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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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.

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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