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Elucidation of the Proton Nuclear Magnetic Resonance Spectrum of Poly(propylene oxide) by Two-Dimensional *J*-Resolved Spectroscopy

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ABSTRACT: Two-dimensional *J*-resolved spectroscopy is applied to the separation of overlapping multiplets in the 500-MHz proton spectrum of poly(propylene oxide). Chemical shifts and homonuclear coupling constants are reported for protons in different stereochemical environments. These values are consistent with spectral parameters previously determined for selectively deuterated polymers. Proton chemical shifts in atactic poly(propylene oxide) are observed to be sensitive to triad stereosequences, but the homonuclear coupling constants for head-to-tail monomer units are the same regardless of stereosequence.

1. Introduction

Proton NMR spectroscopy is potentially a powerful tool for studying the microstructure of synthetic polymers since proton chemical shifts are sensitive to structural variables. Furthermore, proton-proton scalar coupling constants are sensitive to molecular conformation. However, the proton spectra of polymers are often complex because of extensive spectral overlap of multiplets with similar chemical shifts. Homonuclear two-dimensional (2D) *J*-resolved spectroscopy has been widely applied to the separation of overlapping multiplets in the proton spectra of peptides,[1-3] proteins,[4-6] and oligosaccharides.[7-10] However, because of scalar coupling between protons of different monomer units as well as coupling within the monomer unit, the coupling patterns associated with synthetic polymers are generally very complex. Consequently, 2D *J*-resolved spectra of synthetic polymers, especially vinyl polymers, can be difficult to interpret. This was observed by Macura and Brown[11] in the 2D *J*-resolved spectrum of poly(vinyl chloride). Poly(propylene oxide) represents a simpler case for 2D *J*-resolved spectroscopy since scalar coupling between protons of different monomer units is prevented by the oxygen. We report the application of 2D *J*-resolved spectroscopy to the elucidation of the 500-MHz proton spectrum of poly(propylene oxide).

2. Experimental Section

2.1. Materials. The atactic poly(propylene oxide) was a commercial sample supplied by Aldrich Chemical Co. in liquid form (molecular weight ca. 4000). It was initially characterized by ^{13}C NMR and found to have an approximately random stereochemical structure (see section 3). Isotactic poly(propylene oxide) was prepared from (*S*)-propylene oxide (99%, Aldrich Chemical Co.) by using a KOH catalyst and the method of Price and Osgan.[12] This procedure yielded a white crystalline substance with a sharp melting point of 60-61 °C. The intrinsic viscosity, measured in toluene at 25 °C, was 0.171 dL g^{-1}, corresponding to a viscosity-average molecular weight of ca. 14 500.

2.2. NMR Spectroscopy. Two-dimensional *J*-resolved spectroscopy, first performed in 1976 by Ernst and co-workers,[13] employs the spin-echo pulse sequence $90°-t_1/2-180°-t_1/2-t_2$. The 90° pulse flips the net magnetization vector into the *xy* plane, and the individual components dephase during the first interval of length $t_1/2$. The 180° pulse refocuses the spin isochromats which have dephased because of chemical shift differences but not those which have dephased because of *J* coupling. The individual components of a multiplet continue to dephase during the second interval of length $t_1/2$. This results in an apparent precession frequency during t_1 which is dependent only on the scalar coupling constants. At the end of the time t_1, the chemical shift components are completely refocused, and a spin echo is produced. This spin echo is detected as a free induction decay in the time variable t_2. As in all 2D NMR experiments, the evolution time t_1 is systematically incremented and the resultant free induction decay is detected in t_2 for a series of t_1 values. The resultant data matrix is Fourier transformed in both time variables; the first Fourier transform is with respect to t_2 and the second is with respect to t_1. This yields a 2D spectrum as a function of two frequencies, ω_1 and ω_2. In 2D *J*-resolved spectroscopy, the ω_1 frequency reflects only scalar coupling, while the ω_2 frequency reflects both chemical shift and scalar coupling effects. After a "tilt" of 45°,[14] the ω_2 axis reflects only chemical shifts, and the ω_1 axis reflects only *J* coupling. Hence, multiplets which are overlapped in the conventional proton spectrum are separated in the 2D *J*-resolved spectrum.

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All spectra were observed in deuteriochloroform ($CDCl_3$) at 25 °C by using a JEOL GX 500 spectrometer operating at a proton frequency of 500 MHz. Sixteen transients were accumulated for each t_1 increment for all two-dimensional experiments. A four-cycle phase cycling routine was employed to eliminate spectral artifacts, and quadrature detection was employed in both dimensions. The two-dimensional free induction decays were multiplied by a trapezoidal window function in both dimensions prior to Fourier transformation. This was necessary since absolute value spectra were calculated for all two-dimensional experiments.

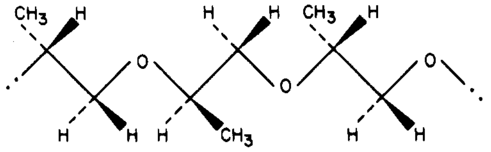
The proton two-dimensional *J*-correlated (COSY) experiment on atactic poly(propylene oxide) was performed with the standard $90° - t_1 - 90° - t_2$ pulse sequence.[15] A recycle time of 3.5 s between transients was used. The data matrix consisted of 256 spectra of 2048 points each and was zero filled to 512 by 2048 points covering 2000 Hz in both dimensions.

Because of the large chemical shift difference between the methyl resonances and the downfield resonances (2 ppm), two-dimensional *J*-resolved spectroscopy was performed in two experiments. The data matrix for the 2D *J*-resolved spectrum of the methyl region of atactic poly(propylene oxide) consisted of 64 spectra of 2048 points each and was zero filled to 128 by 2048 points. The sweep widths were 150 Hz in the chemical shift dimension and 30 Hz in the *J* dimension. The recycle time was 8 s between transients. The data matrix for the 2D *J*-resolved spectrum of the downfield region of atactic poly(propylene oxide) was the same except that the sweep widths were 400 Hz in the chemical shift dimension and 30 Hz in the *J* dimension and the recycle time was 3.5 s between transients.

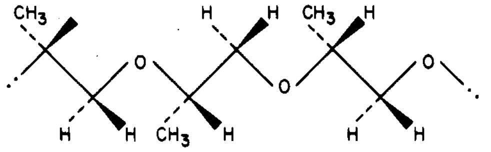
Essentially the same conditions were used for the isotactic polymer. All 2D *J*-resolved spectra were "tilted" by 45°.[14]

3. Results and Discussion

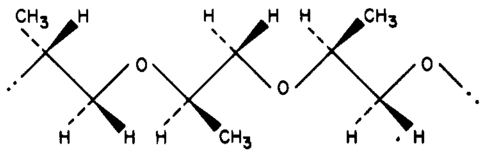
Propylene oxide has an asymmetric α-carbon and may be either *R* or *S*. Hence, polymerization of propylene oxide may in principle generate four species of stereochemical triads:



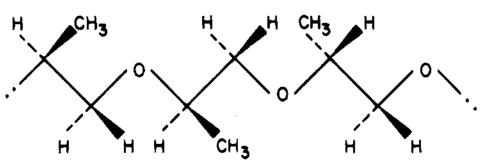
isotactic, *RRR* or *SSS*



syndiotactic, *RSR* or *SRS*



heterotactic-1 *RRS* or *SSR*



heterotactic-2 *SRR* or *RSS*

The 500-MHz proton spectrum of isotactic poly(propylene oxide) is shown in Figure 1. The methyl protons correspond to the upfield doublet with a splitting of 6.4 Hz. Two-dimensional *J*-correlated spectroscopy (COSY) indicates that in the atactic polymer spectrum (vide infra) the methine proton corresponds to the most downfield resonance, and the same is assumed for the isotactic spectrum. The methylene protons are nonequivalent because of the neighboring chiral center. The multiplets corresponding to the methine and methylene protons are distorted by strong coupling effects. However, the chemical shift of the upfield methylene proton is significantly different from that of the other protons and the multiplet observed for this proton is essentially first order. The larger splitting corresponds to germinal coupling between the methylene protons ($J_{gem} = -9.9$ Hz), and the smaller splitting corresponds to vicinal coupling between the upfield methylene proton and the methine proton ($J_{vic} = 5.0$ Hz). Spectral simulation (see inset in Figure 1) indicates that the other vicinal coupling constant, between the methine proton and the downfield methylene proton, is also 5.0 Hz. These values are in good agreement with coupling constants determined previously.[16-20]

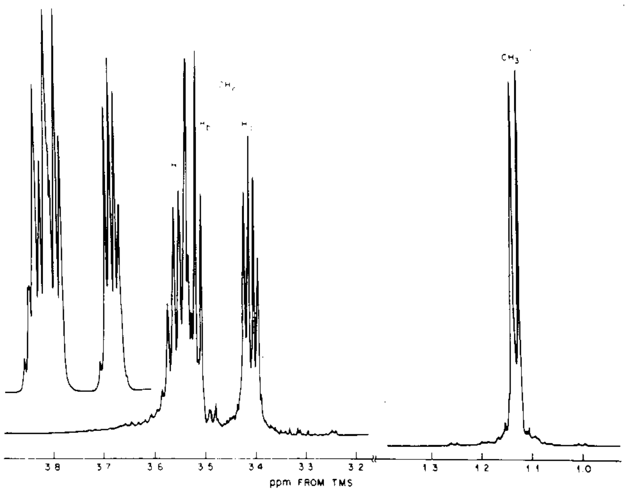


Figure 1. 500-MHz proton spectrum of isotactic poly(propylene oxide), 20% solution in $CDCl_3$. Sixteen transients were accumulated at 25 °C by using a 90° pulse and a pulse interval of 8 s. The inset spectrum is a simulation of the downfield portion of the observed spectrum using the following parameters. Chemical shifts (ppm from Me_4Si): CH, 3.56; CH_2, H_a, 3.53; CH_2, H_b, 3.41; CH_3, 1.126. Coupling constants (Hz): $J_{CH-CH_{2(a)}}$, 5.00; $J_{CH-CH_{2(b)}}$, 5.00; J_{CH_3-CH}, 6.40; $J_{CH_{2(a)}-CH_{2(b)}}$(gem), -9.90.

The 500-MHz proton spectrum of atactic poly(propylene oxide), shown in Figure 2, is complicated by overlap of multiplets corresponding to different stereochemical sequences. The methylene protons are nonequivalent in every environment. Although the proton spectrum of the isotactic polymer can be fairly readily analyzed, that of the atactic spectrum requires selective deuteration or spectral simulation. Spectral overlap obscures the fine structure and prevents accurate measurement of chemical shifts and coupling constants of protons in different stereochemical environments. These problems are solved by two-dimensional *J*-resolved spectroscopy. The simulation of the methyl region (see inset in Figure 2) will be discussed after we consider the 2D spectrum.

The methyl region of the 2D *J*-resolved spectrum of atactic poly(propylene oxide) is shown in Figure 3. Five main doublets are clearly visible; the chemical shifts of these doublets differ by an average of 2 Hz, but the coupling constants are all 6.4 Hz. In contrast, the methyl region of the 2D *J*-resolved spectrum of isotactic poly(propylene oxide), which is not shown, exhibits a single doublet with a splitting of 6.4 Hz. The chemical shift of this doublet (1.126 ppm) corresponds to the most upfield doublet in the spectrum of the atactic polymer, which is therefore assigned to isotactic triad sequences.

Table I
Relative Intensities Obtained from Spectral Simulation of the Methyl Region of Atactic Poly(propylene oxide)

doublet no.[a]	chemical shift[b]	intensity, %	doublet no.[a]	chemical shift[b]	intensity, %
1	1.142	11.5	4	1.130	9.5
2	1.139	9.5	5	1.126[c]	40.2
3	1.135	27.3			

[a] A coupling constant of 6.4 Hz and a line width of 2.2–3.0 Hz were used for all doublets. [b] ppm from Me_4Si measured from 2D J-resolved spectrum. [c] Corresponds to doublet observed for isotactic poly(propylene oxide).

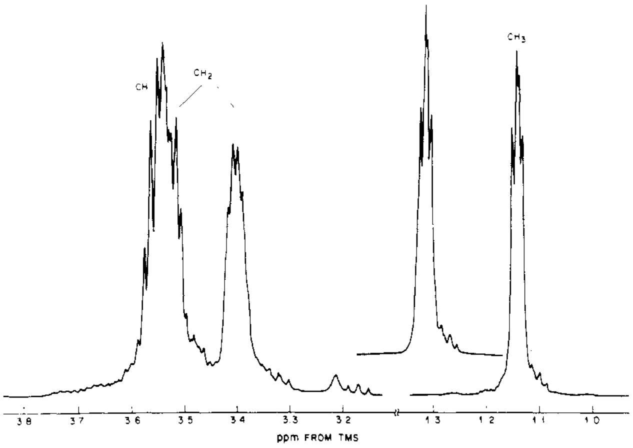


Figure 2. 500-MHz proton spectrum of atactic poly(propylene oxide), 20% solution in $CDCl_3$. Sixteen transients were accumulated at 25 °C by using a 90° pulse and a pulse interval of 8 s. The inset spectrum is a simulation of the methyl region produced by addition of 6.4-Hz doublets. See text and Table I.

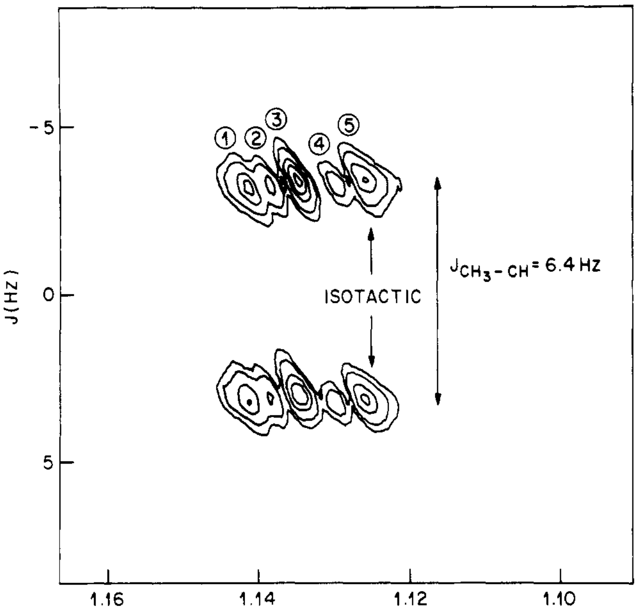


Figure 3. Contour plot of the methyl region of the 2D J-resolved spectrum of atactic poly(propylene oxide). Only large peaks are visible at these contour levels.

The chemical shifts and coupling constants measured from the methyl region of the 2D J-resolved spectrum of atactic poly(propylene oxide) were used in a curve-fitting simulation of the normal proton spectrum in order to obtain the relative intensities of the five doublets. A good fit was obtained with the parameters summarized in Table I. The five components observed in the 2D J-resolved spectrum of atactic poly(propylene oxide) can be interpreted in terms of triad sequences with some splitting due to longer sequences. Methyl resonances 1 and 2 together comprise one triad sequence; the splitting into two components is caused by chemical shift contributions from next nearest neighbors. Resonance 3 corresponds to another triad sequence, and resonance 5 corresponds to the isotactic triad sequence, as we have seen. However, there must be part of another triad overlapping the isotactic triad since the relative intensity of component 5 (40.2%) is too large to correspond only to the isotactic triad. Furthermore, doublet 5 is broader in the chemical shift dimension than the other doublets. Therefore, component 4 and part of component 5 together comprise another triad; the splitting is again due to next nearest neighbor contributions.

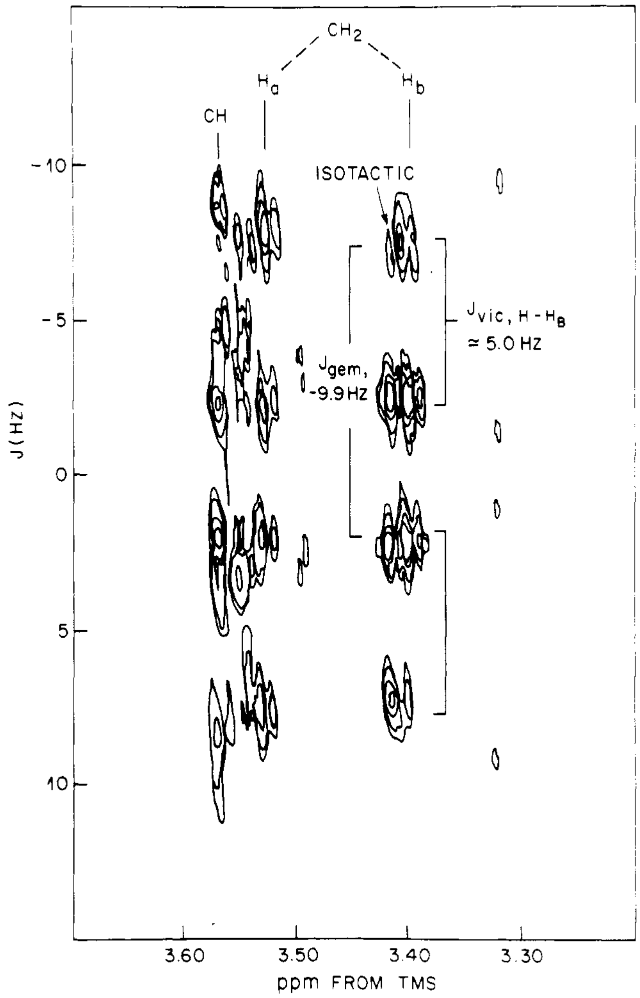


Figure 4. Contour plot of the downfield region of the 2D J-resolved spectrum of atactic poly(propylene oxide). Only large peaks are visible at these contour levels.

There are several possibilities for the origin of these next nearest neighbor chemical shift contributions. Apparently, for some triad sequences, the contribution from one next nearest neighbor is significant, whereas the contribution from the other next nearest neighbor is too small to be observed. The exact cause cannot be determined from this study.

The downfield regions of the 2D J-resolved spectra of atactic and isotactic poly(propylene oxide) are shown in Figures 4 and 5, respectively. The upfield methylene

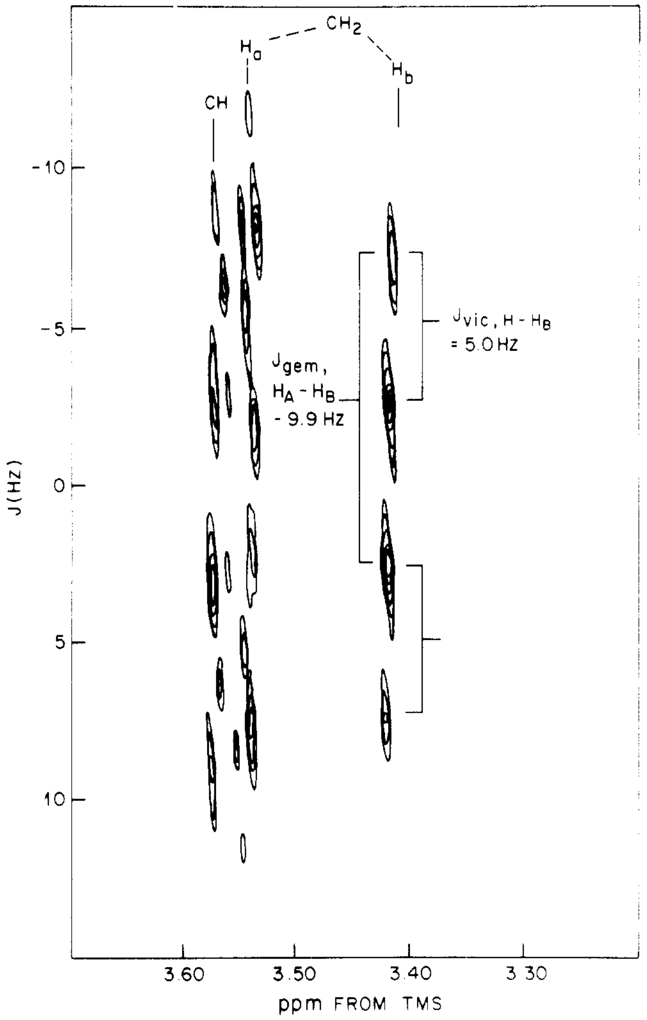


Figure 5. Contour plot of the downfield region of the 2D *J*-resolved spectrum of isotactic poly(propylene oxide).

proton, H_b, of the atactic polymer is characterized by three multiplets; the chemical shifts are different (3.420, 3.405, 3.392 ppm), but the coupling constants ($J_{gem} = -9.9$ Hz, $J_{vic} = 5.0$ Hz) are the same. Only one of these multiplets is visible in the 2D *J*-resolved spectrum of isotactic poly(propylene oxide). Therefore, the three multiplets observed in the 2D *J*-resolved spectrum of atactic poly(propylene oxide) are due to methylene protons in different stereosequences. In this case, the four triad sequences are incompletely resolved; only three different chemical shifts are observed. Although the most downfield of these multiplets (3.420 ppm) can be assigned to the isotactic triad by comparison to the chemical shift of the multiplet observed in the 2D *J*-resolved spectrum of isotactic poly(propylene oxide), the other multiplets cannot be definitively assigned. However, it is probable that they correspond to the two heterotactic sequences (unresolved) and the isotactic sequence, in order of increasing chemical shift.

The most downfield regions (3.5–3.6 ppm) of the 2D *J*-resolved spectra of both atactic and isotactic poly(propylene oxide) are too complex to be interpreted. This is caused by strong coupling effects due to a small chemical shift difference between the methine proton and the downfield methylene proton in every stereochemical environment. Strong coupling causes additional lines to occur in the 2D *J*-resolved spectrum, and spectral parameters cannot be measured directly from the *J*-resolved spectrum of strongly coupled protons.[21]

It should be noted that the multiplets corresponding to the upfield methylene proton, H_b, are essentially unaffected by the small chemical shift difference between the downfield methylene proton, H_a, and the methine proton, and these multiplets can be interpreted as first-order coupling patterns at 500 MHz. However, the intensities of the lines in these multiplets are affected by strong coupling at lower field strengths and are indicative of the relative signs of the coupling constants. In particular, results obtained at 250 MHz indicate that the geminal and vicinal coupling constants are of opposite sign.[21,22] The geminal coupling constant is assumed to be negative, in accordance with extensive previous findings, and the vicinal coupling constant is therefore taken as positive.

Thus far, the discussion has been restricted to the most intense lines in the 2D *J*-resolved spectra. There are a number of weak lines in the conventional proton spectrum of atactic poly(propylene oxide), and some of these lines are also present in the spectrum of isotactic poly(propylene oxide). These weak lines are observed in the 2D *J*-resolved spectra when lower contours are plotted to reveal less intense lines. For example, there is a series of at least five weak doublets upfield from the main doublets in the methyl region of the 2D *J*-resolved spectrum of atactic poly(propylene oxide); all of the coupling constants are 6.4 Hz as in the main doublets. There are also numerous weak multiplets in the downfield region of the 2D *J*-resolved spectrum of atactic poly(propylene oxide). These weak signals most probably correspond to protons in head-to-head:tail-to-tail inverted units. In the spectra of the atactic polymer they may also be attributable in part to end groups. Weak signals due to inverted units are observed in the ^{13}C NMR spectrum of atactic poly(propylene oxide); these signals are approximately 10% as intense as the main head-to-tail ^{13}C signals.[23] However, the weak proton signals cannot be definitively assigned at this time.

4. Conclusions

Two-dimensional *J*-resolved spectroscopy allows us to observe the fine structure in the proton NMR spectrum of atactic poly(propylene oxide). Homonuclear chemical shifts and coupling constants have been measured for protons in different stereochemical environments, and these values are consistent with the spectral parameters previously determined for selectively deuterated poly(propylene oxide).[16-19] Proton chemical shifts in atactic poly(propylene oxide) were observed to be sensitive to triad stereosequences, but the measured homonuclear coupling constants were the same regardless of the stereosequence. This implies that the conformation within the monomer unit is the same for monomers in different stereosequences within the polymer. This conclusion is in agreement with rotational isomeric state calculations which indicate that there are no substantial differences in rotamer populations associated with different stereosequences.[24]

Although only the isotactic resonances could be assigned unambiguously in the 2D *J*-resolved spectrum of atactic poly(propylene oxide), this example illustrates the potential of 2D *J*-resolved spectroscopy for elucidation of proton spectra of synthetic polymers. Overlapping multiplets which differ in chemical shift by only 2 Hz were well separated in the 2D *J*-resolved spectrum. Furthermore, coupling constants which were obscured in the conventional spectrum were easily measured from the 2D *J*-resolved spectrum.

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^{13}C NMR Microstructural Analysis of Chlorinated Poly(vinyl chloride) in Terms of Three-Carbon Sequences

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ABSTRACT: Using previously determined peak assignments at 50.3 MHz, we have developed a quantitative ^{13}C NMR analysis of chlorinated poly(vinyl chloride) (CPVC) microstructure in terms of three-carbon sequences. The analysis is sensitive to chlorine level and yields the concentrations of 11 three-carbon sequences, the weight percent chlorine, the amount of tacticity of residual PVC, and the sequence lengths of unchlorinated vinyl chloride units and CHCl carbons. We have characterized a series of CPVC's (57–69% chlorine) prepared by solution photochlorination, as well as several 66%-chlorine CPVC's made by various processes. The sequence length of the vinyl chloride units ("residual PVC") for the solution-chlorinated polymers correlated well with the second heat of melting determined by DSC. This result confirmed that the heat of melting arises from the residual PVC in these polymers. The CPVC's (66% chlorine) prepared by using different processes had different levels of residual PVC, vinyl chloride sequence lengths, and total amounts and distributions of CCl_2-centered sequences. In solution, the various tactic sequences were chlorinated to approximately equal extents. For the heterogeneous processes, the residual PVC contained greater relative proportions of syndiotactic sequences, reflecting the reduced rate of chlorination of PVC crystallites relative to the amorphous regions. The use of higher frequency (100 MHz) did not significantly improve the peak resolution in much of the CPVC spectrum, even with computer resolution enhancement.

Introduction

In a previous report,[1] we described how the free-radical chlorination of poly(vinyl chloride) produces a polymer, chlorinated poly(vinyl chloride) (CPVC), for which no structural repeat unit can be written. On the basis of ^{13}C NMR data, we know that CPVC's are composed of CH_2, CHCl, and CCl_2 groups occurring in many sequence combinations along the polymer chain. Configurational isomerism of CHCl-containing sequences in both the chlorinated and unchlorinated regions must also be considered. A description of CPVC based on sequences of vinyl or other monomers, as is often done for chemically modified homopolymers,[2,3] is not readily feasible.

Many of the ^{13}C chemical shifts of three- to five-carbon sequences have been assigned in the 50.3-MHz spectrum.[1,4] Here we present a method for the quantitative characterization of CPVC based on the concentrations of 11 three-carbon sequences, residual PVC, the average sequence lengths of unchlorinated vinyl chloride units and CHCl groups, and the tacticity of the residual PVC. We use this analysis to characterize a series of CPVC's of different chlorine contents prepared by solution photochlorination. Several CPVC's made by different processes but at a single chlorine level are also compared. The effect of the chlorination process on the CPVC microstructure and the tacticity of the residual PVC is discussed, as well as the use of higher magnetic fields and resolution enhancement techniques to improve the CPVC analysis.

Experimental Section

CPVC. The CPVC's were prepared by solution photochlorination of Geon 103EP poly(vinyl chloride) (The BF Goodrich Co.) in tetrachloroethane at 80 °C. Gaseous chlorine was fed (0.25 g/min) to the poly(vinyl chloride) solution (50 g/L) under ultraviolet irradiation (300-W Hg lamp). The polymer was precipitated with methanol, recovered by filtration, washed with a large volume of methanol, and vacuum-dried overnight at 25–30 °C. The processes used to prepare the nonsolution CPVC's are referenced in Table IV.

NMR Spectra. The 50.3-MHz ^{13}C NMR spectra were obtained on a Bruker WH-200 wide-bore, cryomagnet Fourier transform NMR spectrometer. The spectral data were acquired on approximately 20 wt % solutions in 4:1 1,2,4-trichlorobenzene/benzene-d_6 at 110 °C by using 20-mm sample tubes. Chemical shifts were measured relative to internal HMDS at 2.00 ppm from Me_4Si. Typical accumulation conditions were as follows: pulse repetition time, 7.5 s; 90° pulse, 35 μs; spectral width, 12 kHz in 8K data points; line broadening from sensitivity enhancement, 1.5–3 Hz; time of accumulation, 5–15 h. Integrated areas were measured from electronic integrals.

The 100-MHz ^{13}C spectra were obtained on a Bruker WH-400 narrow-bore NMR spectrometer using 10-mm tubes. The accumulation conditions were as follows: pulse repetition time, 3.5 s; 90° pulse, 13 μs; spectral width, 15 kHz; transform size, 16K. Resolution enhancement was performed as previously described.[5]

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