(1767 cm^{-1}), C–O–C (1235 cm^{-1}), and C–Cl (828 cm^{-1}) stretching bands. The trimethylsilyl ether **8** can be prepared: The O–H band is replaced by the expected $OSi(CH_3)_3$ bands (2957, 1252, 868, and 841 cm^{-1}). Reaction of PCTFE–OH with thionyl chloride does not yield the expected chloride. Instead, the sulfite **9** is formed is evidenced by the OS(O)O band (907 cm^{-1}). Another expected absorbance due to OS(O)O overlaps the PCTFE peak at 1194 cm^{-1}. This reaction does not follow the typical pathway of solution alcohol–thionyl chloride reactions.[13] The chlorosulfite intermediate is trapped by a surface hydroxyl group to yield **9** faster than SO_2 is eliminated to form the chloride **6**. Treatment of PCTFE–OH with adipoyl chloride renders the diester **10** and a negligible amount[14] of the half ester/half acid chloride. A single carbonyl stretching band (1734 cm^{-1}) appears in the ATR IR spectrum.

It was possible to obtain elemental analyses of the modified surfaces by XPS, which were consistent with the chemistry detailed in Figure 1.[15] Table I summarizes this data. Elemental analysis of surface **3** indicates that its actual structure is 80% III and 20% II. Calculated values for surfaces **4**–**10** are based on this structure, that is, four functional groups per five PCTFE repeat units. These data complement the ATR IR spectra, confirming ambiguous intepretations, particularly for surfaces **6**, **9**, and **10**.

Acknowledgment. We are grateful to the Office of Naval Research and the University of Massachusetts Institute for Interface Science (supported by IBM) for financial support. T.J.M. acknowledges the support of the National Science foundation in the form of a Presidential Young Investigator Award.

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(9) There is a large body of work on the surface modification of polymers containing hydroxyl groups, e.g., poly(vinyl alcohol) and cellulose. For examples, see ref 16–19. These materials are not appropriate for surface studies of the type reported here. They interact extensively with polar solvents (swell and dissolve) and are not chemically resistant, and the derivatized materials contain unreacted hydroxyl groups, which make analyses difficult. We found[19] that it is difficult to control the extent of these reactions.

(10) The numerators of the fractions appearing below the structures in Figure 1 are the advancing contact angles; the denominators are the receding contact angles. Doubly distilled (Gilmont still) water was the probe fluid and a Rame-Hart telescopic goniometer was used to perform analyses. Advancing contact angles were determined by measuring the tangent normal to the drop at the drop–surface intersection as water was added to the drop (using a Gilmont syringe) and the drop advanced. Receding contact angles were measured as water was removed from the drop and the drop receded.

(11) We have carried out several of these reactions on PCTFE–OH samples with 50-Å-thick modified layers and the contact angle and X-ray photoelectron spectroscopy indicate that identical reactions occur; however, ATR IR spectra provide little information.

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

Inaba and Kashiwagi[1] recently presented calculations concerning the effects of the initial polydispersity of molecular weight in a specialization of the general chain mechanism of thermal degradation formulated by Simha, Wall, and Blatz[2] to chain scission initiation. As the description by Inaba and Kashiwagi of the previous literature dealing with this problem was inaccurate and incomplete, we take this opportunity to describe some of the highlights related to it. In addition we point out an inadequacy in a simplification used by them. Gordon[3] showed that the rate equations could be solved for the special case of end-group initiation and no chain transfer if the initial molecular weight distribution were "most probable" (actually the "exponential" approximation to it). He found equations connecting the evolution of sample weight and molecular weight and showed that explicit separate expressions for the average molecular weight and sample weight vs. time in terms of the rate constants could be found under the above circumstances. Simha[4] found that equations connecting sample weight and molecular weight could be obtained under the more general circumstances of the complete mechanism that includes scission initiation and chain transfer and under arbitrary initial distribution. Boyd[5] showed that the complete general mechanism rate equations could be solved and explicit separate molecular weight and sample weight equations found under the circumstance of an initial "most probable" distribution. It is important to realize that the results of Gordon and Boyd showing that the *form* of the "most probable" distribution is preserved if present initially are a consequence of the mechanism and not an assumption. The sample weight can be considered to be the first moment of the molecular weight distribution and the number-average molecular weight to be the ratio of the first to zeroth moment. Thus the equations connecting molecular weight and sample weight evolution referred to above are equations connecting the zeroth and first moments of the molecular weight distribution. Boyd and Lin[6,7] showed that, in general, equations connecting the n-th and $(n + 1)$-th moments (end-group initiation) or n-th, $(n + 1)$-th, and $(n + 2)$-th moments (scission initiation) can be derived. This summarizes the situation with respect to exact results;

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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Received November 11, 1986

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