The glycol obtained in the first reaction can further react with paraformaldehyde to give the polymer described above. It should be stressed that the reason for disregarding possible random reactions between different active groups is the necessity of making the condensation mechanism conform to experimental results, according to which the methylenic groups should not be between an oxygen atom and a sulfur atom.

The details of the mechanism of the cationic polymerization of 1-oxa-3-thiacyclopentane are at present obscure. A kinetic mechanism which might explain the structure obtained implies either that bond scission occurs in a rigorously alternate order at i bonds and at j bonds on the monomer or that the formation of a cyclic dimer takes place probably according to the following mechanism:[17]
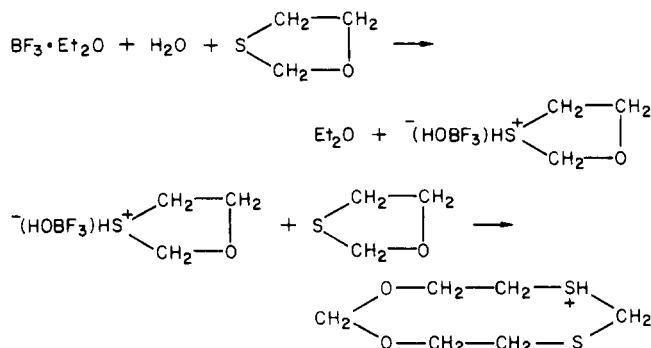
In this case the polymerization should proceed by a process of ring expansion in a way similar to that proposed by Plesch and Westermann[13] for the polymerization of 1,3-dioxolane.

Very recently, Kawakami et al.[11] have discussed the reaction mechanism of the polymerization of 1-oxa-3-thiacyclopentane with oxonium salts. According to these authors, the foreseeable structure of the polymer, $CH_2CH_2OCH_2S$, might be modified by extensive chain transfer or back-biting in the polymerization system; hence the complexity of the NMR spectrum and the low molecular weight of the reaction product. In our case, however, the clear and simple NMR spectra as well as the relatively high molecular weight ($\bar{M}_n$ = 5000) of the polymer suggest that chain-transfer reactions are not present, possibly as a consequence of a different mechanism of polymerization.

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Raman Spectral Evidence for Molecular Orientation in Native Cellulosic Fibers

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Studies of the Raman spectra of individual native fibers have revealed new information concerning ordering of molecular chains within the cell walls. Cellulose, the primary polysaccharide component of the walls, is the β-1,4-linked polymer of anhydroglucose. It is unique among cell wall polysaccharides in that all heavy-atom linkages to the pyranose rings are equatorial and that the methine CH bonds are all axial with respect to the individual anhydroglucose residues. Previous investigations, utilizing X-ray diffractometry and birefringence, detected the average angle of the molecular chains relative to the axes of the fibers.[1,2] The Raman spectra suggest that there is also a preferential orientation of the anhydroglucose units in tangential planes and a correlated preferential orientation of the methine CH bonds in the radial direction.

The evidence for preferential orientation is derived from the response of the intensities of characteristic bands in the spectra of single fibers to changes in the polarization of the incident exciting radiation relative to the axis of the fiber.

Three spectra are presented. The first two were recorded on a Spex 1401 double monochromator in the back-scattering mode. The unfolded schematic representation in Figure 1 shows the relative polarizations of the incident exciting radiation and the Raman scattered light in each recording mode; the depolarized spectra were identical for both orientations of the incident beam. The laser-illuminated portion of the fiber was imaged in the plane of the entrance slit such that the fiber axis was parallel to the slit. The signal received was thus an average, characteristic of the portion of the fiber image admitted through the entrance slit. Figure 2 is the spectrum of a Ramie fiber; Ramie is known to have molecular chains essentially parallel to the fiber axis.[3] Manifestations of this molecular orientation are noted in the changes in relative intensities of a number of the polarized bands when incident-beam polarization is altered. In particular, the 1098-cm⁻¹ skeletal band[4] is very intense in the parallel mode and much reduced in the perpendicular mode. The reverse is true of the methine stretching bands at 2920 cm⁻¹,[5] and this, of course, reflects the orientation of all the methine CH bonds essentially perpendicular to the direction of the cellulose chain.

Figure 3 shows analogous spectra of a cotton fiber recorded in the same modes. As was perhaps to be expected from a fiber with a variable fibril angle,[6] the intensity of the 1098-cm⁻¹ skeletal was of the same order of magnitude in both modes. The unexpected feature in this spectrum was that the methine stretching band does not follow a
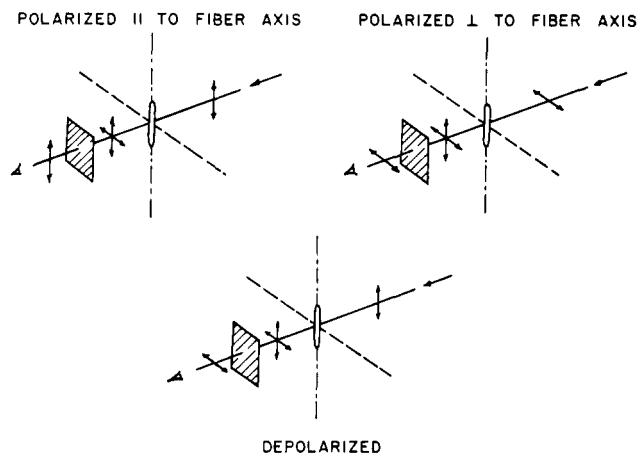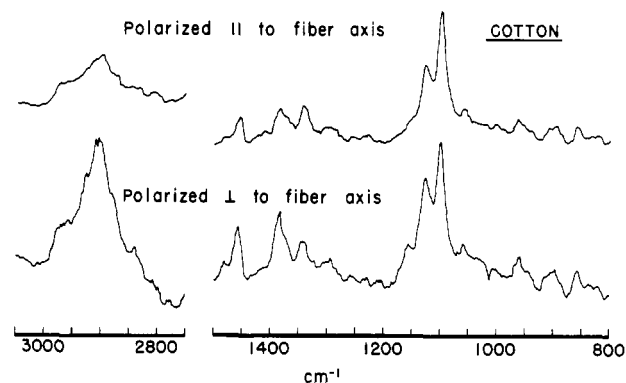
Figure 1. Unfolded representation of the back-scattering experiments showing relative polarizations of incident and Raman scattered light.
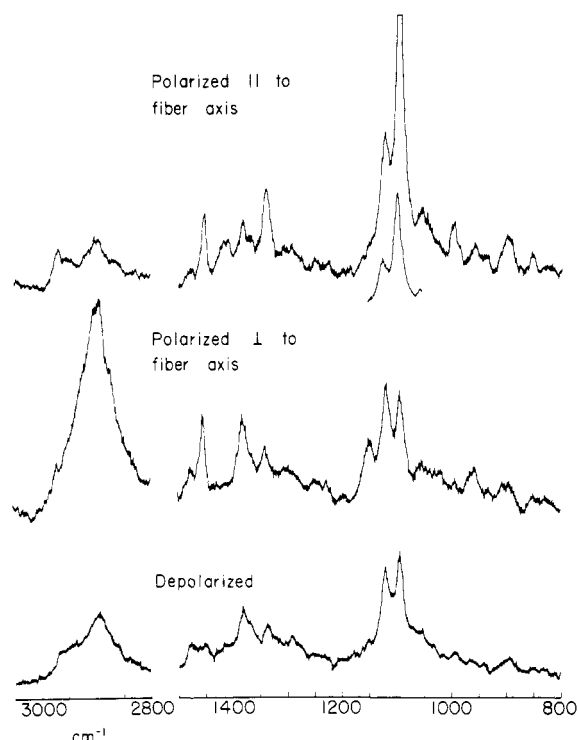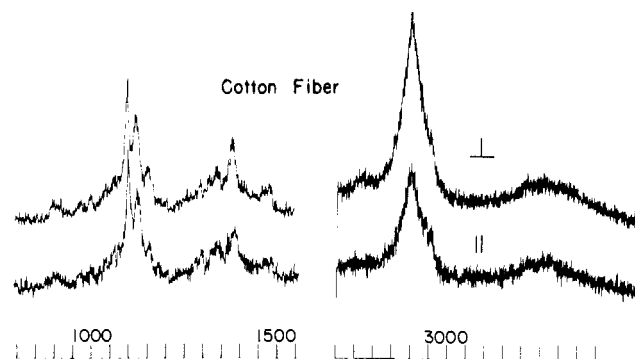

Figure 2. Raman spectra of Ramie fibers (fiber axis parallel to the slit).

Figure 3. Raman spectra of cotton fiber (fiber axis parallel to the slit).

Figure 4. Raman spectra of cotton fiber (fiber axis perpendicular to the slit).

similar pattern but is significantly more intense in the perpendicular mode. It appears that an orientation effect above and beyond that of the fibril angle is present. It was proposed that such an effect could be due to a preferential orientation of the methine groups in the radial direction and the anhydroglucose rings in the tangential direction,[7] but further testing of this interpretation seemed wise in light of the complex morphology of native cotton fibers.

The interpretation proposed received confirmation from the spectra shown in Figure 4. These were recorded in a back-scattering mode developed for a Jobin Yvon Ramanor spectrometer. However, in this instance the axis of the fiber was imaged perpendicular to the entrance slit. Thus it was possible to record the spectra of a section of fiber no longer than the width of the slit. By translating the fiber parallel to the direction of its axis, and thus moving its image in the plane of the slit perpendicular to the slit, it was possible to locate a point at which the intensity of the 1098-cm^{-1} skeletal band was the same for

both orientations of the polarization of the incident beam, suggesting an average fibril angle of 45° within this segment. Here again, however, the intensity of the methine band at 2920 cm^{-1} was significantly higher in the perpendicular mode than in the parallel mode. It appears unlikely that the consistency of the behavior of the methine band shown in Figure 4, with that represented in Figure 3 is coincidental. Rather it seems more plausible that both observations are indicative of preferential orientation of the methine CH bonds in planes perpendicular to the fiber axis. The type of orientation suggested can be described in reference to a cylindrical coordinate system with its axis coincident with the fiber axis. In such a system the methine CH bonds are preferentially oriented in radial directions; it follows also that the anhydroglucose rings are predominantly in tangential planes.

In terms of the orientation of the axes of cellulosic unit cells, the implication of the present finding is that c axes, which are approximately parallel to the methine CH bonds, are preferentially oriented in radial directions, and a axes, which are approximately parallel to the planes of the pyranose rings, are preferentially oriented in tangential directions. The b axes, which are approximately coincident with the chain direction, are, of course, aligned parallel to the fibrils.[8]

If the extended cellulose chains are thought of as ribbons, with the anhydroglucose rings in the plane and the methine CH bonds perpendicular to the plane, the ordering detected can be compared to helical winding of the ribbons about the lumen of the fiber. A coherence to the organization of adjacent chains is implied, since their planes are tangential to the lumen and thus parallel to each other. The coherence in the arrangement of the cellulose chains suggests the possibility that, in the native state, the molecules are organized into lamellae rather than as fibrillar aggregates, as generally proposed.

Although rigorously the present spectral evidence can be interpreted along the lines indicated above only for the case of 45° fibril angles, the ordering of the molecules which it suggests is expected to occur more generally. The ordering indicated by the spectra implies that a higher degree of anisotropy prevails in the organization of cellulose in cell walls than had previously been recognized.

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Figure 1. Logarithmic plot of $\pi(283/T)$ in g cm^{-2} against polymer concentration in g cm^{-3} for poly(vinyl acetate) in two solvents at two temperatures each as identified.

# Concentration Dependence of Osmotic Pressure in the Semidilute Range

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From scaling laws, it has been predicted[1,2] that the osmotic pressure (π) of a polymer solution in the semidilute range of concentration (c) should in athermal solvents be proportional to $(cRT/M)(c/c^*)^{5/4}$ and hence to $c^{9/4}$. Here M is the molecular weight and c^* is a critical concentration above which the molecular coils overlap each others' domains and may be defined as $M/N_0 s^3$; N_0 is Avogadro's number and s is the radius of gyration. The semidilute concentration range corresponds to $c > c^*$. This relation has been tested by Jannink and co-workers[3] from data of Cotton and co-workers[4] on polystyrene, but the concentration included only a very narrow range in which the $^9/_4$ exponent was valid. Other tests have been deduced indirectly from light scattering measurements.[3,5,6]

Extensive osmotic pressure data obtained by Browning[7] in this laboratory in 1948 can be used to test this prediction. Solutions of a poly(vinyl acetate) fraction with $\bar{M}_n$ = 280 000 in methyl ethyl ketone and 1,2,3-trichloropropane were measured at two temperatures in each solvent over a concentration range up to $c = 0.067$ g/cm^3. In Figure 1, osmotic pressures reduced to a temperature of 283 K by multiplication by $283/T$ are plotted logarithmically against c in g/cm^3. In each solvent, data at the two temperatures fall together and over a considerable concentration range are described precisely by a line with slope $^9/_4$.

The proportionality constants in the two solvents are clearly different. Although both solvents are "good" (the exponent for intrinsic viscosity in the Mark–Houwink
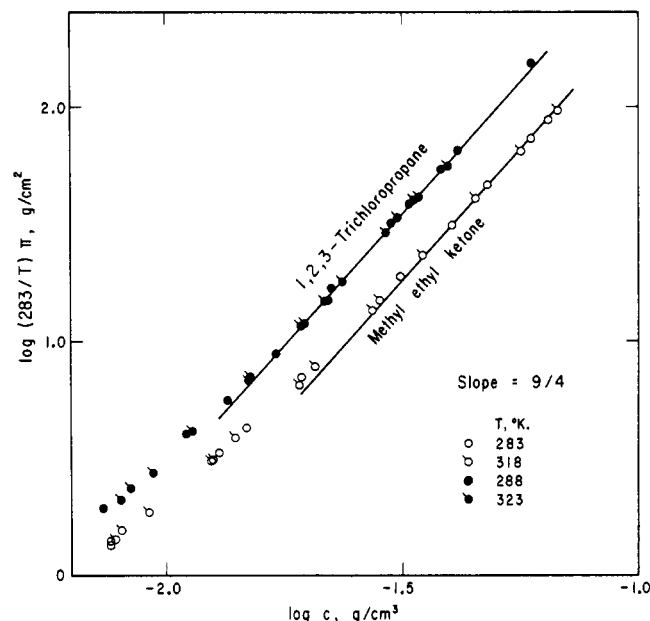
equation is 0.71 for methyl ethyl ketone[8]), they are actually "better" than athermal since the partial molal heats of dilution obtained from an earlier analysis[7] are negative, and are more so for the 1,2,3-trichloropropane. The difference in π/T for the two solvents at a given c could be attributed to the $(c^*)^{-5/4}$ factor and would correspond to a c^* ratio of 0.60 for 1,2,3-trichloropropane/methyl ethyl ketone. Another consequence of scaling laws[1] is that the second virial coefficient A_2 should be proportional to s^3 and hence to $(c^*)^{-1}$. These coefficients are[7] 8.0 and 5.0 × 10^{-4} cm^3 g^{-2} for 1,2,3-trichloropropane and methyl ethyl ketone, respectively, corresponding to a c^* ratio of 0.62, in good agreement. A similar ratio would be expected from the inverse ratio of the intrinsic viscosities. The intrinsic viscosity of this sample is available only in methyl ethyl ketone (98 mL/g at 25 °C); however, a qualitative comparison can be made from the specific viscosities of another (unfractionated) sample at a concentration of 0.01 g/cm^3, which are[9] 1.95 and 1.31, respectively; the inverse ratio is 0.67.

The absolute values of c^* are somewhat elusive. They can be estimated from the second virial coefficient by combining the definition $c^* = M/N_0 s^3$ with a relation quoted by Fujita[10] for the interpenetration function $\Psi(z)$, which should be approximately 0.25 for this molecular weight; c^* is 0.040 g/cm^3 in methyl ethyl ketone and 0.025 g/cm^3 in 1,2,3-trichloropropane. These correspond to points on the lower portions of the linear regions of the curves in Figure 1. Alternatively, from the empirical approximation[11] that $c^* \simeq 3/[\eta]$, in methyl ethyl ketone c^* = 0.031 g/cm^3. On the other hand, the rheological symptoms generally attributed to the onset of entanglement coupling appear at a somewhat higher concentration. The critical molecular weight M_C for the effect of entanglements on viscosity is[12] 22 600 for undiluted poly(vinyl acetate). Dilution increases it[12] by a factor of v_2^{-1} (where v_2, the volume fraction of polymer, is c/ρ and ρ is the polymer density), so the critical entanglement concentration for this molecular weight is 0.10 g/cm^3. The solutions described here may be considered to be semidilute but not entangled.