

Supporting Information

Single Component Polymerization of Diisocynoacetates toward Polyimidazoles

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Experimental Section

Materials. Methyl isocyanoacetate, 1,4-dibromobutane, 1,6-dibromohexane, 1,8-dibromooctane, hydroquinone and other chemicals and reagents were purchased from Energy and used as received without further purification. Silver acetate was ordered from Aladdin. The acetonitrile, acetone, DMF and DMSO were purchased from Guangzhou Chemical Reagent Factory.

Instruments. FT-IR spectra were recorded on a Bruker Vector 33 FT-IR spectrometer as thin films on KBr pellets. ^1H and ^{13}C NMR spectra were measured on a Bruker AV 600, Bruker AV 500 in DMSO- d_6 using tetramethylsilane (TMS; $\delta = 0$) as internal reference. Kinetic polymerization spectra were performed on a ReactIR 15 from Mettler Toledo International Inc. Elemental analyses were carried out through a Vario EL-III elemental analyzer. High-resolution mass spectra (HRMS) were recorded on a GCT premier CAB 048 mass spectrometer operated in MALDI-TOF mode. Gas chromatography–mass spectrometry (GC-MS) was performed on an Agilent GC-6890/MS-5973. The weight average molecular weights (M_w), number average molecular weights (M_n), and polydispersity indices (M_w/M_n) of the polymers were evaluated by a Waters Associates gel permeation chromatography (GPC) system equipped with a RI detector. DMF containing 0.05 M LiBr was used as the solvent to dissolve the polymers. The solutions were filtered through 0.22 μm PTFE syringe-type filters before being injected into the GPC system and DMF containing 0.05 M LiBr was used as the eluent at a flow rate of 1.0 mL min^{-1} . A set of linear PMMA standards (Waters) covering the M_w range of 10^3 – 10^7 was utilized for M_w and PDI calibration.

Monomer preparation. The synthetic routes to monomers M1–M4 are shown in Scheme 2. The synthetic routes to monomer M5 and M6 are shown in Schemes S2 and S3. Detailed experimental

procedures for the synthesis of **M2** are given below as an example.

Potassium 2-isocyanoacetate (**3**): To a solution of the methyl isocyanoacetate (1.982 g, 20 mmol) in THF (40.0 mL) and water (10.0 mL) was added potassium hydroxide (1.122 g, 20 mmol), and the resultant mixture was stirred at room temperature for 5 h. The solvent was then removed in vacuum and the resultant salt **3** was used without further purification.

Hexane-1,6-diyl bis(2-isocyanoacetate) (**M2**): Into a 250 mL round-bottom flask were added potassium 2-isocyanoacetate (**3**) (2.46 g, 20 mmol) and DMF (50 mL) under nitrogen. After potassium 2-isocyanoacetate was completely dissolved, 1,6-dibromohexane (2.39 g, 9.8 mmol) was injected. The solution was stirred at 60 °C for 12 h, and then the formed precipitates were removed by filtration and washed with ethyl acetate. The filtrate was extracted by EA/water in order to remove DMF. After the organic layer was dried with anhydrous magnesium sulfate, the solvent was removed by a rotary evaporator under reduced pressure, and the crude product was purified by a silica gel column chromatography using PE/EA (2:1 v/v) as eluent. White crystal of **M2** was obtained in 73.4% yield (1.810 g). FT-IR (KBr), ν (cm⁻¹): 2247 (-N⁺≡C⁻ stretching), 1680 (carbonyl group stretching). ¹H NMR (600 MHz, DMSO-*d*₆), δ (TMS, ppm): 4.685 (s, 4H, CH₂), 4.131 (t, *J* = 6.6 MHz, 4H, CH₂), 1.595 (t, *J* = 6.6 MHz, 4H, CH₂), 1.333 (t, *J* = 6.6 MHz, 4H, CH₂). ¹³C NMR (150 MHz, DMSO-*d*₆), δ (ppm): 165.6, 159.2, 66.1, 44.2, 28.4, 25.3. Element Analysis for C₁₂H₁₆N₂O₄: Calcd: C, 57.13; H, 6.39; N, 11.10. Found: C, 57.21; H, 6.31; N, 11.15.

Polymerization. All the polymerizations were carried out under nitrogen using a standard Schlenk technique. A typical procedure for the synthesis of **PII** is given below as an example. A 10 mL Schlenk tube equipped with a magnetic stirrer was placed with hexane-1,6-diyl bis(2-isocyanoacetate) **M2** (252 mg, 1 mmol) and silver acetate (6.8 mg, 0.04 mmol). The Schlenk

tube was evacuated under vacuum and flushed with dry nitrogen three times. 2 mL of acetonitrile or DMF was then injected and the resulting solution was stirred for 2 h at room temperature. The reaction mixture was then added dropwise into 200 mL of hexane/chloroform (20:1 v/v) *via* a cotton filter to precipitate without any filtration. The precipitate was allowed to stand overnight and collected by filtration. The polymer was washed with hexane and dried under vacuum at room temperature to a constant weight.

Preparation of Model Compound. The synthetic route to model compound **2** is shown in Scheme 1. Into a 10 mL Schlenk tube was placed silver acetate (6.8 mg, 0.04 mmol). After being evacuated and refilled with nitrogen for three times, acetonitrile (2.0 mL) and methyl isocyanoacetate (0.198 g, 2 mmol) were injected into the tube using a hypodermic syringe. The mixture was stirred at 30 °C for 2 h. After solvent evaporation, the crude product was purified by flash column chromatography using ethyl acetate as eluent to give the product as a colorless solid (0.188 g, 95%). ¹H NMR (600 MHz, DMSO-*d*₆), δ (TMS, ppm): 7.67 (s, 1H, *CH*), 7.54 (s, 1H, *CH*), 4.78 (s, 2H, *CH*₂CO₂Me), 3.89 (s, 3H, OCH₃), and 3.80 (s, 3H, OMe). ¹³C NMR (125 MHz, DMSO-*d*₆), δ (ppm): 166.9, 161.0, 138.1, 130.2, 125.9, 50.8, 49.5.

Post modification of PII. Into a 10 mL Schlenk tube was placed **PII** (112 mg). After being evacuated and refilled with nitrogen for three times, 2 mL DMF was injected. After **PII** was dissolved, 5 mmol (0.598 mL) of benzyl bromide was injected into the tube using a hypodermic syringe. The mixture was stirred at room temperature for 12 h. The reaction mixture was then added into 200 mL of hexane/chloroform (20:1 v/v) *via* a cotton filter to precipitate without any filtration. The precipitate was allowed to stand overnight. The product was collected from the bottom of the flask using a spatula. The polymer was washed with methanol and dried under

vacuum at room temperature to a constant weight. Gray solid (70 mg, 37%), M_w : 11200; M_w/M_n : 1.12, ^1H NMR (500 MHz, $\text{DMSO}-d_6$), δ (TMS, ppm): 9.57, 8.66, 7.41, 7.32, 5.80, 5.37, 4.26, 4.16, 1.61, 1.32. ^{13}C NMR (125 MHz, $\text{DMSO}-d_6$), δ (ppm): 167, 162.8, 157.5, 141.9, 134.8, 130.8, 129.4, 128.2, 123.4, 66.4, 52.2, 50.8, 36.3, 34.8, 31.2, 28.2, 25.3.

Characterization Data of PI: White powder; yield: 85%. M_w : 24 400; M_w/M_n : 1.73. IR (KBr), ν (cm^{-1}): 3140, 3120, 2960, 2568, 1740, 1712, 1555, 1206, 973, 772. ^1H NMR (500 MHz, $\text{DMSO}-d_6$), δ (TMS, ppm): 7.91, 7.75, 5.048, 4.734, 4.172, 1.719, 1.669. ^{13}C NMR (125 MHz, $\text{DMSO}-d_6$), δ (ppm): 168.9, 163.1, 140.2, 132.5, 127.9, 65.2, 63.9, 60.8, 47.8, 24.3.

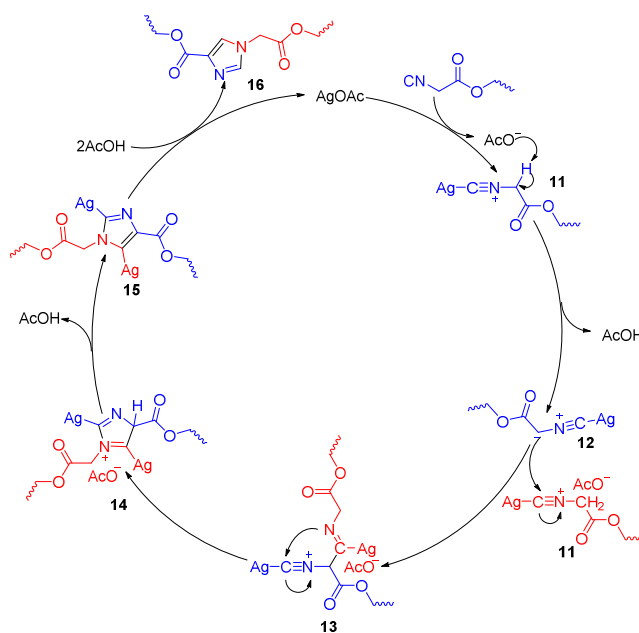
Characterization Data of PII: White powder; yield: 96%. M_w : 50 300; M_w/M_n : 2.06. IR (KBr), ν (cm^{-1}): 3270, 3128, 2936, 2860, 1747, 1718, 1384, 1211, 987, 772. ^1H NMR (500 MHz, $\text{DMSO}-d_6$), δ (TMS, ppm): 7.893, 7.737, 5.031, 4.172, 4.103, 1.636, 1.579, 1.394, 1.355, 1.299. ^{13}C NMR (125 MHz, $\text{DMSO}-d_6$), δ (ppm): 168.7, 162.8, 140.2, 132.4, 128.0, 65.7, 63.9, 61.1, 48.2, 28.8, 25.4.

Characterization Data of PIII: White powder; yield: 81%. M_w : 65 900; M_w/M_n : 2.28. IR (KBr), ν (cm^{-1}): 3142, 3120, 2933, 2854, 1745, 1714, 1555, 1218, 982, 772. ^1H NMR (500 MHz, $\text{DMSO}-d_6$), δ (TMS, ppm): 7.882, 7.731, 5.028, 4.154, 4.096, 1.631, 1.571, 1.278, 1.259. ^{13}C NMR (125 MHz, $\text{DMSO}-d_6$), δ (ppm): 168.7, 163.1, 140.2, 132.4, 128.0, 65.7, 63.8, 61.0, 47.9, 32.9, 31.9, 28.8, 25.7.

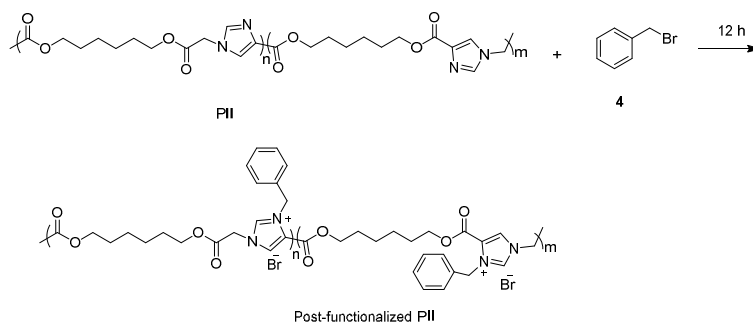
Characterization Data of PIV: White powder; yield: 82%. M_w : 31 700; M_w/M_n : 1.80. FT-IR (KBr), ν (cm^{-1}): 3138, 2989, 2951, 2211, 2163, 1737, 1710, 1550, 1202, 972. ^1H NMR (500 MHz, $\text{DMSO}-d_6$), δ (TMS, ppm): 7.970, 7.768, 7.421, 5.231, 5.099, 4.78. ^{13}C NMR (125 MHz, $\text{DMSO}-d_6$), δ (ppm): 168.6, 165.2, 162.2, 140.3, 137.4, 136.0, 132.4, 128.9, 67.2, 65.2, 47.9, 44.8.

Characterization Data of PV: White powder; yield: 82%. M_w : 33 500; M_w/M_n : 2.08. IR (KBr), ν (cm^{-1}): 3141, 2936, 2856, 1761, 1717, 1510, 1229, 1024, 820, 732. ^1H NMR (500 MHz, $\text{DMSO-}d_6$), δ (TMS, ppm): 7.880, 7.729, 6.815, 5.016, 4.144, 3.857, 1.657, 1.616, 1.413, 1.378, 1.346. ^{13}C NMR (125 MHz, $\text{DMSO-}d_6$), δ (ppm): 168.7, 162.8, 153.1, 140.5, 132.7, 128.3, 115.7, 68.3, 66.3, 65.4, 64.2, 48.2, 44.2, 29.1, 28.5, 25.4.

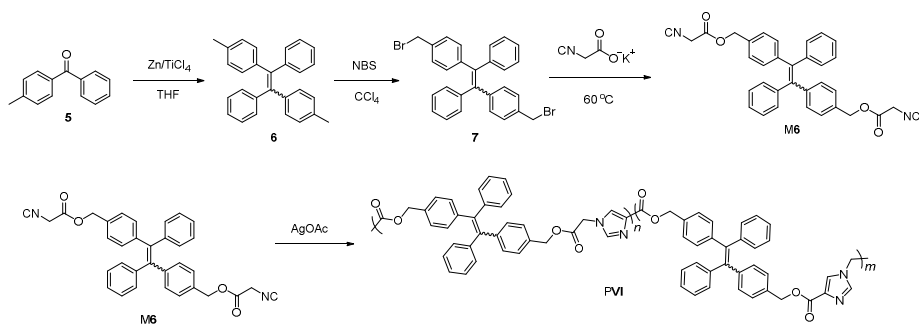
Characterization Data of PVI: White powder; yield: 88%. M_w : 15 600; M_w/M_n : 1.47. IR (KBr), ν (cm^{-1}): 3041, 2167, 1745, 1674, 1545, 1502, 1445, 1381, 1310, 1189, 1110, 982, 761, 696. ^1H NMR (500 MHz, $\text{DMSO-}d_6$), δ (TMS, ppm): 7.947, 7.739, 7.112, 6.985, 5.150, 5.052. ^{13}C NMR (125 MHz, $\text{DMSO-}d_6$), δ (ppm): 168.5, 162.8, 143.6, 140.9, 134.0, 132.2, 128.3, 127.1, 67.3, 66.7, 65.2, 48.0, 36.3, 31.2.



Scheme S1. Proposed mechanism of the reaction of diisocyanoacetates.



Scheme S2. Post-functionalization of PII.



Scheme S3. Synthetic routes to M6 and PVI.

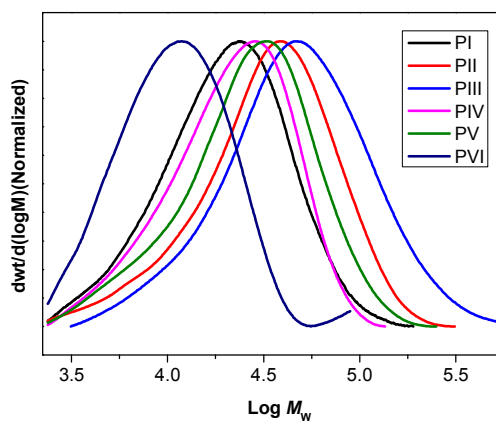


Figure S1. GPC traces of PI-PVI.

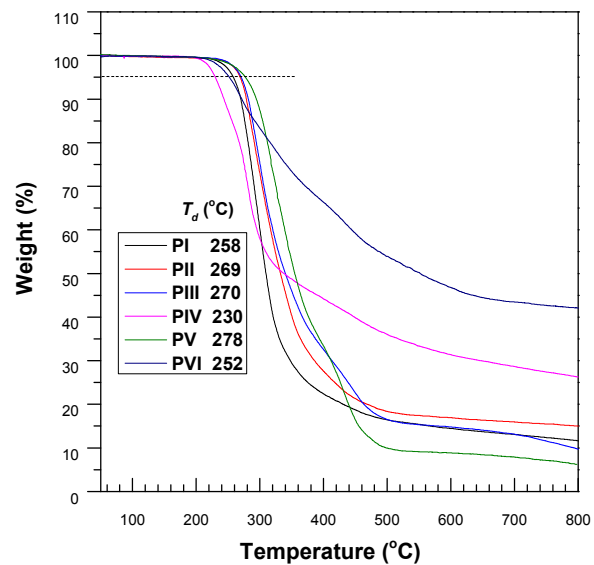


Figure S2. TGA curves of PI-PVI. T_d represents the temperature of 5% weights loss.

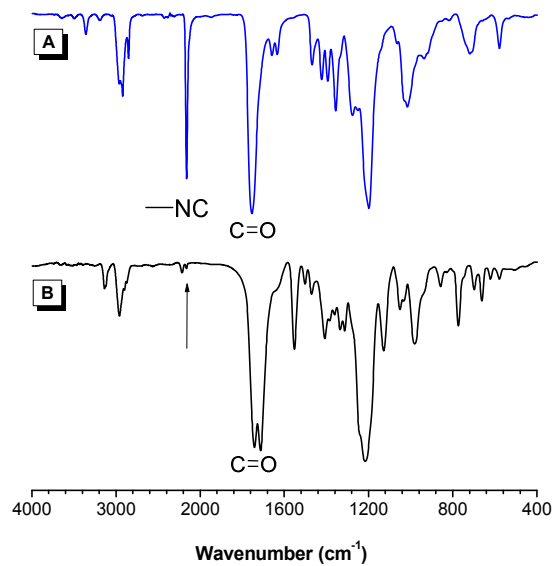


Figure S3. FT-IR spectra of (A) monomer M1 and (B) polymer PI.

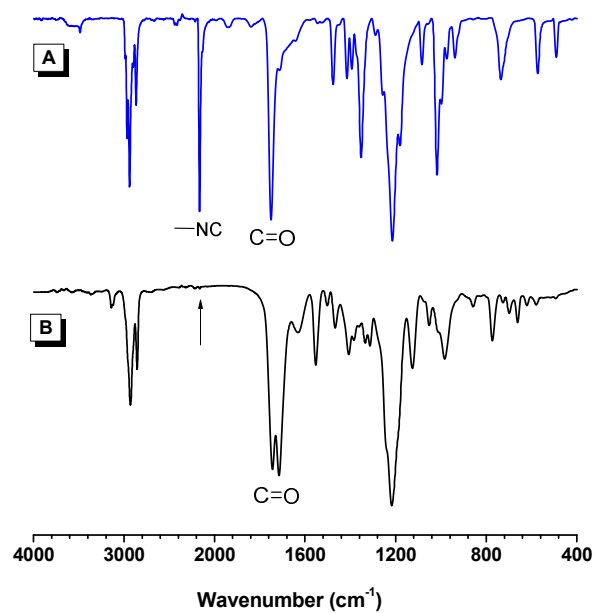


Figure S4. FT-IR spectra of (A) monomer M3 and (B) polymer PIII.

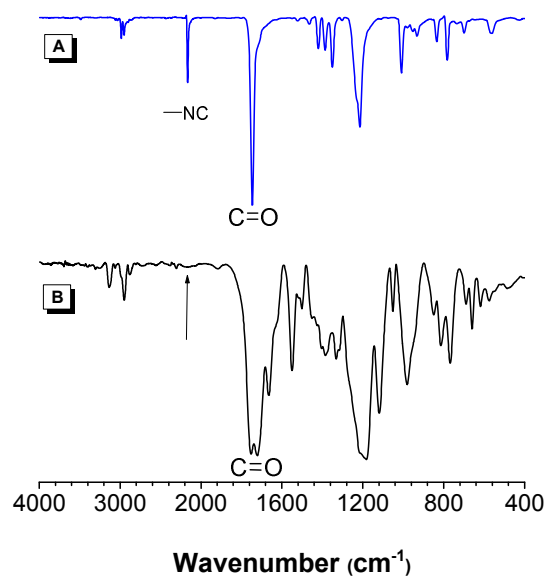


Figure S5. FT-IR spectra of (A) monomer M4 and (B) polymer PIV.

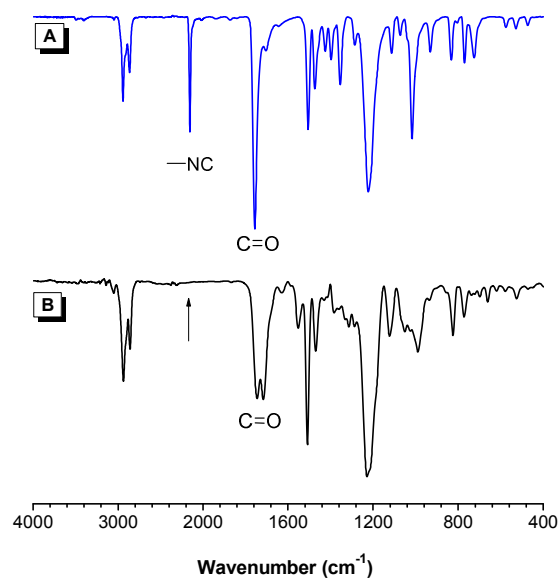


Figure S6. FT-IR spectra of (A) monomer M5 and (B) polymer PV.

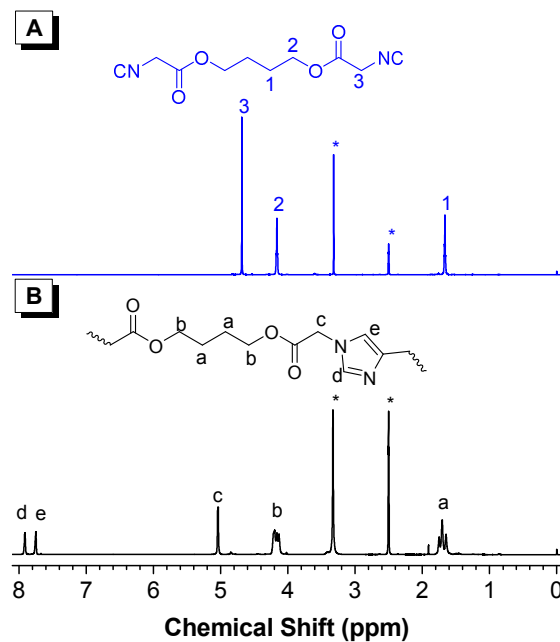


Figure S7. ^1H NMR spectra of (A) monomers M1 (B) polymer PI in $\text{DMSO-}d_6$. The solvent and water peaks are marked with asterisks.

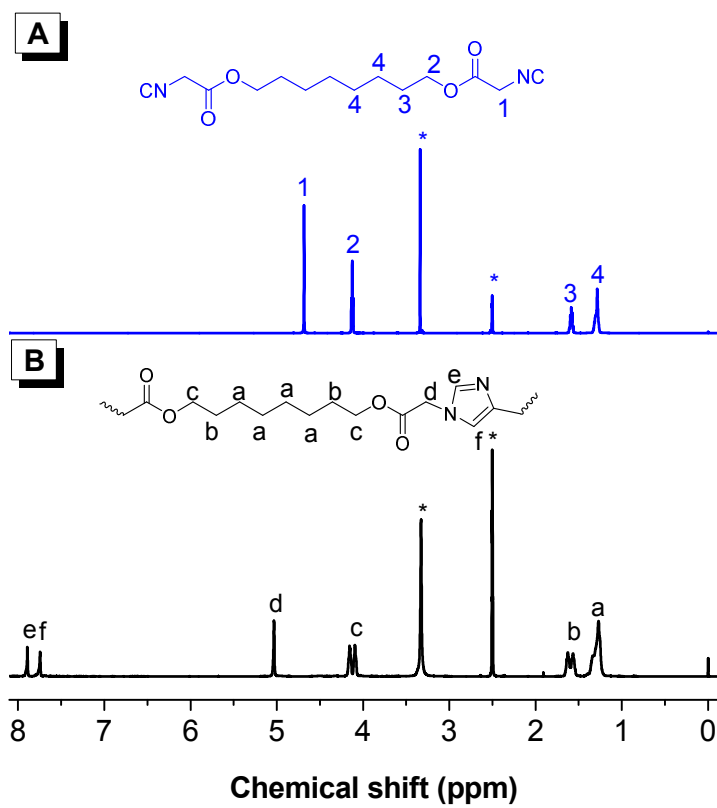


Figure S8. ^1H NMR spectra of (A) monomer M3 (B) polymer PIII in $\text{DMSO-}d_6$. The solvent and water peaks are marked with asterisks.

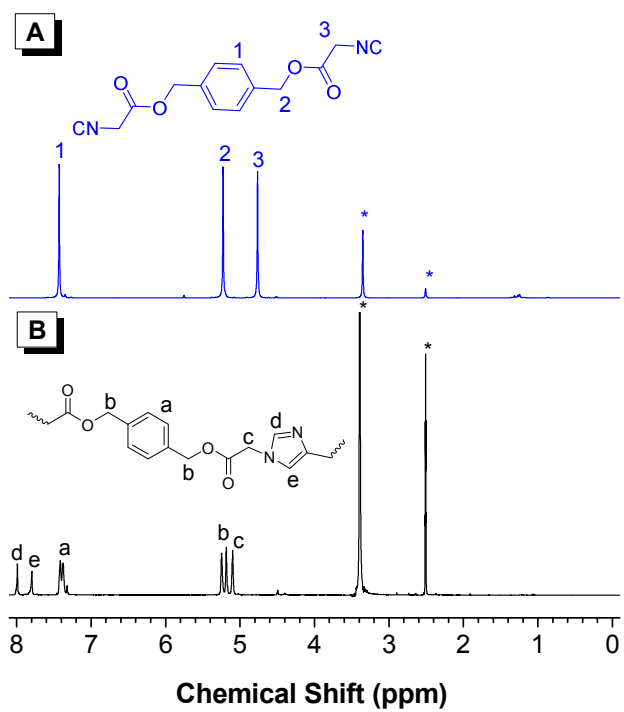


Figure S9. ^1H NMR spectra of (A) monomer M4 (B) polymer PIV in $\text{DMSO-}d_6$. The solvent and water peaks are marked with asterisks.

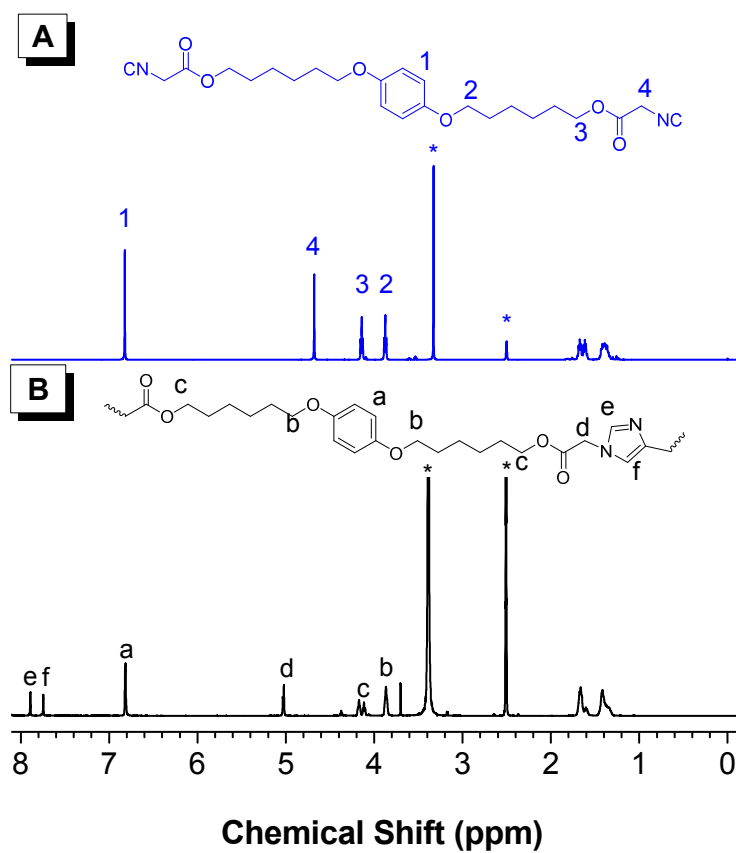


Figure S10. ^1H NMR spectra of (A) monomer M5 (B) polymer PV in $\text{DMSO-}d_6$. The solvent and water peaks are marked with asterisks.

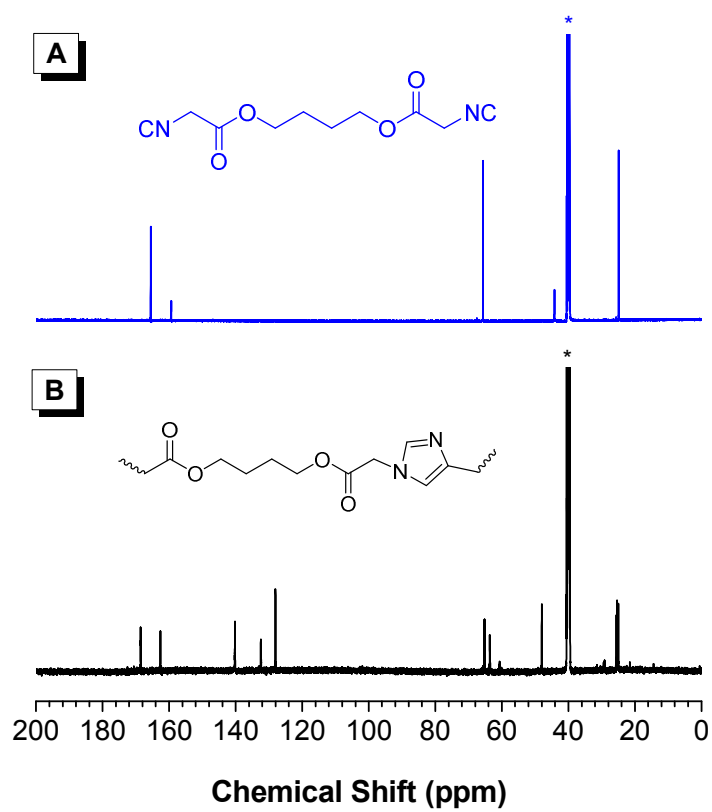


Figure S11. ^{13}C NMR spectra of (A) monomer M1 (B) polymer PI in $\text{DMSO-}d_6$. The solvent peaks are marked with asterisks.

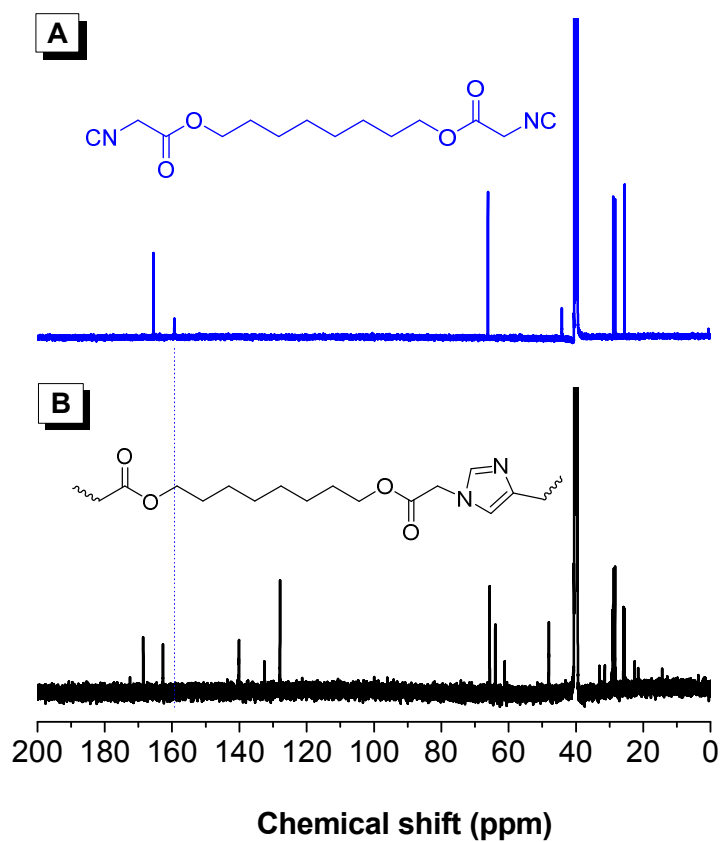


Figure S12. ^{13}C NMR spectra of (A) monomer M3 (B) polymer PIII in $\text{DMSO-}d_6$. The solvent peaks are marked with asterisk.

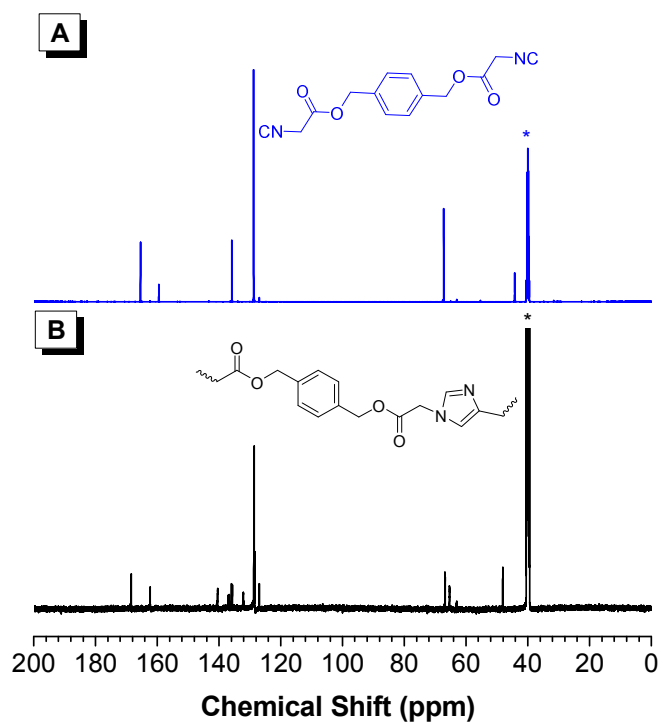


Figure S13. ^{13}C NMR spectra of (A) monomer M4 (B) polymer PIV in $\text{DMSO}-d_6$. The solvent peaks are marked with asterisk.

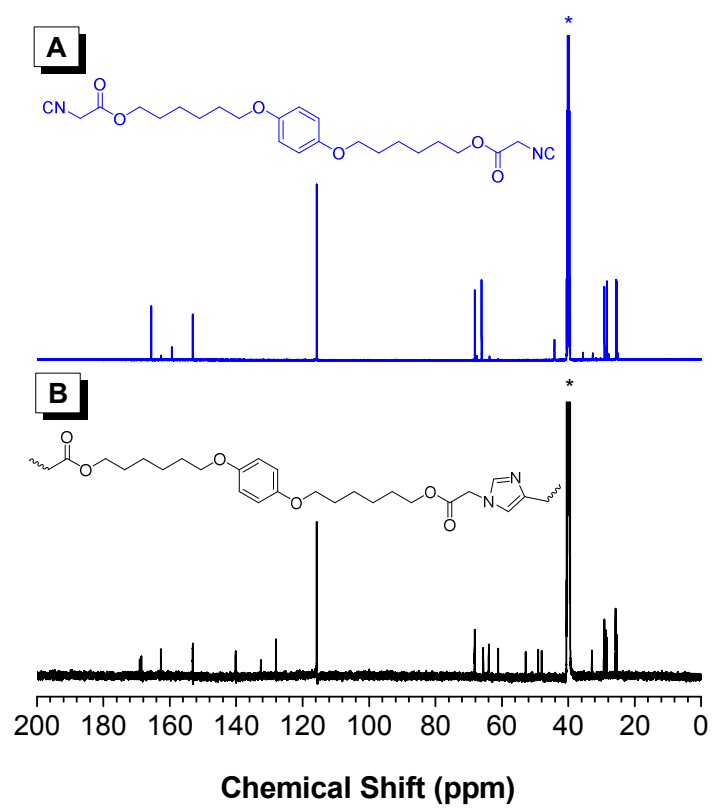


Figure S14. ^{13}C NMR spectra of (A) monomer M5 (B) polymer PV in $\text{DMSO}-d_6$. The solvent peaks are marked with asterisk.

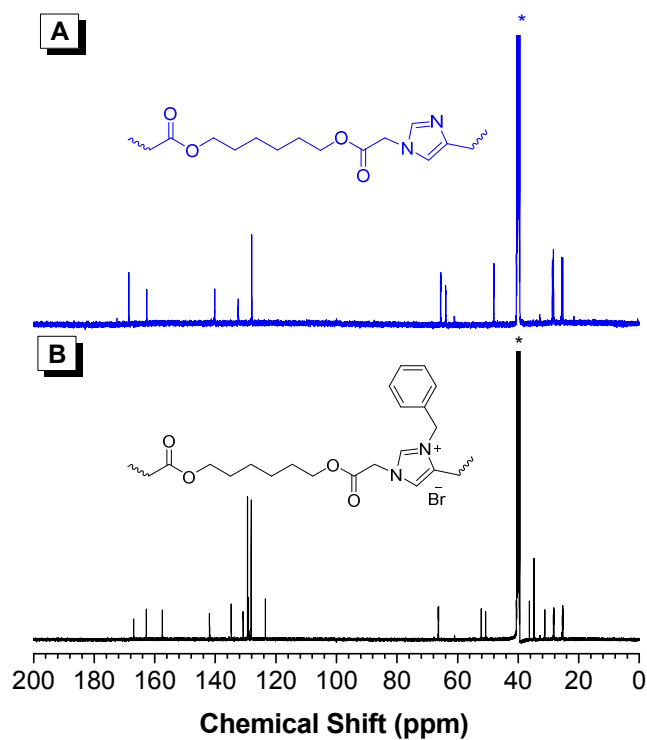


Figure S15. ^{13}C NMR spectra of (A) PII and (B) ionic-PII in $\text{DMSO-}d_6$. The solvent peaks are marked with asterisk.

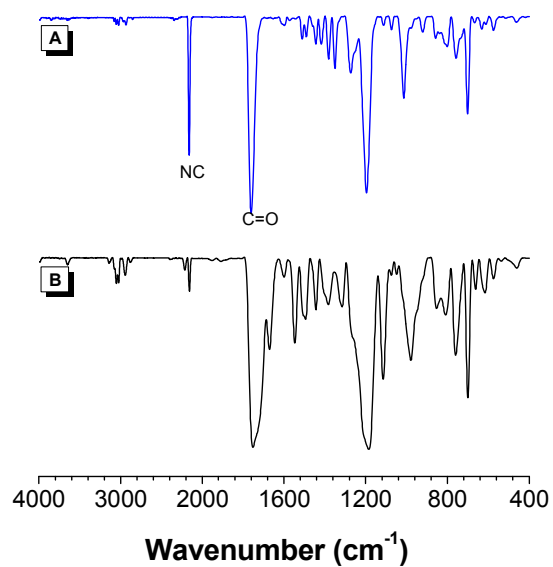


Figure S16. FT-IR spectra of (A) monomer M6 and (B) polymer PVI.

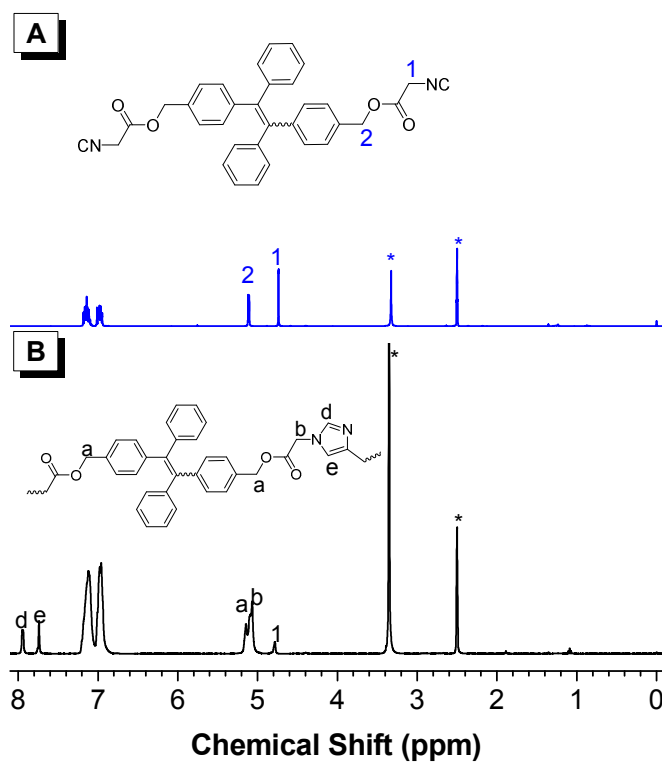


Figure S17. ^1H NMR spectra of (A) monomer M6 (B) polymer PVI in $\text{DMSO-}d_6$. The solvent and water peaks are marked with asterisks.

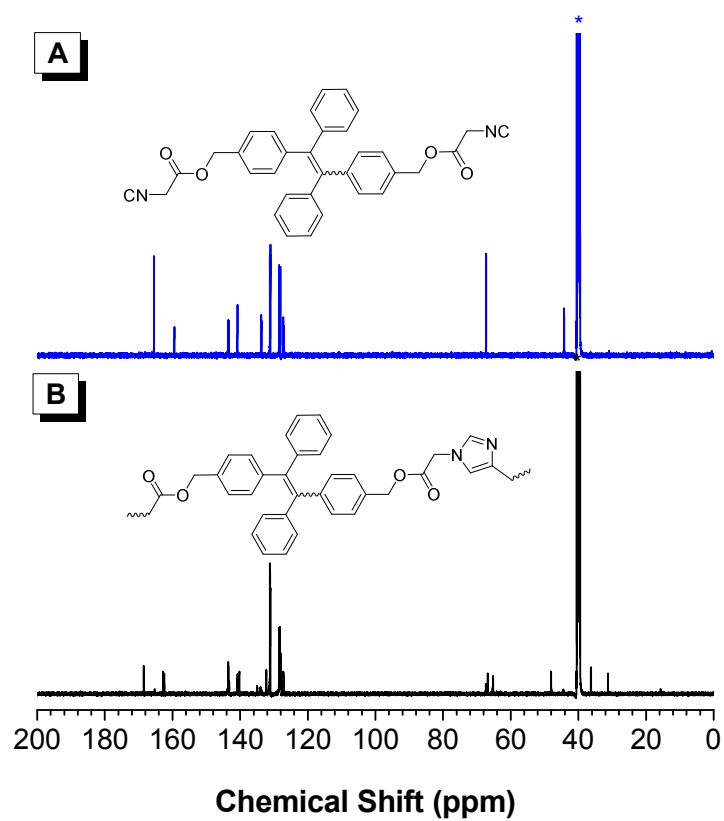


Figure S18. ^{13}C NMR spectra of (A) monomer M6 (B) polymer PVI in $\text{DMSO}-d_6$. The solvent peaks are marked with asterisk.

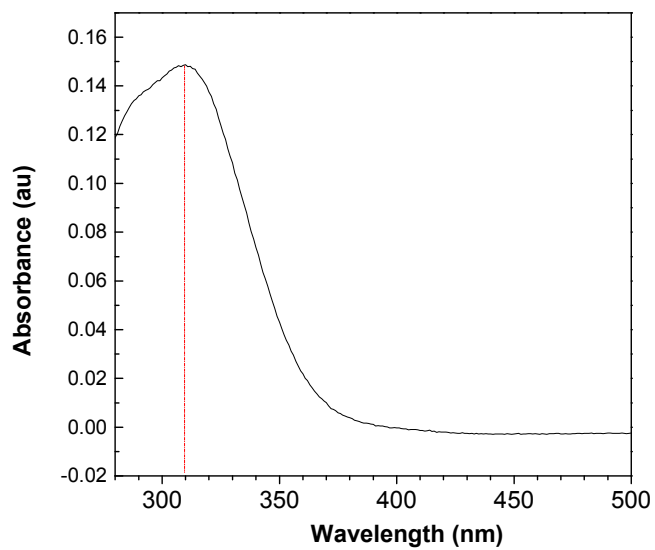


Figure S19. UV spectra of PVI in DMF solution. Polymer concentration: $10\mu\text{m}$.