termediate in MTG chemistry, but the observation that **1** can form in HZSM-5 from a known MTG intermediate removes a major objection to mechanisms such as those in Scheme I. Furthermore, with the ability to generate significant quantities of **1** in HZSM-5, it should be possible to further explore these mechanisms.

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Helix-Sense Reversal of Isotactic Chloral Oligomers in Solution[1]

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We report the observation of helix-sense reversal of linear chloral oligomers (degree of polymerization, DP = 4–6) in solution by NMR spectroscopy and determination of the inversion barrier, which has been found to be dependent on DP.

Some synthetic polymers such as polychloral,[2] poly(triphenylmethyl methacrylate),[3] and poly(*tert*-butyl isocyanide)[4] are known to show optical activity arising entirely from conformational asymmetry (macromolecular asymmetry) when the polymers are prepared by helix-sense selective polymerization. The helix of the optically active polymers seems to be rigid in solution[5,6] or slowly undergoes racemization to a nearly 1:1 mixture of the right- and left-handed helices.[7] The helical conformation of polyisocyanates is less stable, and consequently, right- and left-handed states exist in equilibrium.[8] Although the one-handed helicity of the polymers is apparent from their optical activity, it has been difficult to determine the helical polymer structures and thermodynamic parameters for the helix–helix transition; one reason for the difficulty is that those polymers are, as usual synthetic macromolecular compounds are, mixtures of very similar but not identical molecules (distribution of DP, slight difference in tacticity, etc.).

Recently, we were able to resolve the *tert*-butoxy-initiated, acetate end-capped, purely isotactic pentamer of chloral **1** into the two enantiomers (*R,R,R,R,R* and *S,S,S,S,S* isomers) by HPLC using a chiral stationary phase.[9] The (*R,R,R,R,R*)-(−)-**1**[10] was found to adopt the right-handed 4_1-helical conformation in solution at 35 °C[11] *as well as* in the crystalline state.[12] This conclusion is based on the dihedral angle dependence of $^3J_{COCH}$ coupling constants obtained from the ^{13}C NMR spectrum. The helical-sense preference was ascribed to the conformational energy difference (ΔE) between the right-handed and left-handed helical states, which was estimated as 2.7 kcal/mol[13] by molecular mechanics calculation.[14,15]

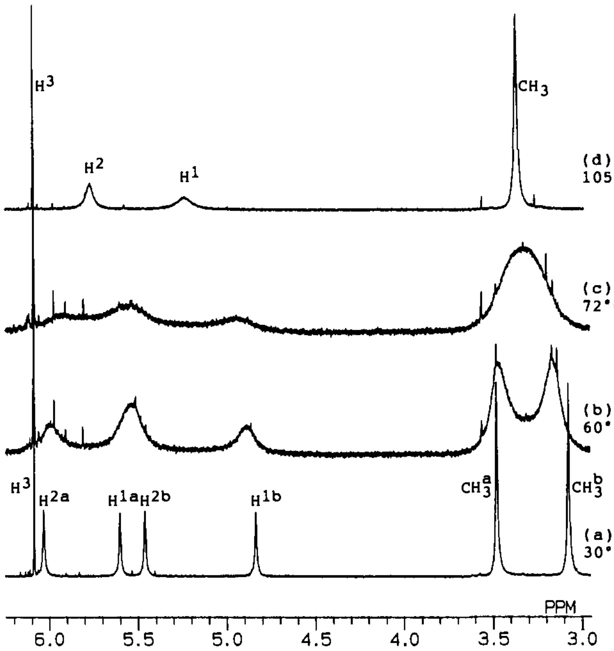
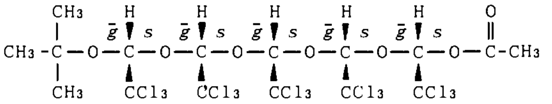
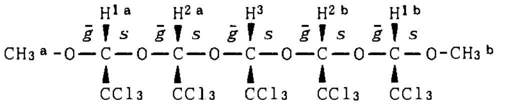


Figure 1. ^1H NMR spectra (500 MHz) of **2** in toluene-d_8 at (a) 30 °C, (b) 60 °C, (c) 72 °C, and (d) 105 °C.



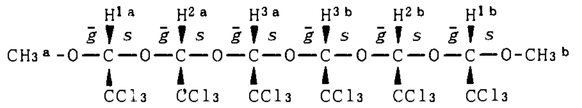
$$CH_3\text{-}\underset{CH_3}{\overset{CH_3}{C}}\text{—}O\text{—}\underset{CCl_3}{\overset{\substack{H\\ \bar{g}\ \ s}}{C}}\text{—}O\text{—}\underset{CCl_3}{\overset{\substack{H\\ \bar{g}\ \ s}}{C}}\text{—}O\text{—}\underset{CCl_3}{\overset{\substack{H\\ \bar{g}\ \ s}}{C}}\text{—}O\text{—}\underset{CCl_3}{\overset{\substack{H\\ \bar{g}\ \ s}}{C}}\text{—}O\text{—}\underset{CCl_3}{\overset{\substack{H\\ \bar{g}\ \ s}}{C}}\text{—}O\text{—}\overset{O}{\overset{\|}{C}}\text{-}CH_3$$

1



$$CH_3{}^a\text{-}O\text{—}\underset{CCl_3}{\overset{\substack{H^{1a}\\ \bar{g}\ \ s}}{C}}\text{—}O\text{—}\underset{CCl_3}{\overset{\substack{H^{2a}\\ \bar{g}\ \ s}}{C}}\text{—}O\text{—}\underset{CCl_3}{\overset{\substack{H^{3}\\ \bar{g}\ \ s}}{C}}\text{—}O\text{—}\underset{CCl_3}{\overset{\substack{H^{2b}\\ \bar{g}\ \ s}}{C}}\text{—}O\text{—}\underset{CCl_3}{\overset{\substack{H^{1b}\\ \bar{g}\ \ s}}{C}}\text{—}O\text{-}CH_3{}^b$$

2



$$CH_3{}^a\text{-}O\text{—}\underset{CCl_3}{\overset{\substack{H^{1a}\\ \bar{g}\ \ s}}{C}}\text{—}O\text{—}\underset{CCl_3}{\overset{\substack{H^{2a}\\ \bar{g}\ \ s}}{C}}\text{—}O\text{—}\underset{CCl_3}{\overset{\substack{H^{3a}\\ \bar{g}\ \ s}}{C}}\text{—}O\text{—}\underset{CCl_3}{\overset{\substack{H^{3b}\\ \bar{g}\ \ s}}{C}}\text{—}O\text{—}\underset{CCl_3}{\overset{\substack{H^{2b}\\ \bar{g}\ \ s}}{C}}\text{—}O\text{—}\underset{CCl_3}{\overset{\substack{H^{1b}\\ \bar{g}\ \ s}}{C}}\text{—}O\text{-}CH_3{}^b$$

3

The purely isotactic and symmetrical pentamer carrying a methyl group at both ends, **2**, is the (*R,R,S,S*)-(±) isomer in which the right- and left-handed helical conformations are no longer

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(12) Crystal data for (*R,R,R,R,R*)-(−)-**1** ($C_{16}H_{17}O_7Cl_{15}$): orthorhombic, $P2_12_12_1$, a = 16.354 (3) Å, b = 18.961 (4) Å, c = 10.767 (2) Å, Z = 4, D(calcd) = 1.698 g/cm^3. The 318 variables were refined with 3023 unique reflections ($3° < 2\theta < 55°$) with $|F_o| > 3\sigma(|F_o|)$ to yield R = 5.65% and R_w = 6.94%. More complete crystallographic details will be described elsewhere: Ute, K.; Oka, K.; Matsuura, Y.; Hatada, K.; Vogl, O., to be submitted to *Polym. J.*

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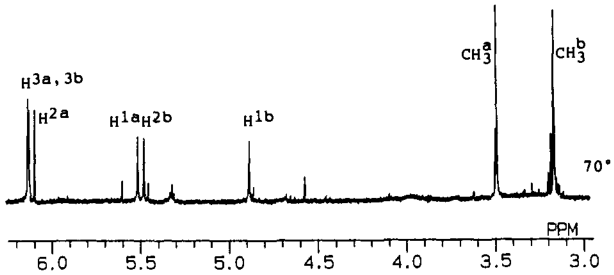
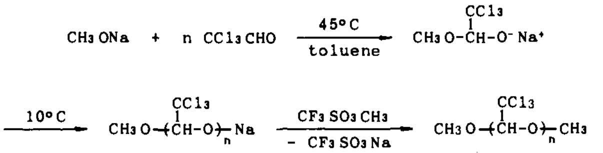


Figure 2. A 500 MHz ^{1}H NMR spectrum of **3** in toluene-d_8 at 70 °C.

diastereomeric states but enantiomeric states with equal probability ($\Delta E = 0$). The pentamer **2**, the hexamer **3**, and the tetramer **4** were isolated by gel permeation chromatography from the oligomer mixture **5**, which was prepared by the cryotachensic polymerization[16] of chloral (50.5 mmol) initiated with sodium methoxide (10.0 mmol) in toluene at 45 °C and terminated with methyl trifluoromethanesulfonate (21.2 mmol) at 10 °C. Each oligomer was purified by recrystallization from ethanol containing a small amount of chloroform.[17]



$$CH_3ONa + n\ CCl_3CHO \xrightarrow[\text{toluene}]{45\,°C} CH_3O\text{-}\overset{CCl_3}{\overset{|}{C}}H\text{-}O^-Na^+$$

$$\xrightarrow{10\,°C} CH_3O\text{-}(\overset{CCl_3}{\overset{|}{C}}H\text{-}O)_n\text{-}Na \xrightarrow[-\ CF_3SO_3Na]{CF_3SO_3CH_3} CH_3O\text{-}(\overset{CCl_3}{\overset{|}{C}}H\text{-}O)_n\text{-}CH_3$$

5

A 500 MHz ^{1}H NMR spectrum of **2** measured in toluene-d_8 at 30 °C showed signals due to methyl groups at 3.08 and 3.48 ppm and those due to methine protons at 4.84, 5.46, 5.60, and 6.03 ppm (Figure 1a);[18] these peaks are relatively broad. The sharp signal at 6.09 ppm is attributed to the methine proton of the central monomer unit of **2** (H^3). The nonequivalency of the two methyl groups and of the five acetal methine protons indicates that **2** exists in solution at 30 °C in a highly preferred conformation, probably the 4_1-helical conformation approximating the repeat gauche(−)–skew(+) ($\bar{g}s$)[19] sequences (or the repeat $\bar{s}g$ sequences). The signals, except for the signal due to H^3, became broader at 60 °C (Figure 1b), and the signals due to methyl groups coalesced at 72 °C (Figure 1c); the spectrum appeared finally as four signals with an intensity ratio of 6:2:2:1 at 105 °C (Figure 1d). Cooling the sample solution to 35 °C again completely reproduced the spectrum shown in Figure 1a. The results clearly show that the rate of helix-sense reversal becomes too fast at 72 °C for the time scale of 500 MHz NMR to distinguish the right-handed $(\bar{g}s)_5$ and left-handed $(\bar{s}g)_5$ helical states of **2**. From the spectra, the activation energy (E_a) and the rate of transition from one helical sense to the opposite sense were determined to be 16.4 kcal/mol and 3.9 s^{-1} at 20 °C, respectively. Though the coalescence temperature for the methine signals was somewhat higher (ca. 80 °C), the methine signals had a larger shift difference, and thus the E_a value estimated from the methine signals agreed with that determined from the methoxy signals (ca. 16.3 kcal/mol).

In a similar manner, the coalescence temperature for the methyl groups of the tetramer **4** was determined as 4 °C. E_a was calculated as 12.7 kcal/mol, which was 3.7 kcal/mol smaller than that for the pentamer **2**.

The hexamer **3** showed a total of seven signals with narrow line widths at 3.16, 3.48, 4.88, 5.47, 5.51, 6.09, and 6.12 (two singlets) ppm due to two methyl groups and six methine protons[18] even at 70 °C (Figure 2), indicating that the rate of the helix-sense reversal is much slower than the rate for **2**. This suggests the possibility that the symmetrical oligomers **5** over the pentamer level may be optically resolved at room temperature based entirely on conformational asymmetry.

The present results also suggest that the $(\bar{g}s)_5$ and $(\bar{s}g)_5$ states of (R,R,R,R,R)-(−)-**1** in solution may be distinguished by NMR spectroscopy, although the fraction of the $(\bar{s}g)_5$ state should be difficult to detect on account of the large ΔE between the two diastereomeric states. Another isotactic pentamer with a smaller ΔE (e.g., the ethoxy-initiated, methoxy-terminated pentamer) might make it possible to determine the fraction of the $(\bar{g}s)_5$ and $(\bar{s}g)_5$ states in solution by NMR spectroscopy at temperatures below the coalescence point.[20]

The purely isotactic oligomers of chloral provide unique and ideal models for the quantitative investigation of the properties of helical polymers because the oligomers have a high tendency to crystallize and very simple ^{1}H and ^{13}C NMR spectra. As far as we are aware, there is no other analogue of linear low molecular weight compounds showing such slow interconversion between enantiomeric helical states.

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(17) The crystals of **2** and **4** started to decompose at 182 and 178 °C, respectively, before melting.

(18) The assignment of the ^{1}H NMR signals was unambiguously made together with that of ^{13}C NMR signals by the procedure (the ^{13}C NMR selective ^{1}H-decoupling method) described in the previous papers.[11b,16c] Dihedral angle dependence of the $^3J_{COCH}$ coupling constants suggested that the backbone conformations of **1** and **2** were essentially identical.

(19) For the notations of the internal rotation angle, see: Tadokoro, H. In *Structure of Crystalline Polymers*; John Wiley & Sons: New York, 1979; p 14.

(20) Very recently, this was confirmed for the ethoxy-initiated, methoxy-terminated, purely isotactic pentamer of chloral. The ratio of the two helical states was 17:8 in chloroform-d at 0 °C: Ute, K.; Kashimoto, H.; Hatada, K.; Vogl, O., manuscript in preparation.

Design and Synthesis of a Knot from Single-Stranded DNA

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The possibility that polymers can be knotted was pointed out by Frisch and Wasserman 30 years ago.[1] Numerous investigators have attempted to form knots in small-molecule systems;[2,3] recently, a synthetic knot has been reported.[4,5] Large, double-stranded DNA molecules are knotted by recombination enzymes using double-strand breaks,[6–9] whereas large single-stranded DNA molecules can be knotted by type I topoisomerases.[10] The plectonemic structure of the nucleic acid double helix[11] offers a convenient way for controlling the braiding of one part of a molecule about another part. This feature has recently been used to construct a multiply catenated cubelike DNA structure, in which every nucleotide is designed to be paired.[12] Likewise, single-stranded DNA containing complementary regions interspersed between relatively unstructured oligo-dT tracts is an ideal substance for the design and synthesis of knots. In contrast to previous approaches,[2,4] the braiding part of the molecular backbone

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