Determination of ¹³C NMR Shifts for Carbons Beta and Gamma to Oxygen in Poly(Olefin Sulfone)s

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Abstract: We have established parameters that enable the prediction of ¹³C NMR chemical shifts for carbons β and γ to a sulfoxide or sulfone oxygen(s). Carbons β were found to be moved upfield by ~ 21 ppm and those γ downfield by ~ 7.7 ppm in chloroform. We tested these parameters by sequentially oxidizing poly(butyl thirane) to its corresponding polysulfone and assigned the new peaks observed in the ¹³C NMR on the basis of their proximity to the oxygen atom(s).

Keywords: ¹³C NMR; Liquid crystalline; NMR; Poly(butyl thirane); Poly(olefin sulfone)

INTRODUCTION

Poly(olefin sulfone)s (POSs) have been shown to form helical conformations and display main chain liquid crystalline behavior in the bulk.[1] The helical regions formed have been observed to have a variable pitch,[2] perhaps due to the random chirality within the backbone of the polymers.

It has been suggested that increasing the tacticity of the polymer backbone may stabilize the helix and enhance the liquid crystalline properties.[3] Various approaches, including stereoselective ring opening polymerization[4] and asymmetric induction,[5] have been successful in producing isotactic polysulfones. The introduction of a chiral sulfoxide group as a replacement for the sulfone group offers the possibility of even greater stereoregularity, but can result in complicated nuclear magnetic resonance (NMR) spectra due to adjacent chiral centers. Being able to predict the chemical shifts of carbons β and γ to sulfoxide or sulfone oxygen atoms can readily ease spectral interpretation of compounds that contain this functionality. Similar parameters have been established for hydrocarbons,[6] alcohols,[7] and amines.[8]

We have previously charted the chemical shifts of carbons adjacent to sulfone groups in POSs, where the determination was based on the replacement of an SO_2 group with a CH_2 group. Here, we have designed a simpler and more accurate approach where the determination is based on the replacement of an SO_2 group with an SO or S group.[9] To establish these parameters we have prepared linear polymers without chiral centers. The first of these was synthesized by reaction of equimolar quantities of 1,2-ethanedithiol and 1,7-octadiene (Figure 1(a)). It was then oxidized by a 0.15 molar equivalence of peracetic acid to yield a polymer in which only a small amount of isolated sulfoxide groups are present (Figure 1(b)). The second, prepared from divinyl sulfone and 1,2-ethanedithiol, produced repeat structures in which sulfone groups were present at every third sulfur atom (Figure 1(c)). From the first polymer, parameters for carbons β and γ to a sulfoxide oxygen may be calculated, and parameters for carbons β and γ to sulfone oxygens may be
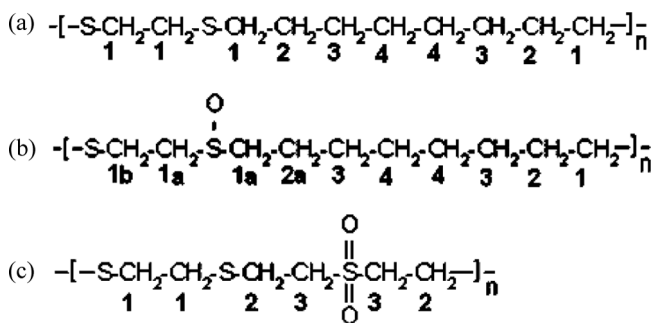
Figure 1. Structures of (a) the 1,2-ethanedithiol-1,7-octadiene addition product, (b) the 1,2-ethanedithiol-1,7-octadiene addition product oxidized by 0.15 M equivalents of peracetic acid, and (c) the 1,2-ethanedithiol-divinyl sulfone addition product.

determined from the second polymer. With these parameters established, they can then be tested by progressively oxidizing a sample of poly(butyl thirane) to its sulfone using increasing amounts of peracetic acid. The new shifts observed in the ^{13}C NMR will be assigned with the aid of the established parameters.

EXPERIMENTAL SECTION

Materials

The materials 1,2 epoxyhexane, peracetic acid (36–40%), tert-butyl-hydroperoxide (70%), sodium, divinyl sulfone, 1,7-octadiene, 1,2-ethane-dithiol, azobisisobutyronitrile (AIBN), and $CDCl_3$ were purchased from Aldrich. Potassium thiocyanate was obtained from Lancaster and sulfur dioxide from BOC.

Synthesis of 1,7-Octadiene-1,2-Ethanedithiol Addition Product

First, 1,2-ethanedithiol (2.65 g, 2.7 mmol), 1,7-octadiene (3.00 g, 2.7 mmol), and AIBN (0.10 g, 0.61 mmol) were dissolved in chloroform (15 mL) and placed in a Carrius reaction tube. The contents were then degassed using the freeze-pump-thaw technique and sealed under vacuum. The reaction tube was incubated in a Carrius oven at 50°C for 24 h. The contents were then cooled and the product precipitated from acidified methanol. The polymer was purified by repeated dissolution in chloroform and precipitation from acidified methanol and dried in a vacuum desiccator to yield 4.39 g, 80.0%. This polymer was oxidized by 0.15 molar equivalents of peracetic acid as outlined below for poly (butyl thirane).

Synthesis of 1,2-Ethanedithiol-Divinyl Sulfone Addition Product

First, 1,2-ethanedithiol (4.62 g, 4.9 mmol), divinyl sulfone (5.89 g, 4.9 mmol), and AIBN (0.1 g, 0.61 mmol) were dissolved in chloroform (20 mL) and placed in a Carrius reaction tube. The contents were then degassed using the freeze-pump-thaw technique and sealed under vacuum. The reaction tube was incubated in a Carrius oven at 50°C for 24 h. The contents were then cooled and the product precipitated from acidified methanol. The polymer was purified by repeated dissolution in chloroform and precipitation from acidified methanol and dried in a vacuum desiccator to yield 8.70 g, 83.0%.

Synthesis of Butyl Thirane

First, 1,2 epoxyhexane (101.56 g, 1.01 mmol) was added to a solution of potassium thiocyanate (123.17 g, 1.27 mmol) dissolved in a distilled water (200 mL)/industrial alcohol (125 mL) solvent mix. The solution was stirred vigorously for 48 h at room temperature after which the thirane was extracted using diethyl ether (2 × 75 mL). The organic layer was washed with brine, then water, and dried over anhydrous sodium sulfate. Excess solvent was removed by rotary evaporation yielding butyl thirane, a clear liquid with a characteristic pungent odor. Yield = 94 g, 80%; 300 MHz ^{1}H-NMR (CDCl$_3$): 0.95 ppm (3H, t, −CH$_3$), 1.32–1.60 (6H, m, 3 × −CH$_2$), 2.2 ppm (1H, d, 0.5 −CH$_2$−O−), 2.5 ppm (1H, d, 0.5 CH$_2$−O−), 2.94 ppm (1H, m, −CH−O−).

Synthesis of Poly(butyl thirane)

Sodium metal (7.9 mg) and an excess of t-butyl alcohol (2 mL) were placed in a self-seal vacuum tube. The tube was evacuated and placed in an oven at 60°C overnight to allow the catalyst to form. Excess alcohol was removed under vacuum, liberating the catalyst as a grey-white powder. Butyl thirane (5 g, 43 mmol) was added and the tube resealed under vacuum following degassing by the freeze-pump-thaw procedure. The tube was then placed in an oven at 60°C for 96 h after which the product was precipitated from acidified methanol solution to give a viscous brown oil. The product was twice further dissolved in chloroform, precipitated from methanol, and dried in a vacuum overnight. Yield = 3.5 g, 70%.

Progressive Oxidation of Poly(butyl thirane)

Poly(butyl thirane) (0.5 g, 4.30 mmol) was dissolved in chloroform (10 mL) and to it was added the appropriate amount of peracetic acid for 0.15 M equivalents oxidation (0.13 g, 0.65 mmol), 0.5 M (0.43 g, 2.15 mmol), 0.85 M (0.73 g, 3.66 mmol), 1.0 M (0.86 g, 4.30 mmol), and 4.0 M (3.44 g, 17.2 mmol). The solution was stirred at ambient temperature for 72 h. The product was washed with saturated sodium bicarbonate and the organic layer dried over anhydrous magnesium sulfate. The chloroform was reduced to ∼2 mL, the product precipitated from acidified methanol, and dried overnight at 30°C in a vacuum oven.

^{13}C-NMR Spectroscopy

All spectra were recorded on a GE GN Ω500 MHz spectrometer operating at 125.8 MHz. Samples were prepared by dissolving 100 mg of the

sample in 1.5 mL of CDCl$_3$. Chemical shifts are reported in parts per million (δ) downfield of tetramethylsilane (TMS). The number of scans for each spectrum was 30 K, the spectral width 0–120 ppm and temperature 323 K.

RESULTS AND DISCUSSION

Figure 2(a) shows the ^{13}C NMR of the 1,2 ethanedithiol-1,7-octadiene copolymer that was oxidized by a 0.15 M equivalence of peracetic acid. This low level of oxidation results in isolated sulfoxide residues along the polymer chain. Four main sets of shifts were observed at 28.7, 29.1, 29.8, and 32.5 ppm. These represent C-1, C-2, C-3, and C-4 of the parent polysulfide polymer (shown in Figure 1(a)). After oxidation new shifts at
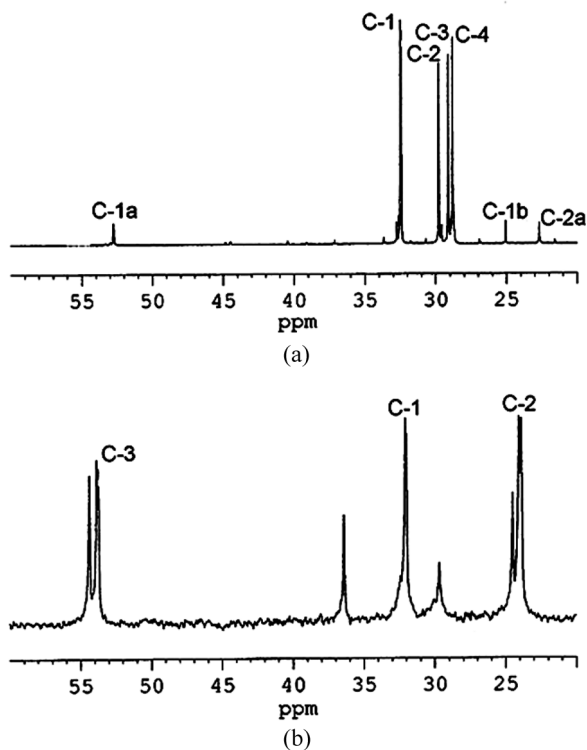
Figure 2. ^{13}C NMR spectra of (a) 1,2 ethanedithiol-1,7-octadiene addition product oxidized by 0.15 M equivalents of peracetic acid and (b) 1,2 ethanedithiol-divinyl sulfone addition product.

22.7, 25.1, and 52.7 were observed, as well as some smaller, less intense peaks. The shift furthest upfield at 22.7 ppm is assigned as C-2a and results from a γ oxygen (γ_O) effect (-7.1 ppm) on C-2 from the isolated sulfoxide oxygen. The shift at 25.1 ppm is assigned as C-1b and results from γ_O effect (-7.5 ppm), this time on carbon C-1. Carbons C-1a, which flank the sulfoxide group, suffer β_O effects and are found downfield at 52.7 ppm, reflecting an effect of 20.2 ppm. The remaining less intense peaks result from a small amount of disulfoxides and sulfones that were present at some residues.

The ^{13}C NMR of the divinyl 1,2 ethanedithiol-divinyl sulfone copolymer is shown in Figure 2(b), the structure of which is shown in Figure 1(c). Three main shifts were observed at 53.8, 32.0, and 24.1 ppm, with fine structure that reflects unreacted vinyl groups in some sulfone residues. The peak at 32.0 ppm represents carbons C-1, which are isolated from the sulfone group and are instead flanked by sulfide groups. These carbons do not suffer any effects from the sulfone oxygens, and their chemical shift compares well with the analogous carbon in Figure 2(a). The shift at 24.1 ppm represents carbons C-2, which are γ to the sulfone oxygens and are found upfield from C-1 by an increment of -8.0 ppm. The shifts centered at 53.8 ppm represent carbons C-3, which suffer a β effect from the sulfone oxygens and experience a downfield shift of 21.8 ppm relative to C-1. Thus we can assign a β_{O_2} effect of 21.8 ppm and a γ_{O_2} effect of -8.0 ppm, quite close to the values obtained for the sulfoxide of 20.2 and -7.5 ppm respectively, although of a slightly smaller magnitude.

These parameters were then used to assign new peaks observed in the ^{13}C NMR spectrum of poly(butyl thirane) that was oxidized using 0.15, 0.5, 0.85, 1.0, and 4.0 molar equivalents of peracetic acid. The plot shown in Figure 3 is expanded for the backbone carbons and the first side chain methylene carbon. Five possible structures are envisaged for the different oxidation levels, the two extremes being the polysulfide and the polysulfone. Between these extremes are the three other possible structures: at low levels of oxidation where a sulfoxide residue is in isolation among sulfide residues, at intermediate levels of oxidation where two sulfoxide residues are adjacent to one another, and at higher levels of oxidation where a sulfoxide residue is adjacent to a sulfone. All five structures are shown in Figure 4. Using the parameters established previously, the estimated chemical shifts were calculated and are presented in Table 1 along with the observed shifts.

For the polymer oxidized at the 0.15 M level, a structure such as that shown in Figure 4(b) is appropriate. Four new sets of shifts were observed centered at 35.5, 41.0, 55.5, and 60.5 ppm. The broad set of shifts from 52.5 to 57.0 ppm is due to C-3b, which suffers a β_O effect, and is in very good agreement with the predicted shift of 57.4 ppm.
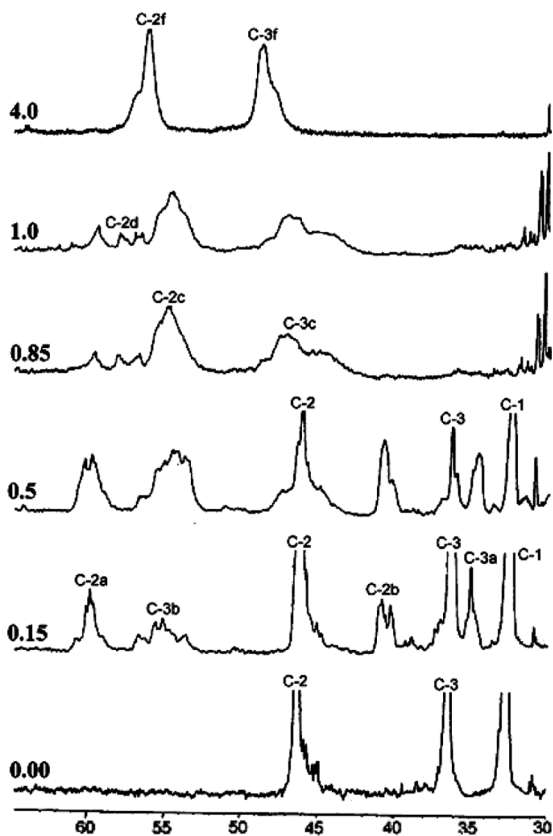
Figure 3. ^{13}C NMR spectra for the progressive oxidation of poly(butyl thirane) showing an expansion of the main chain region. The numbers in bold at the left of the plots show the molar equivalents of oxidizing agent used in the oxidation.

Stereochemical effects are apparent here, with this resonance showing triad sensitivity. The resonance at 58.2–60.1 ppm most likely represents C-2a, which also experiences a β_O effect. That it is further upfield than its predicted 67.3 ppm is probably due to the electron-donating effect of the butyl side chains that partially neutralize the inductive effect of the sulfoxide (note that methylene carbon C-3b, which did not have this electron-donating effect, did experience the full β_O effect). The C-2a resonance displays evidence of triad sensitivity over 3.0 ppm, which we attribute to the relative stereochemistry of the methine carbons at C-2a and C-2b and the sulfoxide. The shifts between 40.1 and 40.9 are due to C-2b, which experiences a γ_O effect and compares favorably with the predicted value of 39.6 ppm. Again this peak showed stereochemical
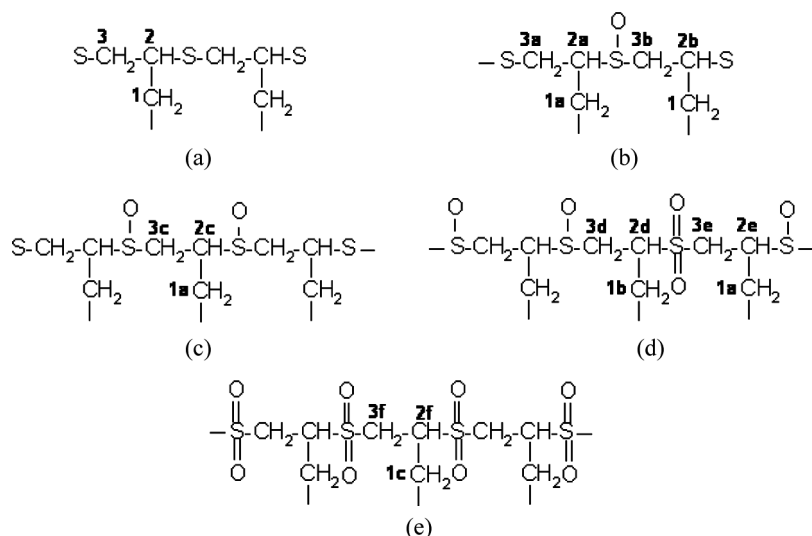
Figure 4. Proposed structures of poly(butyl thirane) oxidized with (a) 0.00, (b) 0.15 and 0.50, (c) 0.85, (d) 1.00, and (e) 4.00 molar equivalents of peracetic acid. Only the backbone and first side chain methylene carbons are shown for convenience.

Table 1. Estimated and observed ^{13}C NMR shifts for first side chain carbon 1 and backbone carbons 2 and 3 in poly(butyl thirane), which have varying β and γ oxygen effects

Carbon	Effect(s) experienced	Predicted shift (ppm)	Observed shift (ppm)
1			33.5
2			47.1
3			37.2
1a	γ_O	$33.5 - 7.5 = \mathbf{26}$	28.0
2a	β_O	$47.1 + 20.2 = \mathbf{67.3}$	58.2–61.0
2b	γ_O	$47.1 + 7.5 = \mathbf{39.6}$	40.1–41.9
3a	γ_O	$37.2 - 7.5 = \mathbf{29.7}$	34.8–35.4
3b	β_O	$37.2 + 20.2 = \mathbf{57.4}$	52.5–57.0
2c	$\beta_O + \gamma_O$	$47.1 + 20.2 - 7.5 = \mathbf{59.9}$	53.5–56.0
3c	$\beta_O + \gamma_O$	$37.2 + 20.2 - 7.5 = \mathbf{49.9}$	43.2–48.2
1b	γ_{O_2}	$33.5 - 8.0 = \mathbf{22.5}$	27.7–28.0
2d	$\beta_{O_2} + \gamma_O$	$47.1 + 21.8 - 7.5 = \mathbf{61.4}$	57.5–59.0
3d	$\beta_O + \gamma_{O_2}$	$37.2 + 20.2 - 8.0 = \mathbf{49.4}$	43.2–48.2
2e	$\beta_O + \gamma_{O_2}$	$47.1 + 20.2 - 8.0 = \mathbf{59.3}$	53.5–56.0
3e	$\beta_{O_2} + \gamma_O$	$37.2 + 21.8 - 7.5 = \mathbf{51.5}$	43.2–48.2
2f	$\beta_{O_2} + \gamma_{O_2}$	$47.1 + 21.8 - 8.0 = \mathbf{60.9}$	56.0–58.5
3f	$\beta_{O_2} + \gamma_{O_2}$	$37.2 + 21.8 - 8.0 = \mathbf{51}$	47.5–49.9

effects and displayed dyad level splitting. The resonance at 34.8–35.4 ppm, which we have labeled C-3a, is somewhat further downfield than its predicted value of 29.7 ppm, the reason for this being unclear. The shift for the side chain methylene carbon C-1a, which suffered a γ_O effect, moved upfield by the expected -7.5 ppm and cannot be observed in the expanded region of Figure 3. The location of this carbon in the side chain means it cannot receive any β_O effects, and so no downfield shifts are observed for it.

The spectrum for the 0.5 M oxidized polymer is quite similar to that for the 0.15 M oxidized polymer. One noticeable difference is that the intensity of carbons 1, 2, and 3 of the parent polysulfide polymer (Figure 4(a)) become diminished due to their increased conversion to the sulfoxide. Consequently, the resonances formed as a result of experiencing β_O and γ_O effects grow. For the 0.85 M and 1.0 M oxidation levels, structures like those shown in Figure 4(c) and 4(d) respectively are appropriate. Two new sets of shifts are observed representing C-2c and C-3c. Both of these carbons are flanked by two sulfoxide groups and so experience both β_O and γ_O effects. The resonance observed between 53.5 and 56.0 ppm is labeled C-2c and is slightly upfield of its predicted 59.9 ppm, again most likely due again to the inductive effect of the butyl side chain. The broad resonance for C-3c between 43.2 and 48.2 ppm is very close to the predicted 49.9 ppm. The broad nature of these resonances is due to both sterochemical effects and a stiffening of the backbone resulting from the presence of small amounts of sulfone residues, which are known to lock backbone residues in a helical conformation. The peak centered at 58.5 ppm and labeled C-2d represents a methine carbon that experienced both a β_{O_2} and a γ_O effect, the slightly greater magnitude effect of the β_{O_2} effect(with respect to β_O) moving it slightly further downfield. Direct evidence for the existence of C-3d, C-2e, and C-3e cannot be observed in Figure 3, but most likely they are present within the broad range of shifts we have already labeled C-2c and C-3c. Note that these two resonances are much broader than those of the sulfone (C-2f and C-3f).

On complete oxidation (structure shown in Figure 4(e)), peaks C-2c and C-3c disappear and are replaced by two downfield resonances at 47.5–49.9 ppm (C-3f) and 56.0–58.5 ppm (C-2f), both of which compare favorably with the predicted values.

CONCLUSIONS

From the preparation of linear polymers devoid of sterochemical features it was possible to determine the effect that sulfoxide and sulfone oxygens have on the chemical shift of carbons adjacent to them. Using these

values new peaks observed in the ^{13}C NMR spectrum of poly(butyl thirane) that was sequentially oxidized to its sulfone were assigned. The establishment of these parameters should make it easier for future analysis of structures containing sulfoxide and sulfone functionality.

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