5178 *Macromolecules* **1997,** *30,* 5178−5180

Preparation and Characterization of a Stable, Polymer-Bound, Linear Hemiacetal

Pierre A. Berger,* Joel R. Garbow, Arijit M. DasGupta, and Edward E. Remsen

Monsanto Company, 800 North Lindbergh Boulevard,
St. Louis, Missouri 63167

Received April 15, 1997

Introduction

Hemiacetals are well-established intermediates[1] in the formation and hydrolysis of acetals, though their extreme instability makes them difficult to isolate and characterize.[2] Although special steps such as incorporation of stressed ring systems or bulky substituents[3] stabilize hemiacetals sufficiently to allow isolation, few examples of isolated, stable, linear, acyclic hemiacetals are known.[4,5]

In a recent NMR study of poly(vinyl butyral) (PVB) we observed peaks in the solution- and solid-state spectra of acid-treated PVB that could not be assigned on the basis of spectra previously reported[6] for PVB. We present here an analysis of NMR spectra for acid-treated PVB that is consistent with the formation of a linear, acyclic hemiacetal. This is, to the best of our knowledge, the first isolation and characterization of a stable, linear, acyclic, polymer-bound hemiacetal.[7]

Experimental Section

The preparation method used in the acid treatment of PVB in methanol solution was critical for producing stable hemiacetals. Dried PVB in methanol solution (4% w/v), prepared to a volume of 2.5 mL, was acidified by dropwise addition of 200 μL of 1 N HCl. The addition of acid initiated polymer precipitation, which was completed by immediately adding 2.5 mL of deionized water. The polymer was isolated and dried by vacuum filtration after washing with deionized water until the filtrate had a pH between 6 and 7. The washed polymer was then dried over P_2O_5 for 24 h before NMR characterization. Residual chloride analysis via X-ray fluorescence revealed no measurable chloride ion in the dried polymer. Molecular weight analysis via size-exclusion chromatography/low-angle laser light scattering[10] indicated no chain degradation resulted from the acid treatment of the PVB.

Results and Discussion

Changes in the polymer due to acid treatment were apparent in its solution-state ^{13}C NMR spectrum, portions of which are shown in Figure 1. For example, the relative intensities of characteristic acetal resonances of the *meso tt* and *rac tt* ring types of PVB,[6] at 102 and 96 ppm, respectively, were dramatically altered. As shown in Figure 1, the *rac tt* peak of the parent PVB (Figure 1A) nearly disappeared and was replaced by a new resonance at 106 ppm (Figure 1B) after acid treatment. By contrast, little change was observed in the *meso tt* peak. The corresponding solid-state carbon spectra of PVB and acid-treated PVB, shown in Figure 2, display the same pattern of change noted in solution-state spectra. Figure 2A is nearly identical to the solid-state ^{13}C NMR spectrum of PVB reported previously.[11] The signal associated with the *rac tt* carbons (Figure 2A) nearly disappears after acid treatment (Figure 2B).

The solution-state ^{13}C NMR spectrum of the acid-treated polymer also showed three additional peaks at chemical shifts of 35.9, 18.7, and 14.5 ppm, having two, two, and three directly attached protons, respectively. On the basis of proton homonuclear correlation (COSY) data, these signals are assigned, together with the acetal carbon at 106 ppm, to a C_4 chain. Spectral changes due to acid treatment are also seen in the carbinol (65−77 ppm) and chain methylene (37−47 ppm) regions of the ^{13}C spectrum. Note, in particular, the strong reduction of the ring carbinols belonging to the *rac tt* ring (∼70 ppm), and the appearance of the new peaks (∼68 ppm) between the *rac tt* ring and alcohol carbinol (∼65−67 ppm) resonances. Although changes in the chain-methylene carbon region of the spectrum are difficult to interpret, they clearly reflect changes in the polymer conformation and/or microstructure[8] induced by the acid treatment.

NMR relaxation data provide additional evidence for hemiacetal formation. Solution-state $T_1(C)$'s for all carbon types in the acid-treated PVB increased dramatically compared with their corresponding values in untreated PVB. For example, $\langle T_1(C)\rangle$ increased from 0.4 to 4.3 s for the C2 acetal carbon (see Figure 1 for carbon numbering scheme) and from 0.4 to 4.5 s for the C11 methylene carbons. These data indicate high-frequency (megahertz regime) motions of the polymer chain change greatly upon acid treatment. Similar changes are observed in the low-frequency cooperative motions of large polymer-chain segments probed by rotating-frame proton and carbon relaxation measurements in the solid state. Measured relaxation times were consistently shorter for the acid-treated PVB compared to the untreated polymer (e.g., $\langle T_{1\rho}(H)\rangle = 9.3$ ms (PVB), 6.2 ms (acid-treated PVB); $\langle T_{1\rho}(C)\rangle$ [C4/C6 backbone methine carbons] = 30 ms (PVB), 10 ms (acid-treated PVB)), indicating these motions are considerably more efficient in causing relaxation in the acid-treated polymer.

To determine if acid-induced changes in PVB were due to an unstable intermediate, the temporal stability of the solution-state spectrum was tested over a 12 month period. During this time the samples were kept at room temperature in capped NMR tubes. The spectrum slowly changed and ultimately yielded the original spectrum of the parent PVB.

The thermal stability of the isolated polymer was evaluated by heating the solid polymer to 80 °C for approximately 16 h. No changes were observed in the solution-state spectrum of the dissolved polymer after this treatment.

The consistency between solution- and solid-state spectra conclusively demonstrates that observed solution-state spectral changes are not artifacts produced by reaction between the polymer and the methanol-d_4 solvent. This result, in conjunction with temporal and thermal stability findings, conclusively demonstrates that acid treatment of PVB produces a stable, isolatable compound.

The structural change in PVB indicated collectively by the solution- and solid-state spectra and relaxation data was the formation of a flexible, hemiacetal-containing C_4 chain due to the hydrolysis of *rac tt* acetal rings. This novel species is shown as structure **IV** in the acid hydrolysis mechanism for PVB acetals rings (Scheme 1). The preference shown toward the *rac tt* ring in the hydrolysis is consistent with the current model of acetal decomposition. Although not fully understood, it is generally accepted that in acidic media acetal decomposition proceeds through a concerted mechanism via intermediate **II** in the above mechanism.[2,12,13] In this scheme, breaking of the carbon−

---

* Address correspondence to this author.

S0024-9297(97)00516-0 CCC: $14.00

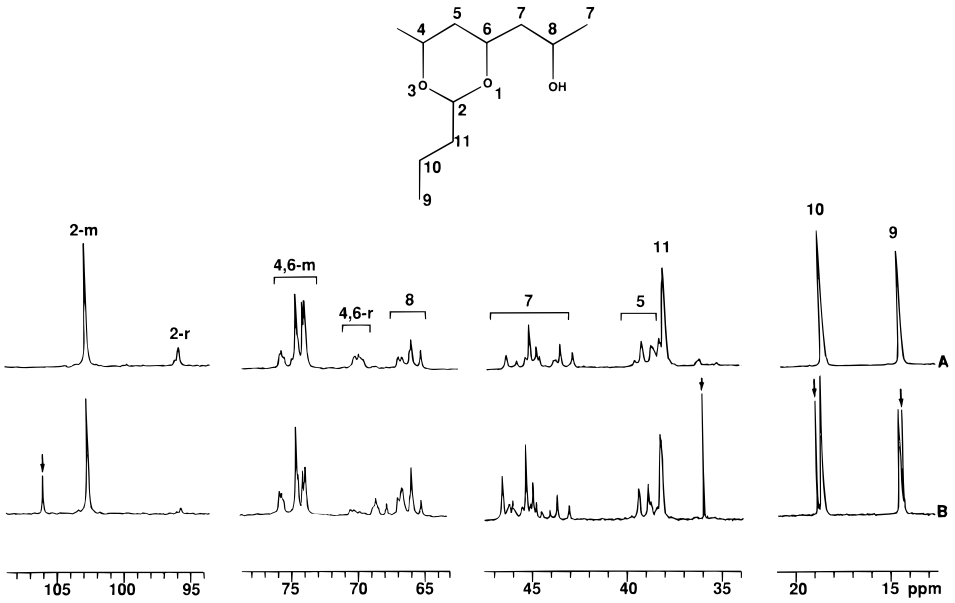


Figure 1. 100 MHz solution-state ^{13}C NMR spectrum of PVB dissolved in CD_3OD (0.7 g/mL) before (A) and after (B) acid treatment. The peaks attributed to the hemiacetal carbon (106 ppm) and the hemiacetal sidechain carbons (35.9, 18.7, and 14.5 ppm) are indicated by arrows in trace B. The spectra were acquired at 40 °C.

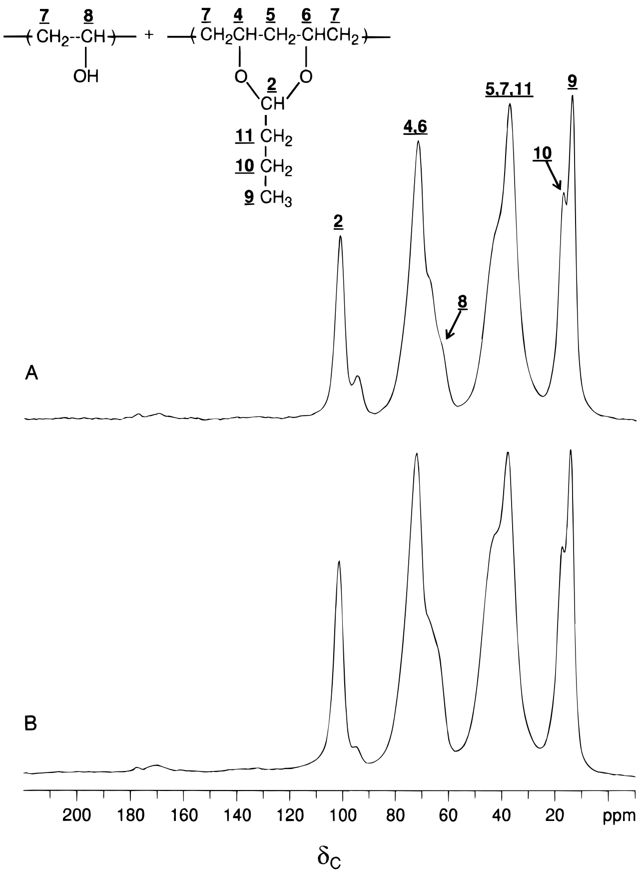
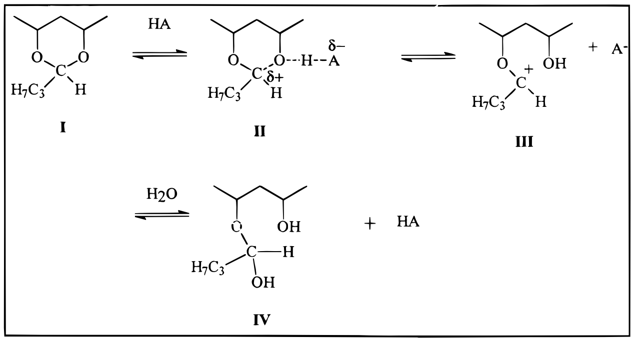


Figure 2. Cross-polarization magic-angle spinning (CPMAS) ^{13}C NMR spectra of PVB (A) and acid-treated PVB (B). Samples were spun at the magic angle at a rate of 3 kHz. CPMAS ^{13}C NMR were obtained at 31.9 MHz following 2-ms matched, 50 kHz $^{1}H-^{13}C$ cross-polarization contacts. High-power ^{1}H decoupling ($H_1(H)$ = 65 kHz) was used during data acquisition, and the recycle delay between repetitions of the experiment was 1 s.

Scheme 1



oxygen bond is the rate-determining step.[13] The pathway is highly stereospecific and acid-catalyzed cyclization back to the acetal may involve S_N^2 displacement of water from the protonated hemiacetal.[11] It should, therefore, come as no surprise that it is the *rac tt* symmetry that gives rise to a stable hemiacetal. This view is consistent with the strain of the *rac tt* ring.[6] In addition, the conformation of the *rac tt* ring is inappropriate for the axial alignment of entering, exiting, and central atoms that is required for S_N2 displacement.[14,15] The apparent thermal and temporal stability of the hemiacetal may also be a consequence of the conformational alignment requirements of the S_N2 displacement reaction. However, further investigation of the kinetics of hemiacetal decay into *rac tt* rings is needed to confirm this hypothesis.

Acknowledgment. The authors express their appreciation to C. Ling for providing X-ray fluorescence analyses.

References and Notes

(1) Carey, F. A.; Sundberg, R. J. *Advanced Organic Chemistry, Part A: Structure and Mechanism*, 3rd ed.; Plenum Press: New York, 1990.
(2) Hurd, C. *J. Chem. Educ.* **1966**, *43*, 527.
(3) Bergstrom, R. G. In *The Chemistry of Ethers, Crown Ethers, Hydroxy Groups and their Sulfur Analogs*; Patai, S., Ed.; John Wiley & Sons: New York, 1980; Part 2, p 881.
(4) Miller, J. F.; Spaltenstein, A. *Tetrahedron Lett.* **1996,** *37*, 2521.
(5) Erickson, J. L. E.; Campbell, C. R. *Tetrahedron Lett.* **1981,** *22*, 3815.

(6) Berger, P. A.; Remsen, E. E.; Leo, G. C.; David, D. J. *Macromolecules* **1992,** *24,* 2189.

(7) Previously, Schlothauer et al.[8] have described the presence of hemiacetals in PVB. However, we believe these claims are incorrect and are based on an erroneous interpretation of the *rac tt* acetal peak. The interpretation of the ^{13}C NMR spectrum of PVB in terms of two cyclic acetal peaks, belonging to two ring conformations (denoted as *rac tt* and *meso tt*) is well supported.[6,9] Additional supporting evidence includes observation that (a) the two acetal carbons have nearly identical solution T_1s and (b) the ratio of the integrals of the ring carbinol and acetal peaks (^{13}C and ^{1}H) is 2/1; the intepretation of the *rac tt* acetal peak as a hemiacetal peak would typically result in a 1.8/1 ratio.

(8) Lebek, B.; Scholthauer, K.; Krause, A.; Marschner, H. *Acta Polym*. **1989**, *40,* 92. Schlothauer, K.; Schulz, B.; Marschner, H.; Krause, A. *Ibid.* **1987**, *38,* 250. Lebek, B.; Krause, A.; Schlothauer, K.; Marschner, H. *Ibid.* **1992**, *43,* 140.

(9) Bruch, M. D.; Bonesteel, J. K. *Macromolecules* **1986**, *19,* 1622.

(10) Remsen, E. E. *J. Appl. Polym. Sci.* **1991**, *42,* 503.

(11) Schaefer, J.; Garbow, J. R.; Stejskal, E. O.; Lefelar, J. A. *Macromolecules* **1987**, *20*, 1271.

(12) Reddy, C. P.; Rao, R. B. *Tetrahedron* **1982**, *38,* 1825.

(13) Nakamura, N.; Suzuki, K. *J. Polym. Sci., Part A: Polym Chem*. **1996**, *34,* 3319.

(14) Hine, J. *Structural Effects on Equilibria on Organic Chemistry*; John Wiley & Sons: New York, 1975; p 284.

(15) Morrison, R. T.; Boyd, R. K. *Organic Chemistry*; Prentice Hall: New York, 1983; p 216.

MA970516B