At high vacuum and by the action of the electron beam, the epoxy resin is degraded, giving rise to the observed contrast without additional staining. The PS is black while the original holes of the microfoam are light. For the weakly cross-linked network the starting material was homogeneous, while the semi-IPN with higher cross-link density already was phase separated. In the first case a finely dispersed bicontinuous structure with average dimensions of about 50 nm is observed, while in the case of the phase-separated starting material larger holes on the order of 500–1000 nm as well as the finely dispersed structure is observed. Dynamic mechanical analysis of the phase-separated semi-IPN shows a sharp loss maximum, which corresponds to "pure" PVME and a broad second relaxation maximum arising from the PS-rich phase but still contains considerable amounts of PVME.[12] Extraction of the PVME in these phase-separated systems is only possible if the phase-separated structure already is bicontinuous (on the large length scale) or if the PS-rich phase undergoes spinodal-like phase separation, providing the necessary channels for material transport. According to the morphological picture given in Figure 3b, both situations may occur simultaneously. The morphological features give strong support to spinodal-like phase separation induced by the interaction of water with homogeneous semi-IPN's. Preliminary permeation studies show that such bicontinuous microfoams may have interesting properties as barrier materials. The generation of microfoams via solvent-induced phase separation of miscible polymer system provides unique possibilities for structural control in such materials.

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Registry No. (S)(MA)(HMDA) (copolymer), 41497-14-7; PVME, 9003-09-2.

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Structural Changes of Native Cellulose Crystals Induced by Annealing in Aqueous Alkaline and Acidic Solutions at High Temperatures

In the previous paper[1] we have reported on the basis of cross-polarization/magic angle spinning (CP/MAS) ^{13}C NMR analyses that native cellulose crystals, which may be roughly classified into cotton–ramie type (cellulose I$_a$) and bacterial–valonia type (cellulose I$_b$),[2,3] are transformed into a new type of crystals by annealing above 260 °C with saturated steam. Since the CP/MAS ^{13}C NMR spectrum of the new type of crystals is very close to that of cellulose I$_a$, we refer to these crystals as cellulose I$_a'$. Although the same crystal transformation was also observed for the cases of the regenerations from cellulose triacetate I[4] and cellulose III$_1$,[5] the degree of crystallinity significantly decreases and the morphology of the microfibrils seems to undergo appreciable changes in these two cases. In contrast, the annealing with saturated steam induces almost no change in crystallinity[1] and the preliminary electron microscopic observation has also revealed no significant change in the morphological structure of the microfibrils. Therefore, the examination of the transformation process induced by this annealing will lead to better understanding of the crystal structure of native cellulose. In particular, the detailed comparison of the crystal structures of intact and annealed valonia celluloses seems to provide an important clue to solve the controversial problems[3] related to a new proposal that native cellulose crystals are a composite of two allomorphs,[6,7] because both samples are highly crystalline and the ordering in crystals is also very high.

In this annealing, we used glass fiber sheets to put each sample between them and to anneal it in the vapor phase without the contact with the liquid phase.[1] However, the glass fiber sheets have been found to play an unexpected important role in preventing the decomposition of the cellulose samples, because the vigorous decomposition of cellulose occurs without them at high temperatures. Since the dissociation of H_2O is greatly enhanced at high temperatures,[8] the increase of H ions, which may promote the decomposition reaction, will be suppressed by the glass fiber sheets. In order to find better annealing conditions, we have investigated annealing effects of native cellulose samples in different aqueous alkaline and acidic solutions at high temperatures. In this paper we report that the same transformation of valonia and cotton cellulose crystals as previously reported is reproduced by annealing in 0.1 N NaOH aqueous solution above 260 °C without the decomposition. The annealing effect of tunicate cellulose is also reported for comparison.

Valonia macrophysa, cotton, and tunicate celluloses, which were purified by the conventional method, were subjected to annealing in different aqueous NaOH or HCl solutions at 220–280 °C for 30 min. After it was washed with deionized water, each sample was packed in a MAS rotor with an O-ring seal together with an appropriate amount of deionized water. CP/MAS ^{13}C NMR mea-

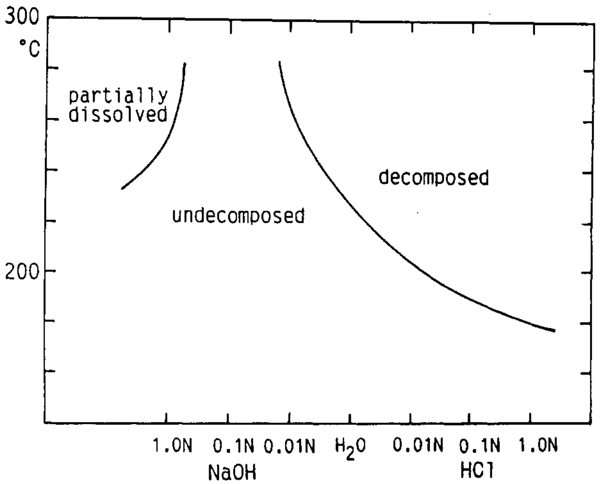

Figure 1. Apparent structural changes of the cotton cellulose sample annealed at different temperatures in aqueous alkaline and acidic solutions.

surements were carried out at room temperature on a JEOL JNM-FX200 spectrometer equipped with a VT/MAS system operating at 50 MHz under 4.7 T. A cylinder-type MAS rotor with an O-ring seal, which was modified from a commercial rotor made of aluminum oxide and poly(amide–imide) resins,[9] was used for hydrated cellulose samples. ^1H and ^{13}C radio-frequency field strengths $\gamma B_1/2\pi$ were 65.8 kHz for the CP process, while the ^1H field strength was reduced to 54.3 kHz in the dipolar decoupling process. The MAS rate was 3.5 kHz and the contact time for the CP process was 1 ms throughout this work. The chemical shift relative to tetramethylsilane was determined by using the crystalline peak at 32.89 ppm of linear polyethylene as an internal standard.

Figure 1 shows schematically the changes in the appearance of the cotton cellulose sample when annealed at different temperatures in aqueous NaOH or HCl solutions. In the media with lower pH values than for 0.01 N NaOH solution cellulose molecules are significantly decomposed at high temperatures, which are recognized by the fragmentation, partial dissolution, and deep coloration of the samples. For example, the vigorous decomposition occurs above 240 °C in water. The critical temperature for the onset of the decomposition tends to decrease with increasing HCl concentration. In contrast to this, no apparent change is observed for the annealing in 0.1–0.5 N NaOH solutions even at 280 °C. Further increase in the NaOH concentration induces partial dissolution of cellulose at higher temperatures, although the cellulose samples are not colored unlike in the media with lower pH values. Therefore, the crystal structures of the samples in region "undecomposed" shown in Figure 1 have been examined by CP/MAS ^{13}C NMR spectroscopy.

Figure 2 shows 50-MHz CP/MAS ^{13}C NMR spectra of valonia cellulose annealed at 220–260 °C for 30 min in 0.1 N NaOH solution. Almost the same changes in fine splittings of resonance lines can be observed as the case of the annealing with saturated steam in the presence of the glass fiber sheets.[1] Marked triplets of C1 and C4 resonance lines, which are characteristic of the spectra for cellulose I_b type samples, are gradually changed into enhanced doublets with increasing annealing temperature. From the line-shape analysis of the C1 and C4 resonances it is concluded that the spectrum of the sample annealed at 260 °C is cellulose I_a' type, in good accord with the previous result.[1] Almost the same spectrum was obtained for cotton cellulose, which belongs to cellulose I_a, when it was annealed under the same condition. In this case, however, the spectrum of the crystalline component had to be selectively observed using Torchia's pulse sequence as previously reported,[1] because the contributions of the crystalline and noncrystalline components are overlapped with each other particularly in the C1 resonance line of the conventional CP/MAS ^{13}C NMR spectrum. As a result, we have found more convenient and reliable annealing conditions under which the transformations from celluloses I_a and I_b to cellulose I_a' are readily induced, compared to the annealing with saturated steam with an aid of the glass fiber sheets. In addition, it should be noted that the percent mass recovery of the annealed sample is more than 90% and the molecular weight is reduced by about 40%.[10] This also indicates that the transformation to cellulose I_a' proceeds in the 0.1 N NaOH solution without vigorous degradation.

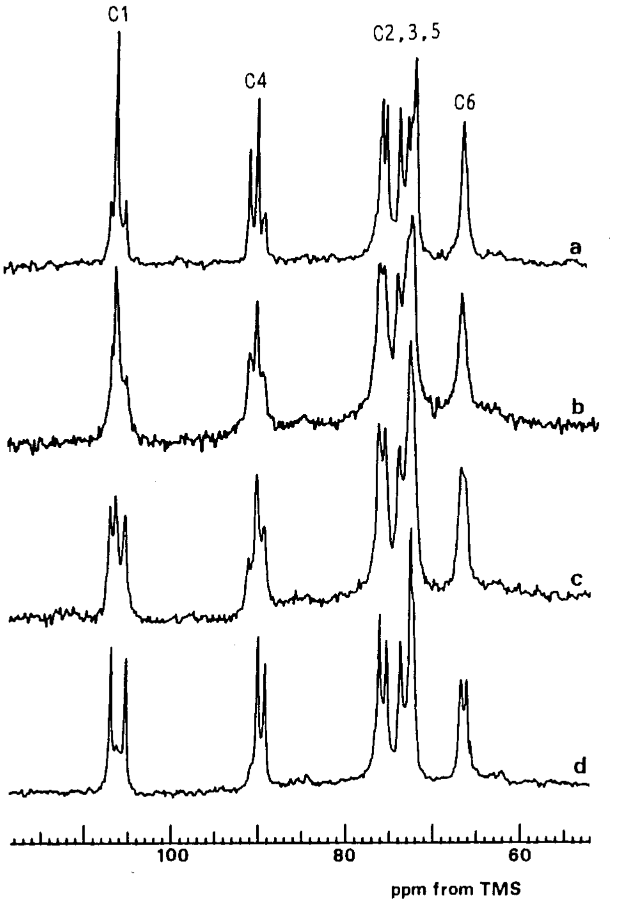

Figure 2. 50-MHz CP/MAS ^{13}C NMR spectra of valonia cellulose annealed at different temperatures in the 0.1 N NaOH solution: (a) original; (b) 220 °C; (c) 240 °C; (d) 260 °C.

Figure 3 shows wide-angle X-ray diffractograms of valonia cellulose and the sample annealed at 260 °C in the 0.1 N NaOH solution. Here each sample was cut into small fragments and pressed into a plate for the X-ray measurements. Some preferential orientation may still exist, because the diffraction intensity of the (110) plane is extraordinally low. Nevertheless, the peaks of the ($\bar{1}10$) and (200) planes appreciably shift to the wider angle side for the annealed sample, while the diffraction from the (110) plane stays almost constant. This suggests that the unit cell of cellulose crystals may be changed to some extent by the annealing. The detailed structural analysis is in progress for the sonicated microfibrils of valonia cellulose annealed at different temperatures by electron diffraction measurements.

Finally we should note the annealing effect of tunicate cellulose, because the CP/MAS ^{13}C NMR spectrum of this

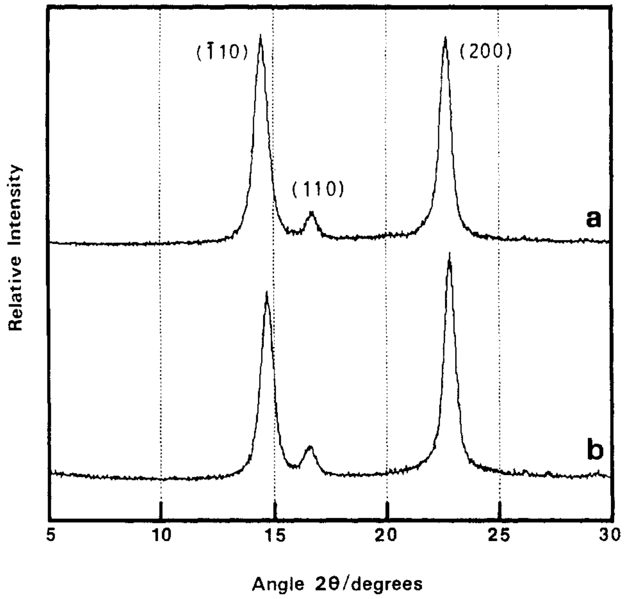

Figure 3. X-ray diffractograms of valonia cellulose (a) and the sample annealed at 260 °C in the 0.1 N NaOH solution (b).

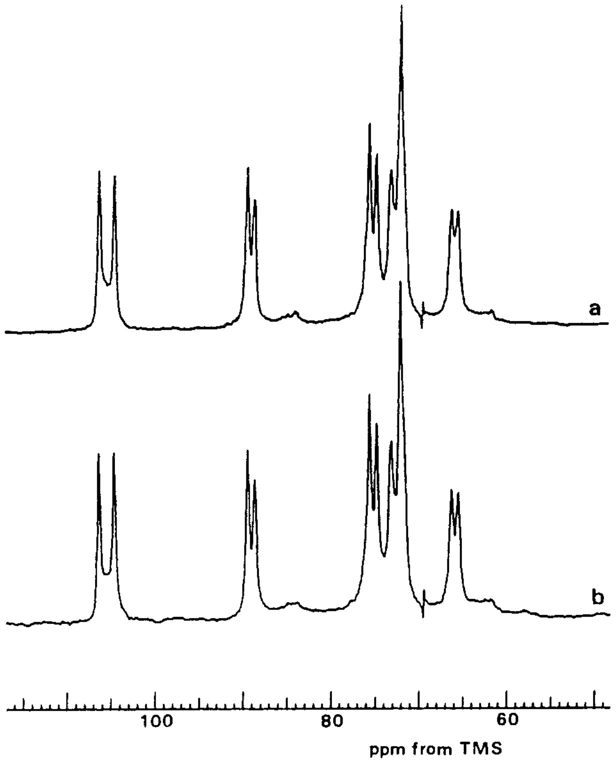

Figure 4. 50-MHz CP/MAS ^{13}C NMR spectra of tunicate cellulose (a) and the sample annealed at 260 °C in the 0.1 N NaOH solution (b).

cellulose sample seems to be very close to that of cellulose I_α' or cellulose I_β, which was defined by Atalla and VanderHart,[6,7] as first pointed out by Belton et al.[11] Figure 4 shows CP/MAS ^{13}C NMR spectra of tunicate cellulose and the sample annealed at 260 °C in the 0.1 N NaOH solution. In accord with the previous report,[11] the multiplets of the C1, C4, and C6 lines of the intact sample, which are virtually doublets, are very similar to those of cellulose I_α' or cellulose I_β. Moreover, no change in the multiplicities can be observed for the annealed sample. This may confirm that the crystal structure of tunicate cellulose is originally cellulose I_α' or cellulose I_β. Further discussion will be given elsewhere after detailed line-shape analyses are conducted for the C1 and C4 lines.

Registry No. NaOH, 1310-73-2; HCl, 7647-01-0; cellulose, 9004-34-6.

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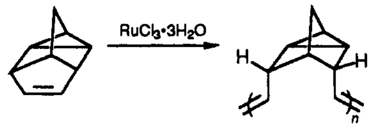
Ring-Opening Metathesis Polymerization of Deltacyclene via a Ruthenium Catalyst

The ring-opening metathesis polymerization (ROMP) of cycloalkenes was first reported in a patent in 1957 by Eleuterio and in the open literature by Truett in 1960.[2] Both synthetic and mechanistic aspects of the reaction have held the attention of chemists since that time.[3,4] We were intrigued by the possibility of preparing new materials having a combination of rigidity and strain through ROMP of suitable monomers. The homo-Diels–Alder reaction,[5] in which a highly strained deltacyclic olefin-containing compound is synthesized by cycloaddition of norbornadiene with an acetylene, provides such a monomer. The polymers derived from metathesis of this cycloalkene meet these criteria since they contain an inflexible carbon backbone, a cyclopropane ring, and a repeating sequence of olefins, which are held in close proximity due to the diendo orientation in the nortricyclane framework (eq 1).



(1)

The homo-Diels–Alder reaction has been known for almost 30 years, and the synthesis of deltacyclene was first reported in 1965.[6] Of the two routes available to provide large quantities of deltacyclene, we preferred the method developed by Lyons since it requires a single step and proceeds at room temperature.[7] However, the yields ob-

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