Reports

Cellulose: Its Regeneration in the Native Lattice

Abstract. *The regeneration of cellulose from solutions in 85 percent phosphoric acid into glycerol at 170°C resulted in its recovery wholly in the native or cellulose I lattice. Identification of the structure of the regenerated material is based on comparisons of its x-ray diffractogram and its Raman spectrum with those of the native fiber, cellulose II, and cellulose IV.*

Cellulose occurs in nature predominantly in a lattice type characterized as native cellulose or cellulose I (*1*, *2*). The processes of mercerization and regeneration that are used industrially produce another polymorph generally identified as cellulose II. A variety of treatments can be applied to either cellulose I or cellulose II to produce other less common and less well characterized polymorphs usually identified as celluloses III, IV, and x (*2*). Although a number of procedures have been described for preparing each of the other polymorphs, the possibility of regenerating cellulose in the native or I lattice has remained an open question. We now report what we believe to be the first instance of regeneration of cellulose in which it is recovered wholly in the native lattice.

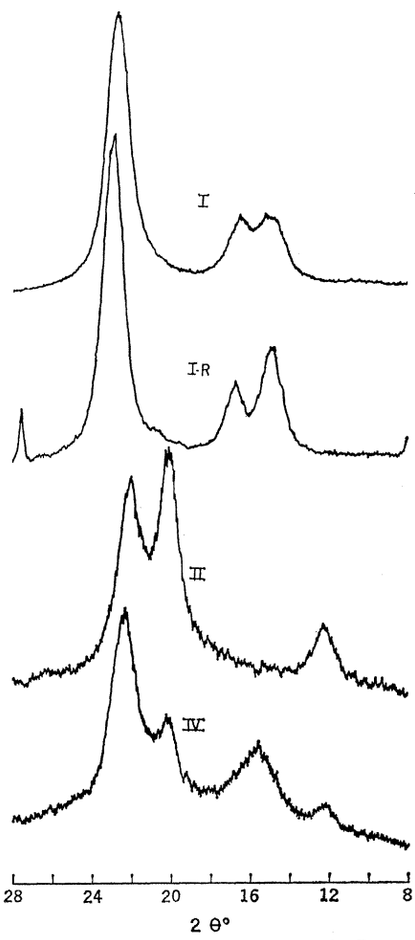

Fig. 1. X-ray diffractograms (θ is Bragg angle).

The question of regenerability of cellulose in the native lattice has been of interest beyond the characterization of polymorphy in cellulose, for it has been introduced in discussions of the plausibility of mechanisms proposed for biosynthesis (*3*). The fact that cellulose I had not been regenerated from solution has encouraged the view that the native cellulose lattice is a metastable form attainable in the course of the biosynthesis during which polymerization and crystallization occur simultaneously (*4*). The general view that cellulose I is metastable has also been reinforced by the observation that the cellodextrins crystallize in unit cells that converge to the unit cell of cellulose II (*5*).

In a number of previous studies cellulose I was considered to have been recovered after regeneration. Early observations of cellulose IV were mistaken for cellulose I because of the similarity of their diffractograms, but the IV form has since been recognized as a distinct polymorph (*2*). In two more recent studies (*6*, *7*) a precipitate consisting of 10 percent cellulose I and 90 percent cellulose II has been reported. However, the conditions of preparation and the nature of the precipitate raise the question of insoluble residues.

The observations that are the basis of the present report are part of a broader investigation of polymorphy in cellulose. The experiments were concerned with regeneration from 85 percent phosphoric acid into water at room temperature or near boiling, or into glycerol at temperatures up to 170°C (*8*). The powdered celluloses recovered were characterized by x-ray diffractometry and Raman spectroscopy. Selected samples were also investigated by scanning electron microscopy (SEM), and their degrees of polymerization (DP) were determined viscometrically on the basis of the correlation by Swenson (*9*).

The primary concern of this report is the sample regenerated at 170°C which appears to precipitate in the native lattice; discussion of celluloses regenerated under other conditions are included for perspective only. In Fig. 1 the diffractograms for the following samples are compared: I, acid-hydrolyzed cotton; I-R, regenerated at 170°C in glycerol; II, regenerated in water at room temperature; and IV, regenerated in glycerol at 150°C. Diffractograms I and II are typical of the types usually reported for celluloses I and II (*2*); IV is primarily a cellulose IV pattern but also includes indications of a small residue of cellulose II. Diffractogram I-R is what would be expected from a high crystallinity cellulose I; the designation I-R indicates regeneration. The extra peak above $2\theta = 27°$ in the I-R diffractogram (see Fig. 1) is due to titanium dioxide added to the particular sample for calibration purposes.

Because of the similarities between the diffractograms of celluloses I and IV (which in the past led to some confusion), it was thought wise to develop independent comparisons of the I-R sample with native cellulose. Other studies have shown that the Raman spectrum of cellulose, particularly in

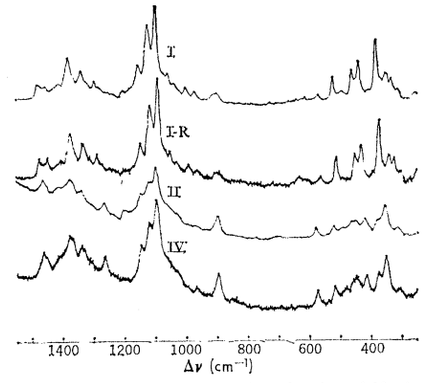

Fig. 2. Raman spectra ($\Delta\nu$ is the shift in the exciting frequency).

the region below 600 cm^{-1}, is sensitive to polymorphic variations (*10*). The Raman spectra of the four samples were, therefore, recorded, and they are compared in Fig. 2, in which it is clear that although the spectrum of cellulose IV is quite similar to that of cellulose II, the spectrum of I-R is almost identical to that of the native cellulose I. There is thus very little question that the sample recovered at 170°C is a high crystallinity cellulose in the native lattice.

In view of the questions raised above concerning the problem of residues in previous studies, it is well to consider the possibility in the present instance. We believe that a number of our observations exclude this possibility. The SEM micrographs of the I-R sample revealed structures that are spongy and stringy, and they are much larger than the pore sizes of the filters used for clarification of the solutions. Furthermore, the structures had no similarity to the morphological features of the native fiber. The DP of sample I-R is 60; it is unlikely that cellulose of such low DP would resist dissolution in 85 percent phosphoric acid. Indeed, sample I-R can be redissolved in phosphoric acid quite readily. Finally, and perhaps most convincing, if we were observing an artifact due to residues it would be difficult to explain recovery of celluloses II and IV from the same solutions when they are regenerated respectively at room temperature and at 150°C.

Although the implications of our observations are manifold, they cannot be developed fully here. It seems clear that the native lattice can no longer be regarded as attainable only through biosynthesis. The conditions under which it was regenerated, although quite remote from those prevailing during synthesis of the cell walls in a living plant, must have factors in common with the biosynthetic process. The thermodynamic condition of the regenerated material is not clear; the conditions of regeneration involve heterogeneities in temperature and solvent environment. Whether they are as dispersive as the conditions thought to generate structure in biological systems (*11*) remains an open question. The role of phosphate ester groups must also be considered, for their rapid hydrolysis in regeneration may contribute to the energetics of the process.

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References and Notes

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8. Cellulose powders were dissolved in phosphoric acid at a consistency between 1 and 3 percent. The solutions were filtered through fritted glass with pore sizes in the 2- to 5-μm range and allowed to stand at room temperature for 2 to 3 weeks before regeneration. They were then added drop by drop to the regeneration baths under cover of nitrogen. Under all conditions the cellulose appeared to precipitate on contact. The precipitates were washed repeatedly in distilled deionized water, freeze-dried, and pressed into pellets for the diffractometric and spectral studies. The diffractograms were obtained with a North American Phillips diffractometer with use of nickel filtered copper Kα radiation. The Raman spectra were recorded on a Spex Raman system in which the 5145 A line of a Coherent Radiation 52A laser was used for excitation.
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12. We thank B. Dimick for valuable critical discussion and J. Hultman for the diffractometric measurements. This work was supported by institutional funds of The Institute of Paper Chemistry and they are gratefully acknowledged.

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Mirex: An Unrecognized Contaminant of Fishes from Lake Ontario

Abstract. *A perchlorinated, cage-structured hydrocarbon, $C_{10}Cl_{12}$, also known as mirex or Dechlorane, has been identified in fish samples from the Bay of Quinte, Lake Ontario, Canada. The compound coelutes with polychlorinated biphenyls (PCB's) in residue cleanup procedures and under standard gas chromatographic conditions. Mirex has never been registered for use as an insecticide in Canada, nor does it appear to be in use in any area of the United States discharging water into Lake Ontario or its tributaries. It seems likely, therefore, that this compound is another widespread environmental contaminant of extremely high geochemical stability and as yet only superficially investigated biological activities. Under standard gas chromatographic conditions its peak is superimposed on that of the PCB's, and, as a result, the presence of mirex may have been unrecognized and it may therefore have been misinterpreted as a PCB isomer.*

In recent years, pesticides in general and the DDT group (*1*) in particular have been of increasing concern to environmental protection agencies around the world. A wide variety of aquatic and terrestrial samples have been and are still being monitored for residual contaminants, and the results indicate that the evidence of pesticides is widespread. Until 1966, neither the presence of polychlorinated biphenyls (PCB's) (*2*) nor their interference with the DDT analysis was recognized. However, analytical cleanup techniques were rapidly developed to permit differentiation between the DDT group and PCB's, primarily column chromatographic separations of the more polar pesticides from the less polar PCB fractions. It is ironic to find now that still another compound may be hidden under the PCB peaks.

I report here the detection of a perchlorinated hydrocarbon, $C_{10}Cl_{12}$, commonly known as mirex (*3*), in fish samples distinctly remote from areas of any field application of this insecticide (*4*) and its presence in the PCB fraction of residues treated by approved standard procedures (*5*, *6*). Two fish

Table 1. Sample data for PCB and mirex residues from two fishes from the Bay of Quinte, Lake Ontario, Canada; ppm, parts per million; N.D., value not determined.

Part	Weight (g)	PCB's as Aroclor (ppm)			Mirex (ppm)
		1242	1254	1260	
Northern longnose gar [Lepistosteus osseus (*L.*)], *902 g*					
Gonads	32	2.09	1.18	0.44	0.020
Viscera, fat	62	3.14	1.95	0.90	0.041
Liver	17	3.68	2.31	1.08	0.047
Northern pike [Esox lucius (*L.*)], *2930 g*					
Pectoral to pelvic fin	950	N.D.	N.D.	N.D.	0.025
Post-anal fin	280	0.89	1.01	0.48	0.050