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# NMR Assignments of Regioregular Poly(propylene oxide) at the Triad and Tetrad Level

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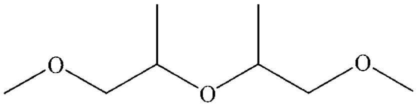
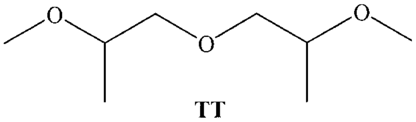
ABSTRACT: Regioregular poly(propylene oxide), PPO, formed by simple base (KOH) and coordinate base (TPP)AlCl, (tetraphenylporphinato)aluminum chloride, ring-opening polymerization of propylene oxide, PO, has been studied by high field $^{13}$C{$^{1}$H} NMR spectroscopy at various concentrations in $CDCl_3$ and $C_6D_6$. The original assignments of Tonelli and Schilling [*Macromolecules* **1986**, *19*, 1337−1343] at the triad and diad sensitivity level have been extended to tetrad sensitivity.

## Introduction

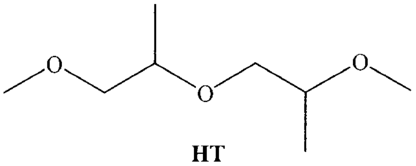
Poly(propylene oxide), PPO, and its lower molecular weight polyether-ols find numerous applications and are bulk commodity materials.[1] They are prepared by ring-opening polymerization, ROP, of the monomer propylene oxide, PO, which can be brought about by base[2] or acid catalysis.[3] Most often, however, a metal-containing complex is involved in the ring-opening polymerization catalysis, and the term coordinate catalysis is employed, and then this is further broken down to coordinate-base or coordinate-acid catalysis.[4] The distinction between acid and base catalysis is evident from the microstructure of the polymer. Acid catalysis yields highly regio-irregular polymers and oligomers together with cyclic ethers.[3] There are many head−head, HH, and tail−tail, TT, junctions in addition to head−tail, HT, junctions which predominate for base catalysis.[2]



**HH**



**TT**



**HT**

From the simple base (KOH promoted) ring-opening of *rac*-PO and *S*-PO, Tonelli and Schilling[5] were able to assign the $^{13}$C{$^{1}$H} NMR spectrum of regioregular PPO at the triad level for the methine carbons (seen in the 75−76 ppm region) and at the diad level for the methylene carbons (seen in the 73−74 ppm region) though, as can be seen from the spectrum shown in Figure 1, there is evidence that the high field signal assigned to the **s** diad is showing further splitting. We recently examined the $^{13}$C{$^{1}$H} NMR spectra of regio-irregular PPO formed from polymerizations induced by various aluminum binolate complexes and proposed several assignments at the triad level based on polymerizations of *rac*-PO, *S*-PO, and 50:50 mixtures of *rac* and *S*-PO.[6] During the course of this work we had occasion to reexamine the $^{13}$C{$^{1}$H} NMR spectra of regioregular PPO, and in so doing we were able to detect a higher level of sensitivity to the microstructure. We report these findings here.

## Results and Discussion

**Polymer Synthesis.** Two samples of PPO were prepared: (1) from KOH polymerization which results in ca. 95% regioregular triads (HTHTHT) and molecular weights of up to ~5000 Da, being limited by base deprotonation of PO[2] at the allylic position: $OH^- + PO \rightarrow H_2O + CH_2{=}CH{-}CH_2O^-$; (ii) from Inoue's living polymerization of PO by initiation with (TPP)AlCl.[7] This gives very high molecular weight polymers with no detectable HH or TT junctions and shows a significant stereoselectivity as described below.

**NMR Studies**. Polymer samples were examined at various concentrations in benzene-$d_6$ and chloroform-*d* at $^{13}$C frequencies of 100, 150, and 200 MHz. A comparison of $^{13}$C{$^{1}$H} spectra of the methine and methylene carbon signals recorded in $CDCl_3$ for the two polymer samples is shown in Figures 2 and 3. The methine carbon resonances (75 ppm region, Figure 2) appear as four signals of equal intensity for the KOH-based sample of PPO readily assignable to the triads **ii**, **is**+**si**, and **ss**. It is not possible to distinguish between **is** and **si**. In the case of the PPO sample prepared employing (TPP)AlCl (Figure 3), there is a significant enhancement of the **ii** stereosequence and a corresponding decrease in the **ss** triad. Even at the highest carbon field, the resolution of the methine carbon is clearly only at the triad level. This presumably is due to the structural nature of the polymer. See Figure 4. At triad sensitivity, the methine carbon is three bonds removed from its nearest methine stereocenters. For a regioregular $(HT)_n$ polymer the next stereocenters are six bonds removed, and even at 200 MHz, the chemical shift is

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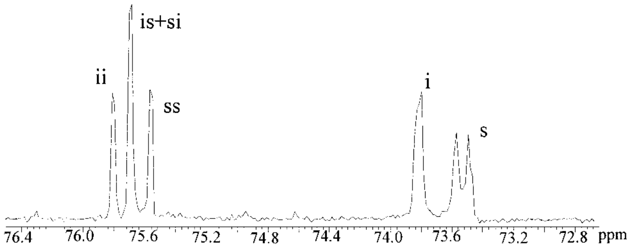

**Figure 1.** $^{13}C\{^1H\}$ NMR (100 MHz, $C_6D_6$) spectrum of PPO obtained from anionic polymerization of PO with KOH.

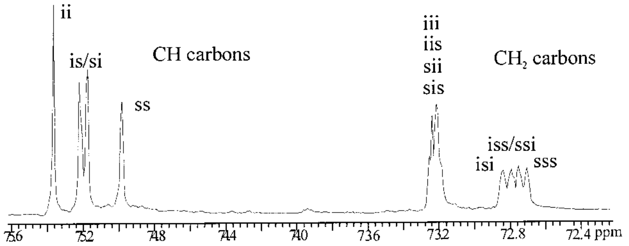

**Figure 2.** $^{13}C\{^1H\}$ NMR (200 MHz, $CDCl_3$) spectrum of PPO obtained from polymerization with KOH.

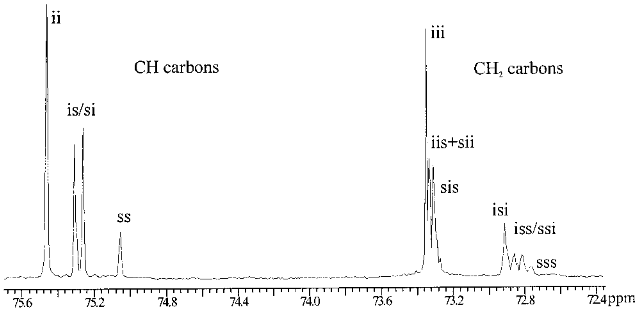

**Figure 3.** $^{13}C\{^1H\}$ NMR (200 MHz, $CDCl_3$) spectrum of PPO obtained from polymerization with (TPP)AlCl.

insensitive to changes in the environment six bonds away in the chemical structure.

In contrast, the methylene carbons in regioregular $(HT)_n$ PPO are asymmetrically disposed with respect to the number of bonds to their neighboring methine stereocenters. In the $^{13}C\{^1H\}$ NMR spectrum of Figure 3, we see seven signals in the methylene carbon region; eight were expected for tetrad sensitivity. It is then tempting and probably correct to interpret this as the methylene carbon of the central PO unit being influenced by stereocenters of the adjacent methine carbons that are one and four bonds to its left and two and five bonds to its right on the structures as drawn in Figure 4.

In the $^{13}C\{^1H\}$ NMR spectrum of the methylene carbons formerly assigned to the **s** diad (see Figure 1), we can see clearly four signals of equal intensity for the PPO prepared by using KOH (Figure 2, 72.5 ppm region). These can be assigned to the **sss**, **ssi**, **iss**, and **isi** tetrads. In the case of PPO prepared by Inoue's catalyst (Figure 3), these four signals are no longer of equal intensity. The downfield signal is significantly more intense and the upfield less intense than the two central signals which appear to share the same intensity. This is, indeed, exactly what we expect since we know that Inoue's catalyst favors the formation of isotactic junctions.[7] From the relative signal intensities of the **ii** and **ss** triads in the methine carbon spectrum, we can reliably estimate the probability ratio of **i**:**s** lies between 2:1 and 3:1. This would predict an intensity ratio for the tetrad resonances **isi**, **iss**, **ssi**, **sss** of 9:3:3:1 for **i**:**s** = 3:1 or 4:2:2:1 for **i**:**s** = 2:1. The assignment of the **iss** and **ssi** tetrad resonances thus remains ambiguous, but those of **sss** and **isi** are firmly established.

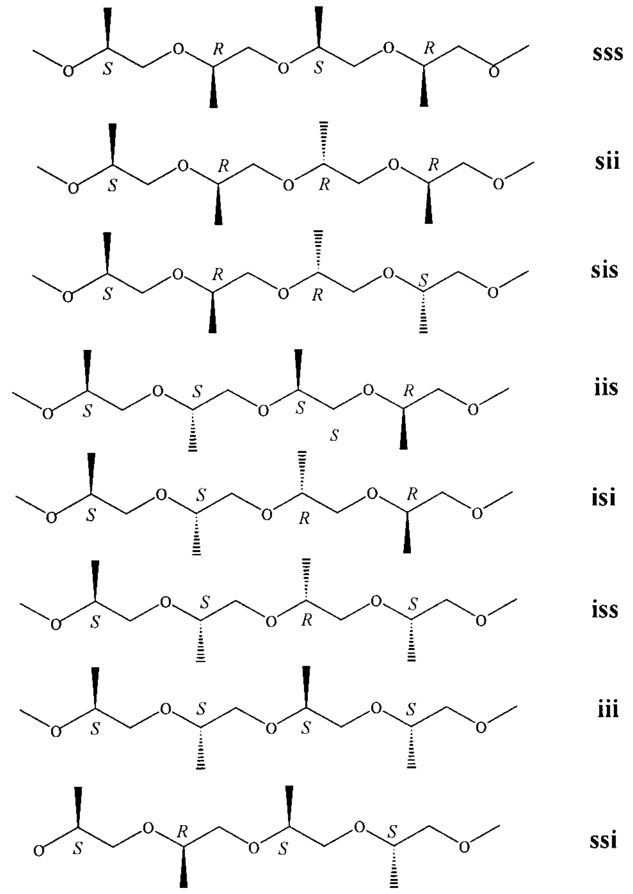

**Figure 4.** Possible stereosequences on a tetrad level for regioregular (HT) PPO.

In the other methylene carbon region, (73 ppm), there should also be four signals corresponding to the tetrads **iii**, **iis**, **sii**, and **sis**. In the $^{13}C\{^1H\}$ NMR spectrum of the sample of PPO from KOH polymerization we see four overlapped resonances (Figure 2), but because of the overlapping nature of the signals, these are not of equal intensity. In the spectrum of PPO derived from Inoue's catalyst system (Figure 3) we see only three signals, of which the downfield signal is clearly of greatest intensity. By the same argument used above, we can identify this as the **iii** signal. The other two signals can be assigned to either **iis** or **sii** and the upfield shoulder to the **sis** signal.

**Concentration Effect**. Experiments were done at different concentrations with both solvents. Typical measurements were done on samples that were 0.1−0.2 g of polymer/mL of solvent (concentrated samples) and 0.02−0.06 g of polymer/mL of solvent (diluted samples) (see Experimental Section). We found there is only a slight change of chemical shift in going from diluted to concentrated solutions. The resonance positions in dilute solutions come further downfield than those in the concentrated ones. The change in $\delta$ is more marked for $CDCl_3$ than for benzene-$d_6$. For instance, for $CDCl_3$, in going from concentration 0.03 to 0.1 g/mL, there is a change of 0.09 ppm, while for benzene-$d_6$ from concentration 0.04 to 0.1 g/mL, the change is 0.02 ppm. Some results on the concentration effect are summarized in Table 1.

**Table 1. Effect of Concentration on the PPO Samples Prepared by Base and Coordinate Catalysis**

| initiator (solvent) | concn (g/mL) | factor | shift (ppm) |
|---|---|---|---|
| TPPAlCl ($CDCl_3$) | 0.03 | 1 | |
| | 0.09 | 3 | 0.04 |
| | 0.1 | 4.6 | 0.09 |
| | 0.2 | 6.25 | 0.13 |
| TPPAlCl ($C_6D_6$) | 0.04 | 1 | |
| | 0.1 | 3.1 | 0.02 |
| KOH ($CDCl_3$) | 0.04 | 1 | |
| | 0.2 | 3.7 | 0.10 |
| KOH ($C_6D_6$) | 0.07 | 1 | |
| | 0.2 | 2.5 | 0.02 |

**Table 2. Concentration Measurements on the Polymer Prepared from Polymerization with KOH**

| sample | polymer (g) | concn (g/mL)[a] | solvent | factor | shift[b] (ppm) |
|---|---|---|---|---|---|
| 1 | 0.031 | 0.04 | $CDCl_3$ | 1 | |
| 2 | 0.12 | 0.2 | $CDCl_3$ | 3.7 | 0.1 |
| 3 | 0.053 | 0.07 | $C_6D_6$ | 1 | |
| 4 | 0.13 | 0.2 | $C_6D_6$ | 2.5 | 0.02 |

[a] All samples were prepared by dissolving the polymer in 0.8 mL of deuterated solvent. [b] Chemical shift calculated as difference from $\delta$ of most diluted sample.

## Concluding Remarks

The combination of employing the two solvents, $C_6D_6$ and $CDCl_3$, along with samples of atactic and partially isotactically enriched regioregular PPO, has allowed the original assignments of Schilling and Tonelli[5] to be extended to tetrad sensitivity for the methylene carbons. The influence of higher field strengths provides better resolution, but only the methylene carbons show tetrad sensitivity. The methine carbons, however, are well-resolved as triads.

## Experimental Section

All syntheses and solvent manipulations were done under an argon atmosphere using standard Schlenk line and drybox techniques. Solvents were distilled from sodium benzophenone ketyl. Propylene oxide was distilled from calcium hydride. (TPP)AlCl was synthesized according to the literature[7] from 5,10,15,20-tetraphenylporphine (Aldrich) and $Et_2AlCl$ (Aldrich). KOH was dried in a vacuum oven at 180 °C prior to use. Deuterated solvents were stored over 4 Å molecular sieves for 24 h prior to use. Polymerization reactions were done under an inert atmosphere.

**NMR Experiments**. $^1H$ and $^{13}C\{^1H\}$ NMR experiments were carried out with a Bruker DPX-400 operating at proton Larmor frequency of 400 MHz equipped with a 5 mm broad-band probe, a Bruker DXR-600 (5 mm broad-band probe), and a Bruker DXR-800 MHz (5 mm triple-resonance inverse TXI probe) spectrometer operating at proton Larmor frequency of 600 and 800 MHz, respectively. Continuous GARP decoupling was used. The parameters used were the following: number of scans, NS = 2048 scans; number of data points, TD = 65 536; sweep width, swh = 26 246.7 Hz (800 MHz) and swh = 21 286.4 Hz (600 MHz); and relaxation time, D1 = 0.4 s and SI = 32 768 (800 MHz) and D1 = 1 s and SI = 65 536 (600 MHz). Their peak frequencies were referenced against the respective solvents, benzene-$d_6$ at 7.15 ppm and chloroform-$d$ at 7.24 ppm.

***rac*-PO/KOH**. KOH (0.064 g, 1.1 mmol) was added to 2 mL of toluene. This solution was added to 5 mL of *rac*-PO (0.0715 mmol). After 24 h, volatiles were evaporated under vacuum to give a white powder that was analyzed by NMR. $M_n$(calc) = 3770 Da.

The data used for concentration studies were recorded by using the $^{13}C\{^1H\}$ 100 MHz spectrometer. See Table 2.

**Table 3. Concentration Measurements on the Polymer Prepared from Polymerization with (TPP)AlCl**

| sample | polymer (g) | concn (g/mL)[a] | solvent | factor | shift[b] (ppm) |
|---|---|---|---|---|---|
| 1 | 0.026 | 0.03 | $CDCl_3$ | 1 | |
| 2 | 0.073 | 0.09 | $CDCl_3$ | 3 | 0.04 |
| 3 | 0.11 | 0.1 | $CDCl_3$ | 4.6 | 0.09 |
| 4 | 0.15 | 0.2 | $CDCl_3$ | 6.25 | 0.1 |
| 5 | 0.035 | 0.04 | $C_6D_6$ | 1 | |
| 6 | 0.14 | 0.1 | $C_6D_6$ | 3.1 | 0.02 |

[a] All samples were prepared by dissolving the polymer in 0.8 mL of deuterated solvent. [b] Chemical shift calculated as difference from $\delta$ of most diluted sample.

For solvent effect studies, solution of concentration 0.1 g/mL was analyzed with 100, 150, and 200 MHz spectrometers. We report here the data obtained with the 200 MHz spectrometer. All NMR experiments were performed at 25 °C.

$^{13}C$ NMR ($C_6D_6$, $\delta$, ppm): 75.78 (CH, **ii**), 75.69 (CH, **is** + **si**), 75.54 (CH, **ss**), 73.81 ($CH_2$, **ii** + **is/ii** + **si**), 73.56 ($CH_2$, **is/si**), 73.49, ($CH_2$, **ss**), 17.87, 17.79 ($CH_3$).

$^{13}C$ NMR ($CDCl_3$, $\delta$, ppm): 75.37 (CH, **ii**), 75.23 (CH, **is/si**), 75.18 (CH, **is/si**), 74.99 (CH, **ss**), 73.26, 73.25, 73.22, 73.20 ($CH_2$, **iii, iis** + **ssi, sis**), 72.85, 72.80, 72.76, 72.71 ($CH_2$, **sss, isi, iss, ssi**), 17.87, 17.79 ($CH_3$).

***rac*-PO/(TPP)AlCl**. (TPP)AlCl (0.1 g, 0.16 mmol) was added to 1 mL of *rac*-PO (0.0143 mol). Heat evolution during reaction was observed. Polymerization went to completion in 24 h, yielding a purple solid. $M_n$(calc) = 5180 Da.

The data used for concentration studies were recorded by using a $^{13}C\{^1H\}$100 MHz spectrometer. See Table 3.

For solvent effect studies, solution of concentration 0.1 g/mL was analyzed with 100, 150, and 200 MHz spectrometers. We report here the data obtained with the 200 MHz spectrometer. All NMR experiments were performed at 25 °C.

$^{13}C$ NMR ($C_6D_6$, $\delta$, ppm): 76.81 (CH, **ii**), 75.70 (CH, **is** + **si**), 75.57 (CH, **ss**), 73.82 ($CH_2$, **ii** + **is/ii** + **si**), 73.58 ($CH_2$, **is/si**), 73.51 ($CH_2$, **ss**), 17.86 ($CH_3$).

$^{13}C$ NMR ($CDCl_3$, $\delta$, ppm): 75.46 (CH, **ii**), 75.30 (CH, **is/si**), 75.26 (CH, **is/si**), 75.05 (CH, **ss**), 73.35, 73.33, 73.31 ($CH_2$, **iii, iis** + **ssi, sis**), 72.91, 72.86, 72.81, 72.77 ($CH_2$, **isi, iss/ssi, sss**), 17.87, 17.79 ($CH_3$).

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**Supporting Information Available:** $^{13}C\{^1H\}$ NMR ($C_6D_6$, 100 MHz) spectrum obtained with (TPP)AlCl showing assignments at the triad level for both methine and methylene carbons; $^{13}C\{^1H\}$ NMR spectra of PPO/TPPAlCl in $C_6D_6$ at 100, 150, and 200 MHz, PPO/TPPAlCl in $CDCl_3$ at 100, 150, and 200 MHz, and PPO/KOH in $CDCl_3$ at 100, 150, and 200 MHz. This material is available free of charge via the Internet at http://pubs.acs.org.

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