Carbon-13 NMR Determination of Poly(propylene oxide) Microstructure

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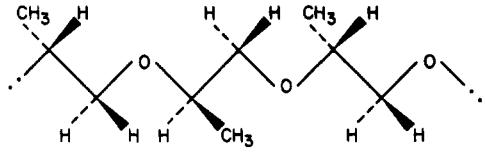
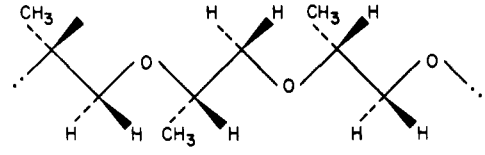
ABSTRACT: The ring-opening polymerization of propylene oxide can produce poly(propylene oxide) (PPO) with a broad range of microstructures. Depending on the optical purity of the cyclic propylene oxide monomer and the mode of ring opening produced by the catalyst, it is possible to obtain stereoregular, crystalline PPO with no head-to-head:tail-to-tail (H–H:T–T) additions, stereoirregular, amorphous PPO with substantial H–H:T–T content, and PPO's with intermediate degrees of microstructural complexity. In the present study we employ ^{13}C NMR spectroscopy to identify the various microstructures present in commercial PPO samples. Our microstructural identifications are materially aided by the multiple-pulse ^{13}C NMR INEPT and DEPT techniques, which permit separate observation of methyl, methylene, and methine carbon resonances. In addition, our ability to predict the relative ^{13}C chemical shifts expected for the carbons in normal (H–T) and defect (H–H:T–T) PPO units, via the γ-gauche effect method, permits a detailed assignment of H–T, H–H:T–T, and end-group resonances and microstructures in PPO.

Introduction

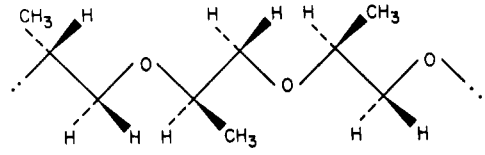
Propylene oxide ($CH_3\overset{\overset{\text{O}}{\frown}}{CH}CH_2$) exists in both the *R* and *S* optical forms due to its asymmetric methine carbon. Providing polymerization[1,2] results from cleavage of only one of the C–O bonds in the cyclic monomer, it is possible in principle to generate four different stereochemical triads in the regioregular, head-to-tail (H–T) PPO polymer. These H–T triads are presented in planar zigzag projection



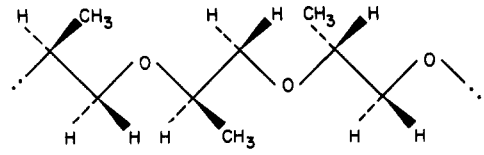
Isotactic, RRR or SSS



Syndiotactic, RSR or SRS

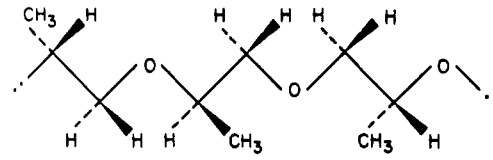


Heterotactic-1 RRS or SSR

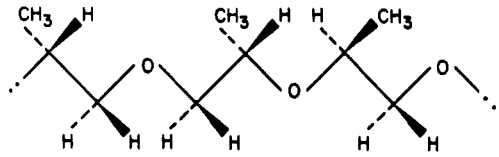


Heterotactic-2 SRR or RSS

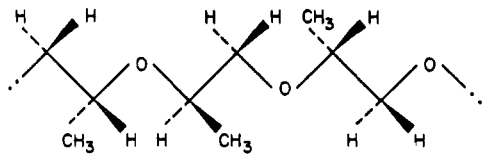
If during the ring-opening polymerization[1,2] both C–O bonds in propylene oxide are subject to cleavage, then, in addition to the H–T PPO triads illustrated above, three additional structural triads are possible for PPO. These are illustrated here for the all-*R* isomers,



(T–H:T–T)



(T–T:H–H)



(H–H:T–H)

where H–T, H–H, T–T, and T–H refer to the directions of neighboring monomers and H is the methine end and T is the methylene end of the monomer unit. Each of these regioirregular triads, with H–H and T–T addition, can be further subdivided on stereochemical grounds as was done above for the regioregular H–T triads. When both stereosequence and regiosequence are considered it is possible that 16 unique structural triads can potentially exist in PPO. It is worth mentioning that independent of regiosequence (H–T, H–H, T–T) an *m* diad consists of *RR* or *SS* neighboring units, while an *r* diad consists of *RS* or *SR* neighboring units. However, the methyl groups in a H–T *m* diad are on opposite sides of the planar zigzag backbone projection while in H–H and T–T *m* diads they are on the same side. The methyl groups in *r* diads are on the same side of the backbone when the diad is H–T and on opposite sides in both H–H and T–T diads. This results directly from the number of bonds separating asymmetric centers in H–T (3 bonds) and in H–H, T–T

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(two, four bonds) regiosequences.

NMR spectroscopy[3] is usually the method of choice for unraveling the microstructural details of polymers. Because the PPO repeat unit contains three protons (two methylene and one methine) whose resonances overlap extensively, it has not been possible to use ^{1}H NMR spectroscopy,[4-9] even at 500 MHz,[9] to determine the microstructure of PPO. Deuteration at the methine carbon simplifies[5-8] the ^{1}H NMR spectra of PPO. Two-dimensional ^{1}H NMR spectroscopy[9] also leads to greater separation of overlapping proton resonances. However, application of these specialized synthetic and spectroscopic techniques has not been completely successful in establishing the microstructures present in PPO.

^{13}C NMR[3,10] generally offers the potential for greater spectroscopic resolution when compared to ^{1}H NMR and might be expected to be better suited for the analysis of PPO microstructure.[11-15] This expectation is realized for regioregular (all H–T) PPO, where the CH and CH_2 carbon resonances are separated by ca. 2 ppm, and permits an unambiguous assignment[15] of PPO stereosequences. However, as we shall demonstrate here, the methine and methylene carbon resonances in regioirregular (H–T, H–H, T–T) PPO do overlap.

The chemical shifts[16-19] of carbon nuclei are sensitive to their neighboring substituents. Carbon substituents α and β to an observed carbon nucleus produce comparable deshielding (~9 ppm), relative to an unsubstituted carbon. The γ substituents, on the other hand, shield the carbon nucleus with a magnitude that depends on the distance between the observed carbon and the γ substituent. The conformationally sensitive γ-effect on ^{13}C NMR chemical shifts has been utilized[20] to predict the chemical shifts observed in polymers, which has facilitated the determination of their microstructure.

The methine and methylene carbons in PPO have the same number and types of α and β substituents (CH, 2 α-carbon, 1 α-oxygen, 1 β-carbon, and 1 β-oxygen; CH_2, 1 α-carbon, 1 α-oxygen, 2 β-carbon, and 1β-oxygen) independent of whether or not they are part of H–T, H–H, or T–T units (see triad representations presented above). In regioregular PPO the H–T methine carbons have two γ-substituents (2 CH) and the methylene carbons three γ-substituents (2 CH_2, CH_3). We therefore expect, as is observed, that the methylene carbons resonate upfield (ca. 2 ppm) from the methine carbons. In regioirregular PPO the H–H methine carbons have three γ-substituents (2 CH_2 and 1 CH_3 or 1 CH, 1 CH_2, and 1 CH_3), as do the H–T methylene carbons, and the T–T methylene carbons have 2 γ-substituents (2 CH or CH and CH_2), like the H–T methine carbons.

We expect the H–H methine and H–T methylene carbon resonances and the T–T methylene and H–T methine resonances to overlap based on their having the same numbers and types of α, β, and γ substituents. Oguni et al.,[15] in the most detailed ^{13}C NMR analysis of PPO microstructure reported to date, failed to consider the potential mixing and overlap of defect (H–H, T–T) and regioregular (H–T) resonances. As a result, we have reanalyzed the ^{13}C NMR spectra of PPO.

We have employed the multiple-pulse INEPT and DEPT techniques[21] to separately identify all observed ^{13}C NMR resonances as to carbon type, i.e., CH, CH_2, or CH_3 carbons. Resonances of minor intensity are attributed to the carbons belonging to the regioirregular portions of the PPO chains and to the chain end structures. Finally, the conformationally sensitive γ-gauche effect method[20] is utilized to calculate the relative ^{13}C chemical shifts expected for all three carbon types (CH, CH_2, CH_3) as a function of PPO microstructure (stereo- and regiosequence).

Experimental Section

The atactic poly(propylene oxide) samples employed in this work were obtained from Aldrich Chemical Co. Molecular weights reported on the basis of KOH hydroxyl number are 1000 and 4000. Both samples are viscous liquids at room temperature and readily miscible in benzene. The isotactic polymer was prepared from (*S*)-(−)-propylene oxide with a KOH catalyst and the method of Price and Osgan.[1] The viscosity-average molecular weight of the isotactic material is found to be 14 500. The 50.3-MHz carbon-13 spectra of PPO were recorded on a Varian XL-200 NMR spectrometer by using 10–40% (v/v) solutions in perdeuterobenzene with hexamethyldisiloxane (HMDS) as an internal reference (2.00 vs. Me_4Si). Spectra were recorded at 23 and 40 °C. The number of scans recorded ranged from 200 to 10 000 with the delay time between sampling pulses equal to ca. 4–5 times the longest carbon T_1 for internal chain units. The INEPT and DEPT multiple-pulse sequences[22] include the use of the compensated 180° pulse. The ^{13}C spin–lattice relaxation times were recorded with the standard 180°–τ–90° inversion–recovery sequence.

Calculation of ^{13}C NMR Chemical Shifts

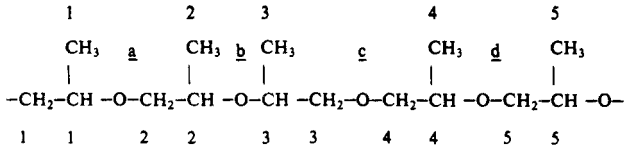
The γ-gauche effect method of calculating ^{13}C NMR chemical shifts in polymers is applied to PPO. Relative ^{13}C chemical shifts are determined by the number and types of γ substituents in a gauche arrangement with the observed carbon nucleus. The carbon nuclei in PPO are shielded by carbon and oxygen γ substituents. From ^{13}C NMR studies[23] of alkanes and their oxygenated derivatives, $\gamma_{c,c} \sim -4$ to -5 ppm and $\gamma_{c,o} \sim -6$ to -8 ppm seem likely for the shieldings produced by C and O γ substituents when in a gauche arrangement with the carbon nuclei in PPO.

The numbers of such γ-gauche arrangements are determined from the bond conformation probabilities calculated for PPO with the RIS model developed by Abe et al.[24] This conformational description developed for regioregular (H–T) PPO was modified so as to permit the calculation of bond probabilities in the H–H and T–T portions of PPO as well. Effects of both stereosequence and regiosequence were explicitly considered when calculating relative ^{13}C NMR chemical shifts in PPO via the γ-gauche method. The results of these calculations for the carbon nuclei in the H–H and T–T structures are given in Table I.

Results

NMR Spectra of Poly(propylene oxide). The carbon-13 NMR spectra of atactic PPO 4000 and isotactic PPO are shown in Figure 1, parts a and b. The methine, methylene, and methyl carbons all display chemical shift sensitivity to the stereochemistry of the polymer chain. The assignments of the head-to-tail portion of the polymer backbone are made by comparison of the two spectra. These results are in agreement with earlier work.[12,15] In contrast to carbon-13 NMR observations for most vinyl polymers, the observed sensitivity of the PPO carbon chemical shifts to stereochemistry is very small. The total spread of shifts is only ca. 0.12, 0.20, and 0.25 ppm for the methyl, methine, and methylene carbons, respectively. This can be contrasted to polypropylene,[25] where the range of chemical shifts due to stereosequences is 2.0, 0.5, and 2.0 ppm for the same carbon types. The reduced sensitivity in PPO reflects the presence of three bonds between the chiral centers in contrast to the two bonds in vinyl polymers. The limited chemical shift sensitivity is predicted by the RIS model.[24] On the basis of γ-gauche

Table I
Calculated ^{13}C NMR Chemical Shifts for Poly(propylene oxide) at 23 °C



carbon	diad[a] a	b	c	d	chem shift, ppm[b]
CH_3 1	m	—	—	—	0.00
2	r	r	—	—	+0.45
2	m	r	—	—	+0.49
2	r	m	—	—	+0.75
2	m	m	—	—	+0.79
3	—	r	—	—	+0.53
3	—	m	—	—	+0.82
4	—	—	—	m	+0.02
4	—	—	—	r	+0.04
5	—	—	—	m	0.00
CH_2 1	m	—	—	—	0.00
2	m	m	—	—	−0.15
2	r	m	—	—	−0.19
2	r	r	—	—	+0.20
2	m	r	—	—	+0.25
3	—	m	—	—	+4.40
3	—	r	—	—	+4.73
4	—	—	—	r	+4.75
4	—	—	—	r	+4.78
5	—	—	—	m	0.00
CH 1	m	—	—	—	0.00
2	m	m	—	—	−4.49
2	r	m	—	—	−4.45
2	m	r	—	—	−4.49
2	r	r	—	—	−4.45
3	—	m	—	—	−4.48
3	—	r	—	—	−4.48
4	—	—	—	r	−0.25
4	—	—	—	m	−0.27
5	—	—	—	m	0.00

[a] The dash (–) indicates either *m* or *r* diad placement. [b] The plus (+) and minus (–) indicate downfield and upfield shifts, respectively, relative to the position of the 1 or 5 (H–T) carbons.

interactions a spread of H–T chemical shifts of ca. 0.05 ppm is predicted for each of the three carbon types.

The methyl carbon, which is attached to the chiral center, is expected to produce four resonances at the triad level in PPO since the two heterotactic sequences are unique. At 23 °C we observe (Figure 1a) only two broad resonances; however, four distinct peaks are visible in spectra recorded at higher sample concentrations (not shown). The small chemical shift differences prevent us from making specific assignments to the head-to-tail methyl carbons, except to note that the isotactic methyl resonance is in the upfield half of the methyl doublet. It should be noted that the chemical shifts of PPO are found to be very sensitive to changes in sample concentration, solvent, or temperature. A significant scrambling of resonances occurs in raising the concentration from 10% to 40%. This effect must be considered when comparing data for different samples.

The methylene carbon displays a clear sensitivity to the diad stereochemical relationship between neighboring chiral centers but exhibts little longer range sensitivity. The chiral methine carbon shows clear separation of the triads, except that the two heterotactic sequences are not resolved. The chemical shifts and spin–lattice relaxation data for these head-to-tail carbons are given in Table II. The relaxation data exhibit no observable dependence on stereochemistry. The fact that the ratio of methine to methylene T_1 values is not 2:1 (i.e., the NT_1 values are not

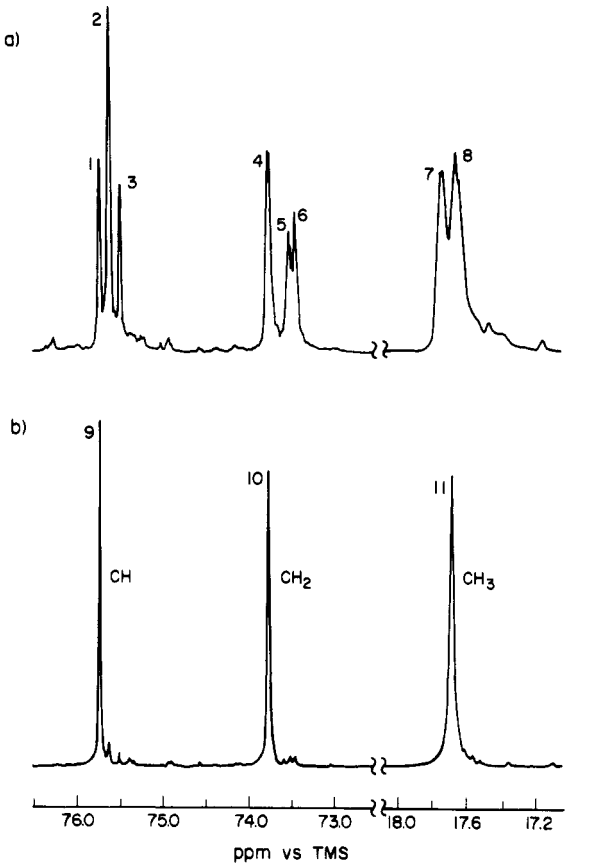


Figure 1. 50.31-MHz ^{13}C NMR spectra of (a) atactic PPO 4000 and (b) isotactic PPO, observed at 23 °C in C_6D_6. See Table II.

Table II
^{13}C NMR Chemical Shifts and Relaxation Data of Head-to-Tail Carbons in Poly(propylene oxide) at 23 °C (Figure 1)

resonance	chem shift, ppm	T_1, s	carbon type	stereosequence
1	75.75	0.78	CH	*mm*
2	75.64	0.80	CH	*mr* + *rm*
3	75.50	0.81	CH	*rr*
4	73.78	0.51	CH_2	*m*
5	73.54	0.50	CH_2	*r*
6	73.47	0.50	CH_2	*r*
7	17.79	1.03	CH_3	*rm, mr, rr*
8	17.71	1.03	CH_3	*mm, rm, mr, rr*
9	75.73		CH	*mm*
10	73.77		CH_2	*m*
11	17.72		CH_3	*mm*

equal) indicates that the relaxation is not entirely dipolar.

In earlier studies of PPO using carbon-13 NMR,[15] confusion developed in assigning carbons of the head-to-head (H–H):tail-to-tail (T–T) defects that result from the catalyst occasionally cleaving the O–CH linkage instead of the O–CH_2 bond. The possibility of mixing of the methine and methylene resonances was not considered. Additionally, spectral analysis of lower molecular weight samples must take into account the contribution of carbon nuclei in the chain-end structures. Our approach in analyzing the carbon spectra of PPO was to first define the type of carbon represented by each resonance, i.e., methine, methylene, or methyl. This was accomplished by the use of the DEPT and INEPT techniques. Second, by analysis of PPO samples differing in molecular weight we assigned those resonances belonging to end-group carbons. The third and final step in the analysis was to assign the resonances of the H–H and T–T defects using the γ–gauche calculations described above.

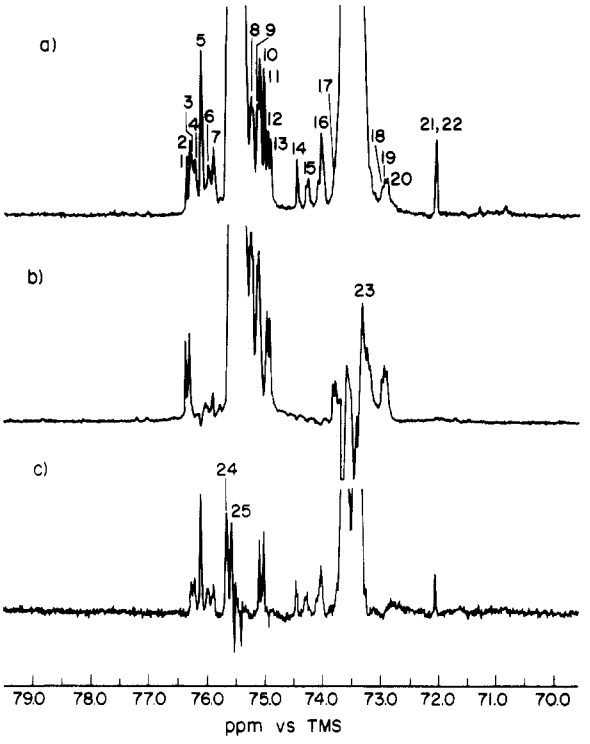


Figure 2. Methine and methylene (a), methine only (b), and methylene only (c) 50.31-MHz ^{13}C NMR DEPT spectra of atactic PPO 4000 observed at 23 °C in C_6D_6.

The DEPT technique permits spectral editing in such a manner that one can produce spectra containing only a specific carbon type. In Figure 2 we show the results of the DEPT measurement on atactic PPO 4000 for the methine and methylene carbons only. At the high vertical gain shown the H–T resonances are off-scale, and we are observing the resonances of the defect H–H and T–T structures as well as the chain-end carbons. In (a) we observe all CH and CH_2 resonances. The spectrum in (b) shows only the CH resonances, while (c) contains only those of the CH_2 carbons. The small negative peaks in (b) and (c) are residual signals from the H–T methylene and methine carbons, respectively. The most striking feature of these editing spectra is that there are clearly methine carbon resonances in the upfield region previously thought to contain exclusively methylene resonances and also there are methylene resonances in the downfield portion of the spectra previously thought to contain only methine resonances. These observations are confirmed by the INEPT spectra (not shown) in which the methylene resonances can be observed with negative intensity while the methine signals appear as positive peaks. Certain H–H:T–T and/or end-group resonances at ca. 73.5 and 75.6 ppm can only be seen in an edited spectrum as they are completely obscured by the H–T peaks in a normal FT spectrum. The comparison of resonances in the three spectra of Figure 2 permits us to establish the identity of each resonance as to carbon type, methine or methylene. These results together with the chemical shift and T_1 data for each carbon are given in Table III. As expected the T_1 values obtained for carbon nuclei near chain ends are longer than those of the internal carbons.

In order to assign resonances produced by various end groups we examined PPO samples with number-average molecular weights of 1000 and 4000 (DP = 17 and 69, respectively). The results of a DEPT measurement on PPO 1000 agree with those of PPO 4000 in establishing the carbon type represented by each NMR resonance. In the PPO 1000 polymer the number of end groups is ca. 3

Table III
^{13}C NMR Chemical Shift Assignments and Relaxation Data of the Methine and Methylene Carbons of Atactic PPO 4000 at 23 °C (Figure 2)

resonance	chem shift, ppm	assignt[a]		T_1, s
1	76.36	-CH-	E	0.93
2	76.29	-CH-	E	0.80
3	76.26	$-CH_2-$	3, 4	0.80
4	76.21	$-CH_2-$	3, 4	0.77
5	76.10	$-CH_2-$	E	1.19
6	75.98	$-CH_2-$	3, 4	0.56
7	75.88	$-CH_2-$	3, 4	0.59
8	75.24	-CH-	E	0.82
9	75.13	-CH-	E	0.81
10	75.08	-CH-, $-CH_2-$	E	0.81
11	75.02	$-CH_2-$	E	0.90
12	74.96	-CH-	E	1.08
13	74.91	-CH-	E	1.18
14	74.46	$-CH_2-$	2	1.04
15	74.26	$-CH_2-$	2	0.50
16	74.02	$-CH_2-$	2	0.51
17	73.82	-CH-	2, 3	
18	72.97	-CH-	2, 3	0.61
19	72.93	-CH-	2, 3	0.64
20	72.87	-CH-	2, 3	0.68
21	72.06	$-CH_2-$	E	2.16
22	72.03	$-CH_2-$	E	2.16
23	73.30	-CH-	2, 3	
24	75.65	$-CH_2-$	E	
25	75.57	$-CH_2-$	E	

[a] E indicates chain end structure; 2, 3, 4 indicates H-H:T-T defect structure (see Table I).

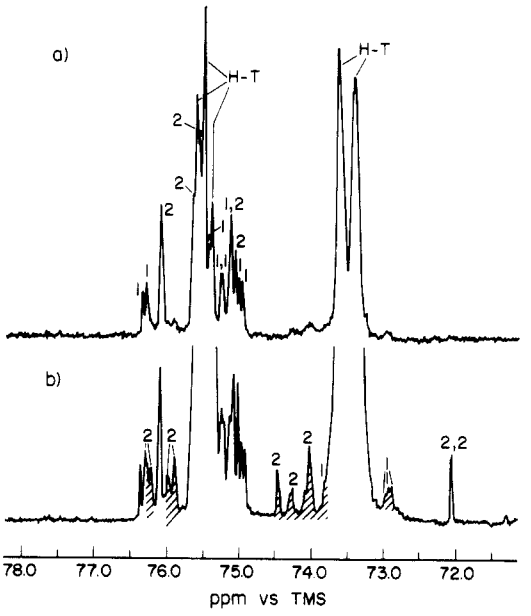


Figure 3. 50.31-MHz ^{13}C NMR spectra of (a) atactic PPO 1000 and (b) atactic PPO 4000 observed at 23 °C in C_6D_6. (1 indicates methine and 2 indicates methylene). The crosshatched resonances result from the H–H:T–T structure.

times that of the H–H:T–T defects. As a result, all of the visible resonances in Figure 3a, other than the labeled H–T peaks, can be attributed to the end groups. We observe that all of the CH and CH_2 end-group resonances occur between 75 and 76.5 ppm, the methine H–T region. The DEPT spectra (not shown) indicate that there are no end-group CH resonances hidden by the H–T methylene resonance at ca. 73.5 ppm. Comparison of the DEPT spectra permit specific assignment of the end-group methine and methylene resonances (1 is methine and 2 is methylene). Note the presence of methylene resonances at ca. 75.6 ppm, which add to the complexity of the H–T

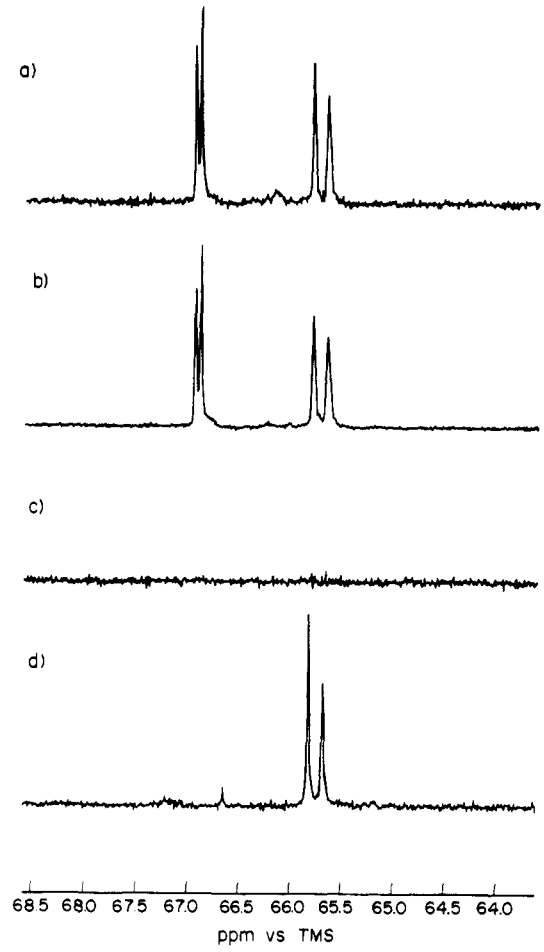


Figure 4. Terminal methine and methylene (a), methine only (b), methylene only (c) 50.31-MHz ^{13}C NMR DEPT spectra of atactic PPO 4000 and (d) methylene and methine of isotactic PPO observed at 23 °C in C_6D_6.

CH region in (a). The chemical shift information obtained from PPO 1000 is used to identify the end-group resonances in PPO 4000, Figure 3b. This comparison of data indicates that only the crosshatched peaks in (b) are the resonances resulting from carbons in the H–H:T–T structure. The identity of carbon types in (b) is obtained from the DEPT spectra of Figure 1. An additional H–H:T–T methine resonance (no. 23) occurs at 73.30 ppm as seen in the DEPT spectrum of Figure 2b.

Additional methine resonances are found in the spectral region 65.5–67 ppm in spectra of the atactic and isotactic PPO samples. They are similar in size to those of other end-group resonances in the low molecular weight atactic sample. As shown in Figure 4 these are all methine resonances. The absence of the resonances at 67 ppm in the isotactic spectrum (d) indicates that they are probably due to the syndiotactic diad at the chain termination. The chemical shift position of these carbons is similar to those expected[23] for a methine carbon in terminal structure 1,

$$\cdots\text{-}CH_2CH(CH_3)OH$$
$$\mathbf{1}$$

produced by protonation of the propagating anion or chain transfer to monomer (see below). However, we find no evidence for a primary alcohol structure, which is postulated to result from the initiation step.[1,26] Model compounds indicate the $-CH_2OH$ resonance will be ca. 68–69 ppm. In spectra of PPO 4000 we find small olefinic resonances as shown in the INEPT spectrum of Figure 5. In this particular spectrum the methylene carbons are negative while the methine resonances are positive. The

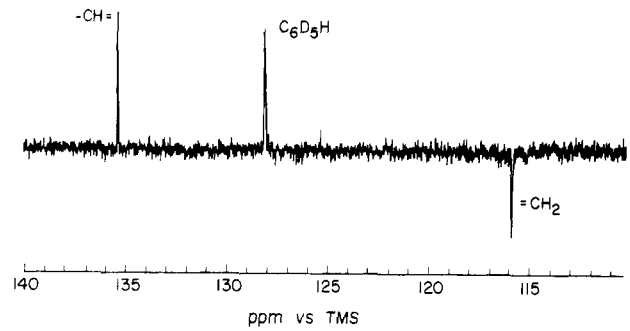


Figure 5. Olefinic region of the 50.31-MHz ^{13}C NMR INEPT spectrum of atactic PPO 4000 observed at 40 °C in C_6D_6.

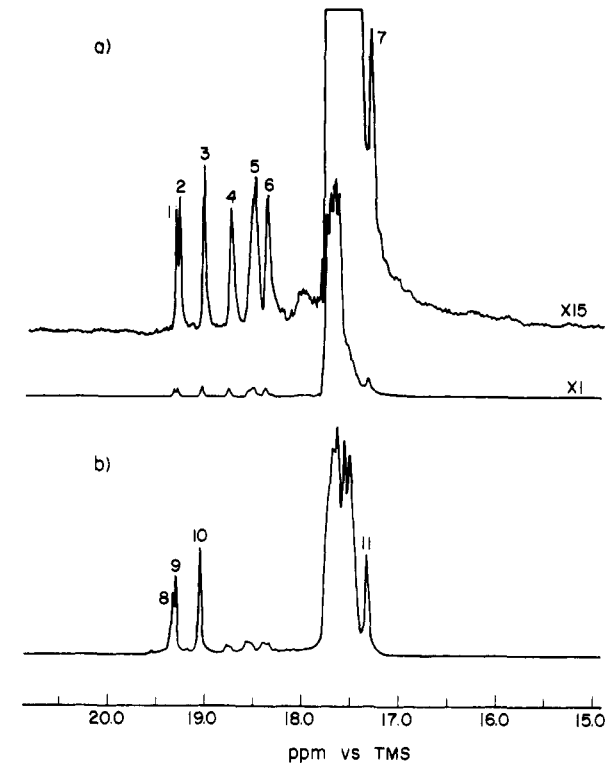
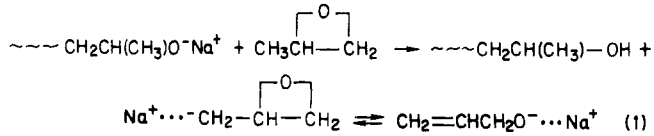


Figure 6. Methyl region of the 50.31-MHz ^{13}C NMR spectra of (a) atactic PPO 4000 and (b) atactic PPO 1000 observed at 23 °C in C_6D_6. See Table IV.

combination of a CH at 135.4 ppm and CH_2 at 115.9 ppm indicates the presence of a terminal $-CH{=}CH_2$ structure.[27] This is very likely the result of chain transfer to monomer.[26]



The terminal $-CH_2O-$ carbon in the vinyl chain end is found at ca. 72.1 ppm, in agreement with published values.[27] The olefinic resonances have an intensity ratio of 1:2 relative to the saturated resonances at 66–67 ppm. The fact that we observe this structure only in the higher molecular weight sample is probably indicative of a higher monomer concentration. The benzene signal at 128 ppm in Figure 5 reflects a protonated species in the perdeuteriobenzene solvent.

The methyl regions of both atactic polymers are shown in Figure 6. All of the methyl resonances occur in the 17–19.5-ppm region. Resonances produced by methyl carbons in or adjacent to an end group can be assigned by the comparison of (a) and (b). As shown in Figure 6a all

Table IV
^{13}C NMR Chemical Shift Assignments and Relaxation Data of the Methyl Carbons of Atactic PPO 4000 at 23 °C (Figure 6)

resonance	chem shift, ppm	assignt[a]	T_1, s
1	19.27	E	1.65
2	19.24	E	1.65
3	18.99	E	1.80
4	18.74	2, 3	0.99
5	18.51	2, 3	0.96
6	18.38	2, 3	0.92
7	17.29	E	1.09
8	19.31	E	
9	19.26	E	
10	19.02	E	
11	17.31	E	

[a] E indicates chain end structure; 2,3 indicates H-H:T-T defect structure (see Table I).

of the H–H:T–T defect resonances are found downfield of the H–T signals at 17.5 ppm.

A summary of the methyl carbon data is given in Table IV. For each carbon identified in Figure 6 we report the chemical shift position, carbon type, assigment (H–T, H–H:T–T defect, or end group), and the spin–lattice relaxation time. We cannot assign the end-group methyls to specific terminal structures. As expected the relaxation times for the chain-end methyl carbons are significantly longer than the value observed for the methyl carbons of internal units.

Comparison of Experimental and Calculated Chemical Shift Data. In order to make assignments of the carbon nuclei in the H–H:T–T structures a comparison was made between the experimental shift data (Figures 2 and 6, and Tables III and IV) and the relative chemical shifts for each carbon type resulting from the γ-gauche calculations (Table I). The calculated data indicates a lack of sensitivity for all carbons to the nature of the stereochemistry across the T–T portion of the chain (diad c, Table I). In addition, for the H–H methyl and methylene carbons 2 and 3, diad b strongly affects the chemical shift while diad a has a much smaller influence on chemical shift. The H–H methine carbons, however, are expected to show only a very small stereochemical dependence.

Using the calculated shift data of Table I, we can make the specific assignments given in Tables III and IV. The H–H methine carbons 2 and 3 are predicted to be significantly upfield of the H–T CH resonances (at ca. 72.8–73.8 ppm) and are observed most clearly in the DEPT editing spectrum (Figure 2b). Methine carbon 4 cannot be resolved from the H–T CH resonances.

For the CH_2 carbons (Figure 2a) we assign the group of resonances[14-16] slightly downfield of the methylene H–T resonances to carbon 2, while the methylene resonances (3, 4, 6, and 7) shifted downfield into the CH H–T region are assigned to carbons 3 and 4. Despite differences in the magnitudes of calculated and observed shifts for the H–H:T–T vs. the H–T methine and methylene carbons,[28] the predicted direction for each carbon permits a consistent set of assignments as given in Tables II and III.

These results illustrate the difficulties faced by early workers in assigning the carbon-13 spectrum of PPO. At first glance one is tempted to simply divide the 73–76 ppm region into two parts, methine and methylene. However, a careful understanding of the shift effects produced by the H–H:T–T structure shows that a large number of methine and methylene resonances should overlap, producing a very complicated spectrum, and that the identity of carbon type can only be ascertained by the DEPT or INEPT editing experiments. In addition, the comparison of samples differing in molecular weight is necessary to identify the chain end carbons.

The methyl carbons of the H–H:T–T structure are assigned in Table IV. The calculated magnitude and the direction of these methyl resonances relative to the H–T resonances agree[28] with the observed results (Figure 6a). The three defect resonances (peaks 4–6) are assigned to carbons 2 and 3 (Table I). Because of the predicted overlap resulting from the stereosequences we cannot make more specific assignments in this region. From the methyl carbon data we can estimate the number of inverted or defect monomer units in PPO 4000 to be ca. 2.2%. The number-average molecular weight ($\bar{M}_n$) based on the end-group resonances is found to be ca. 5400 or DP = 93.

Conclusions

With the aid of multiple-pulse editing techniques and the γ-gauche calculations of relative carbon-13 NMR chemical shifts, we have assigned the carbon-13 spectrum of PPO, including the determination of carbon resonances resulting from chain-end structures. From these results it is possible to quantitatively determine the number-average molecular weight and the amount of H–H:T–T defects resulting from ring opening of the propylene oxide monomer at the CH–O bond. The identification of specific terminal structures can provide insight concerning the mechanism of polymerization as well. As a result, a much more complete understanding of PPO microstructure is obtained.

Acknowledgment. We are indebted to Drs. F. A. Bovey and M. D. Bruch for providing us with the sample of isotactic PPO.

Registry No. Atactic PPO, 25322-69-4; isotactic PPO, 26046-17-3.

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(28) The differences in the magnitudes of the ^{13}C chemical shifts observed and calculated for methine and methylene carbons in the H–H:T–T and H–T structures may stem from the slightly different β substituents[23] present in each of these structural environments. Methine and methylene carbons in both H–H:T–T and H–T structures are β to oxygen ($CHCH_2O$ and CH_2CHO) and the methylene carbons are beta to methyl carbons (CH_2CHCH_3). However, H–T methine and H–H:T–T methylene carbons are β to methylene carbons ($CHOCH_2$ and CH_2OCH_2), while H–T methylene and H–H:T–T methine carbons are β to methine carbons (CH_2OCH and CHOCH) (see Table I). On the other hand, H–H:T–T and H–T methyl carbons have precisely the same α and β substituents. The fact that the calculated and observed methyl chemical shifts agree so closely lends support to the suggestion that slightly different β substituents for H–H:T–T and H–T methine and methylene carbons may be the source of the disparity between the magnitudes of their observed and calculated ^{13}C chemical shifts.

^{13}C NMR Studies of Sequence Distributions in Polymers Having All Rings in the Backbone: 1-Substituted 1,3-Poly(bicyclobutanes)

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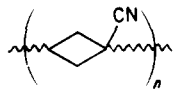
Received September 6, 1985

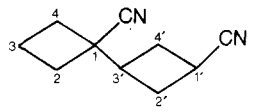
ABSTRACT: To better understand the stereochemistry of the class of unusual polymers having all 1,3-fused cyclobutane rings in the backbone, we obtained ^{13}C NMR results for poly(bicyclobutane-1-carbonitrile) (PBBC), poly(1-(methoxycarbonyl)bicyclobutane) (PMCB), poly(bicyclobutane-1-carboxamide) (PBCA), and some related oligomers. Using chemical shift data for trimers related to PBBC and PMCB, it was possible to assign all of the ^{13}C NMR resonances of the polymers. Triad sequences are observed in the –CN, COO–, and $-CONH_2$ resonances as well as for certain ring carbons in all three polymers. In contrast to vinyl and related polymers, there is a directionality in these polymer sequences that leads to additional multiplicity in the *n*-ad sequences. The quaternary carbons in PBBC and PMCB also exhibit pentad sequences, which are consistent with either Bernoulli or first-order Markov statistics within the experimental error. The ratio of trans/cis ring fusions are similar: 0.68:0.32, 0.66:0.34, and 0.73:0.27 for free radical initiated PBBC, PMCB, and PBCA, respectively.

In a previous NMR study[1] of polymers composed entirely of 1,3-fused cyclobutane rings in the backbone,[2-4] it was shown that the ^{13}C NMR spectrum of poly(bicyclobutane-1-carbonitrile) (PBBC) could be interpreted on the

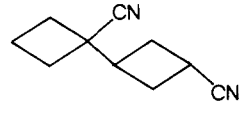


PBBC

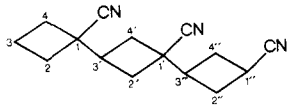
basis of studies of related model compounds. Of particular importance were the NMR spectra of many 3-substituted cyclobutane-1-carbonitriles, which included the two dimers [*cis*- and *trans*-3-(1-cyanocyclobutyl)cyclobutane-1-carbonitrile, **1a** and **1b**] as well as the four trimers **2a–d**.



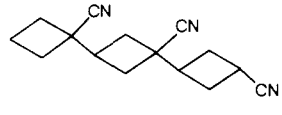
1a (*t*)



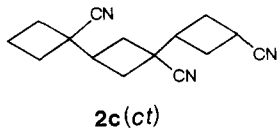
1b (*c*)



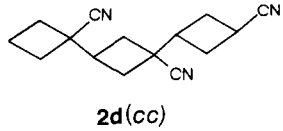
2a (*tt*)



2b (*tc*)



2c (*ct*)

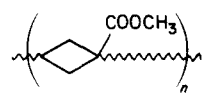


2d (*cc*)

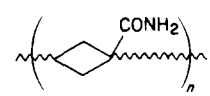
In all of the molecules studied substituents at C3, which were cis to the nitrile, led to nitrile ^{13}C NMR shifts that were 1–1.5 ppm upfield of the trans isomers. On this basis, it was concluded that the nitrile chemical shift provided a very useful probe of cis/trans stereochemistry in 3-substituted cyclobutane-1-carbonitriles as well as in PBBC. With notation of the trimers by the general form RR′R″, where the R's denote the 1-substituted cyclobutane moieties, it was suggested[1] that the ^{13}C NMR spectrum of PBBC arises as the superposition of resonances of the four R′ moieties of the trimers **2a–d**. From the ratios of the integrated intensities of the high-field and low-field CN resonances, for example, it was possible to infer the ratios of trans-to-cis ring enchainments depending on the method of initiation of polymerization.

The oligomers are given different designations than those used previously[1] to avoid confusion in the specification of the sequence distributions. In the present work cis (c) and trans (t) denote ring enchainments, and these are read from left to right. For example, the tc associated with the trimer (**2b**) RR′R″ (R denotes cyanocyclobutyl) implies that R and R″ are in a trans arrangement about R′ and that a cyanocyclobutyl group (R‴) must add in a cis fashion at C1″.

This work extends the previous ^{13}C NMR studies of PBBC to include the detailed assignments of both nitrile and ring carbon resonances and sequence determinations up to pentads. In fact, it will be shown that certain resonances, which were previously thought to be due to impurities,[1] arise because of pentad sequences in the ring carbons. Carbon-13 NMR studies of poly(1-(methoxycarbonyl)bicyclobutane) (PMCB) and related oligomers



PMCB



PBCA

provide an even better example for the appearance of triad and pentad sequences. Moreover, in the absence of all of the model compounds for poly(bicyclobutane-1-carbox-

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