Electronic Supplementary Material (ESI) for Polymer Chemistry.

SUPPORTING INFORMATION

Practical Phosphorylation of Polymers: An Easy Access to Fully Alcohol Soluble Synthetically and Industrially Important Polymers

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Synthetic Procedures

Synthesis of 2-azidoethyl 3-hydroxy-2-(hydroxymethyl)-2-methylpropanoate (1)

The synthesis was carried out according to previously published procedure (see ref. 46 in the main text). (Yield = 7 g, 90%). ^{1}H NMR ($\mathrm{CDCl_3}$, δ): 4.34 (t, 2H, $\mathrm{OC}\mathit{H}_2\mathrm{CH_2N_3}$), 3.91 (d, 2H, $\mathrm{CC}\mathit{H}_2\mathrm{OH}$), 3.75 (d, 2H, $\mathrm{CC}\mathit{H}_2\mathrm{OH}$), 3.52 (t, 2H, $\mathrm{OCH_2C}\mathit{H}_2\mathrm{N_3}$), 2.96 (br, 2H, $\mathrm{O}\mathit{H}$), 1.11 (s, 3H, $\mathrm{CC}\mathit{H}_3$).

Synthesis of 2-azidoethyl 5-methyl-2-oxo-1,3-dioxane-5-carboxylate (2)

1 (5 g, 25.6 mmol) was added to a 250 mL round bottom flask and dissolved in 100 mL of THF. Then the flask was placed in an ice bath and cooled to 0 °C and a solution of ethyl chloroformate (6.8 mL, 71.7 mmol) in 25 mL of THF was added dropwise followed by a solution of triethylamine (14.9 mL, 107.6mmol) in 25 mL of THF. The solution was stirred for 2 h at 0 °C and then at ambient temperature for overnight. The ammonium salt was filtered off and the solvent was evaporated under reduced pressure to give a yellow product that was further purified by washing with diethylether to give **2** as a viscous oil (Yield: 3.3 g, 59%). ^{1}H NMR ($\mathrm{CDCl_3}$, δ): 4.71 (d, 2H, $\mathrm{CC}\mathit{H}_2\mathrm{O}$), 4.38 (t, 2H, $\mathrm{OC}\mathit{H}_2\mathrm{CH_2N_3}$), 4.22 (d, 2H, $\mathrm{CC}\mathit{H}_2\mathrm{O}$), 3.54 (t, 2H, $\mathrm{OCH_2C}\mathit{H}_2\mathrm{N_3}$), 1.37 (s, 3H, $\mathrm{CC}\mathit{H}_3$).

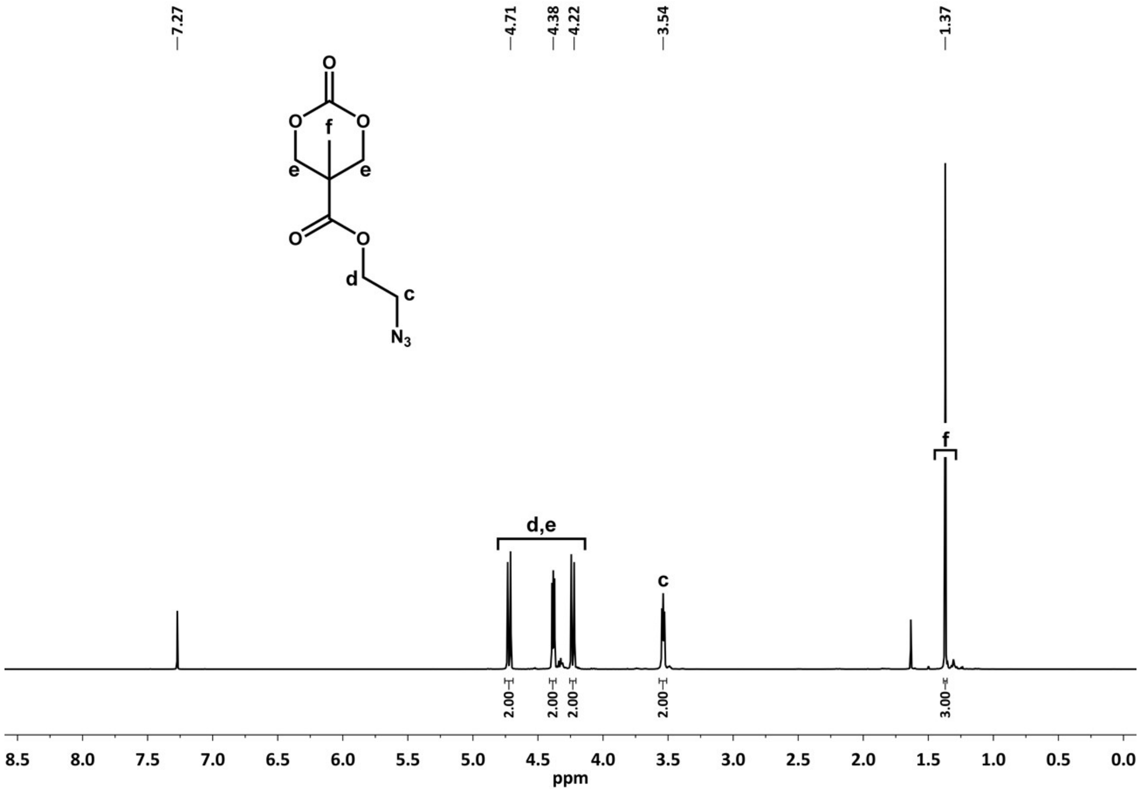


Figure S1. ^{1}H NMR spectrum of **2** in $\mathrm{CDCl_3}$ (500 MHz).

Synthesis of poly(styrene-*co*-chloromethylstyrene) (PSCMS)

The synthesis was carried out according to previously published procedure (see ref. 47 in the main text) (Yield: 1.85g, 39%, M_n= 11.1 kDa). ^{1}H NMR ($CDCl_3$, δ): 7.22- 6.23 (m, Ar*H*), 4.53 (s, ArCH_2Cl), 2.02-1.26 (m, 3H, CH_2C*H*).

Synthesis of azide-functionalized PSCMS (PSCMS-N_3)

PSCMS (1.85 g, 4.85 mmol) was dissolved in 15 mL of DMF and sodium azide (5.85 g, 90 mmol) was added into the round bottom flask, placed into an oil bath thermostated at 60 °C, and stirred for 24 h. After the specified time, the product was filtered and precipitated into excess MeOH. The crude polymer was dissolved in $CHCl_3$ and precipitated into MeOH one more time and filtered. The purified polymer was finally dried in a vacuum oven for 24 h (Yield: 1.41 g, 75%). ^{1}H NMR ($CDCl_3$, δ): 7.06-6.57 (m, 17H, Ar*H*), 4.24 (br, 2H, ArCH_2N_3), 1.80-1.42 (m, 12H, ArC*H*CH_2).

Phosphorylation of PSCMS-N_3 (PSCMS-P)

PS-N_3 (0.1 g, 0.238 mmol) was placed in a dried 25 mL Schlenk tube with a magnetic stir bar and dissolved in 1 mL of MeTHF, and then bis(diethoxyphosphoryl)acetylene (144 mg, 0.476 mmol) was added to this solution. The mixture was degassed via two FPT cycles, placed into an oil bath thermostated at 80 °C, and stirred for 24 h. After the specified time, the reaction mixture was cooled to room temperature and precipitated into cold hexane. The crude polymer was dissolved in $CHCl_3$ and precipitated into cold hexane one more time and the solvent was decanted. The purified polymer was finally dried in a vacuum oven for 24 h (Yield: 114 mg, 66%). ^{1}H NMR ($CDCl_3$, δ): 7.02-6.41 (br, 17H, Ar*H*), 5.89 (br, 2H, ArCH_2N), 4.29-3.98 (m, 8H, P=OOCH_2), 1.73-1.15 (m, 24H, ArC*H*CH_2 & P=OOCH$_2$CH_3). ^{13}C NMR ($CDCl_3$, *δ*): 145.13, 127.93, 125.74, 63.43, 53.56, 40.39, 16.34. ^{31}P NMR ($CDCl_3$, δ): 6.23, 2.08.

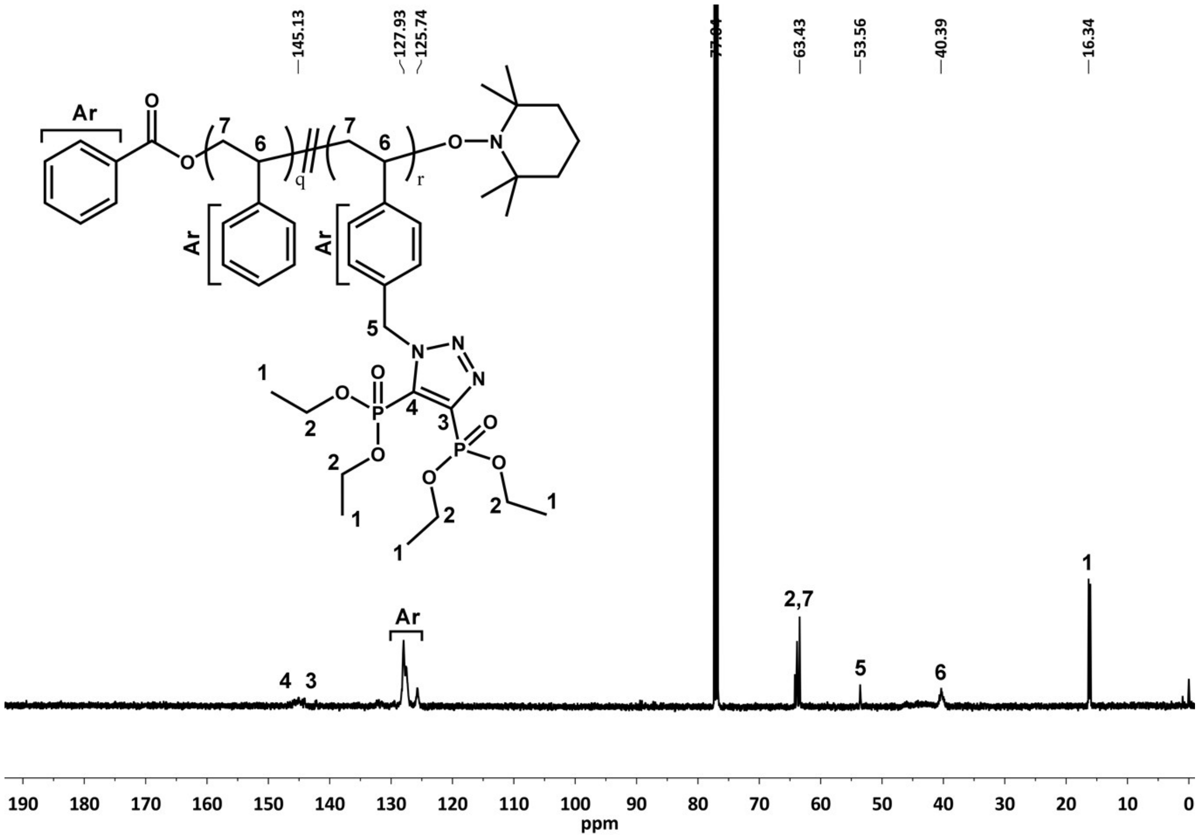


Figure S2. ^{13}C NMR spectrum of **PSCMS-P** in CDCl$_3$ (125 MHz).

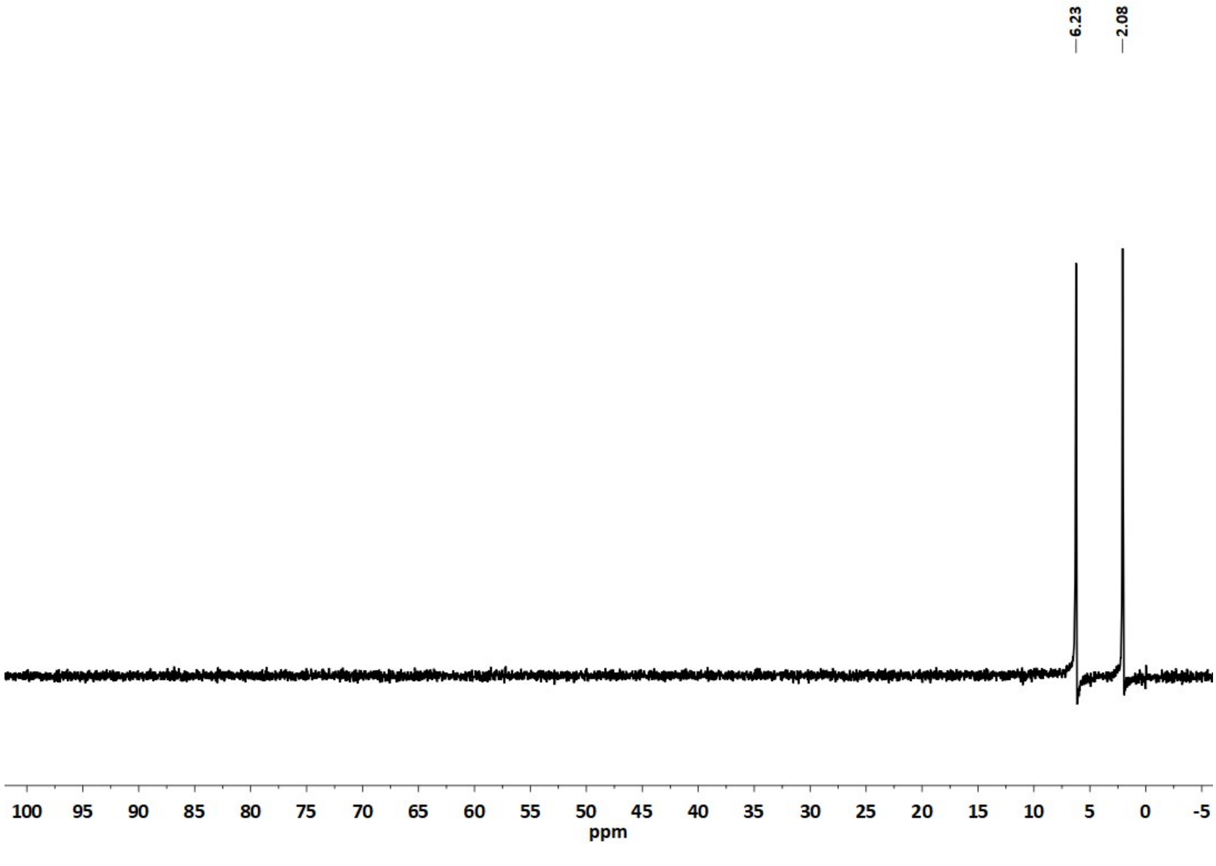


Figure S3. ^{31}P NMR spectrum of **PSCMS-P** in CDCl$_3$ (202 MHz).

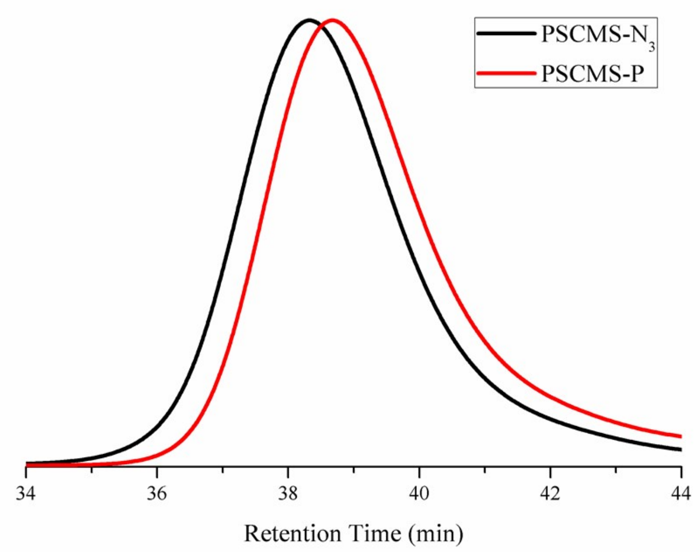


Figure S4. Overlaid GPC traces of **PSCMS-N$_3$** (black) and **PSCMS-P** (red) in THF.

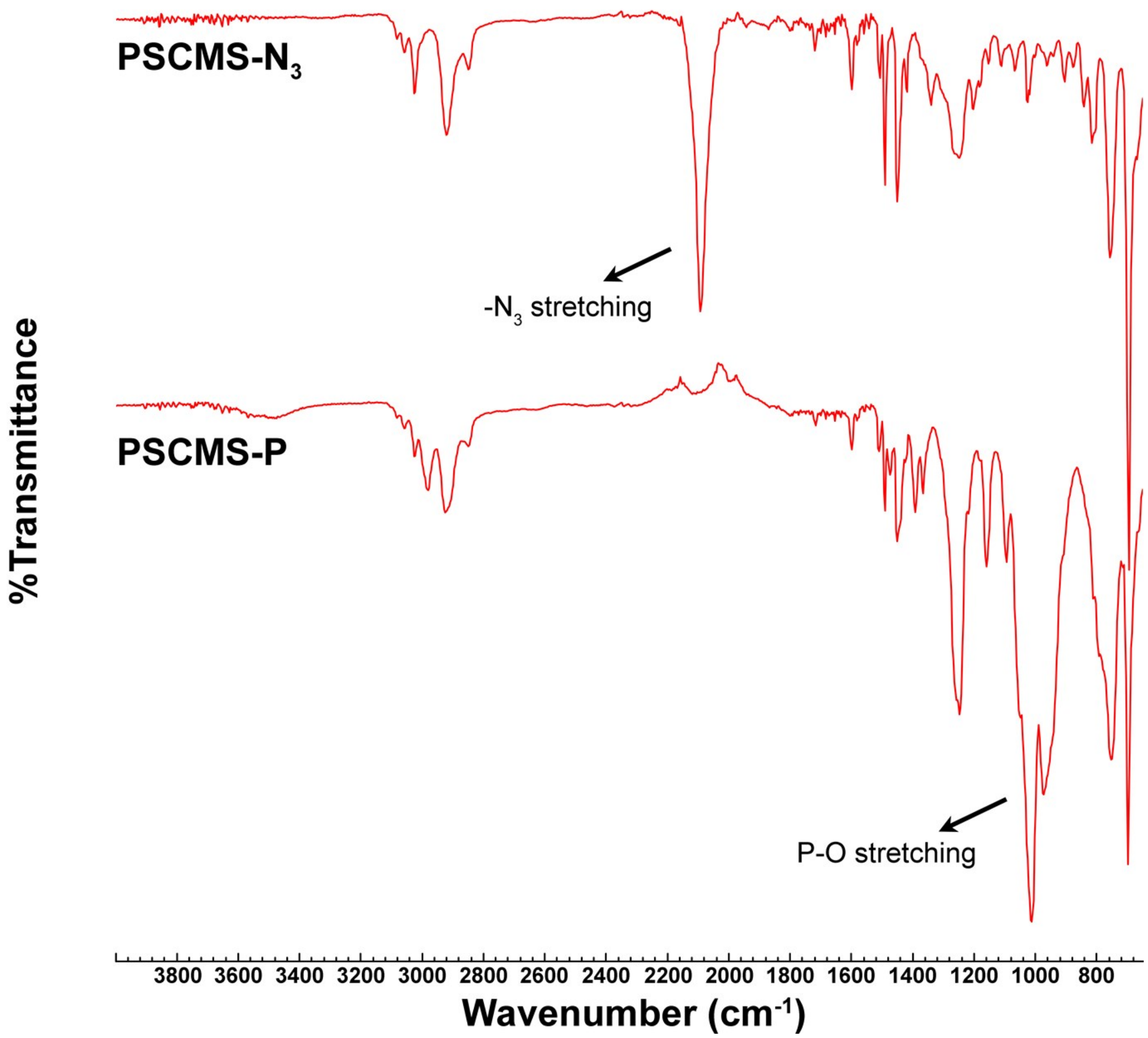


Figure S5. Overlaid FT-IR spectra of **PSCMS-N$_3$** and **PSCMS-P**.

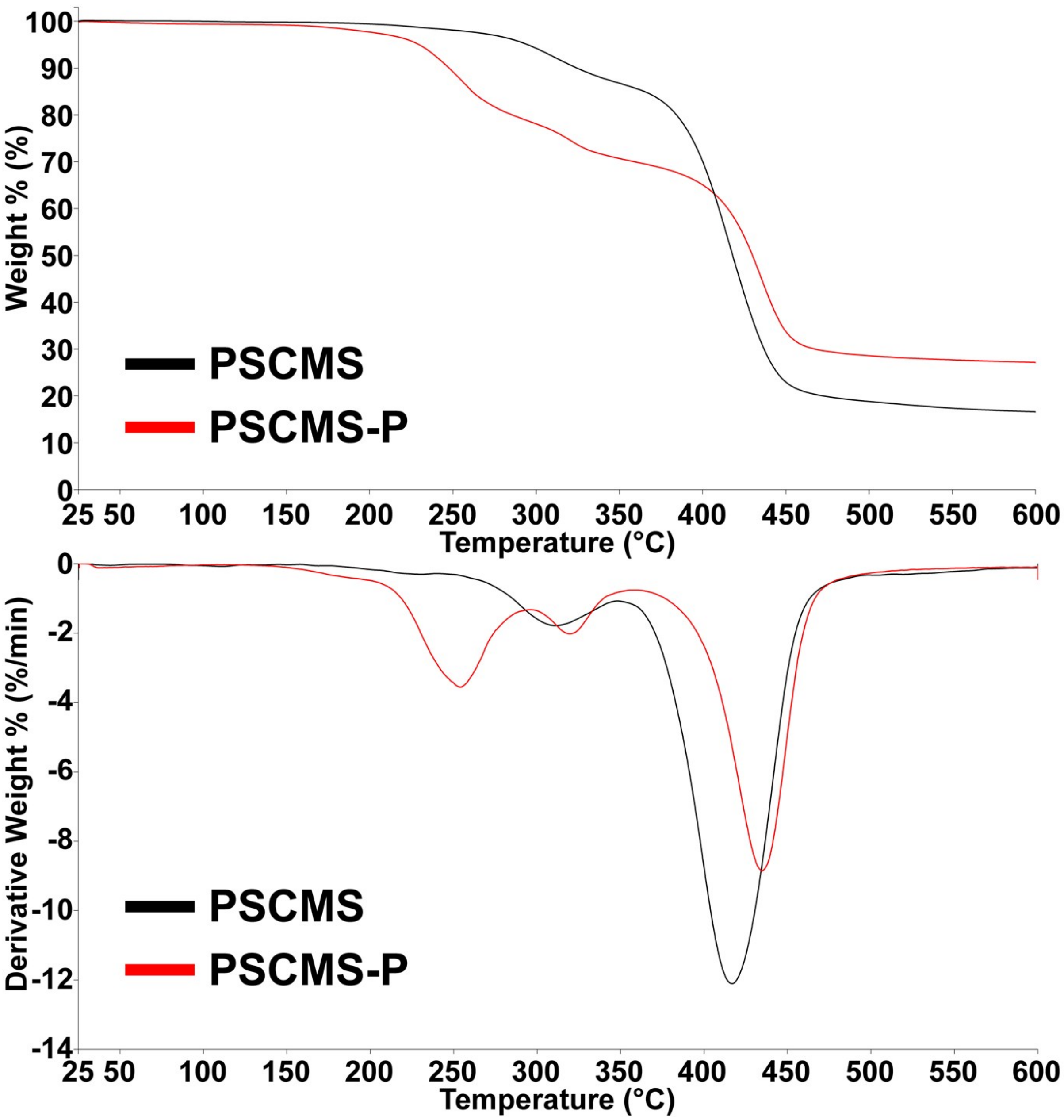


Figure S6. TGA curves of **PSCMS** and **PSCMS-P** (up), and their corresponding derivative curves (down) under nitrogen atmosphere.

Synthesis of polypentafluorostyrene (PPFS)

Pentafluorostyrene (PFS) (3.0 mL, 22 mmol) was placed in a dried Schlenk tube with a magnetic stir bar. Ethyl α-bromoisobutyrate (32.3 µl, 0.22 mmol), PMDETA (45.9 µl, 0.22 mmol), and CuBr (32 mg, 0.22 mmol) was also added in that order. After three FPT cycles, the tube was placed in an oil bath thermostated at 110 ^{o}C. After 1 h, the polymerization was stopped by opening the flask to the open air and diluted with THF. The solution was filtered through a neutral alumina column to remove the copper salts. After partial removal of the solvent, the concentrated solution was precipitated into MeOH. The dissolution-precipitation procedure (THF-MeOH) was repeated two times. The purified polymer was finally dried in vacuum oven for 24 h (Yield: 1.03 g, 24.1% M_n= 10.8 kDa). ^{1}H NMR ($CDCl_3$, δ): 2.75-2.41 (br, 1H, $CH_2C\mathit{H}$), 2.00 (br, 2H, $C\mathit{H}_2CH$). ^{19}F NMR ($CDCl_3$, δ):-141.76, -143.06, -143.82, -153.95, -160.76, -161.26.

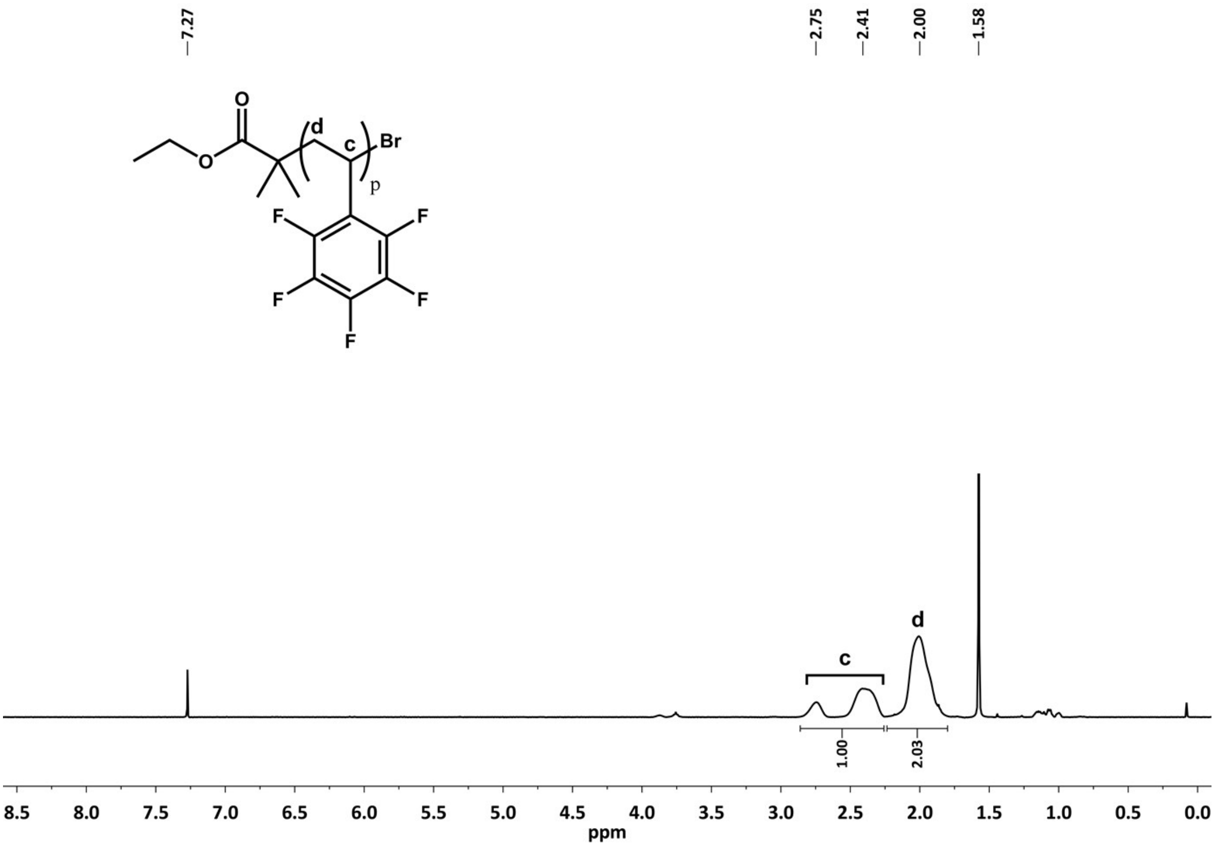


Figure S7. ^{1}H NMR spectrum of **PPFS** in $CDCl_3$ (500 MHz).

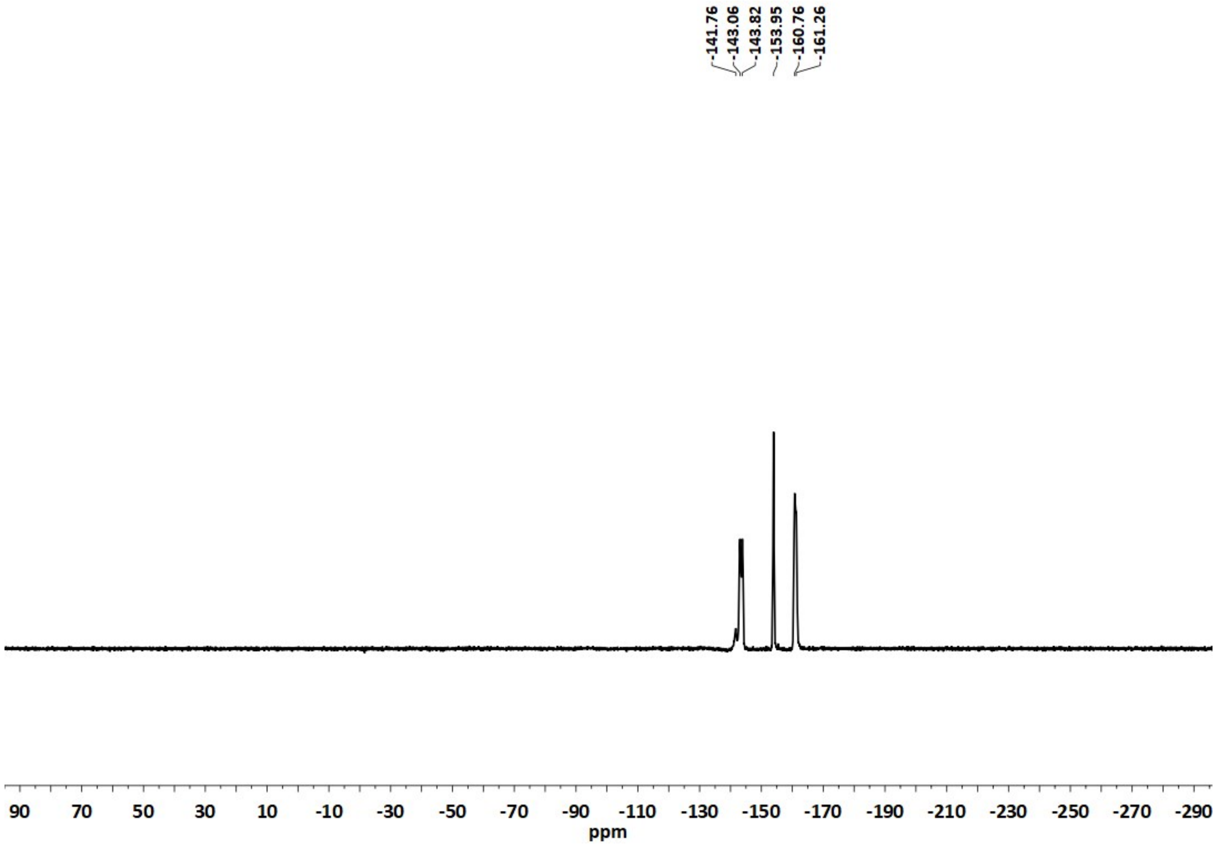


Figure S8. ^{19}F NMR spectrum of **PPFS** in $CDCl_3$ (470 MHz).

Synthesis of azide-functionalized PPFS (PPFS-N_3)

PPFS (0.9 g, 4.63 mmol) was dissolved in 5 mL of DMF and sodium azide (602 mg, 9.27 mmol) was added into the round bottom flask, placed into an oil bath thermostated at 60 ^{o}C, and stirred for 24 h. After the specified time, the product was filtered and precipitated into excess MeOH. The crude polymer was dissolved in $CHCl_3$ and precipitated into MeOH one more time and filtered. The purified polymer was finally dried in a vacuum oven for 24 h (Yield: 720 mg, 71.6%). ^{1}H NMR ($CDCl_3$, δ): 2.72-2.26 (br, 1H, $C_6F_4C\mathit{H}CH_2$), 1.96 (br, 2H, $C_6F_4CHC\mathit{H}_2$). ^{19}F NMR ($CDCl_3$, δ):-141.77, -142.90, -151.19, -151.68, -153.89, -154.20, -160.46, -161.31.

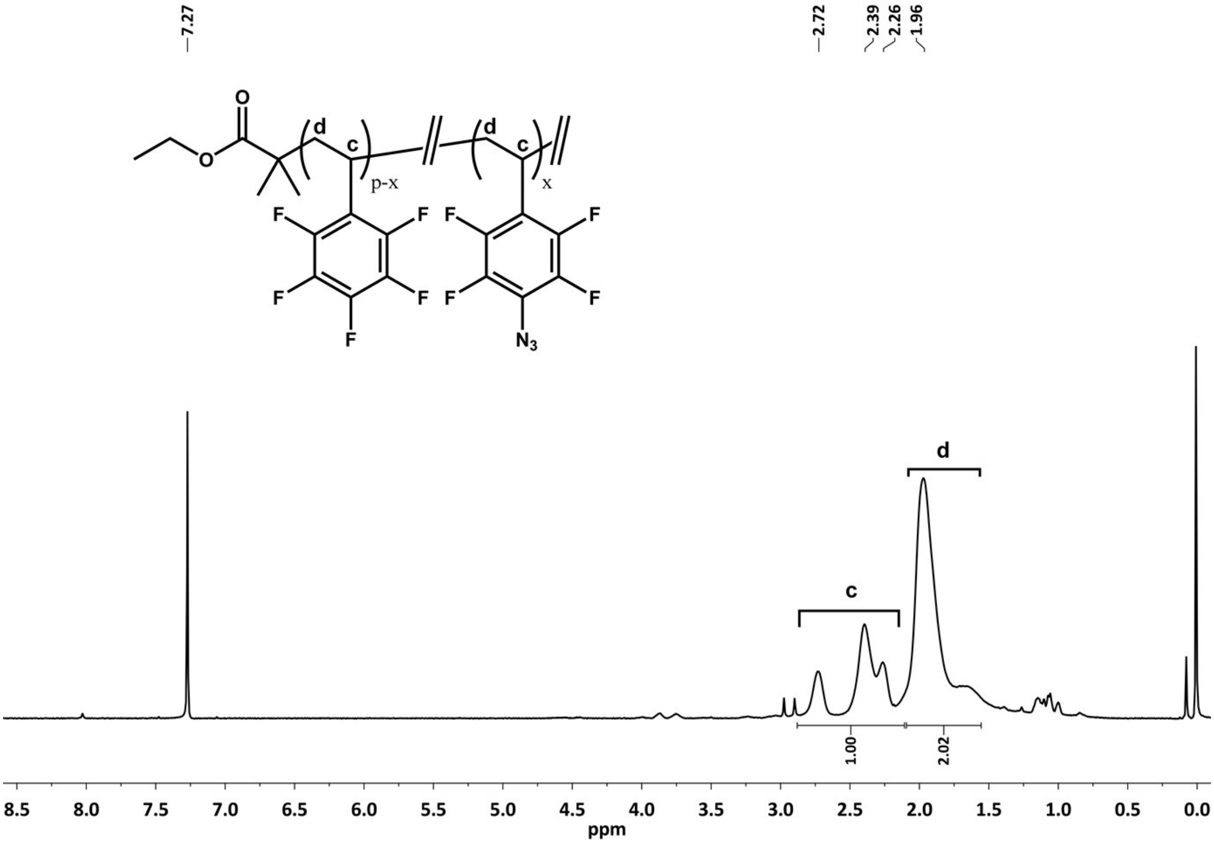


Figure S9. ^{1}H NMR spectrum of **PPFS-N$_3$** in CDCl$_3$ (500 MHz).

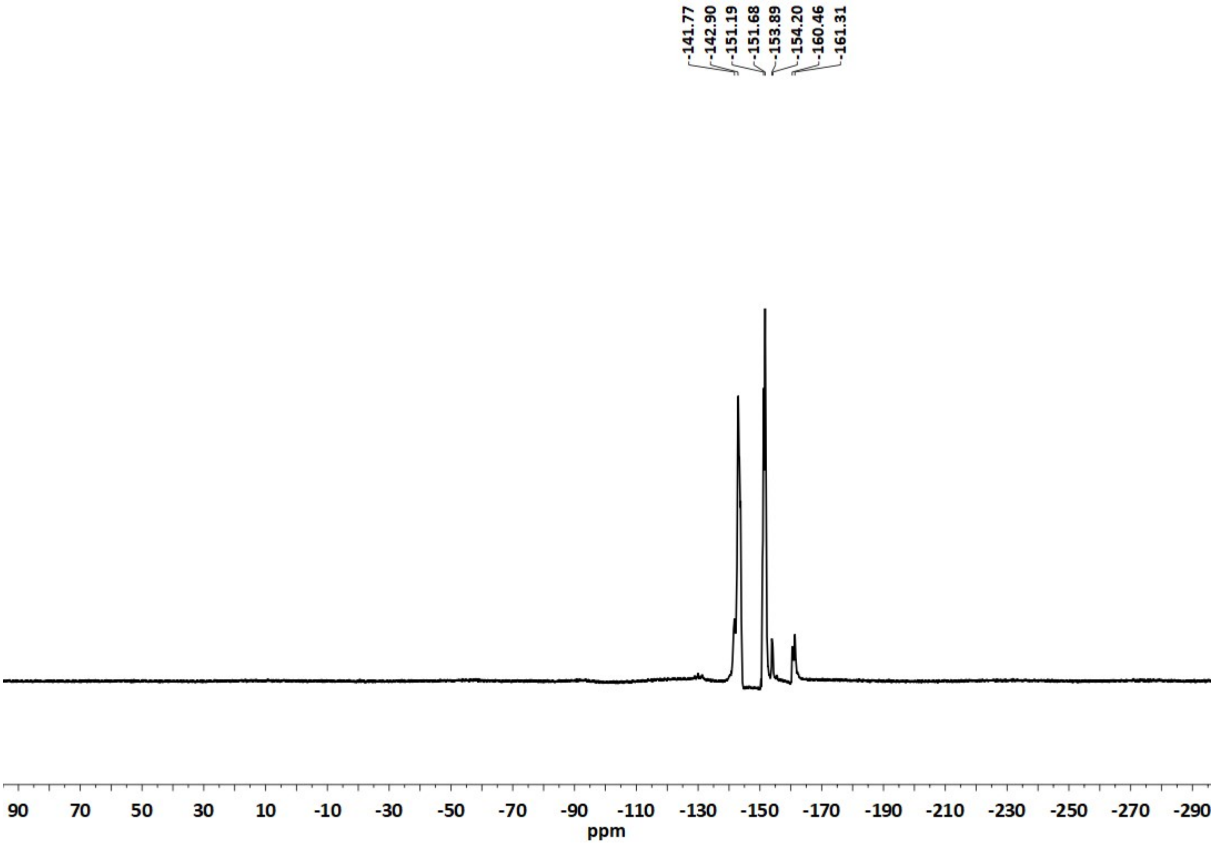
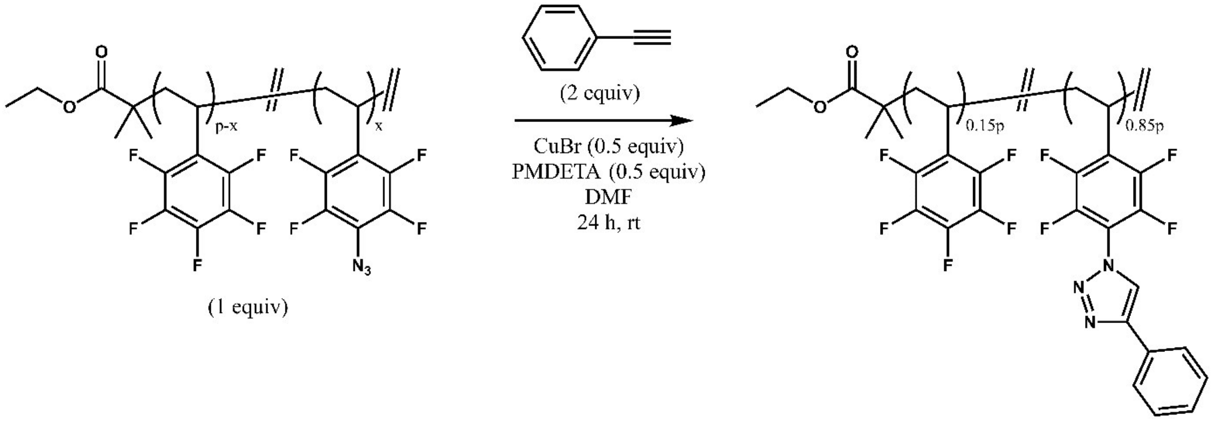


Figure S10. ^{19}F NMR spectrum of **PPFS-N$_3$** in CDCl$_3$ (470 MHz).

Model reaction of PPFS-N$_3$ with phenylacetylene



Scheme S1. Schematic representation of the model reaction between **PPFS-N$_3$** and phenylacetylene.

PPFS-N$_3$ (0.1 g, 0.515 mmol) was placed in a dried 25 mL Schlenk tube with a magnetic stir bar and dissolved in 1 mL of DMF. Phenylacetylene (105 mg, 1.03 mmol), PMDETA (54.2 µL, 0.258 mmol) and CuBr (37 mg, 0.258 mmol) were also added respectively. After degassing via three FPT cycles, the solution was left to stir at room temperature for 24 h. Afterwards, the solution was diluted with THF and passed through a short column of neutral alumina for the removal of copper salts. Excess solvent was evaporated under vacuum and the remaining solution was precipitated into MeOH. The dissolution-precipitation procedure (THF-MeOH) was repeated two times. According to ^{1}H NMR analysis, the azidation efficiency was calculated to be 85% (Yield: 60 mg, 43%). ^{1}H NMR ($CDCl_3$, δ): 8.89-6.62 (m, 6H, Ar*H* & CC*H*N), 2.70-1.51 (m, 3H, C*H*$_2$CH & CH$_2$C*H*).

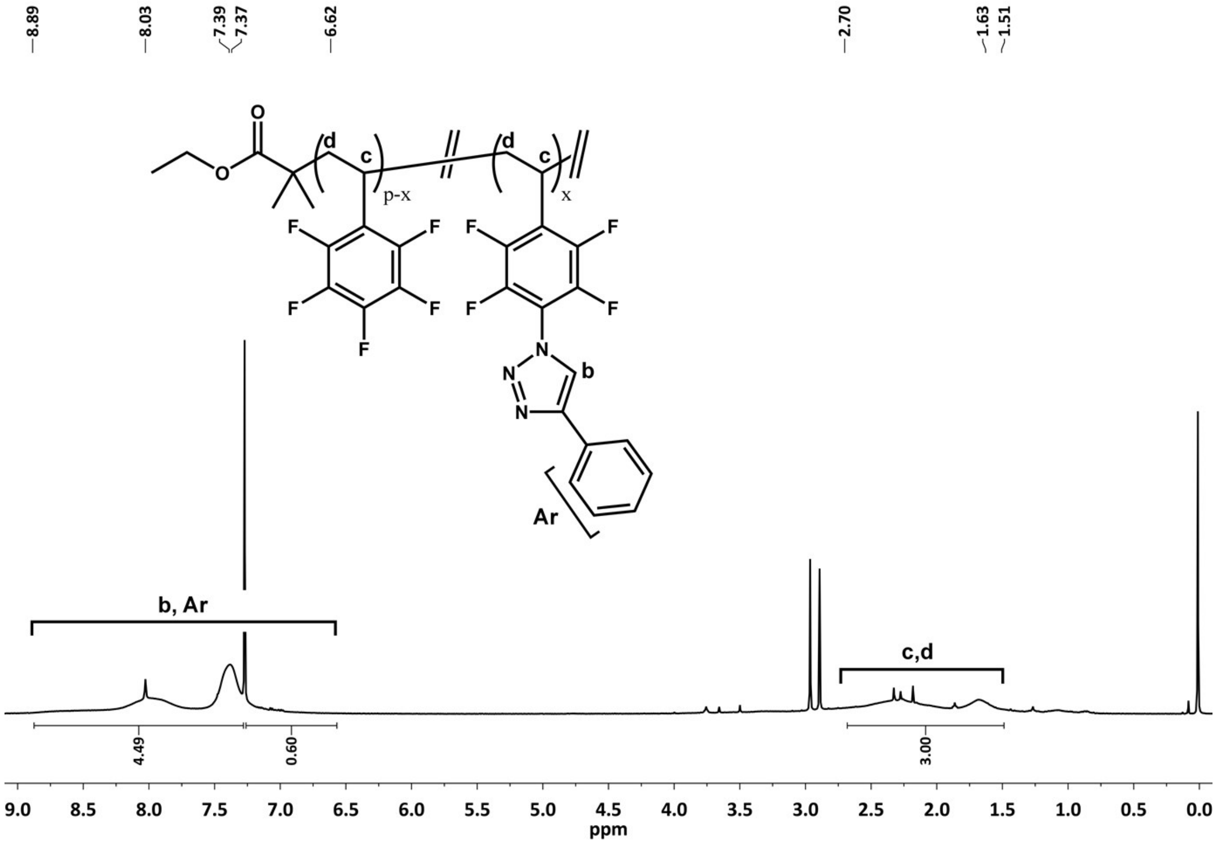


Figure S11. ^{1}H NMR spectrum (in $CDCl_3$) of the resulting polymer obtained from the model reaction between **PPFS-N$_3$** and phenylacetylene (500 MHz).

Phosphorylation of PPFS-N$_3$ (PPFS-P)

PPFS-N$_3$ (0.1 g, 0.46 mmol) was placed in a dried 25 mL Schlenk tube with a magnetic stir bar and dissolved in 1 mL of MeTHF, and then bis(diethoxyphosphoryl)acetylene (274.7 mg, 0.92 mmol) was added to this solution. The mixture was degassed via two FPT cycles, placed into an oil bath thermostated at 80 ^{o}C, and stirred for 24 h. After the specified time, the reaction mixture was cooled to room temperature and precipitated into cold hexane. The crude polymer was dissolved in $CHCl_3$ and precipitated into cold hexane one more time and the solvent was decanted. The purified polymer was finally dried in a vacuum oven for 24 h (Yield: 108 mg, 45%). ^{1}H NMR ($CDCl_3$, δ): 4.35-4.14 (m, 8H, P=OOCH_2), 2.13-1.76 (m, 3H, $C_6F_4CHCH_2$), 1.40-1.29 (m, 12H, P=OOCH_2CH_3). ^{13}C NMR ($CDCl_3$, *δ*): 144.02, 141.81, 115.50, 89.11, 87.29, 64.20, 38.00, 32.56, 16.23.^{19}F NMR ($CDCl_3$, δ): -143.97, -151.34, -160.80. ^{31}P NMR ($CDCl_3$, δ): 4.61, -1.05.

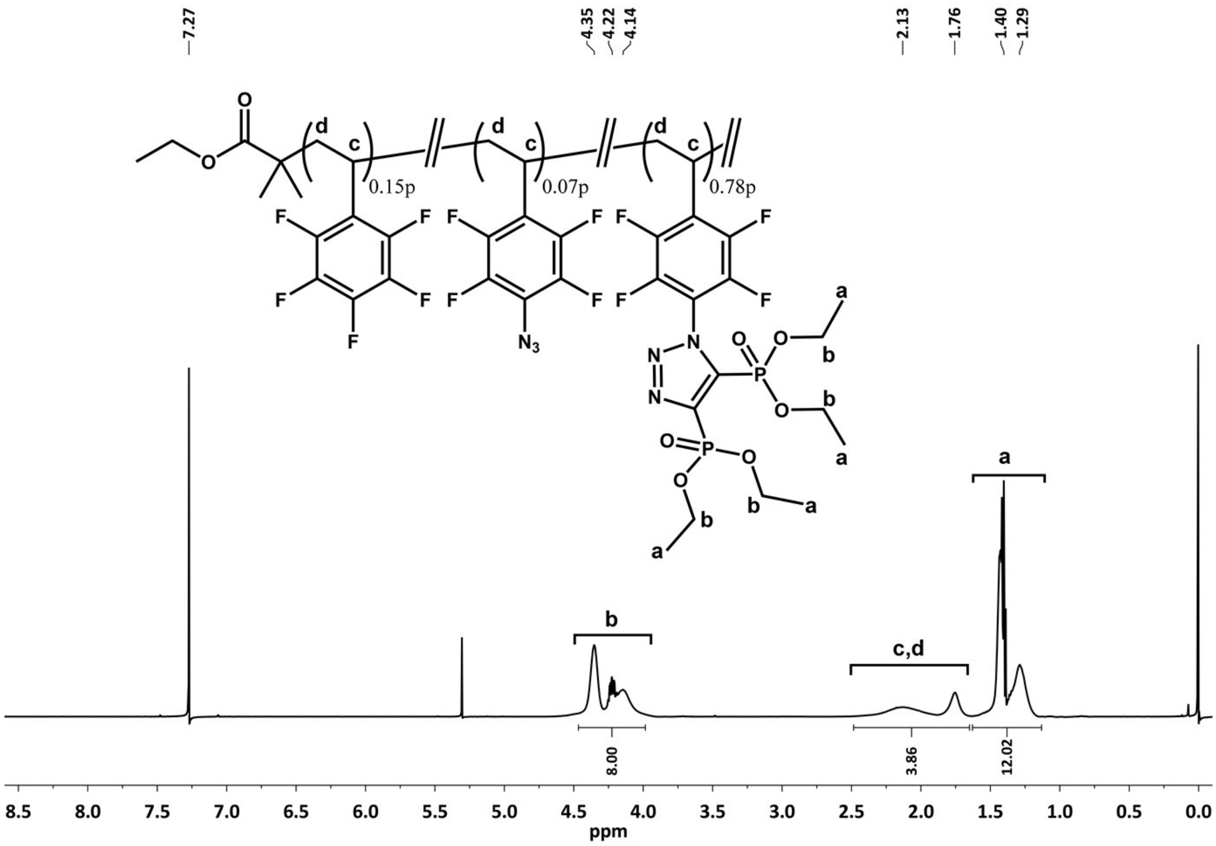


Figure S12. ^{1}H NMR spectrum of **PPFS-P** in $CDCl_3$ (500 MHz).

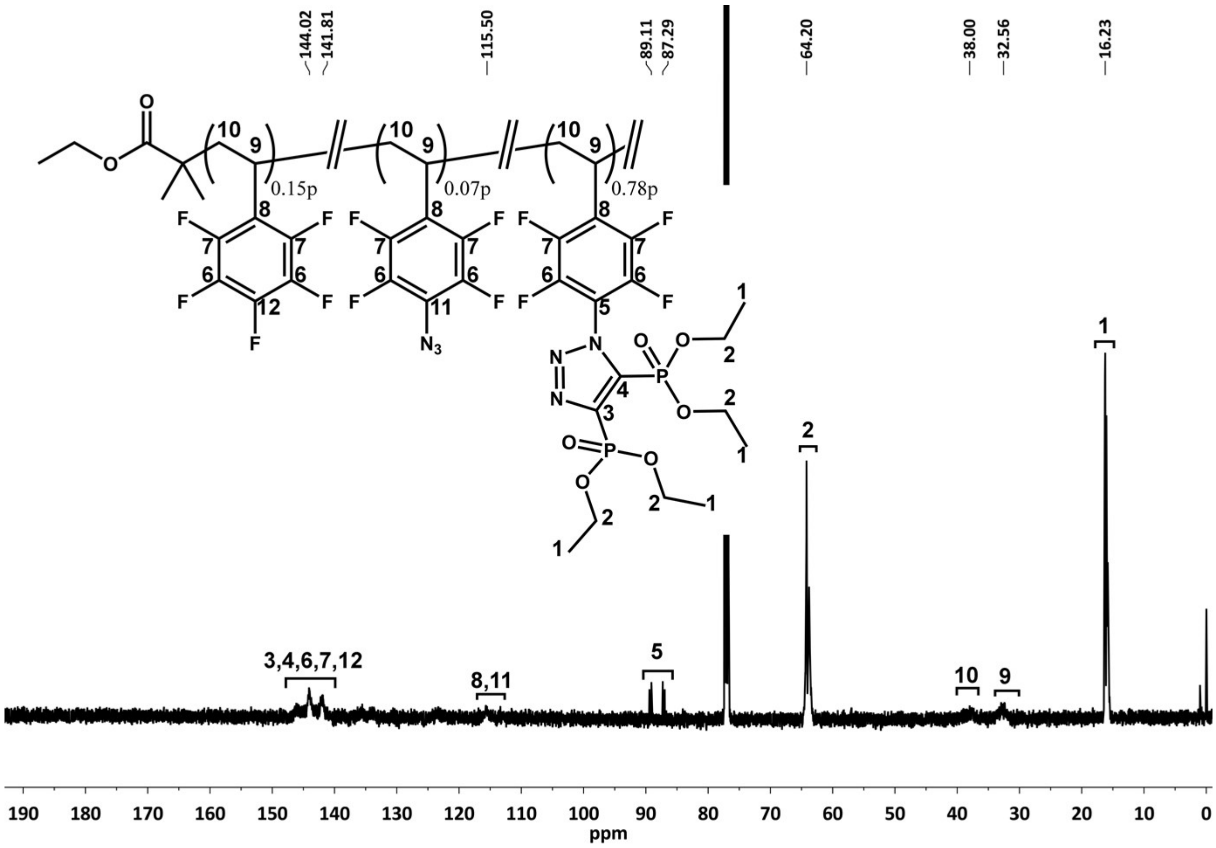


Figure S13. ^{13}C NMR spectrum of **PPFS-P** in $CDCl_3$ (125 MHz).

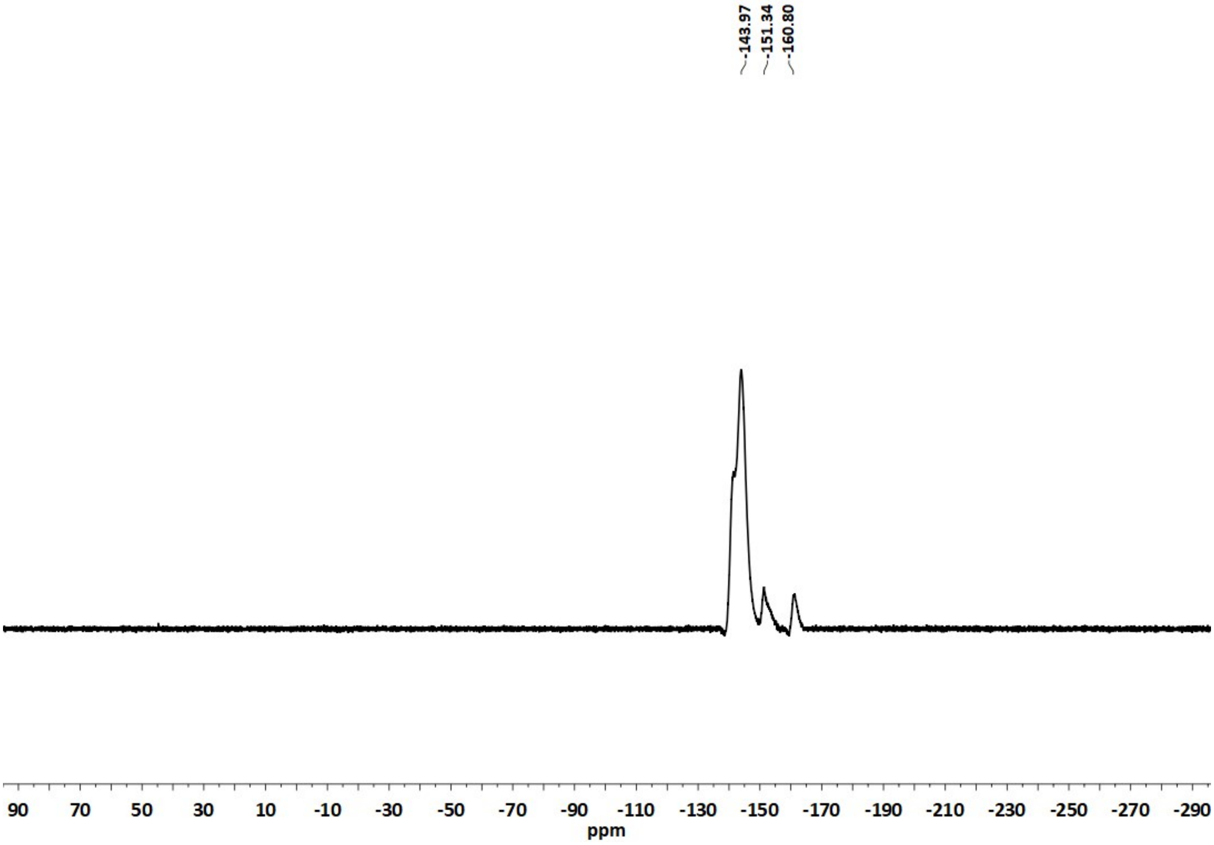


Figure S14. ^{19}F NMR spectrum of **PPFS-P** in $CDCl_3$ (470 MHz).

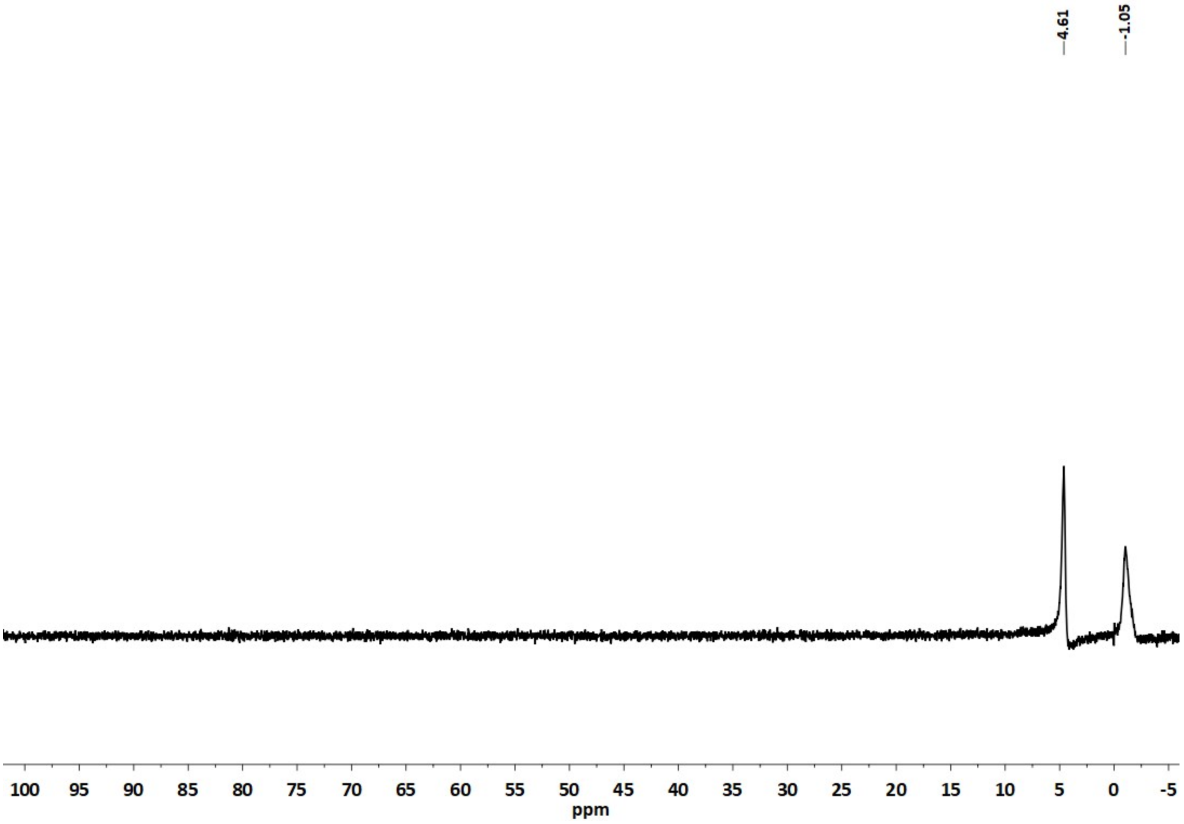


Figure S15. ^{31}P NMR spectrum of **PPFS-P** in $CDCl_3$ (202 MHz).

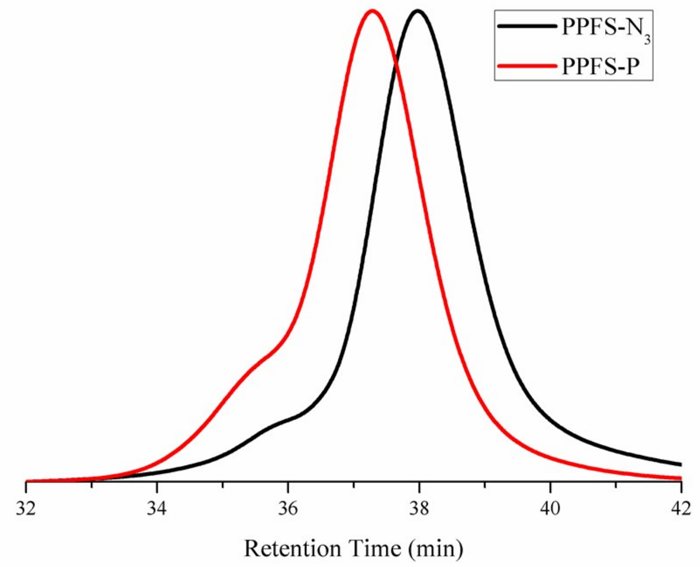


Figure S16. Overlaid GPC traces of **PPFS-N$_3$** (black) and **PPFS-P** (red) in THF.

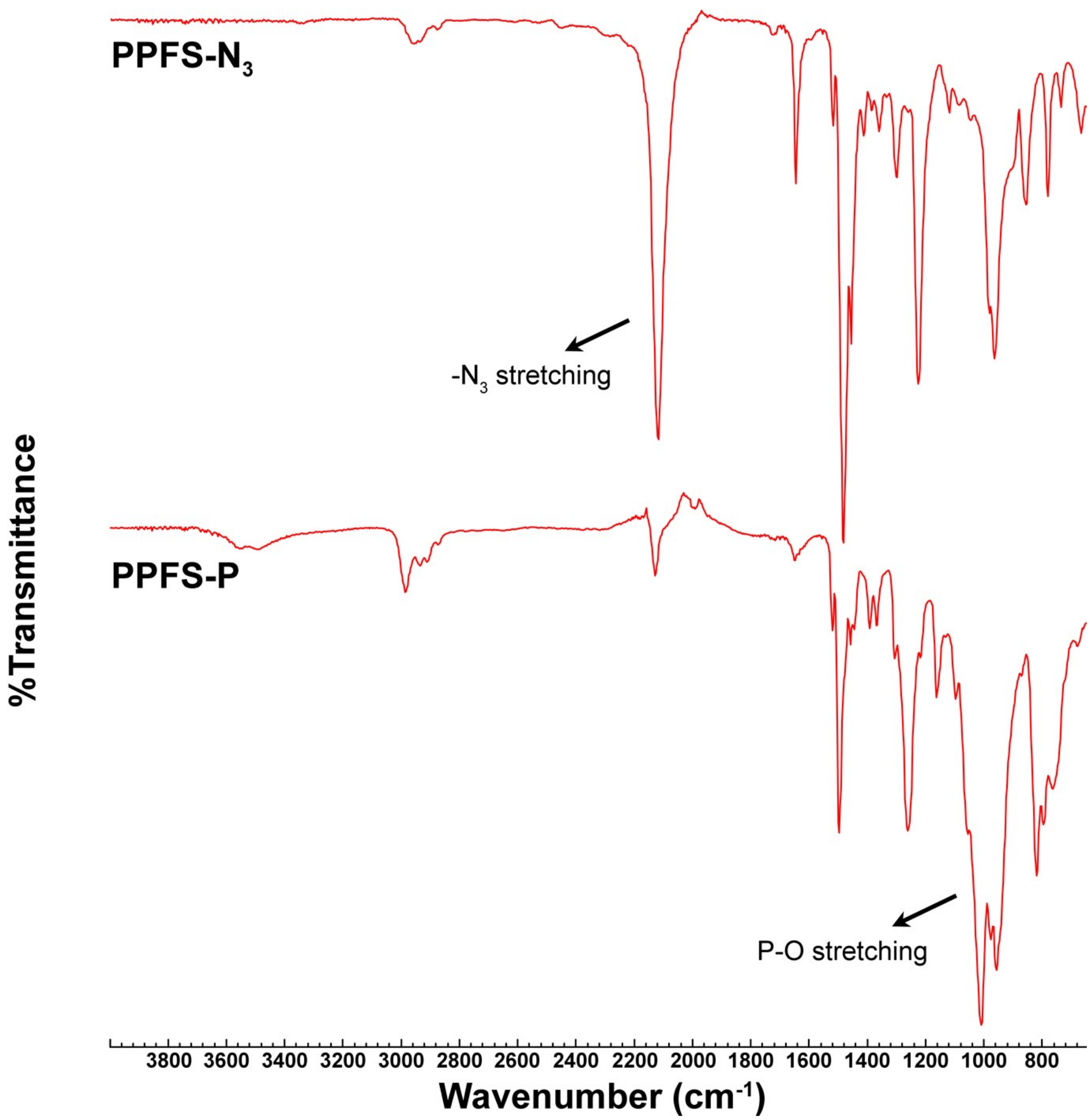


Figure S17. Overlaid FT-IR spectra of **PPFS-N_3** and **PPFS-P**.

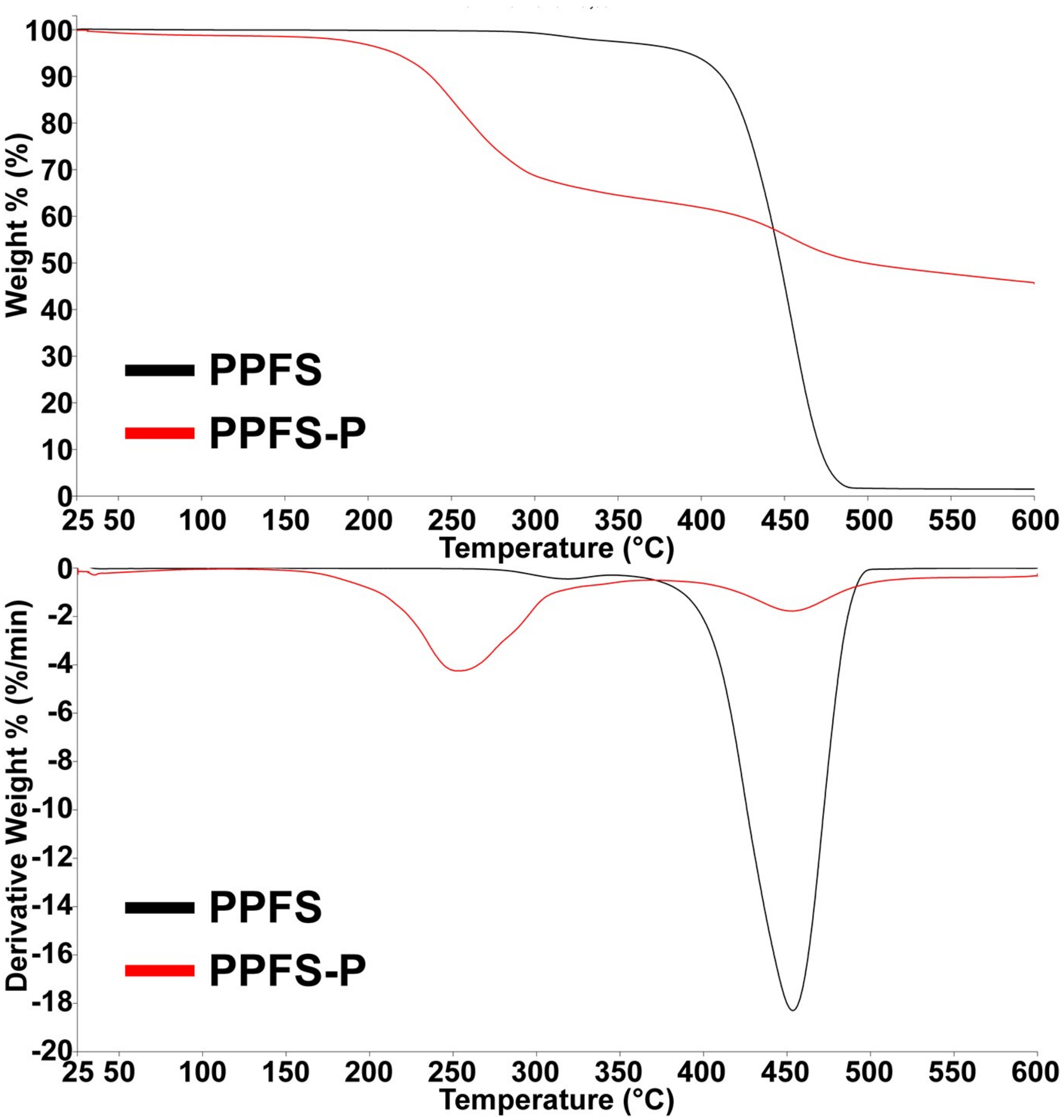


Figure S18. TGA curves of **PPFS** and **PPFS-P** (up), and their corresponding derivative curves (down) under nitrogen atmosphere.

Synthesis of azide-functionalized PE (PE-N_3)

1 (1.0 g, 4.92 mmol) and triethylamine (2.05 mL, 14.8 mmol) were dissolved in 10 mL of CH_2Cl_2 in a round bottom flask and placed in an ice bath. To this mixture, terephthaloyl chloride (999.1 mg, 4.92 mmol) was slowly added while stirring. After 1 h, formed orange solution was precipitated in excess MeOH. The dissolution-precipitation procedure (CH_2Cl_2-MeOH) was repeated two times. The obtained product was dried in a vacuum oven at 40 ^{o}C for 24 h to give yellow solid polymer (Yield = 0.9 g, 55%). ^{1}H NMR (CDCl$_3$, δ): 8.07 (m, 4H, Ar-*H*), 4.63 (m, 4H, OC*H*$_2$CC*H*$_2$O), 4.35 (t, 2H, C=OOC*H*$_2$CH$_2$N$_3$), 3.49 (t, 2H, C*H*$_2$N$_3$), 1.49 (s, 3H, CC*H*$_3$).

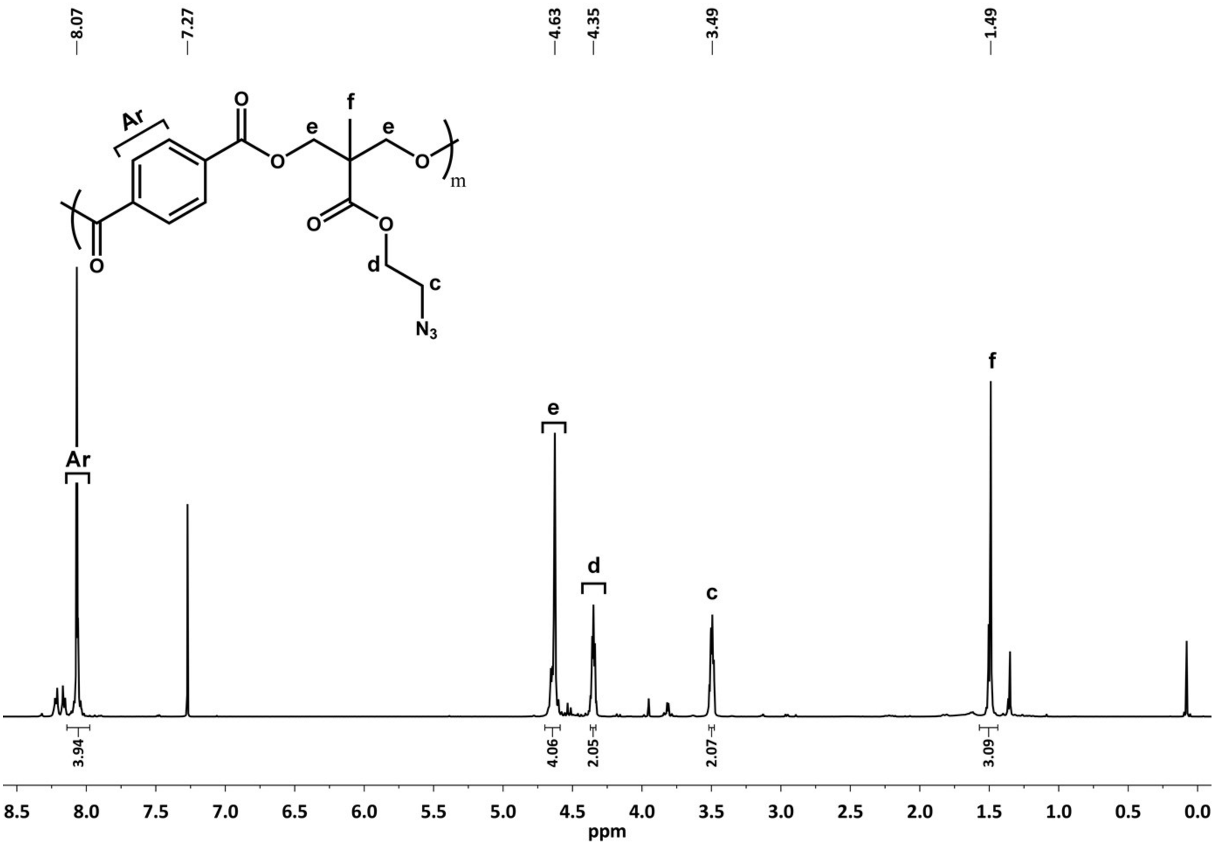


Figure S19. ^{1}H NMR spectrum of **PE-N$_3$** in CDCl$_3$ (500 MHz).

Phosphorylation of PE-N$_3$ (PE-P)

PE-N$_3$ (0.1 g, 0.3 mmol) was placed in a dried 25 mL Schlenk reaction tube with a magnetic stir bar and dissolved in 1 mL of MeTHF, and then bis(diethoxyphosphoryl)acetylene (178.9 mg, 0.6 mmol) was added to this solution. The mixture was degassed via two FPT cycles, placed into an oil bath thermostated at 80 °C, and stirred for 24 h. After the specified time, the reaction mixture was cooled to room temperature and precipitated into cold hexane. The crude polymer was dissolved in CHCl$_3$ and precipitated into cold hexane one more time and the solvent was decanted. The polymer was finally dried in a vacuum oven for 24 h to give yellow solid polymer (Yield = 151 mg, 80%). ^{1}H NMR (CDCl$_3$, δ): 8.06 (m, 4H, Ar-*H*), 5.07 (s, 2H, OCH$_2$C*H*$_2$N), 4.67 (s, 2H, OC*H*$_2$CH$_2$N), 4.55 (m, 4H, OC*H*$_2$CC*H*$_2$O), 4.25 (m, 8H, P=OOC*H*$_2$CH$_3$), 1.37 (m, 15H, P=OOCH$_2$C*H*$_3$ & CC*H*$_3$). ^{13}C NMR (CDCl$_3$, *δ*): 173.61, 172.09, 164.94, 144.02, 133.58, 131.83, 129.72, 65.95, 64.40, 63.45, 49.91, 48.91, 46.76, 17.77, 16.23. ^{31}P NMR (CDCl$_3$, δ): 5.56, 1.85.

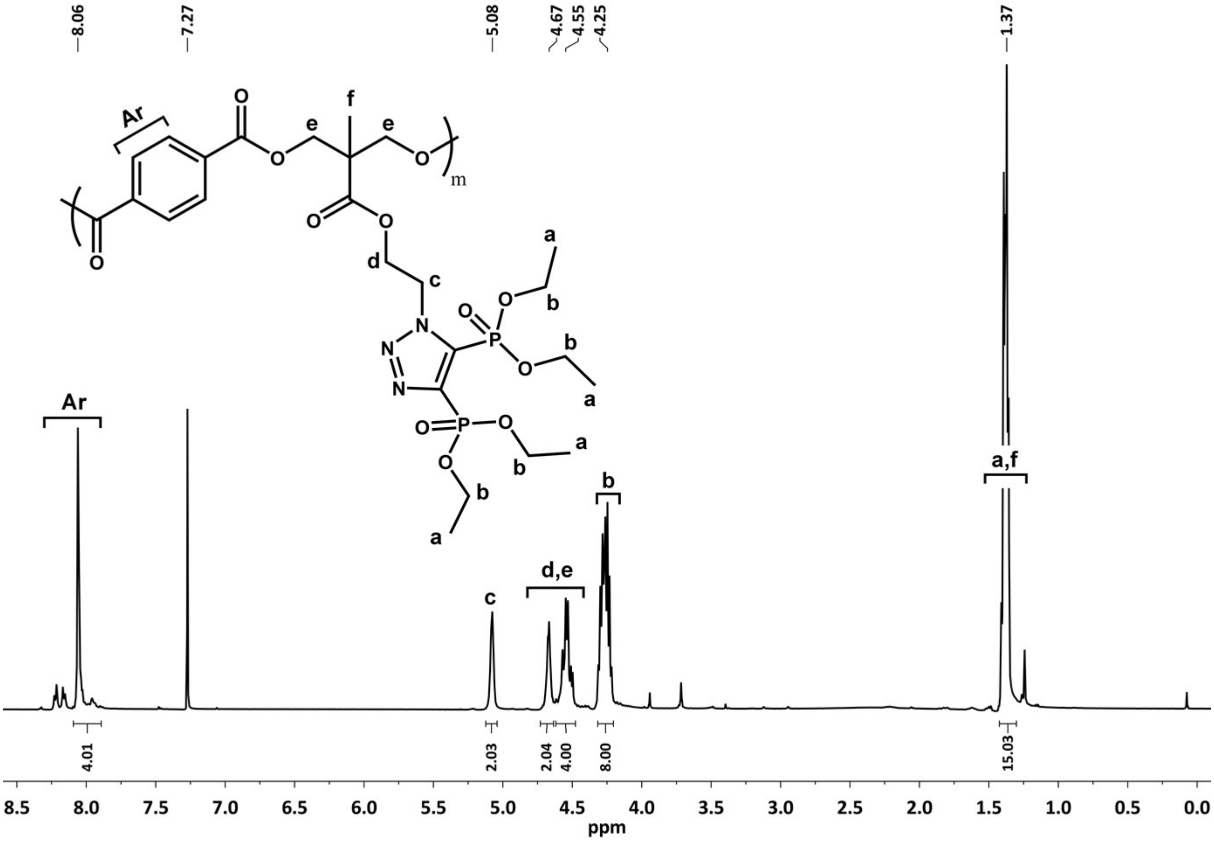


Figure S20. ^{1}H NMR spectrum of **PE-P** in $CDCl_3$ (500 MHz).

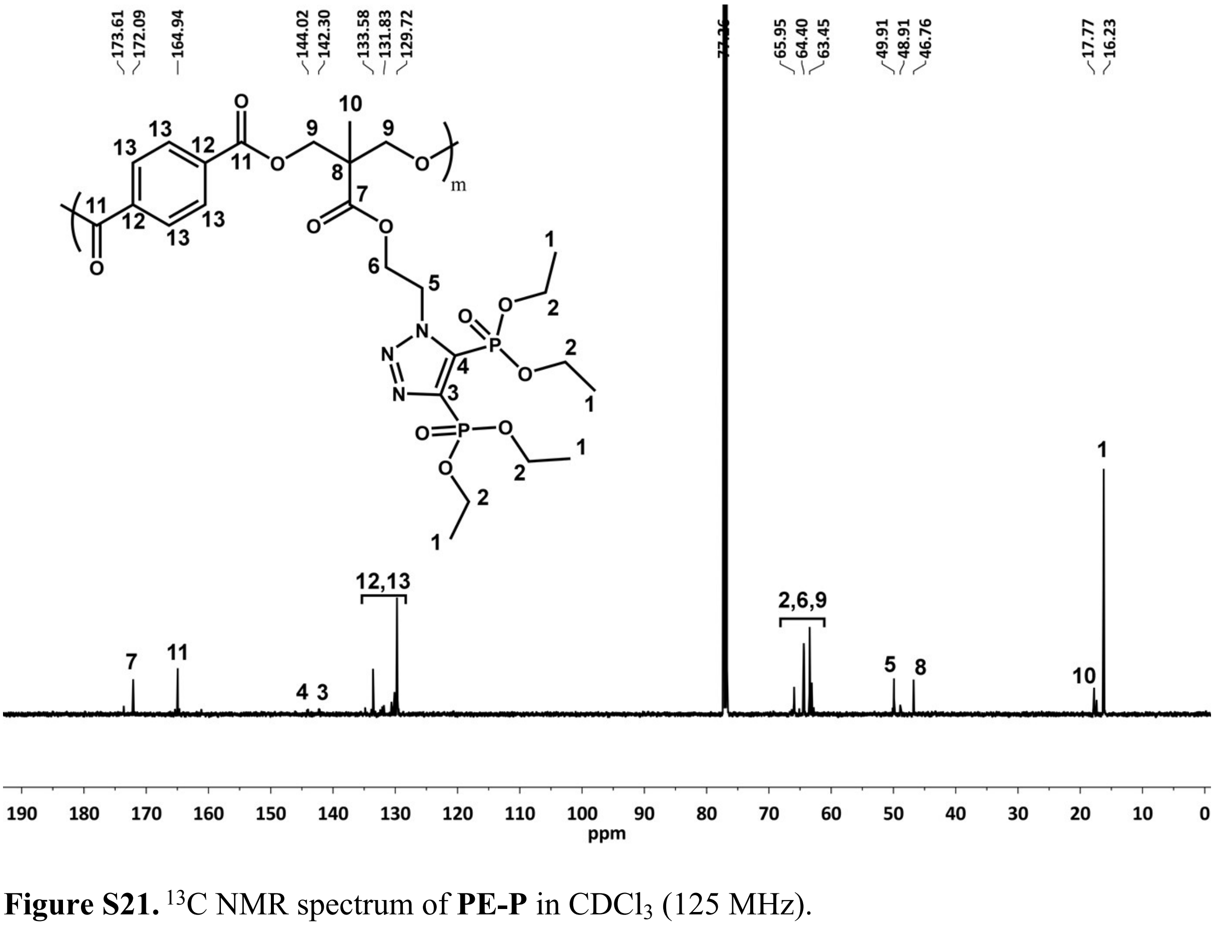


Figure S21. ^{13}C NMR spectrum of **PE-P** in $CDCl_3$ (125 MHz).

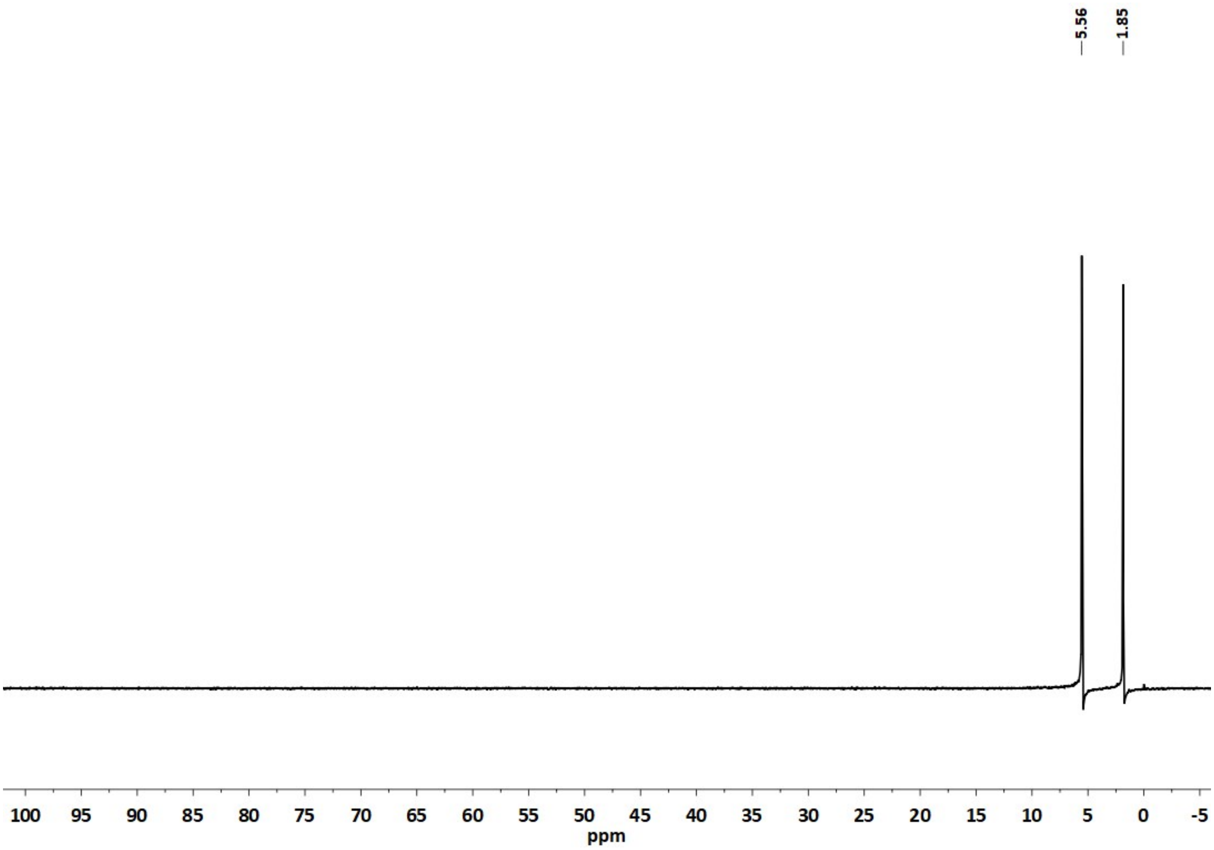


Figure S22. ^{31}P NMR spectrum of **PE-P** in CDCl$_3$ (202 MHz).

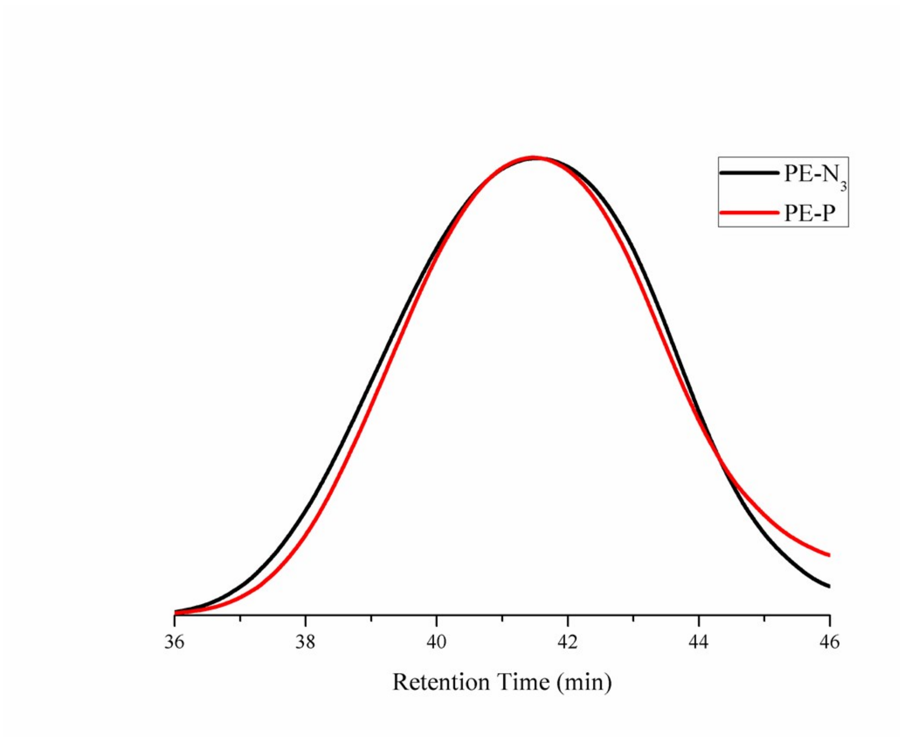


Figure S23. Overlaid GPC traces of **PE-N$_3$** (black) and **PE-P** (red) in THF.

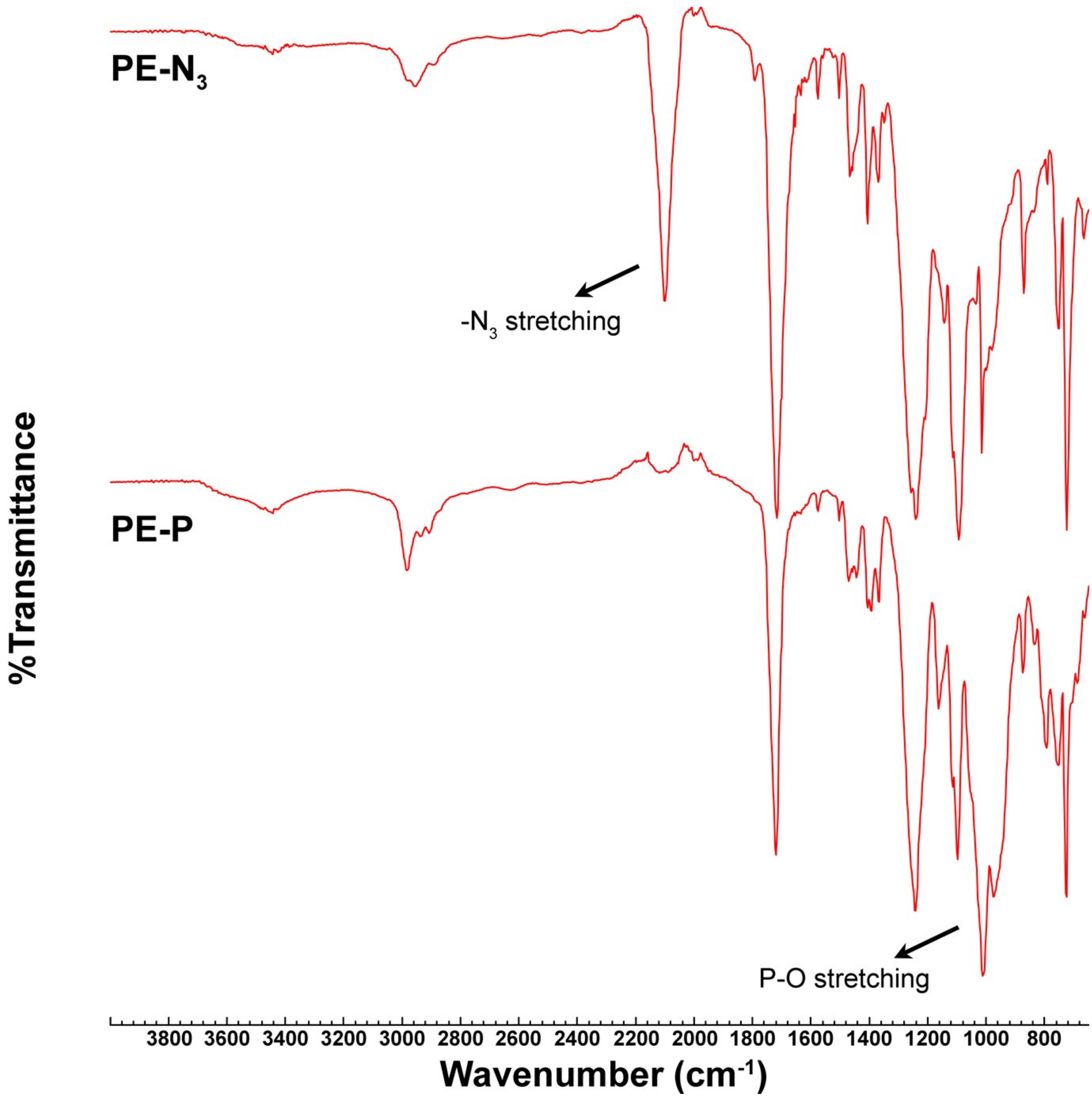


Figure S24. Overlaid FT-IR spectra of **PE-N$_3$** and **PE-P**.

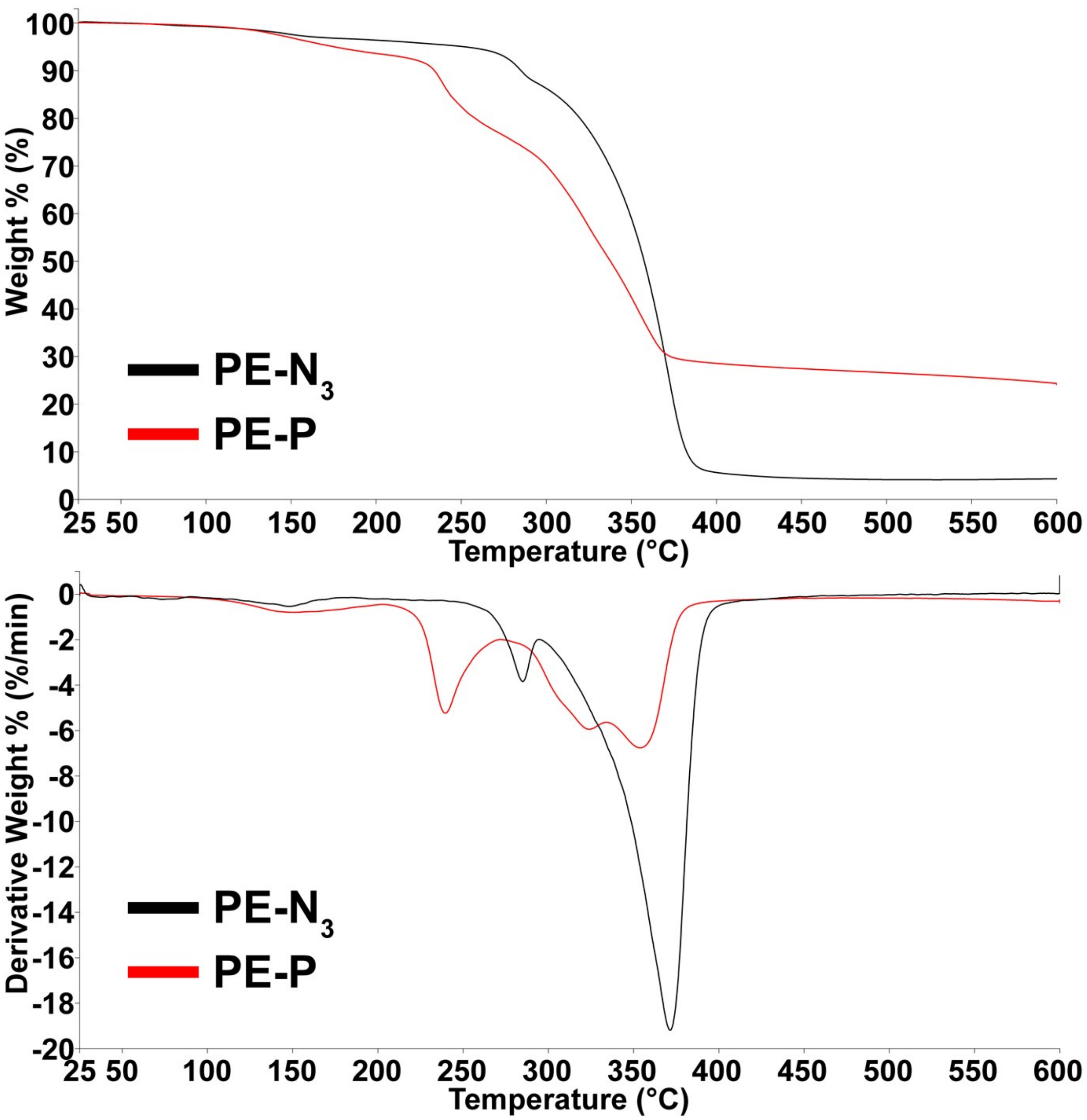


Figure S25. TGA curves of **PE** and **PE-P** (up), and their corresponding derivative curves (down) under nitrogen atmosphere.

Synthesis of azide-functionalized PU (PU-N_3)

HMDI (434.6 mg, 2.58 mmol) was placed in a dried Schlenk tube with a magnetic stir bar and dissolved in 4 mL of DMF. **1** (525 mg, 2.58 mmol) and a few drops of dibutyltin dilaurate was also added to the mixture then the flask was capped. After degassing via three FPT cycles, the tube was placed in an oil bath thermostated at 50 ^{o}C, and stirred for 24 h. After the specified time, the solution was precipitated into MeOH. The crude polymer was dissolved in $CHCl_3$ and precipitated into MeOH one more time. The purified polymer was finally dried in a vacuum oven for 24 h to give transparent viscous polymer (Yield = 0.72 g, 75%). ^{1}H NMR ($CDCl_3$, δ):

5.00 (br, 2H, N*H*), 4.29-4.21 (m, 6H, C*H*$_2$CH$_2$N$_3$ & CC*H*$_2$), 3.49 (m, 2H, CH$_2$C*H*$_2$N$_3$), 3.15 (m, 4H, C=ONHC*H*$_2$), 1.49 (s, 4H, NHCH$_2$C*H*$_2$CH$_2$), 1.32-1.25 (m, 7H, CC*H*$_3$ & NHCH$_2$CH$_2$C*H*$_2$C*H*$_2$).

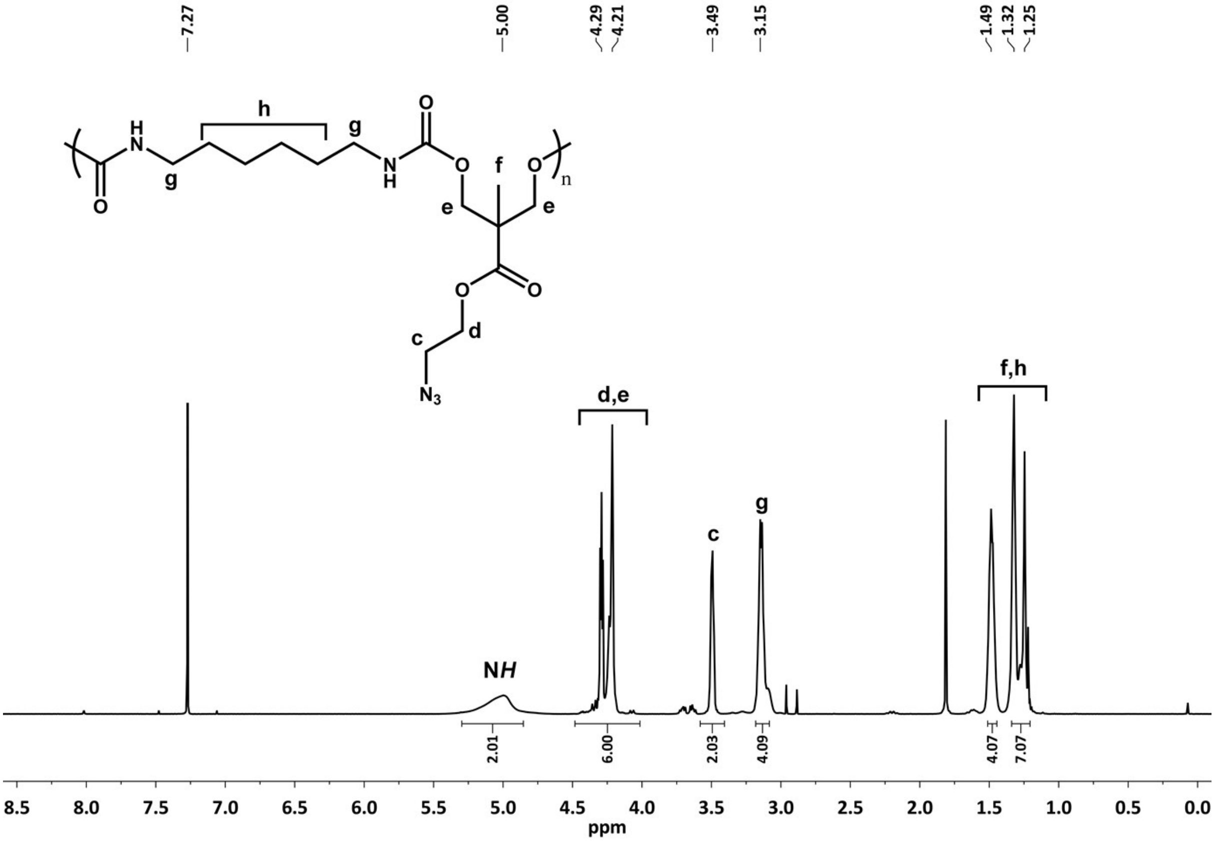


Figure S26. ^{1}H NMR spectrum of **PU-N$_3$** in CDCl$_3$ (500 MHz).

Phosphorylation of PU-N$_3$ (PU-P)

PU-N$_3$ (0.1 g, 0.27 mmol) was placed in a dried 25 mL Schlenk tube with a magnetic stir bar and dissolved in 1 mL of MeTHF, and then bis(diethoxyphosphoryl)acetylene (160.6 mg, 0.54 mmol) was added to this solution. The mixture was degassed via two FPT cycles, placed into an oil bath thermostated at 80 °C, and stirred for 24 h. After the specified time, the reaction mixture was cooled to room temperature and precipitated into cold hexane. The crude polymer was dissolved in CHCl$_3$ and precipitated into cold hexane one more time and the solvent was decanted. The polymer was finally dried in a vacuum oven for 24 h to give viscous transparent polymer (Yield = 139 mg, 77%). ^{1}H NMR (CDCl$_3$, δ): 5.42 (br, 2H, N*H*), 5.04 (s, 2H, OCH$_2$C*H*$_2$N), 4.64 (s, 2H, OC*H*$_2$CH$_2$N), 4.28 (m, 12H, P=OOC*H*$_2$CH$_3$ & OC*H*$_2$CC*H*$_2$O), 3.13 (s, 4H, NHC*H*$_2$), 1.49-1.12 (m, 23H, CC*H*$_3$, P=OOCH$_2$C*H*$_3$ & NHCH$_2$C*H*$_2$C*H*$_2$). ^{13}C NMR (CDCl$_3$, *δ*): 172.87, 156.15, 143.94, 142.08, 131.77, 130.06, 89.42, 86.96, 65.63, 64.33, 63.39, 62.47, 53.43, 50.38, 48.95, 47.06, 40.89, 29.74, 26.33, 17.31, 16.22. ^{31}P NMR ($CDCl_3$, δ): 5.61, 1.82.

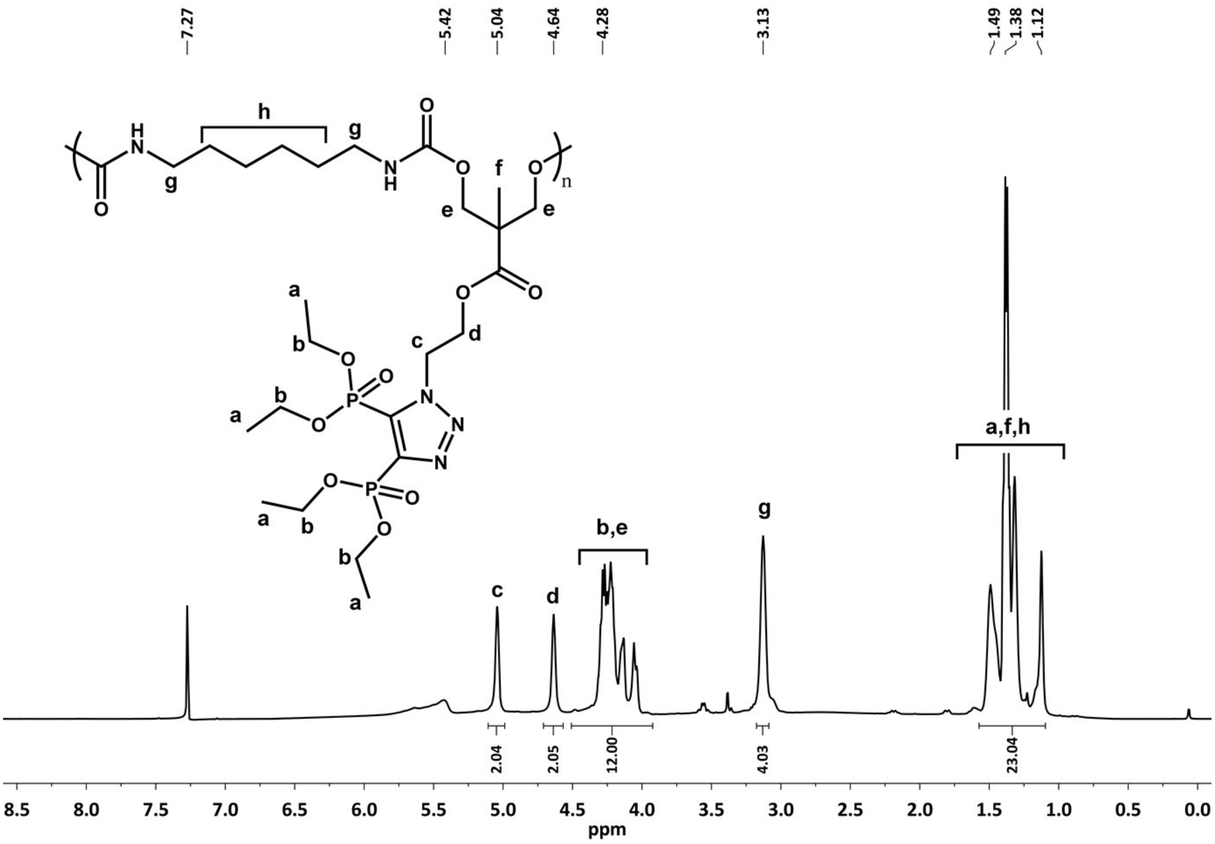


Figure S27. ^{1}H NMR spectrum of **PU-P** in $CDCl_3$ (500 MHz).

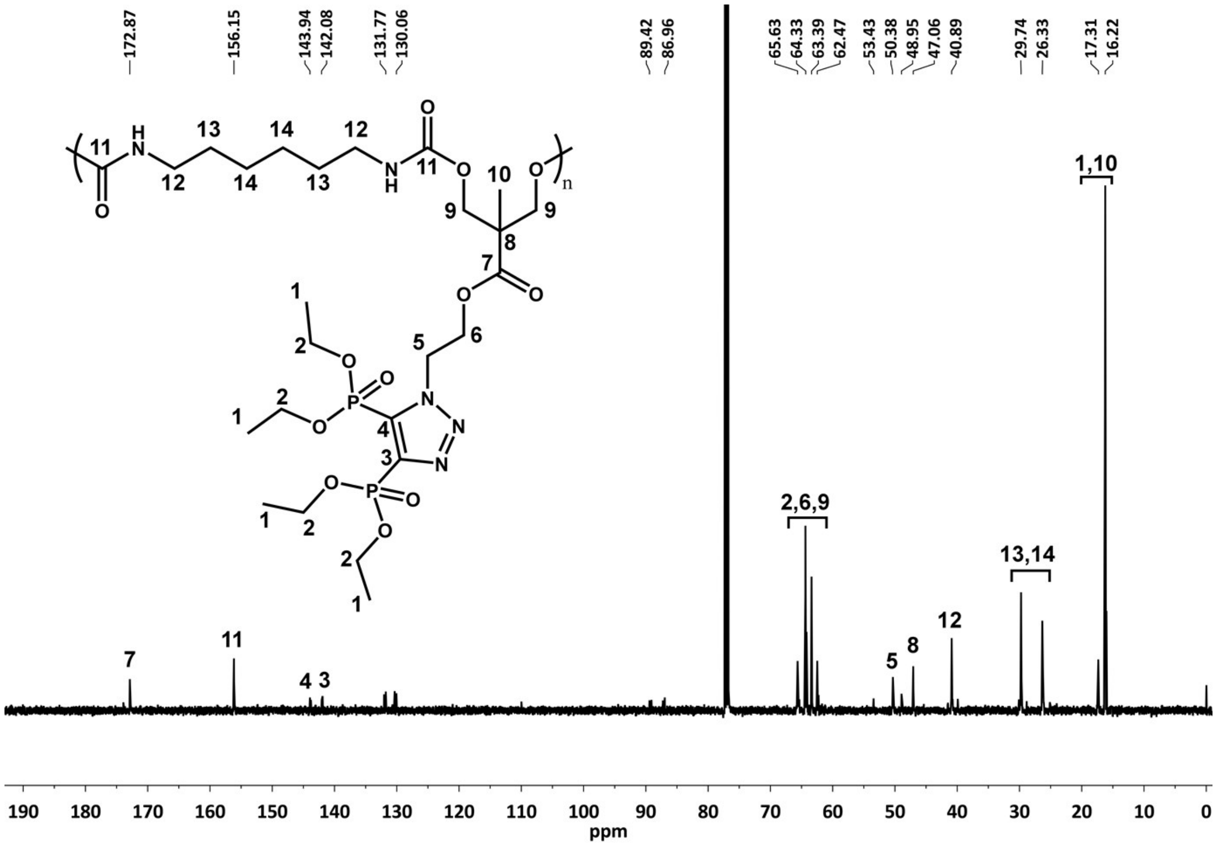


Figure S28. ^{13}C NMR spectrum of **PU-P** in $CDCl_3$ (125 MHz).

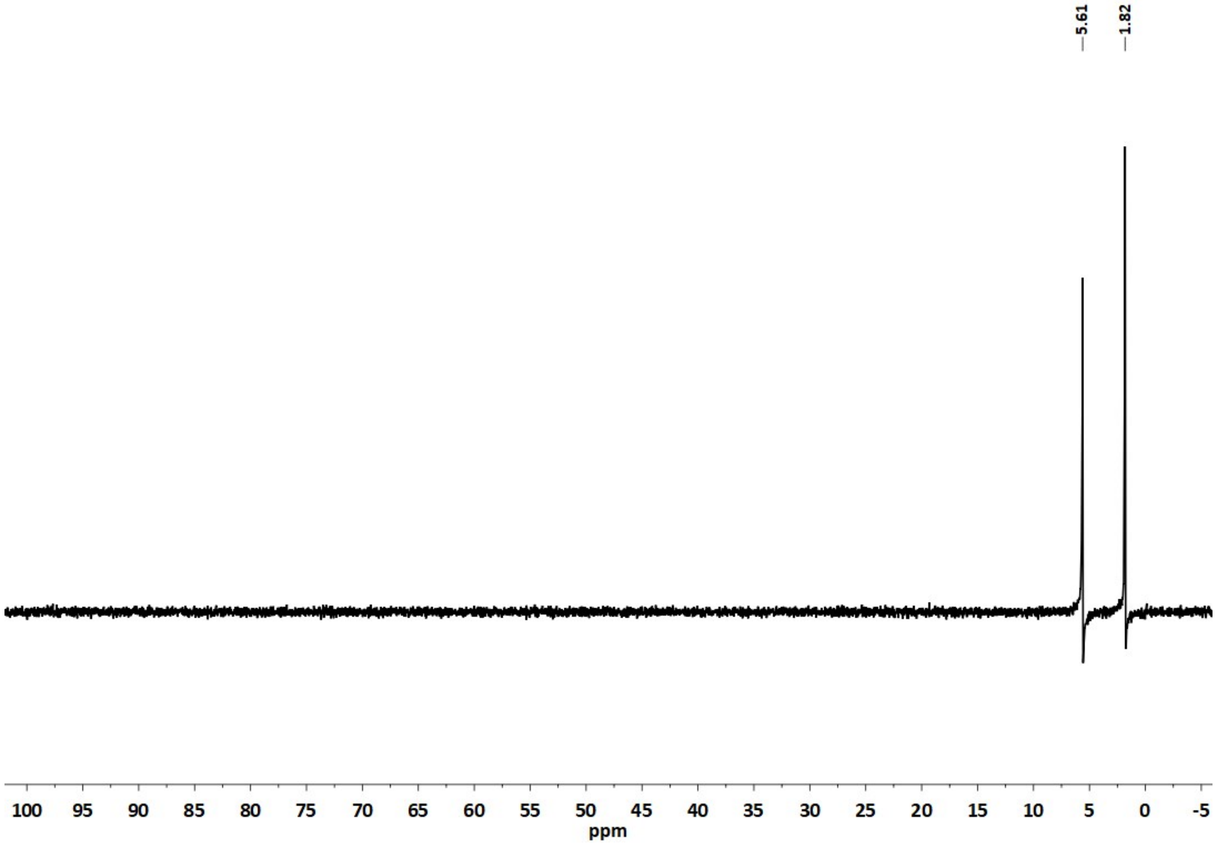


Figure S29. ^{31}P NMR spectrum of **PU-P** in $CDCl_3$ (202 MHz).

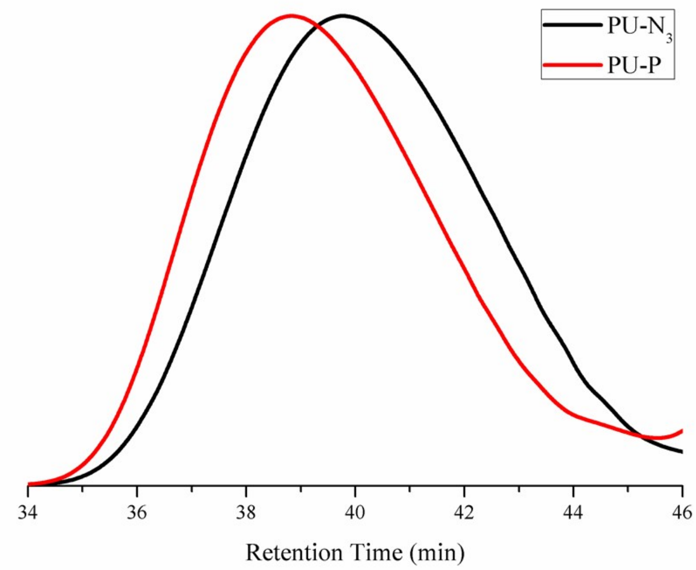


Figure S30. Overlaid GPC traces of **PU-N_3** (black) and **PU-P** (red) in THF.

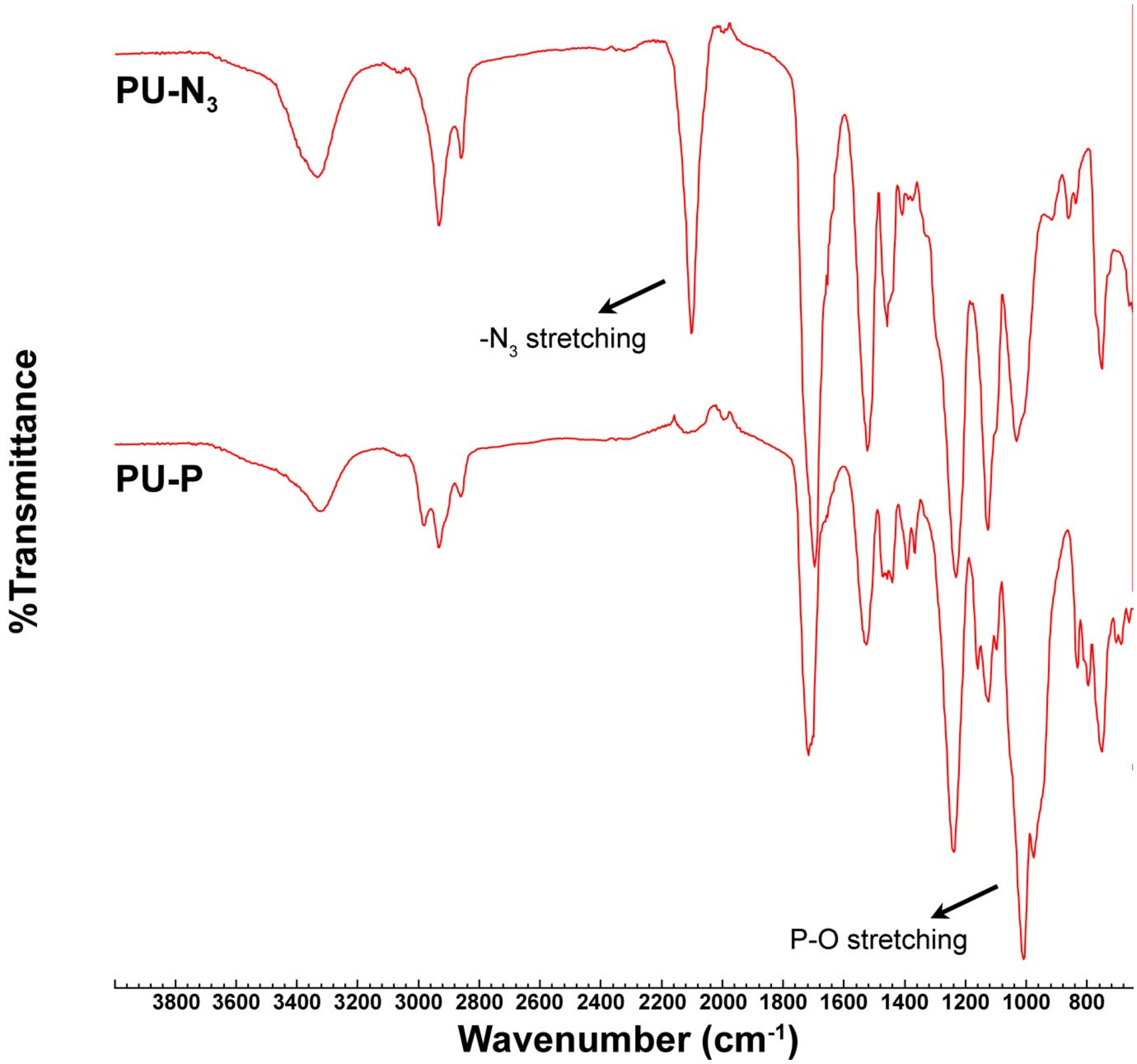


Figure S31. Overlaid FT-IR spectra of **PU-N_3** and **PU-P**.

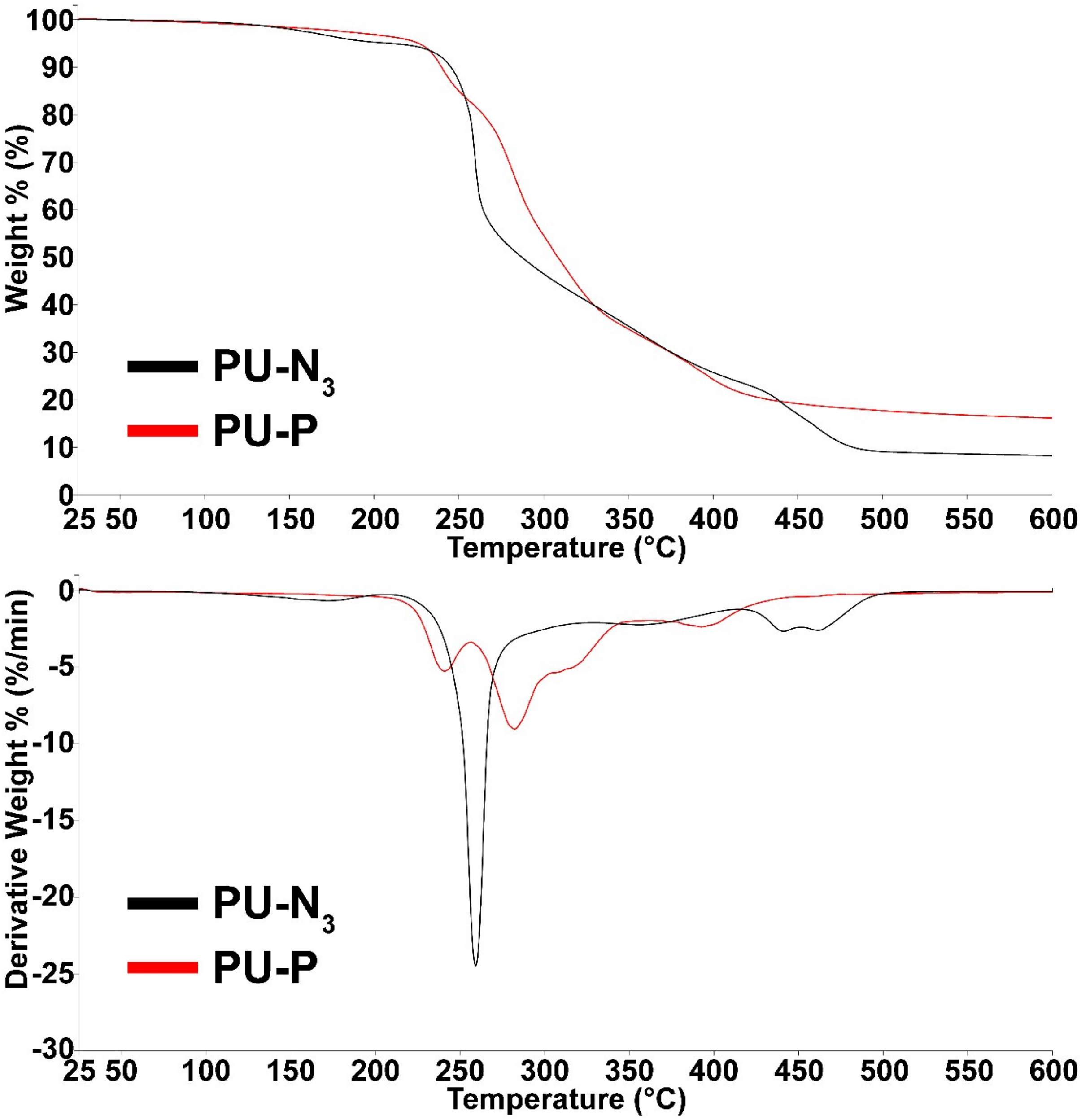


Figure S32. TGA curves of **PU** and **PU-P** (up), and their corresponding derivative curves (down) under nitrogen atmosphere.

Synthesis of azide-functionalized PC (PC-N_3)

2 (1.12 g, 4.88 mmol) was added to a 25 mL Schlenk tube with a magnetic stir bar and dissolved in 5 mL of CH_2Cl_2. Benzyl alcohol (10.2 μL, 0.097 mmol) and DBU (14.5 μL, 0.097 mmol) were also added in that order then the flask was capped. After degassing via three FPT cycles, the tube was placed in an oil bath thermostated at 40 °C, and stirred for 14 h. After the specified time, the solution was concentrated by evaporation and precipitated into MeOH. The dissolution-precipitation procedure (CH_2Cl_2-MeOH) was repeated two times. The purified polymer was finally dried in a vacuum oven for 24 h to give transparent viscous polymer (Yield: 340 mg, 30.4%). ^{1}H NMR (CDCl$_3$, δ): 7.38 (m, Ar*H*), 4.32 (m, 6H, OC*H*$_2$), 3.49 (m, 2H, C*H*$_2$N$_3$), 1.31 (m, 3H, CC*H*$_3$).

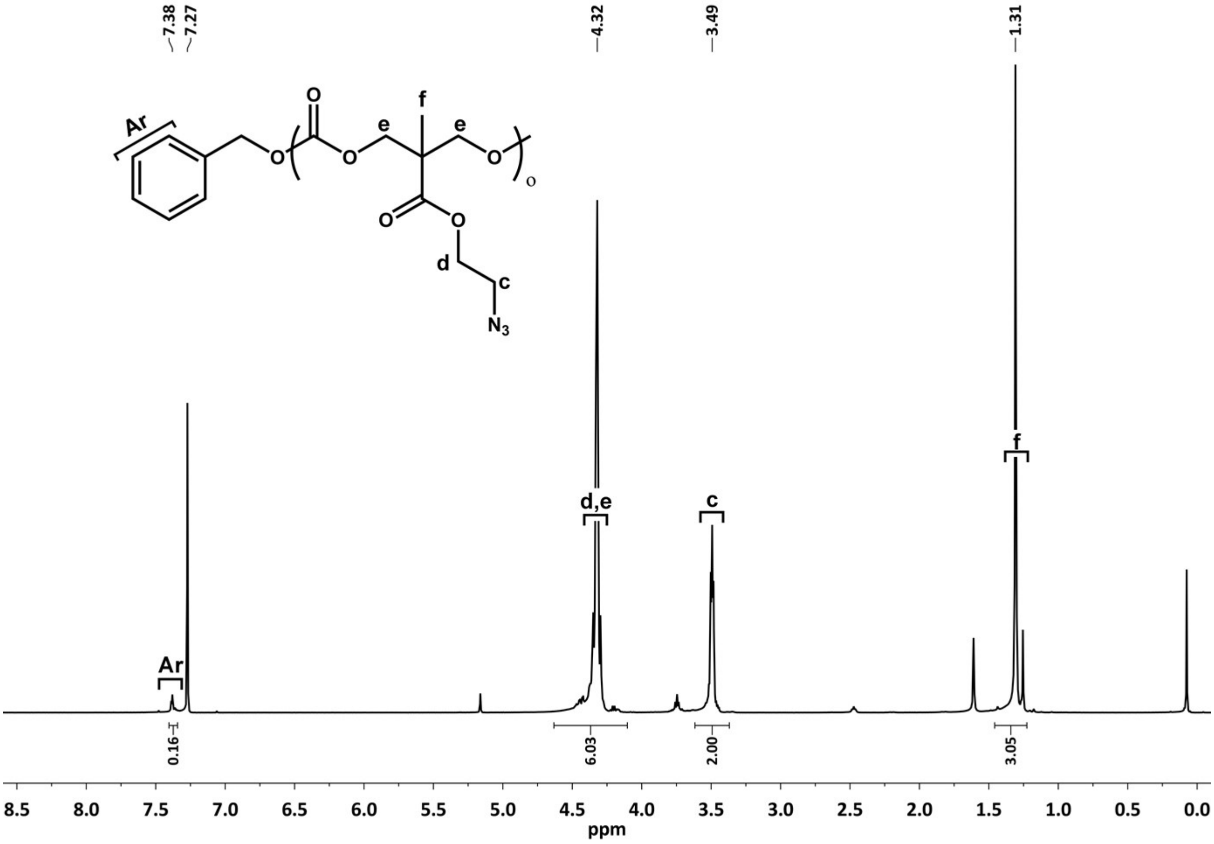


Figure S33. ^{1}H NMR spectrum of **PC-N$_3$** in CDCl$_3$ (500 MHz).

Phosphorylation of PC-N$_3$ (PC-P)

PC-N$_3$ (0.1 g, 0.438 mmol) was placed in a dried 25 mL Schlenk tube with a magnetic stir bar and dissolved in 1 mL of MeTHF, and then bis(diethoxyphosphoryl)acetylene (261 mg, 0.876 mmol) was added to this solution. The mixture was degassed via two FPT cycles, placed into an oil bath thermostated at 80 °C, and stirred for 24 h. After the specified time, the reaction mixture was cooled to room temperature and precipitated into cold hexane. The crude polymer was dissolved in CHCl$_3$ and precipitated into cold hexane one more time and the solvent was decanted. The purified polymer was finally dried in a vacuum oven for 24 h (Yield: 160 mg, 69.3%). ^{1}H NMR (CDCl$_3$, δ): 7.38 (m, Ar*H*) 5.05 (m, 2H, NC*H*$_2$), 4.61 (m, 2H, NCH$_2$C*H*$_2$), 4.25 (m, 12H, CC*H*$_2$ & P=OOC*H*$_2$), 1.38 (m, 12H, P=OOCH$_2$C*H*$_3$), 1.19 (s, 3H, CC*H*$_3$). ^{13}C NMR (CDCl$_3$, *δ*): 173.41, 171.62, 154.57, 154.25, 143.91, 142.03, 132.09, 130.11, 128.57, 68.42, 64.36, 63.45, 63.01, 49.88, 48.57, 46.50, 17.15, 16.24. ^{31}P NMR (CDCl$_3$, δ): 5.66, 1.88.

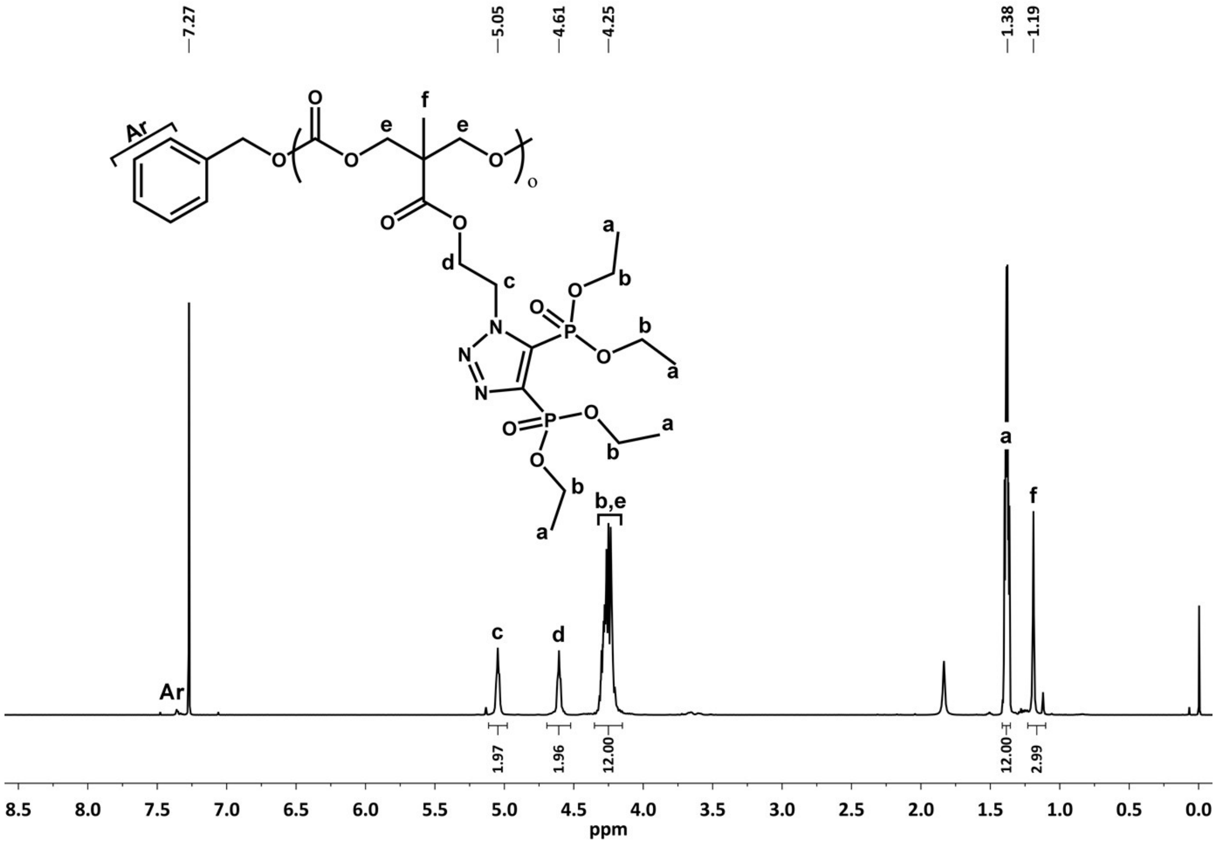


Figure S34. ^{1}H NMR spectrum of **PC-P** in $CDCl_3$ (500 MHz).

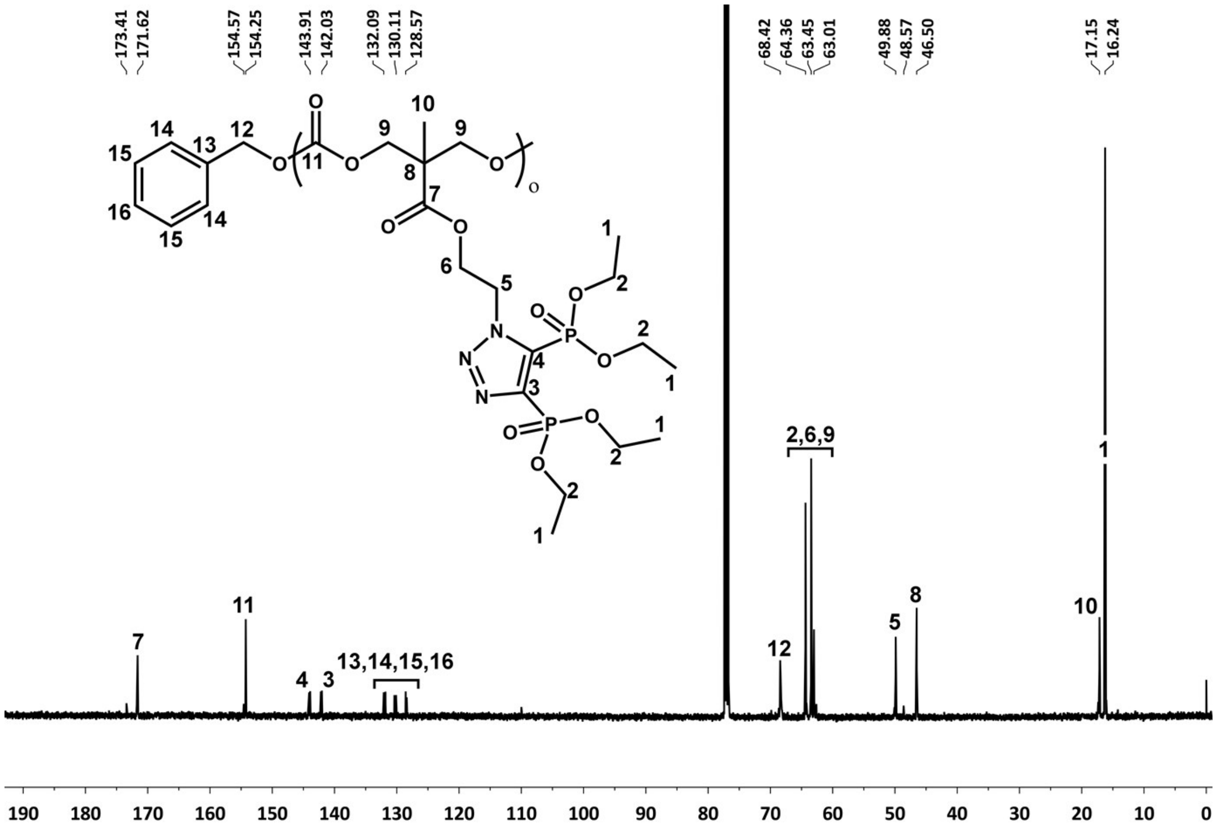


Figure S35. ^{13}C NMR spectrum of **PC-P** in $CDCl_3$ (125 MHz).

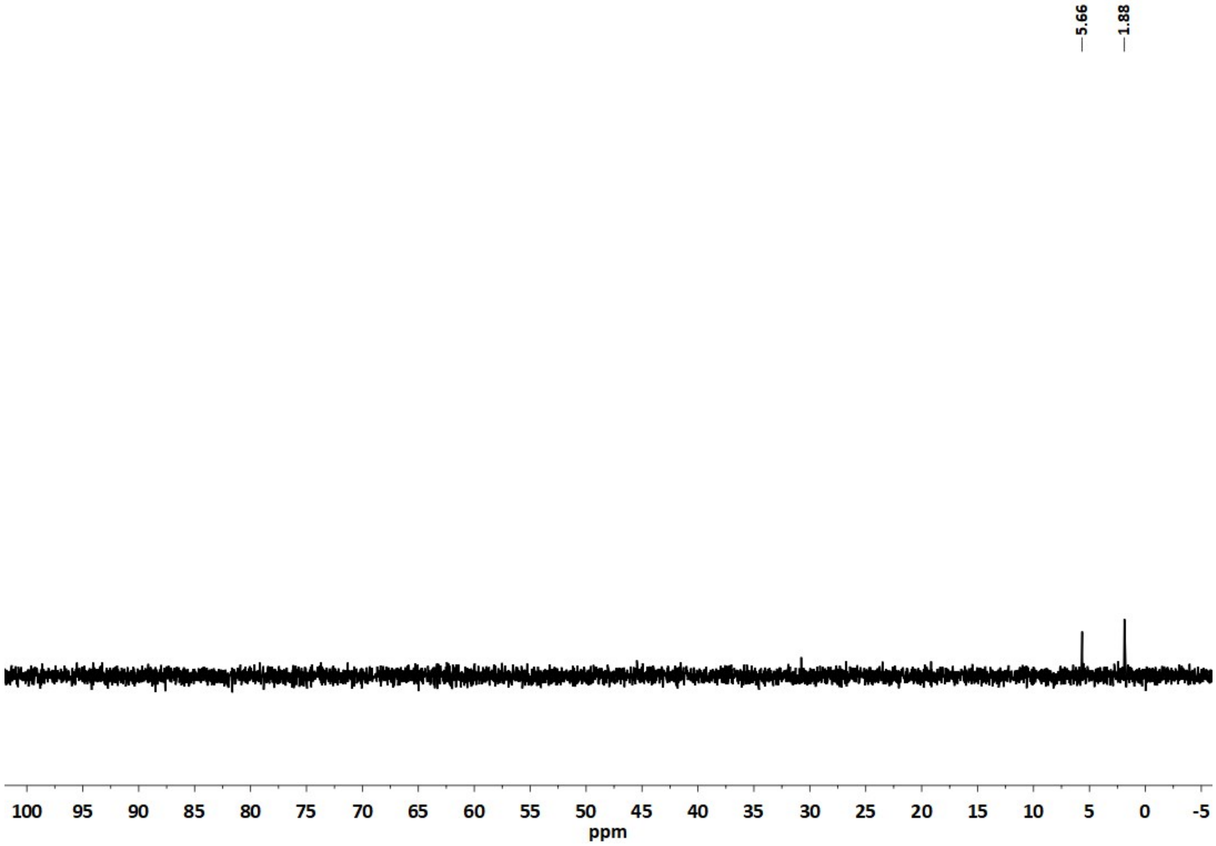


Figure S36. ^{31}P NMR spectrum of **PC-P** in $CDCl_3$ (202 MHz).

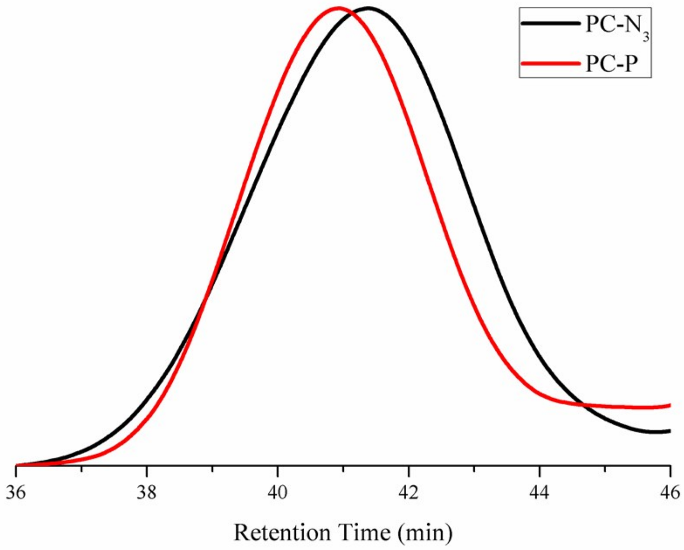


Figure S37. Overlaid GPC traces of **PC-N_3** (black) and **PC-P** (red) in THF.

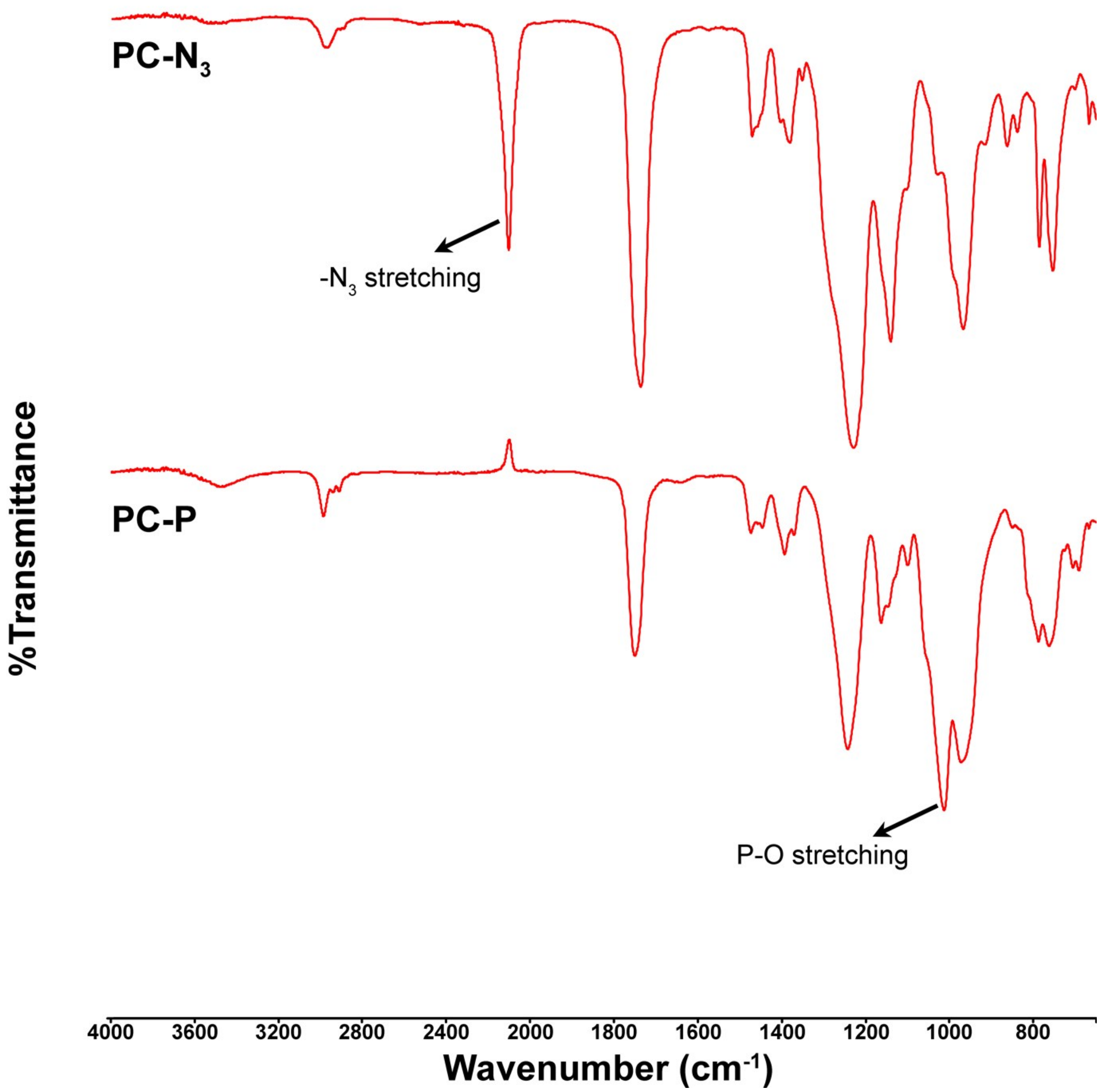


Figure S38. Overlaid FT-IR spectra of **PC-N$_3$** and **PC-P**.

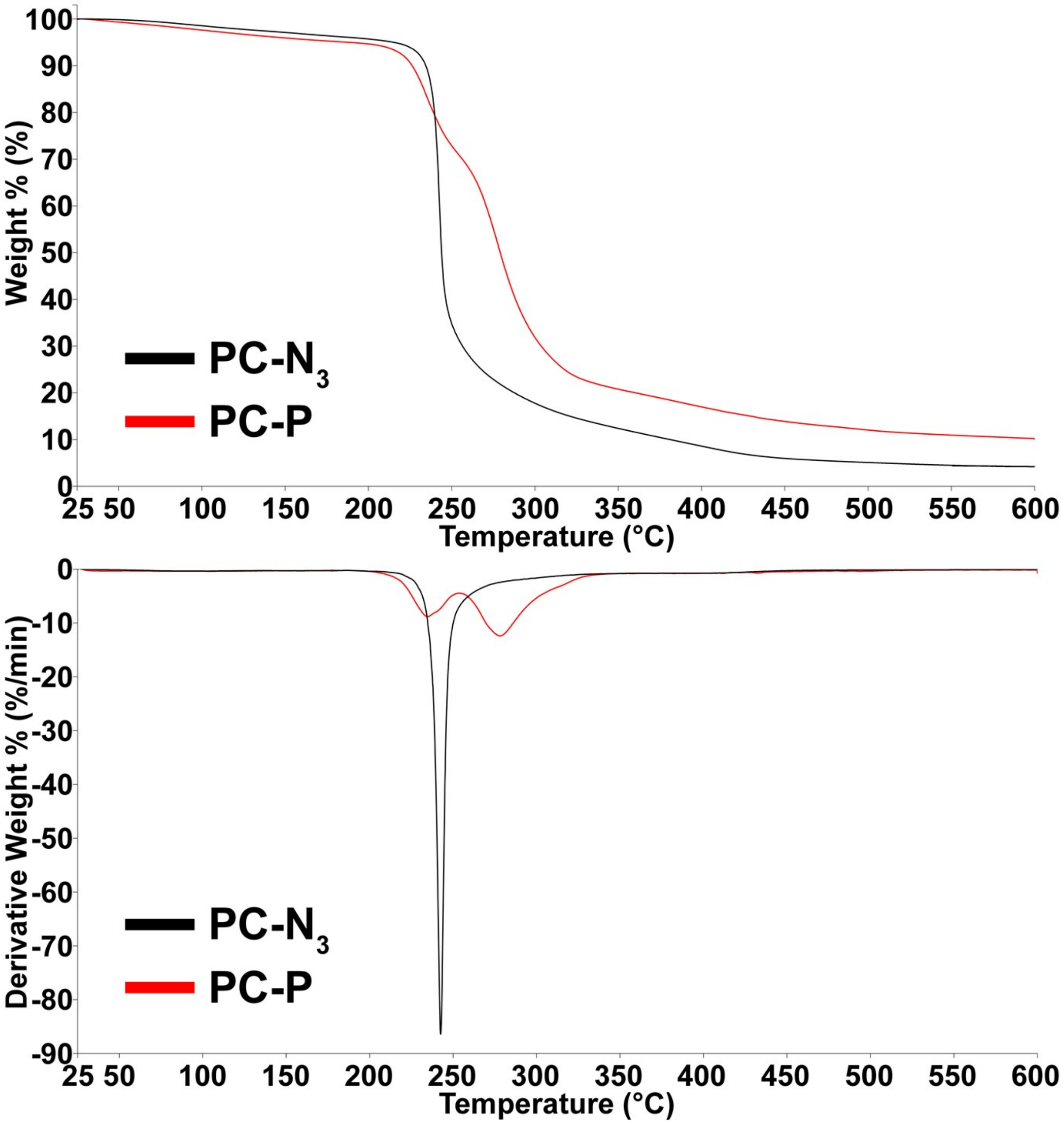


Figure S39. TGA curves of **PC** and **PC-P** (up), and their corresponding derivative curves (down) under nitrogen atmosphere.

Synthesis of azide-functionalized PVC (PVC-N_3)

The azidation of PVC was carried out according to previously published procedure (see ref. 48 in the main text) (Yield: 1.81g, 85%). ^{1}H NMR ($CDCl_3$, δ): 4.61-3.45 (m, 2H, C*H*Cl & C*H*N_3) 2.09-1.28 (m, 4H, CClHC*H*$_2$ & CN_3C*H*$_2$).

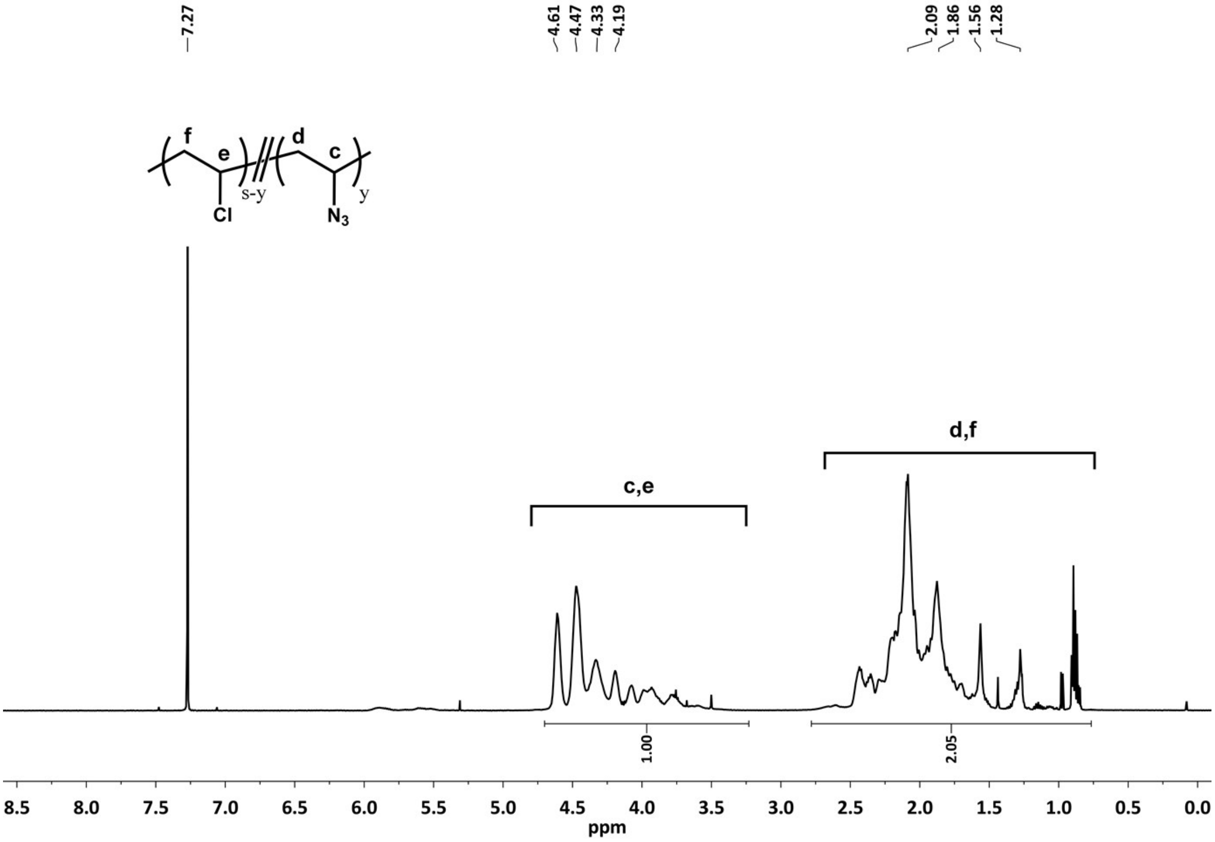
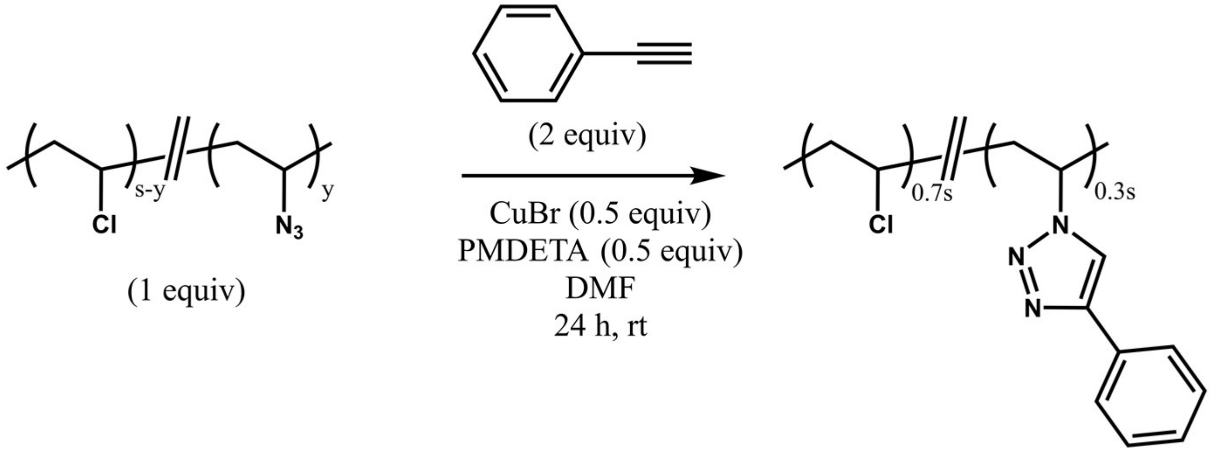


Figure S40. ^{1}H NMR spectrum of **PVC-N$_3$** in CDCl$_3$ (500 MHz).

Model reaction of PVC-N$_3$ with phenylacetylene



Scheme S2. Schematic representation of the model reaction between **PVC-N$_3$** and phenylacetylene.

PVC-N$_3$ (0.1 g, 1.60 mmol) was placed in a dried 25 mL Schlenk tube with a magnetic stir bar and dissolved in 1 mL of DMF. Phenylacetylene (327 mg, 3.20 mmol), PMDETA (0.167 mL, 0.80 mmol) and CuBr (120 mg, 0.80 mmol) were also added respectively. After degassing via three FPT cycles, the solution was left to stir at room temperature for 24 h. Afterwards, the solution was diluted with THF and passed through a short column of neutral alumina for the removal of copper salts. Excess solvent was evaporated under vacuum and the remaining solution was precipitated into MeOH. The dissolution-precipitation procedure (THF-MeOH) was repeated two times. According to ^{1}H NMR analysis, the azidation efficiency was calculated to be 30% (Yield: 65 mg, 45%).^{1}H NMR (DMSO-d6, δ): 8.77-8.11 (m, 3H, CC*H*N), 7.82-7.32 (m, 15H, Ar*H*), 5.16-3.57 (m, 10H, ClC*H* & N_3C*H*), 2.91-1.83 (br, 20H, ClCHCH_2 & NCHCH_2).

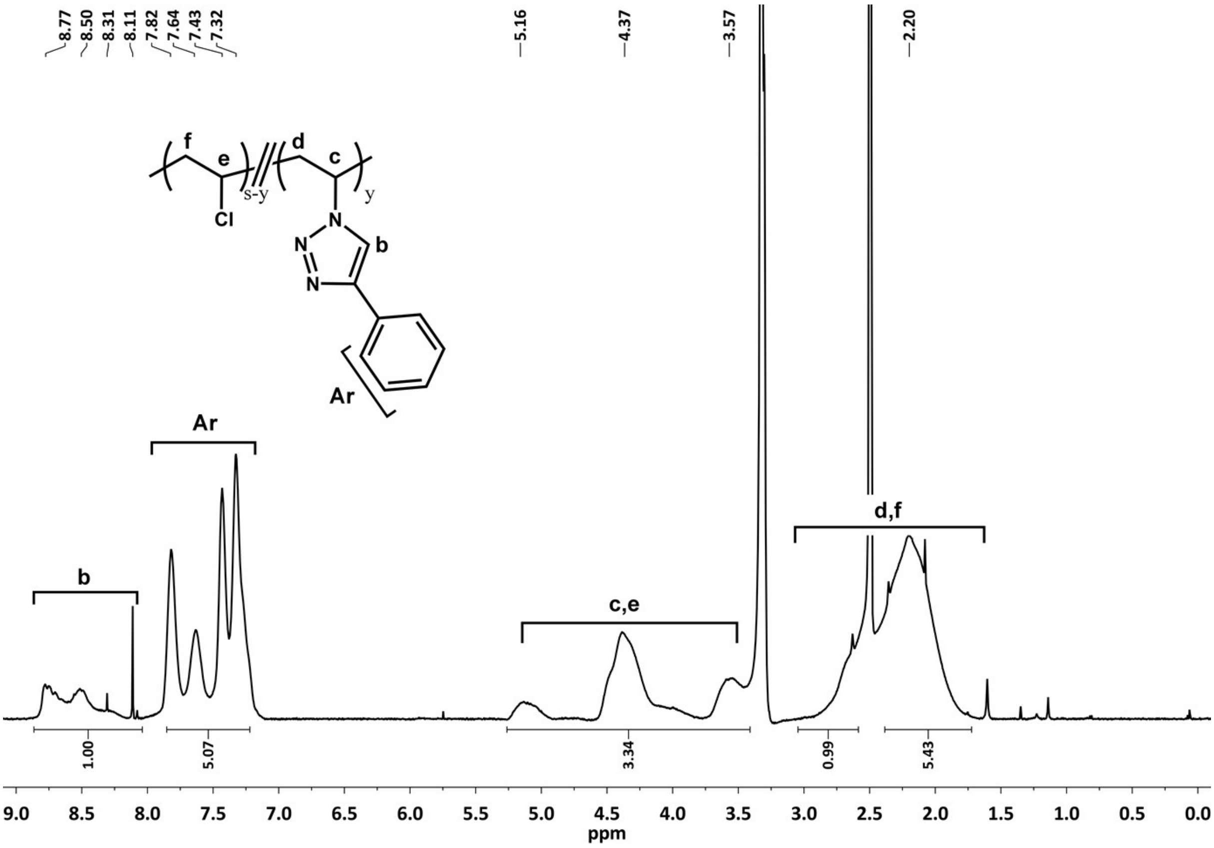


Figure S41. ^{1}H NMR spectrum (in d-DMSO) of the resulting polymer obtained from the model reaction between **PVC-N$_3$** and phenylacetylene (500 MHz).

Phosphorylation of PVC-N$_3$ (PVC-P)

PVC-N$_3$ (0.1 g, 0.47 mmol) was placed in a dried 25 mL Schlenk tube with a magnetic stir bar and dissolved in 1 mL of MeTHF, and then bis(diethoxyphosphoryl)acetylene (281.6 mg, 0.94 mmol) was added to this solution. The mixture was degassed via two FPT cycles, placed into an oil bath thermostated at 80 °C, and stirred for 24 h. After the specified time, the reaction mixture was cooled to room temperature and precipitated into cold hexane. The crude polymer was dissolved in $CHCl_3$ and precipitated into cold hexane one more time and the solvent was decanted. The purified polymer was finally dried in a vacuum oven for 24 h (Yield: 202 mg, 84%). ^{1}H NMR (CDCl$_3$, δ): 5.98 (br, 1H, NC*H*), 4.26 (br, 12H, P-OC*H*$_2$ & ClC*H*), 2.72-1.79 (br, 10H, ClCHC*H*$_2$ & NCHC*H*$_2$) 1.38 (s, 12H, P=OOCH$_2$C*H*$_3$). ^{13}C NMR (CDCl$_3$, *δ*): 143.71, 141.08, 64.20, 63.49, 56.88, 55.82, 46.84, 44.53, 16.29. ^{31}P NMR (CDCl$_3$, δ): 5.86, 1.91.

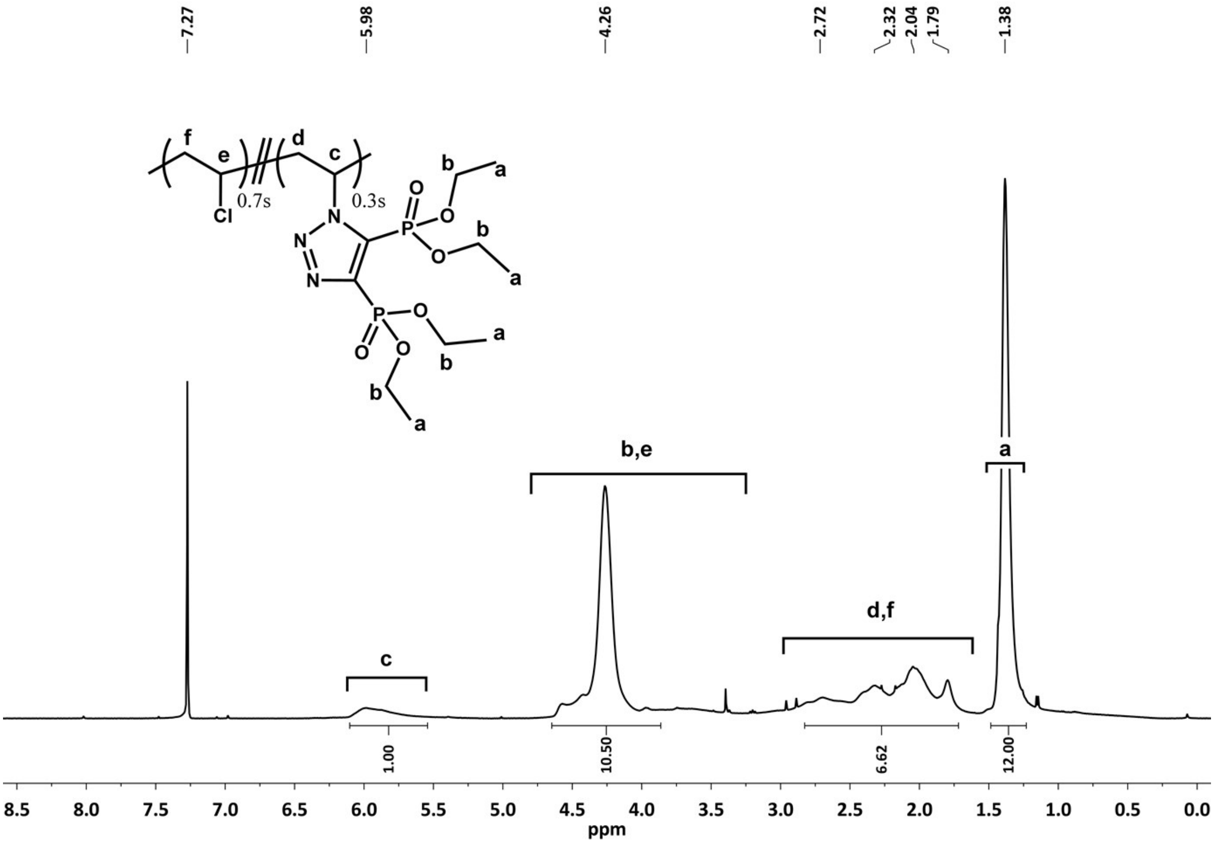


Figure S42. ^{1}H NMR spectrum of **PVC-P** in CDCl$_3$ (500 MHz).

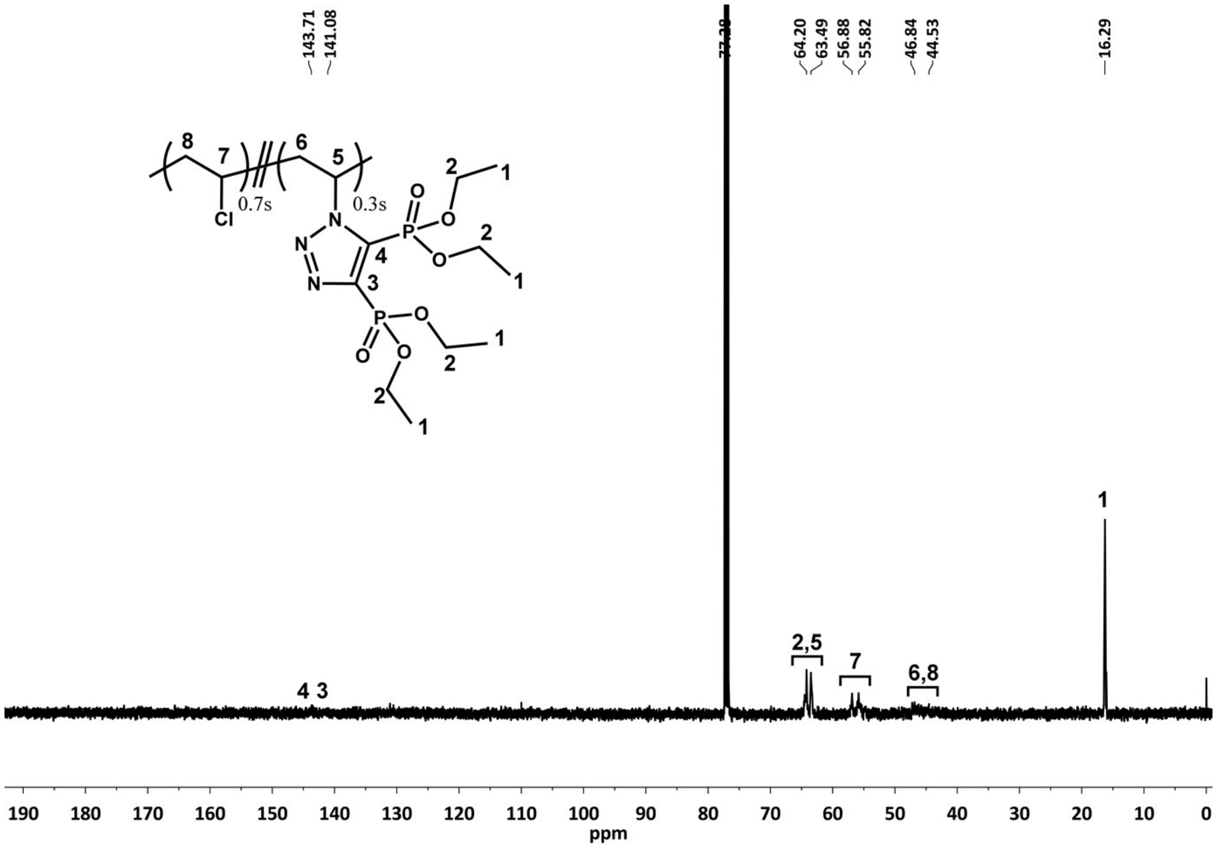


Figure S43. ^{13}C NMR spectrum of **PVC-P** in $CDCl_3$ (125 MHz).

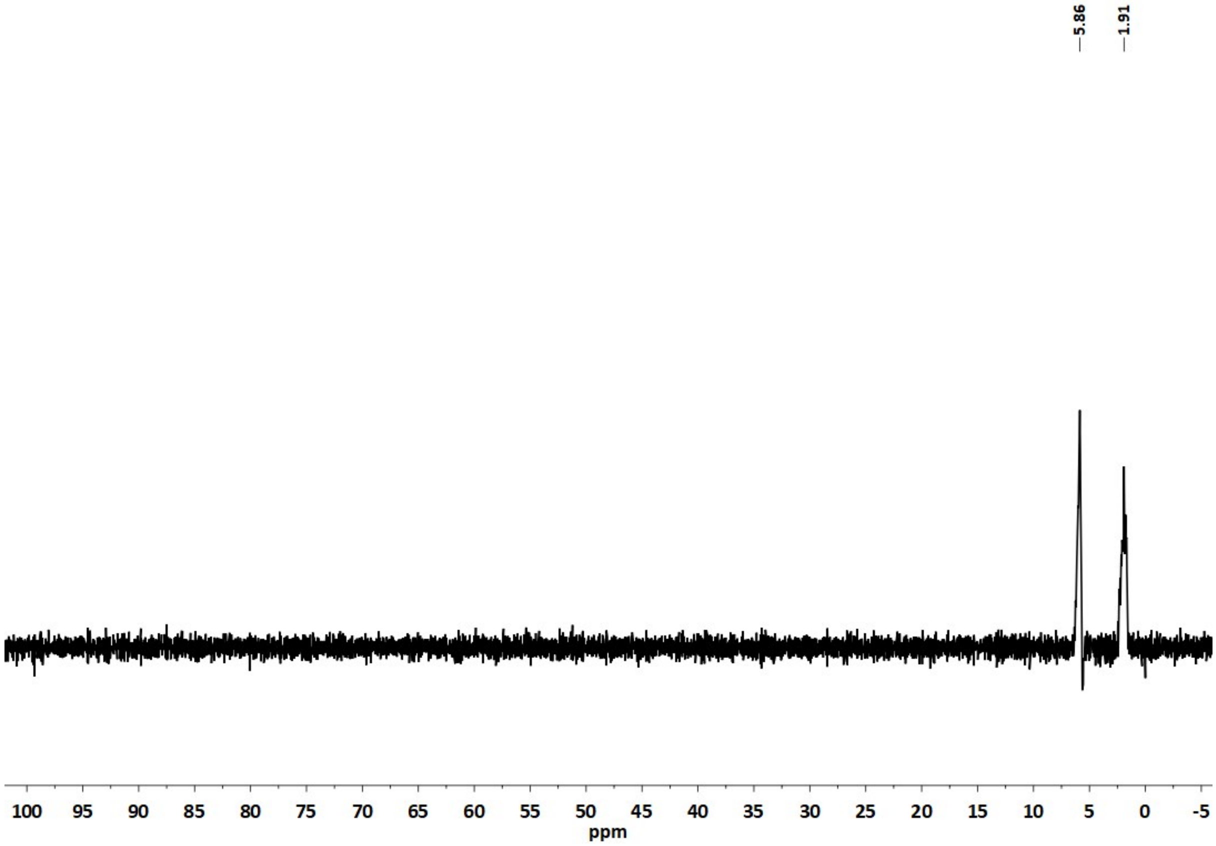


Figure S44. ^{31}P NMR spectrum of **PVC-P** in $CDCl_3$ (202 MHz).

Synthesis of azide-functionalized PECH (PECH-N_3)

The azidation of PECH was carried out according to previously published procedure (see ref. 49 in the main text) (Yield = 2.01 g, 94%). ^{1}H NMR ($CDCl_3$, δ): 3.66 (m, 3H, $\mathrm{C}H_2\mathrm{CHO}$ & $\mathrm{CH_2C}H\mathrm{O}$), 3.41 (m, 2H, $\mathrm{C}H_2\mathrm{N_3}$).

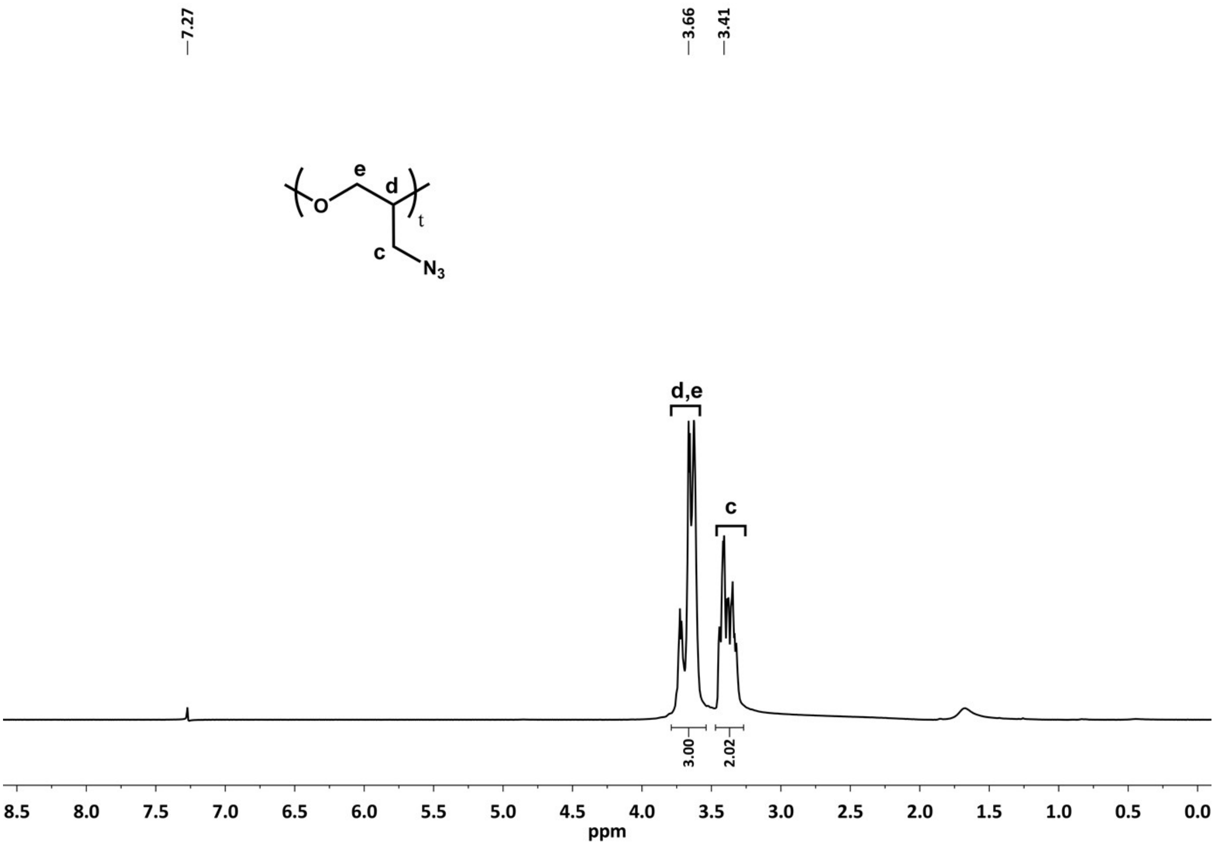


Figure S45. ^{1}H NMR spectrum of **PECH-N_3** in $CDCl_3$ (500 MHz).

Phosphorylation of PECH-N_3 (PECH-P)

PECH-N_3 (0.1 g, 1.01mmol) was placed in a dried 25 mL Schlenk tube with a magnetic stir bar and dissolved in 1 mL of MeTHF, and then bis(diethoxyphosphoryl)acetylene (602 mg, 2.02mmol) was added to this solution. The mixture was degassed via two FPT cycles, placed into an oil bath thermostated at 80 °C, and stirred for 24 h. After the specified time, the reaction mixture was cooled to room temperature and precipitated into cold hexane. The crude polymer was dissolved in $CHCl_3$ and precipitated into cold hexane one more time and the solvent was decanted. The polymer was finally dried in a vacuum oven for 24 h to give transparent viscous polymer (Yield = 360 mg, 90%). ^{1}H NMR ($CDCl_3$, δ): 4.78 (br, 2H, $\mathrm{C}H_2\mathrm{N}$), 4.22 (m, 8H, $\mathrm{P{=}OOC}H_2$), 3.99-3.48 (m, 3H, $\mathrm{CH_2C}H\mathrm{O}$ & $\mathrm{C}H_2\mathrm{CHO}$), 1.35 (m, 12H, $\mathrm{CH_2C}H_3$). ^{13}C NMR ($CDCl_3$, *δ*): 143.64, 141.57, 87.29, 64.19, 63.24, 51.72, 16.27. ^{31}P NMR ($CDCl_3$, δ): 6.33, 2.08.

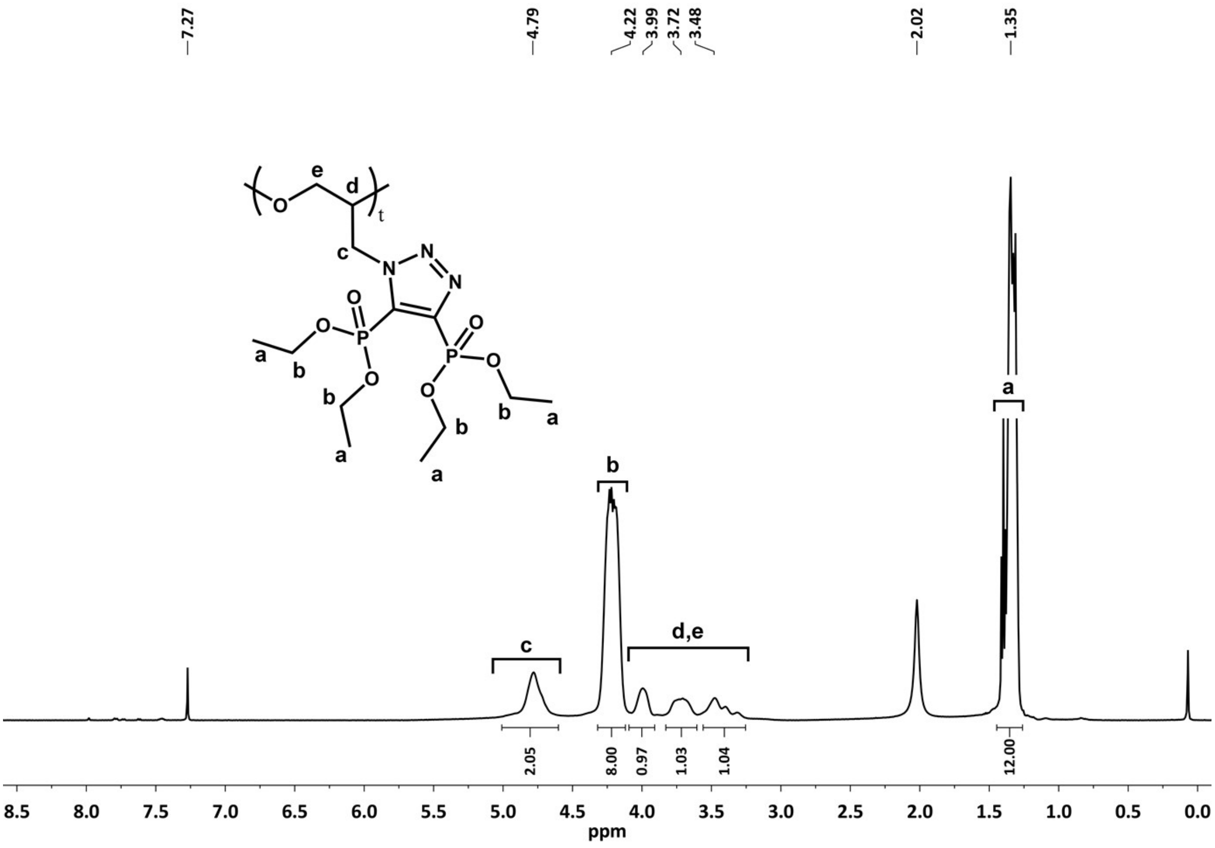


Figure S46. ^{1}H NMR spectrum of **PECH-P** in $CDCl_3$ (500 MHz).

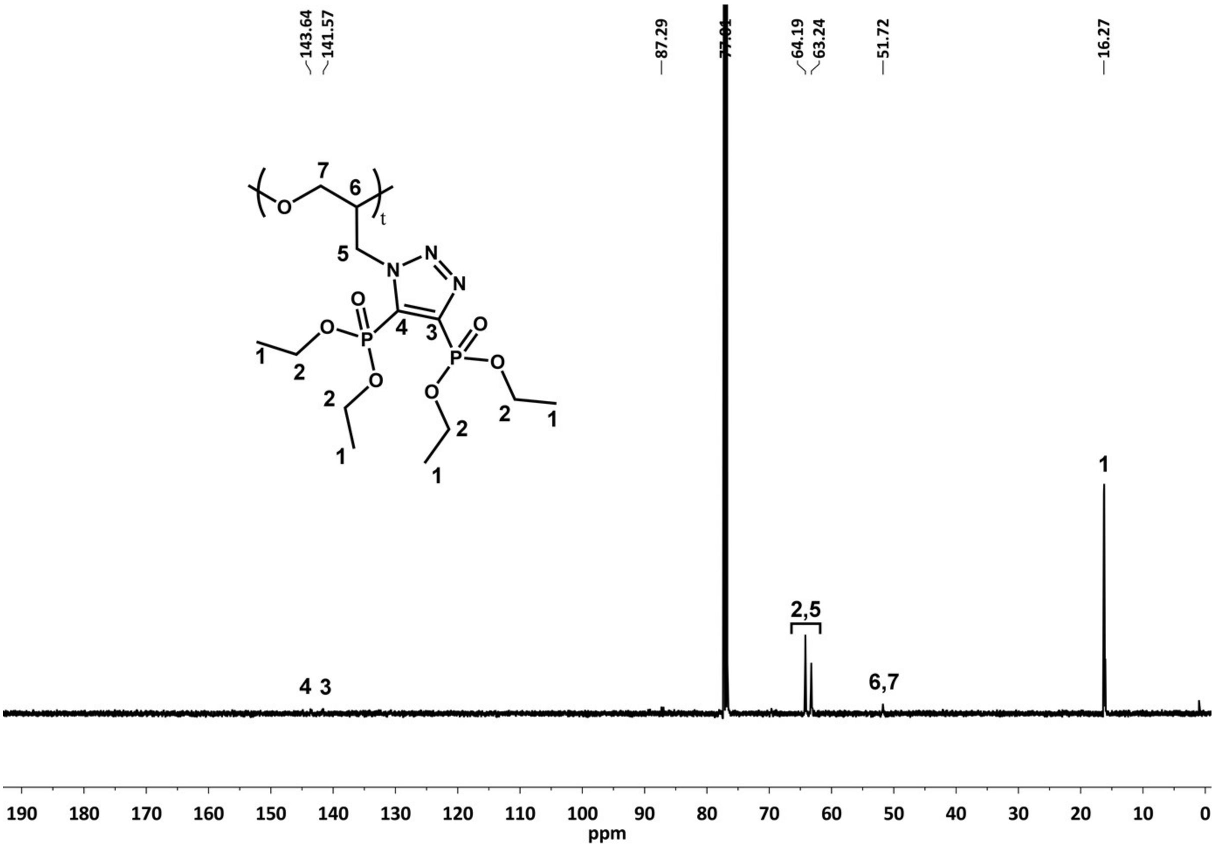


Figure S47. ^{13}C NMR spectrum of **PECH-P** in $CDCl_3$ (125 MHz).

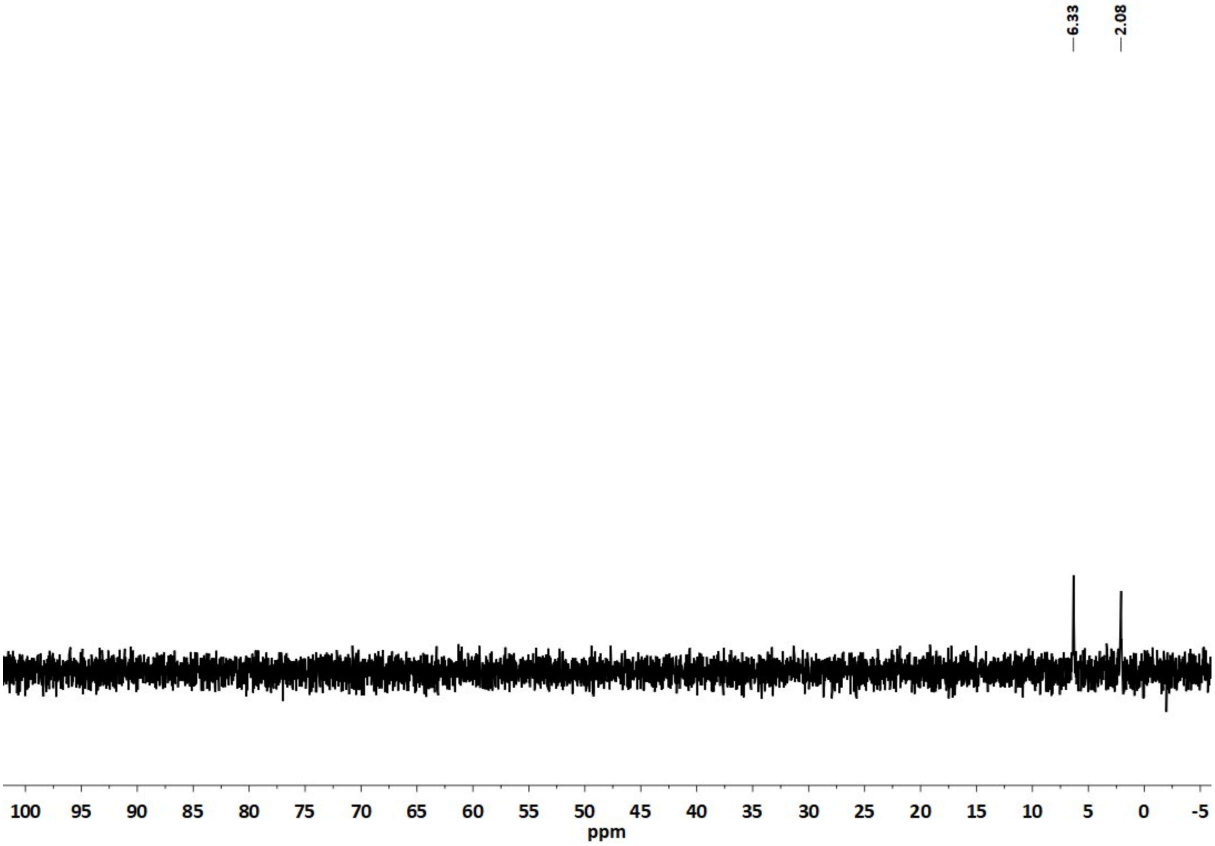


Figure S48. ^{31}P NMR spectrum of **PECH-P** in $CDCl_3$ (202 MHz).

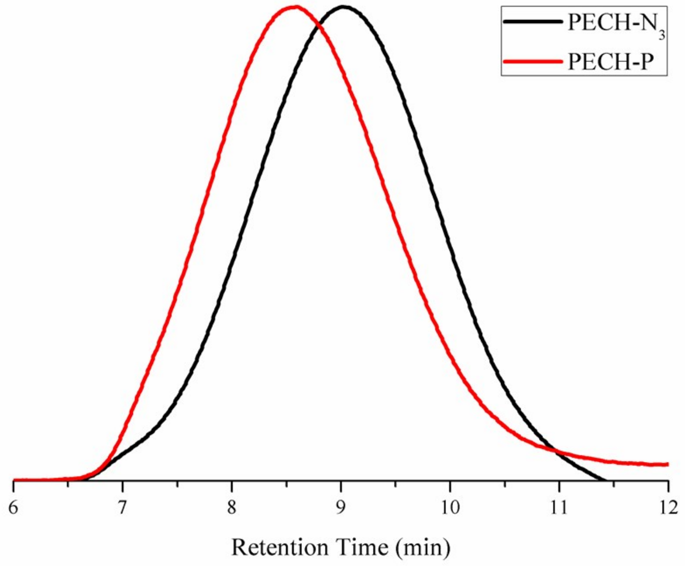


Figure S49. Overlaid GPC traces of **PECH-N_3** (black) and **PECH-P** (red) in THF.

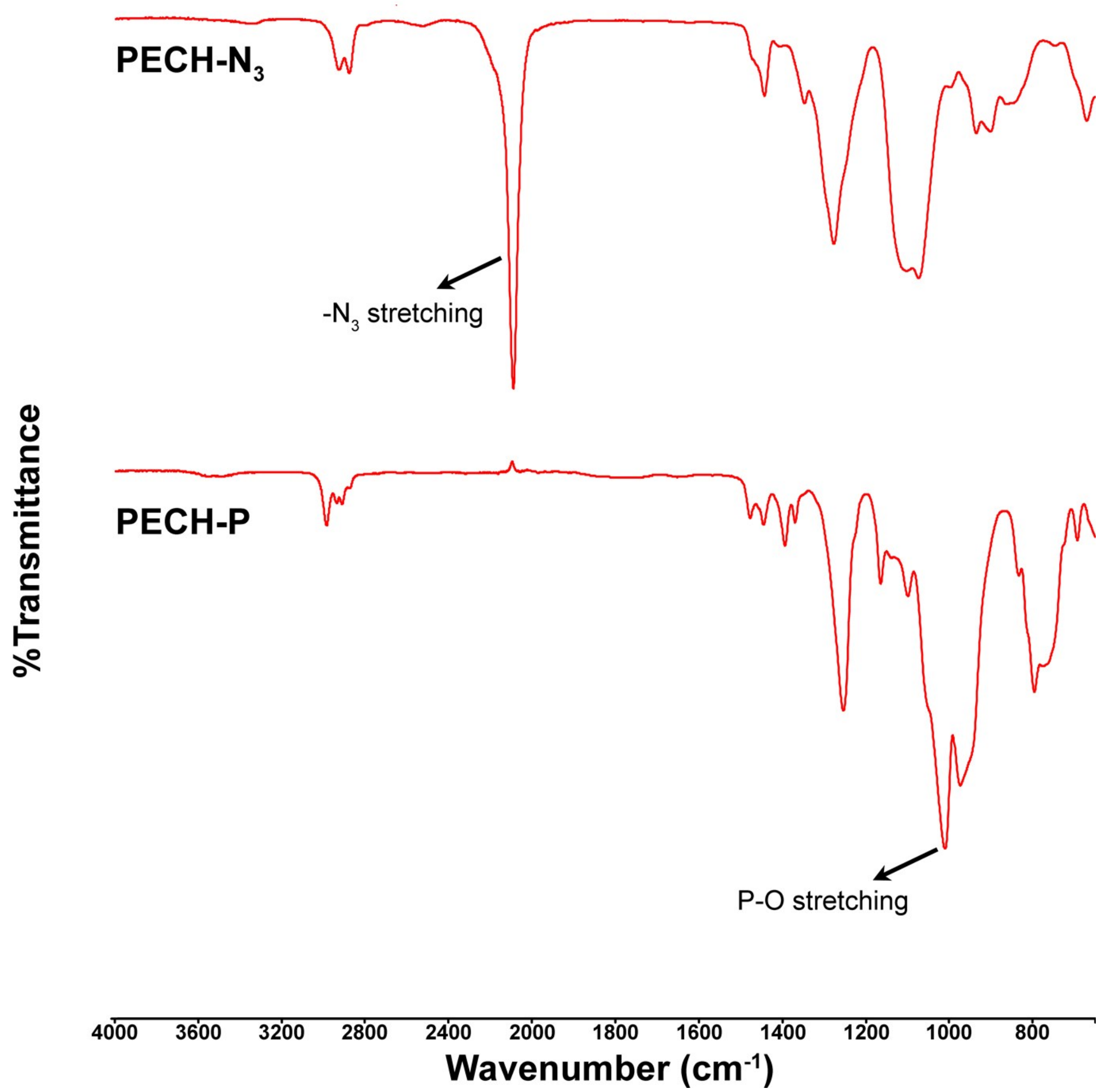


Figure S50. Overlaid FT-IR spectra of **PECH-N_3** and **PECH-P**.

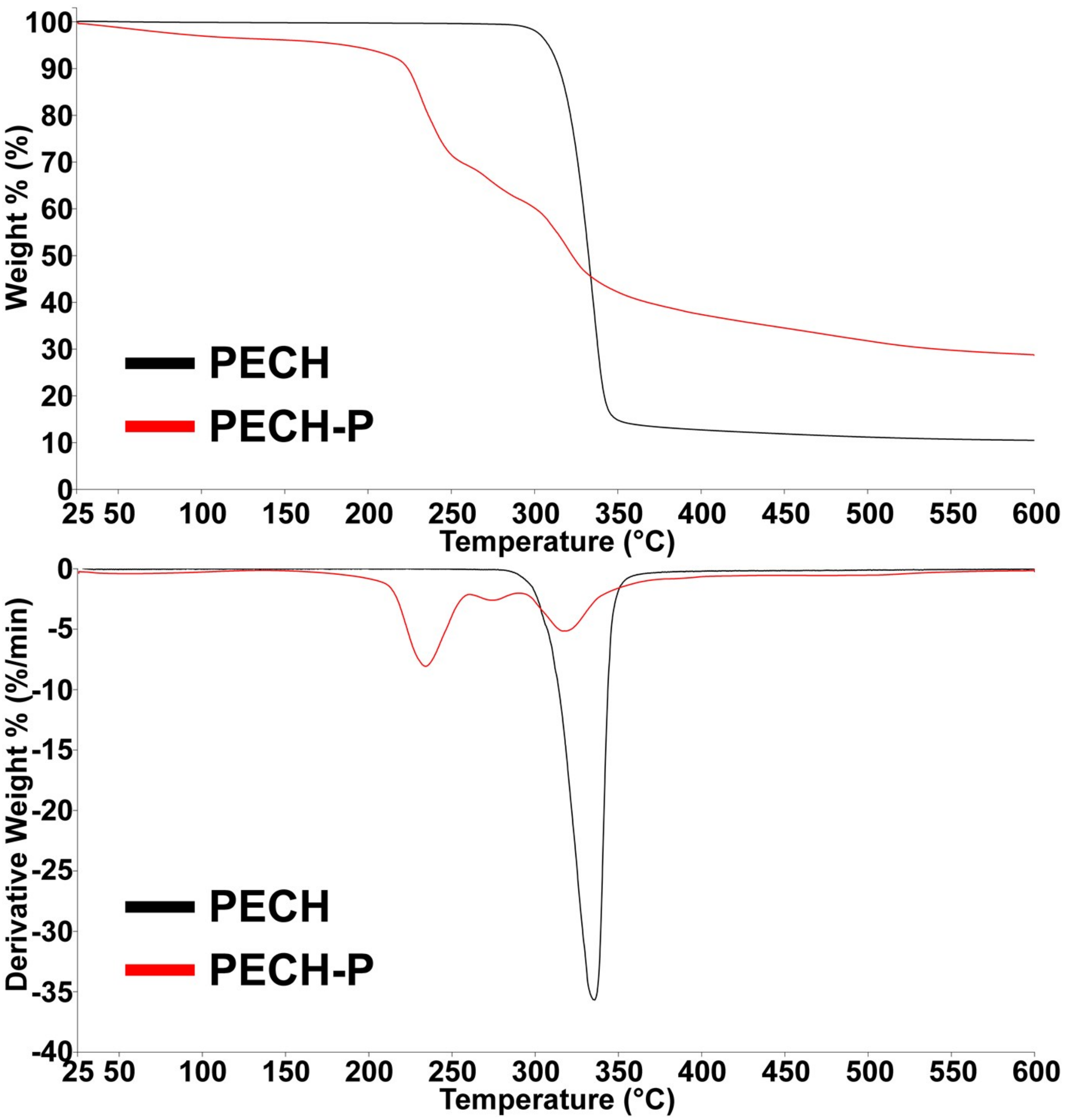


Figure S51. TGA curves of **PECH** and **PECH-P** (up), and their corresponding derivative curves (down) under nitrogen atmosphere.