Supporting Information

Multifunctional and biodegradable polyphosphazenes for use as macromolecular anti-cancer drug carriers

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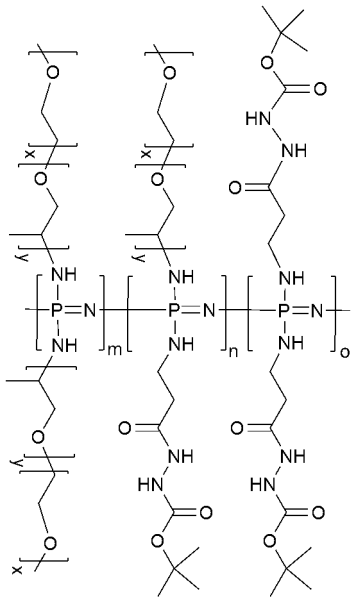
Characterisation data for polymers **1-4**



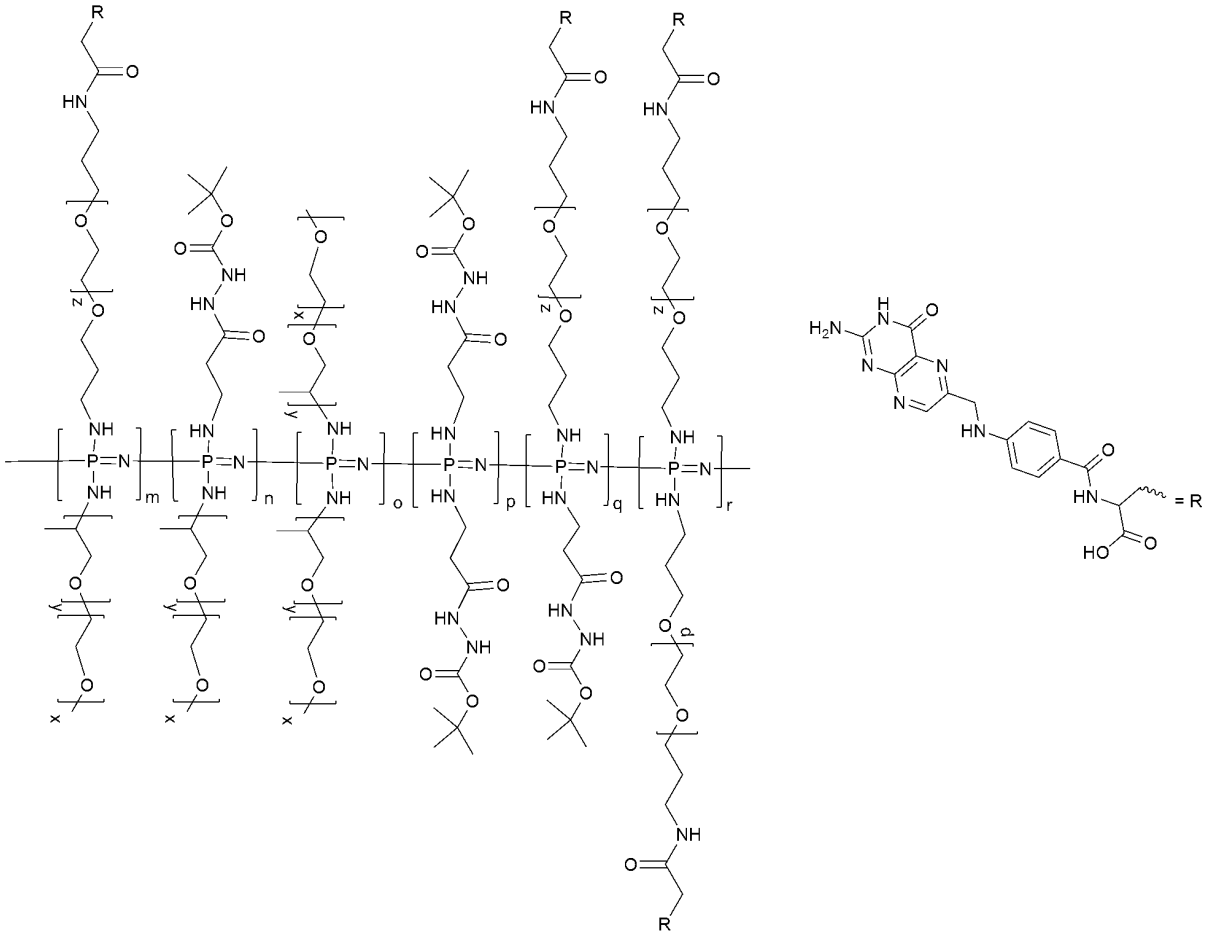
Polymer **1**: FTIR (solid) *ν*max/cm^{-1} = 3277 (N-H), 2881 (C-H), 1740 (C=O), 1688 (C=O) and 1106 (P=N); ^{1}H-NMR ($CDCl_3$): δ = 1.12 (br, 14H), 1.43 (s, 9H), 3.37 (s, 6H), 3.64 (m, 170H); ^{31}P NMR ($CDCl_3$): δ = -1.5 (ppm). GPC (g mol^{-1}) M_n = 32360, M_w = 41188.

Polymer **2**: FTIR (solid) *ν*max/cm^{-1} = 3290 (N-H), 2865 (C-H), 1736 (C=O), 1688 (C=O) and 1104 (P=N). ^{1}H-NMR ($CDCl_3$): δ = 1.13 (d, 16H), 1.47 (s, 9H), 3.38 (s, 6H), 3.64 (m, 144H). ^{31}P NMR ($CDCl_3$): δ = -0.7 (ppm). GPC (g mol^{-1}) M_n = 31319, M_w = 46172.

Polymer **3**: FTIR (solid) *ν*max/cm^{-1} = 3268 (N-H), 2872 (C-H), 1723 (C=O), 1673 (C=O) and 1094 (P=N). ^{1}H-NMR ($CDCl_3$): δ = 1.13 (d, 1H) 1.46 (s, 9H), 3.38 (m, 0.3H), 3.65 (s, 9H). ^{31}P NMR ($CDCl_3$): δ = – 0.3(ppm). GPC (g mol^{-1}) M_n = 13968, M_w = 18220.

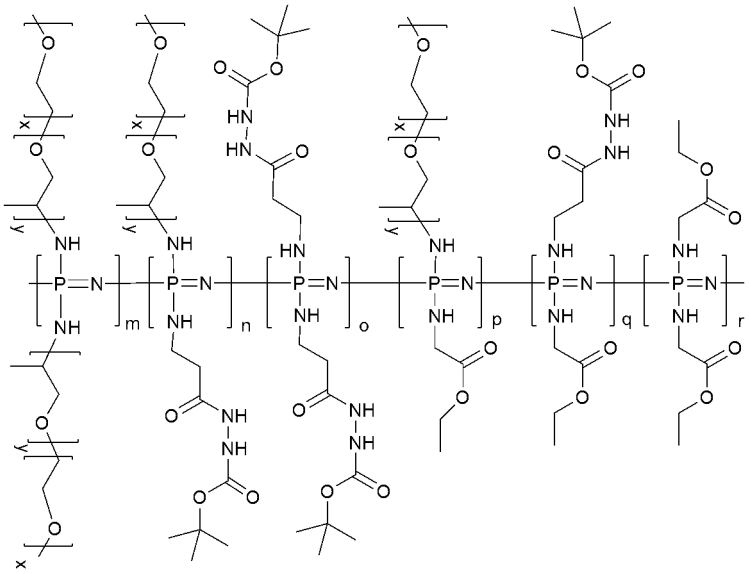
Polymer **4**: FTIR (solid) *v*max/cm^{-1} = 3266 (N-H), 2863 (C-H), 1727 (C=O), 1647 (C=O) and 1101 (P=N). ^{1}H-NMR ($CDCl_3$): δ = 1.15 (d, 30H) 1.49 (s, 9H), 3.62 (b, 124H). ^{31}P NMR ($CDCl_3$): δ = - 1.2 (ppm). GPC (g mol^{-1}) M_n = 48954, M_w = 63799.

Characterisation data for polymer **5**



Polymer **5**: UV-Vis λmax (H_2O)/nm 256, 283 and 368 (ε/dm^3 mol^{-1} cm^{-1} 26900, 25100 and 9120). FTIR (solid) *v*max/cm^{-1} = 3289 (N-H), 2882 (C-H), 1653 (C=O), and 1107 (P=N). ^{1}H-NMR ($CDCl_3$): δ = 1.11 (d, 15H), 1.41 (s, 9H), 3.35 (6H), 3.61 (s, 178H). ^{31}P NMR ($CDCl_3$): δ= -0.8 (ppm). GPC (g mol^{-1}) M_n = 35391, M_w = 51216.

Characterisation data for polymers **6-8**



Polymer **6**: FTIR (solid) *v*max/cm^{-1} = 3292 (N-H), 2867 (C-H), 1739 (C=O), 1683 (C=O), and 1104 (P=N). ^{1}H-NMR (500MHz, $CDCl_3$): δ= 1.14 (d, br, 9.2H), 1.26 (br, 6.4H), 1.45 (s, 9H), 3.38 (s, 4H), 3.65 (br, 108H). ^{31}P NMR ($CDCl_3$): δ (ppm) -0.3. GPC (g mol^{-1}) M_n = 63197, M_w = 100688.

Polymer **7**: FTIR (solid) *v*max/cm^{-1} = 3289 (N-H), 2866 (C-H), 1739 (C=O), 1692 (C=O), and 1107 (P=N). ^{1}H-NMR (200MHz, $CDCl_3$): δ= 1.12 (d, br, 10H), 1.26 (t, 4.5H), 1.44 (s, 9H), 3.38 (s, 5H), 3.65 (br, 120H). ^{31}P NMR ($CDCl_3$): δ (ppm) – 0.6. GPC (g mol^{-1}) M_n = 75681, M_w = 104429.

Polymer **8**: FTIR (solid) *v*max/cm^{-1} = 3281 (N-H), 2866 (C-H), 1793 (C=O), 1691 (C=O), and 1108 (P=N). ^{1}H-NMR (200MHz, $CDCl_3$): δ= 1.12 (d, br, 12H), 1.26 (t, 4.2H), 1.44 (s, 9H), 3.38 (s, 4H), 3.65 (br, 120H). ^{31}P NMR ($CDCl_3$): δ (ppm) 0.8. GPC (g mol^{-1}) M_n = 68467, M_w = 103219.

Example FTIR and NMR spectra for polymers 1 and 6

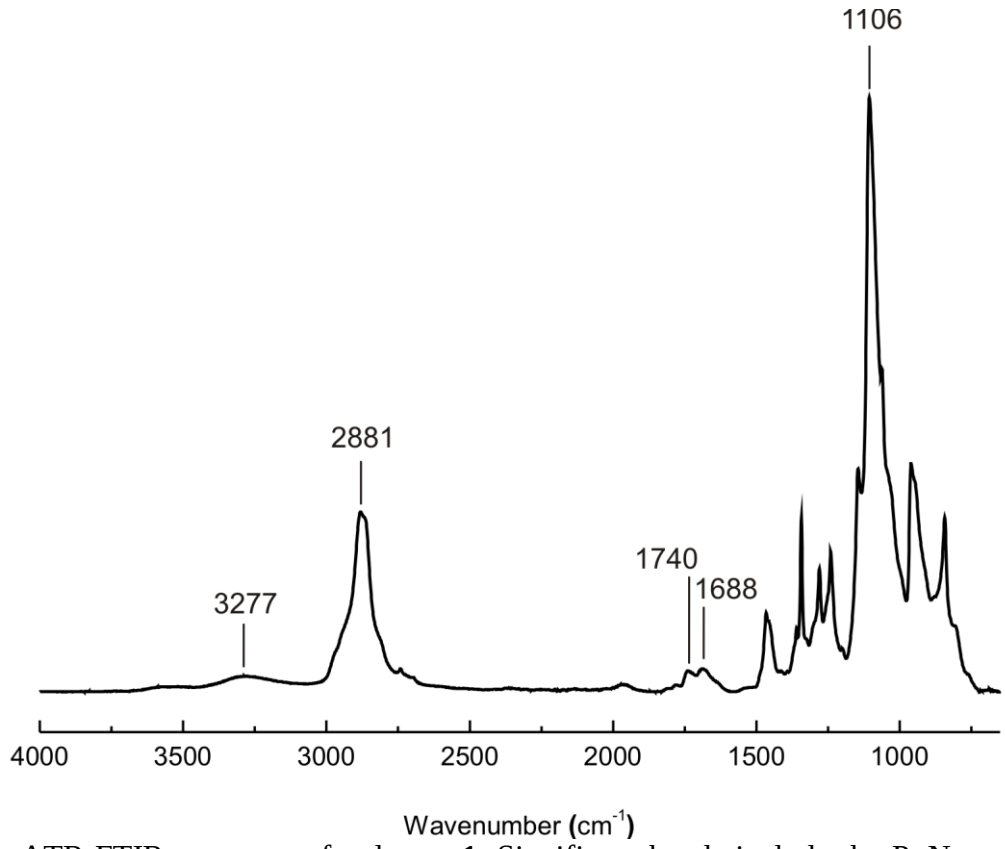


Figure 1: ATR-FTIR spectrum of polymer **1**. Significant bands include the P=N stretching band of the polyphosphazene main chain at 1106 cm^{-1}, the C=O bands at 1740 and 1688 cm^{-1} stemming from the hydrazone linker, a relatively large C-H band, predominantly from the polyalkylene oxide side chains at 2881 cm^{-1} and the NH bands at 3277 cm^{-1} and 3500 cm^{-1}.

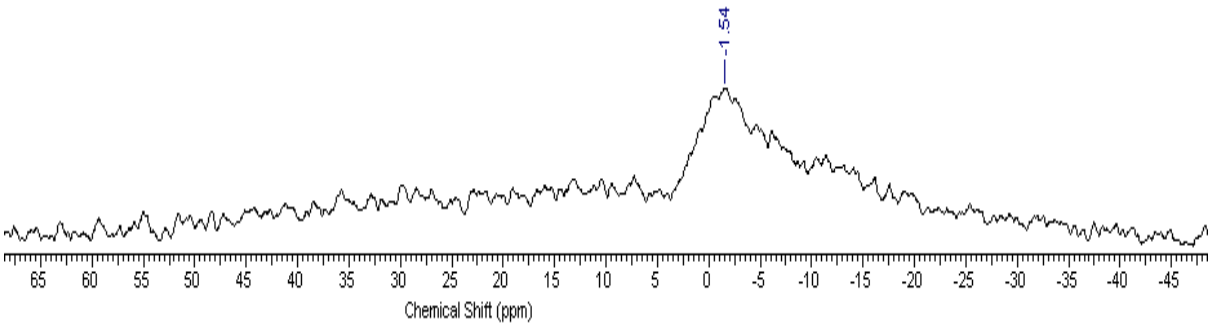


Figure 2: ^{31}P NMR of polymer **1**. A single broad peak is observed due to the mixed substitution of the phosphazene backbone.

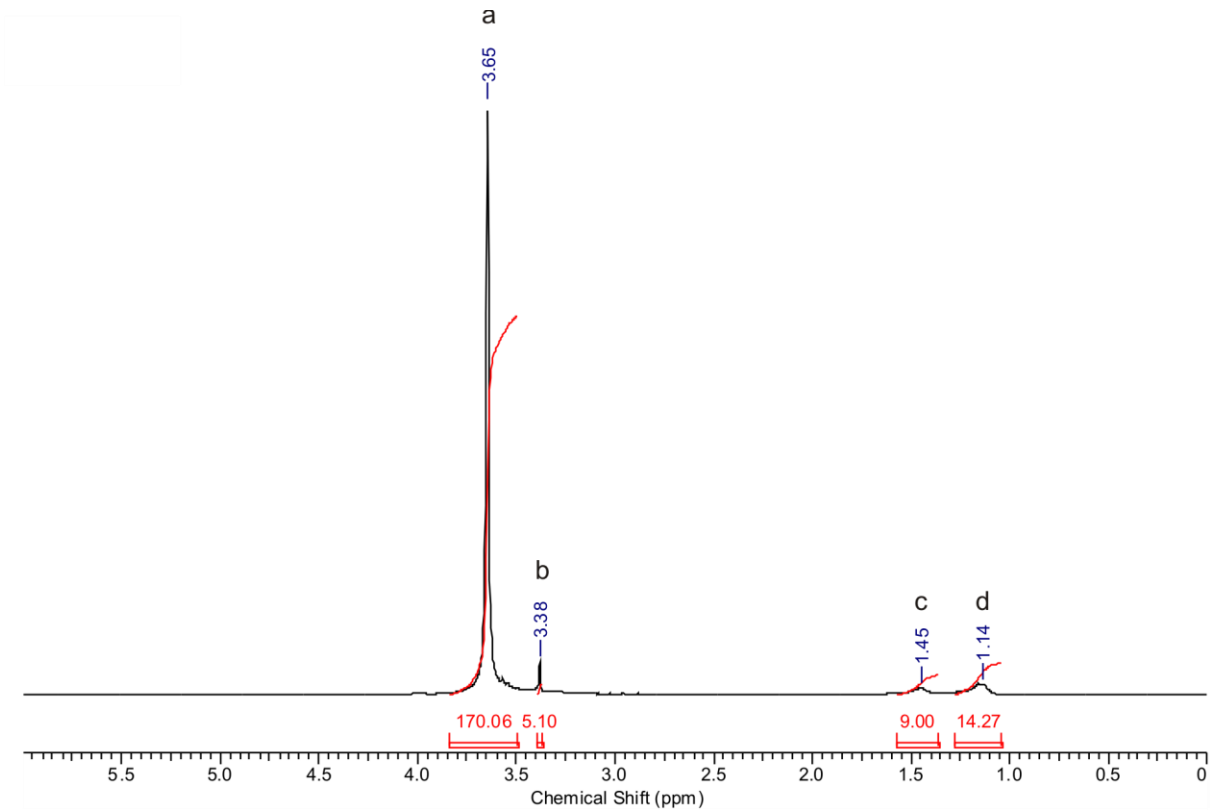


Figure 3: ^{1}H NMR of polymer 1 showing: a) Polyalkylene oxide CH_2 protons, b) -OCH_3 end groups c) Boc protecting group of the hydrazone linker and d) CH_3- groups from the PPO groups of the polyalkylene oxide side chains.

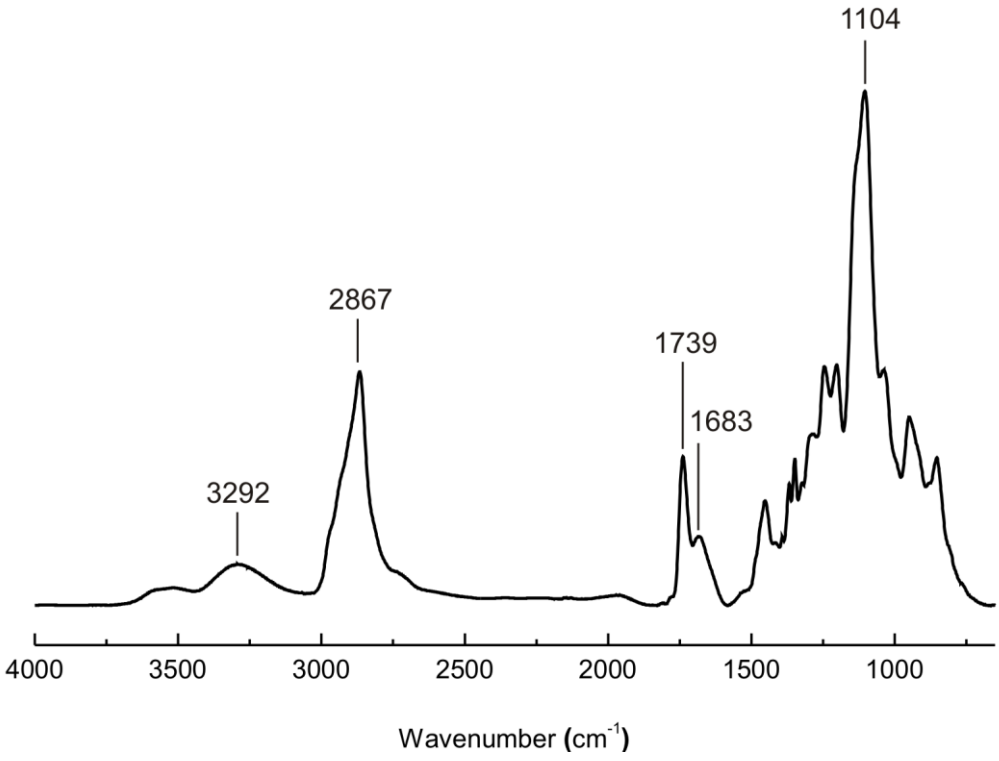


Figure 4: ATR-FTIR spectrum of polymer **6**. Relevant bands include the P=N stretching band of the polyphosphazene main chain at 1104cm^{-1}, the C=O bands stemming from both

the linker and the ethyl glycinate side groups, a relatively large C-H band, predominantly from the polyalkylene oxide side chains at 2867 cm^{-1} and the NH bands at 3292 cm^{-1} and 3500 cm^{-1}.

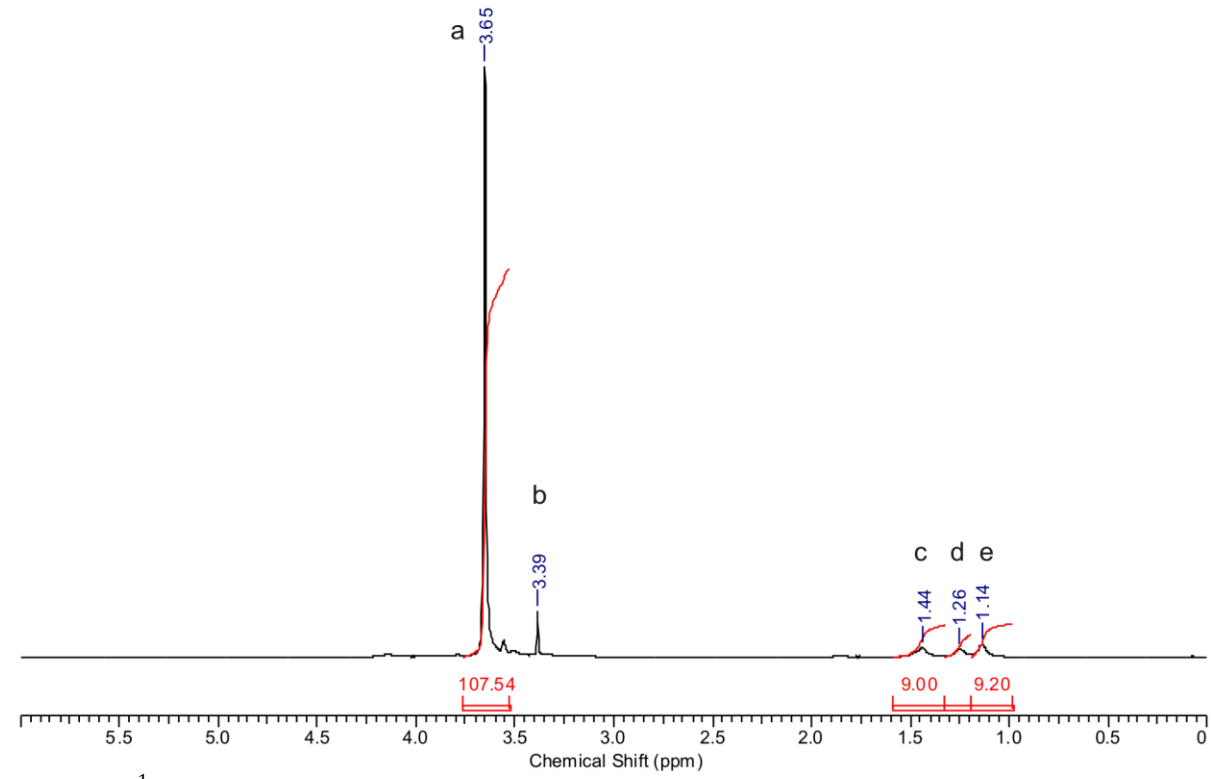


Figure 5: ^{1}H NMR spectrum of polymer **6** showing: a) Polyalkylene oxide CH_2 protons, b) -OCH_3 end groups c) boc protecting group of the hydrazone linker d) CH_3 groups of the ethyl glycinate groups and e) CH_3- groups from the PPO groups of the polyalkylene oxide side chains.

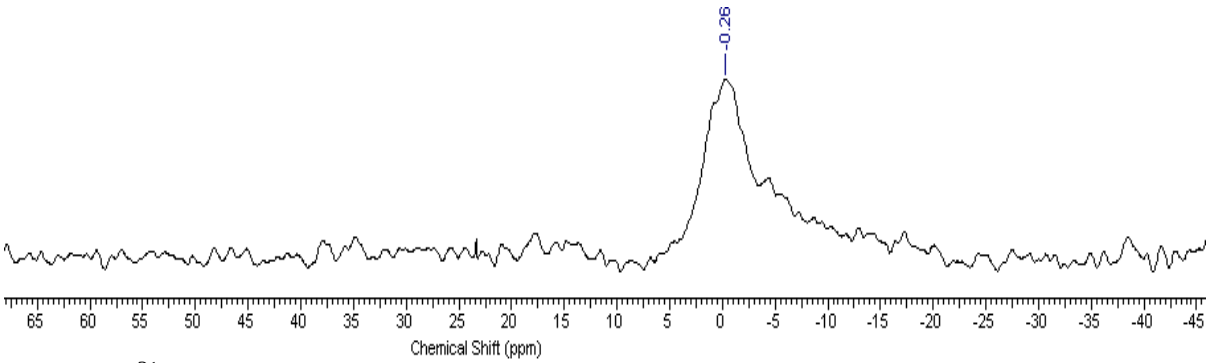


Figure 6: ^{31}P NMR of polymer **6**. A single broad peak is observed due to the mixed substitution of the phosphazene backbone.