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Characterization of Acetal Ring Conformations in Poly(vinyl acetal) Resins Using Two-Dimensional Nuclear Magnetic Resonance Spectroscopy

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ABSTRACT: The ^{1}H and ^{13}C NMR spectra of poly(vinyl butyral) and poly(vinyl formal) were reexamined by two-dimensional homonuclear and heteronuclear correlation spectroscopy. On the basis of these results the geometry of the two major 1,3-dioxane ring systems was established. The thermodynamically less favored ring exhibited a twisted conformation instead of a trans-substituted chair conformation as has been commonly accepted. The implications of this result on the overall chain dimension and conformation, as supported by molecular modeling studies, are discussed.

Introduction

The study of the microstructure of synthetic polymers is justified by the assumption that composition, stereosequence distribution, and dynamic interactions determine some of their macroscopic properties. Of all the available spectroscopic techniques for such studies, high-resolution nuclear magnetic resonance (NMR) spectroscopy has proved to be one of the most versatile, informative, and generally applicable in this field. Its limitations are mainly dictated by the solubility of the polymer in an appropriate solvent, by the correlation times that determine the lifetime of the nuclear spin states, and by the inhomogeneous broadening of peaks.

The application of NMR to the study of polymers was pioneered by Bovey and co-workers[1] in the 1960s and led to the determination of tacticities. However, the correct assignment of the peaks was a formidable problem and subject to ambiguities. New ground was broken with the advent of two-dimensional NMR (2D NMR) and high-field superconducting magnets. In the 2D NMR experiment,[2] spectra are acquired simultaneously along two identical or different frequency axes, and correlated spin states give rise to crosspeaks at the intersections of the respective peak positions on these axes. In this way, overlapping patterns in one dimension are expanded in two-dimensional space. 2D NMR not only results in increased resolution and dispersion but also provides a solution to the peak assignment problem; this approach has appropriately been dubbed "absolute configuration assignment".[3]

The power of 2D NMR in polymer microstructure characterization has been demonstrated in several cases.[3–5] In the present study its application to the determination of acetal ring conformations in poly(vinyl acetal) resins is described.

Experimental Section

Sample Preparation. Poly(vinyl butyral) (PVB) and poly(vinyl formal) (PVF) resins used in this study were provided by Dr. G. C. Cartier, Monsanto Chemical Co. A typical PVB resin had a weight-average molecular weight (M_w) of 200 000 and contained 18.5 wt % residual poly(vinyl alcohol) (PVA), which corresponds to 54 mol % acetal. The set of PVB resins used in this study ranged in PVA content from 11.5 to 27 wt %, corresponding to 46–70 mol % cyclic acetal content. Molecular weight was determined by size-exclusion chromatography/low-angle laser light scattering (SEC/LALLS) as recently described[6] and residual PVA content was obtained by a standard titration method.[7] The PVF resin had a M_w of 100 000 g/mol and contained 6 wt % residual PVA and 11 wt % poly(vinyl acetate). This translates to 76 mol % acetal content.

An acetate derivative of the PVB was prepared by reacting 5 mL of a 0.5% (w/v) solution of the PVB in anhydrous pyridine (Alltech Associates) with 5 mL of acetic anhydride (Alltech Associates). The reaction was allowed to proceed at 45 °C for 6 h. The acetate-derivatized PVB was precipitated by the addition of 150 mL of water to the reaction mixture. The polymer was collected and washed exhaustively with water to remove traces of pyridine and acetic acid. The wet polymer was pressed dry between filter paper after vacuum filtration to remove excess water. The polymer was further dried under vacuum for 24 h.

The M_w for the acetate-derivatized PVB was determined by SEC/LALLS using THF as the polymer solvent. The measured M_w for the polymer indicated that acetylation did not degrade the polymer chain as observed by previous investigators.[8]

Polymers used to prepare NMR solutions were dried in vacuo at 50 °C for 48 h and then dissolved under moderate heating in an appropriate perdeuterated solvent (benzene or methanol). The concentrations ranged from 6 to 9% (w/w) for natural abundance ^{13}C NMR in 10-mm-diameter tubes and from 1 to 2% (w/w) for proton NMR in 5-mm-diameter tubes.

Spectroscopy. NMR experiments were carried out with a Varian VXR400 NMR spectrometer operating at 400- and 100-MHz nominal proton and carbon frequency, respectively. The rf frequencies were generated by direct synthesis. The probe temperature was regulated at 25 °C. One set of spectra was acquired in the −40 to +100 °C range. The data system of the VXR400 spectrometer was supplemented with a 140 Mbyte disk, which provided sufficient storage space for 4K × 4K transforms. Homonuclear correlation (COSY) spectra were acquired according to the method of States et al.[9] and homonuclear broad-band decoupled heteronuclear shift correlation experiments (HETCOR) according to Bax.[10] The spectra were referenced with respect to the deuterated solvent peak. The 2D data were zero-filled and weighted prior to Fourier transformation as appropriate. Data processing was carried out either on-line with Varian software (Version 6.2) or off-line with Varian VNMR software resident on a VAX mainframe computer.

Results and Discussion

The Geometry of the Acetal Ring. The acetal carbons of poly(vinyl butyral) (PVB) were assigned in the ^{13}C spectrum to the absorptions centered at 102.7 and 95.9 ppm, shown in Figure 1A. Identical patterns were observed over a wide range of compositions ranging from 46 to 70 mol % acetal in PVB and reacetylated PVB. Correspond-

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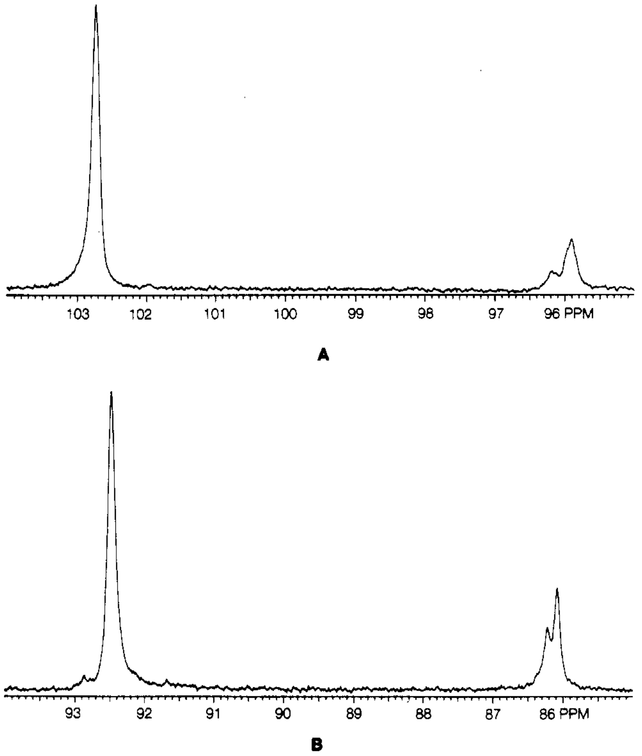

Figure 1. 100-MHz carbon-13 spectrum of the acetal carbons of (A) PVB (9% (w/w) in methanol-d_4) and PVF (6% (w/w) in DMSO-d_6) at 25 °C. Both free induction decays were weighted with a 1-Hz line-broadening function.

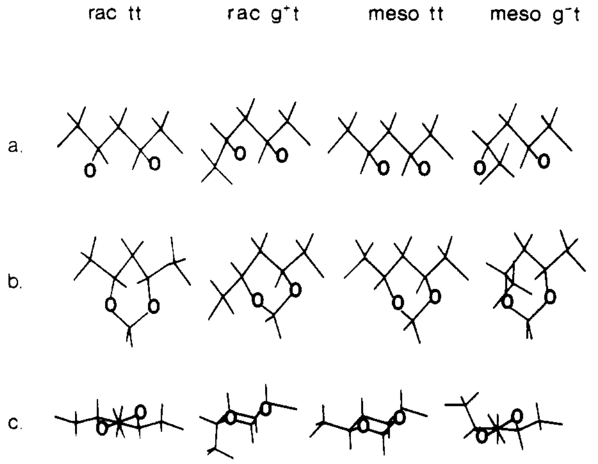

Figure 2. (a) Diads of poly(vinyl alcohol) rotomers that have the proper geometry for forming 1,3-dioxane rings are shown for the *dd* (meso) and *ld* (racemic) conformers. The racemic g^+g^+ and meso g^-g^+ rotomers, which are favorable for ring closure, are strongly excluded for steric reasons and are omitted from the figure. (b and c) the cyclic acetals; (c) the molecule has been rotated along the axis of the polymer chain to highlight the characteristic features of the chair and twist conformations.

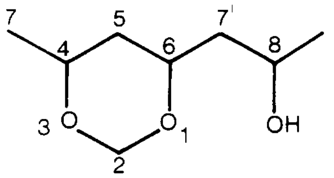

Figure 3. Numbering of the atoms in the polymer chain according to the nomenclature of the 1,3-dioxane ring.

ing acetal carbon resonances for poly(vinyl formal) (PVF) appeared at 92.5 and 86.1 ppm as shown in Figure 1B. In both polymers the upfield peak was clearly split into two overlapping though distinct components. The acetal peaks were identified by their chemical shifts, which clearly separate them from carbons with only one oxygen neighbor. Specific assignments have been attempted.[11-14] The results of the present study are in agreement with a recent[15] NMR study of PVB. In this study, the acetal peaks were assigned to different acetal ring conformations designated as "meso" and "racemic". This terminology indicates that ring conformations originate from the addition of butyraldehyde to either meso or racemic diads of the parent poly(vinyl alcohol) (PVA). A schematic representation of the rotomers for PVA and the corresponding ring conformations that result from acetalization of PVA are shown in Figure 2.

The assignment of the meso peak, at 102.7 ppm in PVB and 92.5 ppm in PVF, to a chair conformation with all-equatorial substituents (derived from the meso tt rotomer, see Figure 2) is firmly supported by the trends of chemical shifts in substituted 1,3-dioxanes.[16] This conformation yields the largest carbon chemical shift value due to a +5 ppm shift contribution from equatorial substituents at C_4 and C_6. The acetal rings are numbered following the convention for 1,3-dioxane rings, and their flanking methylenes are labeled as C_7 and $C_{7'}$, as shown in Figure 3.

The racemic peak, at 95.9 ppm in PVB and 86.1 ppm in PVF, could not be assigned unequivocally on the basis of the above mentioned criteria, although it is sometimes referred to in the literature[13] as the "trans" peak, belonging to a chair conformation with the polymer chain extending in equatorial and axial positions (derived from the racemic g^+t rotomer, see Figure 2). More definitive data for the racemic peak assignment was provided by a comparison of the HETCOR spectra of PVB and PVF shown in Figure 4. The HETCOR spectrum of PVB showed the expected one-to-one correlation between the acetal carbon and the directly bonded proton, for both the meso and the racemic ring. In PVF, however, the meso acetal carbon correlated with two nonequivalent protons, as expected, while the racemic acetal carbons correlated only with one proton. This observation is inconsistent with the inequivalence of these protons expected for the trans chair conformation derived from the racemic g^+t rotomer.

Before discussing these observations in detail a comment should be made regarding the splitting of the peak at 96 ppm in PVB and at 86 ppm in PVF. It is apparent from Figure 4 that both components have very similar proton and carbon-13 chemical shifts and that the acetal protons are equivalent in PVF. Therefore neither component originates from the racemic g^+t conformation. The splitting is not a reflection of selective hydrogen bonding, since it was also observed in acetylated PVB. It may reflect compositional sequences, but the reduction of a complex pattern to two main components over a wide range of compositions has to be explained by highly directed and nonrandom distribution of adjacent monomer units. Further studies along these lines are in progress.

The only known stable conformation that allows equivalence of these protons is the 2,5-twist conformation (derived from the racemic tt rotomer, see Figure 2). It is well-known[17] that cyclohexanes with large substituents that would result in trans configurations escape into a twist conformation in order to make the substituents more equatorial. Evidence for the stability of the 2,5-twist conformer in 1,3-dioxanes has been reported[16] in carbon-13 NMR spectra of *trans*-2,2,4,6-tetramethyl-1,3-dioxane in which the two 2,2-methyl groups had identical carbon-13 chemical shifts. This conformation has been commonly referred to as the 2,5-twist; but we prefer the term "racemic tt" conformation, to indicate the rotational state

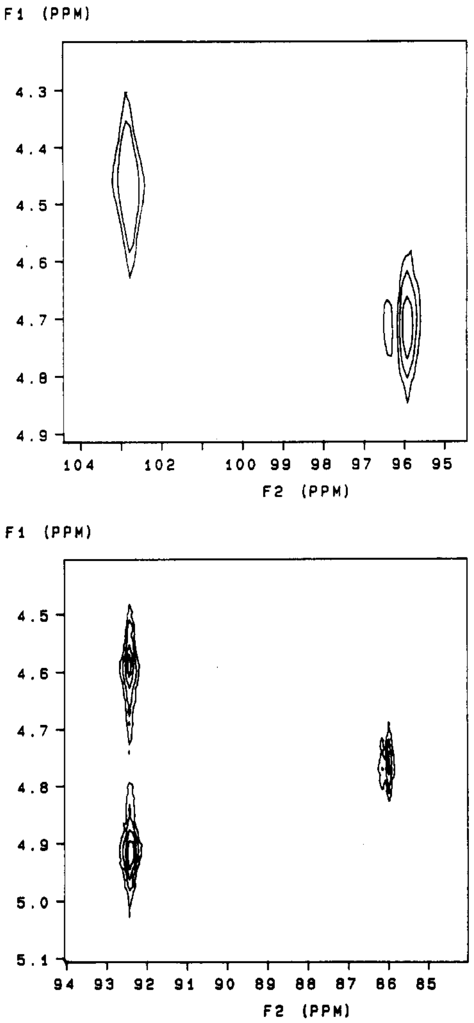

Figure 4. Carbon-hydrogen heteronuclear correlation experiment at 100-MHz carbon-13 frequency showing the acetal region of (a) PVB (8.5% (w/w) in DMSO-d_6) and (b) PVF (6% (w/w) in DMSO-d_6), at 25 °C. The data were acquired as 2K × 256 data sets and zero-filled to 2K × 1K.

from which it is derived. By analogy, we refer to the meso ring as "meso tt".

An alternate possibility, that the symmetry of the 1,3-dioxane ring rapidly interconverts on the NMR time scale the two minimum energy conformations of the 4,6-trans-substituted chair (equatorial/axial and axial/equatorial), has been considered in the literature.[13] However, this conclusion was only supported[13] by the resonance of the acetal protons in PVF measured at one temperature. Concurrent averaging would be expected for the carbinol protons at C_4 and C_6 as well but was not observed. Indeed, the interconversion could not take place without affecting the polymer backbone over its entire extent. NMR spectra of PVB recorded between −40 and 100 °C, in the present study, showed no spectral changes indicating a dynamic situation involving reorganization of the chain conformation of this magnitude. In a model compound, 2,4,6-trimethyl-1,3-dioxane, interconversion between two racemic chair conformations has likewise failed to be detected between −77 and +150 °C.[18]

In PVF, one would expect to find further confirmation for the particular symmetry of the racemic tt conformation in the ring methylene carbon-proton (C_5–H_5) correlations. However, the H_5 methylene protons are, in contrast to the further-removed acetal protons (H_2), sensitive to the compositional and conformational sequencing (which manifests itself in the dihedral angle between H_5 and H_7 protons) of the polymer chain and are therefore inequivalent.

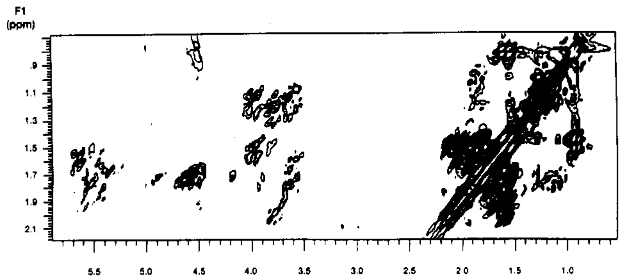

Figure 5. Double-quantum filtered homonuclear correlation experiment of PVB-acetate (1.5% (w/w) in benzene-d_6) at 400-MHz proton frequency, at 25 °C.

The existence of the racemic tt ring conformation in PVB could not be as clearly established because an equivalent correlation experiment to that applied to PVF could not be performed for PVB. However, it would be difficult to attribute to coincidence the fact that the chemical shift patterns of the acetal as well as the carbinol carbons are identical for PVB and PVF, except for a shift caused by substitution on C_2. The two acetal absorptions, meso tt and racemic tt, were separated by 6.8 and 6.4 ppm in PVB and PVF, respectively. In other words, the absolute chemical shifts of the rings were shifted by practically the same amount. If the upfield acetal resonance of PVB was due to the racemic g^+t conformation, it would be expected to be shifted upfield by about 3 ppm from its observed position.[16] Concurrently, downfield shifts of the order of 2 ppm would be predicted for the carbinol carbons.[16]

The COSY spectrum of an acetylated PVB is shown in Figure 5. Acetylation shifted the nonring carbinol protons far downfield into the 5.33–5.8 ppm range and allowed them to be observed separately from the ring carbinol protons appearing between 3.5 and 4.2 ppm. The correlation pattern of the nonring carbinol protons defines the chemical shift range of the H_7 protons, from 1.5 to 1.9 ppm. The ring carbinol crosspeak pattern is therefore divided into a lower portion, corresponding to coupling with H_7, and an upper portion, corresponding to coupling with H_5, in the 1.0–1.4 ppm range. The racemic tt $H_{4,6}$ protons are downfield from the meso tt protons[15] and give rise to separate cross patterns with the H_7 protons. The correlation pattern at the intersection of the H_5 and H_7 protons covers a slightly different range of chemical shifts than expected from the above interpretation. This simply reflects the dihedral angle dependence of the three-bond coupling in the $H_{4,6}$ to H_5 and $H_{4,6}$ to H_7 correlations.

Effect of Acetal Ring Conformation on Polymer Chain Dimensions. From studies of polymer chain dimensions of PVB and PVA[19,20] acetalization of PVA has been shown to produce larger chain dimension for PVB relative to the corresponding dimensions of the parent PVA. These findings are consistent with the hindered internal rotation due to the formation of six-membered acetal rings in the polymer chain backbone. The characterization of poly(vinyl acetal) chain dimension has also been related to specific acetal ring conformation. Numerous studies[15,19,20] have relied on the cis chair (meso tt in Figure 2) and trans chair (racemic g^+t in Figure 2) models to suggest that the cis chair results in an extended polymer chain, while the trans chair produces a bend in the polymer chain that shortens the overall polymer chain dimension. In a recent study[21] of poly(vinyl octanal) (PVO), proton NMR data and *F*–*A* isotherms determined for Langmuir–

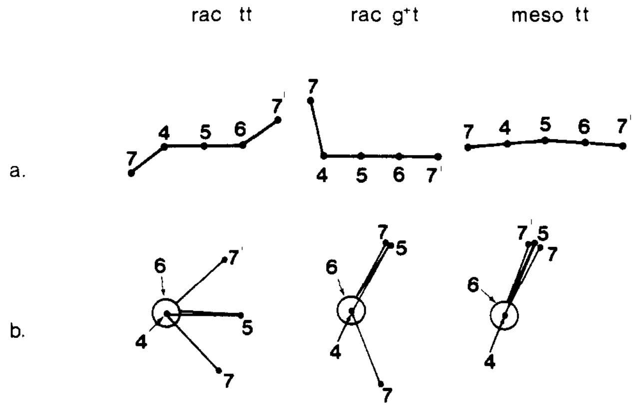

Figure 6. Visualization of spatial relationships in the rings derived from racemic tt, racemic g$^+$t, and meso tt rotomers. (a) Projection with the plane containing C_4, C_5, and C_6 perpendicular to the plane of the paper; (b) projection with the line connecting C_4 and C_6 perpendicular to the plane of the paper.

Blodgett films were used to propose a chain structure for PVO that was schematically represented as an extended chain (due to cis chairs) interspersed with randomly distributed bends (due to trans chairs).

On the basis of the results of the present study, the use of the cis chair and trans chair models may not be appropriate for the analysis of poly(vinyl acetal) chain structure and dimension. Deeper insight into the chain perturbations produced by each acetal ring conformation was obtained by constructing molecular models[22] that highlighted the differences in polymer chain bond lengths and angles. As expected, the distance defined by a line connecting C_7 and $C_{7'}$ carbons for the racemic g$^+$t (trans chair) conformation (4.62 Å) is significantly shorter than the corresponding distance for the meso tt (cis chair) conformation (5.06 Å). However, the C_7–$C_{7'}$ distance of the racemic tt (2,5-twist) conformation (5.07 Å) only differs from that of the meso tt conformation by 0.01 Å. The proposed shortening of poly(vinyl acetal) chain dimension due to conformations other than meso tt must, therefore, be due to more subtle differences between the meso tt and racemic tt conformations.

Formation of a meso tt conformation allows a 1,3-dioxane chair to form with minimal angular distortion, and carbons C_7, C_4, C_6, and C_7 remain almost coplanar. The formation of the racemic tt conformation, however, entails a distortion from the ideal trans conformation by almost 30°; hence the planes defined by C_7, C_4, and C_5 and by $C_{7'}$, C_6, and C_5 intersect at an 88° angle (this is the same as saying that the dihedral angle formed by C_7–C_4–C_6–$C_{7'}$ is 88°). The different geometries can be visualized by looking at two projections shown in Figure 6, one along the plane defined by the backbone ring carbons C_4, C_5, and C_6, the other along the line connecting C_4 and C_6. Both the meso tt and racemic g$^+$t conformations can be formed with little distortion. In the meso tt conformation, the backbone carbons are still coplanar (Figure 6b).

The formation of the racemic tt conformation involves a dihedral angle distortion of almost 30° from the ideal all-trans geometry, and the C_4–C_7 and C_6–$C_{7'}$ bonds form an angle of 88°. However, the disturbance of the racemic tt conformation on the overall polymer chain conformation and dimension is not as dramatic as might be expected. Viewed along the plane of the backbone ring carbons (Figure 6a), the racemic tt conformation is seen to be as elongated as the meso tt conformation and does not show the pronounced bend of the racemic g$^+$t conformation. Similarly, viewed in the direction of the carbinol carbons (Figure 6b), the polymer chain is shown to extend from the racemic tt conformation in directions that are intermediate between those in the meso tt and the racemic g$^+$t conformations. Therefore, it is probable that neither the bond distance nor the geometry of the racemic tt conformation justify the bend model based on the racemic g$^+$t conformation.

While the C_7–$C_{7'}$ distances of the racemic tt and meso tt conformations differ only slightly, the angular backbone changes associated with C_7–$C_{7'}$ directions resulting from racemic tt ring formation, when averaged over many repeating units, may produce changes in polymer chain dimension.

Another important consideration pertaining to polymer chain dimension but not explicitly addressed by the proposed acetal ring conformations is the polymer chain dynamics associated with different ring conformations. Clearly the racemic tt conformation represents the more stressed of the two ring conformations. However, it is presently a matter of speculation that the racemic tt conformation provides sufficient flexibility to affect polymer chain dimension. If flexibility differences exist between the meso tt and racemic tt rings, this effect should also be manifested in the relaxation behavior of the nuclear spins. Further studies, particularly the detailed measurement of carbon correlation times for the different rings, will be needed to test this hypothesis.

Conclusions

It is well-known that acetalization of PVA results in the formation of two types of 1,3-dioxane rings, one of which, the meso tt (cis chair), is thermodynamically favored. In this study we have presented conclusive evidence based on NMR spectroscopy for the particular conformation of each ring. The major ring was confirmed to be the all-equatorial chair conformation (meso tt). In PVF, only the 2,5-twist (racemic tt) conformation was found to be compatible with the observed equivalence of the acetal protons of the minor ring. By chemical shift analogy, the same conformation was attributed to the corresponding ring in PVB. This assignment was further corroborated by the self-consistency it provided to the interpretion of all the 2D NMR data.

Distances determined from molecular models of the acetal rings showed that the racemic tt conformation does not introduce significant lengthening or shortening of the polymer chain. This finding sharply contradicts assumptions in the literature, that the minor ring causes bends in the polymer chain. These assumptions were based on the incorporation of only chair conformations, which yielded a bent configuration resulting from simultaneous axial and equatorial chain propagation. It is therefore suggested that the racemic tt conformation has a more subtle influence on the properties of the polymer chain, either by dynamics or through interchain molecular interactions.

References and Notes

(1) Bovey, F. A. *Polymer Conformation and Configuration*; Academic Press: New York, 1969.
(2) Ernst, R.; Bodenhausen, G.; Wokaun, A. *Principles of Nuclear Magnetic Resonance in One and Two Dimensions*; Oxford University Press: New York, 1987.
(3) Gippert, G. P.; Brown, L. R. *Polym. Bull.* **1984**, *11*, 585.
(4) Schilling, F. C.; Bovey, F. A.; Bruch, M. D., Kozlowski, S. A. *Macromolecules* **1985**, *18*, 1418.
(5) Cheng, H. N.; Lee, G. H. *Polym. Bull.* **1985**, *13*, 549.
(6) Remsen, E. E. *J. Appl. Polym. Sci.* **1991**, *42*, 503.
(7) ASTM Method D 1396-73 *Chemical Analysis of Poly(Vinyl Butyral)*; ASTM: 1916 Race St., Philadelphia, PA 19103.

(8) Scholtens, B. J. R.; Bijsterbosch, J. *J. Polym. Sci., Polym. Phys. Ed.* **1979**, *17*, 1771.
(9) States, D. J.; Haberkorn, R. A.; Ruben, D. J. *J. Magn. Reson.* **1982**, *48*, 286.
(10) Bax, A. D. *J. Magn. Reson.* **1983**, *53*, 517.
(11) Schlothauer, K.; Schulz, B.; Marschner, H.; Krause, A. *Acta Polym.* **1987**, *38*, 249.
(12) Lebek, B.; Schlothauer, K.; Krause, A.; Marschner, H. *Acta Polym.* **1989**, *40*, 92.
(13) Fujii, K.; Shibatani, Y.; Fujiwara, Y.; Ohyanagi, J.; Ukida, J.; Matsumoto, M. *J. Polym. Sci., Polym. Lett. Ed.* **1966**, *B4*, 787.
(14) Schaefer, J.; Garbow, J. R.; Stejskal, E. O.; Lefelar, J. A. *Macromolecules* **1987**, *20*, 1271.
(15) Bruch, M. D.; Bonesteel, J. K. *Macromolecules* **1986**, *19*, 1622.
(16) Pihlaja, K.; Kivimaki, M.; Myllyniemi, A. M.; Nurmi, T. *J. Org. Chem.* **1982**, *47*, 4688.
(17) Duddeck, A. H. *Topics Stereochem.* **1986**, *16*, 219.
(18) Fujiwara, Y.; Fujiwara, S. *Bull. Chem. Soc. Jpn.* **1964**, *37*, 1010.
(19) Matsuda, H.; Katsuya, K.; Inagaki, H. *Kogyo Kagaku Zashi* (*J. Ind. Chem.*) **1970**, *73*, 390.
(20) Cotts, P. M.; Ouano, A. C. In *Microdomains in Polymer Solutions*; Dubin, P., Ed.; Plenum Press: New York, 1985.
(21) Watanabe, M.; Kosaka, Y.; Oguchi, K.; Sanui, K.; Ogata, N. *Macromolecules* **1988**, *21*, 2997.
(22) Molecular models were obtained with aid of the graphics program MACROMODEL v.2.0, Columbia University, 1986.