Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

Electronic supporting information

Al^{i}Bu$_3$: Unprecedented Main-Group Metal Catalyst for Helical-Sense-Selective Polymerization of Chiral Aryl Isocyanides and Copolymerization with Achiral Aryl Isocyanides

Xiaolu Wu,[‡a] Xinwen Yan,[‡a] Zhi Yang,[a] Shaowen Zhang,[a] Xiaofang Li,[*a] Yuping Dong,[*b] Junge Zhi[*a]

Table of Contents

Figure S2. ^{1}H NMR spectrum of N-(naphthalen-2-yl)formamide (**2**).

Figure S3. ^{1}H NMR spectrum of 2-naphthyl isocyanide (**a**).

Figure S4. ^{13}C NMR spectrum of 2-naphthyl isocyanide (**a**).

Figure S5. ^{1}H NMR spectrum of 3-isopropyloxycarbonyl phenyl isocyanide (**b**).

Figure S6. ^{1}H NMR spectrum of ethyl 4-aminobenzoate (**7**).

Figure S7. ^{1}H NMR spectrum of 4-ethoxycarbonyl phenyl isocyanide (**c**).

Figure S8. ^{13}C NMR spectrum of 4-ethoxycarbonyl phenyl isocyanide (**c**).

Figure S9. ^{1}H NMR spectrum of (*1S*,*2R*,*5S*)-2-isopropyl-5-methylcyclohexyl 4-isocyanobenzoate (**d**).

Figure S10. ^{13}C NMR spectrum of (*1S*,*2R*,*5S*)-2-isopropyl-5-methylcyclohexyl 4-isocyanobenzoate (**d**).

Figure S11. ^{1}H NMR spectrum of (*1R*,*2S*,*5R*)-2-isopropyl-5-methylcyclohexyl 4-isocyanobenzoate (**e**).

Figure S12. ^{13}C NMR spectrum of (*1R*,*2S*,*5R*)-2-isopropyl-5-methylcyclohexyl 4-isocyanobenzoate (**e**).

Figure S13. ^{1}H NMR spectrum of 4-isocyano-4'-(1,2,2-triphenylvinyl)-1,1'-biphenyl (**f**).

Figure S14. ^{13}C NMR spectrum of 4-isocyano-4'-(1,2,2-triphenylvinyl)-1,1'-biphenyl (**f**).

Figure S15. ^{1}H NMR spectrum of polymers in $CDCl_3$ at 25 ^{o}C.

Figure S16. ^{1}H NMR spectra of poly(D-IMCI-*co*-ITPB)s and poly(D-IMCI) (Table 1, entry 4 and Table 2, entries 1-5).

Figure S17. ^{1}H NMR spectra of poly(L-IMCI-*co*-ITPB)s and poly(L-IMCI) (Table 1, entry 5 and Table 2, entries 6-10).

Figure S18. ^{1}H NMR spectra of poly(D-IMCI-*co*-IPI)s and poly(D-IMCI) (Table 1, entry 4 and Table 2, entries 11-15).

Figure S19. ^{1}H NMR spectra of poly(L-IMCI-*co*-IPI)s and poly(L-IMCI) (Table 1, entry 5 and Table 2, entries 16-20).

Figure S20. FT-IR spectra of (A) EPI, (B) ITPB, (C) D-IMCI, (D) L-IMCI, (E) IPI.

Figure S21. FT-IR spectra of (A) poly(EPI), (B) poly(ITPB), (C) poly(D-IMCI), (D) poly(L-IMCI), (E) poly(IPI).

Figure S22. AIE nature characterization of (A) ITPB monomer and it corresponding (B) poly(ITPB) (Table 1, entry 6) in THF/water mixture.

Figure S23. Plots of fluorescence intensity vs water fraction in THF/water mixture (0.01 mol of ITPB unit/mL).

Figure S24. AIE nature characterization of poly(D-IMCI-*co*-ITPB)s in THF/water mixture.

Figure S25. AIE nature characterization of poly(L-IMCI-*co*-ITPB)s in THF/water mixture.

Figure S26. AIE nature characterization of ITPB monomer and it corresponding poly(ITPB) (Table 1, entry 6) in THF/water mixture.

Figure S27. AIE nature characterization of poly(D-IMCI-*co*-ITPB)s in THF/water mixture.

Figure S28. AIE nature characterization of poly(L-IMCI-*co*-ITPB)s in THF/water mixture.

Figure S29. FT-IR spectrum of NI and the compound obtained from the reaction of Al^iBu_3/activator with **4** equiv. of NI.

Figure S30. High resolution ESI-MS spectra of NI oligomer obtained by the Al^iBu_3/activator binary systems in PhCl.

Figure S31. GPC curve of poly(IPI) obtained by cationic Aluminum complex in Table 1, entry 2.

Figure S32. GPC curve of poly(EPI) obtained by cationic Aluminum complex in Table 1, entry 3.

Figure S33. GPC curve of poly(D-IMCI) obtained by cationic Aluminum complex in Table 1, entry 4.

Figure S34. GPC curve of poly(L-IMCI) obtained by cationic Aluminum complex in Table 1, entry 5.

Figure S35. GPC curve of poly(ITPB) obtained by cationic Aluminum complex in Table 1, entry 6.

Figure S36. GPC curve of poly(EPI) obtained by cationic Aluminum complex in Table 1, entry 7.

Figure S37. GPC curve of poly(EPI) obtained by cationic Aluminum complex in Table 1, entry 8.

Figure S38. GPC curve of poly(EPI) obtained by cationic Aluminum complex in Table 1, entry 9.

Figure S39. GPC curve of poly(EPI) obtained by cationic Aluminum complex in Table 1, entry 10.

Figure S40. GPC curve of poly(EPI) obtained by cationic Aluminum complex in Table 1, entry 11.

Figure S41. GPC curve of poly(EPI) obtained by cationic Aluminum complex in Table 1, entry 12.

Figure S42. GPC curve of poly(EPI) obtained by cationic Aluminum complex in Table 1, entry 13.

Figure S43. GPC curve of poly(EPI) obtained by cationic Aluminum complex in Table 1, entry 14.

Figure S44. GPC curve of poly(EPI) obtained by cationic Aluminum complex in Table 1, entry 15.

Figure S45. GPC curve of poly(EPI) obtained by cationic Aluminum complex in Table 1, entry 16.

Figure S46. GPC curve of poly(EPI) obtained by cationic Aluminum complex in Table 1, entry 17.

Figure S47. GPC curve of poly(EPI) obtained by cationic Aluminum complex in Table 1, entry 18.

Figure S48. GPC curve of poly(D-IMCI-*co*-ITPB) obtained by cationic Aluminum complex in Table 2, entry 1.

Figure S49. GPC curve of poly(D-IMCI-*co*-ITPB) obtained by cationic Aluminum complex in Table 2, entry 2.

Figure S50. GPC curve of poly(D-IMCI-*co*-ITPB) obtained by cationic Aluminum complex in Table 2, entry 3.

Figure S51. GPC curve of poly(D-IMCI-*co*-ITPB) obtained by cationic Aluminum complex in Table 2, entry 4.

Figure S52. GPC curve of poly(D-IMCI-*co*-ITPB) obtained by cationic Aluminum complex in Table 2, entry 5.

Figure S53. GPC curve of poly(L-IMCI-*co*-ITPB) obtained by cationic Aluminum complex in Table 2, entry 6.

Figure S54. GPC curve of poly(L-IMCI-*co*-ITPB) obtained by cationic Aluminum complex in Table 2, entry 7.

Figure S55. GPC curve of poly(L-IMCI-*co*-ITPB) obtained by cationic Aluminum complex in Table 2, entry 8.

Figure S56. GPC curve of poly(L-IMCI-*co*-ITPB) obtained by cationic Aluminum complex in Table 2, entry 9.

Figure S57. GPC curve of poly(L-IMCI-*co*-ITPB) obtained by cationic Aluminum complex in Table 2, entry 10.

Figure S58. GPC curve of poly(D-IMCI-*co*-IPI) obtained by cationic Aluminum complex in Table 2, entry 11.

Figure S59. GPC curve of poly(D-IMCI-*co*-IPI) obtained by cationic Aluminum complex in Table 2, entry 12.

Figure S60. GPC curve of poly(D-IMCI-*co*-IPI) obtained by cationic Aluminum complex in Table 2, entry 13.

Figure S61. GPC curve of poly(D-IMCI-*co*-IPI) obtained by cationic Aluminum complex in Table 2, entry 14.

Figure S62. GPC curve of poly(D-IMCI-*co*-IPI) obtained by cationic Aluminum complex in Table 2, entry 15.

Figure S63. GPC curve of poly(L-IMCI-*co*-IPI) obtained by cationic Aluminum complex in Table 2, entry 16.

Figure S64. GPC curve of poly(L-IMCI-*co*-IPI) obtained by cationic Aluminum complex in Table 2, entry 17.

Figure S65. GPC curve of poly(L-IMCI-*co*-IPI) obtained by cationic Aluminum complex in Table 2, entry 18.

Figure S66. GPC curve of poly(L-IMCI-*co*-IPI) obtained by cationic Aluminum complex in Table 2, entry 19.

Figure S67. GPC curve of poly(L-IMCI-*co*-IPI) obtained by cationic Aluminum complex in Table 2, entry 20.

EXPERIMENTAL SECTION

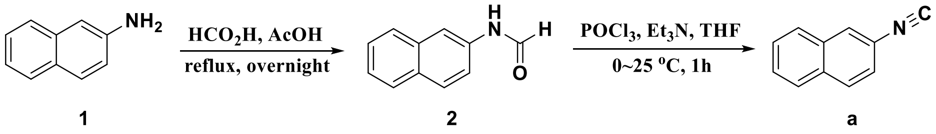
Materials.

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 were purified by a solvent purification system (SPS-800, Mbraun), and dried over fresh Na chips in the glovebox. $Al^{i}Bu_3$, $[Ph_3C][B(C_6F_5)_4]$, $[PhMe_2NH][B(C_6F_5)_4]$, and $B(C_6F_5)_3$ were purchased from Tosoh Finechem Corporation and used without purification. The isocyanide monomers were synthesized according to the literatures. The deuterated solvents toluene-d8 (99.6 atom% D) and chloroform-d1 (99.8 atom% D) were obtained from Cambridge Isotope .

General Methods.

^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance (Ⅲ HD 400 MHz) spectrometer. The molecular weights and the molecular weight distributions of the EPI polymers 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 the D-(or L-)IMCI-ITPB 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 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.

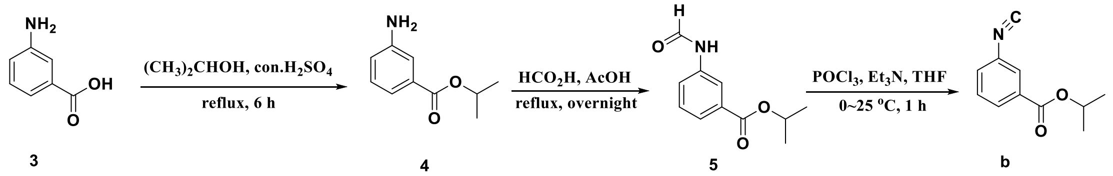
Scheme S1. Synthesis of 2-naphthyl Isocyanide (NI)



Synthesis of N-(naphthalen-2-yl)formamide (2): compound **1** (5 g, 34.92 mmol) was dissolved in a mixture solvents of formic acid (50 mL) and acetic acid (10 mL), the resulting mixture was refluxed overnight. After the reaction mixture was cooled to room temperature, the solvents were removed by evaporation. The residue was dissolved in CH_2Cl_2 (200 mL) and washed with saturated aqueous Na_2CO_3 (2 × 50 mL), the separated organic phase was dried over anhydrous Na_2SO_4, concentrated under reduced pressure, and the residue was purified by column chromatography (silica gel, 3 : 1 – 1 : 1 hexane to ethylacetate, v/v) to afford compound **2** as a white solid (4.95 g, 82.8% yield). ^{1}H NMR (d6-DMSO, 400 MHz): δ 7.41 (dt, *J* = 0.8, 7.2 Hz, 1H), 7.48 (dt, *J* = 0.8, 7.2 Hz, 1H), 7.57 (dd, *J* = 2.0, 8.8 Hz, 0.8H), 7.67 (d, *J* = 1.6 Hz, 0.2H), 7.78 (d, *J* = 8.4 Hz, 0.2H), 7.83 (t, *J* = 6.8 Hz, 1.5H), 7.86 (d, *J* = 5.6 Hz, 0.6H), 7.88 (d, *J* = 5.2 Hz, 0.5H), 8.30 (d, *J* = 1.2 Hz, 0.7H), 8.37 (d, *J* = 1.6 Hz, 0.7H), 8.94 (d, *J* = 11.2 Hz, 0.2H), 10.33 (d, *J* = 11.2 Hz, 0.2H), 10.40 (s, 0.8H).

Synthesis of 2-naphthyl Isocyanide (a): compound **2** (4.95 g, 28.9 mmol) and triethylamine (27.0 mL, 193.6 mmol) were dissolved in dry THF (60 mL) under an atmosphere of nitrogen, after the mixture was cooled to 0 °C, $POCl_3$ (4.5 mL, 49.3 mmol) was added dropwise to the mixture, the resulting mixture was slowly warm to room temperature and stirred for 1h, 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 CH_2Cl_2 (3 × 70 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, 12:1 hexane to ethyl acetate, v/v) to afford the desired compound **a** as a white solid (3.81 g, 86% yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.86 (dd, *J* = 1.8, 8.6 Hz, 1H), 7.11-7.16 (m, 3H), 7.21 (s, 1H), 7.23-7.25 (m, 1H), 7.32-7.37 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 123.34, 123.88, 125.79, 127.61, 127.77, 127.96, 127.99, 129.72, 132.74, 132.86, 164.31.

Scheme S2. Synthesis of 3-isopropyloxycarbonyl phenyl isocyanide (IPI)

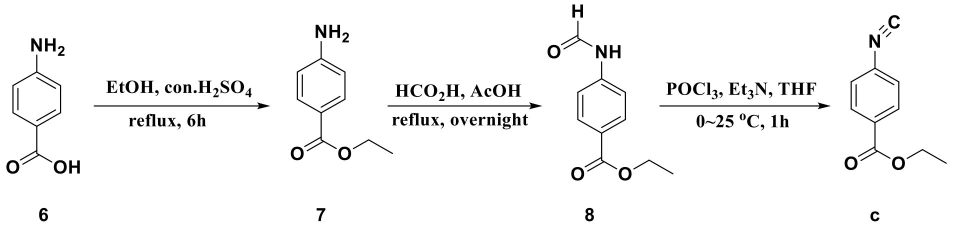


Synthesis of isopropyl 3-aminobenzoate (4): To a solution of **3** (3.42 g, 25 mmol) in 100 mL of $(CH_3)_2CHOH$ was slowly added 13.6 mL of aqueous con. H_2SO_4 (250 mmol) at room temperature. The mixture was refluxed for 6 h, cooled to room temperature, neutralized with a saturated K_2CO_3 aqueous solution and extracted with ethyl acetate (3 × 70 mL), the combined organic phases were washed with brine (2 × 50 mL), dried over anhydrous Na_2SO_4 and concentrated in vacuo, the residue was purified by column chromatography (silica gel, 5 : 1 – 3 : 1 hexane to ethyl acetate, v/v) to afford compound **4** as a white solid (4.06 g, 91% yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.41 (d, *J* = 7.6 Hz, 1H), 7.34 (s, 1H), 7.18 (t, *J* = 7.7 Hz, 1H), 6.83 (d, *J* = 7.9 Hz, 1H), 5.32 – 5.13 (m, 1H), 3.77 (s, 2H), 1.34 (d, *J* = 6.3 Hz, 6H).

Synthesis of isopropyl 3-formamidobenzoate (5): the synthetic procedure was the same with that of compound **2**, and the crude product was directly used for the next step without further purification.

Synthesis of 3-isopropyloxycarbonyl phenyl isocyanide (b): the synthetic procedure was the same with that of compound **a**. (brown solid, 75% yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.07 (dt, *J* = 7.7, 1.5 Hz, 1H), 8.03 (d, *J* = 1.5 Hz, 1H), 7.58 – 7.52 (m, 1H), 7.48 (t, *J* = 7.8 Hz, 1H), 5.26 (dt, *J* = 12.5, 6.3 Hz, 1H), 1.38 (d, *J* = 6.3 Hz, 7H).

Scheme S3. Synthesis of 4-ethoxycarbonyl phenyl isocyanide (EPI)

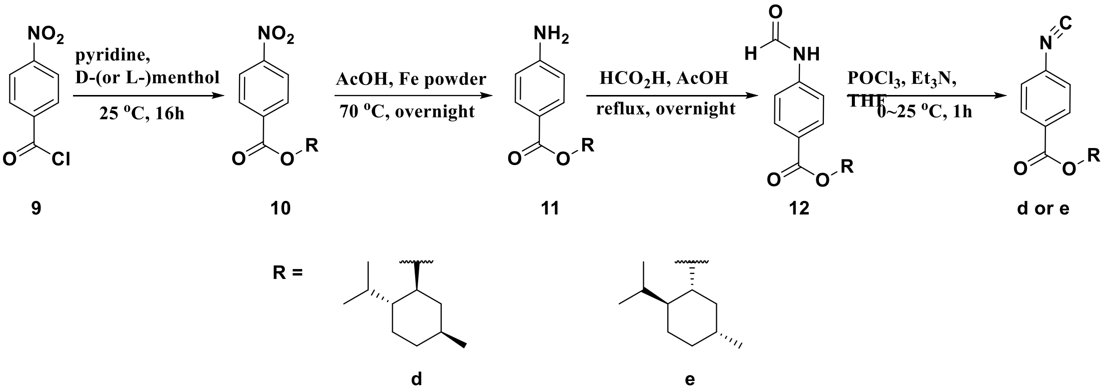


Synthesis of ethyl 4-aminobenzoate (7): To a solution of **6** (3.43 g, 25 mmol) in 100 mL of EtOH was slowly added 13.6 mL of aqueous con. H_2SO_4 (250 mmol) at room temperature. The mixture was refluxed for 6 h, cooled to room temperature, neutralized with a saturated K_2CO_3 aqueous solution and extracted with ethyl acetate (3 × 70 mL), the combined organic phases were washed with brine (2 × 50 mL), dried over anhydrous Na_2SO_4 and concentrated in vacuo, the residue was purified by column chromatography (silica gel, 5 : 1 – 3 : 1 hexane to ethyl acetate, v/v) to afford compound **7** as a white solid (3.90 g, 94% yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.36 (t, *J* = 7.0 Hz, 3H), 4.06 (br, 2H), 4.31 (q, *J* = 7.2 Hz, 2H), 6.63 (d, *J* = 8.8 Hz, 2H), 7.85 (d, *J* = 8.4 Hz, 2H).

Synthesis of ethyl 4-formamidobenzoate (8): the synthetic procedure was the same with that of compound **2**, and the crude product was directly used for the next step without further purification.

Synthesis of 4-ethoxycarbonyl phenyl isocyanide (c): the synthetic procedure was the same with that of compound **a**. (brown solid, 82% yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.40 (t, *J* = 7.2 Hz, 3H), 4.39 (q, *J* = 7.2 Hz, 2H), 7.43 (d, *J* = 8.4 Hz, 2H), 7.43 (d, *J* = 8.4 Hz, 2H), 8.08 (dt, *J* = 2.0, 8.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 14.33, 61.66, 126.48, 129.94, 130.88, 131.38, 165.06, 167.10.

Scheme S4. 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 (10d): Under nitrogen atmosphere, compound **9** (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 CH_2Cl_2 (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 **10d** as a yellow solid (2.40 g, 81% yield) ^{1}H NMR (CDCl$_3$, 400 MHz): 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 (11d): Under nitrogen atmosphere, compound **10d** (2.40 g, 7.86 mmol) was dissolved in 30 mL of acetic acid, then iron powder (4.4 g, 78.6 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, 4 : 1 hexane to ethyl acetate, v/v) to afford the desired compound **11d** as yellow oil (1.61 g, 75% yield) ^{1}H NMR (CDCl$_3$, 400 MHz): δ 0.78 (d, *J* = 7.2 Hz, 3H), 0.90 (d, *J* = 6.8 Hz, 3H), 0.91 (d, *J* = 6.4 Hz, 3H), 0.85-0.96 (m, 1H), 1.02-1.14 (m, 2H), 1.48-1.54 (m, 2H), 1.69-1.72 (m, 2H), 1.94-1.98 (m, 1H), 2.09-2.12 (m, 1H), 4.04 (s, 2H), 4.87 (dt, *J* = 4.4, 10.8 Hz, 1H), 6.63 (d, *J* = 8.4 Hz, 2H), 7.85 (d, *J* = 8.8 Hz, 2H).

Synthesis of (*1S,2R,5S*)-2-isopropyl-5-methylcyclohexyl 4-formamidobenzoate (12d): compound **11d** (1.61 g, 5.85 mmol) was dissolved in a mixture of formic acid (16 mL) and acetic acid (3 mL), the resulting mixture was refluxed overnight. After the reaction mixture was cooled to room temperature, the solvents were removed under reduced pressure, the residue was washed with saturated aqueous Na$_2$CO$_3$ (10 mL) and filtered, the filter cake was washed twice with water and dried in vacuum to afford crude compound **12d** as a white solid (1.70 g, crude), this compound was used directly for the next step without purification.

Synthesis of (*1S,2R,5S*)-2-isopropyl-5-methylcyclohexyl 4-isocyanobenzoate (d): compound **12d** (1.70 g, crude) and triethylamine (5.2 mL, 37.5 mmol) were dissolved in dry THF (15 mL) under an atmosphere of nitrogen, after the mixture was cooled to 0 °C, POCl$_3$ (0.9 mL, 9.5 mmol) was added dropwise to the mixture, the resulting mixture was slowly warm to room temperature and stirred for 1h, then the reaction mixture was slowly poured into 20 mL saturated aqueous Na$_2$CO$_3$ and stirred at room temperature for 0.5 h, the mixture was extracted with CH$_2$Cl$_2$ (3 × 20 mL), the combined organic layers were washed with brine, dried over anhydrous Na$_2$SO$_4$ and concentrated under reduced pressure, the residue was purified by column chromatography (neutral Al$_2$O$_3$, 12 : 1 hexane to ethyl acetate, v/v) to afford the desired compound **d** as a black syrup (1.35 g, 81% yield for two steps) ^{1}H NMR (CDCl$_3$, 400 MHz): δ 0.77 (d, *J* = 6.8 Hz, 3H), 0.91 (dd, *J* = 5.6, 6.8 Hz, 6H), 0.86-0.96 (m, 1H), 1.05-1.17 (m, 2H), 1.50-1.59 (m, 2H), 1.70-1.74 (m, 2H), 1.86-1.94 (m, 1H), 2.07-2.12 (m, 1H), 4.93 (dt, *J* = 4.4, 10.8 Hz, 1H), 7.43 (d, *J* = 8.4 Hz, 2H), 8.07 (dt, *J* = 2.0, 8.8 Hz, 2H); ^{13}C NMR (CDCl$_3$, 100 MHz): δ 16.60, 20.82, 22.10, 23.71, 26.66, 31.53, 34.32, 40.98, 47.30, 75.75, 126.48, 129.88, 130.90, 131.74, 164.58, 167.05.

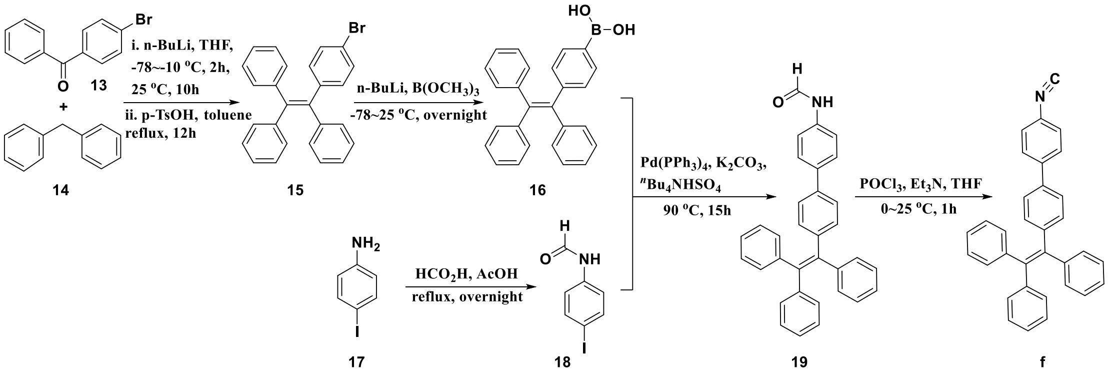
The synthesis of (*1R,2S,5R*)-2-isopropyl-5-methylcyclohexyl 4-isocyanobenzoate (**e**) was the same with that of (*1S,2R,5S*)-2-isopropyl-5-methylcyclohexyl 4-isocyanobenzoate (**d**).

Synthesis of (*1R,2S,5R*)-2-isopropyl-5-methylcyclohexyl 4-nitrobenzoate (10e): (yellow solid, 83% yield). ^{1}H NMR (CDCl$_3$, 400 MHz): δ 0.79 (d, *J* = 6.8 Hz, 3H), 0.93 (t, *J* = 6.2 Hz, 6H), 0.88-0.98 (m, 1H), 1.08-1.19 (m, 2H), 1.54-1.61 (m, 2H), 1.71-1.78 (m, 2H), 1.85-1.97 (m, 1H), 2.13 (d, *J* = 12.0 Hz, 1H), 4.97 (dt, *J* = 4.4, 10.8 Hz, 1H), 8.20 (d, *J* = 9.2 Hz, 2H), 8.28 (d, *J* = 8.8 Hz, 2H).

Synthesis of (*1R,2S,5R*)-2-isopropyl-5-methylcyclohexyl 4-aminobenzoate (11e): (yellow oil, 72% yield). ^{1}H NMR (DMSO-d6, 400 MHz): δ 0.73 (d, *J* = 6.8 Hz, 3H), 0.87 (t, *J* = 7.4 Hz, 6H), 0.82-0.92 (m, 1H), 0.97-1.09 (m, 2H), 1.43-1.49 (m, 2H), 1.62-1.66 (m, 2H), 1.82-1.89 (m, 1H), 1.92-1.95 (m, 1H), 4.72 (dt, *J* = 4.4, 10.8 Hz, 1H), 5.92 (s, 2H), 6.56 (d, *J* = 8.8 Hz, 2H), 7.62 (d, *J* = 8.8 Hz, 2H).

Synthesis of (*1R,2S,5R*)-2-isopropyl-5-methylcyclohexyl 4-isocyanobenzoate (e): (black syrup, 80% yield). ^{1}H NMR (CDCl$_3$, 400 MHz): δ 0.78 (d, *J* = 6.8 Hz, 3H), 0.92 (t, *J* = 6.4 Hz, 6H), 0.87-0.90 (m, 1H), 1.04-1.18 (m, 2H), 1.51-1.60 (m, 2H), 1.70-1.76 (m, 2H), 1.86-1.94 (m, 1H), 2.08-2.13 (m, 1H), 4.93 (dt, *J* = 4.4, 11.2 Hz, 1H), 7.43 (d, *J* = 8.4 Hz, 2H), 8.07 (dt, *J* = 2.0, 8.8 Hz, 2H); ^{13}C NMR (CDCl$_3$, 100 MHz): δ 16.63, 20.86, 22.13, 23.74, 26.69, 31.57, 34.35, 41.01, 47.35, 75.81, 126.52, 129.92, 130.94, 131.78, 164.63, 167.03.

Scheme S5. 4-isocyano-4'-(1,2,2-triphenylvinyl)-1,1'-biphenyl (ITPB)



Synthesis of (2-(4-bromophenyl)ethene-1,1,2-triyl)tribenzene (15): Under nitrogen atmosphere, compound **14** (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 compound **13** (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 CH$_2$Cl$_2$ (3 × 100 mL), the combined organic layers were dried over anhydrous Na$_2$SO$_4$ 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 **15** as a white solid (11.7 g, 68% yield). ^{1}H NMR (CDCl$_3$, 400 MHz): δ 6.89 (d, *J* = 8.2 Hz, 2H), 7.08 (m, 15H), 7.22 (d, *J* = 8.2 Hz, 2H).

Synthesis of (4-(1,2,2-triphenylvinyl)phenyl)boronic acid (16): Under nitrogen atmosphere, compound **15** (2 g, 4.86 mmol) was dissolved in 20 mL of dry THF, after the solution was cooled to -78 ^{o}C, *n*-BuLi (2.43 mL, 2.4 M in hexane) was added dropwise and the mixture was stirred at -78 ^{o}C for 30 min. Then a solution of trimethyl borate (0.76 g, 7.29 mmol) in dry THF (10 mL) was added dropwise, the resulting mixture was stirred at -78 ^{o}C for 30 min, 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 **16** as white solid (2.40 g, crude), this compound was used directly for the next step without purification.

Synthesis of N-(4-iodophenyl)formamide (18): the synthetic procedure was the same with that of compound **2**, and the crude product was directly used for the next step without further purification.

Synthesis of N-(4'-(1,2,2-triphenylvinyl)-[1,1'-biphenyl]-4-yl)formamide (19): Under nitrogen atmosphere, compound **16** (6 g, crude), compound **18** (3.33 g, crude) were dissolved in a mixture solvents of toluene (100 mL) and water (50 mL), then $Pd(PPh_3)_4$ (386 mg, 0.33 mmol), K_2CO_3 (2.75 g, 19.9 mmol) and tetrabutylammonium hydrogen sulfate (452 mg, 1.33 mmol) were added, the resulting mixture was stirred at 90 ^{o}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 **19** as a light yellow solid (6.5 g). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.02-7.13 (m, 18H), 7.17 (s, 0.5H), 7.31 (dd, *J* = 2.0, 8.4 Hz, 2H), 7.51-7.58 (m, 3H), 7.64 (d, *J* = 11.6 Hz, 0.6H), 8.39 (d, *J* = 1.6 Hz, 0.5H), 8.71 (d, *J* = 11.6 Hz, 0.4H).

Synthesis of 4-isocyano-4'-(1,2,2-triphenylvinyl)-1,1'-biphenyl (f): the synthetic procedure was the same with that of compound **a**. (light green solid, 79% yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.03-7.15 (m, 17H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.40 (d, *J* = 8.4 Hz, 2H), 7.56 (dt, *J* = 1.6, 8.4, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 125.50, 126.36, 126.69, 126.73, 126.76, 126.83, 127.81, 127.84, 127.90, 127.95, 131.43, 131.46, 131.50, 132.15, 137.06, 140.28, 141.75, 141.99, 143.64, 143.69, 144.02, 164.69.

A typical procedure for the polymerization of 4-ethoxycarbonyl phenyl isocyanide (EPI) (Table 1, entry 3): In the glove box, a 50 mL round bottom flask was charged with a solution of $[Ph_3C][B(C_6F_5)_4]$ (7.8 mg, 8.46 μmol) in chlorobenzene (2 mL), then $Al^{i}Bu_3$ (85 μL, 85 μmol, 1 mol/L in toluene) was added, the resulting mixture was stirred at 25 ^{o}C for 1 min and then added to a solution of 4-ethoxycarbonyl phenyl isocyanide (150 mg, 0.851 mmol) in chlorobenzene (3 mL). The reaction mixture was stirred at 25 ^{o}C for 1 min, then the flask was taken out of the glove box and the reaction mixture was poured into methanol (100 mL) to precipitate the polymer product, the yellow polymer solid was collected by filtration, and dried in vacuo at 40 ^{o}C to a constant weight (132 mg, 88% yield), The product obtained is soluble thoroughly in $CHCl_3$ at 25 ^{o}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, a 50 mL round bottom flask was charged with a solution of $[Ph_3C][B(C_6F_5)_4]$ (2.1 mg, 2.3 μmol) in chlorobenzene (2 mL), then $Al^{i}Bu_3$ (23 μL, 23 μmol, 1 mol/L in toluene) was added, the resulting mixture was stirred at 25 ^oC for 3 min, then a solution of (*1S,2R,5S*)-2-isopropyl-5-methylcyclohexyl 4-isocyanobenzoate (66 mg, 0.23 mmol) and 4-isocyano-4'-(1,2,2-triphenylvinyl)-1,1'-biphenyl (100 mg, 0.23 mmol) in chlorobenzene (3 mL) was added, the reaction mixture was stirred at 25 ^oC for 3 min, then the flask was taken out of the glove box and the reaction mixture was poured into methanol (100 mL) to precipitate the copolymer product, the orange copolymer solid was collected by filtration, and dried in vacuo at 40 ^oC to a constant weight (86 mg, 52% yield), The product obtained is soluble thoroughly in $CHCl_3$ and THF at 25 ^oC.

A typical procedure for the copolymerization of (*1S,2R,5S*)-2-isopropyl-5-methylcyclohexyl 4-isocyanobenzoate (D-IMCI) with 3-isopropyloxycarbonyl phenyl isocyanide (IPI) (Table 2, entry 13): In the glove box, a 50 mL round bottom flask was charged with a solution of $[Ph_3C][B(C_6F_5)_4]$ (2.1 mg, 2.3 μmol) in chlorobenzene (2 mL), then $Al^{i}Bu_3$ (23 μL, 23 μmol, 1 mol/L in toluene) was added, the resulting mixture was stirred at 25 ^oC for 3 min, then a solution of (*1S,2R,5S*)-2-isopropyl-5-methylcyclohexyl 4-isocyanobenzoate (66 mg, 0.23 mmol) and 3-isopropyloxycarbonyl phenyl isocyanide (44 mg, 0.23 mmol) in chlorobenzene (3 mL) was added, the reaction mixture was stirred at 25 ^oC for 3 min, then the flask was taken out of the glove box and the reaction mixture was poured into methanol (100 mL) to precipitate the copolymer product, the orange copolymer solid was collected by filtration, and dried in vacuo at 40 ^oC to a constant weight (76 mg, 70% yield), The product obtained is soluble thoroughly in $CHCl_3$ and THF at 25 ^oC.

Calculation of the IMCI contents of the copolymers

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

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

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 isopropy.

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

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

In which I_{H1} 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 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.

Solvent separation experiments

4 mg of poly(D-IMCI) or poly(L-IMCI) was added into 1.5 mL of toluene, the mixture was shaken for about 1 min and all of the solid dissolved in toluene completely. 4 mg of poly(ITPB) or poly(IPI) was added into 1.5 mL of toluene and exhibited poor solubility, after shaken for about 1 hour there was still some solid precipitated in the solution. Then 6 mg of the copolymer product (Table 2, entry 3 and Table 2, entry 18) was added into 6 mL of toluene, the mixture was shaken for about 5 min and the solid dissolved in toluene completely.

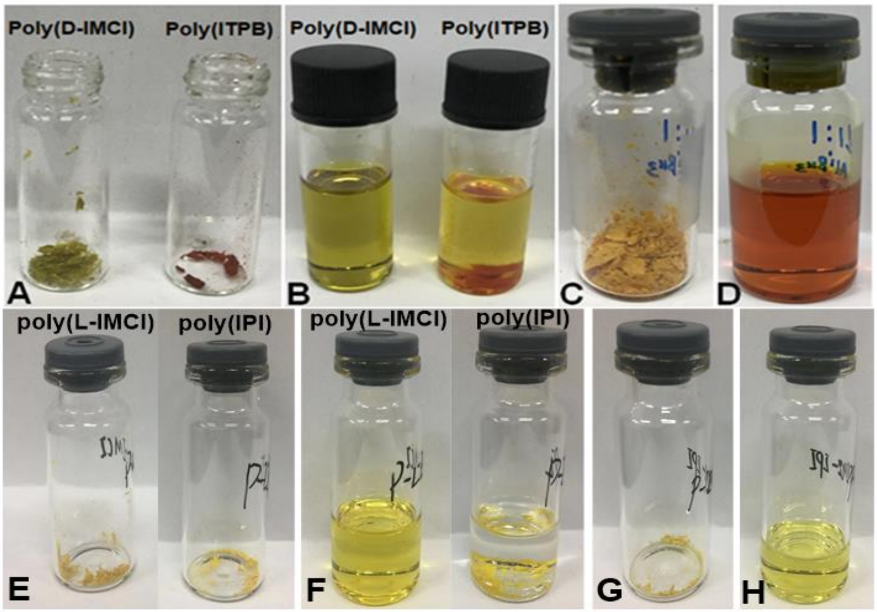


Figure S1. Photos of solubility of poly(D-IMCI) (A-B, left), poly(ITPB) (A-B, right), copolymer product (Table 2, entry 3) (C-D) in toluene, poly(L-IMCI) (E-F, left), poly(IPI) (E-F, right), copolymer product (Table 2, entry 18) (G-H) in toluene.

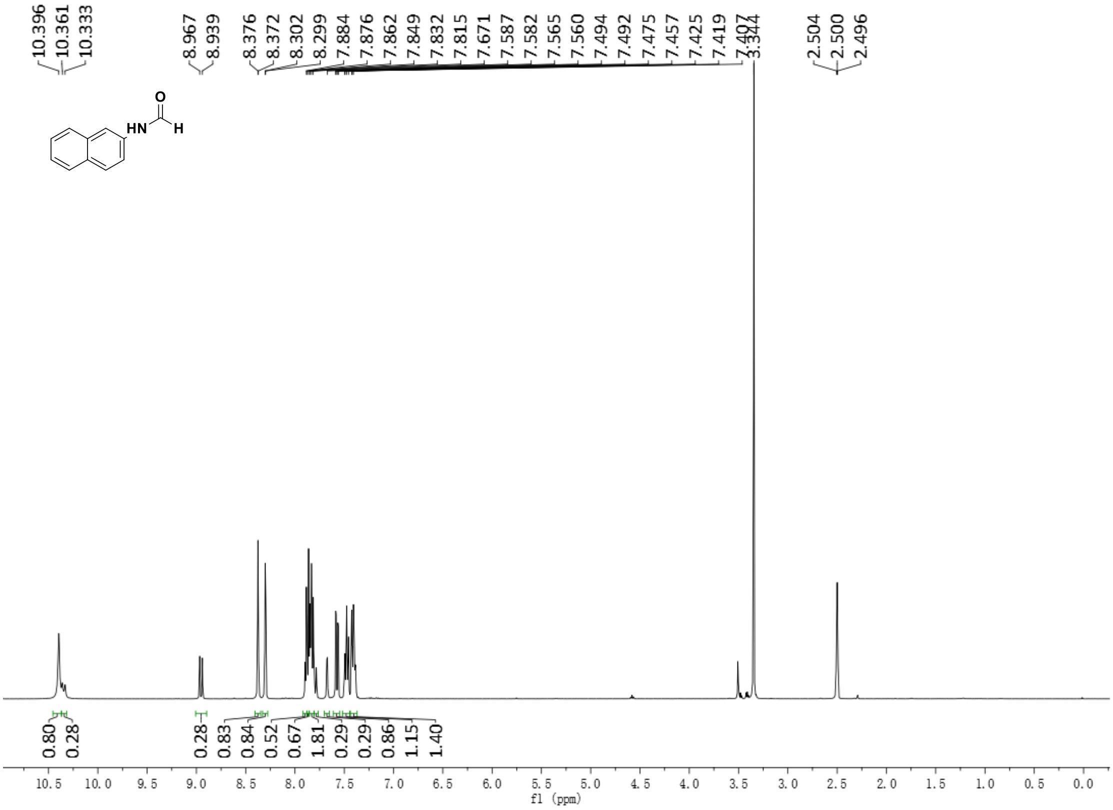


Figure S2. ^{1}H NMR spectrum of N-(naphthalen-2-yl)formamide (**2**) in DMSO-d6 at 25 ^{o}C.

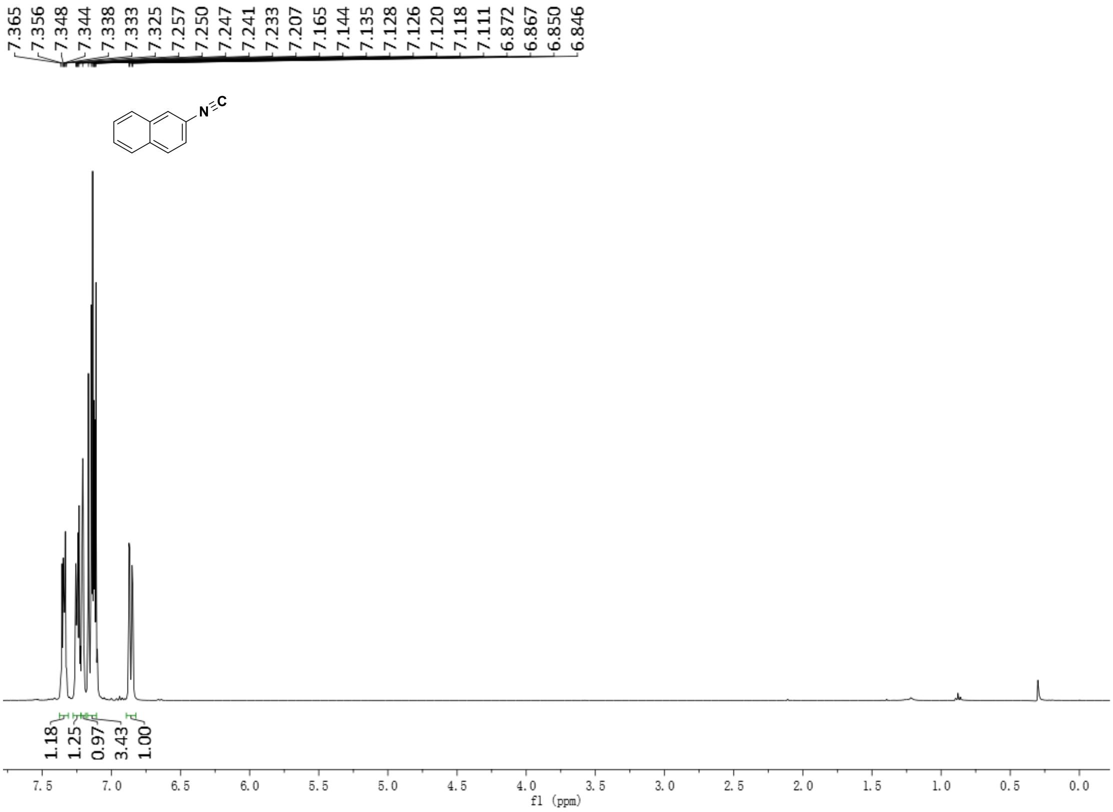


Figure S3. ^{1}H NMR spectrum of 2-naphthyl isocyanide (**a**) in $CDCl_3$ at 25 ^{o}C.

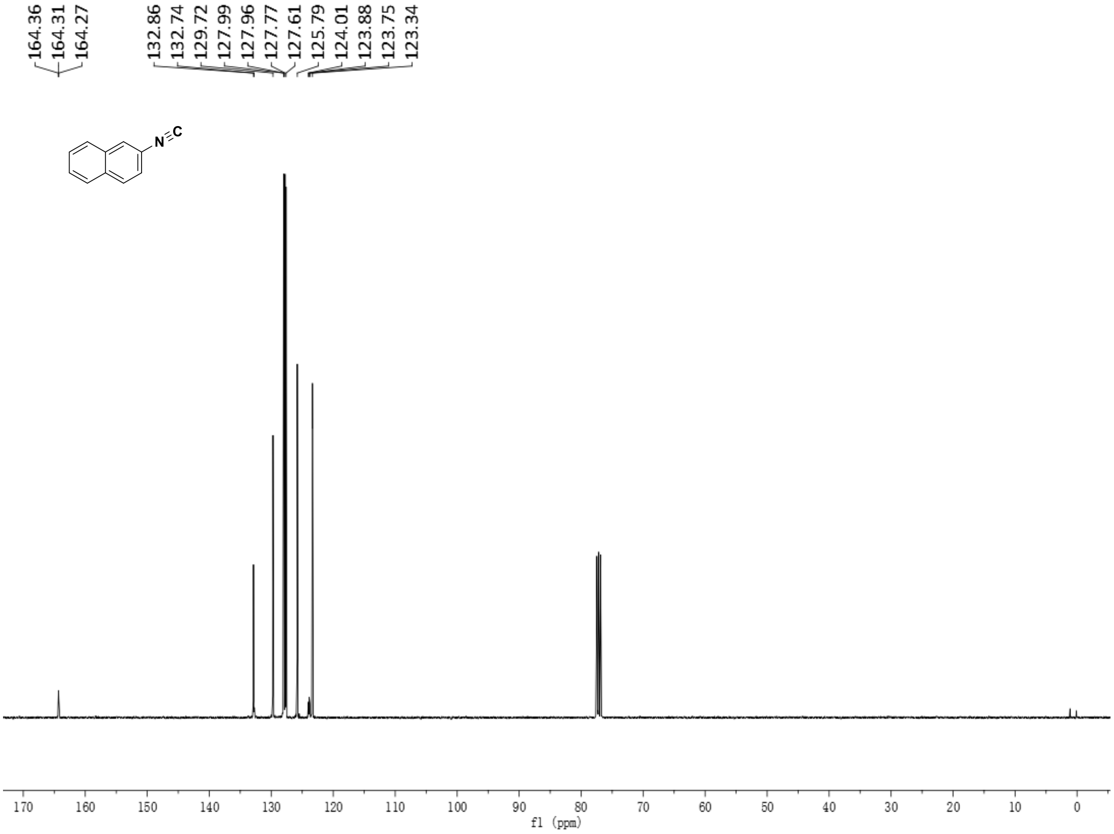


Figure S4. ^{13}C NMR spectrum of 2-naphthyl isocyanide (**a**) in $CDCl_3$ at 25 ^{o}C.

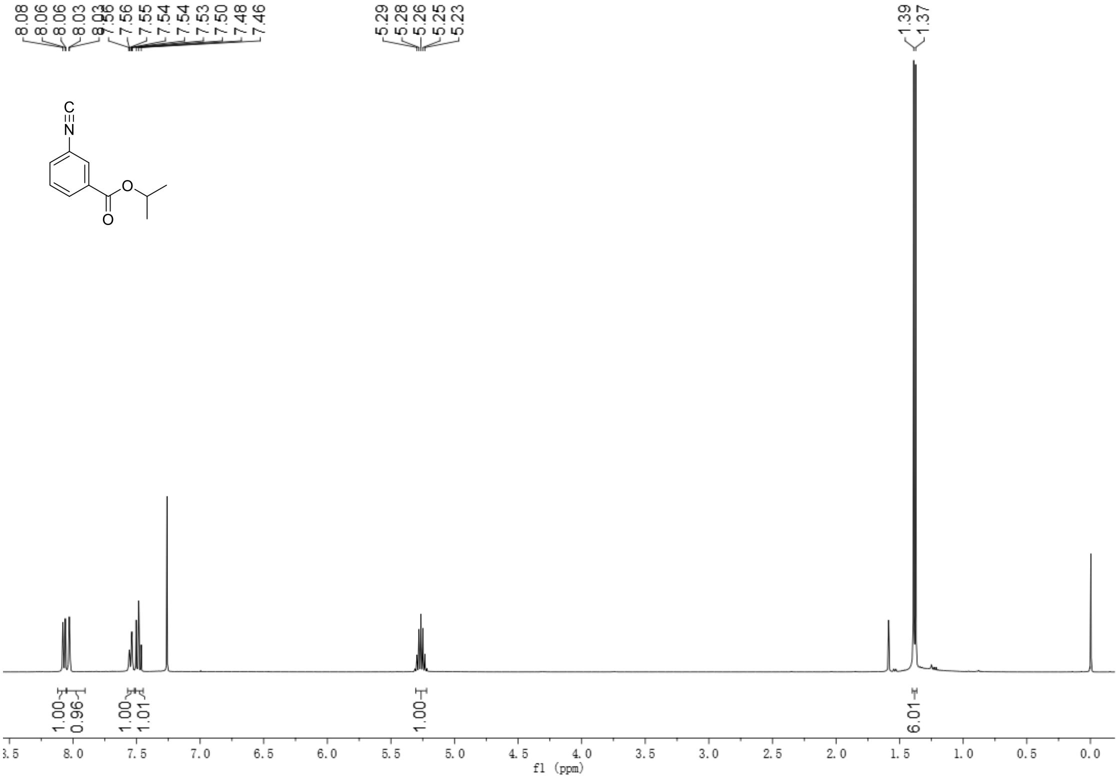


Figure S5. ^{1}H NMR spectrum of 3-isopropyloxycarbonyl phenyl isocyanide (**b**) in $CDCl_3$ at 25 ^{o}C.

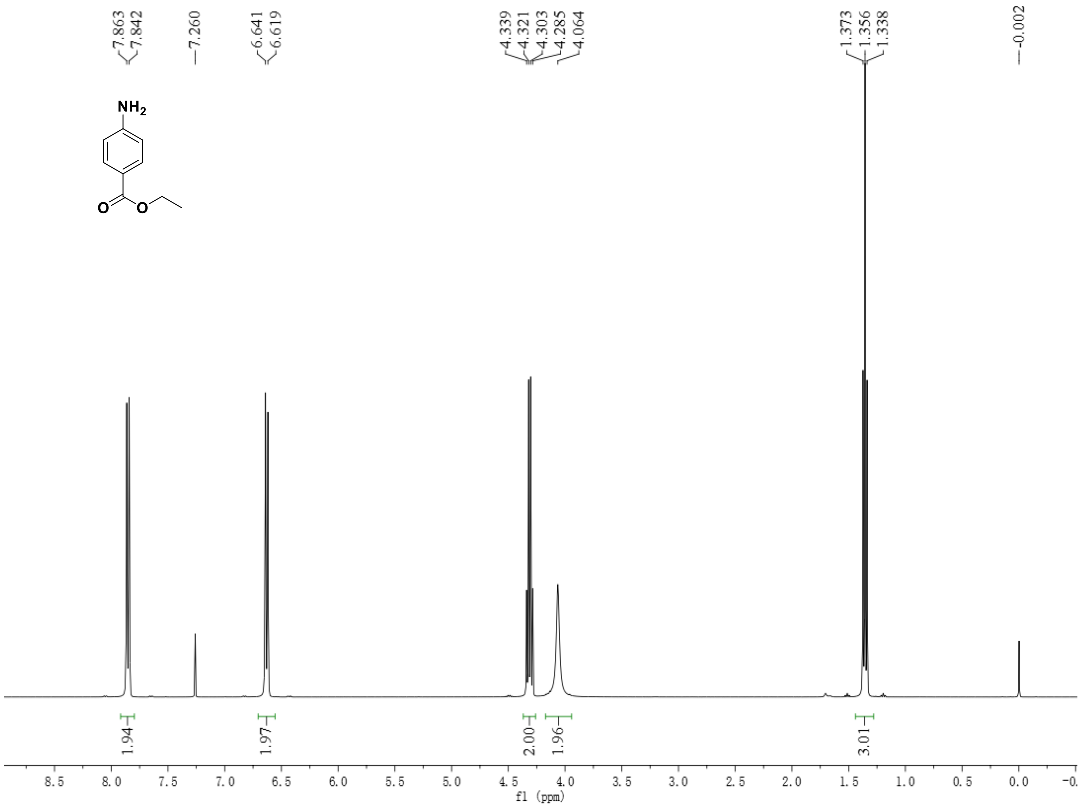


Figure S6. ^{1}H NMR spectrum of ethyl 4-aminobenzoate (**7**) in $CDCl_3$ at 25 °C.

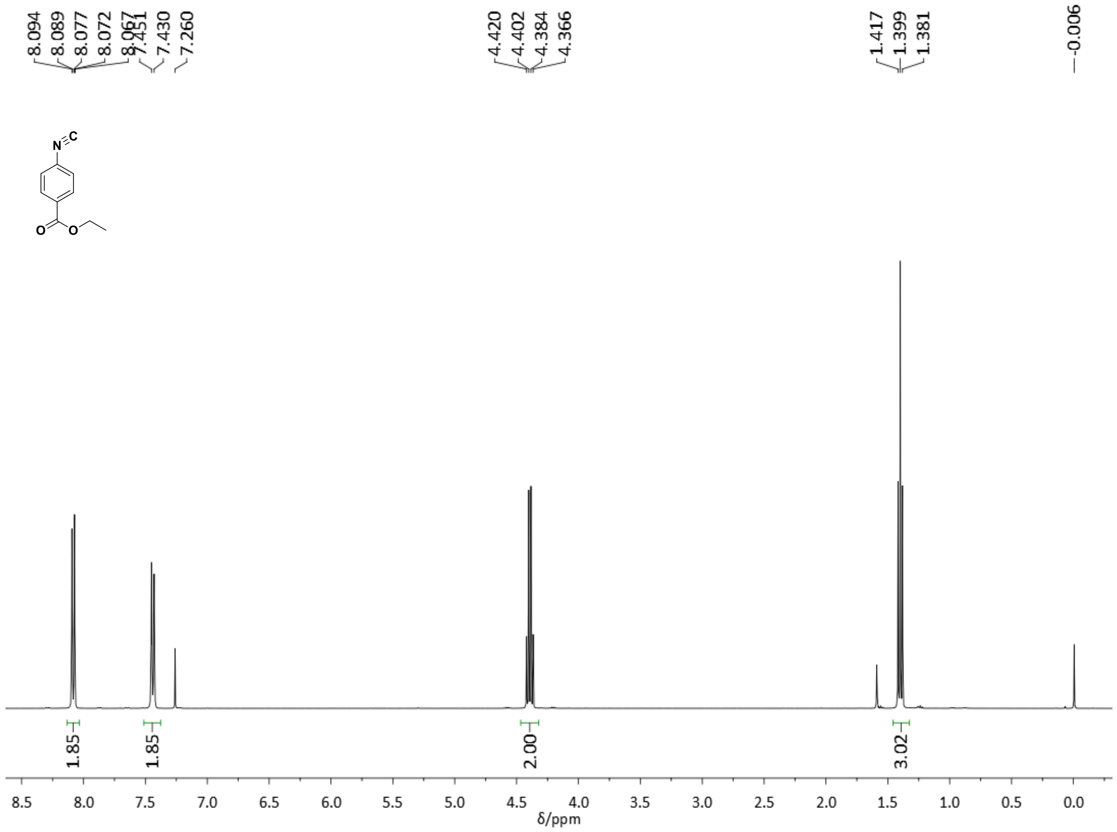


Figure S7. ^{1}H NMR spectrum of 4-ethoxycarbonyl phenyl isocyanide (**c**) in $CDCl_3$ at 25 °C.

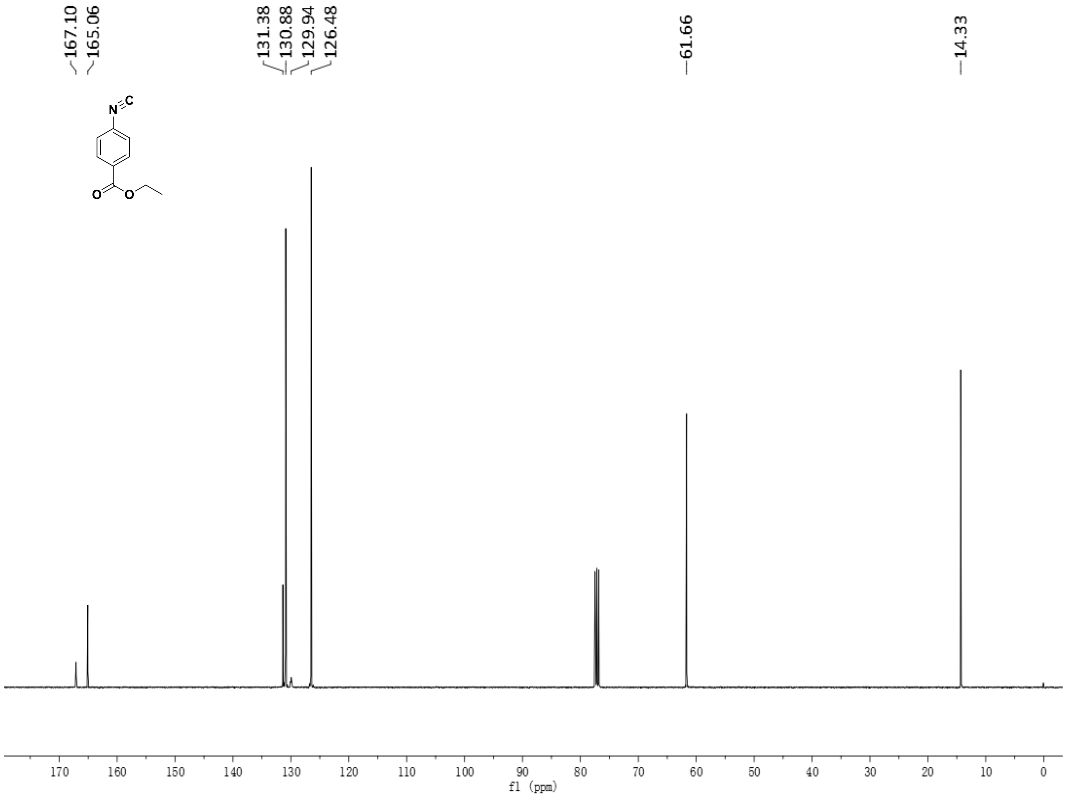


Figure S8. ^{13}C NMR spectrum of 4-ethoxycarbonyl phenyl isocyanide (**c**) in CDCl$_3$ at 25 ^{o}C.

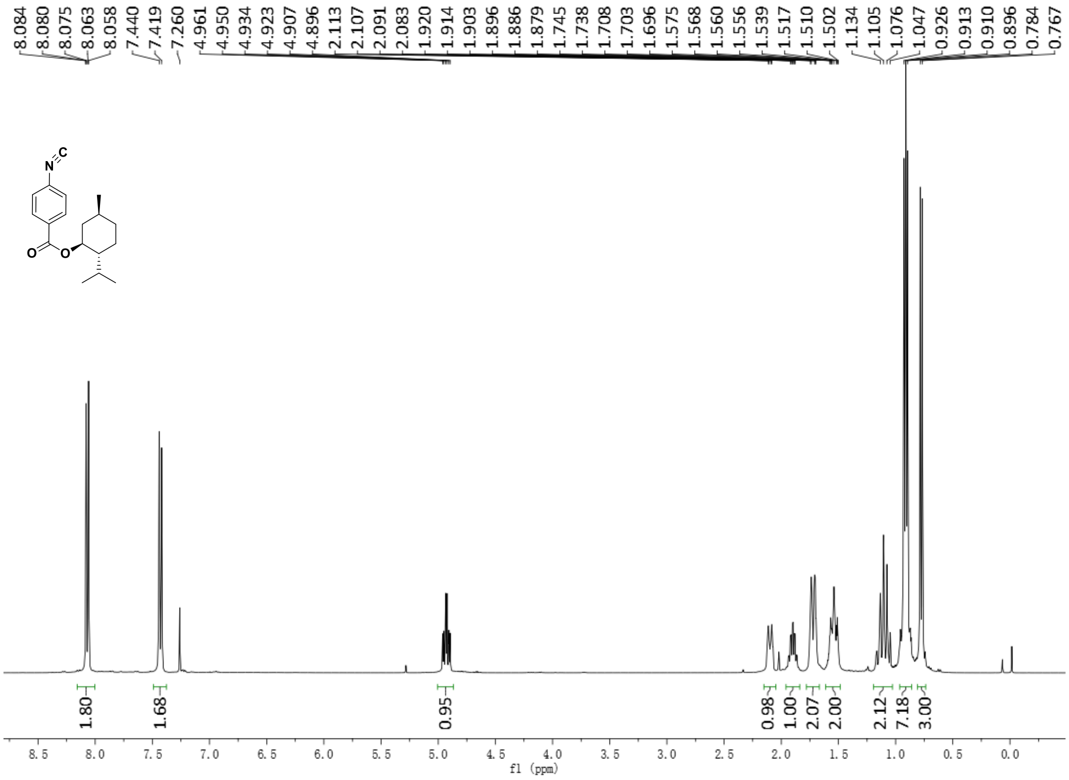


Figure S9. ^{1}H NMR spectrum of (*1S*,*2R*,*5S*)-2-isopropyl-5-methylcyclohexyl 4-isocyanobenzoate (**d**) in CDCl$_3$ at 25 ^{o}C.

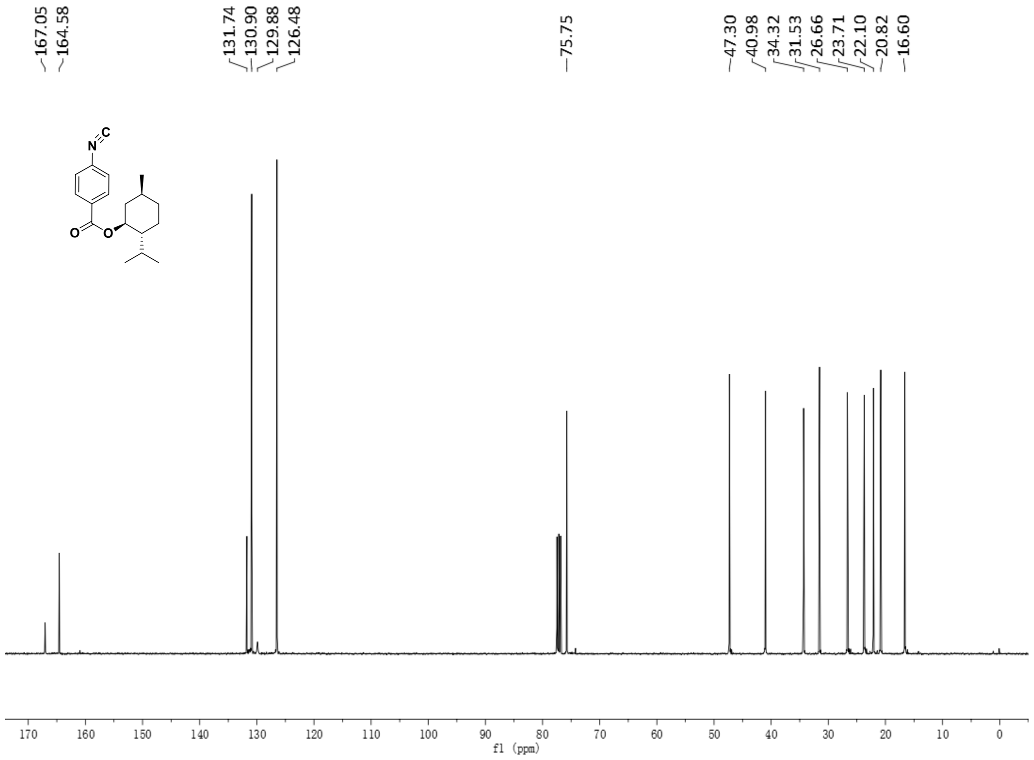


Figure S10. ^{13}C NMR spectrum of (*1S*,*2R*,*5S*)-2-isopropyl-5-methylcyclohexyl 4-isocyanobenzoate (**d**) in CDCl$_3$ at 25 ^{o}C.

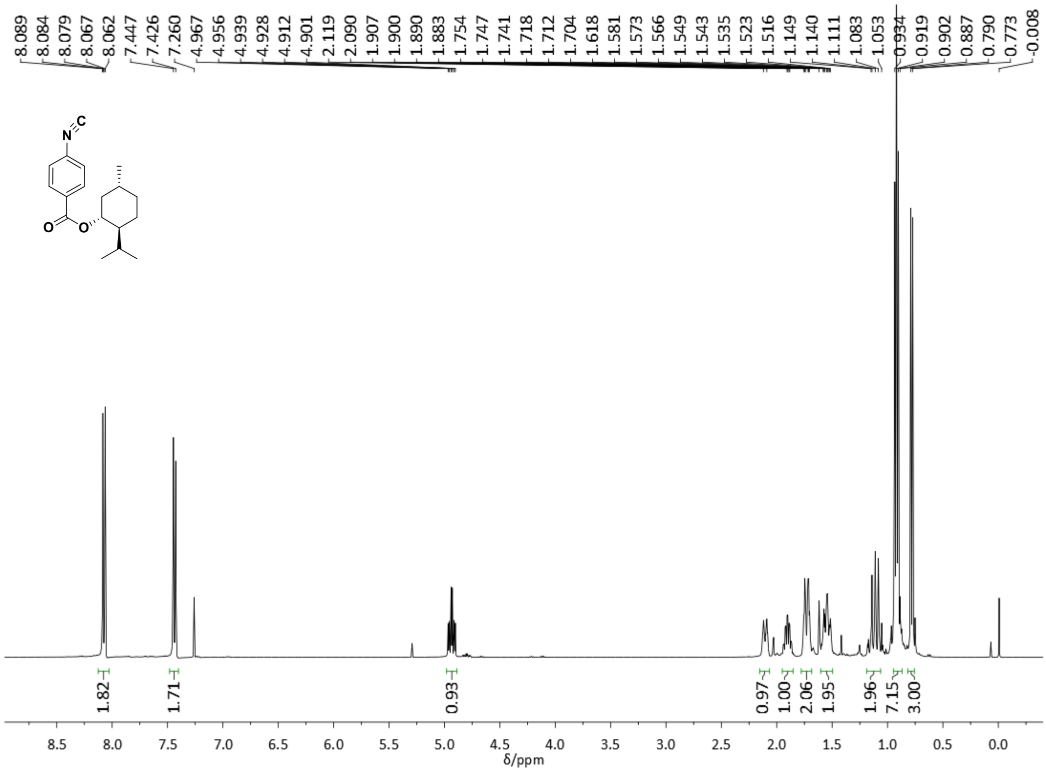


Figure S11. ^{1}H NMR spectrum of (*1R*,*2S*,*5R*)-2-isopropyl-5-methylcyclohexyl 4-isocyanobenzoate (**e**) in CDCl$_3$ at 25 ^{o}C.

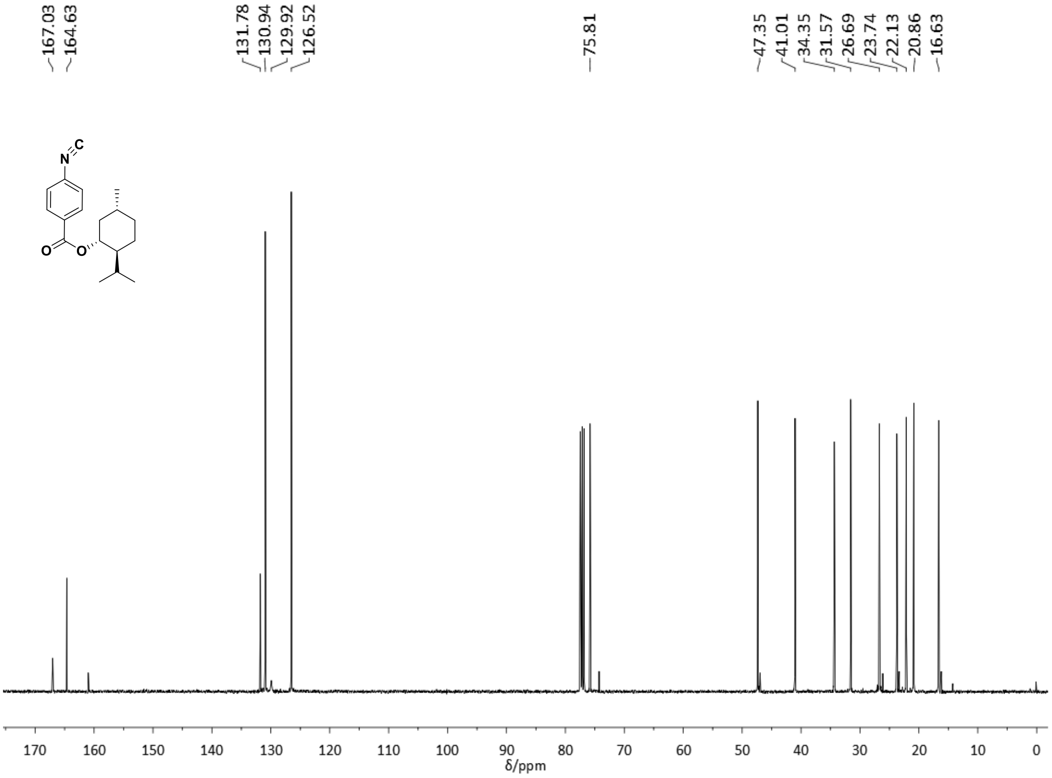


Figure S12. ^{13}C NMR spectrum of (*1R,2S,5R*)-2-isopropyl-5-methylcyclohexyl 4-isocyanobenzoate (**e**) in $CDCl_3$ at 25 °C.

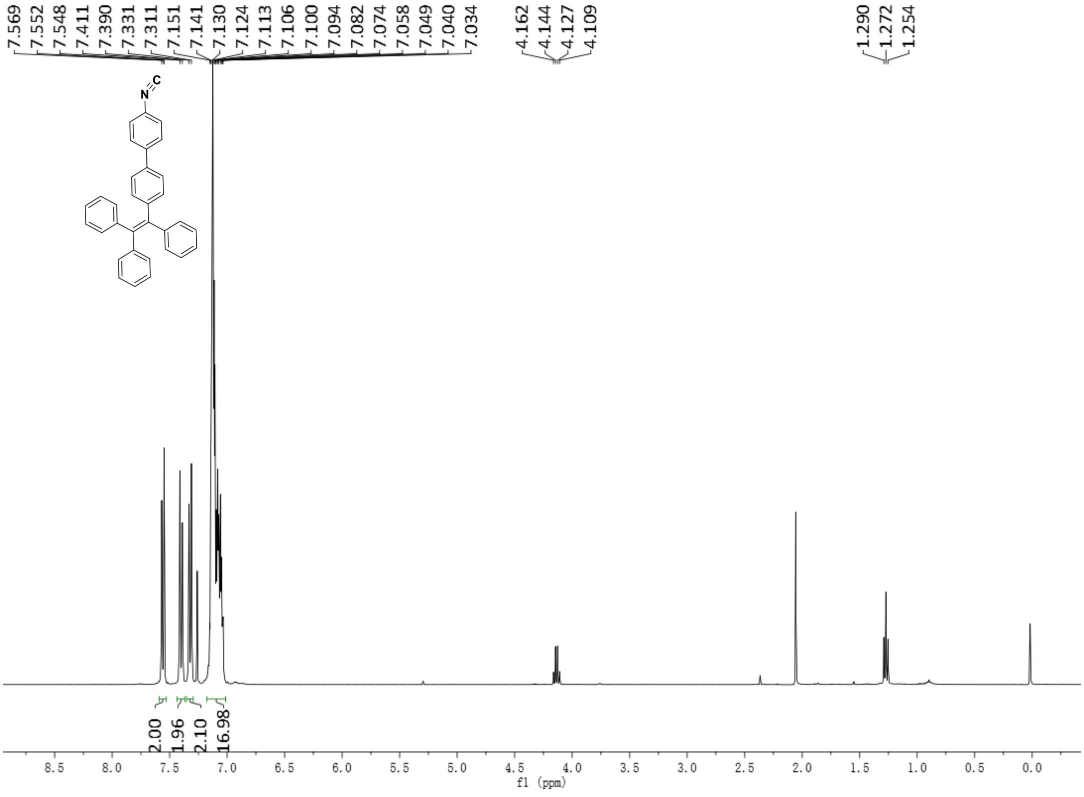


Figure S13. ^{1}H NMR spectrum of 4-isocyano-4'-(1,2,2-triphenylvinyl)-1,1'-biphenyl (**f**) in $CDCl_3$ at 25 °C.

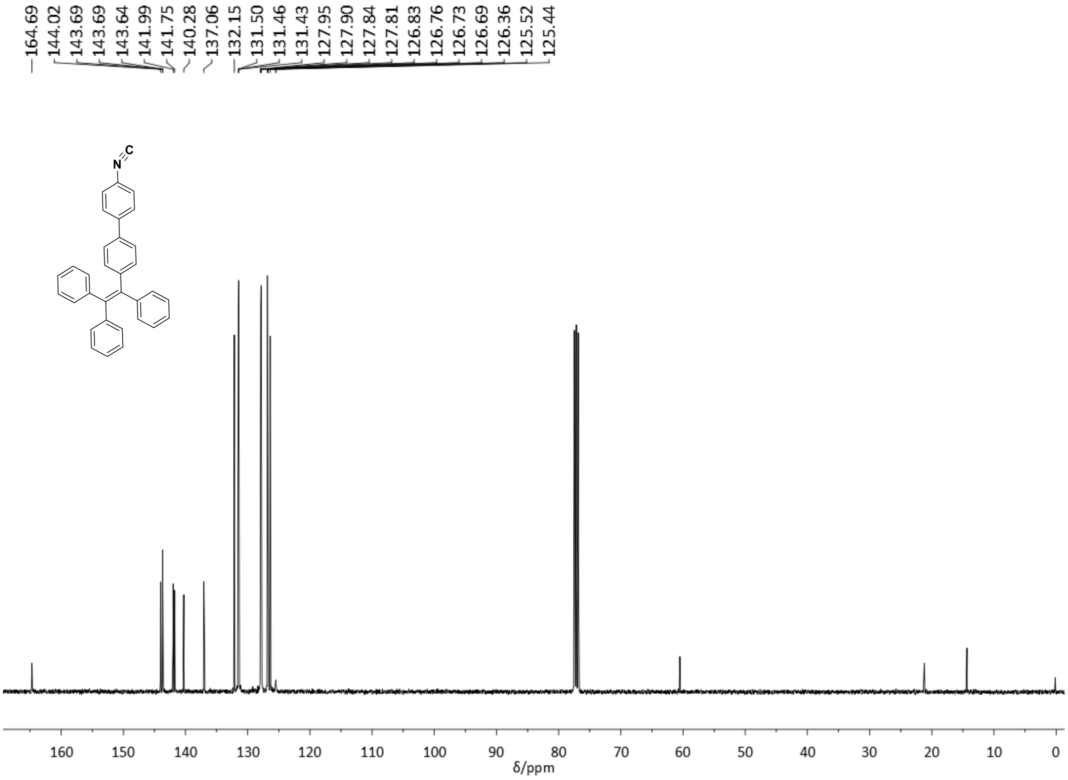


Figure S14. ^{13}C NMR spectrum of 4-isocyano-4'-(1,2,2-triphenylvinyl)-1,1'-biphenyl (**f**) in $CDCl_3$ at 25 ^{o}C.

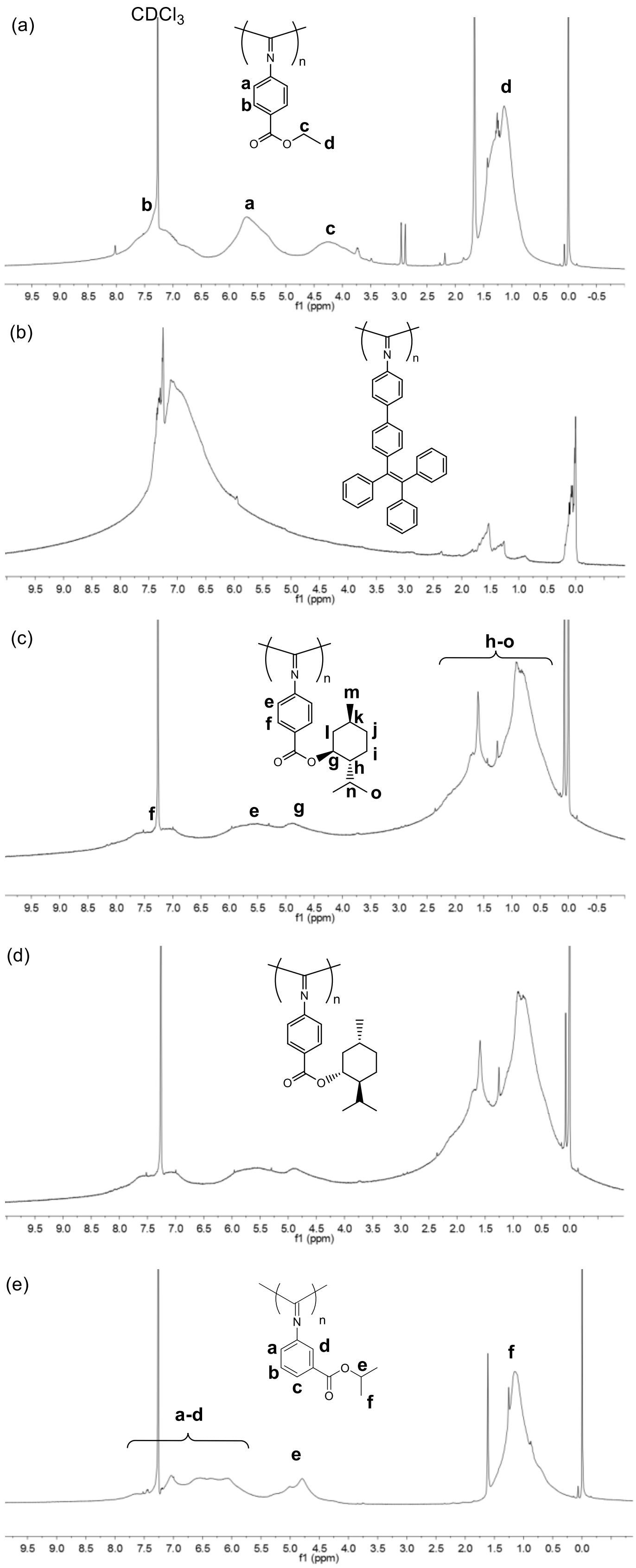


Figure S15. ^{1}H NMR spectrum of polymers (a) poly(EPI) (Table 1, entry 3), (b) poly(ITPB) (Table 1, entry 6), (c) poly(D-IMCI) (Table 1, entry 4), (d) poly(L-IMCI) (Table 1, entry 5), (e) poly(IPI) (Table 1, entry 2) in $CDCl_3$ at 25 ^oC.

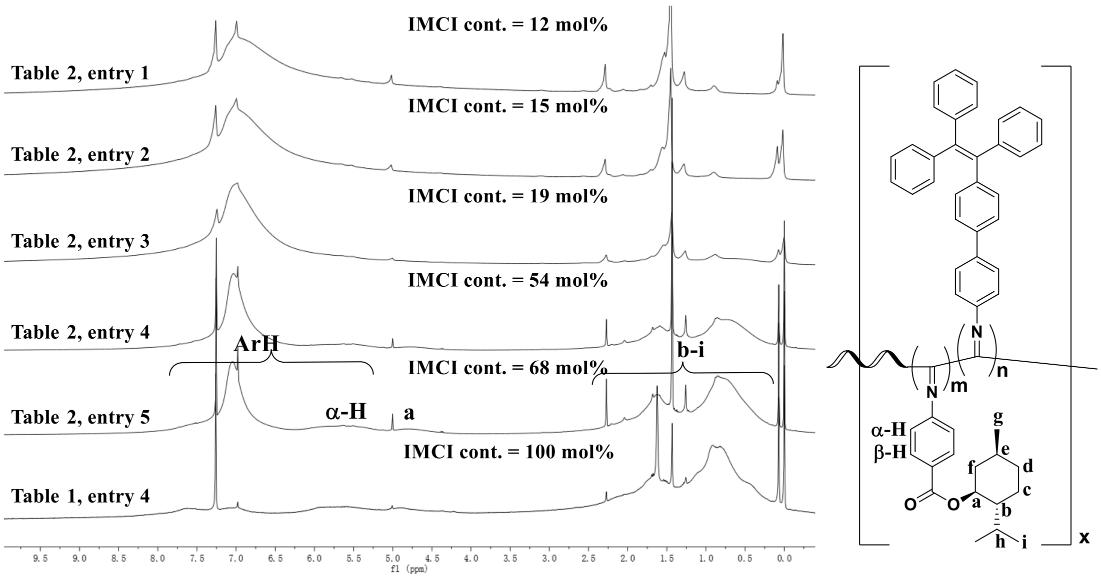


Figure S16. ^{1}H NMR spectra of poly(D-IMCI-*co*-ITPB)s and poly(D-IMCI) (Table 1, entry 4 and Table 2, entries 1-5)

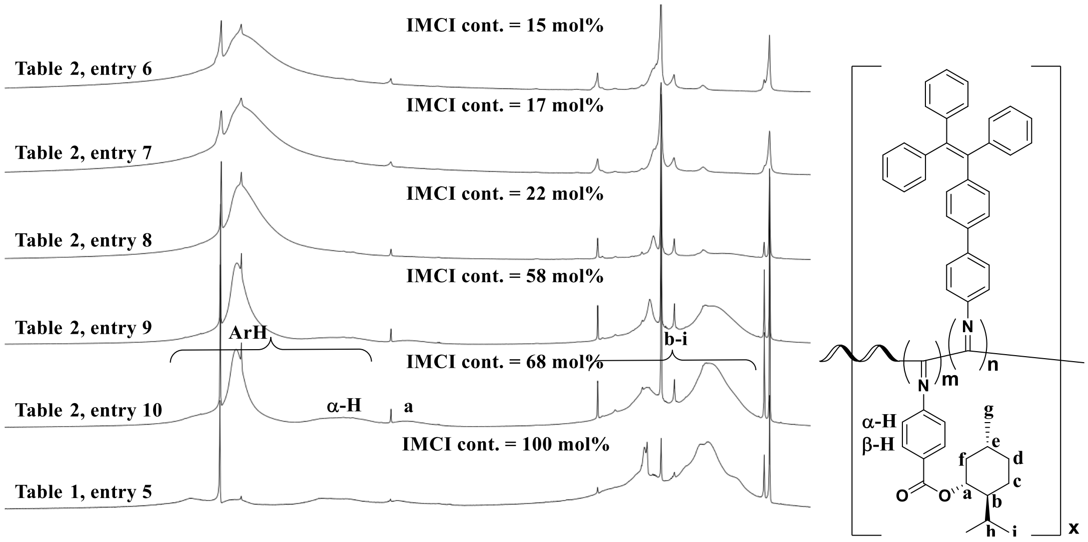


Figure S17. ^{1}H NMR spectra of poly(L-IMCI-*co*-ITPB)s and poly(L-IMCI) (Table 1, entry 5 and Table 2, entries 6-10)

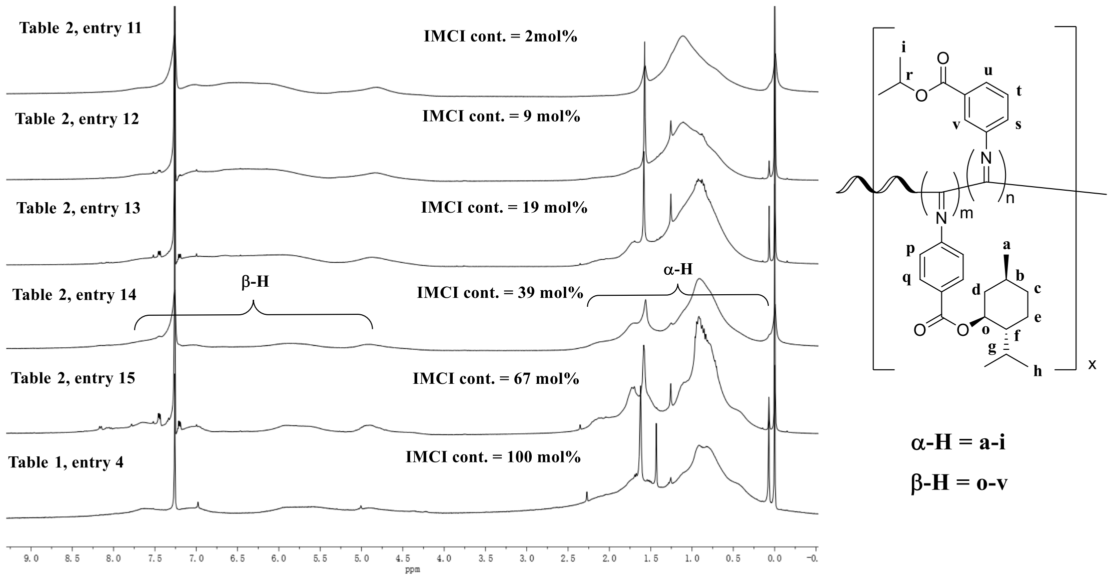


Figure S18. ^{1}H NMR spectra of poly(D-IMCI-*co*-IPI)s and poly(D-IMCI) (Table 1, entry 4 and Table 2, entries 11-15)

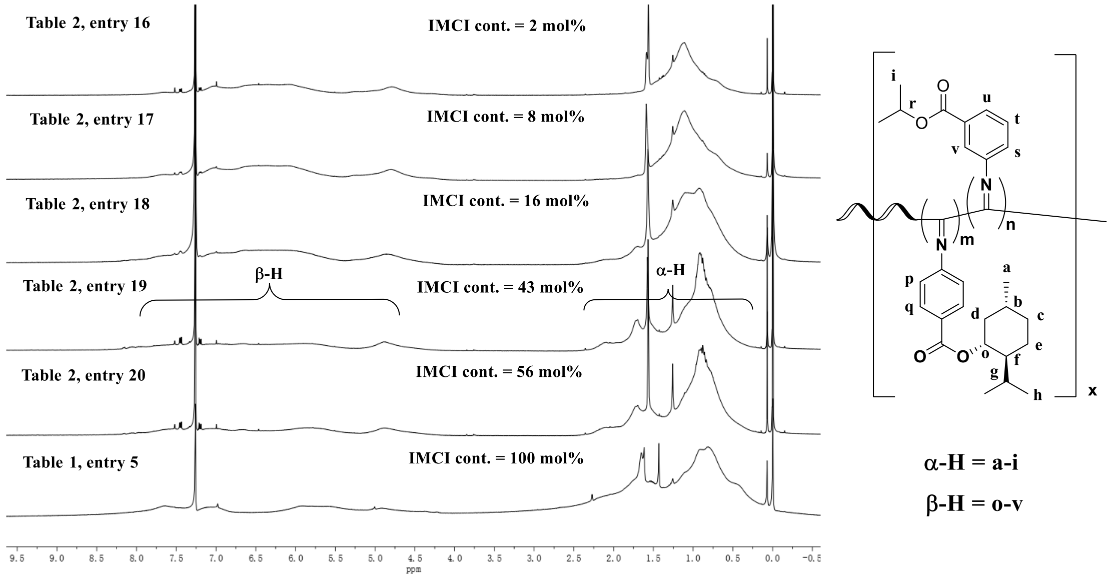


Figure S19. ^{1}H NMR spectra of poly(L-IMCI-*co*-IPI)s and poly(L-IMCI) (Table 1, entry 5 and Table 2, entries 16-20)

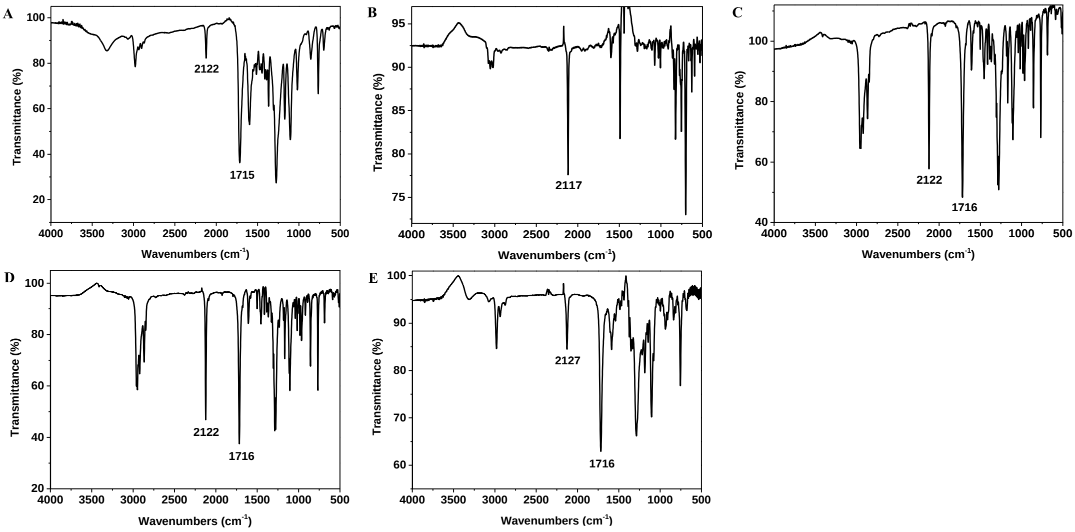


Figure S20. FT-IR spectra of (A) EPI, (B) ITPB, (C) D-IMCI, (D) L-IMCI and (E) IPI.

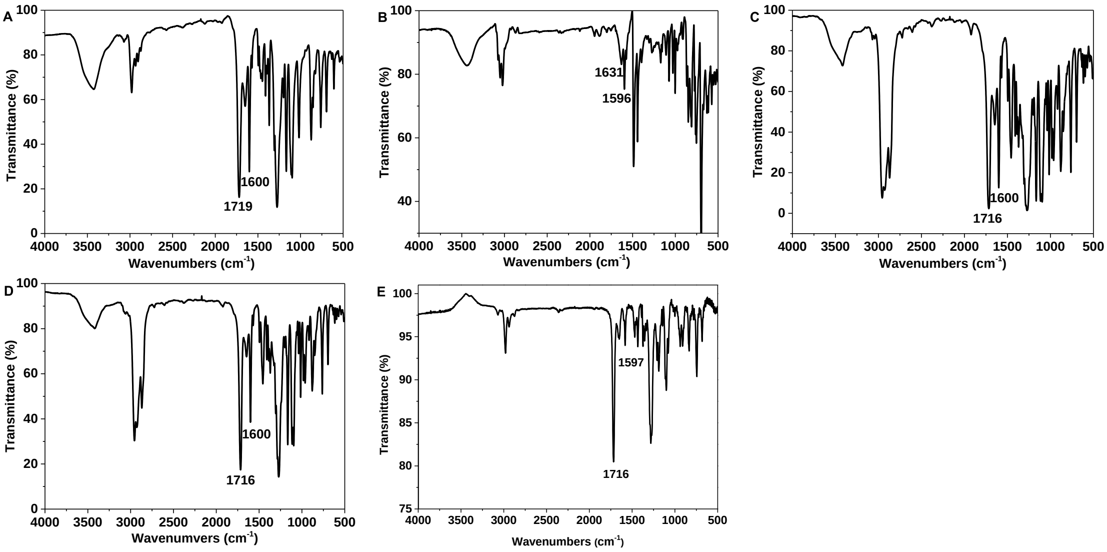


Figure S21. FT-IR spectra of (A) poly(EPI), (B) poly(ITPB), (C) poly(D-IMCI), (D) poly(L-IMCI) and (E) poly(IPI).

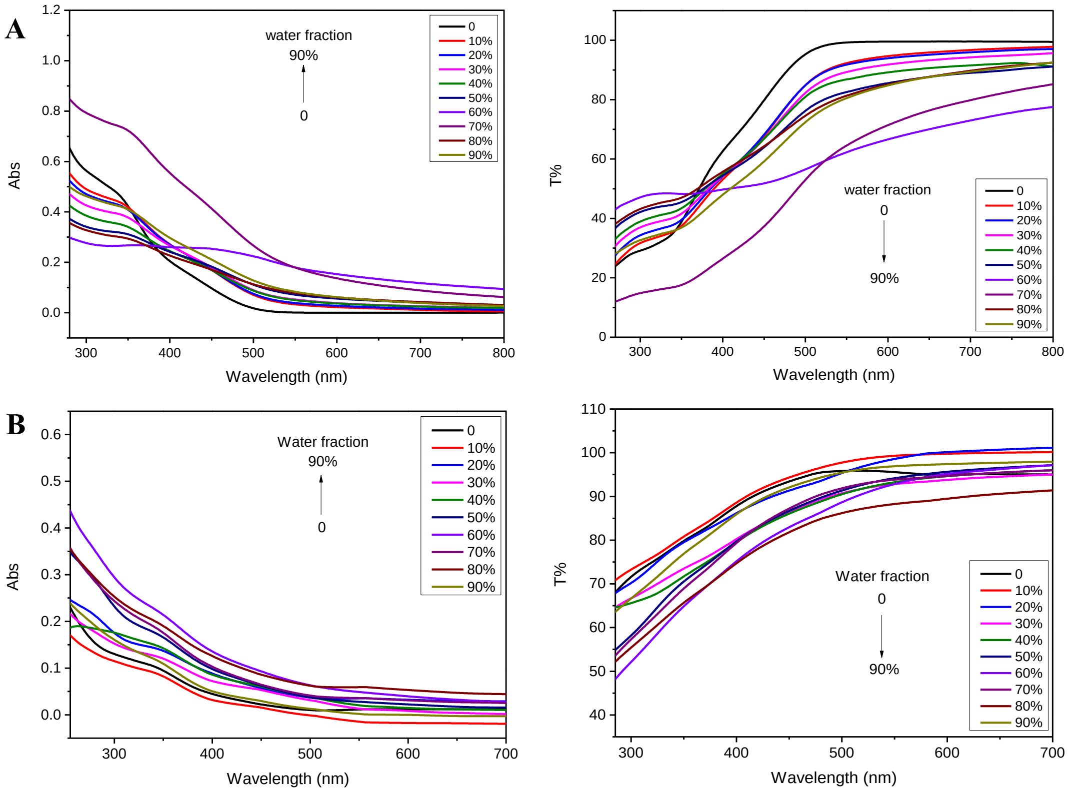


Figure S22. AIE nature characterization of (A) ITPB monomer and it corresponding (B) poly(ITPB) (Table 1, entry 6) in THF/water mixture. The UV absorption spectra with the water fraction in THF/water mixture ranging from 0 to 90% (left side). The UV/Vis transmittance spectra with the water fraction in THF/water mixture ranging from 0 to 90% (right side).

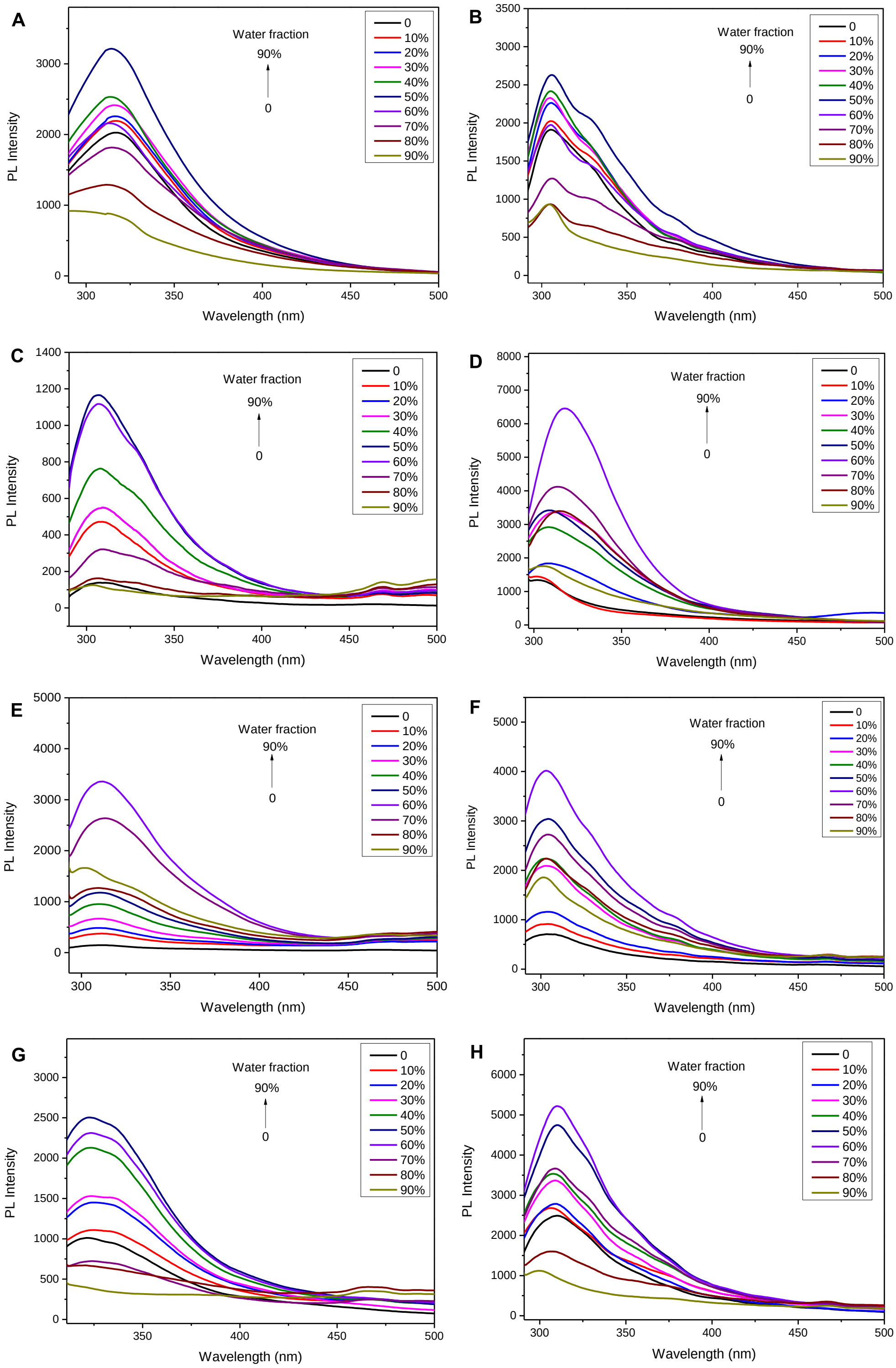


Figure S23. Plots of fluorescence intensity vs water fraction in THF/water mixture (0.01 mol of ITPB unit/mL). (A) poly(D-IMCI-*co*-ITPB) (Table 2, entry 1), (B) poly(D-IMCI-*co*-ITPB) (Table 2, entry 2), (C) poly(D-IMCI-*co*-ITPB) (Table 2, entry 3), (D) poly(L-IMCI-*co*-ITPB) (Table 2, entry 5), (E) poly(L-IMCI-*co*-ITPB) (Table 2, entry 7), (F) poly(L-IMCI-*co*-ITPB) (Table 2, entry 8), (G) poly(L-IMCI-*co*-ITPB) (Table 2, entry 9), (H) poly(L-IMCI-*co*-ITPB) (Table 2, entry 10) (conditions for A-H: EX wavelength: 290 nm, EX slit: 5 nm, EM slit: 5 nm, 700 V)

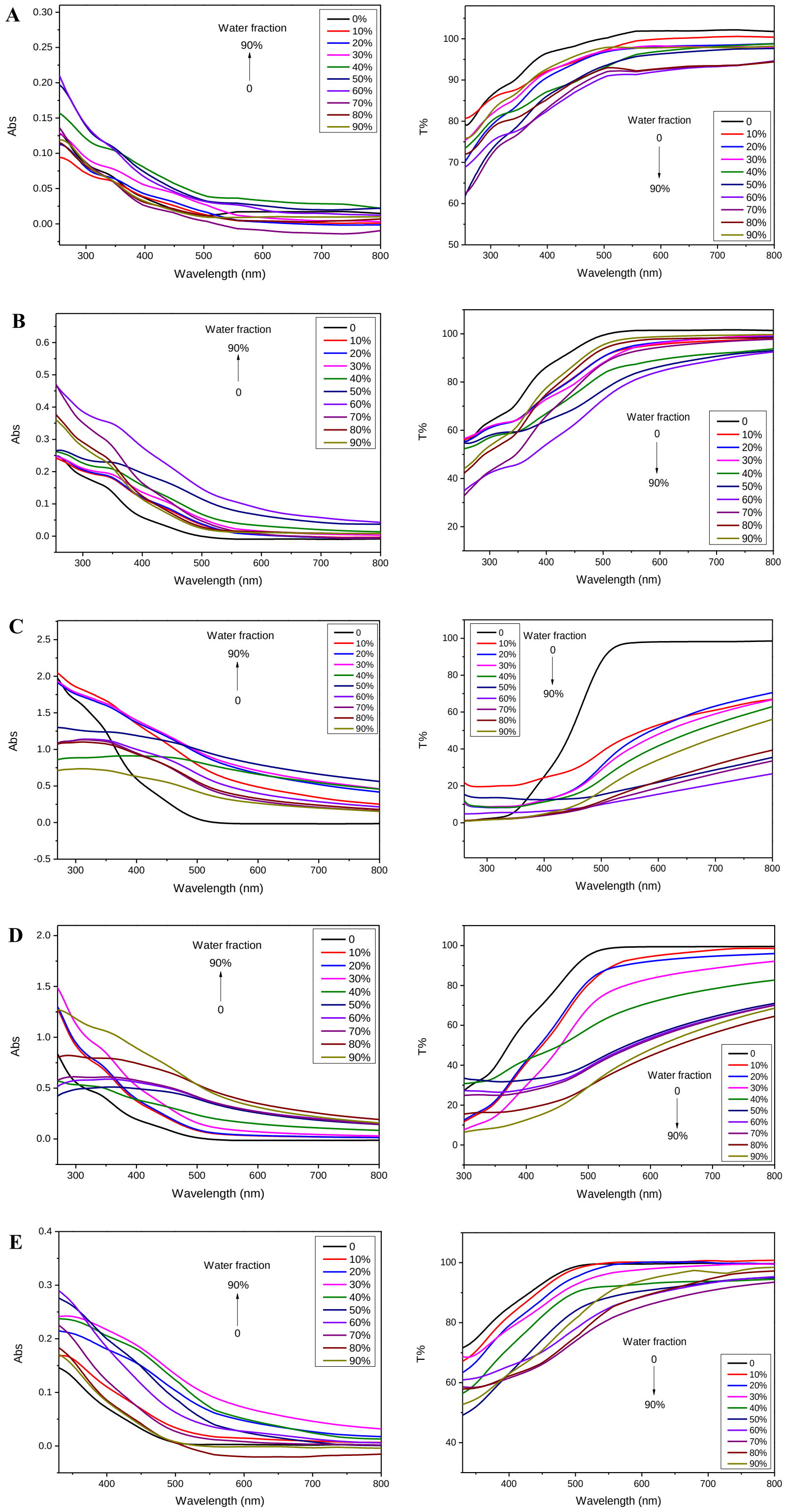


Figure S24. AIE nature characterization of (A) poly(D-IMCI-*co*-ITPB) (Table 2, entry 1), (B) poly(D-IMCI-*co*-ITPB) (Table 2, entry 2), (C) poly(D-IMCI-*co*-ITPB) (Table 2, entry 3), (D) poly(D-IMCI-*co*-ITPB) (Table 2, entry 4), (E) poly(D-IMCI-*co*-ITPB) (Table 2, entry 5) in THF/water mixture. The UV absorption spectra with the water fraction in THF/water mixture ranging from 0 to 90% (left side). The UV/Vis transmittance spectra with the water fraction in THF/water mixture ranging from 0 to 90% (right side).

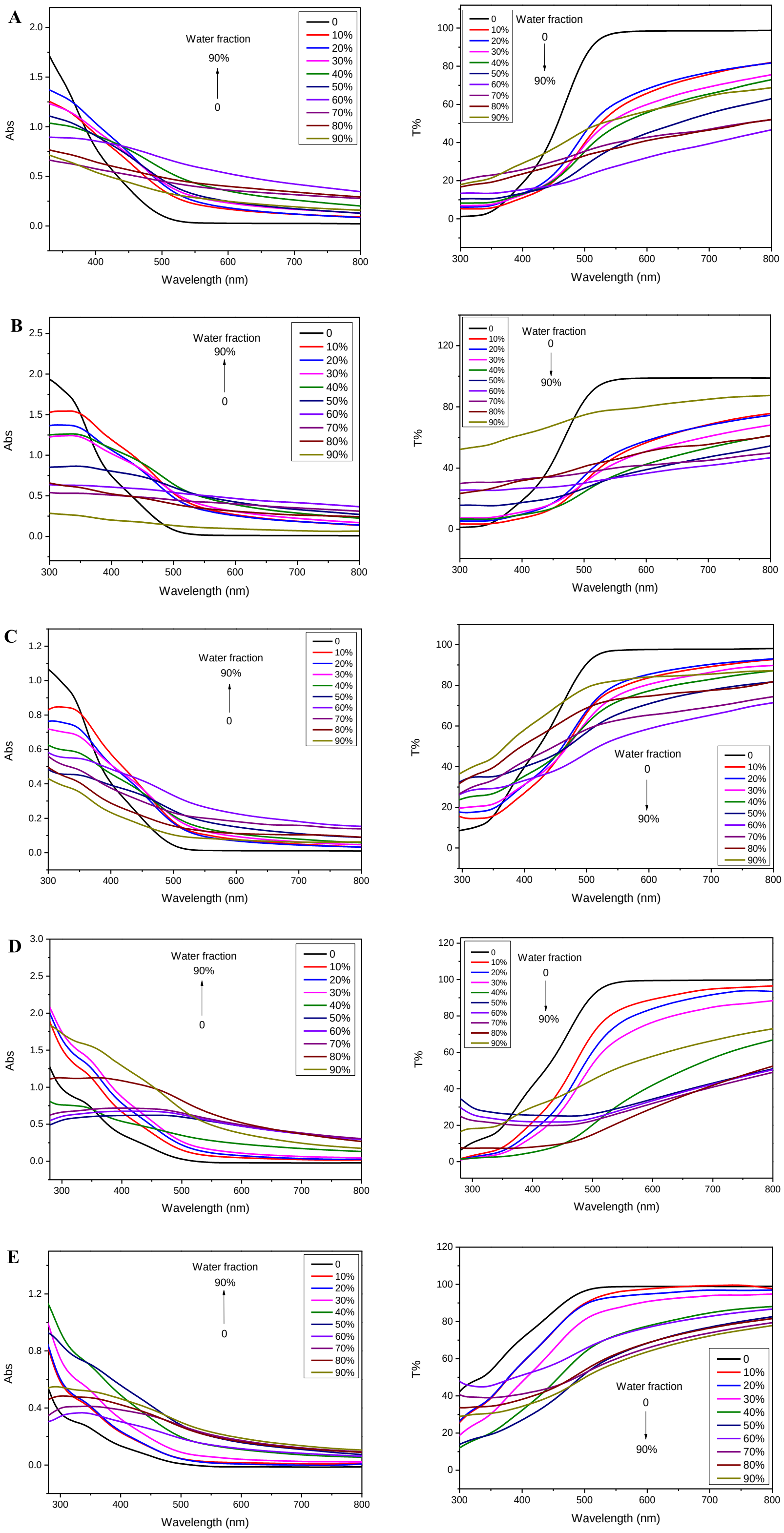


Figure S25. AIE nature characterization of (A) poly(L-IMCI-*co*-ITPB) (Table 2, entry 6), (B) poly(L-IMCI-*co*-ITPB) (Table 2, entry 7), (C) poly(L-IMCI-*co*-ITPB) (Table 2, entry 8), (D) poly(L-IMCI-*co*-ITPB) (Table 2, entry 9), (E) poly(L-IMCI-*co*-ITPB) (Table 2, entry 10) in THF/water mixture. The UV absorption spectra with the water fraction in THF/water mixture ranging from 0 to 90% (left side). The UV/Vis transmittance spectra with the water fraction in THF/water mixture ranging from 0 to 90% (right side).

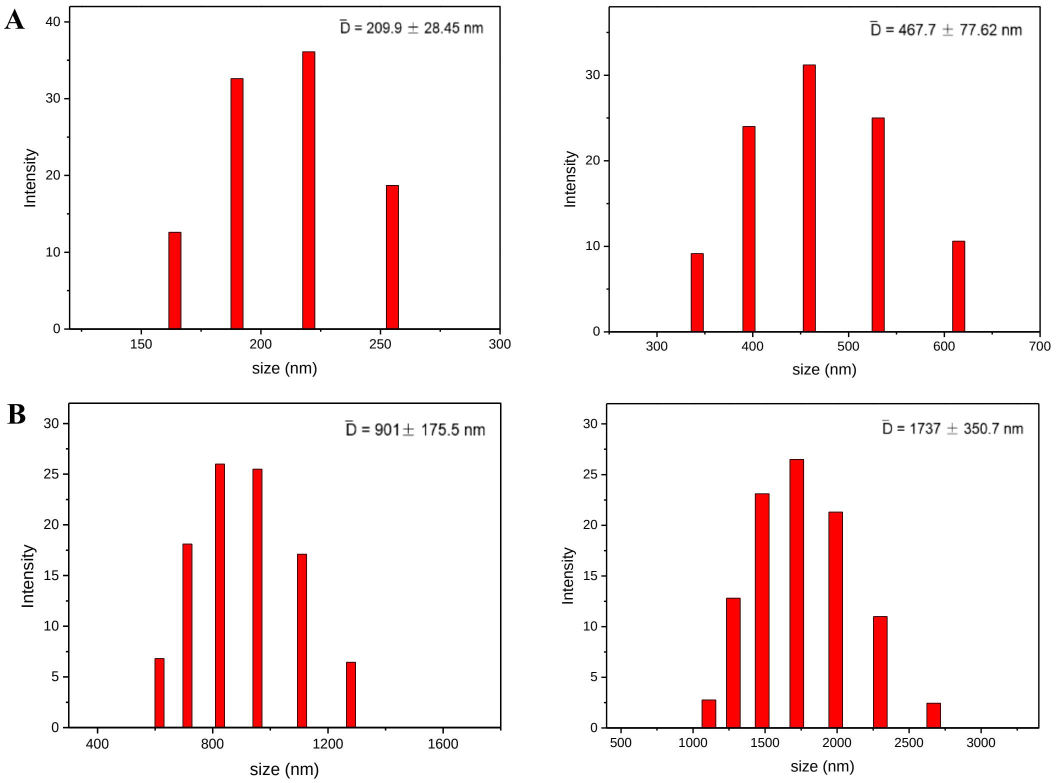


Figure S26. AIE nature characterization of ITPB monomer and it corresponding poly(ITPB) (Table 1, entry 6) in THF/water mixture. (A) Dynamic light scattering measurement of ITPB at 0% water fraction in THF-water mixture (left side) and at 80% water fraction in THF-water mixture (right side). (B) Dynamic light scattering measurement of poly(ITPB) at 0% water fraction in THF-water mixture (left side) and at 50% water fraction in THF-water mixture (right side).

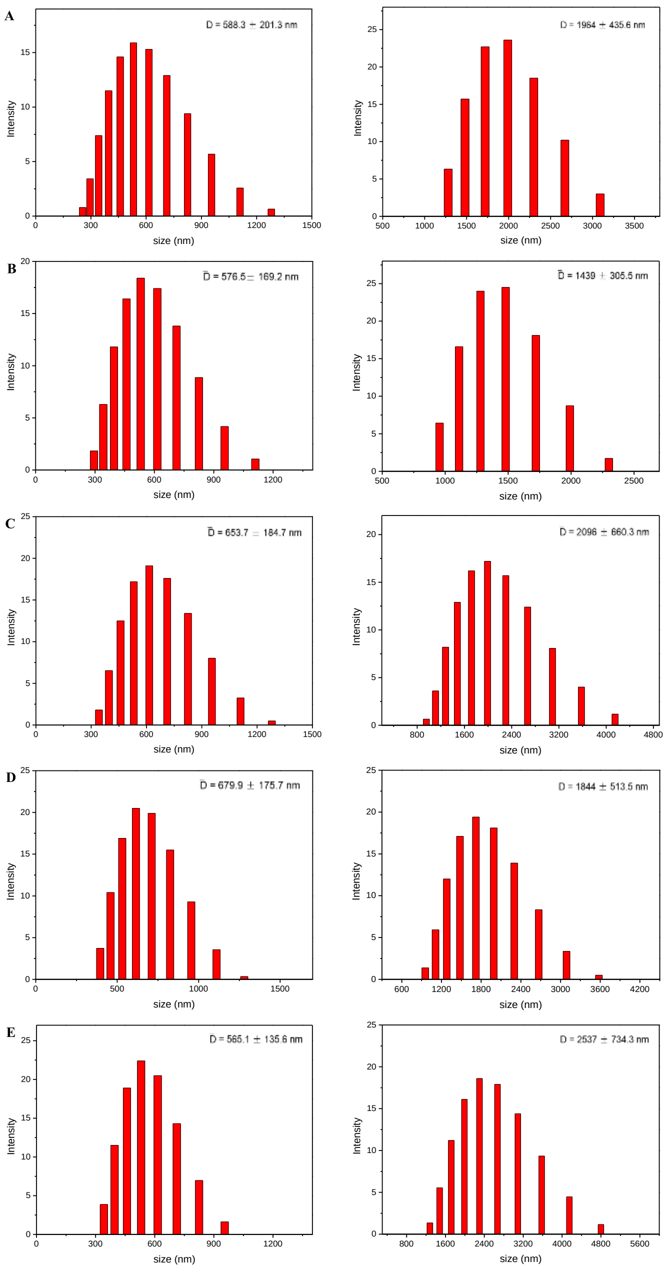


Figure S27. AIE nature characterization of poly(D-IMCI-*co*-ITPB)s in THF/water mixture. (A) Dynamic light scattering measurement of poly(D-IMCI-*co*-ITPB) (Table 2, entry 1) at 0% water fraction in THF-water mixture (left side) and at 50% water fraction in THF-water mixture (right side). (B) Dynamic 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 50% water fraction in THF-water mixture (right side). (C) Dynamic light scattering measurement of poly(D-IMCI-*co*-ITPB) (Table 2, entry 3) at 0% water fraction in THF-water mixture (left side) and at 50% water fraction in THF-water mixture (right side). (D) Dynamic light scattering measurement of poly(D-IMCI-*co*-ITPB) (Table 2, entry 4) at 0% water fraction in THF-water mixture (left side) and at 60% water fraction in THF-water mixture (right side). (E) Dynamic light scattering measurement of poly(D-IMCI-*co*-ITPB) (Table 2, entry 5) at 0% water fraction in THF-water mixture (left side) and at 60% water fraction in THF-water mixture (right side).

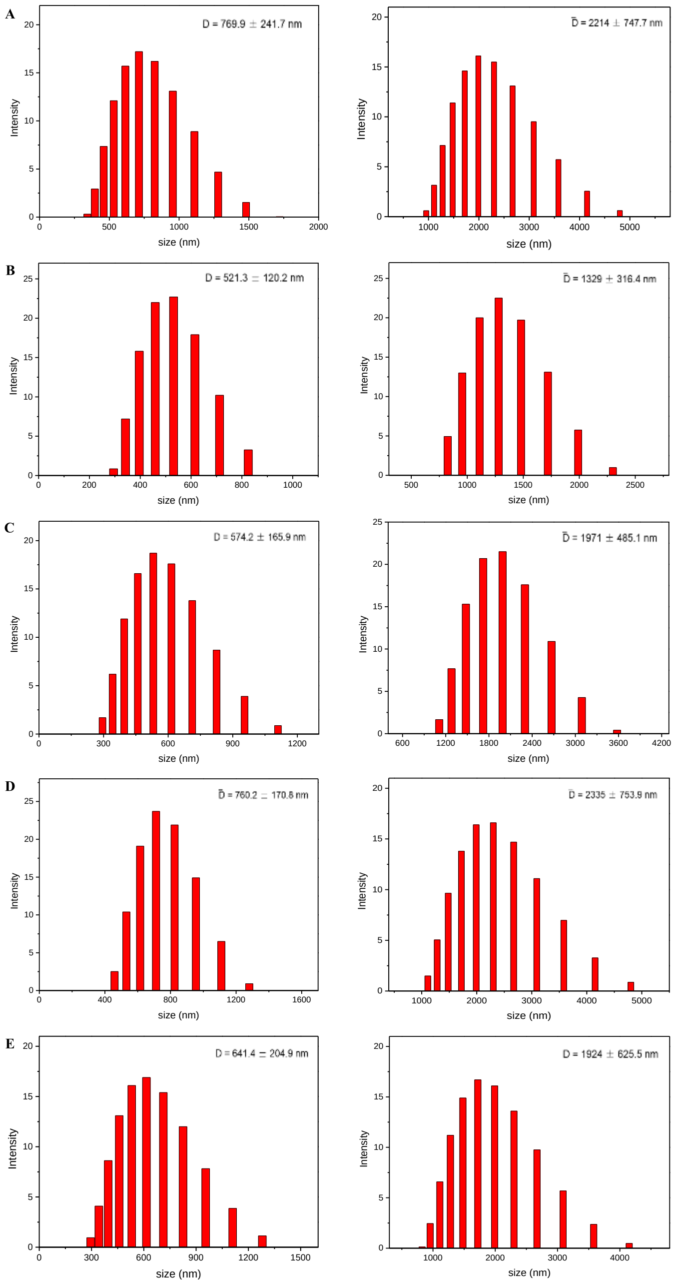


Figure S28. AIE nature characterization of poly(L-IMCI-*co*-ITPB)s in THF/water mixture. (A) Dynamic light scattering measurement of poly(L-IMCI-*co*-ITPB) (Table 2, entry 6) at 0% water fraction in THF-water mixture (left side) and at 70% water fraction in THF-water mixture (right side). (B) Dynamic light scattering measurement of poly(L-IMCI-*co*-ITPB) (Table 2, entry 7) at 0% water fraction in THF-water mixture (left side) and at 60% water fraction in THF-water mixture (right side). (C) 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 60% water fraction in THF-water mixture (right side). (D) Dynamic light scattering measurement of poly(L-IMCI-*co*-ITPB) (Table 2, entry 9) at 0% water fraction in THF-water mixture (left side) and at 50% water fraction in THF-water mixture (right side). (E) Dynamic light scattering measurement of poly(L-IMCI-*co*-ITPB) (Table 2, entry 10) at 0% water fraction in THF-water mixture (left side) and at 60% water fraction in THF-water mixture (right side).

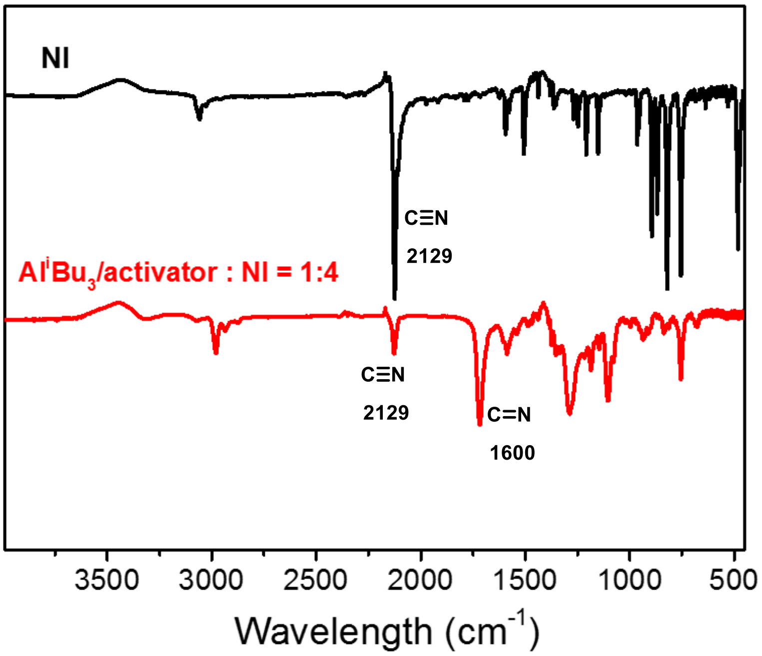


Figure S29. FT-IR spectrum of NI and the compound obtained from the reaction of Al^{i}Bu$_3$/activator with **4** equiv. of NI.

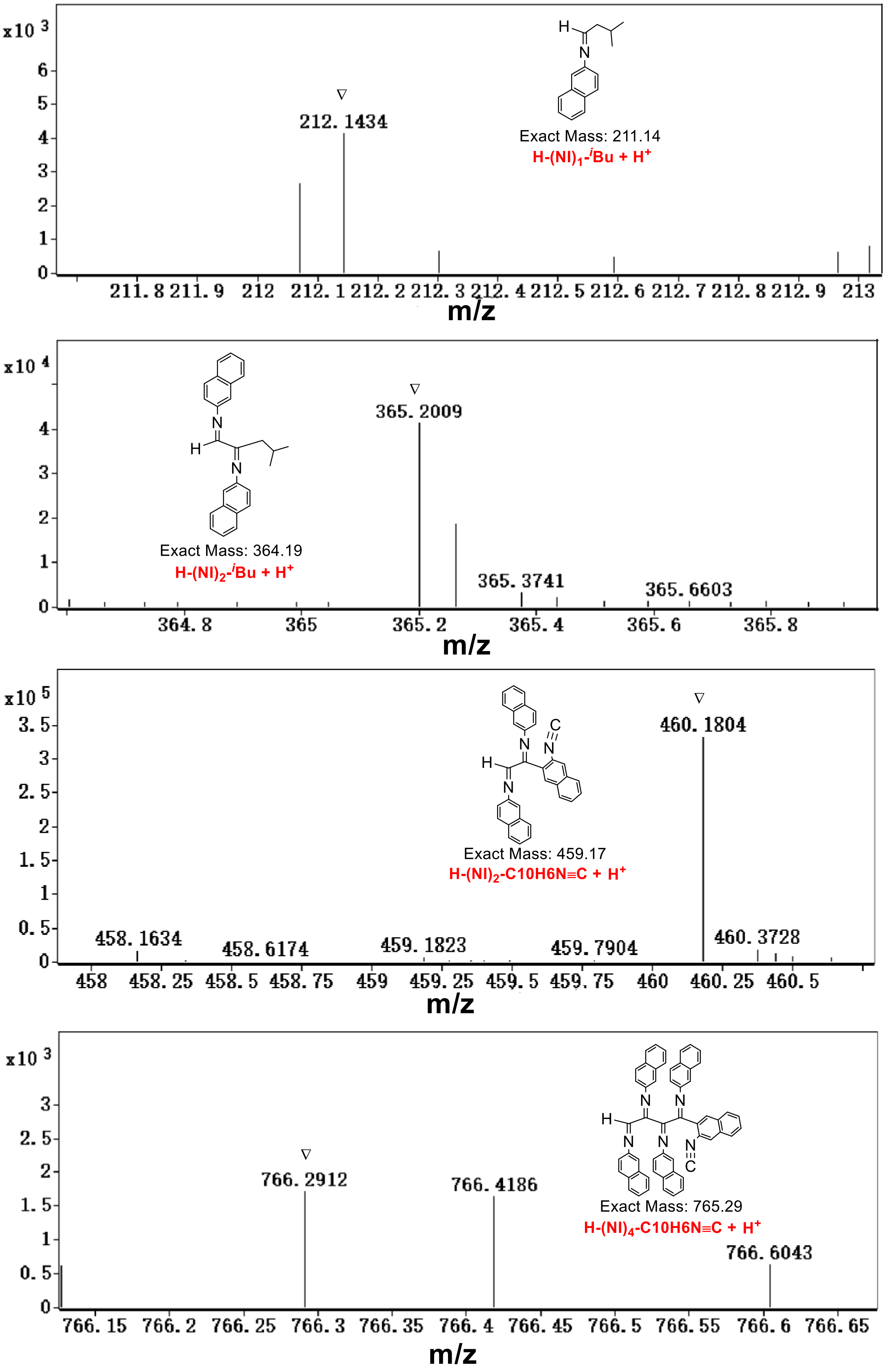
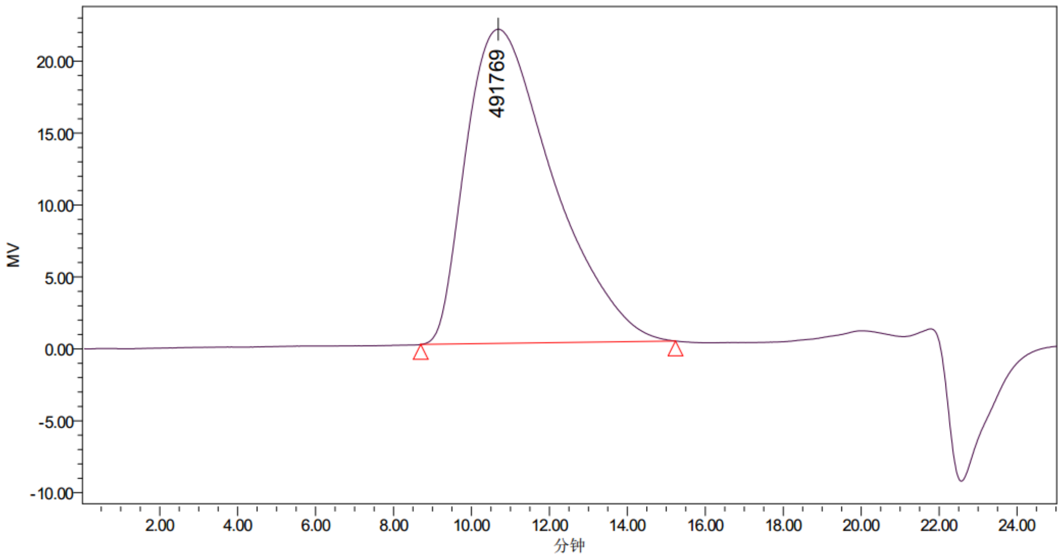


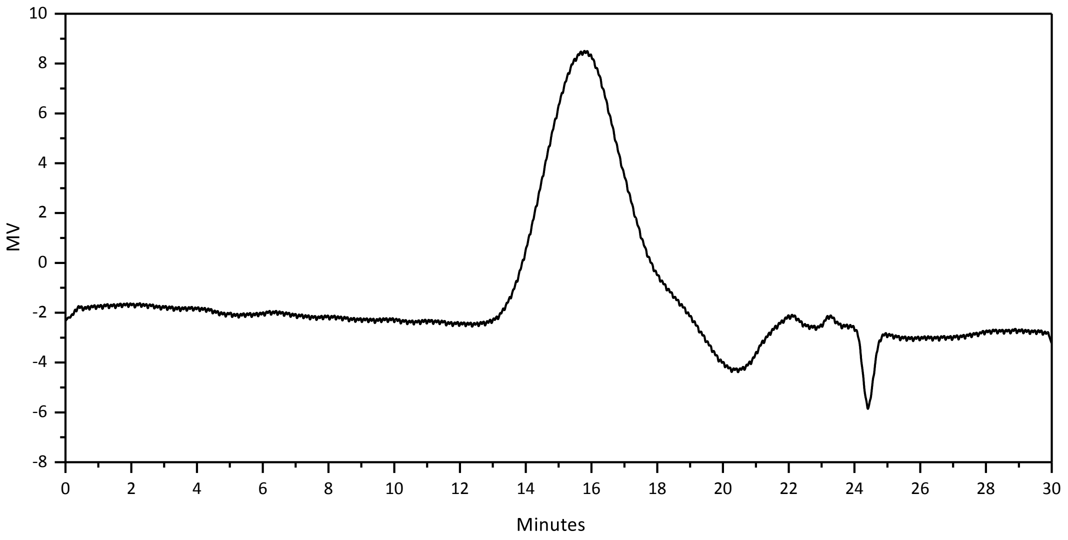
Figure S30. High resolution ESI-MS spectra of NI oligomer obtained by the Al^{i}Bu$_3$/activator binary systems in PhCl.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		10.687	10.687	10.687	188938	520632	491769	1089676	1738002	2.092986

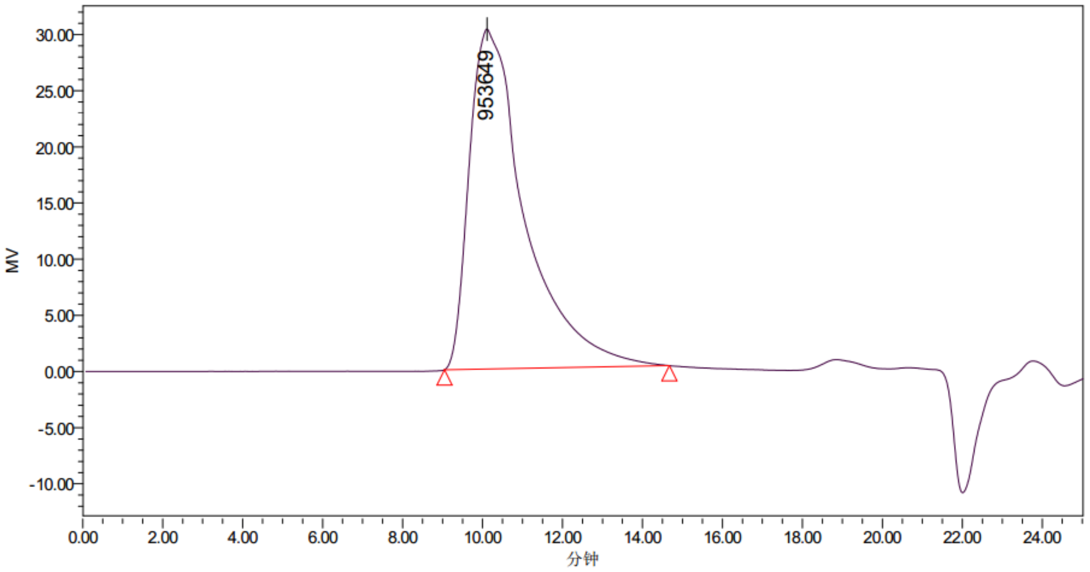
Figure S31. GPC curve of poly(IPI) obtained by cationic Aluminum complex in Table 1, entry 2.



Broad Unknown Relative Peak Table

	Distributionn Name	Mn (Daltons)	Mw (Daltons)	Mp (Daltons)	Mz (Daltons)	polydispersity	Mz/Mw
1		175702	608228	355534	1573708	3.46170	2.58736

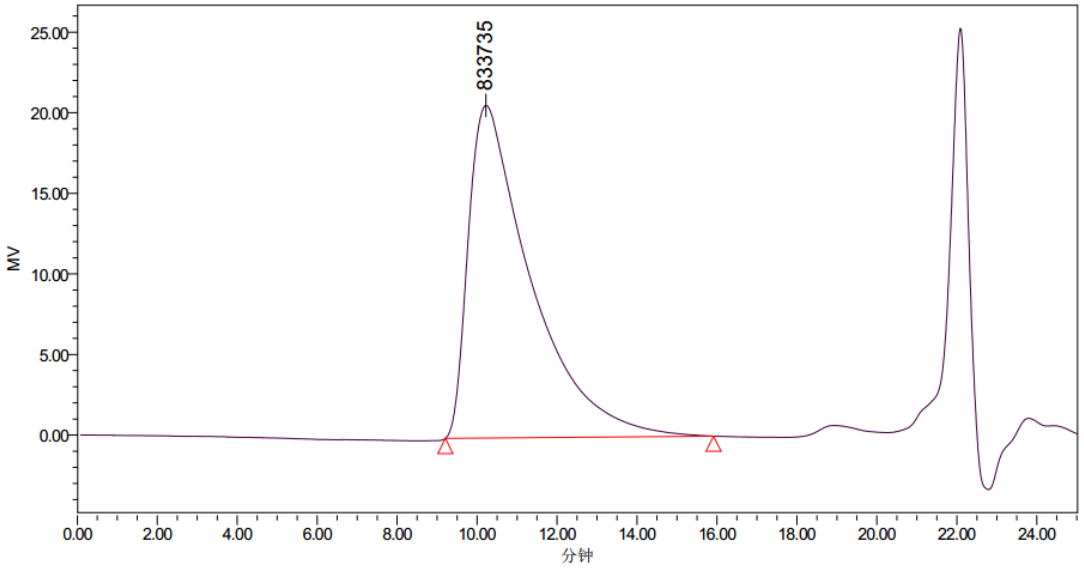
Figure S32. GPC curve of poly(EPI) obtained by cationic Aluminum complex in Table 1, entry 3.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		10.110	10.110	10.110	359956	774783	953649	1165729	1495519	1.504587

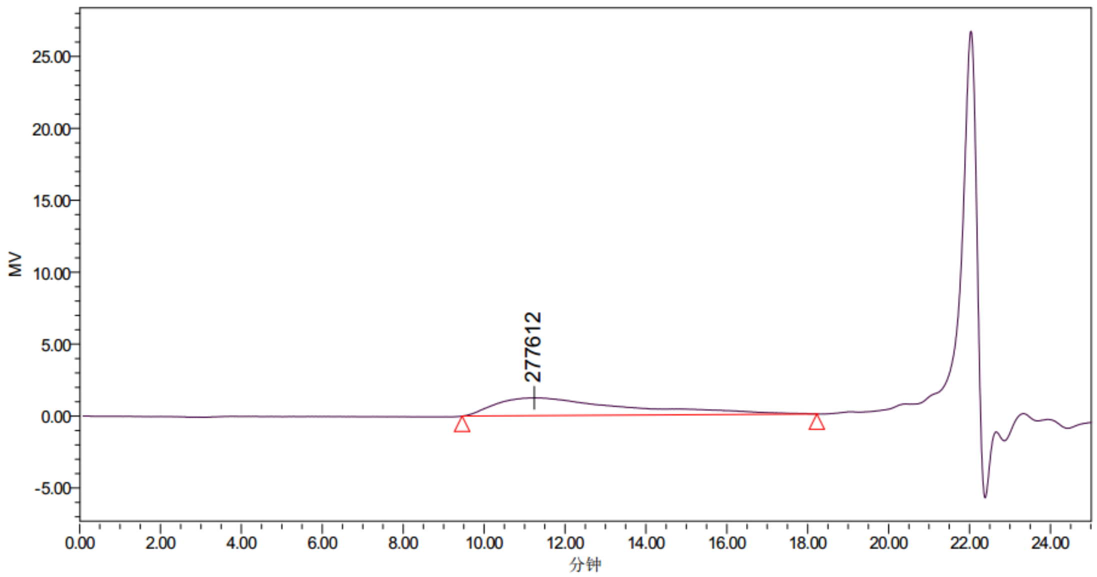
Figure S33. GPC curve of poly(D-IMCI) obtained by cationic Aluminum complex in Table 1, entry 4.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		10.223	10.223	10.223	247311	611981	833735	965223	1242116	1.577212

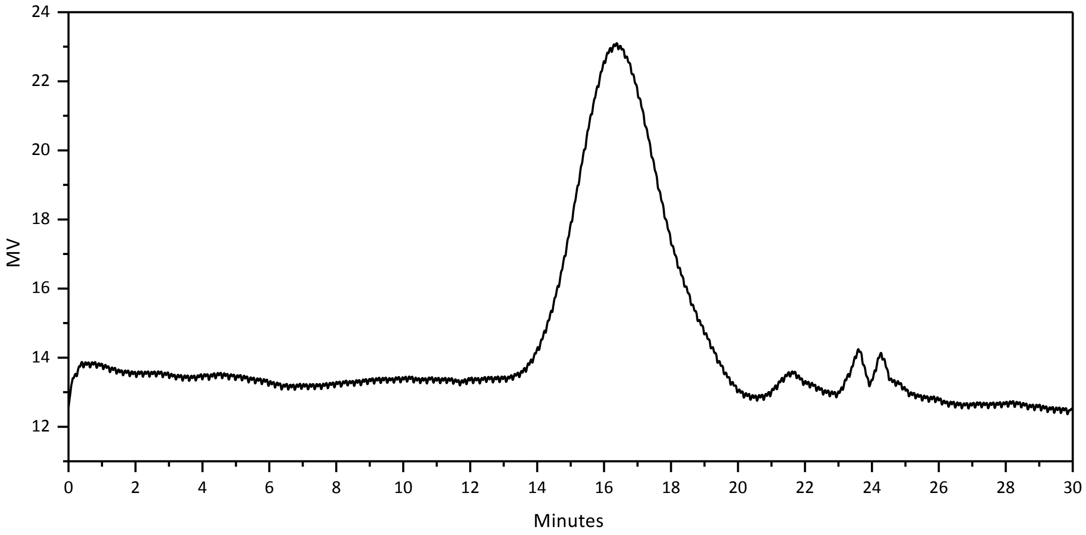
Figure S34. GPC curve of poly(L-IMCI) obtained by cationic Aluminum complex in Table 1, entry 5.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		11.242	11.242	11.242	42394	240529	277612	594131	894547	2.470106

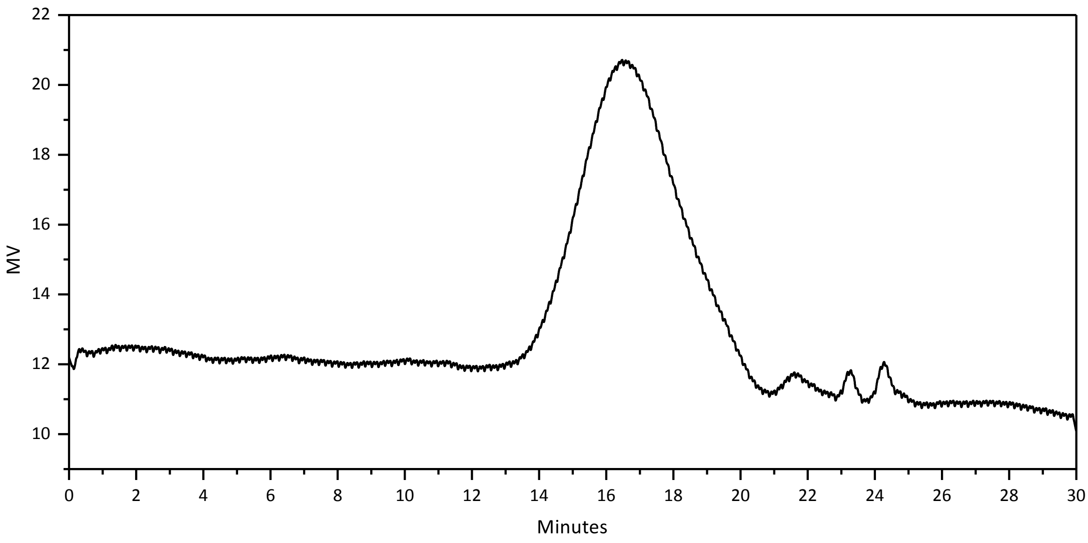
Figure S35. GPC curve of poly(ITPB) obtained by cationic Aluminum complex in Table 1, entry 6.



Broad Unknown Relative Peak Table

	Distributionn Name	Mn (Daltons)	Mw (Daltons)	Mp (Daltons)	Mz (Daltons)	polydispersity	Mz/Mw
1		92384	335743	219647	908251	3.63421	2.70520

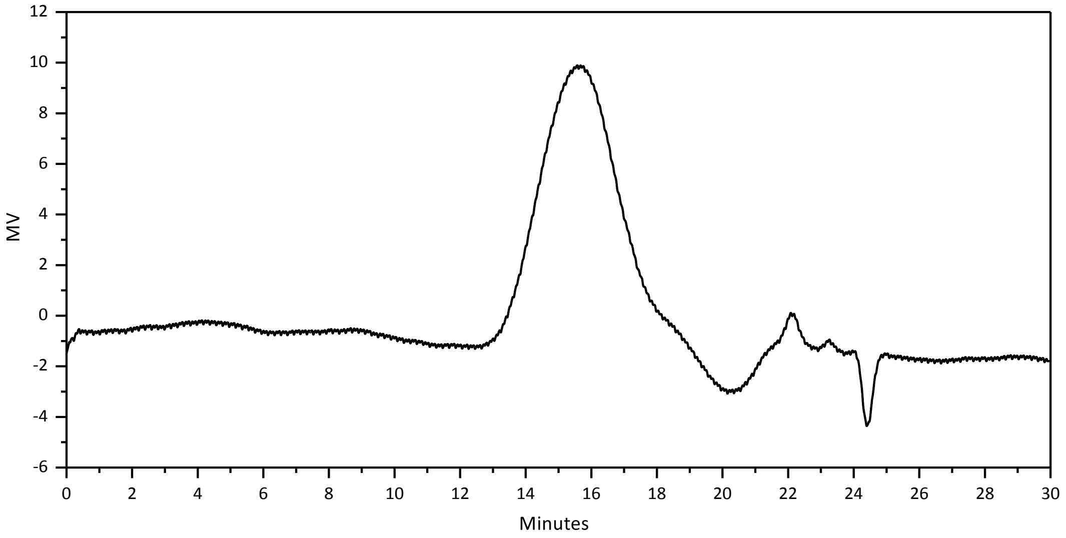
Figure S36. GPC curve of poly(EPI) obtained by cationic Aluminum complex in Table 1, entry 7.



Broad Unknown Relative Peak Table

	Distributionn Name	Mn (Daltons)	Mw (Daltons)	Mp (Daltons)	Mz (Daltons)	polydispersity	Mz/Mw
1		63859	349503	185478	1410692	5.47304	4.03628

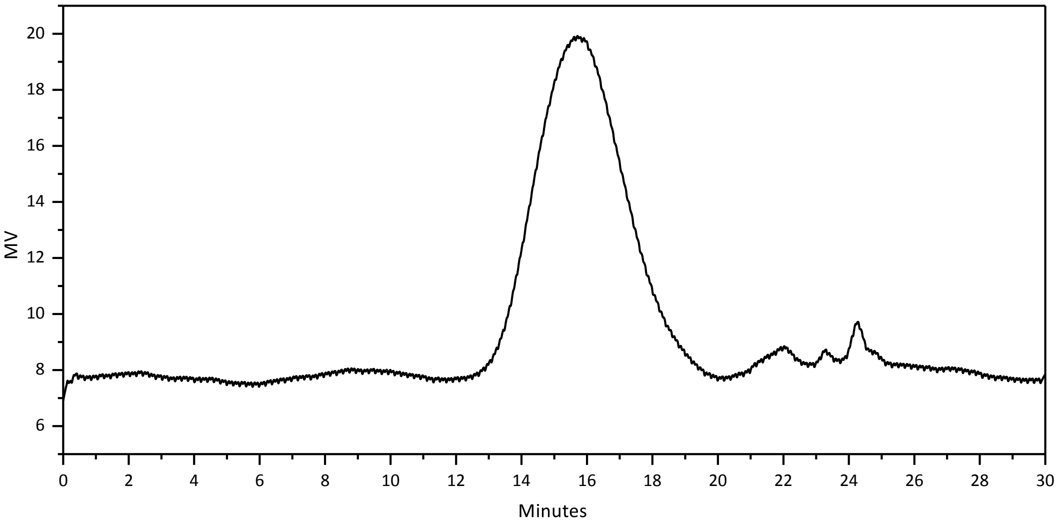
Figure S37. GPC curve of poly(EPI) obtained by cationic Aluminum complex in Table 1, entry 8.



Broad Unknown Relative Peak Table

	Distributionn Name	Mn (Daltons)	Mw (Daltons)	Mp (Daltons)	Mz (Daltons)	polydispersity	Mz/Mw
1		232934	682225	396842	1593774	2.92883	2.33614

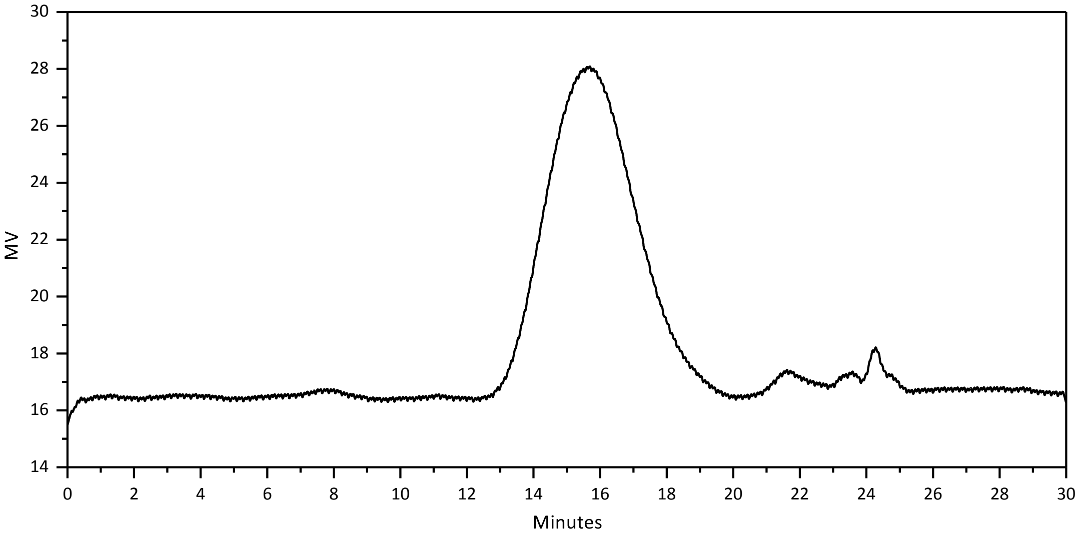
Figure S38. GPC curve of poly(EPI) obtained by cationic Aluminum complex in Table 1, entry 9.



Broad Unknown Relative Peak Table

	Distributionn Name	Mn (Daltons)	Mw (Daltons)	Mp (Daltons)	Mz (Daltons)	polydispersity	Mz/Mw
1		176735	686862	386399	2046966	3.88639	2.98017

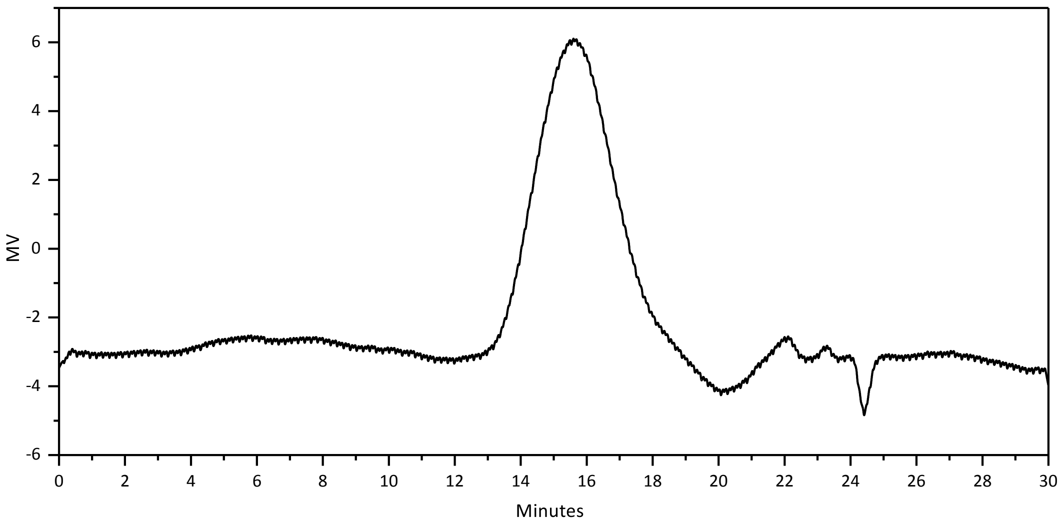
Figure S39. GPC curve of poly(EPI) obtained by cationic Aluminum complex in Table 1, entry 10.



Broad Unknown Relative Peak Table

	Distributionn Name	Mn (Daltons)	Mw (Daltons)	Mp (Daltons)	Mz (Daltons)	polydispersity	Mz/Mw
1		188042	685364	420833	1788946	3.64474	2.61021

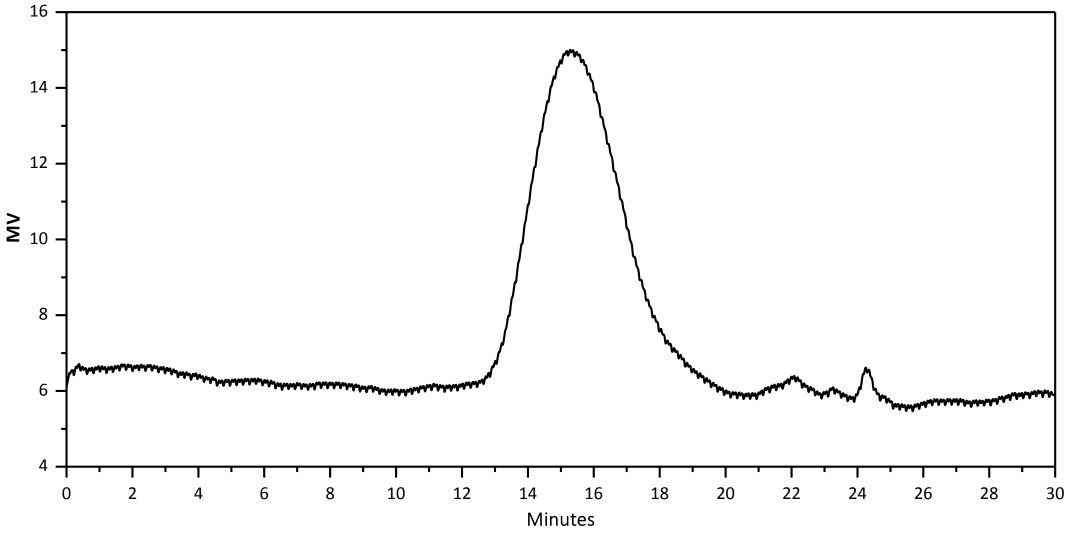
Figure S40. GPC curve of poly(EPI) obtained by cationic Aluminum complex in Table 1, entry 11.



Broad Unknown Relative Peak Table

	Distributionn Name	Mn (Daltons)	Mw (Daltons)	Mp (Daltons)	Mz (Daltons)	polydispersity	Mz/Mw
1		256918	642866	424145	1356625	2.50222	2.11028

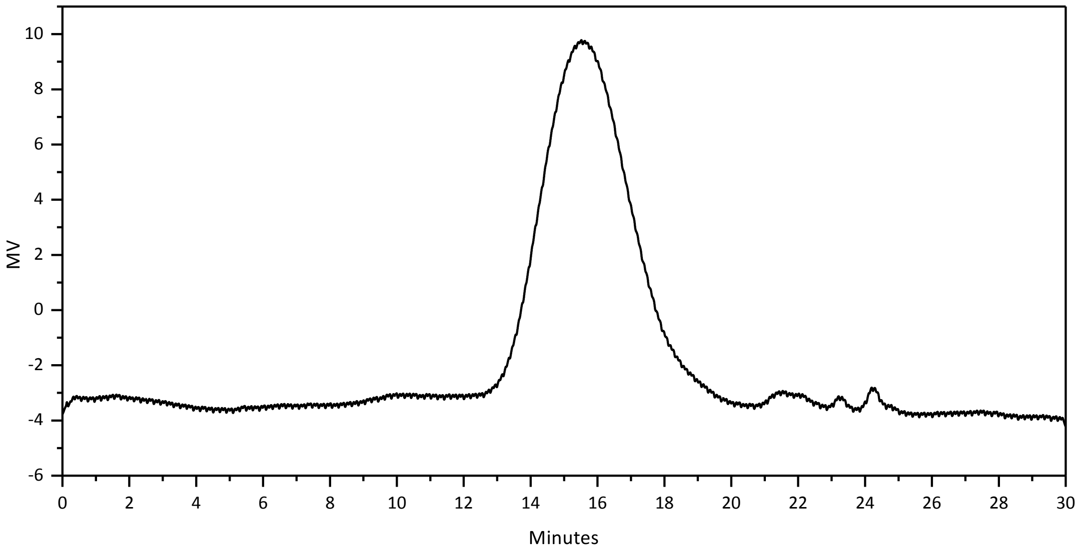
Figure S41. GPC curve of poly(EPI) obtained by cationic Aluminum complex in Table 1, entry 12.



Broad Unknown Relative Peak Table

	Distributionn Name	Mn (Daltons)	Mw (Daltons)	Mp (Daltons)	Mz (Daltons)	polydispersity	Mz/Mw
1		165129	899032	600807	2724886	5.44442	3.03091

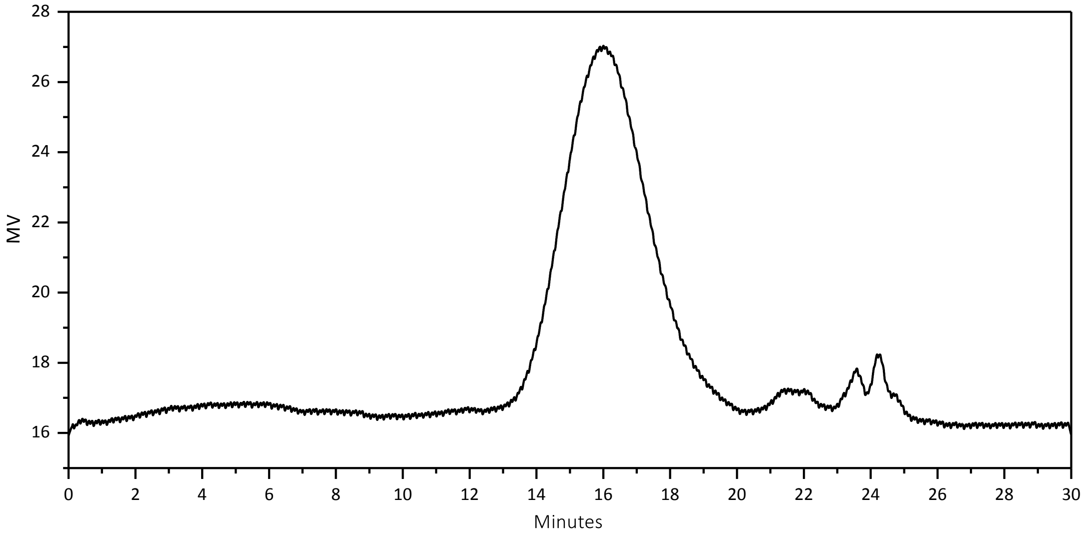
Figure S42. GPC curve of poly(EPI) obtained by cationic Aluminum complex in Table 1, entry 13.



Broad Unknown Relative Peak Table

	Distributionn Name	Mn (Daltons)	Mw (Daltons)	Mp (Daltons)	Mz (Daltons)	polydispersity	Mz/Mw
1		189312	745486	493060	2163595	3.93787	2.90226

Figure S43. GPC curve of poly(EPI) obtained by cationic Aluminum complex in Table 1, entry 14.

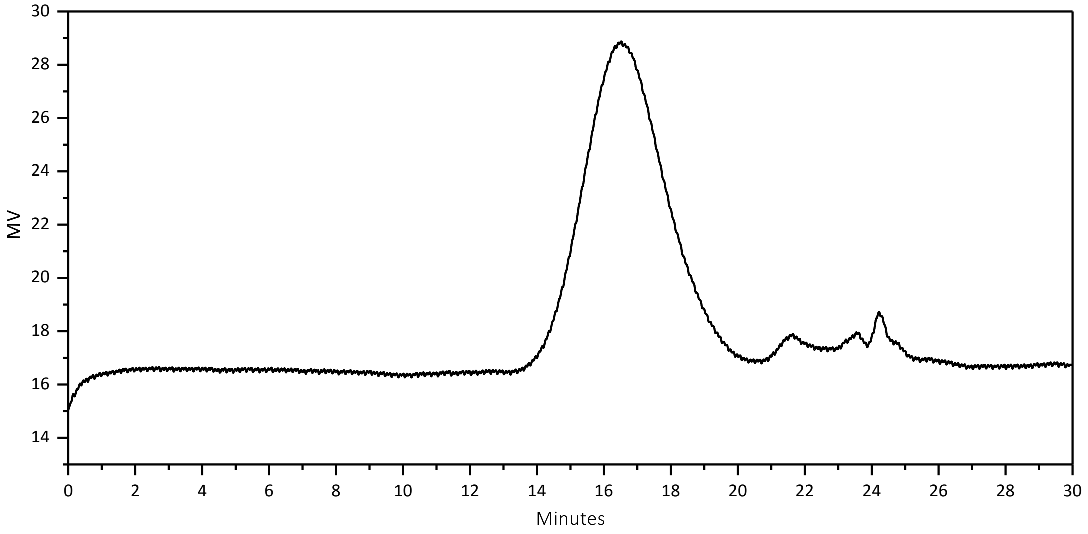


Broad Unknown Relative Peak Table

	Distributionn Name	Mn (Daltons)	Mw (Daltons)	Mp (Daltons)	Mz (Daltons)	polydispersity	Mz/Mw
1		142084	462844	292881	1140673	3.25754	2.46448

Figure S44. GPC curve of poly(EPI) obtained by cationic Aluminum complex in Table 1, entry

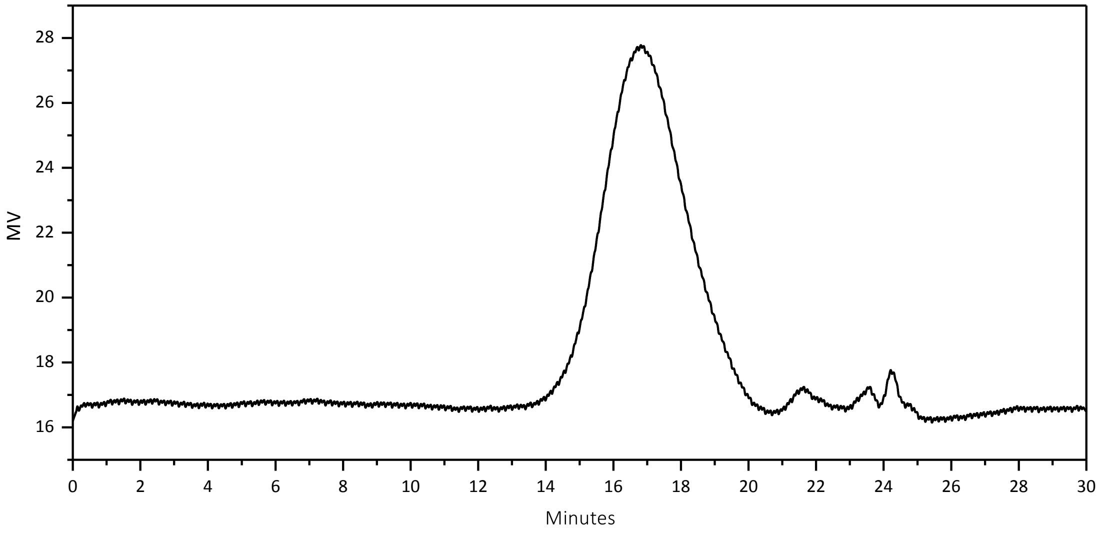
15.



Broad Unknown Relative Peak Table

	Distributionn Name	Mn (Daltons)	Mw (Daltons)	Mp (Daltons)	Mz (Daltons)	polydispersity	Mz/Mw
1		83402	267113	193797	630258	3.20272	2.35952

Figure S45. GPC curve of poly(EPI) obtained by cationic Aluminum complex in Table 1, entry 16.

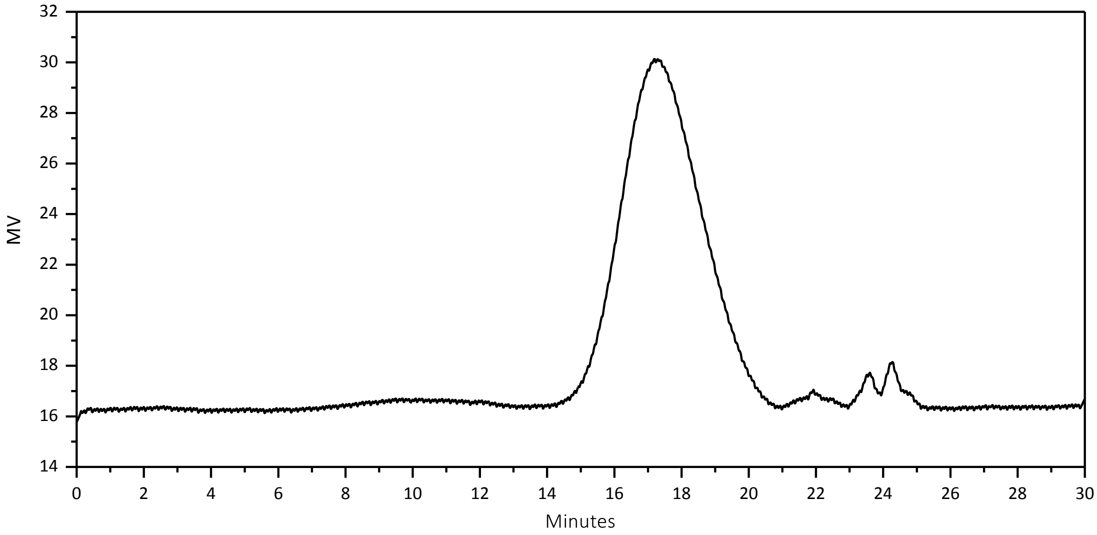


Broad Unknown Relative Peak Table

	Distributionn Name	Mn (Daltons)	Mw (Daltons)	Mp (Daltons)	Mz (Daltons)	polydispersity	Mz/Mw
1		67643	219321	139692	606268	3.24233	2.76430

Figure S46. GPC curve of poly(EPI) obtained by cationic Aluminum complex in Table 1, entry

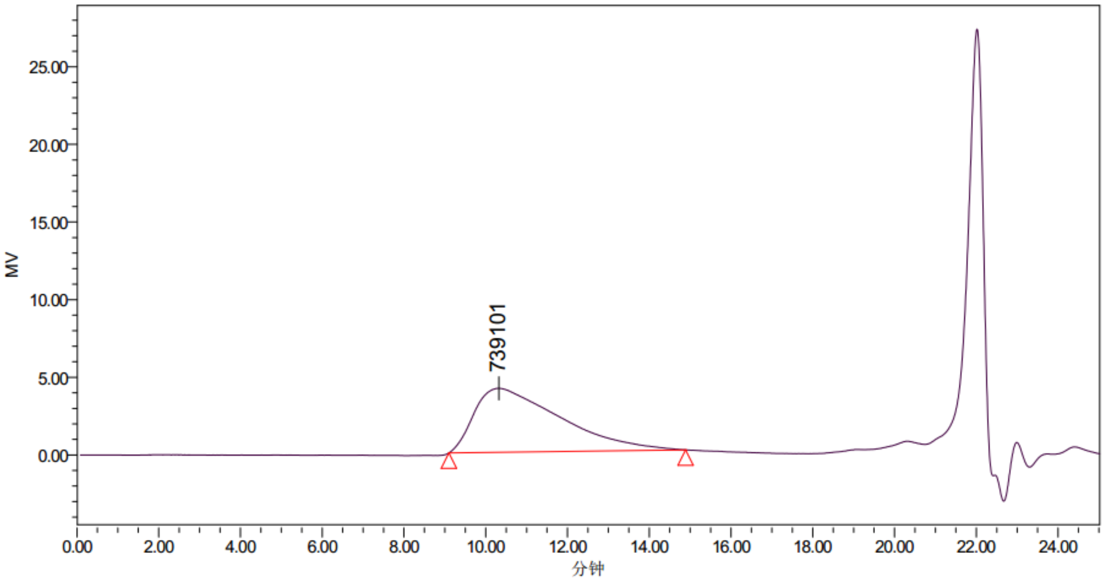
17.



Broad Unknown Relative Peak Table

	Distributionn Name	Mn (Daltons)	Mw (Daltons)	Mp (Daltons)	Mz (Daltons)	polydispersity	Mz/Mw
1		45276	123026	90410	256303	2.71724	2.08332

Figure S47. GPC curve of poly(EPI) obtained by cationic Aluminum complex in Table 1, entry 18.

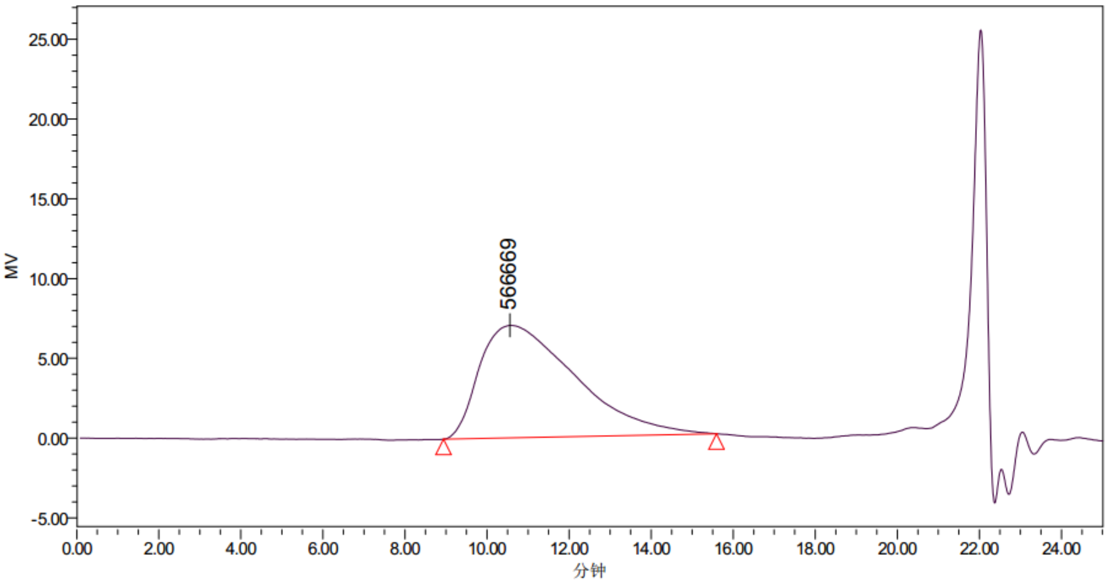


GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		10.325	10.325	10.325	208468	577947	739101	1083105	1521525	1.874057

Figure S48. GPC curve of poly(D-IMCI-*co*-ITPB) obtained by cationic Aluminum complex in

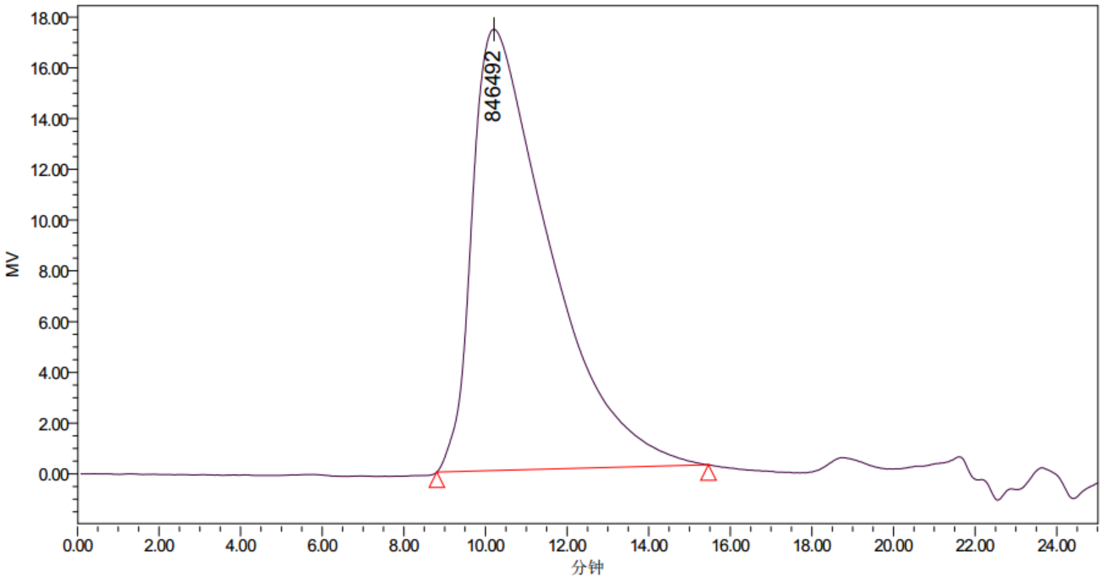
Table 2, entry 1.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		10.558	10.558	10.558	167854	502774	566669	1022794	1531489	2.034300

Figure S49. GPC curve of poly(D-IMCI-*co*-ITPB) obtained by cationic Aluminum complex in Table 2, entry 2.

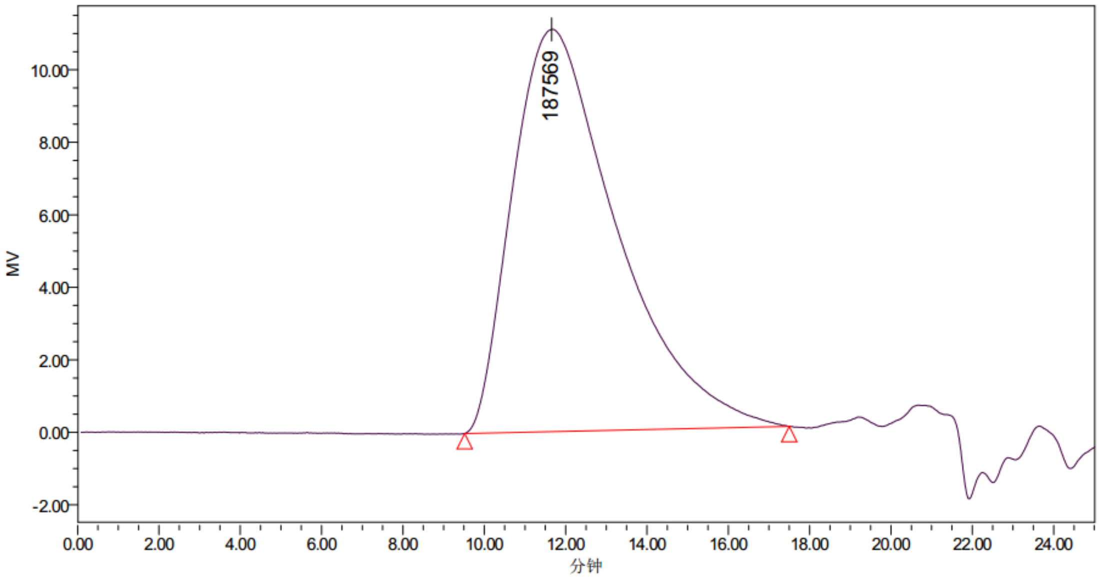


GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		10.210	10.210	10.210	227964	648683	846492	1211986	1802848	1.868379

Figure S50. GPC curve of poly(D-IMCI-*co*-ITPB) obtained by cationic Aluminum complex in

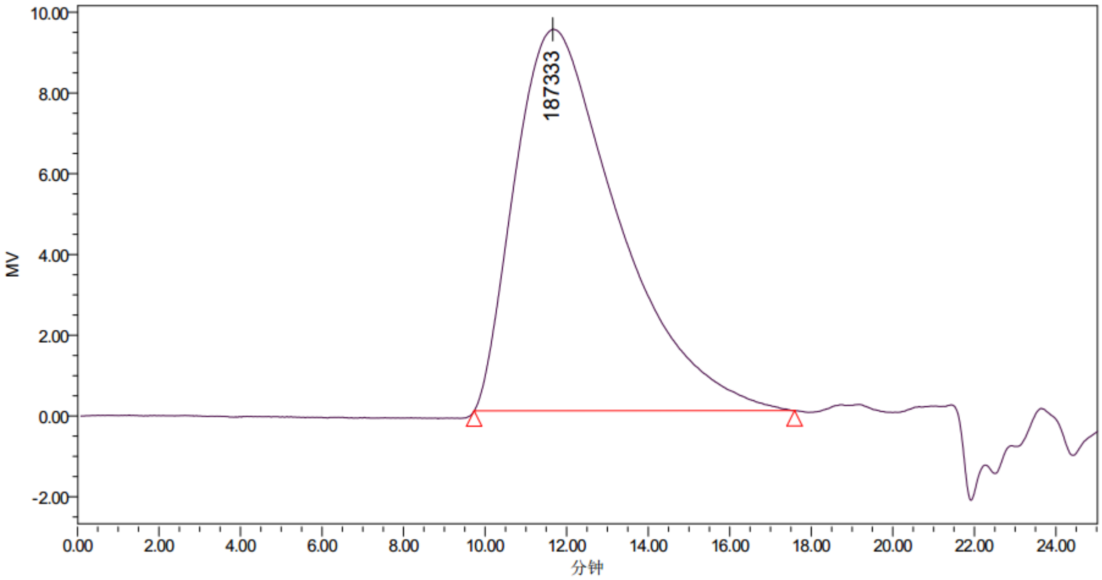
Table 2, entry 3.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		11.658	11.658	11.658	70236	200224	187569	412394	645036	2.059663

Figure S51. GPC curve of poly(D-IMCI-*co*-ITPB) obtained by cationic Aluminum complex in Table 2, entry 4.

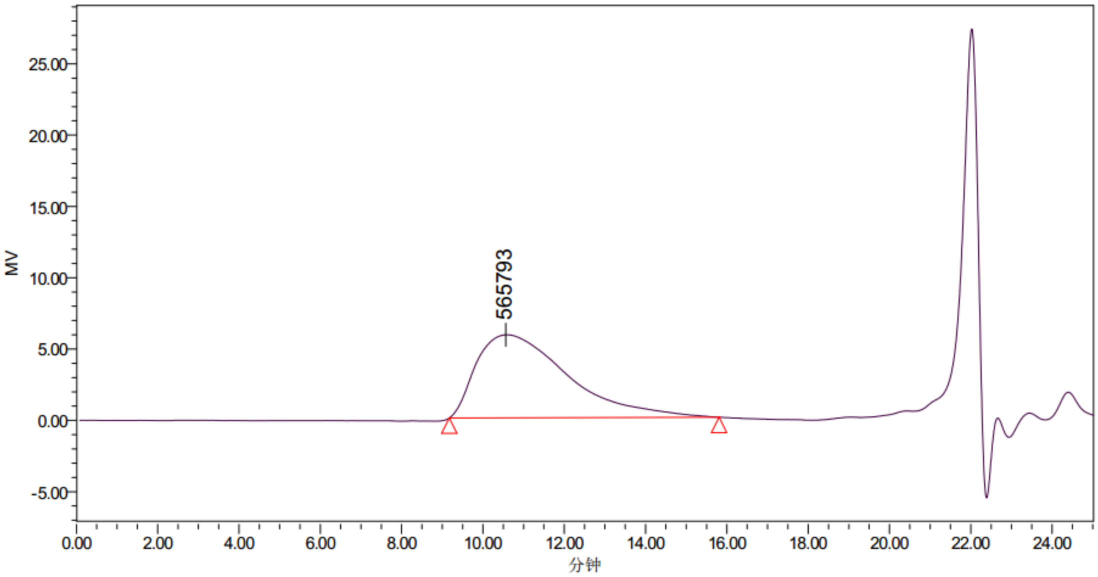


GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		11.660	11.660	11.660	69431	191866	187333	380873	575800	1.985102

Figure S52. GPC curve of poly(D-IMCI-*co*-ITPB) obtained by cationic Aluminum complex in

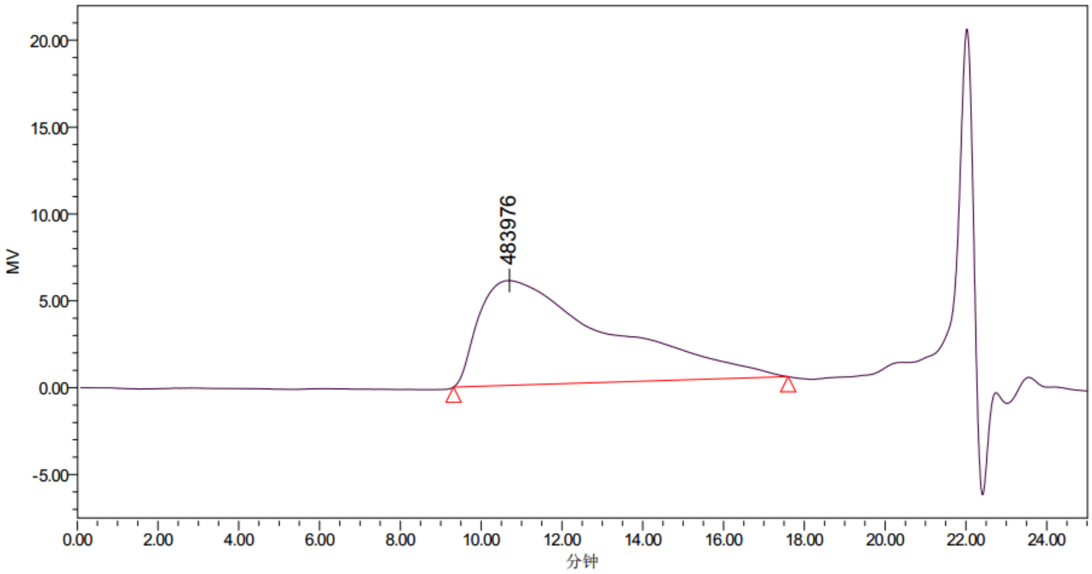
Table 2, entry 5.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		10.560	10.560	10.560	164598	496596	565793	954825	1357301	1.922740

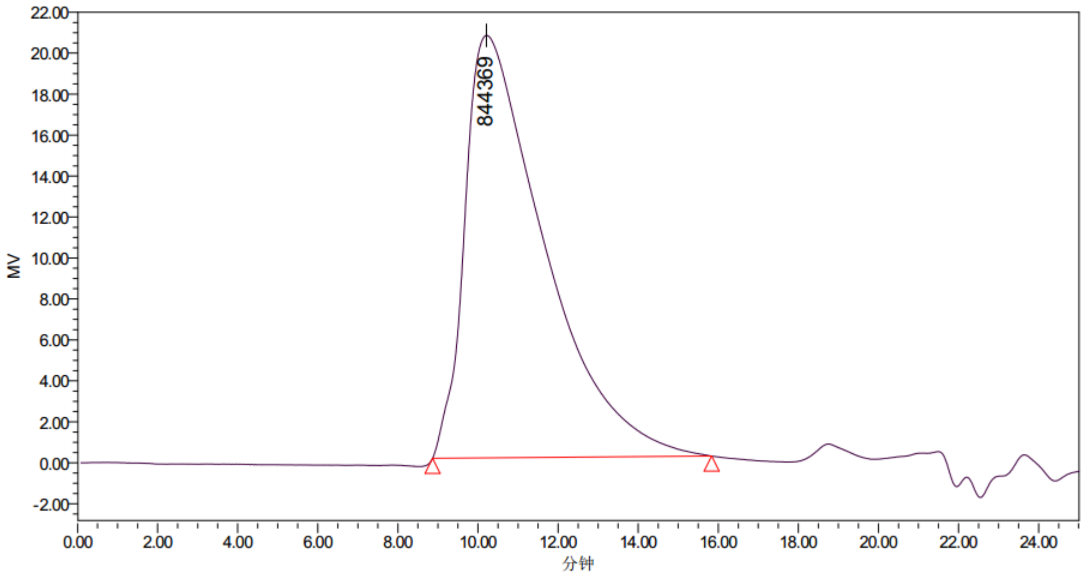
Figure S53. GPC curve of poly(L-IMCI-*co*-ITPB) obtained by cationic Aluminum complex in Table 2, entry 6.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		10.702	10.702	10.702	53596	317359	483976	772497	1108902	2.434143

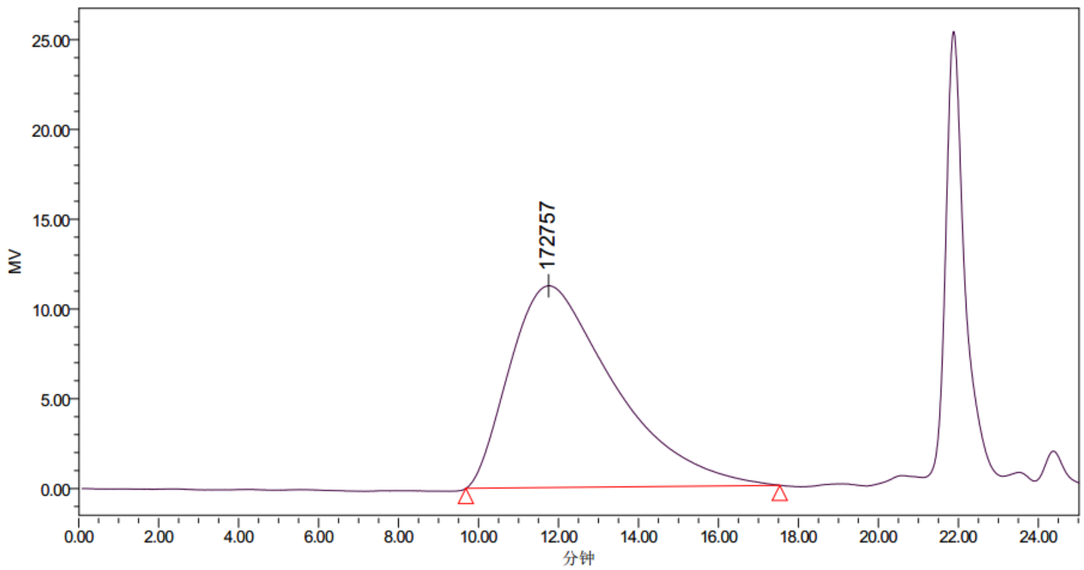
Figure S54. GPC curve of poly(L-IMCI-*co*-ITPB) obtained by cationic Aluminum complex in Table 2, entry 7.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		10.212	10.212	10.212	206678	637623	844369	1243797	1875078	1.950676

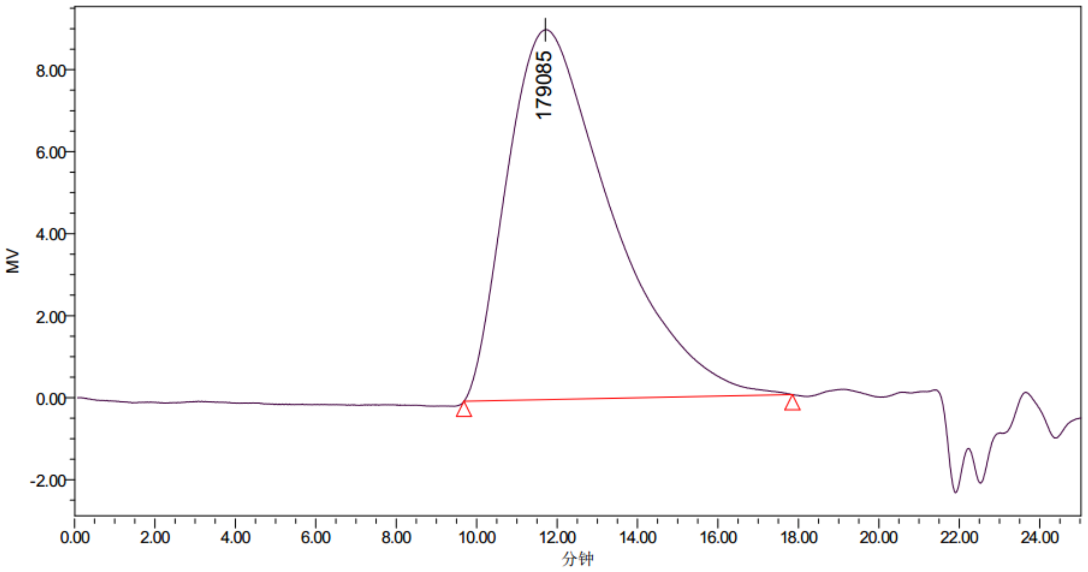
Figure S55. GPC curve of poly(L-IMCI-*co*-ITPB) obtained by cationic Aluminum complex in Table 2, entry 8.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		11.750	11.750	11.750	64496	181799	172757	374291	582445	2.058822

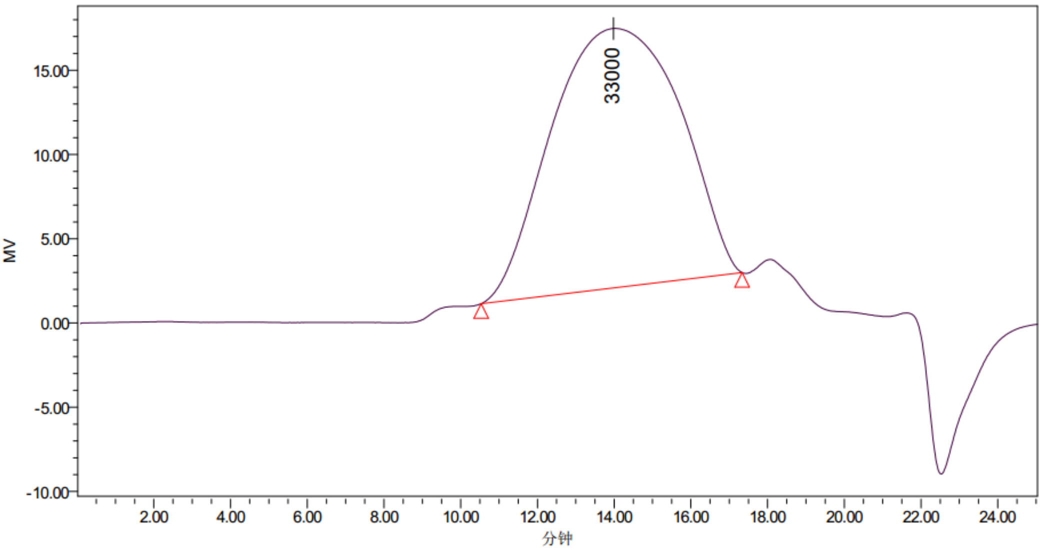
Figure S56. GPC curve of poly(L-IMCI-*co*-ITPB) obtained by cationic Aluminum complex in Table 2, entry 9.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		11.710	11.710	11.710	66191	187372	179085	382444	590673	2.041090

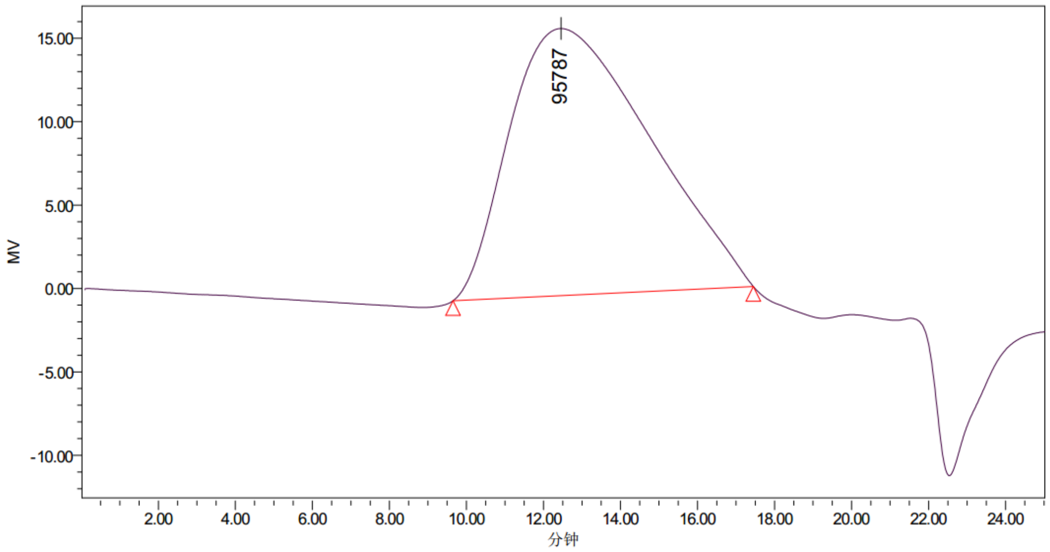
Figure S57. GPC curve of poly(L-IMCI-*co*-ITPB) obtained by cationic Aluminum complex in Table 2, entry 10.



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		13.983	13.983	13.983	24014	50050	33000	105815	180375	2.114190	3.603892

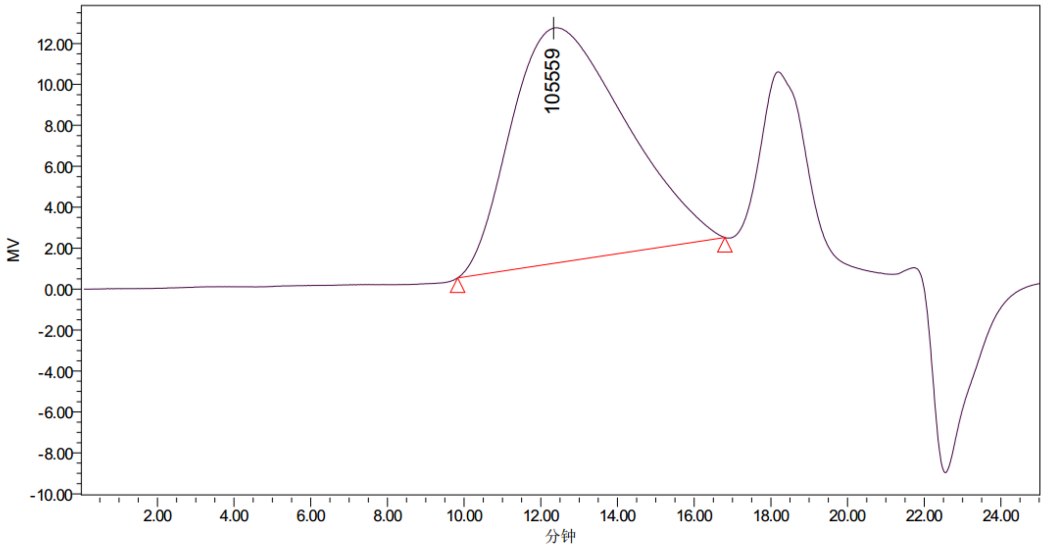
Figure S58. GPC curve of poly(D-IMCI-*co*-IPI) obtained by cationic Aluminum complex in Table 2, entry 11.



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		12.456	12.456	12.456	35324	117786	95787	316310	562503	2.685457	4.775628

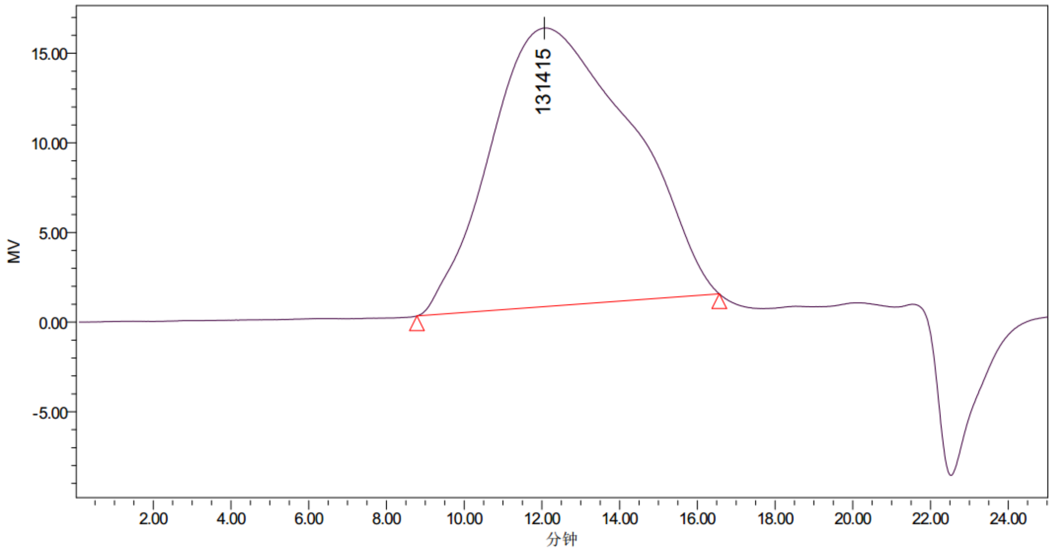
Figure S59. GPC curve of poly(D-IMCI-*co*-IPI) obtained by cationic Aluminum complex in Table 2, entry 12.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		12.333	12.333	12.333	47979	119206	105559	260255	435681	2.183233

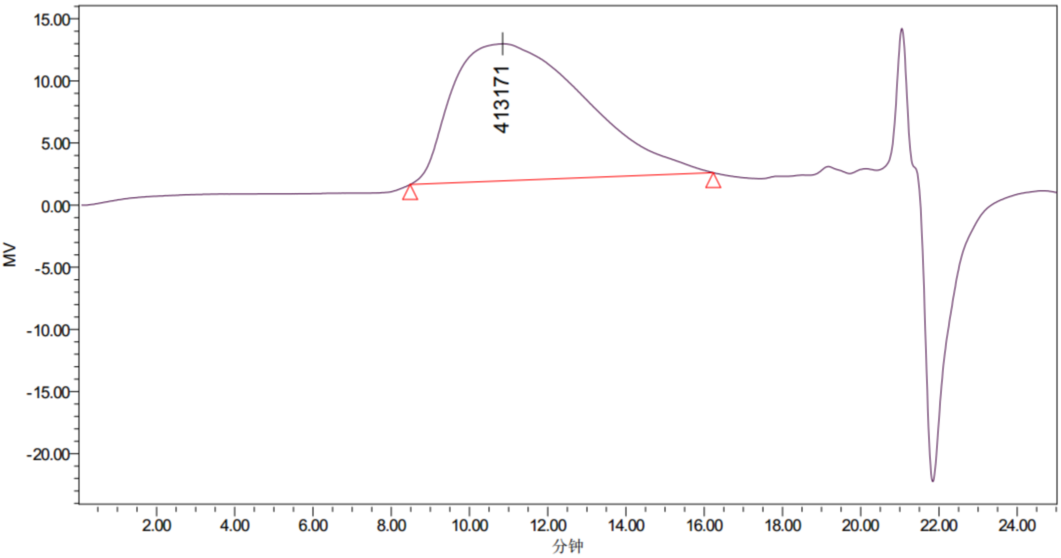
Figure S60. GPC curve of poly(D-IMCI-*co*-IPI) obtained by cationic Aluminum complex in Table 2, entry 13.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		12.066	12.066	12.066	51547	211679	131415	867725	1866372	4.099256

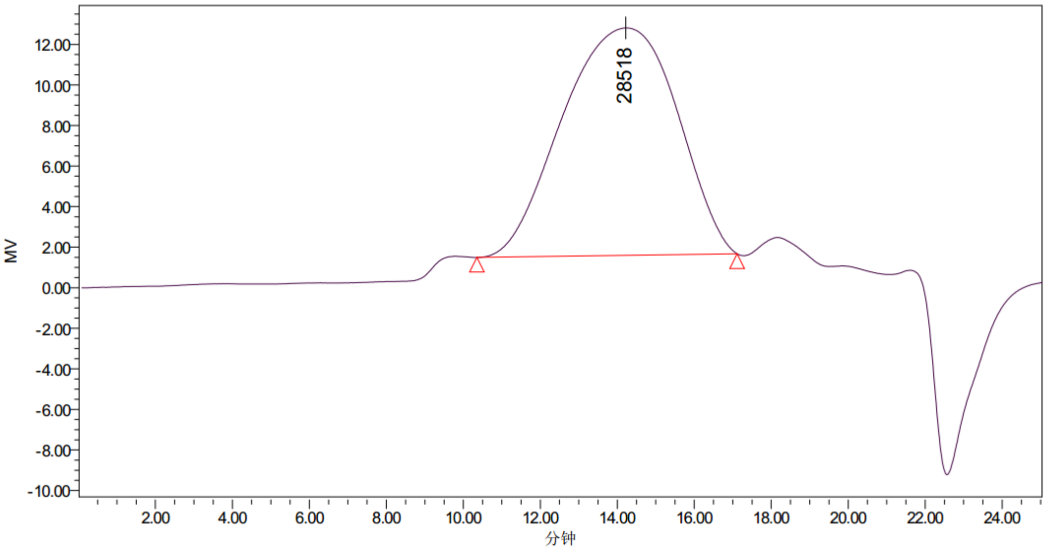
Figure S61. GPC curve of poly(D-IMCI-*co*-IPI) obtained by cationic Aluminum complex in Table 2, entry 14.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		10.850	10.850	10.850	108042	576199	413171	1786953	3089361	3.101279

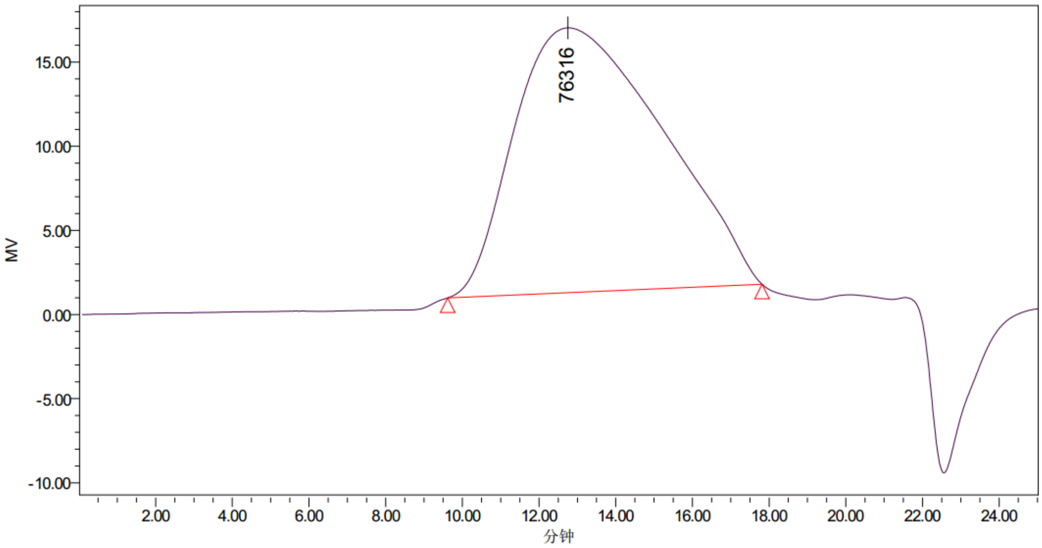
Figure S62. GPC curve of poly(D-IMCI-*co*-IPI) obtained by cationic Aluminum complex in Table 2, entry 15.



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		14.219	14.219	14.219	25407	47355	28518	95190	167169	2.010141	3.530111

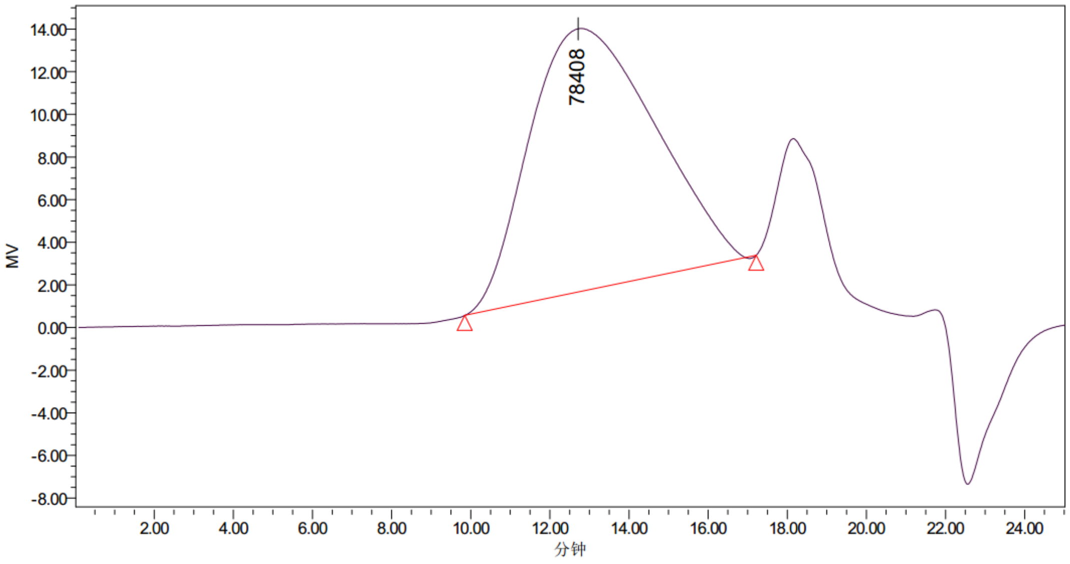
Figure S63. GPC curve of poly(L-IMCI-*co*-IPI) obtained by cationic Aluminum complex in Table 2, entry 16.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1		12.753	12.753	12.753	27712	93189	76316	262296	497635	2.814667	5.340056

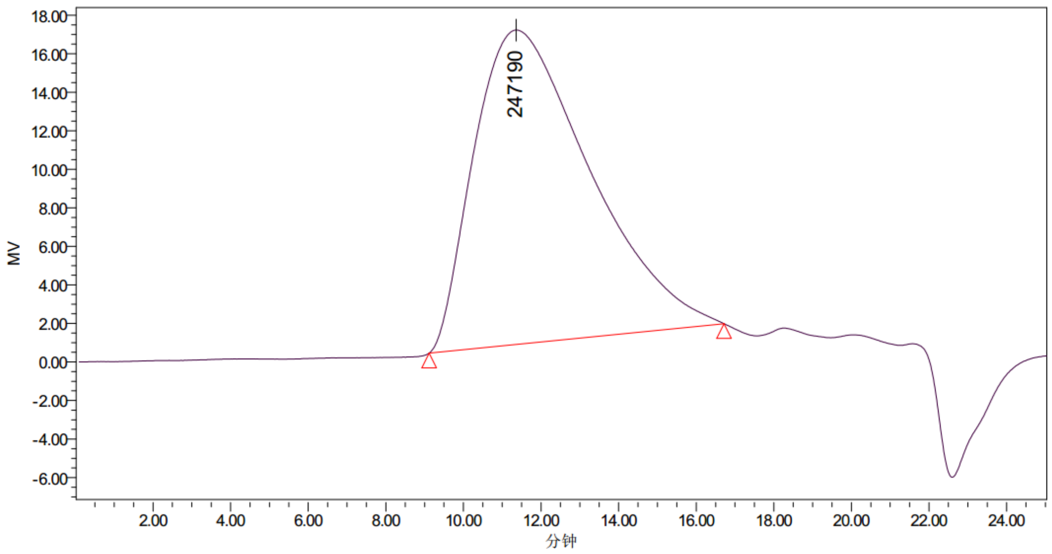
Figure S64. GPC curve of poly(L-IMCI-*co*-IPI) obtained by cationic Aluminum complex in Table 2, entry 17.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1		12.717	12.717	12.717	39513	96594	78408	219047	383171	2.267711	3.966828

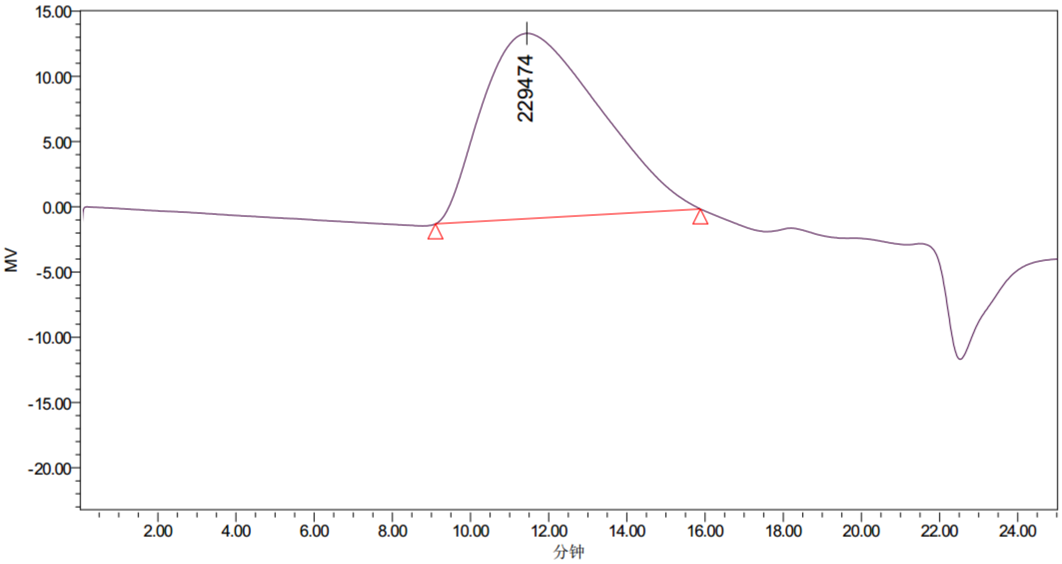
Figure S65. GPC curve of poly(L-IMCI-*co*-IPI) obtained by cationic Aluminum complex in Table 2, entry 18.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		11.362	11.362	11.362	79565	288542	247190	728613	1210946	2.525151

Figure S66. GPC curve of poly(L-IMCI-*co*-IPI) obtained by cationic Aluminum complex 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		11.440	11.440	11.440	87867	286064	229474	734313	1242380	2.566955

Figure S67. GPC curve of poly(L-IMCI-*co*-IPI) obtained by cationic Aluminum complex in Table 2, entry 20.