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Communications to the Editor

Transformation of Native Cellulose Crystals Induced by Saturated Steam at High Temperatures

Cross-polarization/magic-angle spinning (CP/MAS) ^{13}C NMR spectroscopy has proved to be very useful in characterizing crystalline and noncrystalline regions of cellulose.[1–24] However, the origin of the fine multiplicities appearing in the crystalline resonance lines still remains a controversial problem. Two models[10,11,15] have been proposed, which indicate that all native celluloses are a mixture of two crystalline modifications although each modification is differently defined in the two models. In contrast to these proposals, we have recently found by using a computer-line-shape analysis[20] that relative intensities of the C1 and C4 triplets are not explained in terms of a linear combination of two crystalline modifications based on either model. Moreover, the crystalline spectra of native cellulose, which were successfully separated from the noncrystalline components by using the difference in ^{13}C spin–lattice relaxation times T_{1C}, are classified into two types, cotton–ramie type and bacterial–valonia type. Although these spectra were referred to as celluoses I_a and I_b, respectively, both spectra seem to be composites of different crystal forms in accord with previous proposals.[10,11,15] The main cause of the unsuccessful interpretation of the experimental spectra in terms of their models may be inappropriate identification of the spectrum of each pure crystal form.

For the purpose of solving the controversial problem of cellulose crystals, it is very important to obtain more information about cotton–ramie type and bacterial–valonia type crystals, which are also here referred to as celluloses I_a and I_b for convenience although such nomenclature may not be exact in crystallography.[25] In a previous paper[19] we reported that cellulose I_b was readily transformed into cellulose I_a when the sample was regenerated from cellulose triacetate which was prepared under a low swelling condition. Similar transformation from cellulose I_b to I_a was also recognized in the case of the regeneration from cellulose III_I.[21] In contrast to this peculiar transformation of cellulose I_b, cellulose I_a crystals stay almost unchanged during these processes. In an attempt to examine the interconversion between cellulose I_a and I_b in a more direct way, we have studied in this paper the possible transformation of the crystals induced by saturated steam at higher temperatures.

The cellulosic materials used are bacterial and valonia celluloses, the crystals of which are referred to as cellulose I_b, and cotton cellulose, which contains cellulose I_a crystals. After conventional purification, these samples were subjected to annealing by saturated steam at 230–280 °C for 30 min in an autoclave. In this case each sample was kept in the vapor phase by fixing it with glass fiber sheets and stainless steel nets without contact with the liquid phase. CP/MAS ^{13}C NMR measurements, at 50 MHz were performed on a JEOL JNM-FX200 spectrometer using a magnetic field of 4.7 T for the annealed samples in the hydrated state and using a MAS rotor with an O-ring seal.[13,26] The experimental conditions are almost the same as described in the previous papers.[19,20] The chemical shifts relative to tetramethylsilane (Me_4Si) were determined by assuming the crystalline peak of linear polyethylene to appear at 33.6 ppm.[27]

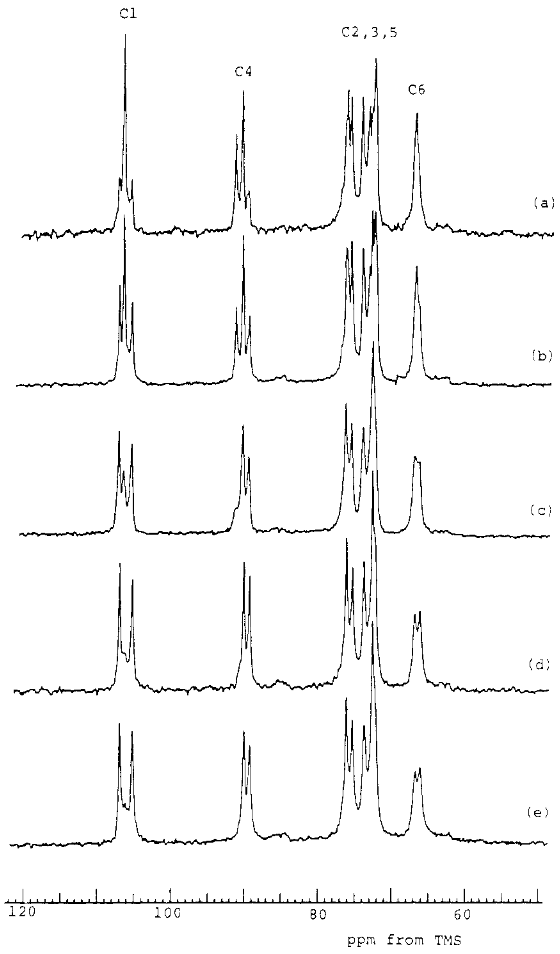

Figure 1. CP/MAS ^{13}C NMR spectra, 50 MHz, of valonia cellulose treated with steam at different temperatures: (a) original; (b) 230 °C; (c) 245 °C; (d) 260 °C; (e) 280 °C.

Figure 1 shows 50-MHz CP/MAS ^{13}C NMR spectra of

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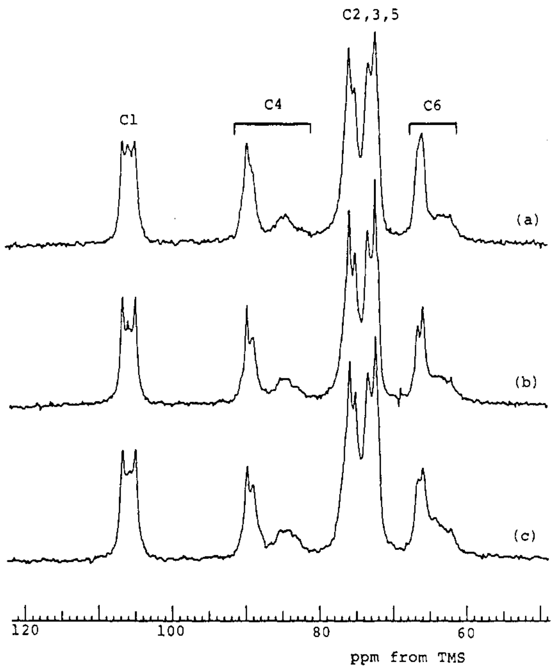

Figure 2. CP/MAS ^{13}C NMR spectra, 50 MHz, of cotton cellulose treated with steam at different temperatures: (a) original; (b) 230 °C; (c) 260 °C.

valonia cellulose which were treated with saturated steam at different temperatures for 30 min in an autoclave. For comparison, the spectrum of original valonia cellulose is also shown in Figure 1a; it exhibits typical cellulose I_b type multiplets.[20] It is clear that these multiplets are converted to different multiplets, which seem to be almost identical with cellulose I_a type multiplets, with increasing steam annealing temperature: in the C1 triplet, the central line decreases in intensity with increasing annealing temperature, whereas the lines on both sides of the triplet increase in intensity. As a result, the C1 line becomes a doublet with almost identical intensities above 260 °C. Concomitantly, the C4 triplet also changes to a doublet as a result of the reduction of the downfield line and the increase of the upfield line. Compared to the change in the lines at both sides of the C4 triplet, the intensity of the central line seemingly stays constant. The C6 line is subjected to almost the same effect as the C1 triplet; this line is also composed of a triplet although it is not clearly recognized in this figure. The annealing induces a reduction of the central line and an increase in intensity of the side lines, resulting in the appearance of the doublet above 260 °C. On the other hand, the C1 and C4 noncrystalline resonances, which correspond to small broad lines at about 85 and 63 ppm,[4,8,9] respectively, do not change significantly in relative intensity, suggesting almost no change in the degree of crystallinity. Similar annealing effects were also observed for bacterial cellulose, which exhibits the same crystalline spectrum (cellulose I_b) as valonia cellulose.

Figure 2 shows the CP/MAS ^{13}C NMR spectra of original and steam-treated cotton celluloses. Since the degree of crystallinity of this sample is not high compared to that of valonia cellulose, it is not easy from this figure to determine the effect of annealing on the crystalline component. Particularly in the C1 resonances the crystalline and noncrystalline contributions are superimposed.

Figure 3 shows the spectra of the crystalline components of the original and annealed cotton celluloses, which were recorded by using the difference in ^{13}C spin–lattice relaxation times between the crystalline and noncrystalline components.[8,9,13,14,18–20] The delay time to suppress the

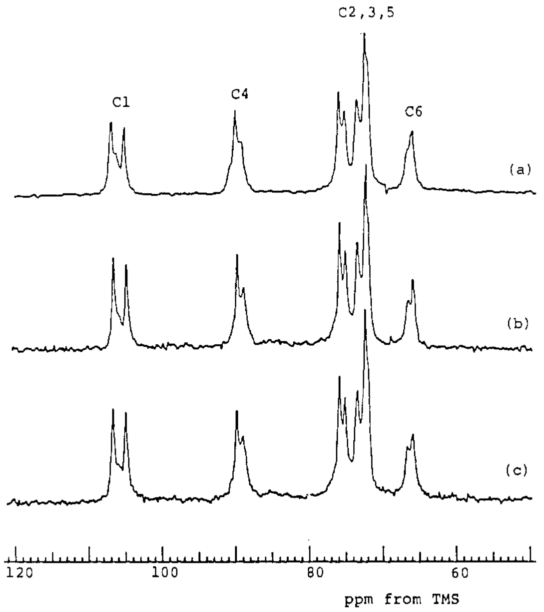

Figure 3. CP/MAS ^{13}C NMR spectra, 50 MHz, of the crystalline components of cotton cellulose treated with steam at different temperatures: (a) original, (b) 230 °C, (c) 260 °C.

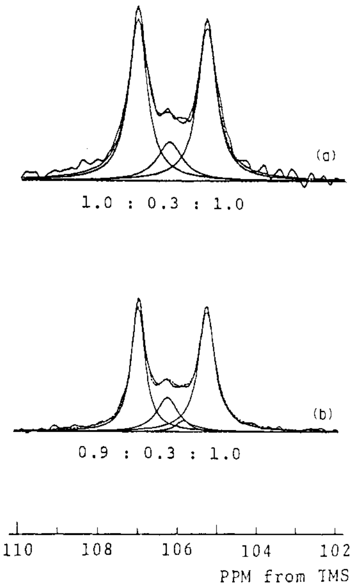

Figure 4. Line-shape analyses for the C1 resonance lines of cotton cellulose (a) and valonia cellulose (b) treated with steam at 260 and 280 °C, respectively.

noncrystalline contribution was 100 s throughout this work. As is clearly seen in Figure 3, the annealing effects are not as evident in cotton celllulose compared to the case of valonia cellulose: the C1 doublet, which is a feature of the cotton–ramie type spectrum (cellulose I_a), is almost unchanged except for a slight decrease in intensity of the central line. In the C4 triplet the change is also very small but the downfield shoulder significantly decreases in intensity at 260 °C. In addition, the C6 doublet is more clearly observed with increasing annealing temperature.

In an attempt to compare the crystalline spectra of both annealed celluloses, C1 and C4 multiplets were resolved into the constituent lines by a computer by assuming each line to be a Lorentzian curve. This assumption seems reasonable for line-shape analyses of solid-state high-resolution ^{13}C NMR spectra of different polymeric materials including cellulose,[20] polyethylene,[29] polypropyrene,[30] etc. Figures 4 and 5 show the results of the line-shape analyses for the C1 and C4 resonances which correspond to the

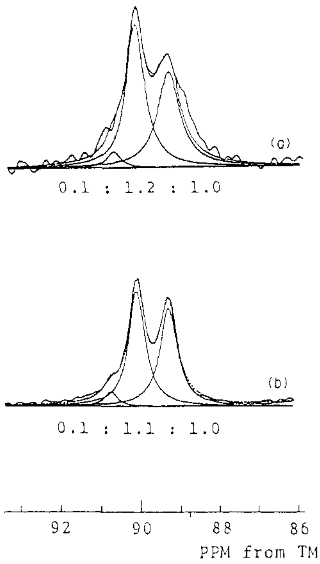

Figure 5. Line-shape analysis for the C4 resonance lines of cotton cellulose (a) and valonia cellulose (b) treated with steam at 260 and 280 °C, respectively.

spectra shown in Figures 1e and 3c. These triplets are well resolved into three Lorentzians except for the C1 resonance of valonia cellulose which additionally contains a small amount of noncrystalline contribution at 105.8 ppm. Interestingly, the integrated intensity ratios for the C1 and C4 triplets, which are indicated under the respective triplets, are almost identical for the two samples. In contrast, these ratios evidently differ from those of the original cotton cellulose; for example, 0.9:0.3:1.0 for the C1 triplet of valonia cellulose and 1.4:0.4:1.0 for that of original cotton cellulose.[20] Here, the latter is the ratio in the unrelaxed state which is calculated by considering the change in relative intensity due to ^{13}C spin–lattice relaxation. The intensity ratios of the C4 triplets, 0.1:1.2:1.0 and 0.1:1.1:1.0, for annealed cotton and valonia celluloses are also different from the ratio 0.4:2.0:1.0 for original cotton cellulose.[20] Here those values are not the unrelaxed ones, but the deviation from the true values seems very small because the C4 triplets in the unrelaxed state shown in Figure 2 are almost the same as those in the partially relaxed state shown in Figure 3. Consequently, the spectra for annealed celluloses with steam above 260 °C differ from the cotton–ramie type which is previously assigned to cellulose I_a.[20] We hereafter refer to this new type of the crystalline spectrum as cellulose I_a'. According to this nomenclature, it is concluded that both celllulose I_a and I_b are transformed into cellulose I_a' by the treatment with saturated steam above 260 °C.

Recently VanderHart and Atalla[10,11,23] have proposed that native celluloses are composites of two crystalline forms which are designated celluloses I_α and I_β and obtained the ^{13}C NMR spectra of these allomorphic forms by taking linear combinations of the spectra of regenerated cellulose I and *Acetobacter* cellulose or of the spectra of the original and hydrolyzed samples of *Cladophora* cellulose. These two the spectra of two candidates for cellulose I_β are very similar to the spectrum of cellulose I_a, for steam-treated cellulose, if the minor differences in the central line of the C1 triplet and the downfield shoulder of the C4 triplet are neglected. As is seen in Figure 1 the minor components in the C1 and C4 triplets do not change above 260 °C and thus it is impossible to obtain the spectrum exactly consisting of C1, C4, and C6 doublets, which corresponds to one of candidates for cellulose I_β, by annealing with steam. However, since the amounts of those components are very small, we can use this sample as a model for one of allomorphic forms of cellulose. Detailed characterization is in progress, using the X-ray diffraction method and electron microscopy.

Finally, we should revise the conclusion of the previous paper[19] concerning the crystals regenerated from cellulose triacetate I (CTA I), on the basis of the line-shape analyses. Although the crystal form thus produced was reported to be cellulose I_a, it should be also assigned to cellulose I_a' because the decrease in intensity is also observed for the C1 central line and the C4 downfield line in the regenerated samples. Therefore, it is concluded that celluloses I_a and I_b are transformed into cellulose I_a' by regeneration from CTA I as well as by treatment with steam above 260 °C. The same conclusion also applies in the case of regeneration from cellulose III_I.[21]

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Registry No. Cellulose, 9004-34-6.

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Acyclic Metathesis Polymerization. The Olefin Metathesis Reaction of 1,5-Hexadiene and 1,9-Decadiene

Since the appearance of Natta and Dall'Asta's report of the polymerization of cyclopentene with a catalyst/cocatalyst metal pair,[1] countless publications have probed the subject of olefin metathesis over the past 20 years.[2] Elegant mechanistic studies have shown that metallocarbenes are the reactive intermediates responsible for this disproportionation reaction,[3] that the reaction is general, and that the reaction has commercial value for the polymerization of strained cyclolefins.[4] These ring opening polymerizations, which are depicted in Figure 1, are thought to be driven by a release of ring strain,[5] and indeed high molecular weight polymers are formed very rapidly by this technique. The polymerization of cyclopentene,[6] norbornene,[7] and cyclooctene[8] have received the most attention during this 20-year period, and the metathesis polymerization of strained rings remains an active field.[9]

In this present paper, we report our efforts to employ olefin metathesis in a step polymerization, condensation-type reaction scheme, as shown in Figure 2, wherein an equilibrium is established such that a volatile compound can be removed to drive the polymerization.[10] Such a reaction would provide a significant opportunity to create a wide variety of new polymer structures, if indeed the metathesis reaction can be precisely controlled. The identity of substituent "R_1" in Figure 2 would be restricted only by factors that govern intramolecular vs. intermolecular metathesis chemistry, since the intent is for intermolecular reactions to predominate. Though the suggestion of doing polycondensation metathesis chemistry is not new,[11] virtually no results have been reported to determine the viability of the approach.

Our first reactions have been done with 1,9-decadiene and 1,5-hexadiene (structures 1 and 2 in Figure 2). These monomers were chosen since their self-metathesis would release an easily identifiable gas (ethylene, R_2 = H) and would yield well-characterized polymers (polyoctenamer and polybutadiene, respectively). Thus, the polymerization technique and not the polymers themselves become the principal object of the study. The 1,5-hexadiene polymerization appeared particularly challenging, since it has been stated that self metathesis does not occur at all for this monomer.[12]

All reactions were carried out under an argon atmosphere, either in bulk or with chlorobenzene as a solvent, and we chose the $WCl_6/EtAlCl_2$ catalyst system (monomer/tungsten 100:1 and tungsten/aluminum 1:4) for our initial experiments. Tungsten hexachloride was stored under argon, and $EtAlCl_2$ was used as received (1 M solution in hexane). In a representative polymerization the monomer and WCl_6 were combined and cooled to −78 °C, followed by the addition of the cocatalyst. The homogeneous reaction mixture was then permitted to warm to 25 °C, and after 30 min the reaction was terminated with a few drops of methanol. In some cases a slight vacuum was applied to the reaction system to remove the gases formed. Gas samples were collected during the reaction and analyzed by gas chromatography.[13]

In the 1,9-decadiene reaction, a large volume of gas was released instantly when the cocatalyst was added to the reaction flask, and GC analysis showed the major com-

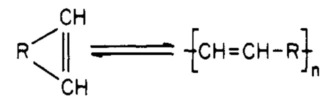

Figure 1. Ring-opening polymerization of strained cycloolefins.

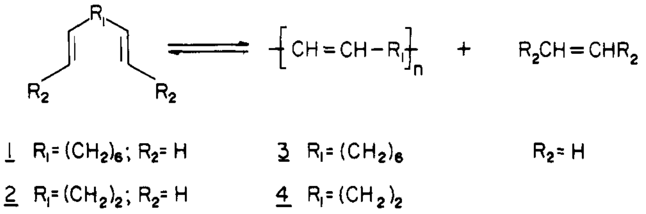

Figure 2. Step propagation, condensation type polymerization of acyclic dienes.

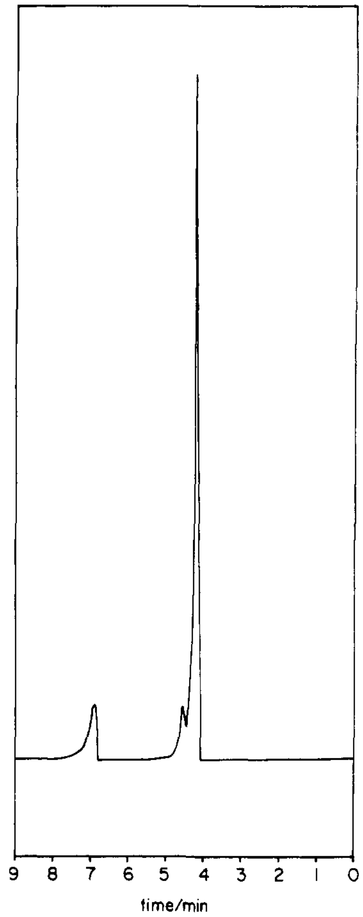

Figure 3. GC chromatogram of the gases released during the 1,9-decadiene reaction. The large peak at 4 min is identified as ethylene by comparison with an authentic sample. Identical results were observed for 1,5-hexadiene.

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