Supporting Information for

Non-cytotoxic, iodinated poly(ethylene oxide) (PEO) block-co-polymer contrast agents for computed tomography (CT) imaging.

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Characterization of PEO-PECH

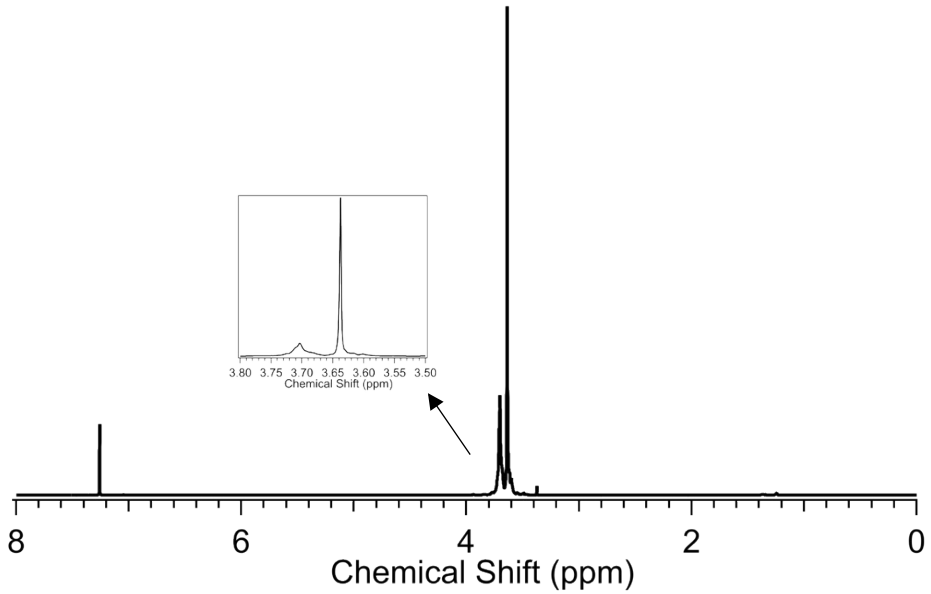


Figure 1. *^{1}H NMR spectrum of PEO-PECH5. ^{1}H NMR (500 MHz, $CDCl_3$)* $\boldsymbol{\delta}$ *3.80 - 3.66 (bm, C**H**-C**H$_2$**Cl), 3.64 - 3.56 (bm, C**H$_2$C H$_2$** and C**H$_2$**CH-CH$_2$Cl)*

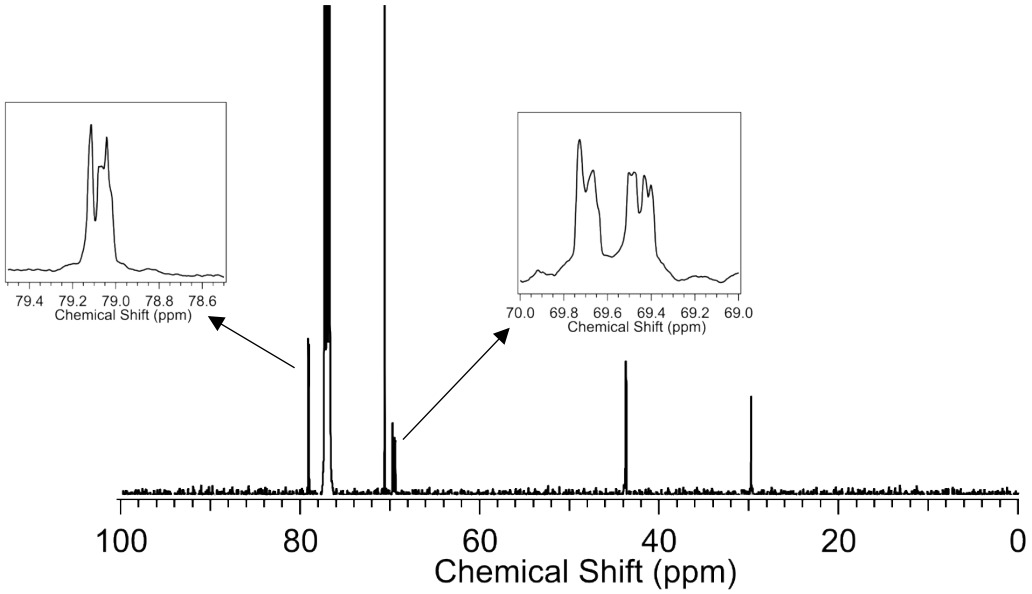


Figure 2. *^{13}C NMR spectrum of PEO-PECH5. ^{13}C NMR (500 MHz, $CDCl_3$)* ***δ*** *79.08 (t, -O-CH_2-**C**H(CH_2Cl)-O-), 70.59 (s, **C**H_2**C**H_2), 69.89 – 69.30 (bm, **C**H_2-CH-CH_2Cl), 43.65 (s, **C**H_2Cl). The peak at 29 ppm is grease.*

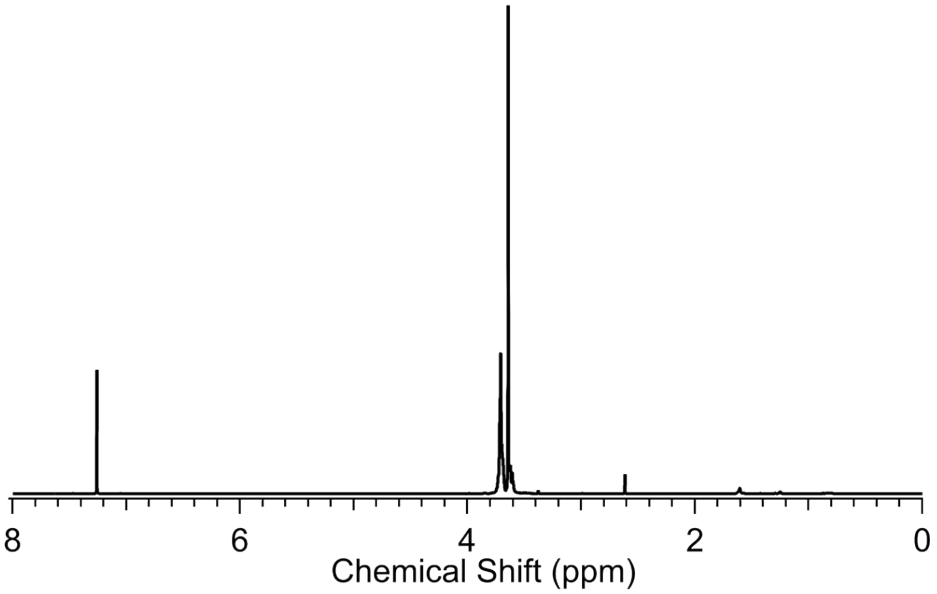


Figure 3. *^{1}H NMR spectrum of PEO-PECH15. ^{1}H NMR (500 MHz, $CDCl_3$)* ***δ*** *3.80 - 3.66 (bm, C**H**-C**H$_2$**Cl), 3.64 - 3.56 (bm, C**H$_2$**C**H$_2$** and C**H$_2$**CH-CH_2Cl)*

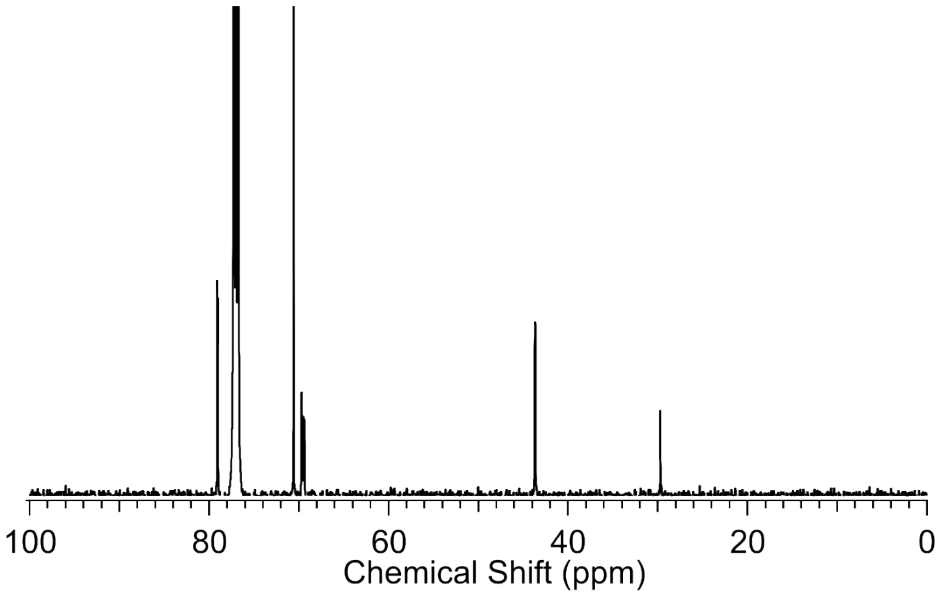


Figure 4. *^{13}C NMR spectrum of PEO-PECH15. ^{13}C NMR (500 MHz, $CDCl_3$)* ***δ*** *79.08 (t, -O-CH_2-**C**H(CH_2Cl)-O-), 70.59 (s, **C**H_2**C**H_2), 69.89 – 69.30 (bm, **C**H_2-CH-CH_2Cl), 43.65 (s, **C**H_2Cl). The peak at 29 ppm is grease.*

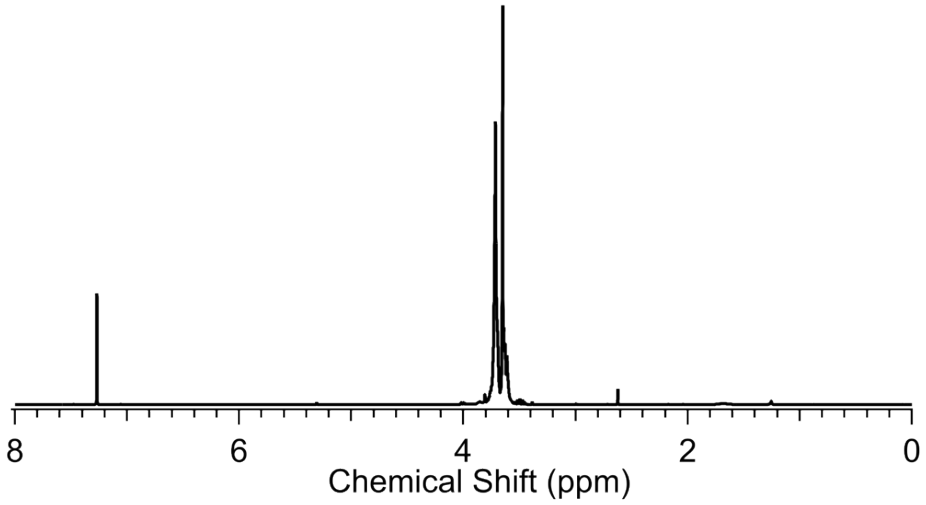


Figure 5. *^{1}H NMR spectrum of PEO-PECH30. ^{1}H NMR (500 MHz, $CDCl_3$)* ***δ*** *3.80 - 3.66 (bm, C**H**-C**H$_2$**Cl), 3.64 - 3.56 (bm, C**H$_2$**C**H$_2$** and C**H$_2$**CH-CH_2Cl)*

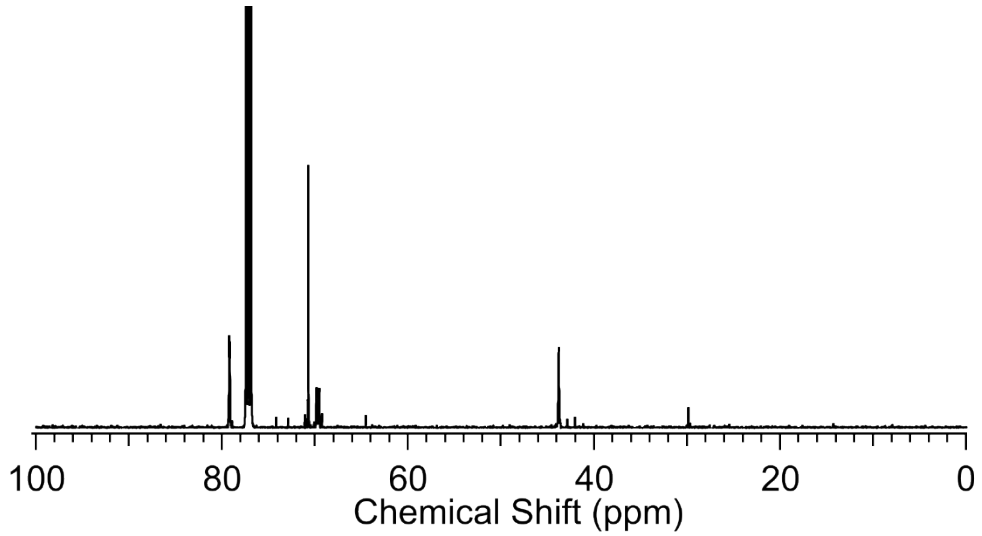


Figure 6. *^{13}C NMR spectrum of PEO-PECH30. ^{13}C NMR (500 MHz, $CDCl_3$) **δ** 79.08 (t, -O-CH_2-**C**H(CH_2Cl)-O-), 70.59 (s, **C**H_2**C**H_2), 69.89 – 69.30 (bm, **C**H_2-CH-CH_2Cl), 43.65 (s, **C**H_2Cl). The peak at 29 ppm is grease.*

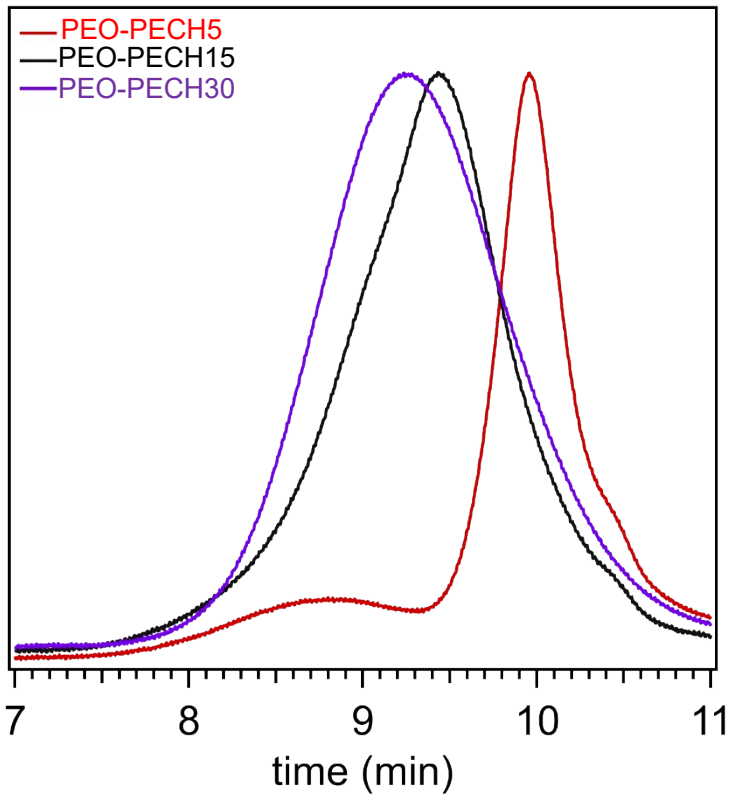


Figure 7. *RI spectra for PEO-PECHX. SEC revealed copolymers with M_n of 9,693 g/mol and Đ of 1.3 for the target PECH block of 5 kg/mol, 21,300 g/mol and Đ of 2.2 for the target PECH block of 15 kg/mol, and 34,615 g/mol and Đ of 2.4 for the target PECH block of 30 kg/mol.*

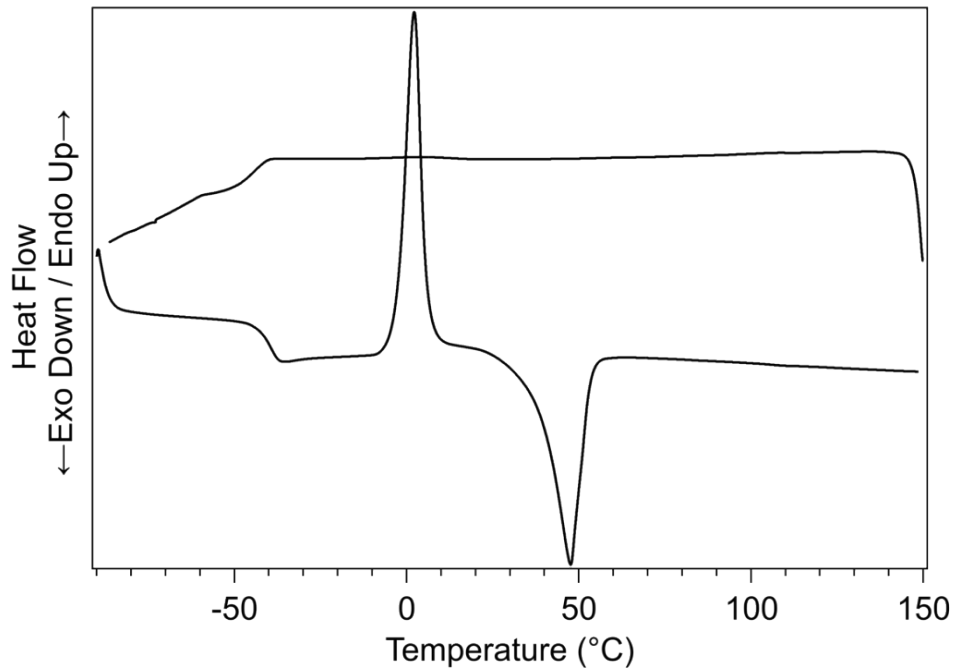


Figure 8. *DSC trace of $PEO_{113}PECH_{50}$ with T_g = -43.2 ℃, Tc = 0 ℃ (ΔH=32.67 J/g), and T_m = 49.3 ℃ (ΔH=57.18 J/g).*

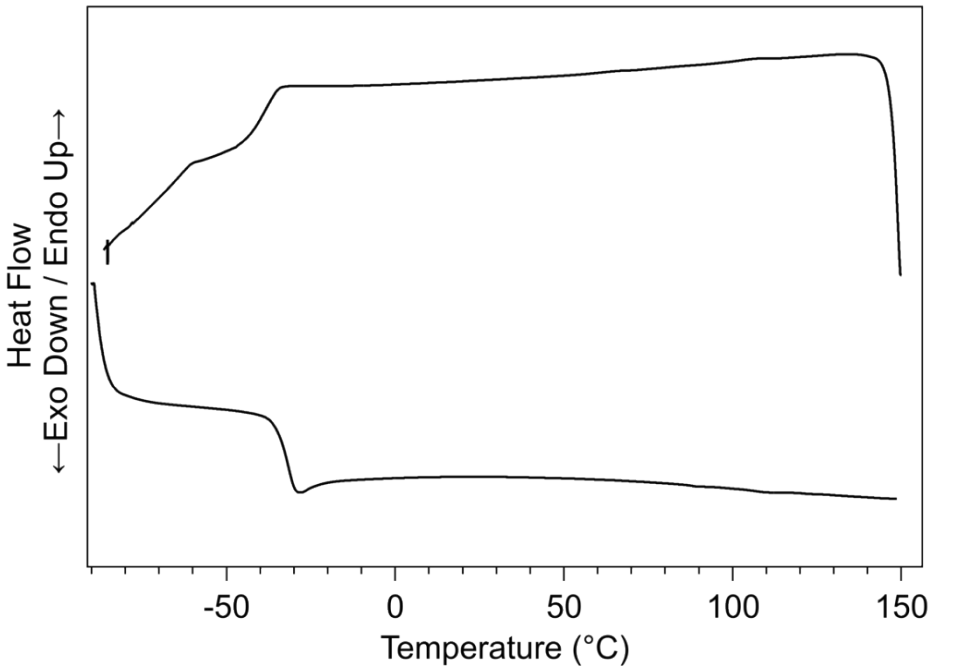


Figure 9. *DSC trace of PEO-PECH15 with T_g = -33.64 ℃.*

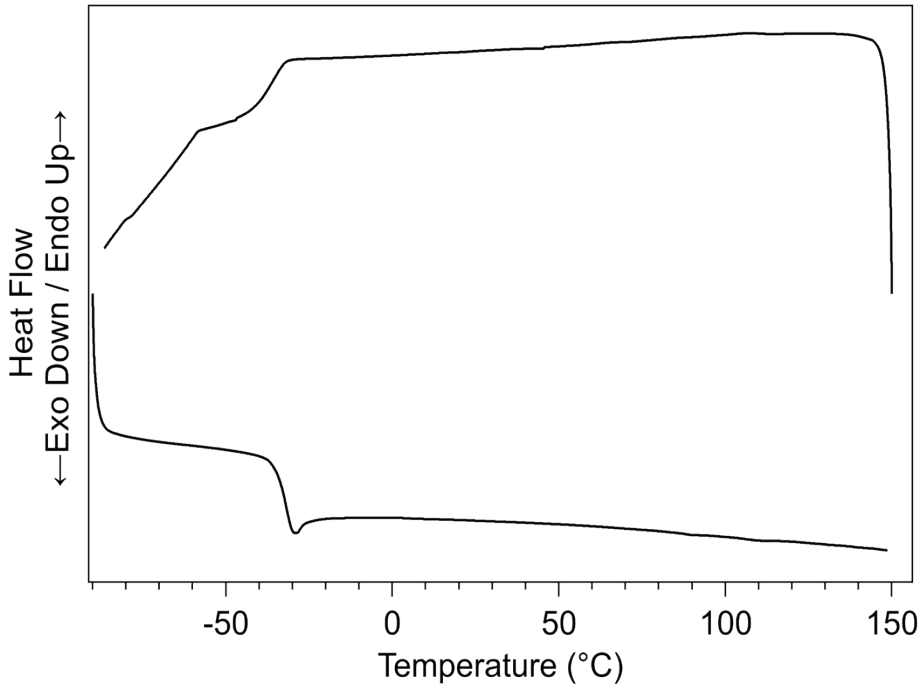


Figure 10. *DSC trace of PEO-PECH30 with T_g = -32.84 ℃.*

Characterization of PEO-PEI

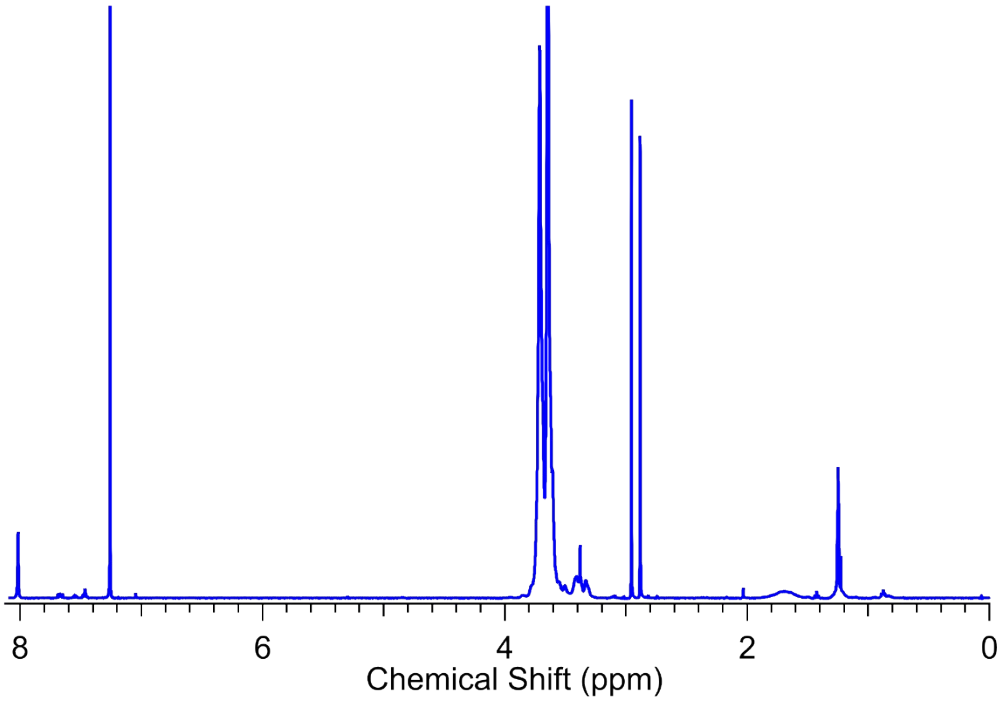


Figure 11. *^{1}H NMR spectrum of PEO-PEI5. ^{1}H NMR (500 MHz, $CDCl_3$)* ***δ*** *3.80 - 3.66 (bm, C**H**-C**H$_2$**I), 3.64 - 3.56 (bm, C**H$_2$CH$_2$** and C**H$_2$** CH-CH$_2$I), 3.46 – 3.24 (bm, CH$_2$CH-C**H$_2$**I). The broad peak at 1.85 – 1.52 is water, the peaks at 8.04, 2.95, and 2.88 are DMF, and the peaks at 1.25 and 0.88 are hexane.*

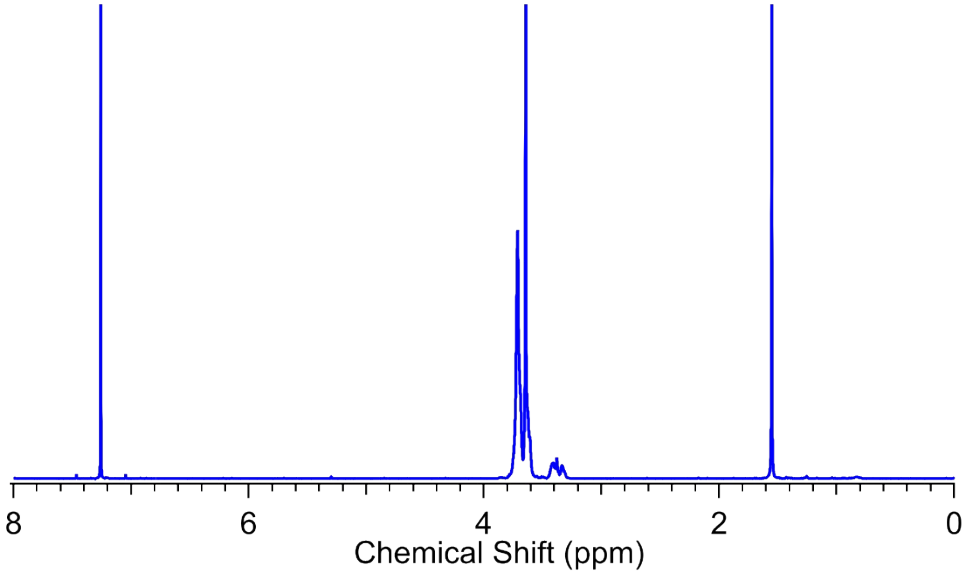


Figure 12. *^{1}H NMR spectrum of PEO-PEI15. ^{1}H NMR (500 MHz, $CDCl_3$)* ***δ*** *3.80 - 3.66 (bm, C**H**-C**H$_2$**I), 3.64 - 3.56 (bm, C**H$_2$**C**H$_2$** and C**H$_2$** CH-CH$_2$I), 3.46 – 3.24 (bm, CH$_2$CH-C**H$_2$**I). The peak at 1.56 is water.*

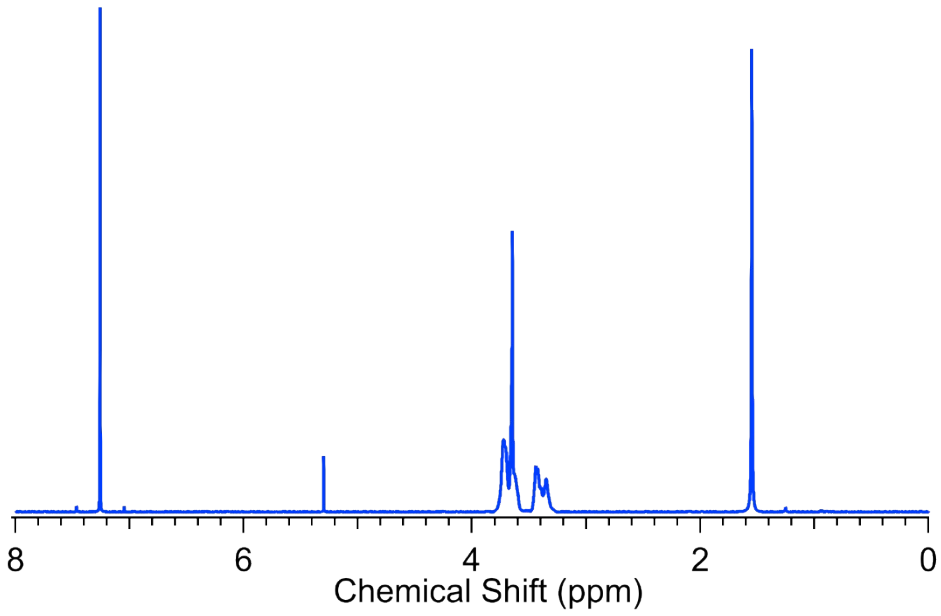


Figure 13. *^{1}H NMR spectrum of PEO-PEI30. ^{1}H NMR (500 MHz, $CDCl_3$)* ***δ*** *3.80 - 3.66 (bm, C**H**-C**H$_2$**I), 3.64 - 3.56 (bm, C**H$_2$C H$_2$** and C**H$_2$** CH-CH$_2$I), 3.46 – 3.24 (bm, CH$_2$CH-C**H$_2$**I). The peak at 1.56 is water.*

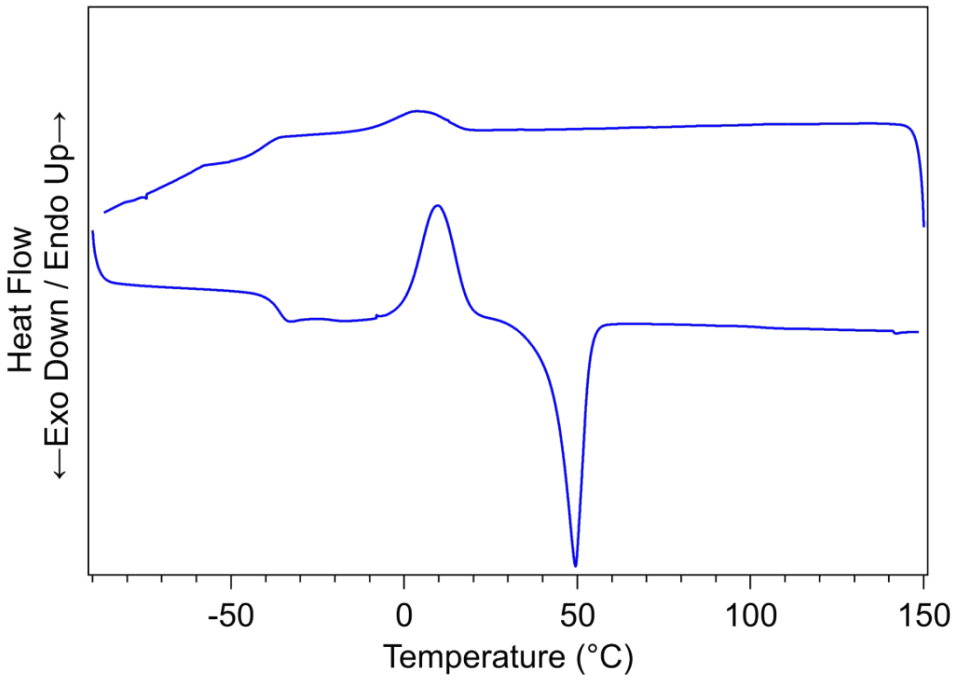


Figure 14. *DSC trace of PEO-PEI5 with T_g = -36.9 ℃, Tc = 9.6 ℃ (ΔH=31.2 J/g), and T_m = 49.3 ℃ (ΔH=44.8 J/g).*

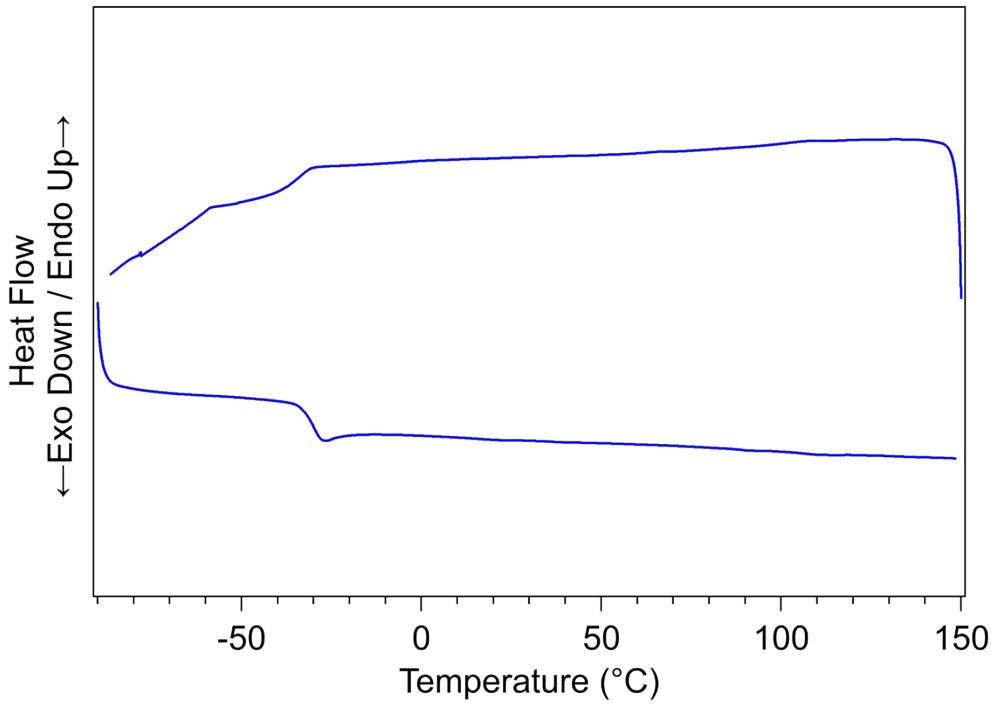


Figure 15. *DSC trace of PEO-PEI15 with T_g = -31.12 ℃.*

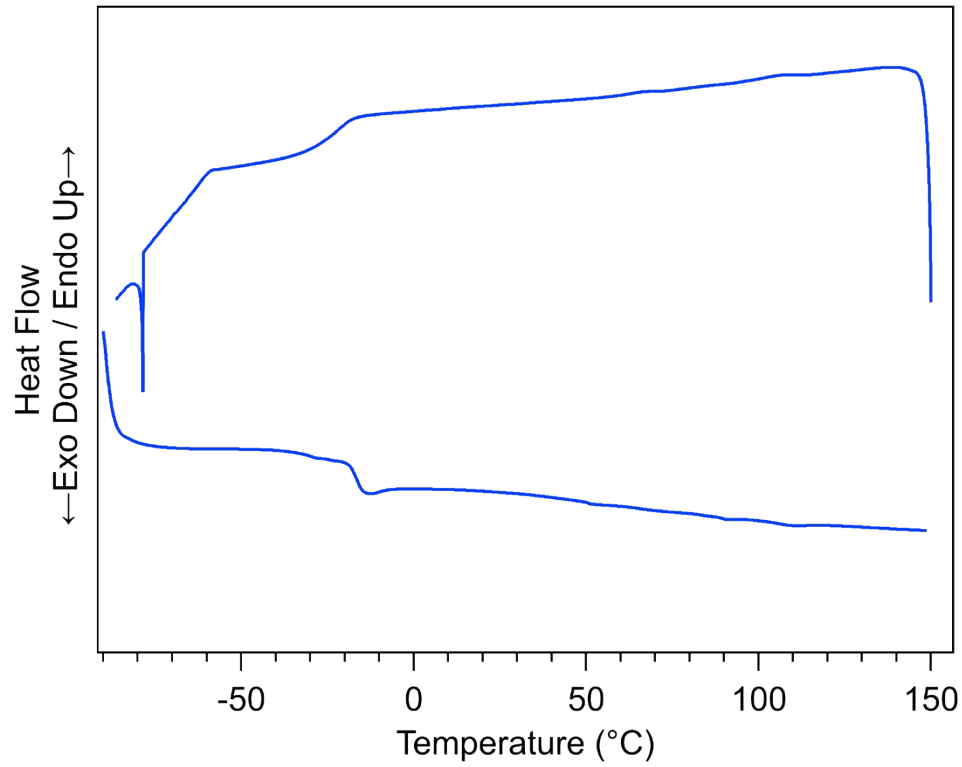


Figure 16. *DSC trace of PEO-PEI30 with Tg = -16.88 ℃.*

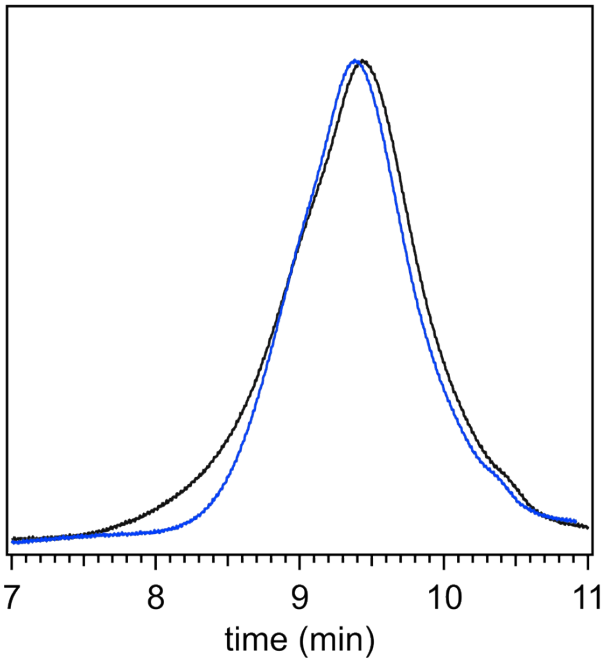
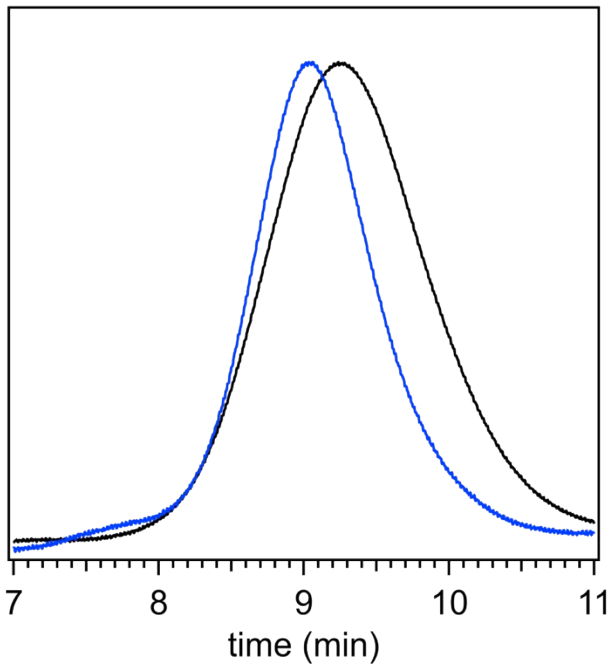


Figure 17. *RI spectra for PEO-PECH15 (black) and PEO-PEI15 (blue). SEC revealed an* M_n *of*



25.5 kg/mol and Đ of 2.1 for PEO-PEI15, an increase of 4,180 g/mol after iodinating.

Figure 18. *RI spectra for PEO-PECH30 (black) and PEO-PEI30 (blue). SEC revealed an M_n of 37.2 g/mol and Đ of 1.9 for PEO-PEI6, increasing after iodinating.*

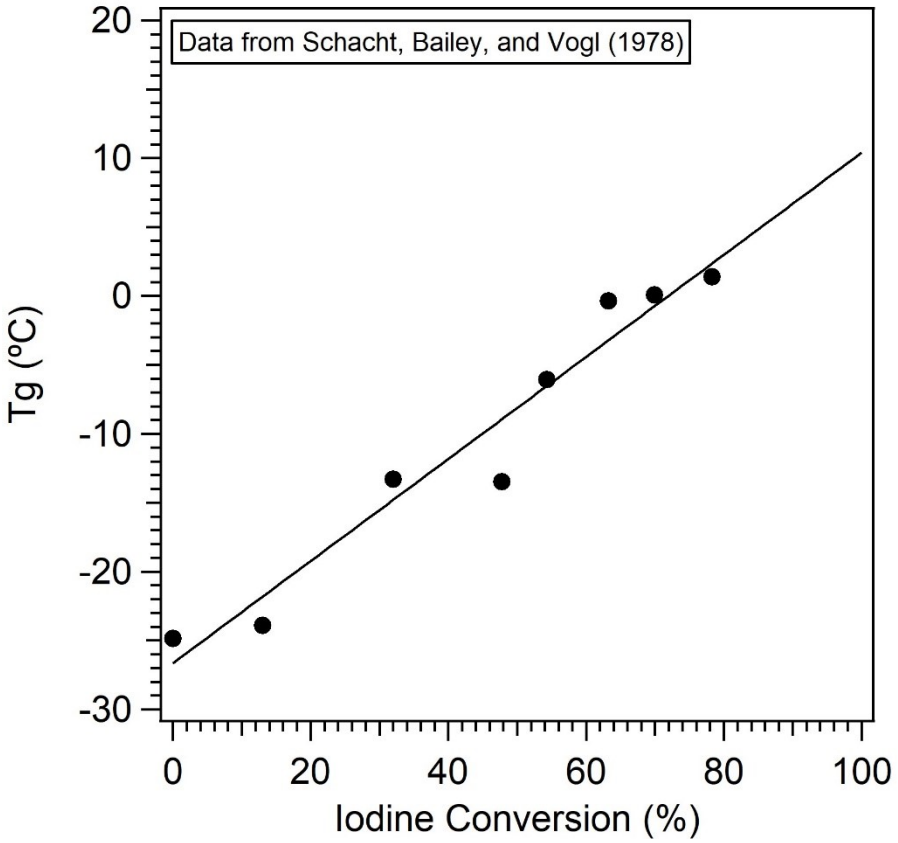


Figure 19. *Plot of the T_g as a function of iodine conversion of PECH from Schacht, Bailey and Vogl (1978). The black line is a linear fit to the data.*

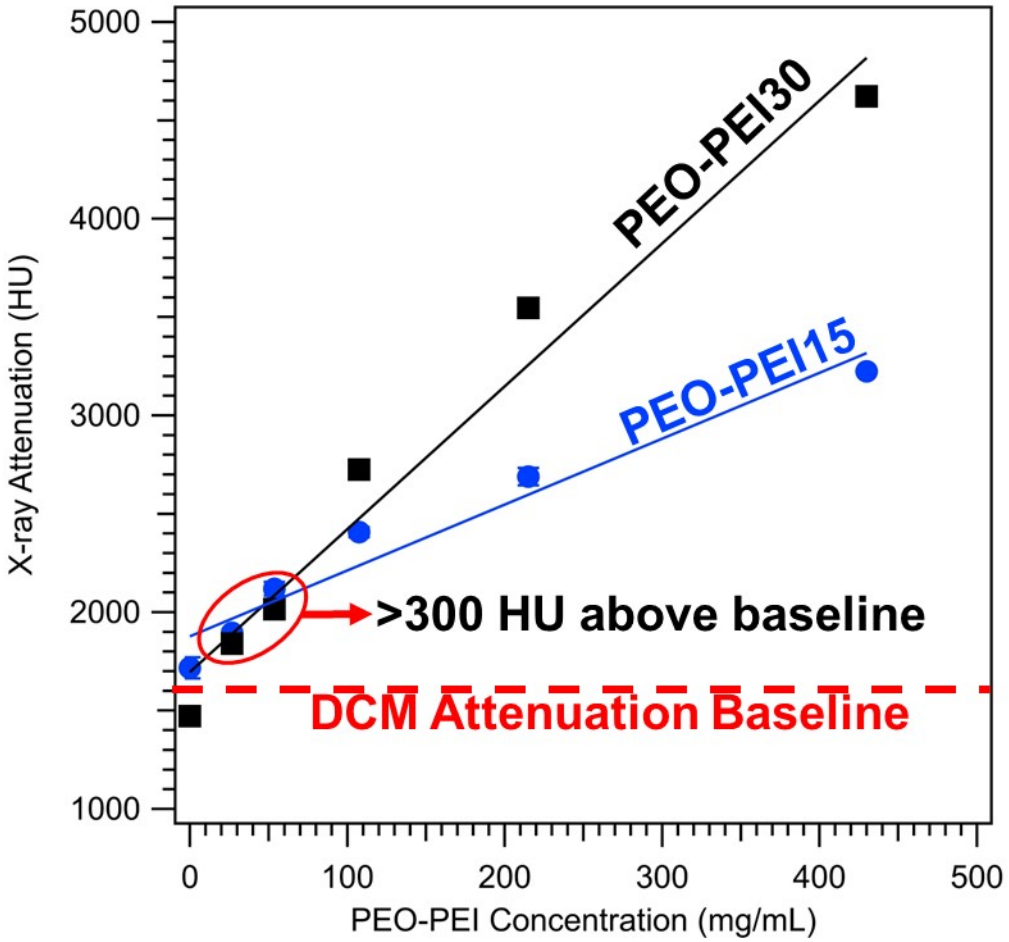


Figure 20. *Linear relationship of X-ray attenuation and polymer concentration for PEO-PEI5 and PEO-PEI30 dissolved in DCM, with slopes of 3.4 HU/mgmL^{-1} and 7.0 HU/mgmL^{-1}, respectively. The X-ray attenuation values here are absolute values without subtraction of the DCM baseline X-ray attenuation of 1594 HU. We have also provided the approximate location (red oval) of where attenuation of the polymer is greater than 300 HU off baseline. Error bars are included in the data and are often smaller than the data symbols.*

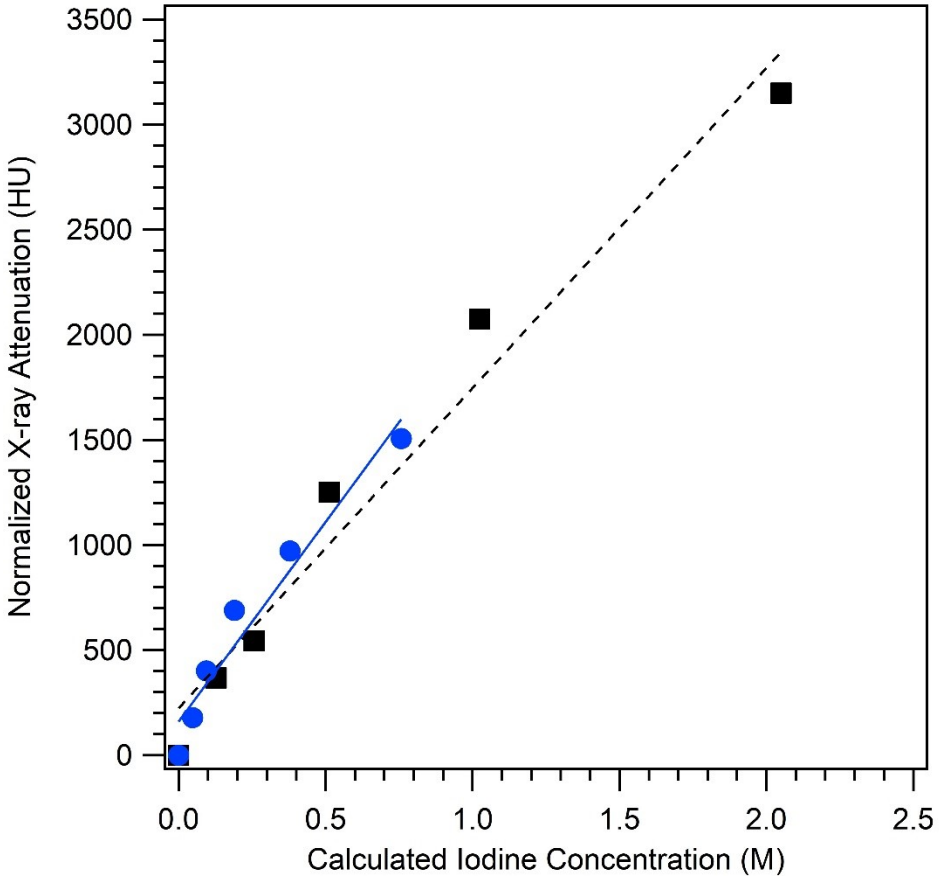


Figure S21. *The normalized* X-ray attenuation as a function of the calculated iodine concentration for PEO-PEI15 (●blue circles) and PEO-PEI30 (■black squares). The data is calculated from the data in **Figure S20**. Here we see a nearly identical attenuation response with respect to the iodine concentration, as expected. The calculation of the iodine concentration takes into account the iodine conversion as determined by ^{1}H NMR spectroscopy. Given the large difference in iodine conversion between the PEO-PEI15 and PEO-PEI30, the data should only be consistent if the conversions are accurate.

Calculations

Example Calculation for PEO-PECH Molecular Weight

1. Set integration of PEO peak at 3.67 to 3.64 ppm to 4.
2. Determine integration of entire backbone from 3.85 – 3.53 ppm
3. Subtract 4 from backbone integration and divide by 5

For PEO-PECH5, backbone integration = 6.33

$$Ratio\ of\ PECH{:}PEO = \frac{6.33 - 4}{5} = 0.46$$

$$Relative\ PECH = \frac{0.46}{1 + 0.46} = 0.32$$

Then, PECH M_n was found by calculating the total number of repeat units (N)

At 5000 g/mol, $PEO_N = 113$

$$Total\ N\ = \frac{113}{1 - 0.32} = 165.6 \sim 165$$

$$PECH_N = 165 - 113 = 52$$

$$PECH\ M_n = 52 * 92.52 = 4{,}872$$

Example Calculation for Iodine Conversion

1. Set integration of PEO peak at 3.67 to 3.64 ppm to 4. This is the number of protons in a EO monomer unit.
2. Determine integration of entire copolymer from 3.85 to 3.24 ppm.
3. Determine integration of C**H$_2$**-I peak at 3.48 – 3.24 ppm
4. Subtract 4 from step 2 which gives the total integration of the polymer related to PECH and PEI.
5. Divide the integral of the C**H$_2$**-I peak by the total from step 4. This gives the relative contribution of the C**H$_2$**-I peak to the total PECH/PEI polymer unit.
6. Since the C**H$_2$**-I contribution only takes into account two protons, the total in step 5 needs to be divided by 0.4 (i.e., 2/5, or 2 of the 5 PECH/PEI protons in a monomeric unit), which gives the percent conversion.

For PEO-PEI5, backbone integration = 6.24 and C**H$_2$**-I peak integration = 0.25

$$6.24 - 4 = 2.24$$

$$\frac{0.25}{2.24} = 0.11$$

$$\frac{0.11}{0.4} = 0.27$$

Example Calculation for Predicted T_g of PEO-PECH with Fox equation

$$Fox\ equation = \frac{1}{T_g} = \frac{w_{PEO}}{T_{gPEO}} + \frac{w_{PECH}}{T_{gPECH}}$$

$$T_{g,PECH} = -26\ °C$$

$$T_{g,PEO} = -73\ °C$$

Example for PEO-PECH5:

$$w_{PEO_{Total}} = \frac{MW_1}{MW_1 + MW_2} = 0.505 \text{ (includes crystalline region)}$$

$$w_{PEO} = \frac{MW_1}{MW_1 + MW_2}(1 - w_{xtal}) = 0.386$$

$$w_{PECH} = 1 - w_1 = 0.614$$

$$\frac{1}{T_g} = 0.0044$$

$$T_g = 227\ K = -45.7\ ^{\circ}C$$