# Appendices

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## Appendix-A (Identification of peaks of NMR Spectra)

### *1. Calculation for peak identification of $^1$H-NMR spectra shown in Figure 3.48*

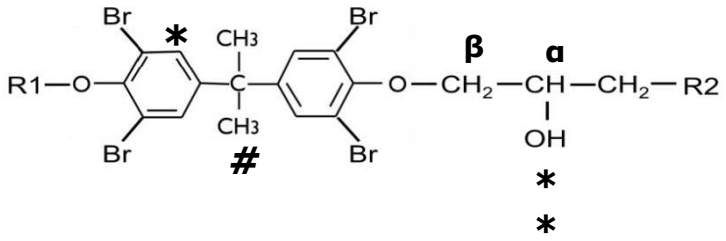



Figure A.0.1- Peak indexing of protons in the HER chain

**a.** Peak at position *

$$Shift = \delta Benzene + \sum \delta\ ortho\ substituent + \sum \delta\ meta\ substituent + \sum \delta\ para\ substituent$$

$$Shift = \delta Benzene + \sum \delta\ ortho\ Br + \delta\ ortho\ C(CH_3)_2R + \sum \delta\ meta\ O + \sum \delta\ para\ Br$$

$$Shift = 7.27 + \sum (0.25 - 0.04) + 0.11 + 0$$

$$Shift = 7.59 \text{ (Actual observed at 7.110 ppm)}$$

**b.** Peak at position α

$$\text{X-CH-Y (Z)} = \text{CH}_3\text{-CH-CH}_3\ (\text{Z}) + \Delta XY$$

$$XCH_2\text{-}\underset{\underset{OH}{|}}{CH}\text{-}CH_2X = X\text{-}\underset{\underset{OH}{|}}{CH}\text{-}Y + \Delta CH_2X$$

= 3.94 + (0.2+0.2)

= 4.34 (Actual peak observed at 4.209 ppm)

**c.** Peak at position β

$$\delta H\ of\ CH_2 = \delta CH_2 + \sigma\ O - Ar + \sigma R$$

= 0.23 + 2.94 + 0.68

= 3.85 (Actual peak observed at 3.683 ppm)

**d.** Peak at position #

Standard shift for $CH_3$ is δ 2.00. In our system it was observed at δ 1.611 (integration factor ~ 7.32 ppm for 6 protons of polymer chain).

**e.** Peak at position **

In alcohols the peak of hydroxyl group is generally seen δ 0.5 – δ 4.0. The position of peak is influenced by the concentration, polarity of solvent, and temperature. H-bonding shifts this peak to higher frequency by lowering the electron density around proton. Temperature rise shifts the peak to lower frequency. In our system the peak of H of O-H is seen at δ 1.321 (after 8 h WPCBs:DMA contact)

## 2. *Calculation for peak identification of $^{13}$C-NMR spectra shown in Figure 3.49*

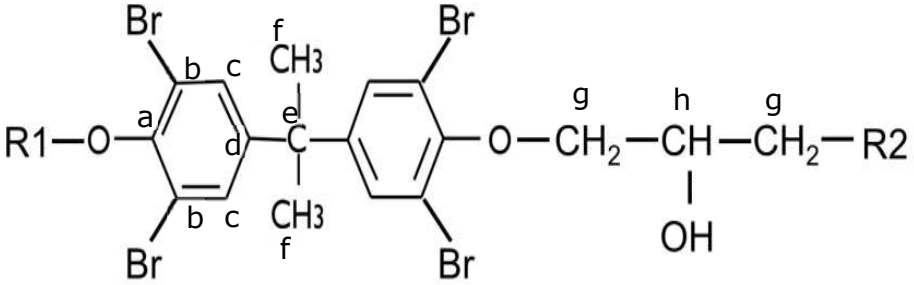



Figure A. 0.2- Peak indexing of carbon atom in the HER chain

a. Aromatic chain shifts-

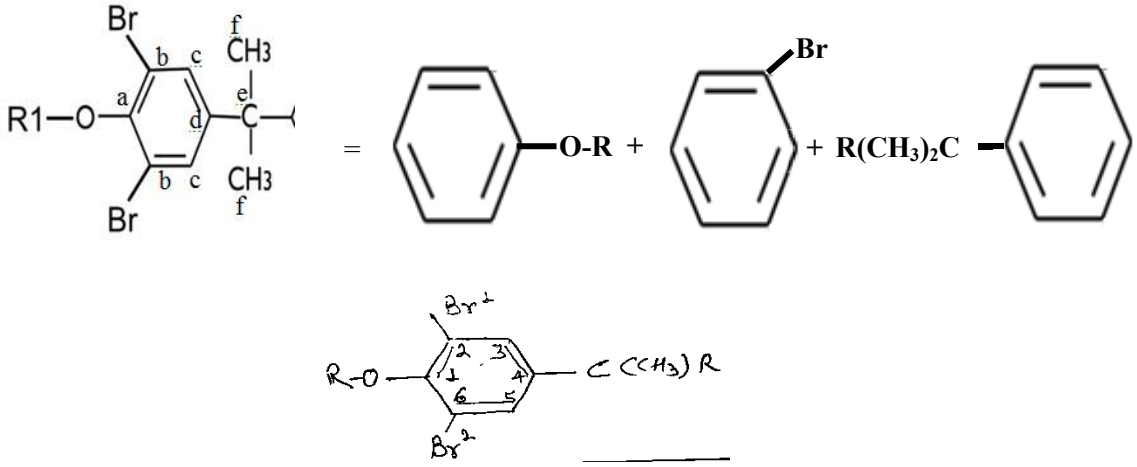



Table A.1- Peaks corresponding to position a, b, c and d position

| Group | Shift of peak at various positions [101] | | | | | |
|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 |
| O-R | 31.4 | -14.4 | 1.6 | -7.7 | 1.6 | -14.4 |
| $R(CH_3)_2C$- | -3.1 | -0.4 | -3.4 | 22.2 | -3.4 | -0.4 |
| Br $^1$ | +3.4 | -5.4 | 3.4 | 2.2 | -1 | 2.2 |
| Br $^2$ | 3.4 | 2.2 | -1 | 2.2 | 3.4 | -5.4 |
| Total shift (Δ) | 35.1 | -18 | 0.6 | 18.9 | 0.6 | -18 |

| δ= δ Benzen +Δ (=128.5+Δ) | 163.1 | 110.5 | 129.1 | 147.3 | 129.1 | 110.5 |
|---|---|---|---|---|---|---|
| Observed | 162.5 | 113.5 | 127.3 | | 127.1 | 113.5 |

b. Shift of ether link-

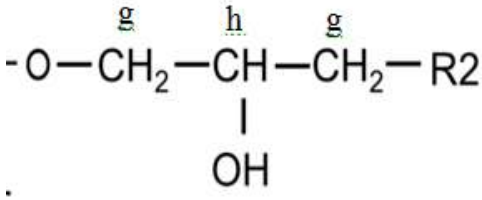
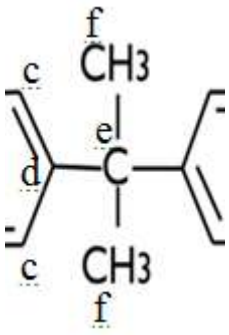



Table A.2- Peaks corresponding to position g and h position

| Position | δ for propane chain | Δ substitution | | δ total | observed |
|---|---|---|---|---|---|
| g | 15.8 | O-R terminal = 8 | O-H = 8 | 31.8 | 30.1 |
| h | 16.3 | | O-H = 41 | 57.3 | 66.5 |
| g | 15.8 | O-R terminal = 8 | O-H = 8 | 31.8 | 30.7 |

c. Shift of $(CH_3)_2C$ linkage of aromatic chain –




Peak at position ***e*** and ***f*** shows vibration corresponding to 68.9 and 25.8 ppm, respectively [238].