Silylium Cations Initiated Sergeants-and-Soldiers Type Chiral Amplification of Helical Aryl Isocyanide Copolymers

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Figure S42. UV absorption and transmittance spectra of poly(D/L-IMCI-*co*-ITPB) (table 2, entry 1-10) in THF/water mixture (copolymer: A (Table 2, entry 1), B (Table 2, entry 2), F (Table 2, entry 6), G (Table 2, entry 7): 0.005 mg/ml; C (Table 2, entry 3), H (Table 2, entry 8): 0.0065 mg/ml; D (Table 2, entry 4), I (Table 2, entry 9): 0.010 mg/ml; E

References

EXPERIMENTAL SECTION

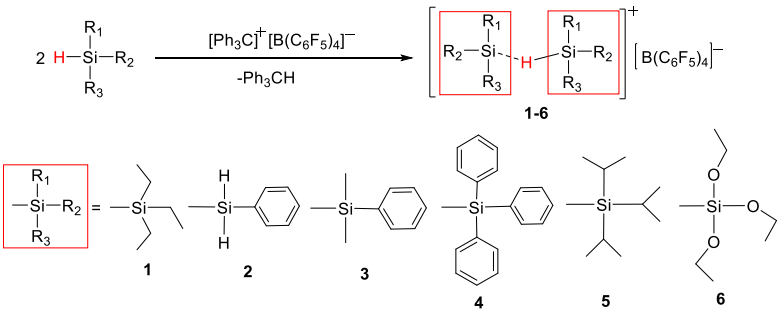
Materials

All manipulations of air and moisture-sensitive compounds were performed under a dry and oxygen-free nitrogen atmosphere by using Schlenk techniques or under a nitrogen atmosphere in an Mbraun glove box. Nitrogen (Beijing AP Beifen Gases Industrial Co., Ltd.) was purified by passing through a Dryclean column (4A molecular sieves, Dalian Replete Science And Technology Co., Ltd.) and a Gasclean column (Dalian Replete Science And Technology Co., Ltd.). The nitrogen in the glovebox was constantly circulated through a copper/molecular sieves catalyst unit. The oxygen and moisture concentrations in the glovebox atmosphere were monitored by an O_2/H_2O Combi-Analyzer (Mbraun) to ensure both were always below 0.1 ppm. Anhydrous THF, hexane and toluene were purified by a solvent purification system (SPS-800, Mbraun), and dried over fresh Na chips in the glovebox. $[Ph_3C]^+[B(C_6F_5)_4]^-$ was purchased from Tosoh Finechem Corporation and used without purification. Et_3SiH was purchased from Aldrich and used as received. The catalyst and the isocyanide monomers were synthesized according to literatures. The deuterated solvents chloroform-d1 (99.8 atom% D) and Chlorobenzene-d5 (99.6 atom% D) were obtained from Cambridge Isotope.

General Method

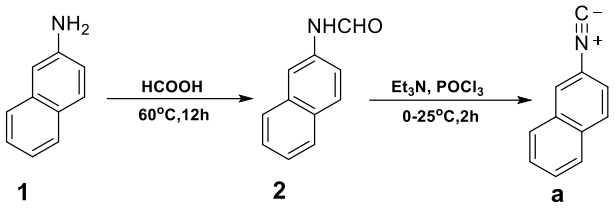
^1H, ^{29}Si, ^{11}B, and ^{13}C NMR spectra were recorded on a Bruker Avance (Ⅲ-HD 400 MHz, 700MHz) spectrometer. The molecular weights and the molecular weight distributions of the EPI polymers and poly(L-IMCI-*co*-EPI)s were determined against polystyrene standard at 25 °C by GPC on a Waters HPLC-515 apparatus, $CHCl_3$ was employed as the eluent at a flow rate of 1 mL/min. The molecular weights and the molecular weight distributions of copolymers were determined against polystyrene standard at 25 °C by GPC on a Waters HLC-8320GPC apparatus, THF was used as the eluent at a flow rate of 1 mL/min. FT-IR spectra were recorded on a Thermo IS5 FT-IR system using KBr pellets at room temperature. The UV-Vis spectra were recorded on a TU-1901 double beam UV-vis spectrophotometer, and the fluorescence spectra were recorded on a HITACHI F-7000 fluorescence spectrophotometer. Quartz cells with 10.0 mm length were used in UV-Vis and fluorescence measurement, and the slit widths were set at 5.0 (or 2.5) nm for both excitation and emission during the fluorescence measurement. Circular dichroism spectra were collected on a Jasco J-810 and the quartz cell length is 1.0 mm. The dynamic light scattering measurement were tested by Zetasizer Nano. The thermosgravimetric analysis (TGA) spectra were tested by DTG-60 spectrometer.

Scheme S1. Synthesis of silylium cations



Synthesis of silylium cations 1–6: 1 was used as an example: Under nitrogen atmosphere, $[Ph_3C]^+[B(C_6F_5)_4]^-$ (0.2 g, 0.22 mmol) was added to a small vial. An excess of triethylsilane (1.5 mL) was added to the $[Ph_3C]^+[B(C_6F_5)_4]^-$ solid and stirred for 48 h.[1] The yellow solid was replaced with a white solid, which was washed several times with pentane, dried under vacuum to give $[(Et_3Si)_2H]^+[B(C_6F_5)_4]^-$ (**1**), stored in a freezer in the glovebox. Yield: 0.15 g (90 %). ^1H NMR (400 MHz, C_6D_5Cl) δ 2.20 (s, 1H), 0.85 – 0.61 (m, 47H); ^{29}Si NMR (700 MHz, C_6D_5Cl) δ 58.54; ^{11}B NMR (700 MHz, C_6D_5Cl) δ 16.00; ^{13}C NMR (700 MHz, C_6D_5Cl) δ 5.86, 5.53, 5.25, 4.97. Catalysts **2–6** are synthesized in the same way as **1**. **5**: ^{29}Si NMR (700 MHz, C_6D_6) δ 105.51.

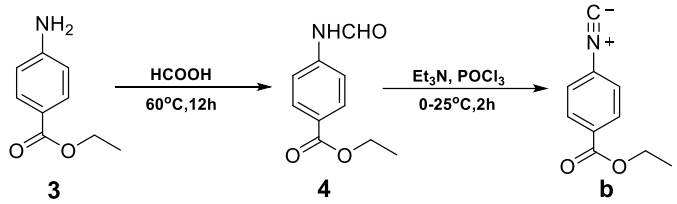
Scheme S2. Synthesis of 2-isocyanonaphthalene (NI)



Synthesis of N-(naphthalen-2-yl)formamide (2) Compound **1** (1.0 g, 7.0 mmol) was dissolved in formic acid (10 mL),the resulting mixture was heated to 60°C for 12 h. After the reaction mixture was cooled to room temperature, the solvents were removed under reduced pressure. The residue was dissolved in DCM (20 mL) and the solution was washed with saturated aqueous Na_2CO_3 (2×20 mL). The separated organic phase was dried over anhydrous Na_2SO_4, concentrated under reduced pressure to afford compound **2** as a red solid (crude product).

Synthesis of 2-isocyanonaphthalene (a) Compound **2** (1 g, crude product) and triethylamine (5 mL) were dissolved in dry DCM (20 mL) under an atmosphere of nitrogen, after the mixture was cooled to 0 °C, $POCl_3$ (1.2 mL) was added dropwise to the mixture, the resulting mixture was slowly warm to room temperature and stirred for 2 h, then the reaction mixture was slowly poured into 50 mL saturated aqueous Na_2CO_3 and stirred at room temperature for 0.5 h, the mixture was extracted with DCM (3 × 50 mL), the combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure, the residue was purified by column chromatography (neutral Al_2O_3, 10:1 hexane to ethyl acetate, v/v) to afford compound **a** as a white solid (0.69 g,78 % yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (ddd, J = 9.7, 9.1, 4.9 Hz, 4H), 7.61 – 7.53 (m, 2H), 7.42 (dd, J = 8.7, 1.6 Hz, 1H).

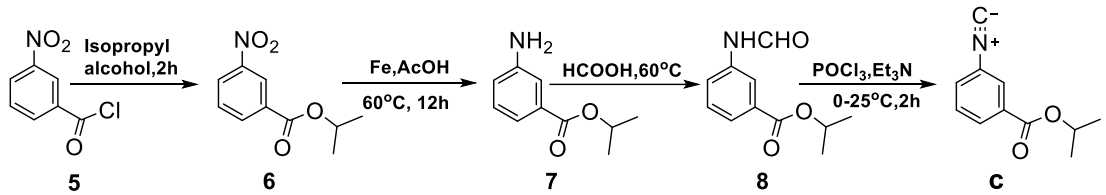
Scheme S3. Synthesis of ethyl 4-isocyanobenzoate (EPI)



Synthesis of ethyl 4-formamidobenzoate (4) The synthetic procedure was the same with that of compound **2** (crude product).

Synthesis of ethyl 4-isocyanobenzoate (b) The synthetic procedure was the same with that of compound **a**. (a brown solid, 73 % yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 – 8.06 (m, 2H), 7.44 (d, J = 8.5 Hz, 2H), 4.39 (q, J = 7.1 Hz, 2H), 1.40 (t, J = 7.1 Hz, 3H).

Scheme S4. Synthesis of isopropyl 3-isocyanobenzoate (IPI)



Synthesis of isopropyl 3-nitrobenzoate (6) To a mixture of Isopropanol(4 mL) and Et_3N(5.2ml) was slowly added a solution of 3-nitrobenzoyl chloride (7.0 g, 37.0 mmol) in 50 mL DCM at nitrogen atmosphere and the resulting mixture was stirred at room temperature for 2 h. Then the solvents were removed under reduced pressure and the residue was dissolved in dichloromethane (30 mL). The solution was washed with saturated Na_2CO_3 aqueous solution and brine, the separated organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure, the residue was purified by column chromatography (silica gel, 10:1 hexane to ethyl acetate, v/v) to afford

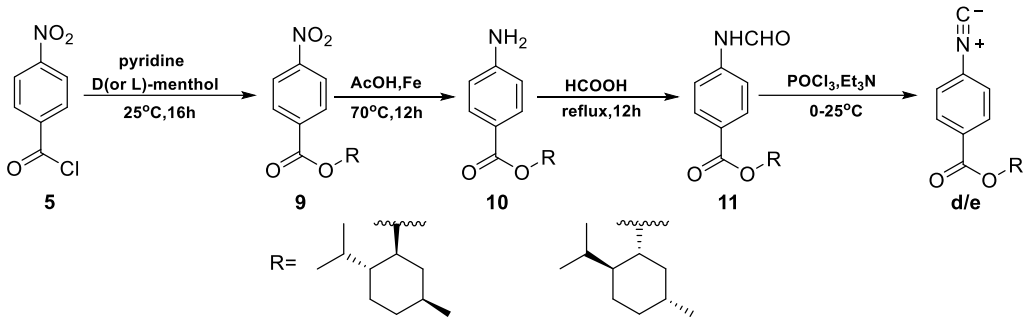
the desired compound **6** as a white solid (2.40 g, 81 % yield) ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 – 8.70 (m, 1H), 8.34 – 8.24 (m, 2H), 7.57 (t, *J* = 8.0 Hz, 1H), 5.22 (dq, *J* = 12.6, 6.3 Hz, 1H), 1.33 (d, *J* = 6.3 Hz, 6H).

Synthesis of isopropyl 3-aminobenzoate (7) Under nitrogen atmosphere, compound **6** (7.5 g, 42mmol) was dissolved in 30 ml of acetic acid, then iron powder (23.5g, 430 mmol) was added in one portion, the resulting mixture was stirred at 70^{o}C overnight. Then the mixture was filtered and the filter cake was washed with ethyl acetate (50 mL), the filtrate was concentrated under reduced pressure, the residue was purified by column chromatography (silica gel, 4:1 hexane to ethyl acetate, v/v) to afford the desired compound **7** as a yellow oil (3.5 g, 51 % yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 – 8.70 (m, 1H), 8.34 – 8.24 (m, 2H), 7.57 (t, *J* = 8.0 Hz, 1H), 5.22 (dq, *J* = 12.6, 6.3 Hz, 1H), 1.33 (d, *J* = 6.3 Hz, 6H).

Synthesis of isopropyl 3-formamidobenzoate (8) The synthetic procedure was the same with that of compound **2** (crude product).

Synthesis of isopropyl 3-isocyanobenzoate (c) The synthetic procedure was the same with that of compound **a**. (a brown oil, 64 % yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 – 8.70 (m, 1H), 8.34 – 8.24 (m, 2H), 7.57 (t, *J* = 8.0 Hz, 1H), 5.22 (dq, *J* = 12.6, 6.3 Hz, 1H), 1.33 (d, *J* = 6.3 Hz, 6H).

Scheme S5. Synthesis of (*1S,2R,5S*)-2-isopropyl-5-methylcyclohexyl 4-isocyanobenzoate (D-IMCI) and (*1R,2S,5R*)-2-isopropyl-5-methylcyclohexyl 4-isocyanobenzoate (L-IMCI)



Synthesis of (*1S,2R,5S*)-2-isopropyl-5-methylcyclohexyl 4-nitrobenzoate (9) Under nitrogen atmosphere, 4-nitrobenzoyl chloride (1.8 g, 9.7 mmol) was dissolved in dry pyridine (20 mL), then D-menthol (1.5 g, 9.7 mmol) was added in one portion and the resulting mixture was stirred at room temperature for 16 h, after removal of pyridine under reduced pressure, the residue was dissolved in dichloromethane (30 mL) and washed with 1 N HCl, saturated $NaHCO_3$ aqueous solution and brine, the separated organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure, the residue was purified by column chromatography (silica gel, 10:1 hexane to ethyl acetate, v/v) to afford the desired compound **9** as a white solid (2.0 g, 68 % yield) . ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.79 (d, *J* = 7.2 Hz, 3H), 0.93 (t, *J* = 6.4 Hz, 6H), 0.88-0.98 (m, 1H), 1.08-1.17 (m, 2H), 1.54-1.62 (m,2H), 1.74 (d, *J* = 12.4 Hz, 2H), 1.88-1.95 (m, 1H), 2.12 (d, *J* = 11.6 Hz, 1H), 4.97 (dt, *J* = 4.4, 11.2 Hz, 1H), 8.20 (d, *J* = 8.8 Hz, 2H), 8.28 (d, *J* = 8.4 Hz, 2H).

Synthesis of (*1S,2R,5S*)-2-isopropyl-5-methylcyclohexyl 4-aminobenzoate (10) The synthetic procedure was the same with that of compound **7**. (a yellow oil, 50 % yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.6 Hz, 2H), 6.64 (d, *J* = 8.6 Hz, 2H), 4.95 – 4.73 (m, 1H), 4.03 (s, 2H), 2.11 (d, *J* = 11.5 Hz, 1H), 1.95 (ddd, *J* = 13.9, 7.0, 2.7 Hz, 1H), 1.77 – 1.67 (m, 2H), 1.52 (ddd, *J* = 13.9, 6.0, 3.0 Hz, 2H), 1.10 (ddd, *J* = 35.1, 18.0, 11.1 Hz, 2H), 0.91 (dd, *J* = 6.8, 3.8 Hz, 7H), 0.78 (d, *J* = 6.9 Hz, 3H).

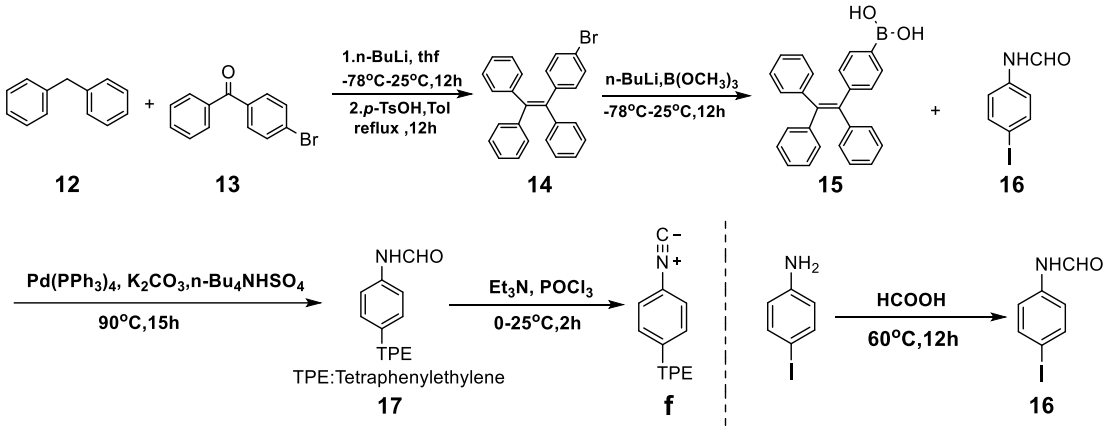
Synthesis of (*1S,2R,5S*)-2-isopropyl-5-methylcyclohexyl 4-formamidobenzoate (11) The synthetic procedure was the same with that of compound **2** (a yellow oil, crude product).

Synthesis of (*1S,2R,5S*)-2-isopropyl-5-methylcyclohexyl 4-isocyanobenzoate (d) The synthetic procedure was the same with that of compound **a**. (a brown solid, 75 % yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 – 8.06 (m, 2H), 7.44 (d, *J* = 8.6 Hz, 2H), 4.94 (td, *J* = 10.9, 4.4 Hz, 1H), 2.21 – 2.04 (m, 1H), 2.00 – 1.83 (m, 1H), 1.74 (dt, *J* = 5.0, 3.0 Hz,

2H), 1.65 – 1.47 (m, 2H), 1.17 – 1.05 (m, 2H), 0.99 – 0.87 (m, 7H), 0.79 (d, *J* = 7.0 Hz, 3H).

Synthesis of (*1R,2S,5R*)-2-isopropyl-5-methylcyclohexyl 4-isocyanobenzoate (e) The synthesis of (*1R*,*2S*,*5R*)-2-isopropyl-5-methylcyclohexyl 4-isocyanobenzoate (**e**) was the same with that of (*1S*,*2R*,5S)-2-isopropyl-5-methylcyclohexyl 4-isocyanobenzoate (**d**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 – 8.04 (m, 2H), 7.44 (d, *J* = 8.6 Hz, 2H), 4.94 (td, *J* = 10.9, 4.4 Hz, 1H), 2.17 – 2.06 (m, 1H), 1.91 (dtd, *J* = 13.9, 7.0, 2.7 Hz, 1H), 1.79 – 1.69 (m, 2H), 1.62 – 1.50 (m, 2H), 1.21 – 1.03 (m, 2H), 1.00 – 0.85 (m, 7H), 0.79 (d, J = 7.0 Hz, 3H).

Scheme S6. Synthesis of 4-isocyano-4'-(1,2,2-triphenylvinyl)-1,1'-biphenyl (ITPB)



Synthesis of (2-(4-bromophenyl)ethene-1,1,2-triyl)tribenzene (14) Under nitrogen atmosphere, diphenylmethane (8.60 g, 51 mmol) was dissolved in 50 mL of dry THF, after the solution was cooled to -78°C, *n*-BuLi (35 mL, 1.6 M in hexane) was added dropwise and the resulting mixture was stirred at -10 °C for 2 h, then (4-bromophenyl)(phenyl)methanone (11.1 g, 42.4 mmol) was added dropwise and the mixture was allowed to warmed to room temperature and stirred for 10 h. Then the reaction mixture was quenched with an aqueous solution of ammonium chloride, extracted with DCM (3×100 mL), the combined organic layers were dried over anhydrous Na_2SO_4 and evaporated to remove the solvent. The residue was dissolved in toluene (100 mL), p-toluene sulfonic acid (1.06 g, 6.20 mmol) was added, the resulting mixture was refluxed for 12 h. after the reaction mixture was cooled to room temperature, the solvent was removed under reduced pressure, the residue was purified by column chromatography (silica gel, 20:1 hexane to ethyl acetate, v/v) to afford the desired compound **14** as a white solid (12.7 g, 73 % yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, *J* = 8.5 Hz, 2H), 7.16 – 7.08 (m, 9H), 7.02 (qd, *J* = 6.2, 2.6 Hz, 6H), 6.92 – 6.87 (m, 2H).

Synthesis of (4-(1,2,2-triphenylvinyl)phenyl)boronic acid (15) Under nitrogen atmosphere, compound 6-1 (12.7 g, 31.0 mmol) was dissolved in 20 ml of dry THF, after the solution was cooled to -78°C, *n*-BuLi (25 mL, 2.4 M in hexane) was added dropwise and the mixture was stirred at -78 °C for 30 min. Then a solution of trimethyl borate (18 mL) in dry THF (10 mL) was added dropwise, the resulting mixture was stirred at -78 °C for 2h, then allowed to warm to room temperature and stirred overnight. The reaction mixture was quenched with 10 % hydrogen chloride aqueous solution, extracted with ethyl acetate (3 × 30 mL), the combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to afford crude compound **15** as white solid (6.8 g, crude product), this compound was used directly for the next step without purification.

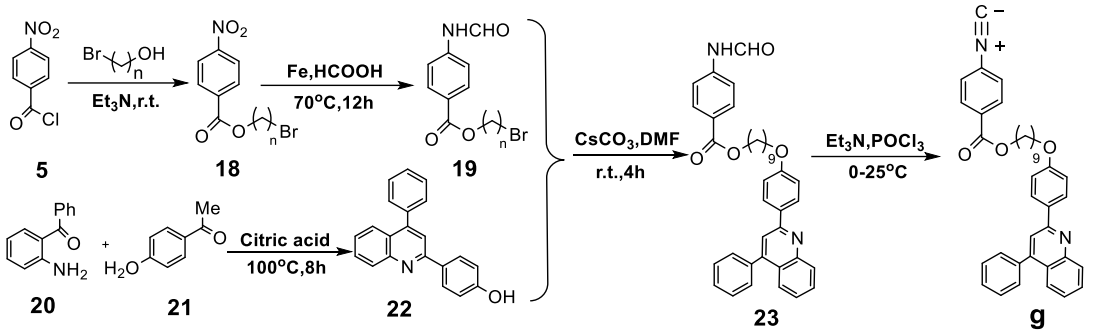
Synthesis of *N*-(4-iodophenyl)formamide (16) The synthetic procedure was the same with that of compound **2** (a brown solid, crude product).

Synthesis of *N*-(4'-(1,2,2-triphenylvinyl)-[1,1'-biphenyl]-4-yl)formamide (17) Under nitrogen atmosphere, compound **15** (6.8 g, crude product), compound **16** (4.5 g, crude product) were dissolved in a mixture solvents of toluene (100 mL) and water (50 mL), then $Pd(PPh_3)_4$ (410 mg, 0.33 mmol), K_2CO_3 (3.10g, 22.4mmol) and tetrabutylammonium hydrogen sulfate (510 mg, 1.5 mmol) were added, the resulting mixture was stirred at 90 °C

for 15 h. after the reaction mixture was cooled to room temperature, the organic layer was separated and the aqueous phase was extracted with ethyl acetate (3 × 80 mL), the combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure, the residue was purified by column chromatography (silica gel, 2:1 hexane: ethyl acetate, v/v) to afford the desired compound **17** as a light yellow solid (5.1 g, 63 % yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (d, J = 11.4 Hz, 1H), 8.39 (d, J = 1.3 Hz, 1H), 7.60 – 7.49 (m, 3H), 7.35 – 7.29 (m, 2H), 7.22 – 6.98 (m, 18H).

Synthesis of 4-isocyano-4'-(1,2,2-triphenylvinyl)-1,1'-biphenyl (f) The synthetic procedure was the same with that of compound **a** (a green solid 0.7 g, 75 % yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, J = 8.5 Hz, 2H), 7.40 (d, J = 8.5 Hz, 2H), 7.31 (d, J = 8.3 Hz, 2H), 7.15 – 7.02 (m, 17H).

Scheme S7. Synthesis of 9-bromononyl 4-nitrobenzoate (BNB)



Synthesis of 9-bromononyl 4-nitrobenzoate (18) Under nitrogen atmosphere, 4-nitrobenzoyl chloride (0.56 g, 3.0 mmol) was dissolved in dry DCM (20ml), then Et_3N(0.5ml) and D-menthol (1.5 g, 9.7 mmol) were added in one portion and the resulting mixture was stirred at room temperature for 8 h.[3] After removal of Et_3N under reduced pressure, the residue was dissolved in DCM (30 mL) and washed with saturated $NaHCO_3$ aqueous solution and brine; the separated organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure, the residue was purified by column chromatography (silica gel, 10:1 hexane to ethyl acetate, v/v) to afford the desired compound **18** as a white solid (0.87 g, 75 % yield) . ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, J = 8.4 Hz, 2H), 8.20 (d, J = 8.5 Hz, 2H), 4.36 (t, J = 6.7 Hz, 2H), 3.40 (t, J = 6.8 Hz, 2H), 1.90 – 1.73 (m, 4H), 1.48 – 1.27 (m, 10H).

Synthesis of 9-bromononyl 4-formamidobenzoate (19) Under nitrogen atmosphere, compound **18** (1.0 g, 2.7 mmol) was dissolved in 12 mL of acetic acid, then iron powder (1.51 g, 27 mmol) was added in one portion, the resulting mixture was stirred at 70 °C overnight. Then the mixture was filtered and the filter cake was washed with ethyl acetate (20 ml), the filtrate was concentrated under reduced pressure, the residue was purified by column chromatography (silica gel, 1:1 hexane to ethyl acetate, v/v) to afford the desired compound **19** as a white solid (0.9 g, 91 % yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, J = 8.4 Hz, 2H), 8.20 (d, J = 8.5 Hz, 2H), 4.36 (t, J = 6.7 Hz, 2H), 3.40 (t, J = 6.8 Hz, 2H), 1.90 – 1.73 (m, 4H), 1.48 – 1.27 (m, 10H).

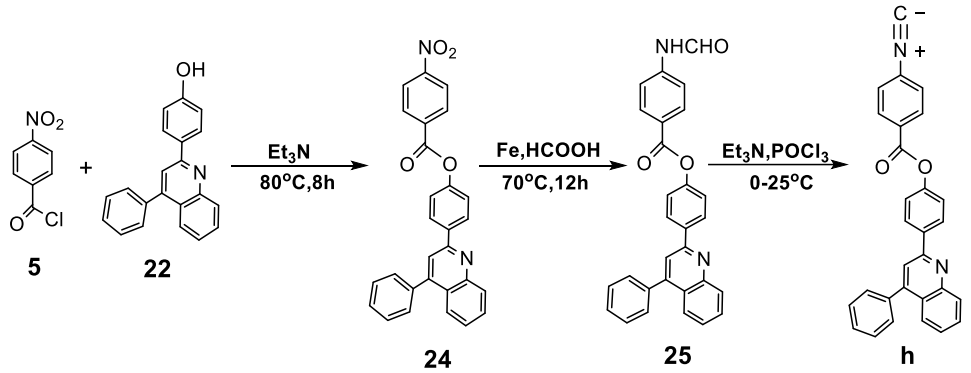
Synthesis of 4-(5-phenylquinolin-7-yl)phenol (22) A mixture of (2-aminophenyl)-(phenyl)methanone (3.96 g, 2 mmol),1-(4-hydroxyphenyl)ethan-1-one (3.0 g, 2.2 mmol) and citric acid (96 mg, 0.50 mmol) were heated for 8h to 100°C.[2] The crude mixture was dissolved in DCM (30 mL) and concentrated under reduced pressure, the residue was purified by column chromatography (silica gel, 5:1 hexane to ethyl acetate, v/v) to afford the desired compound **22** as a white solid (3.3 g, 56 % yield) . ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, J = 7.9 Hz, 1H), 8.14 – 8.06 (m, 2H), 7.88 (dd, J = 8.4, 0.9 Hz, 1H), 7.76 (s, 1H), 7.72 (ddd, J = 8.4, 6.9, 1.4 Hz, 1H), 7.59 – 7.48 (m, 5H), 7.48 – 7.41 (m, 1H), 7.01 – 6.92 (m, 2H), 5.29 (s, 1H).

Synthesis of 9-(4-(5-phenylquinolin-7-yl)phenoxy)nonyl 4-formamidobenzoate (23) To a solution of Compound **22** (1.0 g, 3.4 mmol) in dry DMF(20 mL), cesium carbonate and compound **19** were added under nitrogen atmosphere and the mixture was stirred at room temperature for 4 h.[4] The reaction mixture was quenched with 1N HCl aqueous

solution, extracted with DCM (3 × 30 mL), the combined organic layers washed with saturated Na_2CO_3 aqueous solution and brine, the separated organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure, the residue was purified by column chromatography (silica gel, 1:1 hexane to ethyl acetate, v/v) to afford the desired compound **23** as a white solid (2.0 g, 80 % yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.82 (d, *J* = 11.2 Hz, 1H), 8.39 (s, 1H), 8.24 – 8.10 (m, 3H), 8.02 (t, *J* = 9.1 Hz, 2H), 7.88 (d, *J* = 8.4 Hz, 1H), 7.77 (s, 1H), 7.74 – 7.68 (m, 1H), 7.62 – 7.41 (m, 7H), 7.09 (d, *J* = 8.5 Hz, 1H), 7.02 (d, *J* = 8.7 Hz, 2H), 4.31 (t, *J* = 6.4 Hz, 2H), 4.03 (t, *J* = 6.4 Hz, 2H), 1.79 (qd, *J* = 13.6, 6.5 Hz, 4H), 1.53 – 1.32 (m, 10H).

Synthesis of 9-(4-(5-phenylquinolin-7-yl)phenoxy)nonyl 4-isocyanobenzoate (g) The synthetic procedure was the same with that of compound **a**. (a white solid, 58 % yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (dd, *J* = 15.9, 8.6 Hz, 3H), 8.10 – 8.06 (m, 2H), 7.92 (d, *J* = 8.8 Hz, 1H), 7.88 (d, *J* = 7.8 Hz, 1H), 7.78 (s, 1H), 7.71 (t, *J* = 7.5 Hz, 1H), 7.57 – 7.54 (m, 3H), 7.53 – 7.49 (m, 1H), 7.45 (t, *J* = 7.4 Hz, 3H), 7.03 (d, *J* = 8.8 Hz, 2H), 7.00 (s, 1H), 6.91 (d, *J* = 8.9 Hz, 1H), 4.33 (t, *J* = 6.7 Hz, 2H), 4.04 (t, *J* = 6.5 Hz, 2H), 1.86 – 1.73 (m, 4H), 1.52 – 1.30 (m, 10H).

Scheme S8. Synthesis of 4-(4-phenylquinolin-2-yl)phenyl 4-isocyanobenzoate (PQPI)

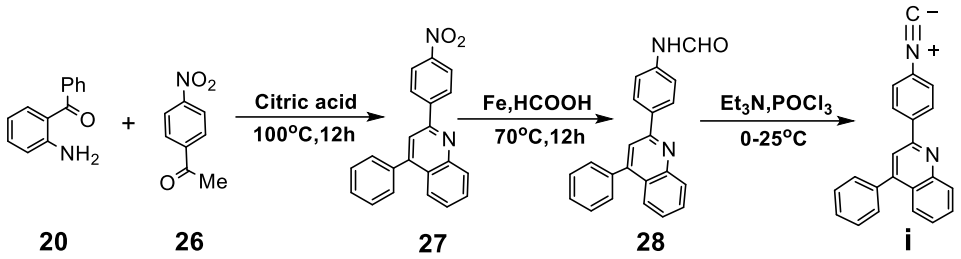


Synthesis of 4-(4-phenylquinolin-2-yl)phenyl 4-nitrobenzoate (24) Under nitrogen atmosphere, 4-nitrobenzoyl chloride (0.78 g, 4.2 mmol) was dissolved in dry DMF (15 mL), then Et_3N(3 mL) and compound **22** (0.60 g, 2 mmol) were added in one portion and the resulting mixture was stirred at 80 °C for 8 h, cooled and then poured into ice-cold water. The precipitate was collected by filtration, washed thoroughly with water and methanol and dried. The crude product was then recrystallized in ethanol, finally dried in vacuum to afford the desired compound 8-1 as a yellow solid (0.5 g, 56 % yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (q, *J* = 9.0 Hz, 4H), 8.34 (d, *J* = 1.4 Hz, 1H), 8.31 (d, *J* = 8.7 Hz, 2H), 7.93 (d, *J* = 8.3 Hz, 1H), 7.83 (s, 1H), 7.76 (t, *J* = 7.5 Hz, 1H), 7.61 – 7.47 (m, 6H), 7.42 (d, *J* = 8.7 Hz, 2H).

Synthesis of 4-(4-phenylquinolin-2-yl)phenyl 4-formamidobenzoate (25) The synthetic procedure was the same with that of compound **24**. (a white solid, 63 % yield). 1H NMR (400 MHz, CDCl3) δ 8.91 (d, *J* = 11.2 Hz, 1H), 8.46 (s, 1H), 8.24 (dt, *J* = 24.6, 11.6 Hz, 5H), 8.05 (d, *J* = 8.4 Hz, 1H), 7.92 (d, *J* = 8.4 Hz, 1H), 7.83 (s, 1H), 7.74 (dd, J = 17.5, 8.2 Hz, 3H), 7.61 – 7.44 (m, 7H), 7.39 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.5 Hz, 1H), 7.20 (d, *J* = 8.4 Hz, 1H).

Synthesis of 4-(4-phenylquinolin-2-yl)phenyl 4-isocyanobenzoate (h) The synthetic procedure was the same with that of compound **a**. (a white solid, 64 % yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 – 8.21 (m, 5H), 7.96 – 7.89 (m, 1H), 7.85 – 7.81 (m, 1H), 7.79 – 7.72 (m, 1H), 7.61 – 7.46 (m, 8H), 7.42 – 7.36 (m, 2H).

Scheme S9. Synthesis of 2-(4-isocyanophenyl)-4-phenylquinoline (IPQ)



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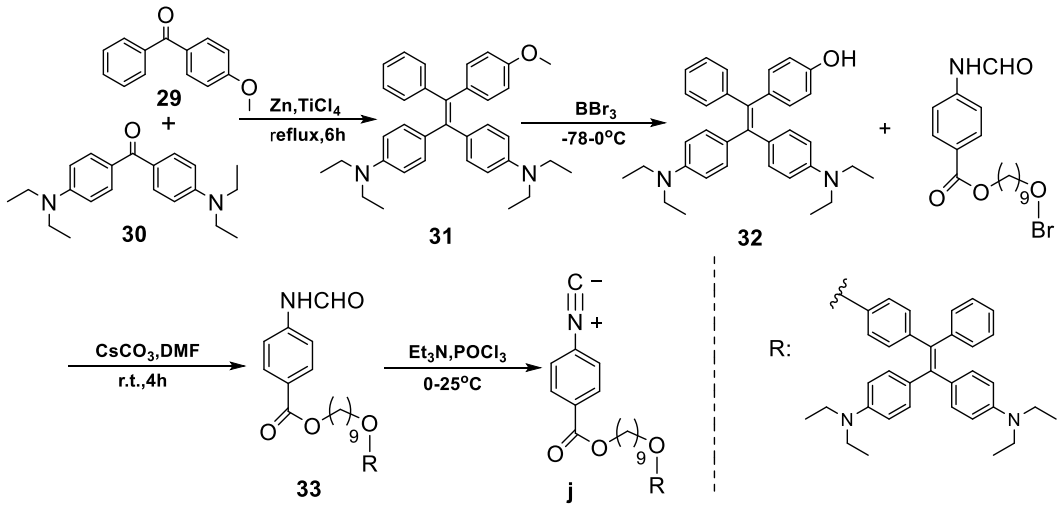
Synthesis of 2-(4-nitrophenyl)-4-phenylquinoline (27) The synthetic procedure was the same with that of compound **22**. (a white solid, 30 % yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 – 8.35 (m, 4H), 8.26 (d, *J* = 8.4 Hz, 1H), 7.95 (d, *J* = 8.4 Hz, 1H), 7.87 (s, 1H), 7.79 (t, *J* = 7.5 Hz, 1H), 7.62 – 7.51 (m, 6H).

Synthesis of N-(4-(4-phenylquinolin-2-yl)phenyl)formamide (28) The synthetic procedure was the same with that of compound **7**. (a white solid, 56 % yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.81 (d, J = 11.4 Hz, 1H), 8.54 (s, 1H), 8.45 (d, *J* = 1.1 Hz, 1H), 8.22 (dd, *J* = 11.8, 5.4 Hz, 3H), 8.02 (s, 1H), 7.90 (dd, *J* = 8.2, 2.9 Hz, 1H), 7.79 (d, *J* = 4.4 Hz, 1H), 7.77 – 7.70 (m, 2H), 7.58 – 7.45 (m, 6H), 7.36 (s, 1H).

Synthesis of 2-(4-isocyanophenyl)-4-phenylquinoline (i) The synthetic procedure was the same with that of compound **a**. (a white solid, 67 % yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 – 8.21 (m, 3H), 7.92 (d, *J* = 7.8 Hz, 1H), 7.80 – 7.74 (m, 2H), 7.61 – 7.47 (m, 8H).

Scheme S10. Synthesis of 9-(4-(2,2-bis(4-(diethylamino)phenyl)-1-phenylvinyl)phenoxy)nonyl 4-isocyanobenzoate (PPNI)



Synthesis of 4,4'-(2-(4-methoxyphenyl)-2-phenylethene-1,1-diyl)bis(N,N-diethylaniline) (31) Under nitrogen atmosphere, compound **29** (1.75 g, 8.26 mmol) and compound **30** (3.08 g, 9.50 mmol) was dissolved in 30 mL of dry tetrahydrofuran, then zinc powder (2.15 g, 33.04 mmol) was added in one portion, the resulting mixture was stirred, then $TiCl_4$ (3.63mL, 33.04mmol) was added dropwise and the mixture was allowed to refluxed for 6 h.[4] Then the reaction mixture was quenched with an aqueous solution of sodium carbonate, extracted with DCM (3×30 mL), the combined organic layers were dried over anhydrous Na_2SO_4 and evaporated to remove the solvent. The residue was purified by column chromatography (silica gel, 1:2 hexane to DCM, v/v) to afford the desired compound **31** as a yellow solid, 60 % yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12–7.00 (m, 8H), 6.98 – 6.92 (m, 3H), 6.91 – 6.83 (m, 4H), 6.64 (dt, *J* = 8.6, 6.5 Hz, 3H), 6.40 (dd, *J* = 11.2, 8.9 Hz, 3H), 3.74 (d, *J* = 3.3 Hz, 3H), 3.28 (p, *J* = 7.0 Hz, 8H), 1.11 (q, *J* = 6.9 Hz, 12H).

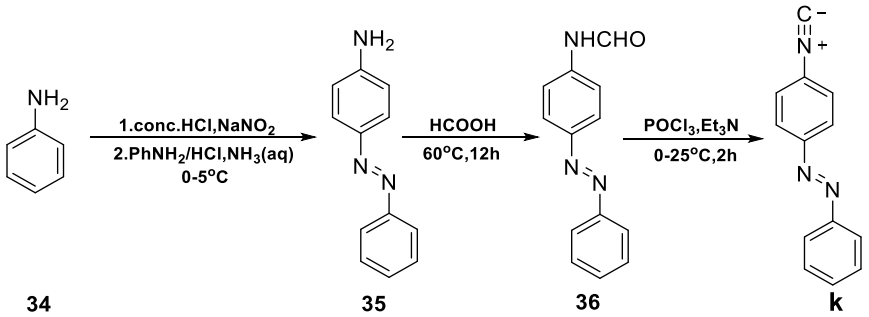
Synthesis of 4-(2,2-bis(4-(diethylamino)phenyl)-1-phenylvinyl)phenol (32) Under nitrogen atmosphere, compound **31** (4.3 g, 8.6 mmol) was dissolved in 30 mL of dry DCM, after the solution was cooled to -78°C, BBr_3 (10

mL, 8.6 mmol) was added dropwise and the resulting mixture was stirred at 0°C for 2 h. Then the reaction solution was quenched with ice water, extracted with DCM (3×30 mL), the combined organic layers were dried over anhydrous Na_2SO_4 and evaporated to remove the solvent. The residue was purified by column chromatography (silica gel, 1:20 MeOH to DCM, v/v) to afford the desired compound **32** as a green solid (0.9 g, 57 % yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06 (s, 6H), 6.88 (s, 6H), 6.56 (s, 2H), 6.40 (s, 3H), 3.91 (s, 1H), 3.28 (s, 8H), 1.11 (d, J = 5.1 Hz, 12H).

Synthesis of 9-(4-(2,2-bis(4-(diethylamino)phenyl)-1-phenylvinyl)phenoxy)nonyl 4-formamidobenzoate (33) The synthetic procedure was the same with that of compound **23**. (a yellow solid, 57 % yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.83 (dd, J = 11.2, 3.7 Hz, 1H), 8.41 (d, *J* = 19.9 Hz, 1H), 8.03 (dd, *J* = 11.9, 5.6 Hz, 3H), 7.61 (dd, *J* = 12.0, 8.8 Hz, 2H), 7.14 – 6.98 (m, 9H), 6.95 – 6.82 (m, 6H), 6.62 (d, *J* = 8.5 Hz, 2H), 6.39 (dd, *J* = 11.5, 8.9 Hz, 4H), 4.30 (t, *J* = 6.5 Hz, 3H), 3.85 (dd, *J* = 14.9, 6.8 Hz, 2H), 3.33 – 3.18 (m, 8H), 1.80 – 1.69 (m, 5H), 1.47 – 1.29 (m, 16H), 1.10 (dt, *J* = 10.8, 5.4 Hz, 12H).

Synthesis of 9-(4-(2,2-bis(4-(diethylamino)phenyl)-1-phenylvinyl)phenoxy)nonyl 4-isocyanobenzoate (j) The synthetic procedure was the same with that of compound **a**. (a yellow oil, 72 % yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 – 8.05 (m, 2H), 7.48 – 7.40 (m, 2H), 7.13 – 6.98 (m, 5H), 6.97 – 6.81 (m, 6H), 6.67 – 6.58 (m, 2H), 6.47 – 6.31 (m, 4H), 4.36 – 4.29 (m, 2H), 3.93 – 3.81 (m, 2H), 3.42 – 3.14 (m, 8H), 1.81 – 1.69 (m, 4H), 1.47 – 1.30 (m, 13H), 1.16 – 1.04 (m, 12H).

Scheme S11. Synthesis of (*E*)-1-(4-isocyanophenyl)-2-phenyldiazene (IPD)



Synthesis of (*E*)-4-(phenyldiazenyl)aniline (35) To a solution of 37 % conc. HCl (13.0 mL) , aniline (4 g, 43.4 mmol)、an aqueous solution of sodium nitrite (3.02 g, 43.4 mmol) was added dropwise in 0 °C, then the mixture was stirred for 1h to an yellow transparent diazonium salt solution. The coupling solution was prepared by using aniline (4 g, 43.4 mmol) and hydrochloric acid (1 N, 44 mL) under vigorous stirring at 0-5 °C. The diazonium salt solution was added dropwise to the coupling solution at 0-5 °C and the solution was stirred for 3h. The final solution was added slowly to ammonia solution (1N, 60 mL) and an yellow-orange crude product was obtained.[5] The crude product was then recrystallized in ethanol, finally dried in vacuum to afford the desired compound **35** as a yellow solid (5.9 g, 69 % yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.79 (m, 4H), 7.53 – 7.45 (m, 2H), 7.43 – 7.38 (m, 1H), 6.78 – 6.71 (m, 2H), 4.04 (s, 2H).

Synthesis of (*E*)-*N*-(4-(phenyldiazenyl)phenyl)formamide (36) The synthetic procedure was the same with that of compound **2**. (a red solid, 81 % yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 (d, *J* = 11.3 Hz, 1H), 8.45 (d, *J* = 1.4 Hz, 1H), 7.99 – 7.84 (m, 4H), 7.72 (d, *J* = 8.8 Hz, 1H), 7.56 – 7.44 (m, 3H), 7.35 (s, 1H), 7.21 (d, *J* = 8.7 Hz, 1H).

Synthesis of (*E*)-1-(4-isocyanophenyl)-2-phenyldiazene (k) The synthetic procedure was the same with that of compound **a**. (a white solid, 65 % yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 (d, J = 11.3 Hz, 1H), 8.45 (d, *J* = 1.4 Hz, 1H), 7.99 – 7.84 (m, 4H), 7.72 (d, *J* = 8.8 Hz, 1H), 7.56 – 7.44 (m, 3H), 7.35 (s, 1H), 7.21 (d, *J* = 8.7 Hz, 1H).

A typical procedure for the polymerization of 4-ethoxycarbonyl phenyl isocyanide (EPI) (Table 1, entry 3)

In the glove box, after $[(Et_3Si)_2H][B(C_6F_5)_4]$ (9.1 mg, 10 μmol) was dissolved in chlorobenzene (1 mL), the resulting mixture was stirred at 25 °C for 5 min. Then a solution of 4-ethoxycarbonyl phenyl isocyanide (87.5 mg, 0.5 mmol)

in chlorobenzene (2 mL) was added in one portion and the resulting mixture was stirred at 25 °C for 1min. The reaction mixture was taken out of the glove box and poured into methanol (100 mL) to precipitate the polymer product. The yellow polymer solid was collected by filtration and dried in vacuum at 40 °C to a constant weight. The product obtained is soluble thoroughly in $CHCl_3$ at 25 °C.

A typical procedure for the copolymerization of (1S,2R,5S)-2-isopropyl-5-methylcyclohexyl 4-isocyanobenzoate (D-IMCI) with 4-isocyano-4'-(1,2,2-triphenylvinyl)-1,1'-biphenyl (ITPB) (Table 2, entry 3)

In the glove box, after $[(Et_3Si)_2H][B(C_6F_5)_4]$ (9.1 mg, 10 μmol) was dissolved in chlorobenzene (1 mL), the resulting mixture was stirred at 25 °C for 5 min. Then a solution of (*1S,2R,5S*)-2-isopropyl-5-methylcyclohexyl 4-isocyanobenzoate (142.6 mg, 0.5 mmol) and 4-isocyano-4'-(1,2,2-triphenylvinyl)-1,1'-biphenyl (216.6 mg, 0.5 mmol) in chlorobenzene (2 mL) was added in one portion and the resulting mixture was stirred at 25 °C for 3min. The reaction mixture was taken out of the glove box and poured into methanol (100 mL) to precipitate the copolymer product. The orange copolymer solid was collected by filtration and dried in vacuum at 40 °C to a constant weight. The product obtained is soluble thoroughly in $CHCl_3$ and THF at 25 °C.

Calculation the activity of catalyst

$$A = m_{polymer} / (n_{cat.} \cdot t)$$

A: the activity of (co)polymerization (g of polymer/($mol_{cat.}$·h)), $m_{polymer}$: the mass of (co)polymer (g), *t*: the reaction time of (co)polymerization (h), $n_{cat.}$: molar amount of catalyst (mol).

$$n_{cat.} = m_{catalyst} / M_{catalyst}$$

$m_{catalyst}$: the mass of catalysts (g), $M_{catalysts}$: the relative molecular weight of catalyst.

Calculation of the IMCI contents of the copolymers

The IMCI contents of the copolymers were calculated from the ^{1}H NMR spectra according to the following formula:

$$\omega(mol\%)_{IMCI} = \{[23(I_{H3}+I_{H4})]/[19(I_{H1}+I_{H2}+I_{H3}+I_{H4})]\}\times 100$$

In which I_{H1} is the integration of the peak at 7.08 ppm which assigned to the aryl protons of ITPB units and the *β*-H of the aryl ring of IMCI units. I_{H2} is the integration of the peak at 5.82 ppm which assigned to the *α*-H of the aryl ring of IMCI units. I_{H3} is the integration of the peak at 4.88 ppm ascribed to the proton of the cyclohexyl carbon connected with the oxygen. I_{H4} is the integration of the peaks between 0.3 to 2.5 ppm which assigned to the rest protons of the cyclohexyl group as well as the substituted methyl and the isopropyl.

The IMCI contents of poly(D-IMCI-*co*-IPI)s and poly(L-IMCI-*co*-IPI)s were calculated from the ^{1}H NMR spectra according to the following formula:

$$\omega(mol\%)IMCI = \{[5\times I_{H4}-6(I_{H1}+I_{H2}+I_{H3})]/[12(I_{H1}+I_{H2}+I_{H3})]\}\times 100$$

In which IH1 is the integration of the peak at 7.08 ppm which assigned to the aryl protons of IPI units and the H of the aryl ring of IMCI units. I_{H2} is the integration of the peak at 5.82 ppm which assigned to the H of the aryl ring of IMCI and IPI units. I_{H3} is the integration of the peak at 4.88 ppm ascribed to the proton of the cyclohexyl carbon connected with the oxygen and the proton of the isopropyl carbon connected with the oxygen. I_{H4} is the integration of the peaks between 0.3 to 2.5 ppm which assigned to the rest protons of the cyclohexyl group as well as the substituted methyl and the isopropy and the rest protons of the isopropyl.

The IMCI contents of poly(D-IMCI-*co*-IPD)s and poly(L-IMCI-*co*-IPD)s were calculated from the ^{1}H NMR spectra according to the following formula:

$$\omega(mol\%)IMCI = \{[5(I_{H3}+I_{H4})]/[23(I_{H2}-I_{H1})+5(I_{H3}+I_{H4})]\}\times 100$$

In which I_{H1} is the integration of the peak at 7.08 ppm which assigned to the aryl protons of IPD units and the H of the aryl ring of IMCI units. I_{H2} is the integration of the peak at 5.82 ppm which assigned to the H of the aryl ring of IMCI units. I_{H3} is the integration of the peak at 4.88 ppm ascribed to the proton of the cyclohexyl carbon connected

with the oxygen. I_{H4} is the integration of the peaks between 0.3 to 2.5 ppm which assigned to the rest protons of the cyclohexyl group as well as the substituted methyl and the isopropyl.

The IMCl contents of poly(D-IMCl-*co*-EPI)s and poly(L-IMCl-*co*-EPI)s were calculated from the ^{1}H NMR spectra according to the following formula:

$$\omega(\text{mol\%})\text{IMCl} = \{[4(2I_{H4}-3I_{H4})]/[41(I_{H1} + I_{H2})]\}\times 100$$

In which I_{H1} is the integration of the peak at 7.08 ppm which assigned to the aryl protons of EPI units and the H of the aryl ring of IMCl units. I_{H2} is the integration of the peak at 5.82 ppm which assigned to the H of the aryl ring of IMCl and EPI units. I_{H3} is the integration of the peak at 4.88 ppm ascribed to the proton of the cyclohexyl carbon connected with the oxygen and the proton of the ethyl carbon connected with the oxygen. I_{H4} is the integration of the peaks between 0.3 to 2.5 ppm which assigned to the rest protons of the cyclohexyl group as well as the substituted ethyl.

Solvent separation experiments

4 mg of poly(D/L-IMCl) (Table 1, entry 18, 20) was added into 2 mL of toluene, the mixture was shaken for about 1h and most of the solid dissolved in toluene completely. 4 mg of poly(ITPB) (Table 1, entry 22) or poly(IPI) (Table 1, entry 17) or poly(IPD) (Table 1, entry 28) was added into 2 mL of toluene and exhibited poor solubility. After shaken for about 1 hour, there was still some solid precipitated in the solution. Then 4 mg of the copolymer products (Table 2, entry 8; Table 2, entry 13; Table 2, entry 28) was added into 2 mL of toluene, the mixture was shaken for 1 min and the solid dissolved in toluene completely.

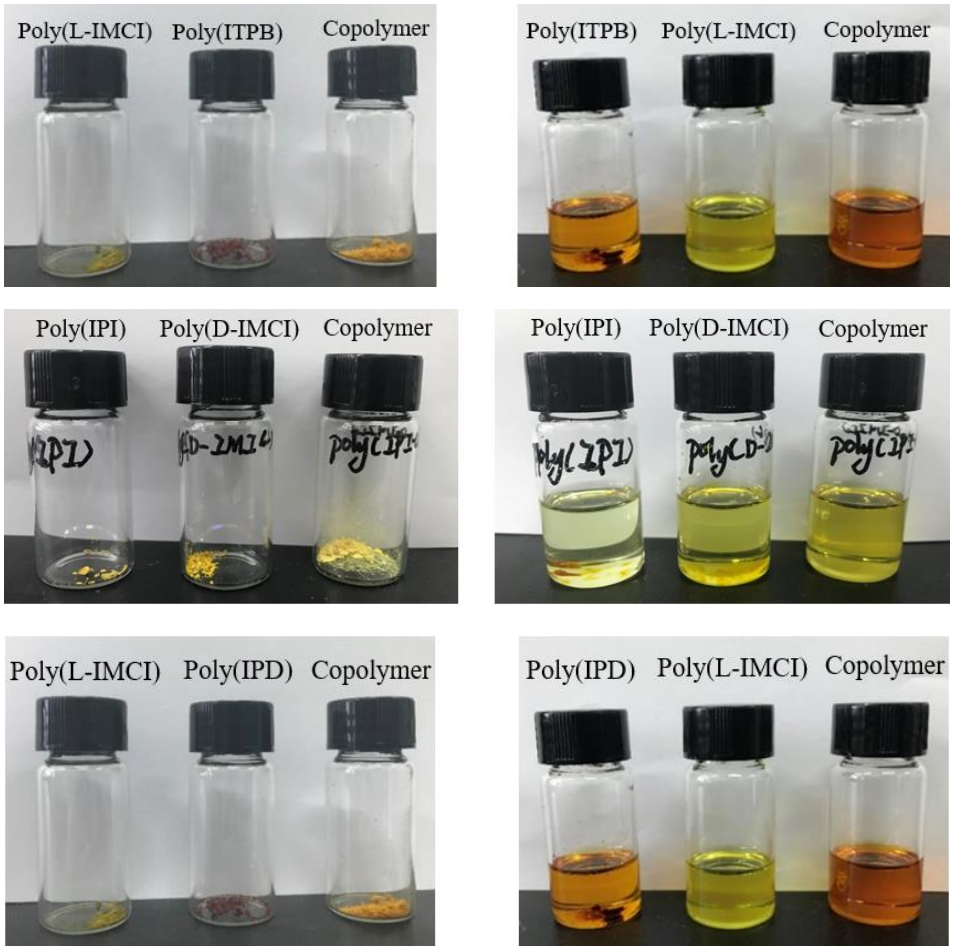


Figure S1. Photos of poly(D/L-IMIC), poly(ITPB), poly(IPI), poly(IPD), copolymers (left) and the solubility of poly(D/L-IMIC), poly(ITPB), poly(IPI), poly(IPD), copolymers (right) in toluene.

Calculation of reactivity ratio of copolymerization

Formula: Fineman-Ross plot:

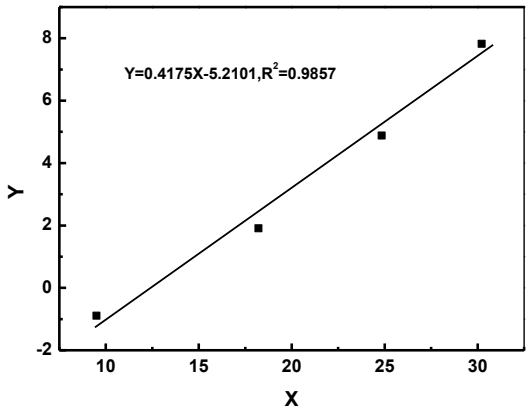
$$\frac{F}{f} \times (f-1) = r_1 \times \frac{F^2}{f} - r_2$$

Copolymerization of L-IMCI with ITPB

F: L-IMCI/ITPB feed ratio in the reaction

f: L-IMCI/ITPB content in the copolymers

L-IMCI (mmol)	ITPE (mmol)	L-IMCI cont. (mol%)	ITPB cont. (mol%)	F	f	X	Y
0.138	0.368	43	57	2.67	0.75	9.50	-0.89
0.138	0.736	61	39	5.33	1.56	18.21	1.91
0.138	1.104	72	28	7.99	2.57	24.84	4.88
0.138	1.472	79	21	10.66	3.76	30.22	7.82



Y = 0.4175X-5.2101, R^2 = 0.9857

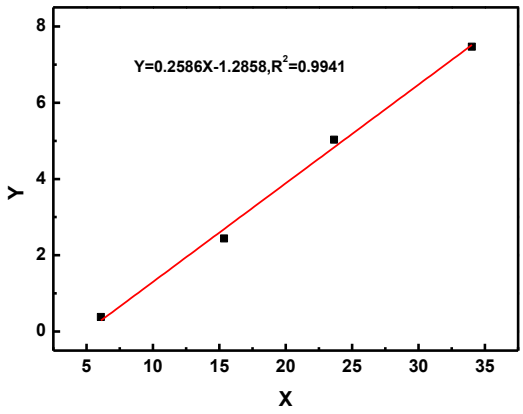
$r_{L\text{-}IMCI} = k_{L\text{-}IMCID\text{-}IMCI}/k_{L\text{-}IMCIITPB}$ = 0.4175, $r_{ITPB} = k_{ITPBITPB}/k_{ITPBL\text{-}IMCI}$ = 5.2101

copolymerization of L-IMCI and IPI

F：L-IMIC/IPI feed ratio in the reaction

f：L-IMIC/IPI content in the copolymers

L-IMCI (mmol)	IPI (mmol)	IPI cont. (mol%)	L-IMCI cont. (mol%)	F	f	X	Y
0.138	0.368	54	46	2.67	1.17	6.09	0.38
0.138	0.736	65	35	5.33	1.85	15.36	2.44
0.138	1.104	73	27	7.99	2.70	23.64	5.03
0.138	1.472	77	23	10.66	3.34	34.02	7.47



Y = 0.2586X-1.2858, R^2 = 0.9941

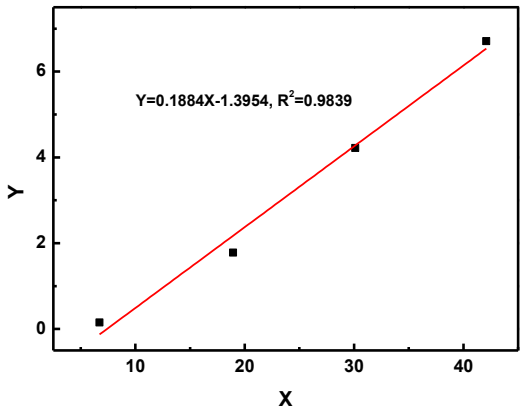
$r_{IPI} = k_{IPIIPI}/k_{IPIL\text{-}IMIC}$ = 0.2586, $r_{L\text{-}IMIC} = k_{L\text{-}IMICL\text{-}IMIC}/k_{L\text{-}IMCIIPI}$ = 1.2858

copolymerization of L-IMCI with IPD

F：IPD/L-IMCI feed ratio in the reaction

f：IPD/L-IMCI content in the copolymers

L-IMCI (mmol)	DNI (mmol)	DNI cont. (mol%)	L-IMCI cont. (mol%)	F	f	X	Y
0.138	0.368	49	51	2.67	1.06	6.73	0.15
0.138	0.736	40	60	5.33	1.50	18.94	1.78
0.138	1.104	36	67	7.99	2.12	30.11	4.22
0.138	1.472	27	73	10.66	2.70	42.09	6.71



Y = 0.1884X-1.3954, R^2 = 0.9839

$r_{DNI} = k_{IPDIPD}/k_{IPDL\text{-}IMIC}$ = 0.2586, $r_{L\text{-}IMIC} = k_{L\text{-}IMICL\text{-}IMIC}/k_{L\text{-}IMCIIPD}$ = 1.3954

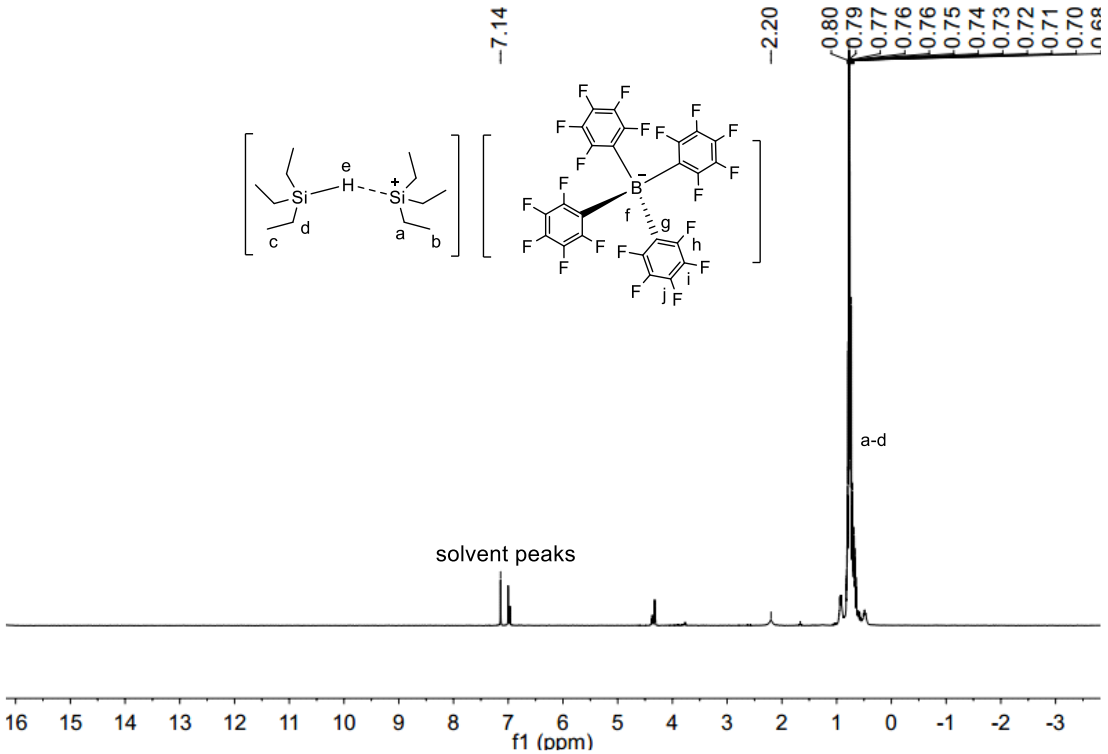


Figure S2. ^{1}H NMR spectrum of catalyst **1** in C_6D_5Cl at 25 °C.

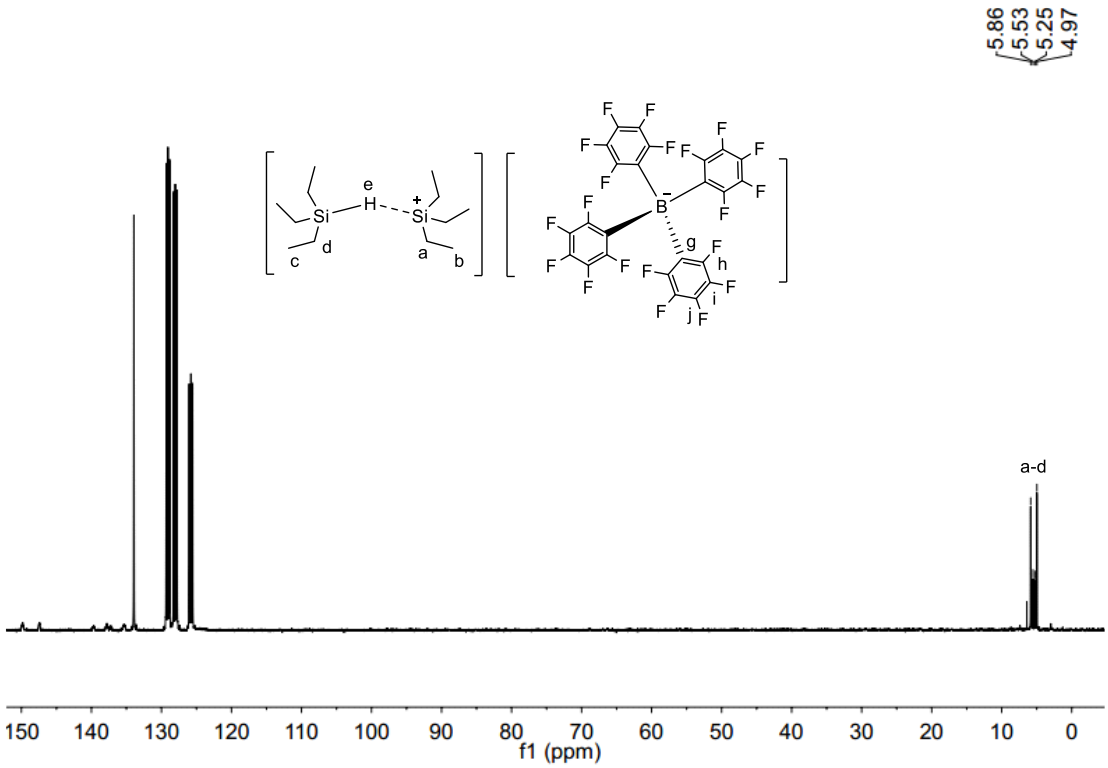


Figure S3. ^{13}C NMR spectrum of catalyst **1** in C_6D_5Cl at 25 °C.

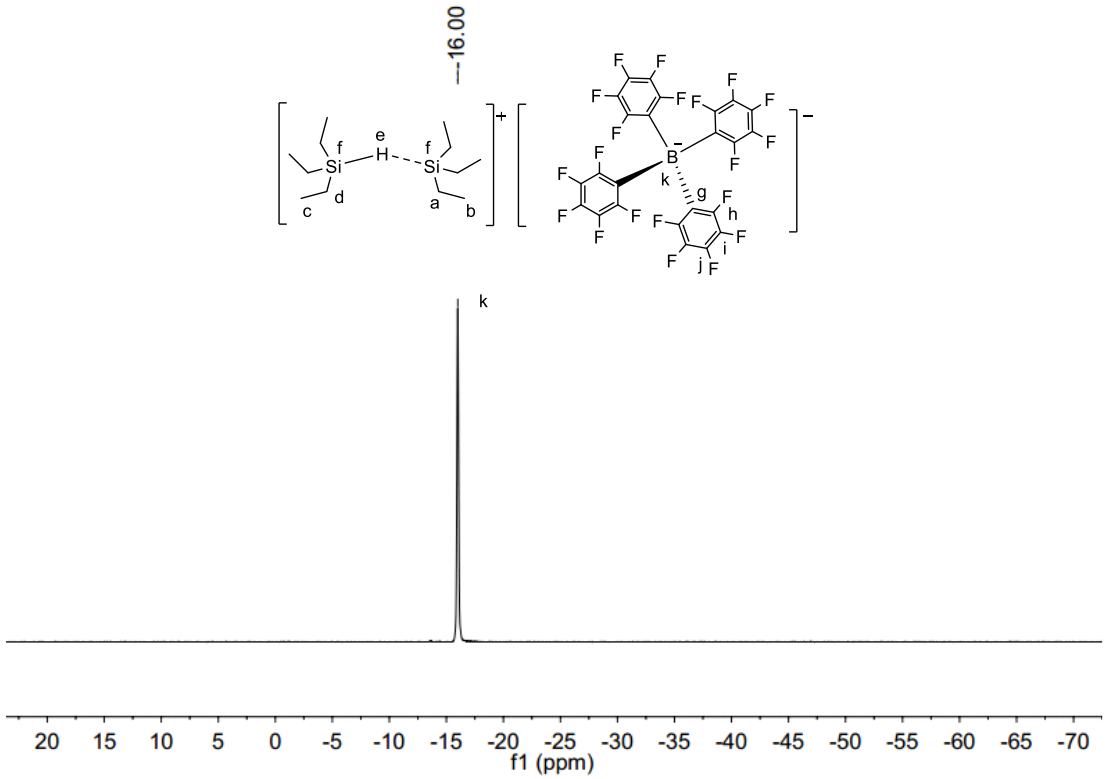


Figure S4. ^{11}B NMR spectrum of catalyst **1** in C_6D_5Cl at 25 °C.

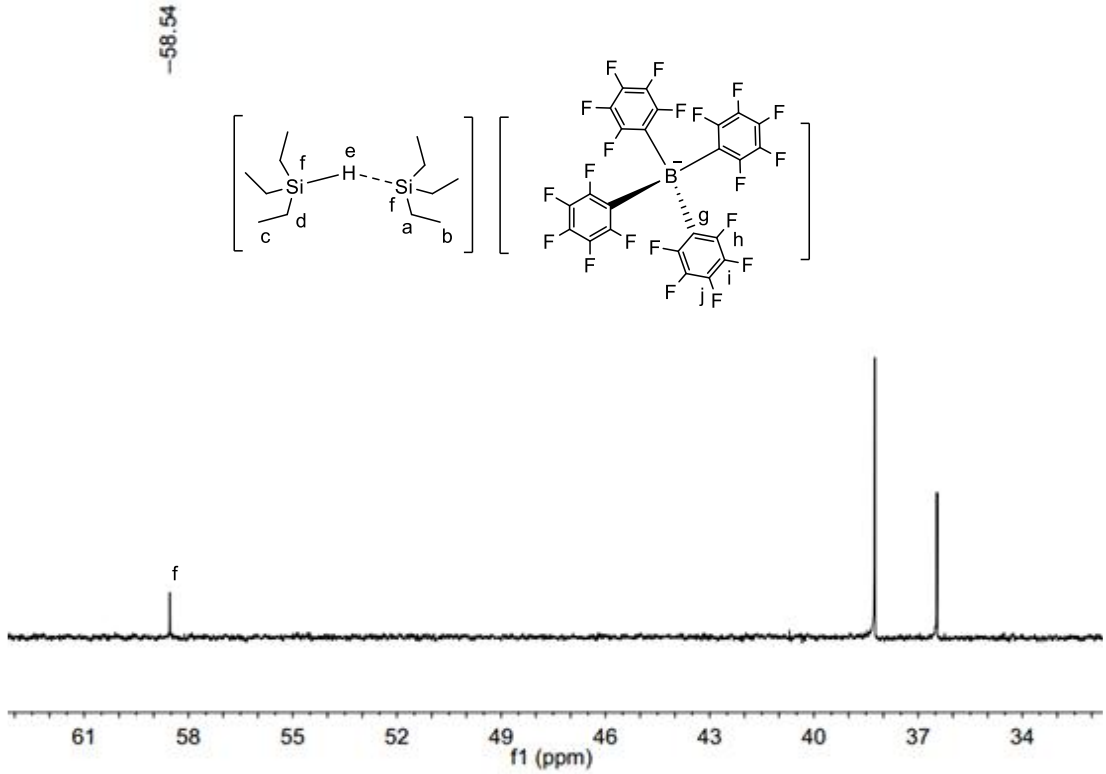


Figure S5. ^{29}Si NMR spectrum of catalyst **1** in C_6D_5Cl at 25 °C.

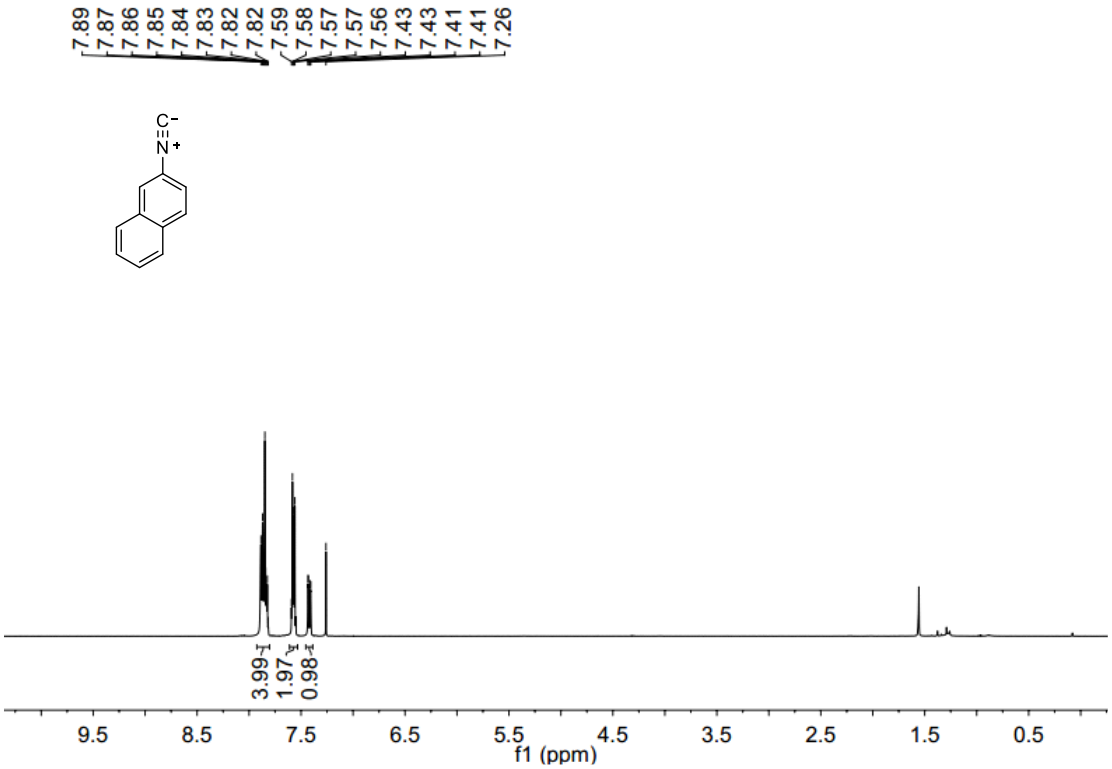


Figure S6. ^{1}H NMR spectrum of 2-naphthyl isocyanide (**a**) in $CDCl_3$ at 25 °C.

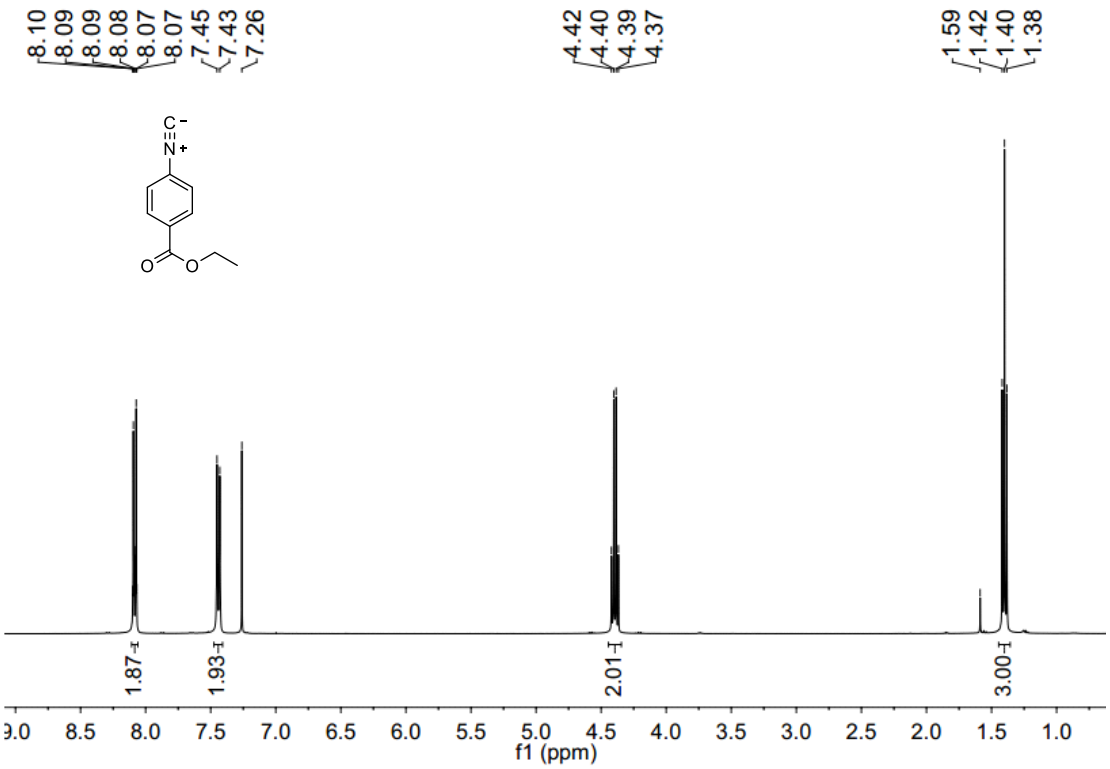


Figure S7. ^{1}H NMR spectrum of 4-ethoxycarbonyl phenyl isocyanide (**b**) in $CDCl_3$ at 25 °C.

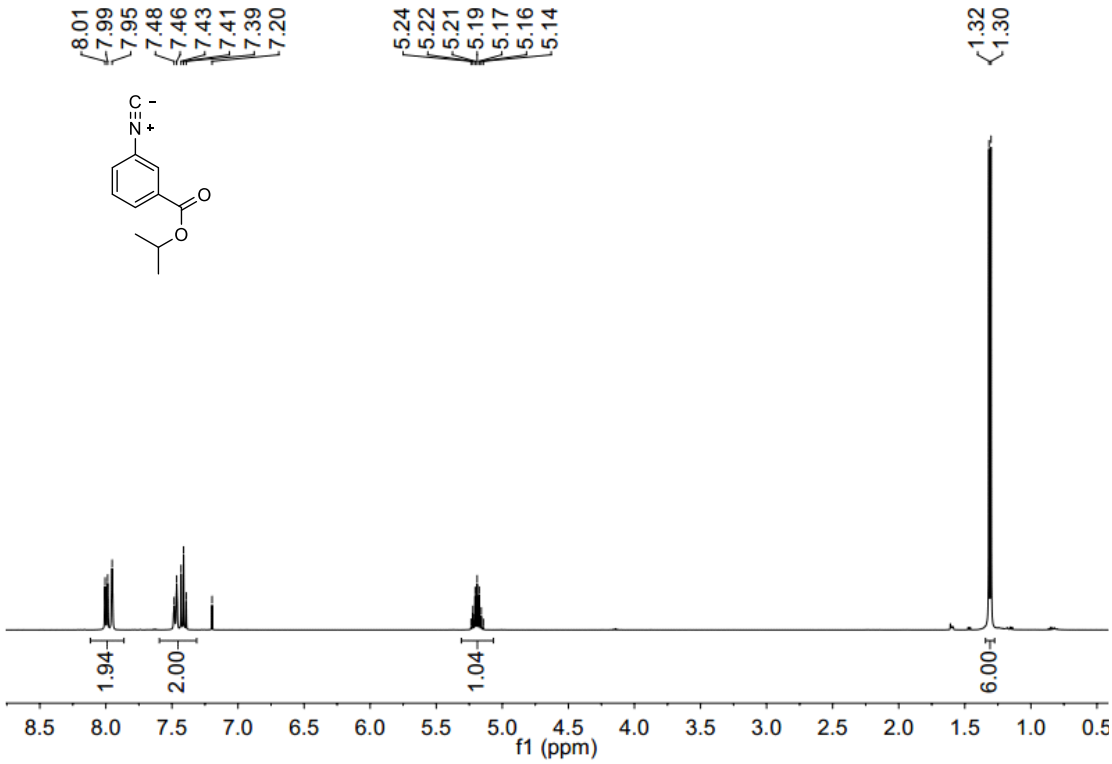


Figure S8. ^{1}H NMR spectrum of 3-isopropyloxycarbonyl phenyl isocyanide (**c**) in $CDCl_3$ at 25 °C.

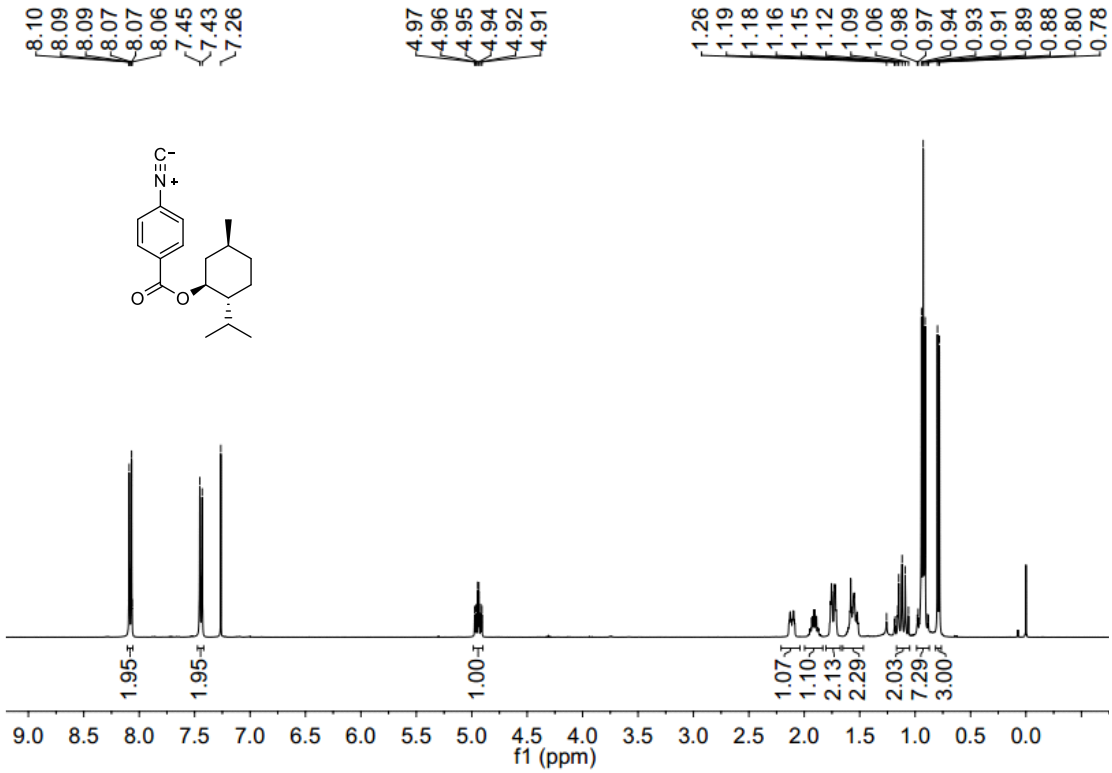


Figure S9. ^{1}H NMR spectrum of (*1S,2R,5S*)-2-isopropyl-5-methylcyclohexyl 4-isocyanobenzoate (**d**) in $CDCl_3$ at 25 °C.

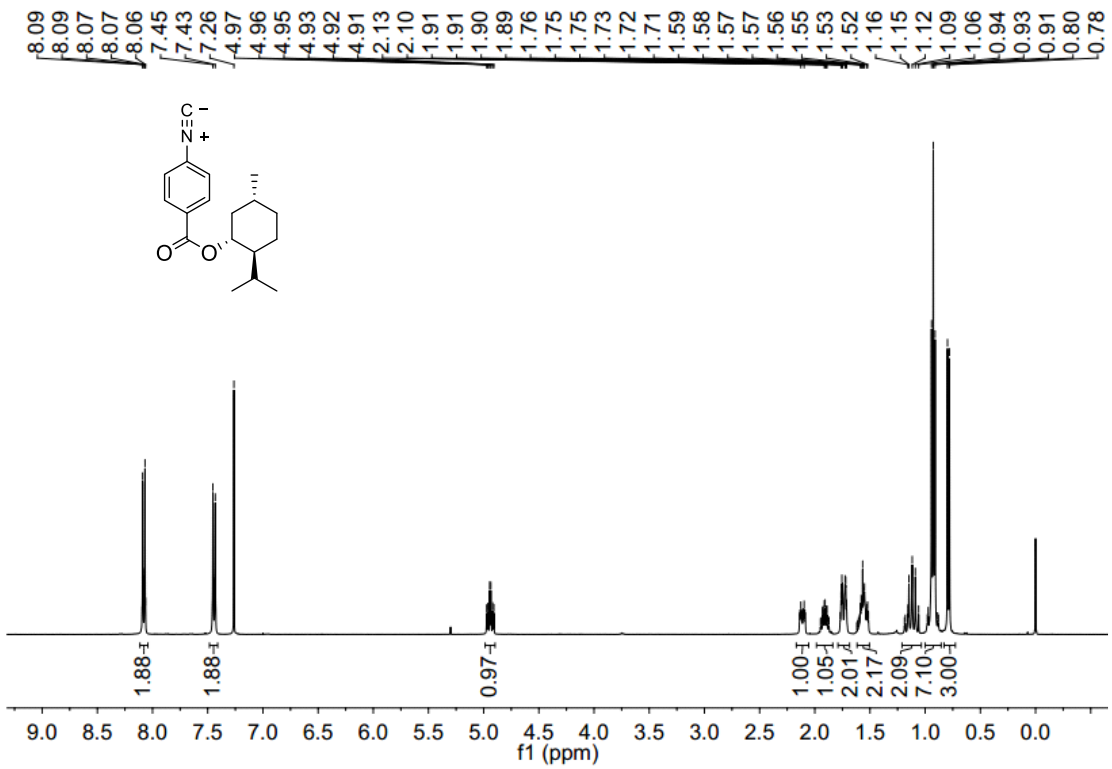


Figure S10. ^{1}H NMR spectrum of (*1R,2S,5R*)-2-isopropyl-5-methylcyclohexyl 4-isocyanobenzoate (**e**) in $CDCl_3$ at 25 ^{o}C.

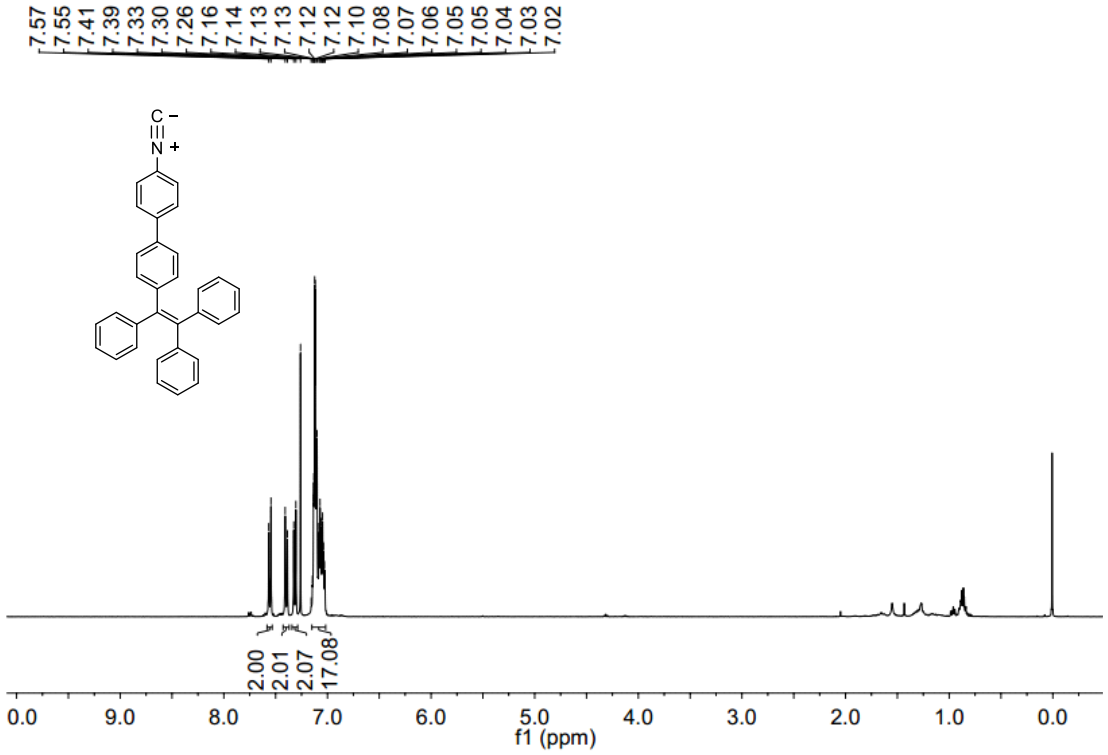


Figure S11. ^{1}H NMR spectrum of 4-isocyano-4'-(1,2,2-triphenylvinyl)-1,1'-biphenyl (**f**) in $CDCl_3$ at 25 ^{o}C.

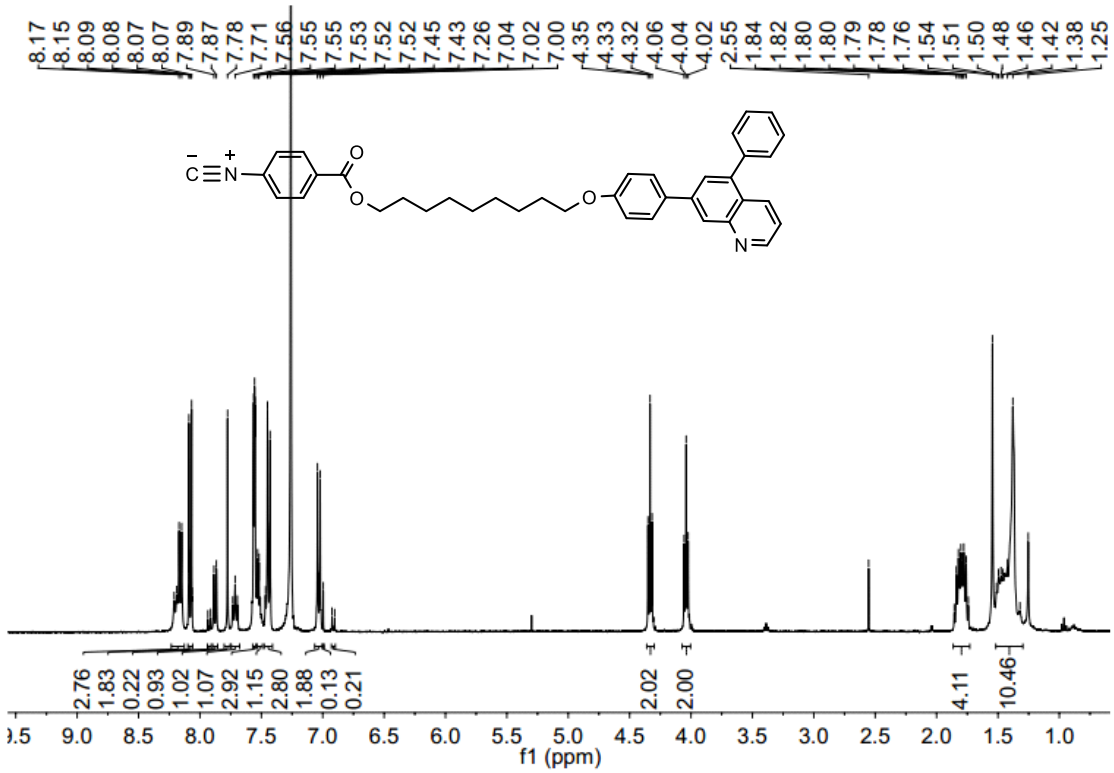


Figure S12. ^{1}H NMR spectrum of 9-(4-(5-phenylquinolin-7-yl)phenoxy)nonyl 4-isocyanobenzoate (**g**) in $CDCl_3$ at 25 ^{o}C.

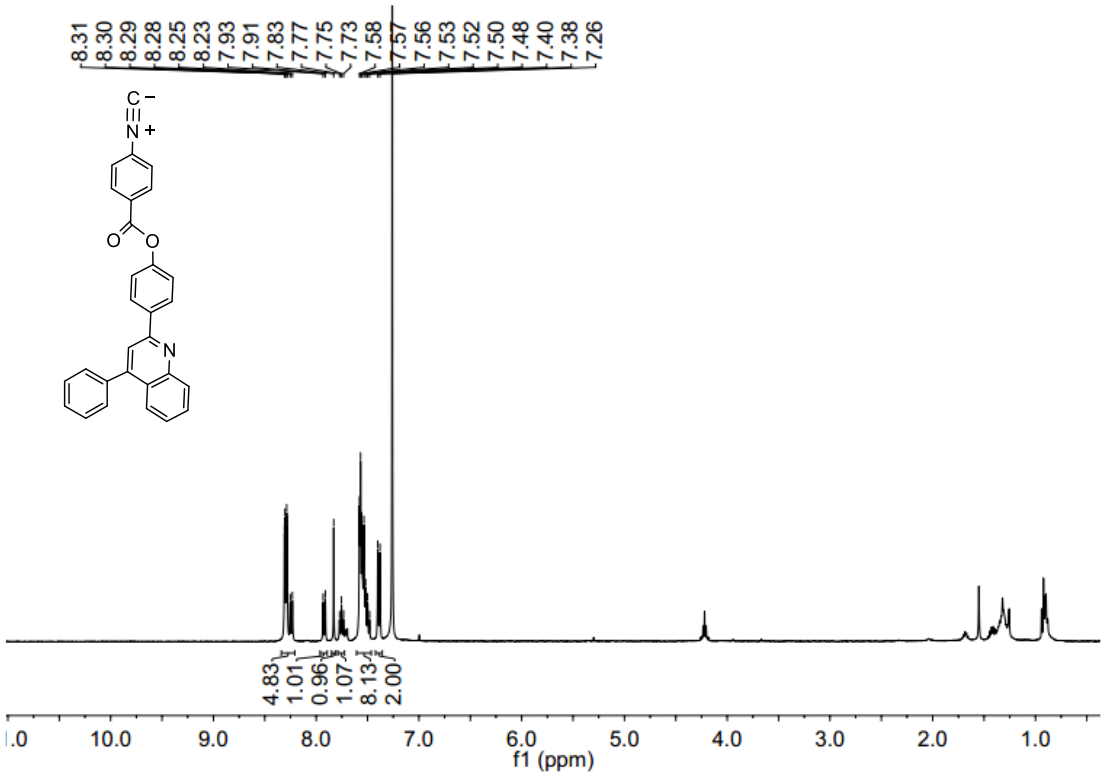


Figure S13. ^{1}H NMR spectrum of 4-(4-phenylquinolin-2-yl)phenyl 4-isocyanobenzoate (**h**) in $CDCl_3$ at 25 ^{o}C.

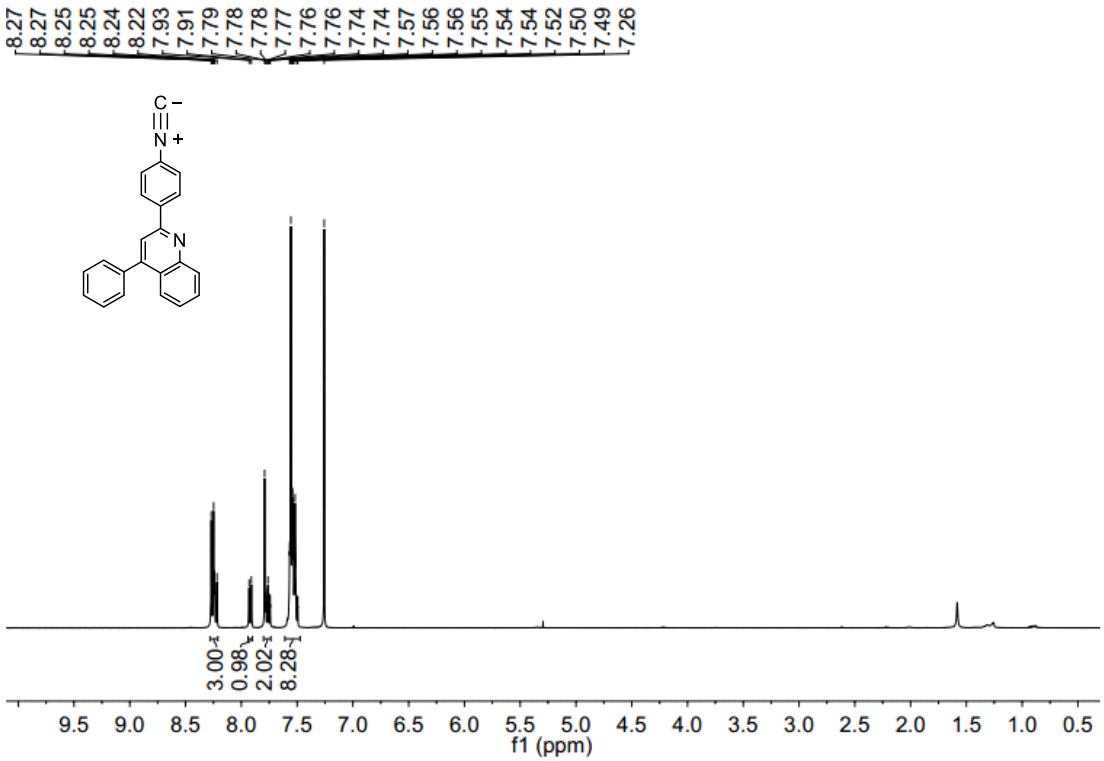


Figure S14. ^{1}H NMR spectrum of 2-(4-isocyanophenyl)-4-phenylquinoline (**i**) in $CDCl_3$ at 25 °C.

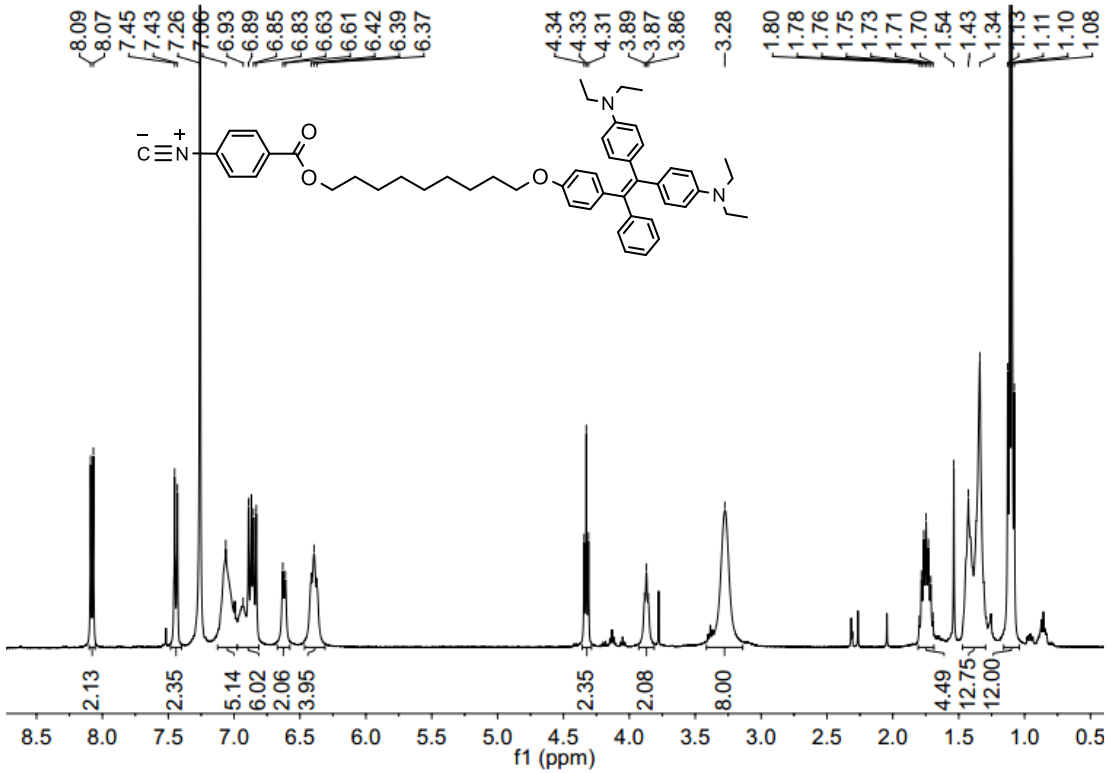


Figure S15. ^{1}H NMR spectrum of 9-(4-(2,2-bis(4-(diethylamino)phenyl)-1-phenylvinyl)phenoxy)nonyl 4-formamidobenzoate (**j**) in $CDCl_3$ at 25 °C.

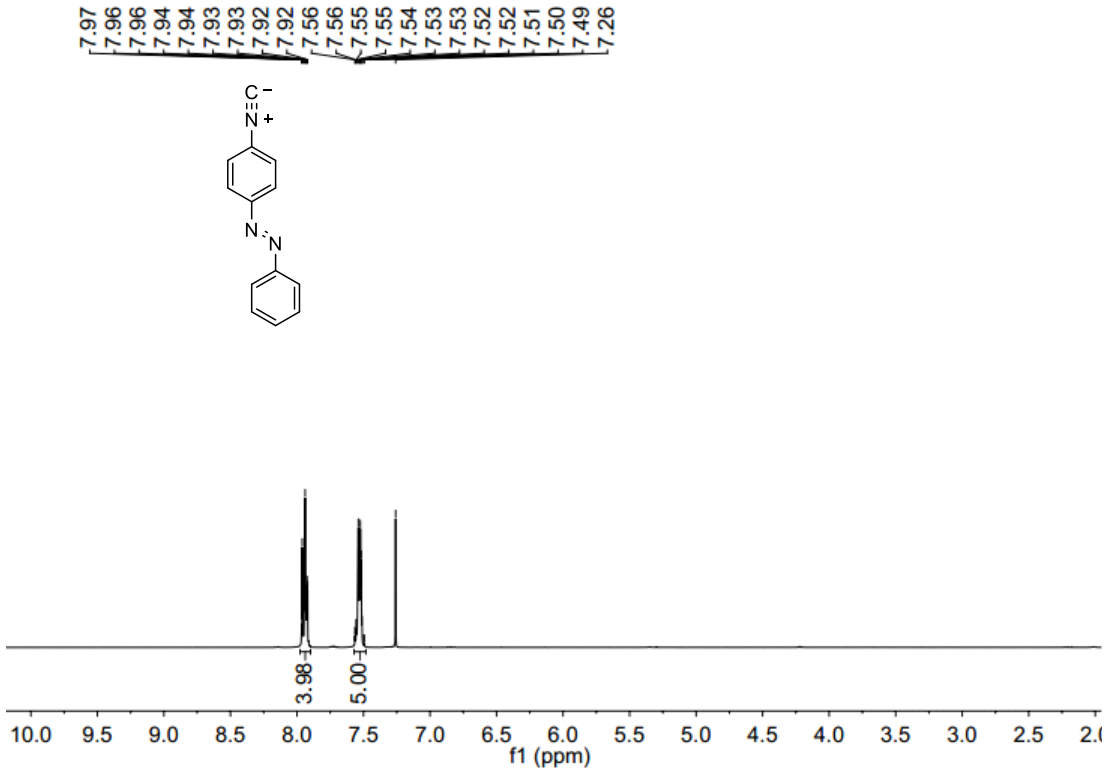


Figure S16. ^{1}H NMR spectrum of (*E*)-1-(4-isocyanophenyl)-2-phenyldiazene(**k**) in $CDCl_3$ at 25 °C.

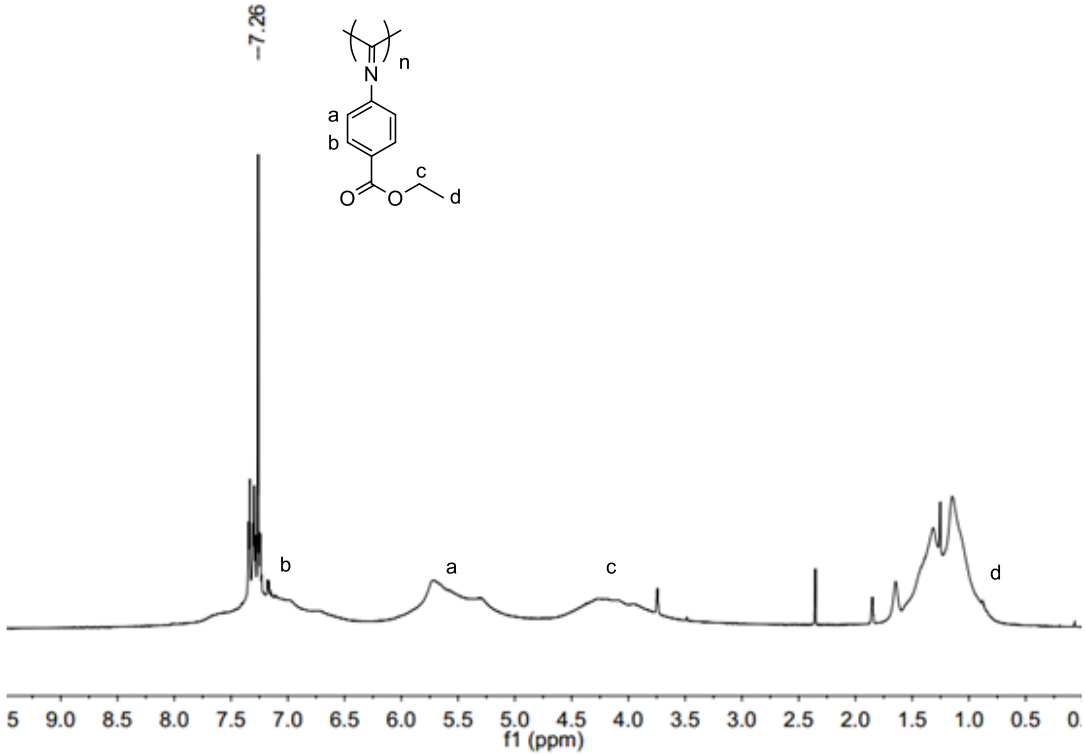


Figure S17. ^{1}H NMR spectrum of poly(EPI) in entry1, Table 1.

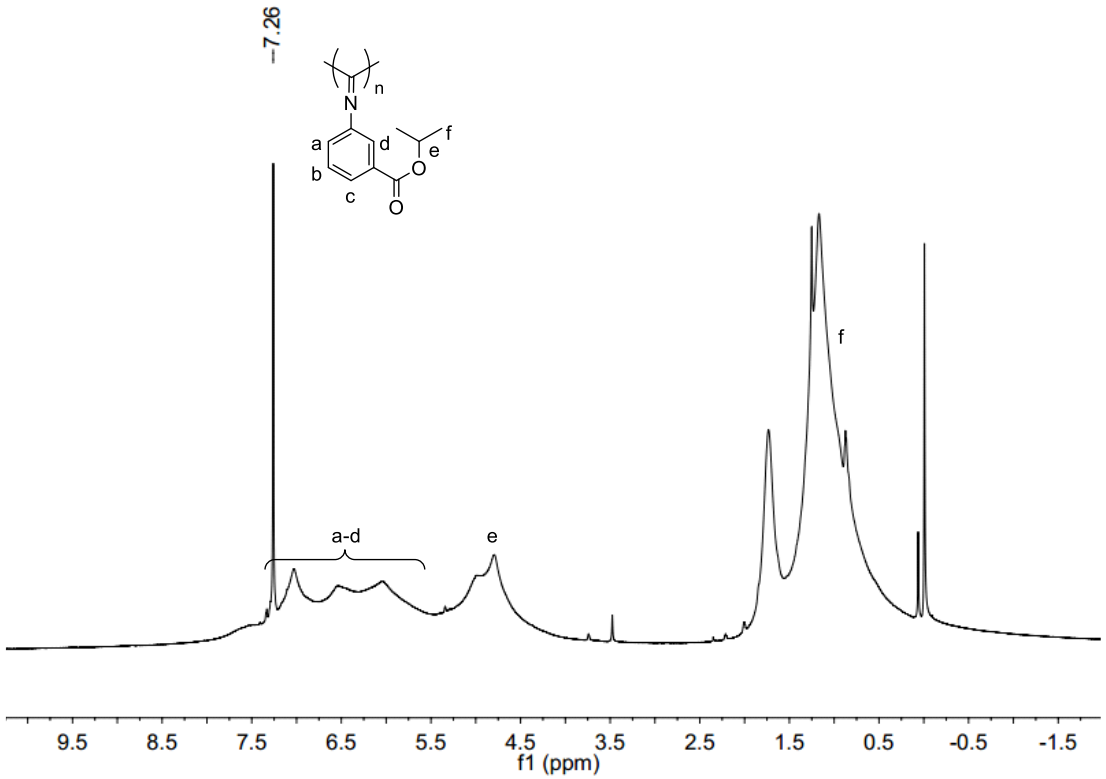


Figure S18. ^{1}H NMR spectrum of poly(IPI) in entry17, Table 1.

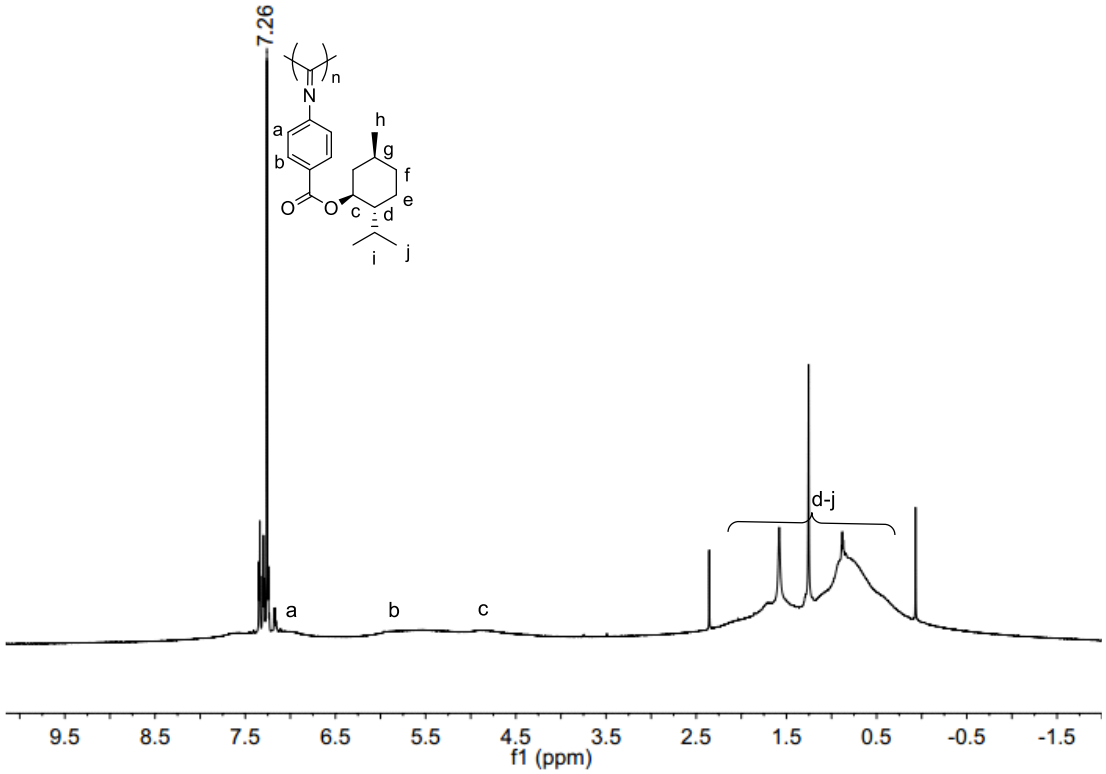


Figure S19. ^{1}H NMR spectrum of poly(D-IMCI) in entry 18, Table 1.

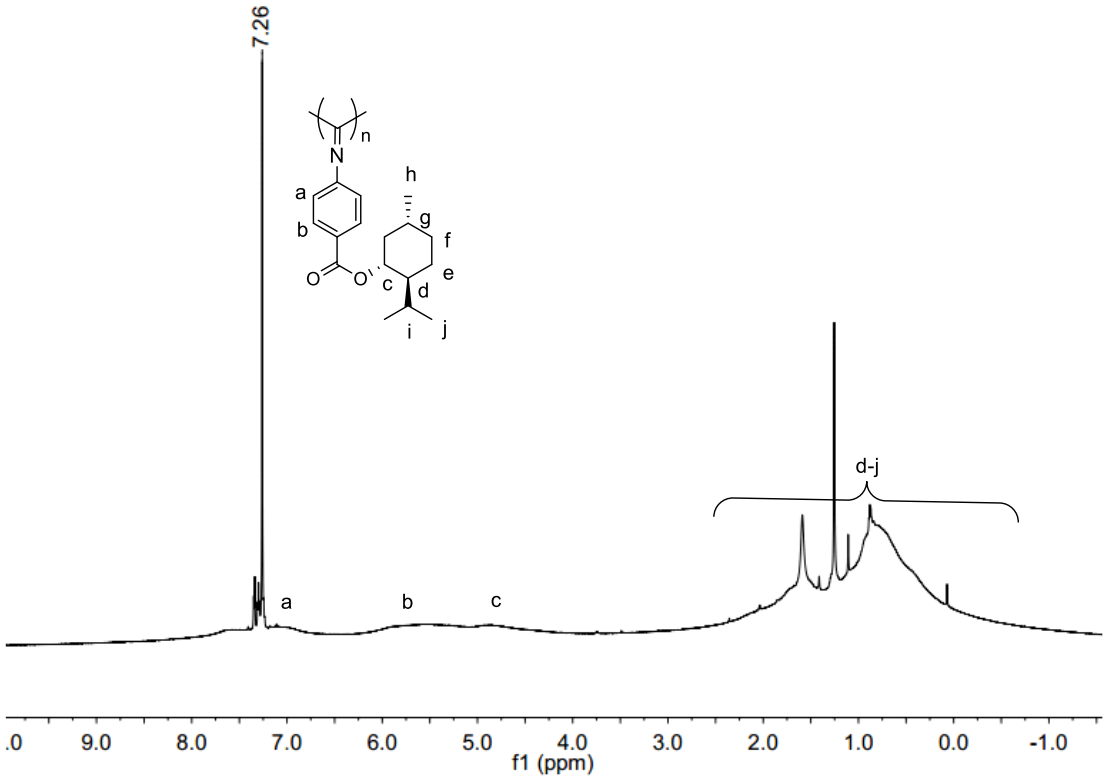


Figure S20. ^{1}H NMR spectrum of poly(L-IMCl) in entry 20, Table 1.

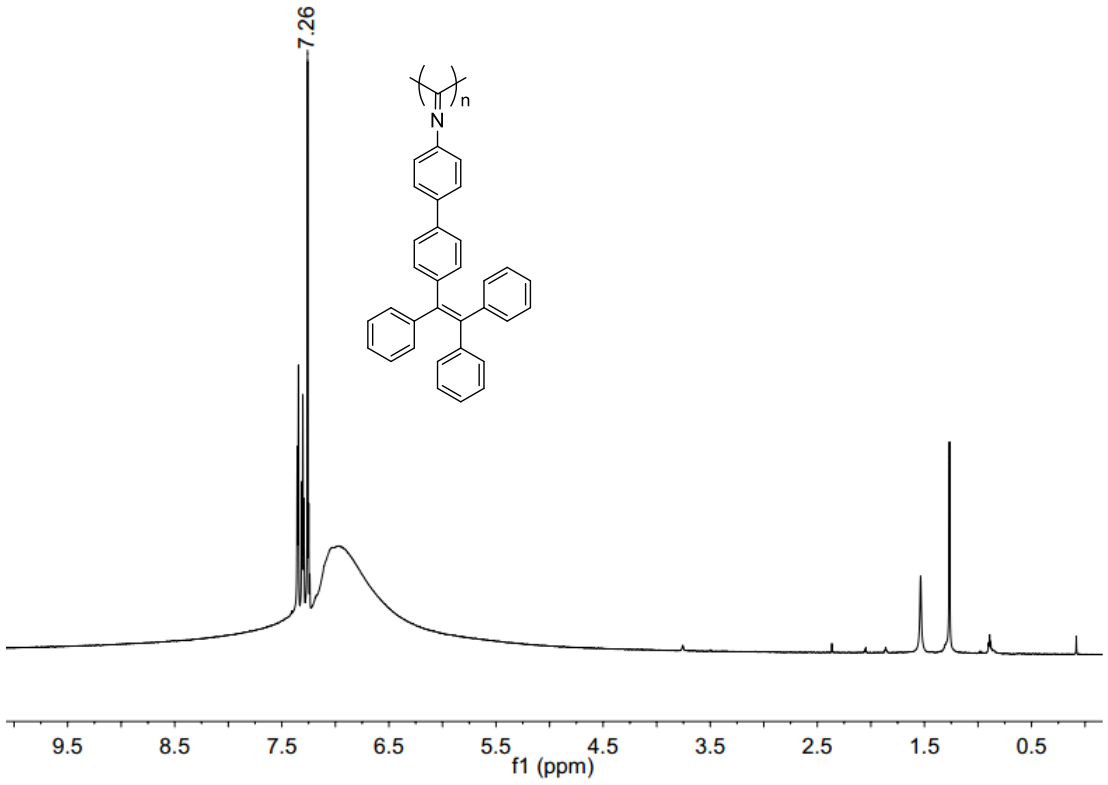


Figure S21. ^{1}H NMR spectrum of poly(ITPB) in entry 22, Table 1.

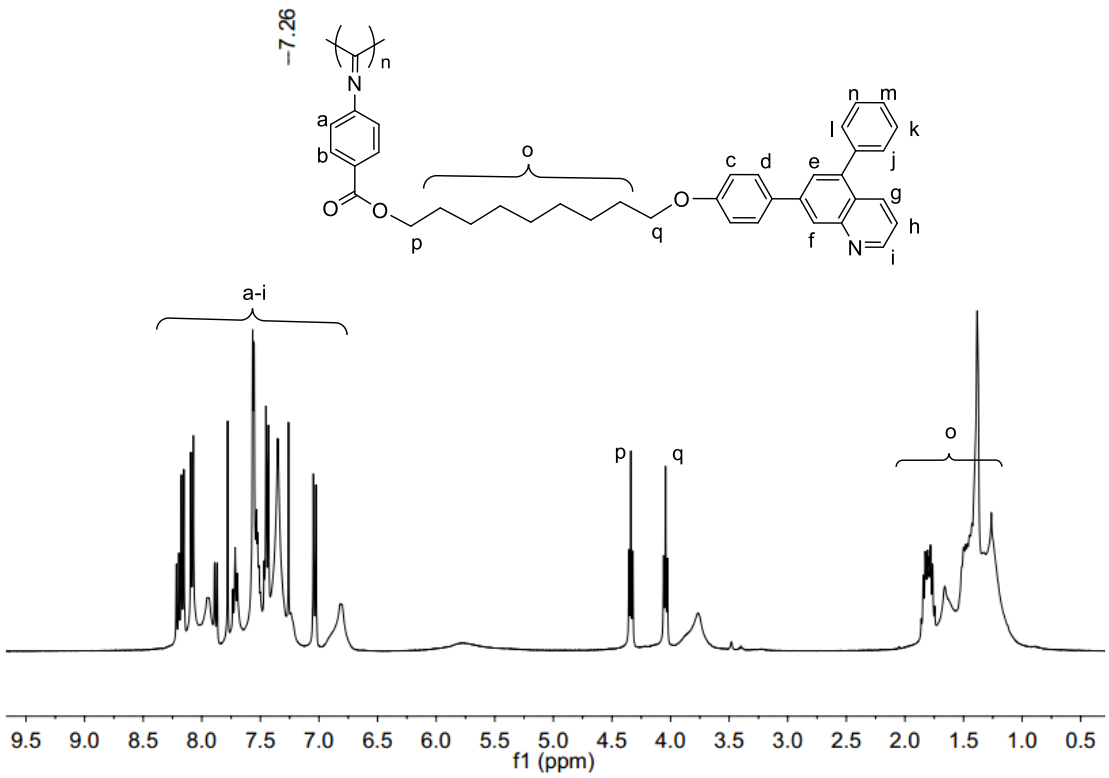


Figure S22. ^{1}H NMR spectrum of poly(BNB) in entry 24, Table 1.

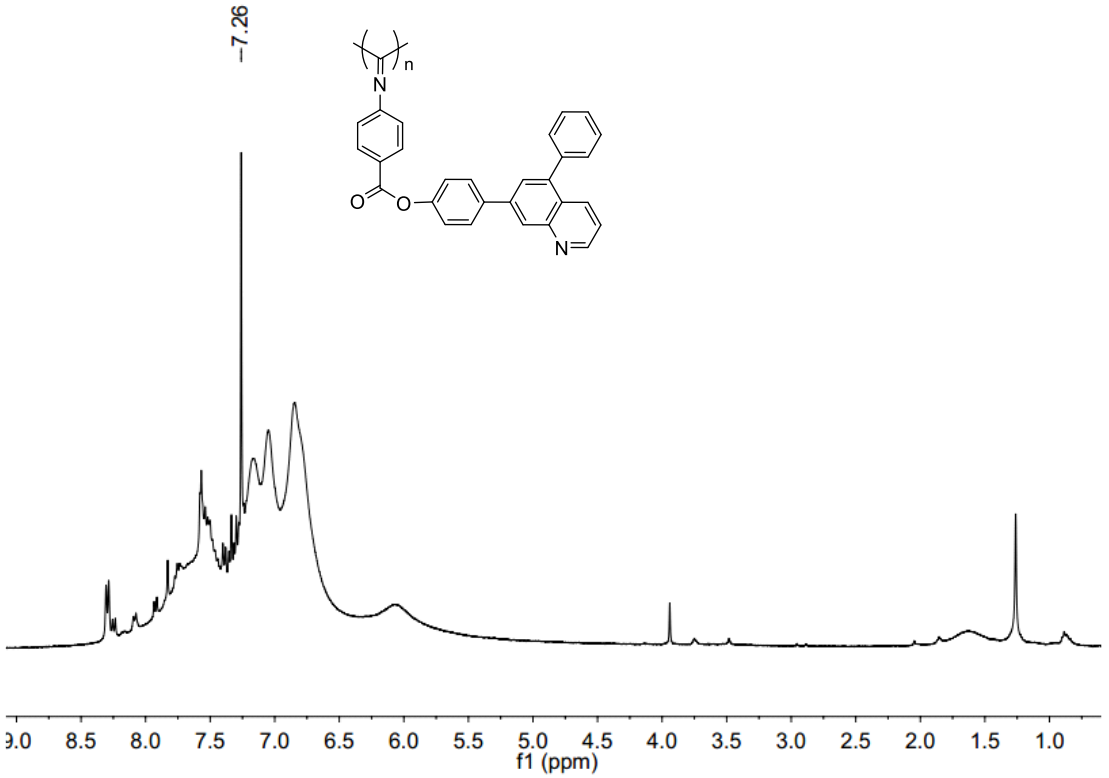


Figure S23. ^{1}H NMR spectrum of poly(PQPI) in entry 25, Table 1.

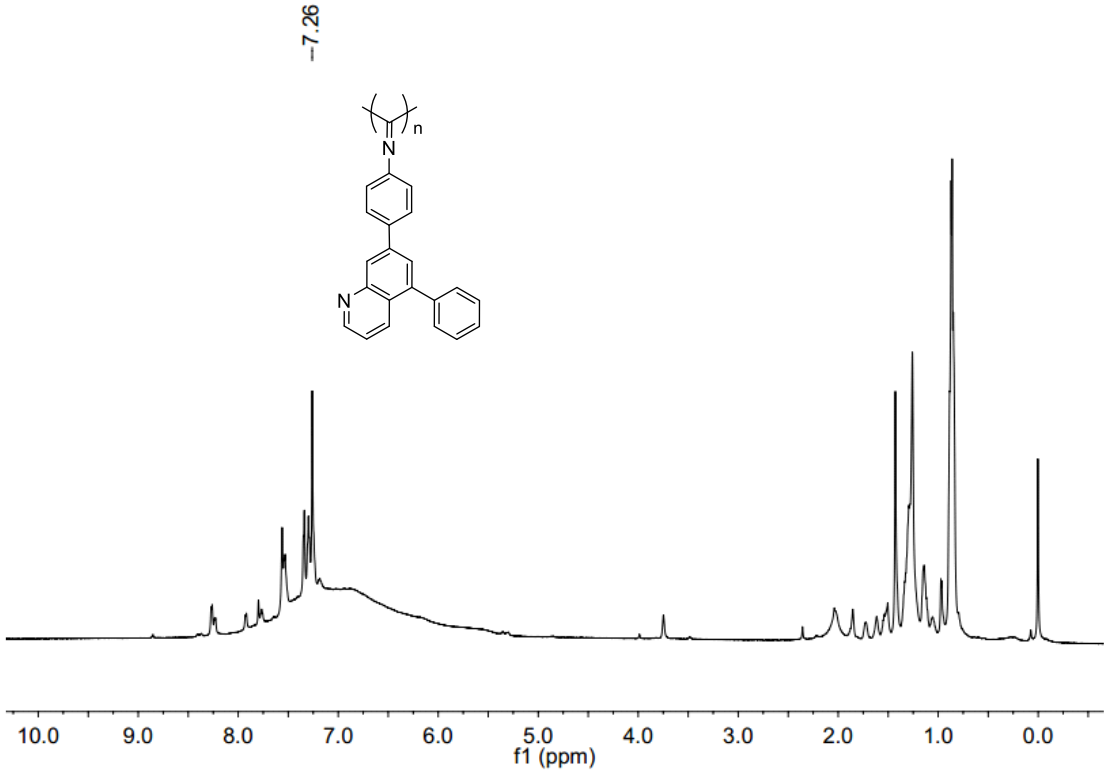


Figure S24. ^{1}H NMR spectrum of poly(IPQ) in entry 26, Table 1.

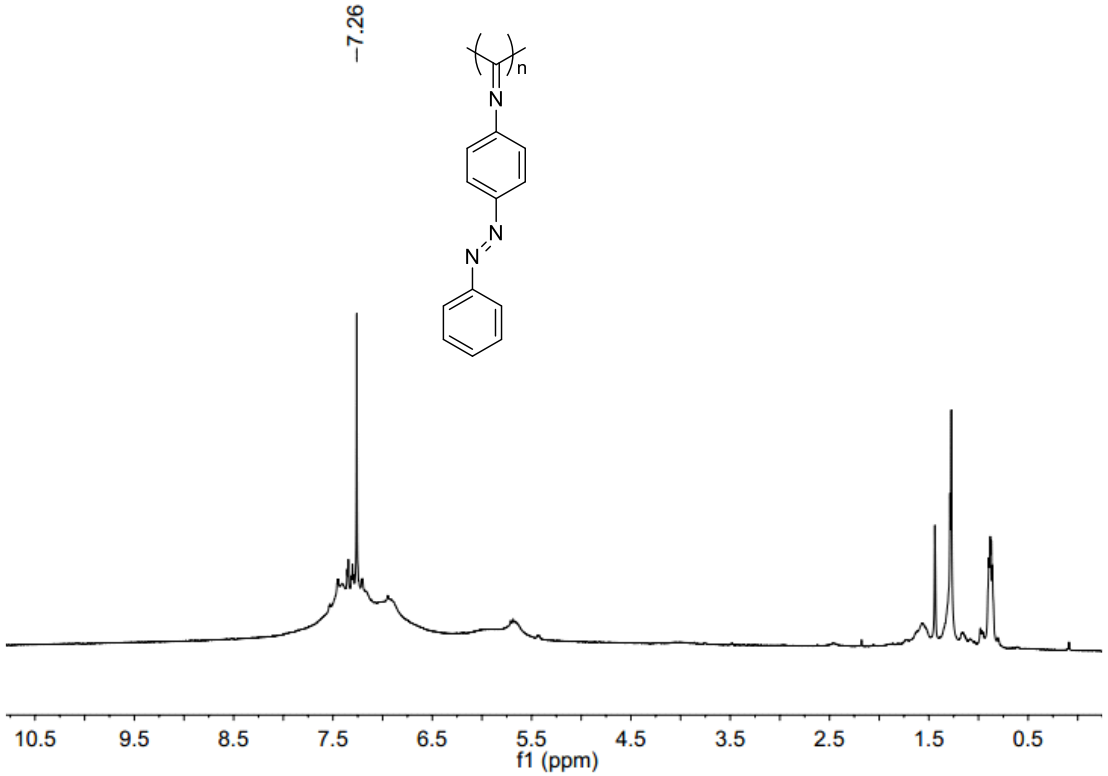


Figure S25. ^{1}H NMR spectrum of poly(IPD) in entry 28 Table 1.

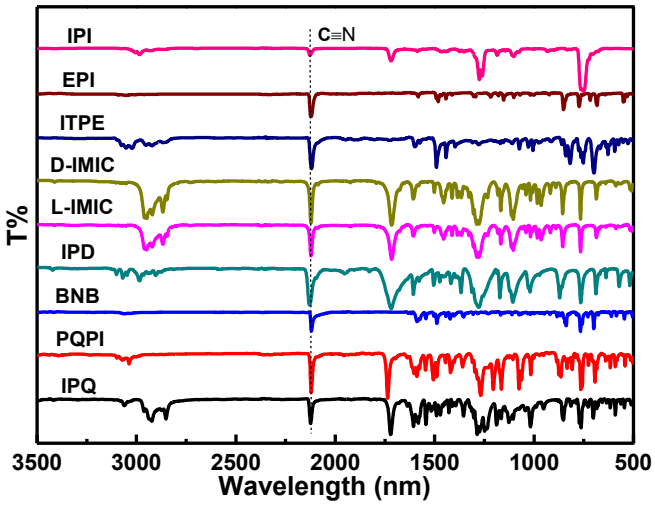


Figure S26. FT-IR spectra of isocyanide monomers EPI (**b**), IPI (**c**), D/L-IMCI (**d**/**e**), ITPB (**f**), BNB (**g**), PQPI (**h**), IPQ (**i**), IPD (**j**).

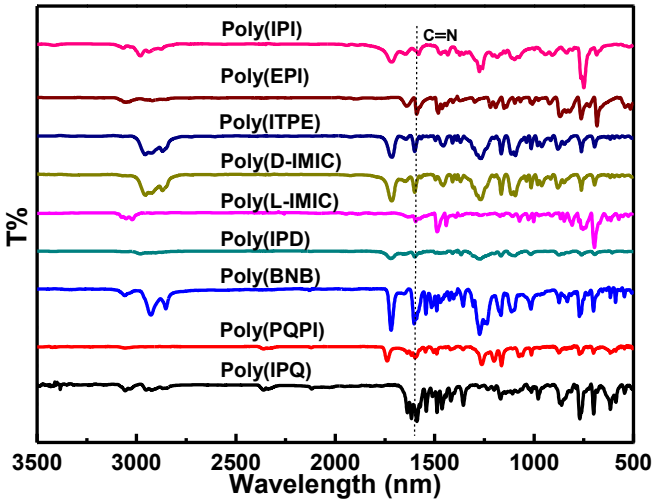
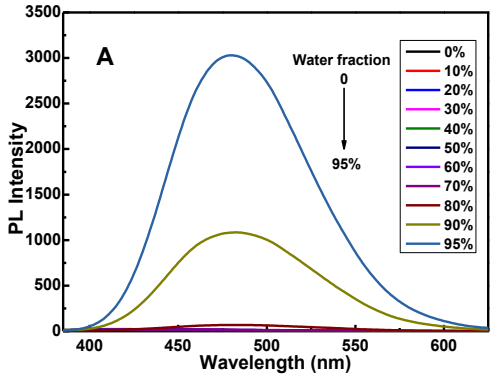


Figure S27. FT-IR spectra of poly(EPI) (Table 1, entry 1), poly(IPI) (Table1, entry17), poly(D-IMCI) (Table 1, entry 18), poly(L-IMCI) (Table 1, entry 20), poly(ITPB) (Table 1, entry 22), poly(BNB) (Table 1, entry 24), poly(PQPI) (Table 1, entry 25), poly(IPQ) (Table 1, entry 26), poly(IPD) (Table 1, entry 28).



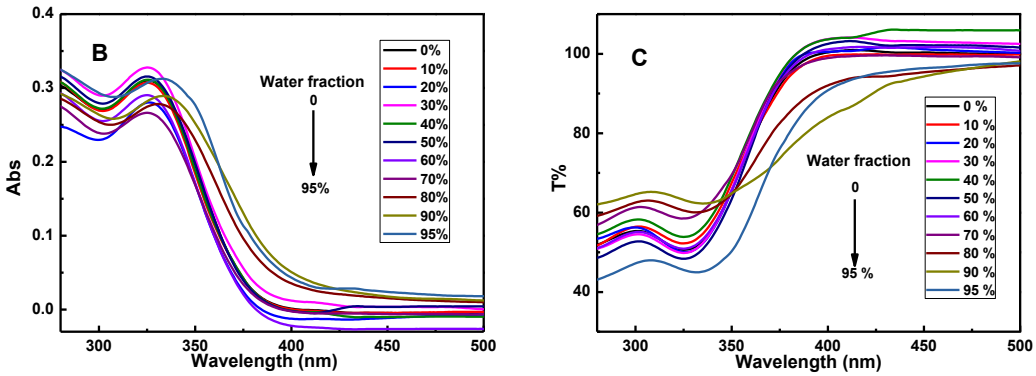


Figure S28. Fluorescence spectra and UV absorption-transmittance spectra of ITPB monomer (excitation wavelength: 325 nm; 0.004 mg/ml) in THF/water mixture.

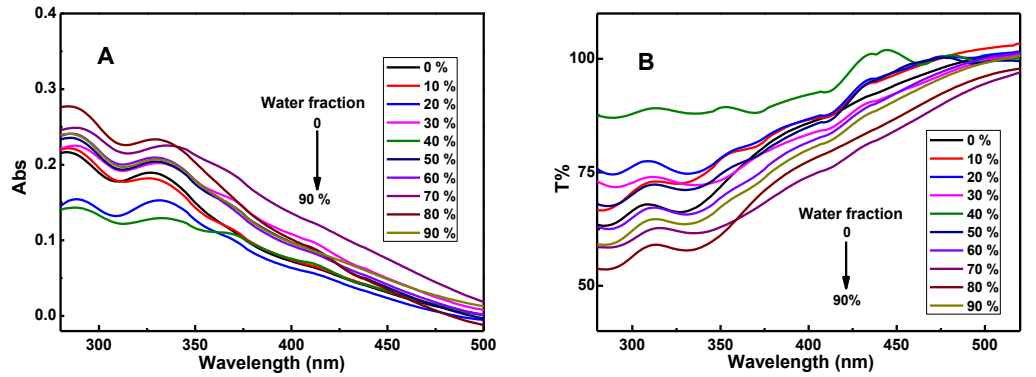


Figure S29. UV absorption and transmittance spectra of poly(ITPB) (Table 1, entry 20) (0.004 mg/ml) in THF/water mixture.

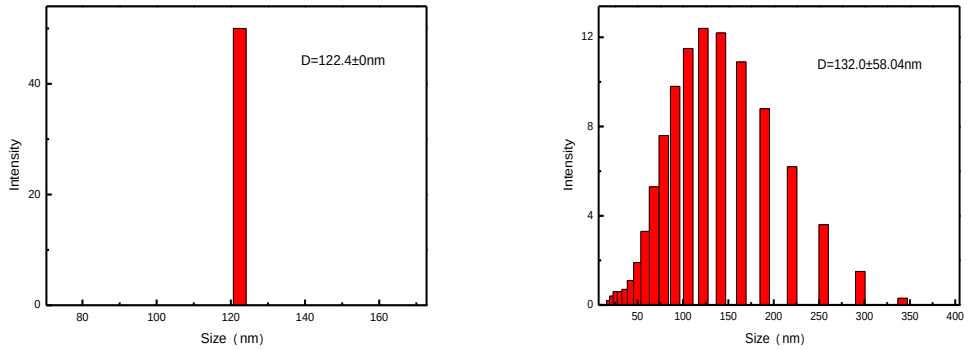


Figure S30. Dynamic light scattering measurement of ITPB mommer at 0 % water fraction in THF/water mixture (left side) and at 95 % water fraction in THF/water mixture (right side).

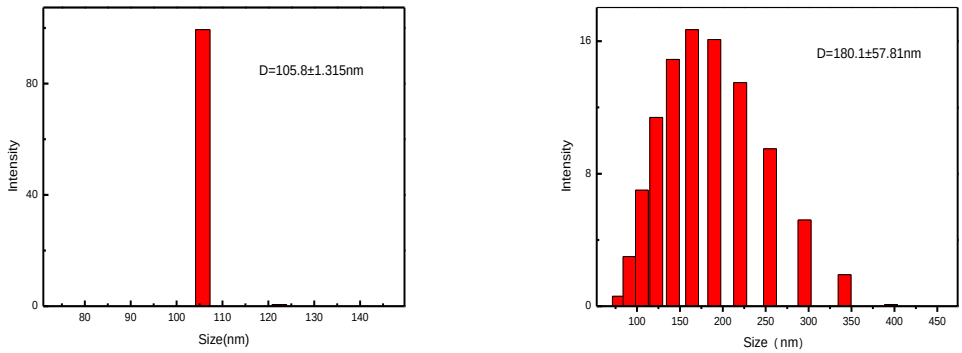


Figure S31. Dynamic light scattering measurement of poly(ITPB) (Table 1, entry 20) at 0 % water fraction in THF/water mixture (left side) and at 70% water fraction in THF/water mixture (right side).

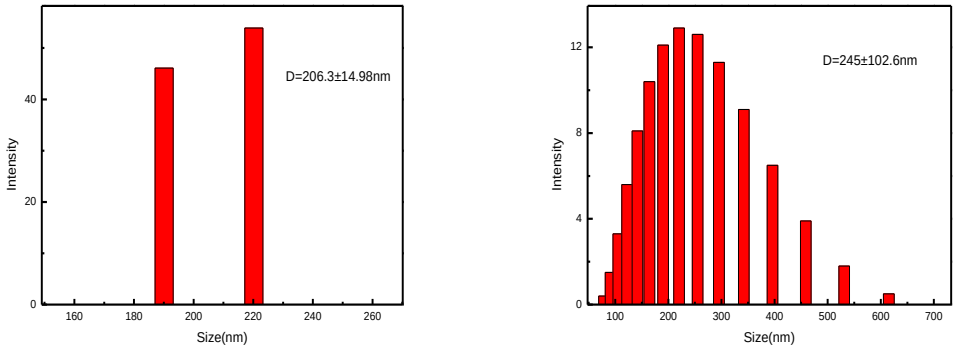


Figure S32. Dynamic light scattering measurement of poly(D-IMCI-*co*-ITPB) (Table 2, entry 2) at 0 % water fraction in THF/water mixture (left side) and at 70% water fraction in THF/water mixture (right side).

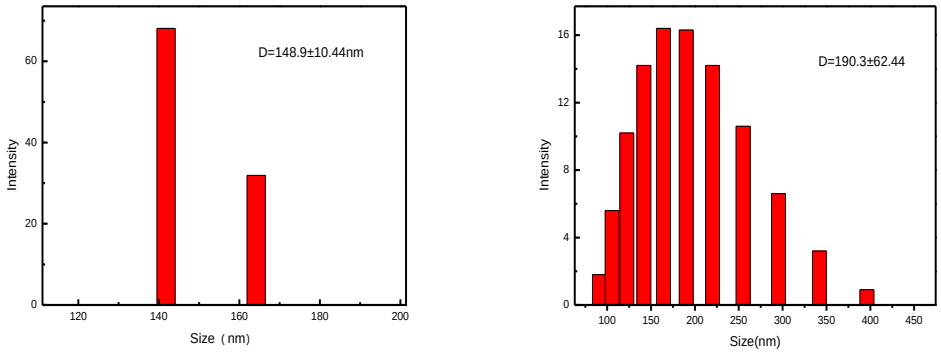


Figure S33. Dynamic light scattering measurement of poly(L-IMCI-*co*-ITPB) (Table 2, entry 8) at 0 % water fraction in THF/water mixture (left side) and at 70% water fraction in THF/water mixture (right side).

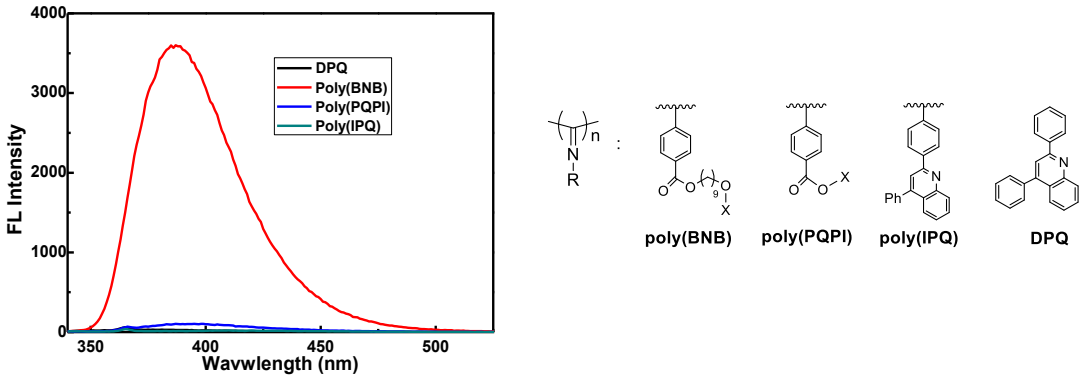


Figure S34. Fluorescence spectra of DPQ unit, poly(BNB), poly(PQPI), poly(IPQ) (repeat unit 10^{-5}M) in THF.

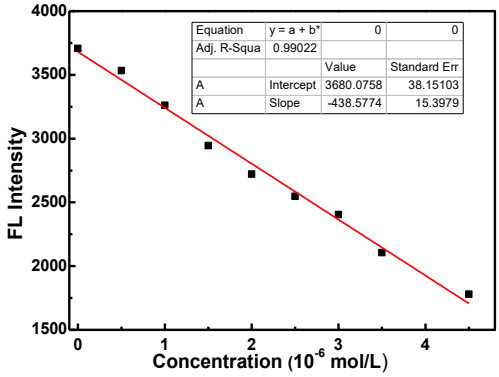


Figure S35. A plot of fluorescence intensity as a function of the iron concentration (5×10^{-7}–4.5×10^{-6} M) in THF.

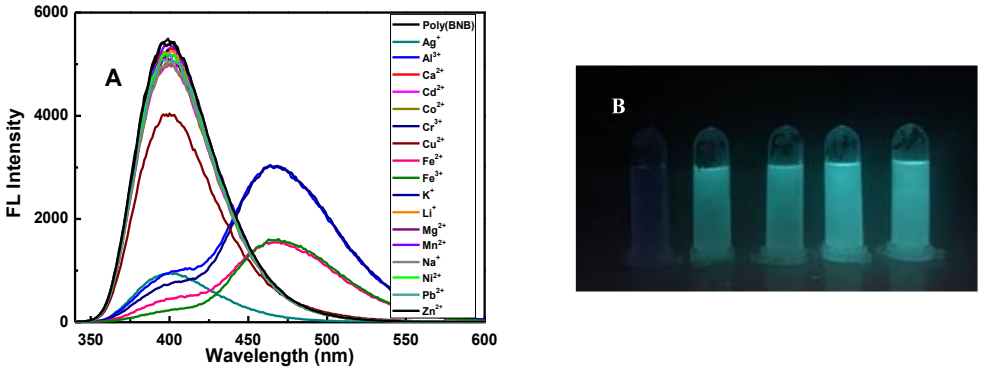


Figure S36. (A) Fluorescence spectra of poly(BNB) (Table 1, entry 24) (10^{-5} M repeat unit) in the absence (blank) and presence of different metal salts (10^{-5} M) in MeOH; (B) Fluorescence emission of poly(BNB) (10^{-5} M repeat unit) in MeOH with Al^{3+}, Cr^{3+}, Fe^{3+}, and Fe^{2+} (10^{-5} M), respectively, under UV lamp irradiation.

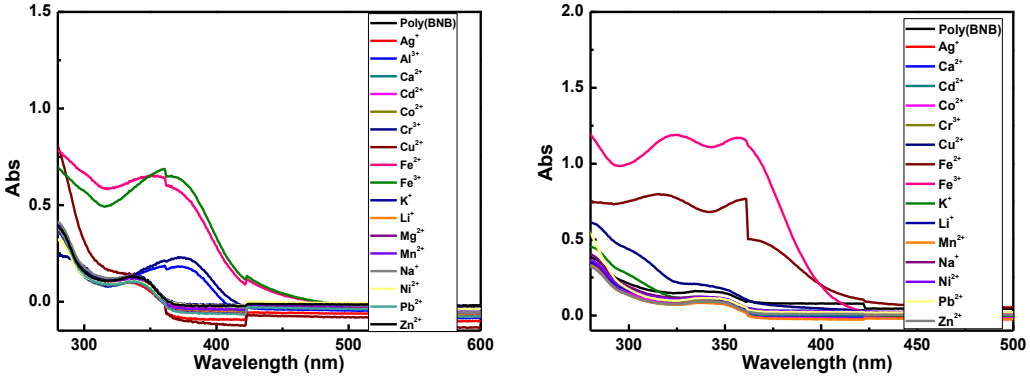


Figure S37. UV absorption spectra of poly(BNB) (10^{-5} M) and poly(BNB) (10^{-5} M) with different metal iron(10^{-5} M) in MeOH(left) and THF(right).

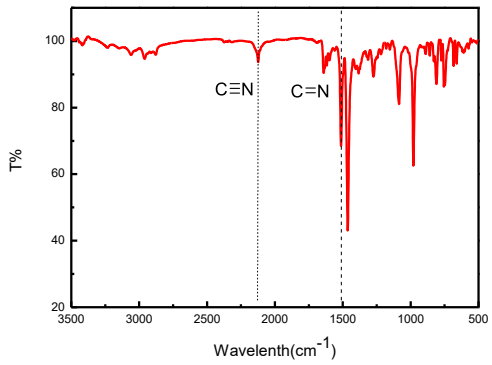


Figure S38. FT-IR spectra of NI oligomer obtained by $[(Et_3Si)_2H][B(C_6F_5)_4]$.

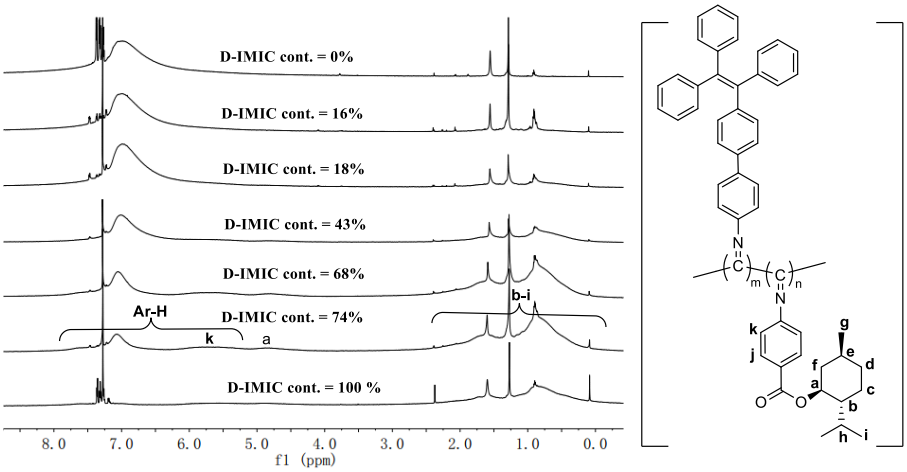


Figure S39. ^{1}H NMR spectra of poly(D-IMCI), poly(ITPB) and poly(D-IMCI-*co*-ITPB)s and (Table 1, entries 18, 22 and Table 2, entries 1-5).

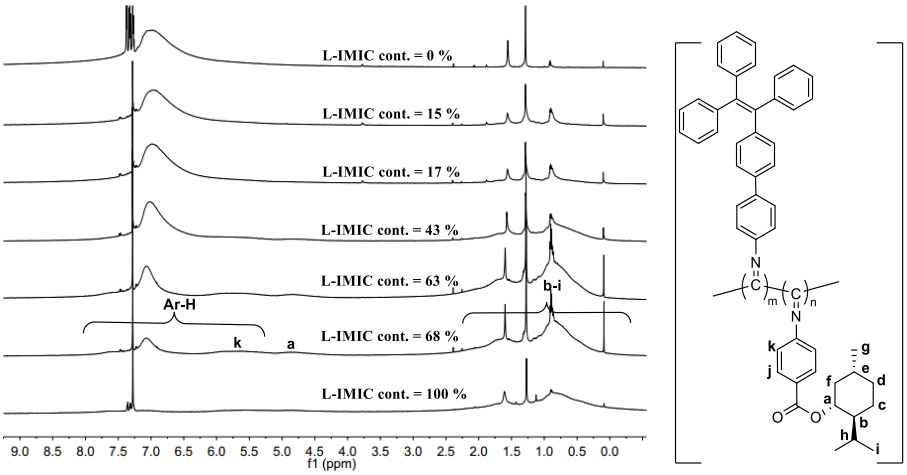
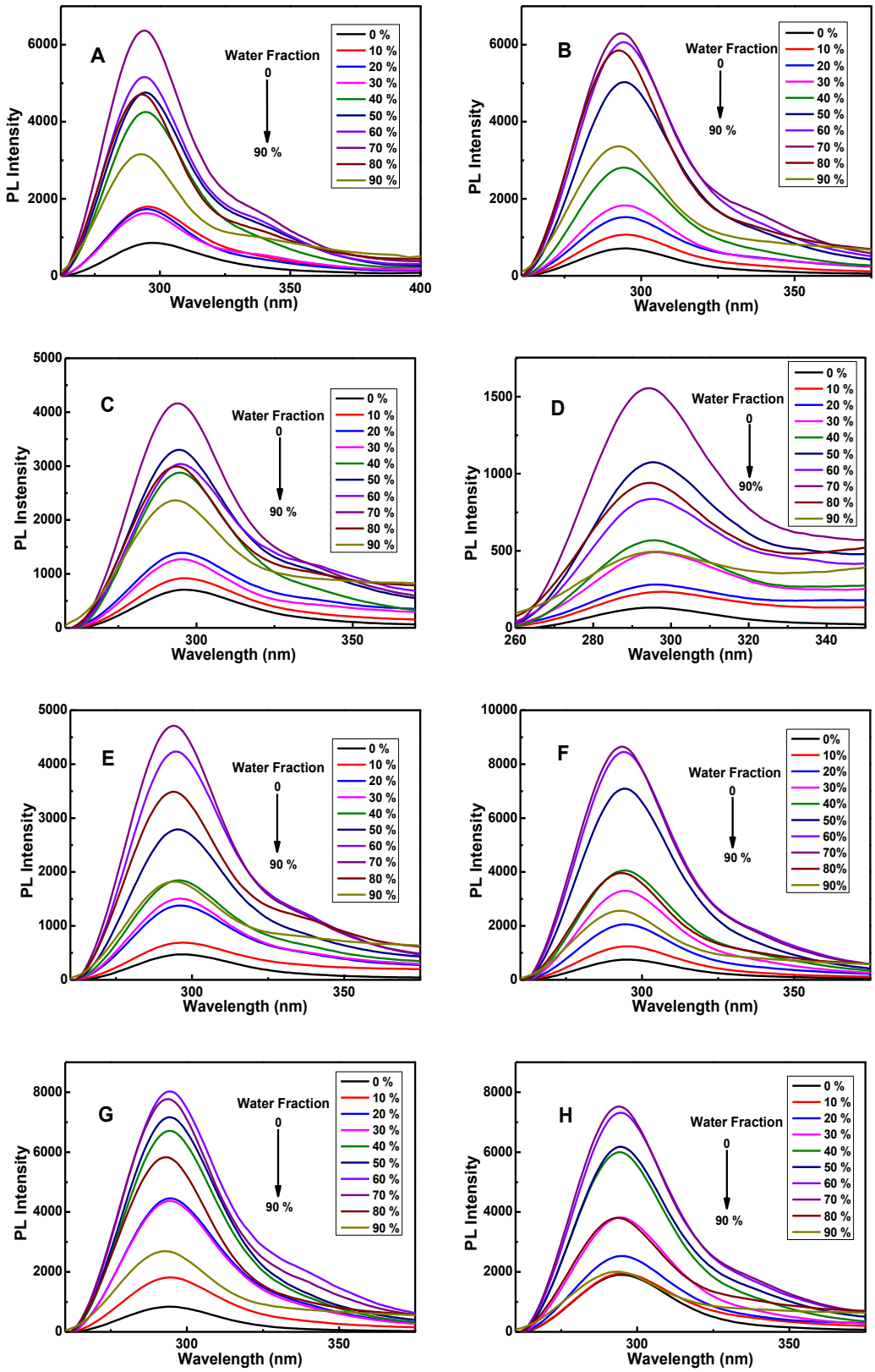


Figure S40. ^{1}H NMR spectra of poly(L-IMCI), poly(ITPB) and poly(L-IMCI-*co*-ITPB)s (Table 1, entries 20, 22 and Table 2, entries 6-10).


A
B
C
D
E
F
G
H
Water Fraction
0
90 %
90%
0 %
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40 %
50 %
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90 %
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80%
90%
PL Intensity
PL Instensity
Wavelength (nm)

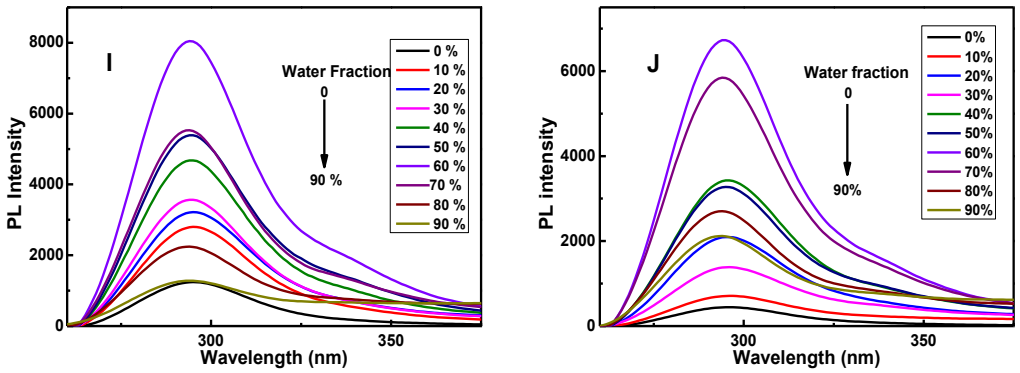
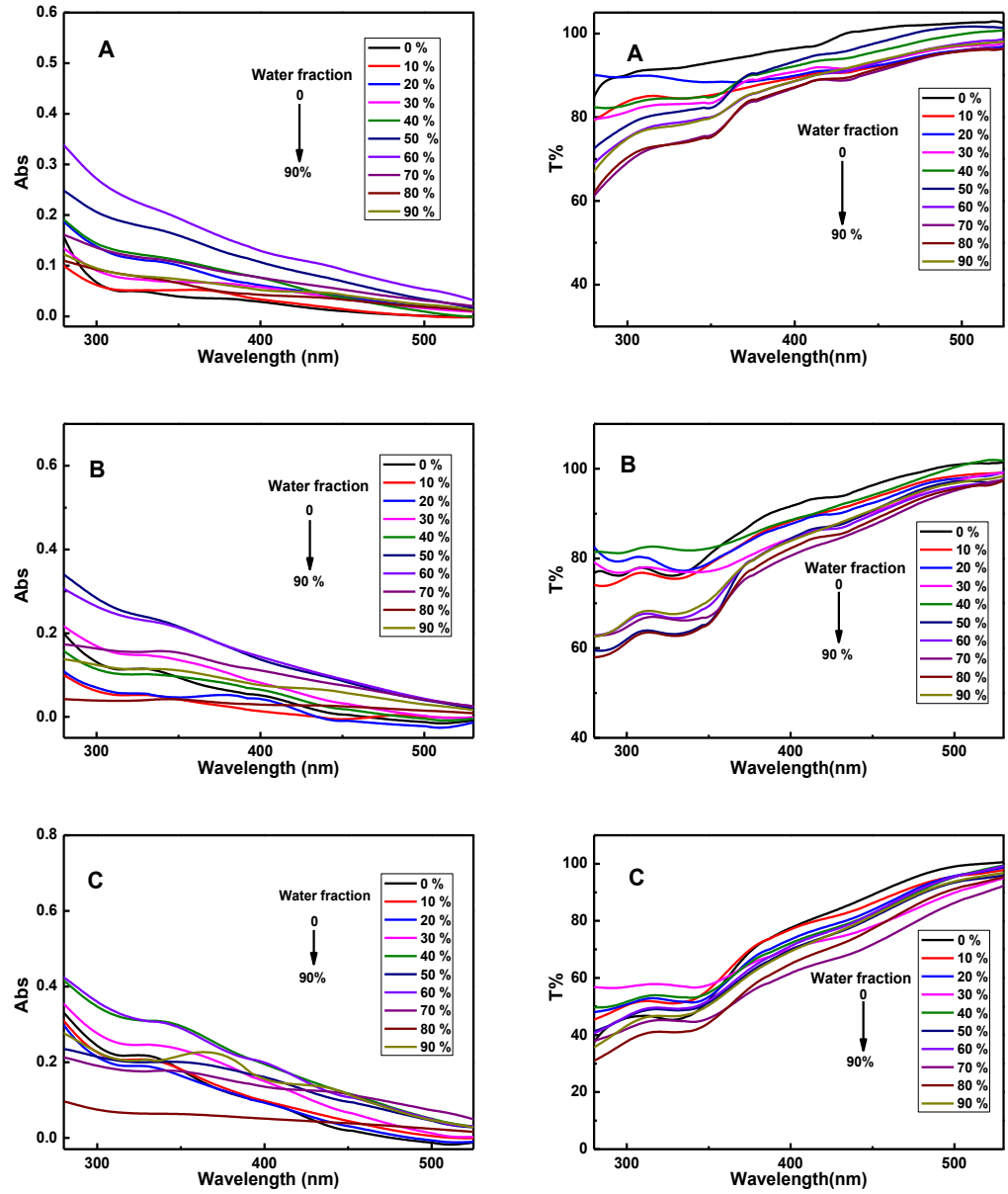
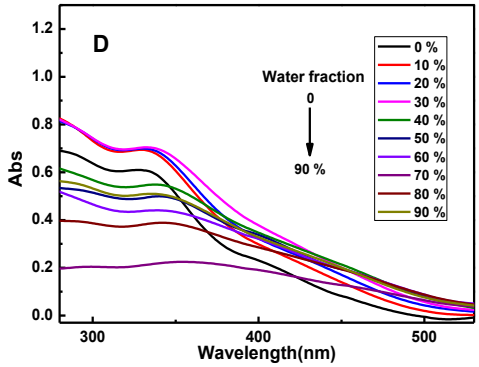


Figure S41. Fluorescence spectra of poly(D/L-IMCI-*co*-ITPB) (table 2, entry1-10) in THF/water mixture (excitation wavelength: 220 nm; copolymer: A (Table 2, entry 1), B (Table 2, entry 2), F (Table 2, entry 6), G (Table 2, entry 7): 0.005 mg/ml; C (Table 2, entry 3), H (Table 2, entry 8): 0.0065 mg/ml; D (Table 2, entry 4), I (Table 2, entry 9): 0.010 mg/ml; E (Table 2, entry 5), J (Table 2, entry 10): 0.015 mg/ml).




D
Water fraction
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90 %
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10 %
20 %
30 %
40 %
50 %
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70 %
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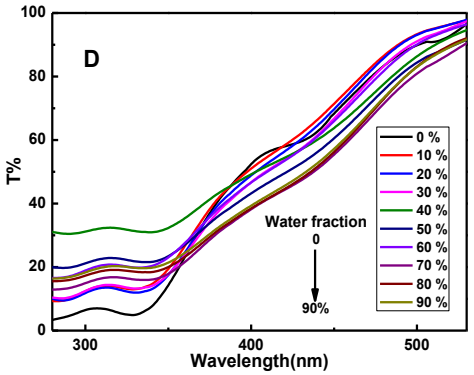
Abs
Wavelength(nm)


D
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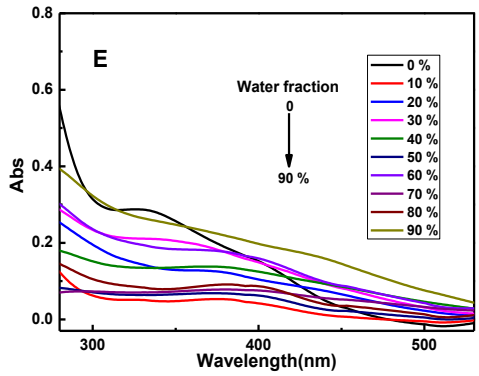
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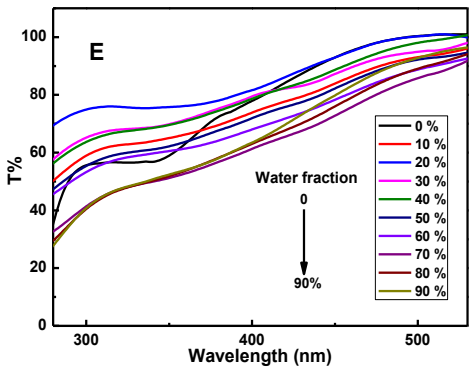
E
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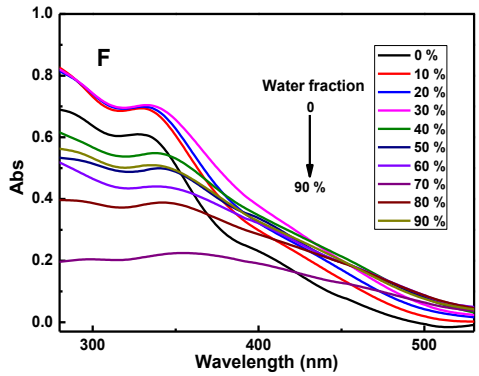
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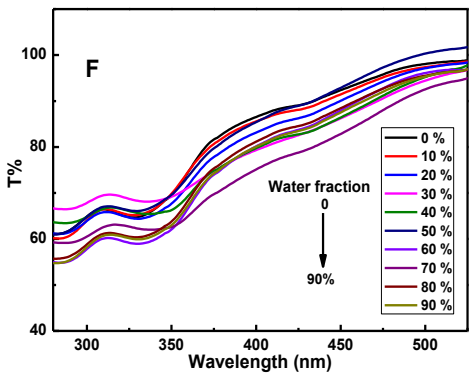
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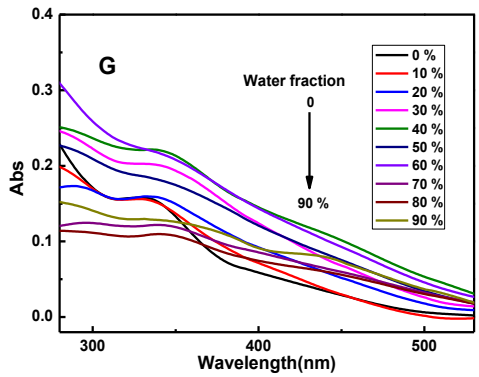
G
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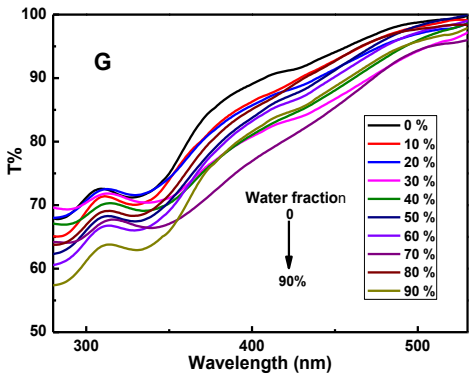
Abs
Wavelength(nm)


G
Water fraction
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T%
Wavelength (nm)

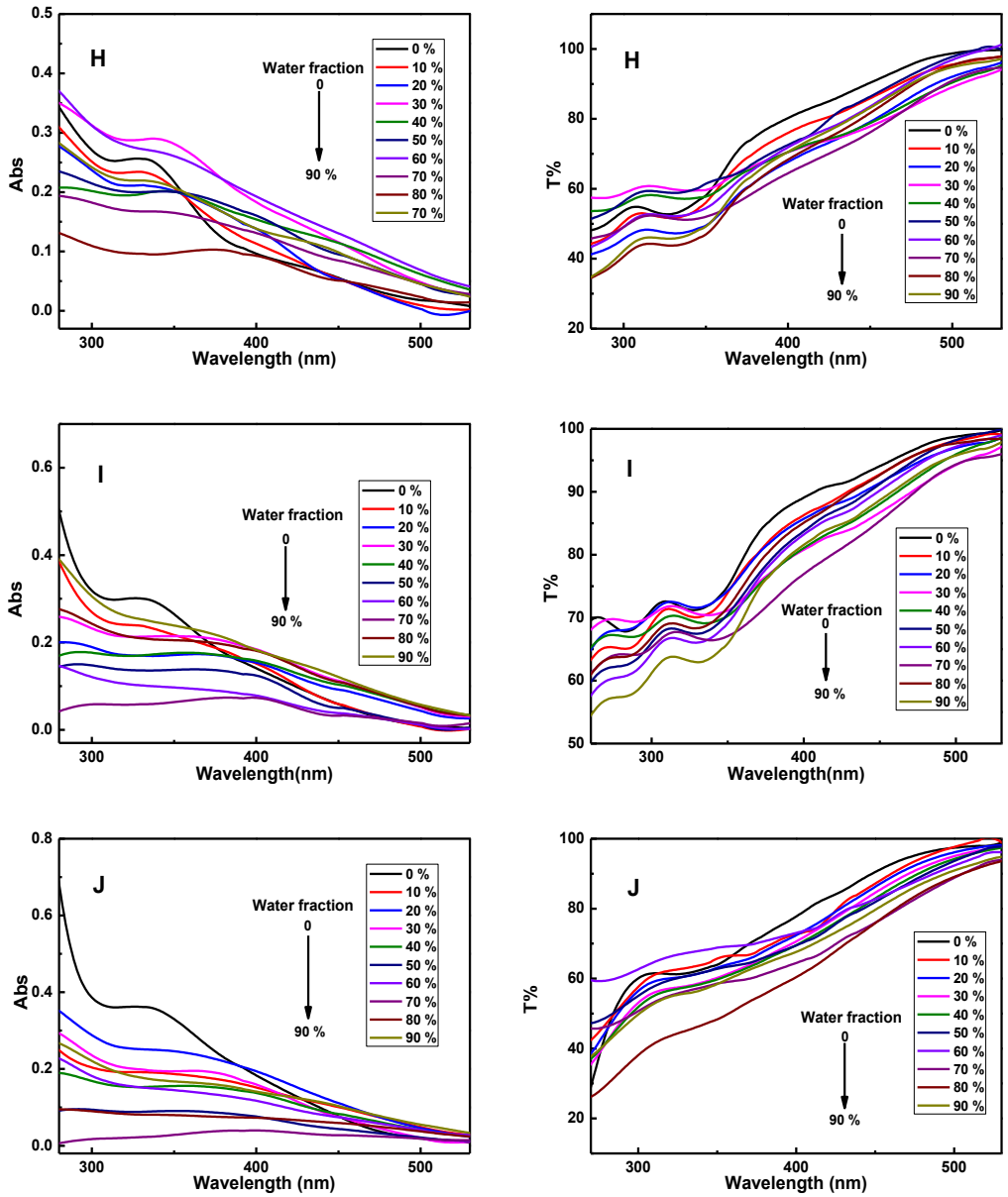


Figure S42. UV absorption and transmittance spectra of poly(D/L-IMCI-*co*-ITPB) (table 2, entry 1-10) in THF/water mixture (copolymer: A (Table 2, entry 1), B (Table 2, entry 2), F (Table 2, entry 6), G (Table 2, entry 7): 0.005 mg/ml; C (Table 2, entry 3), H (Table 2, entry 8): 0.0065 mg/ml; D (Table 2, entry 4), I (Table 2, entry 9): 0.010 mg/ml; E (Table 2, entry 5), J (Table 2, entry 10): 0.015 mg/ml).

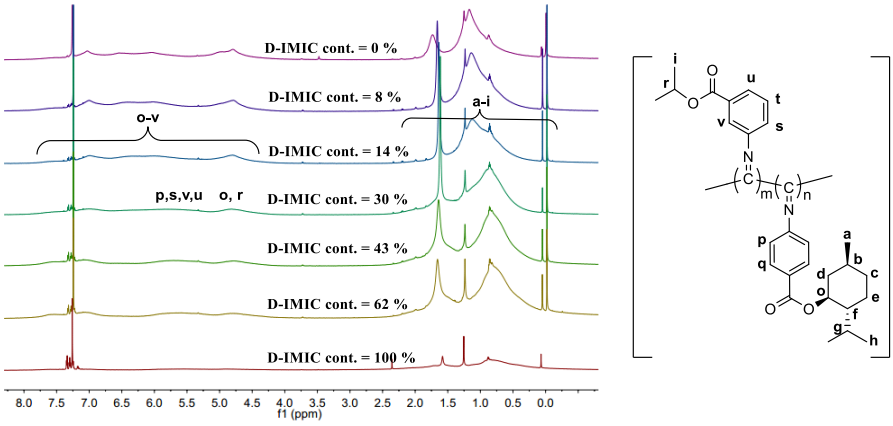


Figure S43. ^{1}H NMR spectra of poly(IPI), poly(D-IMCI) and poly(D-IMCI-*co*-IPI)s (Table 1, entries 17, 18 and Table 2, entries 11-15).

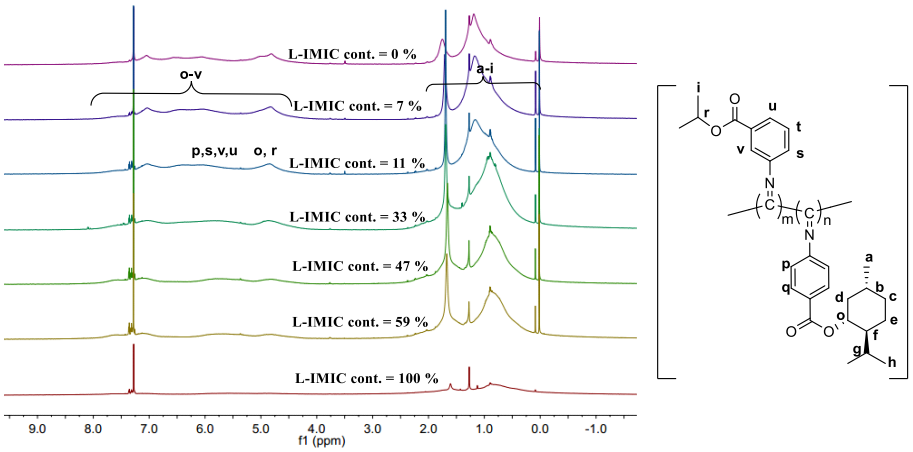


Figure S44. ^{1}H NMR spectra of poly(IPI), poly(L-IMCI) and poly(L-IMCI-*co*-IPI)s (Table 1, entries 17, 20 and Table 2, entries 16-20).

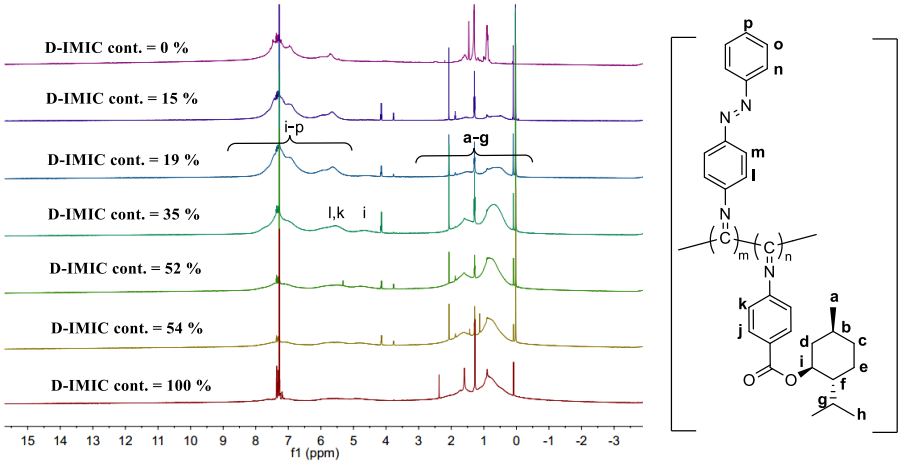


Figure S45. ^{1}H NMR spectra of poly(D-IMCI), poly(IPD) and poly(D-IMIC-*co*-IPD)s (Table 1, entries 18, 28 and Table 2, entries 21-25).

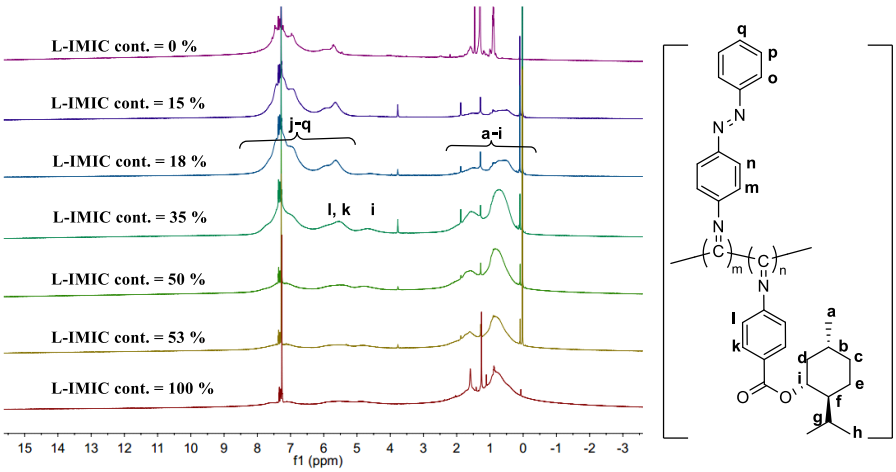


Figure S46. ^{1}H NMR spectra of poly(L-IMCI), poly(IPD) and poly(L-IMIC-*co*-IPD)s (Table 1, entries 20, 28 and Table 2, entries 26-30).

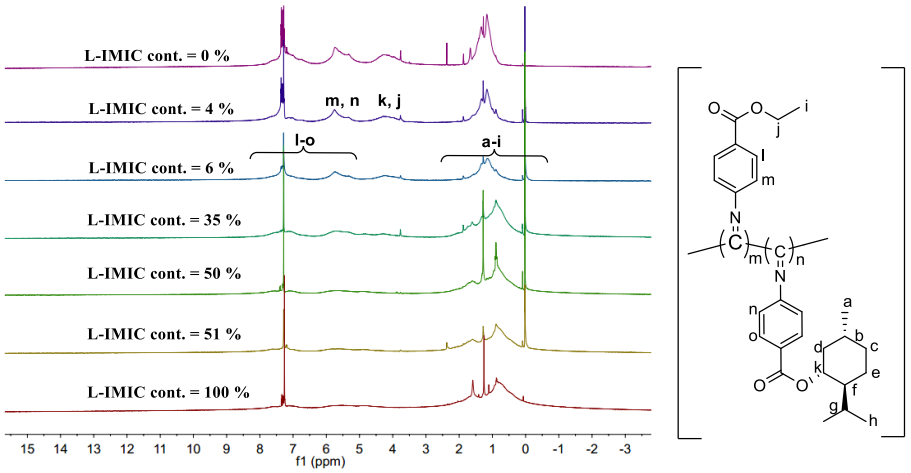
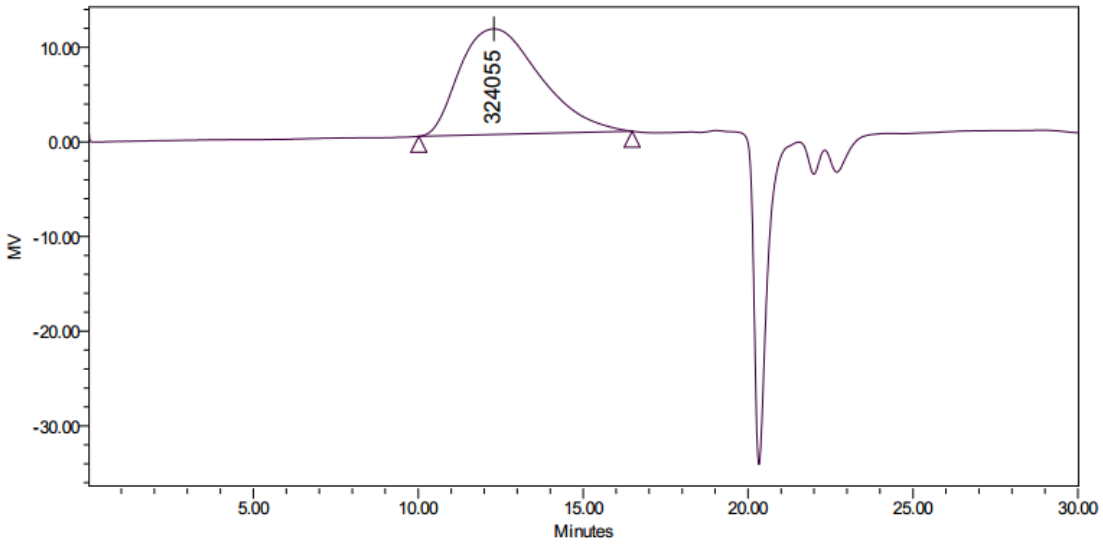


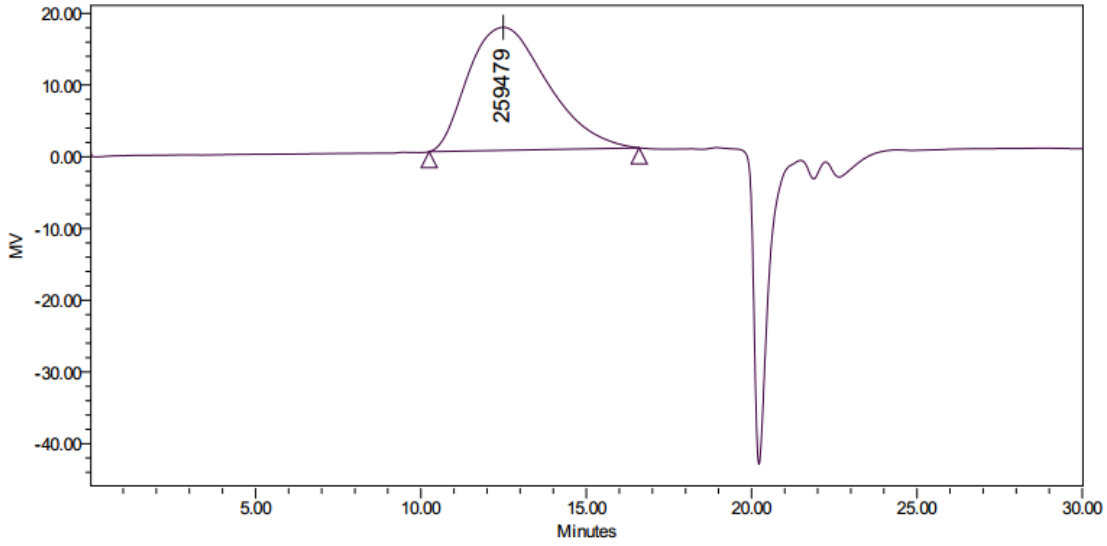
Figure S47. ^{1}H NMR spectra of poly(L-IMCl), poly(EPI) and poly(L-IMIC-*co*-EPI)s (Table 1, entries 20, 1 and Table 2, entries 31-35).



Broad Unknown Modified Universal Peak Table

	Distribution Name	Mv (Daltons)	K (dl/g)	alpha	Intrinsic Viscosity (dl/g)	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw
1						99380	419555	324055	973823	1553064	4.221743	2.321087

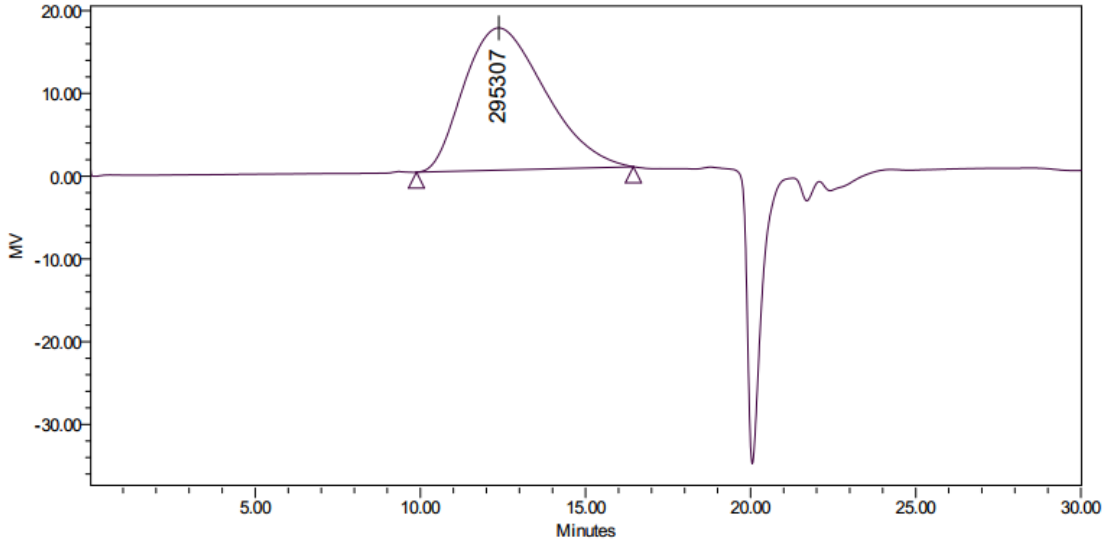
Figure S48. GPC curve of poly(EPI) in Table 1, entry 1.



Broad Unknown Modified Universal Peak Table

	Distribution Name	Mv (Daltons)	K (dl/g)	alpha	Intrinsic Viscosity (dl/g)	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw
1						89614	353163	259479	807066	1275883	3.940943	2.285252

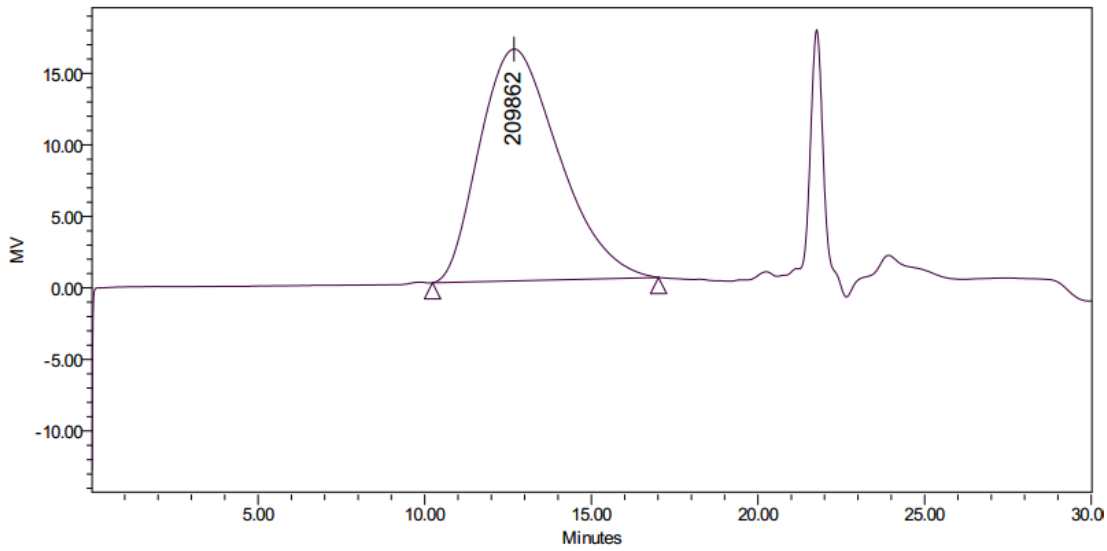
Figure S49. GPC curve of poly(EPI) in Table 1, entry 2.



Broad Unknown Modified Universal Peak Table

	Distribution Name	Mv (Daltons)	K (dl/g)	alpha	Intrinsic Viscosity (dl/g)	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw
1						95602	405689	295307	1011338	1701846	4.243529	2.492891

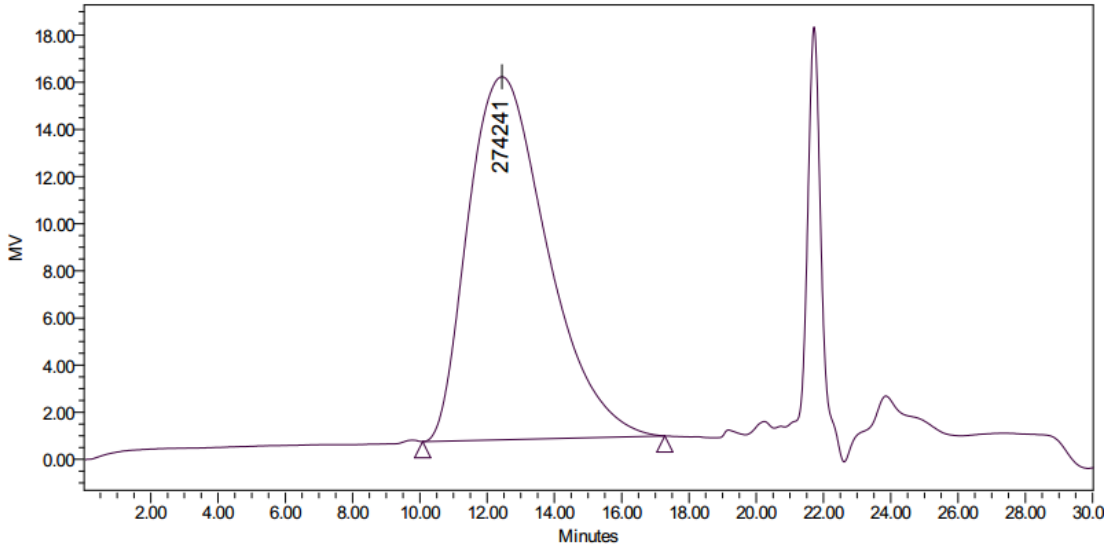
Figure S50. GPC curve of poly(EPI) in Table 1, entry 3.



Broad Unknown Modified Universal Peak Table

	Distribution Name	Mv (Daltons)	K (dl/g)	alpha	Intrinsic Viscosity (dl/g)	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw
1						69662	285021	209862	686674	1147514	4.091472	2.409201

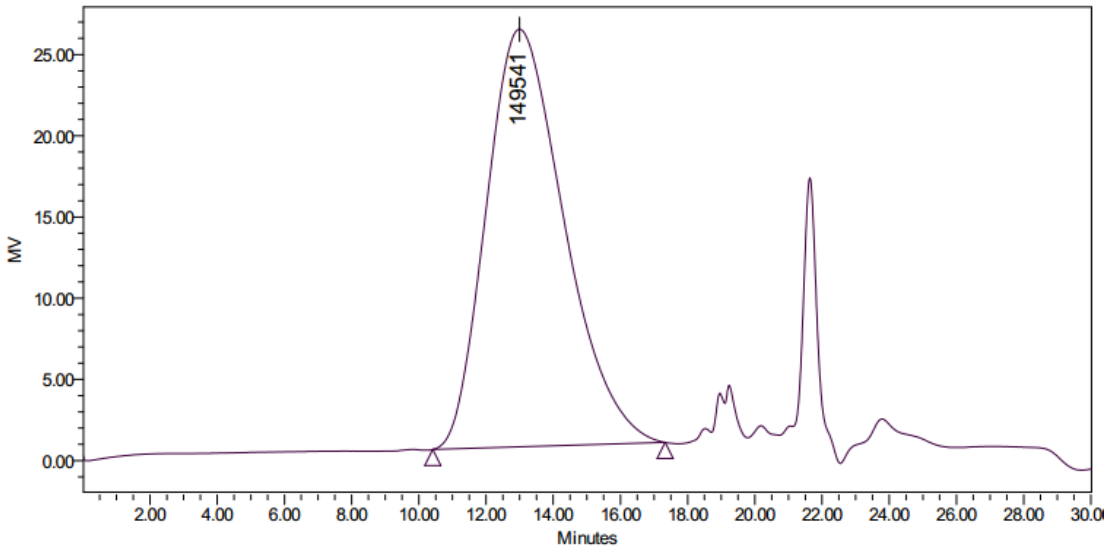
Figure S51. GPC curve of poly(EPI) in Table 1, entry 4.



Broad Unknown Modified Universal Peak Table

	Distribution Name	Mv (Daltons)	K (dl/g)	alpha	Intrinsic Viscosity (dl/g)	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw
1						82143	354236	274241	810693	1302041	4.312433	2.288566

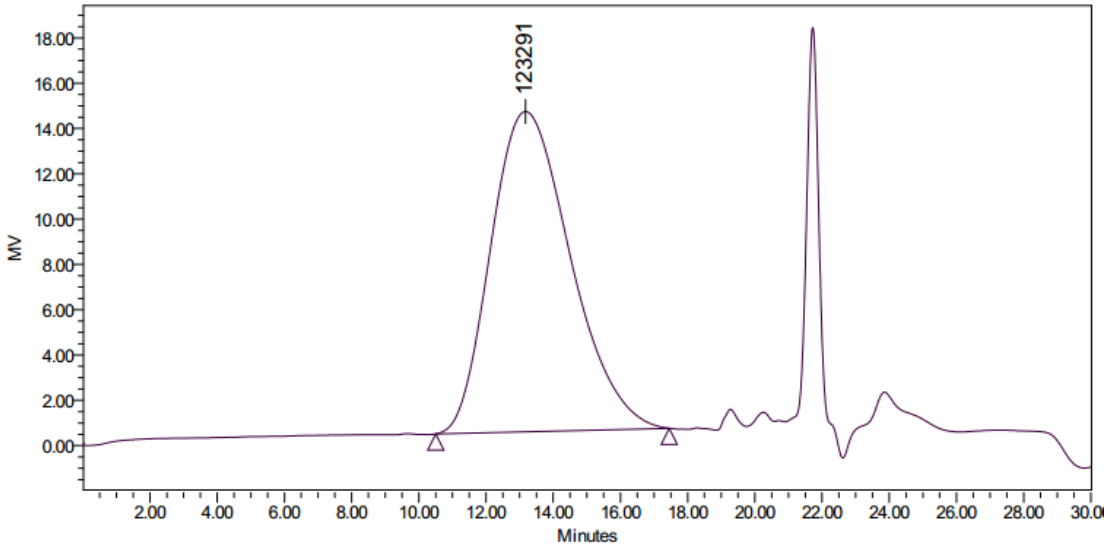
Figure S52. GPC curve of poly(EPI) in Table 1, entry 5.



Broad Unknown Modified Universal Peak Table

	Distribution Name	Mv (Daltons)	K (dl/g)	alpha	Intrinsic Viscosity (dl/g)	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw
1						51452	196611	149541	473038	823767	3.821261	2.405962

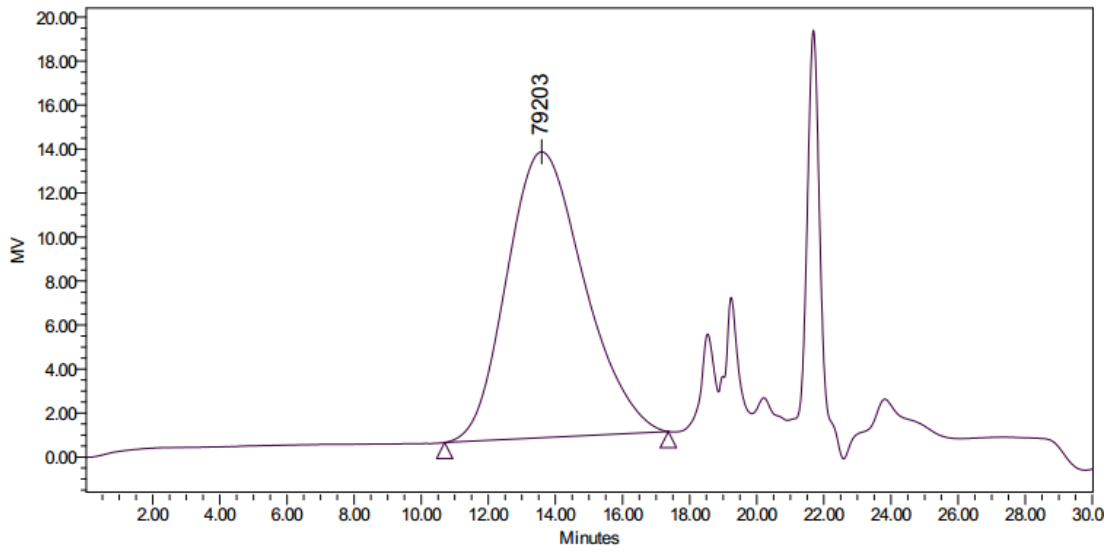
Figure S53. GPC curve of poly(EPI) in Table 1, entry 6.



Broad Unknown Modified Universal Peak Table

	Distribution Name	Mv (Daltons)	K (dl/g)	alpha	Intrinsic Viscosity (dl/g)	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw
1						44653	168002	123291	409413	724300	3.762392	2.436954

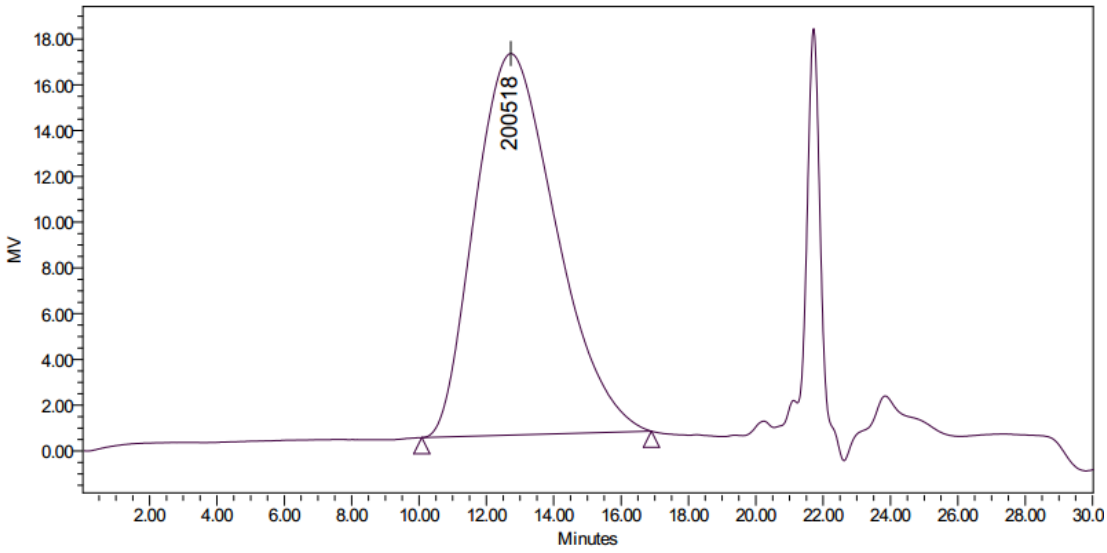
Figure S54. GPC curve of poly(EPI) in Table 1, entry 7.



Broad Unknown Modified Universal Peak Table

	Distribution Name	Mv (Daltons)	K (dl/g)	alpha	Intrinsic Viscosity (dl/g)	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw
1						33069	113144	79203	284615	541335	3.421436	2.515507

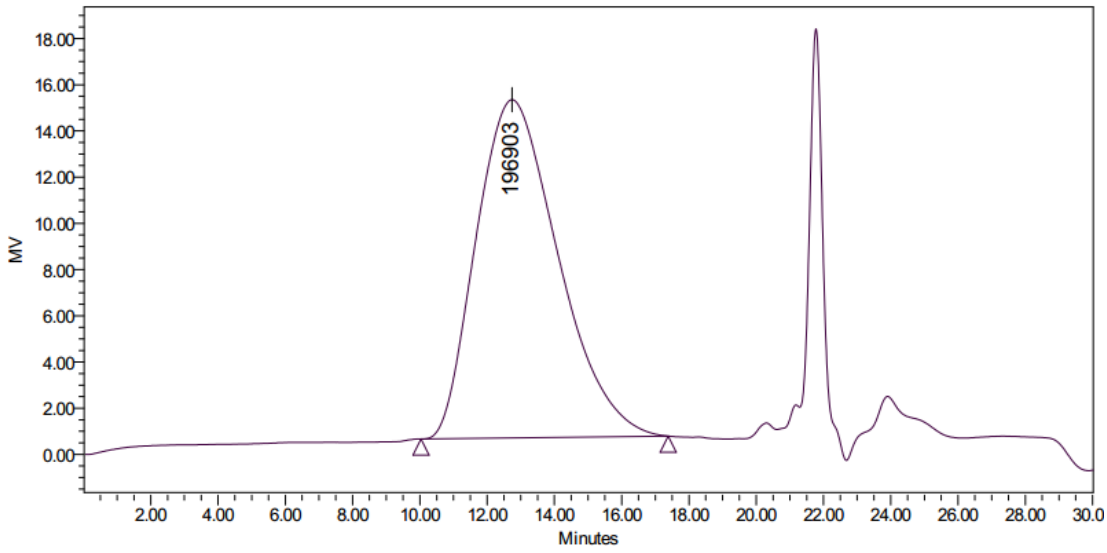
Figure S55. GPC curve of poly(EPI) in Table 1, entry 8.



Broad Unknown Modified Universal Peak Table

	Distribution Name	Mv (Daltons)	K (dl/g)	alpha	Intrinsic Viscosity (dl/g)	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw
1						69470	285287	200518	711086	1217921	4.106645	2.492531

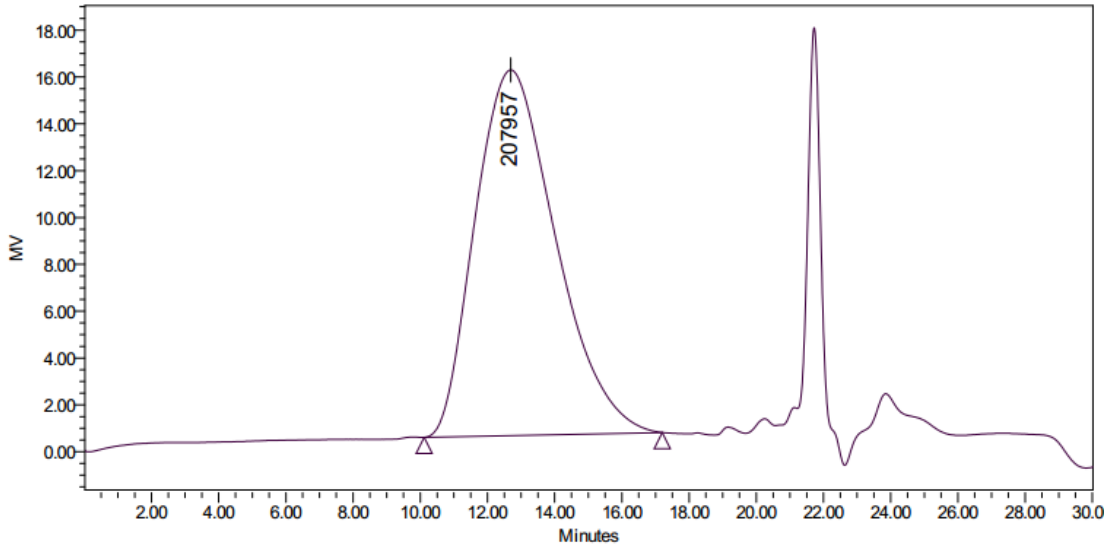
Figure S56. GPC curve of poly(EPI) in Table 1, entry 9.



Broad Unknown Modified Universal Peak Table

	Distribution Name	Mv (Daltons)	K (dl/g)	alpha	Intrinsic Viscosity (dl/g)	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw
1						63333	278039	196903	694242	1183795	4.390093	2.496919

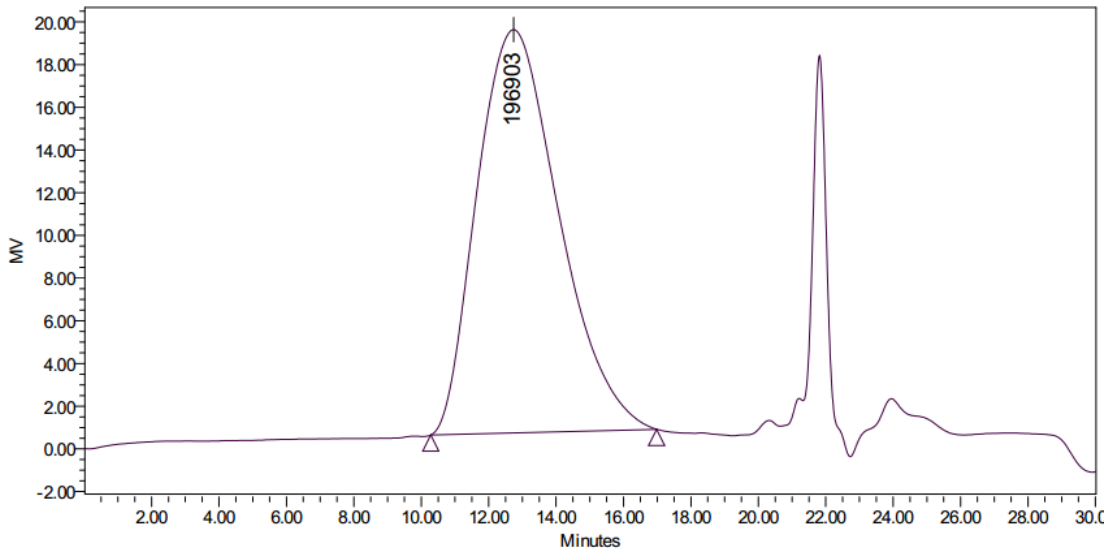
Figure S57. GPC curve of poly(EPI) in Table 1, entry 10.



Broad Unknown Modified Universal Peak Table

	Distribution Name	Mv (Daltons)	K (dl/g)	alpha	Intrinsic Viscosity (dl/g)	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw
1						69720	293069	207957	717670	1213443	4.203489	2.448806

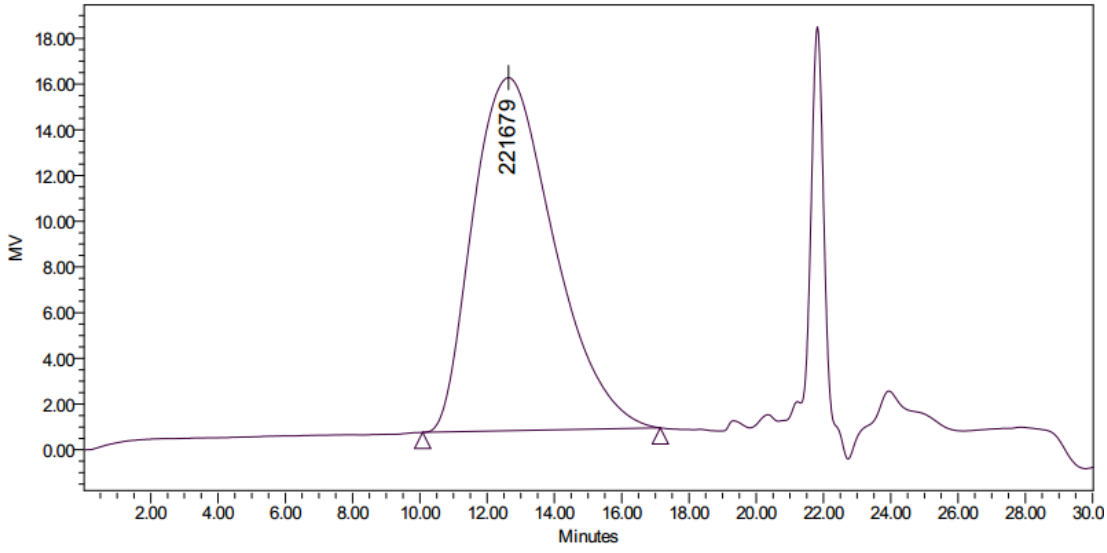
Figure S58. GPC curve of poly(EPI) in Table 1, entry 11.



Broad Unknown Modified Universal Peak Table

	Distribution Name	Mv (Daltons)	K (dl/g)	alpha	Intrinsic Viscosity (dl/g)	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw
1						67748	282710	196903	687657	1139210	4.172967	2.432373

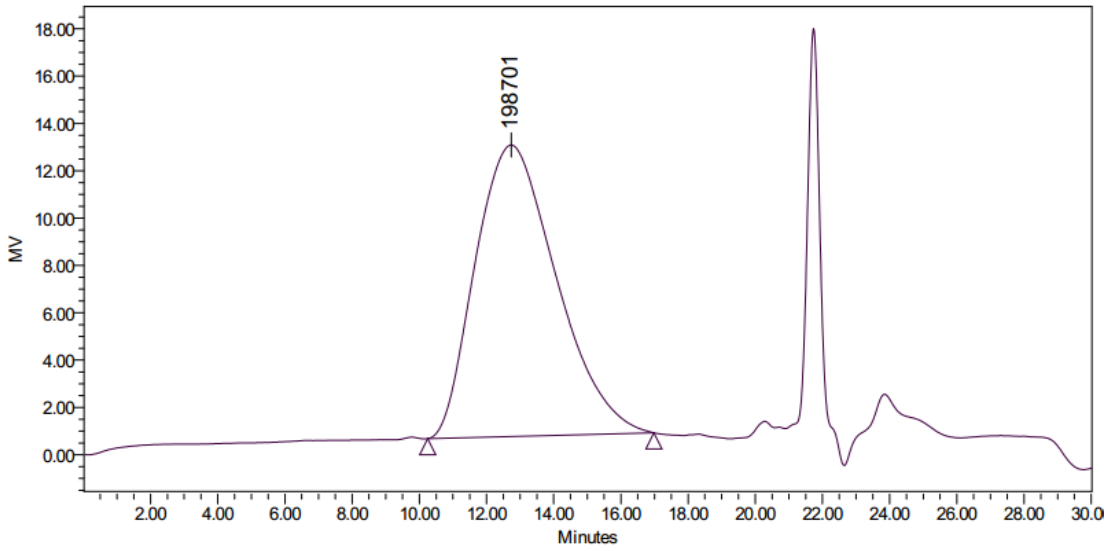
Figure S59. GPC curve of poly(EPI) in Table 1, entry 12.



Broad Unknown Modified Universal Peak Table

	Distribution Name	Mv (Daltons)	K (dl/g)	alpha	Intrinsic Viscosity (dl/g)	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw
1						71713	302167	221679	712672	1167319	4.213543	2.358538

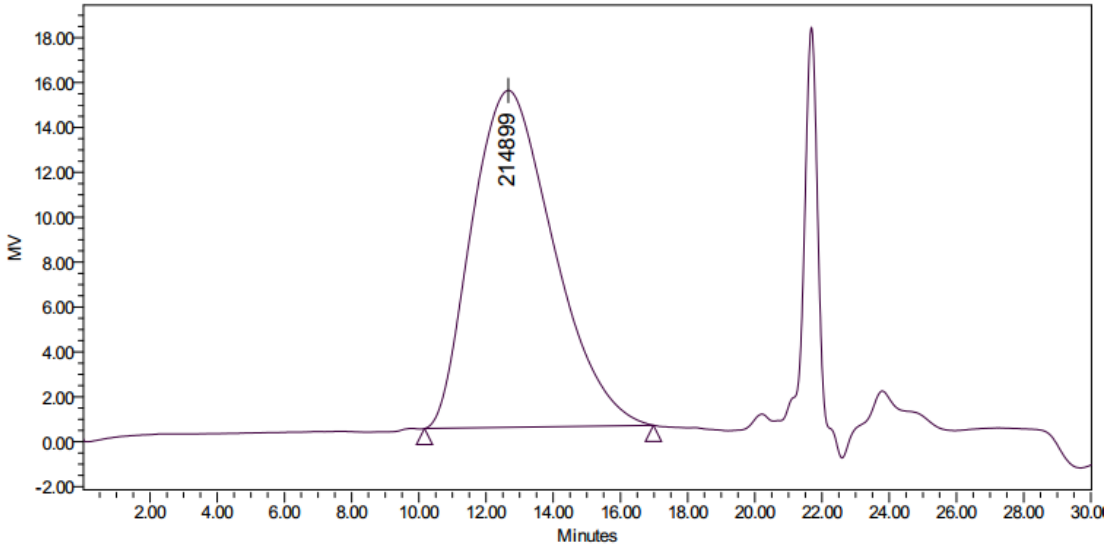
Figure 60. GPC curve of poly(EPI) in Table 1, entry 13.



Broad Unknown Modified Universal Peak Table

	Distribution Name	Mv (Daltons)	K (dl/g)	alpha	Intrinsic Viscosity (dl/g)	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw
1						68089	279930	198701	677565	1123920	4.111215	2.420478

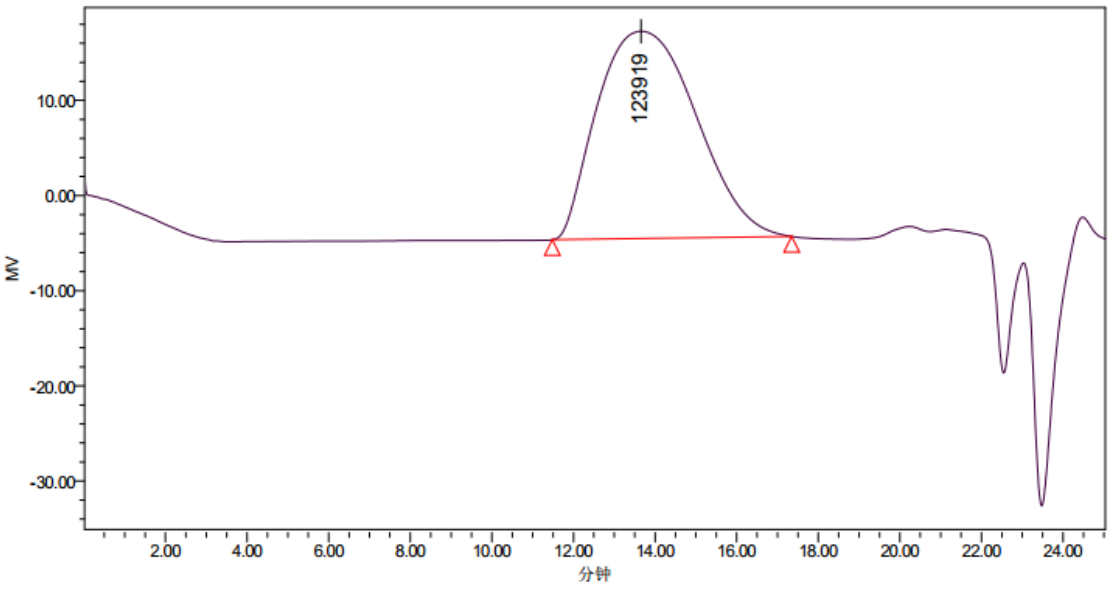
Figure S61. GPC curve of poly(EPI) in Table 1, entry 14.



Broad Unknown Modified Universal Peak Table

	Distribution Name	Mv (Daltons)	K (dl/g)	alpha	Intrinsic Viscosity (dl/g)	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw
1						73048	309722	214899	762290	1271888	4.239970	2.461209

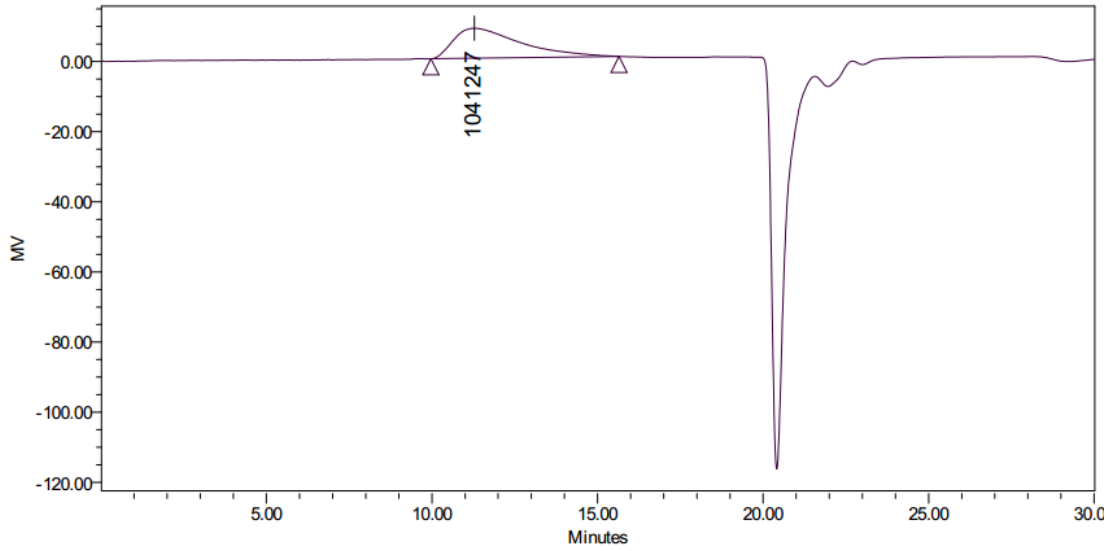
Figure S62. GPC curve of poly(EPI) in Table 1, entry 15.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		13.657	13.657	13.657	64568	206115	123919	590028	1073073	2.862620

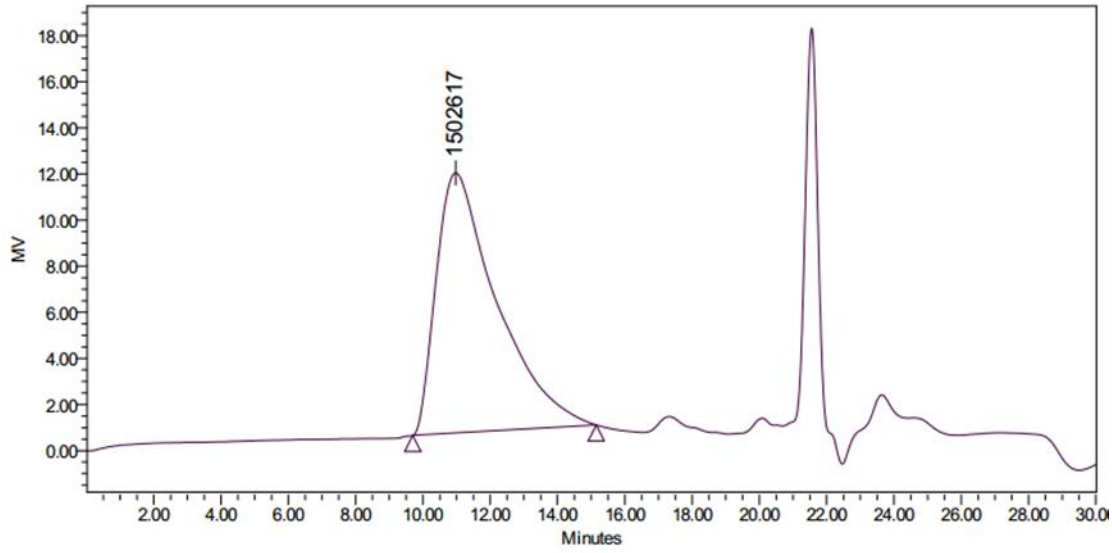
Figure S63. GPC curve of poly(IPI) in Table 1, entry 17.



Broad Unknown Modified Universal Peak Table

	Distribution Name	Mv (Daltons)	K (dl/g)	alpha	Intrinsic Viscosity (dl/g)	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw
1						215458	840579	1041247	1580041	2162687	3.901350	1.879707

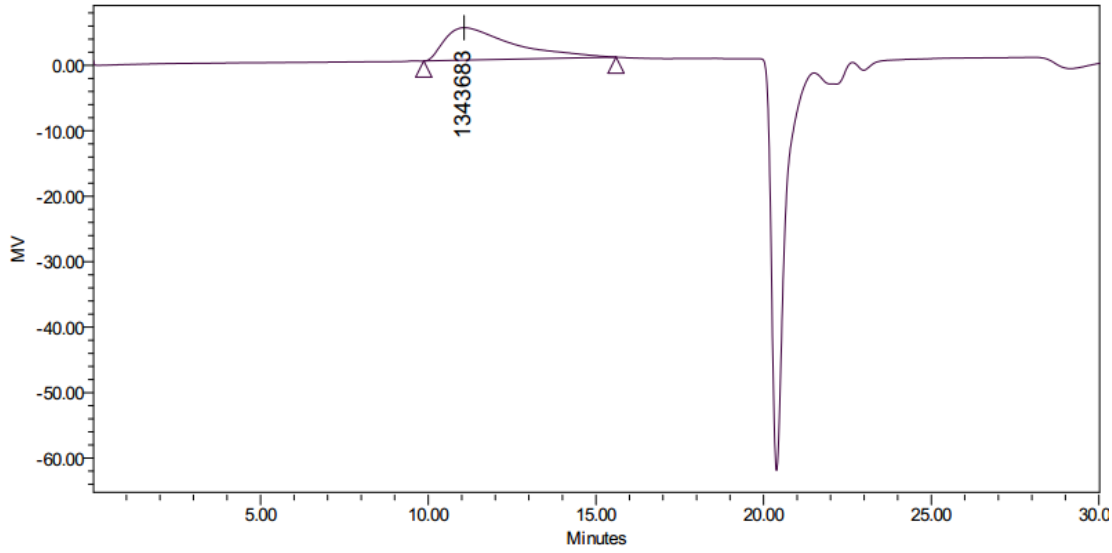
Figure S64. GPC curve of poly(D-IMIC) in Table 1, entry 18.



Broad Unknown Modified Universal Peak Table

	Distribution Name	Mv (Daltons)	K (dl/g)	alpha	Intrinsic Viscosity (dl/g)	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw
1						357051	1234953	1502617	2226555	3021716	3.458757	1.802947

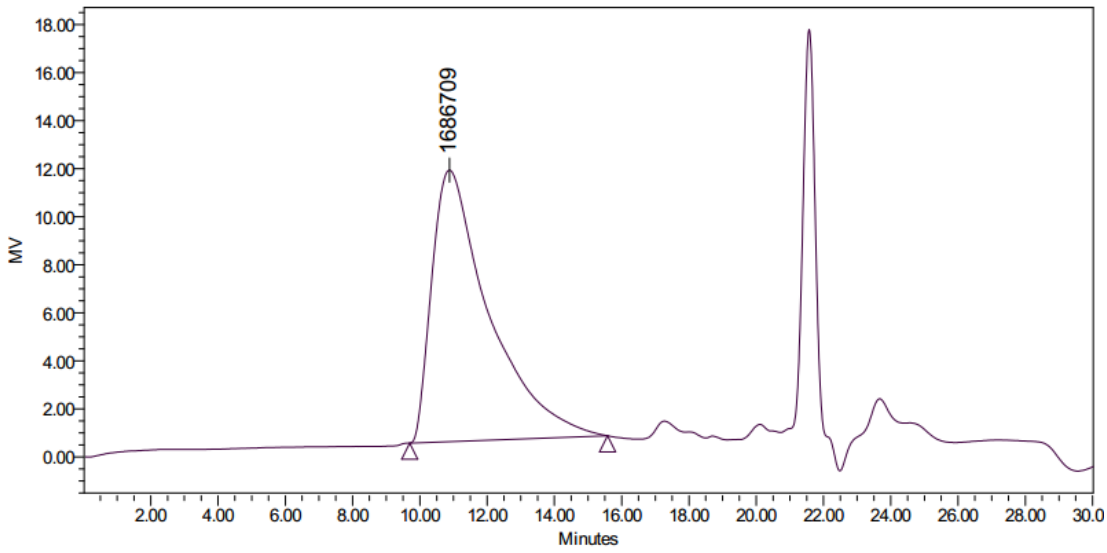
Figure S65. GPC curve of poly(D-IMIC) in Table 1, entry 19.



Broad Unknown Modified Universal Peak Table

	Distribution Name	Mv (Daltons)	K (dl/g)	alpha	Intrinsic Viscosity (dl/g)	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw
1						216071	995795	1343683	1887136	2530938	4.608639	1.895106

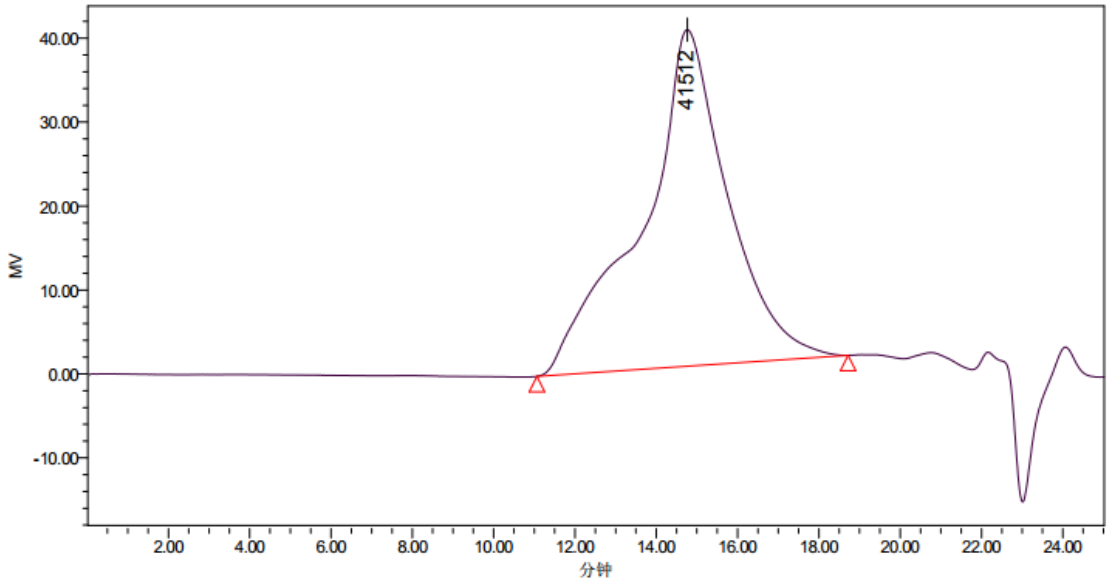
Figure S66. GPC curve of poly(L-IMIC) in Table 1, entry 20.



Broad Unknown Modified Universal Peak Table

	Distribution Name	Mv (Daltons)	K (dl/g)	alpha	Intrinsic Viscosity (dl/g)	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw
1						333832	1303972	1686709	2269851	2990174	3.906073	1.740721

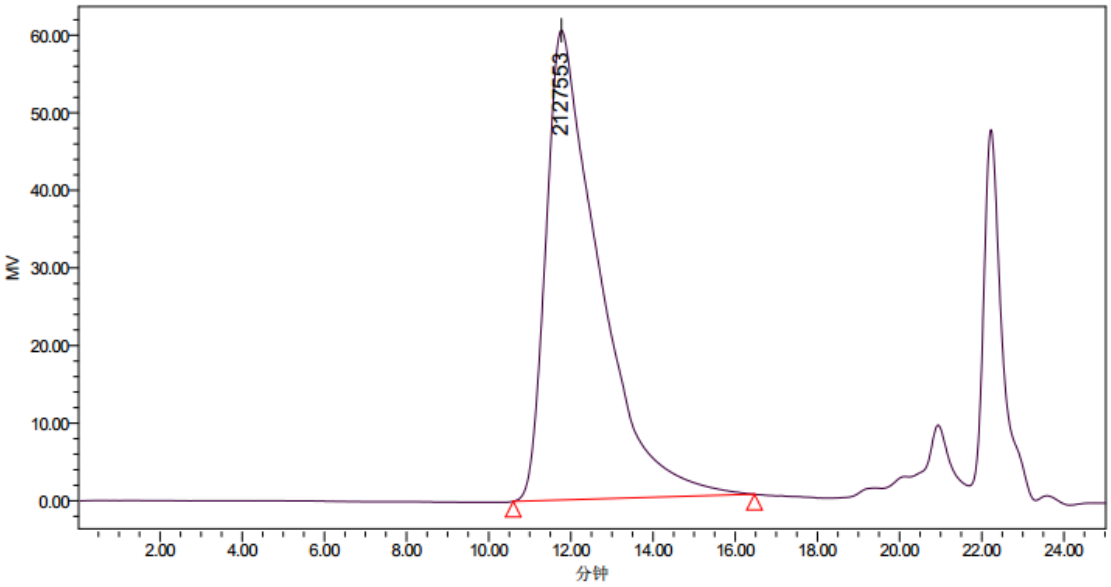
Figure S67. GPC curve of poly(L-IMIC) in Table 1, entry 21.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		14.764	14.764	14.764	33103	170406	41512	1232498	2684363	7.232707

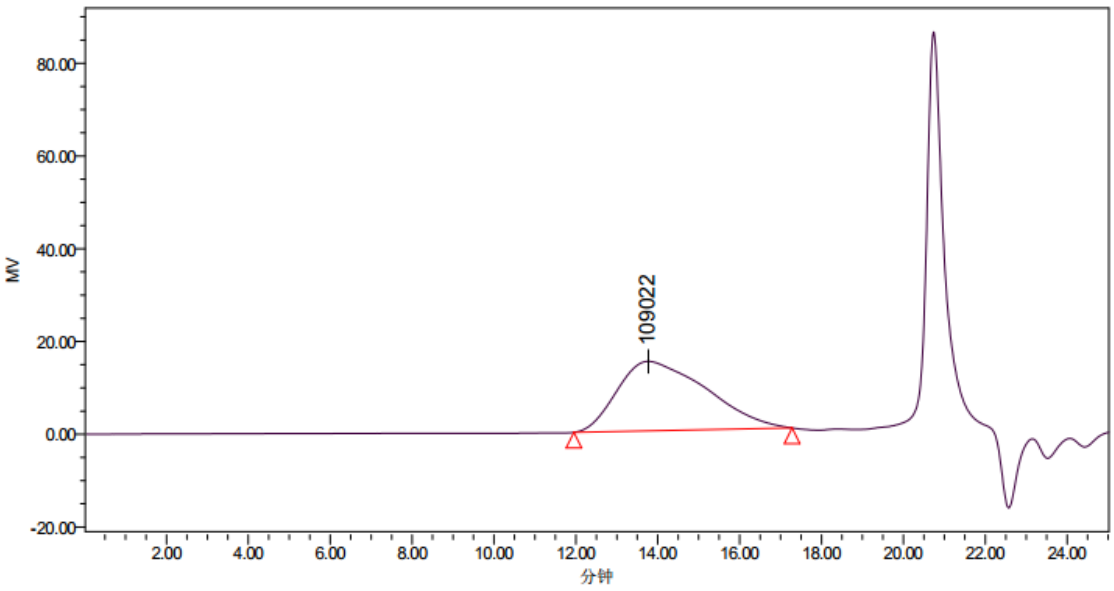
Figure S68. GPC curve of poly(ITPB) in Table 1, entry 22.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		11.772	11.772	11.772	378543	1747850	2127553	3895455	6523868	2.228712

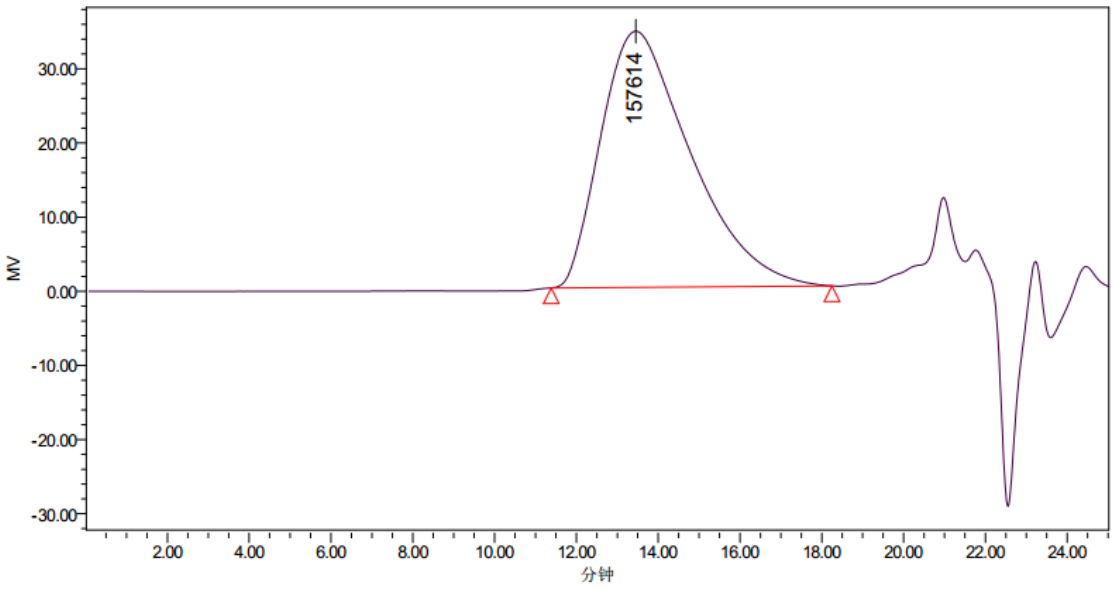
Figure S69. GPC curve of poly(ITPB) in Table 1, entry 23.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		13.771	13.771	13.771	48615	115948	109022	259230	451684	2.235750

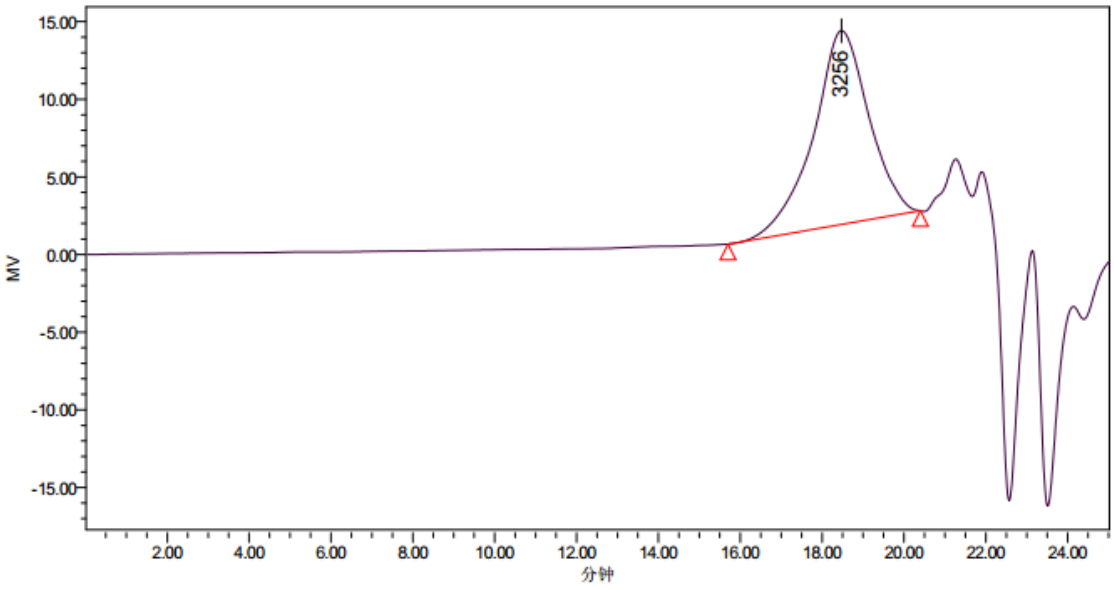
Figure S70. GPC curve of poly(BNB) in Table 1, entry 24.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		13.453	13.453	13.453	60053	204824	157614	570245	1090598	2.784078

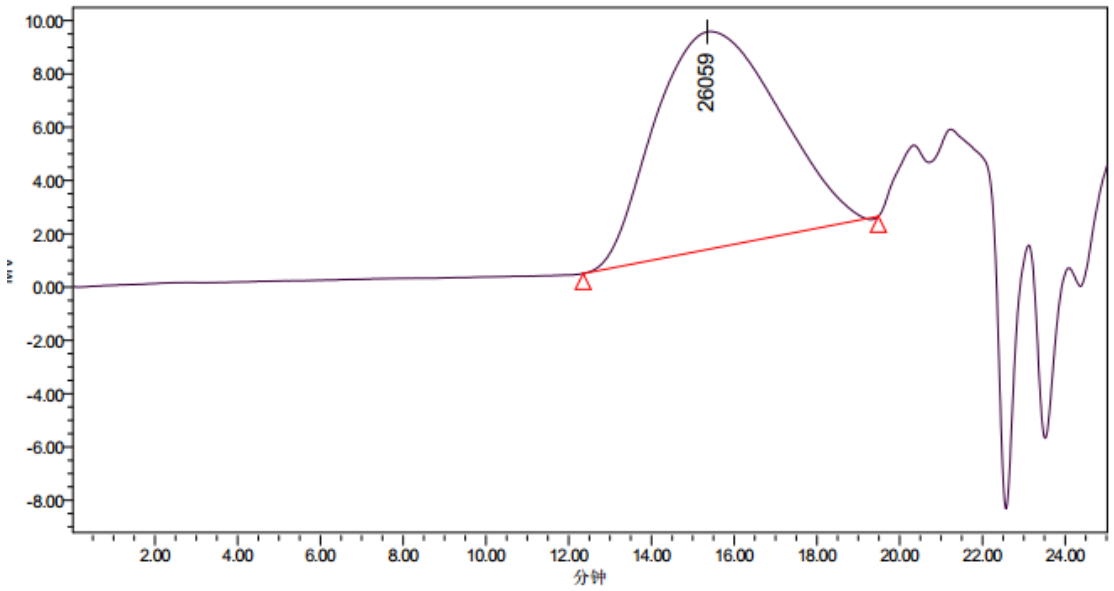
Figure S71. GPC curve of poly(PQPI) in Table 1, entry 25



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1		18.475	18.475	18.475	2819	3677	3256	4703	5891	1.279185	1.602208

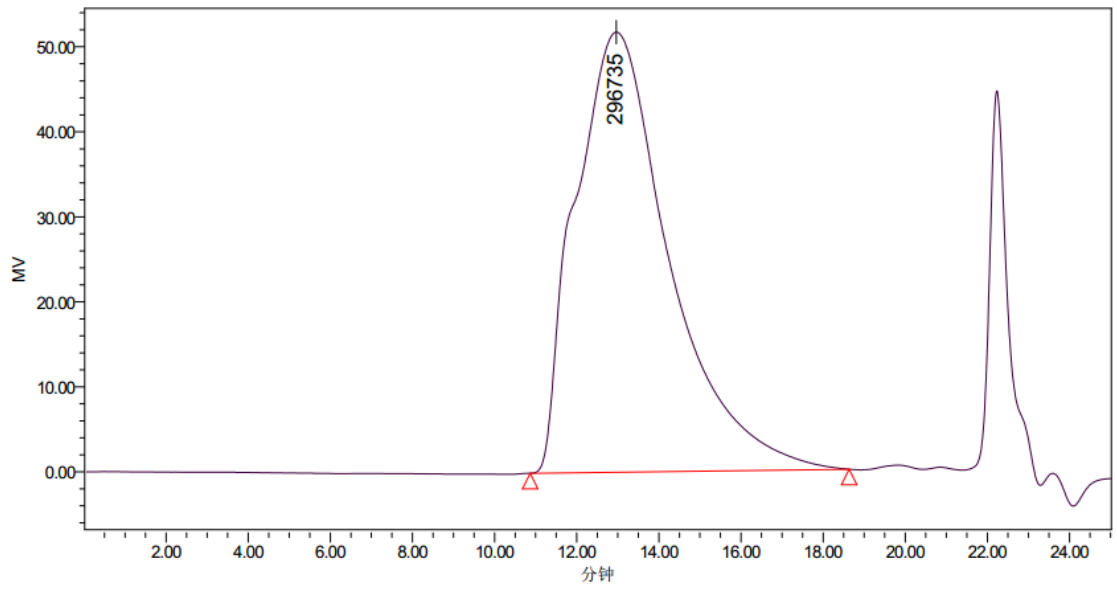
Figure S72. GPC curve of poly(IPQ) in Table 1, entry 26.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1		15.350	15.350	15.350	14977	36151	26059	86868	165736	2.402945	4.584580

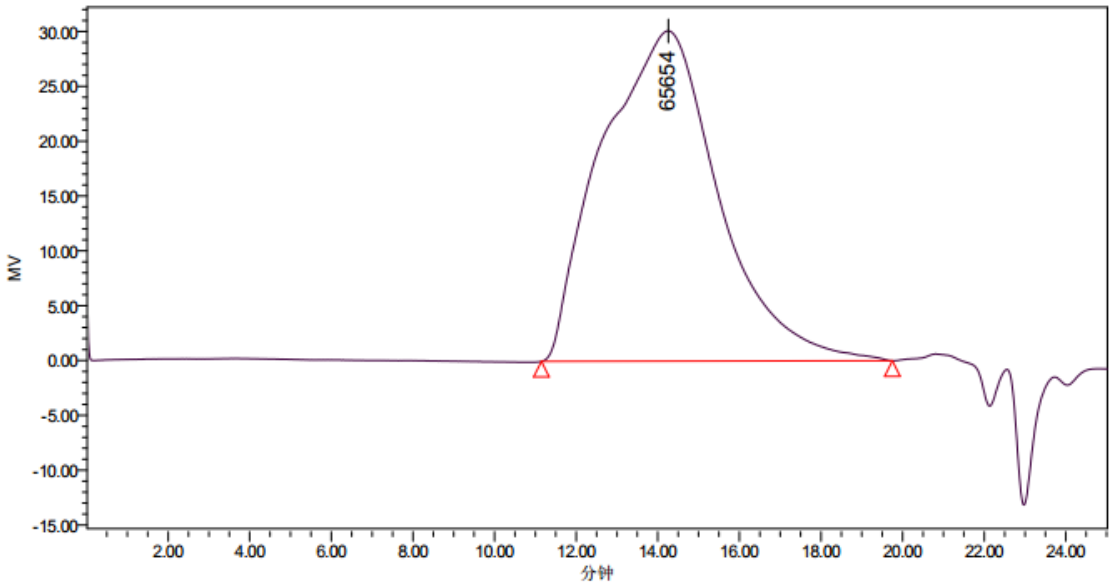
Figure S73. GPC curve of poly(IPD) in Table 1, entry 28.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		12.967	12.967	12.967	86648	569587	296735	1966614	3427610	3.452698

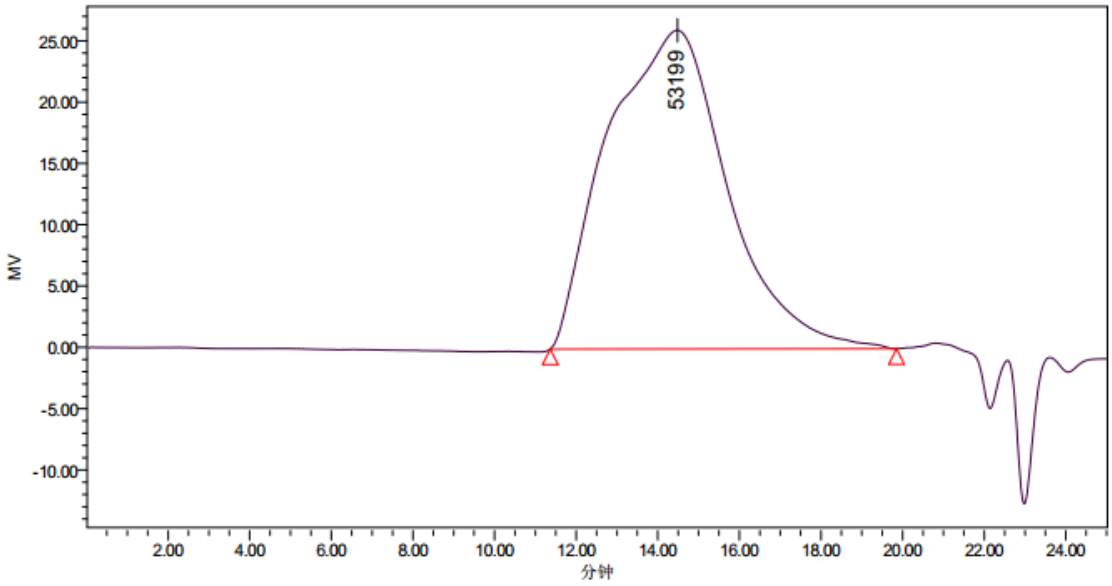
Figure S74. GPC curve of poly(IPD) in Table 1, entry 29.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		14.259	14.259	14.259	38873	254887	65654	117406(	2268873	4.606198

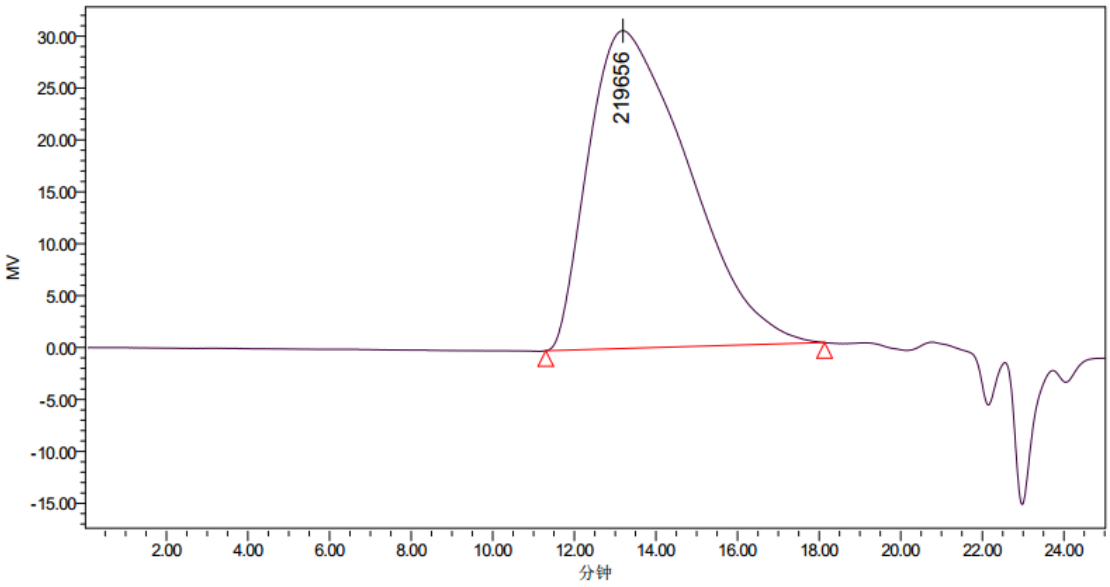
Figure S75. GPC curve of poly(ITPB-*co*-D-IMCl) in Table 2, entry 1.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		14.482	14.482	14.482	34532	198280	53199	856640	1657729	4.320346

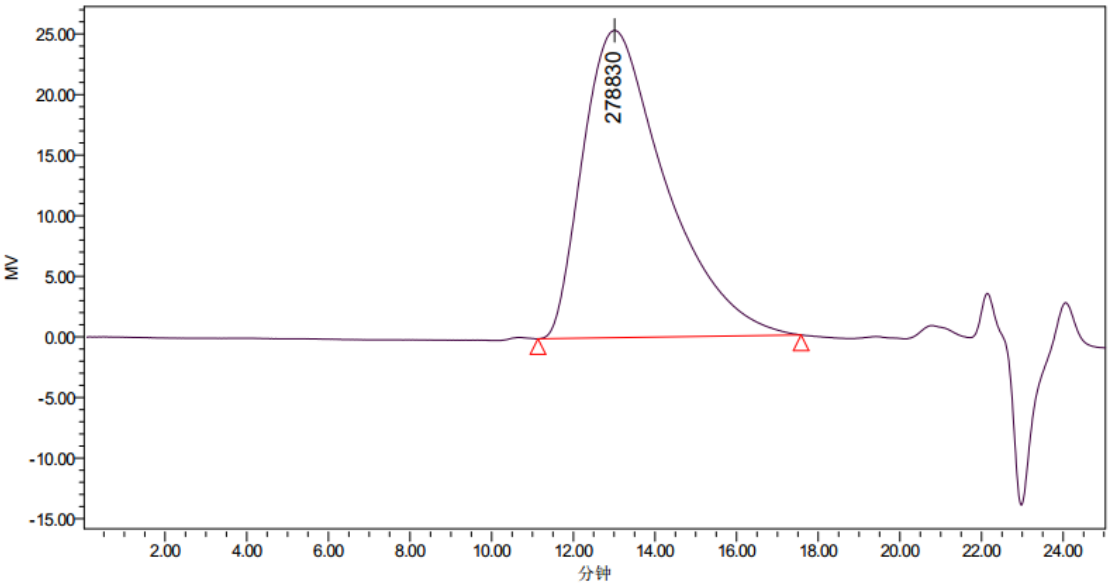
Figure S76. GPC curve of poly(ITPB-*co*-D-IMCl) in Table 2, entry 2.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		13.190	13.190	13.190	63424	264803	219656	816461	1509701	3.083281

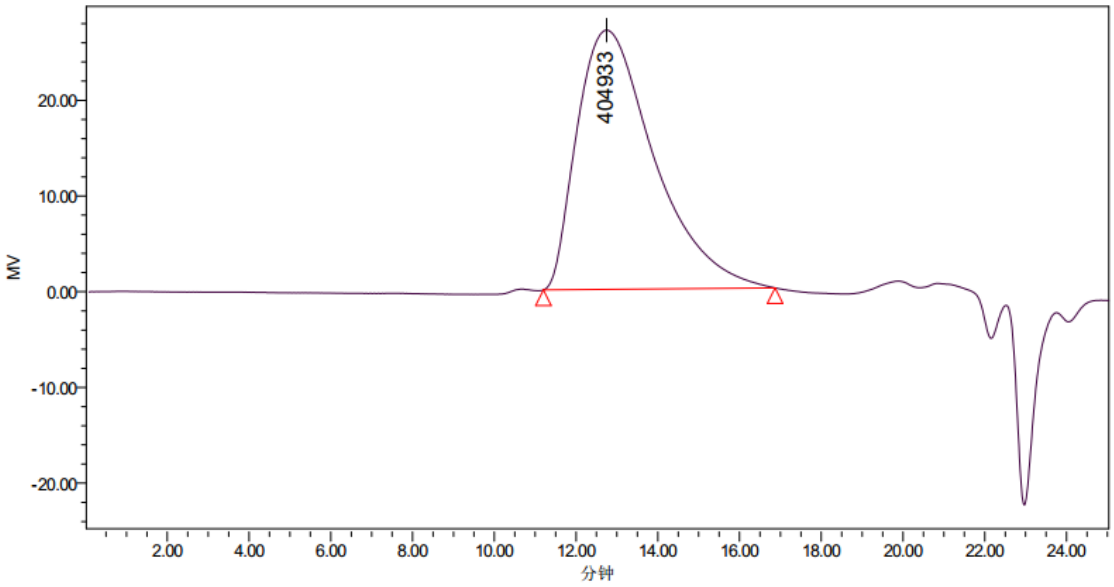
Figure S77. GPC curve of poly(ITPB-*co*-D-IMCl) in Table 2, entry 3.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		13.012	13.012	13.012	90481	352248	278830	981575	1814187	2.786600

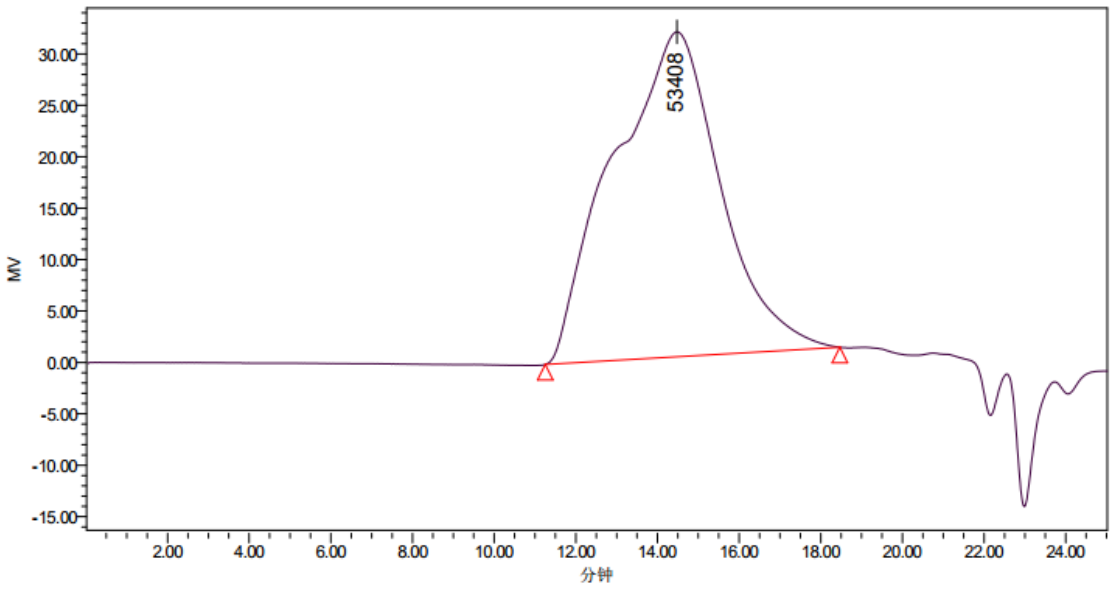
Figure S78. GPC curve of poly(ITPB-*co*-D-IMCl) in Table 2, entry 4.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		12.750	12.750	12.750	131898	492770	404933	1243941	2101771	2.524382

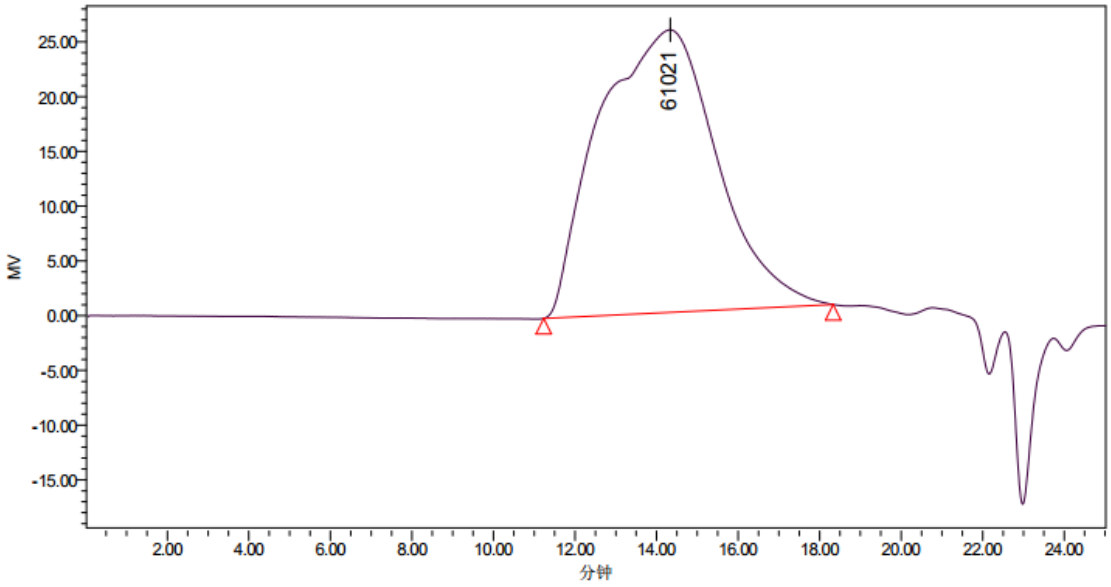
Figure S79. GPC curve of poly(ITPB-*co*-D-IMCl) in Table 2, entry 5.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		14.478	14.478	14.478	43523	213114	53408	956646	1875173	4.488899

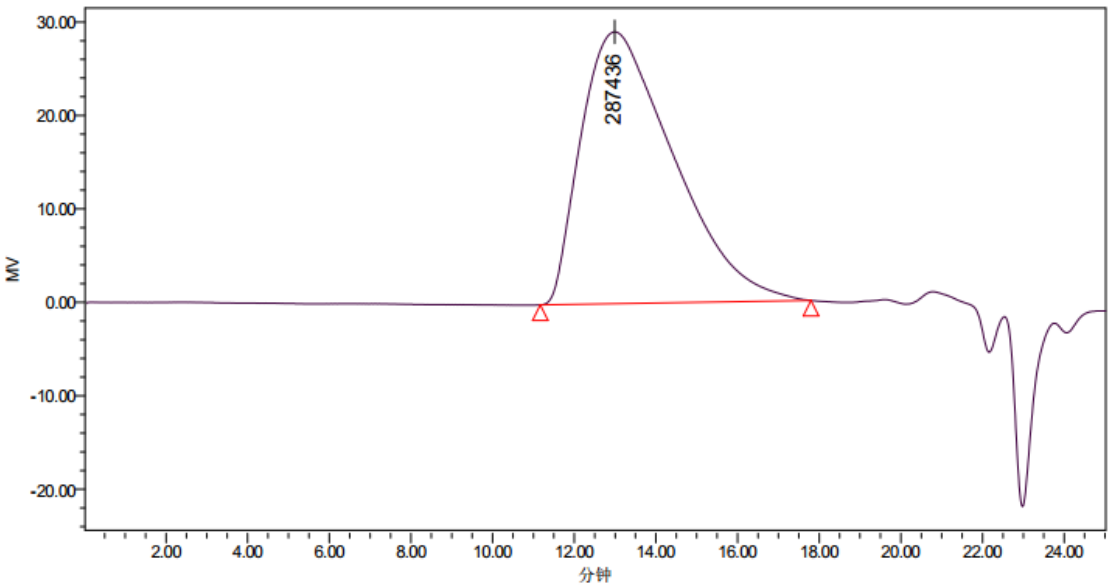
Figure S80. GPC curve of poly(ITPB-*co*-L-IMCl) in Table 2, entry 6.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		14.335	14.335	14.335	47944	246380	61021	1008788	1903372	4.094441

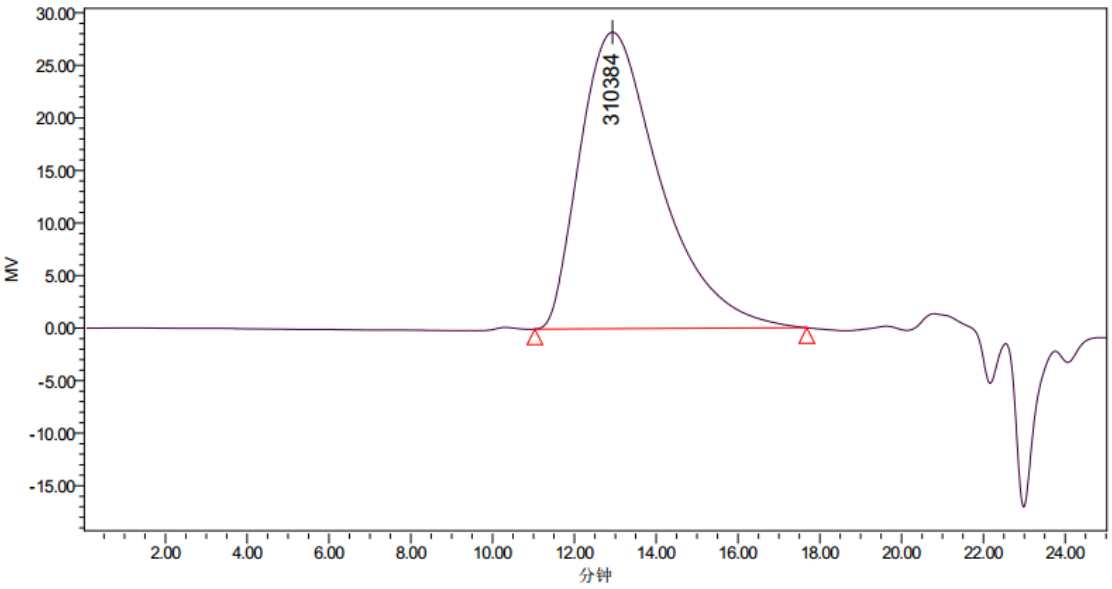
Figure S81. GPC curve of poly(ITPB-*co*-L-IMCl) in Table 2, entry 7.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		12.990	12.990	12.990	81562	357021	287436	1046293	1861634	2.930621

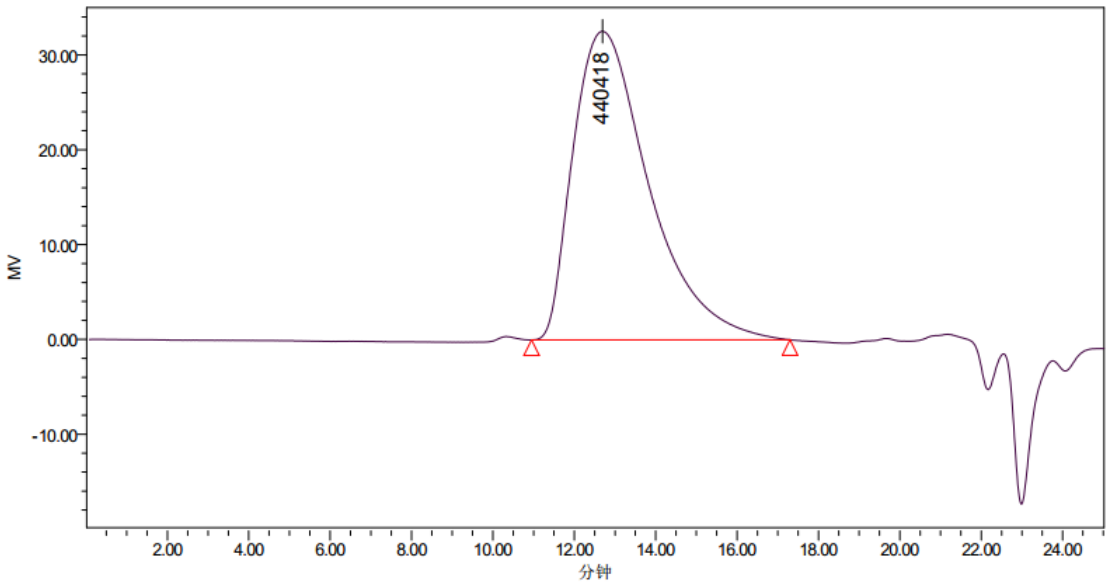
Figure S82. GPC curve of poly(ITPB-*co*-L-IMCl) in Table 2, entry 8.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		12.935	12.935	12.935	106664	430123	310384	1240872	2374240	2.884924

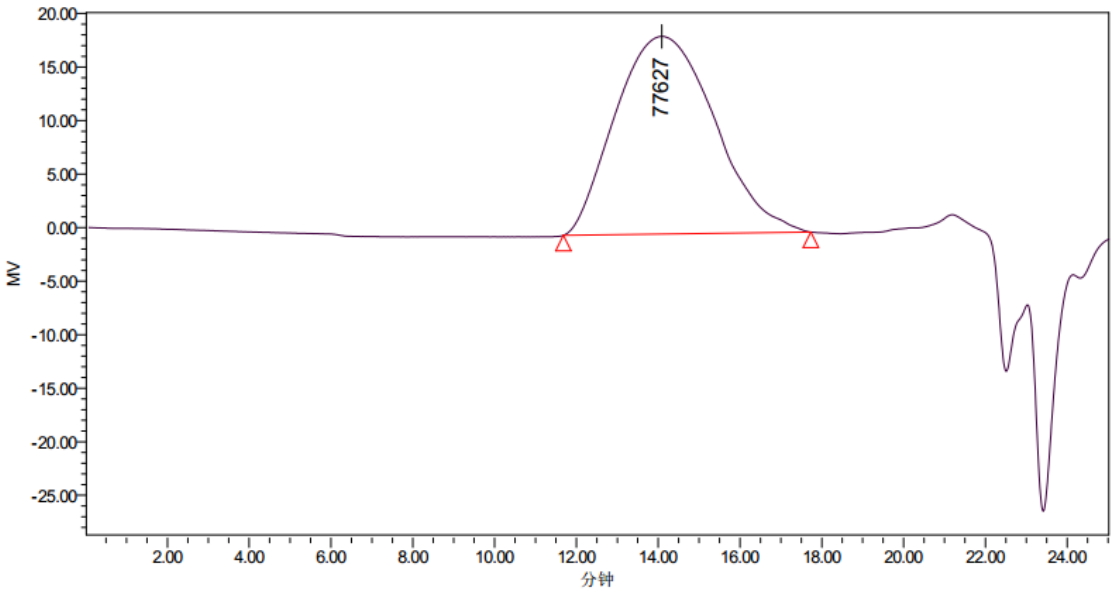
Figure S83. GPC curve of poly(ITPB-*co*-L-IMCl) in Table 2, entry 9.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		12.694	12.694	12.694	136414	549035	440418	1444077	2577459	2.630208

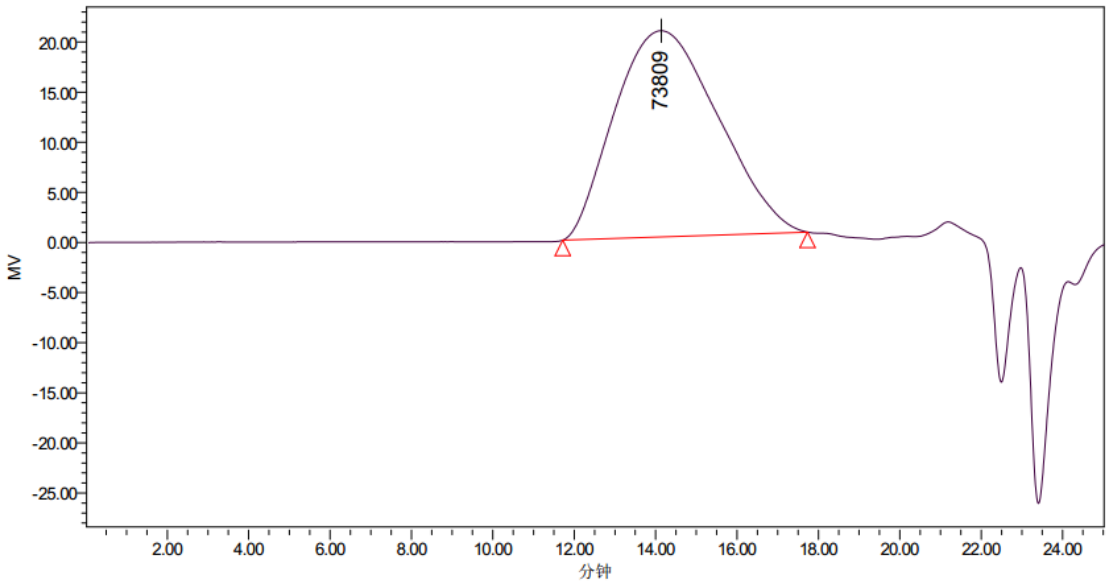
Figure S84. GPC curve of poly(ITPB-*co*-L-IMCl) in Table 2, entry 10.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1		14.090	14.090	14.090	47102	137594	77627	405628	788242	2.948007	5.728759

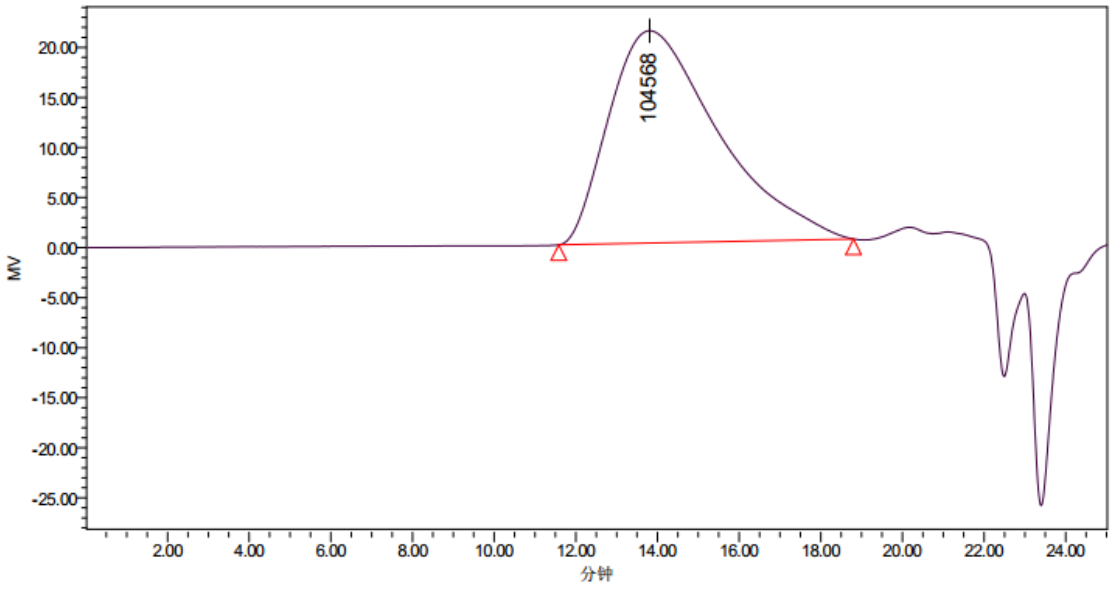
Figure S85. GPC curve of poly(IPI-*co*-D-IMCl) in Table 2, entry 11.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1		14.140	14.140	14.140	41944	126181	73809	378663	736764	3.000954	5.838955

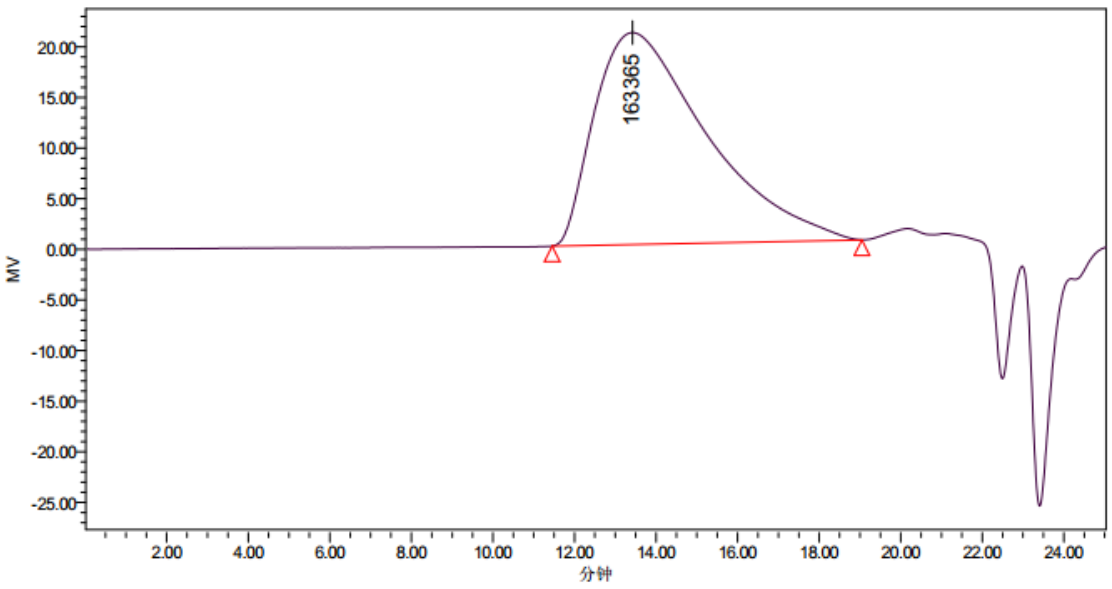
Figure S86. GPC curve of poly(IPI-*co*-D-IMCl) in Table 2, entry 12.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		13.808	13.808	13.808	34205	138858	104568	438372	855216	3.156985

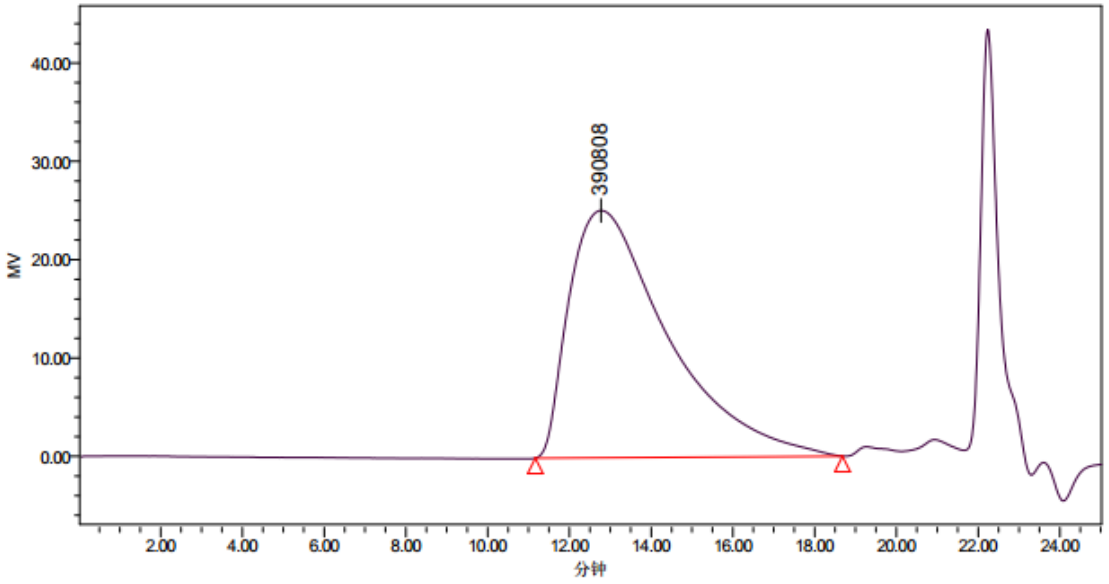
Figure S87. GPC curve of poly(IPI-*co*-D-IMCl) in Table 2, entry 13.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		13.424	13.424	13.424	37461	194506	163365	617050	1120837	3.172394

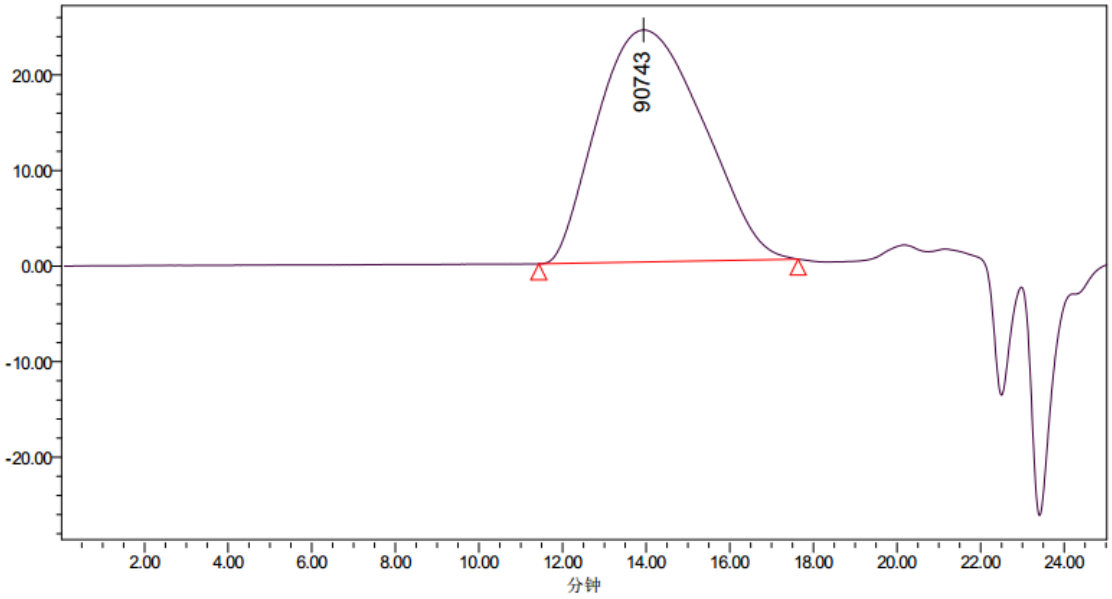
Figure S88. GPC curve of poly(IPI-*co*-D-IMCl) in Table 2, entry 14.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		12.774	12.774	12.774	63518	419917	390808	1272020	2166095	3.029216

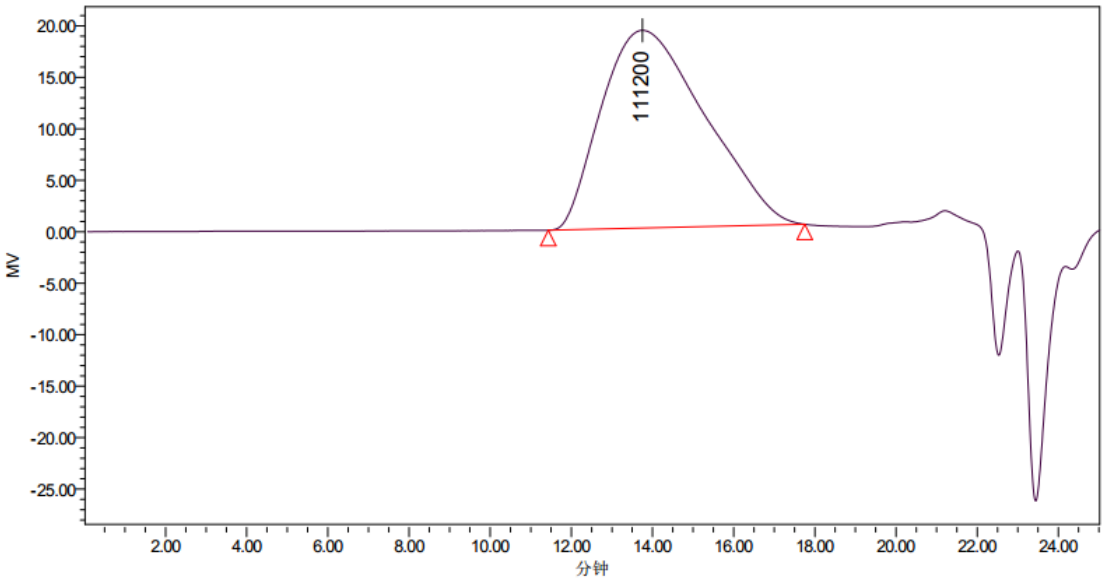
Figure S89. GPC curve of poly(IPI-*co*-D-IMCl) in Table 2, entry 15.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1		13.940	13.940	13.940	48813	152319	90743	475709	953895	3.123104	6.262461

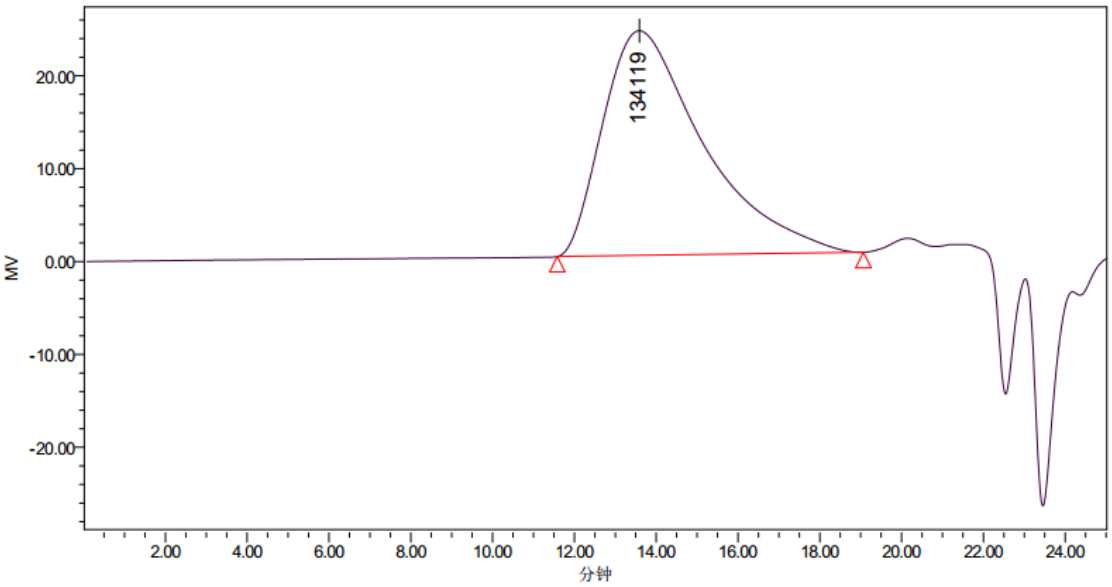
Figure S90. GPC curve of poly(IPI-*co*-L-IMCl) in Table 2, entry 16.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		13.753	13.753	13.753	47503	161857	11120(	496148	964502	3.065349

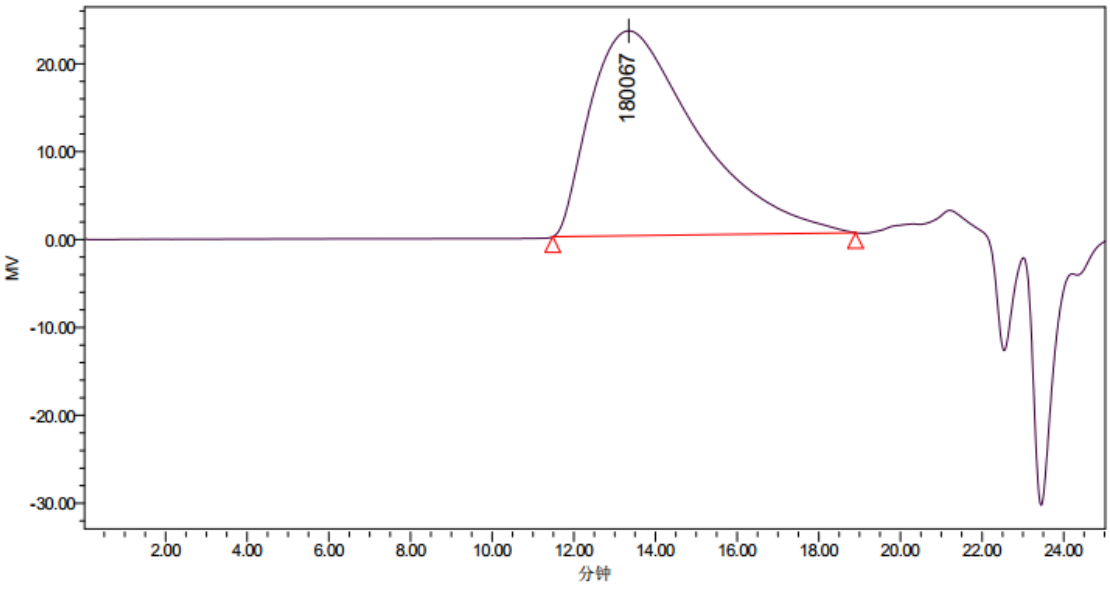
Figure S91. GPC curve of poly(IPI-*co*-L-IMCl) in Table 2, entry 17.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		13.589	13.589	13.589	39878	163384	134119	475900	890888	2.912778

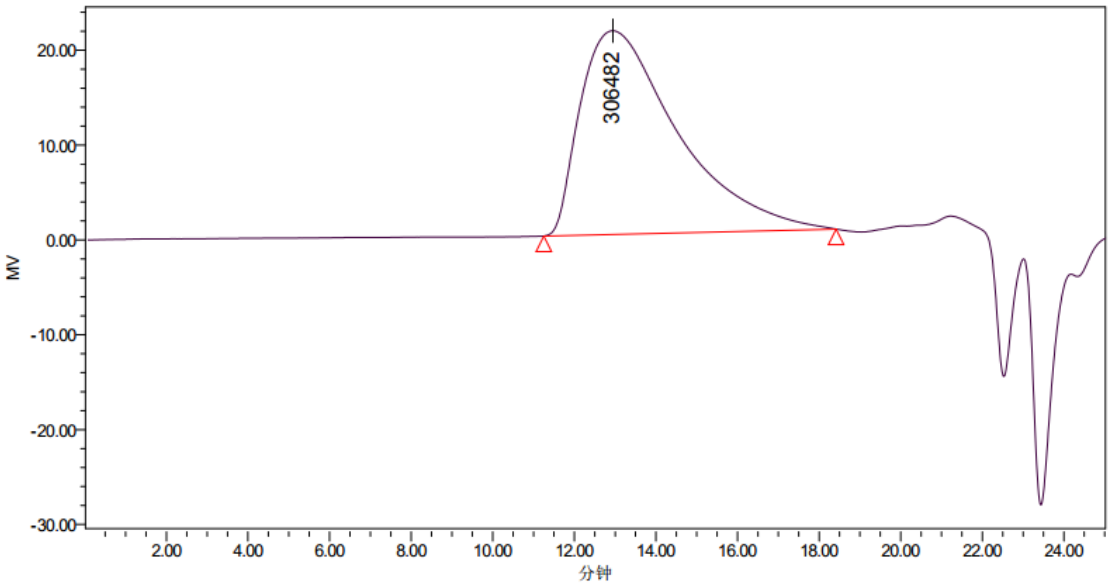
Figure S92. GPC curve of poly(IPI-*co*-L-IMCl) in Table 2, entry 18.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		13.345	13.345	13.345	43492	227524	180067	700422	1227425	3.078455

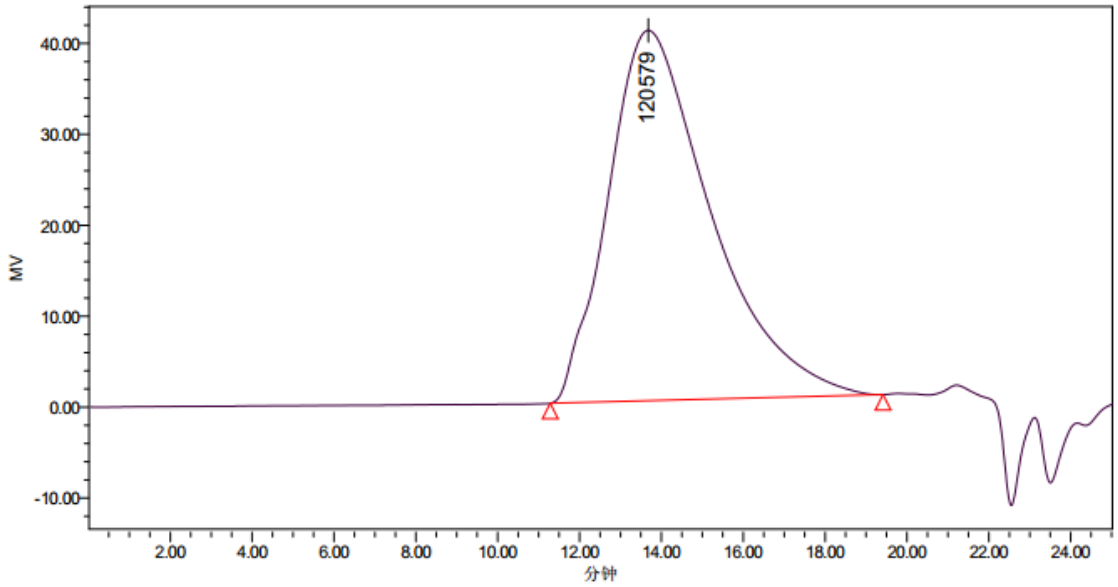
Figure S93. GPC curve of poly(IPI-*co*-L-IMCl) in Table 2, entry 19.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		12.944	12.944	12.944	62817	335375	306482	961135	1642924	2.865851

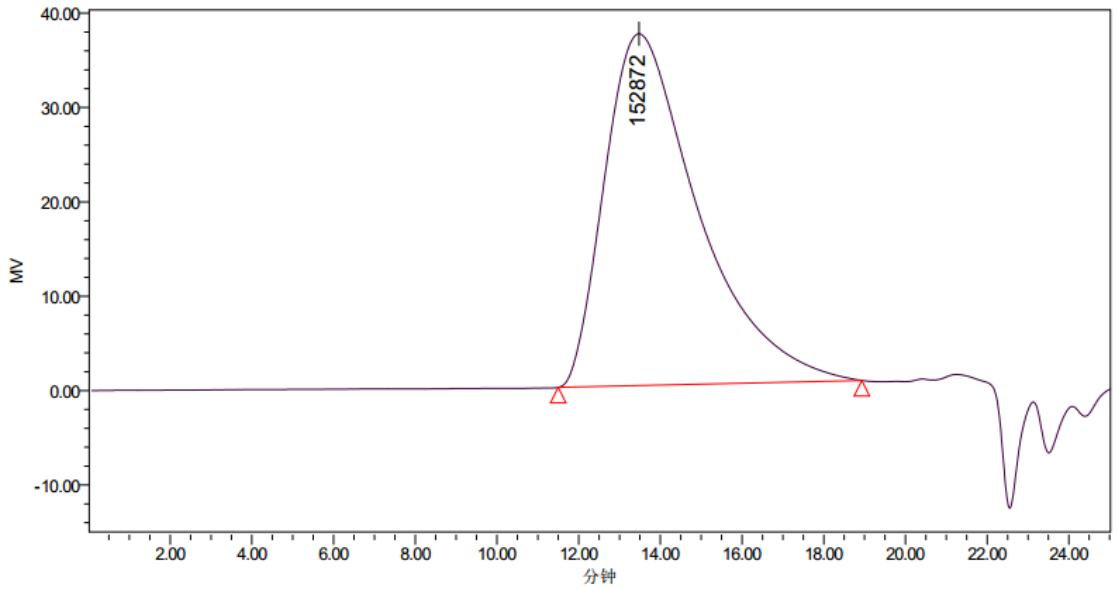
Figure S94. GPC curve of poly(IPI-*co*-L-IMCl) in Table 2, entry 20.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		13.681	13.681	13.681	40252	191238	120579	768139	1629575	4.016669

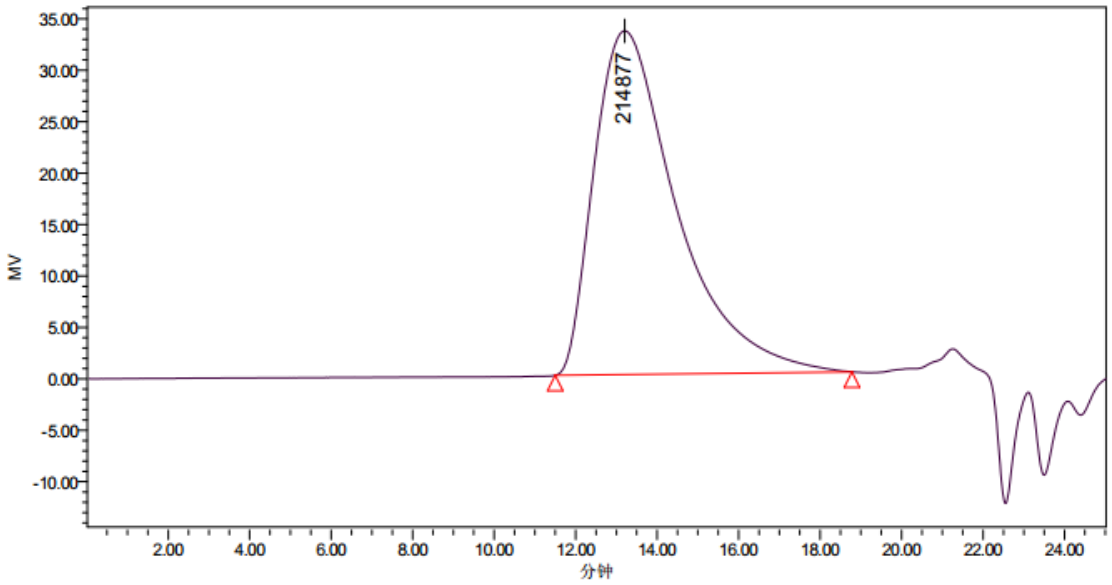
Figure S95. GPC curve of poly(IPD-*co*-D-IMCI) in Table 2, entry 21.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		13.478	13.478	13.478	46939	184787	152872	520335	977242	2.815864

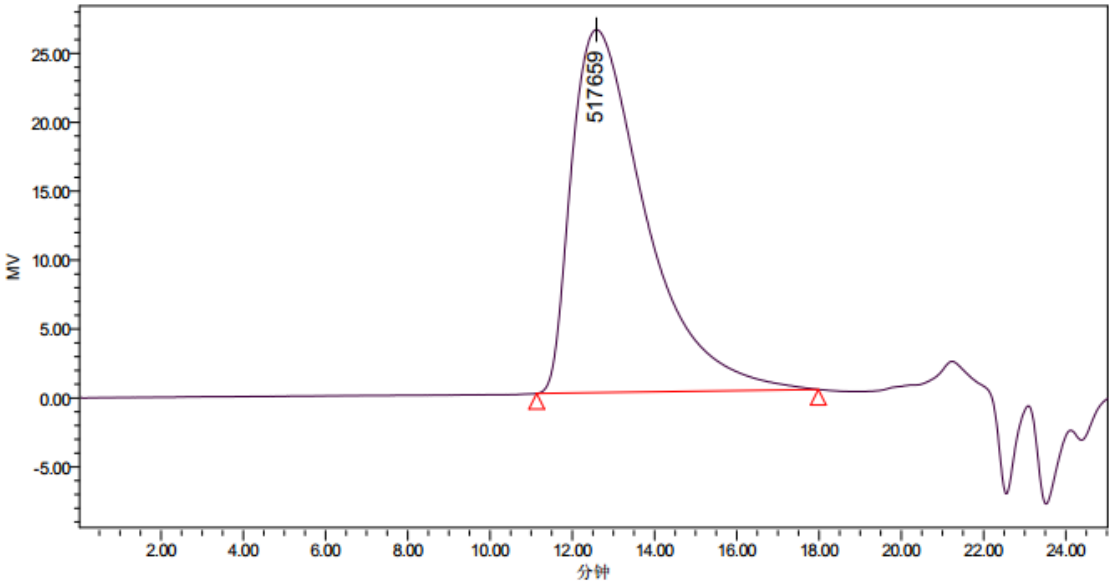
Figure S96. GPC curve of poly(IPD-*co*-D-IMCI) in Table 2, entry 22.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		13.206	13.206	13.206	64713	242856	214877	590364	1008045	2.430916

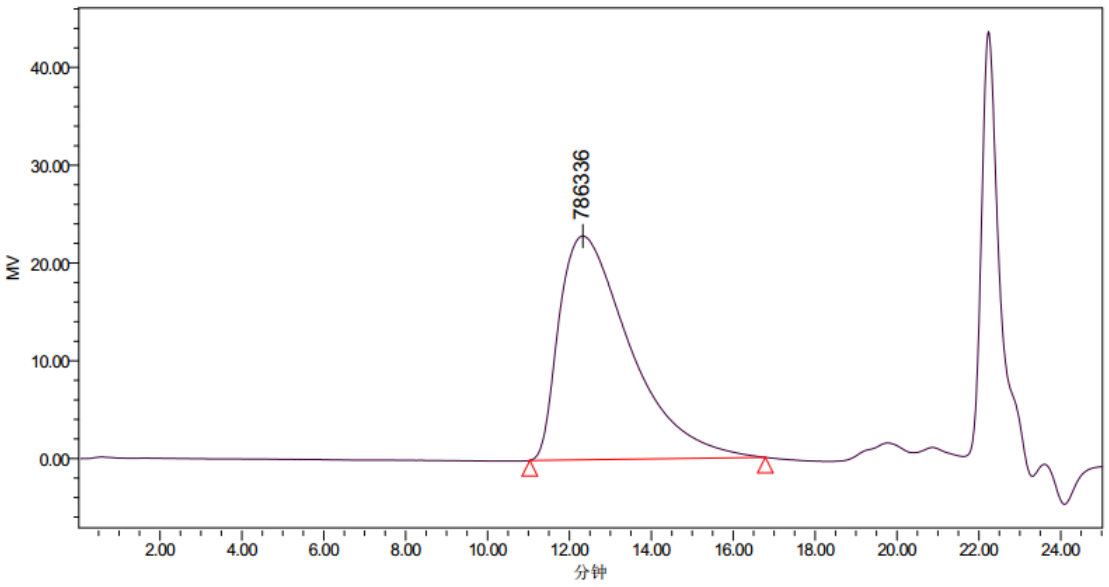
Figure S97. GPC curve of poly(IPD-*co*-D-IMCI) in Table 2, entry 23.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		12.588	12.588	12.588	118282	505364	517659	1183279	1936776	2.341438

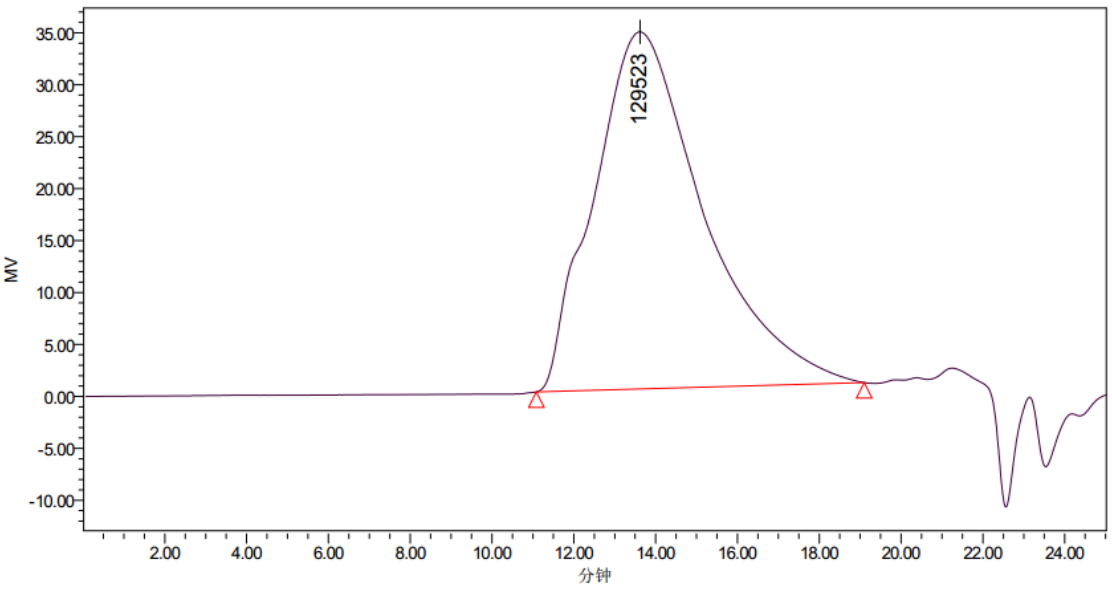
Figure S98. GPC curve of poly(IPD-*co*-D-IMCI) in Table 2, entry 24.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		12.327	12.327	12.327	181934	761048	786336	1784601	2853489	2.344926

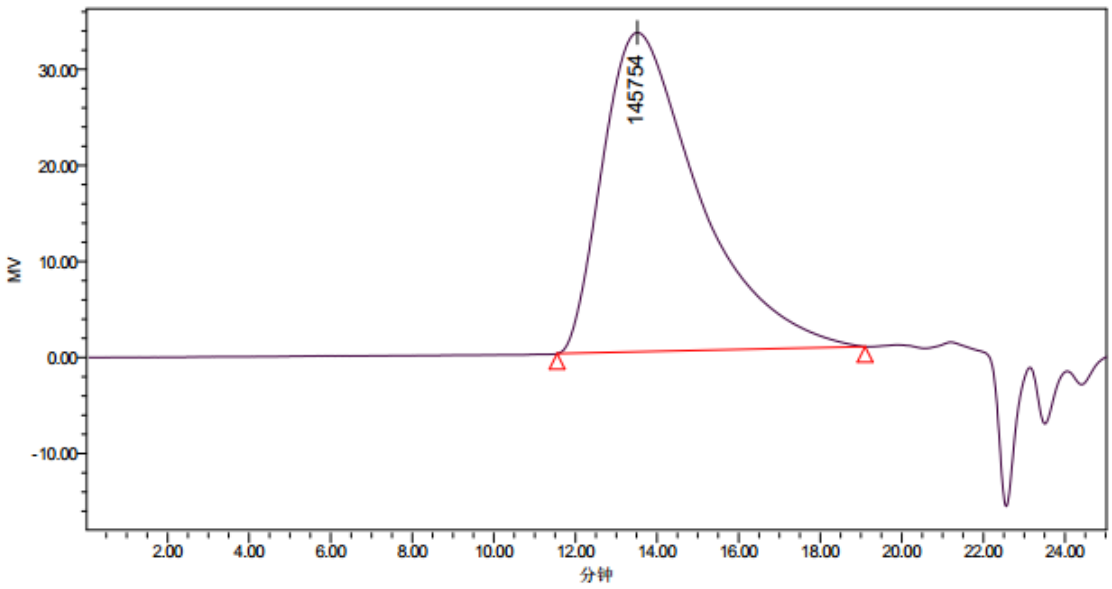
Figure S99. GPC curve of poly(IPD-*co*-D-IMCI) in Table 2, entry 25.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		13.619	13.619	13.619	42411	277289	129523	1300584	2570515	4.690356

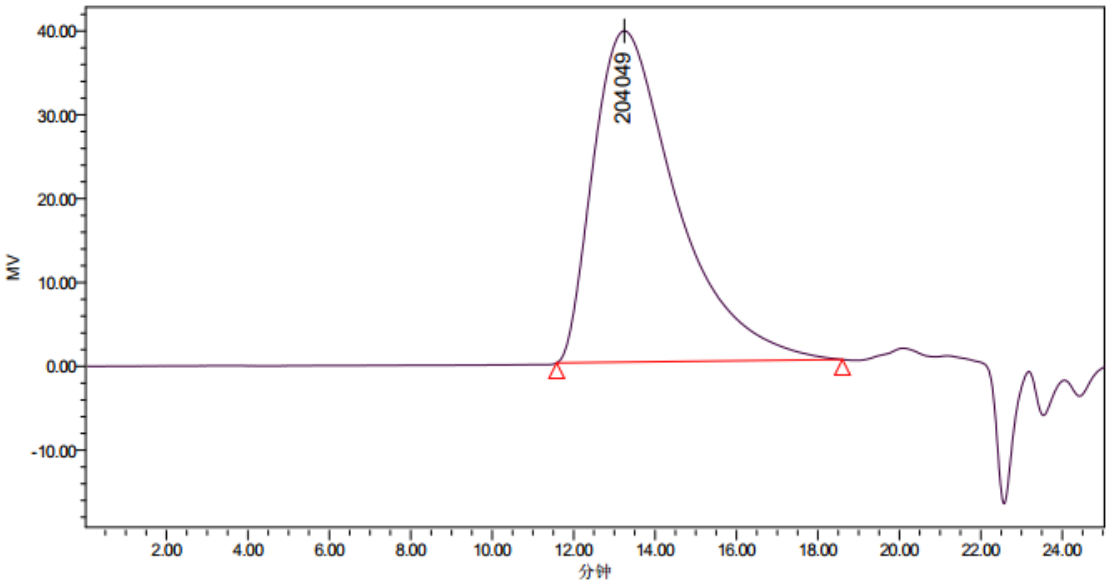
Figure S100. GPC curve of poly(IPD-*co*-L-IMCI) in Table 2, entry 26.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		13.518	13.518	13.518	42686	172601	145754	484901	901250	2.809378

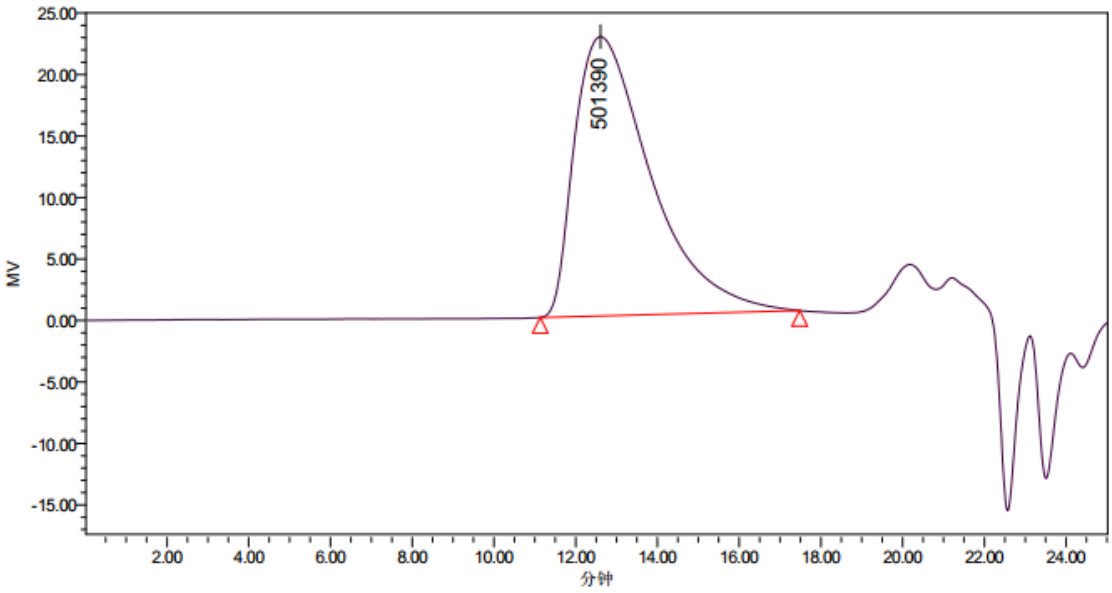
Figure S101. GPC curve of poly(IPD-*co*-L-IMCl) in Table 2, entry 27.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		13.246	13.246	13.246	64498	231587	204049	559001	943343	2.413789

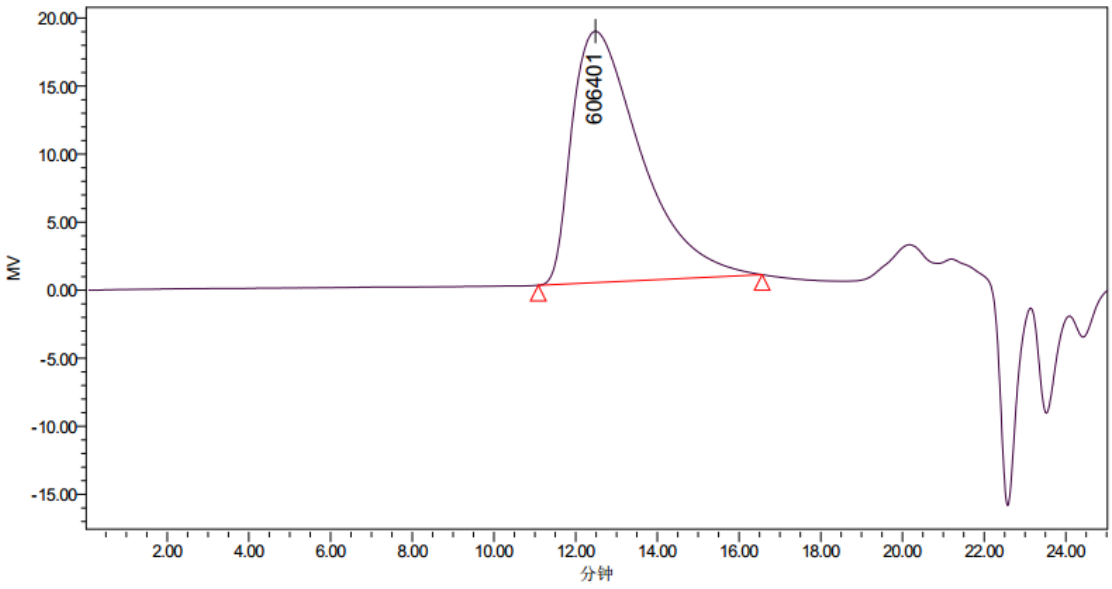
Figure S102. GPC curve of poly(IPD-*co*-L-IMCl) in Table 2, entry 28.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		12.608	12.608	12.608	124265	508166	501390	1221604	2016399	2.403946

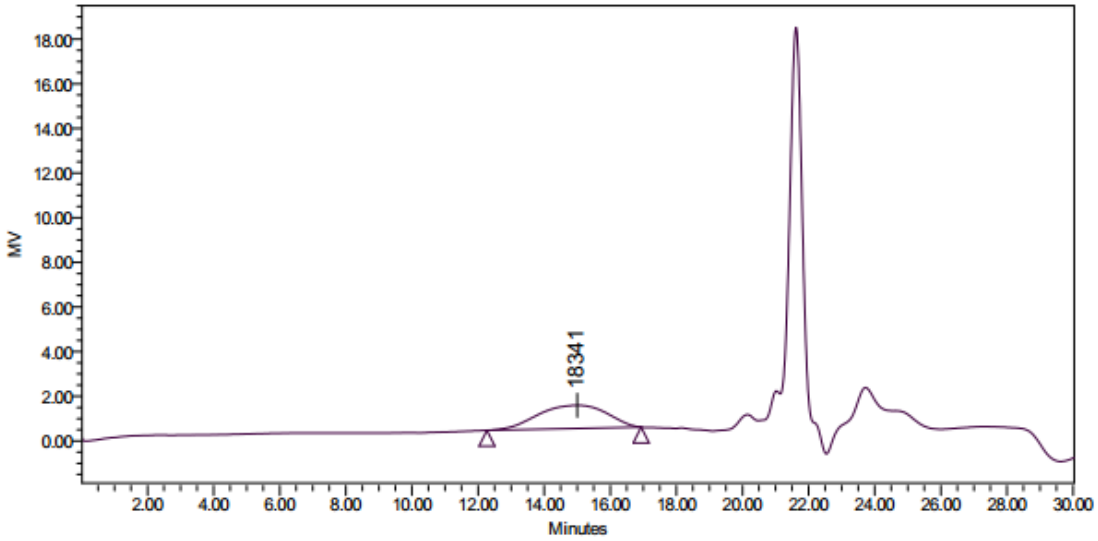
Figure S103. GPC curve of poly(IPD-*co*-L-IMCl) in Table 2, entry 29.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		12.487	12.487	12.487	168382	588739	606401	1307287	2102271	2.220489

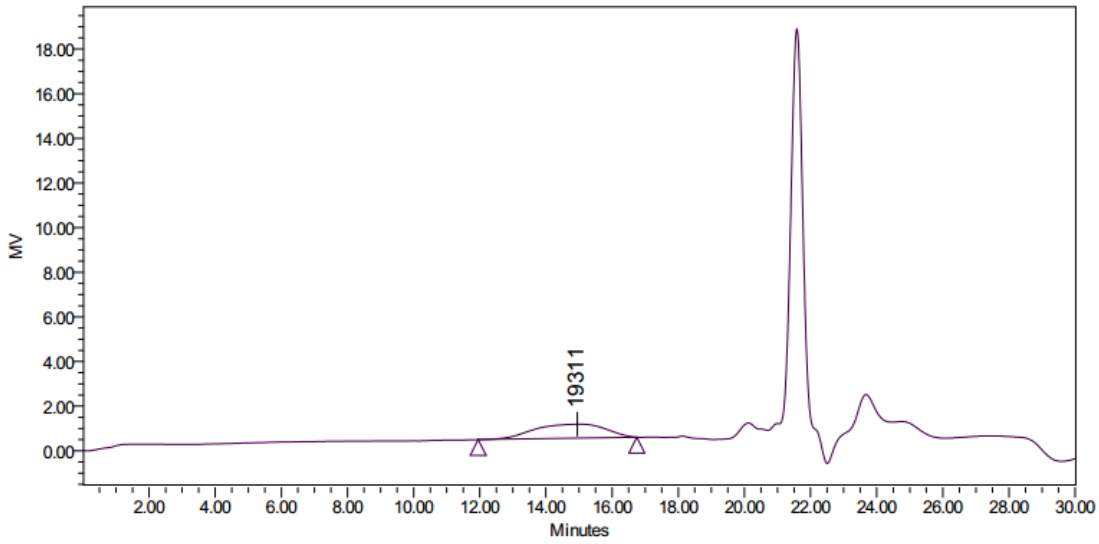
Figure S104. GPC curve of poly(IPD-*co*-L-IMCl) in Table 2, entry 30.



Broad Unknown Modified Universal Peak Table

	Distribution Name	Mv (Daltons)	K (dl/g)	alpha	Intrinsic Viscosity (dl/g)	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw
1						15425	32855	18341	65973	108300	2.129983	2.008036

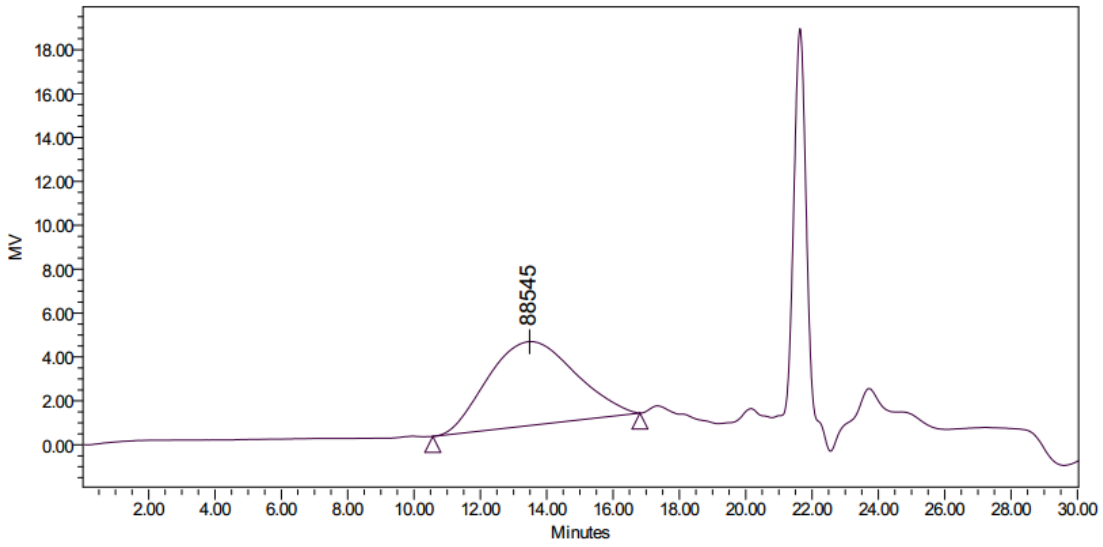
Figure S105. GPC curve of poly(EPI-*co*-L-IMCl) in Table 2, entry 31.



Broad Unknown Modified Universal Peak Table

	Distribution Name	Mv (Daltons)	K (dl/g)	alpha	Intrinsic Viscosity (dl/g)	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw
1						17947	38647	19311	77828	127768	2.153456	2.013807

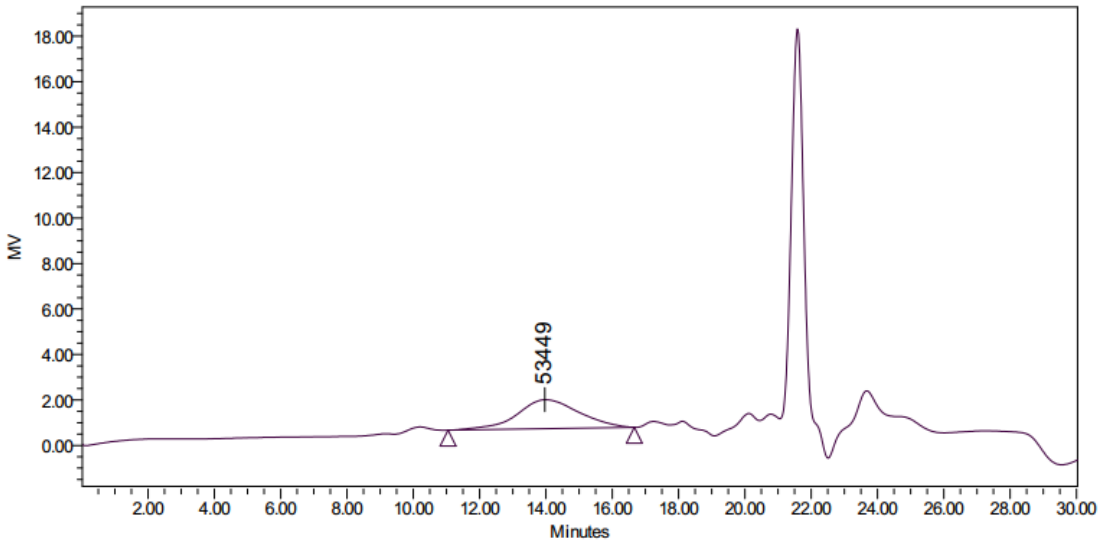
Figure S106. GPC curve of poly(EPI-*co*-L-IMCl) in Table 2, entry 32.



Broad Unknown Modified Universal Peak Table

	Distribution Name	Mv (Daltons)	K (dl/g)	alpha	Intrinsic Viscosity (dl/g)	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw
1						39396	155353	88545	409819	699900	3.943318	2.637987

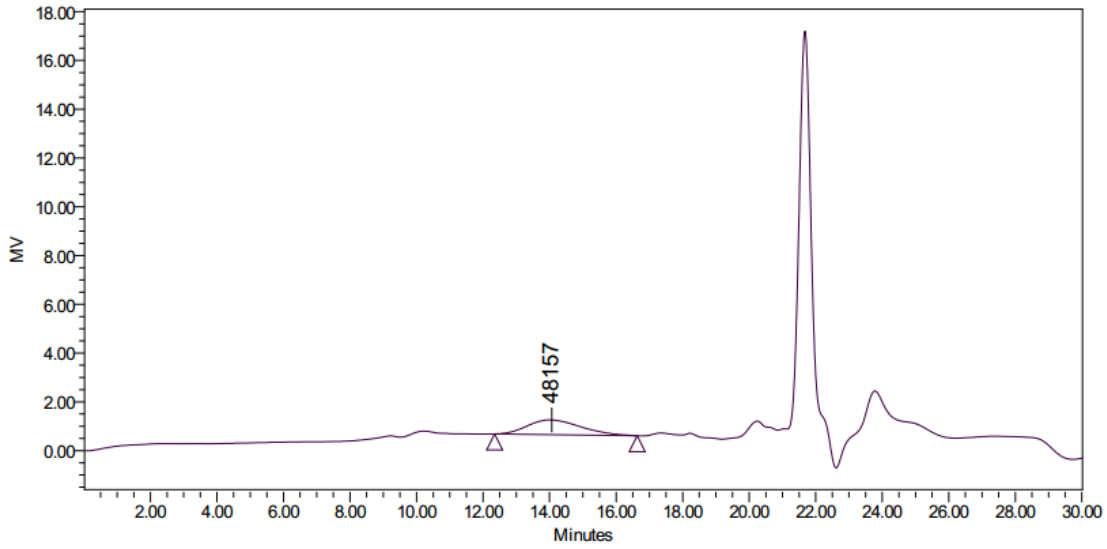
Figure S107. GPC curve of poly(EPI-*co*-L-IMCl) in Table 2, entry 33.



Broad Unknown Modified Universal Peak Table

	Distribution Name	Mv (Daltons)	K (dl/g)	alpha	Intrinsic Viscosity (dl/g)	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw
1						31168	75725	53449	199885	423798	2.429590	2.639631

Figure S108. GPC curve of poly(EPI-*co*-L-IMCl) in Table 2, entry 34.



Broad Unknown Modified Universal Peak Table

	Distribution Name	Mv (Daltons)	K (dl/g)	alpha	Intrinsic Viscosity (dl/g)	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw
1						29753	53352	48157	82584	112599	1.793148	1.547908

Figure S109. GPC curve of poly(EPI-*co*-L-IMCl) in Table 2, entry 35.

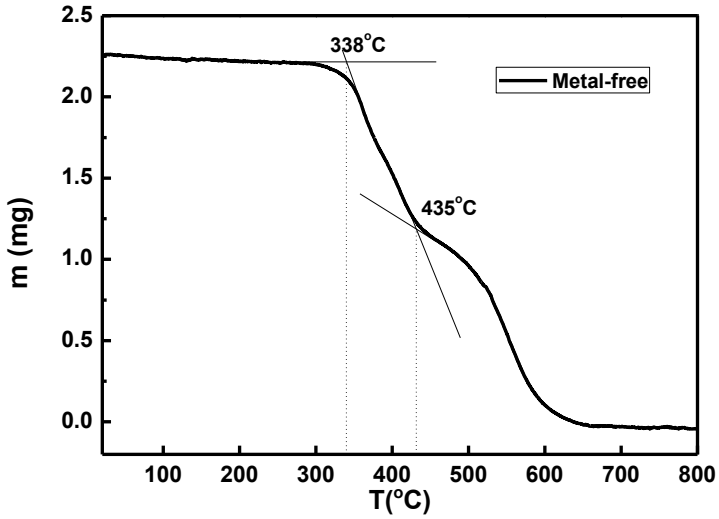


Figure S110. TGA spectrum of PEPI obtained by $[(Et_3Si)_2H]^+[B(C_6F_5)_4]^-$ (Measure condition: Temperature range: 0-1000°C, Temp. Rate：10 °C/min, Atmosphere: Air, Gas Flow: 50 [ml/min]).

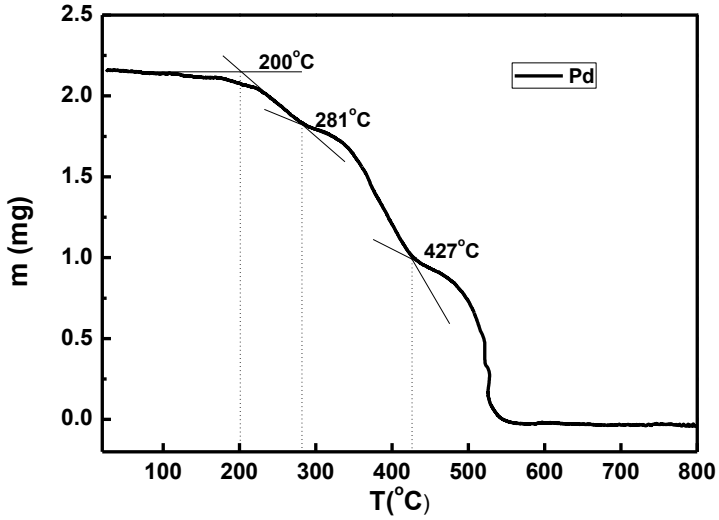


Figure S111. TGA spectrum of PEPI obtained by (Et_2-(S,S)-BOZ)PdC≡CC_6H_5 (Measure condition: Temperature range: 0-1000°C, Temp. Rate:10 °C/min, Atmosphere: Air, Gas Flow: 50 [ml/min]).

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