the general mechanism can be solved for the case of an initial "most probable" distribution and the connections between moments of the molecular weight distribution are known for the general mechanism and arbitrary initial molecular weight distribution.

The Simha, Wall, and Blatz mechanism was formulated in terms of kinetic rate equations. Alternatively, a statistical description may be used and this approach was used by Simha and Montroll[8,9] much earlier for discussing stepwise scission as opposed to chain depolymerization. Gordon[3] used the statistical method in his treatment and thus made the important contribution of establishing the equivalence between the approaches.

With respect to explicit results for other than the initial "most probable" system the situation is the following. Numerical results were obtained by Simha, Wall, and Bram[10] by direct numerical solution by computer of the rate equations for the case of scission initiation and an initial monodisperse distribution. Inaba and Kashiwagi[1] also performed numerical integration and included initial distributions other than monodisperse. Boyd and Lin assumed a flexible analytical form for the molecular weight distribution (the Schulz-Zimm distribution) through the course of the degradation and used their general moment equations to derive a set of three coupled differential equations for the sample weight, molecular weight, and molecular weight distribution or polydispersity parameter. These were solved numerically for an extensive set of initial polydispersities (from very broad to very narrow) and zip lengths for both end-group initiation[6] and scission initiation.[7] In addition to their numerical integration calculations, Inaba and Kashwagi[1] introduced the simplification of regarding the polydispersity parameter as remaining constant through the degradation and arrived at equations representing the molecular weight and sample weight. They presented results for a log normal distribution. This simplification however is not a justifiable one. The effect of chain scission on any initial distribution is to cause it to approach the "most probable" one. The effect is very rapid vs. conversion for short zip lengths and slower but nevertheless inexorable for longer ones. Thus regarding polydispersity as constant is at best only an approximation appropriate at low conversions and long zip lengths. The work of Boyd and Lin[6,7] explores this point in detail.

A summary of much of the previous work on the theory of thermal depolymerization can be found in a review article.[11]

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Richard H. Boyd*
Department of Materials Science and Engineering and Department of Chemical Engineering
University of Utah
Salt Lake City, Utah 84112

Robert Simha
Department of Macromolecular Science
Case Western Reserve University
Cleveland, Ohio 44106

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Reply to Comments on "A Calculation of Thermal Degradation Initiated by Random Scission. 1. Steady-State Radical Concentration"

We greatly regret our inaccurate and incomplete effort in referring to previous works. We appreciate very much the excellent review by Professors Boyd and Simha, which summarizes the previous theoretical studies of thermal degradation based on the free radical mechanism.

Thermal degradation based on random scission initiation, depropagation, and termination reactions with variable polydispersity can be calculated only numerically. However, the numerical solutions cannot be used widely by other people. For this reason, we used the approximation of a constant polydispersity (initial polydispersity) to obtain an approximate analytical solution, although we are aware that polydispersity changes significantly during degradation for the case of small zip length as shown in Fiure 10 in our paper. The key question is then how bad or good the approximate analytical solution is compared with the numerical results without any approximation. This comparison was made in our paper and the results are shown in Figures 2, 3, 6, and 7. The results shown in Figure 3 summarize the comparison. In the Z/x_0 range of 10^{-2}–10^2, the results based on the approximate analytical solution are reasonably close to the numerical results (roughly at most a 7% overestimation). Considering the difficulty in precise measurement of the degree of polymerization, we believe that our approximate analytical solution is useful and can be used by other people. This indicates that the change in polydispersity during degradation appears not to be significantly important if the degradation is based on random scission initiation, depropagation, and termination reactions.

Atsushi Inaba and Takashi Kashiwagi*
Center of Fire Research
National Bureau of Standards
Gaithersburg, Maryland 20899

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Transformation of Native Cellulose Crystals from Cellulose I_b to I_a through Solid-State Chemical Reactions

In the preceding paper[1] we reported that CP/MAS ^{13}C NMR spectra of the crystalline components of valonia and bacterial celluloses differ from those of cotton and ramie celluloses. On the basis of this finding, it has been concluded that there are two types of crystalline spectra for these native celluloses, cotton–ramie type and bacterial–valonia type, which are simply referred to as cellulose I_a and cellulose I_b, respectively. However, the intensity ratios of the subpeaks of the triplets representing the C1 and C4 resonances cannot be described in terms of simple integers. In addition, ^{13}C spin–lattice relaxation times T_{1C} and line widths of the subpeaks are significantly different from each other. These suggest that the crystalline regions of native cellulose may be composed of different crystal structures, in accord with previous proposals.[2-4] It may be difficult at present, however, to explain the origin of the composites of the different crystal forms, particularly because the cause of the fine splitting of the resonance lines is not well understood in solids. Therefore, in an attempt to obtain

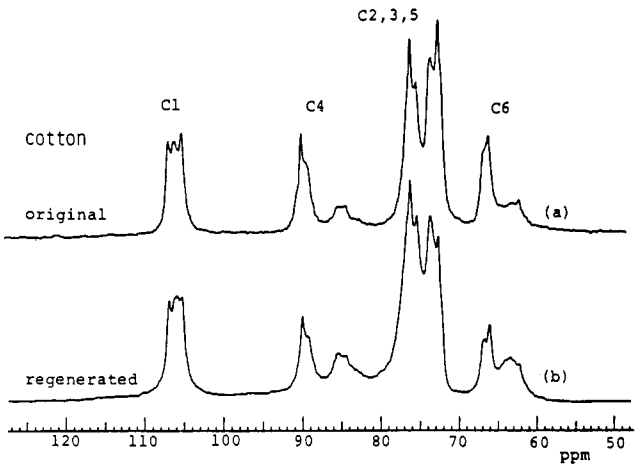

Figure 1. 50-MHz CP/MAS ^{13}C NMR spectra of the original cotton and the cotton regenerated from the triacetate.

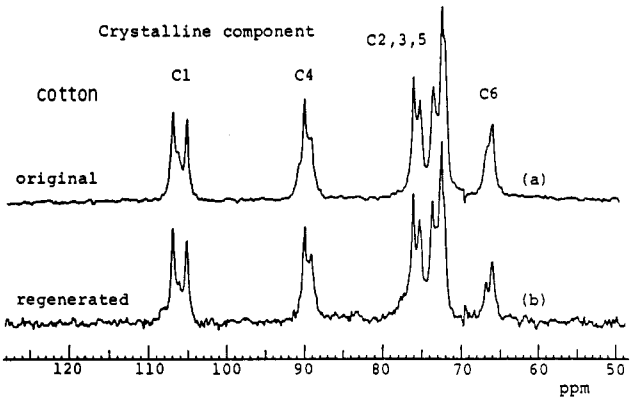

Figure 2. 50-MHz CP/MAS ^{13}C NMR spectra of the crystalline components for original cotton and regenerated cotton.

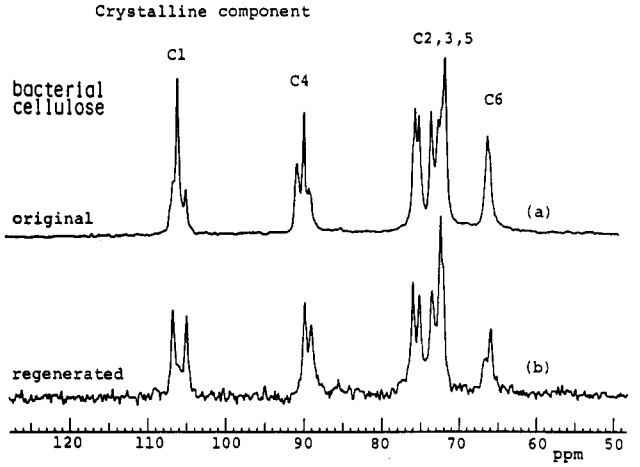

Figure 3. 50-MHz CP/MAS ^{13}C NMR spectra of the crystalline components for original bacterial cellulose and its regenerated cellulose.

further information about the crystal forms of native cellulose, we have examined the possibility of interconversion between cellulose I_a and I_b.

A large number of CP/MAS ^{13}C NMR studies[5] have already been carried out on cellulose polymorphs and their derivatives, but no one has focused on the problem of the transformation between cellulose I_a and I_b. There are several ways to regenerate cellulose I after converting it to other crystal forms of cellulose or cellulose derivatives.[6] Of these processes, solid-state triacetylation followed by saponification has been extensively studied by many investigators.[6] Under conditions of moderate swelling the acetylation of native cellulose with the crystal structure of cellulose I yields cellulose triacetate I (CTA I), and in turn cellulose I can be regenerated by solid-state saponification under low swelling. In this paper we report CP/MAS ^{13}C NMR studies of cotton, bacterial, and valonia celluloses that were regenerated from their triacetates with such solid-state reactions.

Heterogeneous acetylation of cotton, bacterial, and valonia celluloses was carried out by a procedure described by Sprague et al.[7] This procedure involves the pretreatment of the cellulose in 80% acetic acid followed by acetylation in a 50/50 mixture of acetic anhydride and amyl acetate, using 0.2% perchloric acid, for 5 h at 20 °C. The triacetylated samples were also saponified heterogeneously for 19 h at 80 °C in an aqueous solution containing 1 wt % NaOH and 10 wt % sodium acetate. CP/MAS ^{13}C NMR measurements were carried out with JEOL JNM-FX200 spectrometer equipped with a CP/MAS unit operating under a static magnetic field of 4.7 T, using the same experimental conditions as in the previous work.[1]

Figure 1 shows the CP/MAS ^{13}C NMR spectra of original cotton and cotton regenerated from the triacetate, respectively, which were measured in the hydrated state using an MAS rotor with an O-ring seal.[8,9] As already reported,[5,10-14] the respective resonance lines are assigned to the C1, C4, and C6 carbons from the downfield side except for the cluster of resonances at 70–80 ppm which belong to the C2, C3, and C5 carbons. Of these resonances C4 and C6 split into two components, a sharp downfield and a broad upfield component. These sharp and broad components have been assigned to the crystalline and noncrystalline components, respectively.[12-14] Although two such components cannot be explicitly observed in the C1 line, their existence has been confirmed by ^{13}C spin–lattice relaxation analysis.[15] The relative intensity of the noncrystalline components of C4 and C6 carbons against the crystalline components increases when compared with that of original cotton; namely the crystallinity of the regenerated cotton is lower than that of the original cotton.

It has been found that ^{13}C T_1 values of the crystalline and noncrystalline components of cotton are 140–230 and 14–40 s, respectively. On the basis of the large difference in T_1 values, we have recorded the spectra of the crystalline and noncrystalline components of both samples, as shown in Figure 2. The chemical shifts of both samples are the same, although the fine splitting of each carbon of regenerated cellulose is more clearly recognized. It is, therefore, concluded that the cellulose regenerated from triacetylated cotton has the same crystalline regions, cellulose I_a, as that of native cotton.

Figure 3 shows the spectra of the crystalline components of the original bacterial cellulose and its regenerated cellulose, respectively. As is clearly seen in Figure 3a, the spectrum of the bacterial cellulose is different from that of cotton. We have already designated this crystalline spectrum as cellulose I_b, which has been also found for valonia celluloses.[1] In contrast, the spectrum of the regenerated bacterial cellulose is completely different from the original spectrum but almost the same as that of cotton and the regenerated cotton (cellulose I_a), as shown in Figure 3b. Almost the same result was obtained also for valonia cellulose having cellulose I_b. It can be, therefore, concluded that cellulose I_b is converted into cellulose I_a through solid-state acetylation and saponification.

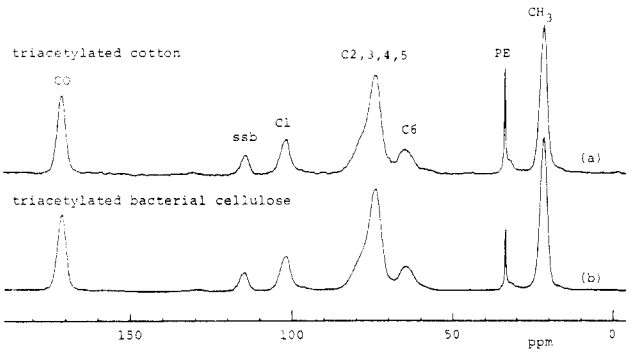

Figure 4. 50-MHz CP/MAS ^{13}C NMR spectra of the triacetylated samples from cotton and bacterial celluloses.

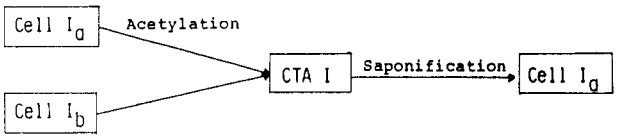

Figure 5. Transformation processes of cellulose crystals by heterogeneous acetylation and saponification.

Marrian and Mann[16] has found the same type of spectrum change in infrared spectroscopy for bacterial and valonia celluloses regenerated from cellulose triacetate, which is in good accord with our results. The same conversion in infrared spectra has also been observed in the case of the regeneration from cellulose III_I, which was prepared by treatment with liquid ammonia at about −50 °C.[16] The examination of the latter process is in progress by CP/MAS ^{13}C NMR spectroscopy.[17]

In order to confirm at which stage the transformation from cellulose I_b to cellulose I_a occurs, we have measured X-ray diffraction patterns and the CP/MAS ^{13}C NMR spectra of triacetylated cotton and bacterial celluloses in the dry state. From X-ray analysis it was difficult to distinguish between the two acetylated samples, and both samples were assigned to cellulose triacetate I (CTA I).[19] Moreover, as shown in Figure 4, the CP/MAS ^{13}C NMR spectra of both samples are almost the same. Thus it has been confirmed that cotton with cellulose I_a and bacterial cellulose with cellulose I_b produce the same crystal form CTA I by the heterogeneous acetylation. Chanzy and Roche[20] studied the change in *Valonia ventricosa* microfibrillar morphology upon the acetylation and saponification by electron microscopy. The structure and orientation for the acetylated and deacetylated microfibrils were identified by selected area diffraction. However, no change could be observed in the fibrillar morphology in both reaction processes. Some significant change in chain conformation and/or packing may occur during solid-state acetylation in the case of bacterial and valonia celluloses, but it is difficult at present to discuss in detail this structural change because the cause of the multiplicities of the resonance lines is unknown and the X-ray diffraction method has not clearly detected such a difference.

In Figure 5, we summarize the transformation process of cellulose I_a and I_b for native cellulose. Cotton and ramie celluloses belong to cellulose I_a, while bacterial and valonia celluloses are assigned to cellulose I_b.[1] The heterogeneous acetylation transforms both groups of native celluloses to the same crystal form CTA I, and these CTA I samples are regenerated to cellulose I_a by heterogeneous saponification. Thus the structural difference in cellulose I_a and I_b disappears during acetylation under the low swelling condition.

Registry No. cellulose, 9004-34-6; cellulose triacetate, 9012-09-3.

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Asako Hirai, Fumitaka Horii,* and Ryozo Kitamaru
Institute for Chemical Research
Kyoto University
Uji, Kyoto 611, Japan

Received November 18, 1986

New Initiator System for the "Living" Anionic Polymerization of *tert*-Alkyl Acrylates

The elegant demonstration[1-3] by a Du Pont Co. research team that the nucleophile-assisted "group-transfer" reaction[4] of silyl ketene silyl acetals could be turned into a "living" polymerization process for alkyl acrylates (and other α,β-unsaturated carbonyl monomers) challenged us to revisit possible pathways toward a "living" anionic polymerization of such monomers. Owing to the general importance of poly(acrylates), it would indeed still be desirable to extend such a "living" control to a higher molecular weight range and especially make it compatible with monomers lacking carbonyl conjugated groups (i.e., styrenes, dienes, heterocyclic monomers, etc.), in order to easily synthesize the corresponding and still unknown block copolymers.

Although many attempts to solve that problem have been reported in the literature,[5-9] none of them has been really successful as yet. In this preliminary communication, we describe a possible answer to that challenge.[10]

The strategy followed here has been to minimize the relative importance of the secondary transfer and termination reactions (usually ascribed to the presence of the

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