the IV lattice is higher. Finally, at a high enough temperature all of the k_{II} is lost, leaving the highly crystalline aggregate of k_I, which is cellulose I.

Two more general observations are relevant here. The cellulose IV polymorph appears to be less a pure polymorph than a category of mixed crystals. This is suggested by the greater variability of the relative intensities of the peaks in its diffractograms. This is one characteristic of mixed polymeric crystalline materials.[20]

The second observation is that the diffractogram of the sample treated at 200° in Fig. 3 is suggestive of the diffractograms reported in the literature for what has been called cellulose X.[14] It cannot be coincidental that it was also prepared by procedures including, at some point, treatment with 85% phosphoric acid or very concentrated hydrochloric acid, and that in those instances the reported DPs were in the 15 to 20 range.

High DP Cellulose

The results of heat treatment of the high DP celluloses can be interpreted in terms of the concepts set forth above together with the considerable constraint of molecular entanglements restraining molecular transformations. Two observations are noteworthy at the outset. First, all high DP celluloses responded in the same manner, producing the IV polymorph, though varying in the degree of order. Second, heat treatment in steam resulted in more rapid ordering than treatment in water.

A plausible interpretation, based on parallels with the low DP celluloses, is that k_I and k_{II} coexist in the amorphous cellulose, and aggregate into type IV crystalline domains upon heat treatment. The constraints of molecular entanglement clearly limit aggregation as cellulose II or transformation of a significant fraction of molecules from the k_I to the k_{II} form. Yet when the amorphous cellulose is wetted prior to treatment in water, this seems to retard the ordering process relative to its rate of progress in steam.

It is not unreasonable to suggest that the wetting results in a small amount of highly localized aggregation as cellulose II, beyond the detection limit, and that the presence of this component retards the progress of the ordering. At higher treatment temperatures, such local aggregates would be disrupted and reaggregation in the IV form would continue.

Another noteworthy observation is that the weight losses upon heat treatment of the high DP material were much less than those for treatment of the much more crystalline low DP materials. This reinforces the view that much of the losses in heat treatment of the latter were due to dissolution rather than to chemical decomposition.

Broader Implications

The results reported above suggest that exposure of cellulosic materials to elevated temperatures, not unlike those occurring in many commercial processes, can cause transformations in molecular conformations and states of aggregation. Such transformations have not been considered in most past analyses because of the difficulty of characterizing the transformations and the morphological heterogeneity of commercial celluloses. Our results suggest a new approach to investigating and assessing the effects, and provide a foundation for exploring their influence on properties.

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