Haloaldehyde Polymers LXII. High Resolution Solid State ^{13}C NMR Spectra of Chloral and Bromal Polymers

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ABSTRACT: Homopolymers of chloral and bromal and copolymers of chloral with bromal were studied by solid-state ^{13}C NMR spectroscopy operated at 100.5 MHz. The cross polarization/magic angle spinning (CP/MAS) measurements of *t*-butoxy-initiated, acetate end-capped polychloral samples showed the trichloromethyl carbon atom and the acetal ^{13}C NMR resonances at 97.2 and 101.0 ppm. The signals due to the end-groups were noticed at 24.1, 29–31, and 178.0 ppm; these signals were observed more clearly in the dipolar decoupling/MAS spectrum. The tribromomethyl carbon and the acetal carbon resonances of polybromal were observed as a single broad peak at 100.9 ppm. The copolymer of chloral and bromal showed the acetal carbon and the tribromomethyl carbon resonances at 100.9 ppm and the trichloromethyl carbon resonance at 98 ppm as a shoulder peak. In the CP/MAS spectrum of the copolymer of chloral and *p*-chlorophenyl isocyanate (5 mol%), the acetal carbon and the trichloromethyl carbon resonances were similar to the ^{13}C resonances in polychloral, suggesting that the *p*-chlorophenyl isocyanate units are segregated in the polychloral chain.

KEY WORDS Polychloral / Polybromal / CP/MAS / DD/MAS / Tacticity
/ Terminal Group / Aldehyde Polymerization /

Polychloral and polybromal are insoluble and infusible polymers. These characteristics limit the techniques available for their characterization.¹ From early IR² and solid-state ^{13}C NMR measurements³ it was recognized that polychloral has a tactic structure and it was suggested that the structure was most likely the isotactic structure. X-Ray studies on rolled samples⁴ and on samples drawn over a hot pin⁵ indicated that polychloral was isotactic and had the structure of a 4/1 helix with a repeat distance of approximately 5.2 Å.⁵ It has been known for some time that the steric repulsion between the

bulky trichloromethyl groups lead the polymerization of chloral to be highly isotactic-specific and conformational specific resulting in a helical polymer structure.

For the same reason, polybromal and copolymers of chloral and bromal were also expected to have highly isotactic structures.

Recently, our knowledge of the polymerizations of chloral and bromal has been greatly advanced by the synthesis and structure determinations of the soluble oligomers. NMR spectroscopy^{6–10} and X-ray single crystal analysis^{7,9–12} allowed the determination of the configuration of the oligomers. The soluble

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oligomers were prepared, as were the polymers previously synthesized, by "cryotachensic" polymerization¹³⁻¹⁵ carried out by using a low monomer to initiator ratio (5:1).

The chloral oligomers from the trimer to the nonamer have been shown to consist of the single diastereomer with a purely-isotactic structure.

It was the objective of this paper to analyze by solid-state ¹³C NMR spectroscopy the homopolymers of chloral and bromal, and also the copolymer of chloral and bromal produced by the cryotachensic polymerization.

EXPERIMENTAL

Homopolymers of chloral and bromal, and copolymers of chloral with bromal were prepared by procedures reported previously.¹⁴⁻¹⁸

Solid-state ¹³C NMR spectra were recorded at 100.5 MHz on a JEOL JNM-GSX400 spectrometer. Magic-angle spinning (MAS) and proton dipolar decoupling (DD) were applied for all spectra. The sample polymer was packed in a 6 mm i.d. rotor made of zirconia; the rotor was spun at a frequency of 6.0 kHz. In cross polarization (CP)/MAS measurements, the contact time was 5.0 ms; 512 scans were accumulated with a delay of 5.0 s between successive sequences. The CP/MAS spectra recorded with contact times ranging from 2.0 to 5.0 ms were essentially identical. Protonated-carbon suppression (PCS, or dipolar dephasing^{19,20}) measurements used a delay time of 20 μs. DD/MAS spectra were obtained by accumulating a total of 1024 transients recorded with a π/2 observation pulse and a recycle time of 6.0 s; the pulse saturation transfer method, in which the ¹³C magnetiza-

tion was enhanced by saturated protons through the nuclear Overhauser effect, was applied. In the DD/MAS spectra, broad background absorbance (line width at half height ≈ 6 kHz) was removed by subtracting the blank (background) data from the time-domain data of each sample before Fourier transformation. The peak height of the background signal was *ca.* 50% of that of polychloral samples.

RESULTS AND DISCUSSION

The ¹³C NMR spectra of solid homopolymers and copolymers of chloral and bromal were investigated by CP/MAS and DD/MAS techniques. Of particular interest to us was the possible characterization of the tacticity of the polymers based on observation of line sharpness, and the end-groups of the various samples of polymers and copolymers.

Homopolymer of Chloral

Figure 1a shows the CP/MAS spectrum of polychloral obtained by polymerization of chloral initiated with lithium *t*-butoxide and terminated with acetic anhydride. Two peaks found at 97.2 and 101.0 ppm were assigned to the trichloromethyl carbon atoms and the main-chain acetal carbon atoms, respectively. When the solid-state NMR spectrum of this polymer was recorded in the PCS mode (Figure 1b), the signal due to the acetal carbon was suppressed because of its short *T*₂. Our assignment is consistent with that of the ¹³C NMR spectrum of the chloral pentamer in solution⁷ in which the carbon atom of the trichloromethyl group resonated at 96.2–97.9 ppm and the acetal carbon atom at 100.3–101.9 ppm.

The symmetrical, rather sharp resonance peaks due to the acetal carbon atom and the trichloromethyl carbon atom in the CP/MAS spectrum suggest that a single tactic (isotactic) structure predominates in the polymer. The previous CP/MAS measurement of poly-

Figure 1. Solid-state ^{13}C NMR spectra of the *t*-butoxy-initiated, acetate end-capped polychloral (measured by the CP/MAS (a), PCS (b), and DD/MAS (c) methods).

chloral (recorded at 38 MHz) detected only the acetal peak at 101.4 ppm and the trichloromethyl peak was not observed; the reason is believed to be the broadening of the trichloromethyl carbon resonance from the chlorine quadrupoles.³

In the CP/MAS spectrum of Figure 1a we can see also small signals at 20–32 ppm which come from the terminal *t*-butoxy and acetyl methyl groups. These signals of the end-groups could be observed more clearly in the DD/MAS spectrum (Figure 1c) in which the resonances from relatively mobile segments of the polymer were enhanced. The signal due to the carbonyl carbon atom of the terminal acetyl group appeared at 178.0 ppm. We have assigned the sharp signals at 95.9 and 102.2 ppm in Figure 1c to the trichloromethyl and acetal carbon atoms of the monomeric units near the end-groups.

Figure 2. CP/MAS ^{13}C NMR spectra of the *t*-butoxy-initiated (a), and bornyloxy-initiated polybromals (b), and of the bornyloxy-initiated copolymer of chloral and bromal (c). All the polymers were acetate end-capped.

Homopolymer of Bromal and Copolymer of Chloral with Bromal

Figure 2a shows the CP/MAS spectrum of *t*-butoxy-initiated, acetate end-capped polybromal. The tribromomethyl and the acetal carbon resonances were observed together at 100.9 ppm. The narrow linewidth of the signal suggests that polybromal also has high stereoregularity. The acetyl methyl resonance at 24.6 ppm and the *t*-butoxy and acetyl carbonyl resonances at 30–50 and 175–190 ppm are stronger than those in polychloral (Figure 1a), indicating that the degree of polymerization of this sample of polybromal is lower than that of the polychloral sample that we described before. Polybromal prepared by initiation with the lithium alkoxide of (–)-borneol and acetate end-capped showed a similar spectrum (Figure 2b) except for broad

signals around 30–55 ppm which we assigned to the bornyloxy moiety.

The CP/MAS spectrum of the copolymer of chloral and bromal (the ratio of monomer feed = 1/1 in moles), which is bornyloxy-initiated and acetate end-capped, is shown in Figure 2c. The small shoulder peak at 98 ppm was assigned to the trichloromethyl carbon as we described before about the homopolymer of chloral.

*Copolymer of Chloral with *p*-Chlorophenyl Isocyanate*

Figure 3a shows the CP/MAS spectrum of the first solid piece of polychloral ever made (March 1963).^{13,21} The sample was “stabilized” by soaking the sample in *p*-chlorophenyl isocyanate. The broad signal at 127–170 ppm with weak intensity suggests that the polychloral sample contains *p*-chlorophenyl isocyanate segments at the end of the polymer chain.

The copolymerization of chloral with isocyanates and ketenes has been described previously.^{22–25} As seen in Figure 3b, the copolymer of chloral and *p*-chlorophenyl isocyanate (5 mol%) gave acetal and tri-

chloromethyl ¹³C NMR signals very similar to those of the chloral homopolymer. The phenyl carbon atoms from the *p*-chlorophenyl isocyanate units in the copolymer contributed to a relatively broad resonance at 127–170 ppm. The observation that the acetal carbon resonance was not altered by the presence of *p*-chlorophenyl isocyanate units indicates that the structure of chloral units in the copolymer is similar to that in the homopolymer. This is consistent with the previously discussed structure²⁵ of segregated *p*-chlorophenyl isocyanate units in the polymer chain.

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Figure 3. CP/MAS ¹³C NMR spectra of the polychloral “stabilized” by soaking polychloral in *p*-chlorophenyl isocyanate (a) and the chloral/*p*-chlorophenyl isocyanate (95/5) copolymer (b).

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