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Electronic Supporting Information

For

Controlled, One-pot Synthesis of Recyclable Poly(1,3-diene)-Polyester Block Copolymers, Catalyzed by Yttrium β-Diketiminate Complexes

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Table of Contents

1.0 General Considerations **S17**

1.1 Polymerization and Methods **S17**

General procedure for the homopolymerization of 1,3-dienes or cyclic esters **S17**

General procedure for the block copolymerization of 1,3-dienes and cyclic esters **S17**

1.2 Characterization Methods **S18**

1.3 Impurity in $[Ph_3C][B(C_6F_5)_4]$ **S19**

Fig. S1 ^{19}F NMR of $[Ph_3C][B(C_6F_5)_4]$ in C_6D_6 at 298 K. **S19**

1.4 Homopolymerization of 1,3-dienes and cyclic esters with 8/$[Ph_3C][B(C_6F_5)_4]$. **S20**

Table S1 Homopolymerization of a range of 1,3-dienes and cyclic esters with precatalyst **8**. **S20**

1.5 Homopolymerization of different feed ratios of IP and CL with 6/$[Ph_3C][B(C_6F_5)_4]$. **S21**

Table S2 Homopolymerization of IP or CL with precatalyst **6**. **S21**

1.6 Recycling PIP-*b*-PCL Copolymers **S22**

General procedure for the degradation of PIP-b-PCL diblocks **S22**

Formation of Alkoxide macroinitiator with recovered IP 50 and $Y[N(SiMe_3)_2]_3$ and repolymerization with CL. **S22**

Fig. S2 ^1H NMR stack of **$Y[N(SiMe_3)_2]_3$** before (bottom) and after recovered IP 50 addition (top) in toluene-d_8 at 298 K. **S22**

Fig. S3 ^1H NMR stack of PIP-*b*-PCL repolymerization with **$Y[N(SiMe_3)_2]_3$** and PIP 50 in toluene-d_8 at 298 K. **S23**

General procedure for the repolymerization of PIP-b-PCL diblocks **S23**

Table S3. Polymerization, depolymerization, and repolymerization of PIP-*b*-PCL. **S24**

2.0 References **S25**

3.0 Nuclear Magnetic Resonance (NMR) Spectroscopy Characterization of Isolated Polymers **S26**

3.1 ^1H NMR Spectroscopy **S26**

Fig. S4 ^1H NMR spectrum of PIP 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 1**, entry 1a in $CDCl_3$ at 298 K (12 h). **S26**

Fig. S5 ^1H NMR spectrum of PIP 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 1**, entry 1(b and c) in $CDCl_3$ at 298 K (12 h). **S26**

Fig. S6 ^1H NMR spectrum of PIP 800 equivalents generated by **8**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 1**, entry 3 in $CDCl_3$ at 298 K (12 h). **S27**

Fig. S7 ^{1}H NMR spectrum of PIP 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 1**, entry 4 in $CDCl_3$ at 298 K (24 h). **S28**
Fig. S8 ^{1}H NMR spectrum of PIP 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 1**, entry 5 in $CDCl_3$ at 298 K (30 min). **S29**
Fig. S9 ^{1}H NMR spectrum of PIP 800 equivalents generated by **8**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 1**, entry 6 in $CDCl_3$ at 298 K (30 min). **S29**
Fig. S10 ^{1}H NMR spectrum of PCL 300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 1**, entry 7 in $CDCl_3$ at 298 K (10 min). **S30**
Fig. S11 ^{1}H NMR spectrum of PCL 300 equivalents generated by **8**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 1**, entry 8 in $CDCl_3$ at 298 K (10 min). **S30**
Fig. S12 ^{1}H NMR spectrum of PCL 300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 1**, entry 9 in $CDCl_3$ at 298 K (2 h). **S31**
Fig. S13 ^{1}H NMR spectrum of PIP-*b*-PCL 550:550 generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 2**, entry 2 in $CDCl_3$ at 298 K. **S32**
Fig. S14 ^{1}H NMR spectrum of PIP-*b*-PCL 550:550 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 2**, entry 2 in $CDCl_3$ at 298 K. **S33**
Fig. S15 ^{1}H NMR spectrum of PIP-*b*-PCL 300:800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 2**, entry 3 in $CDCl_3$ at 298 K. **S34**
Fig. S16 ^{1}H NMR spectrum of PIP 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 3**, entry 1 in $CDCl_3$ at 298 K (IP addition time 0 min). **S35**
Fig. S17 ^{1}H NMR spectrum of PIP 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 3**, entry 2 in $CDCl_3$ at 298 K (IP addition time 30 min). **S36**
Fig. S18 ^{1}H NMR spectrum of PIP-*b*-PCL 800:300 equivalents generated by **6** and 0.5 equivalents of $[Ph_3C][B(C_6F_5)_4]$ from **Table 3**, entry 3 in $CDCl_3$ at 298 K. **S37**
Fig. S19 ^{1}H NMR spectrum of PIP-*b*-PCL 800:300 equivalents generated by **6** and 1.5 equivalents of $[Ph_3C][B(C_6F_5)_4]$ from **Table 3**, entry 4 in $CDCl_3$ at 298 K. **S38**
Fig. S20 ^{1}H NMR spectrum of PMyr 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 4**, entry 1 in $CDCl_3$ at 298 K (30 min). **S39**
Fig. S21 ^{1}H NMR spectrum of PMyr 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 4**, entry 2 in $CDCl_3$ at 298 K (90 min). **S39**
Fig. S22 ^{1}H NMR spectrum of PMyr 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 4**, entry 3 in $CDCl_3$ at 298 K (3 h). **S40**
Fig. S23 ^{1}H NMR spectrum of PS 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 4**, entry 4 in $CDCl_3$ at 298 K (30 min). **S40**
Fig. S24 ^{1}H NMR spectrum of PS 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 4**, entry 5 in $CDCl_3$ at 298 K (20 h). **S41**
Fig. S25 ^{1}H NMR spectrum of PVL 300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 4**, entry 6 in $CDCl_3$ at 298 K (10 min). **S41**
Fig. S26 ^{1}H NMR spectrum of PDL 300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 4**, entry 7 in $CDCl_3$ at 298 K (6 h). **S42**
Fig. S27 ^{1}H NMR spectrum of PIP-*b*-PVL 800:300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 5**, entry 1 in $CDCl_3$ at 298 K. **S42**
Fig. S28 ^{1}H NMR spectrum of PIP-*b*-PDL 800:300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 5**, entry 2 in $CDCl_3$ at 298 K. **S43**
Fig. S29 ^{1}H NMR spectrum of PMyr-*b*-PCL 800:300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 5**, entry 3 in $CDCl_3$ at 298 K. **S43**

Fig. S30 ^{1}H NMR spectrum of PMyr-*b*-PVL 800:300 equivalents generated by **6**/[Ph_3C][$B(C_6F_5)_4$] from **Table 5**, entry 4 in $CDCl_3$ at 298 K. **S44**
Fig. S31 ^{1}H NMR spectrum of PMyr-*b*-PDL 800:300 equivalents generated by **6**/[Ph_3C][$B(C_6F_5)_4$] from **Table 5**, entry 5 in $CDCl_3$ at 298 K. **S44**
Fig. S32 ^{1}H NMR spectrum of PMyr 800 equivalents generated by **8**/[Ph_3C][$B(C_6F_5)_4$] from **Table S1**, entry 1 in $CDCl_3$ at 298 K (30 min). **S45**
Fig. S33 ^{1}H NMR spectrum of PS 800 equivalents generated by **8**/[Ph_3C][$B(C_6F_5)_4$] from **Table S1**, entry 2 in $CDCl_3$ at 298 K (30 min). **S45**
Fig. S34 ^{1}H NMR spectrum of PVL 300 equivalents generated by **8**/[Ph_3C][$B(C_6F_5)_4$] from **Table S1**, entry 3 in $CDCl_3$ at 298 K (10 min). **S46**
Fig. S35 ^{1}H NMR spectrum of PDL 300 equivalents generated by **8**/[Ph_3C][$B(C_6F_5)_4$] from **Table S1**, entry 4 in $CDCl_3$ at 298 K (6 h). **S46**
Fig. S36 ^{1}H NMR spectrum of PIP 300 equivalents generated by **6**/[Ph_3C][$B(C_6F_5)_4$] from **Table S2**, entry 1 in $CDCl_3$ at 298 K (12 h). **S47**
Fig. S37 ^{1}H NMR spectrum of PIP 550 equivalents generated by **6**/[Ph_3C][$B(C_6F_5)_4$] from **Table S2**, entry 2 in $CDCl_3$ at 298 K (12 h). **S48**
Fig. S38 ^{1}H NMR spectrum of PCL 550 equivalents generated by **6**/[Ph_3C][$B(C_6F_5)_4$] from **Table S2**, entry 3 in $CDCl_3$ at 298 K (2 h). **S49**
Fig. S39 ^{1}H NMR spectrum of PCL 800 equivalents generated by **6**/[Ph_3C][$B(C_6F_5)_4$] from **Table S2**, entry 4 in $CDCl_3$ at 298 K (2 h). **S50**
Fig. S40 ^{1}H NMR spectrum of PCL 800 equivalents generated by **6** from **Table S2**, entry 5 in $CDCl_3$ at 298 K (No [Ph_3C][$B(C_6F_5)_4$] added) (10 min). **S51**
Fig. S41 ^{1}H NMR spectrum of PIP 50 equivalents generated by **6**/[Ph_3C][$B(C_6F_5)_4$] from **Table S3**, entry 1 in $CDCl_3$ at 298 K (12 h). **S51**
Fig. S42 ^{1}H NMR spectrum of PIP-*b*-PCL 50:50 equivalents generated by **6**/[Ph_3C][$B(C_6F_5)_4$] from **Table S3**, entry 2 in $CDCl_3$ at 298 K. **S52**
Fig. S43 ^{1}H NMR spectrum of recovered PIP 50 equivalents after hydrolysis of PIP-*b*-PCL 50:50 equivalents from **Table S3**, entry 3 in $CDCl_3$ at 298 K (12 h). **S52**
Fig. S44 ^{1}H NMR spectrum of repolymerized PIP-*b*-PCL 50:50 equivalents generated by **Y[N(SiMe$_3$)$_2$]$_3$** from **Table S3**, entry 4 in $CDCl_3$ at 298 K. **S53**
Fig. S45 ^{1}H NMR spectrum of PIP-*b*-PCL 50:50 equivalents generated by **6**/[Ph_3C][$B(C_6F_5)_4$] (1 mL of toluene) from **Table S3**, entry 5 in $CDCl_3$ at 298 K. **S53**
3.2 ^{13}C NMR Spectroscopy **S54**

Fig. S46 ^{13}C NMR spectrum of PIP 800 equivalents generated by **6**/[Ph_3C][$B(C_6F_5)_4$] from **Table 1**, entry 1a in $CDCl_3$ at 298 K (12 h). **S54**
Fig. S47 ^{13}C NMR spectrum of PIP equivalents generated by **6**/[Ph_3C][$B(C_6F_5)_4$] from **Table 1**, entry 1(b, c) in $CDCl_3$ at 298 K (12 h). **S54**
Fig. S48 ^{13}C NMR spectrum of PIP 800 equivalents generated by **8**/[Ph_3C][$B(C_6F_5)_4$] from **Table 1**, entry 3 in $CDCl_3$ at 298 K (12 h). **S55**
Fig. S49 ^{13}C NMR spectrum of PIP 800 equivalents generated by **6**/[Ph_3C][$B(C_6F_5)_4$] from **Table 1**, entry 4 in $CDCl_3$ at 298 K (24 h). **S56**
Fig. S50 ^{13}C NMR spectrum of PIP 800 equivalents generated by **6**/[Ph_3C][$B(C_6F_5)_4$] from **Table 1**, entry 5 in $CDCl_3$ at 298 K (30 min). **S57**
Fig. S51 ^{13}C NMR spectrum of PIP 800 equivalents generated by **8**/[Ph_3C][$B(C_6F_5)_4$] from **Table 1**, entry 6 in $CDCl_3$ at 298 K (30 min). **S57**

Fig. S52 ^{13}C NMR spectrum of PCL 300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 1**, entry 7 in $CDCl_3$ at 298 K (10 min). **S58**
Fig. S53 ^{13}C NMR spectrum of PCL 300 equivalents generated by **8**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 1**, entry 8 in $CDCl_3$ at 298 K (10 min). **S58**
Fig. S54 ^{13}C NMR spectrum of PCL 300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 1**, entry 9 in $CDCl_3$ at 298 K (2 h). **S59**
Fig. S55 ^{13}C NMR spectrum of PIP-*b*-PCL 800:300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 2**, entry 1 in $CDCl_3$ at 298 K. **S60**
Fig. S56 ^{13}C NMR spectrum of PIP-*b*-PCL 550:550 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 2**, entry 2 in $CDCl_3$ at 298 K. **S61**
Fig. S57 ^{13}C NMR spectrum of PIP-*b*-PCL 300:800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 2**, entry 3 in $CDCl_3$ at 298 K. **S62**
Fig. S58 ^{13}C NMR spectrum of PIP 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 3**, entry 1 in $CDCl_3$ at 298 K (IP addition time 0 min). **S63**
Fig. S59 ^{13}C NMR spectrum of PIP 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 3**, entry 2 in $CDCl_3$ at 298 K (IP addition time 30 min). **S64**
Fig. S60 ^{13}C NMR spectrum of PIP-*b*-PCL 800:300 equivalents generated by **6** and 0.5 equivalents of $[Ph_3C][B(C_6F_5)_4]$ from **Table 3**, entry 3 in $CDCl_3$ at 298 K. **S65**
Fig. S61 ^{13}C NMR spectrum of PIP-*b*-PCL 800:300 equivalents generated by **6** and 1.5 equivalents of $[Ph_3C][B(C_6F_5)_4]$ from **Table 3**, entry 4 in $CDCl_3$ at 298 K. **S66**
Fig. S62 ^{13}C NMR spectrum of PMyr 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 4**, entry 1 in $CDCl_3$ at 298 K (30 min). **S67**
Fig. S63 ^{13}C NMR spectrum of PMyr 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 4**, entry 2 in $CDCl_3$ at 298 K (90 min). **S67**
Fig. S64 ^{13}C NMR spectrum of PMyr 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 4**, entry 3 in $CDCl_3$ at 298 K (3 h). **S68**
Fig. S65 ^{13}C NMR spectrum of PS 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 4**, entry 4 in $CDCl_3$ at 298 K (30 min). **S68**
Fig. S66 ^{13}C NMR spectrum of PS 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 4**, entry 5 in $CDCl_3$ at 298 K (20 h) **S69**
Fig. S67 ^{13}C NMR spectrum of PVL 300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 4**, entry 6 in $CDCl_3$ at 298 K (10 min). **S69**
Fig. S68 ^{13}C NMR spectrum of PDL 300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 4**, entry 7 in $CDCl_3$ at 298 K (30 min). **S70**
Fig. S69 ^{13}C NMR spectrum of PIP-*b*-PVL 800:300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 5**, entry 1 in $CDCl_3$ at 298 K. **S70**
Fig. S70 ^{13}C NMR spectrum of PIP-*b*-PDL 800:300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 5**, entry 2 in $CDCl_3$ at 298 K. **S71**
Fig. S71 ^{13}C NMR spectrum of PMyr-*b*-PCL 800:300 equivalents generated by 6/$[Ph_3C][B(C_6F_5)_4]$ from Table 5, entry 3 in $CDCl_3$ at 298 K. **S71**
Fig. S72 ^{13}C NMR spectrum of PMyr-*b*-PVL 800:300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 5**, entry 4 in $CDCl_3$ at 298 K. **S72**
Fig. S73 ^{13}C NMR spectrum of PMyr-*b*-PDL 800:300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 5**, entry 5 in $CDCl_3$ at 298 K. **S72**
Fig. S74 ^{13}C NMR spectrum of PMyr 800 equivalents generated by **8**/$[Ph_3C][B(C_6F_5)_4]$ from **Table S1**, entry 1 in $CDCl_3$ at 298 K (30 min). **S73**

Fig. S75 ^{13}C NMR spectrum of PS 800 equivalents generated by **8**/$[Ph_3C][B(C_6F_5)_4]$ from **Table S1**, entry 2 in $CDCl_3$ at 298 K (30 min). **S73**
Fig. S76 ^{13}C NMR spectrum of PVL 300 equivalents generated by **8**/$[Ph_3C][B(C_6F_5)_4]$ from **Table S1**, entry 3 in $CDCl_3$ at 298 K (10 min). **S74**
Fig. S77 ^{13}C NMR spectrum of PDL 300 equivalents generated by **8**/$[Ph_3C][B(C_6F_5)_4]$ from **Table S1**, entry 4 in $CDCl_3$ at 298 K (6 h). **S74**
Fig. S78 ^{13}C NMR spectrum of PIP 300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table S2**, entry 1 in $CDCl_3$ at 298 K (12 h). **S75**
Fig. S79 ^{13}C NMR spectrum of PIP 550 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table S2**, entry 2 in $CDCl_3$ at 298 K (12 h). **S76**
Fig. S80 ^{13}C NMR spectrum of PCL 550 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table S2**, entry 3 in $CDCl_3$ at 298 K (12 h). **S77**
Fig. S81 ^{13}C NMR spectrum of PCL 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table S2**, entry 4 in $CDCl_3$ at 298 K (12 h). **S78**
Fig. S82 ^{13}C NMR spectrum of PCL 800 equivalents generated by **6** from **Table S2**, entry 5 in $CDCl_3$ at 298 K (No $[Ph_3C][B(C_6F_5)_4]$ added) (10 min). **S79**
Fig. S83 ^{13}C NMR spectrum of PIP 50 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table S3**, entry 1 in $CDCl_3$ at 298 K (12 h). **S79**
Fig. S84 ^{13}C NMR spectrum of PIP-*b*-PCL 50:50 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table S3**, entry 2 in $CDCl_3$ at 298 K. **S80**
Fig. S85 ^{13}C NMR spectrum of recovered PIP 50 equivalents after hydrolysis of PIP-*b*-PCL 50:50 from **Table S3**, entry 3 in $CDCl_3$ at 298 K (12 h). **S80**
Fig. S86 ^{13}C NMR spectrum of PIP-*b*-PCL 50:50 equivalents generated by **$Y[N(SiMe_3)_2]_3$** from **Table S3**, entry 4 in $CDCl_3$ at 298 K (6 h). **S81**
Fig. S87 ^{13}C NMR spectrum of PIP-*b*-PCL 50:50 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ (1 mL of toluene) from **Table S3**, entry 5 in $CDCl_3$ at 298 K. **S81**

3.3 Diffusion-Ordered Spectroscopy (DOSY) **S82**

Fig. S88 DOSY NMR spectrum of PIP-*b*-PCL 800:300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 2**, entry 1a in $CDCl_3$ at 298 K. **S82**
Fig. S89 DOSY NMR spectrum of PIP-*b*-PCL 800:300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 2**, entry 1b in $CDCl_3$ at 298 K. **S83**
Fig. S90 DOSY NMR spectrum of PIP-*b*-PCL 800:300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 2**, entry 1c in $CDCl_3$ at 298 K. **S84**
Fig. S91 DOSY NMR spectrum of PIP-*b*-PCL 550:550 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 2**, entry 2a in $CDCl_3$ at 298 K. **S85**
Fig. S92 DOSY NMR spectrum of PIP-*b*-PCL 550:550 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 2**, entry 2b in $CDCl_3$ at 298 K. **S86**
Fig. S93 DOSY NMR spectrum of PIP-*b*-PCL 550:550 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 2**, entry 2c in $CDCl_3$ at 298 K. **S87**
Fig. S94 DOSY NMR spectrum of PIP-*b*-PCL 300:800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 2**, entry 3a in $CDCl_3$ at 298 K. **S88**
Fig. S95 DOSY NMR spectrum of PIP-*b*-PCL 300:800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 2**, entry 3b in $CDCl_3$ at 298 K. **S89**
Fig. S96 DOSY NMR spectrum of PIP-*b*-PCL 300:800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 2**, entry 3c in $CDCl_3$ at 298 K. **S90**

Fig. S97 DOSY NMR spectrum of PIP-*b*-PCL 800:300 equivalents generated by **6** and 0.5 equivalents of $[Ph_3C][B(C_6F_5)_4]$ from **Table 3**, entry 3a in $CDCl_3$ at 298 K. **S91**
Fig. S98 DOSY NMR spectrum of PIP-*b*-PCL 800:300 equivalents generated by **6** and 0.5 equivalents of $[Ph_3C][B(C_6F_5)_4]$ from **Table 3**, entry 3b in $CDCl_3$ at 298 K. **S92**
Fig. S99 DOSY NMR spectrum of PIP-*b*-PCL 800:300 equivalents generated by **6** and 0.5 equivalents of $[Ph_3C][B(C_6F_5)_4]$ from **Table 3**, entry 3c in $CDCl_3$ at 298 K. **S93**
Fig. S100 DOSY NMR spectrum of PIP-*b*-PCL 800:300 equivalents generated by **6** and 1.5 equivalents of $[Ph_3C][B(C_6F_5)_4]$ from **Table 3**, entry 4a in $CDCl_3$ at 298 K. **S94**
Fig. S101 DOSY NMR spectrum of PIP-*b*-PCL 800:300 equivalents generated by **6** and 1.5 equivalents of $[Ph_3C][B(C_6F_5)_4]$ from **Table 3**, entry 4b in $CDCl_3$ at 298 K. **S95**
Fig. S102 DOSY NMR spectrum of PIP-*b*-PCL 800:300 equivalents generated by **6** and 1.5 equivalents of $[Ph_3C][B(C_6F_5)_4]$ from **Table 3**, entry 4c in $CDCl_3$ at 298 K. **S96**
Fig. S103 DOSY NMR spectrum of PIP-*b*-PVL 800:300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 5**, entry 1 in $CDCl_3$ at 298 K. **S97**
Fig. S104 DOSY NMR spectrum of PIP-*b*-PDL 800:300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 5**, entry 2 in $CDCl_3$ at 298 K. **S98**
Fig. S105 DOSY NMR spectrum of PMyr-*b*-PCL 800:300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 5**, entry 3 in $CDCl_3$ at 298 K. **S99**
Fig. S106 DOSY NMR spectrum of PMyr-*b*-PVL 800:300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 5**, entry 3 in $CDCl_3$ at 298 K. **S100**
Fig. S107 DOSY NMR spectrum of PMyr-*b*-PDL 800:300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 5**, entry 5 in $CDCl_3$ at 298 K. **S101**
Fig. S108 DOSY NMR spectrum of PIP-*b*-PCL 50:50 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ of from **Table S3**, entry 2 in $CDCl_3$ at 298 K. **S102**
Fig. S109 DOSY NMR spectrum of repolymerized PIP-*b*-PCL 50:50 equivalents generated by $\mathbf{Y[N(SiMe_3)_2]_3}$ from **Table S3**, entry 4 in $CDCl_3$ at 298 K. **S103**
4.0 Fourier-Transform Infrared (FT-IR) Spectroscopy Characterization of Isolated Polymers **S104**
Fig. S110 FT-IR spectrum of PIP 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 1**, entry 1 (12 h). **S104**
Fig. S111 FT-IR spectrum of PIP 800 equivalents generated by **8**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 1**, entry 3 (12 h). **S104**
Fig. S112 FT-IR spectrum of PIP 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 1**, entry 4 (24 h). **S105**
Fig. S113 FT-IR spectrum of PIP 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 1**, entry 5 (30 min). **S105**
Fig. S114 FT-IR spectrum of PIP generated by **8**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 1**, entry 6 (30 min). **S106**
Fig. S115 FT-IR spectrum of PCL generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 1**, entry 7 (10 min). **S106**
Fig. S116 FT-IR spectrum of PCL 300 equivalents generated by **8**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 1**, entry 8 (10 min). **S107**
Fig. S117 FT-IR spectrum of PCL 300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 1**, entry 9 (2 h). **S107**
Fig. S118 FT-IR spectrum of PIP-*b*-PCL 800:300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 2**, entry 1. **S108**

Fig. S119 FT-IR spectrum of PIP-*b*-PCL 550:550 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 2**, entry 2. **S108**
Fig. S120 FT-IR spectrum of PIP-*b*-PCL 300:800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 2**, entry 3. **S109**
Fig. S121 FT-IR spectrum of PIP 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 3**, entry 1 (IP addition time 0 min). **S109**
Fig. S122 FT-IR spectrum of PIP 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 3**, entry 2 (IP addition time 30 min). **S110**
Fig. S123 FT-IR spectrum of PIP-*b*-PCL 800:300 equivalents generated by **6** and 0.5 equivalents of $[Ph_3C][B(C_6F_5)_4]$ from **Table 3**, entry 3. **S110**
Fig. S124 FT-IR spectrum of PIP-*b*-PCL 800:300 equivalents generated by **6** and 1.5 equivalents of $[Ph_3C][B(C_6F_5)_4]$ from **Table 3**, entry 4. **S111**
Fig. S125 FT-IR spectrum of PMyr 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 4**, entry 1 (30 min). **S111**
Fig. S126 FT-IR spectrum of PMyr 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 4**, entry 2 (90 min). **S112**
Fig. S127 FT-IR spectrum of PMyr 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 4**, entry 3 (3 h). **S112**
Fig. S128 FT-IR spectrum of PS 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 4**, entry 4 (30 min). **S113**
Fig. S129 FT-IR spectrum of PS 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 4**, entry 5 (20 h). **S113**
Fig. S130 FT-IR spectrum of PVL 300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 4**, entry 6 (10 min). **S114**
Fig. S131 FT-IR spectrum of PDL 300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 4**, entry 7 (6 h). **S114**
Fig. S132 FT-IR spectrum of PIP-*b*-PVL 800:300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 5**, entry 1. **S115**
Fig. S133 FT-IR spectrum of PIP-*b*-PDL 800:300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 5**, entry 2. **S115**
Fig. S134 FT-IR spectrum of PMyr-*b*-PCL 800:300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 5**, entry 3. **S116**
Fig. S135 FT-IR spectrum of PMyr-*b*-PVL 800:300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 5**, entry 4. **S116**
Fig. S136 FT-IR spectrum of PMyr-*b*-PDL 800:300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 5**, entry 5. **S117**
Fig. S137 FT-IR spectrum of PMyr 800 equivalents generated by **8**/$[Ph_3C][B(C_6F_5)_4]$ from **Table S1**, entry 1 (30 min). **S117**
Fig. S138 FT-IR spectrum of PS 800 equivalents generated by **8**/$[Ph_3C][B(C_6F_5)_4]$ from **Table S1**, entry 2 (30 min). **S118**
Fig. S139 FT-IR spectrum of PVL 300 equivalents generated by **8**/$[Ph_3C][B(C_6F_5)_4]$ from **Table S1**, entry 3 (10 min). **S118**
Fig. S140 FT-IR spectrum of PDL 300 equivalents generated by **8**/$[Ph_3C][B(C_6F_5)_4]$ from **Table S1**, entry 4 (6 h). **S119**
Fig. S141 FT-IR spectrum of PIP 300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table S2**, entry 1 (12 h). **S119**

Fig. S142 FT-IR spectrum of PIP 550 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table S2**, entry 2 (12 h). **S120**
Fig. S143 FT-IR spectrum of PCL 550 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table S2**, entry 3 (2 h). **S120**
Fig. S144 FT-IR spectrum of PCL 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table S2**, entry 4 (2 h). **S121**
Fig. S145 FT-IR spectrum of PCL 300 equivalents generated by **6** from **Table S2**, entry 5 (No $[Ph_3C][B(C_6F_5)_4]$ added) (10 min). **S121**
Fig. S146 FT-IR spectrum of PIP 50 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table S3**, entry 1 (12 h). **S122**
Fig. S147 FT-IR spectrum of PIP-*b*-PCL 50:50 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table S3**, entry 2. **S122**
Fig. S148 FT-IR spectrum of recovered PIP 50 equivalents after hydrolysis of PIP-*b*-PCL 50:50 from **Table S3**, entry 3 (12 h). **S123**
Fig. S149 FT-IR spectrum of PIP-*b*-PCL 50:50 equivalents generated by **$Y[N(SiMe_3)_2]_3$** from **Table S3**, entry 4 (6 h). **S123**

5.0 Gel Permeation Chromatography (GPC) Characterization of Isolated Polymers **S124**

Fig. S150 GPC spectrum of PIP 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 1**, entry 1a (12 h): (left) LS; (right) RI. **S124**
Fig. S151 GPC spectrum of PIP 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 1**, entry 1b (12 h): (left) LS; (right) RI. **S124**
Fig. S152 GPC spectrum of PIP 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 1**, entry 1c (12 h): (left) LS; (right) RI. **S125**
Fig. S153 GPC spectrum of PIP 800 equivalents generated by **8**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 1**, entry 3 (12 h): (left) LS; (right) RI. **S125**
Fig. S154 GPC spectrum of PIP 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 1**, entry 4a (24 h): (left) LS; (right) RI. **S126**
Fig. S155 GPC spectrum of PIP 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 1**, entry 4b (24 h): (left) LS; (right) RI. **S126**
Fig. S156 GPC spectrum of PIP 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 1**, entry 4c (24 h): (left) LS; (right) RI. **S127**
Fig. S157 GPC spectrum of PIP 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 1**, entry 5 (30 min): (left) LS; (right) RI. **S127**
Fig. S158 GPC spectrum of PIP 800 equivalents generated by **8**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 1**, entry 6 (30 min): (left) LS; (right) RI. **S128**
Fig. S159 GPC spectrum of PCL 300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 1**, entry 7 (10 min): (left) LS; (right) RI. **S128**
Fig. S160 GPC spectrum of PCL 300 equivalents generated by **8**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 1**, entry 8 (10 min): (left) LS; (right) RI. **S129**
Fig. S161 GPC spectrum of PCL 300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 1**, entry 9a (2 h): (left) LS; (right) RI. **S129**
Fig. S162 GPC spectrum of PCL 300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 1**, entry 9b (2 h): (left) LS; (right) RI. **S130**
Fig. S163 GPC spectrum of PCL 300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 1**, entry 9c (2 h): (left) LS; (right) RI. **S130**

Fig. S164 GPC spectrum of PIP-*b*-PCL 800:300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 2**, entry 1a: (left) LS; (right) RI. **S131**
Fig. S165 GPC spectrum of PIP-*b*-PCL 800:300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 2**, entry 1b: (left) LS; (right) RI. **S131**
Fig. S166 GPC spectrum of PIP-*b*-PCL 800:300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 2**, entry 1c: (left) LS; (right) RI. **S132**
Fig. S167 GPC spectrum of PIP-*b*-PCL 550:550 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 2**, entry 2a: (left) LS; (right) RI. **S132**
Fig. S168 GPC spectrum of PIP-*b*-PCL 550:550 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 2**, entry 2b: (left) LS; (right) RI. **S132**
Fig. S169 GPC spectrum of PIP-*b*-PCL 550:550 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 2**, entry 2c: (left) LS; (right) RI. **S133**
Fig. S170 GPC spectrum of PIP-*b*-PCL 300:800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 2**, entry 3a: (left) LS; (right) RI. **S133**
Fig. S171 GPC spectrum of PIP-*b*-PCL 300:800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 2**, entry 3b: (left) LS; (right) RI. **S134**
Fig. S172 GPC spectrum of PIP-*b*-PCL 300:800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 2**, entry 3c: (left) LS; (right) RI. **S134**
Fig. S173 GPC spectrum of PIP 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 3**, entry 1a (IP addition time 0 min): (left) LS; (right) RI. **S134**
Fig. S174 GPC spectrum of PIP 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 3**, entry 1b (IP addition time 0 min): (left) LS; (right) RI. **S135**
Fig. S175 GPC spectrum of PIP 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 3**, entry 1c (IP addition time 0 min): (left) LS; (right) RI. **S135**
Fig. S176 GPC spectrum of PIP 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 3**, entry 2a (IP addition time 30 min): (left) LS; (right) RI. **S135**
Fig. S177 GPC spectrum of PIP 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 3**, entry 2b (IP addition time 30 min): (left) LS; (right) RI. **S136**
Fig. S178 GPC spectrum of PIP 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 3**, entry 2c (IP addition time 30 min): (left) LS; (right) RI. **S136**
Fig. S179 GPC spectrum of PIP-*b*-PCL 800:300 generated by **6** and 0.5 equivalents of $[Ph_3C][B(C_6F_5)_4]$ from **Table 3**, entry 3a: (left) LS; (right) RI. **S136**
Fig. S180 GPC spectrum of PIP-*b*-PCL 800:300 generated by **6** and 0.5 equivalents of $[Ph_3C][B(C_6F_5)_4]$ from **Table 3**, entry 3b: (left) LS; (right) RI. **S137**
Fig. S181 GPC spectrum of PIP-*b*-PCL 800:300 generated by **6** and 0.5 equivalents of $[Ph_3C][B(C_6F_5)_4]$ from **Table 3**, entry 3c: (left) LS; (right) RI. **S137**
Fig. S182 GPC spectrum of PIP-*b*-PCL 800:300 generated by **6** and 1.5 equivalents of $[Ph_3C][B(C_6F_5)_4]$ from **Table 3**, entry 4a: (left) LS; (right) RI. **S137**
Fig. S183 GPC spectrum of PIP-*b*-PCL 800:300 generated by **6** and 1.5 equivalents of $[Ph_3C][B(C_6F_5)_4]$ from **Table 3**, entry 4b: (left) LS; (right) RI. **S138**
Fig. S184 GPC spectrum of PIP-*b*-PCL 800:300 generated by **6** and 1.5 equivalents of $[Ph_3C][B(C_6F_5)_4]$ from **Table 3**, entry 4c: (left) LS; (right) RI. **S138**
Fig. S185 GPC spectrum of PMyr generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 4**, entry 1 (30 min): (left) LS; (right) RI. **S139**
Fig. S186 GPC spectrum of PMyr generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 4**, entry 2 (90 min): (left) LS; (right) RI. **S139**

Fig. S187 GPC spectrum of PMyr generated by **6**/[Ph_3C][$B(C_6F_5)_4$] from **Table 4**, entry 3 (3 h): (left) LS; (right) RI. **S140**
Fig. S188 GPC spectrum of PS generated by **6**/[Ph_3C][$B(C_6F_5)_4$] from **Table 4**, entry 4 (30 min): (left) LS; (right) RI. **S140**
Fig. S189 GPC spectrum of PS generated by **6**/[Ph_3C][$B(C_6F_5)_4$] from **Table 4**, entry 5 (20 h): (left) LS; (right) RI. **S141**
Fig. S190 GPC spectrum of PVL generated by **6**/[Ph_3C][$B(C_6F_5)_4$] from **Table 4**, entry 6 (10 min): (left) LS; (right) RI. **S141**
Fig. S191 GPC spectrum of PDL generated by **6**/[Ph_3C][$B(C_6F_5)_4$] from **Table 4**, entry 7 (6 h): (left) LS; (right) RI. **S141**
Fig. S192 GPC spectrum of PIP-*b*-PVL 800:300 equivalents generated by **6**/[Ph_3C][$B(C_6F_5)_4$] from **Table 5**, entry 1: (left) LS; (right) RI. **S142**
Fig. S193 GPC spectrum of PIP-*b*-PDL 800:300 equivalents generated by **6**/[Ph_3C][$B(C_6F_5)_4$] from **Table 5**, entry 2: (left) LS; (right) RI. **S142**
Fig. S194 GPC spectrum of PMyr-*b*-PCL 800:300 equivalents generated by **6**/[Ph_3C][$B(C_6F_5)_4$] from **Table 5**, entry 3: (left) LS; (right) RI. **S143**
Fig. S195 GPC spectrum of PMyr-*b*-PVL 800:300 equivalents generated by **6**/[Ph_3C][$B(C_6F_5)_4$] from **Table 5**, entry 4: (left) LS; (right) RI. **S143**
Fig. S196 GPC spectrum of PMyr-*b*-PDL 800:300 equivalents generated by **6**/[Ph_3C][$B(C_6F_5)_4$] from **Table 5**, entry 5: (left) LS; (right) RI. **S143**
Fig. S197 GPC spectrum of PMyr 800 equivalents generated by **8**/[Ph_3C][$B(C_6F_5)_4$] from **Table S1**, entry 1 (30min): (left) LS; (right) RI. **S144**
Fig. S198 GPC spectrum of PS 800 equivalents generated by **8**/[Ph_3C][$B(C_6F_5)_4$] from **Table S1**, entry 2 (30 min): (left) LS; (right) RI. **S144**
Fig. S199 GPC spectrum of PVL 300 equivalents generated by **8**/[Ph_3C][$B(C_6F_5)_4$] from **Table S1**, entry 3 (10 min): (left) LS; (right) RI. **S144**
Fig. S200 GPC spectrum of PDL 300 equivalents generated by **8**/[Ph_3C][$B(C_6F_5)_4$] from **Table S1**, entry 4 (6 h): (left) LS; (right) RI. **S145**
Fig. S201 GPC spectrum of PIP 300 equivalents generated by **6**/[Ph_3C][$B(C_6F_5)_4$] from **Table S2**, entry 1a (12 h): (left) LS; (right) RI. **S145**
Fig. S202 GPC spectrum of PIP 300 equivalents generated by **6**/[Ph_3C][$B(C_6F_5)_4$] from **Table S2**, entry 1b (12 h): (left) LS; (right) RI. **S145**
Fig. S203 GPC spectrum of PIP 300 equivalents generated by **6**/[Ph_3C][$B(C_6F_5)_4$] from **Table S2**, entry 1c (12 h): (left) LS; (right) RI. **S146**
Fig. S204 GPC spectrum of PIP 550 equivalents generated by **6**/[Ph_3C][$B(C_6F_5)_4$] from **Table S2**, entry 2a (12 h): (left) LS; (right) RI. **S146**
Fig. S205 GPC spectrum of PIP 550 equivalents generated by **6**/[Ph_3C][$B(C_6F_5)_4$] from **Table S2**, entry 2b (12 h): (left) LS; (right) RI. **S146**
Fig. S206 GPC spectrum of PIP 550 equivalents generated by **6**/[Ph_3C][$B(C_6F_5)_4$] from **Table S2**, entry 2c (12 h): (left) LS; (right) RI. **S147**
Fig. S207 GPC spectrum of PCL 550 equivalents generated by **6**/[Ph_3C][$B(C_6F_5)_4$] from **Table S2**, entry 3a (2 h): (left) LS; (right) RI. **S147**
Fig. S208 GPC spectrum of PCL 550 equivalents generated by **6**/[Ph_3C][$B(C_6F_5)_4$] from **Table S2**, entry 3b (2 h): (left) LS; (right) RI. **S148**
Fig. S209 GPC spectrum of PCL 550 equivalents generated by **6**/[Ph_3C][$B(C_6F_5)_4$] from **Table S2**, entry 3c (2 h): (left) LS; (right) RI. **S148**

Fig. S210 GPC spectrum of PCL 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table S2**, entry 4a (2 h): (left) LS; (right) RI. **S148**
Fig. S211 GPC spectrum of PCL 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table S2**, entry 4b (2 h): (left) LS; (right) RI. **S149**
Fig. S212 GPC spectrum of PCL 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table S2**, entry 4c (2 h): (left) LS; (right) RI. **S149**
Fig. S213 GPC spectrum of PCL 300 equivalents generated by **6** from **Table S2**, entry 5 (No $[Ph_3C][B(C_6F_5)_4]$ added) (10 min): (left) LS; (right) RI. **S150**
Fig. S214 GPC spectrum of PIP 50 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table S3**, entry 1 (12 h): (left) LS; (right) RI. **S150**
Fig. S215 GPC spectrum of PIP-*b*-PCL 50:50 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table S3**, entry 2: (left) LS; (right) RI. **S151**
Fig. S216 GPC spectrum of recovered PIP 50 equivalents after hydrolysis of PIP-*b*-PCL 50:50 from **Table S3**, entry 3 (12 h): (left) LS; (right) RI. **S151**
Fig. S217 GPC spectrum of repolymerized PIP-*b*-PCL 50:50 equivalents generated by **$Y[N(SiMe_3)_2]_3$** from **Table S3**, entry 4 (6 h): (left) LS; (right) RI. **S152**
Fig. S218 GPC spectrum of PIP-*b*-PCL 50:50 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ (1 mL of toluene) from **Table S3**, entry 5: (left) LS; (right) RI. **S152**

6.0 Thermogravimetric Analysis (TGA) of Isolated Polymers **S153**

Fig. S219 TGA curve of PIP 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 1**, entry 1a (12 h). **S153**
Fig. S220 TGA curve of PIP 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 1**, entry 1b (12 h). **S153**
Fig. S221 TGA curve of PIP 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 1**, entry 1c (12 h). **S154**
Fig. S222 TGA curve of PIP 800 equivalents generated by **8**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 1**, entry 3 (12 h). **S154**
Fig. S223 TGA curve of PIP 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 1**, entry 4 (24 h). **S155**
Fig. S224 TGA curve of PIP 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 1**, entry 5 (30 min). **S155**
Fig. S225 TGA curve of PIP 800 equivalents generated by **8**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 1**, entry 6 (30 min). **S156**
Fig. S226 TGA curve of PCL 300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 1**, entry 7 (10 min). **S156**
Fig. S227 TGA curve of PCL 300 equivalents generated by **8**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 1**, entry 8 (10 min). **S157**
Fig. S228 TGA curve of PCL 300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 1**, entry 9a (2 h). **S157**
Fig. S229 TGA curve of PCL 300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 1**, entry 9b (2 h). **S158**
Fig. S230 TGA curve of PCL 300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 1**, entry 9c (2 h). **S158**
Fig. S231 TGA curve of PIP-*b*-PCL 800:300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 2**, entry 1a. **S159**

Fig. S232 TGA curve of PIP-*b*-PCL 800:300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 2**, entry 1b. **S159**
Fig. S233 TGA curve of PIP-*b*-PCL 800:300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 2**, entry 1c. **S160**
Fig. S234 TGA curve of PIP-*b*-PCL 550:550 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 2**, entry 2a. **S160**
Fig. S235 TGA curve of PIP-*b*-PCL 550:550 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 2**, entry 2b. **S161**
Fig. S236 TGA curve of PIP-*b*-PCL 550:550 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 2**, entry 2c. **S161**
Fig. S237 TGA curve of PIP-*b*-PCL 300:800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 2**, entry 3a. **S162**
Fig. S238 TGA curve of PIP-*b*-PCL 300:800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 2**, entry 3b. **S162**
Fig. S239 TGA curve of PIP-*b*-PCL 300:800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 2** entry 3c. **S163**
Fig. S240 TGA curve of PIP 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 3**, entry 1a (IP addition time 0 min). **S163**
Fig. S241 TGA curve of PIP 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 3**, entry 1b (IP addition time 0 min). **S164**
Fig. S242 TGA curve of PIP 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 3**, entry 1c (IP addition time 0 min). **S164**
Fig. S243 TGA curve of PIP 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 3**, entry 2a (IP addition time 30 min). **S165**
Fig. S244 TGA curve of PIP 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 3**, entry 2b (IP addition time 30 min). **S165**
Fig. S245 TGA curve of PIP 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 3**, entry 2c (IP addition time 30 min). **S166**
Fig. S246 TGA curve of PIP-*b*-PCL 800:300 equivalents generated by **6** and 0.5 equivalents of $[Ph_3C][B(C_6F_5)_4]$ from **Table 3**, entry 3a. **S166**
Fig. S247 TGA curve of PIP-*b*-PCL 800:300 equivalents generated by **6** and 0.5 equivalents of $[Ph_3C][B(C_6F_5)_4]$ from **Table 3**, entry 3b. **S167**
Fig. S248 TGA curve of PIP-*b*-PCL 800:300 equivalents generated by **6** and 0.5 equivalents of $[Ph_3C][B(C_6F_5)_4]$ from **Table 3**, entry 3c. **S167**
Fig. S249 TGA curve of PIP-*b*-PCL 800:300 equivalents generated by **6** and 1.5 equivalents of $[Ph_3C][B(C_6F_5)_4]$ from **Table 3**, entry 4a. **S168**
Fig. S250 TGA curve of PIP-*b*-PCL 800:300 equivalents generated by **6** and 1.5 equivalents of $[Ph_3C][B(C_6F_5)_4]$ from **Table 3**, entry 4b. **S168**
Fig. S251 TGA curve of PIP-*b*-PCL 800:300 equivalents generated by **6** and 1.5 equivalents of $[Ph_3C][B(C_6F_5)_4]$ from **Table 3**, entry 4c. **S169**
Fig. S252 TGA curve of PMyr 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 4**, entry 1 (30 min). **S169**
Fig. S253 TGA curve of PMyr 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 4**, entry 2 (90 min). **S170**
Fig. S254 TGA curve of PMyr 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 4**, entry 3 (3 h). **S170**

Fig. S255 TGA curve of PS 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 4**, entry 4 (30 min). **S171**
Fig. S256 TGA curve of PS 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 4**, entry 5 (24 h). **S171**
Fig. S257 TGA curve of PVL 300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 4**, entry 6 (10 min). **S172**
Fig. S258 TGA curve of PDL 300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 4**, entry 7 (6 h). **S172**
Fig. S259 TGA curve of PIP-*b*-PVL 800:300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 5**, entry 1. **S173**
Fig. S260 TGA curve of PIP-*b*-PDL 800:300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 5**, entry 2. **S173**
Fig. S261 TGA curve of PMyr-*b*-PCL 800:300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 5**, entry 3. **S174**
Fig. S262 DSC curve of PMyr-*b*-PVL 800:300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 5**, entry 4. **S174**
Fig. S263 TGA curve of PMyr-*b*-PDL 800:300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 5**, entry 5. **S175**
Fig. S264 TGA curve of PMyr 800 equivalents generated by **8**/$[Ph_3C][B(C_6F_5)_4]$ from **Table S1**, entry 1 (30 min). **S175**
Fig. S265 TGA curve of PS 800 equivalents generated by **8**/$[Ph_3C][B(C_6F_5)_4]$ from **Table S1**, entry 2 (30 min). **S176**
Fig. S266 TGA curve of PVL 300 equivalents generated by **8**/$[Ph_3C][B(C_6F_5)_4$ from **Table S1**, entry 3 (10 min). **S176**
Fig. S267 TGA curve of PDL 300 equivalents generated by **8**/$[Ph_3C][B(C_6F_5)_4]$ from **Table S1**, entry 4 (6 h). **S177**
Fig. S268 TGA curve of PIP 300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table S2**, entry 1a (12 h). **S177**
Fig. S269 TGA curve of PIP 300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table S2**, entry 1b (12 h). **S178**
Fig. S270 TGA curve of PIP 300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table S2**, entry 1c (12 h). **S178**
Fig. S271 TGA curve of PIP 550 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table S2**, entry 2a (12 h). **S179**
Fig. S272 TGA curve of PIP 550 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table S2**, entry 2b (12 h). **S179**
Fig. S273 TGA curve of PIP 550 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table S2**, entry 2c (12 h). **S180**
Fig. S274 TGA curve of PCL 550 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table S2**, entry 3a (2 h). **S180**
Fig. S275 TGA curve of PCL 550 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table S2**, entry 3b(2 h). **S181**
Fig. S276 TGA curve of PCL 550 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table S2**, entry 3c (2 h). **S181**
Fig. S277 TGA curve of PCL 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table S2**, entry 4a (2 h). **S182**

Fig. S278 TGA curve of PCL 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table S2**, entry 4b (2 h). **S182**
Fig. S279 TGA curve of PCL 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table S2**, entry 4c (2 h). **S183**
Fig. S280 TGA curve of PCL 300 equivalents generated by **6** from **Table S2**, entry 5 (No $[Ph_3C][B(C_6F_5)_4]$ added) (10 min). **S183**
Fig. S281 TGA curve of PIP 50 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table S3**, entry 1 in $CDCl_3$ at 298 K (12 h). **S184**
Fig. S282 TGA curve of PIP-*b*-PCL 50:50 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table S3**, entry 2. **S184**
Fig. S283 TGA curve of recovered PIP 50 equivalents after hydrolysis of PIP-*b*-PCL 50:50 from **Table S3**, entry 3 (12 h). **S185**
Fig. S284 TGA curve of PIP-*b*-PCL 50:50 equivalents generated by $\mathbf{Y[N(SiMe_3)_2]_3}$ from **Table S3**, entry 4 (6 h). **S185**

7.0 Differential Scanning Calorimetry (DSC) Characterization of Isolated Polymers **S186**

Fig. S285 DSC curve of PIP generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 1**, entry 1 (12 h). **S186**
Fig. S286 DSC curve of PIP 800 equivalents generated by **8**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 1**, entry 3 (12 h). **S186**
Fig. S287 DSC curve of PIP 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 1**, entry 4 (24 h). **S187**
Fig. S288 DSC curve of PIP 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 1**, entry 5 (30 min). **S187**
Fig. S289 DSC curve of PIP 800 equivalents generated by **8**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 1**, entry 6 (30 min). **S188**
Fig. S290 DSC curve of PCL 300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 1**, entry 7 (10 min). **S188**
Fig. S291 DSC curve of PCL 300 equivalents generated by **8**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 1**, entry 8 (10 min). **S189**
Fig. S292 DSC curve of PCL 300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 1**, entry 9 (2 h). **S189**
Fig. S293 DSC curve of PIP-*b*-PCL 800:300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 2**, entry 1. **S190**
Fig. S294 DSC curve of PIP-*b*-PCL 550:550 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 2**, entry 2. **S190**
Fig. S295 DSC curve of PIP-*b*-PCL 300:800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 2**, entry 3. **S191**
Fig. S296 DSC curve of PIP 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 3**, entry 1 (IP addition time 0 min). **S191**
Fig. S297 DSC curve of PIP 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 3**, entry 2 (IP addition time 30 min). **S192**
Fig. S298 DSC curve of PIP-*b*-PCL 800:300 equivalents generated by **6** and 0.5 equivalents of $[Ph_3C][B(C_6F_5)_4]$ from **Table 3**, entry 3. **S192**
Fig. S299 DSC curve of PIP-*b*-PCL 800:300 equivalents generated by **6** and 1.5 equivalents of $[Ph_3C][B(C_6F_5)_4]$ from **Table 3**, entry 4. **S193**

Fig. S300 DSC curve of PMyr 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 4**, entry 1 (30 min). **S193**
Fig. S301 DSC curve of PMyr 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 4**, entry 2 (90 min). **S194**
Fig. S302 DSC curve of PMyr 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 4**, entry 3 (3 h). **S194**
Fig. S303 DSC curve of PS 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 4**, entry 4 (30 min). **S195**
Fig. S304 DSC curve of PS 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 4**, entry 5 (20 h). **S195**
Fig. S305 DSC curve of PVL 300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 4**, entry 6 (10 min). **S196**
Fig. S306 DSC curve of PDL 300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 4**, entry 7 (6 h). **S196**
Fig. S307 DSC curve of PIP-*b*-PVL 800:300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 5**, entry 1. **S197**
Fig. S308 DSC curve of PIP-*b*-PDL 800:300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 5**, entry 2. **S197**
Fig. S309 DSC curve of PMyr-*b*-PCL 800:300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 5**, entry 3. **S198**
Fig. S310 DSC curve of PMyr-*b*-PVL 800:300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 5**, entry 4. **S198**
Fig. S311 DSC curve of PMyr-*b*-PDL 800:300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 5**, entry 5. **S199**
Fig. S312 DSC curve of PMyr 800 equivalents generated by **8**/$[Ph_3C][B(C_6F_5)_4]$ from **Table S1**, entry 1 (30 min). **S199**
Fig. S313 DSC curve of PS 800 equivalents generated by **8**/$[Ph_3C][B(C_6F_5)_4]$ from **Table S1**, entry 2 (30 min). **S200**
Fig. S314 DSC curve of PVL 300 equivalents generated by **8**/$[Ph_3C][B(C_6F_5)_4]$ from **Table S1**, entry 3 (10 min). **S200**
Fig. S315 DSC curve of PDL 300 equivalents generated by **8**/$[Ph_3C][B(C_6F_5)_4]$ from **Table S1**, entry 4 (6 h). **S201**
Fig. S316 DSC curve of PIP 300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table S2**, entry 1 (12 h). **S201**
Fig. S317 DSC curve of PIP 550 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table S2**, entry 2 (12 h). **S202**
Fig. S318 DSC curve of PCL 550 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table S2**, entry 3 (2 h). **S202**
Fig. S319 DSC curve of PCL 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table S2**, entry 4 (2 h). **S203**
Fig. S320 DSC curve of PCL 300 equivalents generated by **6** from **Table S2**, entry 5 (No $[Ph_3C][B(C_6F_5)_4]$ added) (10 min). **S203**
Fig. S321 DSC curve of PIP-*b*-PCL 50:50 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table S3**, entry 2. **S204**
Fig. S322 DSC curve of PIP-*b*-PCL 50:50 equivalents generated by $\mathbf{Y[N(SiMe_3)_2]_3}$ from **Table S3**, entry (6 h). **S204**

1. General Considerations

All reactions involving air and moisture sensitive compounds were carried out using Schlenk line techniques or in a Vacuum Atmospheres OMNI-LAB glovebox under an oxygen free, N_2 atmosphere. Solvents used in air free reactions (toluene, hexanes, pentane, and tetrahydrofuran) were purchased from Fisher, sparged under ultrahigh purity (UHP) grade argon and passed through two columns of drying agent in a JCMeyer solvent purification system and dispensed directly into the glovebox. All other solvents were used without further purification. Deuterated NMR solvents, C_6D_6, $CDCl_3$, and toluene-d_8 were purchased from Cambridge Isotope Laboratories and were used as received. Toluene-d_8 and C_6D_6 suitable for air sensitive compounds were dried by stirring over Na/benzophenone for two days, followed by three freeze-pump-thaw cycles and vacuum transferred into a flame-dried Straus flask and stored in a glovebox under a N_2 atmosphere. Complexes {MeC(2,6-^{i}Pr)$_2$C$_6$H$_3$NH)CHC(Me[N(2-OMeC$_6$H$_4$)]}Y(CH$_2$SiMe$_3$)$_2$ (**6**), [1] {CH(CHC(Me[N(2-OMeC$_6$H$_4$)$_2$]}Y(CH$_2$SiMe$_3$)$_2$ (**7**)[2], and {CH$_3$C(2,6-(^{i}Pr)$_2$C$_6$H$_3$NH)CHC(CH$_3$)(NCH$_2$-NMe$_2$)}Y(CH$_2$SiMe$_3$)$_2$ (**8**)[3] and Y[N(SiMe$_3$)$_2$]$_3$[4] were synthesized following literature procedure. Isoprene, purchased from Sigma-Aldrich, was dried over 4Å molecular sieves for 7 days, followed by three freeze-pump-thaw cycles and a vacuum transfer into a flame-dried Straus flask and stored in a glovebox at -35 ºC under a N_2 atmosphere. ε-Caprolactone, ε-decalactone, δ-valerolactone, and β-myrcene were purchased from Sigma-Aldrich and were dried over CaH_2 for 3 days followed by three freeze-pump-thaw cycles and a vacuum transfer to a flame-dried Straus flask and stored in a glovebox at -35 ºC under a N_2 atmosphere. All other reagents and chemicals were obtained from commercial vendors (Sigma-Aldrich, TCI, Alfa Aesar, and VWR) and were used without further purification.

1.1 Polymerization Methods

General procedure for the homopolymerization of 1,3-dienes or cyclic esters

In a glovebox, catalyst **6**-**8** (10 μmol, 200 μL of a 0.5 M stock solution) was placed in a stir bar charged 20 mL vial and diluted in toluene (7 mL). Trityl (tetrakis(pentafluorophenyl)borate [Ph$_3$C][B(C$_6$F$_5$)$_4$] (10 μmol, 1 mL of a 0.01 M stock solution) was add to the vial and the mixture was stirred for 10 min. Olefin (300-800 equiv.) was added by micro syringe in one portion, and the polymerization was carried out for the designated time with constant stirring during which the reaction turned from orange to gold. The reaction mixture was poured into a large quantity of ethanol (100 mL) to give colorless copolymer that was dried in a vacuum oven at 40 ºC for 12 h to a constant weight (0.90 g, 100%).

General procedure for the block copolymerization of 1,3-dienes and cyclic esters

In a glovebox, catalyst **6**-**8** (10 μmol, 200 μL of a 0.5 M stock solution) was placed in a stir bar charged 20 mL vial and diluted in toluene (7 mL). Trityl (tetrakis(pentafluorophenyl)borate [Ph$_3$C][B(C$_6$F$_5$)$_4$] (10 μmol, 1 mL of a 0.01 M stock solution) was add to the vial and reaction was stirred for 10 min. Olefin (300-800 equiv.) was added by micro syringe in one portion, and the polymerization was carried out for the designated time with constant stirring during which the reaction turned from orange to gold. Then cyclic ester (300-800 equiv.) was added by micro syringe to the above system and polymerization was continued for the designated time. The gel like reaction mixture was poured into a large quantity of ethanol (100 mL) to give colorless copolymer that was dried in a vacuum oven at 40 ºC for 12 h to a constant weight (0.90 g, 100%).

Note: All conditions that deviate from this general procedure are clearly indicated in each table.

1.2 Characterization Methods

NMR Spectroscopy. ^{1}H, ^{13}C, and ^{19}F, NMR spectra were recorded using a Varian Mercury 400 MHz, Varian 500 MHz, or Varian 600 MHz spectrometers. Chemical shifts are referenced to residual protons in the deuterated solvent or the deuterated solvent itself for ^{1}H (7.26 ppm for $CDCl_3$, 2.08 for toluene-d_8) or ^{13}C (77.16 ppm for $CDCl_3$) NMR spectra. All NMR spectra were recorded at room temperature in specified deuterated solvents. Representative peak assignments shown for each homopolymer, isoprene,[5,6] β-myrcene,[7] Styrene,[8] ε-caprolactone,[8] δ-valerolactone,[9] and ε-decalactone.[10]

Fourier Transform Infrared Spectroscopy (FT-IR). FT-IR spectra were recorded using an Agilent Cary 630 FT-IR equipped with a Diamond ATR sampling accessory. Accompanying MicroLab FT-IR software was used to acquire 72 scans at 4 cm^{-1} resolution with a spectral range of 400-4000 cm^{-1}.

Gel Permeation Chromatography (GPC). GPC analyses were conducted using an Agilent 1260 Infinity II GPC System equipped with a Wyatt DAWN HELEOS-II and a Wyatt Optilab T-rEX as well as an Agilent 1260 Infinity autosampler and UV-detector. The GPC system was equipped with an Agilent PolyPore column (5 micron, 4.6 mmID) which was calibrated using monodisperse polystyrene standards, eluted with THF at 30 ºC at 0.3 mL/min. The number average molar mass and dispersity values were determined from multi-angle light scattering (MALS) using *dn/dc* values calculated by 100 % mass recovery method from the refractive index (RI) signal.

Thermal Gravimetric Analysis (TGA). All TGA traces were recorded using Mettler-Toledo STARe System TGA/DSC 3+ equipped with STARe software, a TA SDTA Sensor LF, XP1 Balance, and a sample robot except for four samples (**S239**-**S242**). Data from these four samples were collected on a TGA Q50 instrument. Sample weight of purified polymer was between 5-15 mg was sealed in 40 μL aluminum crucible fitted with a pierceable lid. General method involves heating from 25 ºC to 500 ºC at a scan rate of 10 ºC/min under a constant flow of N_2 (15 mL/min).

Differential Scanning Calorimetry (DSC). DSC traces were recorded using a Perkin-Elmer DSC 8000 and processed with Pyris software. Sample weight of purified polymer was between 7-30 mg measured out on a microbalance and sealed in standard Perkin-Elmer Aluminum Pans. Data was collected at a consistent scan rate of 10 ºC/min under a N_2 flow of 20 mL/min. General collection method involved 1) 5 min isothermal step at -80 ºC, 2) heating step from -80 ºC to 100º C, 3) 5 min isothermal step, 4) cooling step from 100 ºC to -80 ºC. These 4 steps were repeated through two additional heating and cooling cycles. All T_g and T_m values reported are from the 3rd heating scan. Any deviations from this method involved a temperature range shift.

1.3 Impurity in $[Ph_3C][B(C_6F_5)_4]$

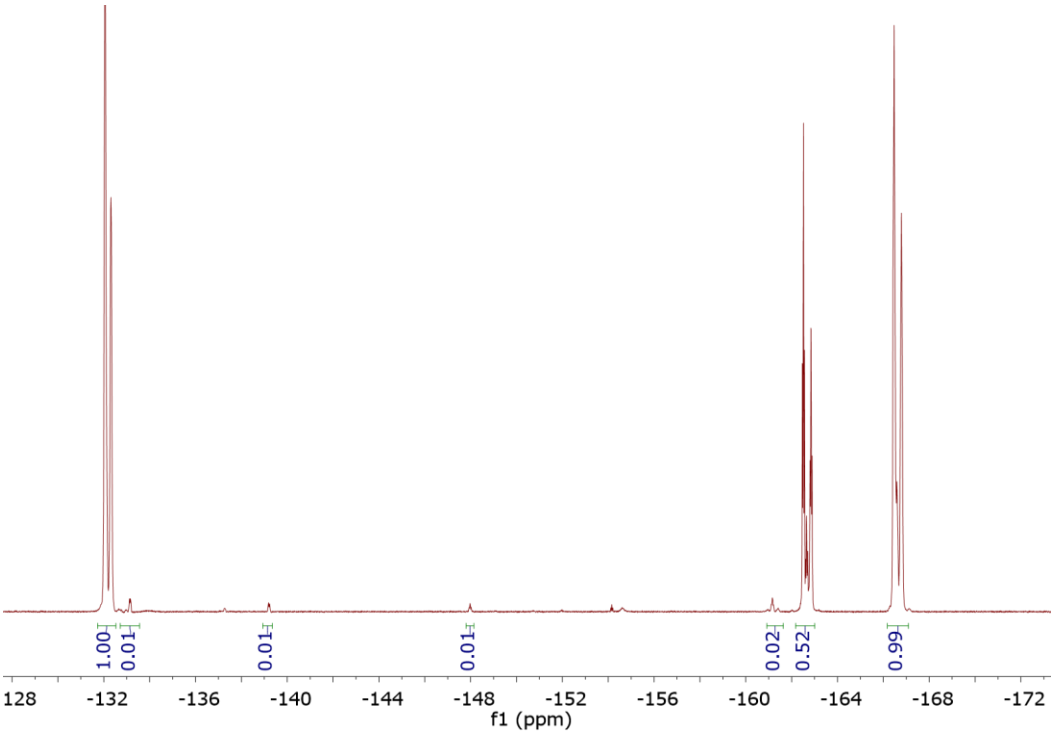
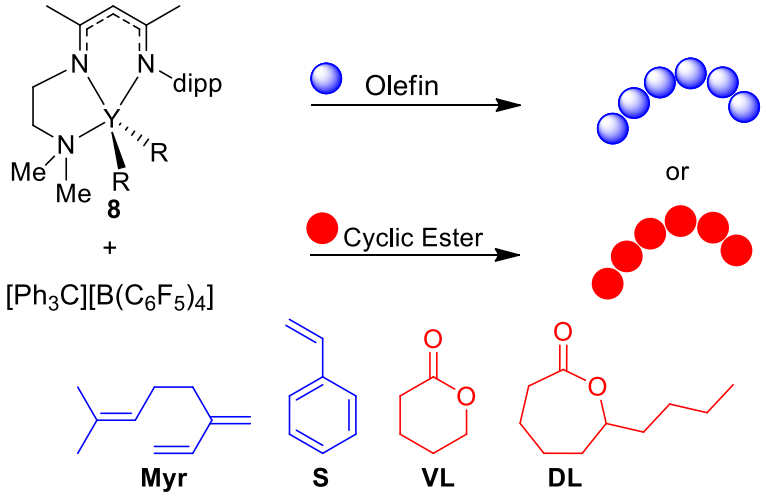


Fig. S1. ^{19}F NMR spectrum of $[Ph_3C][B(C_6F_5)_4]$ in C_6D_6 at 298 K.

1.4 Homopolymerization of 1,3-dienes and cyclic esters with 8/[Ph_3C][$B(C_6F_5)_4$].

Table S1. Homopolymerization of a range of 1,3-dienes and cyclic esters with pre-catalyst **8**.[a]

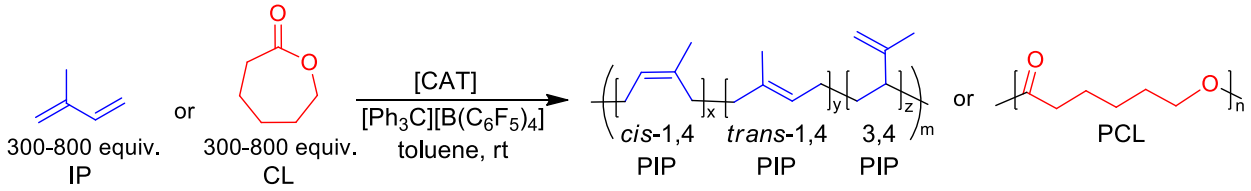


Entry	Monomer	Time	Temp. (°C)	Conv. (%)[b]	M_n (kDa)[c]	Đ[c]	Microstructure[d] *Cis*-1,4/*Trans*-1,4/3,4	T_g (°C)[e]	T_m (°C)[e]
1	Myr	30 min	rt	19	12	1.14	4/93/3	-65	—
2	S	30 min	rt	13	4.9	2.03	—	87	—
3	VL	10 min	rt	82	26	1.27	—	—	54
4	DL	6 h	60	69	42	1.07	—	-51	—

[a]Conditions: **8**,10 μmol; [Ph_3C][$B(C_6F_5)_4$], 10 μmol; toluene, 10 mL; [olefin]/**8**= 800; [cyclic ester]/ **8**= 300. [b]Determined by ^{1}H NMR spectroscopy of crude reaction mixtures, comparing monomer peaks to polymer. [c]Determined by gel permeation chromatography (GPC) in THF using a Wyatt DAWN HELEOS II MALS detector. [d]1,4 and 3,4 selectivity determined by ^{1}H NMR. *Cis*-1,4 and *trans*-1,4 selectivity determined by ^{13}C NMR. [e]Determined by low temperature differential scanning calorimetry (DSC).

1.5 Homopolymerization of different feed ratios of IP and CL with 6/[Ph_3C][$B(C_6F_5)_4$].

Table S2. Homopolymerization of IP or CL with pre-catalyst **6**.[a]



Entry	Monomer	Feed Ratio	M_n (kDa)[b]	Đ[b]	Microstructure[c] *Cis*-1,4/*Trans*-1,4/3,4	T_g (°C)[d]	T_m (°C)[d]
1	IP	300	50.8(13.1)	1.11(1)	19/79/2	-68	—
2	IP	550	67.4(13.3)	1.05(1)	46/52/2	-65	—
3	CL	550	103(4.71)	1.33(1)	—	—	54
4	CL	800	112(3.62)	1.36(1)	—	—	58
5[e]	CL	300	51	1.26	—	—	55

[a]Conditions: **6**, 10 μmol; [Ph_3C][$B(C_6F_5)_4$], 10 μmol; toluene, 10 mL; room temperature; IP 12 h; CL 2 h; entries 1-4 are done in triplicate; full conversion was seen in all cases. [b]Determined by gel permeation chromatography (GPC) in THF using a Wyatt DAWN HELEOS II MALS detector. [c]1,4 and 3,4 selectivity determined by ^{1}H NMR. *Cis*-1,4 and *trans*-1,4 selectivity determined by ^{13}C NMR. [d]Determined by low temperature differential scanning calorimetry (DSC). [e]No [Ph_3C][$B(C_6F_5)_4$] added.

1.6 Recycling PIP-*b*-PCL copolymers.

General procedure for the degradation of PIP-b-PCL diblocks

In a 100 mL round bottom flask, charged with a stir bar, PIP-*b*-PCL 50:50 (0.2 g, 55 kDa) was dissolved in THF (~25 mL). A 2 M NaOH aqueous solution (50 mL) was then added, and the reaction flask was fitted with a reflux condenser and heated to 100 ºC for 12 h. After cooling, the solution was neutralized with acetic acid. The organic fraction was separated, and the aqueous fraction was washed with THF (25 mL) 3 times. Organic fractions were combined and washed twice with 2 M $NaHCO_3$ (50 mL) followed by a brine wash (40 mL), dried over $MgSO_4$, and filtered. The volatiles were evaporated *in vacuo* to afford a colorless gel. The residue was redissolved in toluene (5 mL) and colorless polymer was crashed out using cooled EtOH. Polymer was dried on a vacuum line at 45 ºC for 3 days, then transferred to a high vacuum line for an additional day before being stored at -35 ºC in a glovebox (75 mg, 63% mass loss).

Formation of Alkoxide macroinitiator with recovered IP 50 and $Y[N(SiMe_3)_2]_3$ and repolymerization with CL

NMR scale PIP-*b*-PCL repolymerization was carried out in a J-young tube in toluene-d_8. Initial ^{1}H NMR of the $Y[N(SiMe_3)_2]_3$ showed a singlet at 0.23 ppm corresponding to yttrium bound $N(SiMe_3)_2$ (Fig. S2, bottom). Upon addition of PIP-OH 50 an immediate loss of the 0.23 ppm peak as well as formation of a new downfield $HN(SiMe_3)_2$ peak was seen (Fig. S2, top). Subsequent addition of CL lead to immediate appearance of a peak a 3.92 ppm which corresponds to PCL (Fig. S3, middle). Full conversion of PCL was seen after 6 h (Fig. S3, top).

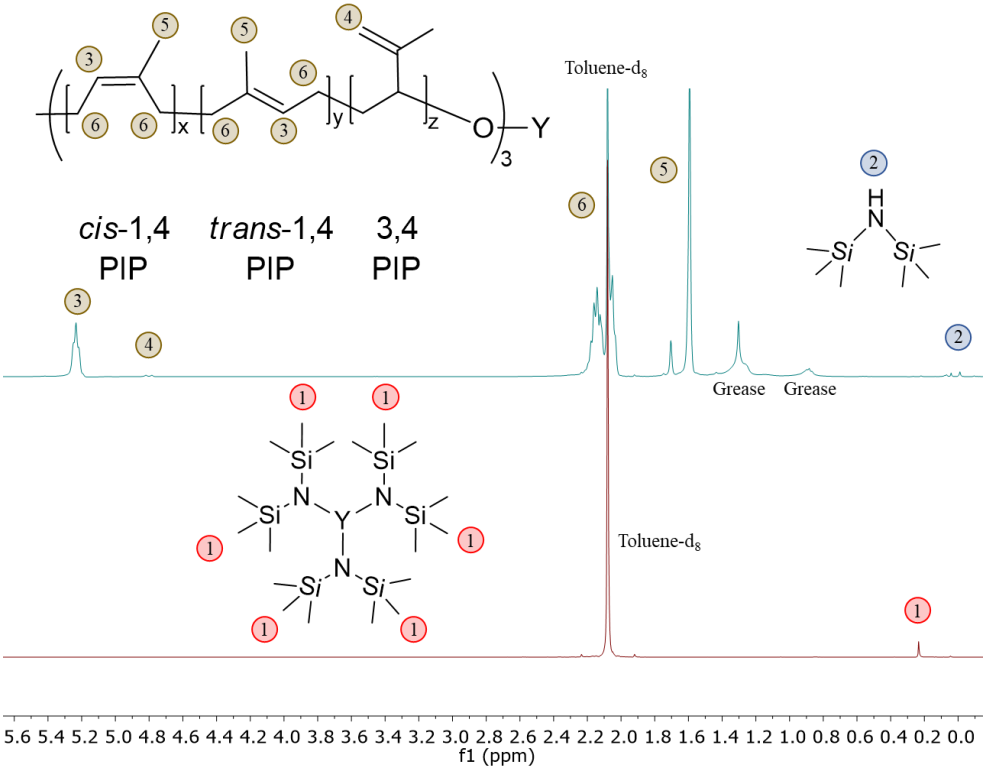


Fig. S2. ^{1}H NMR stack of $Y[N(SiMe_3)_2]_3$ before (bottom) and after recovered IP 50 addition (top) in toluene-d_8 at 298 K.

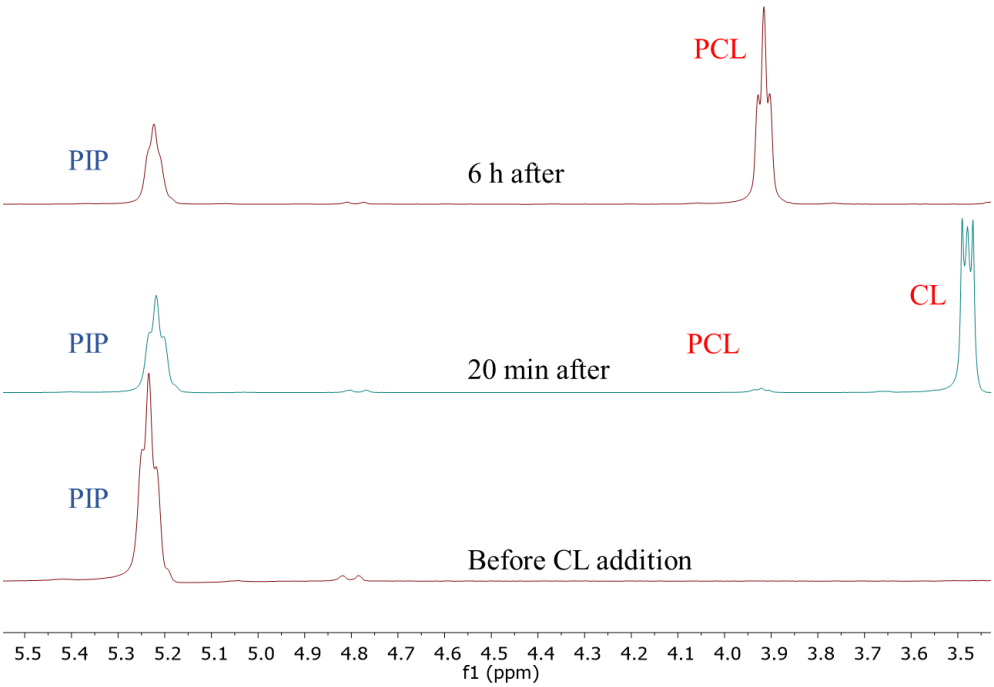


Fig. S3. ^{1}H NMR stack of PIP-*b*-PCL repolymerization with Y[N(SiMe$_3$)$_2$]$_3$ and PIP 50 in toluene-d$_8$ at 298 K. After macroinitiator formation (bottom), 20 min after CL addition (middle), and 6 h after CL addition (top).

General procedure for the repolymerization of PIP-b-PCL diblocks

In a glovebox, yttrium tris[N,N-bis(trimethylsilyl)amide] (Y[N(SiMe$_3$)$_2$]$_3$) (1 equiv., 47 μL of a 0.01 M stock solution, 0.47 μmol) was dissolved in toluene (2 mL) and transferred to a stir bar charged Schlenk flask. PIP-OH (2.5 equiv., 0.05 g, 43 kDa) was dissolved in toluene (5 mL) and slowly added. After stirring for 10 min, ε-caprolactone (125 equiv., 8 μL, 58 μmol) was added to the reaction. Reaction was removed from the glovebox and placed on a Schlenk line. The side arm of the Schlenk flask was evacuated and backfilled with dry N$_2$ three times and the reaction mixture was heated to 70 ºC for 6 h under N$_2$ atmosphere. The colorless reaction mixture was poured into a large quantity of ethanol (50 mL) to quench the polymerization. The collected colorless polymer was dried in a vacuum oven at 40 ºC for 12 h to a constant weight of 0.152 g.

Table S3. Polymerization, depolymerization, and repolymerization of PIP-*b*-PCL.[a]

Entry	Cat.	Initiator: Activator	Monomer (M_1:M_2)	Time (h)	Feed Ratio	M_n (kDa)[e]	Đ[e]	Microstructure[f] *Cis*-1,4/*Trans*-1,4/3,4	Eff (%)[g]
1	**6**	Alkyl: Borate	IP: —	12	50:0	42	1.15	42/56/2	8
2	**6**	Alkyl: Borate	IP:CL	12:2	50:50	55	1.09	45/53/2	17
3[b]	**NaOH**	—	—	12	—	43	1.15	41/58/1	—
4[c]	**$Y[N(SiMe_3)_2]_3$**	Alkoxide (PIP-OH): —	CL	6	0:125	56	1.16	42/57/1	85
5[d]	**6**	Alkyl: Borate	IP:CL	12:2	50:50	21	1.12	34/65/1	43

[a]Conditions: **6**, 10 μmol; $[Ph_3C][B(C_6F_5)_4]$, 10 μmol; toluene, 10 mL toluene; room temperature; IP 12 h; CL 2 h; full conversion was seen in all cases. [b]NaOH, 2M (50 mL); THF, 25 mL; 100 ºC; 12 h; full degradation of PCL was seen. [c]**$Y[N(SiMe_3)_2]_3$**, 0.47 μmol; PIP-OH, 43 kDa; toluene, 7 mL; 70 ºC, 6 h. [d]Same conditions as entries 1 and 2 except toluene volume decreased to 1 mL. [e]Determined by gel permeation chromatography (GPC) in THF using a Wyatt DAWN HELEOS II MALS detector. [f]1,4 and 3,4 selectivity determined by ^{1}H NMR. *Cis*-1,4 and *trans*-1,4 selectivity determined by ^{13}C NMR. [g]Catalyst efficiency, calculated by M_n(theor.)/M_n(exp.).

2.0 References

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3.0 Nuclear Magnetic Resonance (NMR) Spectroscopy Characterization of Isolated Polymers

3.1 ^{1}H NMR Spectroscopy

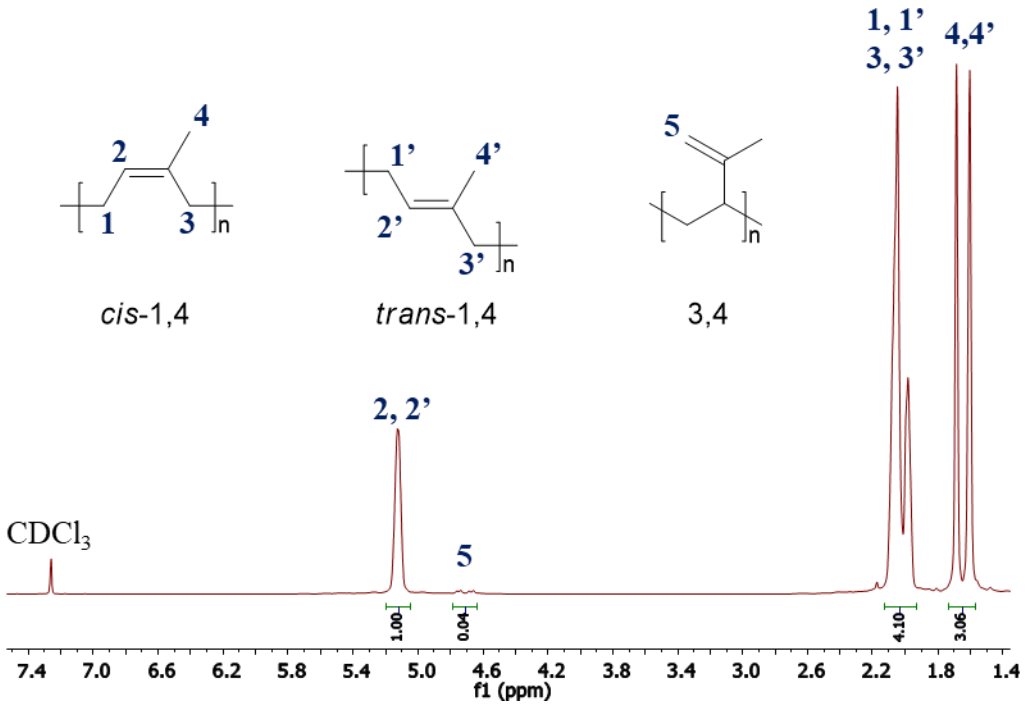

Fig. S4 ^{1}H NMR spectrum of PIP 800 equivalents generated by **6**/[Ph_3C][$B(C_6F_5)_4$] from **Table 1**, entry 1a in $CDCl_3$ at 298 K (12 h). Representative peak assignment for PIP. Peak 5 used to calculate 3,4 selectivity.

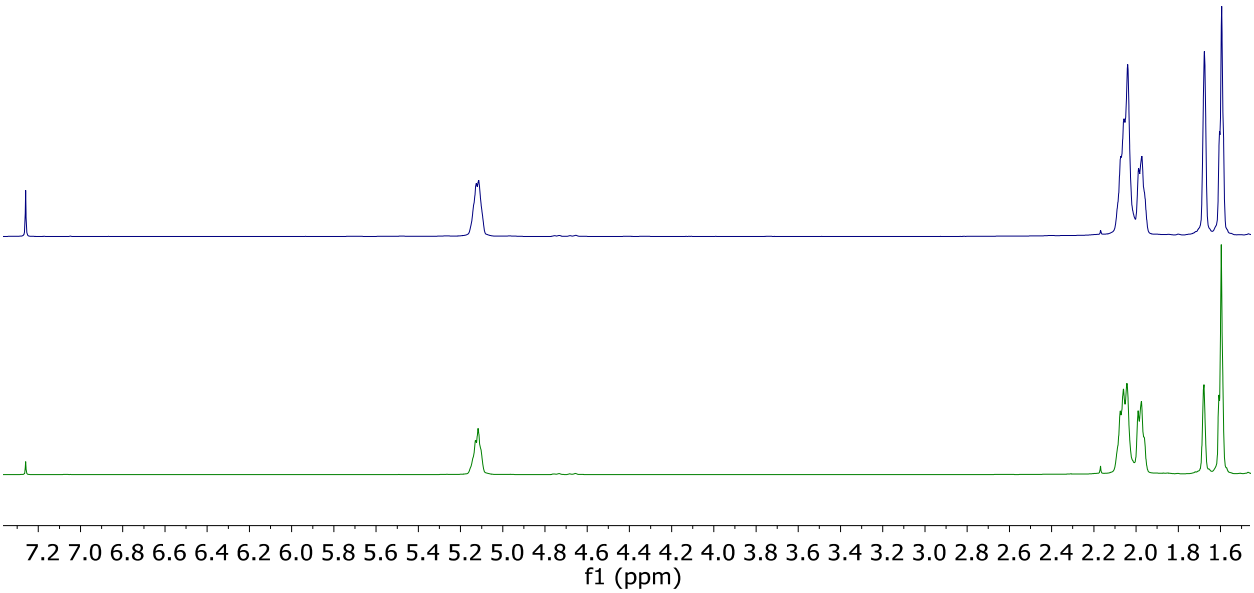

Fig. S5 ^{1}H NMR spectrum of PIP 800 equivalents generated by **6**/[Ph_3C][$B(C_6F_5)_4$] from **Table 1**, entry 1(b and c) in $CDCl_3$ at 298 K (12 h).

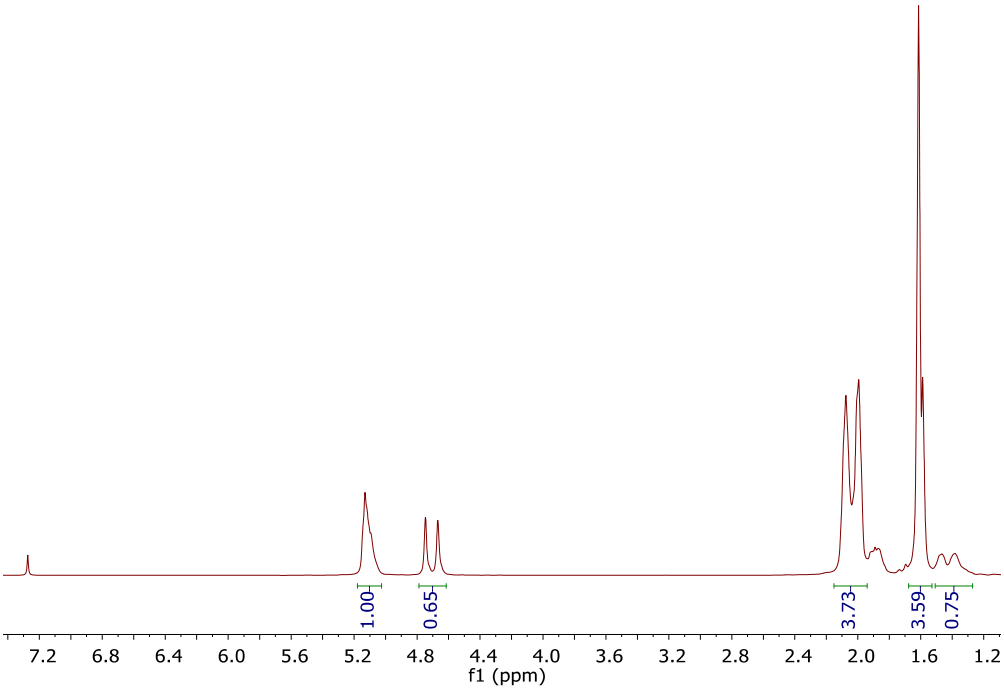

Fig. S6 ^{1}H NMR spectrum of PIP 800 equivalents generated by **8**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 1**, entry 3 in $CDCl_3$ at 298 K (12 h).

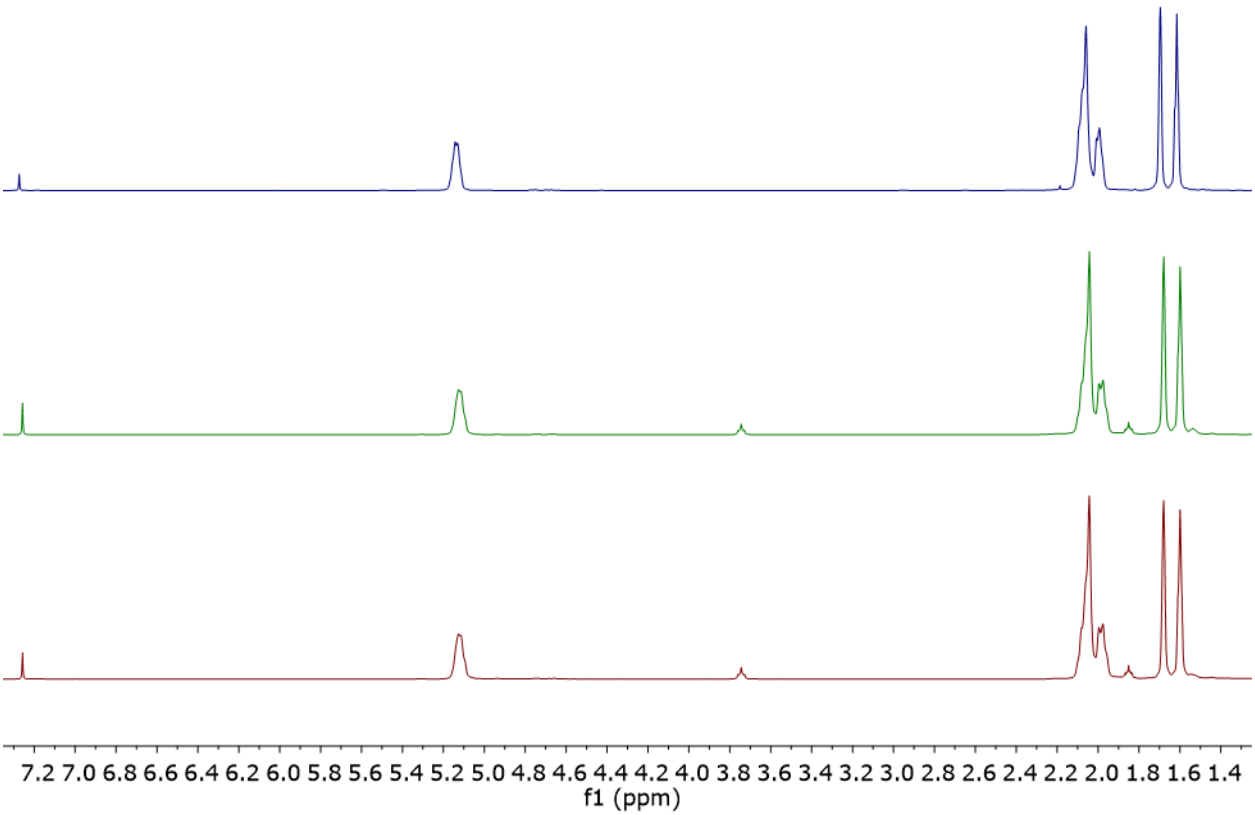

Fig. S7 ^{1}H NMR spectrum of PIP 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 1**, entry 4 in $CDCl_3$ at 298 K (24 h).

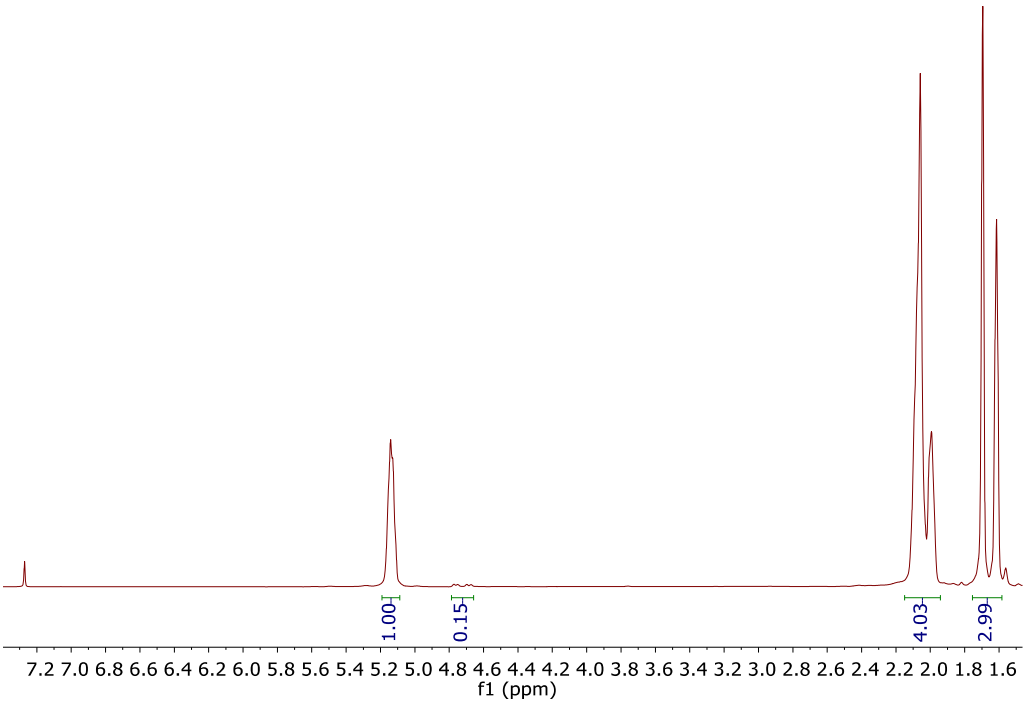

Fig. S8 ^{1}H NMR spectrum of PIP 800 equivalents generated by **6**/[Ph_3C][$B(C_6F_5)_4$] from **Table 1**, entry 5 in $CDCl_3$ at 298 K (30 min).

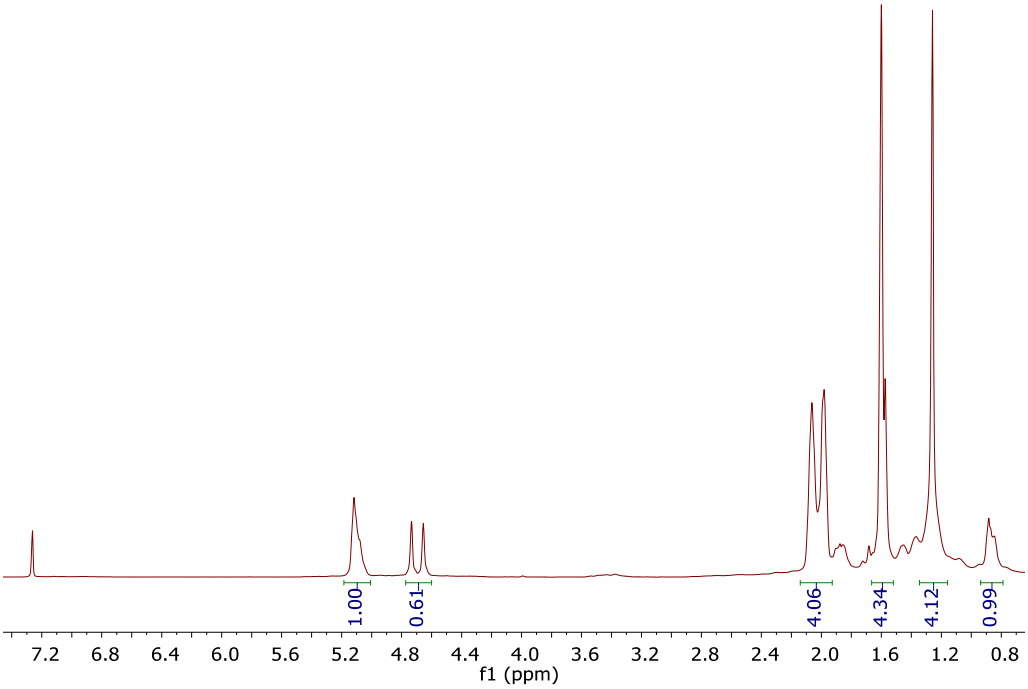

Fig. S9 ^{1}H NMR spectrum of PIP 800 equivalents generated by **8**/[Ph_3C][$B(C_6F_5)_4$] from **Table 1**, entry 6 in $CDCl_3$ at 298 K (30 min).

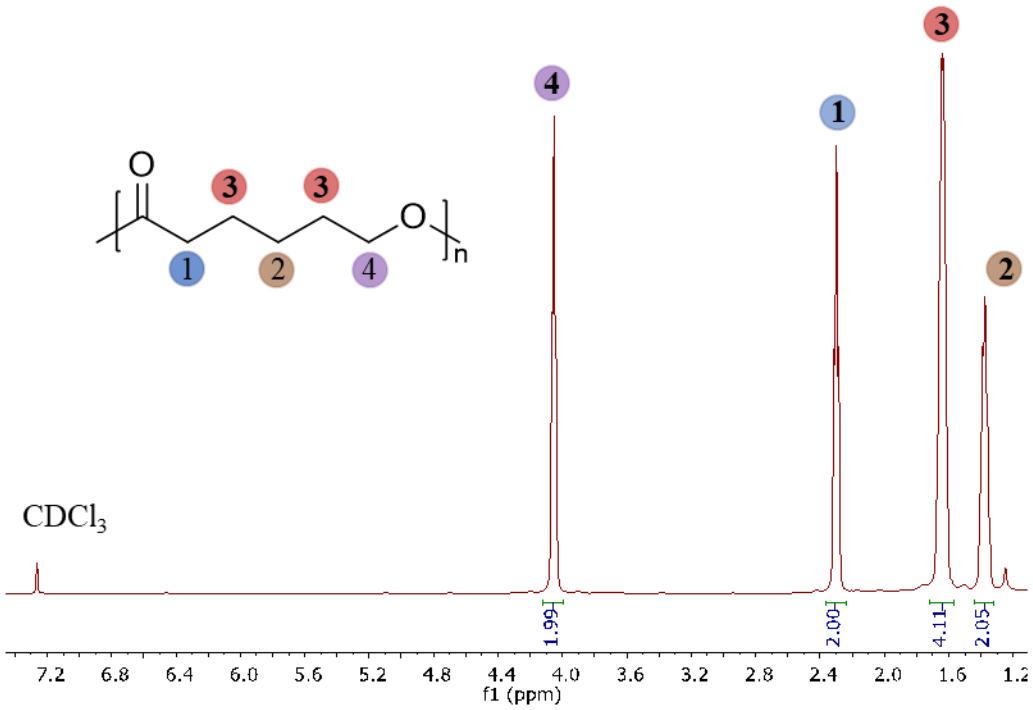

Fig. S10 ^{1}H NMR spectrum of PCL 300 equivalents generated by **6**/[Ph_3C][$B(C_6F_5)_4$] from **Table 1**, entry 7 in $CDCl_3$ at 298 K (10 min). Representative peak assignment for PCL.

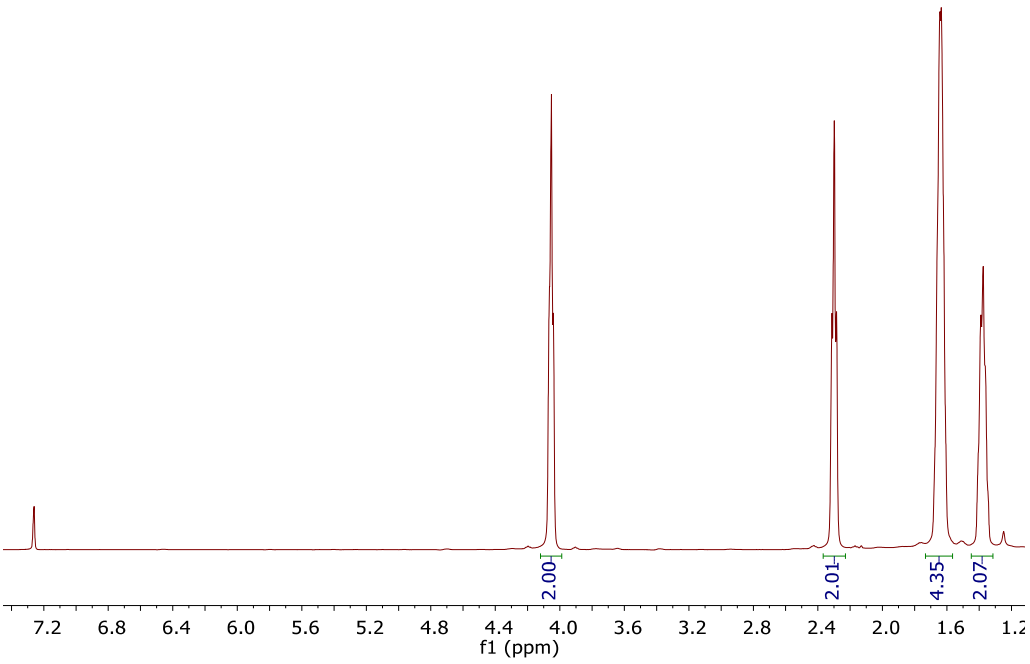

Fig. S11 ^{1}H NMR spectrum of PCL 300 equivalents generated by **8**/[Ph_3C][$B(C_6F_5)_4$] from **Table 1**, entry 8 in $CDCl_3$ at 298 K (10 min).

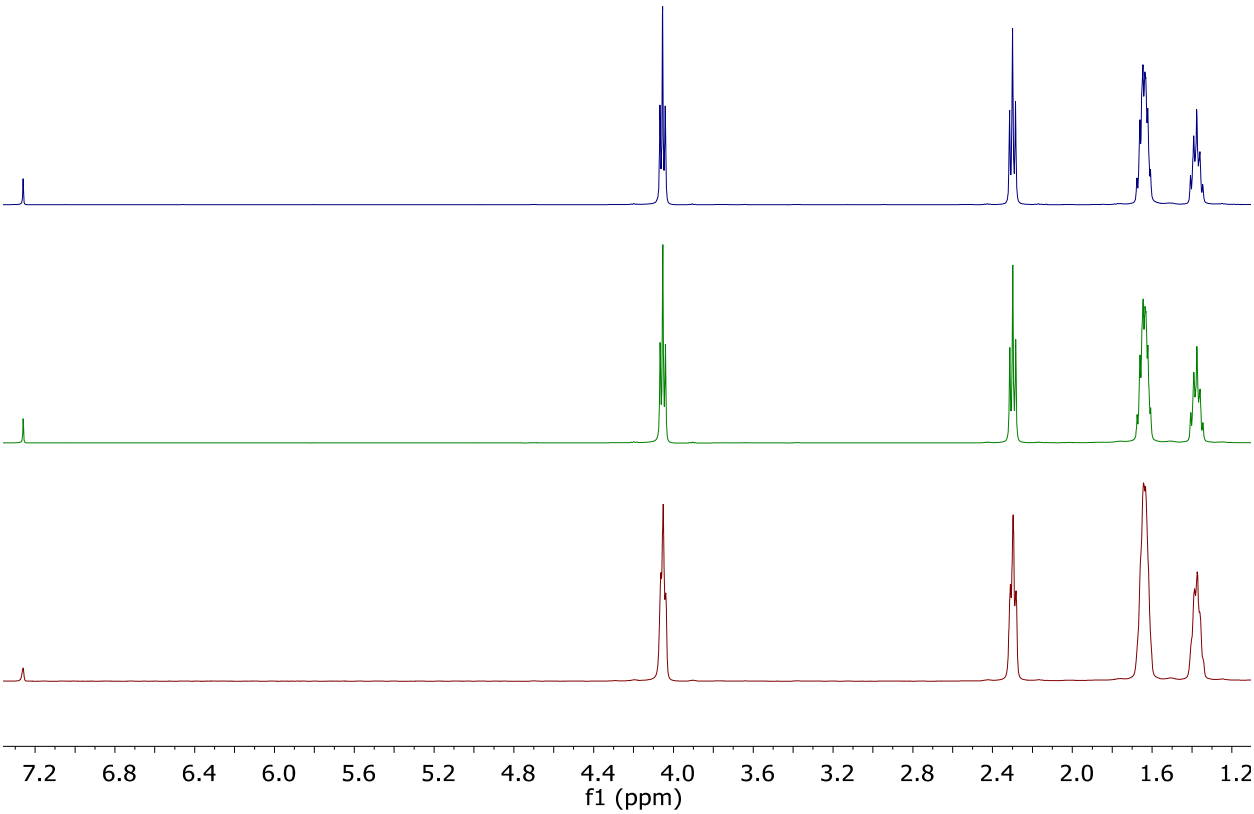

Fig. S12 ^{1}H NMR spectrum of PCL 300 equivalents generated by **6**/[Ph_3C][$B(C_6F_5)_4$] from **Table 1**, entry 9 in $CDCl_3$ at 298 K (2 h).

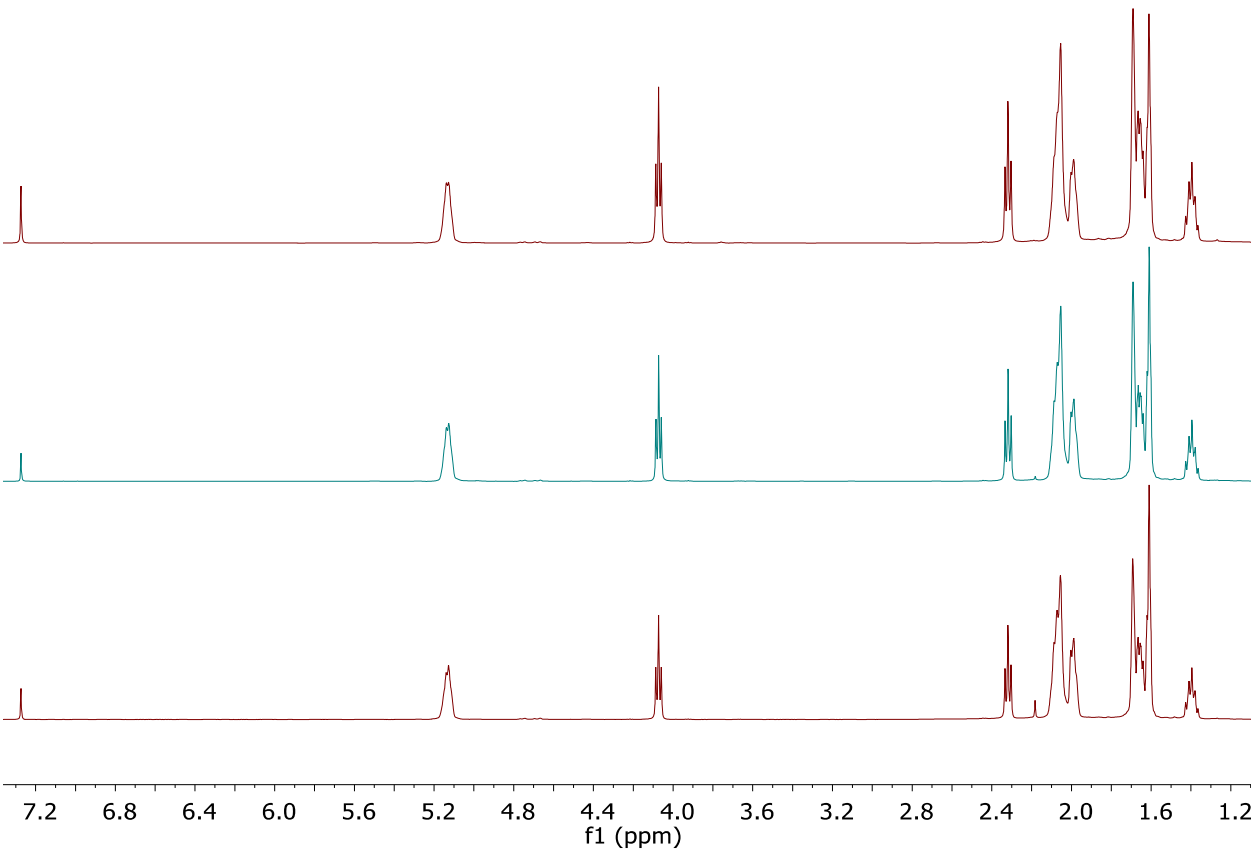

Fig. S13 ^{1}H NMR spectrum of PIP-*b*-PCL 800:300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 2**, entry 1 in $CDCl_3$ at 298 K.

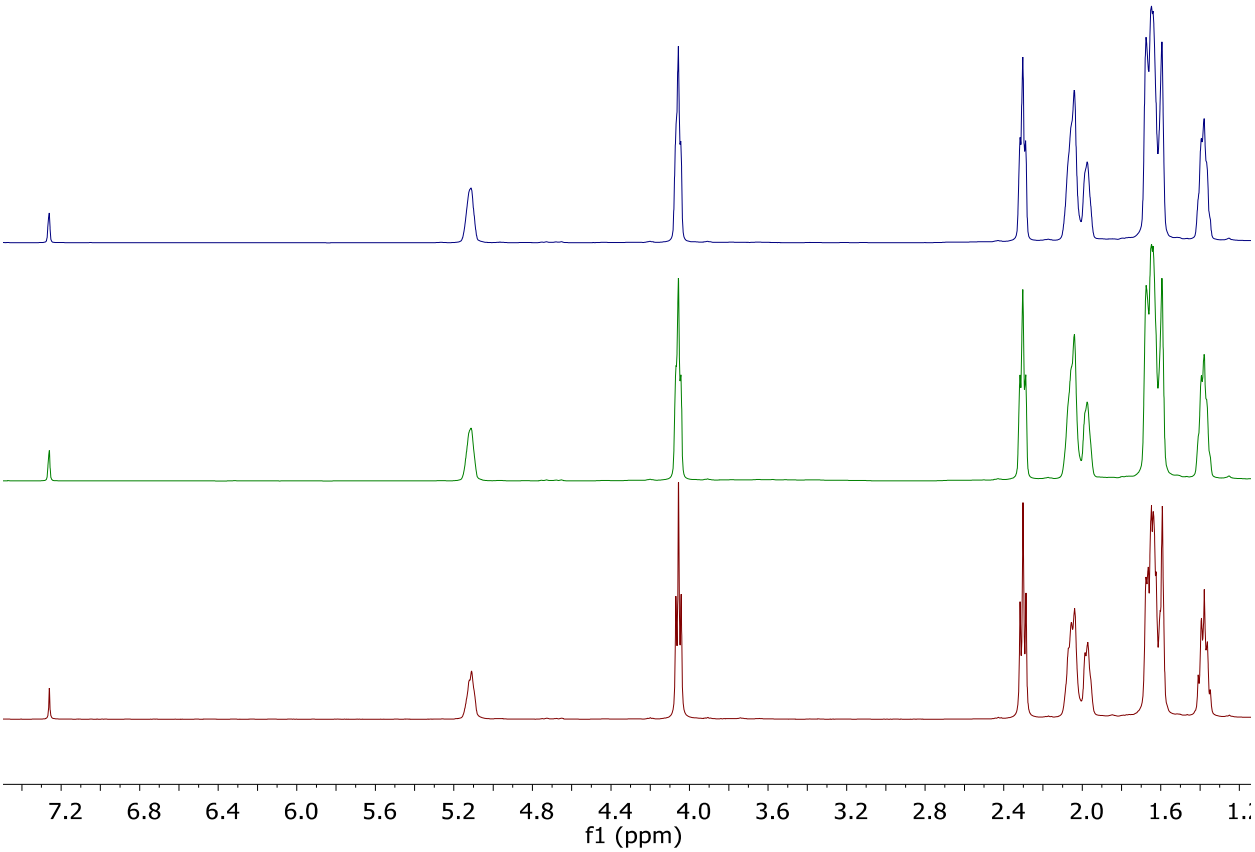

Fig. S14 ^{1}H NMR spectrum of PIP-*b*-PCL 550:550 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 2**, entry 2 in $CDCl_3$ at 298 K.

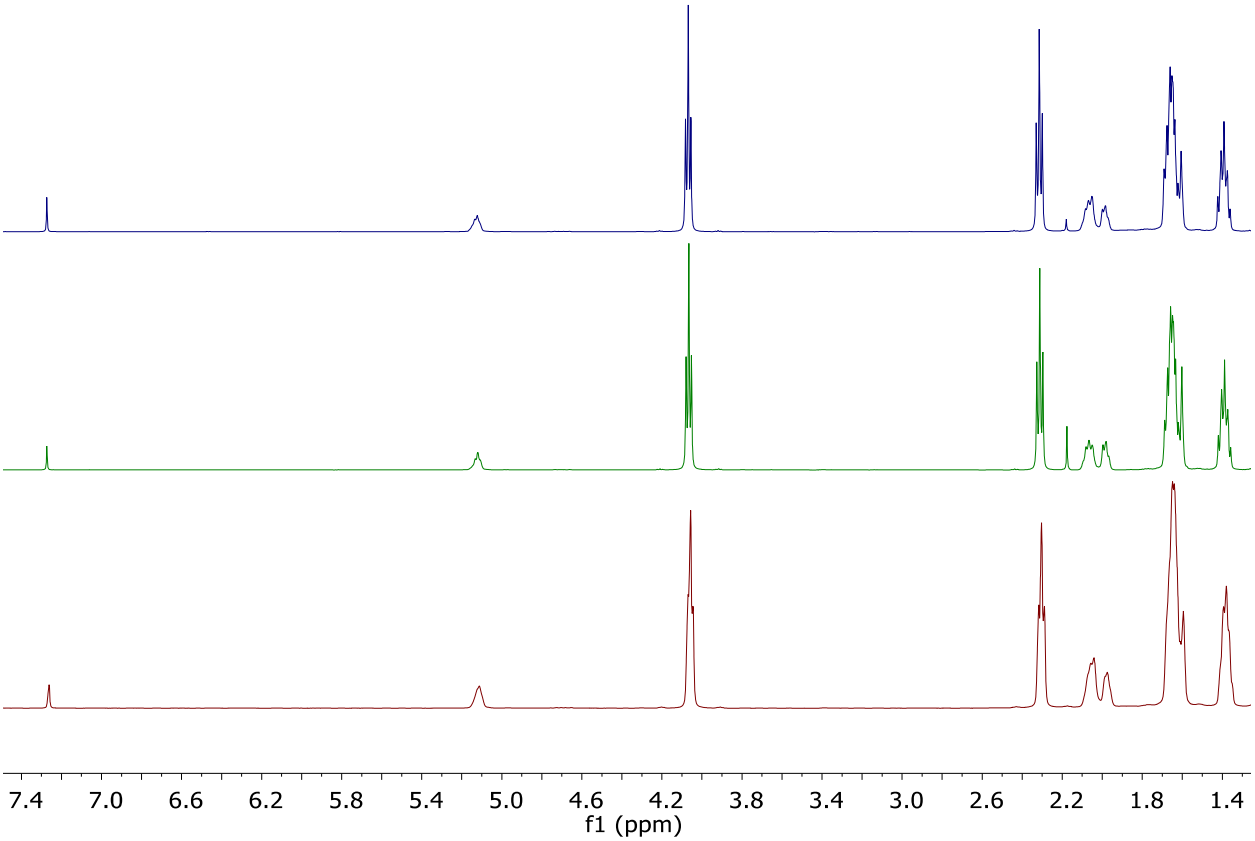

Fig. S15 ^{1}H NMR spectrum of PIP-*b*-PCL 300:800 equivalents generated by **6**/[Ph_3C][$B(C_6F_5)_4$] from **Table 2**, entry 3 in $CDCl_3$ at 298 K.

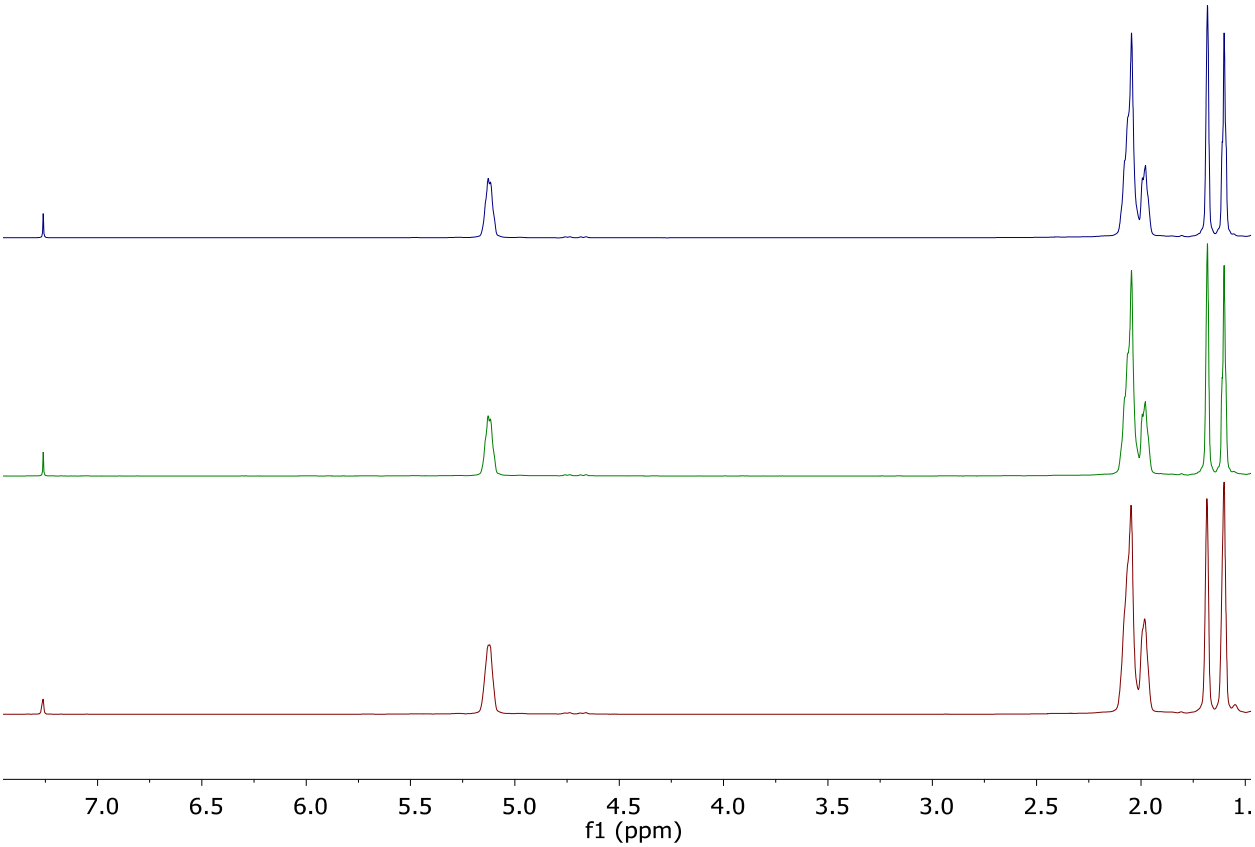

Fig. S16 ^{1}H NMR spectrum of PIP 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 3**, entry 1 in $CDCl_3$ at 298 K (IP addition time 0 min).

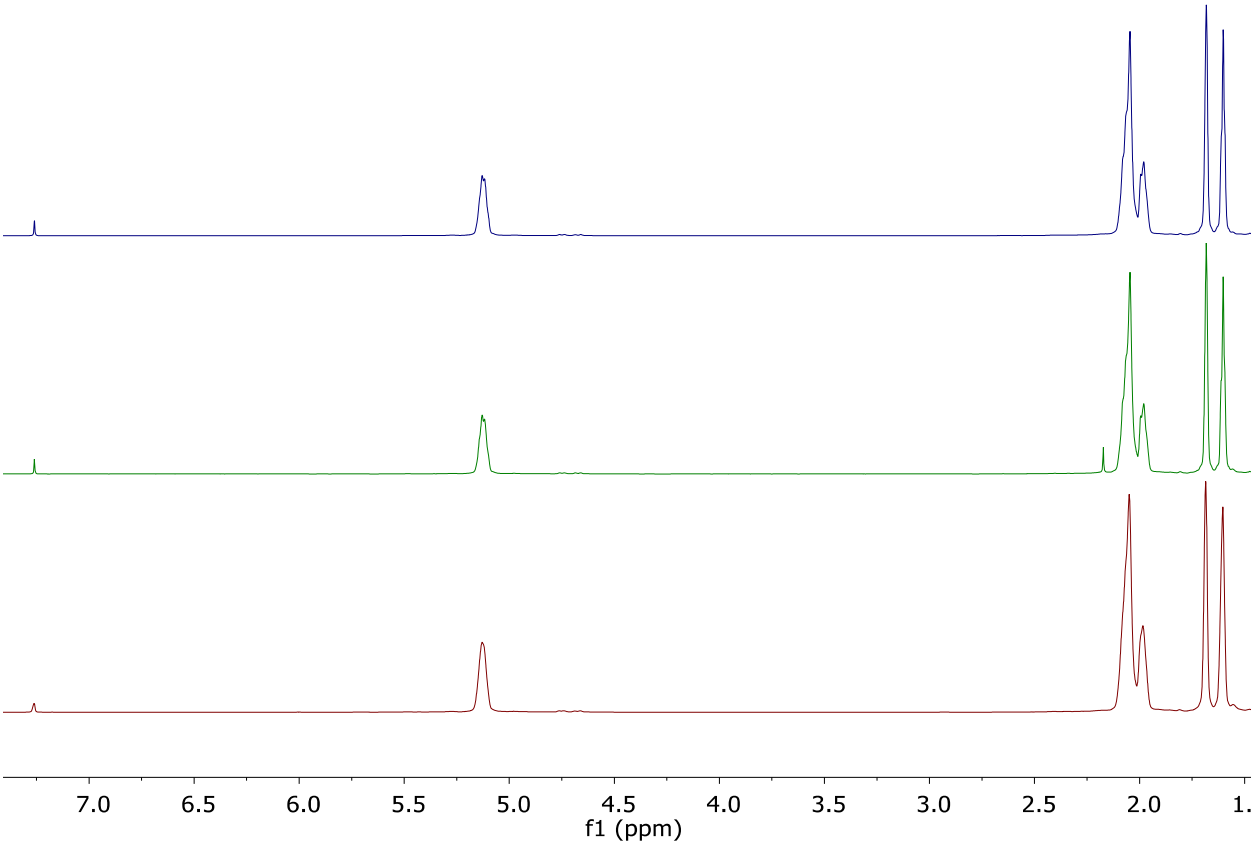

Fig. S17 ^{1}H NMR spectrum of PIP 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 3**, entry 2 in $CDCl_3$ at 298 K (IP addition time 30 min).

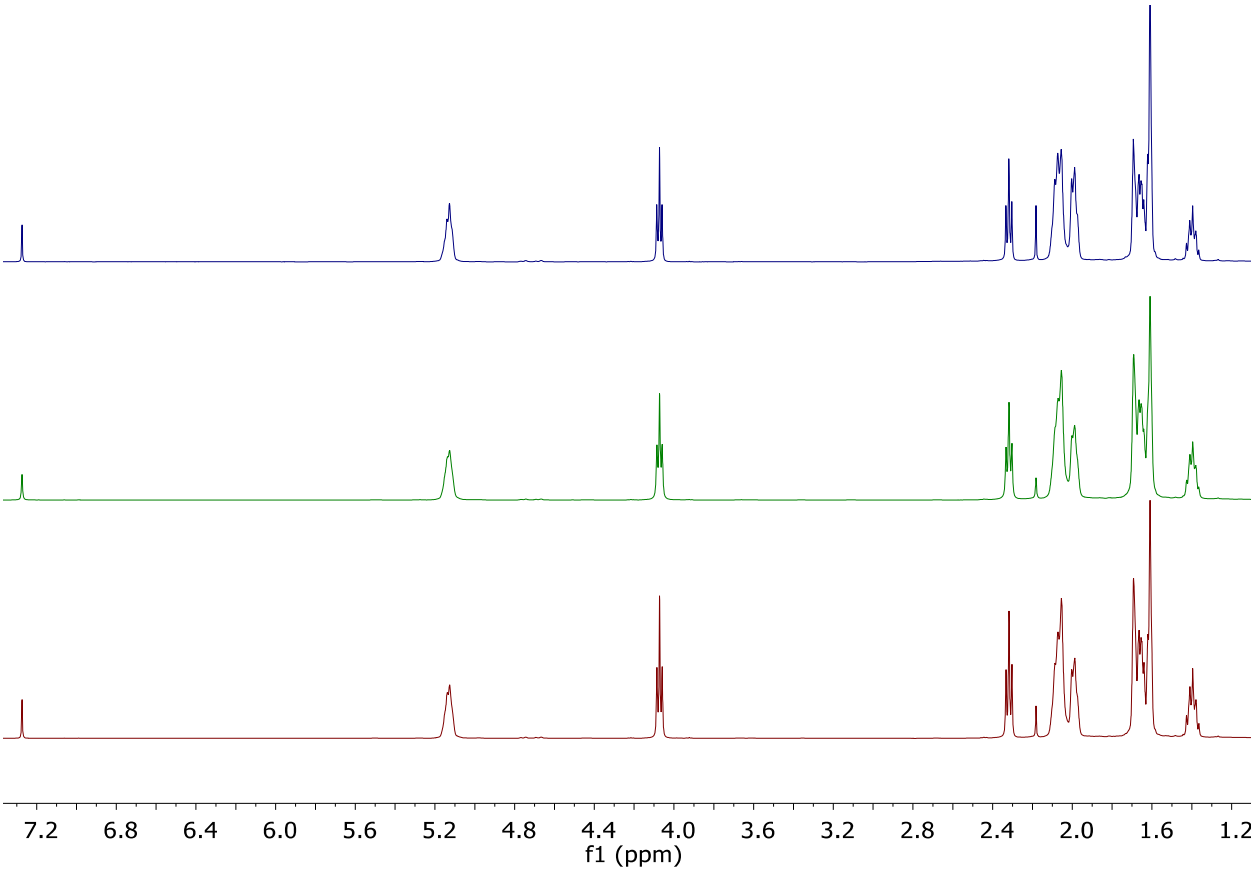

Fig. S18 ^{1}H NMR spectrum of PIP-*b*-PCL 800:300 equivalents generated by **6** and 0.5 equivalents of $[Ph_3C][B(C_6F_5)_4]$ from **Table 3**, entry 3 in $CDCl_3$ at 298 K.

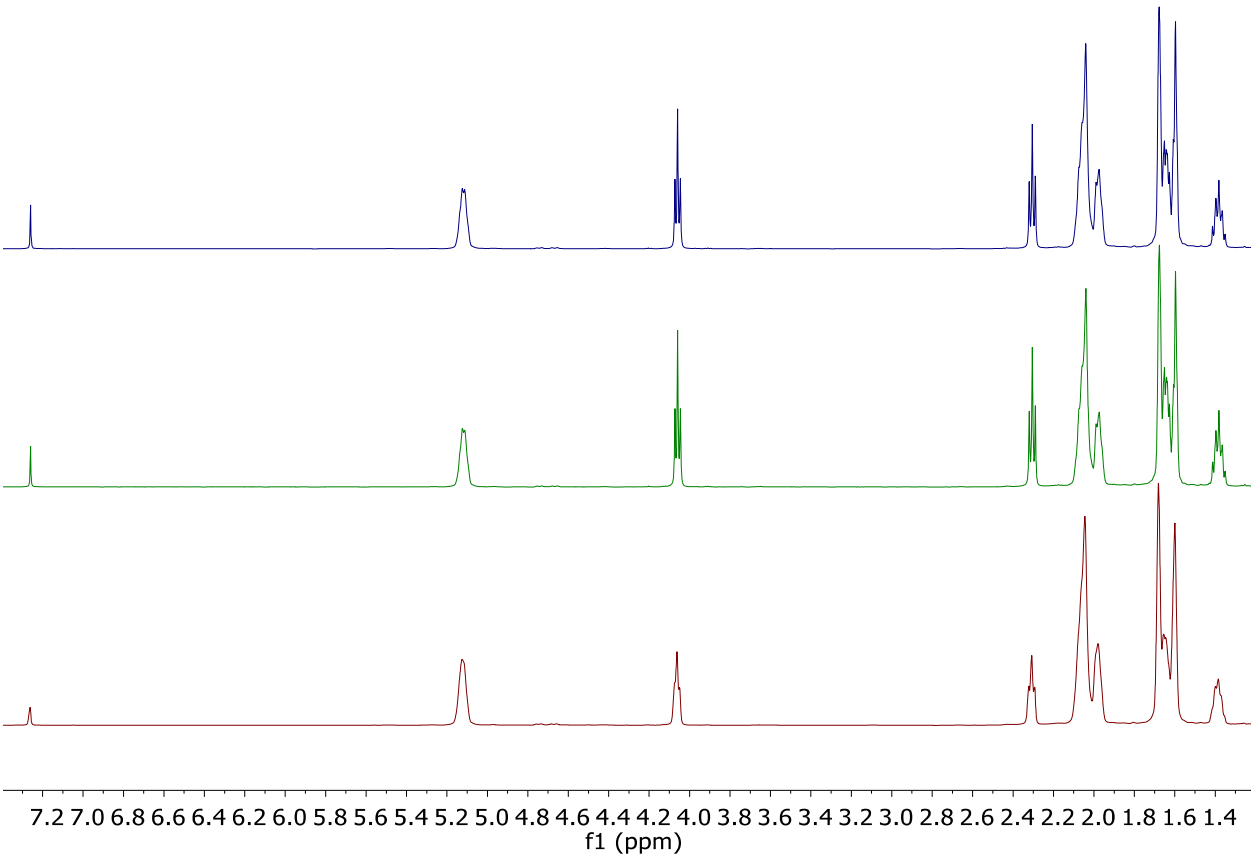

Fig. S19 ^{1}H NMR spectrum of PIP-*b*-PCL 800:300 equivalents generated by **6** and 1.5 equivalents of $[Ph_3C][B(C_6F_5)_4]$ from **Table 3**, entry 4 in $CDCl_3$ at 298 K.

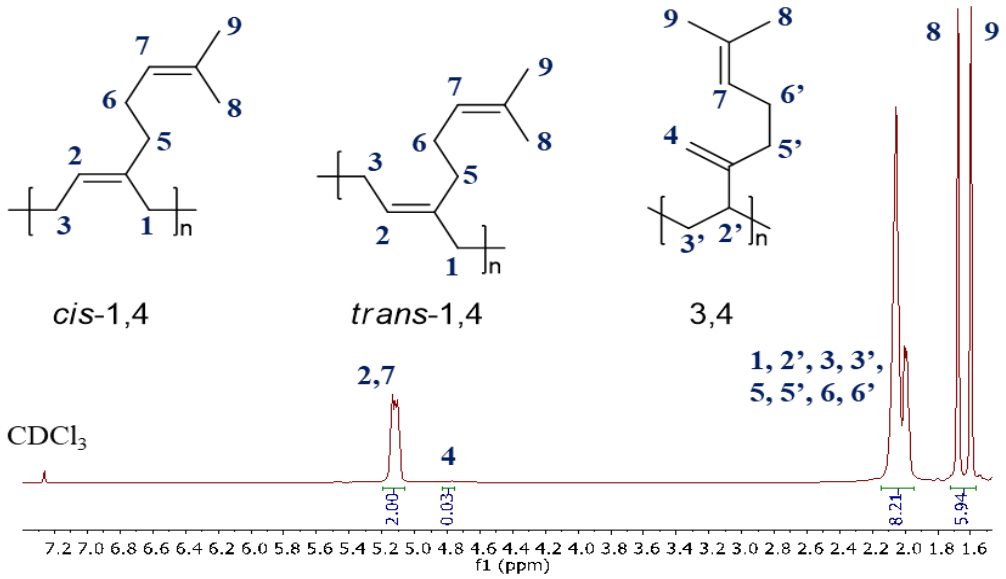

Fig. S20 ^{1}H NMR spectrum of PMyr 800 equivalents generated by **6**/[Ph_3C][$B(C_6F_5)_4$] from **Table 4**, entry 1 in $CDCl_3$ at 298 K (30 min). Representative peak assignment for PMyr.

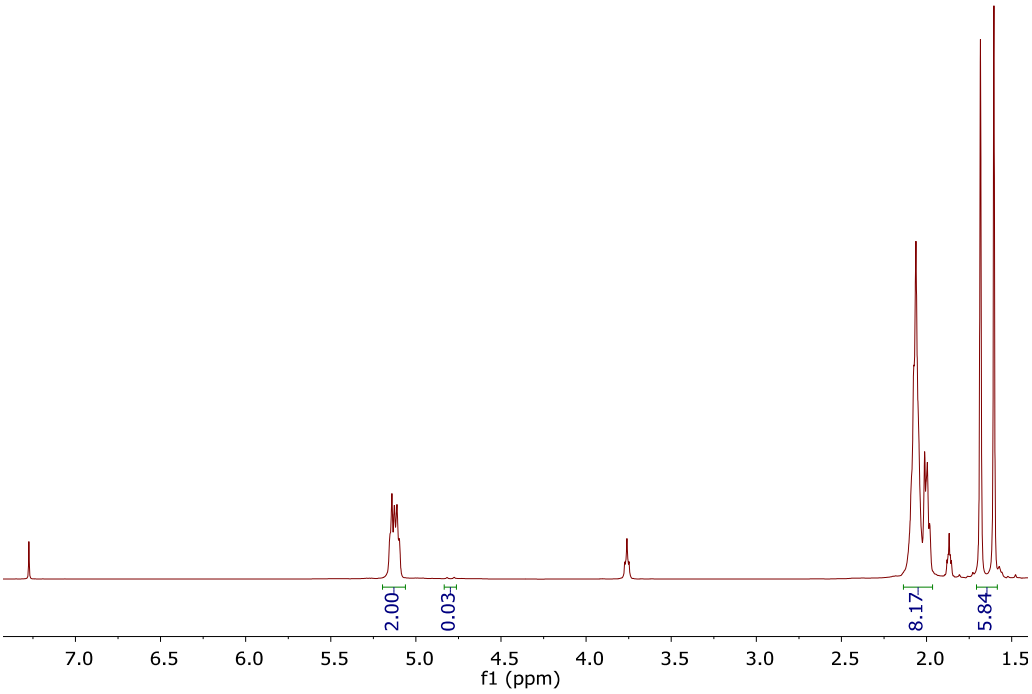

Fig. S21 ^{1}H NMR spectrum of PMyr 800 equivalents generated by **6**/[Ph_3C][$B(C_6F_5)_4$] from **Table 4**, entry 2 in $CDCl_3$ at 298 K (90 min).

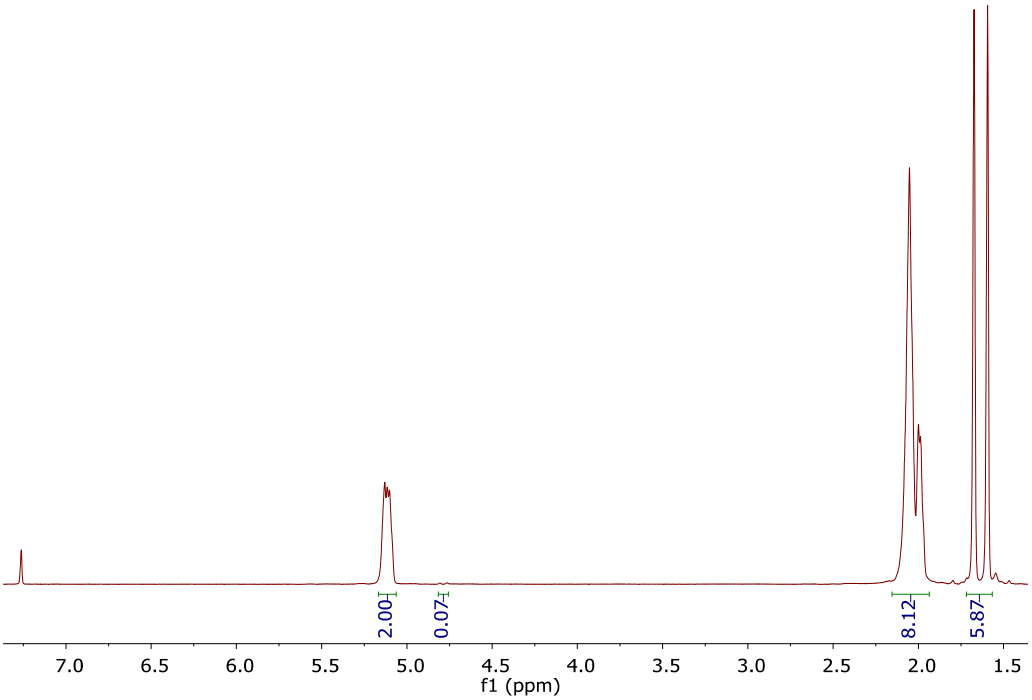

Fig. S22 ^{1}H NMR spectrum of PMyr 800 equivalents generated by **6**/[Ph_3C][$B(C_6F_5)_4$] from **Table 4**, entry 3 in $CDCl_3$ at 298 K (3 h).

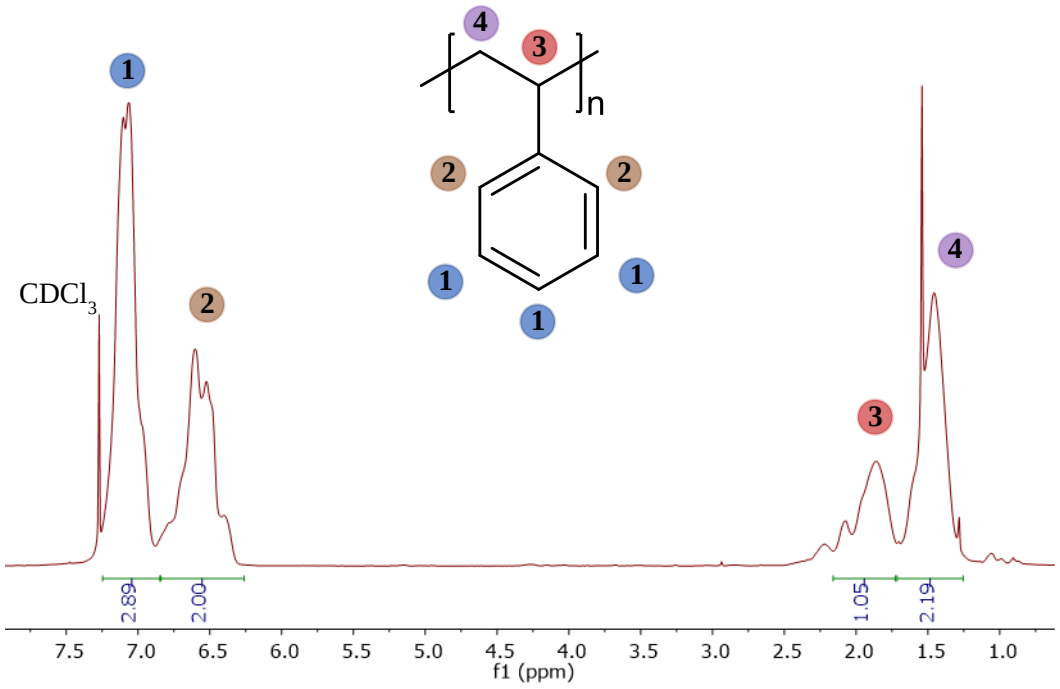

Fig. S23 ^{1}H NMR spectrum of PS 800 equivalents generated by **6**/[Ph_3C][$B(C_6F_5)_4$] from **Table 4**, entry 4 in $CDCl_3$ at 298 K (30 min). Representative peak assignment for PS.

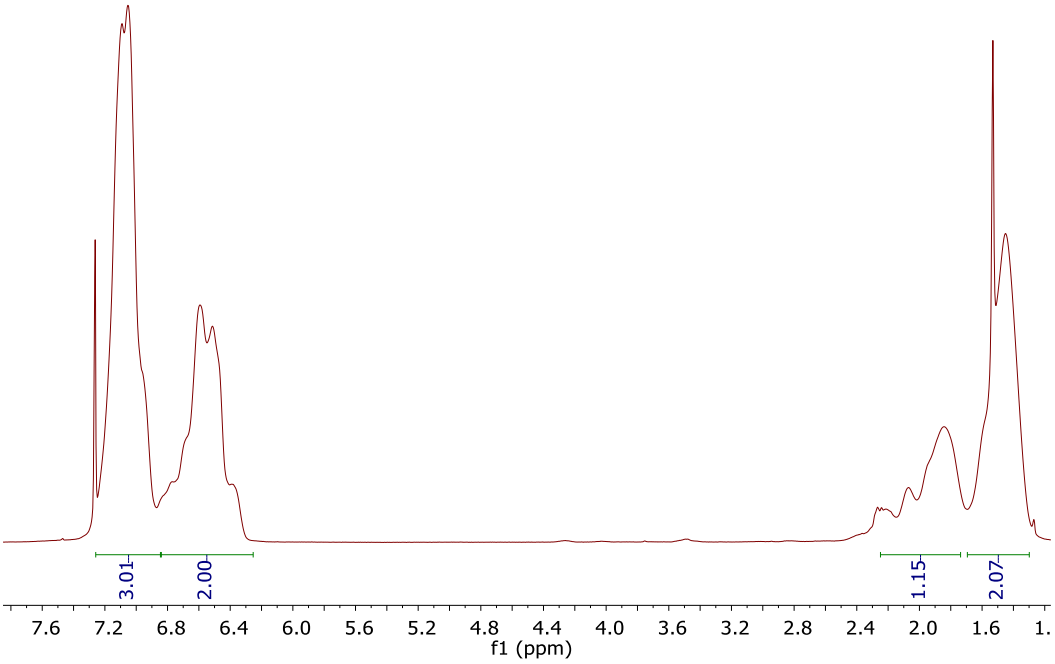

Fig. S24 ^{1}H NMR spectrum of PS 800 equivalents generated by **6**/[Ph_3C][$B(C_6F_5)_4$] from **Table 4**, entry 5 in $CDCl_3$ at 298 K (20 h).

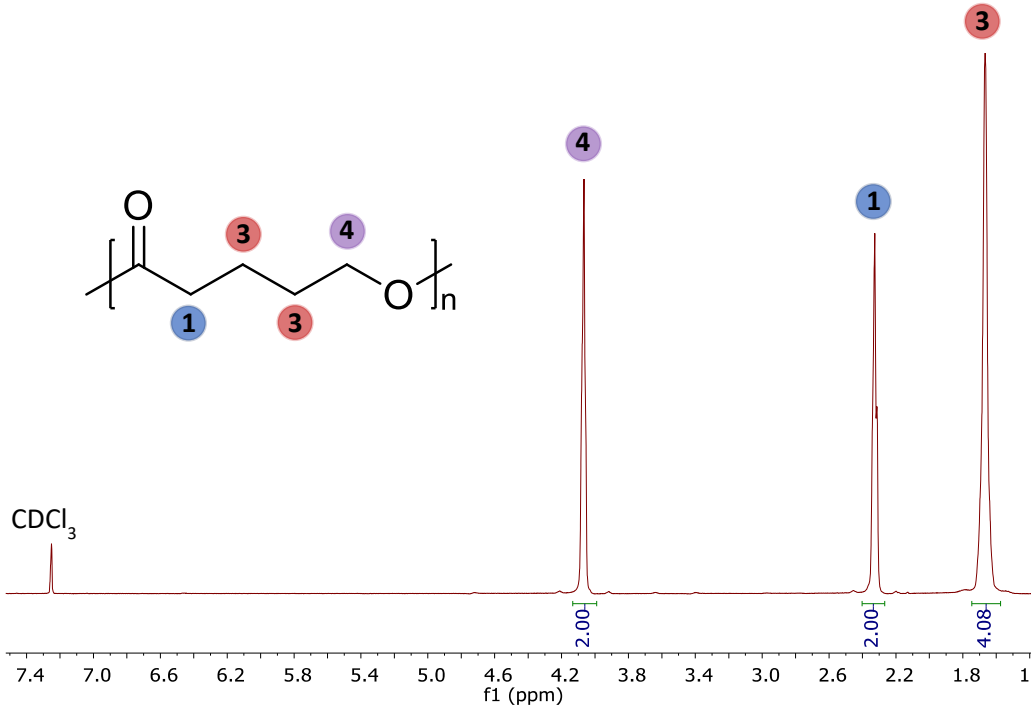

Fig. S25 ^{1}H NMR spectrum of PVL 300 equivalents generated by **6**/[Ph_3C][$B(C_6F_5)_4$] from **Table 4**, entry 6 in $CDCl_3$ at 298 K (10 min). Representative peak assignment for PVL.

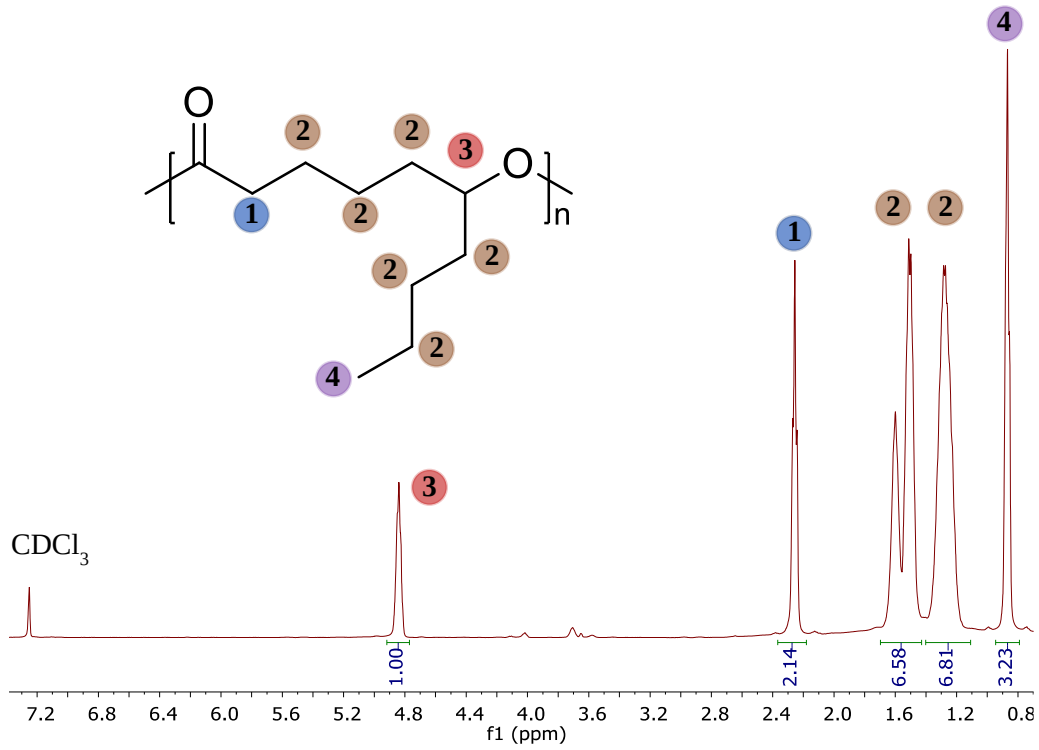

Fig. S26 ^{1}H NMR spectrum of PDL 300 equivalents generated by **6**/[Ph_3C][$B(C_6F_5)_4$] from **Table 4**, entry 7 in $CDCl_3$ at 298 K (6 h). Representative peak assignment for PDL.

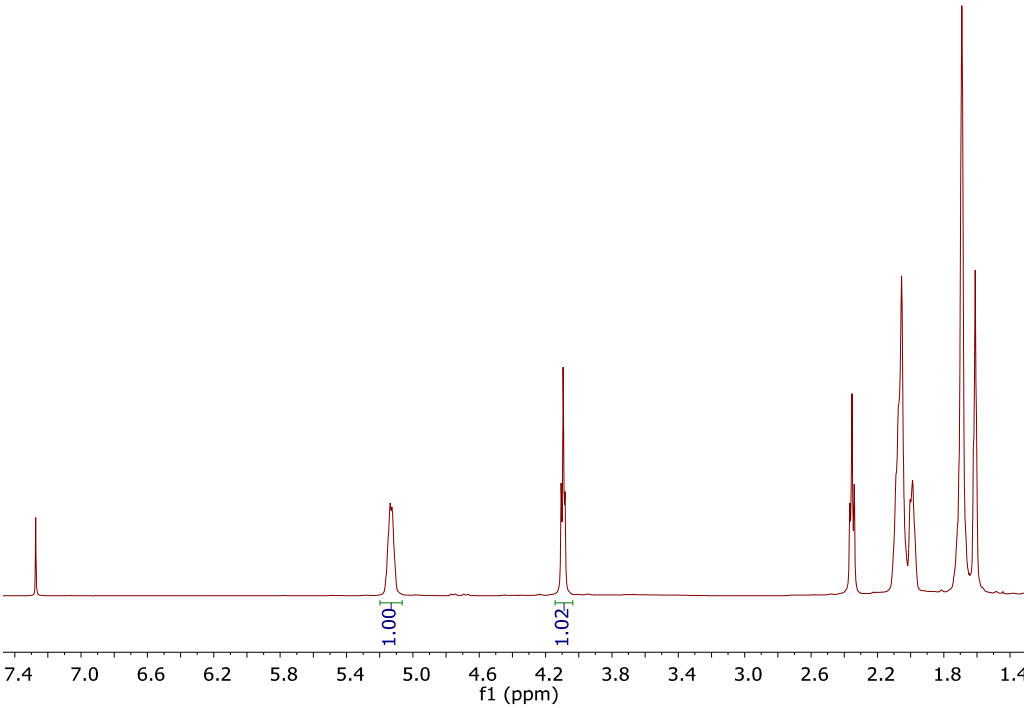

Fig. S27 ^{1}H NMR spectrum of PIP-*b*-PVL 800:300 equivalents generated by **6**/[Ph_3C][$B(C_6F_5)_4$] from **Table 5**, entry 1 in $CDCl_3$ at 298 K.

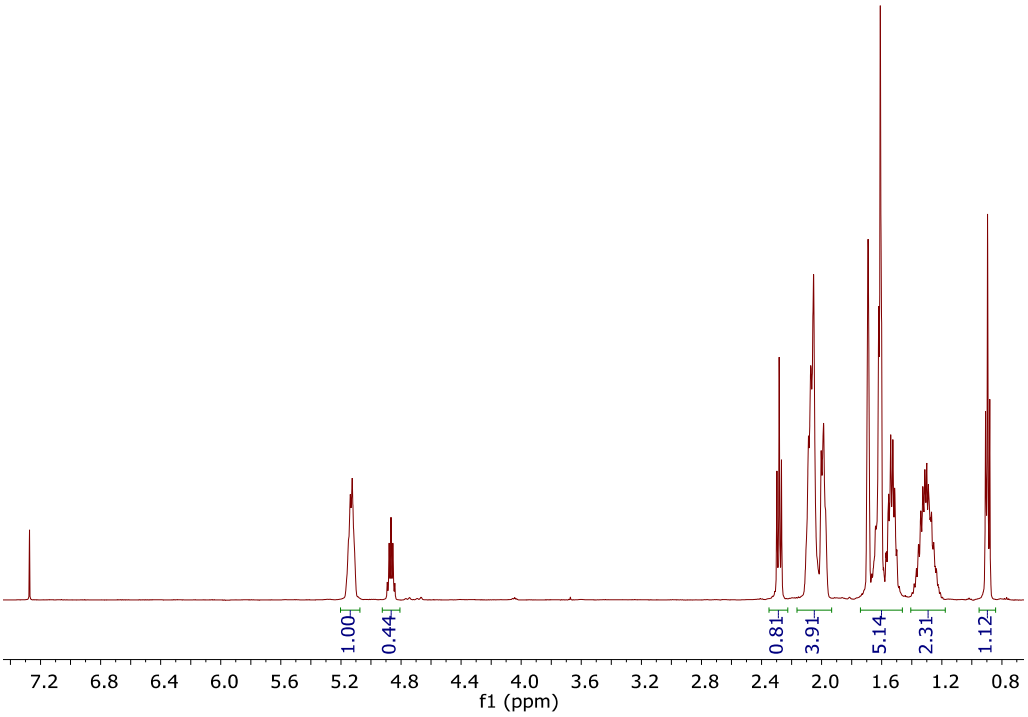

Fig. S28 ^{1}H NMR spectrum of PIP-*b*-PDL 800:300 equivalents generated by **6**/[Ph_3C][$B(C_6F_5)_4$] from **Table 5**, entry 2 in $CDCl_3$ at 298 K.

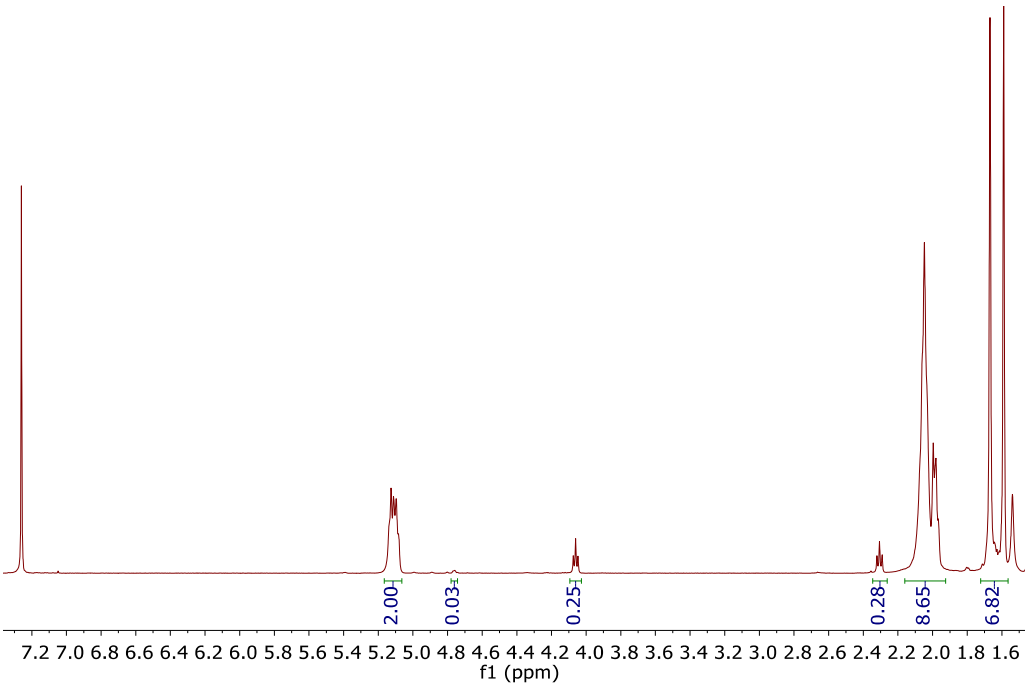

Fig. S29 ^{1}H NMR spectrum of PMyr-*b*-PCL 800:300 equivalents generated by **6**/[Ph_3C][$B(C_6F_5)_4$] from **Table 5**, entry 3 in $CDCl_3$ at 298 K.

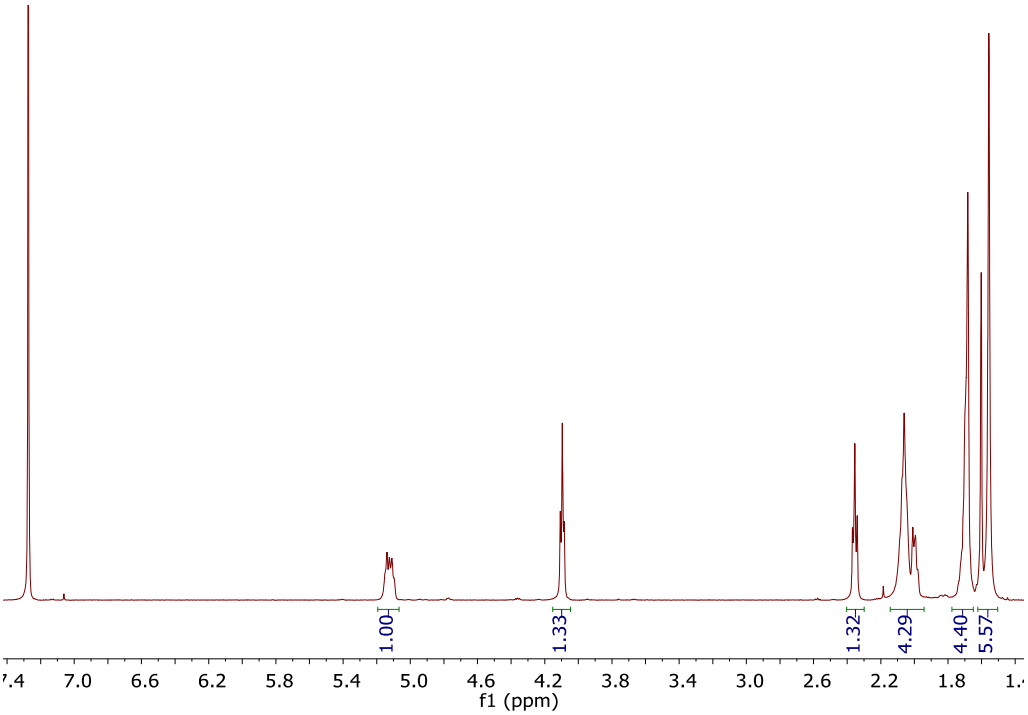

Fig. S30 ^{1}H NMR spectrum of PMyr-*b*-PVL 800:300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 5**, entry 4 in $CDCl_3$ at 298 K.

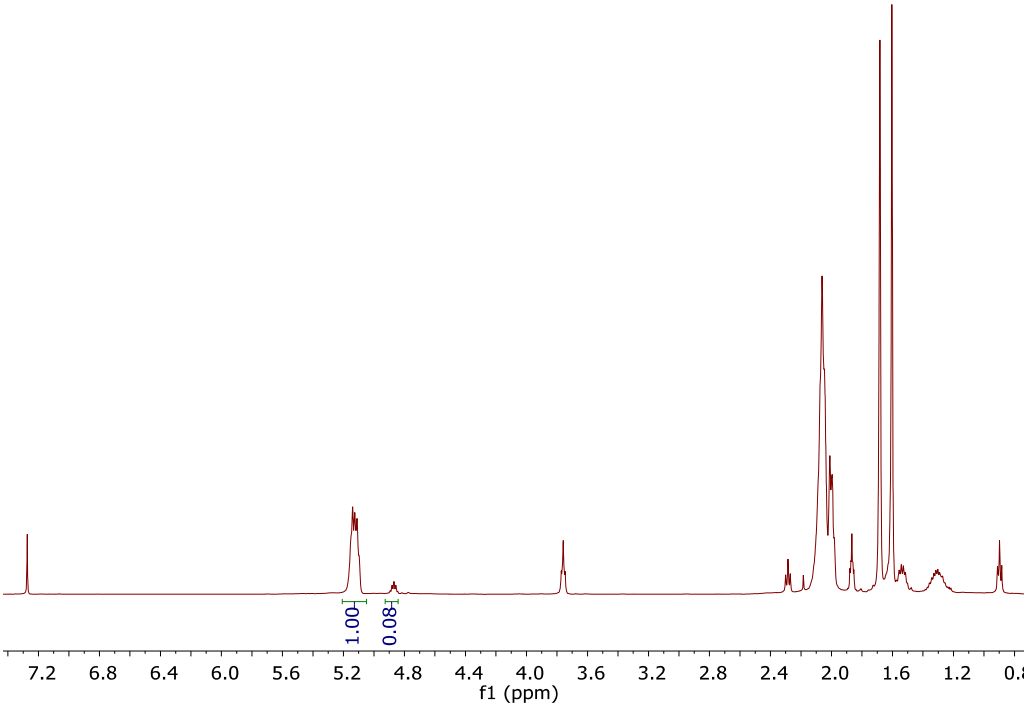

Fig. S31 ^{1}H NMR spectrum of PMyr-*b*-PDL 800:300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 5**, entry 5 in $CDCl_3$ at 298 K.

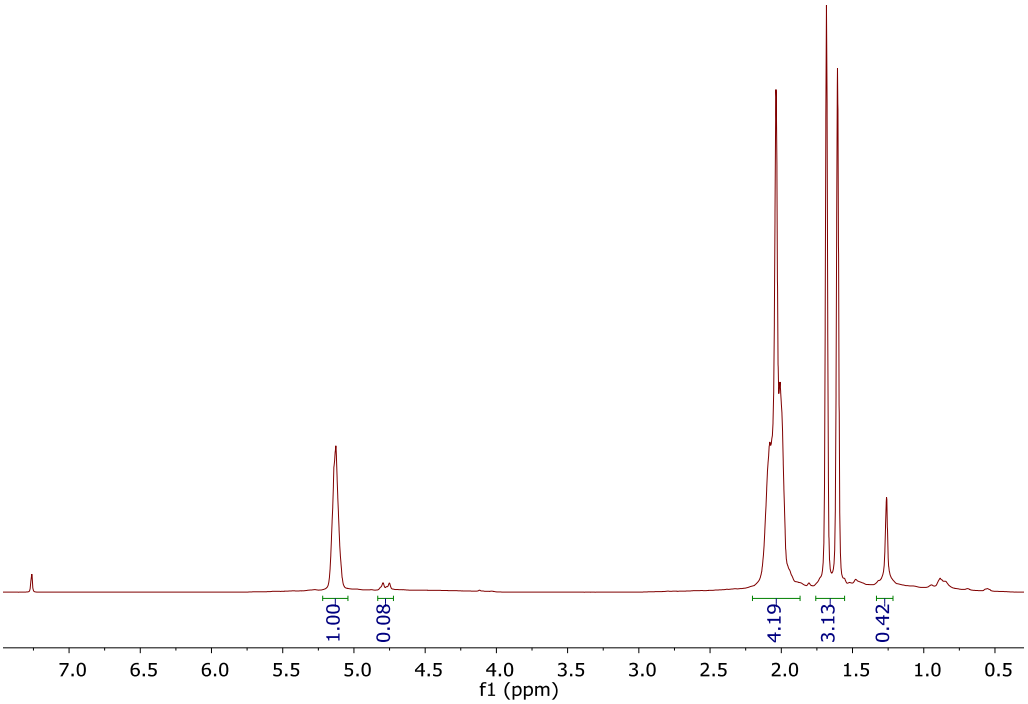

Fig. S32 ^{1}H NMR spectrum of PMyr 800 equivalents generated by **8**/$[Ph_3C][B(C_6F_5)_4]$ from **Table S1**, entry 1 in $CDCl_3$ at 298 K (30 min).

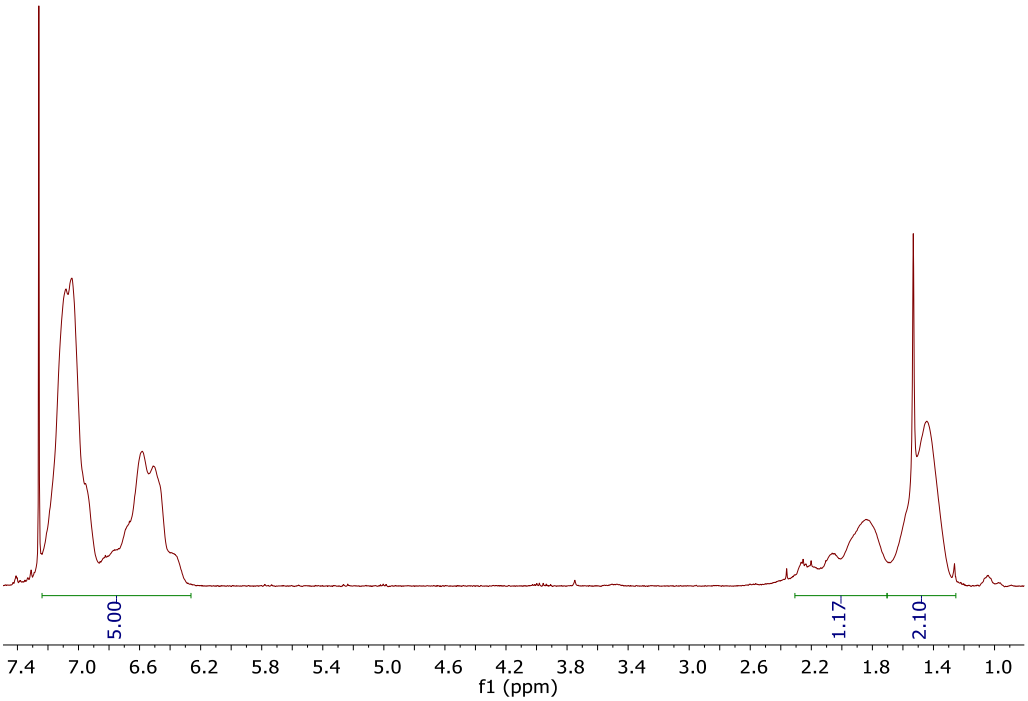

Fig. S33 ^{1}H NMR spectrum of PS 800 equivalents generated by **8**/$[Ph_3C][B(C_6F_5)_4]$ from **Table S1**, entry 2 in $CDCl_3$ at 298 K (30 min).

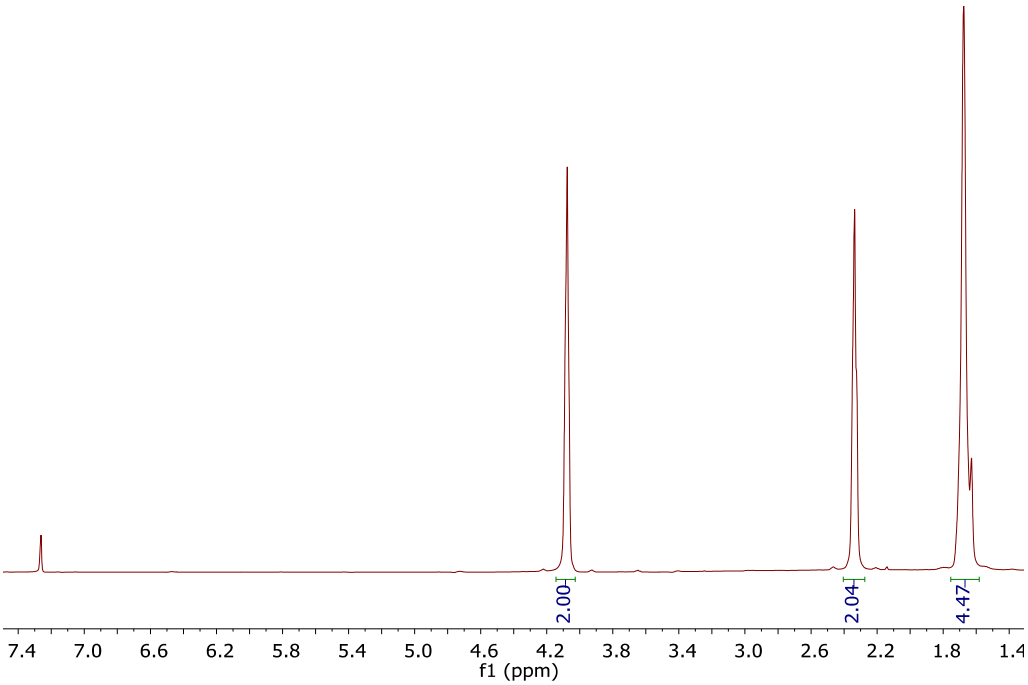

Fig. S34 ^{1}H NMR spectrum of PVL 300 equivalents generated by **8**/[Ph_3C][$B(C_6F_5)_4$] from **Table S1**, entry 3 in $CDCl_3$ at 298 K (10 min).

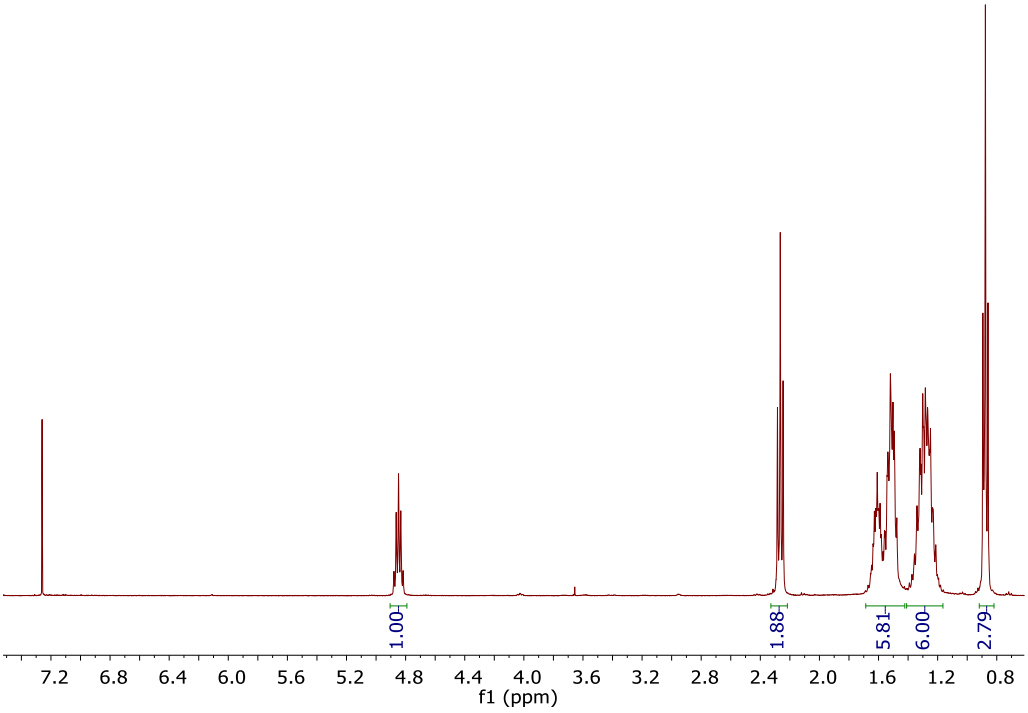

Fig. S35 ^{1}H NMR spectrum of PDL 300 equivalents generated by **8**/[Ph_3C][$B(C_6F_5)_4$] from **Table S1**, entry 4 in $CDCl_3$ at 298 K (6 h).

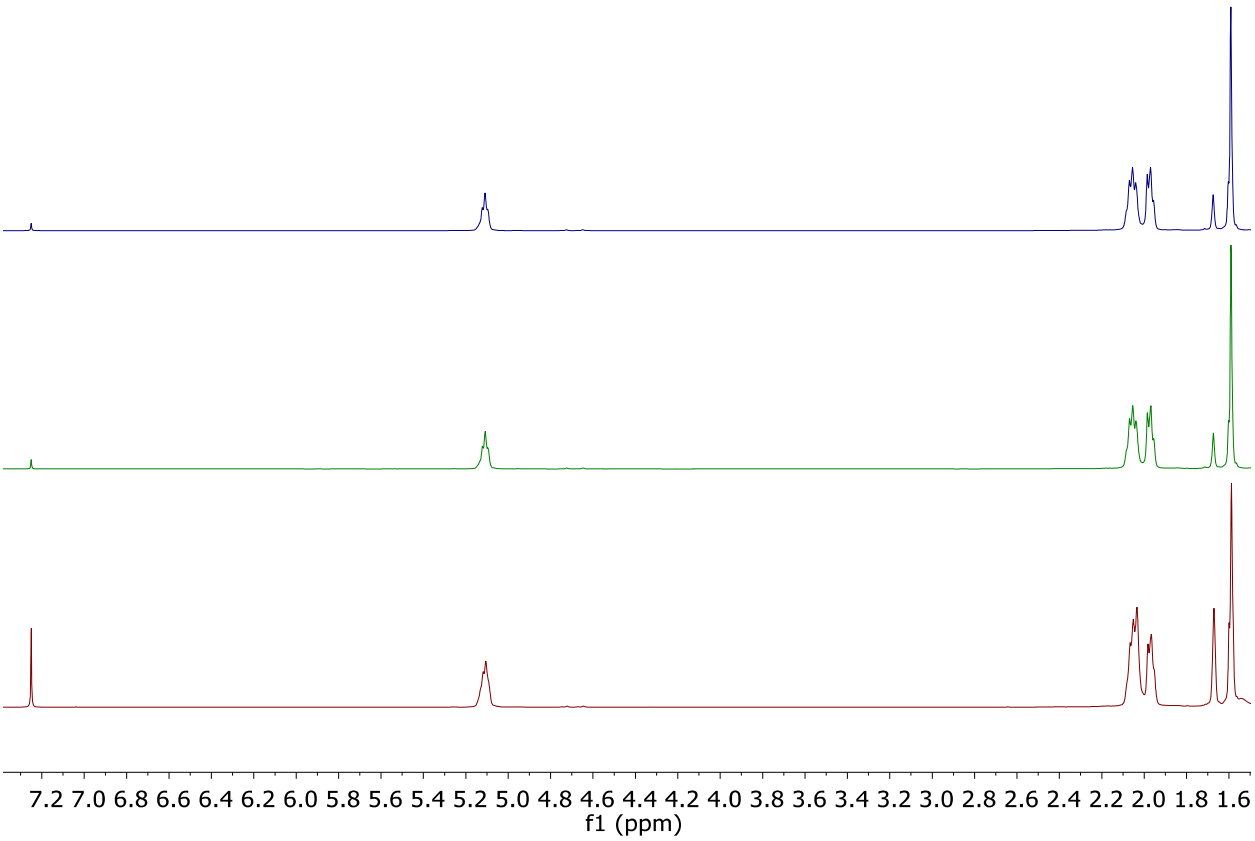

Fig. S36 ^{1}H NMR spectrum of PIP 300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table S2**, entry 1 in $CDCl_3$ at 298 K (12 h).

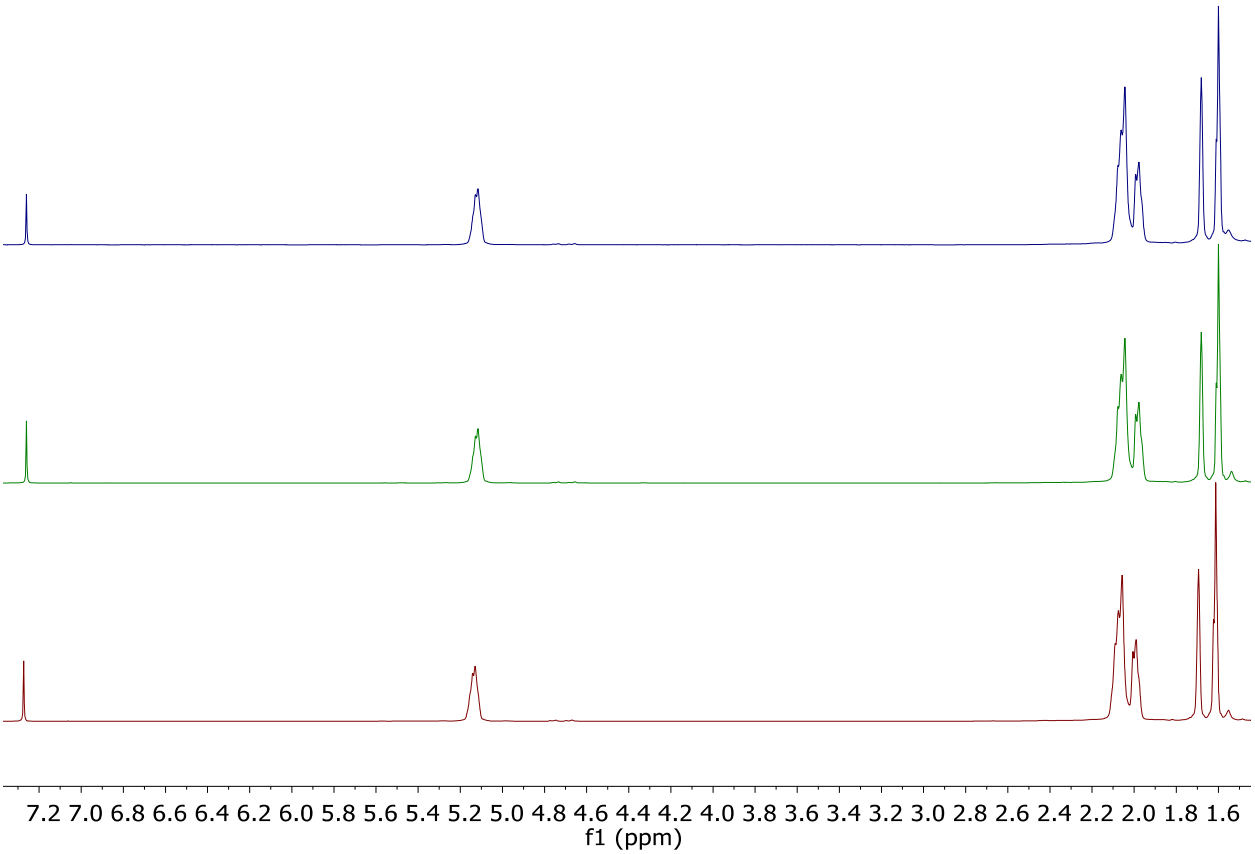

Fig. S37 ^{1}H NMR spectrum of PIP 550 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table S2**, entry 2 in $CDCl_3$ at 298 K (12 h).

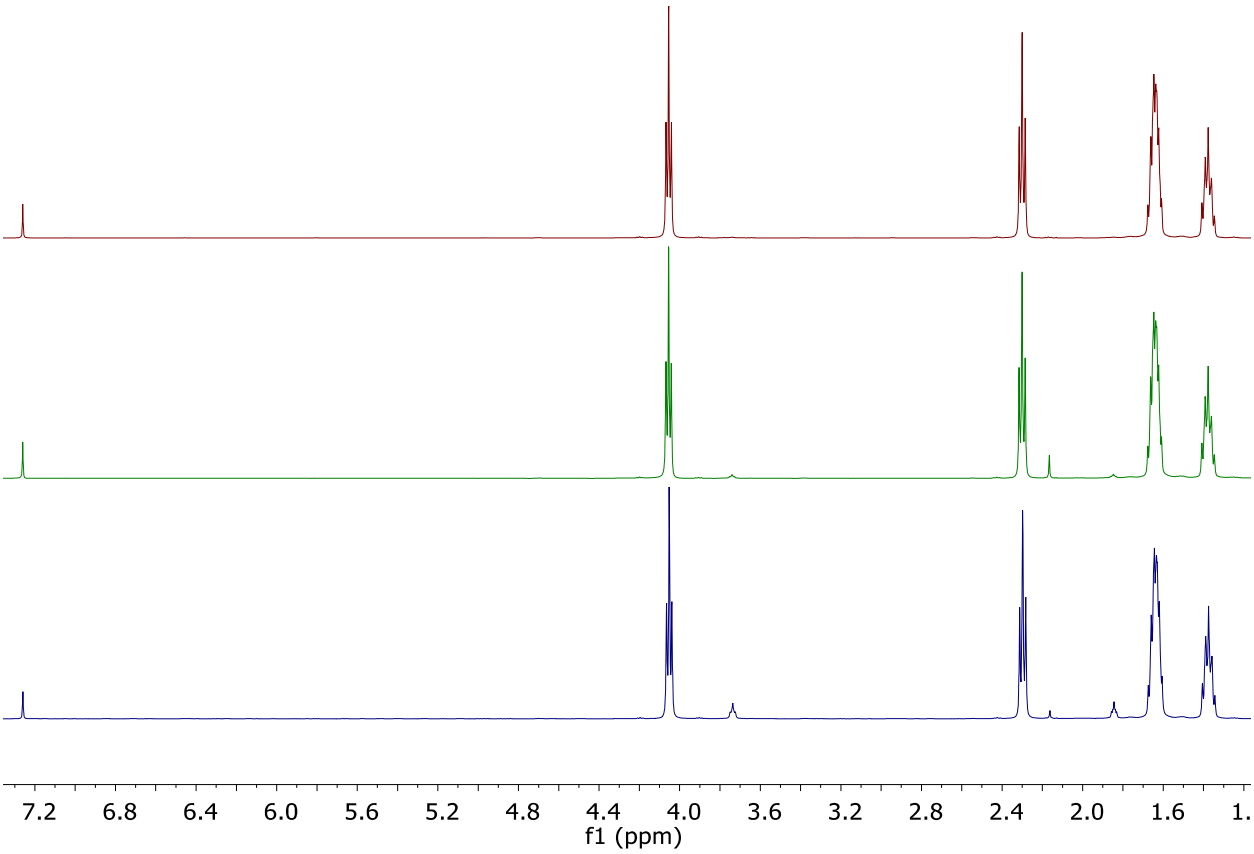

Fig. S38 ^{1}H NMR spectrum of PCL 550 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table S2**, entry 3 in $CDCl_3$ at 298 K (2 h).

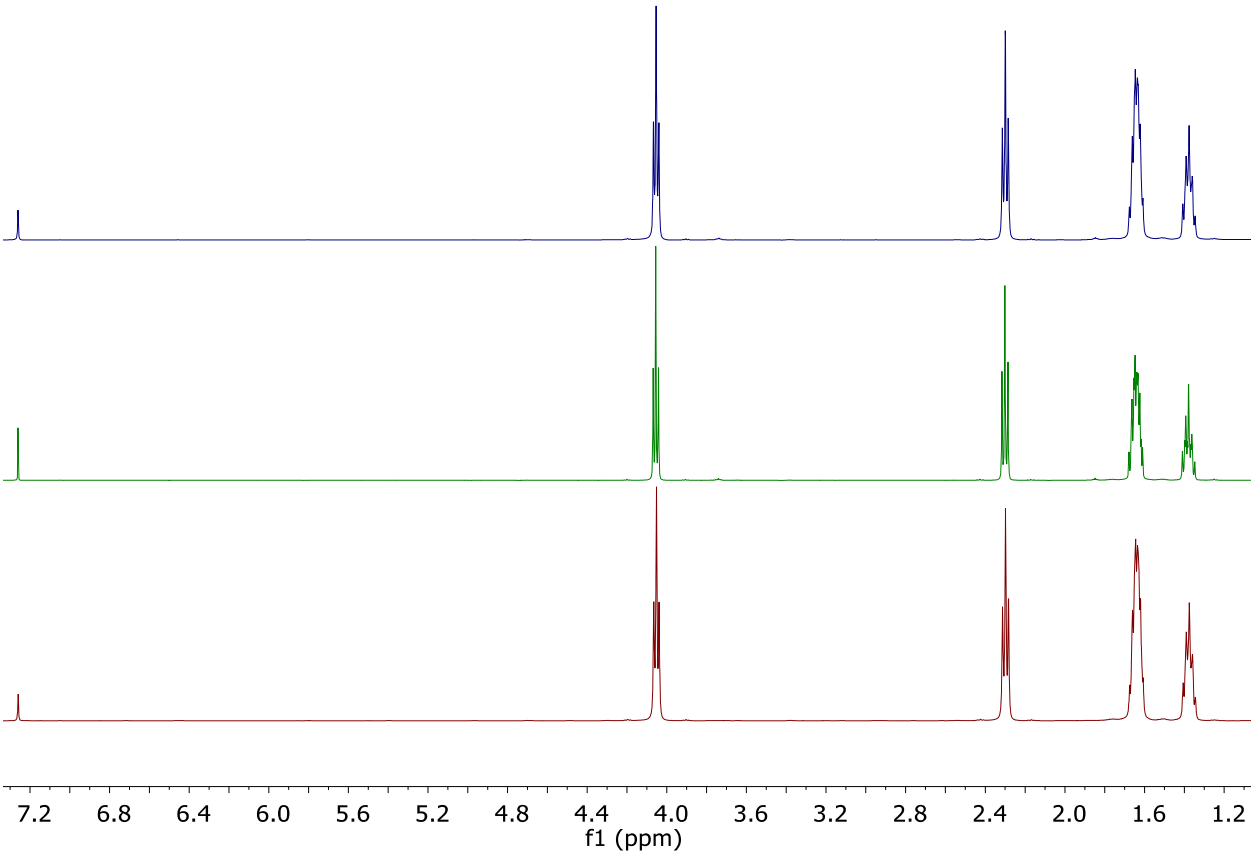

Fig. S39 ^{1}H NMR spectrum of PCL 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table S2**, entry 4 in $CDCl_3$ at 298 K (2 h).

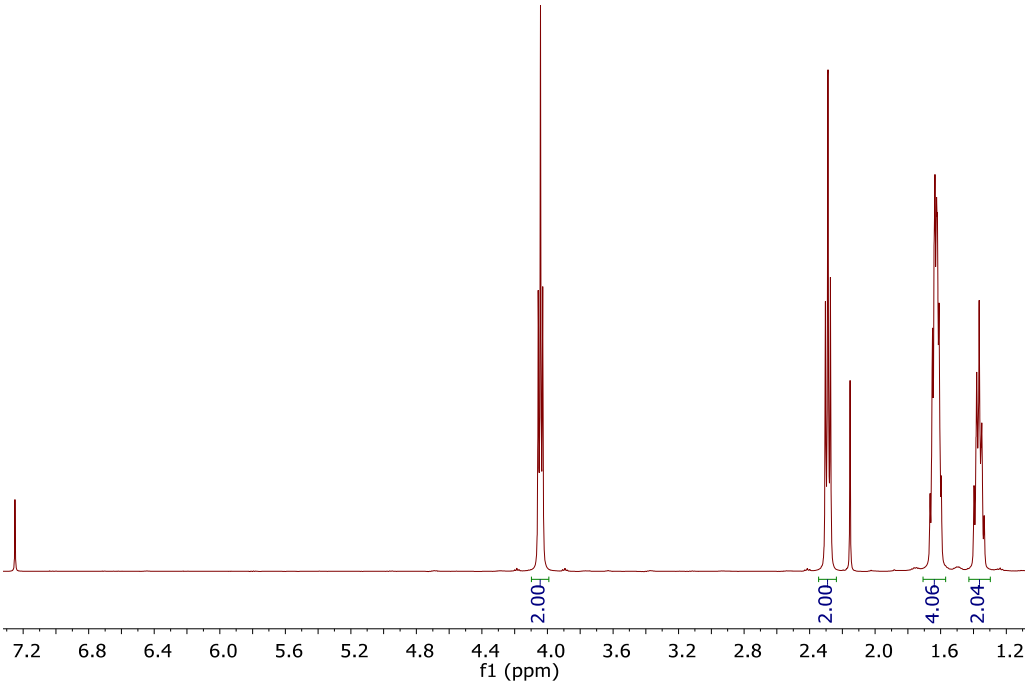

Fig. S40 ^{1}H NMR spectrum of PCL 800 equivalents generated by **6** from **Table S2**, entry 5 in $CDCl_3$ at 298 K (No $[Ph_3C][B(C_6F_5)_4]$ added) (10 min).

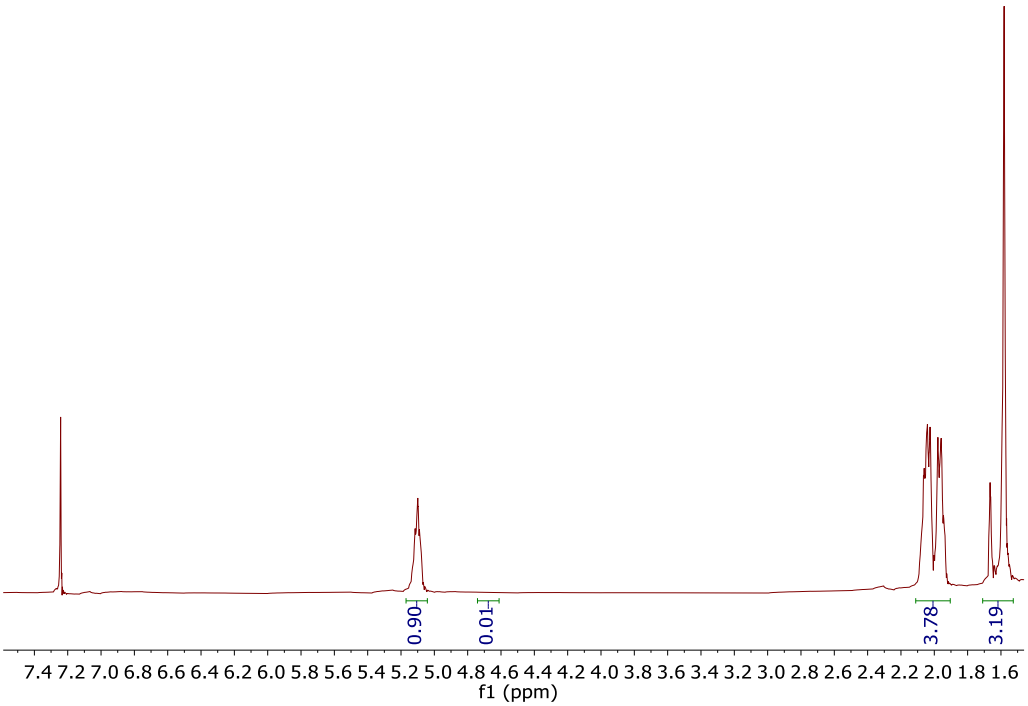

Fig. S41 ^{1}H NMR spectrum of PIP 50 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table S3**, entry 1 in $CDCl_3$ at 298 K (12 h).

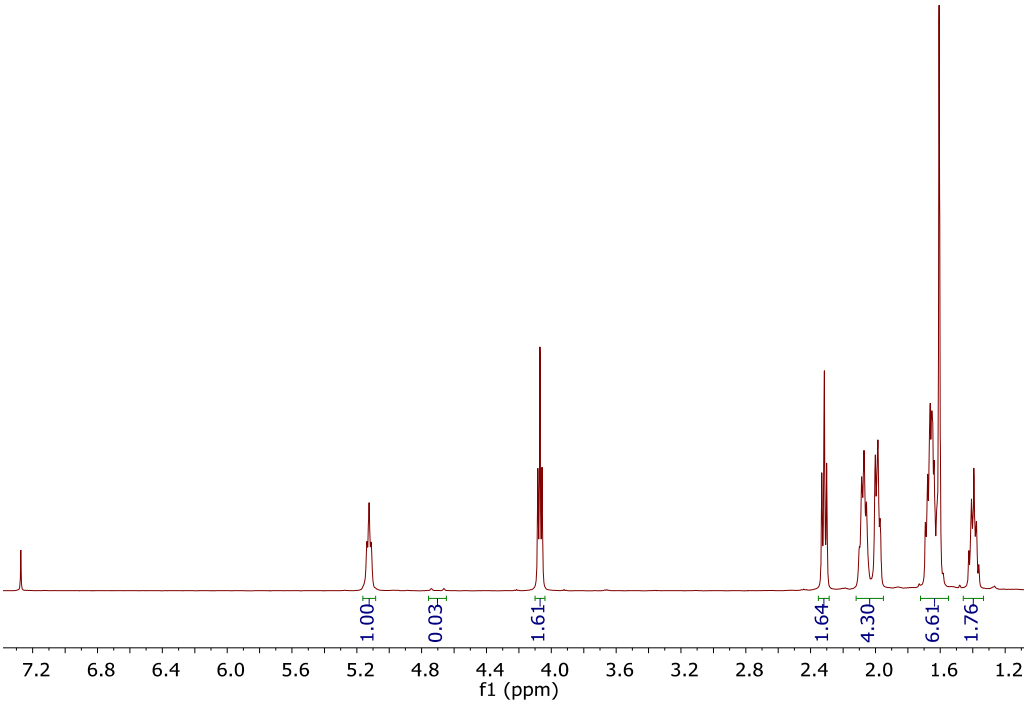

Fig. S42 ^{1}H NMR spectrum of PIP-*b*-PCL 50:50 equivalents generated by **6**/[Ph_3C][$B(C_6F_5)_4$] from **Table S3**, entry 2 in $CDCl_3$ at 298 K.

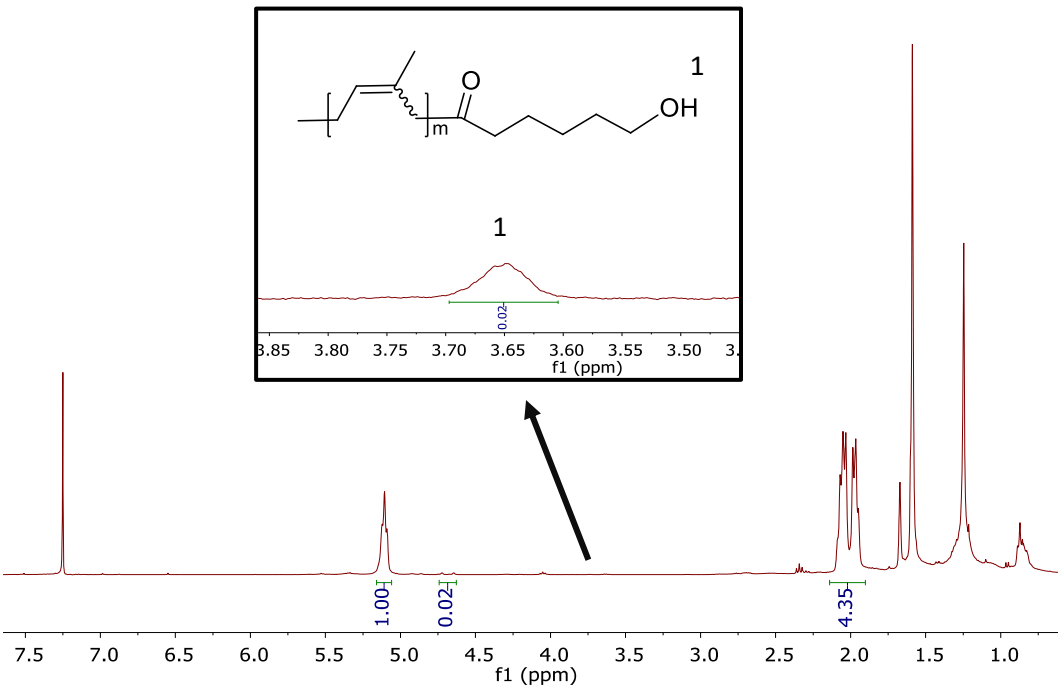

Fig. S43 ^{1}H NMR spectrum of recovered PIP 50 equivalents after hydrolysis of PIP-*b*-PCL 50:50 equivalents from **Table S3**, entry 3 in $CDCl_3$ at 298 K (12 h). Alcohol Peak at 3.65 ppm.

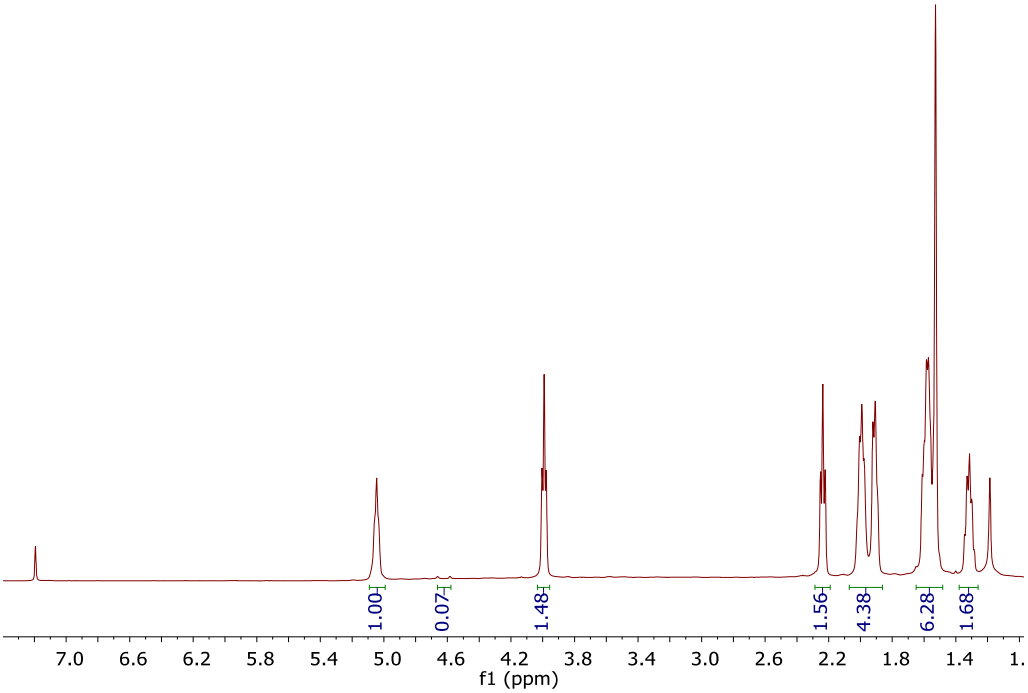

Fig. S44 ^{1}H NMR spectrum of repolymerized PIP-*b*-PCL 50:50 equivalents generated by **Y[N(SiMe$_3$)$_2$]$_3$** from **Table S3**, entry 4 in $CDCl_3$ at 298 K.

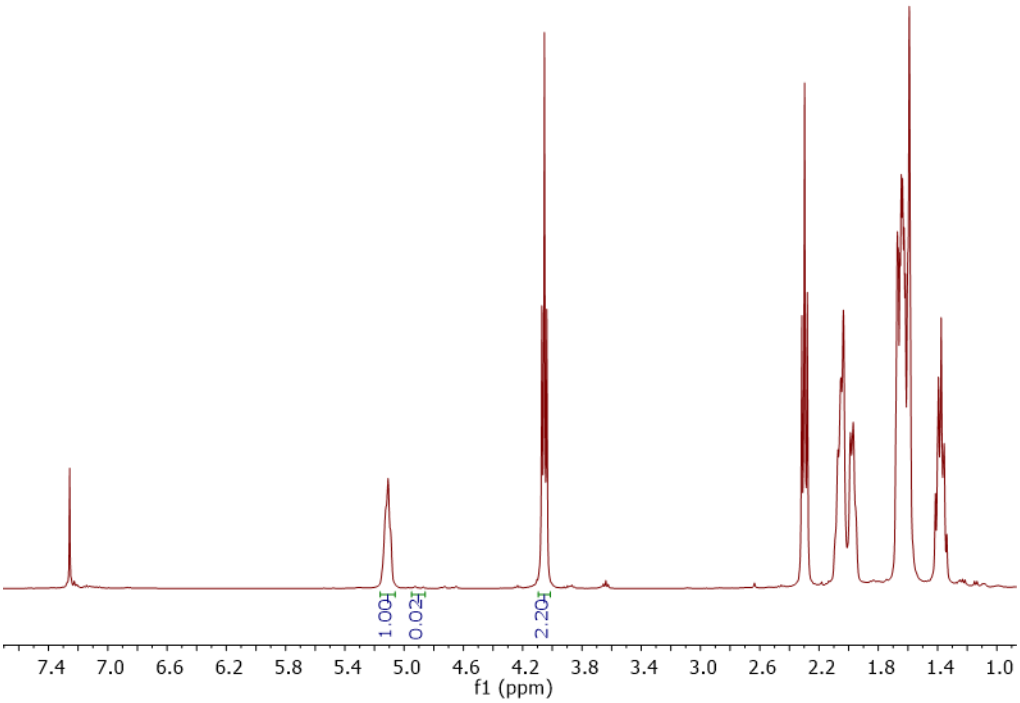

Fig. S45 ^{1}H NMR spectrum of PIP-*b*-PCL 50:50 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ (1 mL of toluene) from **Table S3**, entry 5 in $CDCl_3$ at 298 K.

3.2 ^{13}C NMR Spectroscopy

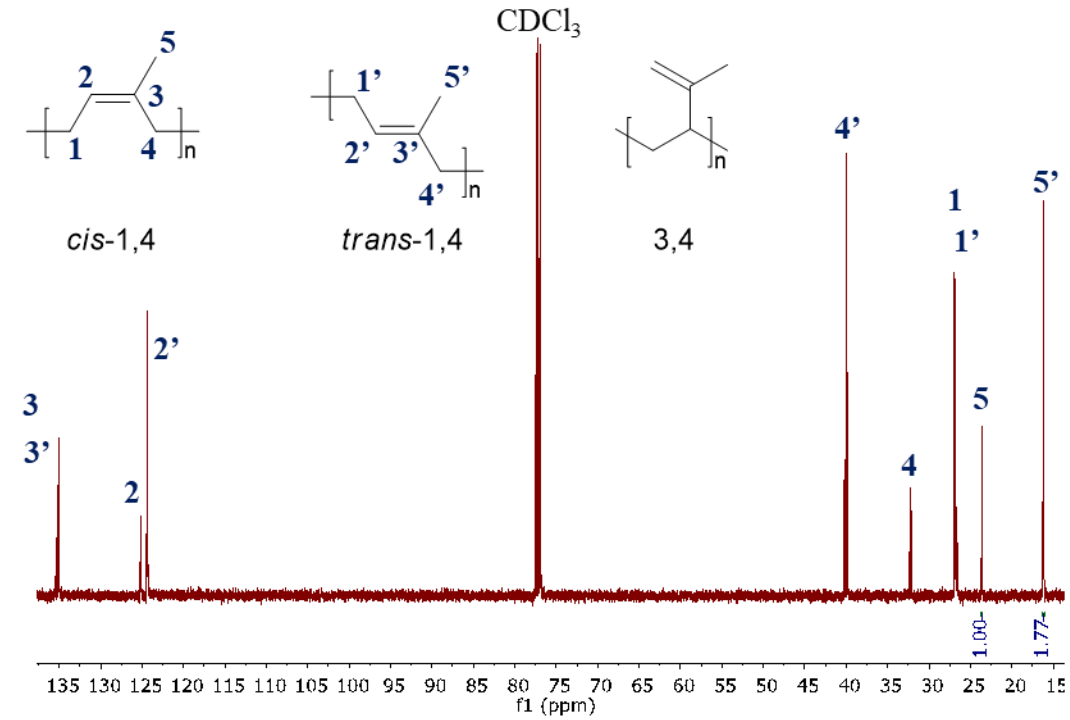

Fig. S46 ^{13}C NMR spectrum of PIP 800 equivalents generated by **6**/[Ph_3C][$B(C_6F_5)_4$] from **Table 1**, entry 1a in $CDCl_3$ at 298 K (12 h). Representative peak assignment for PIP. *Cis*-1,4-PIP verses *trans*-1,4-PIP calculated based on peaks 5 and 5'.

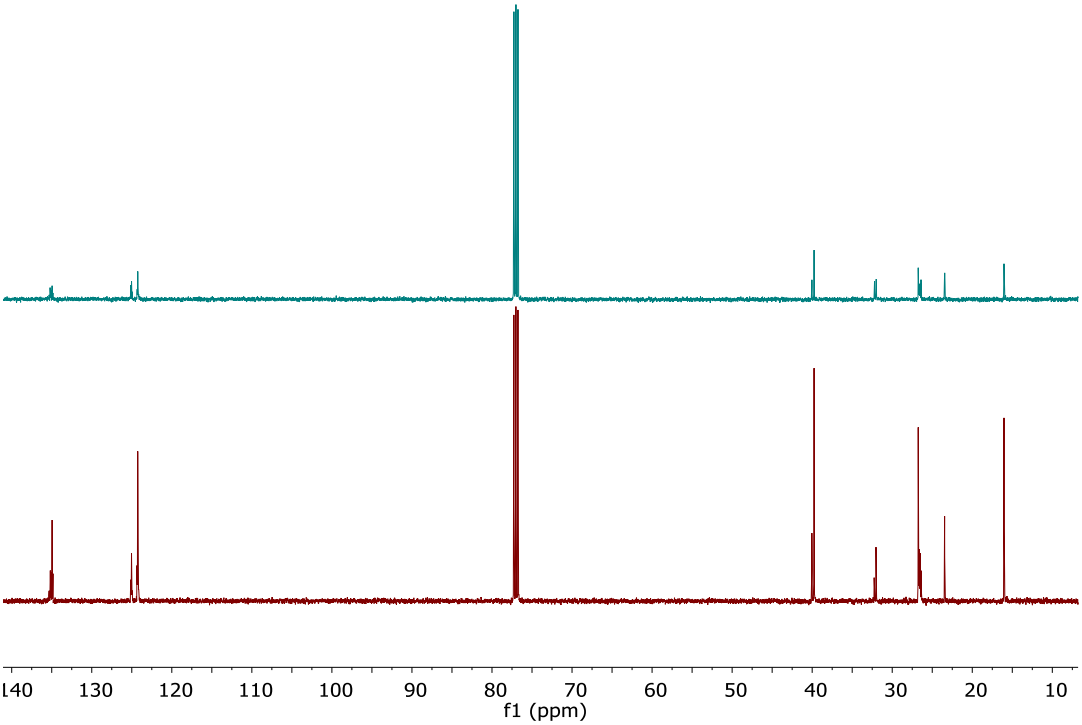

Fig. S47 ^{13}C NMR spectrum of PIP equivalents generated by **6**/[Ph_3C][$B(C_6F_5)_4$] from **Table 1**, entry 1(b, c) in $CDCl_3$ at 298 K (12 h).

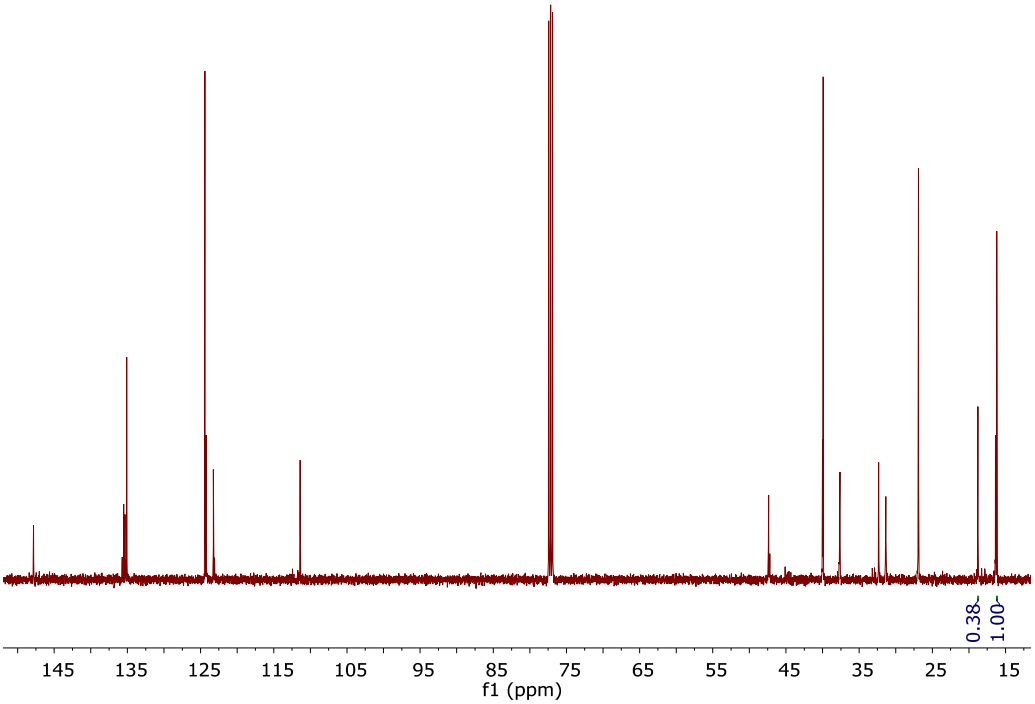

Fig. S48 ^{13}C NMR spectrum of PIP 800 equivalents generated by **8**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 1**, entry 3 in $CDCl_3$ at 298 K (12 h).

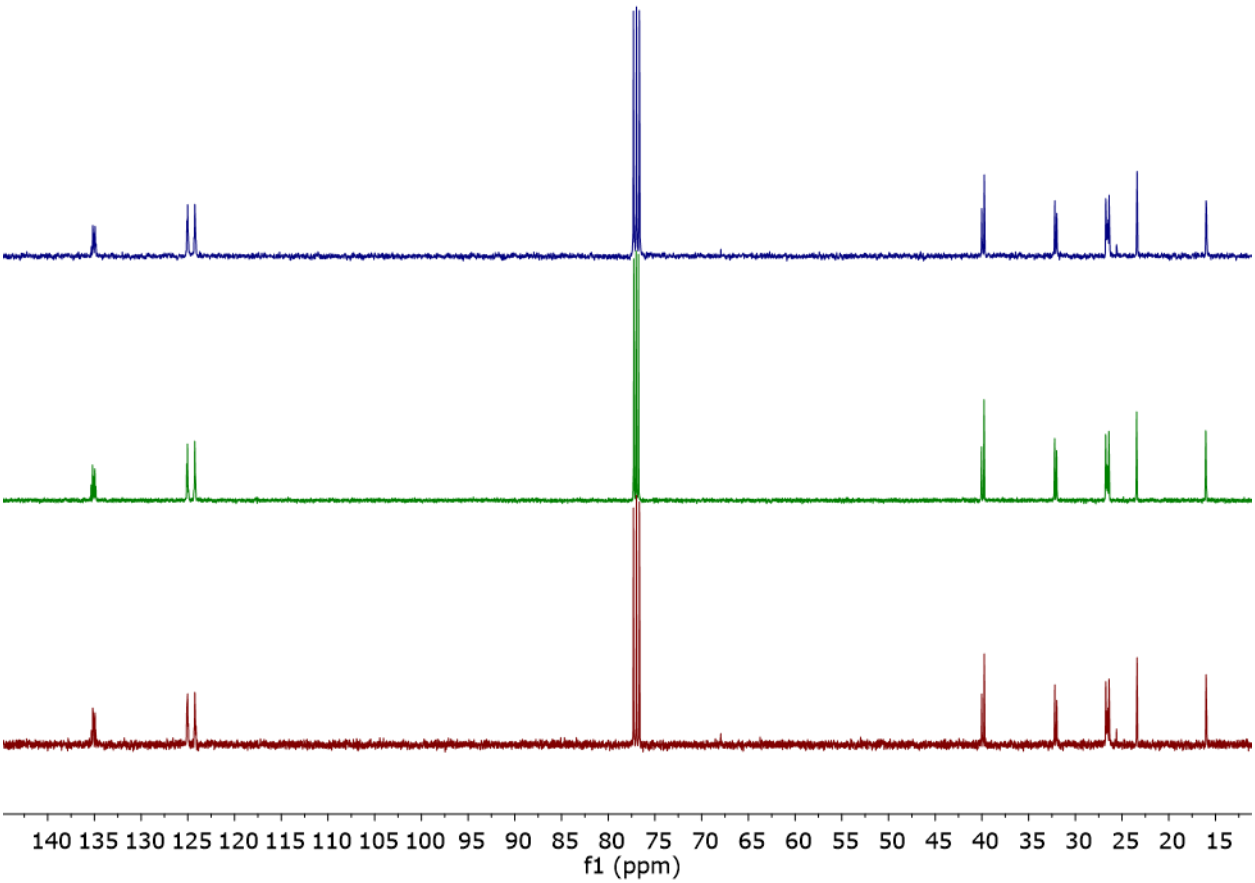

Fig. S49 ^{13}C NMR spectrum of PIP 800 equivalents generated by **6**/[Ph_3C][$B(C_6F_5)_4$] from **Table 1**, entry 4 in $CDCl_3$ at 298 K (24 h).

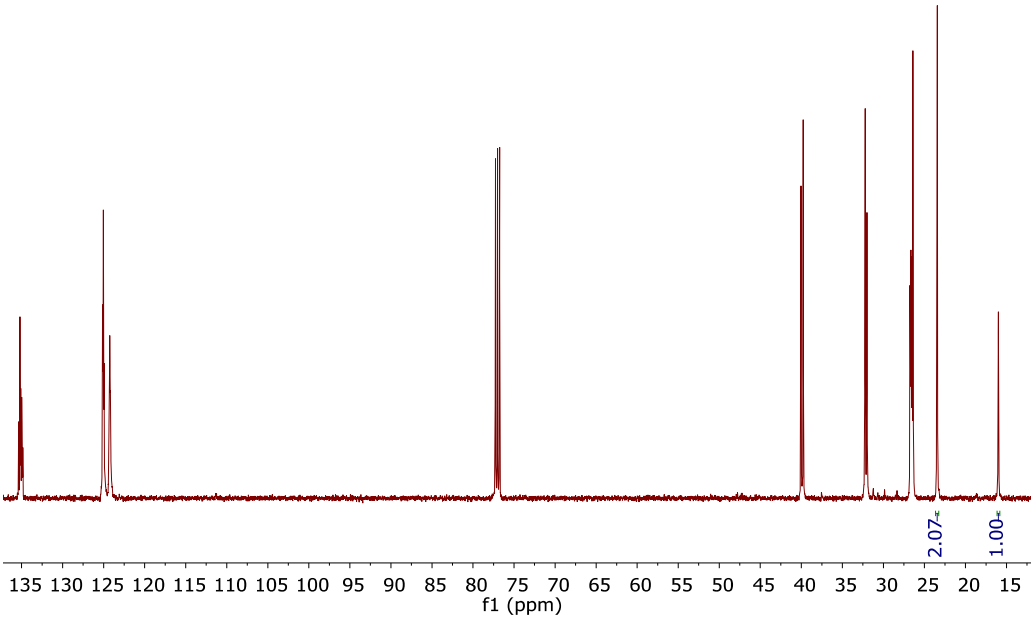

Fig. S50 ^{13}C NMR spectrum of PIP 800 equivalents generated by **6**/[Ph_3C][$B(C_6F_5)_4$] from **Table 1**, entry 5 in $CDCl_3$ at 298 K (30 min).

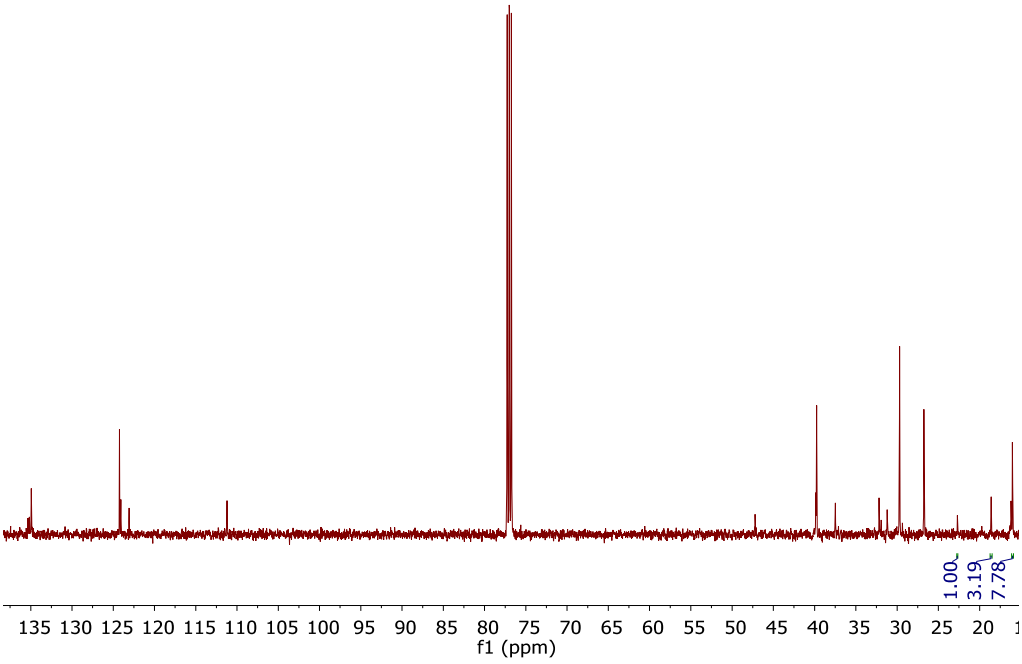

Fig. S51 ^{13}C NMR spectrum of PIP 800 equivalents generated by **8**/[Ph_3C][$B(C_6F_5)_4$] from **Table 1**, entry 6 in $CDCl_3$ at 298 K (30 min).

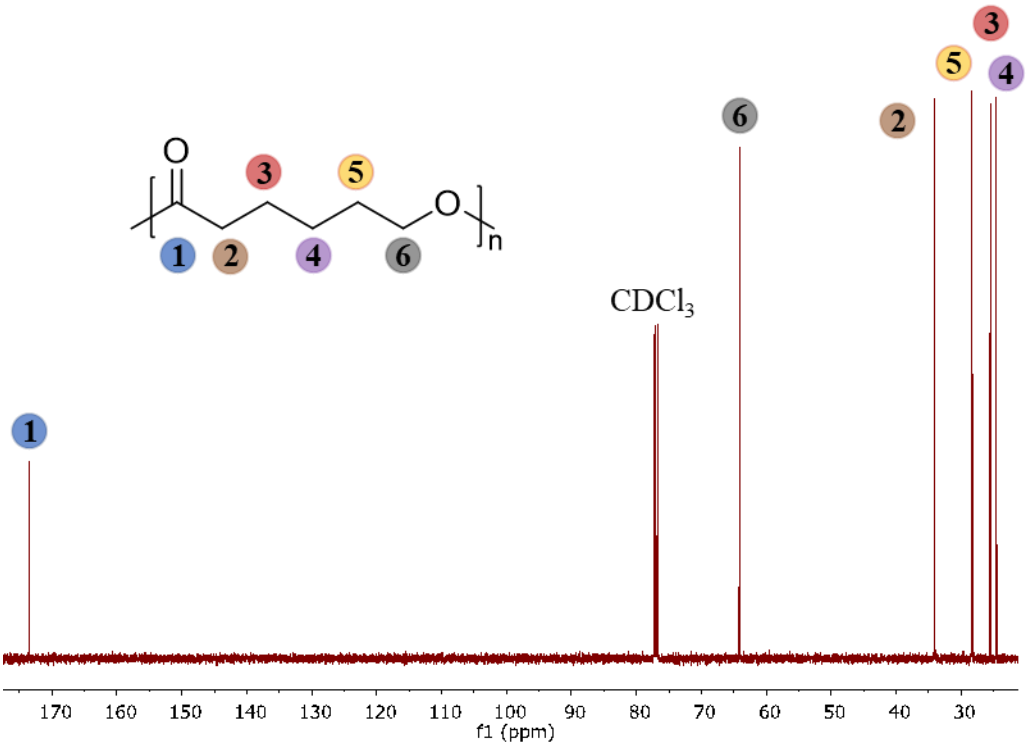

Fig. S52 ^{13}C NMR spectrum of PCL 300 equivalents generated by **6**/[Ph_3C][$B(C_6F_5)_4$] from **Table 1**, entry 7 in $CDCl_3$ at 298 K (10 min). Representative peak assignment for PCL.

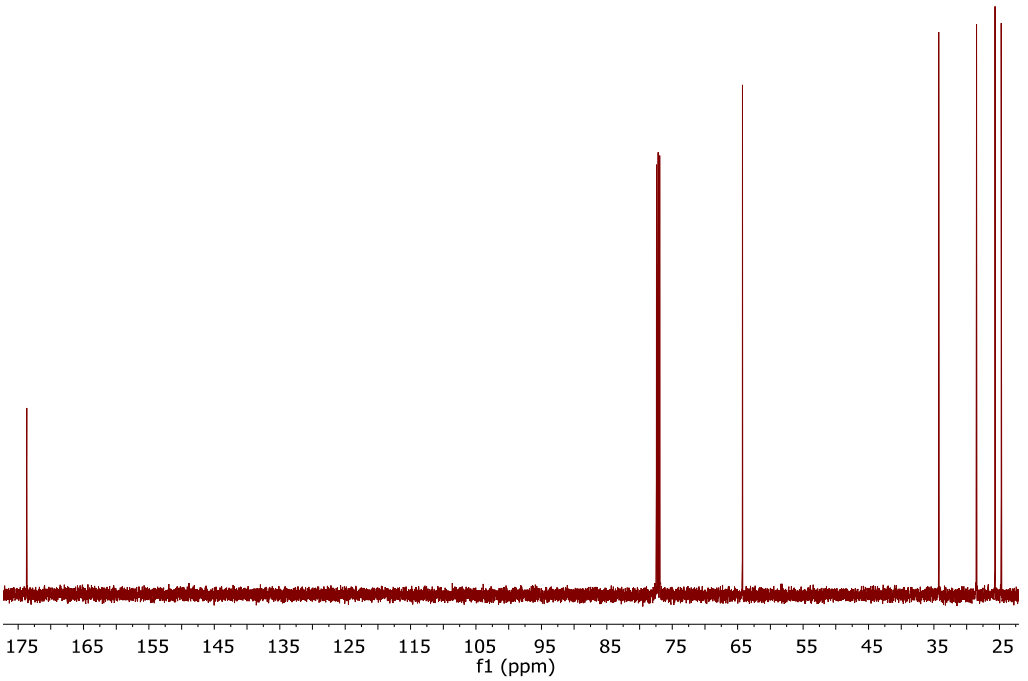

Fig. S53 ^{13}C NMR spectrum of PCL 300 equivalents generated by **8**/[Ph_3C][$B(C_6F_5)_4$] from **Table 1**, entry 8 in $CDCl_3$ at 298 K (10 min).

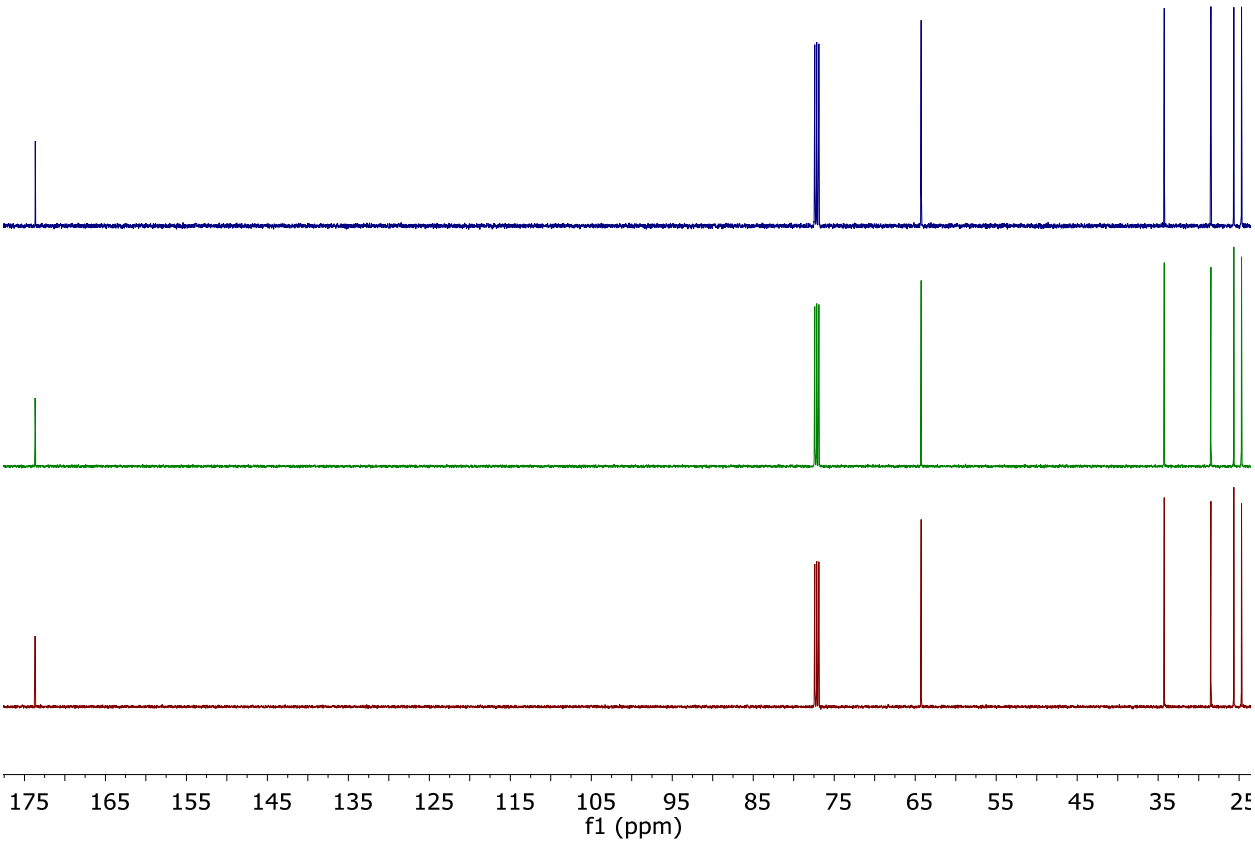

Fig. S54 ^{13}C NMR spectrum of PCL 300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 1**, entry 9 in $CDCl_3$ at 298 K (2 h).

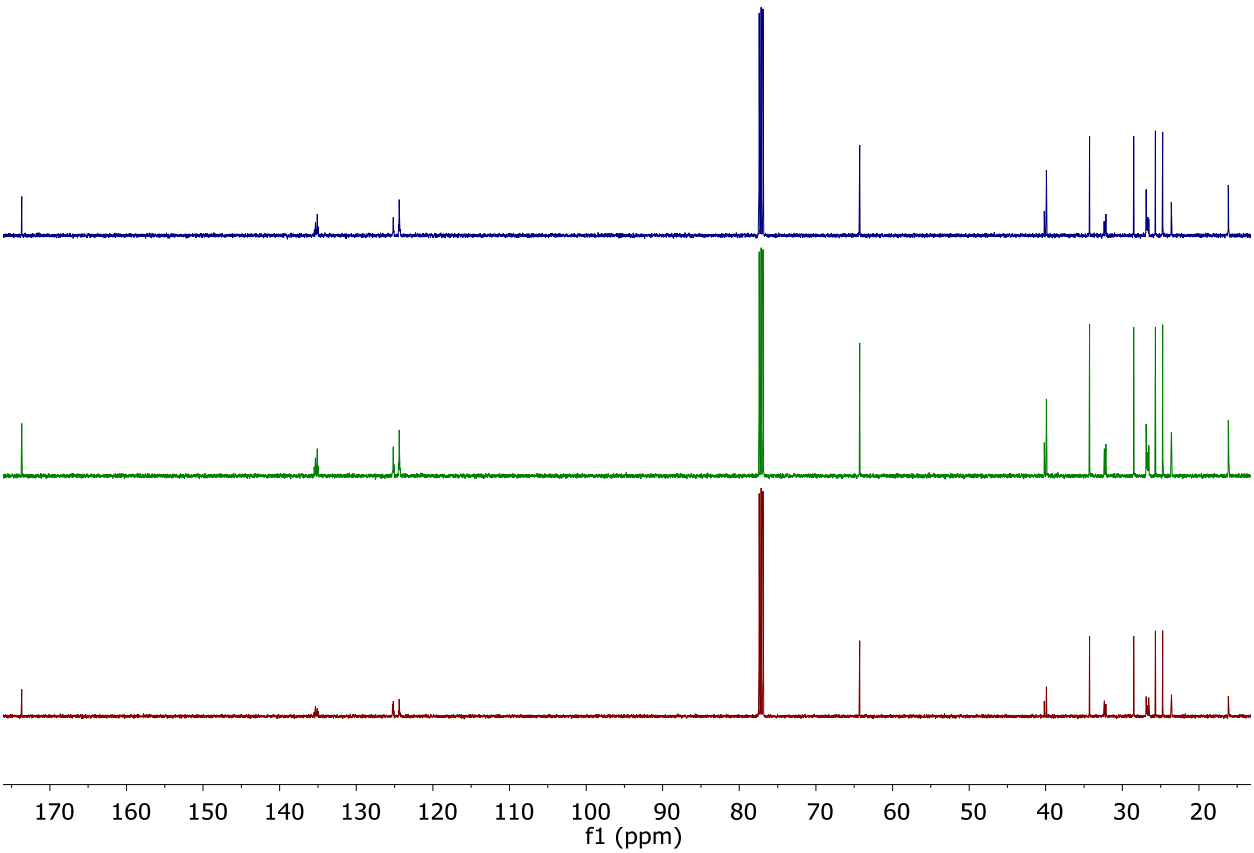

Fig. S55 ^{13}C NMR spectrum of PIP-*b*-PCL 800:300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 2**, entry 1 in $CDCl_3$ at 298 K.

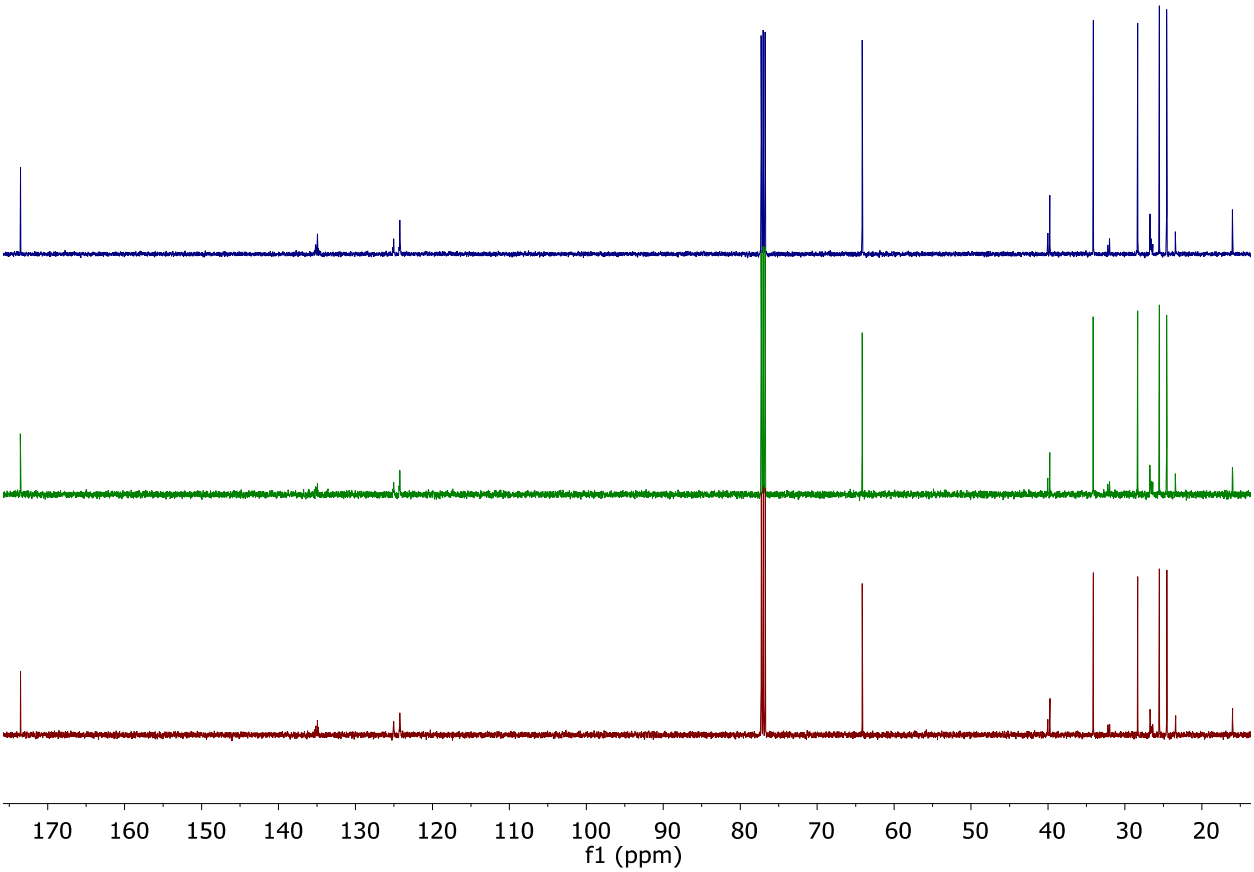

Fig. S56 ^{13}C NMR spectrum of PIP-*b*-PCL 550:550 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 2**, entry 2 in $CDCl_3$ at 298 K.

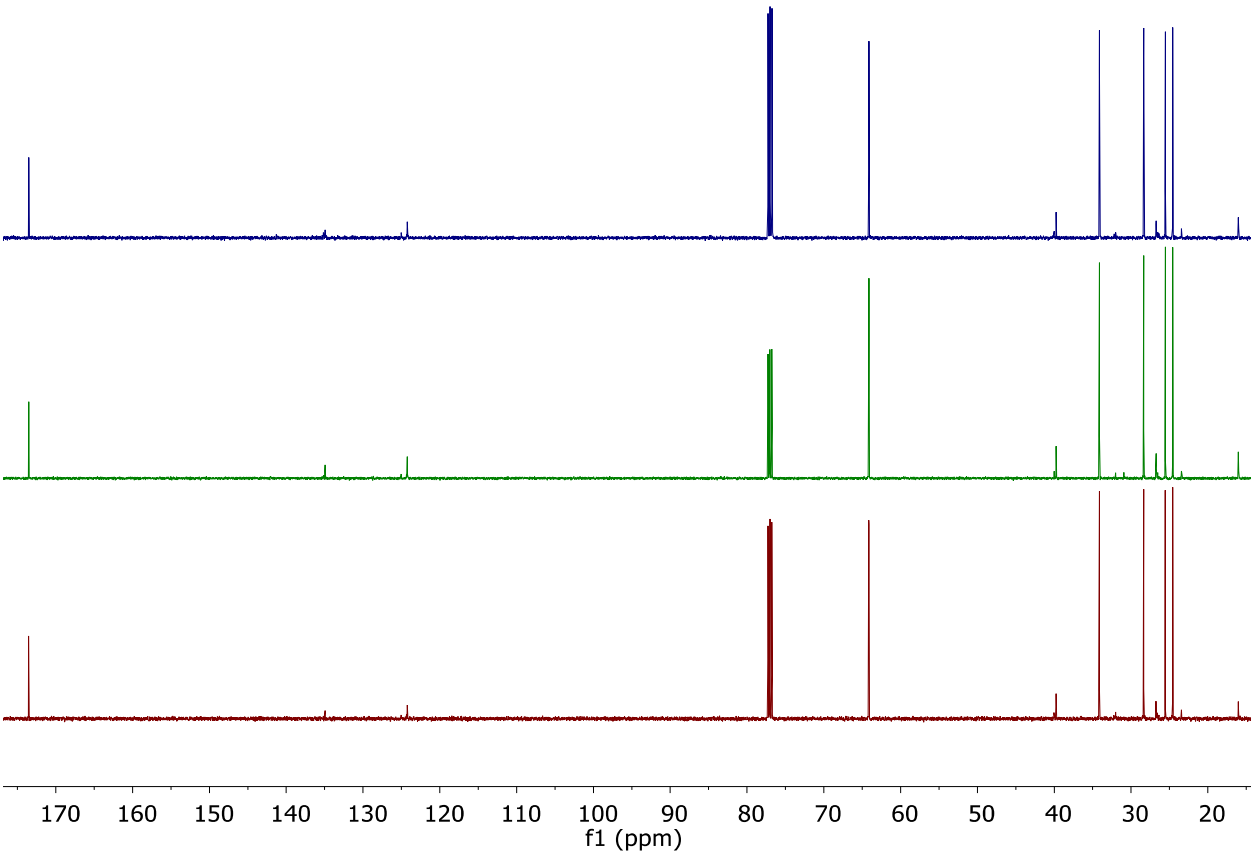

Fig. S57 ^{13}C NMR spectrum of PIP-*b*-PCL 300:800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 2**, entry 3 in $CDCl_3$ at 298 K.

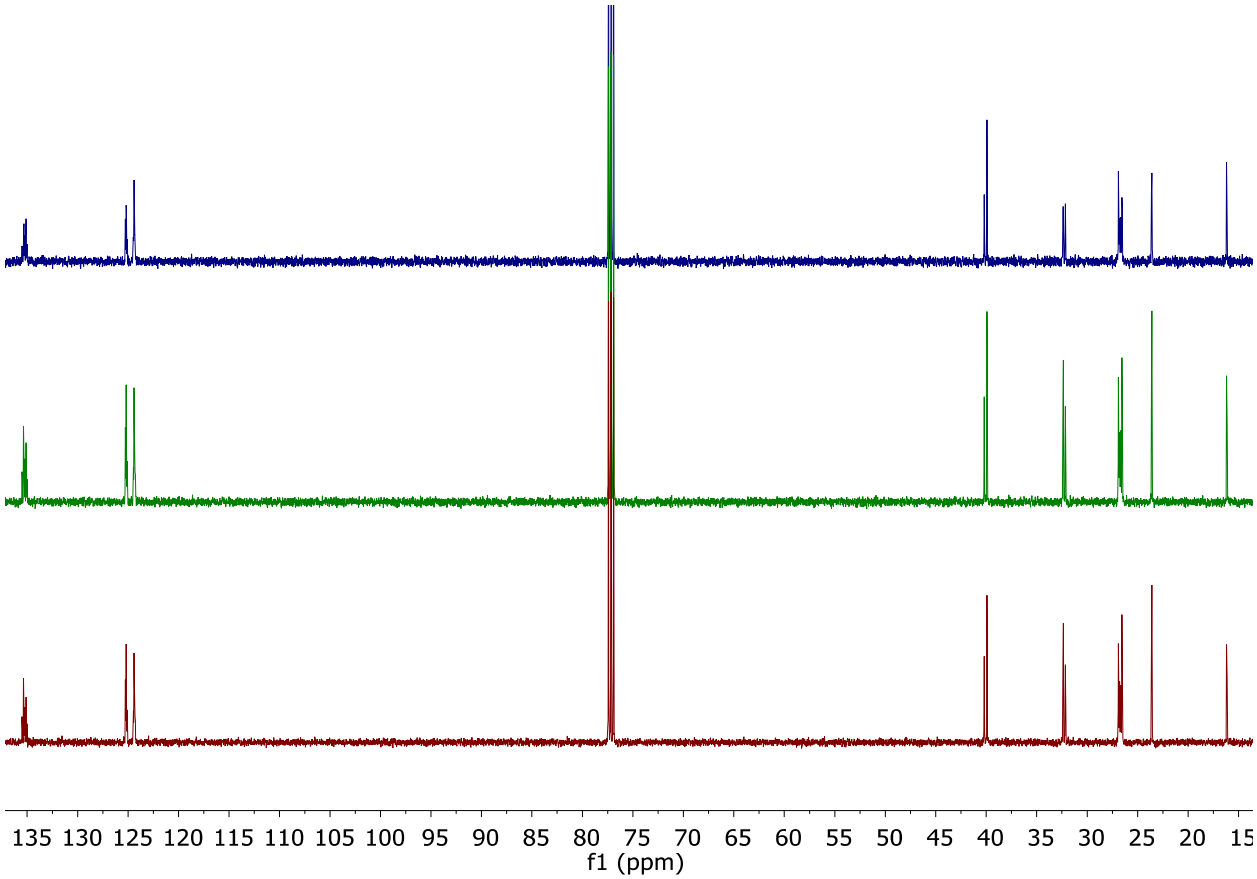

Fig. S58 ^{13}C NMR spectrum of PIP 800 equivalents generated by **6**/[Ph_3C][$B(C_6F_5)_4$] from **Table 3**, entry 1 in $CDCl_3$ at 298 K (IP addition time 0 min).

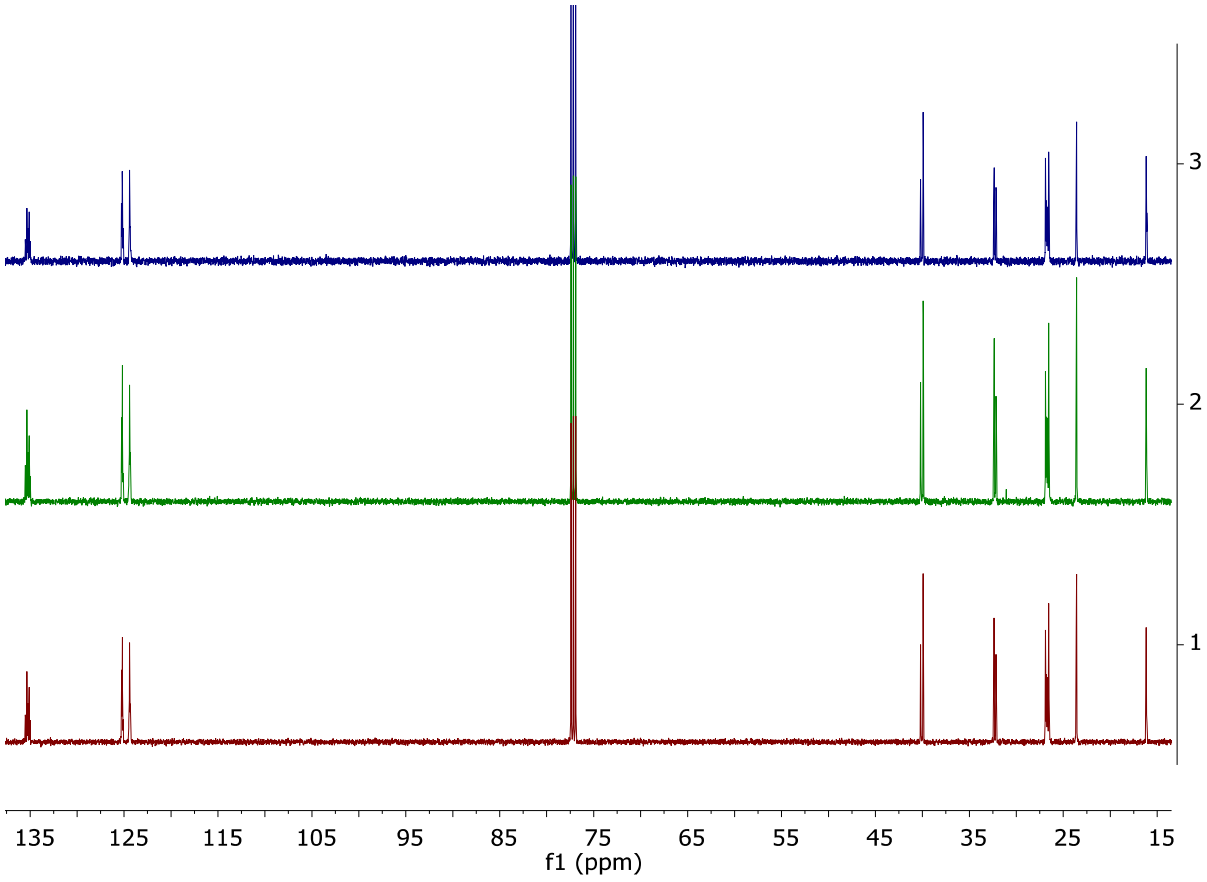

Fig. S59 ^{13}C NMR spectrum of PIP 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 3**, entry 2 in $CDCl_3$ at 298 K (IP addition time 30 min).

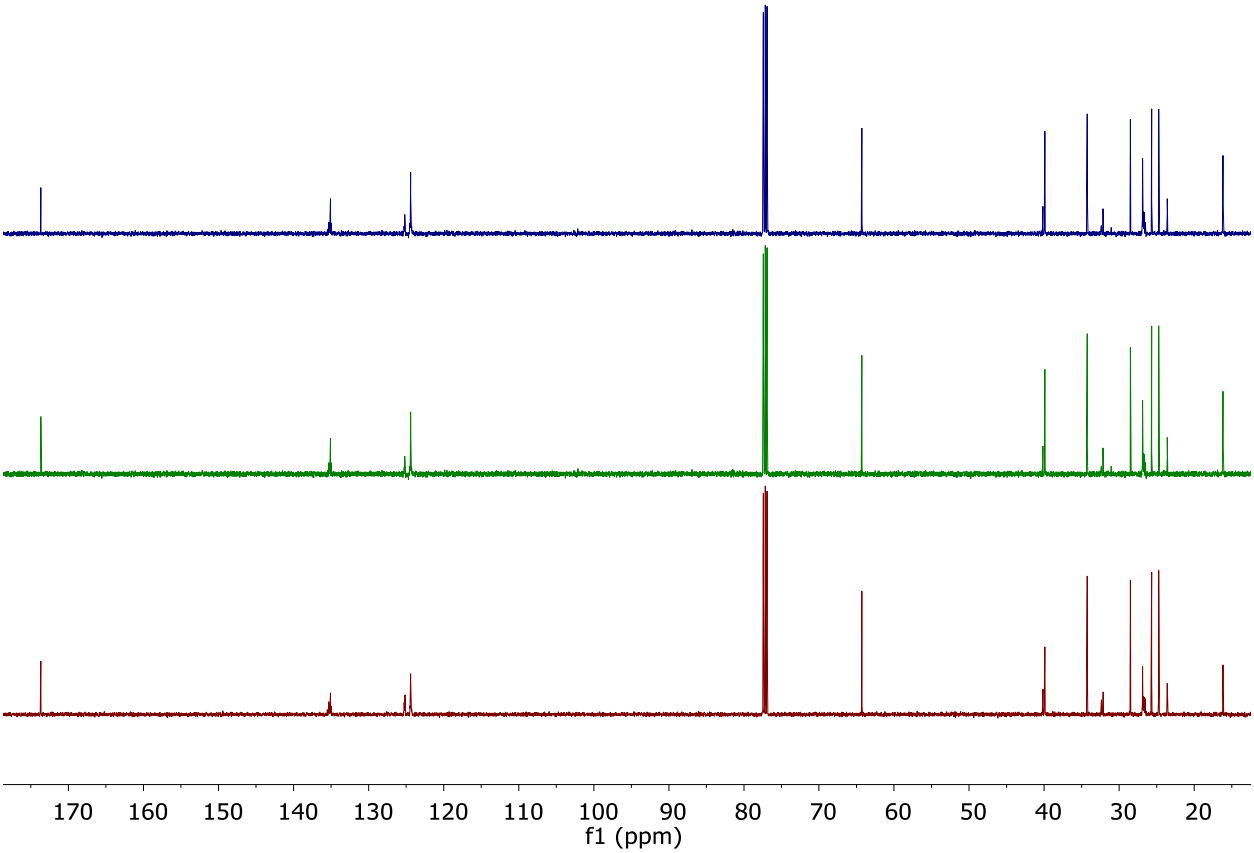

Fig. S60 ^{13}C NMR spectrum of PIP-*b*-PCL 800:300 equivalents generated by **6** and 0.5 equivalents of $[Ph_3C][B(C_6F_5)_4]$ from **Table 3**, entry 3 in $CDCl_3$ at 298 K.

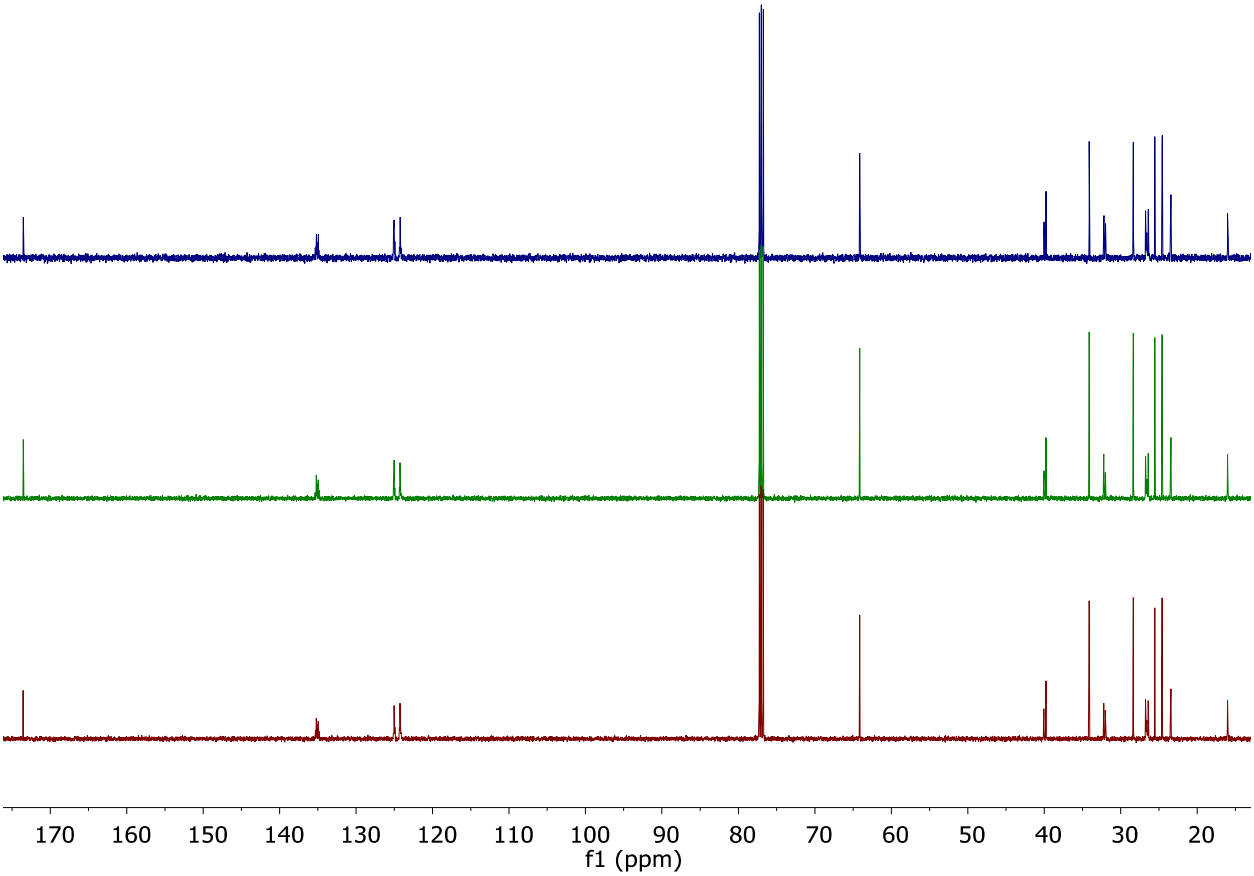

Fig. S61 ^{13}C NMR spectrum of PIP-*b*-PCL 800:300 equivalents generated by **6** and 1.5 equivalents of $[Ph_3C][B(C_6F_5)_4]$ from **Table 3**, entry 4 in $CDCl_3$ at 298 K.

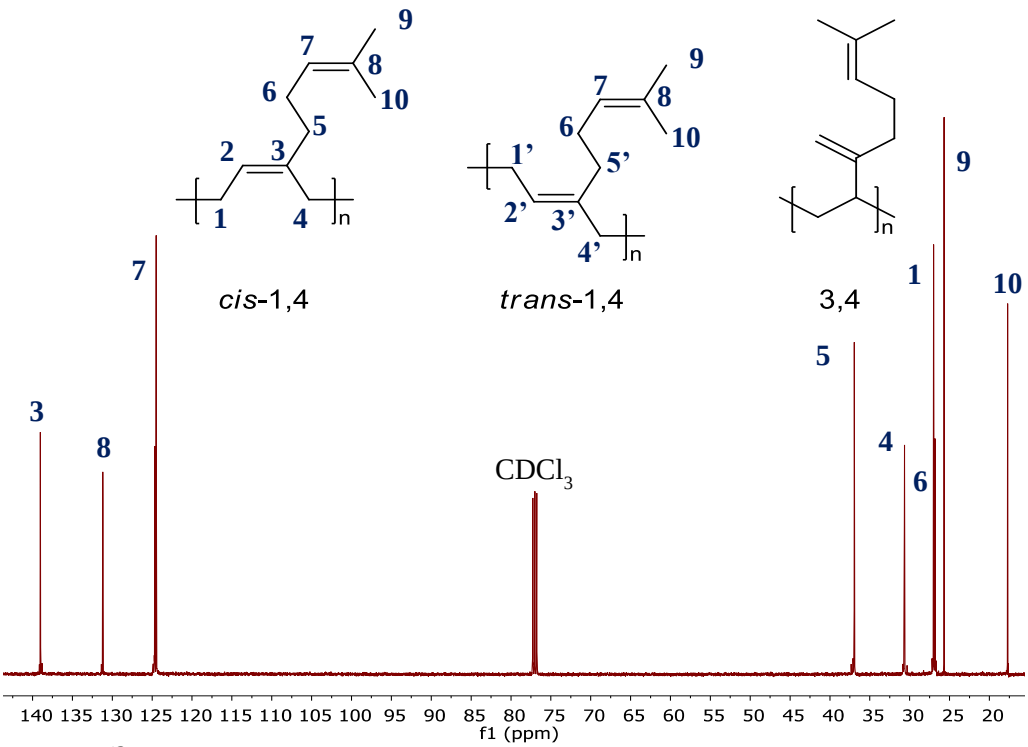

Fig. S62 ^{13}C NMR spectrum of PMyr 800 equivalents generated by **6**/[Ph_3C][$B(C_6F_5)_4$] from **Table 4**, entry 1 in $CDCl_3$ at 298 K (30 min). Representative peak assignment for PMyr.

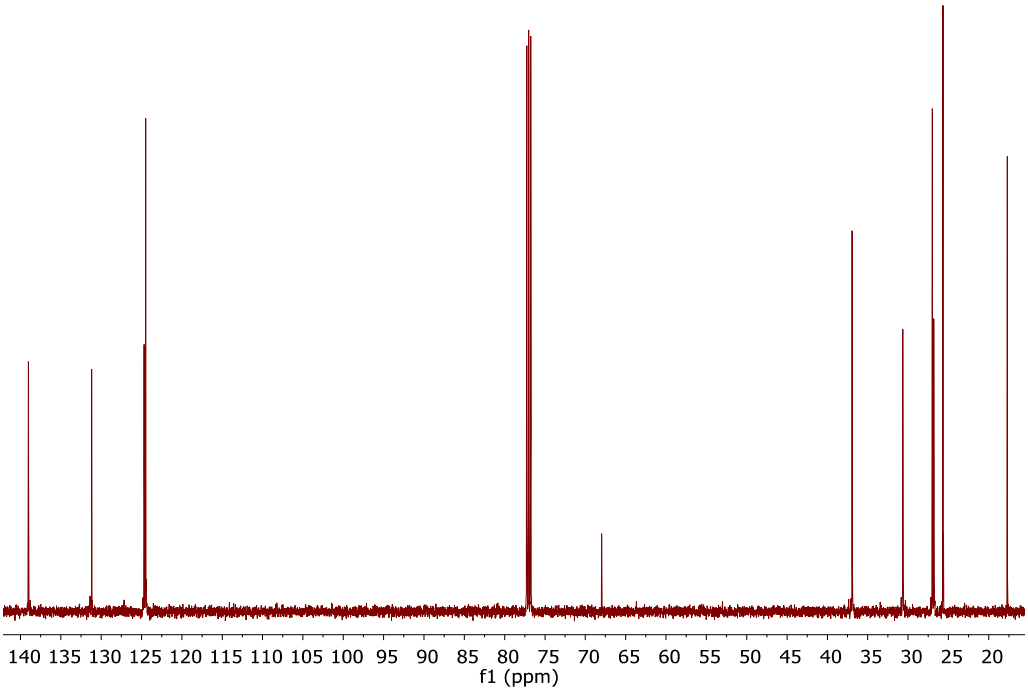

Fig. S63 ^{13}C NMR spectrum of PMyr 800 equivalents generated by **6**/[Ph_3C][$B(C_6F_5)_4$] from **Table 4**, entry 2 in $CDCl_3$ at 298 K (90 min).

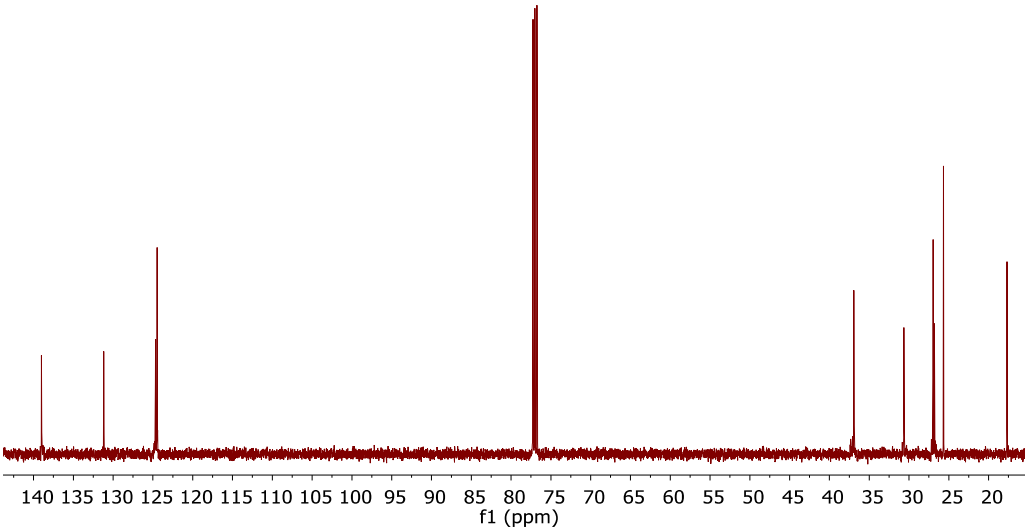

Fig. S64 ^{13}C NMR spectrum of PMyr 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 4**, entry 3 in $CDCl_3$ at 298 K (3 h).

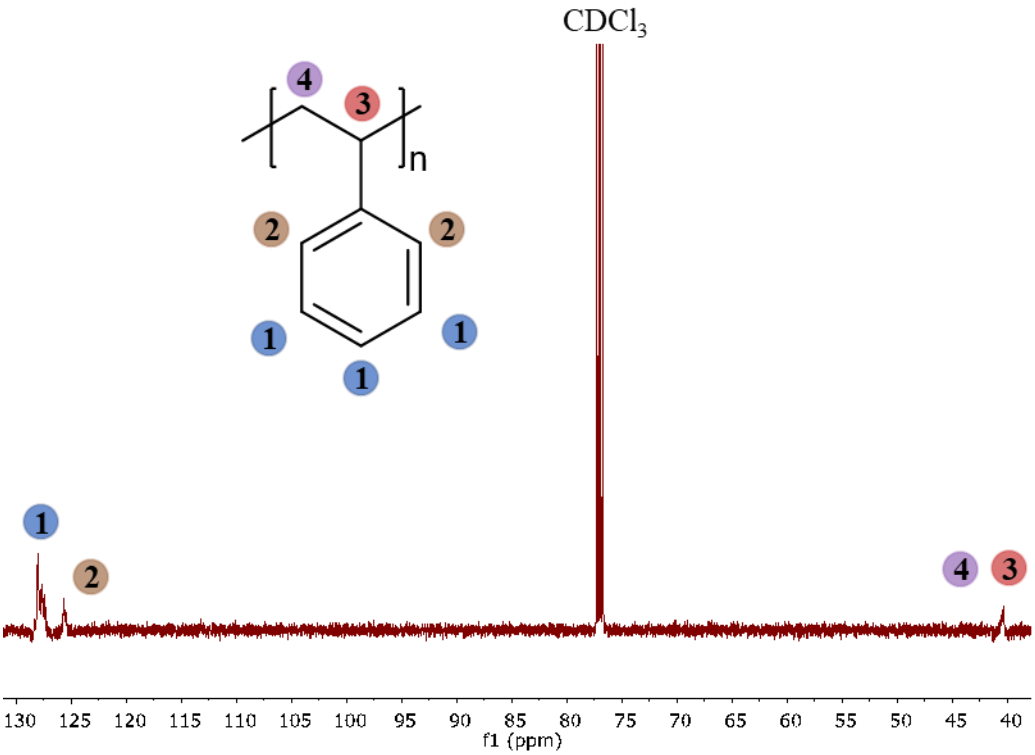

Fig. S65 ^{13}C NMR spectrum of PS 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 4**, entry 4 in $CDCl_3$ at 298 K (30 min). Representative peak assignment for PS.

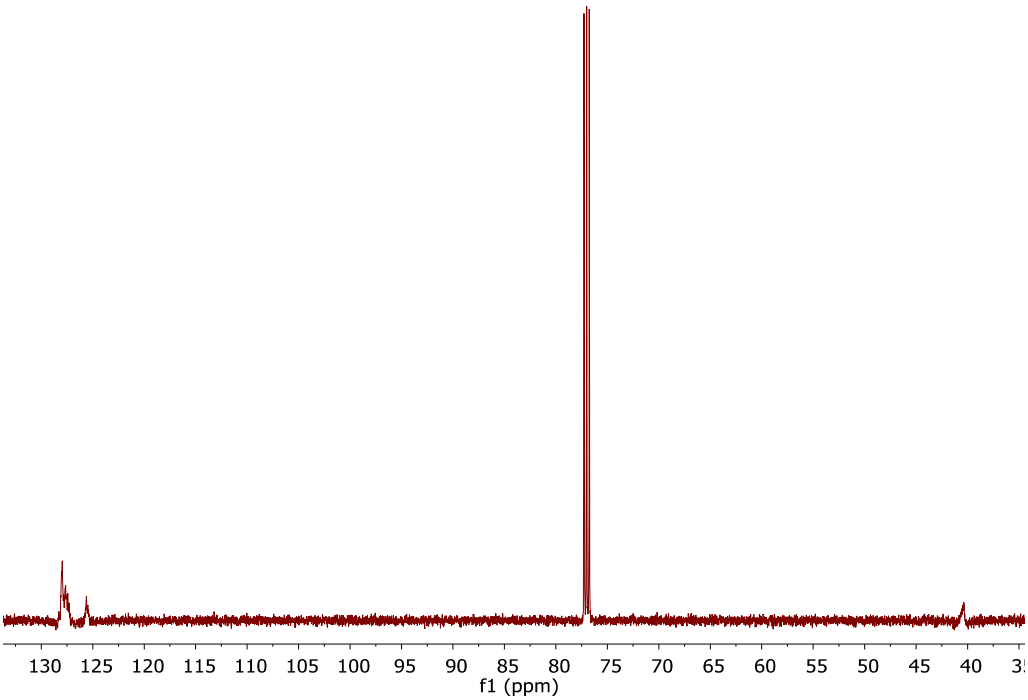

Fig. S66 ^{13}C NMR spectrum of PS 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 4**, entry 5 in $CDCl_3$ at 298 K (20 h).

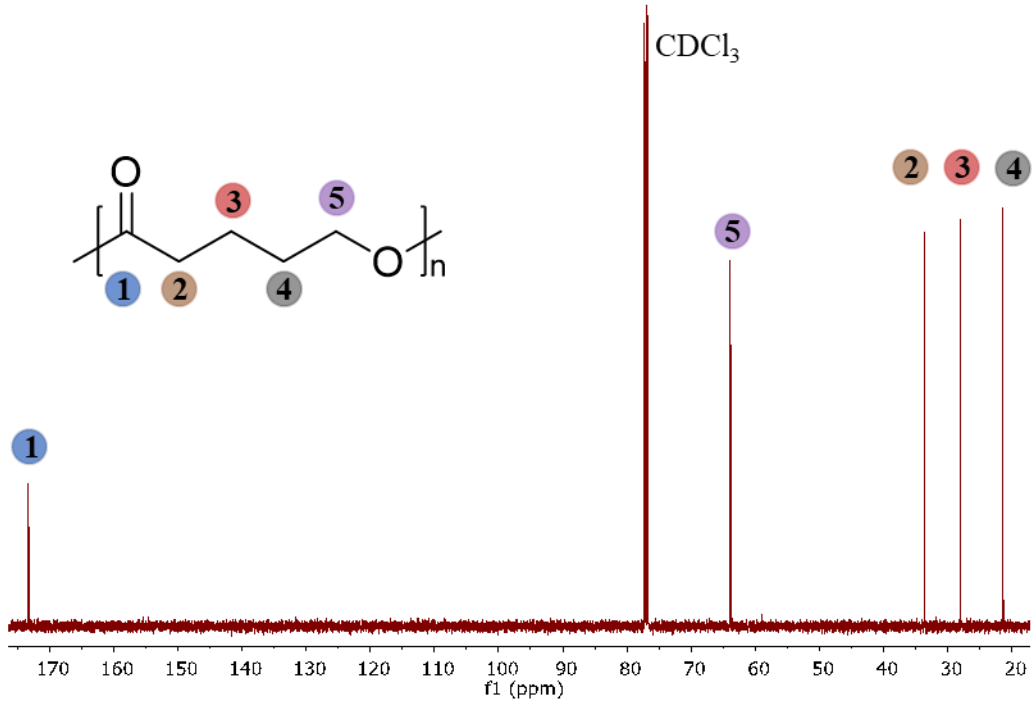

Fig. S67 ^{13}C NMR spectrum of PVL 300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 4**, entry 6 in $CDCl_3$ at 298 K (10 min). Representative peak assignment for PVL.

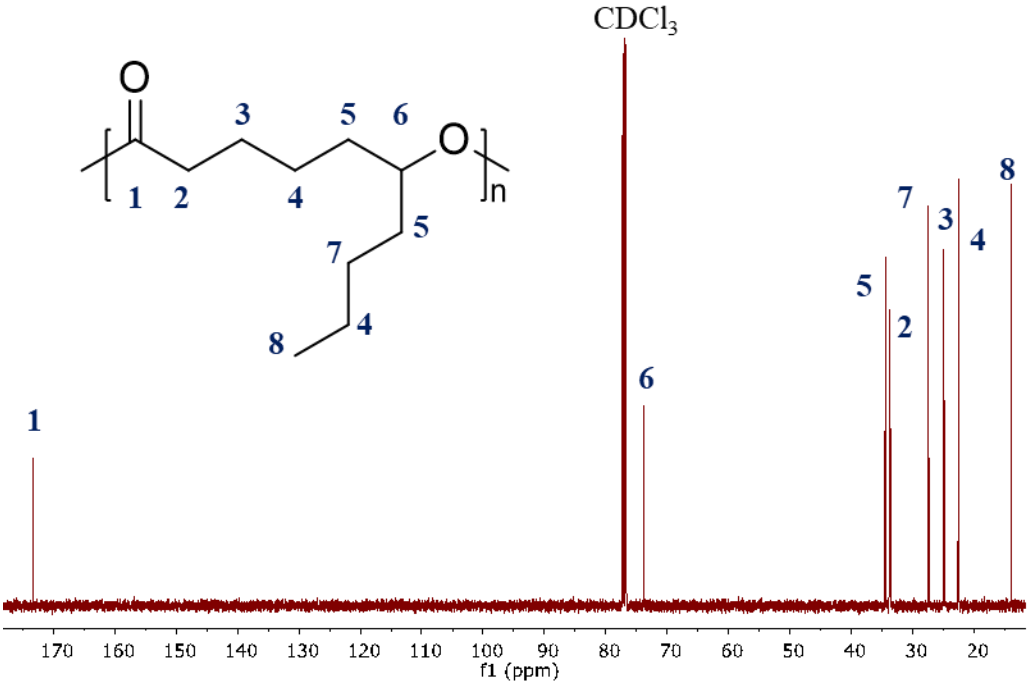

Fig. S68 ^{13}C NMR spectrum of PDL 300 equivalents generated by **6**/[Ph_3C][$B(C_6F_5)_4$] from **Table 4**, entry 7 in $CDCl_3$ at 298 K (30 min). Representative peak assignment for PDL.

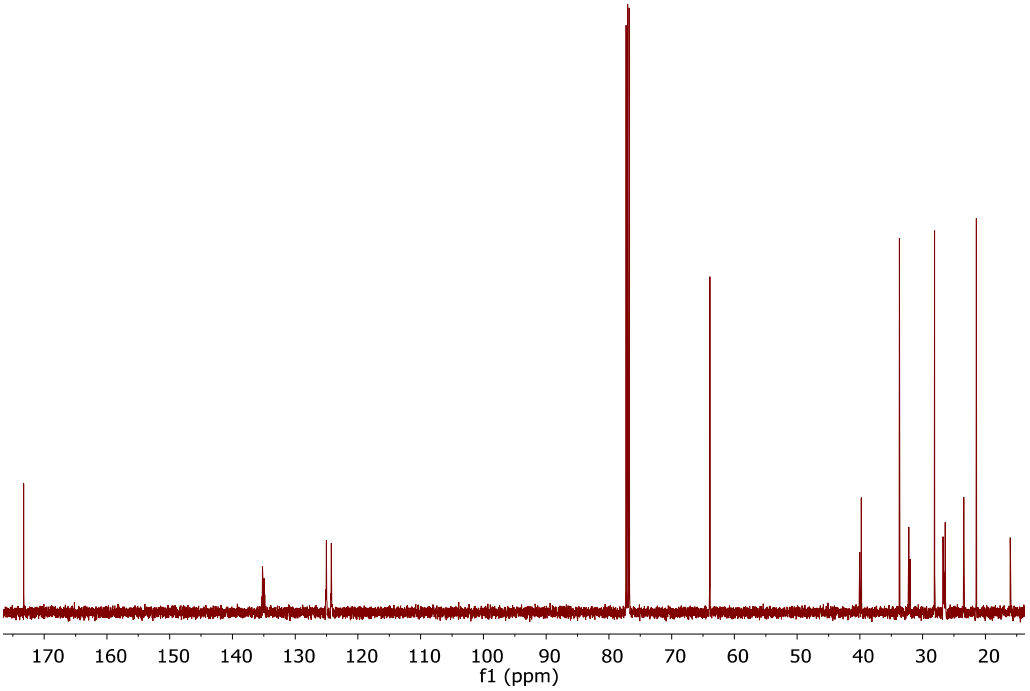

Fig. S69 ^{13}C NMR spectrum of PIP-*b*-PVL 800:300 equivalents generated by **6**/[Ph_3C][$B(C_6F_5)_4$] from **Table 5**, entry 1 in $CDCl_3$ at 298 K.

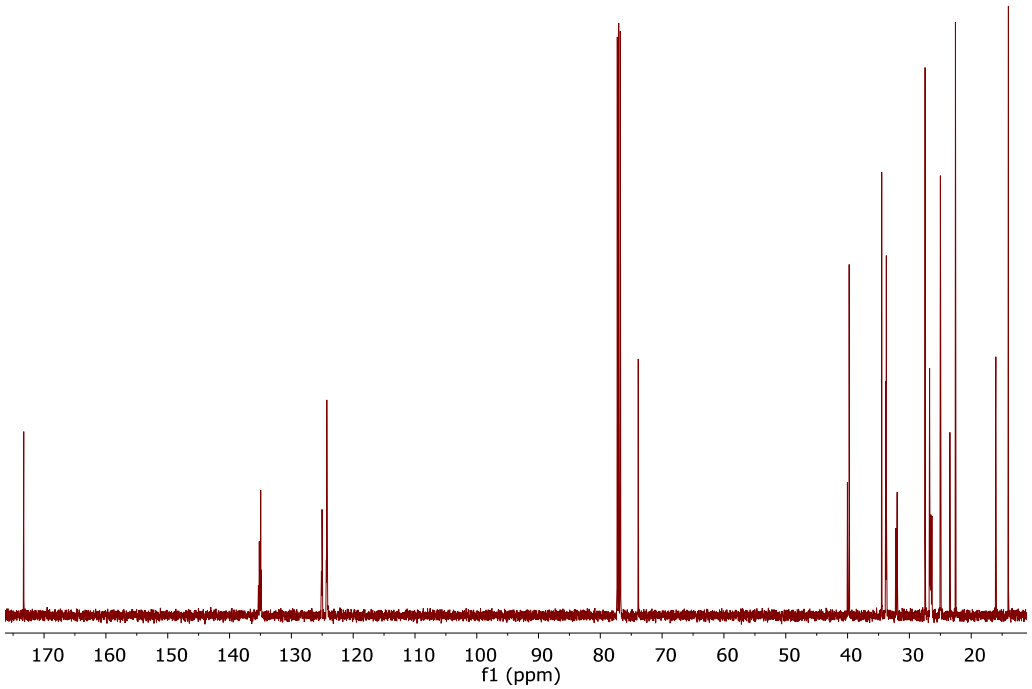

Fig. S70 ^{13}C NMR spectrum of PIP-*b*-PDL 800:300 equivalents generated by **6**/[Ph_3C][$B(C_6F_5)_4$] from **Table 5**, entry 2 in $CDCl_3$ at 298 K.

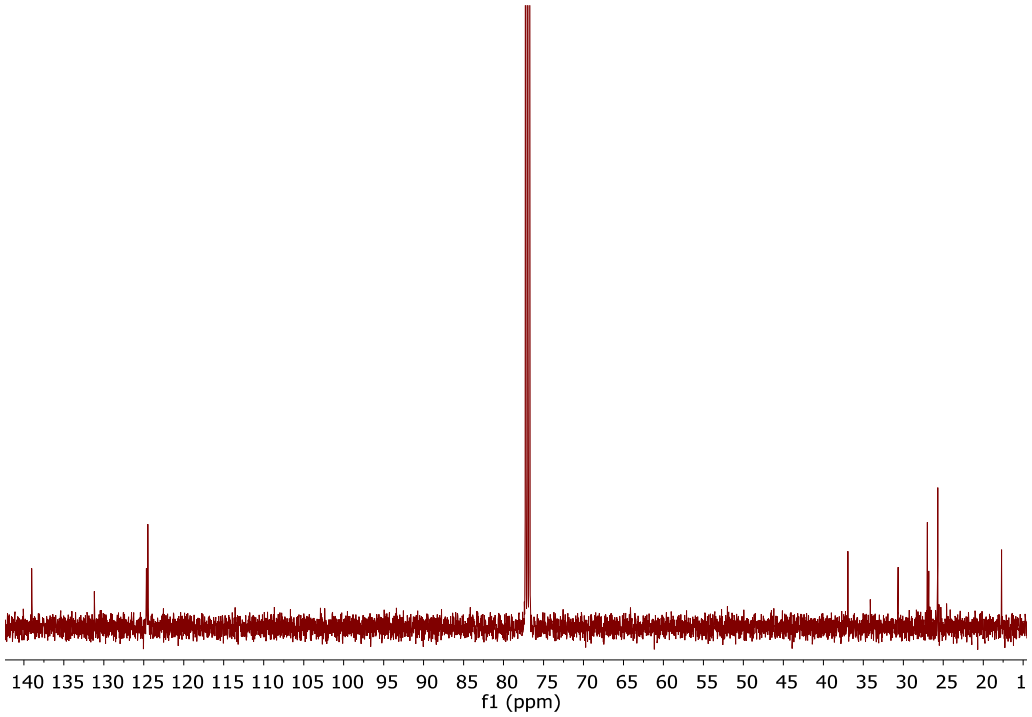

Fig. S71 ^{13}C NMR spectrum of PMyr-*b*-PCL 800:300 equivalents generated by **6**/[Ph_3C][$B(C_6F_5)_4$] from **Table 5**, entry 3 in $CDCl_3$ at 298 K.

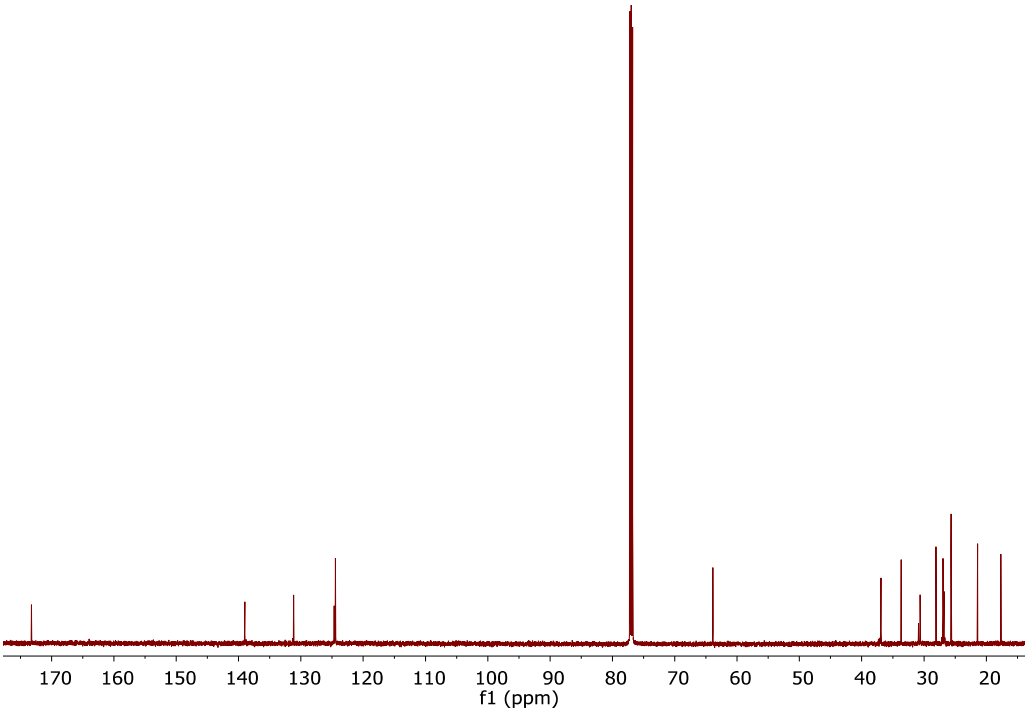

Fig. S72 ^{13}C NMR spectrum of PMyr-*b*-PVL 800:300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 5**, entry 4 in $CDCl_3$ at 298 K.

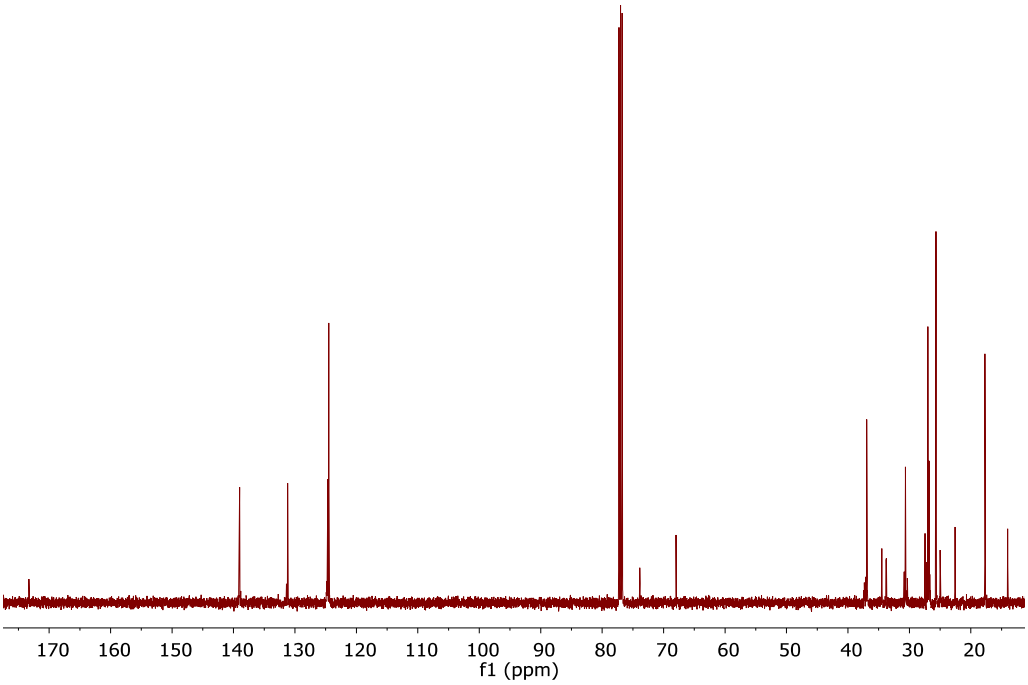

Fig. S73 ^{13}C NMR spectrum of PMyr-*b*-PDL 800:300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 5**, entry 5 in $CDCl_3$ at 298 K.

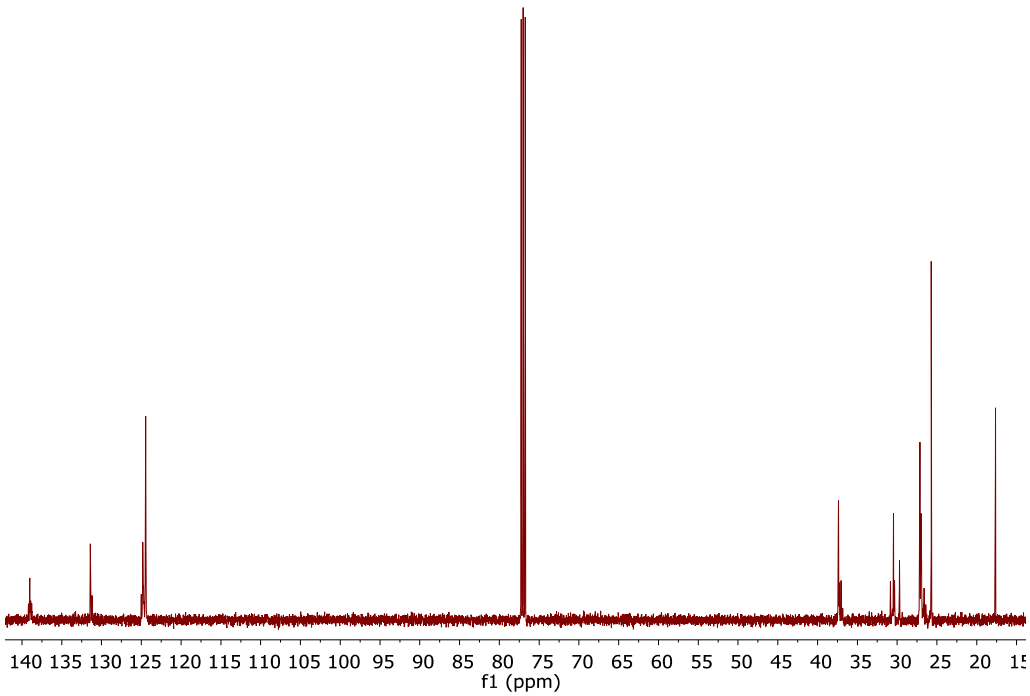

Fig. S74 ^{13}C NMR spectrum of PMyr 800 equivalents generated by **8**/[Ph_3C][$B(C_6F_5)_4$] from **Table S1**, entry 1 in $CDCl_3$ at 298 K (30 min).

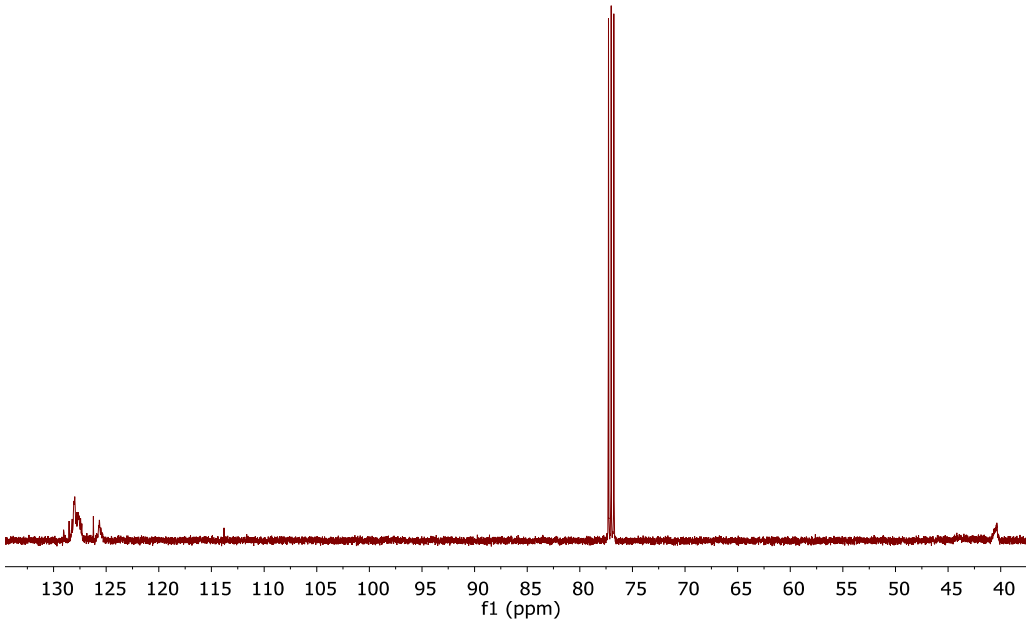

Fig. S75 ^{13}C NMR spectrum of PS 800 equivalents generated by **8**/[Ph_3C][$B(C_6F_5)_4$] from **Table S1**, entry 2 in $CDCl_3$ at 298 K (30 min).

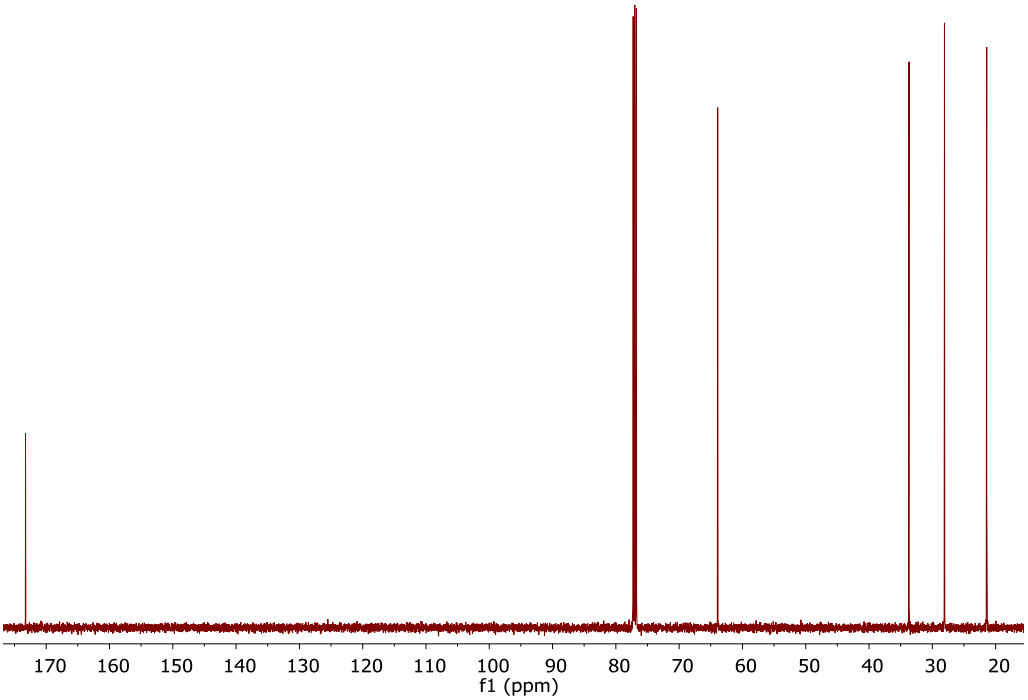

Fig. S76 ^{13}C NMR spectrum of PVL 300 equivalents generated by **8**/$[Ph_3C][B(C_6F_5)_4]$ from **Table S1**, entry 3 in $CDCl_3$ at 298 K (10 min).

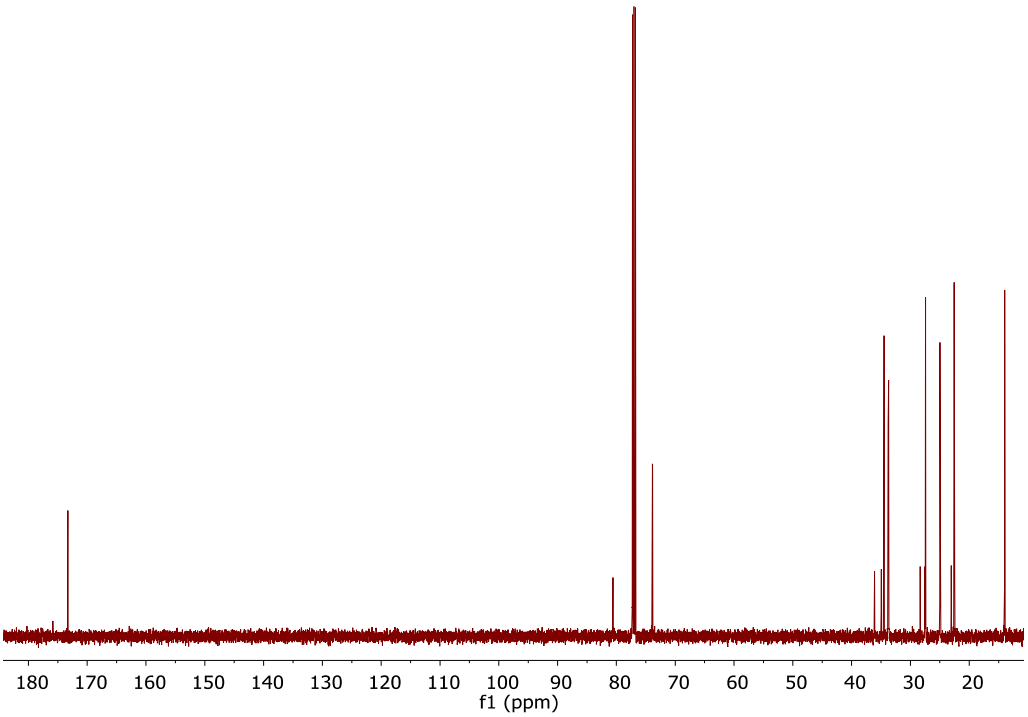

Fig. S77 ^{13}C NMR spectrum of PDL 300 equivalents generated by **8**/$[Ph_3C][B(C_6F_5)_4]$ from **Table S1**, entry 4 in $CDCl_3$ at 298 K (6 h).

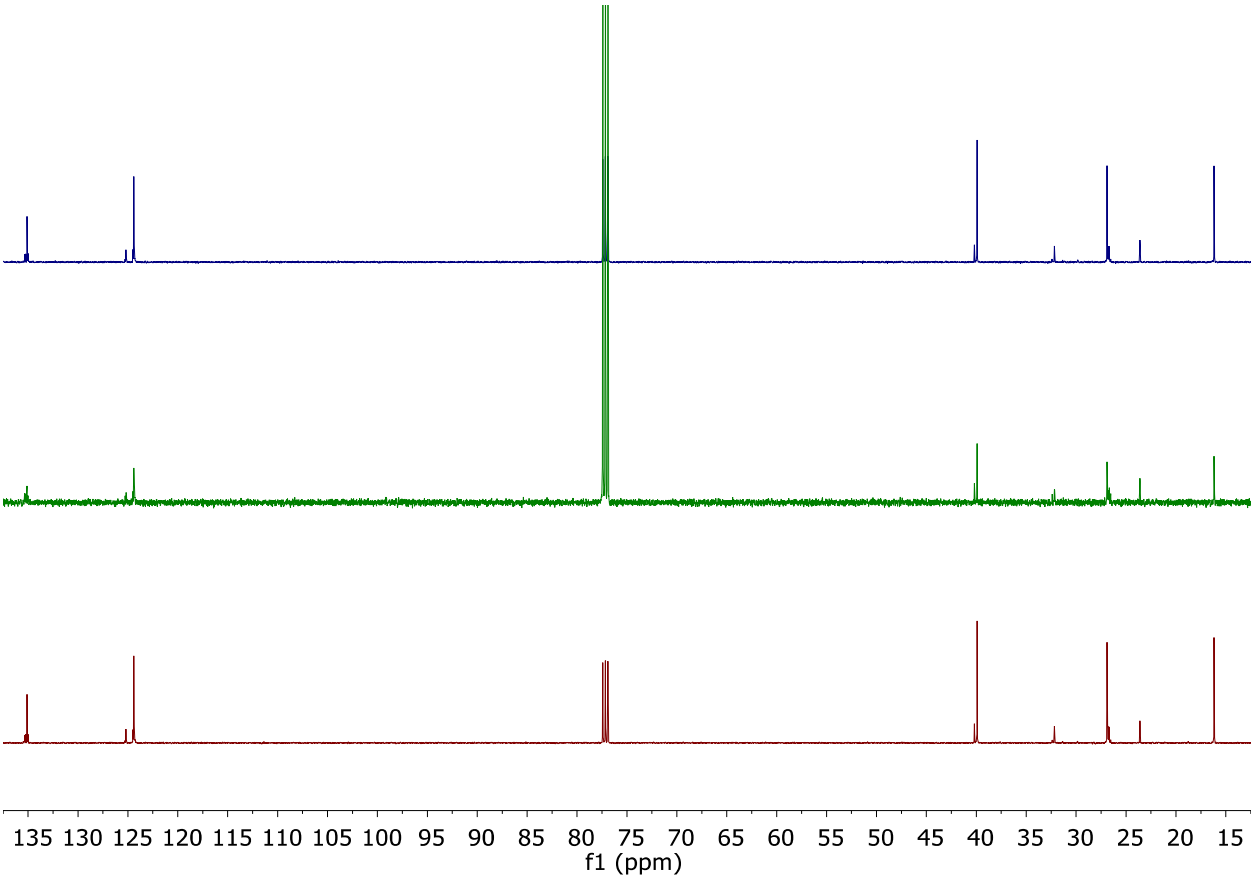

Fig. S78 ^{13}C NMR spectrum of PIP 300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table S2**, entry 1 in $CDCl_3$ at 298 K (12 h).

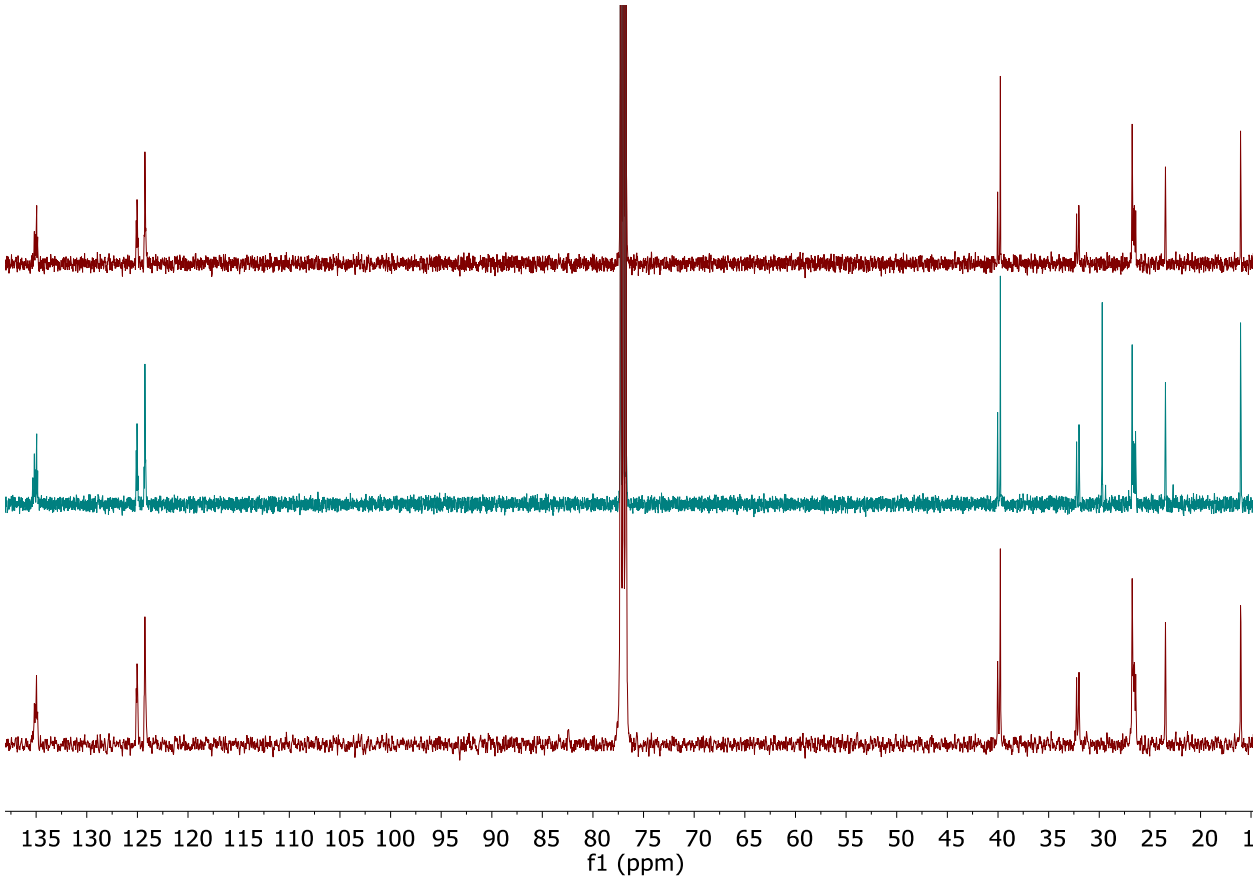

Fig. S79 ^{13}C NMR spectrum of PIP 550 equivalents generated by **6**/[Ph_3C][$B(C_6F_5)_4$] from **Table S2**, entry 2 in $CDCl_3$ at 298 K (12 h).

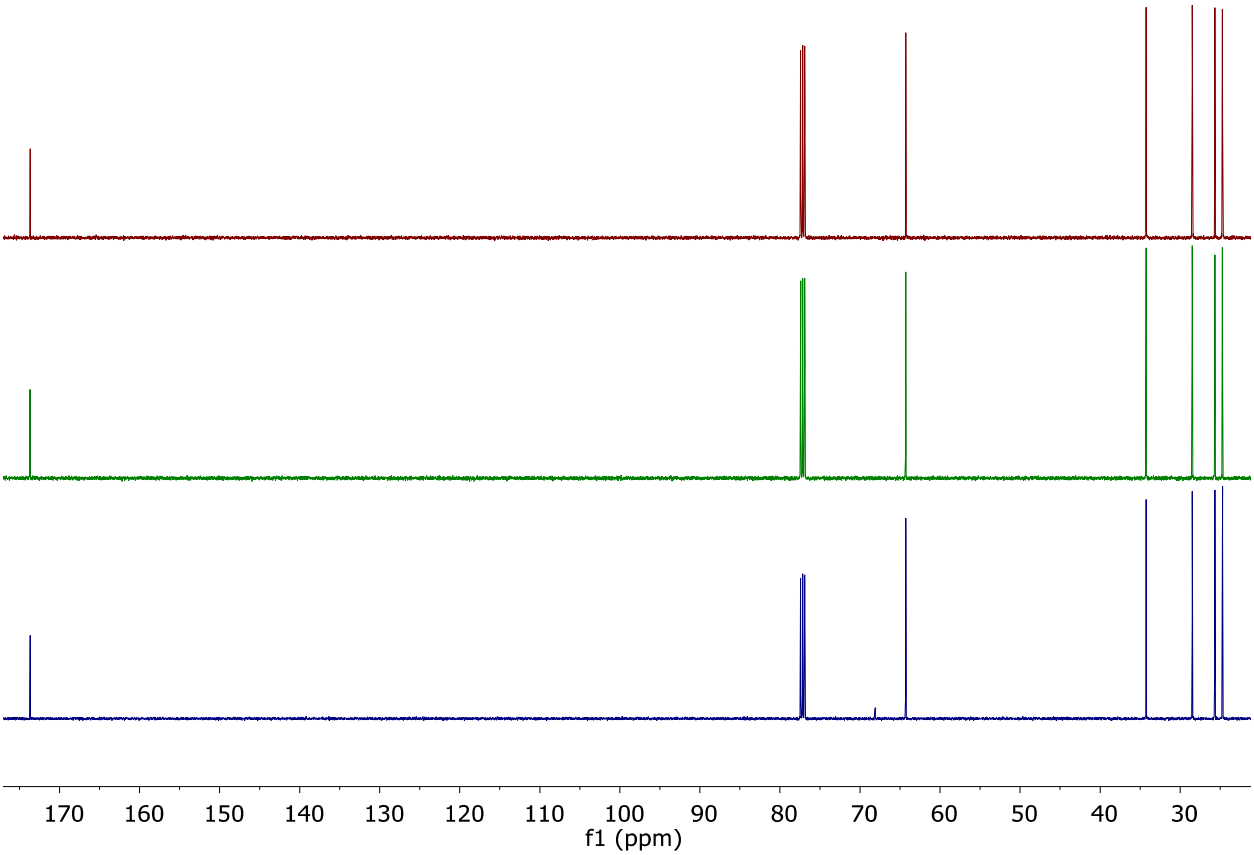

Fig. S80 ^{13}C NMR spectrum of PCL 550 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table S2**, entry 3 in $CDCl_3$ at 298 K (12 h).

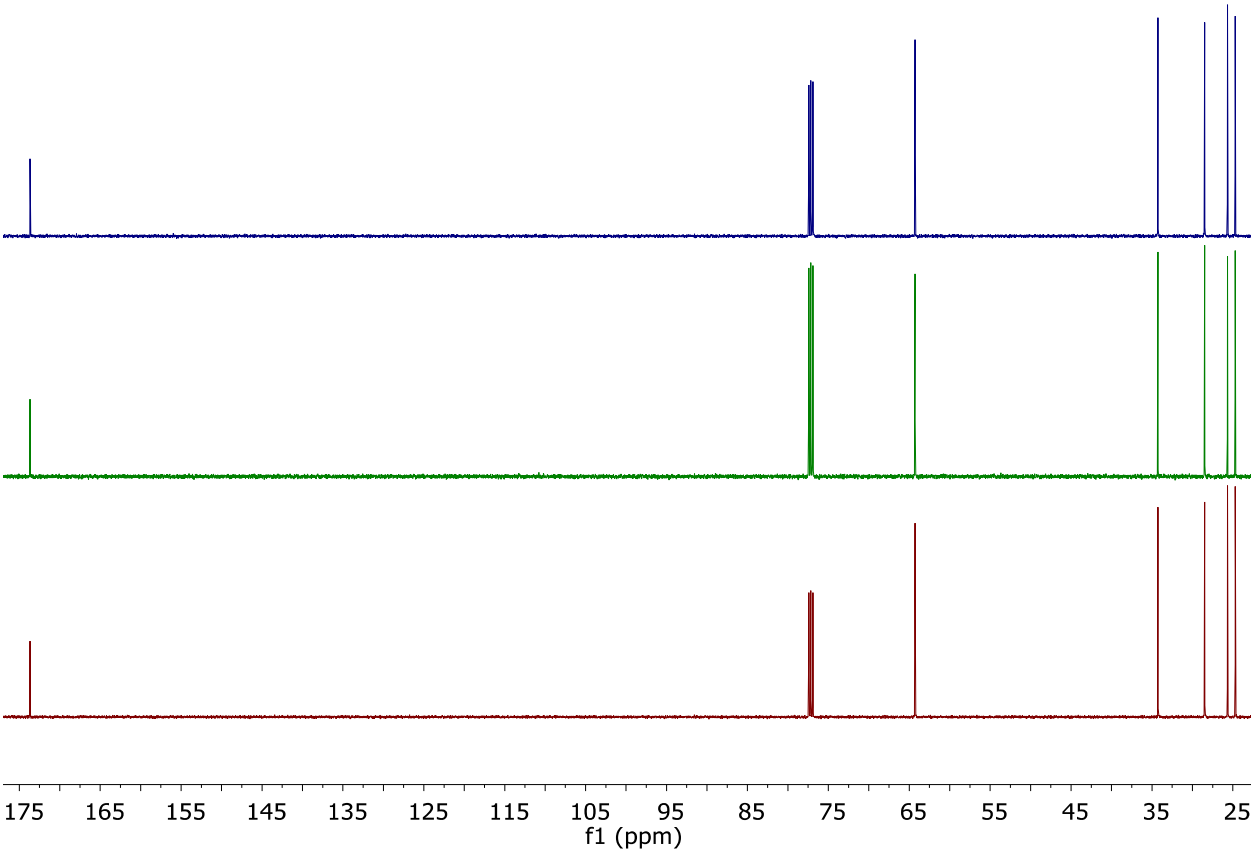

Fig. S81 ^{13}C NMR spectrum of PCL 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table S2**, entry 4 in $CDCl_3$ at 298 K (12 h).

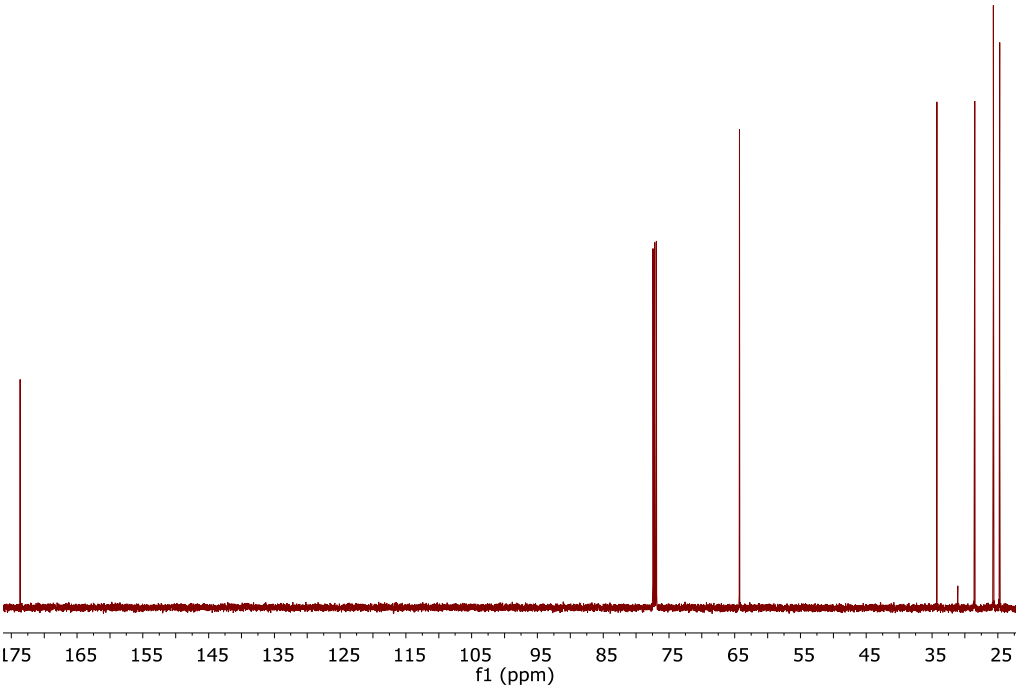

Fig. S82 ^{13}C NMR spectrum of PCL 800 equivalents generated by **6** from **Table S2**, entry 5 in $CDCl_3$ at 298 K (No $[Ph_3C][B(C_6F_5)_4]$ added) (10 min).

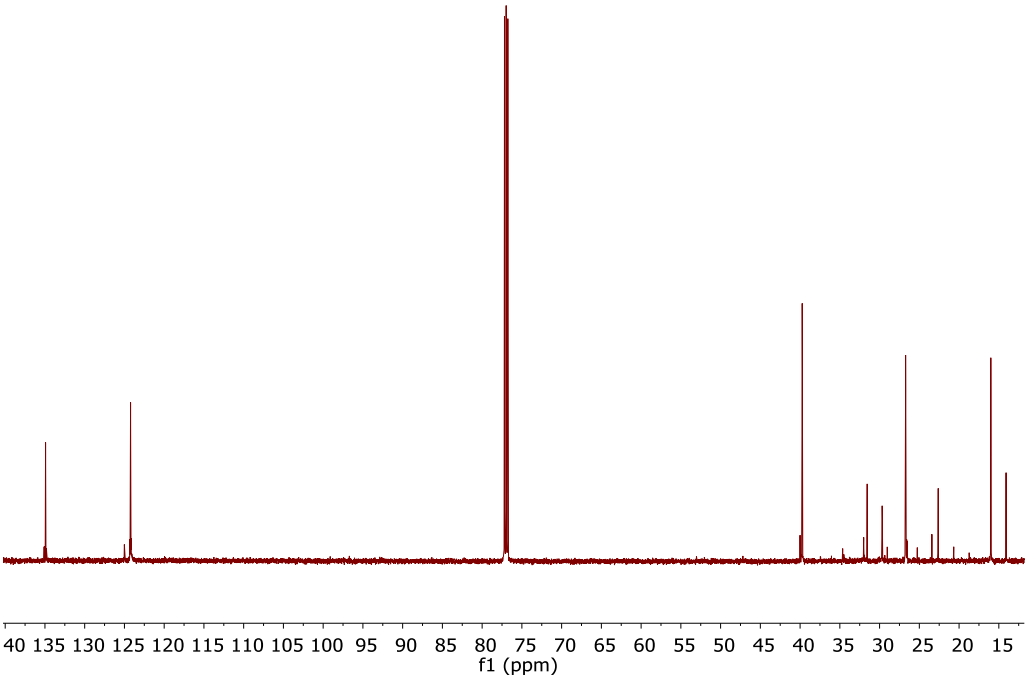

Fig. S83 ^{13}C NMR spectrum of PIP 50 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table S3**, entry 1 in $CDCl_3$ at 298 K (12 h).

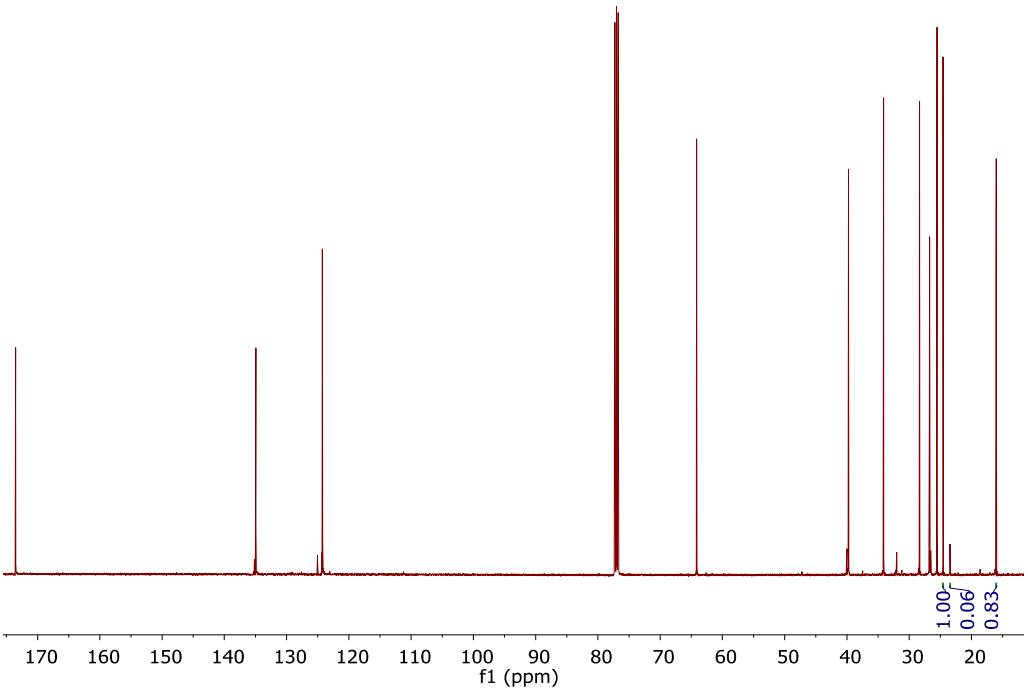

Fig. S84 ^{13}C NMR spectrum of PIP-*b*-PCL 50:50 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table S3**, entry 2 in $CDCl_3$ at 298 K.

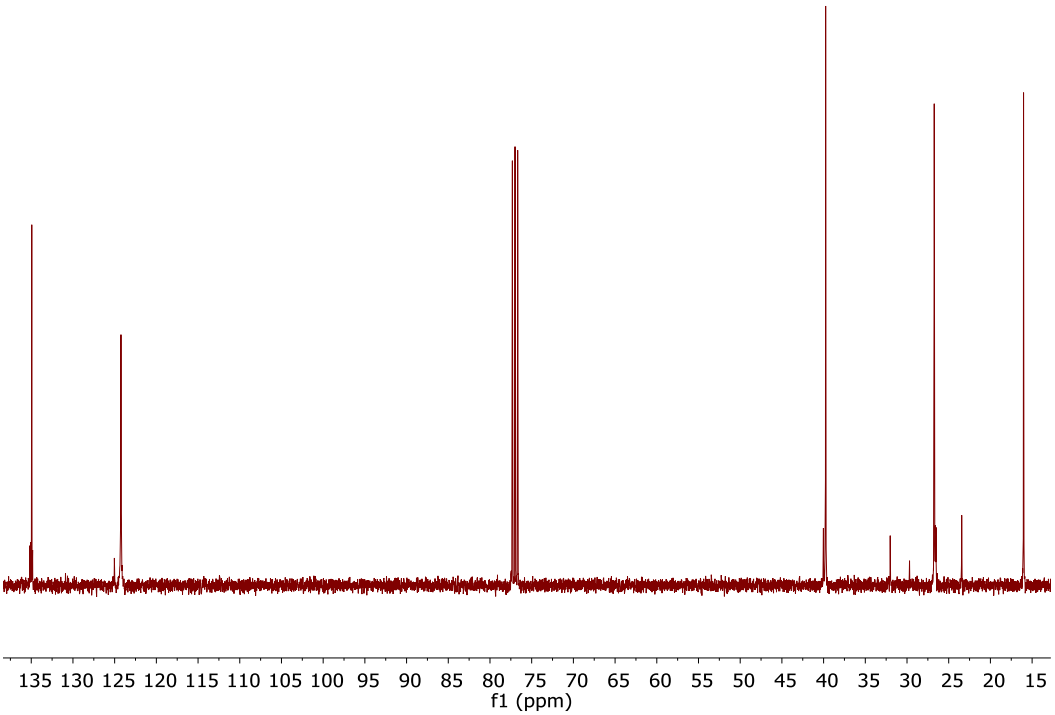

Fig. S85 ^{13}C NMR spectrum of recovered PIP 50 equivalents after hydrolysis of PIP-*b*-PCL 50:50 from **Table S3**, entry 3 in $CDCl_3$ at 298 K (12 h).

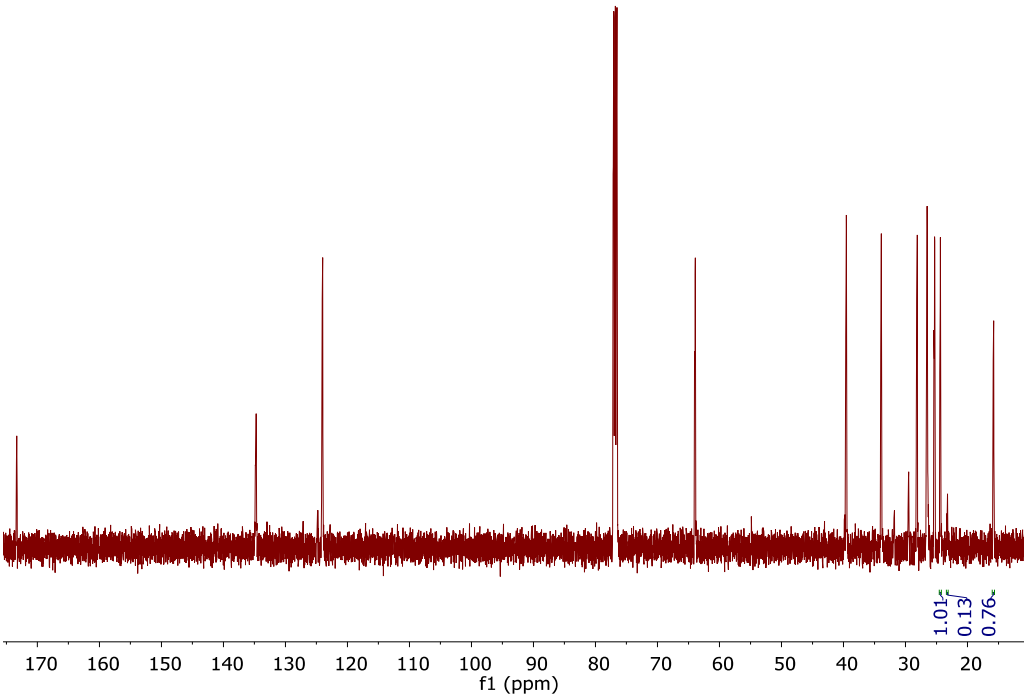

Fig. S86 ^{13}C NMR spectrum of PIP-*b*-PCL 50:50 equivalents generated by **Y[N(SiMe$_3$)$_2$]$_3$** from **Table S3**, entry 4 in $CDCl_3$ at 298 K (6 h).

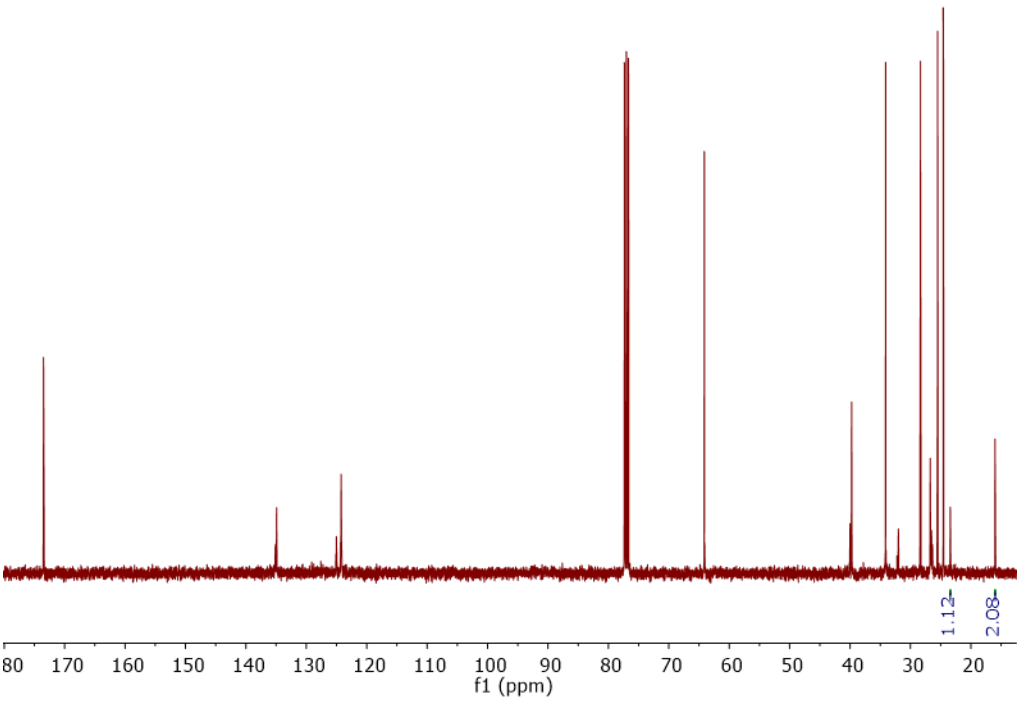

Fig. S87 ^{13}C NMR spectrum of PIP-*b*-PCL 50:50 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ (1 mL of toluene) from **Table S3**, entry 5 in $CDCl_3$ at 298 K.

3.3 Diffusion-Ordered Spectroscopy (DOSY)

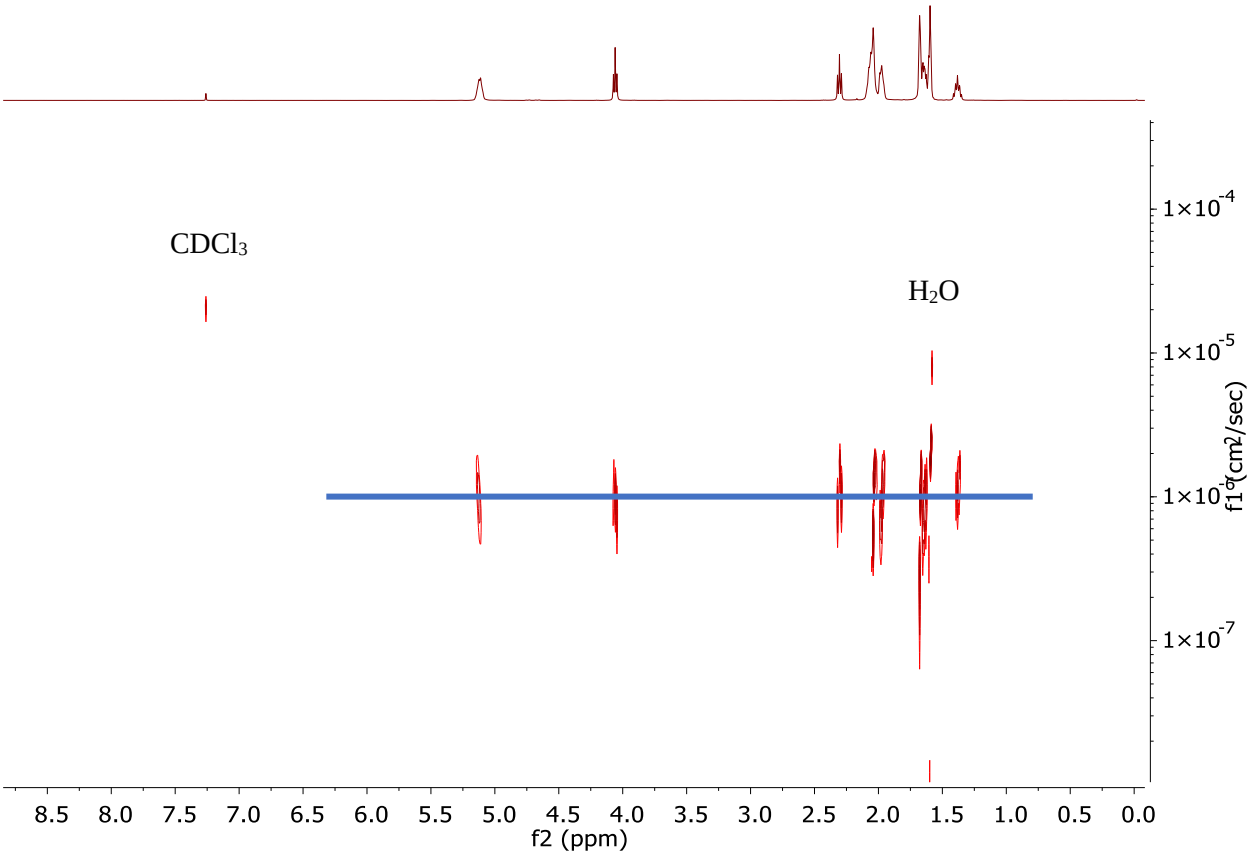

Fig. S88 DOSY NMR spectrum of PIP-*b*-PCL 800:300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 2**, entry 1a in $CDCl_3$ at 298 K.

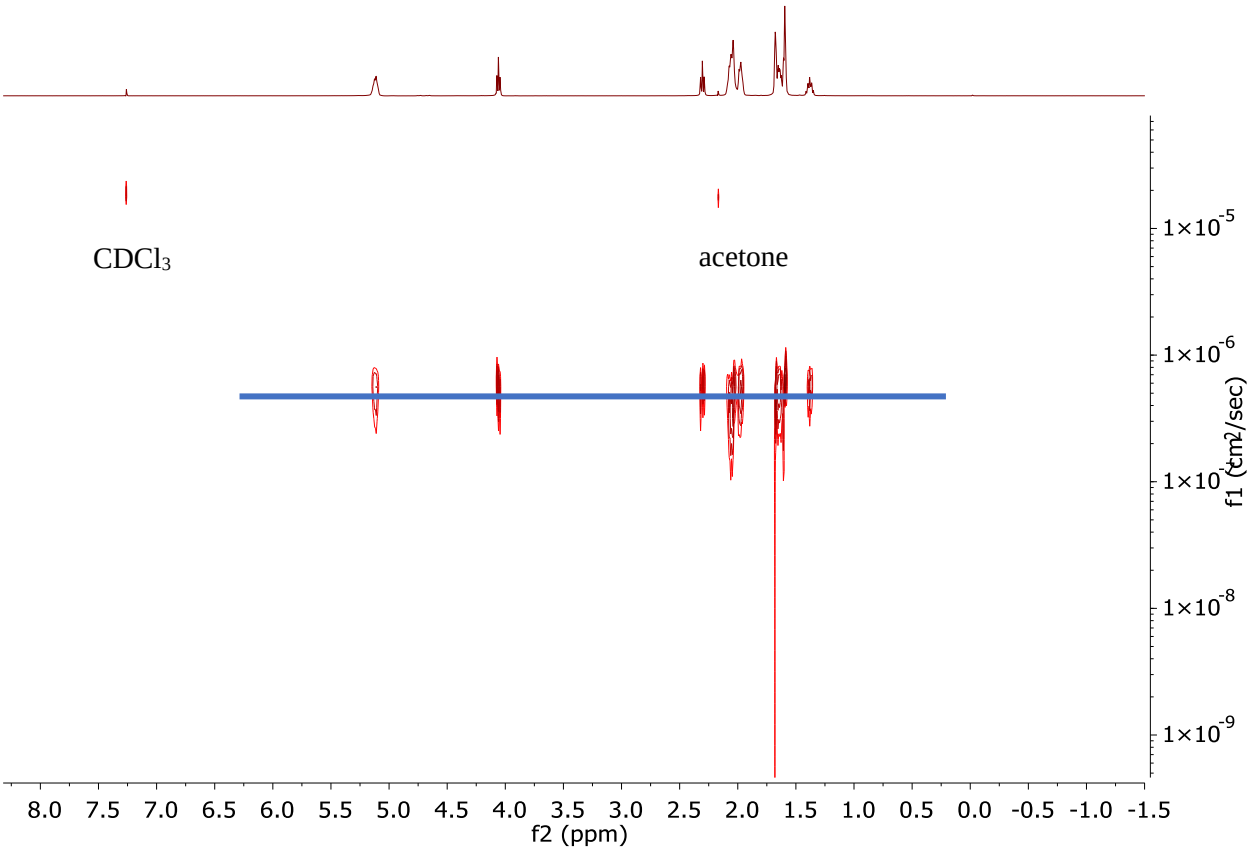

Fig. S89 DOSY NMR spectrum of PIP-*b*-PCL 800:300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 2**, entry 1b in $CDCl_3$ at 298 K.

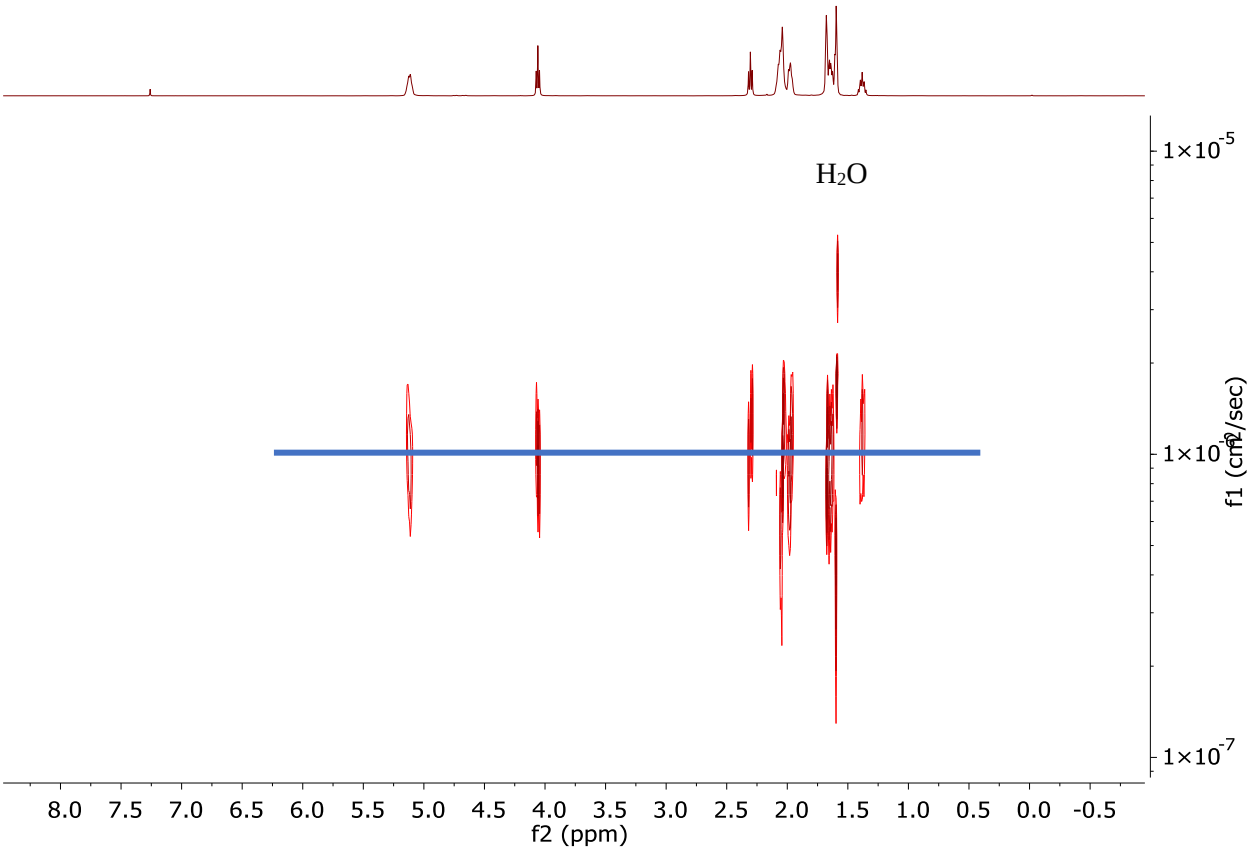

Fig. S90 DOSY NMR spectrum of PIP-*b*-PCL 800:300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 2**, entry 1c in $CDCl_3$ at 298 K.

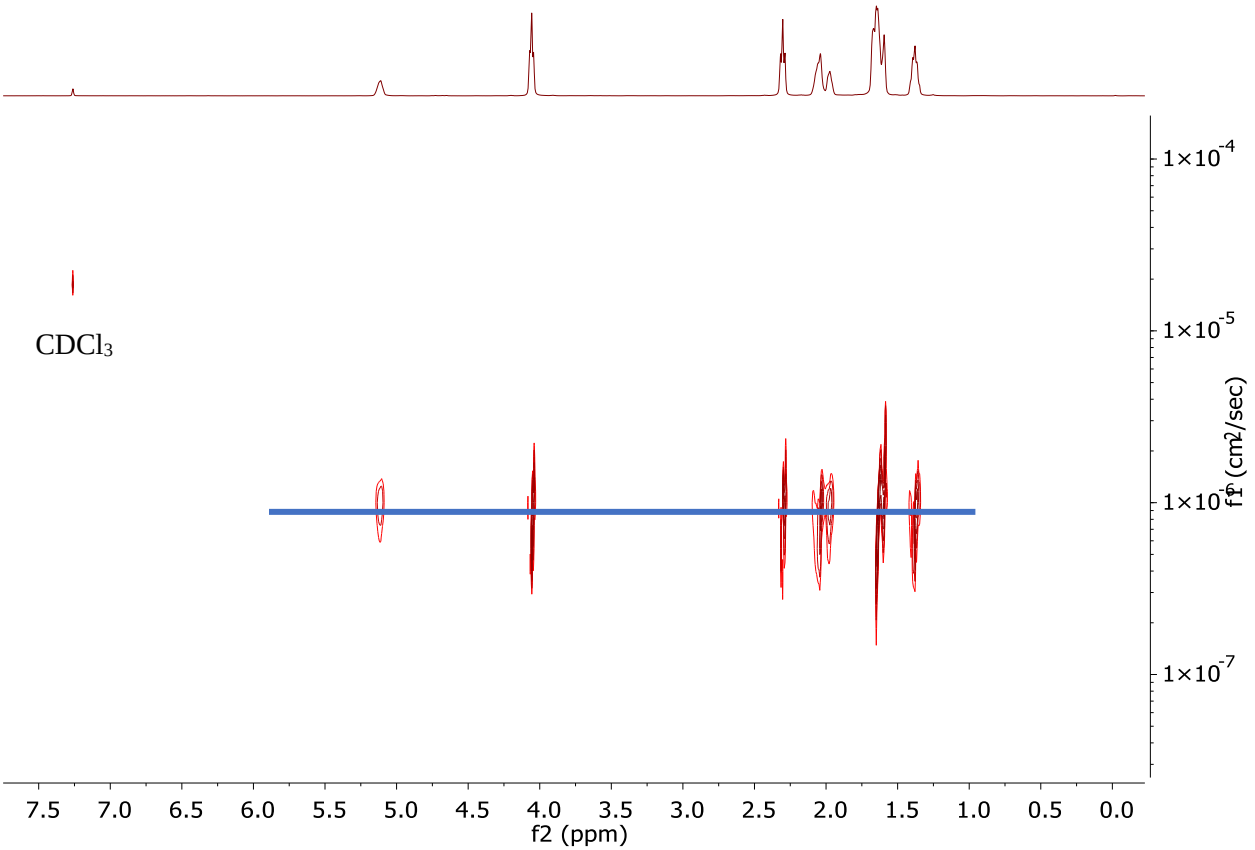

Fig. S91 DOSY NMR spectrum of PIP-*b*-PCL 550:550 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 2**, entry 2a in $CDCl_3$ at 298 K.

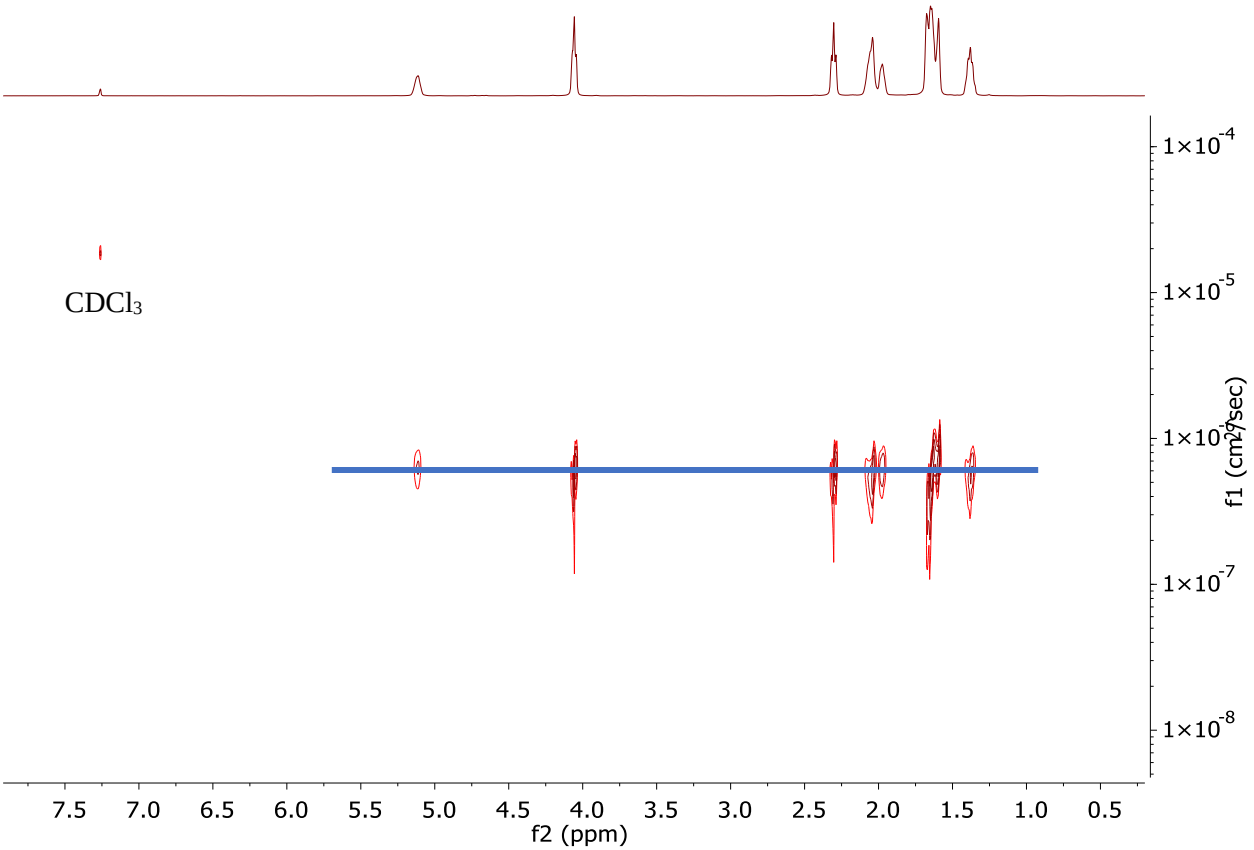

Fig. S92 DOSY NMR spectrum of PIP-*b*-PCL 550:550 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 2**, entry 2b in $CDCl_3$ at 298 K.

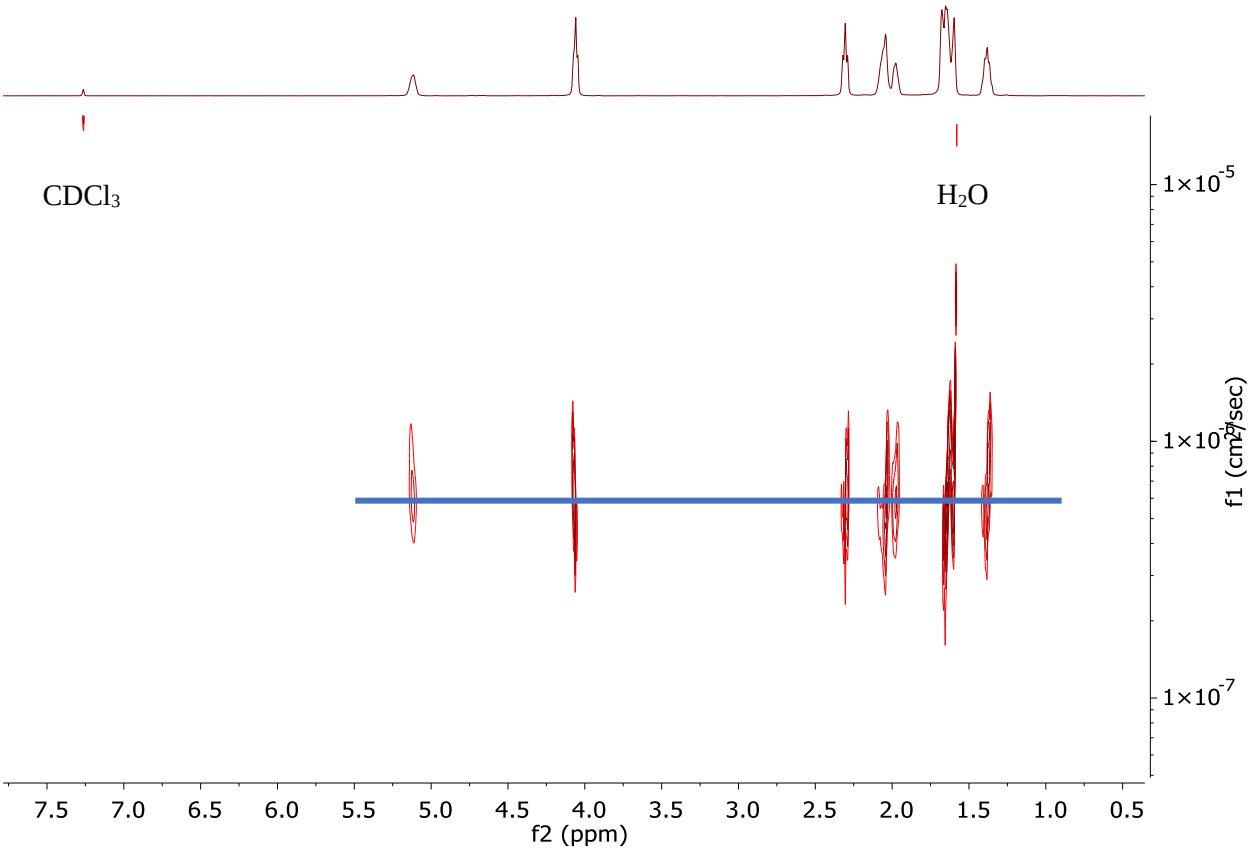

Fig. S93 DOSY NMR spectrum of PIP-*b*-PCL 550:550 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 2**, entry 2c in $CDCl_3$ at 298 K.

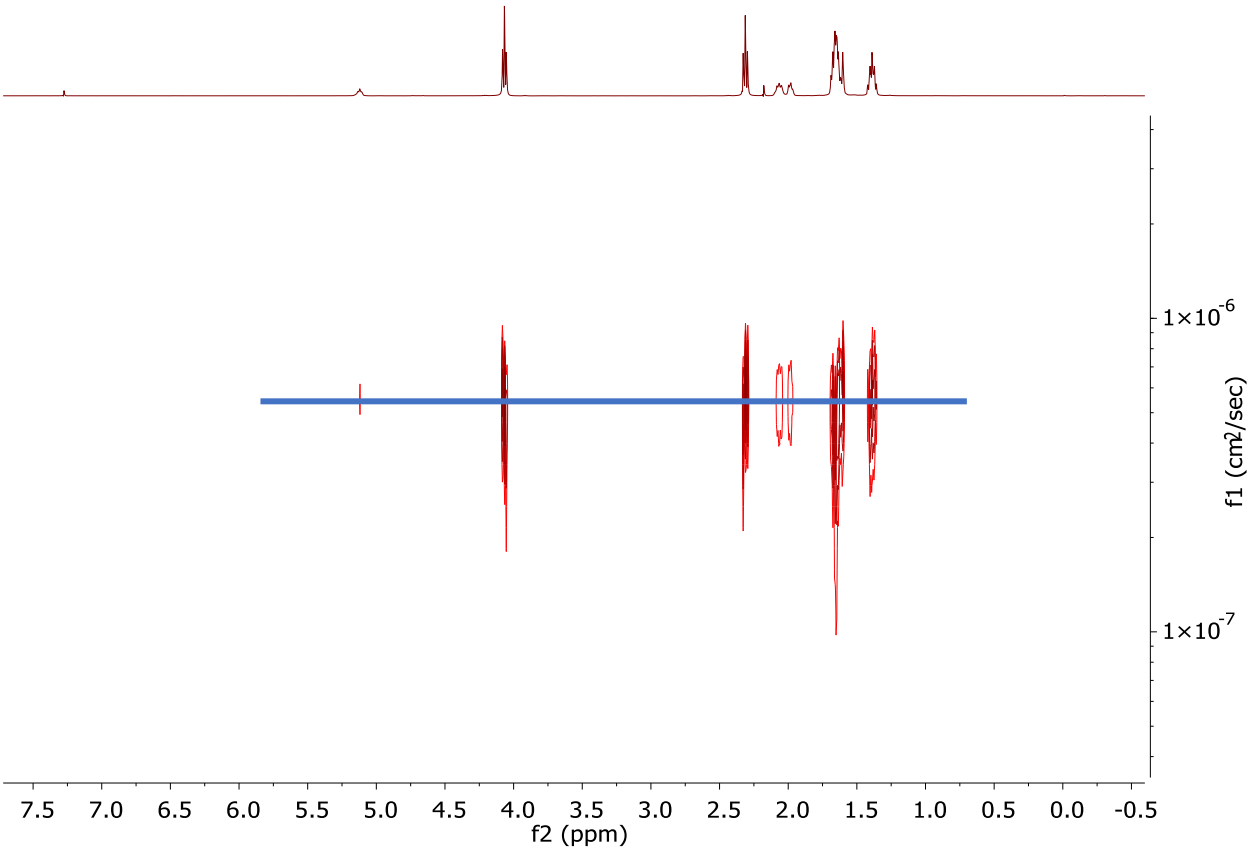

Fig. S94 DOSY NMR spectrum of PIP-*b*-PCL 300:800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 2**, entry 3a in $CDCl_3$ at 298 K.

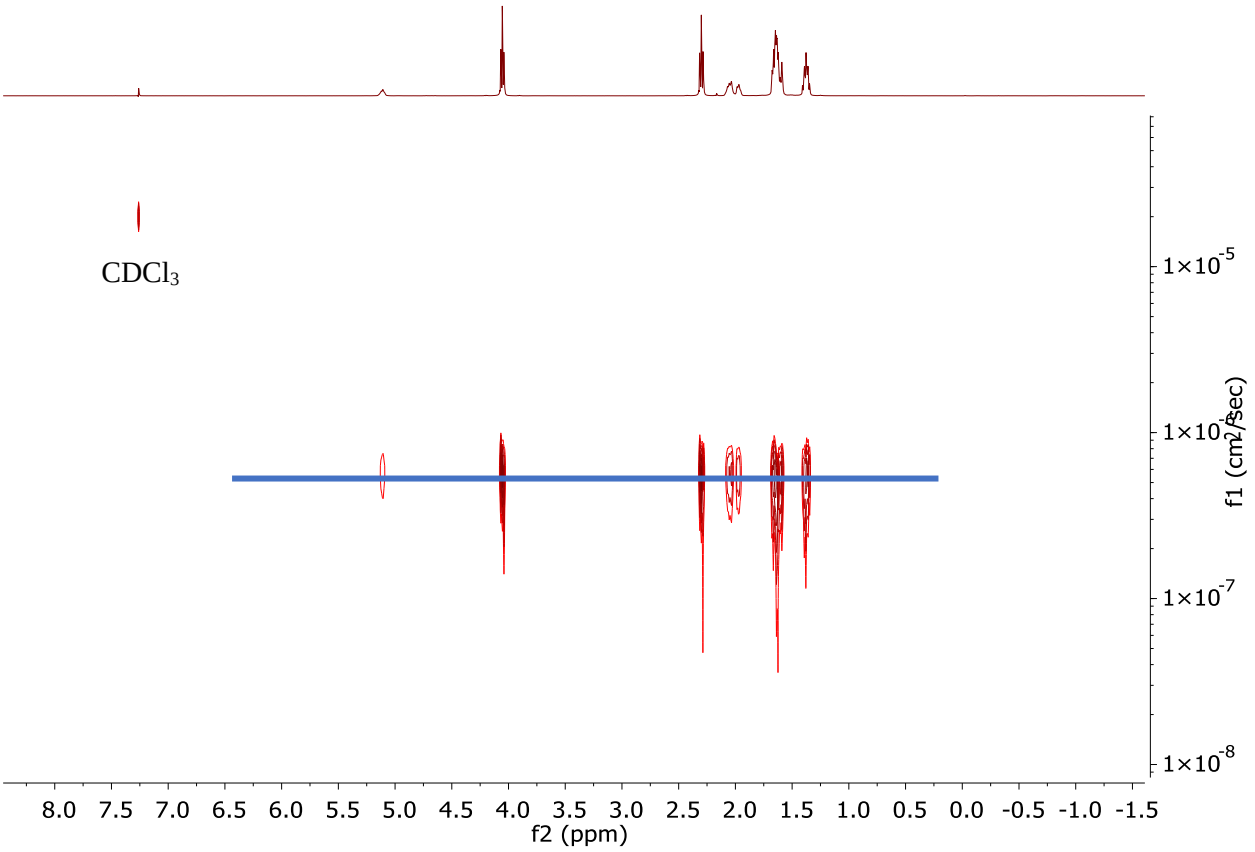

Fig. S95 DOSY NMR spectrum of PIP-*b*-PCL 300:800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 2**, entry 3b in $CDCl_3$ at 298 K.

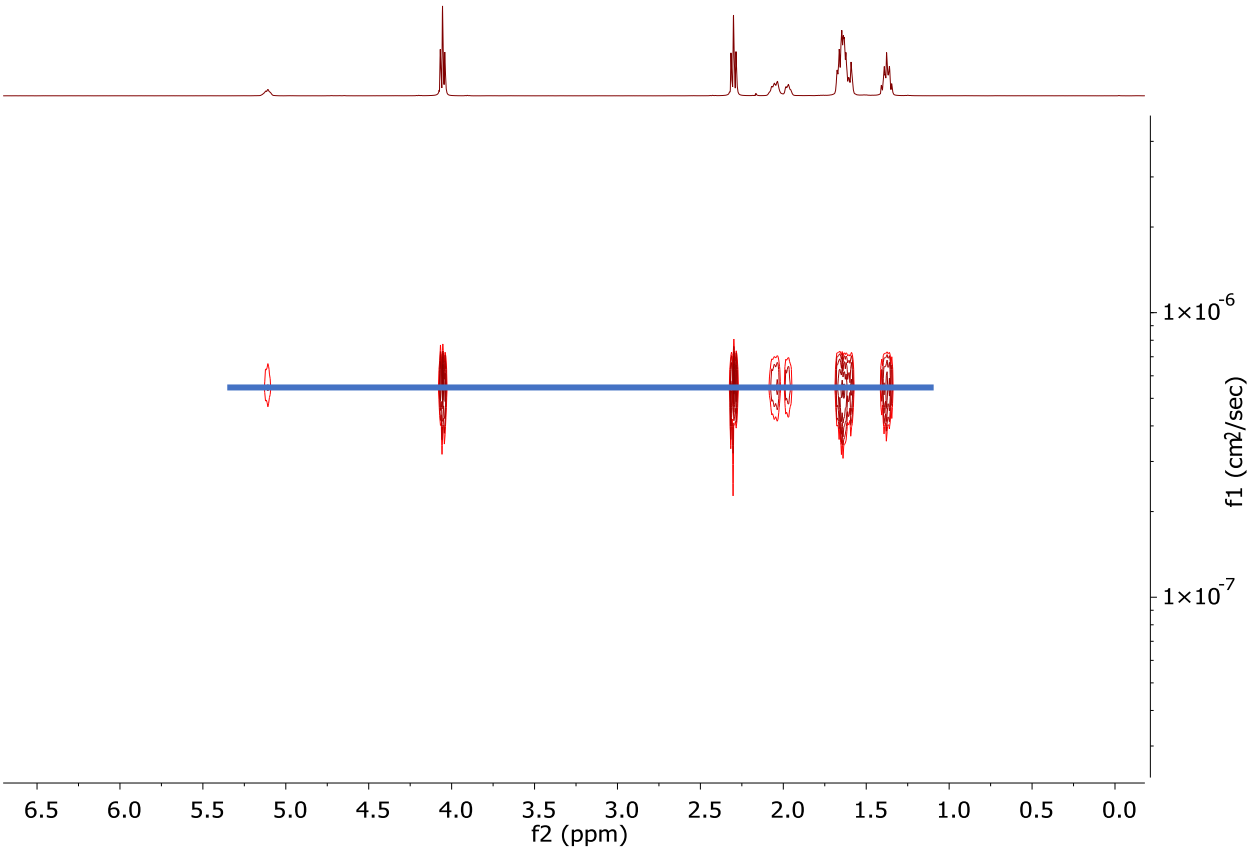

Fig. S96 DOSY NMR spectrum of PIP-*b*-PCL 300:800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 2**, entry 3c in $CDCl_3$ at 298 K.

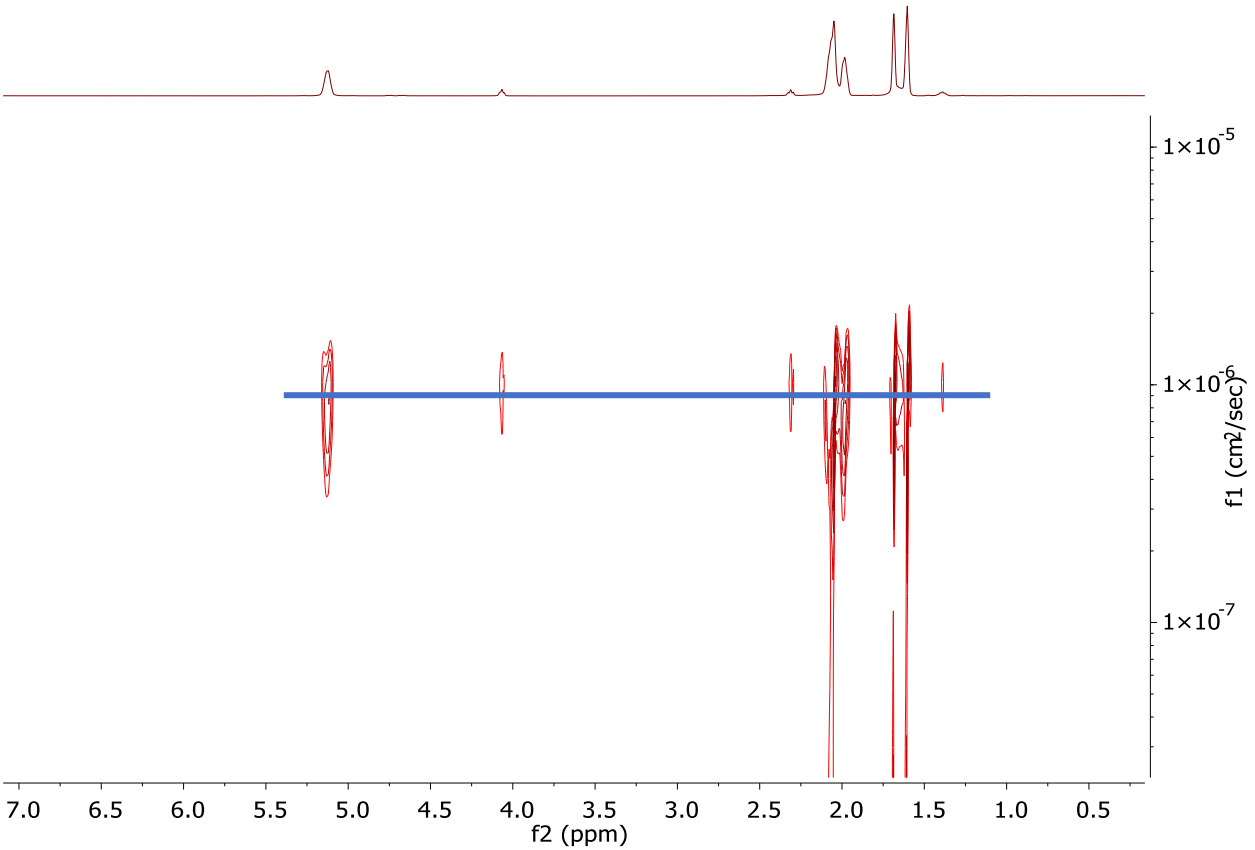

Fig. S97 DOSY NMR spectrum of PIP-*b*-PCL 800:300 equivalents generated by **6** and 0.5 equivalents of $[Ph_3C][B(C_6F_5)_4]$ from **Table 3**, entry 3a in $CDCl_3$ at 298 K.

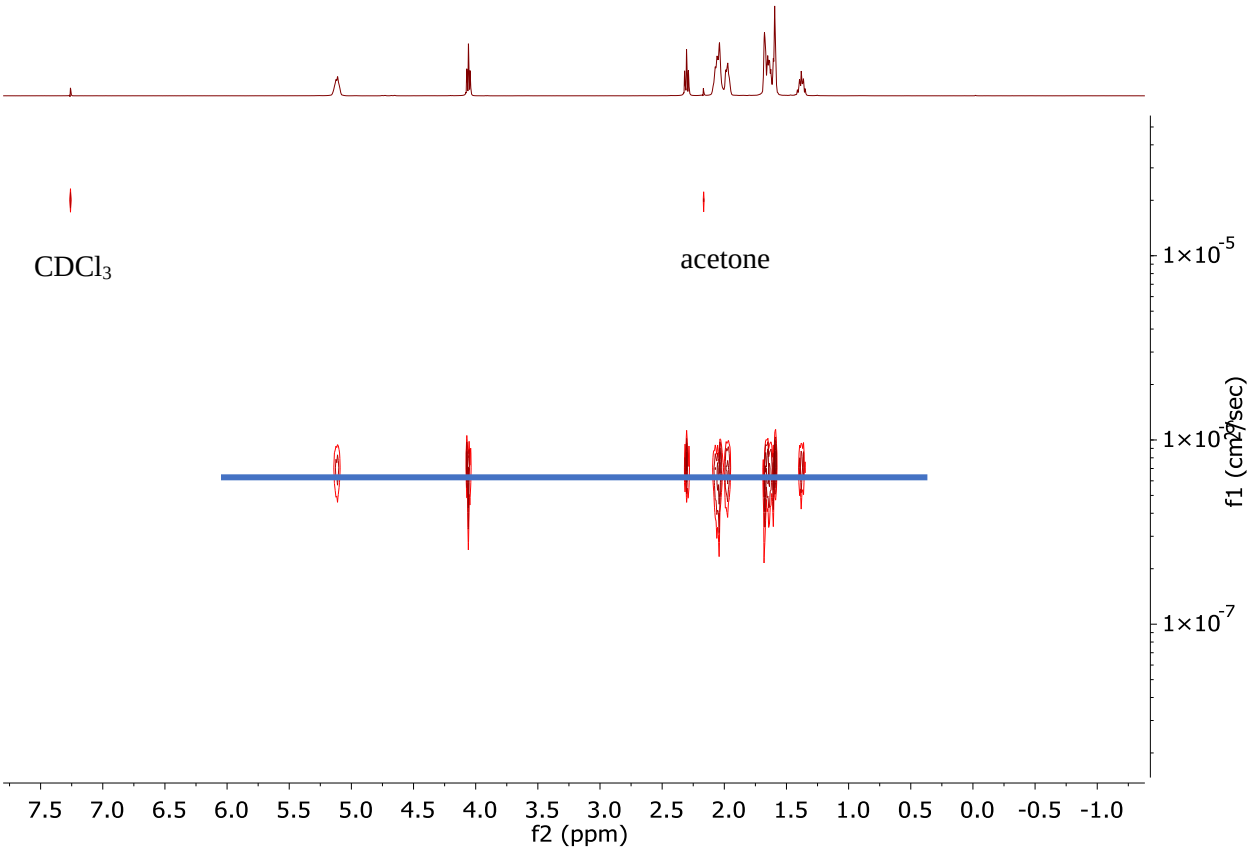

Fig. S98 DOSY NMR spectrum of PIP-*b*-PCL 800:300 equivalents generated by **6** and 0.5 equivalents of $[Ph_3C][B(C_6F_5)_4]$ from **Table 3**, entry 3b in $CDCl_3$ at 298 K.

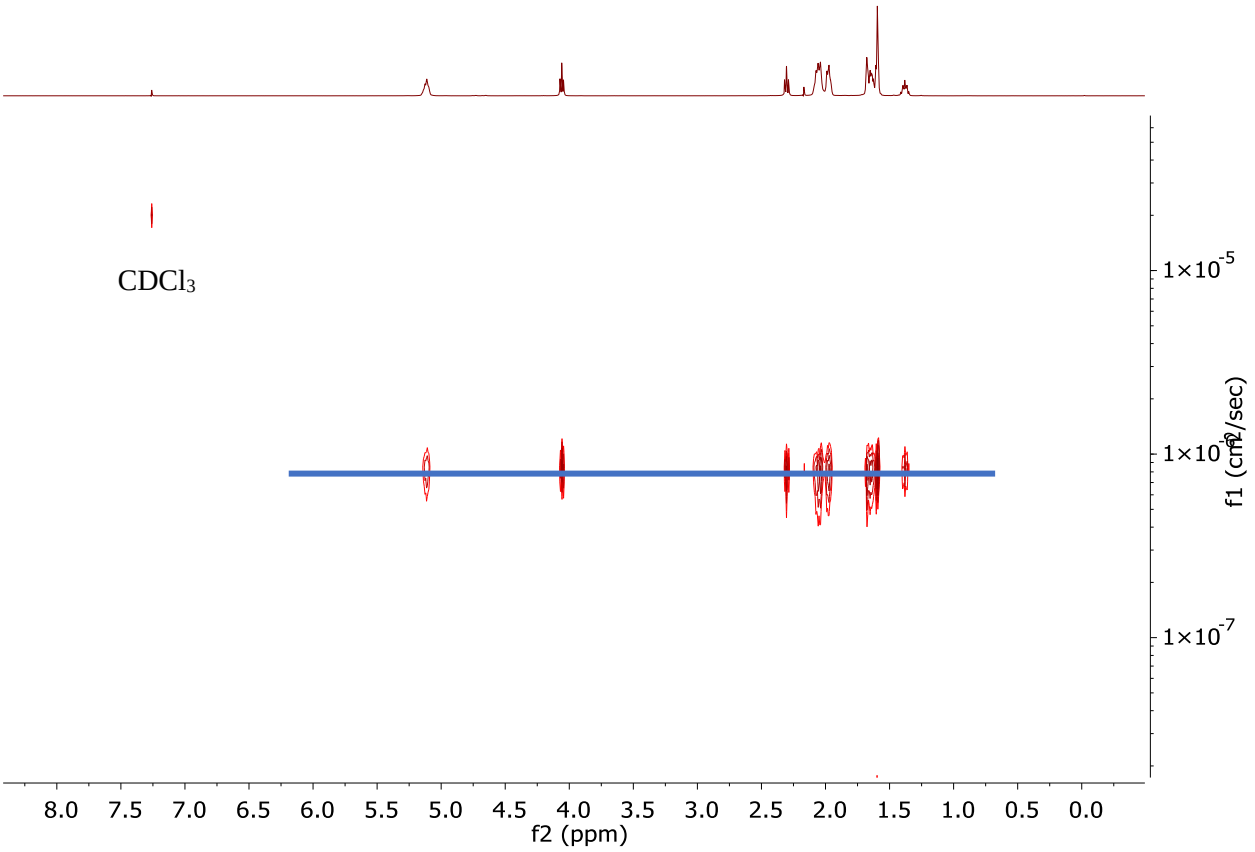

Fig. S99 DOSY NMR spectrum of PIP-*b*-PCL 800:300 equivalents generated by **6** and 0.5 equivalents of $[Ph_3C][B(C_6F_5)_4]$ from **Table 3**, entry 3c in $CDCl_3$ at 298 K.

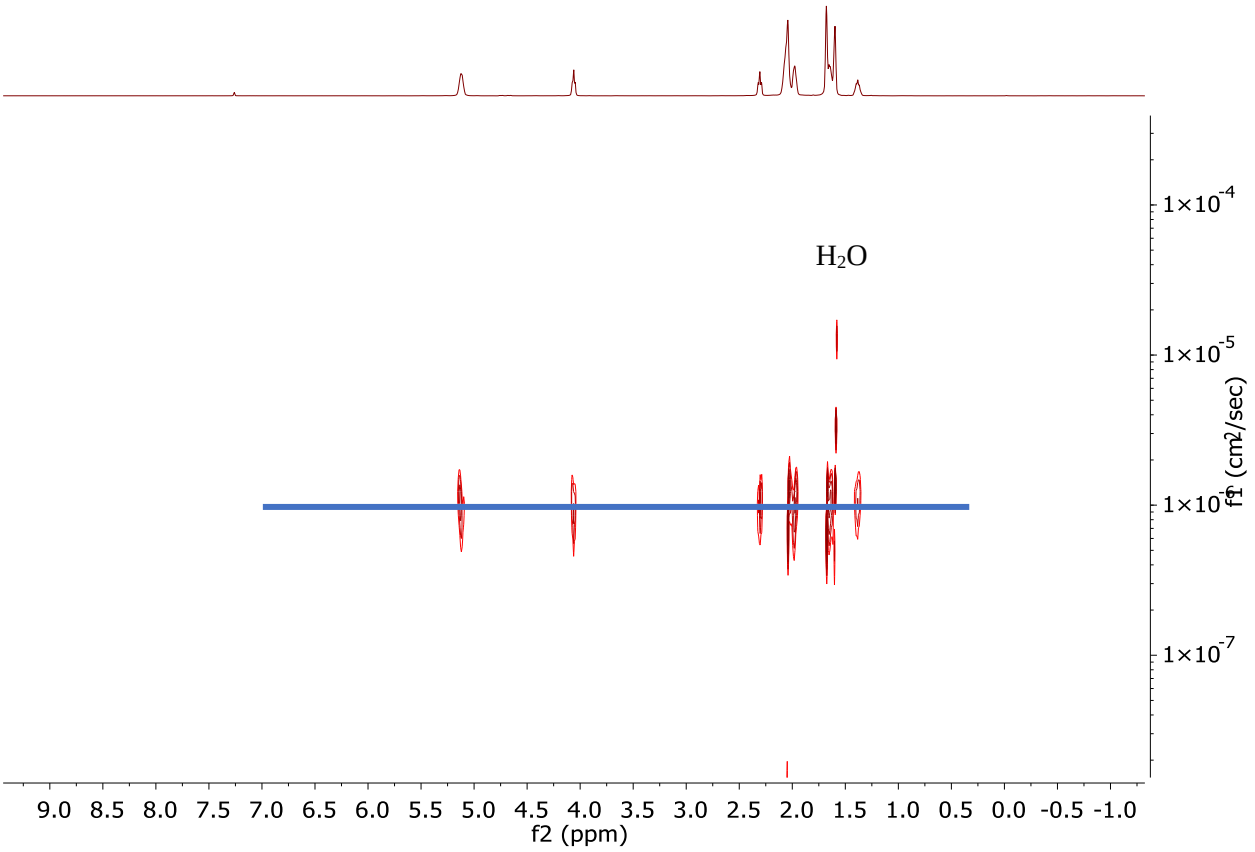

Fig. S100 DOSY NMR spectrum of PIP-*b*-PCL 800:300 equivalents generated by **6** and 1.5 equivalents of $[Ph_3C][B(C_6F_5)_4]$ from **Table 3**, entry 4a in $CDCl_3$ at 298 K.

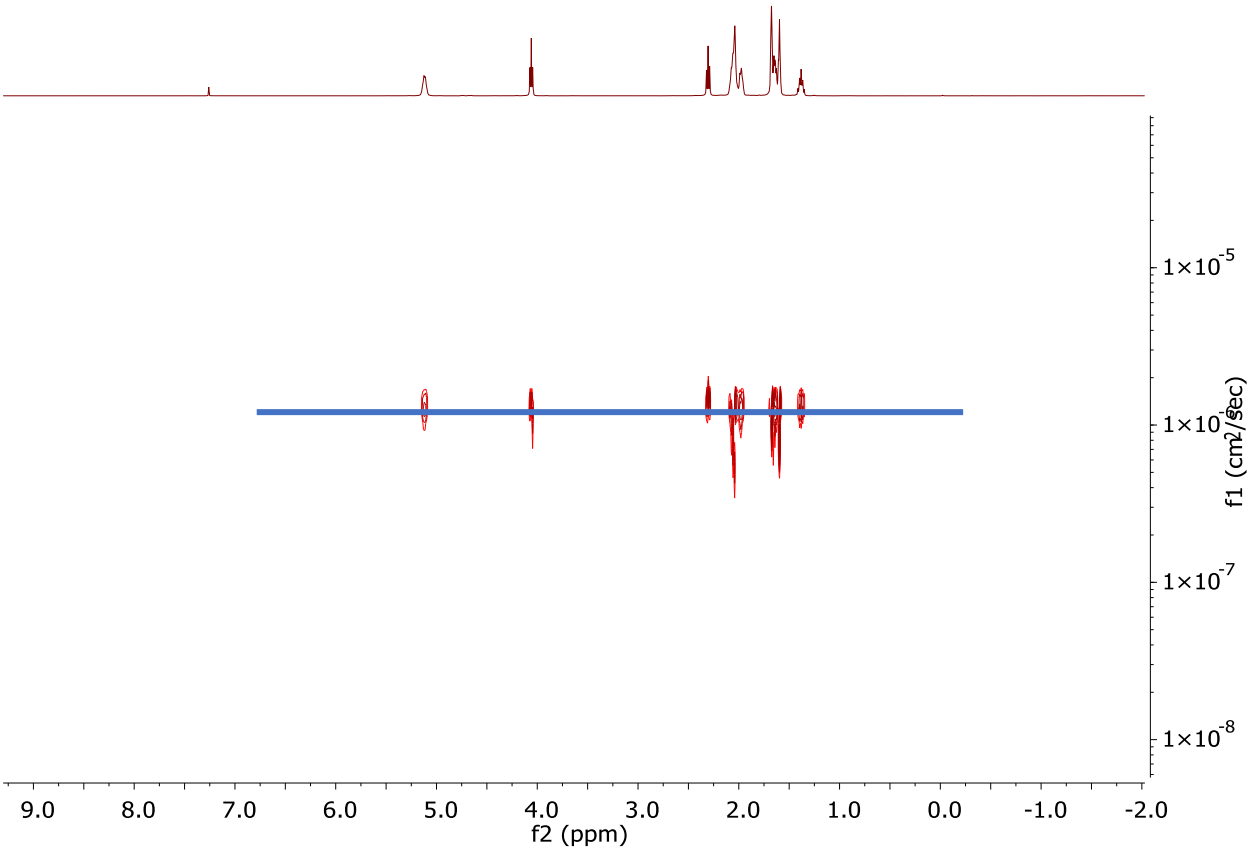

Fig. S101 DOSY NMR spectrum of PIP-*b*-PCL 800:300 equivalents generated by **6** and 1.5 equivalents of $[Ph_3C][B(C_6F_5)_4]$ from **Table 3**, entry 4b in $CDCl_3$ at 298 K.

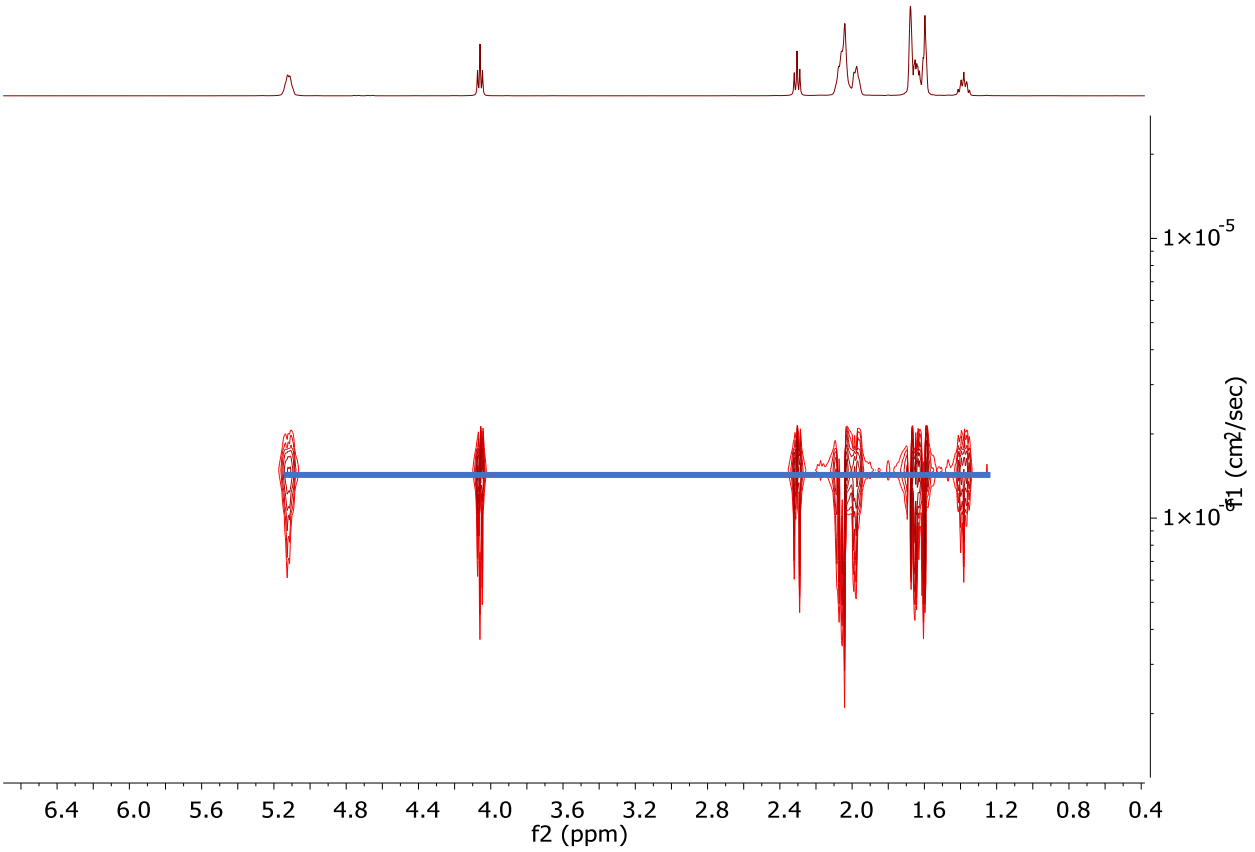

Fig. S102 DOSY NMR spectrum of PIP-*b*-PCL 800:300 equivalents generated by **6** and 1.5 equivalents of $[Ph_3C][B(C_6F_5)_4]$ from **Table 3**, entry 4c in $CDCl_3$ at 298 K.

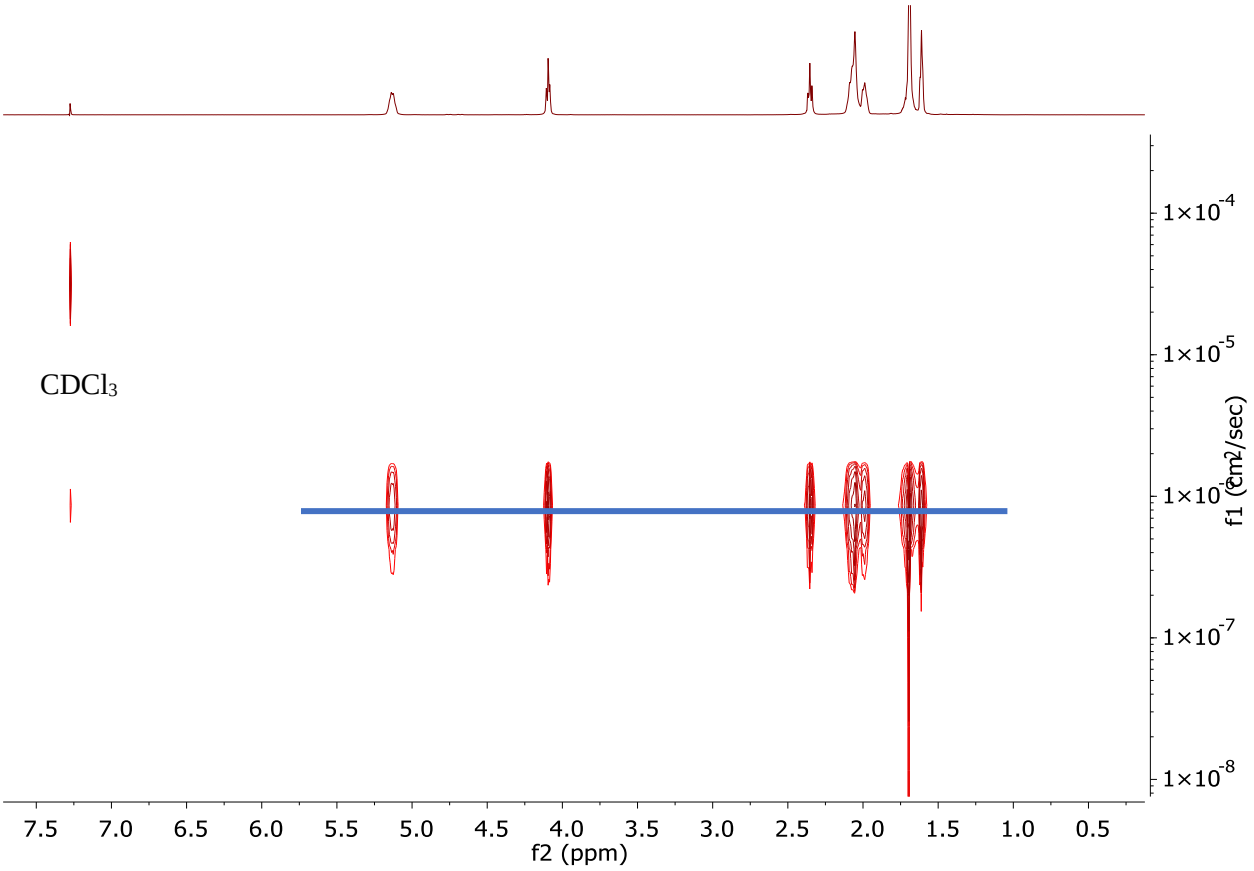

Fig. S103 DOSY NMR spectrum of PIP-*b*-PVL 800:300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 5**, entry 1 in $CDCl_3$ at 298 K.

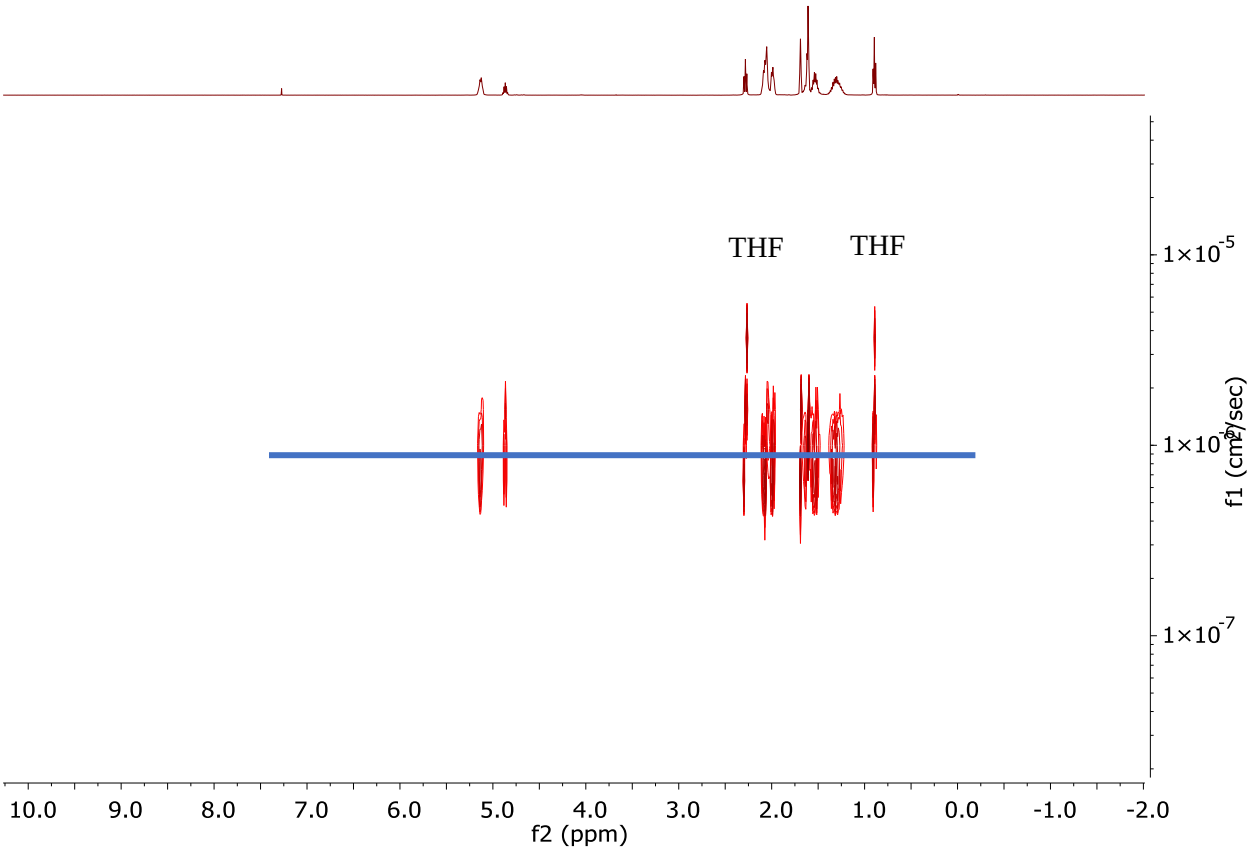

Fig. S104 DOSY NMR spectrum of PIP-*b*-PDL 800:300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 5**, entry 2 in $CDCl_3$ at 298 K.

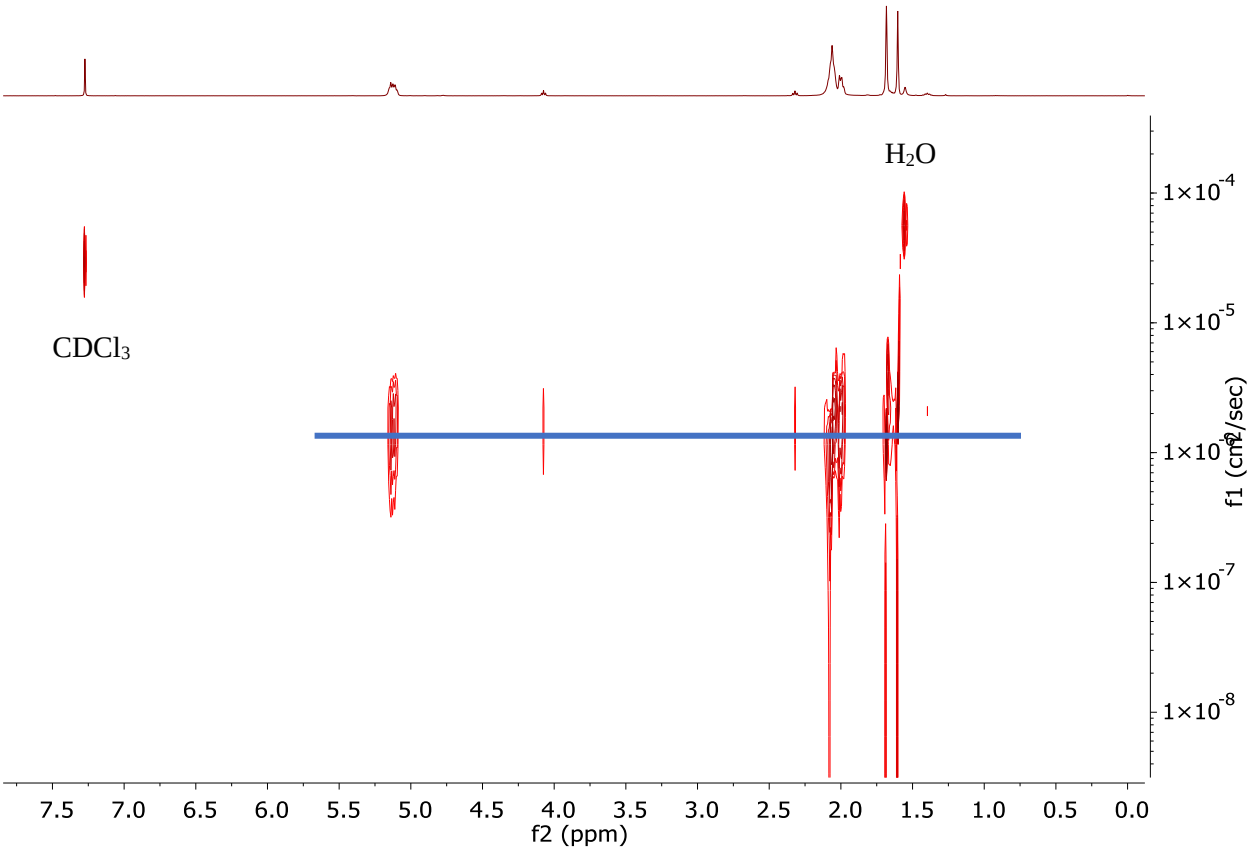

Fig. S105 DOSY NMR spectrum of PMyr-*b*-PCL 800:300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 5**, entry 3 in $CDCl_3$ at 298 K.

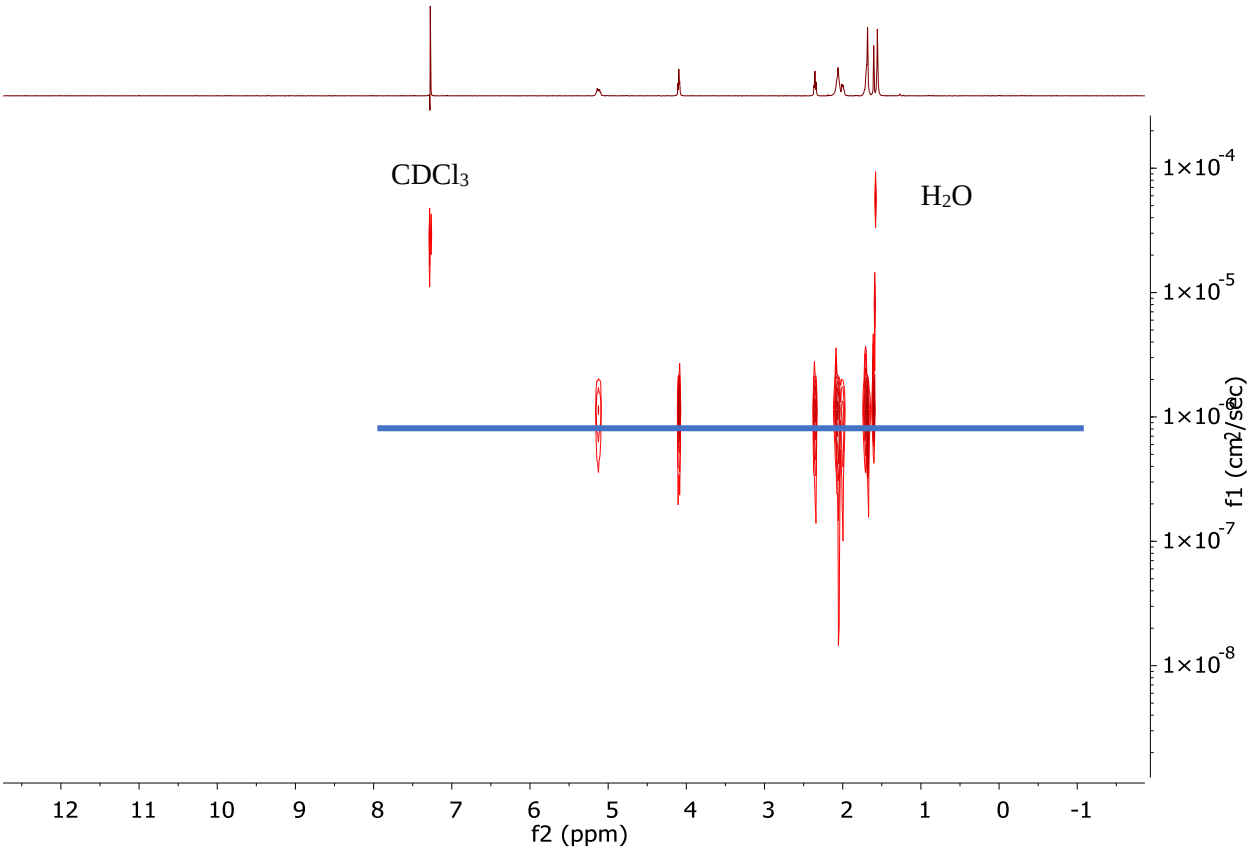

Fig. S106 DOSY NMR spectrum of PMyr-*b*-PVL 800:300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 5**, entry 3 in $CDCl_3$ at 298 K.

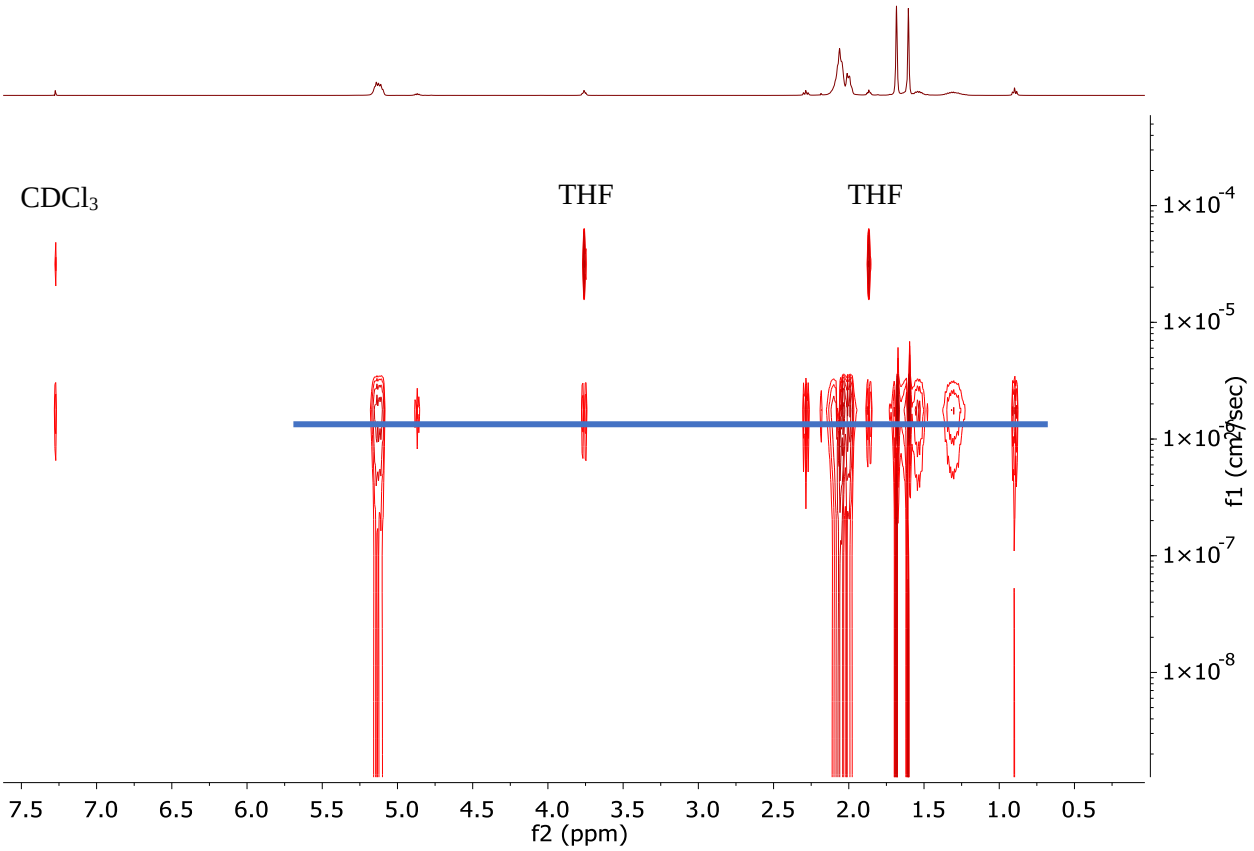

Fig. S107 DOSY NMR spectrum of PMyr-*b*-PDL 800:300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 5**, entry 5 in $CDCl_3$ at 298 K.

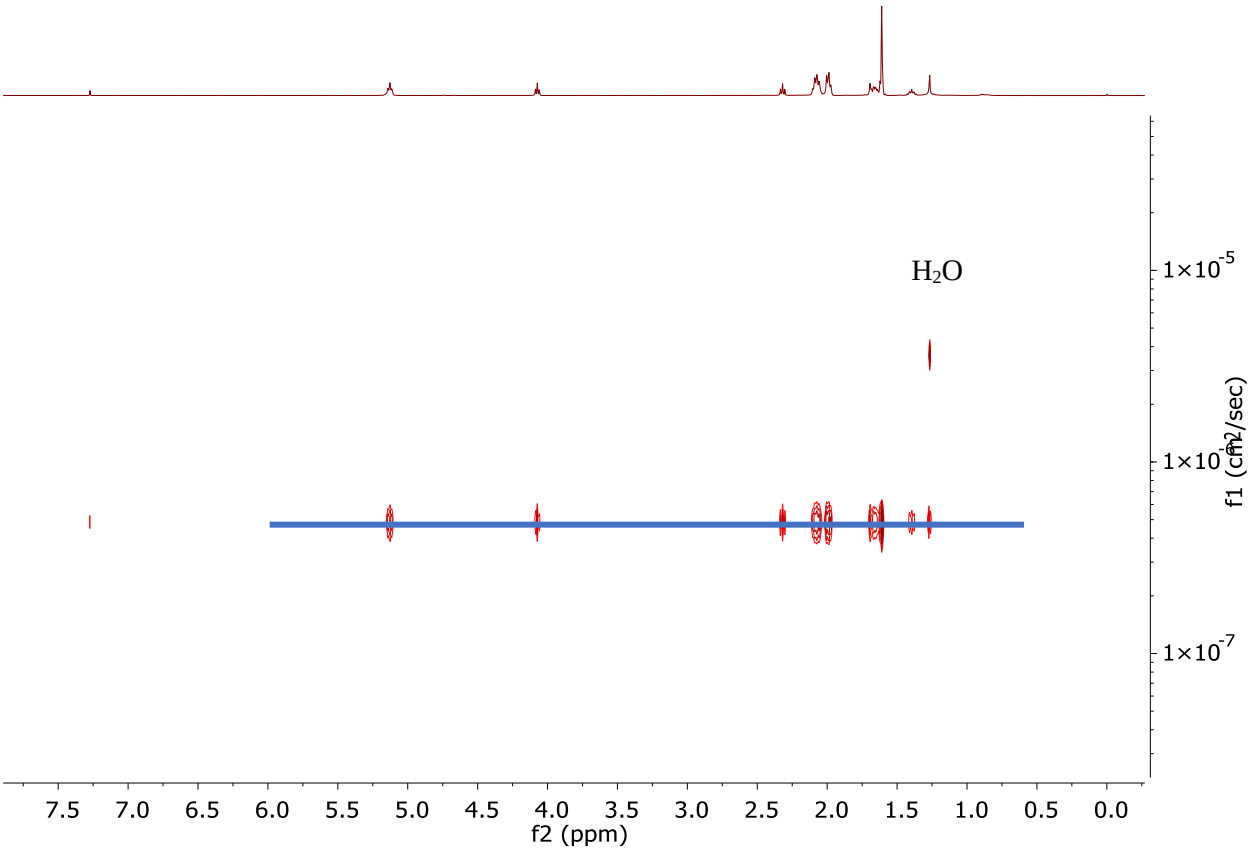

Fig. S108 DOSY NMR spectrum of PIP-*b*-PCL 50:50 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ of from **Table S3**, entry 2 in $CDCl_3$ at 298 K.

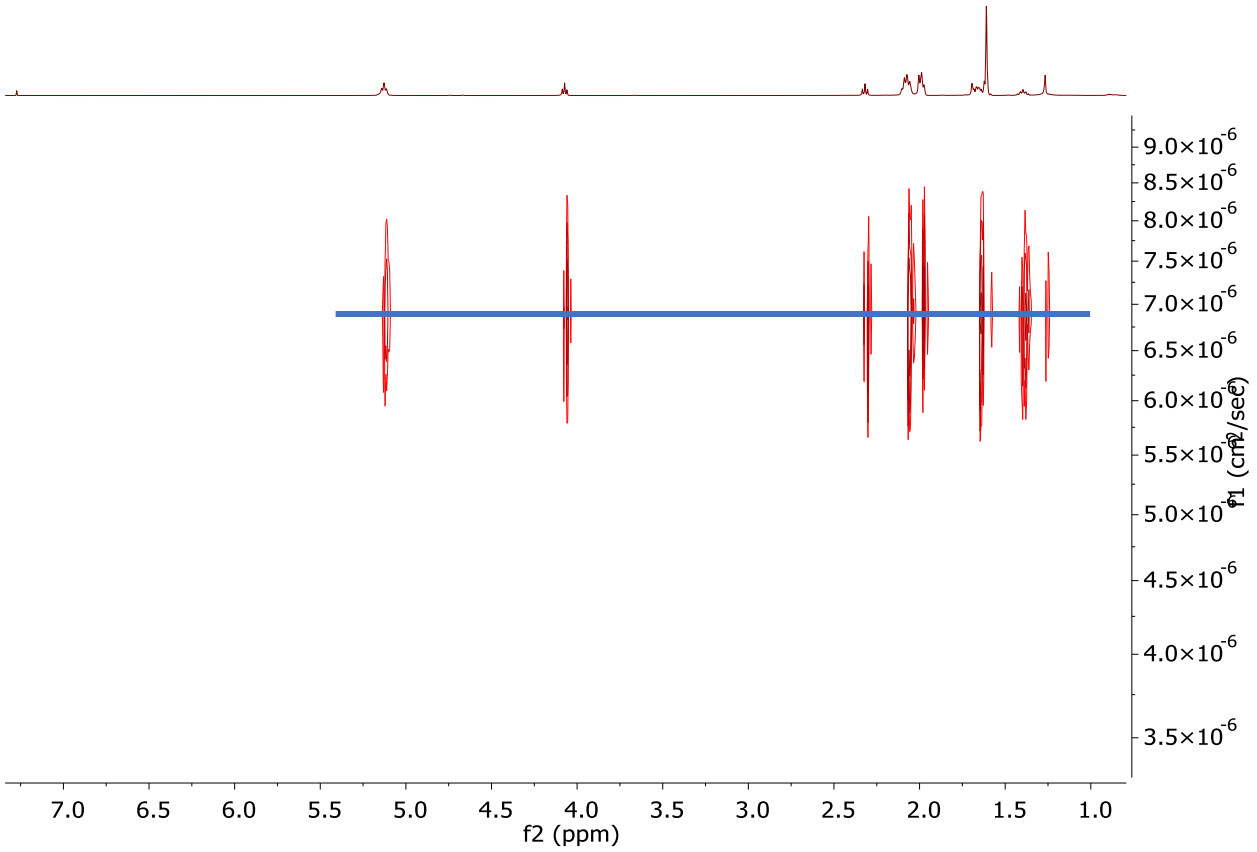

Fig. S109 DOSY NMR spectrum of repolymerized PIP-*b*-PCL 50:50 equivalents generated by **Y[N(SiMe$_3$)$_2$]$_3$** from **Table S3**, entry 4 in $CDCl_3$ at 298 K.

4.0 Fourier-Transform Infrared Spectroscopy (FT-IR) Characterization of Isolated Polymers.

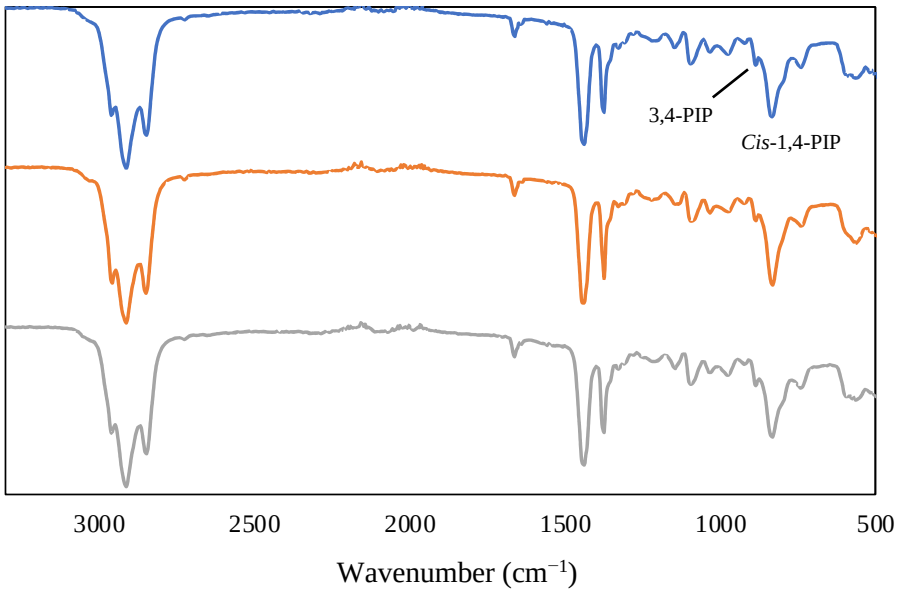

Fig. S110 FT-IR spectrum of PIP 800 equivalents generated by **6**/[Ph_3C][$B(C_6F_5)_4$] from **Table 1**, entry 1 (12 h). Representative 3,4 PIP and *cis*-1,4 PIP peaks shown.

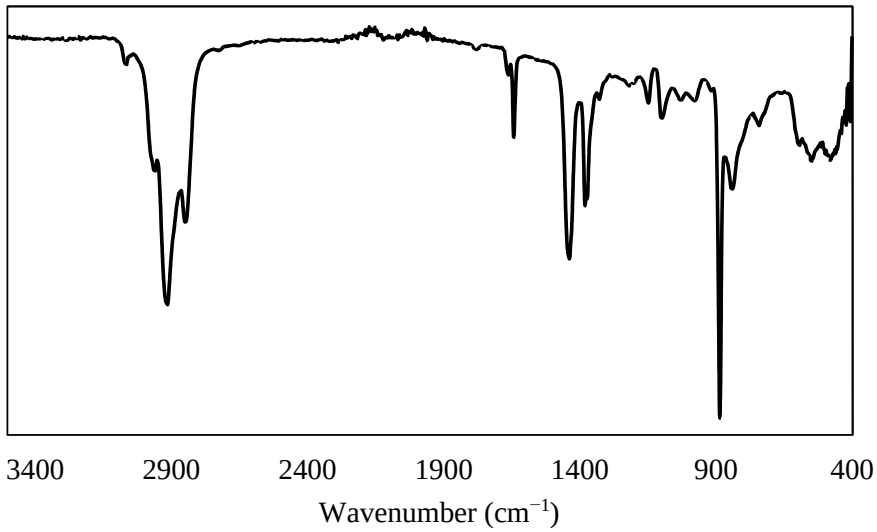

Fig. S111 FT-IR spectrum of PIP 800 equivalents generated by **8**/[Ph_3C][$B(C_6F_5)_4$] from **Table 1**, entry 3 (12 h).

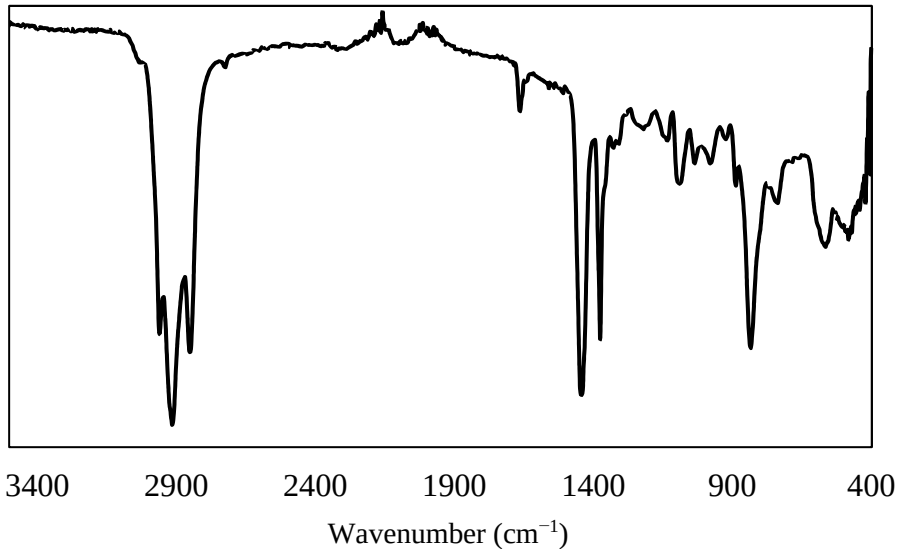

Fig. S112 FT-IR spectrum of PIP 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 1**, entry 4 (24 h).

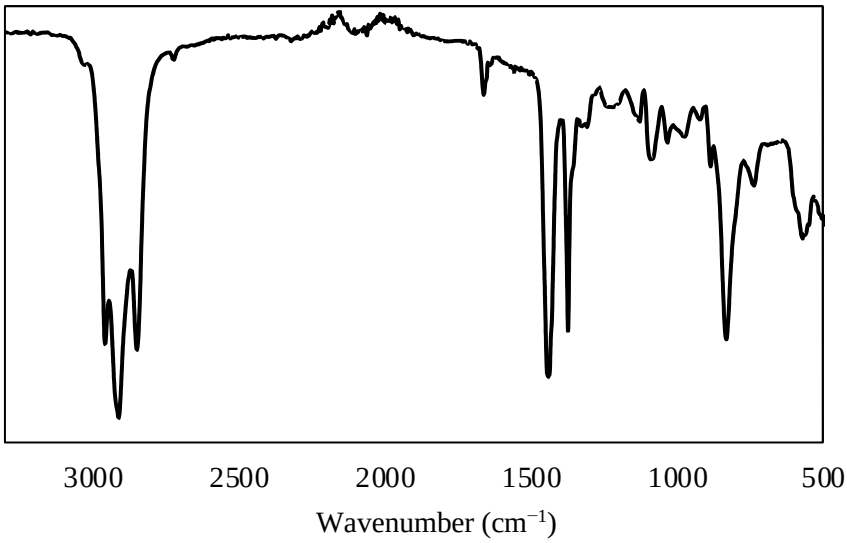

Fig. S113 FT-IR spectrum of PIP 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 1**, entry 5 (30 min).

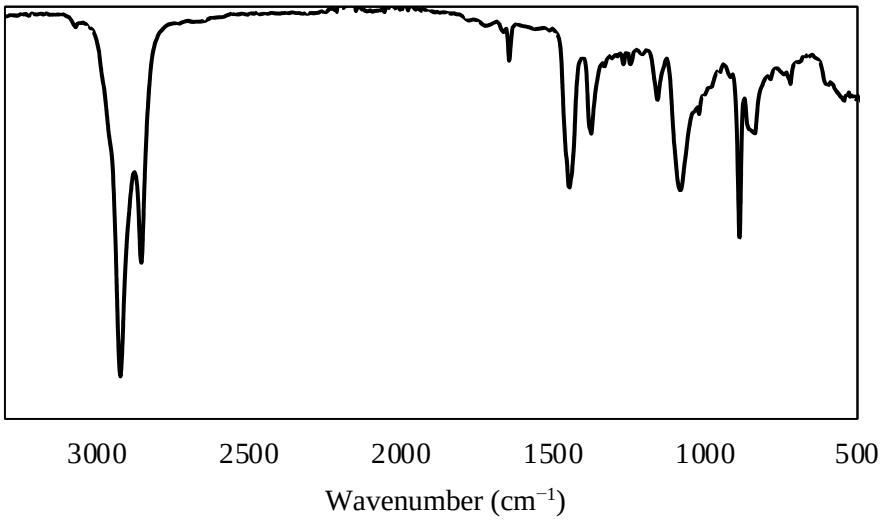

Fig. S114 FT-IR spectrum of PIP generated by **8**/[Ph_3C][$B(C_6F_5)_4$] from **Table 1**, entry 6 (30 min).

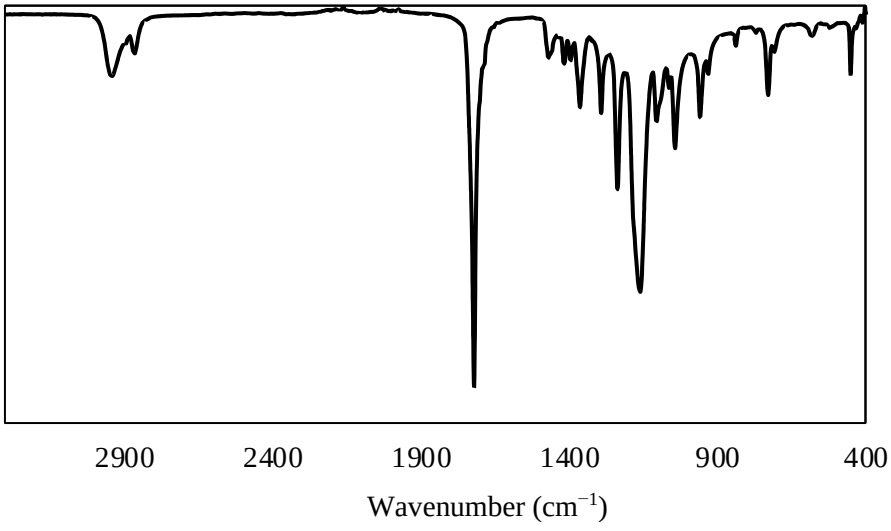

Fig. S115 FT-IR spectrum of PCL generated by **6**/[Ph_3C][$B(C_6F_5)_4$] from **Table 1**, entry 7 (10 min).

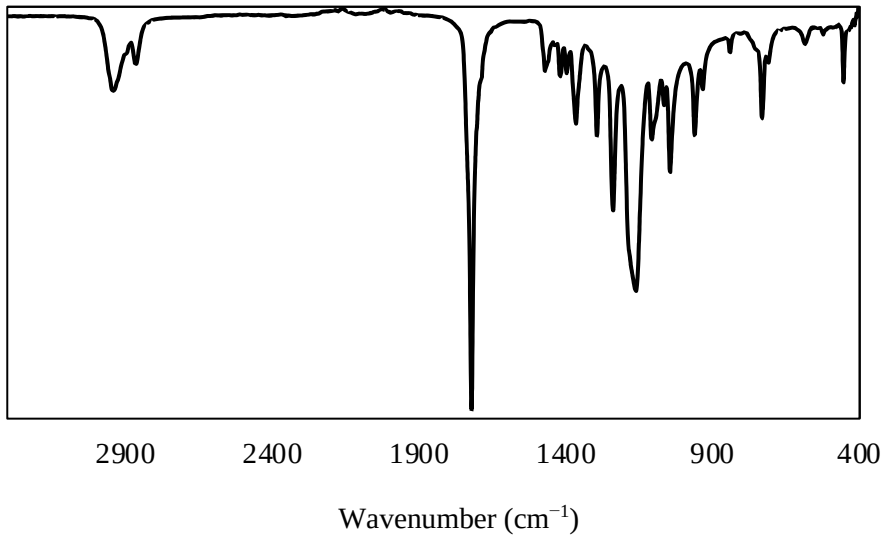

Fig. S116 FT-IR spectrum of PCL 300 equivalents generated by **8**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 1**, entry 8 (10 min).

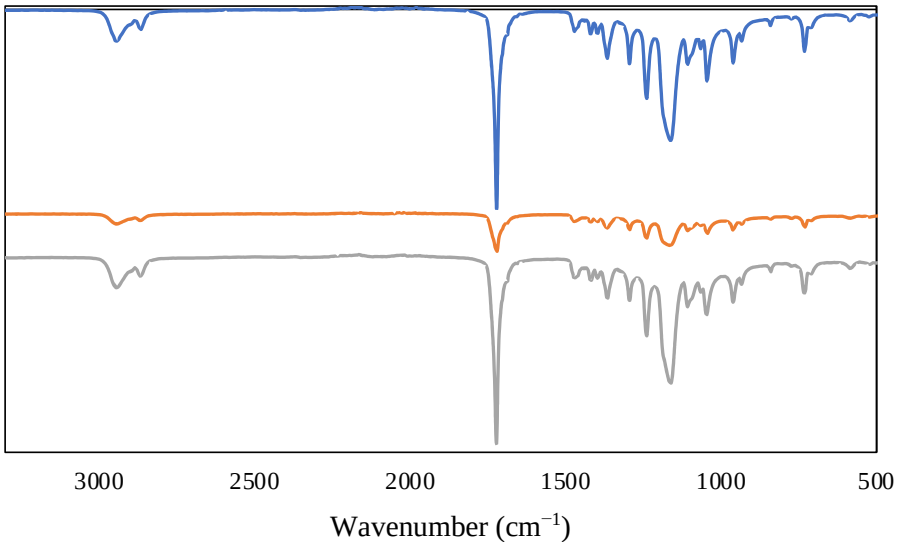

Fig. S117 FT-IR spectrum of PCL 300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 1**, entry 9 (2 h).

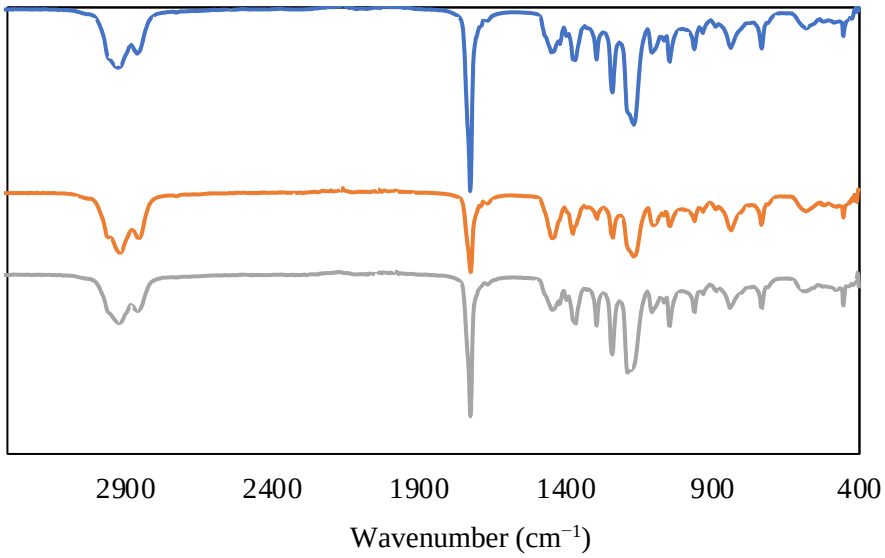

Fig. S118 FT-IR spectrum of PIP-*b*-PCL 800:300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 2**, entry 1.

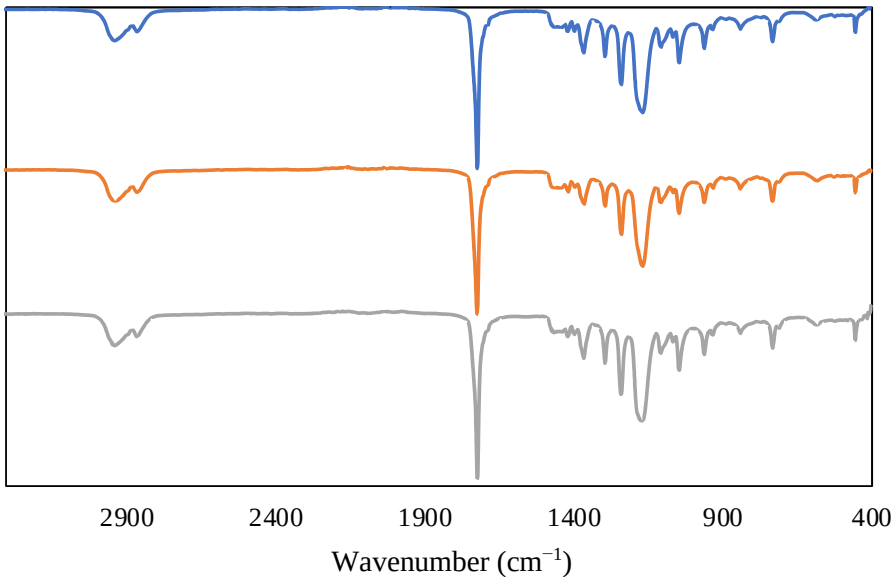

Fig. S119 FT-IR spectrum of PIP-*b*-PCL 550:550 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 2**, entry 2.

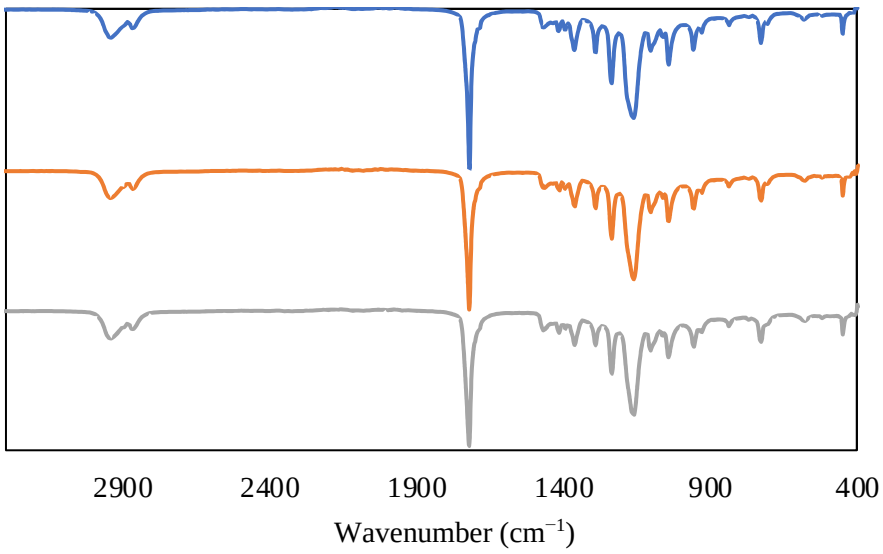

Fig. S120 FT-IR spectrum of PIP-*b*-PCL 300:800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 2**, entry 3.

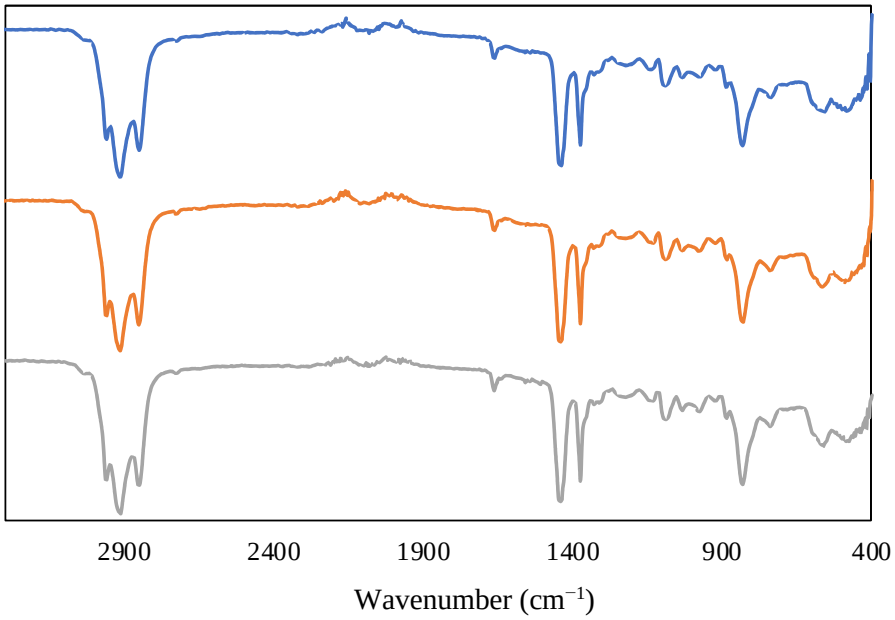

Fig. S121 FT-IR spectrum of PIP 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 3**, entry 1 (IP addition time 0 min).

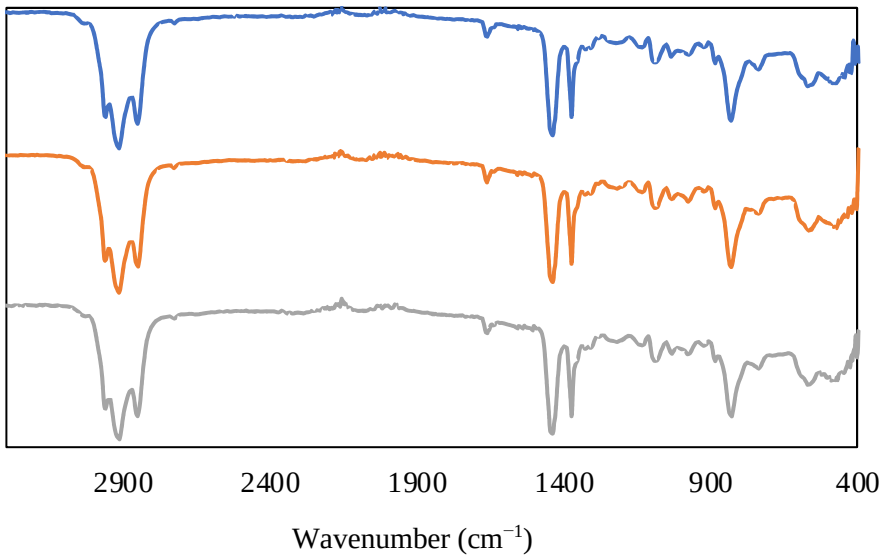

Fig. S122 FT-IR spectrum of PIP 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 3**, entry 2 (IP addition time 30 min).

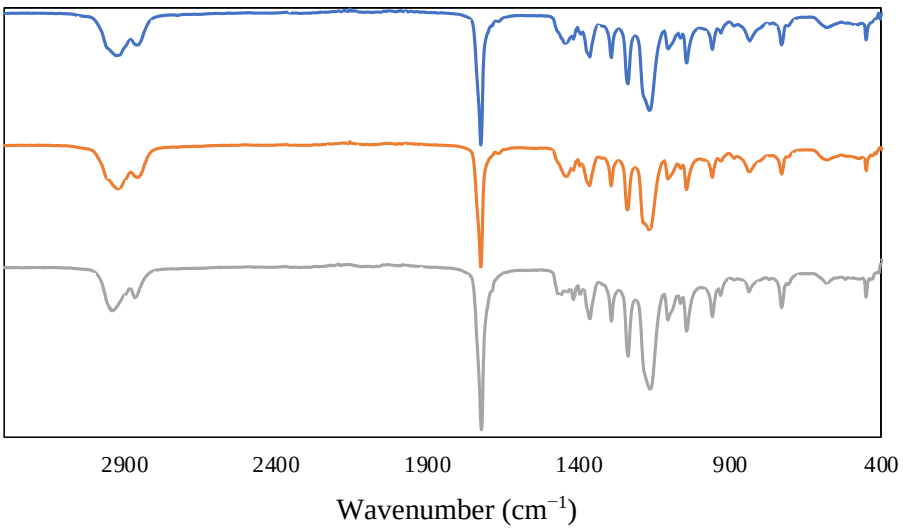

Fig. S123 FT-IR spectrum of PIP-*b*-PCL 800:300 equivalents generated by **6** and 0.5 equivalents of $[Ph_3C][B(C_6F_5)_4]$ from **Table 3**, entry 3.

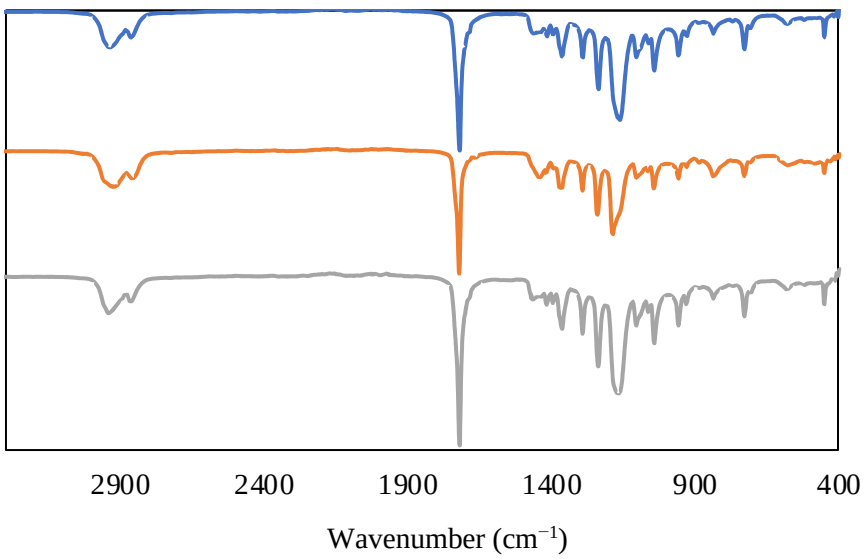

Fig. S124 FT-IR spectrum of PIP-*b*-PCL 800:300 equivalents generated by **6** and 1.5 equivalents of $[Ph_3C][B(C_6F_5)_4]$ from **Table 3**, entry 4.

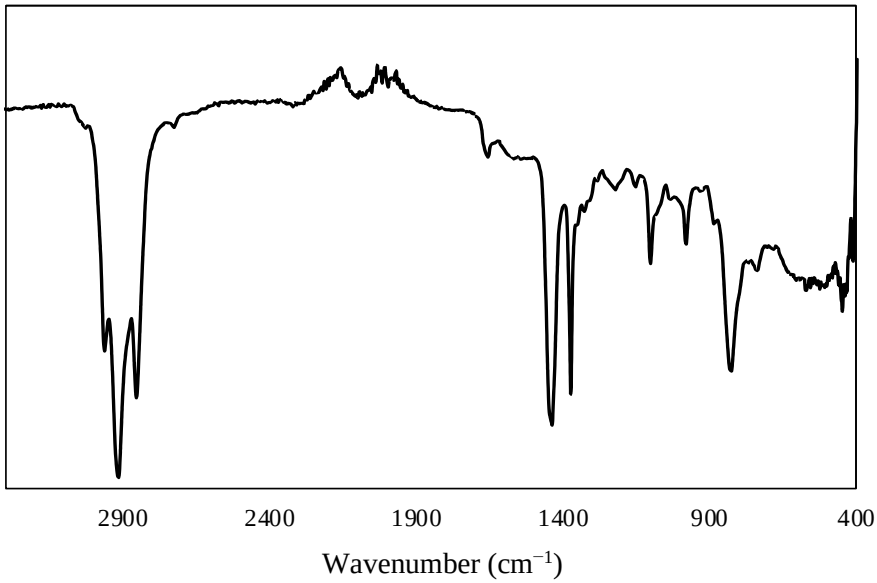

Fig. S125 FT-IR spectrum of PMyr 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 4**, entry 1 (30 min).

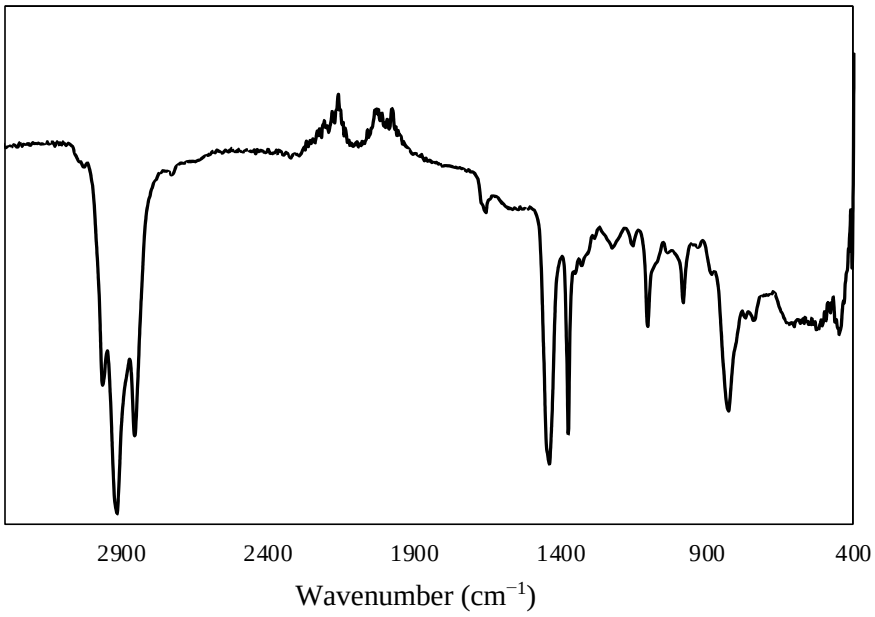

Fig. S126 FT-IR spectrum of PMyr 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 4**, entry 2 (90 min).

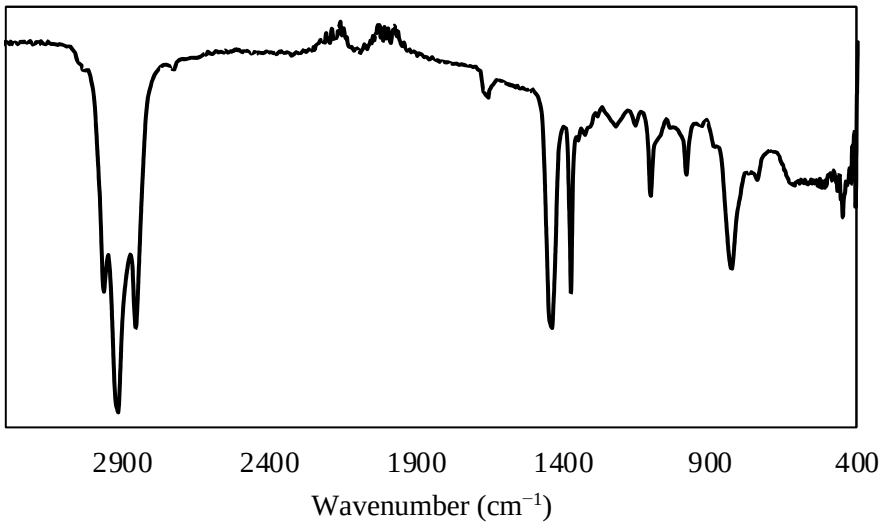

Fig. S127 FT-IR spectrum of PMyr 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 4**, entry 3 (3 h).

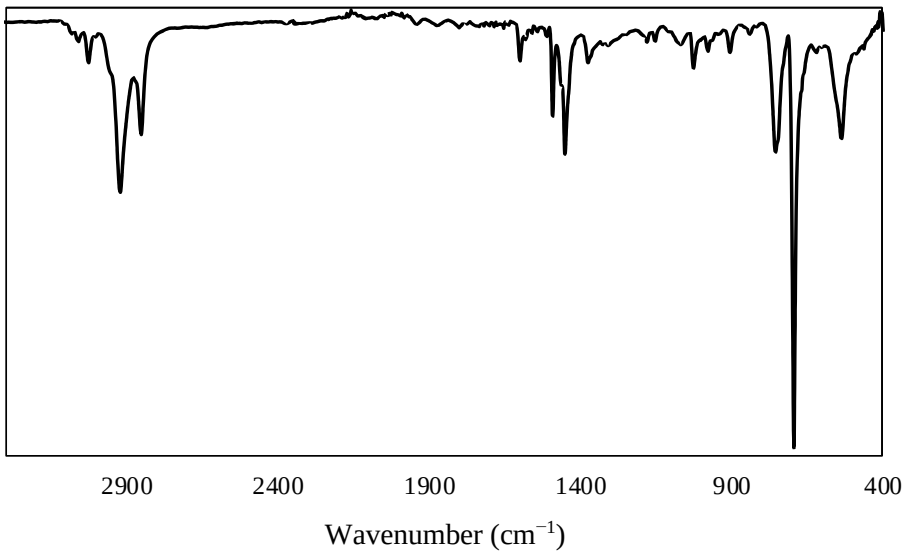

Fig. S128 FT-IR spectrum of PS 800 equivalents generated by **6**/[Ph_3C][$B(C_6F_5)_4$] from **Table 4**, entry 4 (30 min).

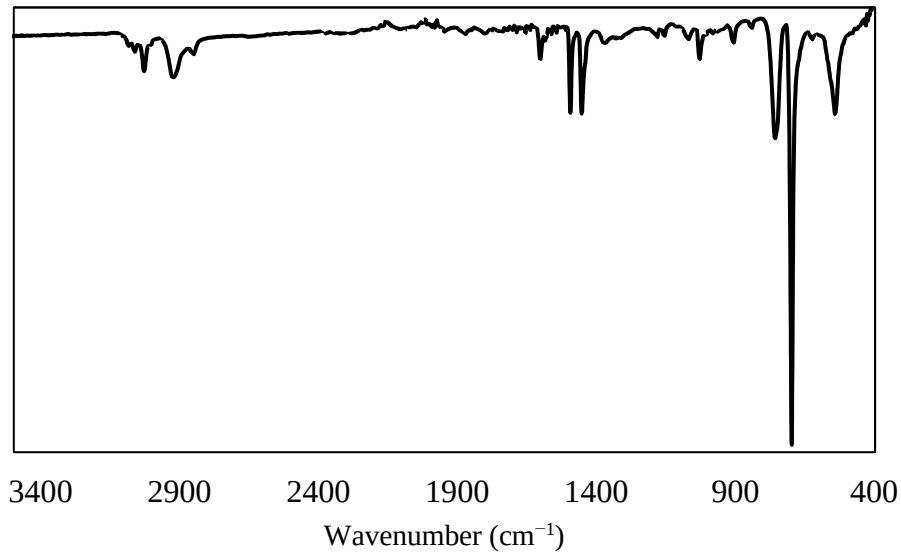

Fig. S129 FT-IR spectrum of PS 800 equivalents generated by **6**/[Ph_3C][$B(C_6F_5)_4$] from **Table 4**, entry 5 (20 h).

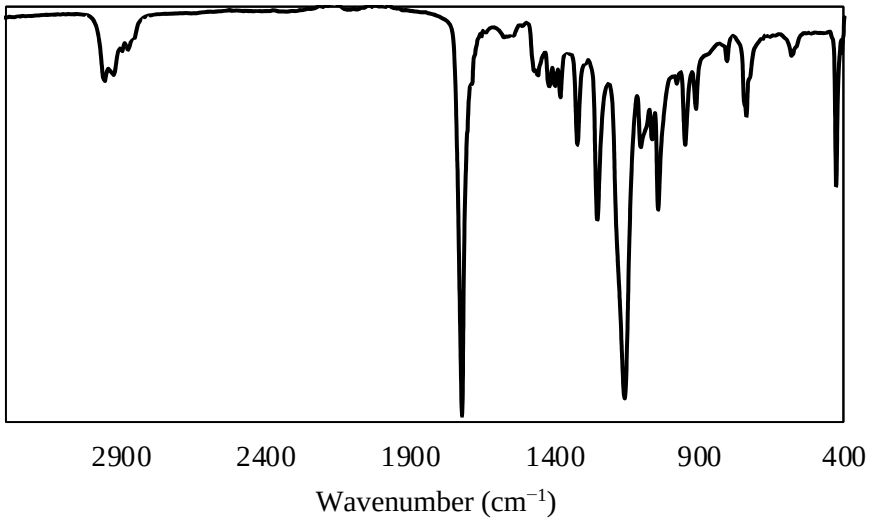

Fig. S130 FT-IR spectrum of PVL 300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 4**, entry 6 (10 min).

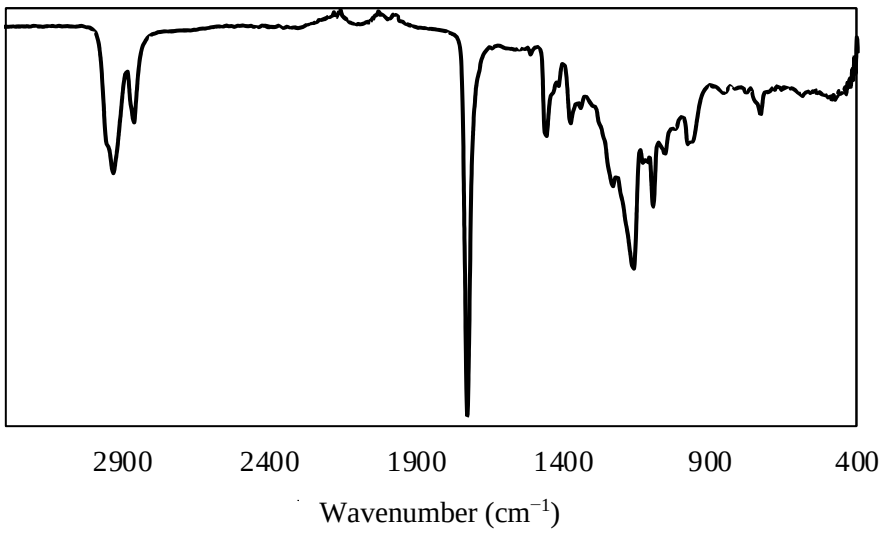

Fig. S131 FT-IR spectrum of PDL 300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 4**, entry 7 (6 h).

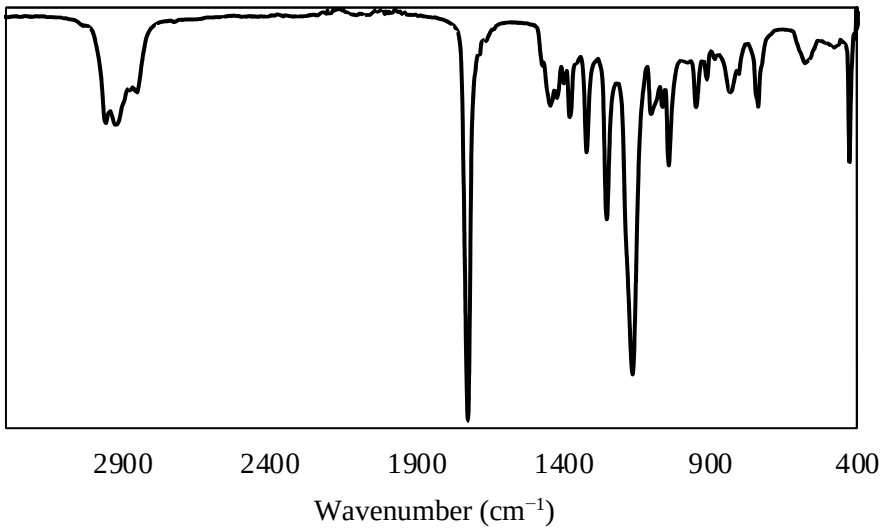

Fig. S132 FT-IR spectrum of PIP-*b*-PVL 800:300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 5**, entry 1.

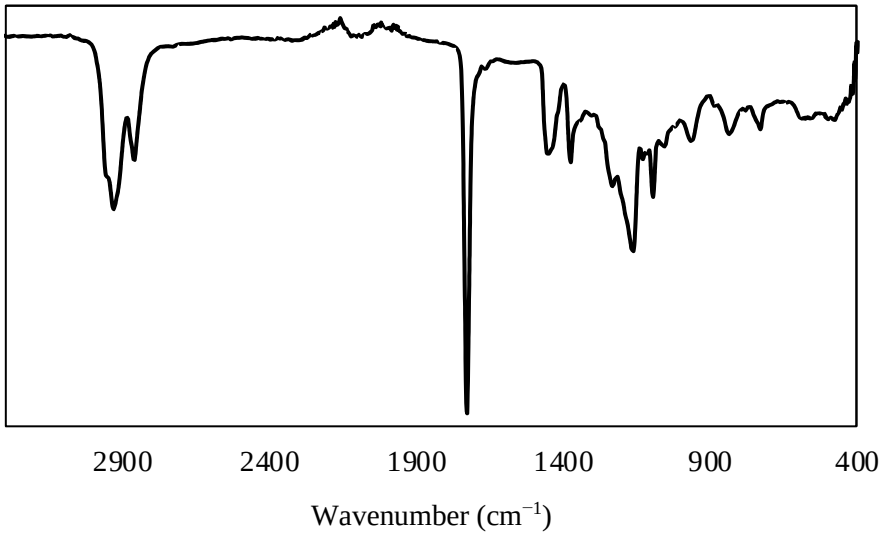

Fig. S133 FT-IR spectrum of PIP-*b*-PDL 800:300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 5**, entry 2.

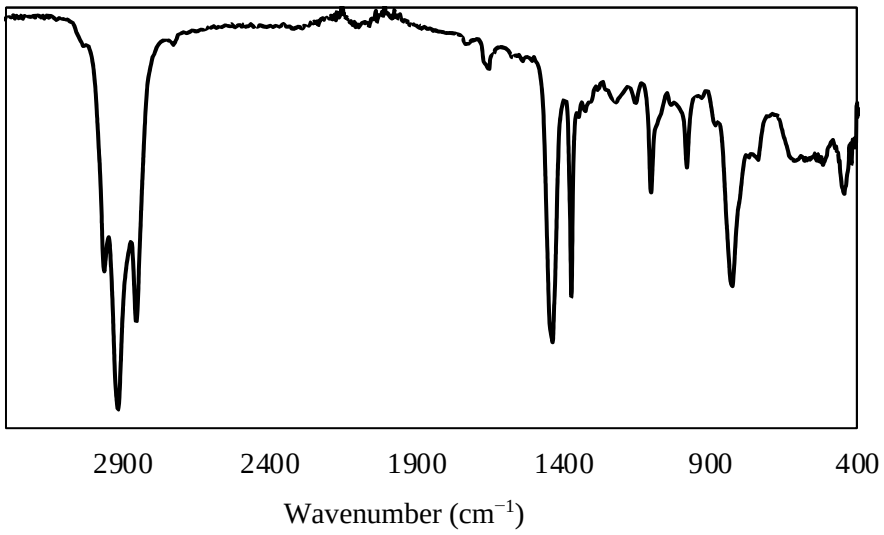

Fig. S134 FT-IR spectrum of PMyr-*b*-PCL 800:300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 5**, entry 3.

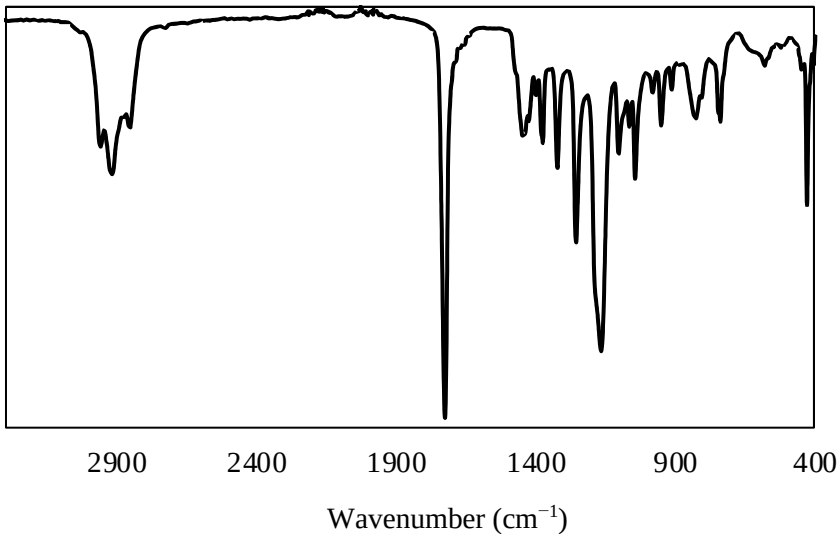

Fig. S135 FT-IR spectrum of PMyr-*b*-PVL 800:300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 5**, entry 4.

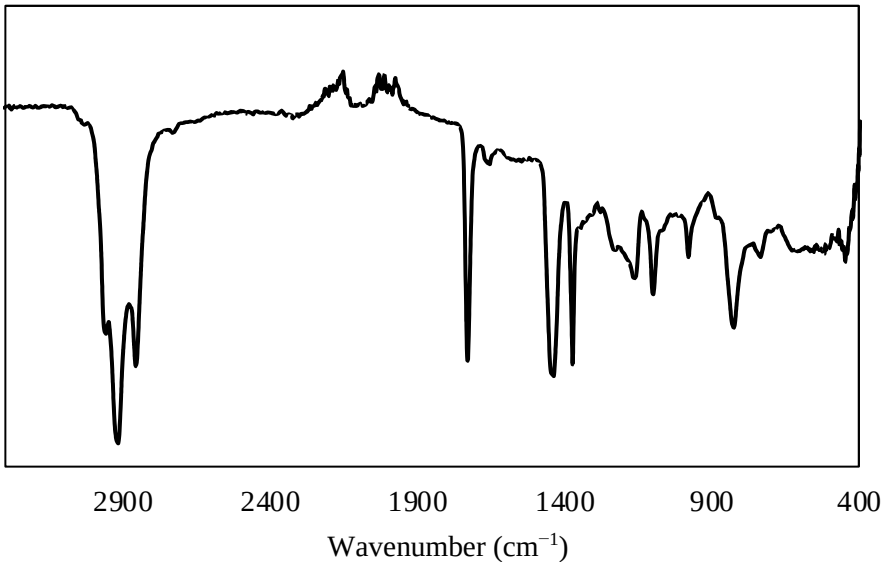

Fig. S136 FT-IR spectrum of PMyr-*b*-PDL 800:300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 5**, entry 5.

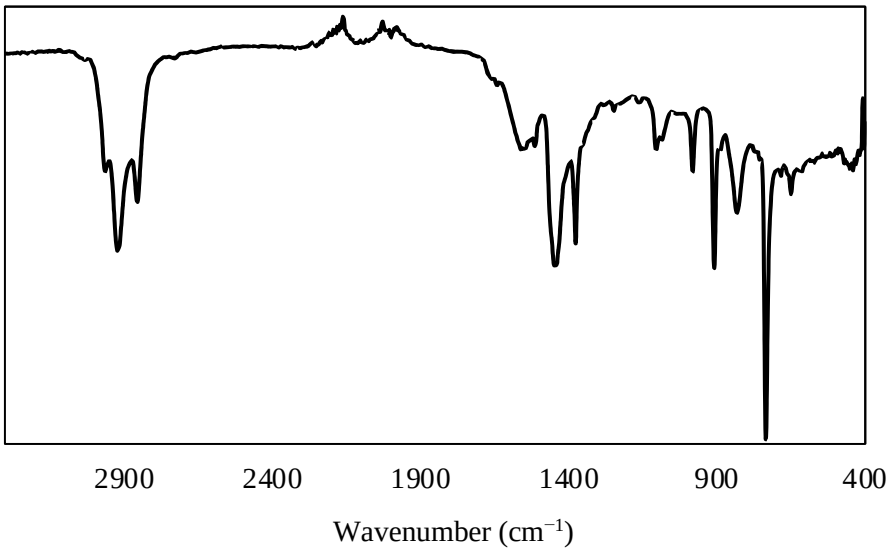

Fig. S137 FT-IR spectrum of PMyr 800 equivalents generated by **8**/$[Ph_3C][B(C_6F_5)_4]$ from **Table S1**, entry 1 (30 min).

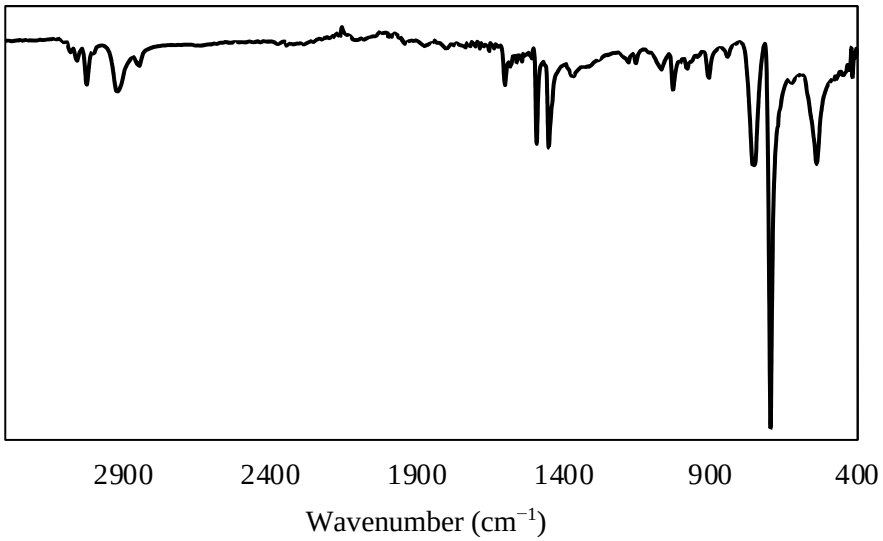

Fig. S138 FT-IR spectrum of PS 800 equivalents generated by **8**/$[Ph_3C][B(C_6F_5)_4]$ from **Table S1**, entry 2 (30 min).

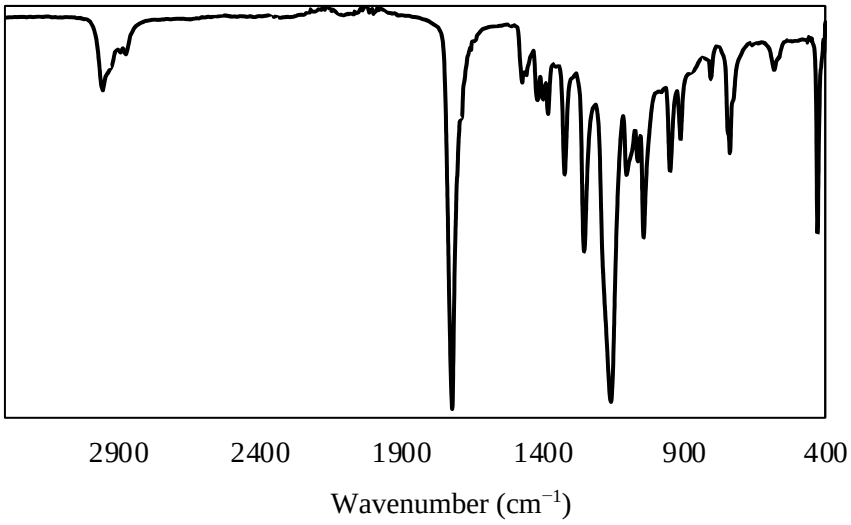

Fig. S139 FT-IR spectrum of PVL 300 equivalents generated by **8**/$[Ph_3C][B(C_6F_5)_4]$ from **Table S1**, entry 3 (10 min).

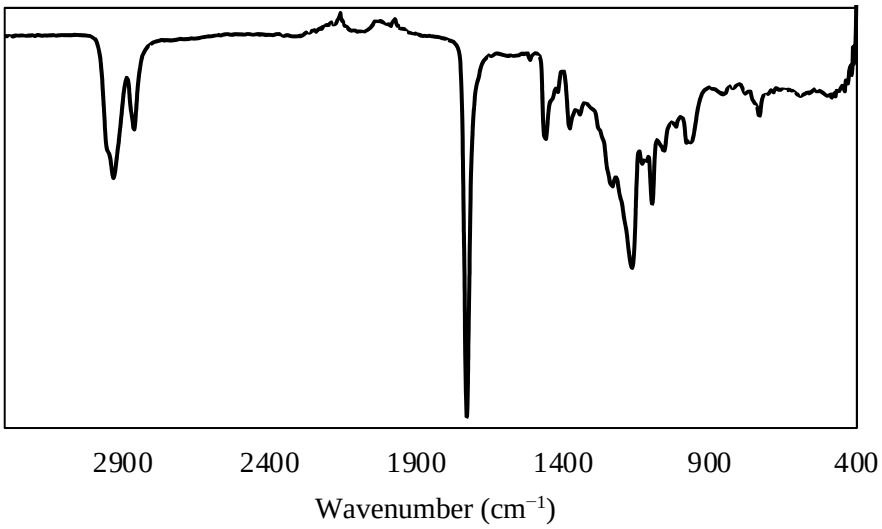

Fig. S140 FT-IR spectrum of PDL 300 equivalents generated by **8**/$[Ph_3C][B(C_6F_5)_4]$ from **Table S1**, entry 4 (6 h).

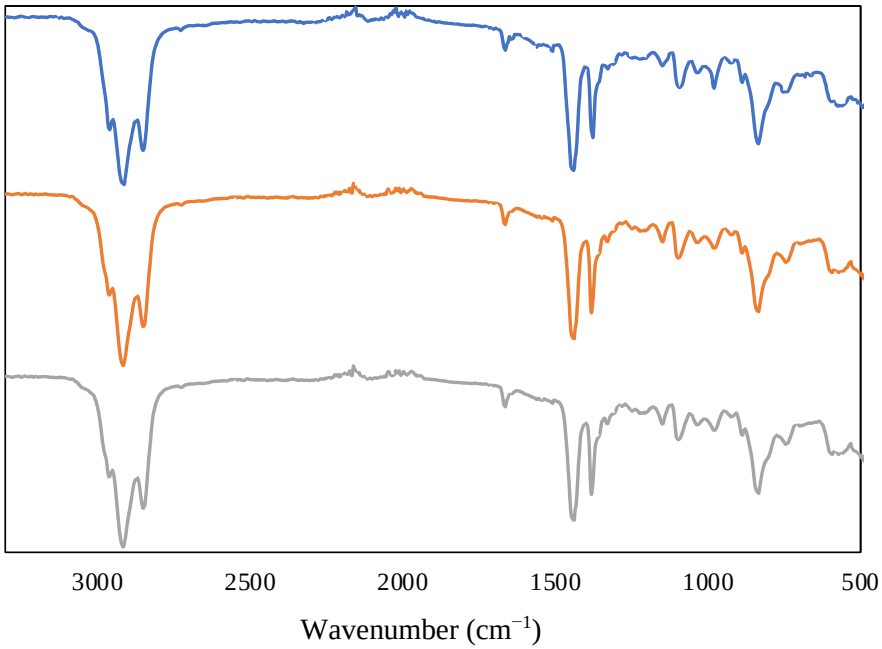

Fig. S141 FT-IR spectrum of PIP 300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table S2**, entry 1 (12 h).

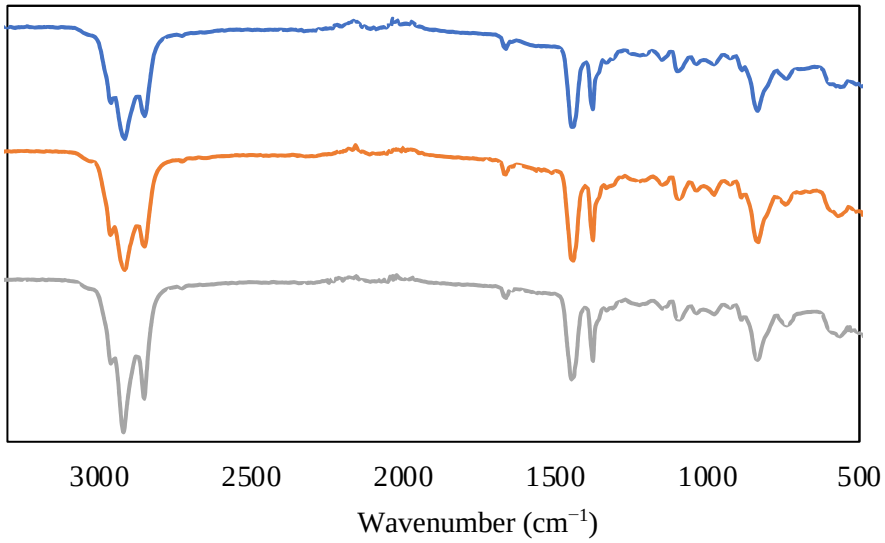

Fig. S142 FT-IR spectrum of PIP 550 equivalents generated by **6**/[Ph_3C][$B(C_6F_5)_4$] from **Table S2**, entry 2 (12 h).

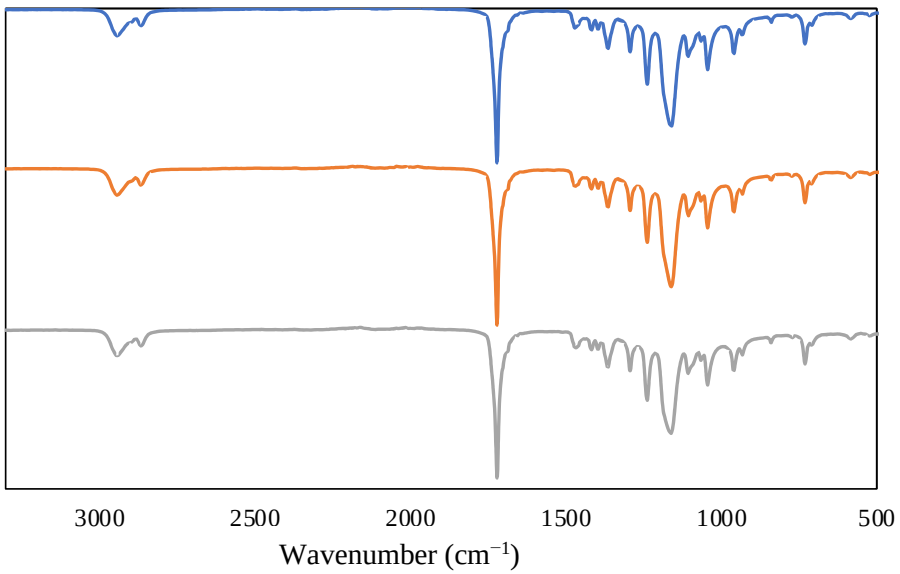

Fig. S143 FT-IR spectrum of PCL 550 equivalents generated by **6**/[Ph_3C][$B(C_6F_5)_4$] from **Table S2**, entry 3 (2 h).

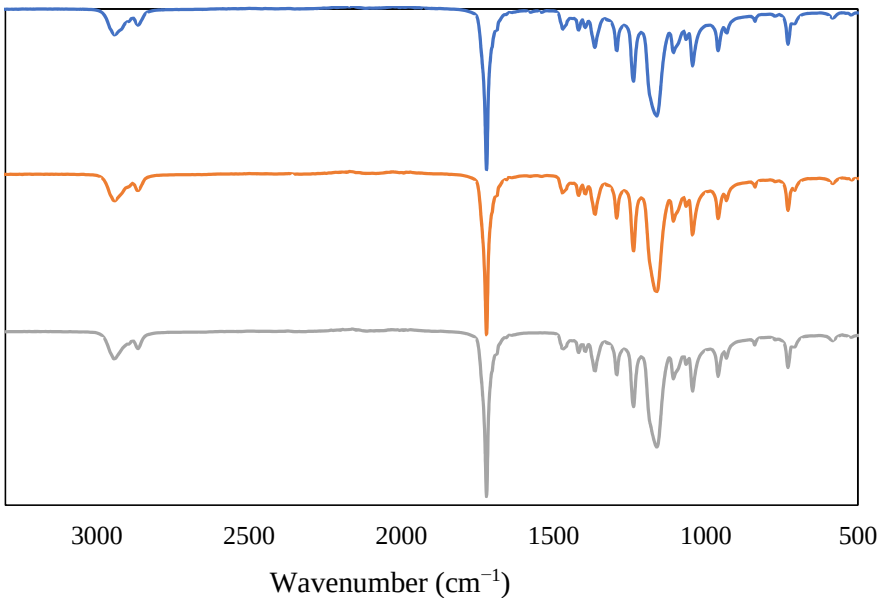

Fig. S144 FT-IR spectrum of PCL 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table S2**, entry 4 (2 h).

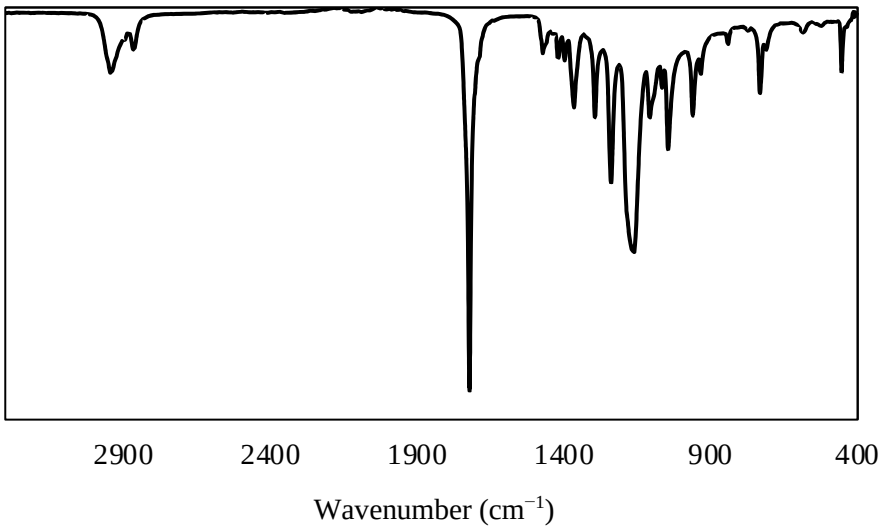

Fig. S145 FT-IR spectrum of PCL 300 equivalents generated by **6** from **Table S2**, entry 5 (No $[Ph_3C][B(C_6F_5)_4]$ added) (10 min).

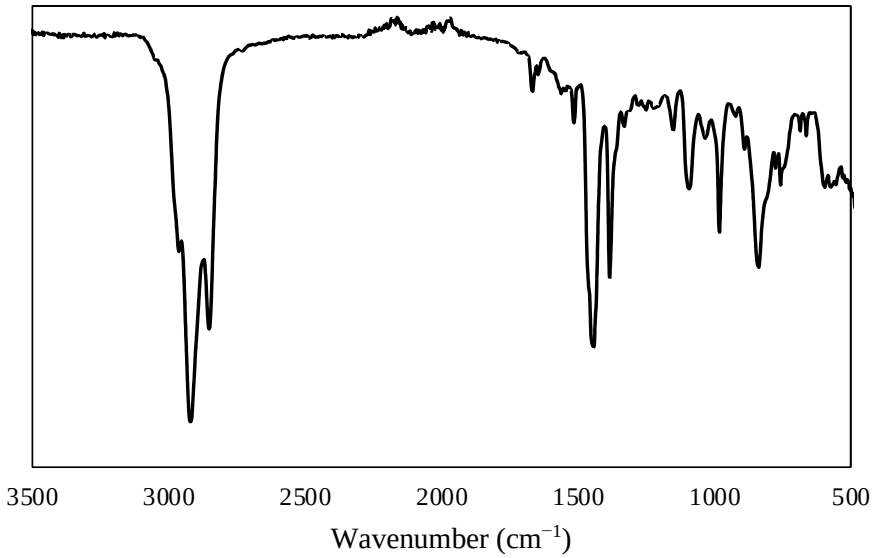

Fig. S146 FT-IR spectrum of PIP 50 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table S3**, entry 1 (12 h).

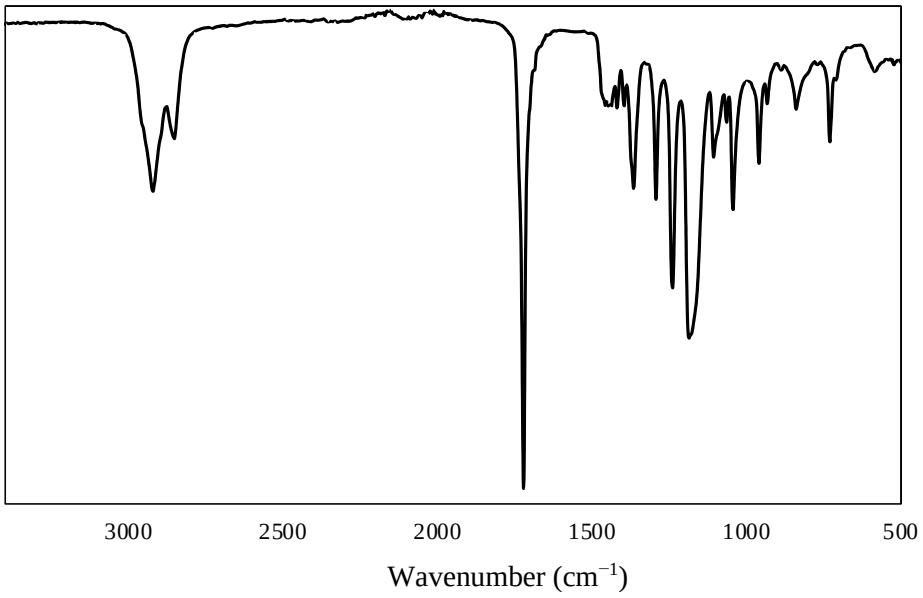

Fig. S147 FT-IR spectrum of PIP-*b*-PCL 50:50 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table S3**, entry 2.

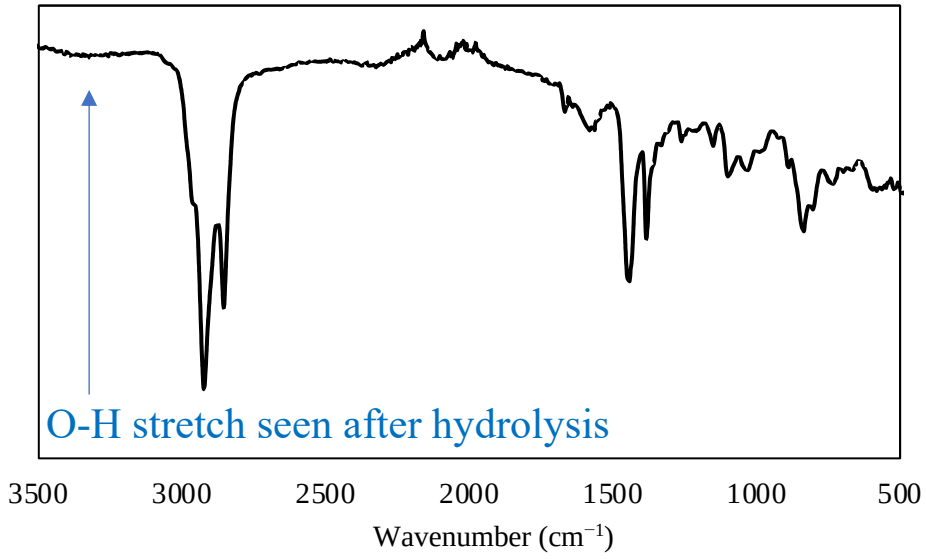

Fig. S148 FT-IR spectrum of recovered PIP 50 equivalents after hydrolysis of PIP-*b*-PCL 50:50 from **Table S3**, entry 3 (12 h).

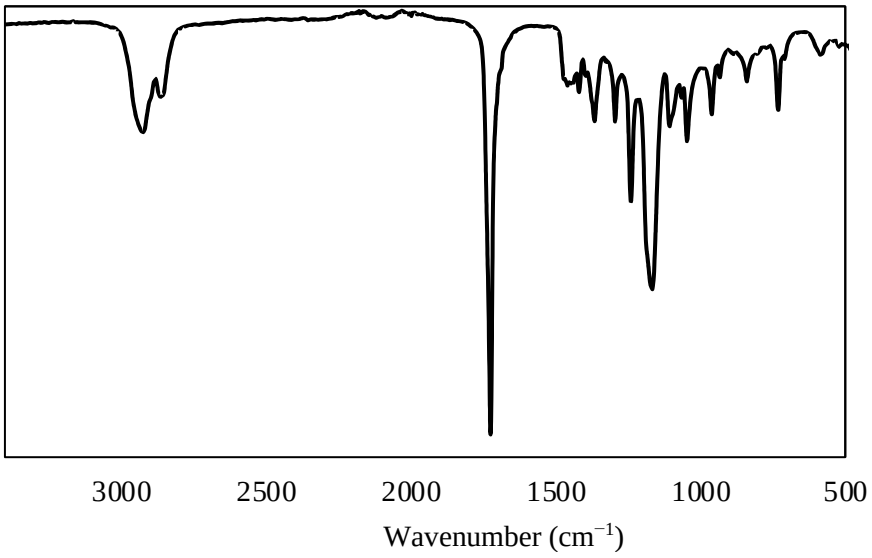

Fig. S149 FT-IR spectrum of PIP-*b*-PCL 50:50 equivalents generated by **Y[N(SiMe$_3$)$_2$]$_3$** from **Table S3**, entry 4 (6 h).

5.0 Gel Permeation Chromatography (GPC) Characterization of Isolated Polymers.

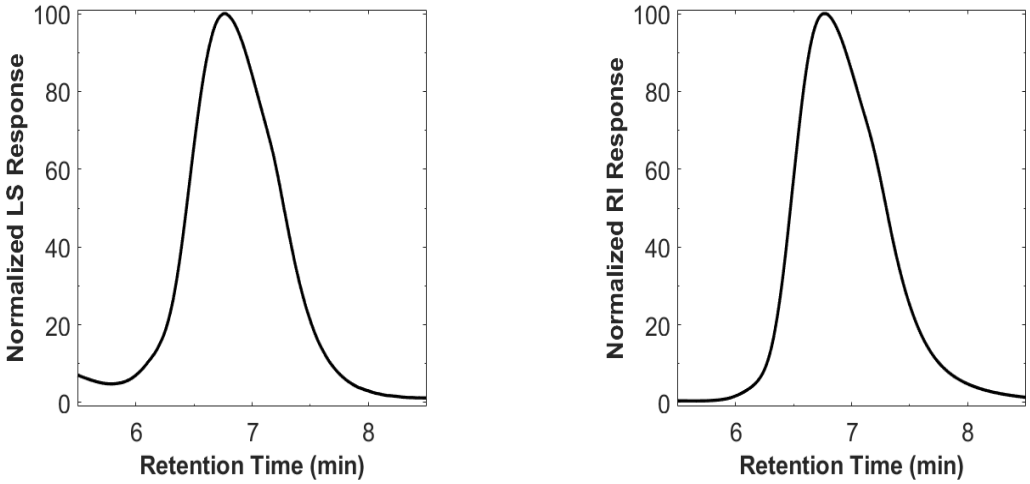

Fig. S150 GPC spectrum of PIP 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 1**, entry 1a (12 h): (left) LS; (right) RI.

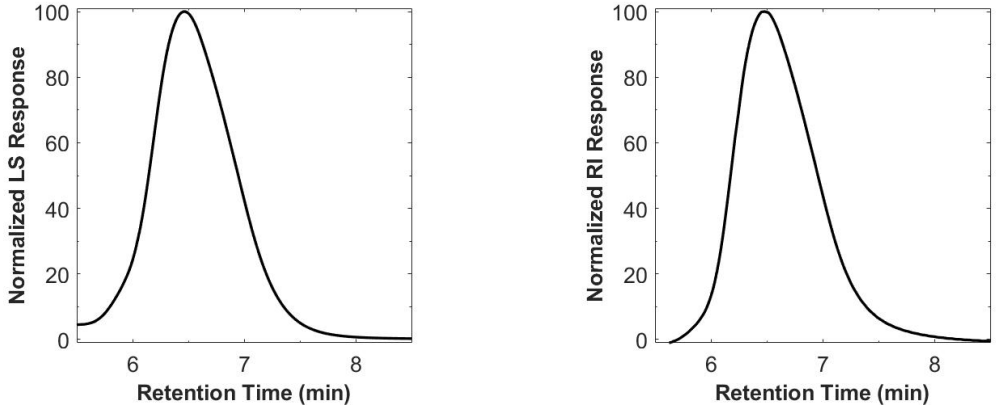

Fig. S151 GPC spectrum of PIP 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 1**, entry 1b (12 h): (left) LS; (right) RI.

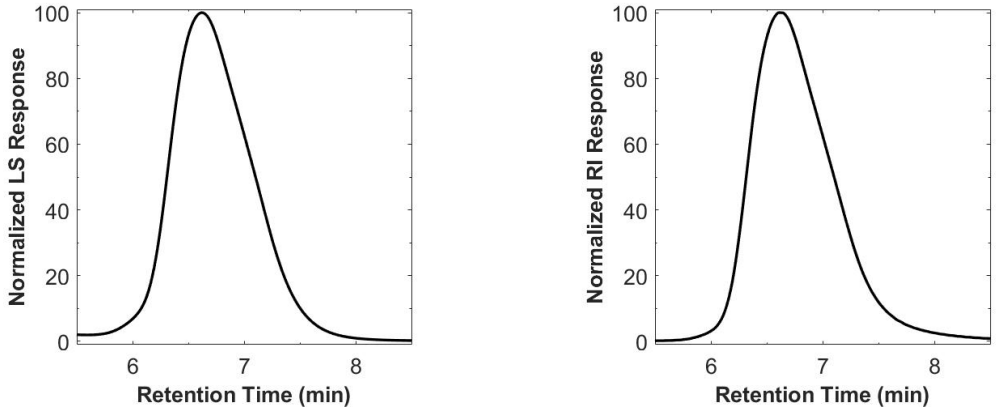

Fig. S152 GPC spectrum of PIP 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 1**, entry 1c (12 h): (left) LS; (right) RI.

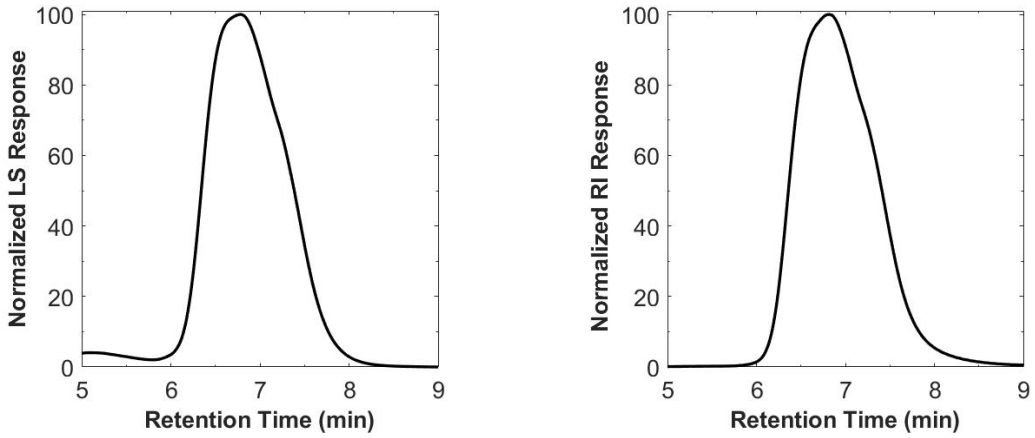

Fig. S153 GPC spectrum of PIP 800 equivalents generated by **8**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 1**, entry 3 (12 h): (left) LS; (right) RI.

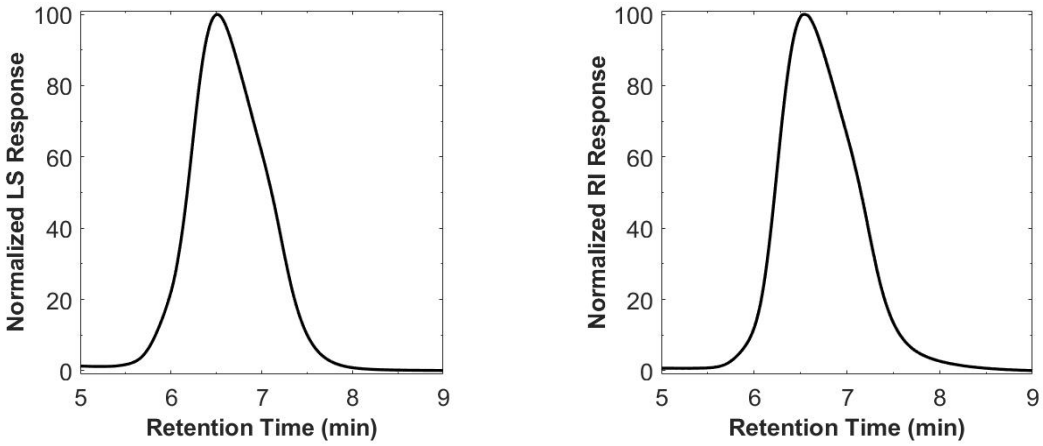

Fig. S154 GPC spectrum of PIP 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 1**, entry 4a (24 h): (left) LS; (right) RI.

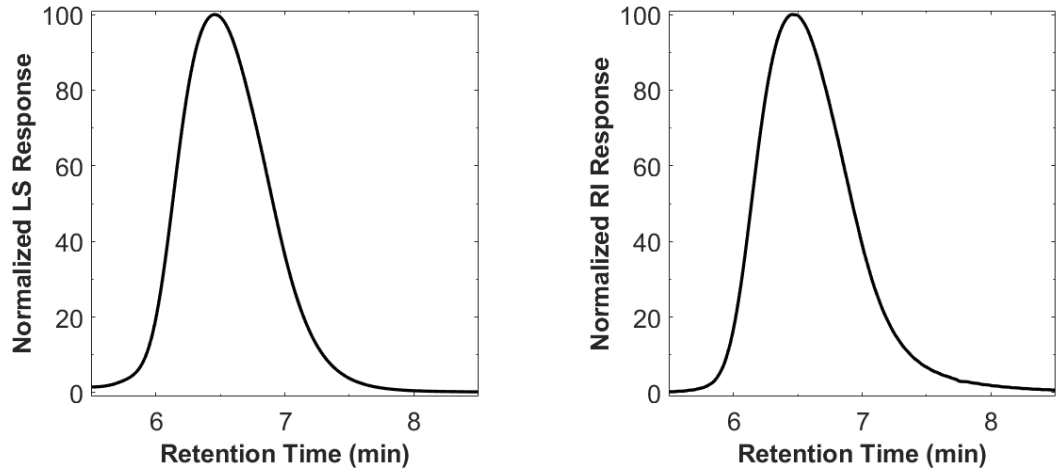

Fig. S155 GPC spectrum of PIP 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 1**, entry 4b (24 h): (left) LS; (right) RI.

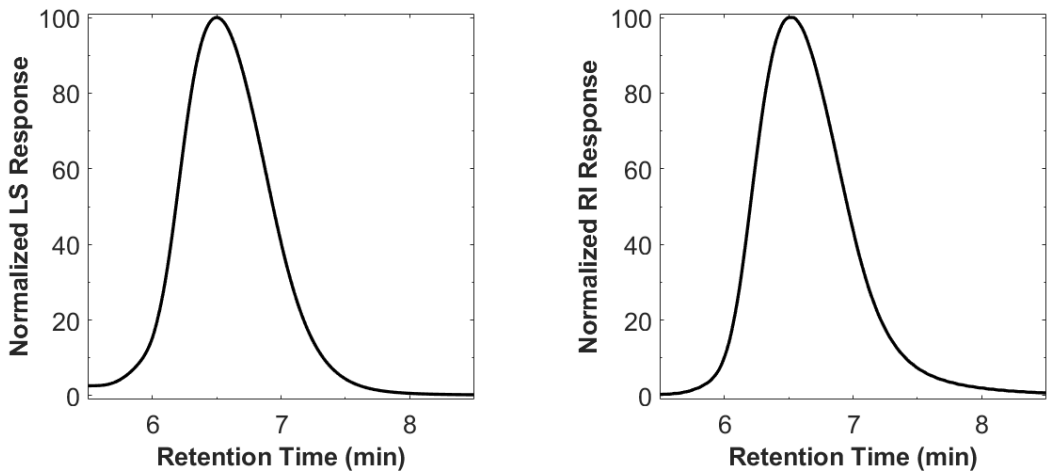

Fig. S156 GPC spectrum of PIP 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 1**, entry 4c (24 h): (left) LS; (right) RI.

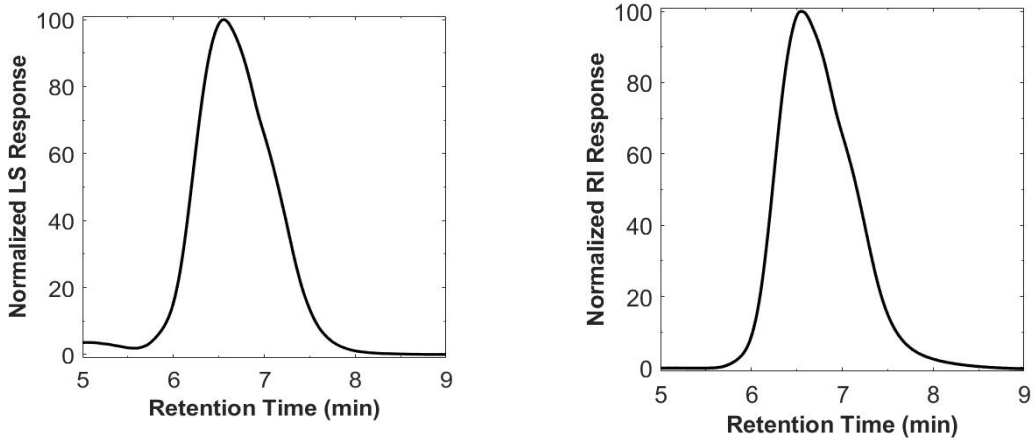

Fig. S157 GPC spectrum of PIP 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 1**, entry 5 (30 min): (left) LS; (right) RI.

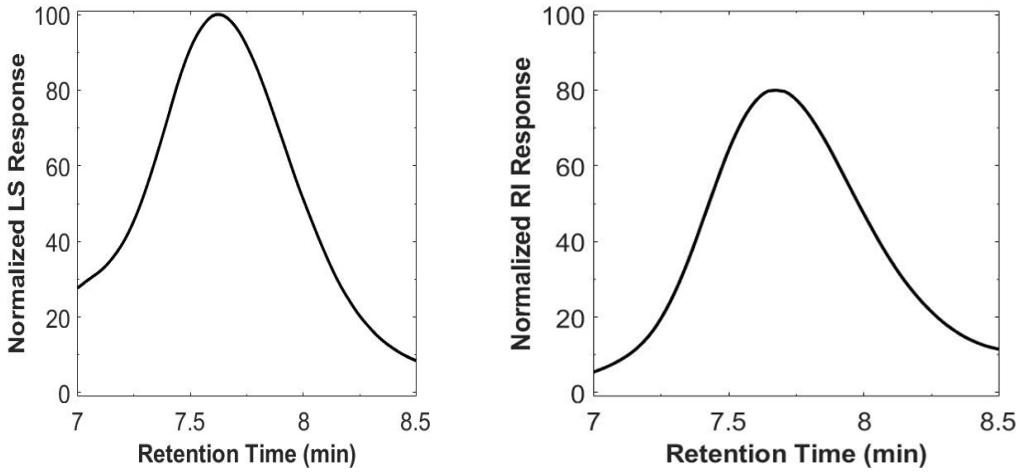

Fig. S158 GPC spectrum of PIP 800 equivalents generated by **8**/[Ph_3C][$B(C_6F_5)_4$] from **Table 1**, entry 6 (30 min): (left) LS; (right) RI.

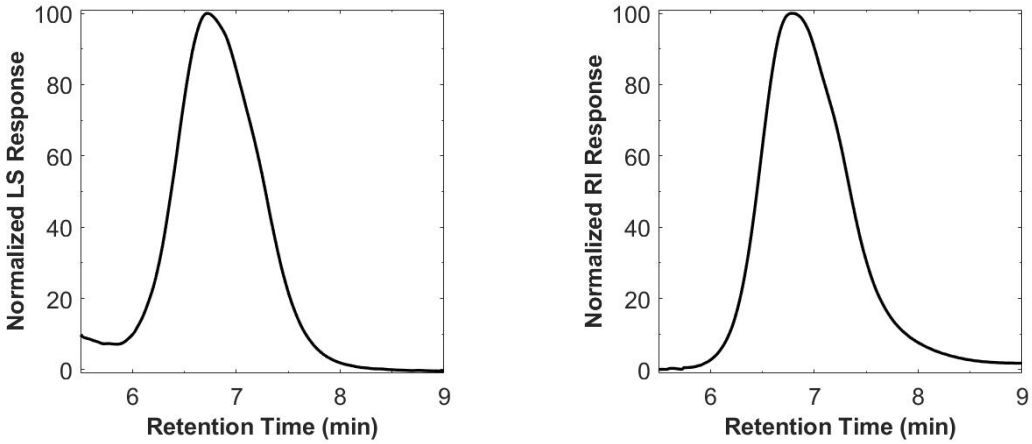

Fig. S159 GPC spectrum of PCL 300 equivalents generated by **6**/[Ph_3C][$B(C_6F_5)_4$] from **Table 1**, entry 7 (10 min): (left) LS; (right) RI.

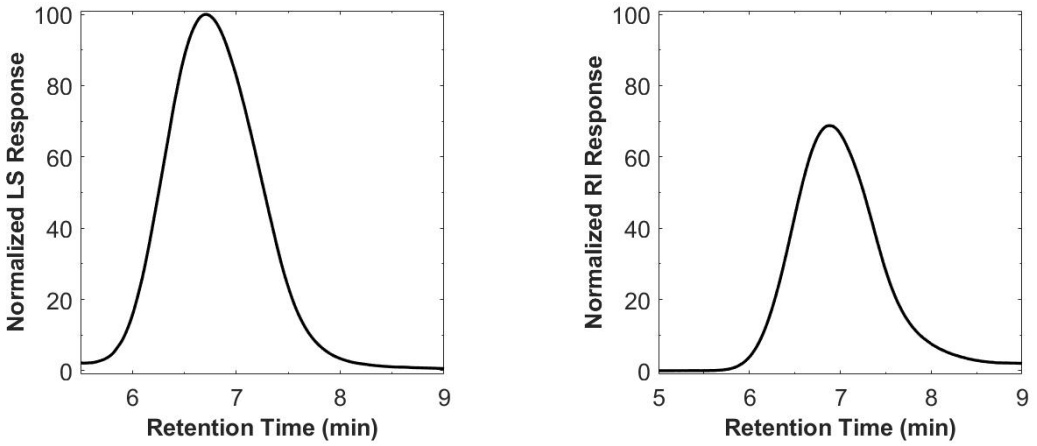

Fig. S160 GPC spectrum of PCL 300 equivalents generated by **8**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 1**, entry 8 (10 min): (left) LS; (right) RI.

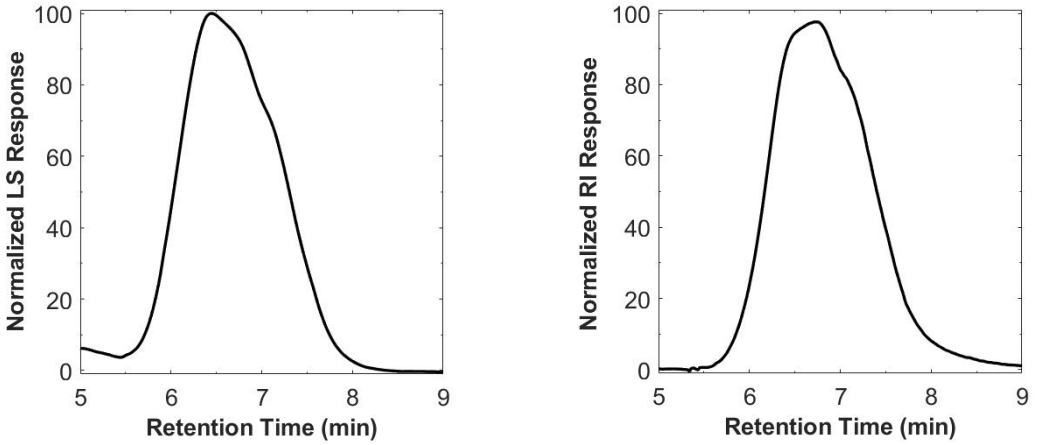

Fig. S161 GPC spectrum of PCL 300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 1**, entry 9a (2 h): (left) LS; (right) RI.

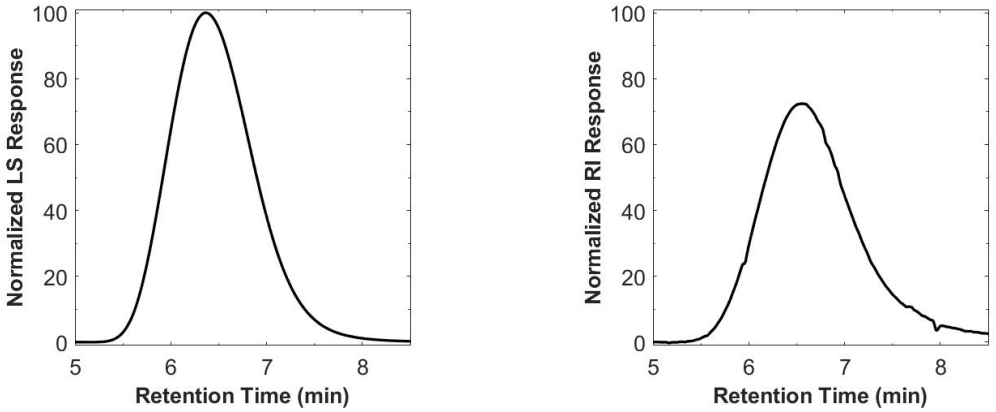

Fig. S162 GPC spectrum of PCL 300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 1**, entry 9b (2 h): (left) LS; (right) RI.

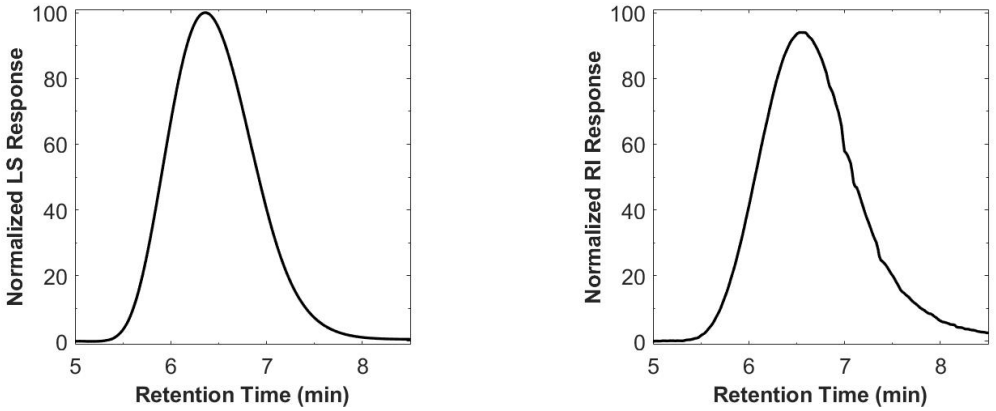

Fig. S163 GPC spectrum of PCL 300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 1**, entry 9c (2 h): (left) LS; (right) RI.

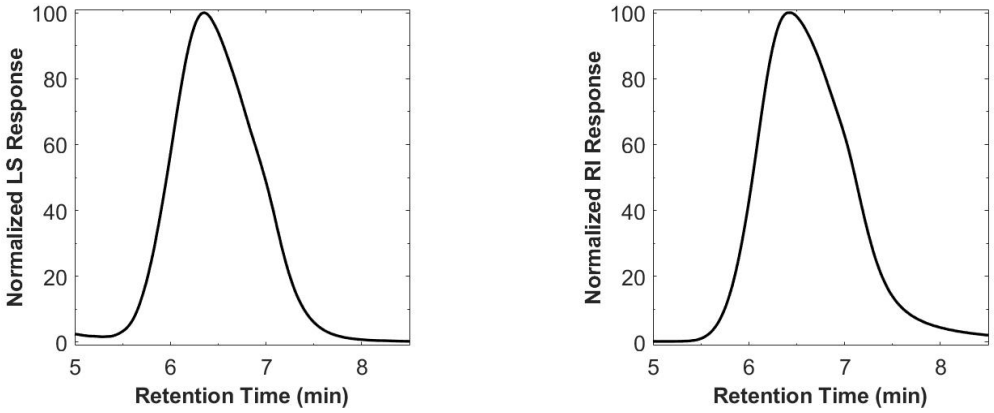

Fig. S164 GPC spectrum of PIP-*b*-PCL 800:300 equivalents generated by **6**/[Ph_3C][$B(C_6F_5)_4$] from **Table 2**, entry 1a: (left) LS; (right) RI.

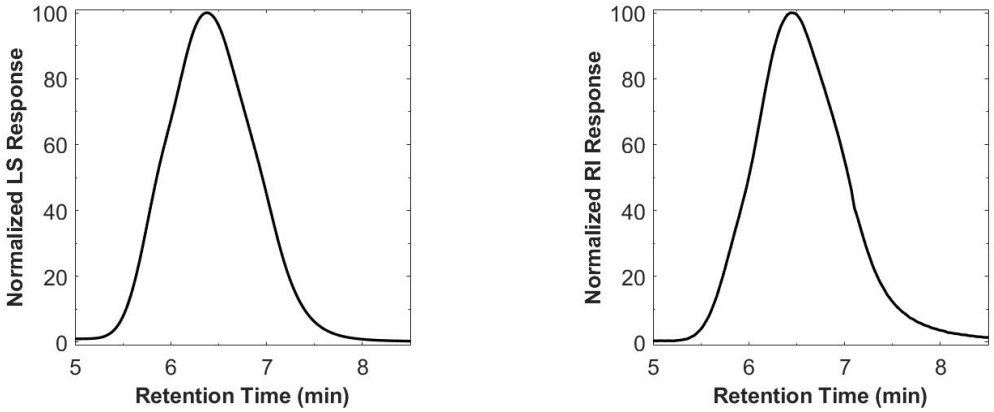

Fig. S165 GPC spectrum of PIP-*b*-PCL 800:300 equivalents generated by **6**/[Ph_3C][$B(C_6F_5)_4$] from **Table 2**, entry 1b: (left) LS; (right) RI.

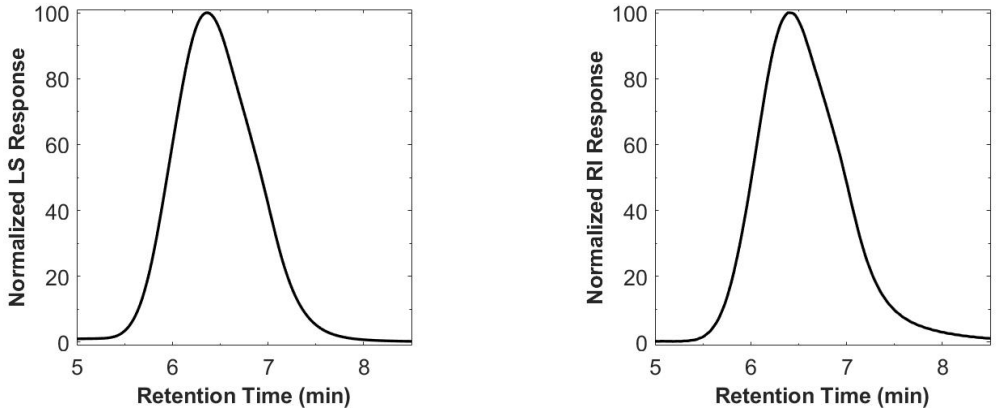

Fig. S166 GPC spectrum of PIP-*b*-PCL 800:300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 2**, entry 1c: (left) LS; (right) RI.

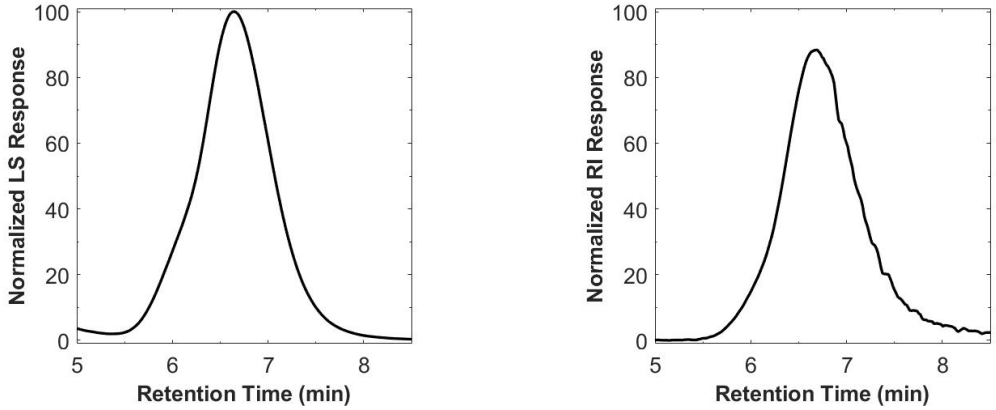

Fig. S167 GPC spectrum of PIP-*b*-PCL 550:550 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 2**, entry 2a: (left) LS; (right) RI.

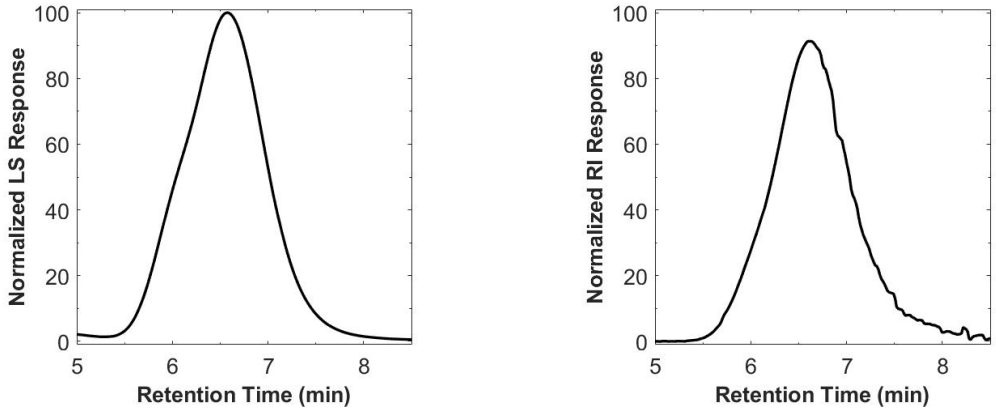

Fig. S168 GPC spectrum of PIP-*b*-PCL 550:550 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 2**, entry 2b: (left) LS; (right) RI.

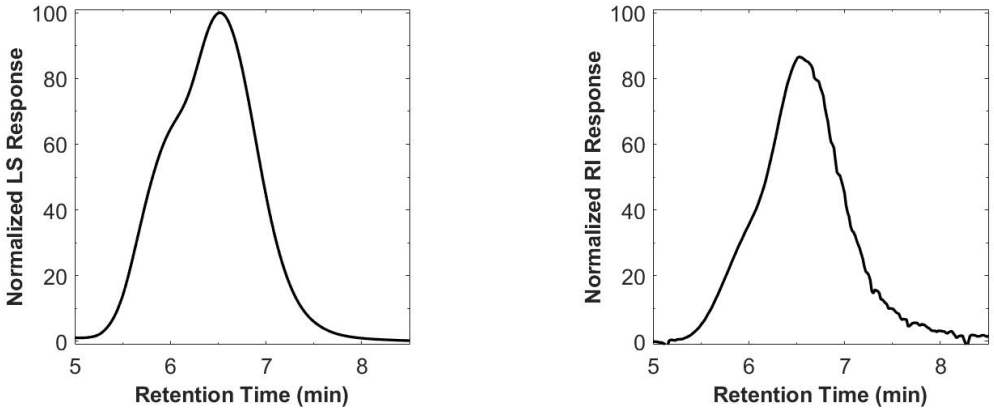

Fig. S169 GPC spectrum of PIP-*b*-PCL 550:550 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 2**, entry 2c: (left) LS; (right) RI.

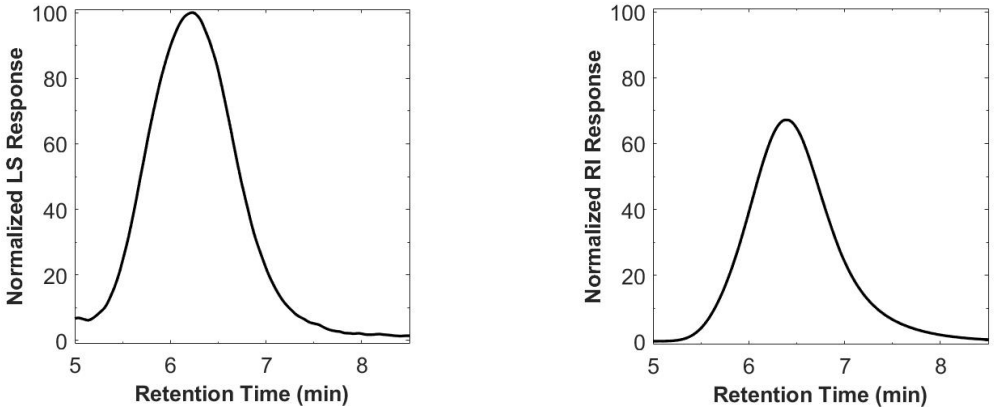

Fig. S170 GPC spectrum of PIP-*b*-PCL 300:800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 2**, entry 3a: (left) LS; (right) RI.

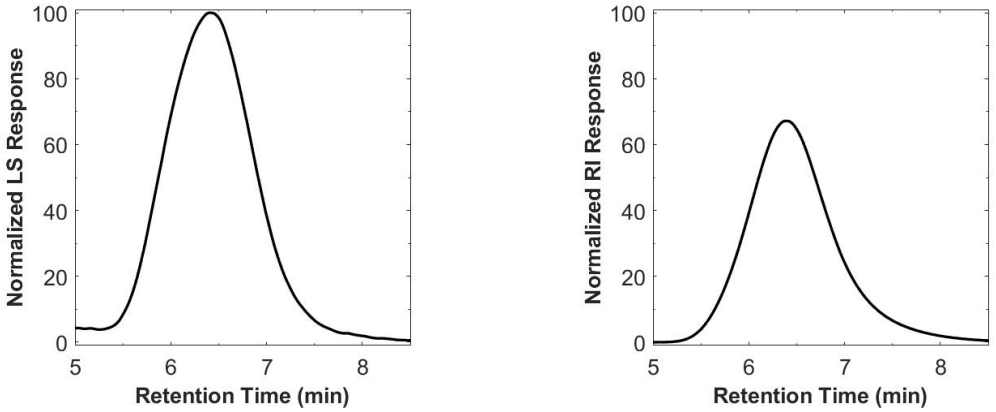

Fig. S171 GPC spectrum of PIP-*b*-PCL 300:800 equivalents generated by **6**/[Ph_3C][$B(C_6F_5)_4$] from **Table 2**, entry 3b: (left) LS; (right) RI.

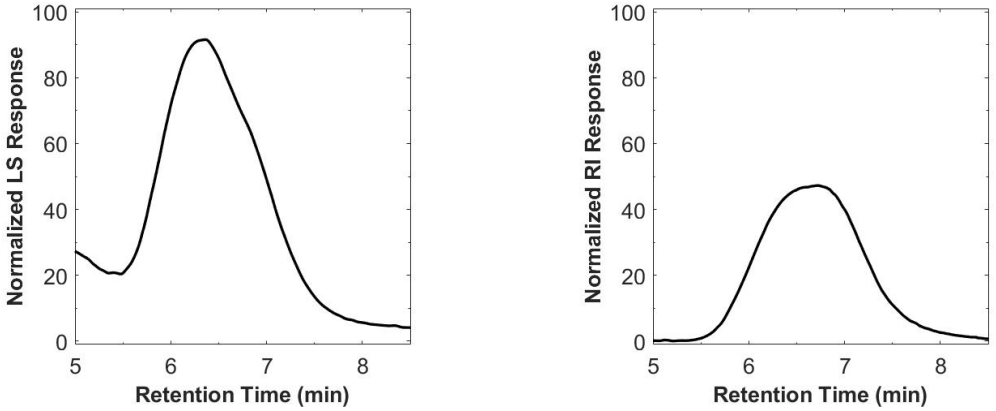

Fig. S172 GPC spectrum of PIP-*b*-PCL 300:800 equivalents generated by **6**/[Ph_3C][$B(C_6F_5)_4$] from **Table 2**, entry 3c: (left) LS; (right) RI.

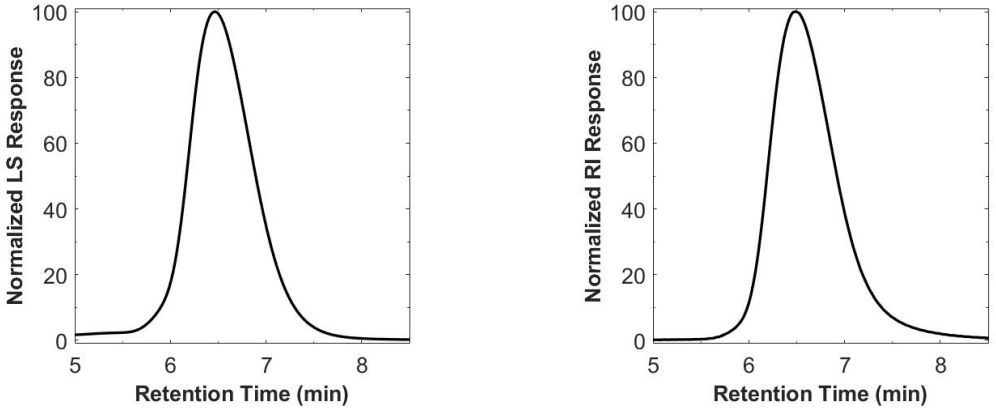

Fig. S173 GPC spectrum of PIP 800 equivalents generated by **6**/[Ph_3C][$B(C_6F_5)_4$] from **Table 3**, entry 1a (IP addition time 0 min): (left) LS; (right) RI.

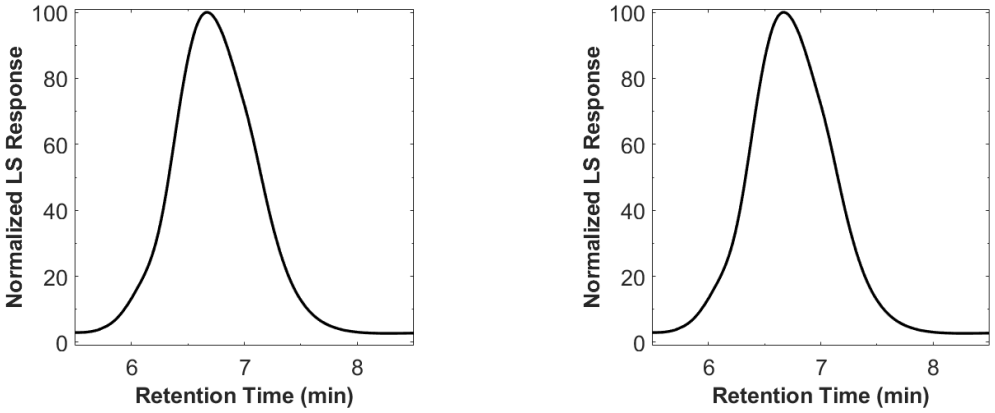

Fig. S174 GPC spectrum of PIP 800 equivalents generated by **6**/[Ph_3C][$B(C_6F_5)_4$] from **Table 3**, entry 1b (IP addition time 0 min): (left) LS; (right) RI.

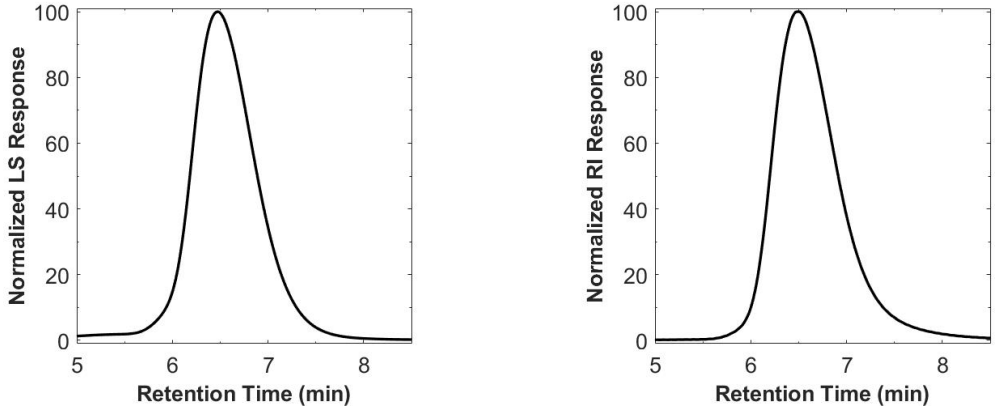

Fig. S175 GPC spectrum of PIP 800 equivalents generated by **6**/[Ph_3C][$B(C_6F_5)_4$] from **Table 3**, entry 1c (IP addition time 0 min): (left) LS; (right) RI.

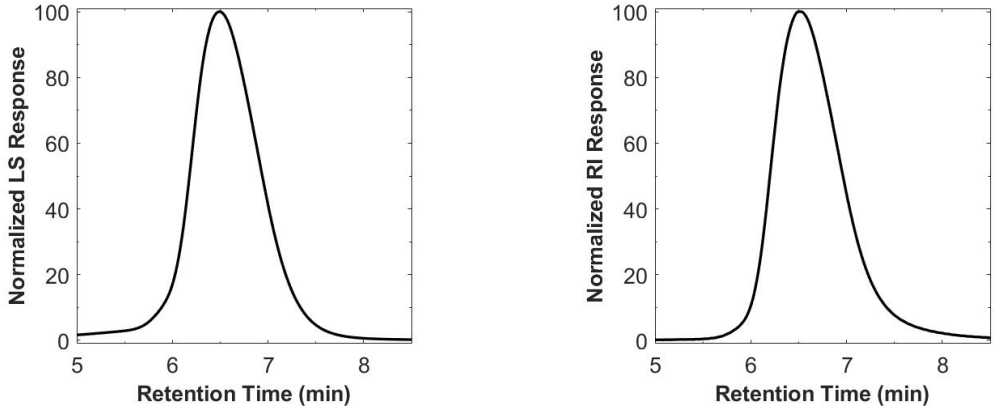

Fig. S176 GPC spectrum of PIP 800 equivalents generated by **6**/[Ph_3C][$B(C_6F_5)_4$] from **Table 3**, entry 2a (IP addition time 30 min): (left) LS; (right) RI.

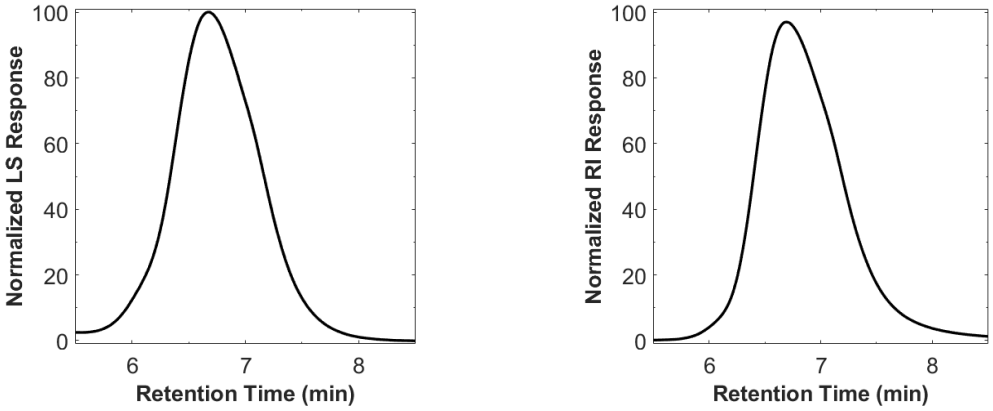

Fig. S177 GPC spectrum of PIP 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 3**, entry 2b (IP addition time 30 min): (left) LS; (right) RI.

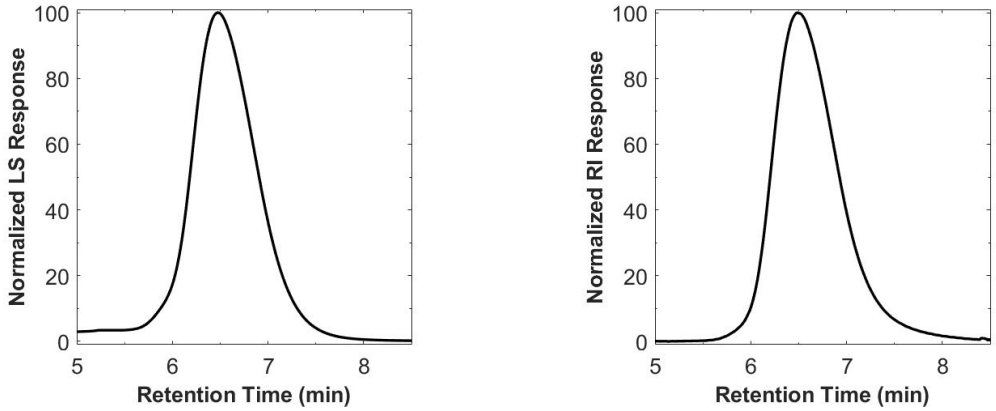

Fig. S178 GPC spectrum of PIP 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 3**, entry 2c (IP addition time 30 min): (left) LS; (right) RI.

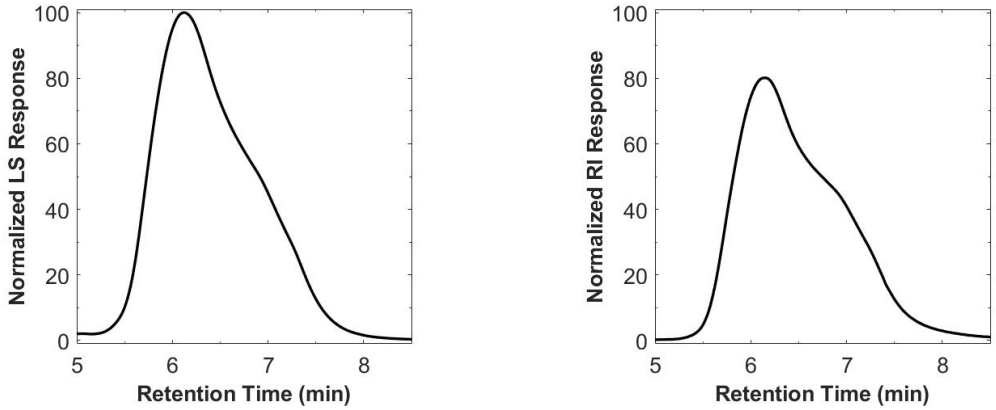

Fig. S179 GPC spectrum of PIP-*b*-PCL 800:300 generated by **6** and 0.5 equivalents of $[Ph_3C][B(C_6F_5)_4]$ from **Table 3**, entry 3a: (left) LS; (right) RI.

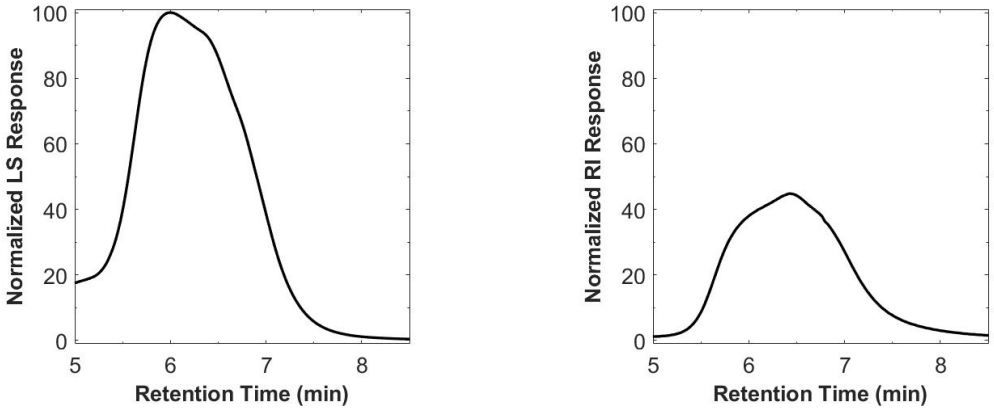

Fig. S180 GPC spectrum of PIP-*b*-PCL 800:300 generated by **6** and 0.5 equivalents of $[Ph_3C][B(C_6F_5)_4]$ from **Table 3**, entry 3b: (left) LS; (right) RI.

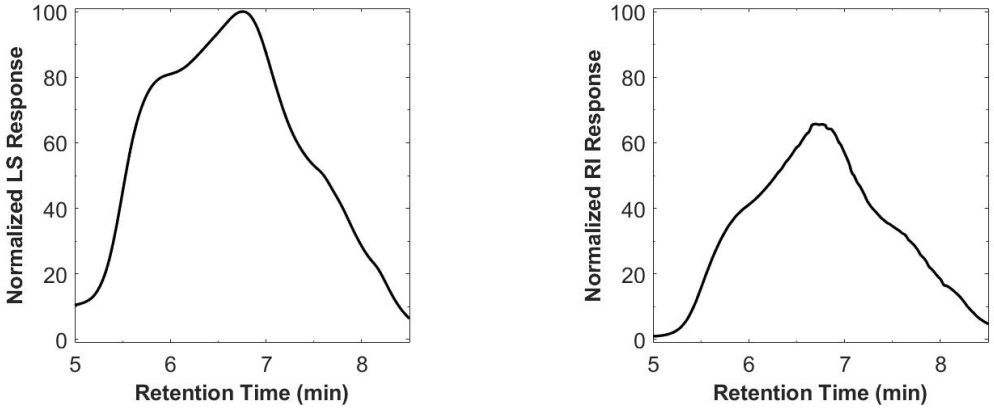

Fig. S181 GPC spectrum of PIP-*b*-PCL 800:300 generated by **6** and 0.5 equivalents of $[Ph_3C][B(C_6F_5)_4]$ from **Table 3**, entry 3c: (left) LS; (right) RI.

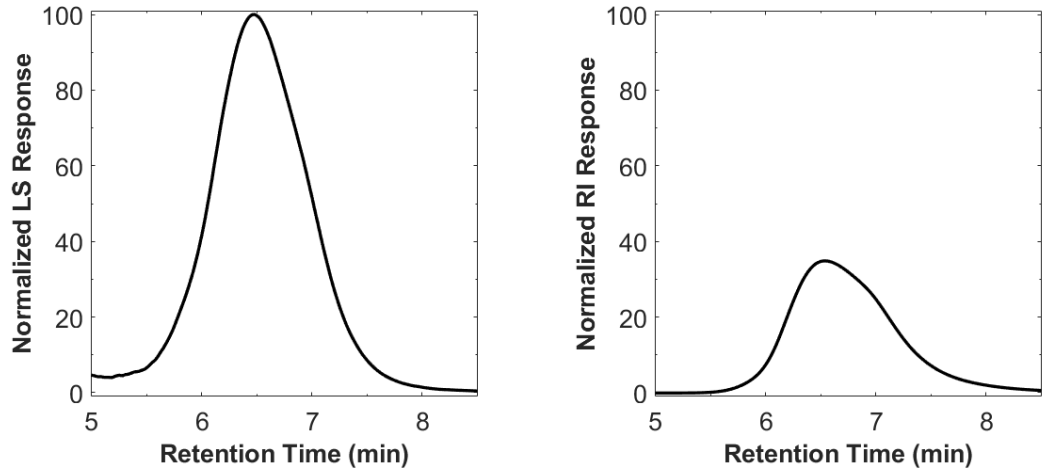

Fig. S182 GPC spectrum of PIP-*b*-PCL 800:300 generated by **6** and 1.5 equivalents of $[Ph_3C][B(C_6F_5)_4]$ from **Table 3**, entry 4a: (left) LS; (right) RI.

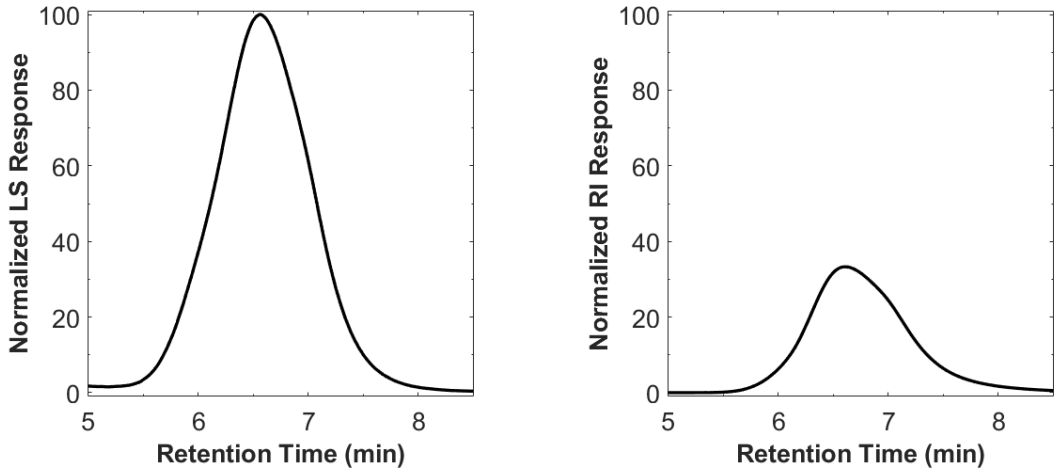

Fig. S183 GPC spectrum of PIP-*b*-PCL 800:300 generated by **6** and 1.5 equivalents of $[Ph_3C][B(C_6F_5)_4]$ from **Table 3**, entry 4b: (left) LS; (right) RI.

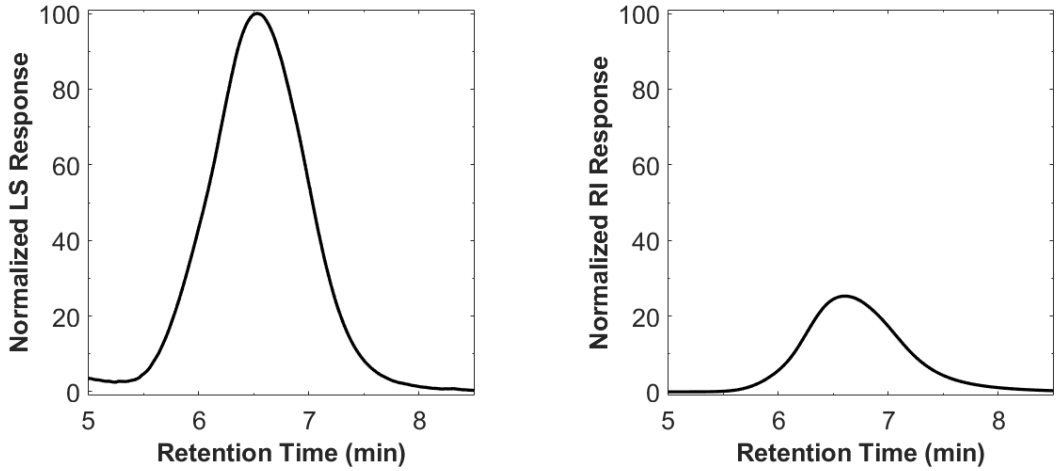

Fig. S184 GPC spectrum of PIP-*b*-PCL 800:300 generated by **6** and 1.5 equivalents of $[Ph_3C][B(C_6F_5)_4]$ from **Table 3**, entry 4c: (left) LS; (right) RI.

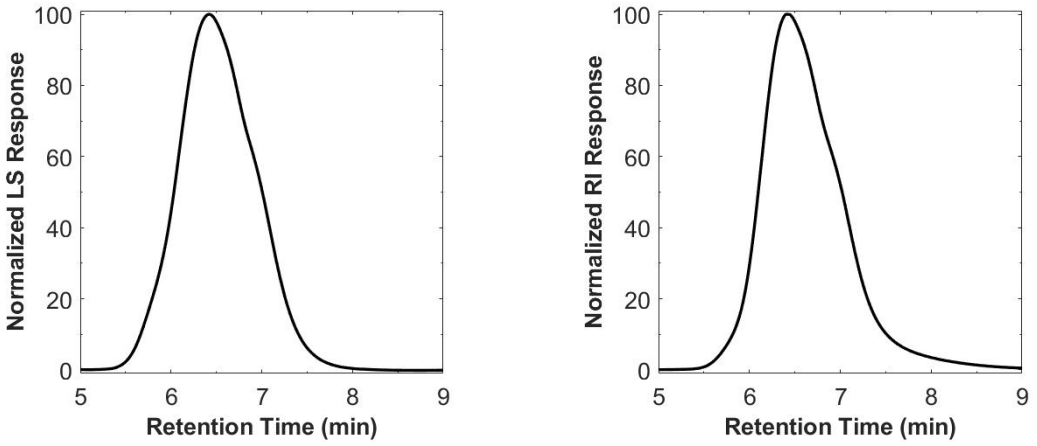

Fig. S185 GPC spectrum of PMyr generated by **6**/[Ph_3C][$B(C_6F_5)_4$] from **Table 4**, entry 1 (30 min): (left) LS; (right) RI.

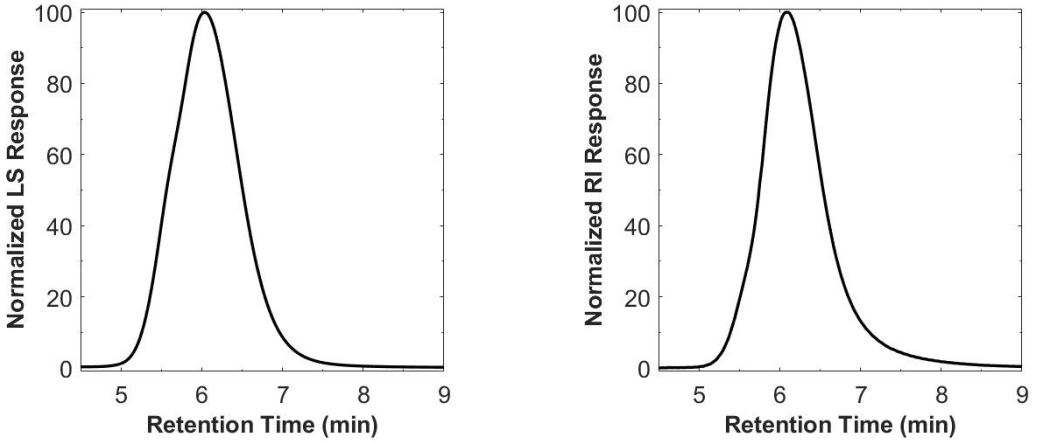

Fig. S186 GPC spectrum of PMyr generated by **6**/[Ph_3C][$B(C_6F_5)_4$] from **Table 4**, entry 2 (90 min): (left) LS; (right) RI.

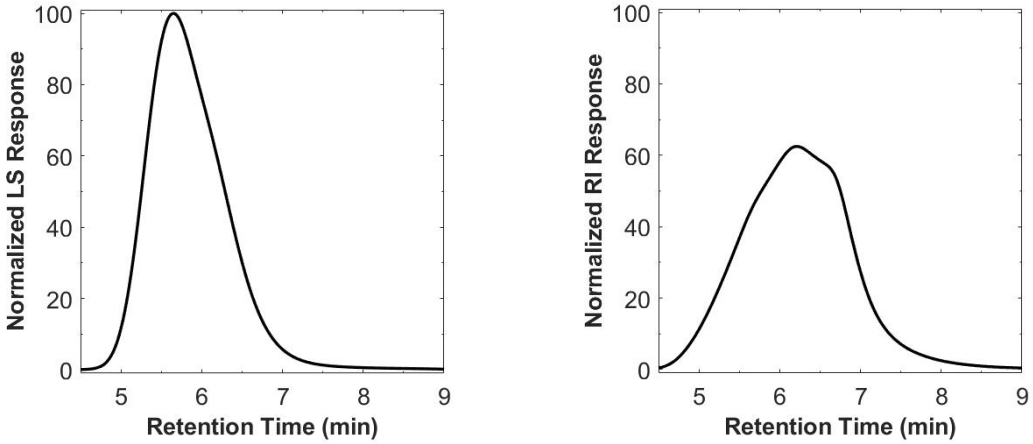

Fig. S187 GPC spectrum of PMyr generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 4**, entry 3 (3 h): (left) LS; (right) RI.

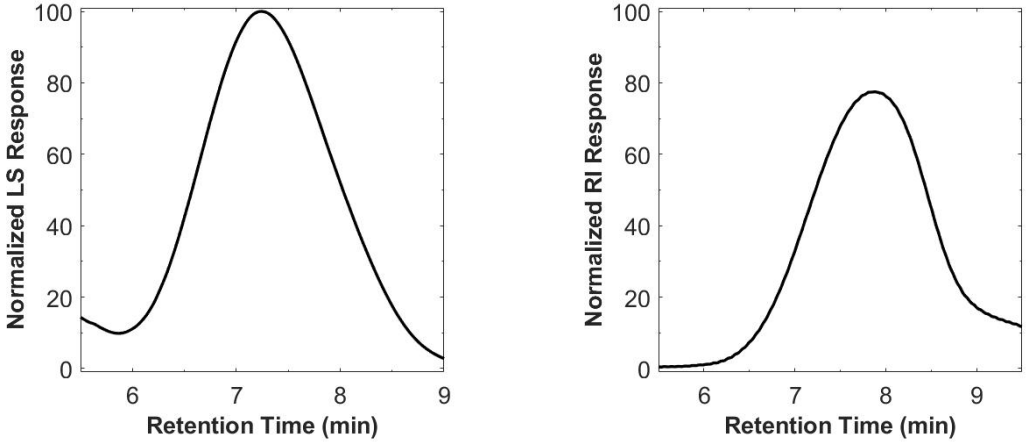

Fig. S188 GPC spectrum of PS generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 4**, entry 4 (30 min): (left) LS; (right) RI.

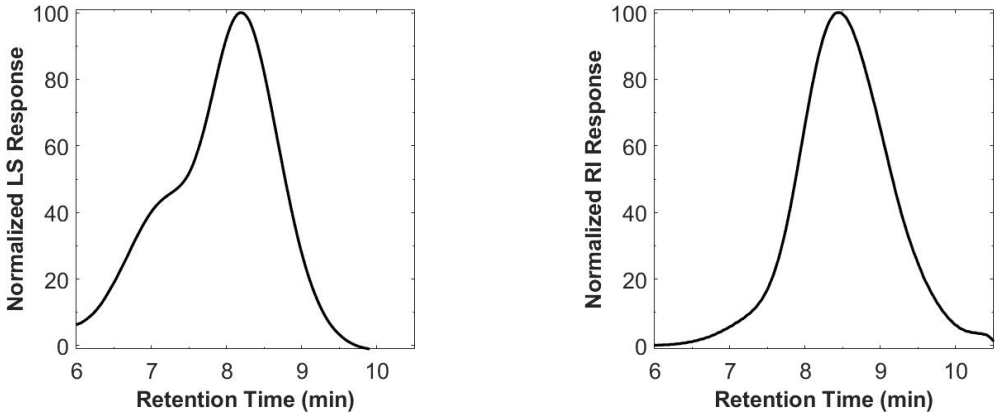

Fig. S189 GPC spectrum of PS generated by **6**/[Ph_3C][$B(C_6F_5)_4$] from **Table 4**, entry 5 (20 h): (left) LS; (right) RI.

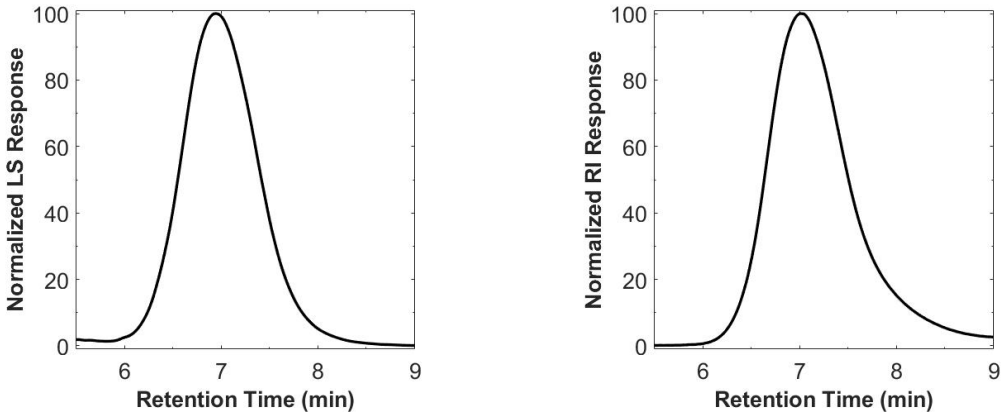

Fig. S190 GPC spectrum of PVL generated by **6**/[Ph_3C][$B(C_6F_5)_4$] from **Table 4**, entry 6 (10 min): (left) LS; (right) RI.

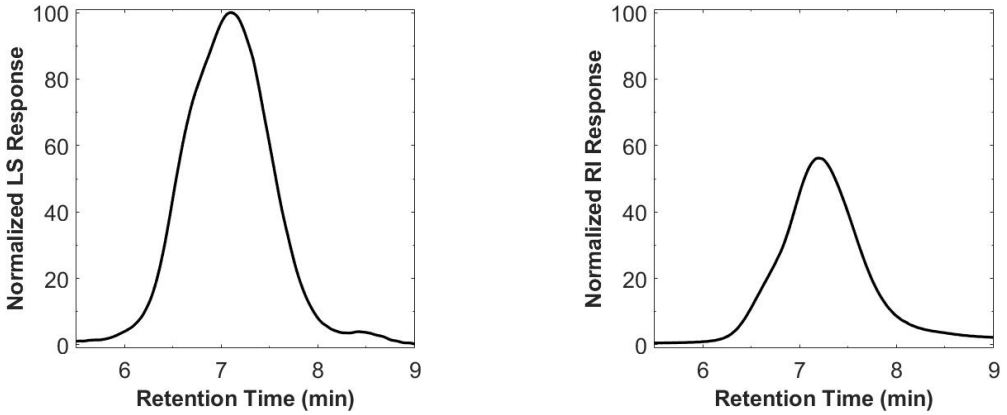

Fig. S191 GPC spectrum of PDL generated by **6**/[Ph_3C][$B(C_6F_5)_4$] from **Table 4**, entry 7 (6 h): (left) LS; (right) RI.

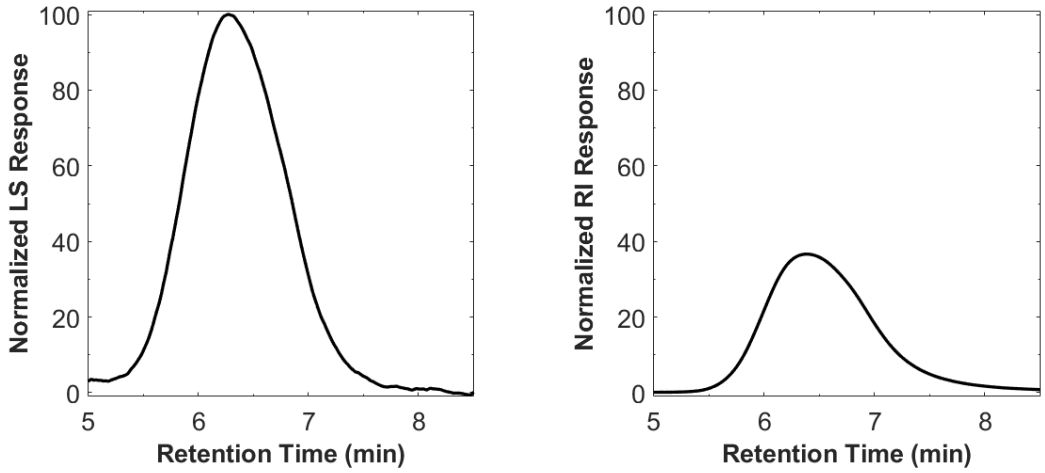

Fig. S192 GPC spectrum of PIP-*b*-PVL 800:300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 5**, entry 1: (left) LS; (right) RI.

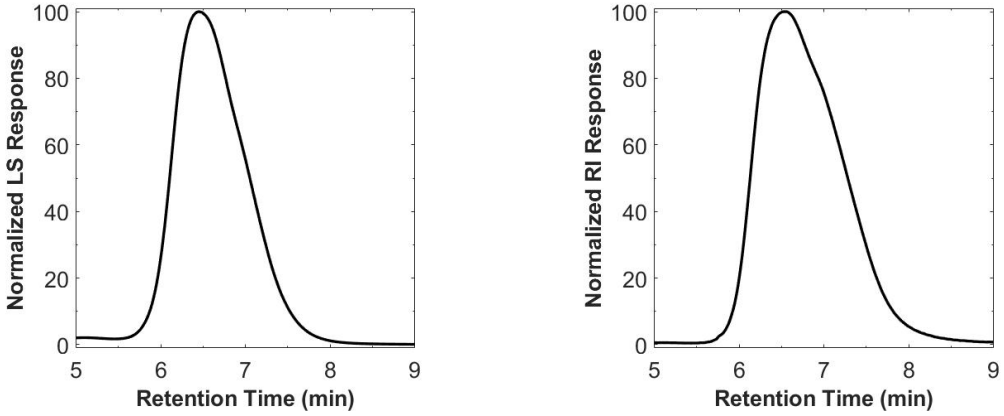

Fig. S193 GPC spectrum of PIP-*b*-PDL 800:300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 5**, entry 2: (left) LS; (right) RI.

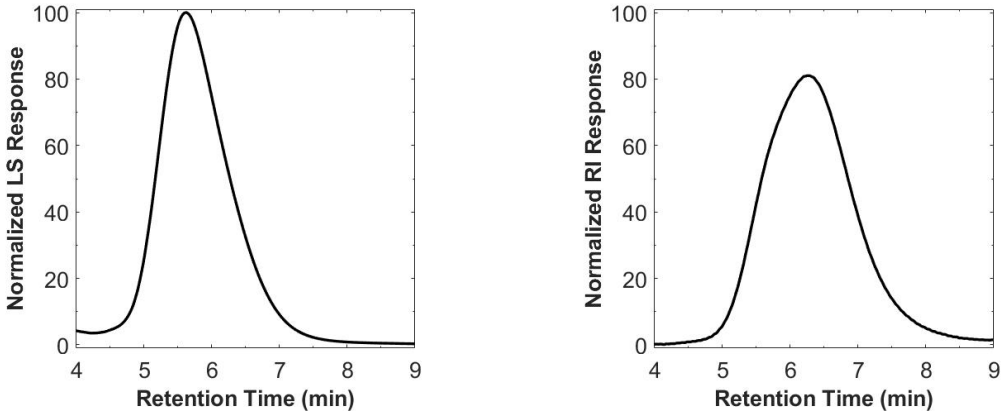

Fig. S194 GPC spectrum of PMyr-*b*-PCL 800:300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 5**, entry 3: (left) LS; (right) RI.

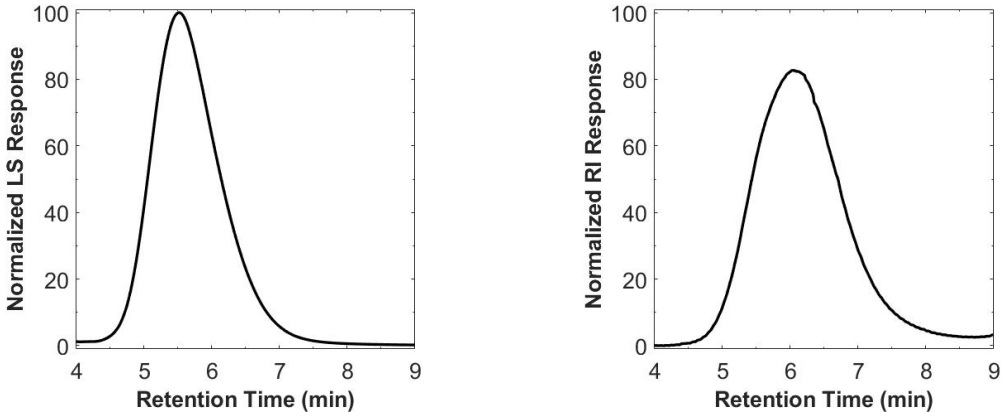

Fig. S195 GPC spectrum of PMyr-*b*-PVL 800:300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 5**, entry 4: (left) LS; (right) RI.

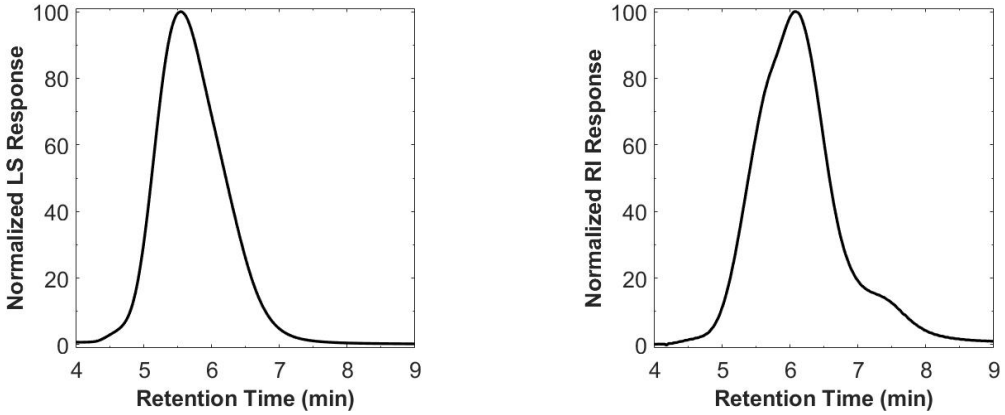

Fig. S196 GPC spectrum of PMyr-*b*-PDL 800:300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 5**, entry 5: (left) LS; (right) RI.

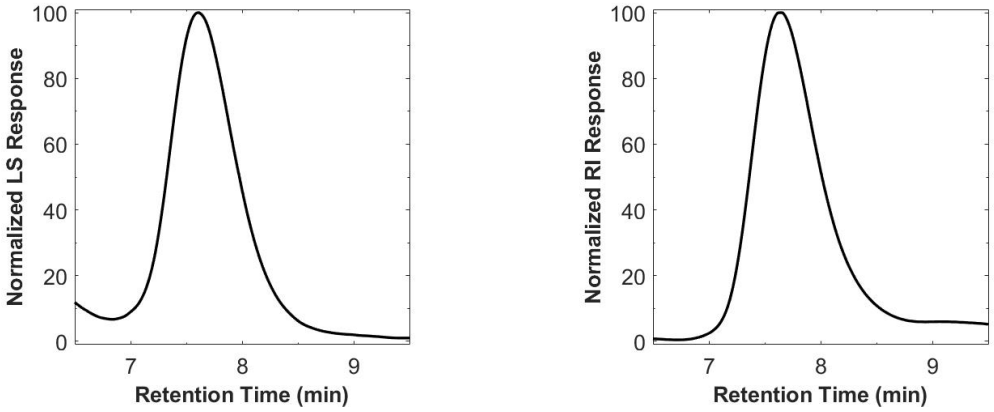

Fig. S197 GPC spectrum of PMyr 800 equivalents generated by **8**/[Ph_3C][$B(C_6F_5)_4$] from **Table S1**, entry 1 (30min): (left) LS; (right) RI.

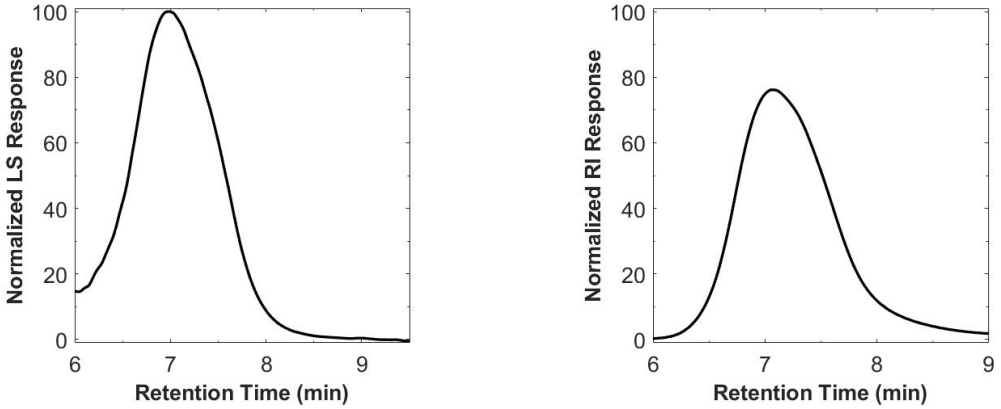

Fig. S198 GPC spectrum of PS 800 equivalents generated by **8**/[Ph_3C][$B(C_6F_5)_4$] from **Table S1**, entry 2 (30 min): (left) LS; (right) RI.

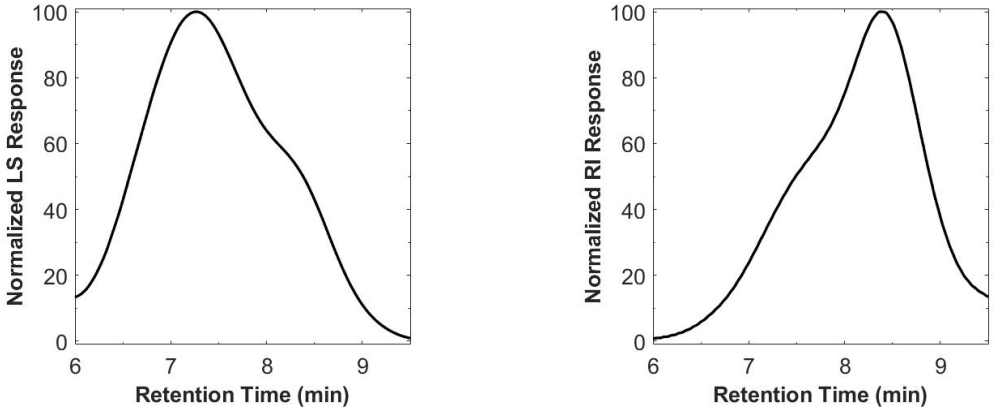

Fig. S199 GPC spectrum of PVL 300 equivalents generated by **8**/[Ph_3C][$B(C_6F_5)_4$] from **Table S1**, entry 3 (10 min): (left) LS; (right) RI.

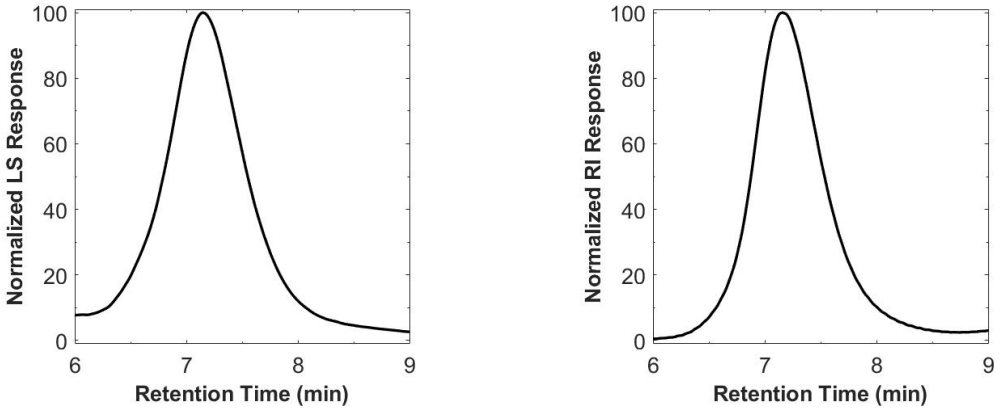

Fig. S200 GPC spectrum of PDL 300 equivalents generated by **8**/[Ph_3C][$B(C_6F_5)_4$] from **Table S1**, entry 4 (6 h): (left) LS; (right) RI.

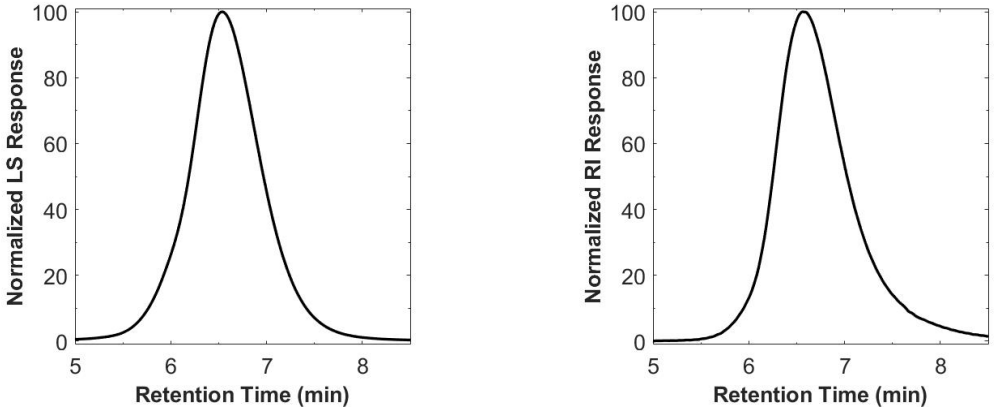

Fig. S201 GPC spectrum of PIP 300 equivalents generated by **6**/[Ph_3C][$B(C_6F_5)_4$] from **Table S2**, entry 1a (12 h): (left) LS; (right) RI.

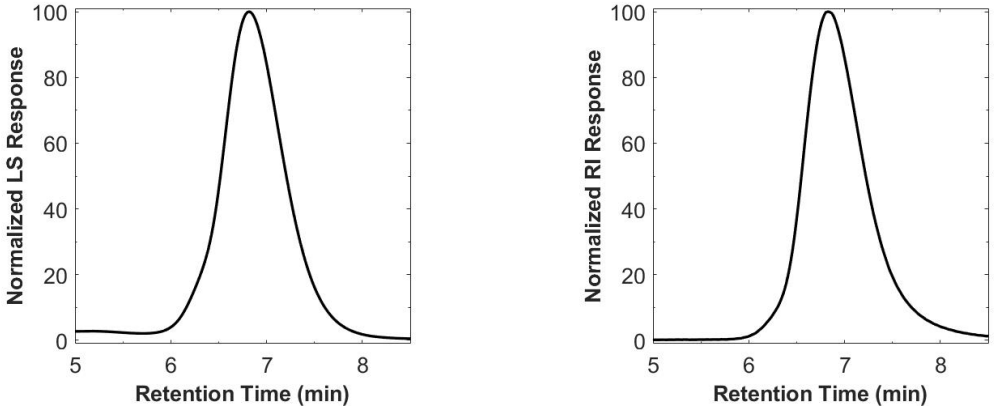

Fig. S202 GPC spectrum of PIP 300 equivalents generated by **6**/[Ph_3C][$B(C_6F_5)_4$] from **Table S2**, entry 1b (12 h): (left) LS; (right) RI.

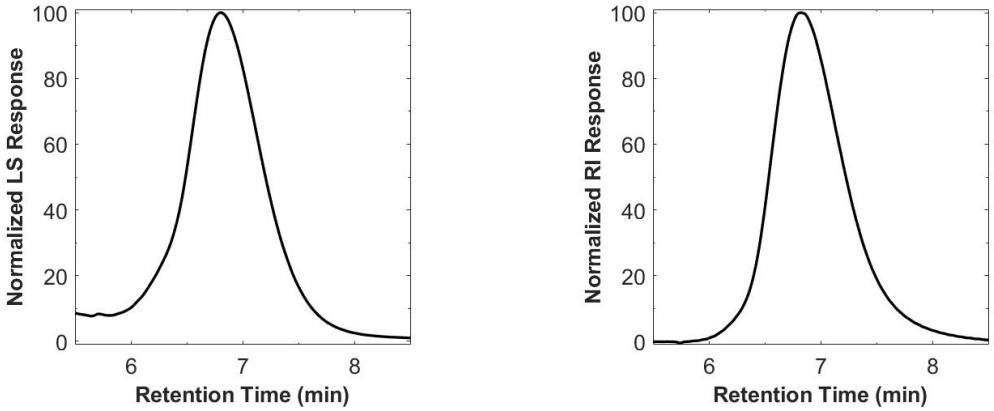

Fig. S203 GPC spectrum of PIP 300 equivalents generated by **6**/[Ph_3C][$B(C_6F_5)_4$] from **Table S2**, entry 1c (12 h): (left) LS; (right) RI.

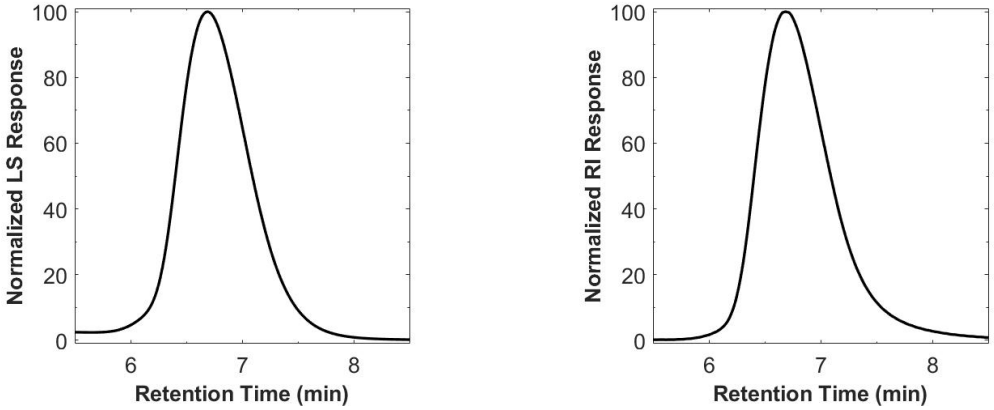

Fig. S204 GPC spectrum of PIP 550 equivalents generated by **6**/[Ph_3C][$B(C_6F_5)_4$] from **Table S2**, entry 2a (12 h): (left) LS; (right) RI.

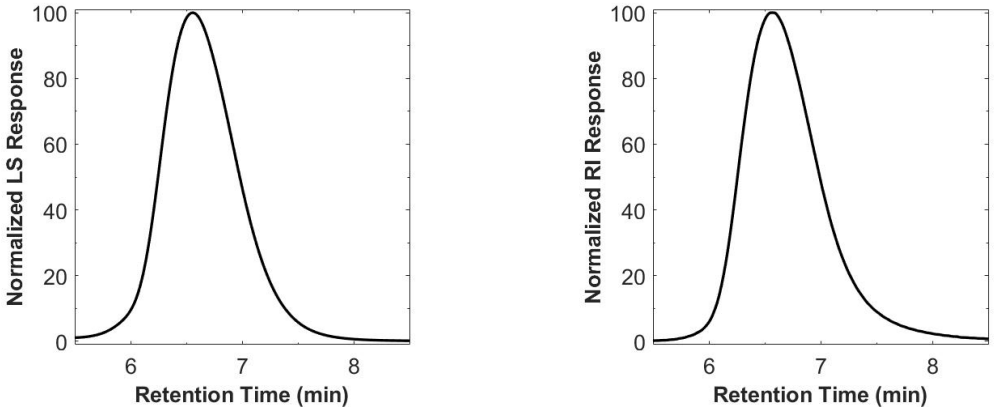

Fig. S205 GPC spectrum of PIP 550 equivalents generated by **6**/[Ph_3C][$B(C_6F_5)_4$] from **Table S2**, entry 2b (12 h): (left) LS; (right) RI.

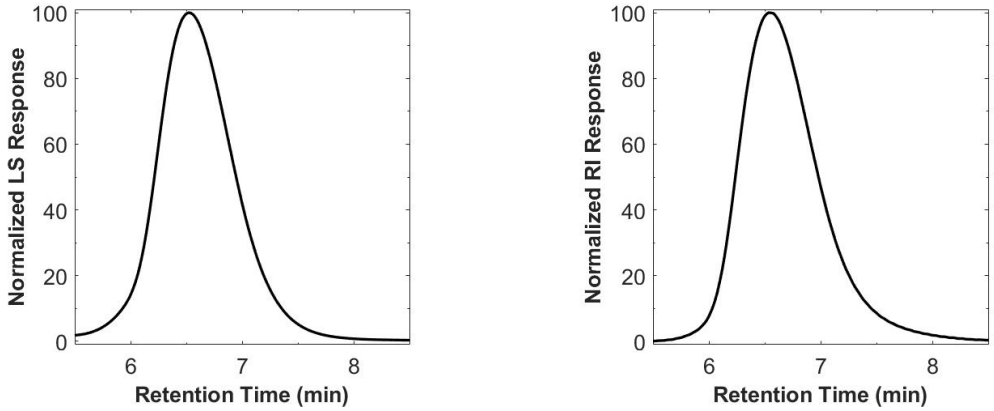

Fig. S206 GPC spectrum of PIP 550 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table S2**, entry 2c (12 h): (left) LS; (right) RI.

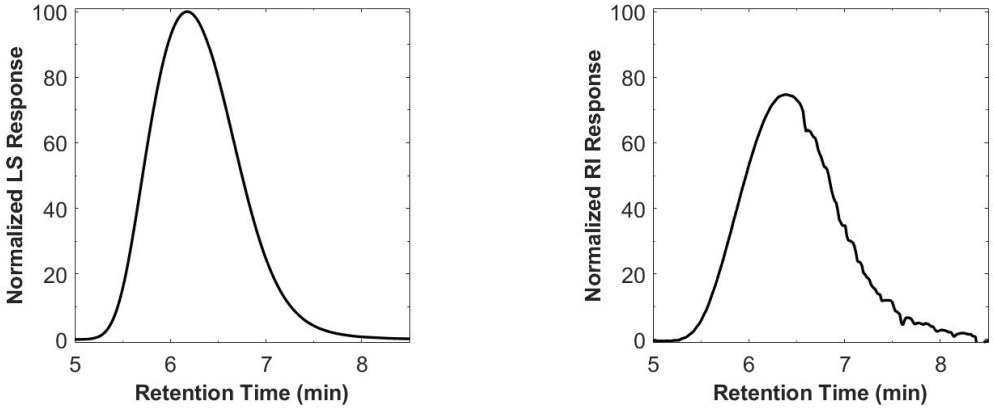

Fig. S207 GPC spectrum of PCL 550 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table S2**, entry 3a (2 h): (left) LS; (right) RI.

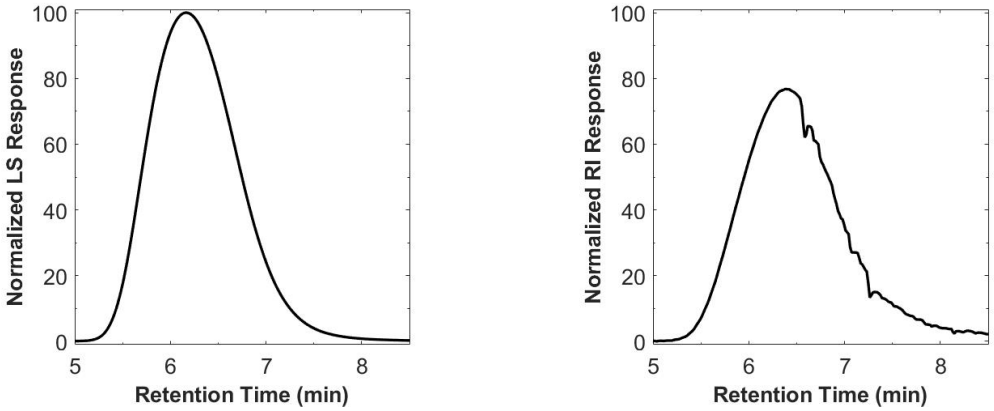

Fig. S208 GPC spectrum of PCL 550 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table S2**, entry 3b (2 h): (left) LS; (right) RI.

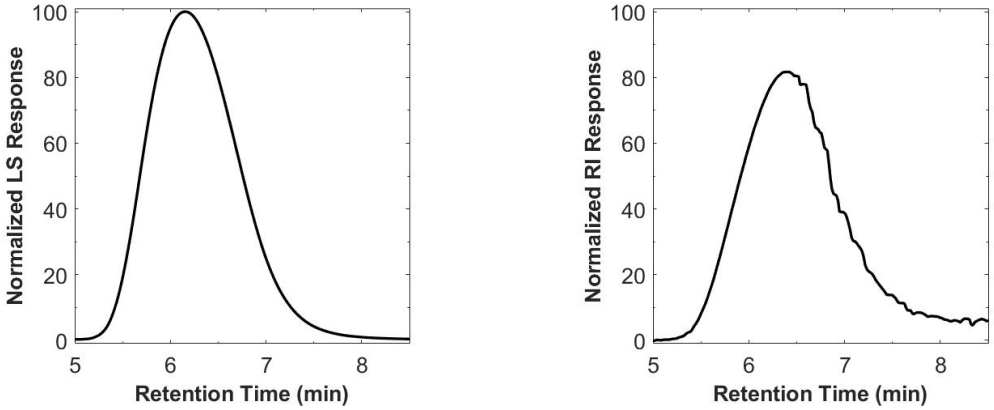

Fig. S209 GPC spectrum of PCL 550 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table S2**, entry 3c (2 h): (left) LS; (right) RI.

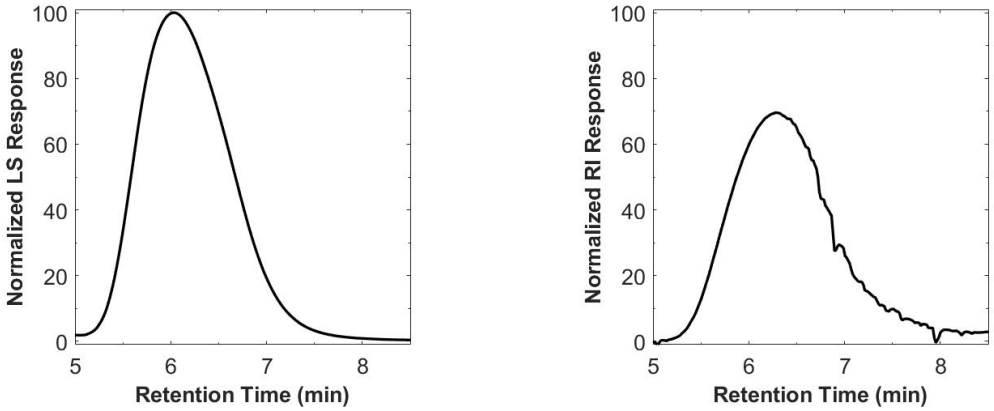

Fig. S210 GPC spectrum of PCL 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table S2**, entry 4a (2 h): (left) LS; (right) RI.

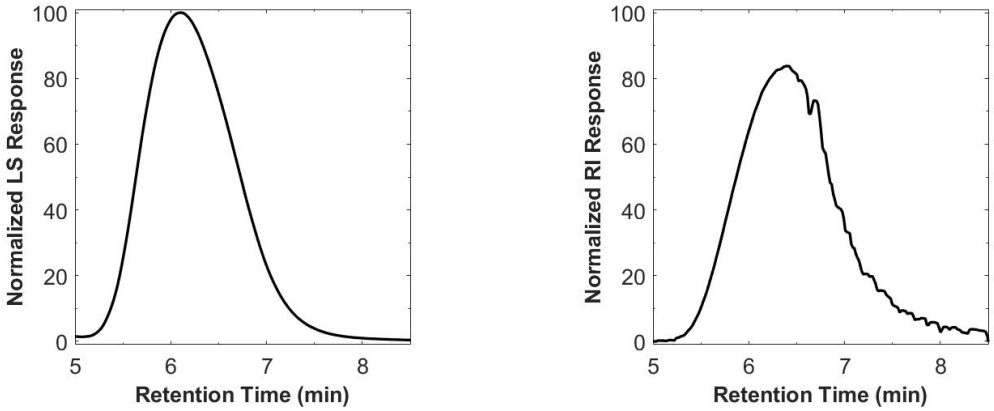

Fig. S211 GPC spectrum of PCL 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table S2**, entry 4b (2 h): (left) LS; (right) RI.

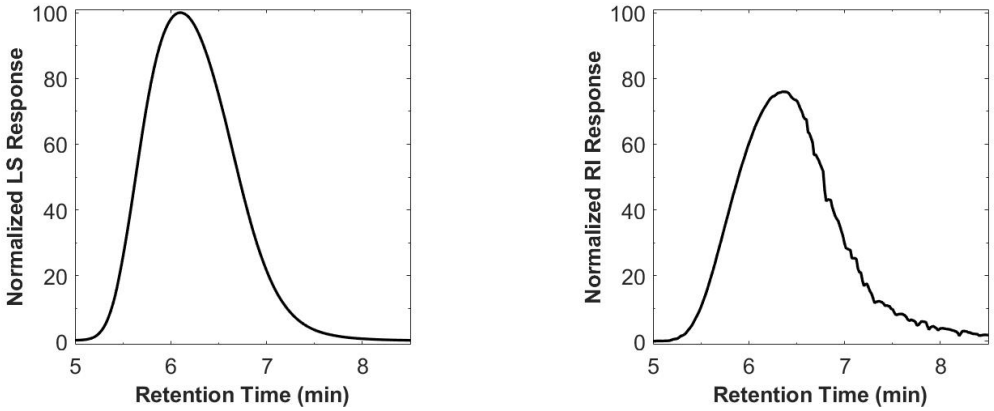

Fig. S212 GPC spectrum of PCL 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table S2**, entry 4c (2 h): (left) LS; (right) RI.

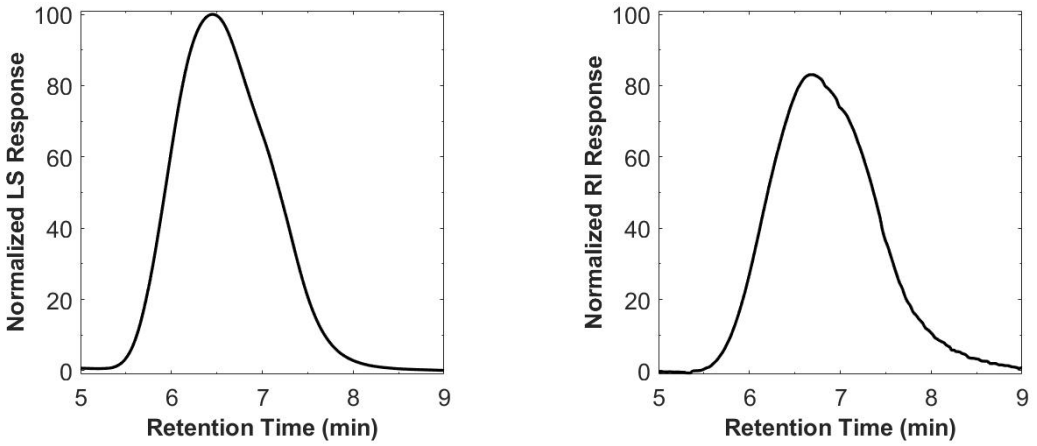

Fig. S213 GPC spectrum of PCL 300 equivalents generated by **6** from **Table S2**, entry 5 (No $[Ph_3C][B(C_6F_5)_4]$ added) (10 min): (left) LS; (right) RI.

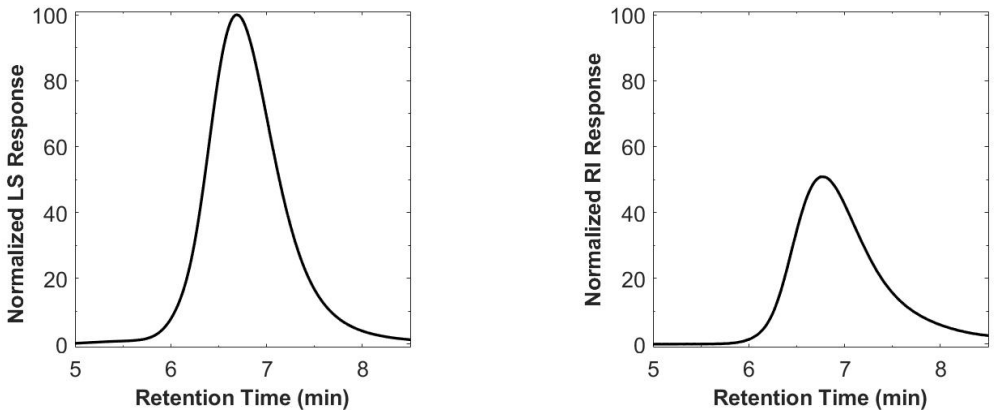

Fig. S214 GPC spectrum of PIP 50 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table S3**, entry 1 (12 h): (left) LS; (right) RI.

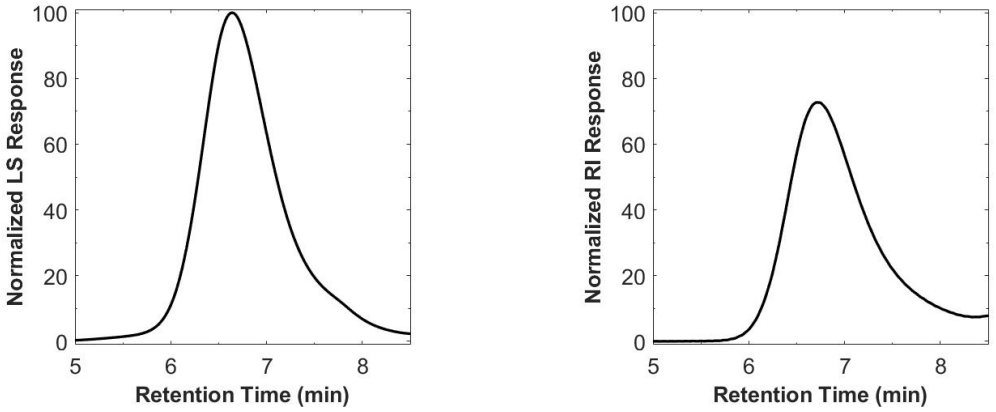

Fig. S215 GPC spectrum of PIP-*b*-PCL 50:50 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table S3**, entry 2: (left) LS; (right) RI.

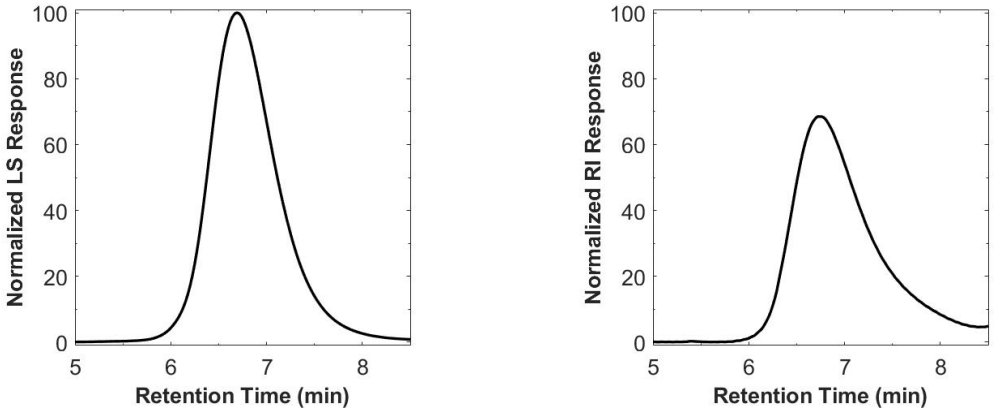

Fig. S216 GPC spectrum of recovered PIP 50 equivalents after hydrolysis of PIP-*b*-PCL 50:50 from **Table S3**, entry 3 (12 h): (left) LS; (right) RI.

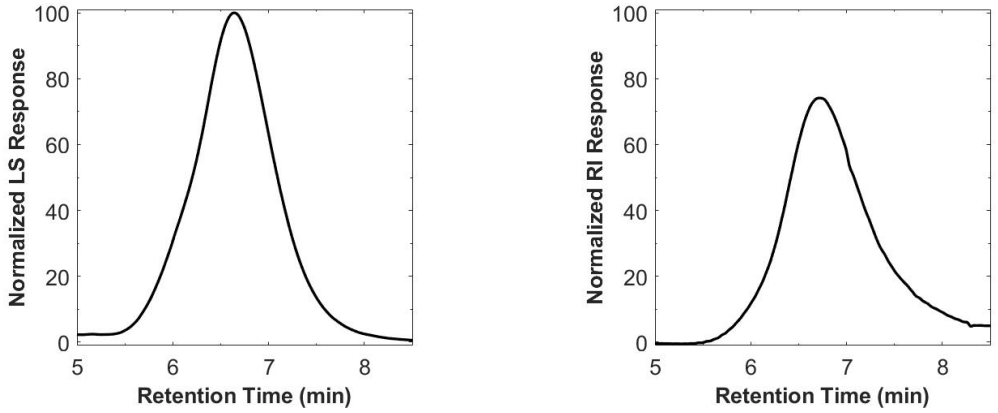

Fig. S217 GPC spectrum of repolymerized PIP-*b*-PCL 50:50 equivalents generated by **Y[N(SiMe$_3$)$_2$]$_3$** from **Table S3**, entry 4 (6 h): (left) LS; (right) RI.

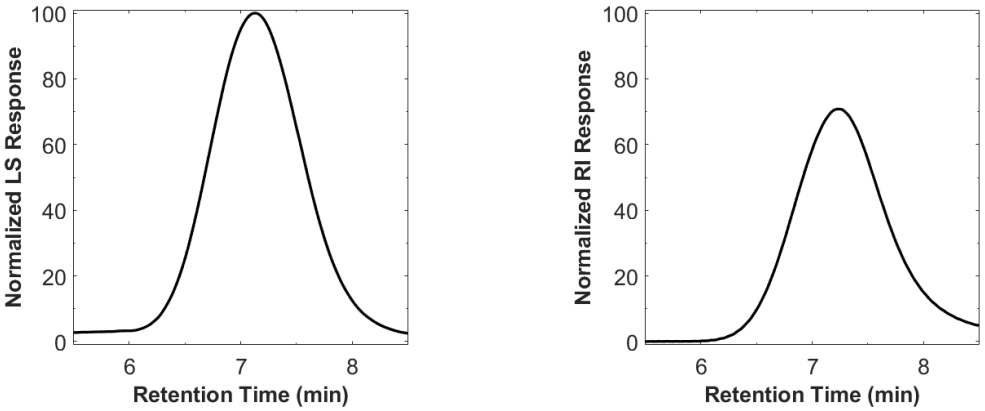

Fig. S218 GPC spectrum of PIP-*b*-PCL 50:50 equivalents generated by **6**/[Ph_3C][$B(C_6F_5)_4$] (1 mL of toluene) from **Table S3**, entry 5: (left) LS; (right) RI.

6.0 Thermogravimetric Analysis (TGA) of Isolated Polymers

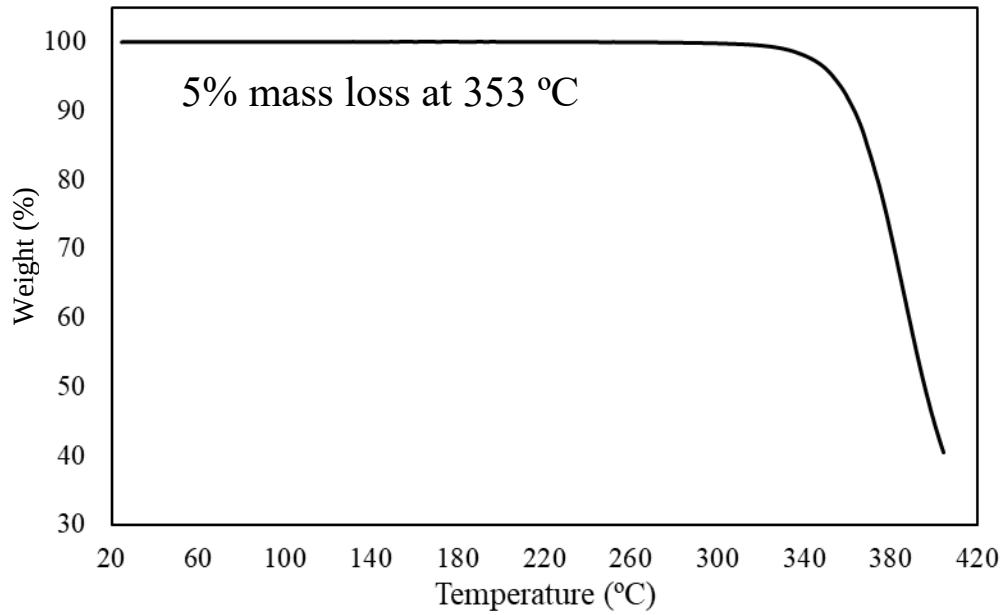

Fig. S219 TGA curve of PIP 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 1**, entry 1a (12 h).

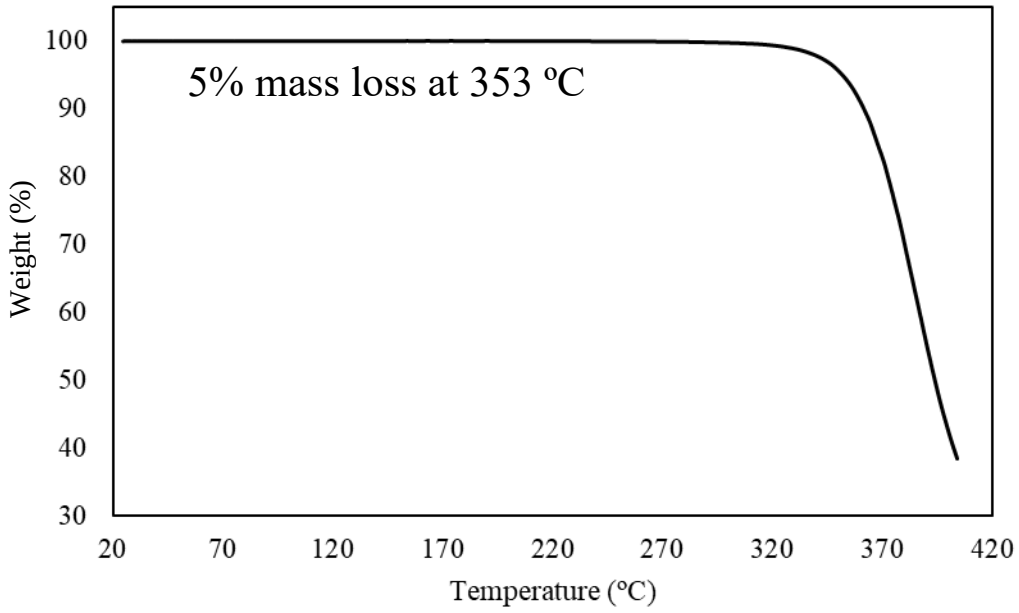

Fig. S220 TGA curve of PIP 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 1**, entry 1b (12 h).

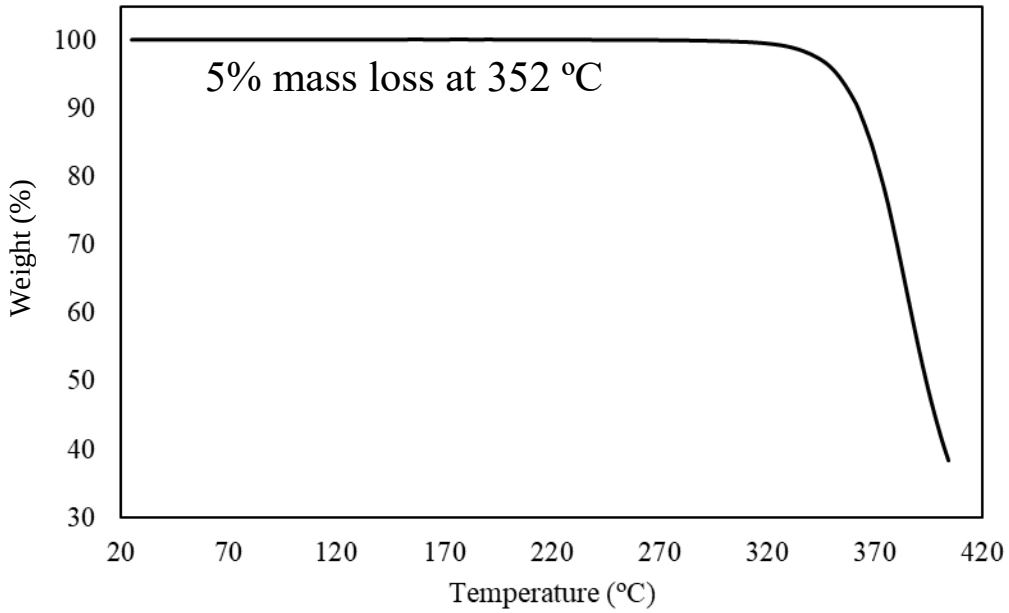

Fig. S221 TGA curve of PIP 800 equivalents generated by **6**/[Ph_3C][$B(C_6F_5)_4$] from **Table 1**, entry 1c (12 h).

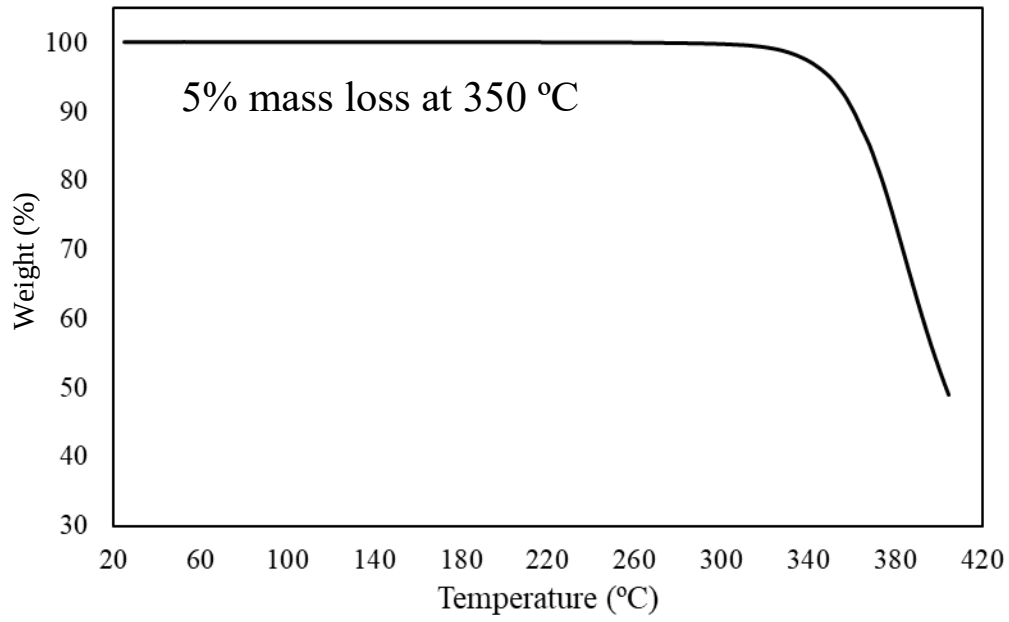

Fig. S222 TGA curve of PIP 800 equivalents generated by **8**/[Ph_3C][$B(C_6F_5)_4$] from **Table 1**, entry 3 (12 h).

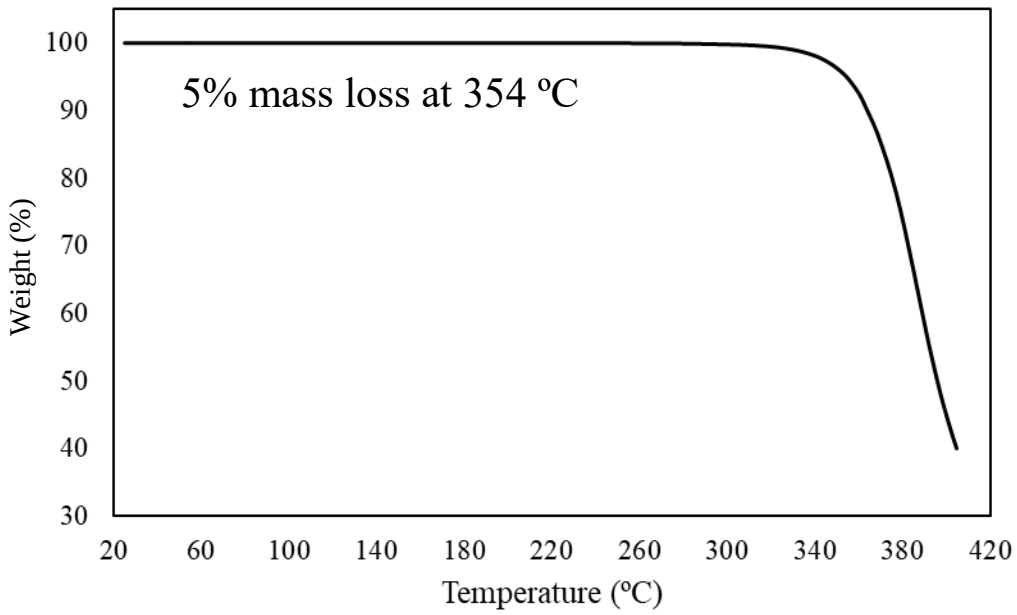

Fig. S223 TGA curve of PIP 800 equivalents generated by **6**/[Ph_3C][$B(C_6F_5)_4$] from **Table 1**, entry 4 (24 h).

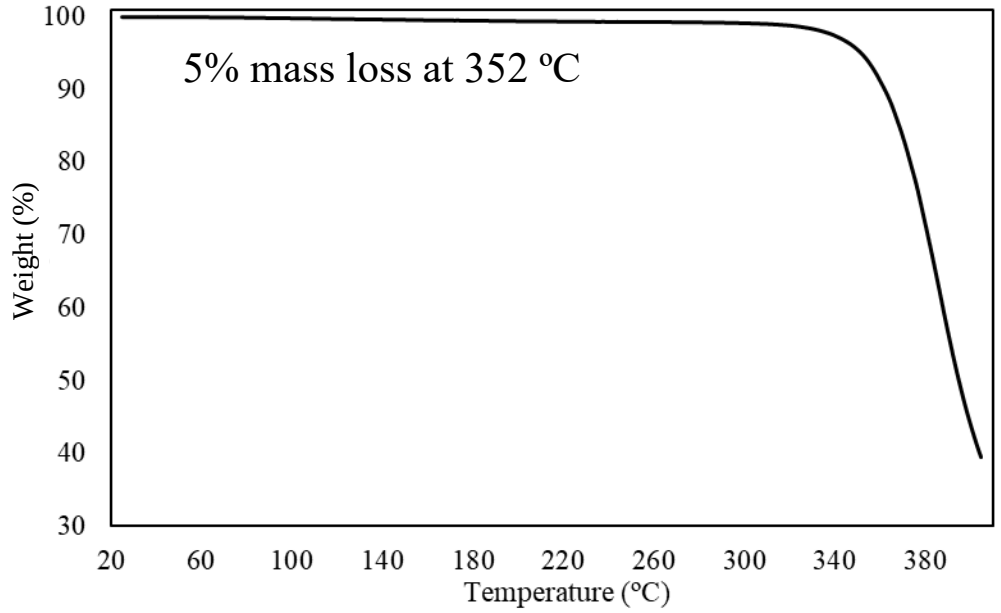

Fig. S224 TGA curve of PIP 800 equivalents generated by **6**/[Ph_3C][$B(C_6F_5)_4$] from **Table 1**, entry 5 (30 min).

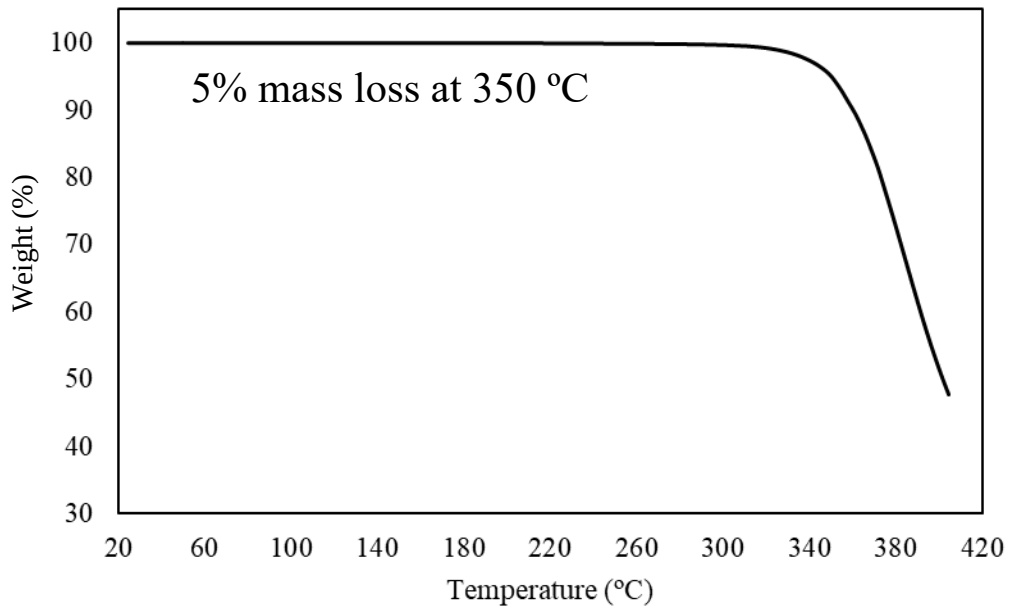

Fig. S225 TGA curve of PIP 800 equivalents generated by **8/**$[Ph_3C][B(C_6F_5)_4]$ from **Table 1**, entry 6 (30 min).

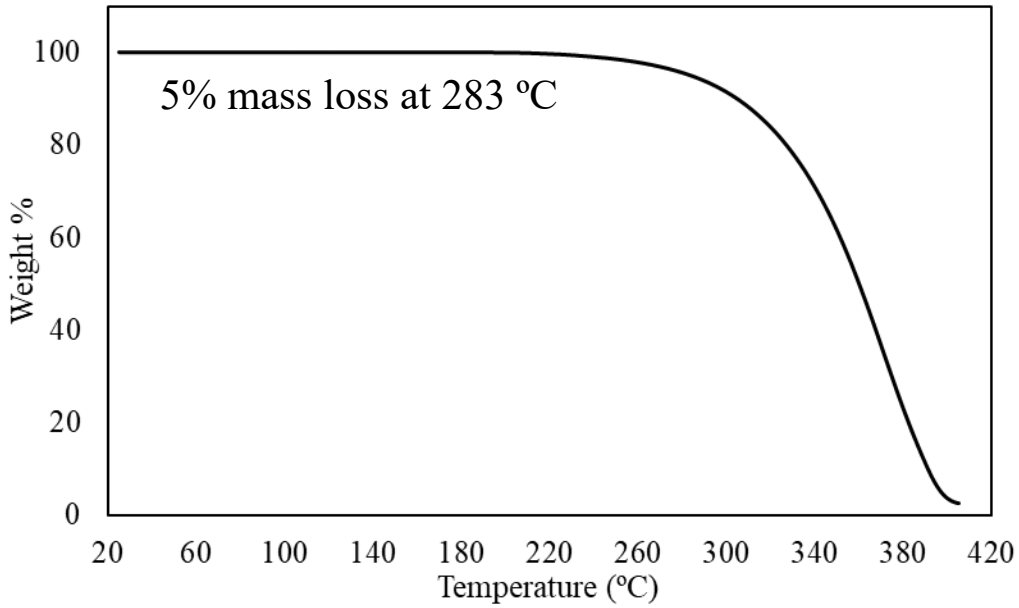

Fig. S226 TGA curve of PCL 300 equivalents generated by **6/**$[Ph_3C][B(C_6F_5)_4]$ from **Table 1**, entry 7 (10 min).

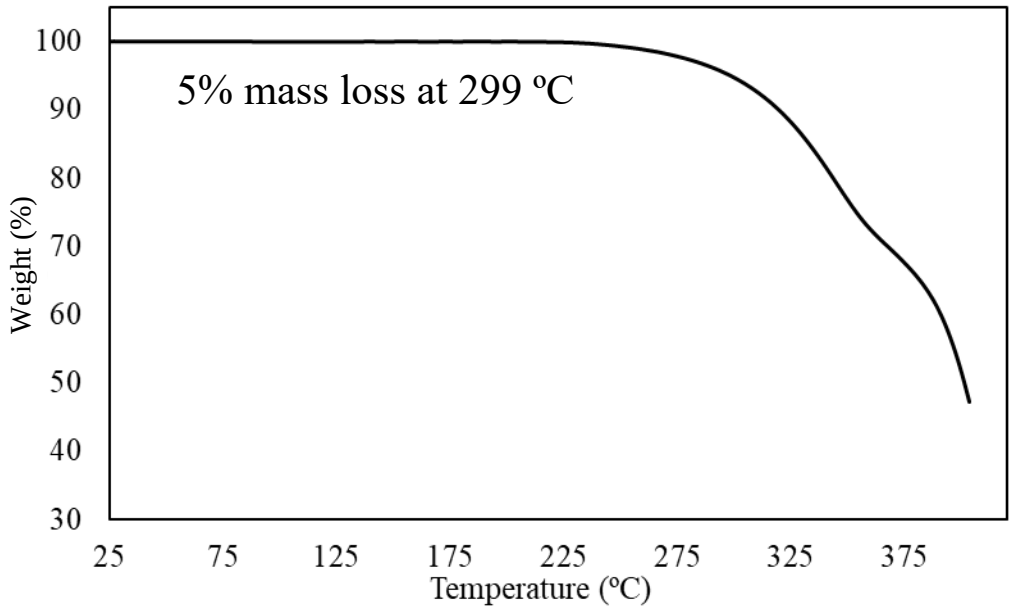

Fig. S227 TGA curve of PCL 300 equivalents generated by **8**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 1**, entry 8 (10 min).

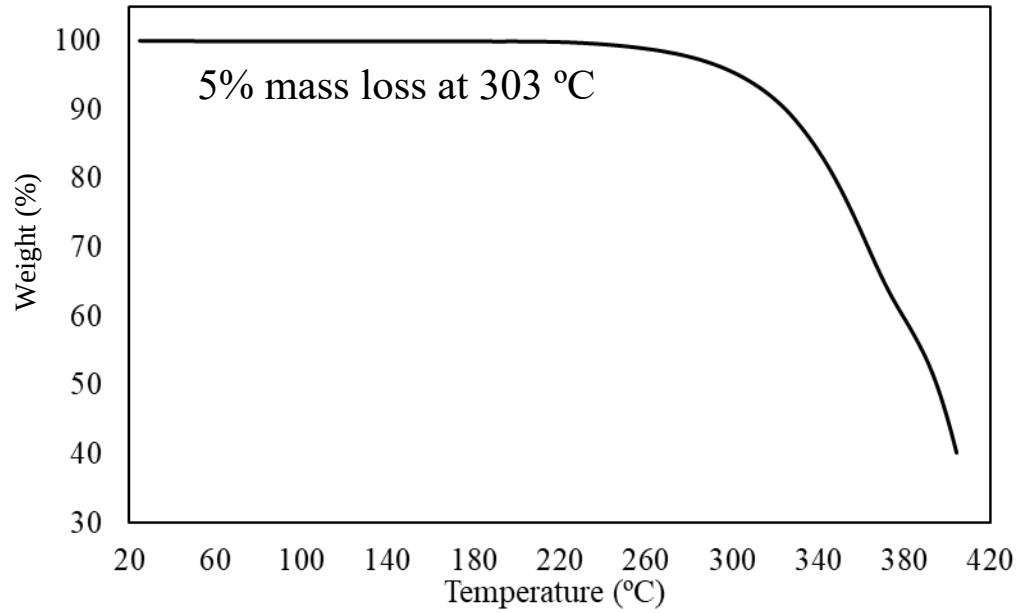

Fig. S228 TGA curve of PCL 300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 1**, entry 9a (2 h).

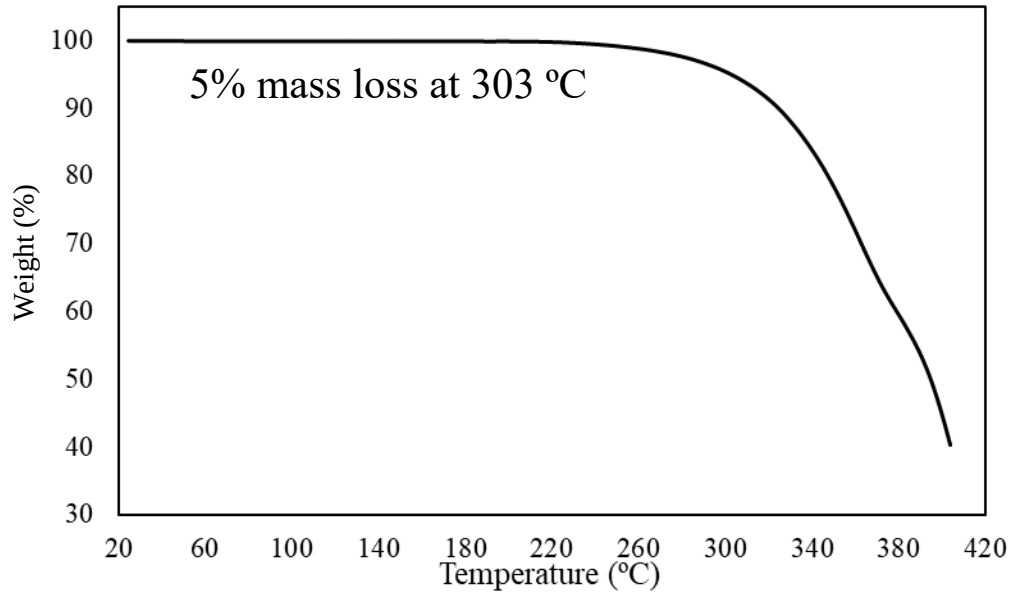

Fig. S229 TGA curve of PCL 300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 1**, entry 9b (2 h).

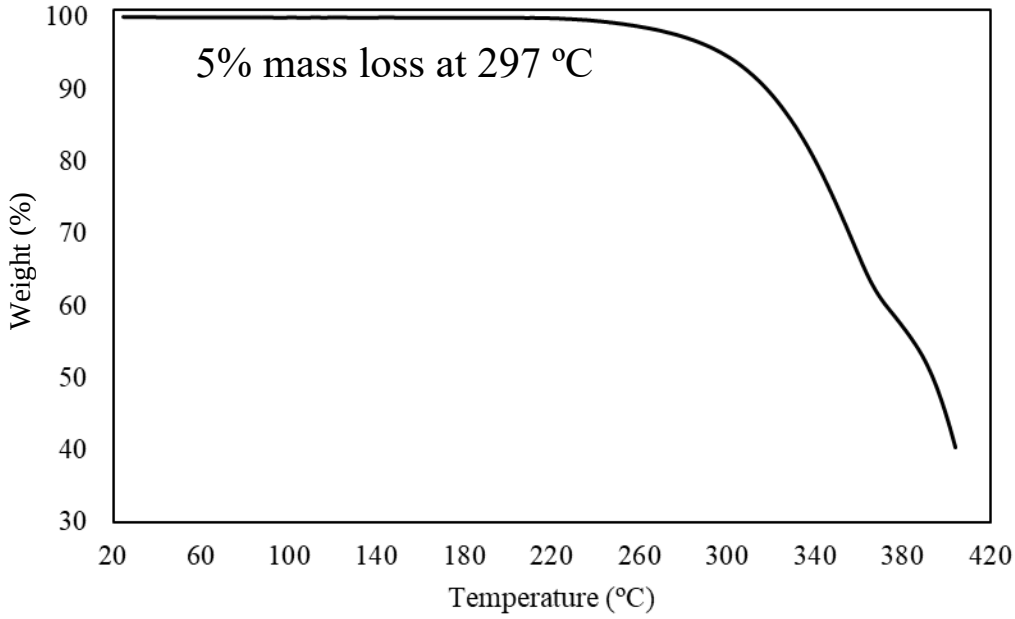

Fig. S230 TGA curve of PCL 300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 1**, entry 9c (2 h).

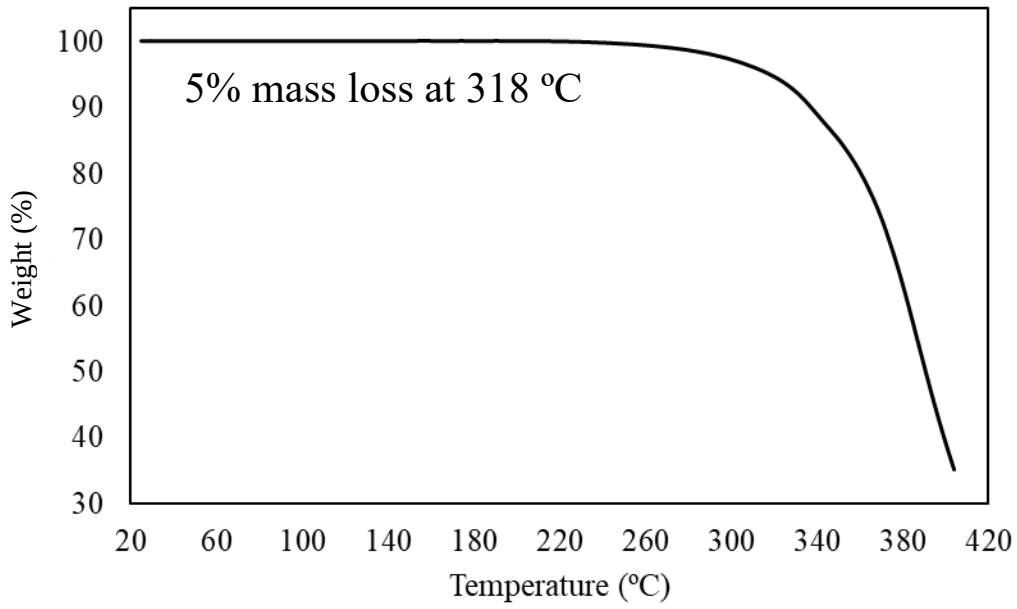

Fig. S231 TGA curve of PIP-*b*-PCL 800:300 equivalents generated by **6**/[Ph_3C][$B(C_6F_5)_4$] from **Table 2**, entry 1a.

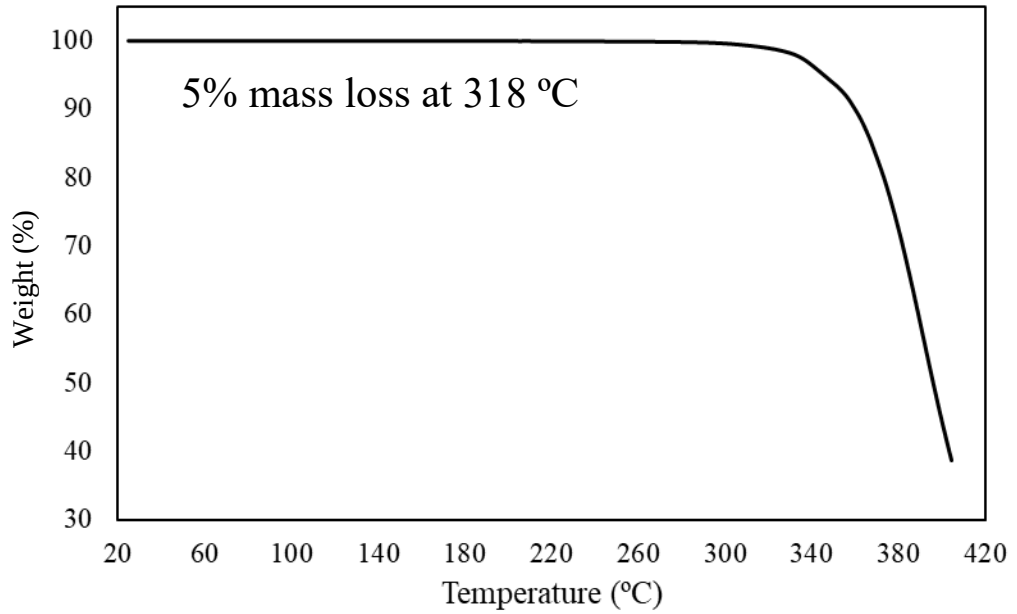

Fig. S232 TGA curve of PIP-*b*-PCL 800:300 equivalents generated by **6**/[Ph_3C][$B(C_6F_5)_4$] from **Table 2**, entry 1b.

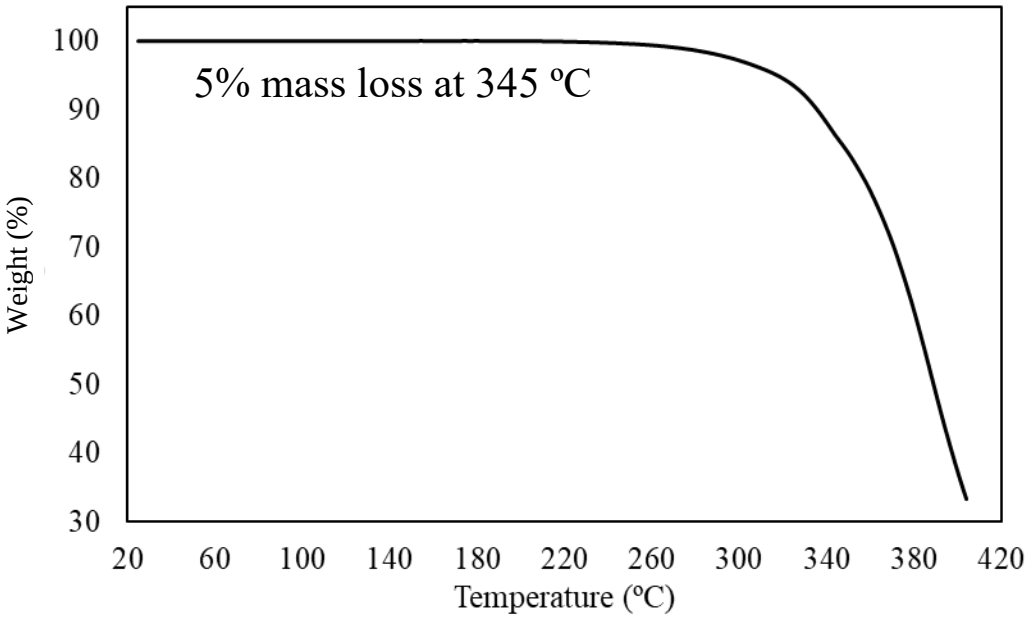

Fig. S233 TGA curve of PIP-*b*-PCL 800:300 equivalents generated by **6**/[Ph_3C][$B(C_6F_5)_4$] from **Table 2**, entry 1c.

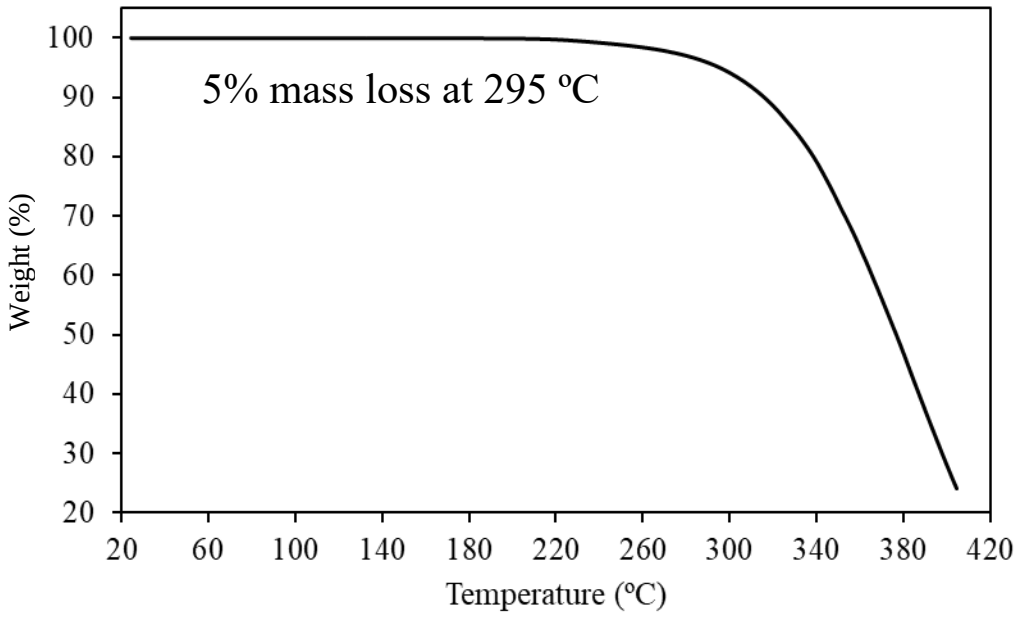

Fig. S234 TGA curve of PIP-*b*-PCL 550:550 equivalents generated by **6**/[Ph_3C][$B(C_6F_5)_4$] from **Table 2**, entry 2a.

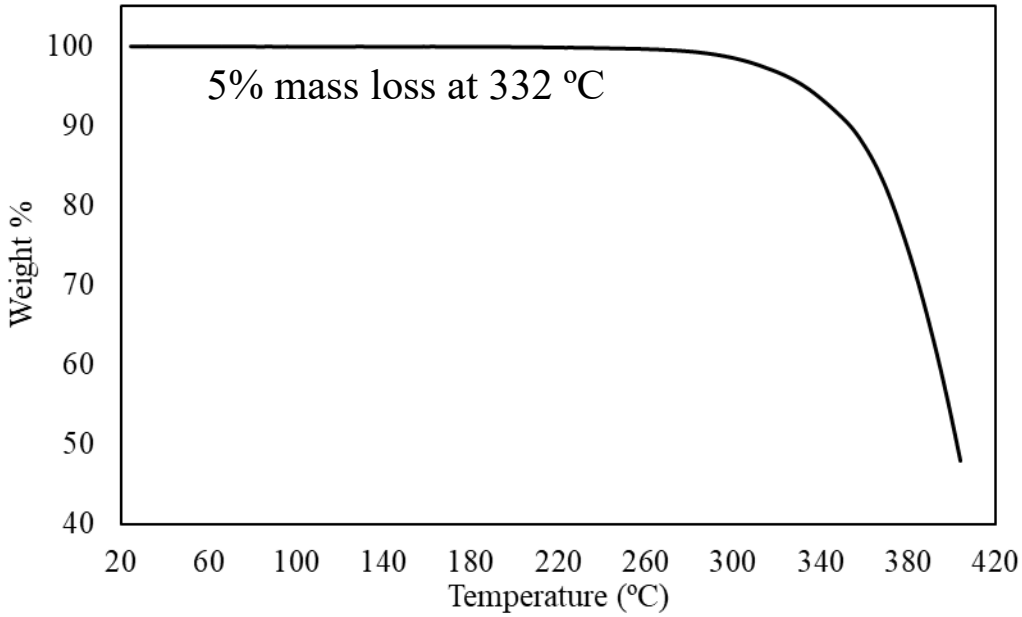

Fig. S235 TGA curve of PIP-*b*-PCL 550:550 equivalents generated by **6**/[Ph_3C][$B(C_6F_5)_4$] from **Table 2**, entry 2b.

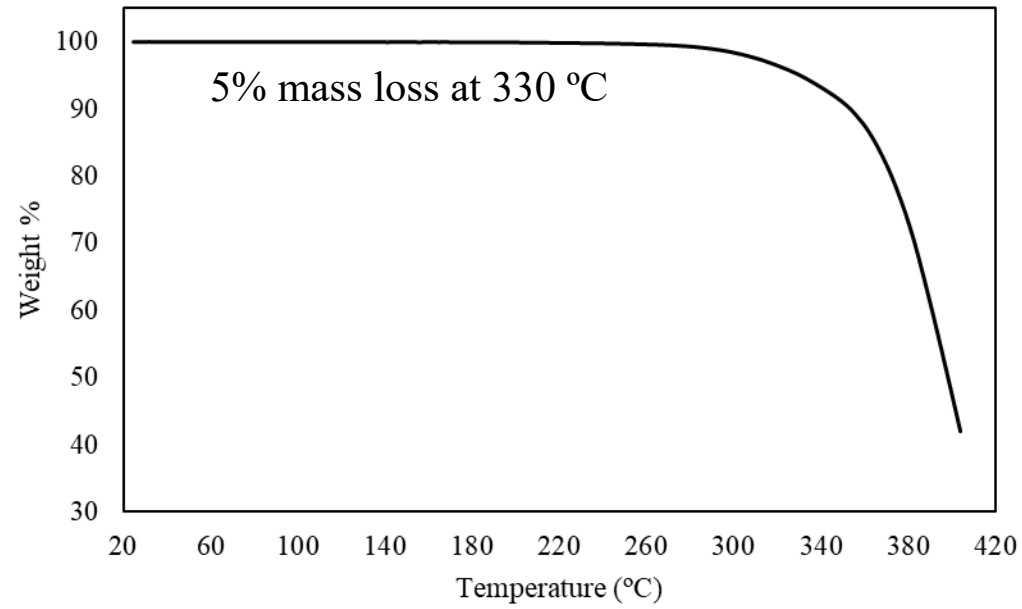

Fig. S236 TGA curve of PIP-*b*-PCL 550:550 equivalents generated by **6**/[Ph_3C][$B(C_6F_5)_4$] from **Table 2**, entry 2c.

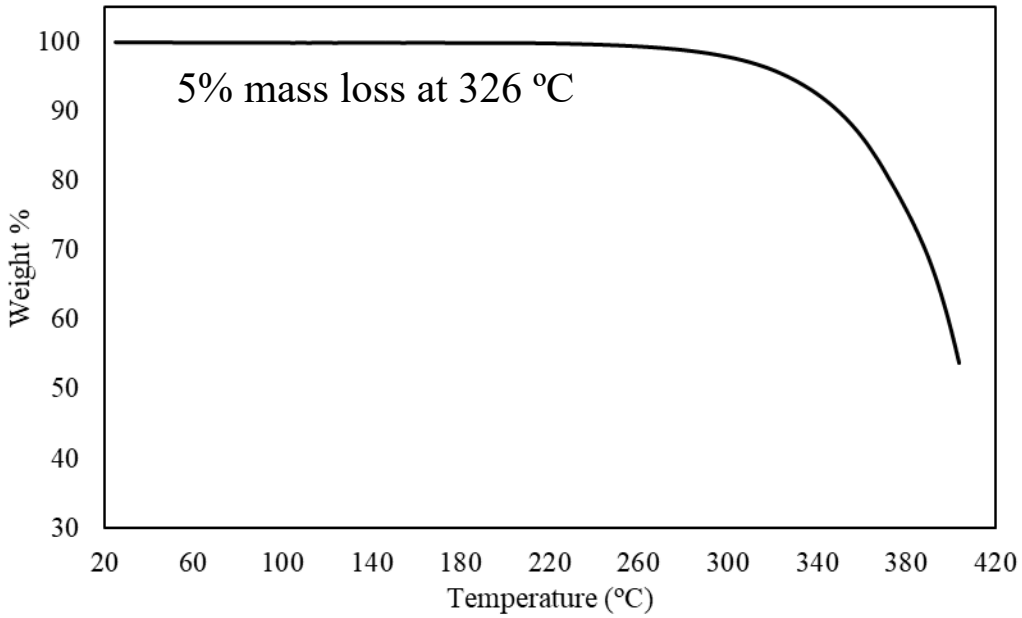

Fig. S237 TGA curve of PIP-*b*-PCL 300:800 equivalents generated by **6**/[Ph_3C][$B(C_6F_5)_4$] from **Table 2**, entry 3a.

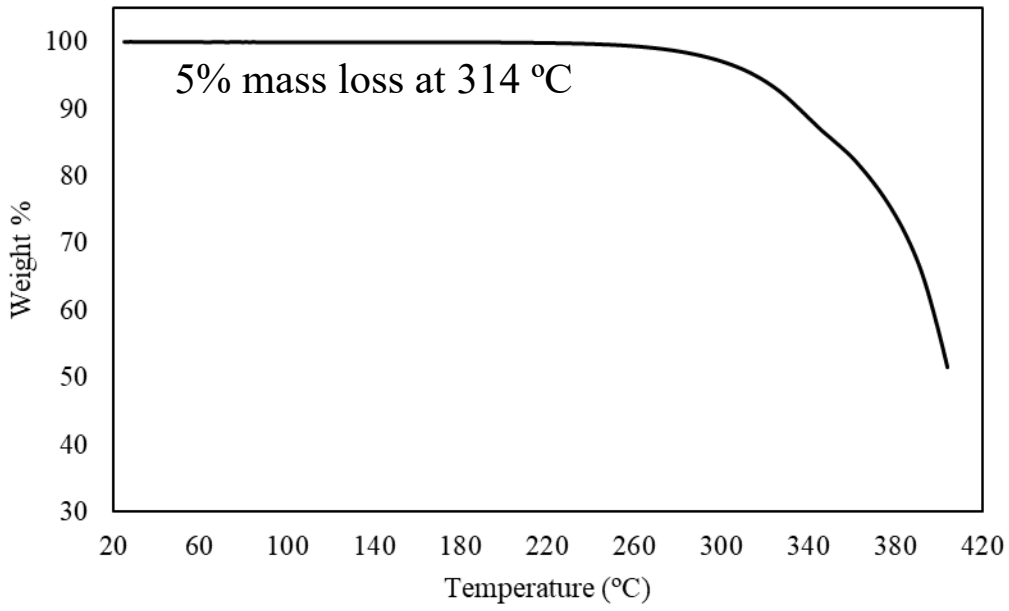

Fig. S238 TGA curve of PIP-*b*-PCL 300:800 equivalents generated by **6**/[Ph_3C][$B(C_6F_5)_4$] from **Table 2**, entry 3b.

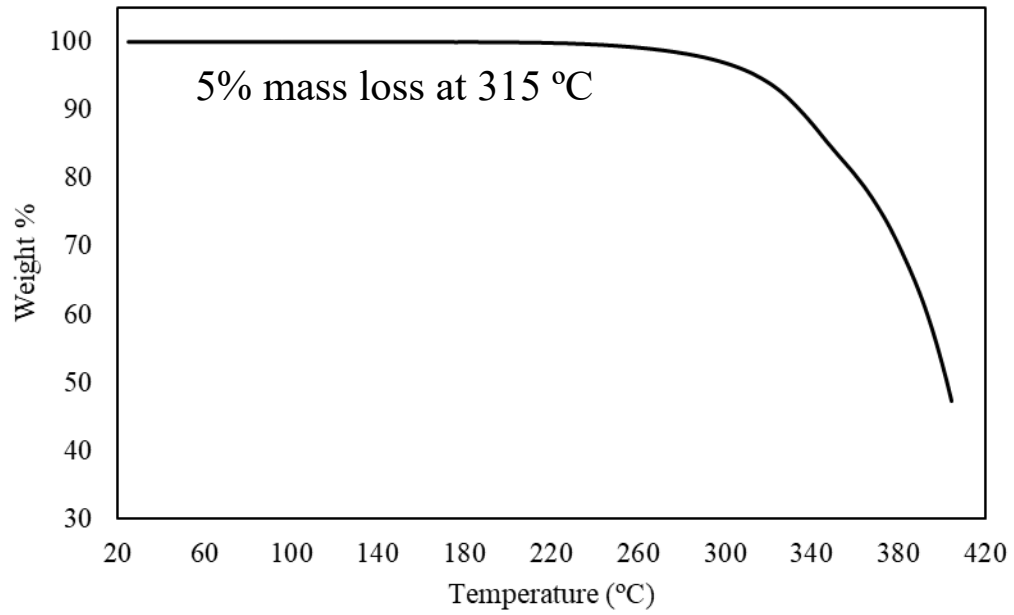

Fig. S239 TGA curve of PIP-*b*-PCL 300:800 equivalents generated by **6**/[Ph_3C][$B(C_6F_5)_4$] from **Table 2** entry 3c.

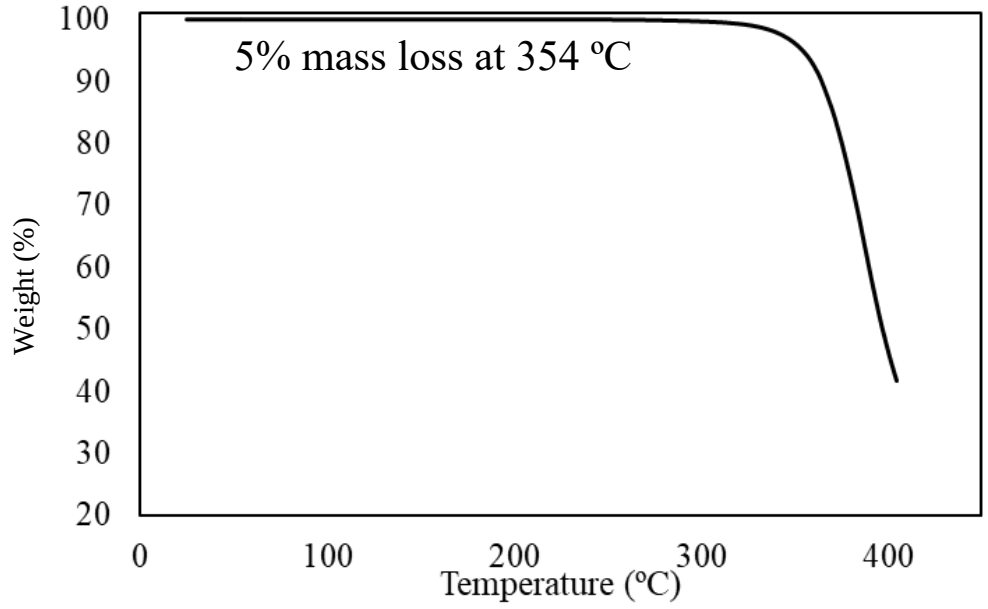

Fig. S240 TGA curve of PIP 800 equivalents generated by **6**/[Ph_3C][$B(C_6F_5)_4$] from **Table 3**, entry 1a (IP addition time 0 min).

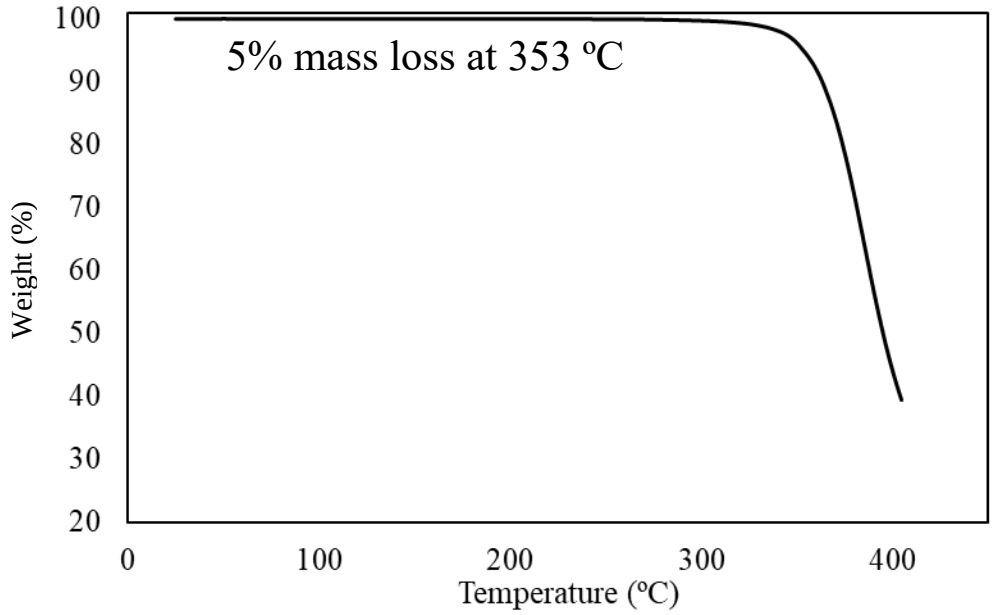

Fig. S241 TGA curve of PIP 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 3**, entry 1b (IP addition time 0 min).

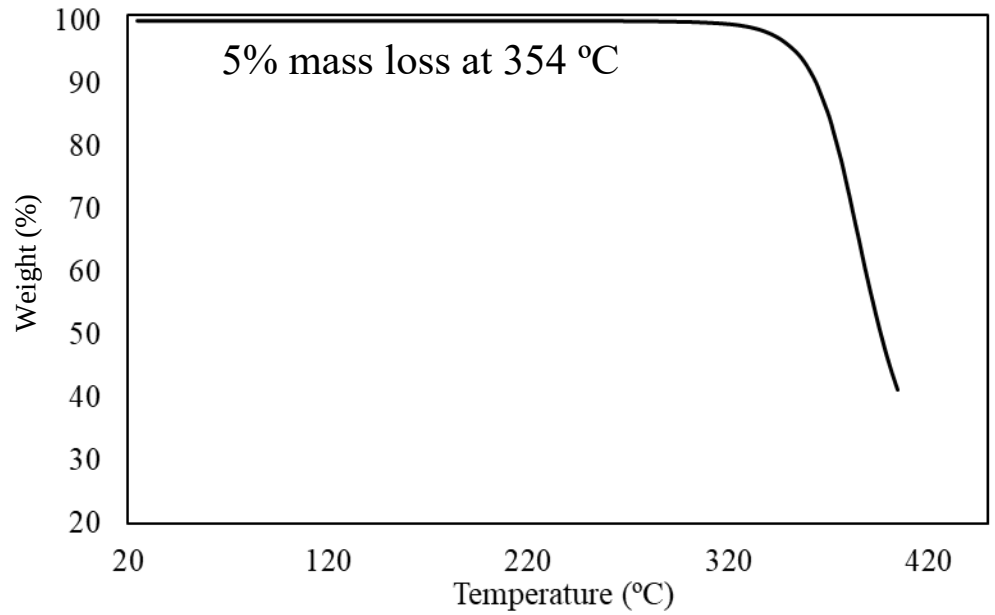

Fig. S242 TGA curve of PIP 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 3**, entry 1c (IP addition time 0 min).

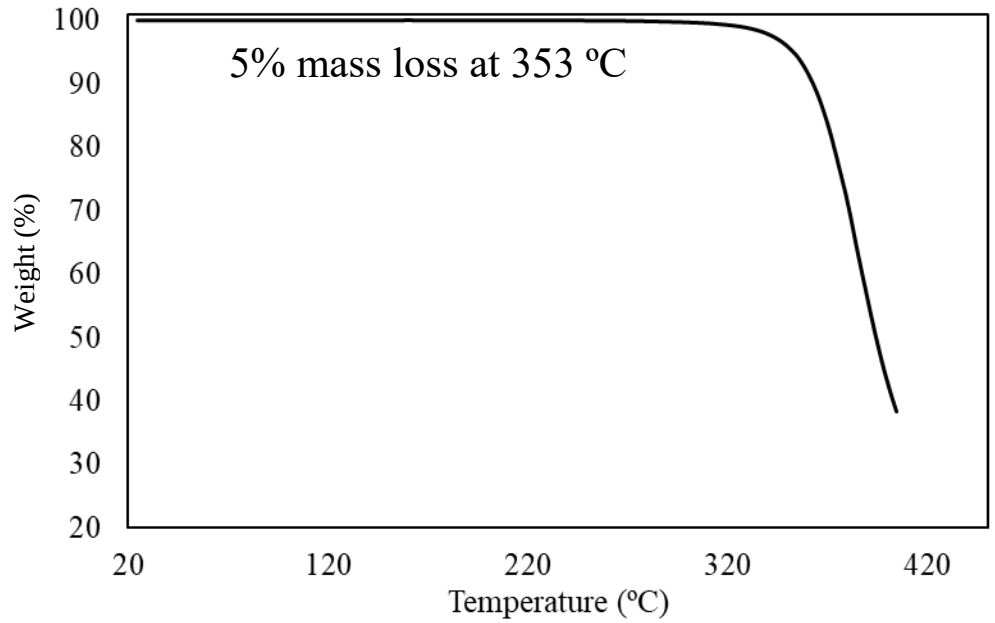

Fig. S243 TGA curve of PIP 800 equivalents generated by **6**/[Ph_3C][$B(C_6F_5)_4$] from **Table 3**, entry 2a (IP addition time 30 min).

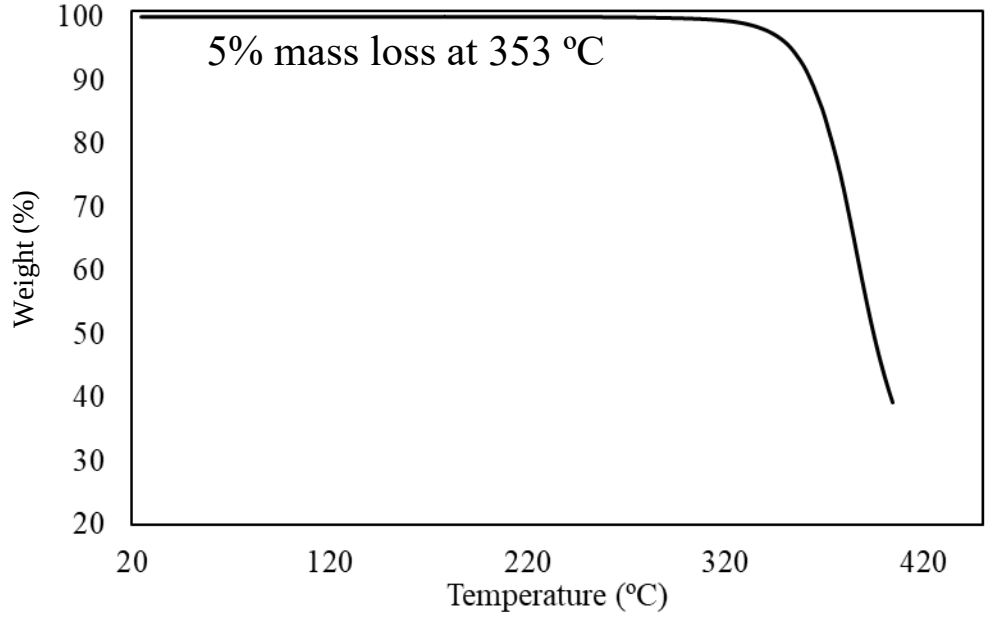

Fig. S244 TGA curve of PIP 800 equivalents generated by **6**/[Ph_3C][$B(C_6F_5)_4$] from **Table 3**, entry 2b (IP addition time 30 min).

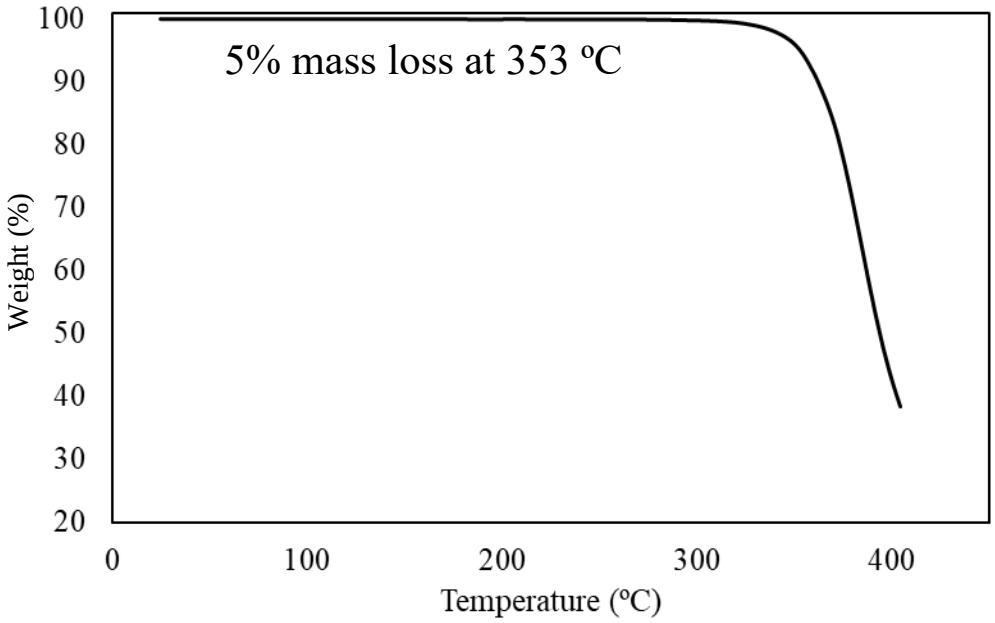

Fig. S245 TGA curve of PIP 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 3**, entry 2c (IP addition time 30 min).

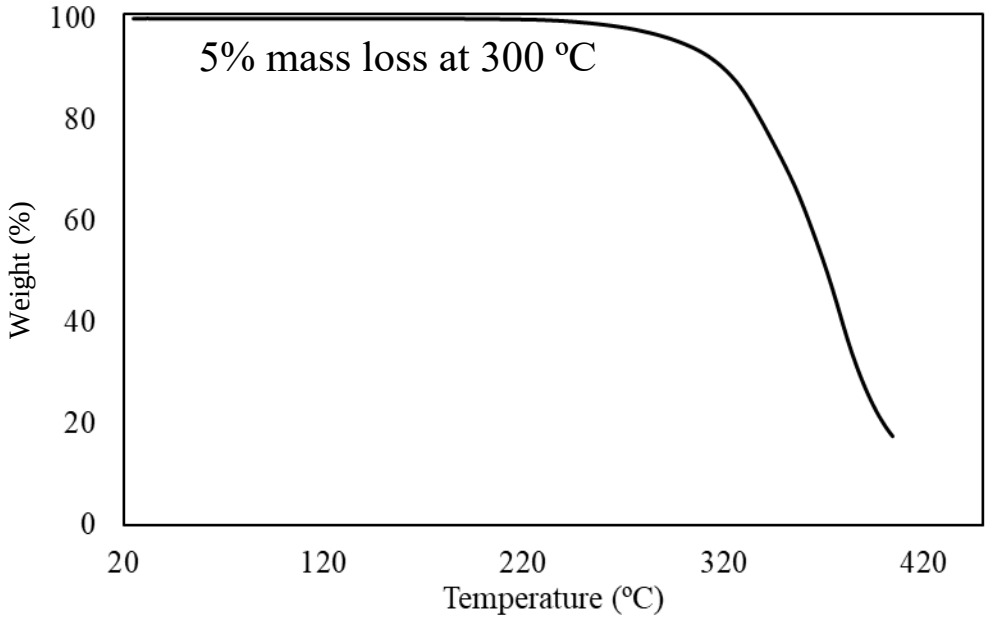

Fig. S246 TGA curve of PIP-*b*-PCL 800:300 equivalents generated by **6** and 0.5 equivalents of $[Ph_3C][B(C_6F_5)_4]$ from **Table 3**, entry 3a.

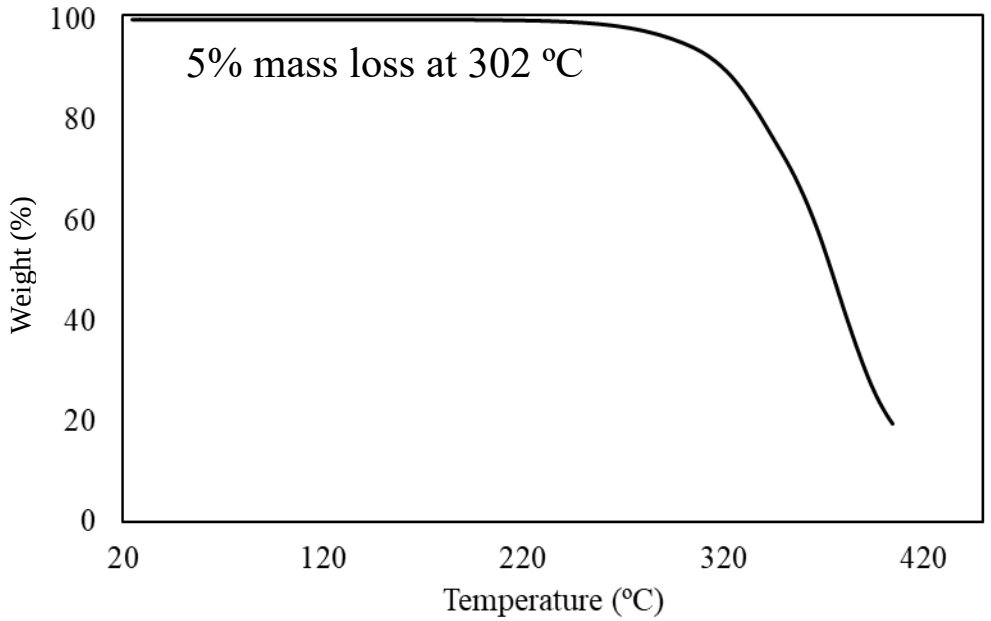

Fig. S247 TGA curve of PIP-*b*-PCL 800:300 equivalents generated by **6** and 0.5 equivalents of $[Ph_3C][B(C_6F_5)_4]$ from **Table 3**, entry 3b.

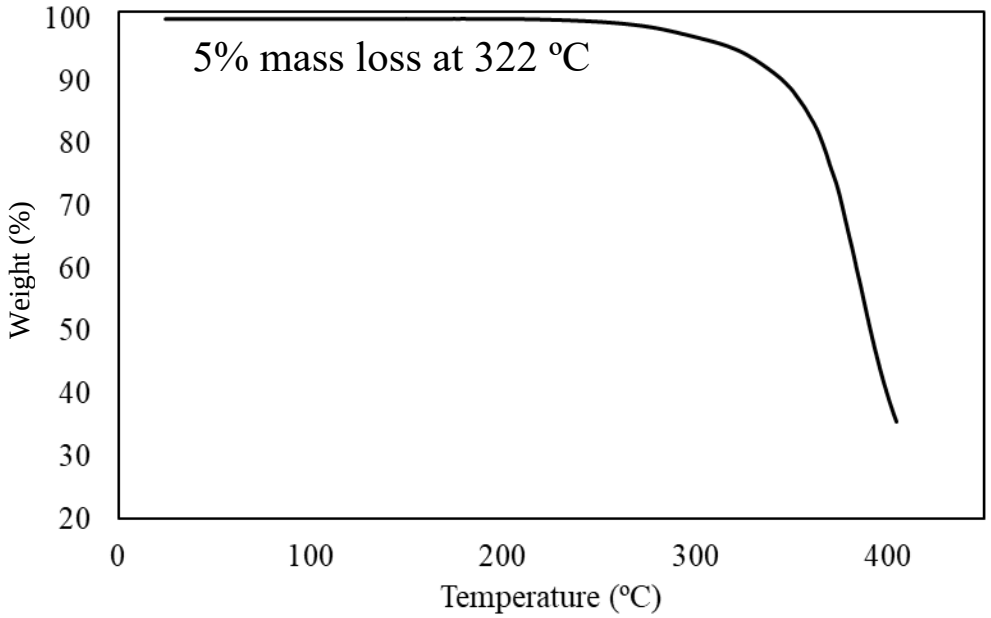

Fig. S248 TGA curve of PIP-*b*-PCL 800:300 equivalents generated by **6** and 0.5 equivalents of $[Ph_3C][B(C_6F_5)_4]$ from **Table 3**, entry 3c.

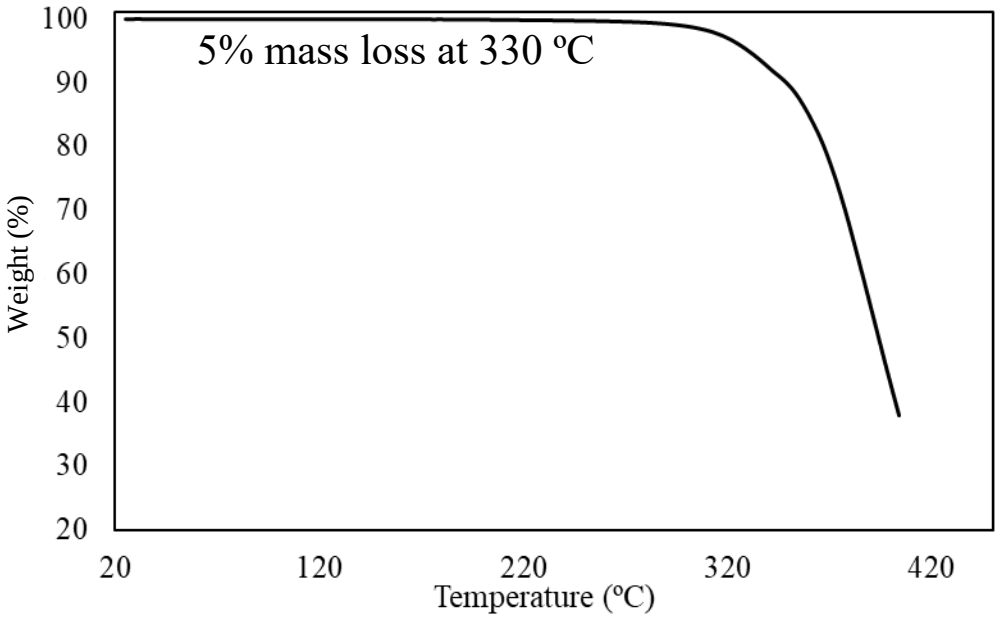

Fig. S249 TGA curve of PIP-*b*-PCL 800:300 equivalents generated by **6** and 1.5 equivalents of $[Ph_3C][B(C_6F_5)_4]$ from **Table 3**, entry 4a.

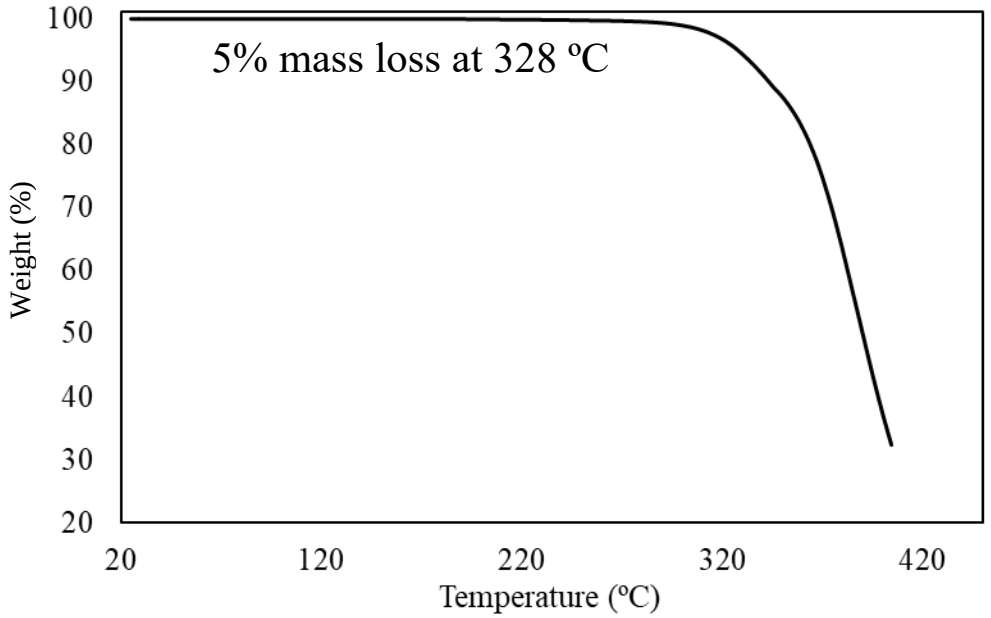

Fig. S250 TGA curve of PIP-*b*-PCL 800:300 equivalents generated by **6** and 1.5 equivalents of $[Ph_3C][B(C_6F_5)_4]$ from **Table 3**, entry 4b.

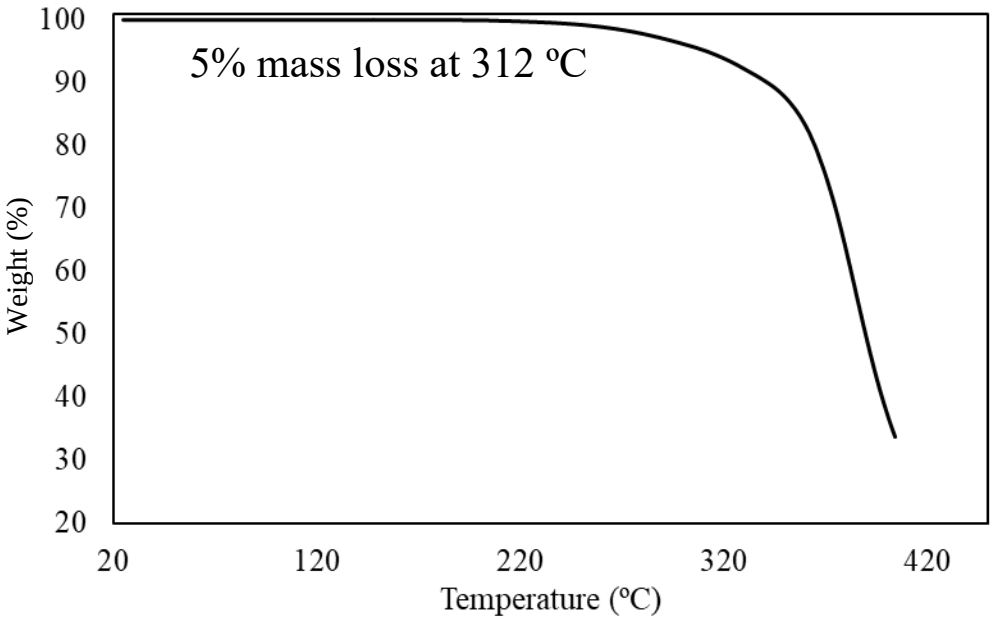

Fig. S251 TGA curve of PIP-*b*-PCL 800:300 equivalents generated by **6** and 1.5 equivalents of $[Ph_3C][B(C_6F_5)_4]$ from **Table 3**, entry 4c.

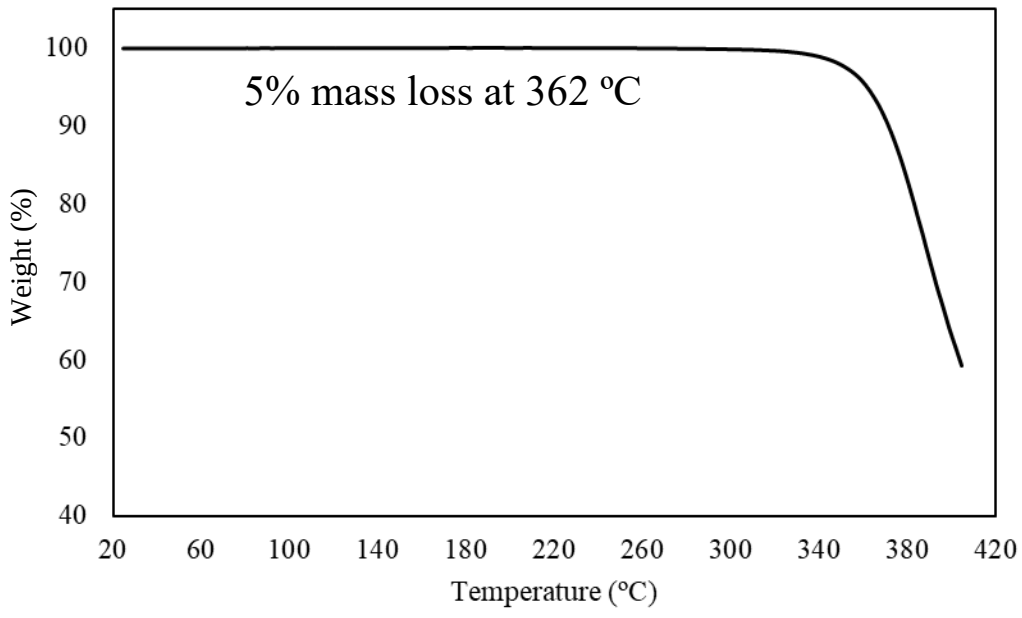

Fig. S252 TGA curve of PMyr 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 4**, entry 1 (30 min).

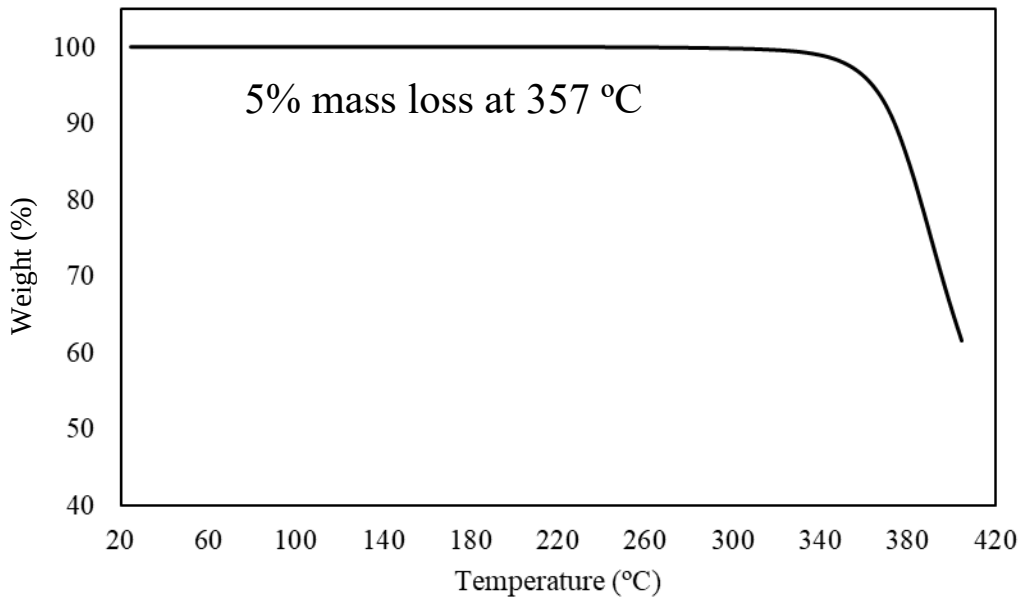

Fig. S253 TGA curve of PMyr 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 4**, entry 2 (90 min).

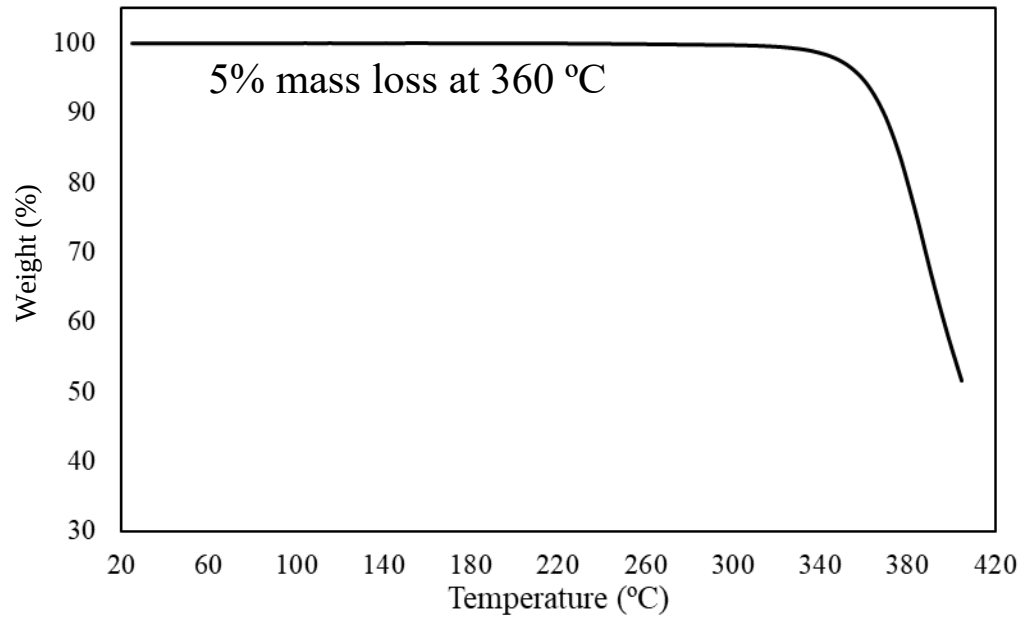

Fig. S254 TGA curve of PMyr 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 4**, entry 3 (3 h).

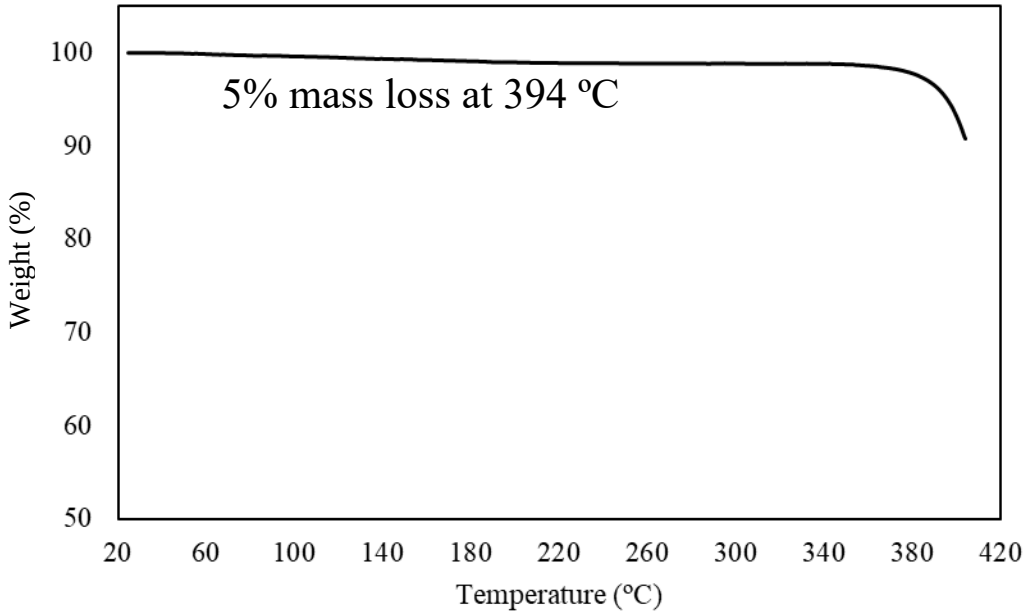

Fig. S255 TGA curve of PS 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 4**, entry 4 (30 min).

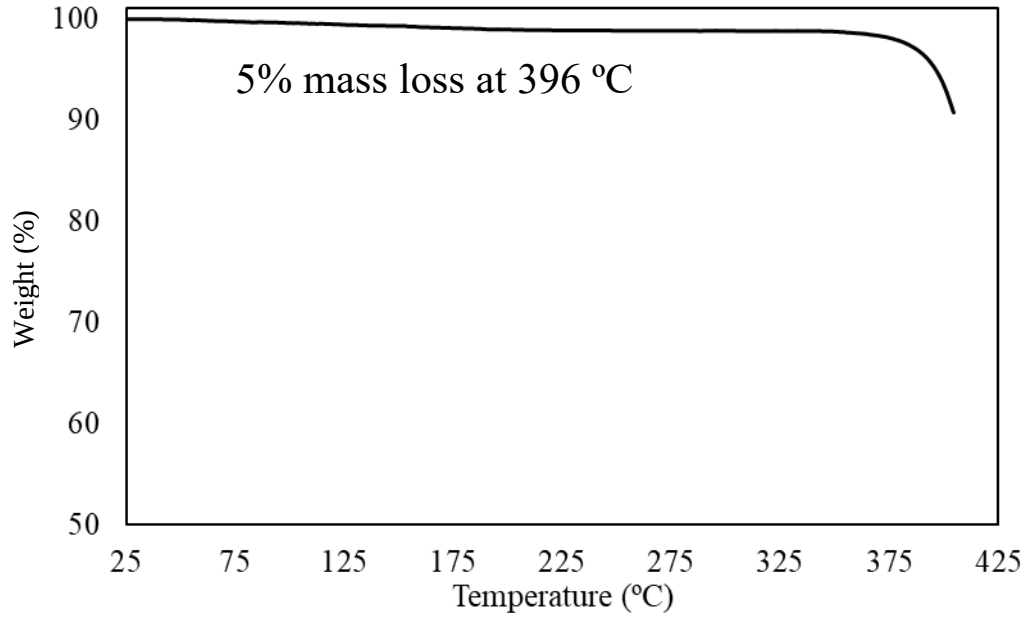

Fig. S256 TGA curve of PS 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 4**, entry 5 (20 h).

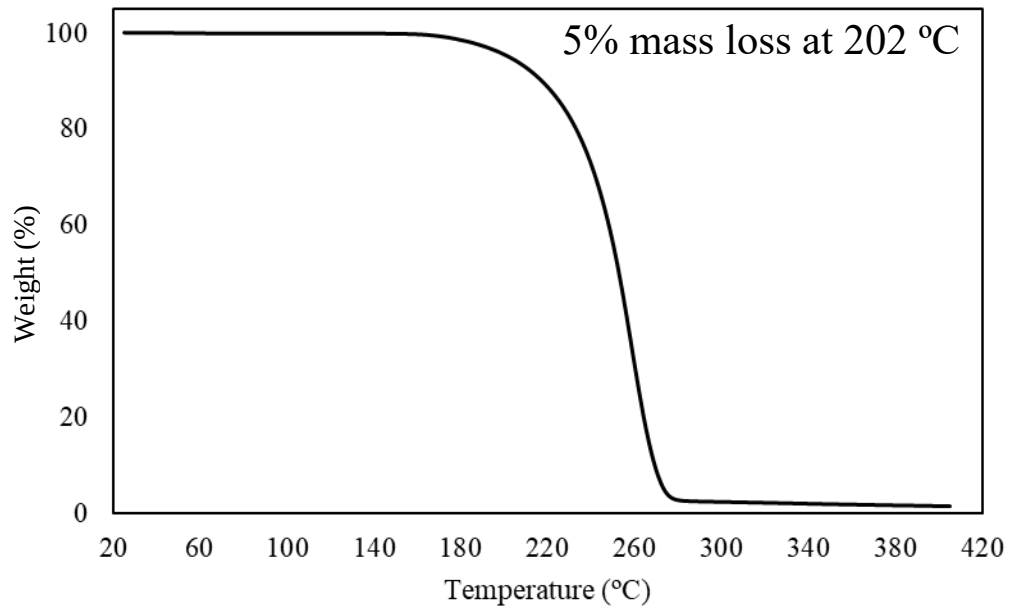

Fig. S257 TGA curve of PVL 300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 4**, entry 6 (10 min).

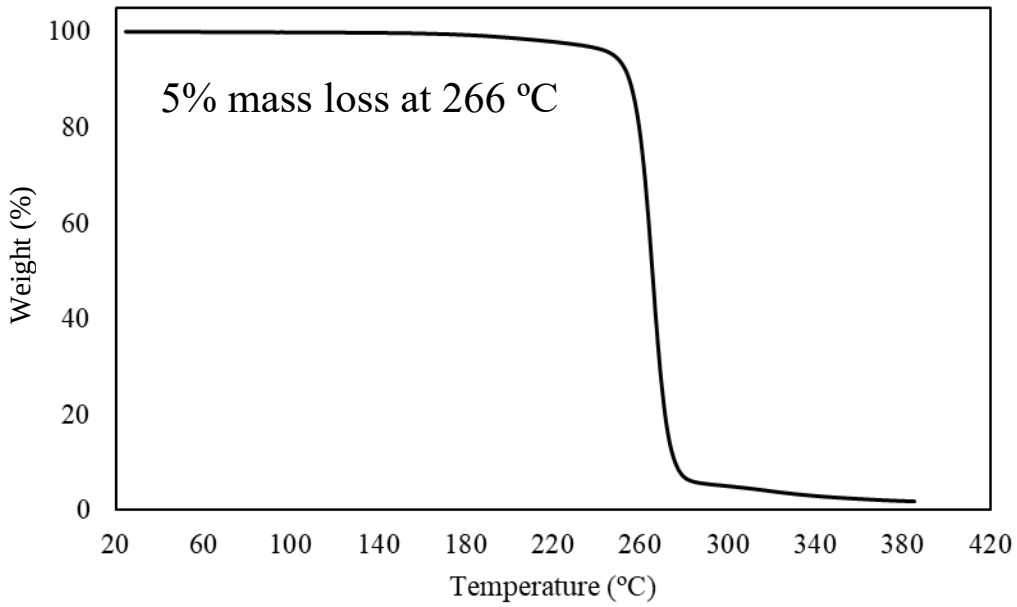

Fig. S258 TGA curve of PDL 300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 4**, entry 7 (6 h).

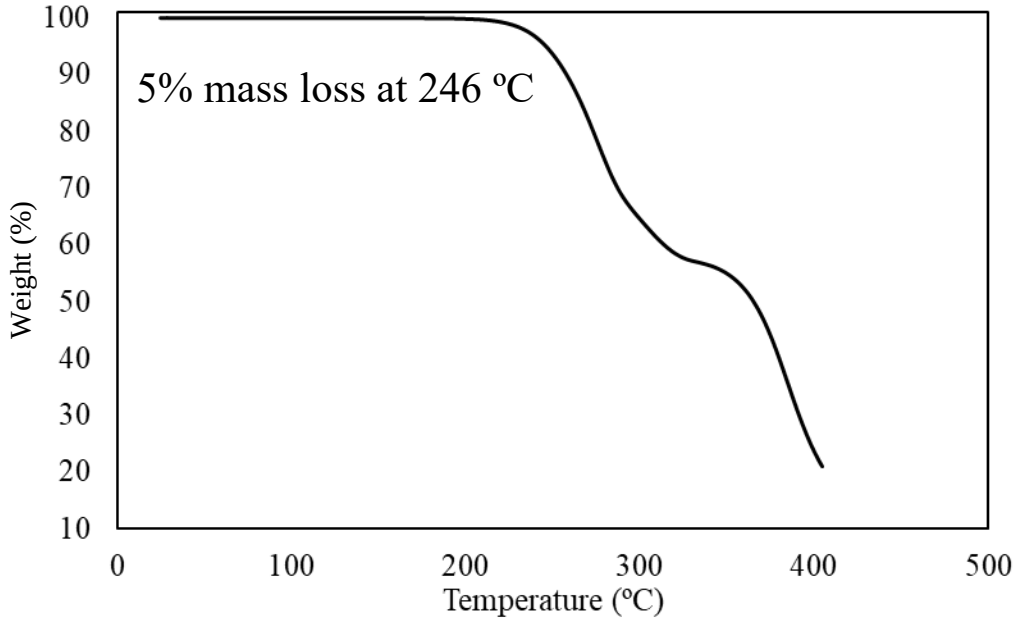

Fig. S259 TGA curve of PIP-*b*-PVL 800:300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 5**, entry 1.

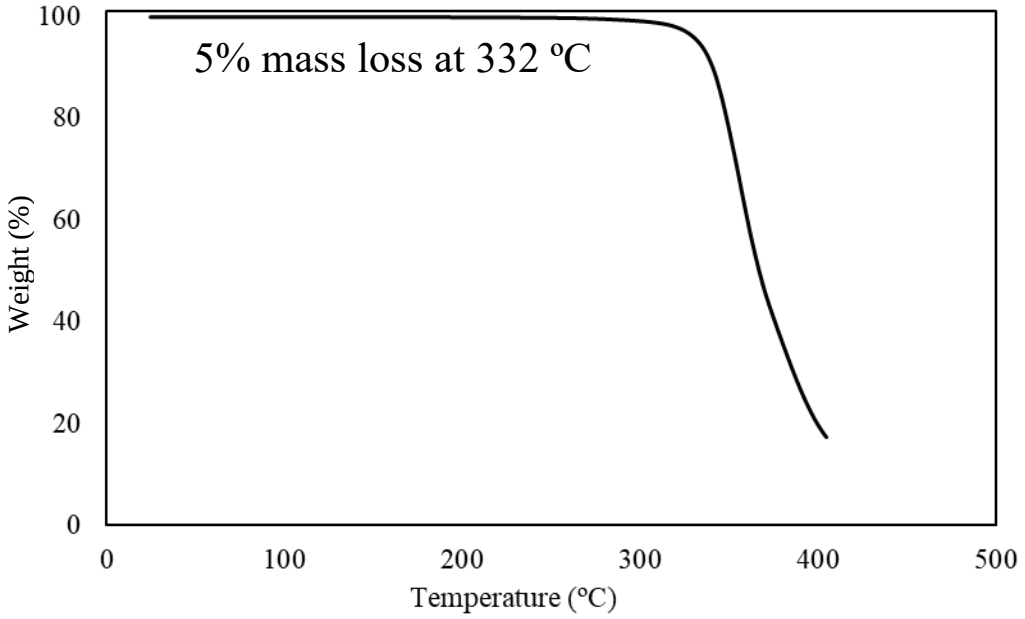

Fig. S260 TGA curve of PIP-*b*-PDL 800:300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 5**, entry 2.

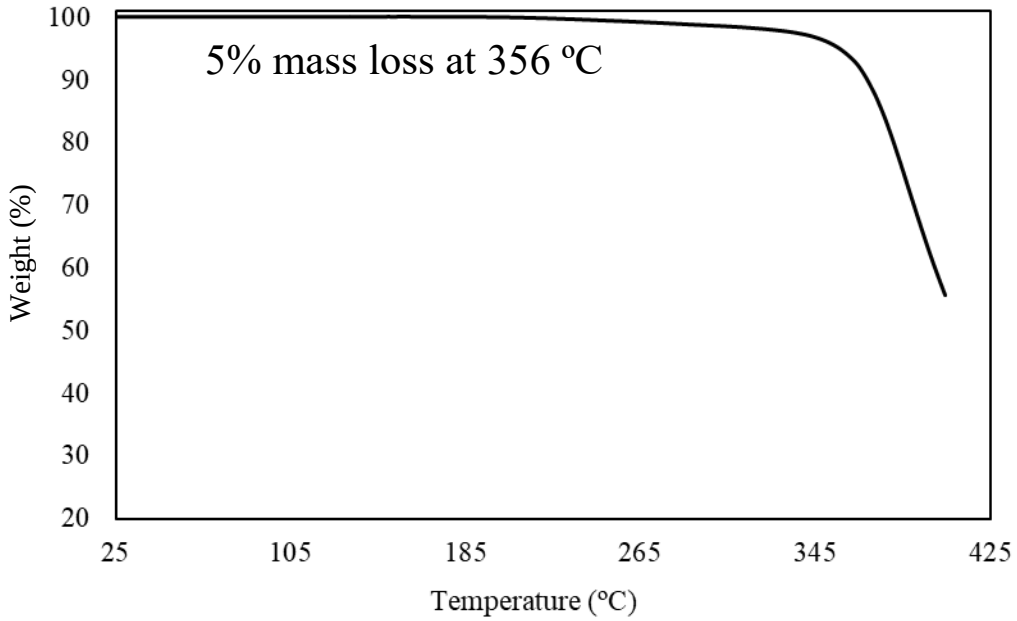

Fig. S261 TGA curve of PMyr-*b*-PCL 800:300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 5**, entry 3.

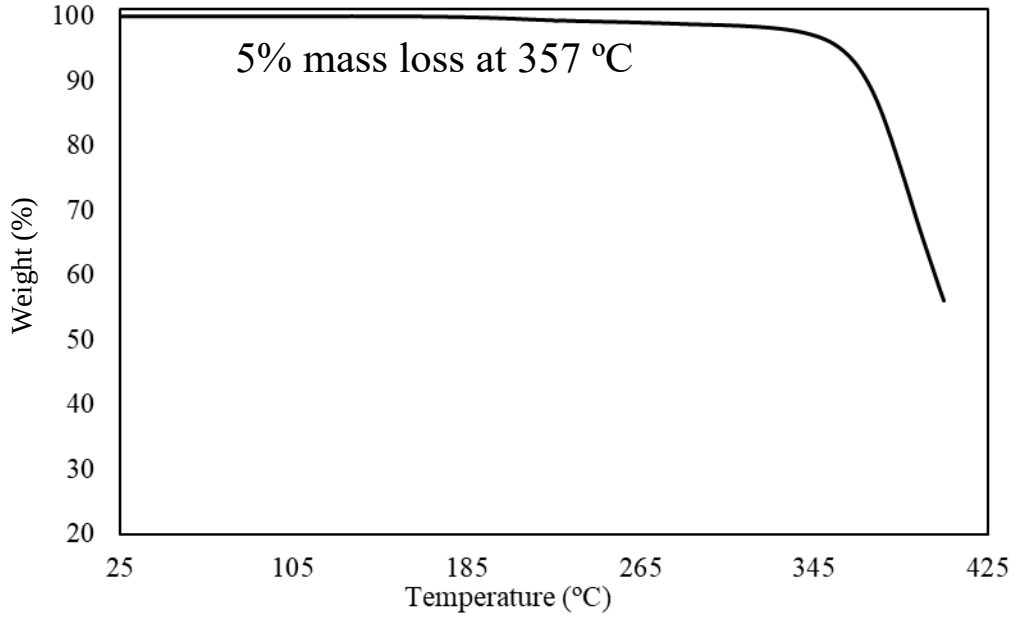

Fig. S262 DSC curve of PMyr-*b*-PVL 800:300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 5**, entry 4.

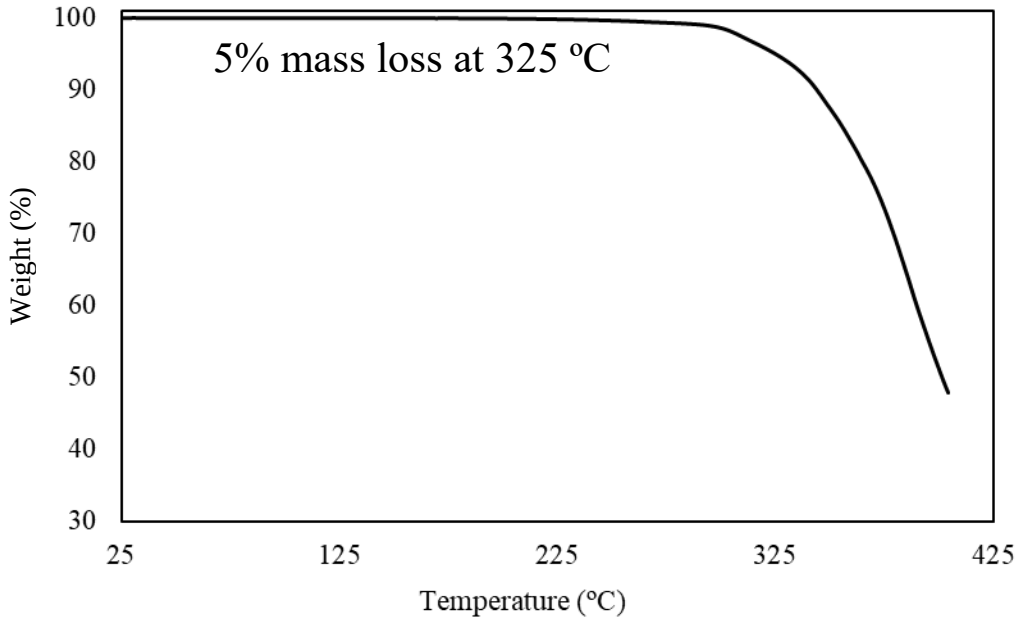

Fig. S263 TGA curve of PMyr-*b*-PDL 800:300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 5**, entry 5.

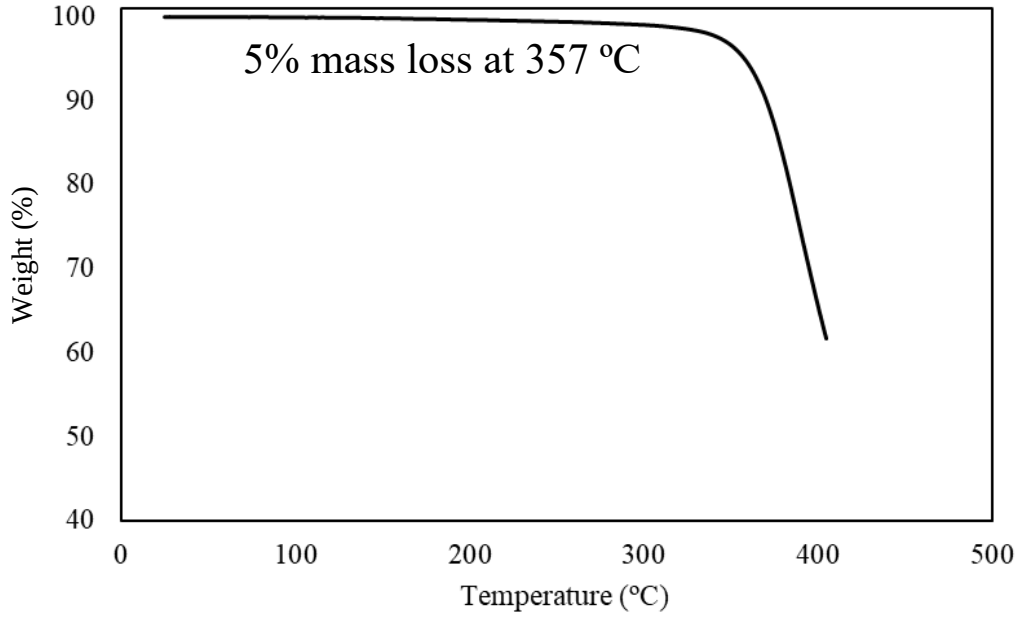

Fig. S264 TGA curve of PMyr 800 equivalents generated by **8**/$[Ph_3C][B(C_6F_5)_4]$ from **Table S1**, entry 1 (30 min).

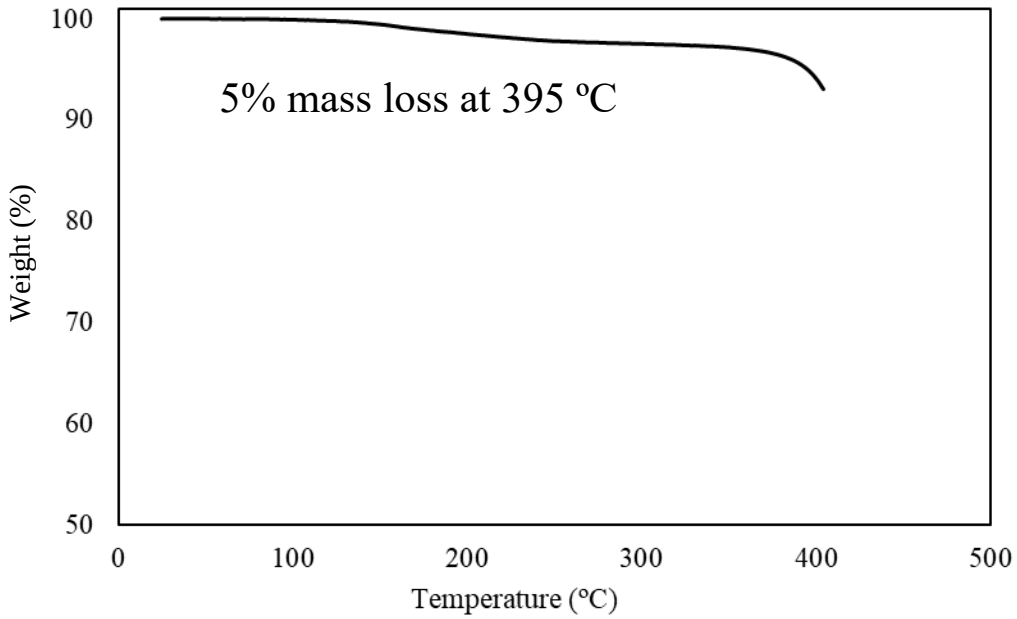

Fig. S265 TGA curve of PS 800 equivalents generated by **8**/$[Ph_3C][B(C_6F_5)_4]$ from **Table S1**, entry 2 (30 min).

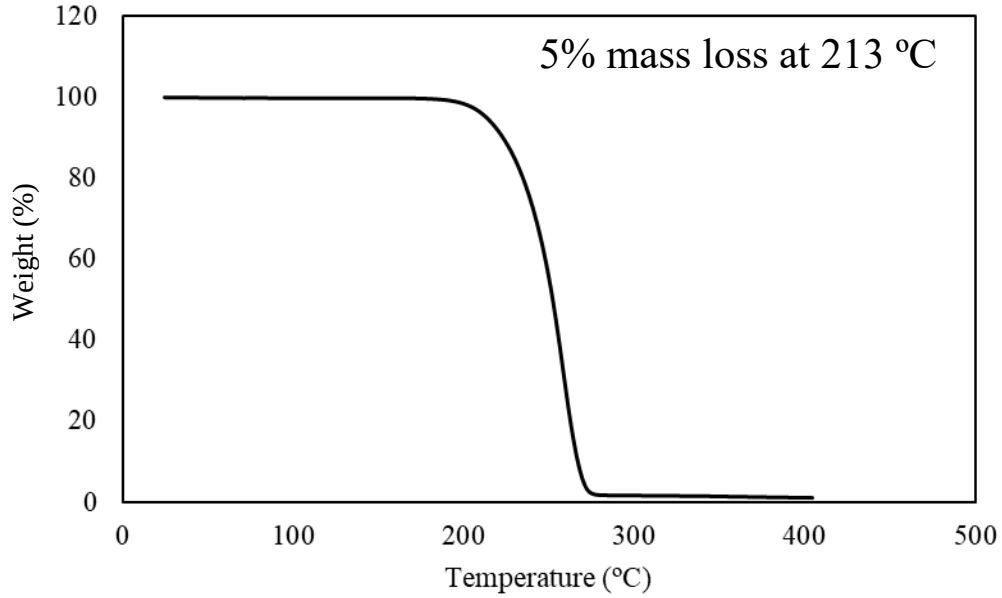

Fig. S266 TGA curve of PVL 300 equivalents generated by **8**/$[Ph_3C][B(C_6F_5)_4$ from **Table S1**, entry 3 (10 min).

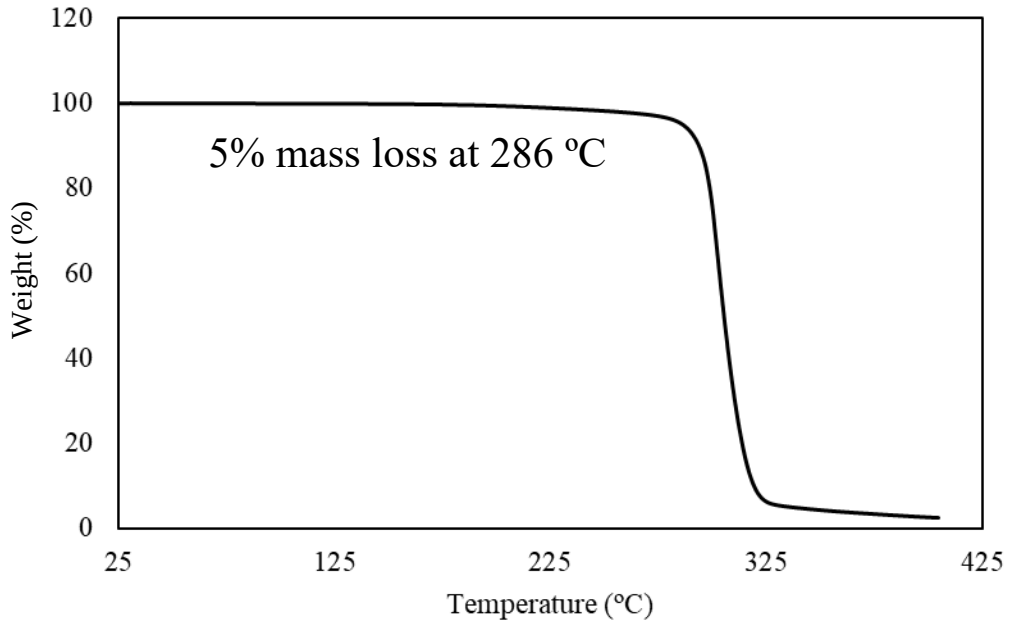

Fig. S267 TGA curve of PDL 300 equivalents generated by **8**/$[Ph_3C][B(C_6F_5)_4]$ from **Table S1**, entry 4 (6 h).

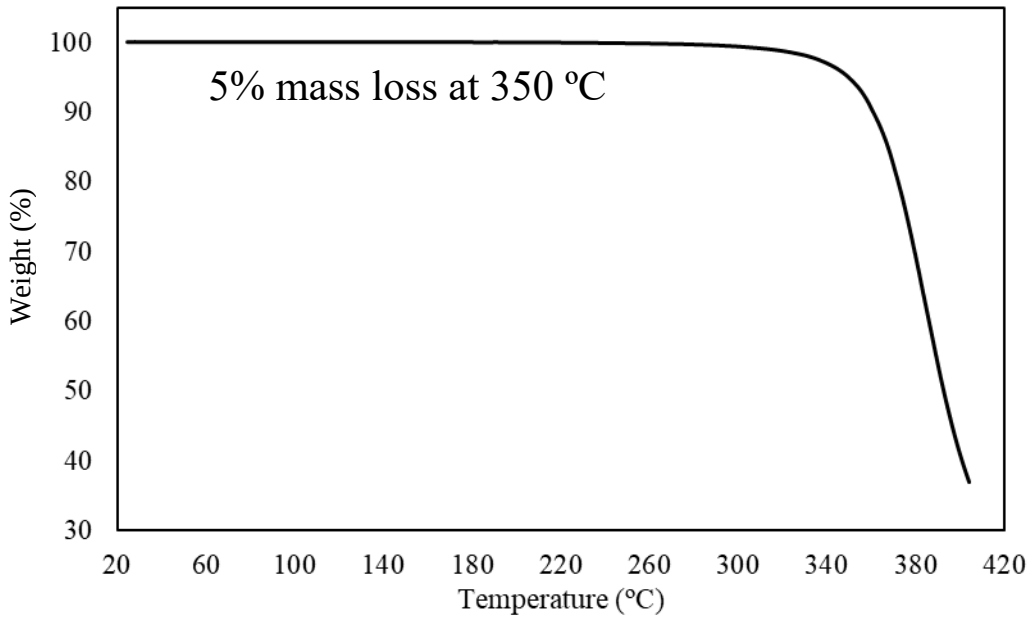

Fig. S268 TGA curve of PIP 300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table S2**, entry 1a (12 h).

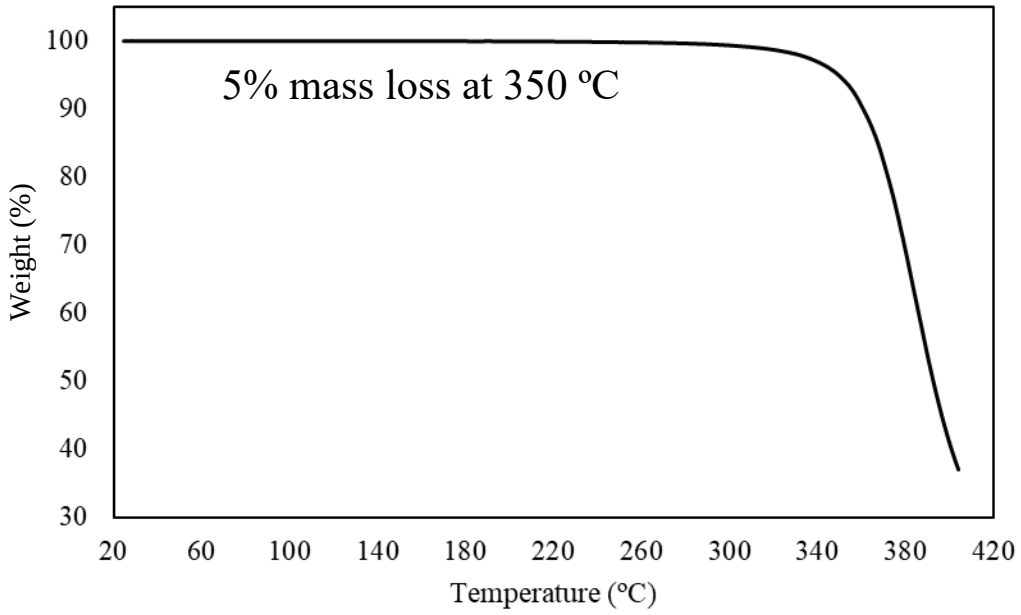

Fig. S269 TGA curve of PIP 300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table S2**, entry 1b (12 h).

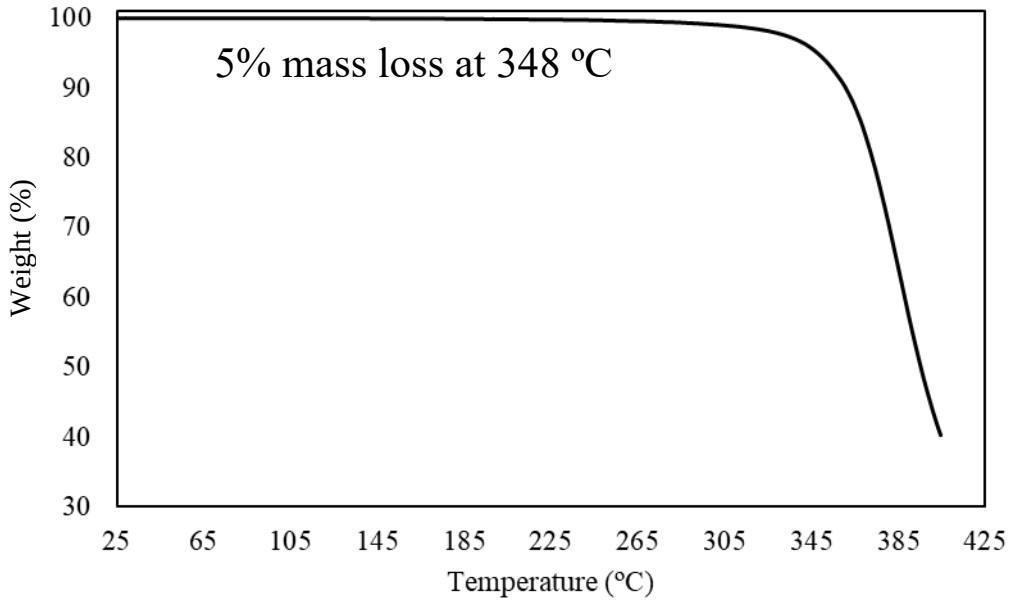

Fig. S270 TGA curve of PIP 300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table S2**, entry 1c (12 h).

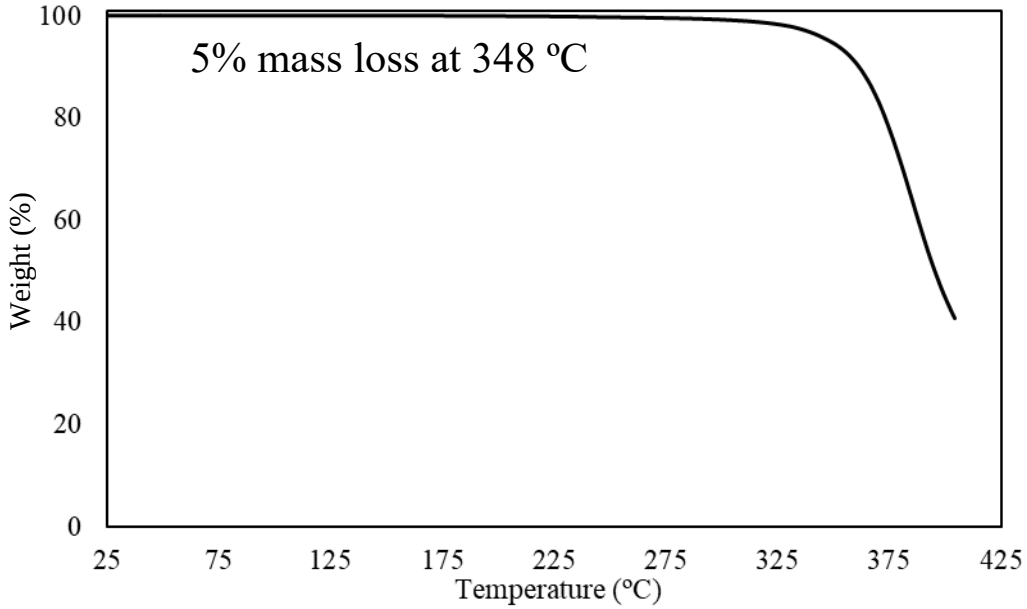

Fig. S271 TGA curve of PIP 550 equivalents generated by **6**/[Ph_3C][$B(C_6F_5)_4$] from **Table S2**, entry 2a (12 h).

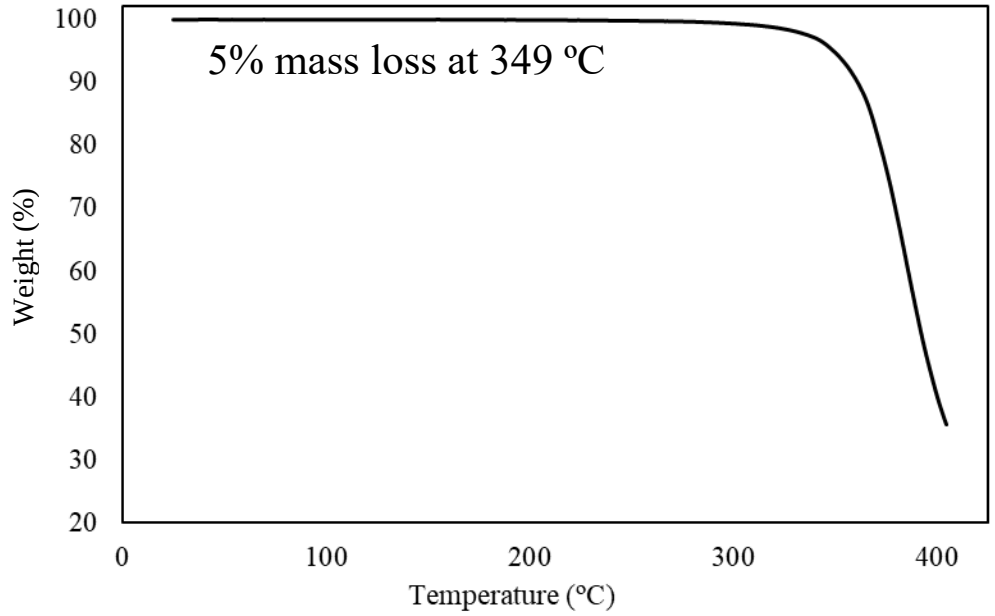

Fig. S272 TGA curve of PIP 550 equivalents generated by **6**/[Ph_3C][$B(C_6F_5)_4$] from **Table S2**, entry 2b (12 h).

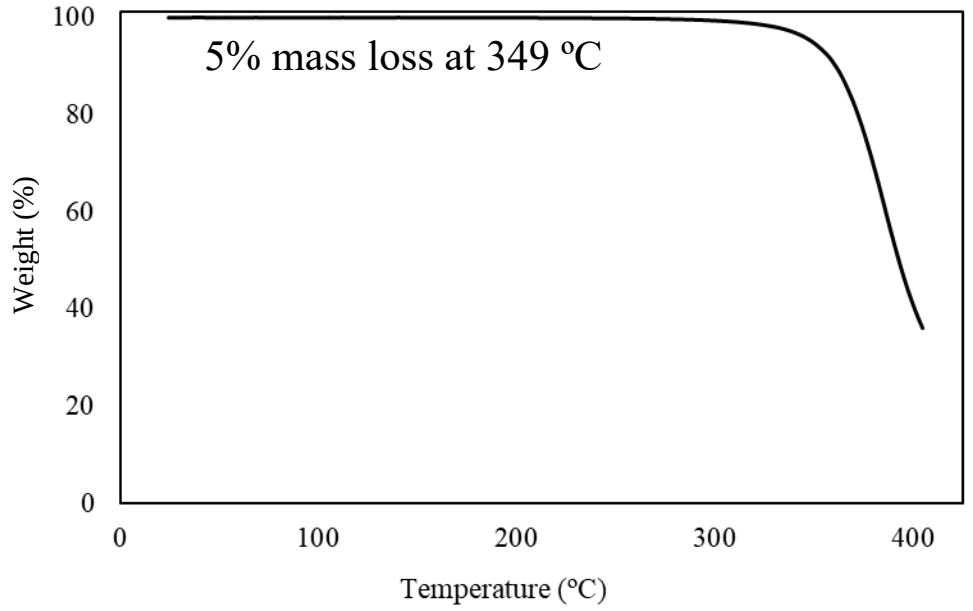

Fig. S273 TGA curve of PIP 550 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table S2**, entry 2c (12 h).

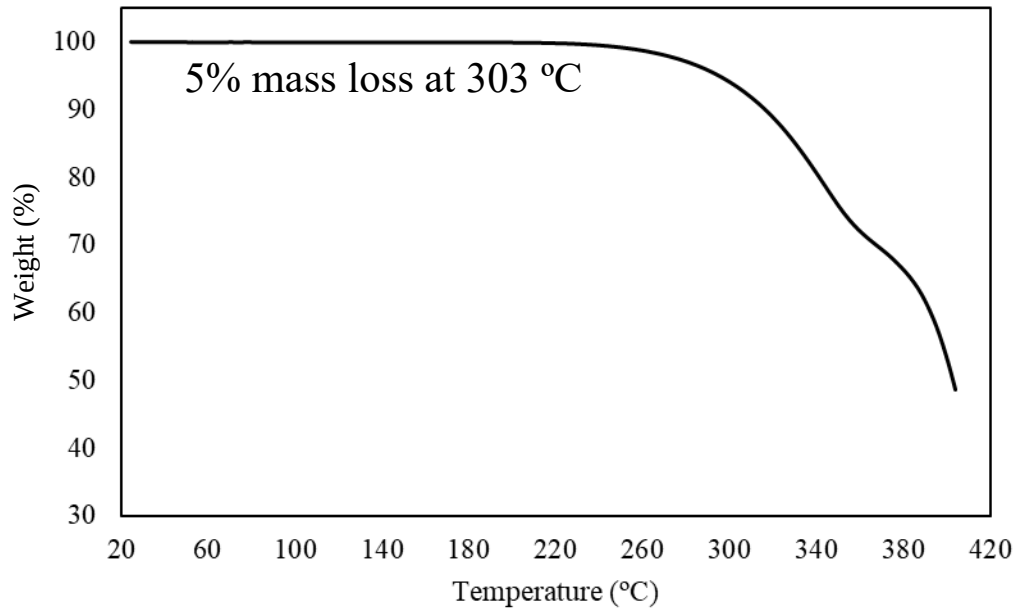

Fig. S274 TGA curve of PCL 550 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table S2**, entry 3a (2 h).

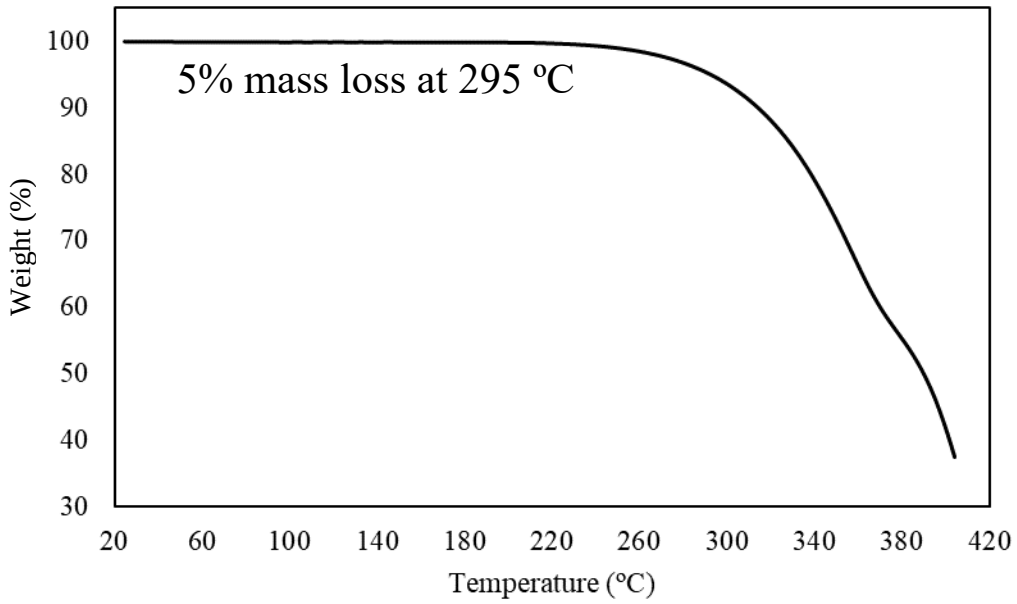

Fig. S275 TGA curve of PCL 550 equivalents generated by **6**/[Ph_3C][$B(C_6F_5)_4$] from **Table S2**, entry 3b (2 h).

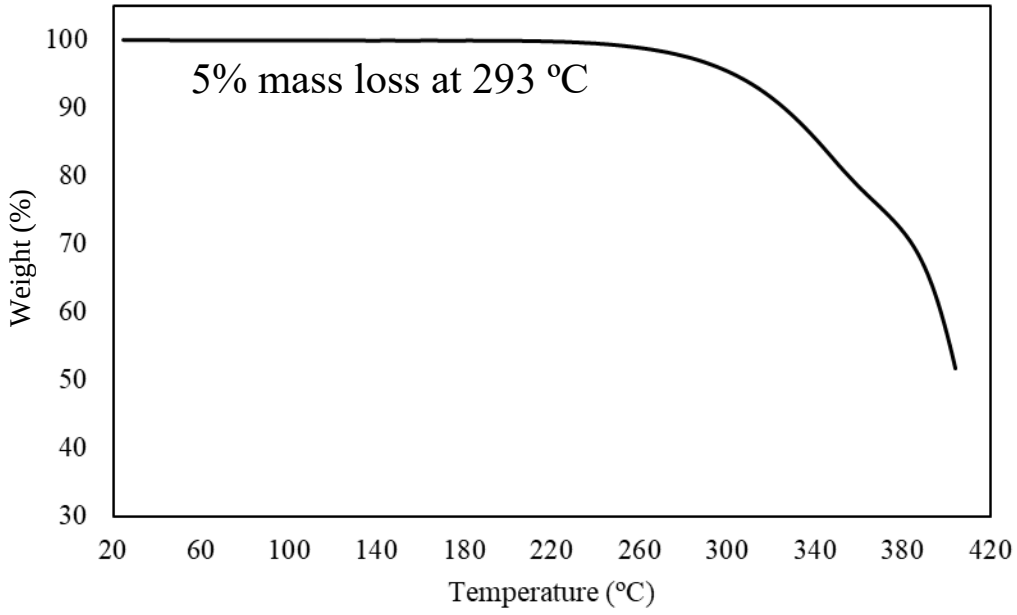

Fig. S276 TGA curve of PCL 550 equivalents generated by **6**/[Ph_3C][$B(C_6F_5)_4$] from **Table S2**, entry 3c (2 h).

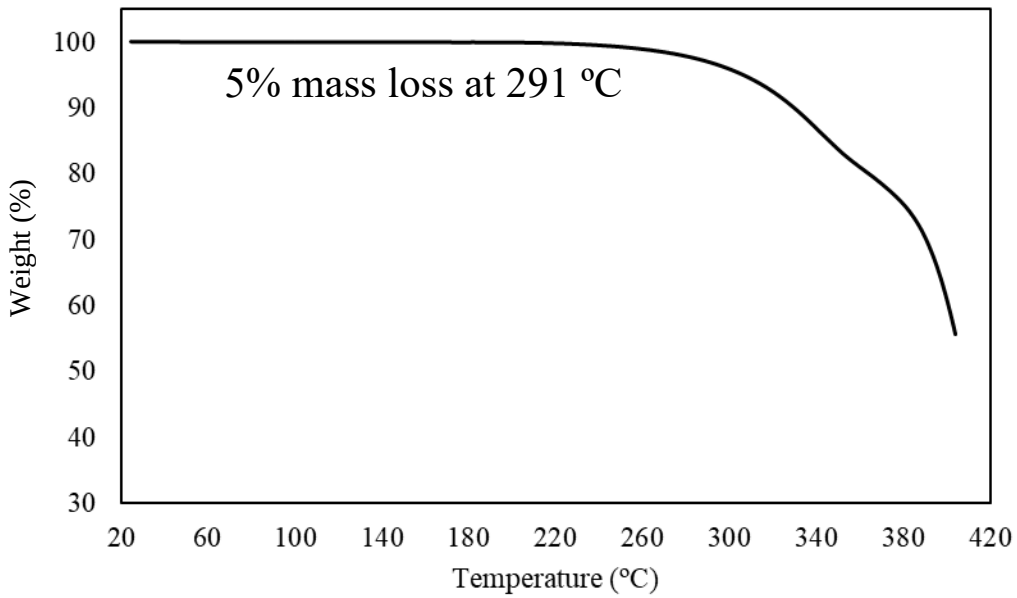

Fig. S277 TGA curve of PCL 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table S2**, entry 4a (2 h).

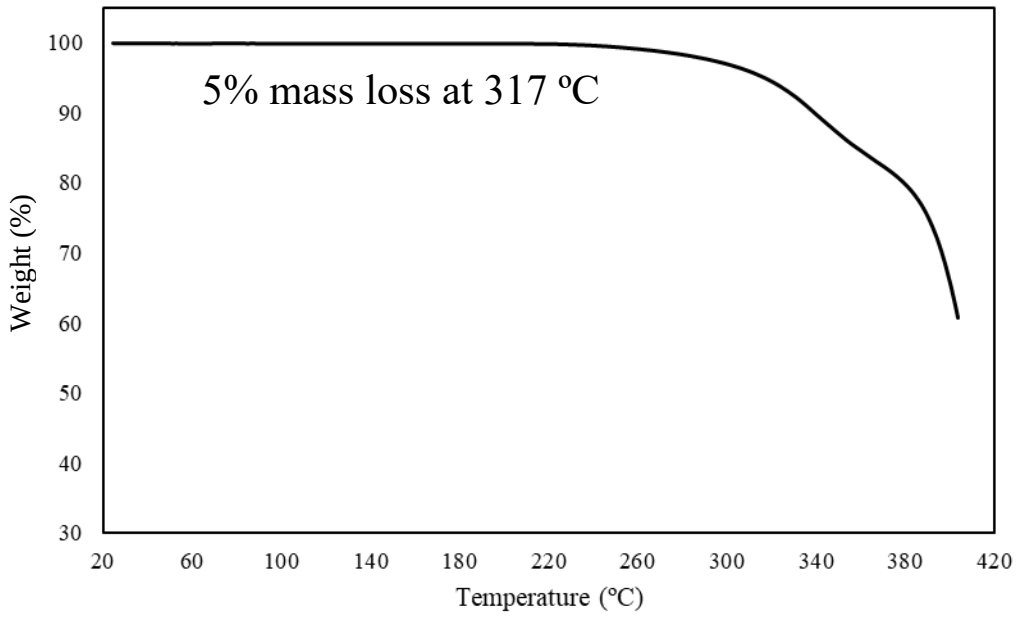

Fig. S278 TGA curve of PCL 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table S2**, entry 4b (2 h).

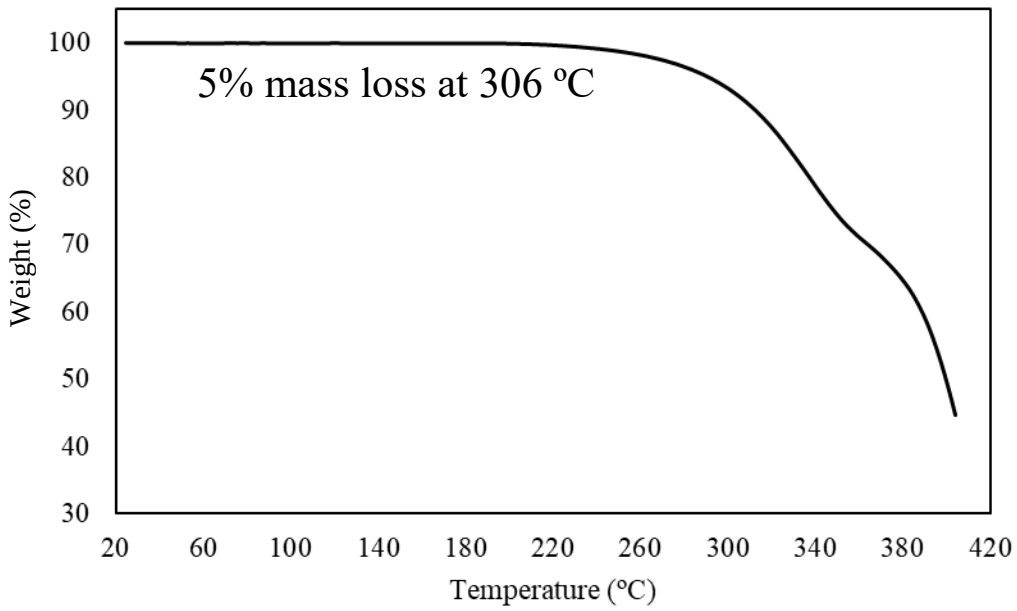

Fig. S279 TGA curve of PCL 800 equivalents generated by **6**/[Ph_3C][$B(C_6F_5)_4$] from **Table S2**, entry 4c (2 h).

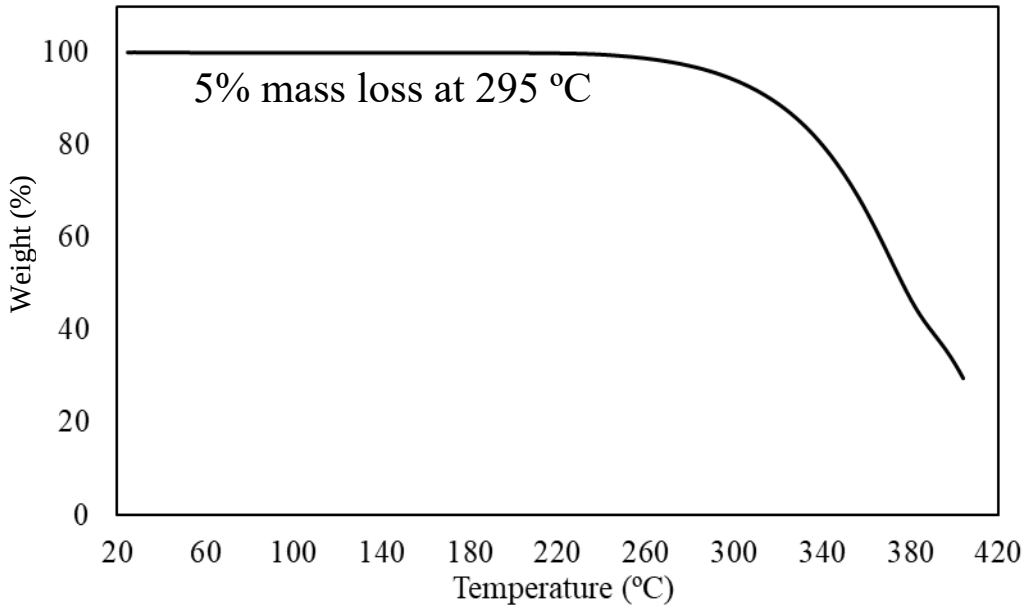

Fig. S280 TGA curve of PCL 300 equivalents generated by **6** from **Table S2**, entry 5 (No [Ph_3C][$B(C_6F_5)_4$] added) (10 min).

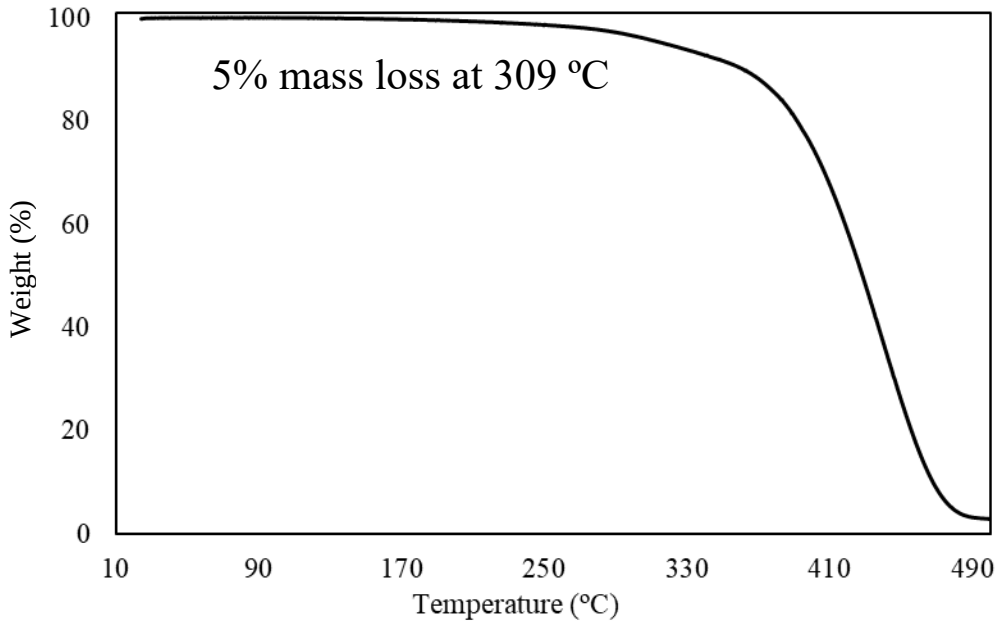

Fig. S281 TGA curve of PIP 50 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table S3**, entry 1 (12 h).

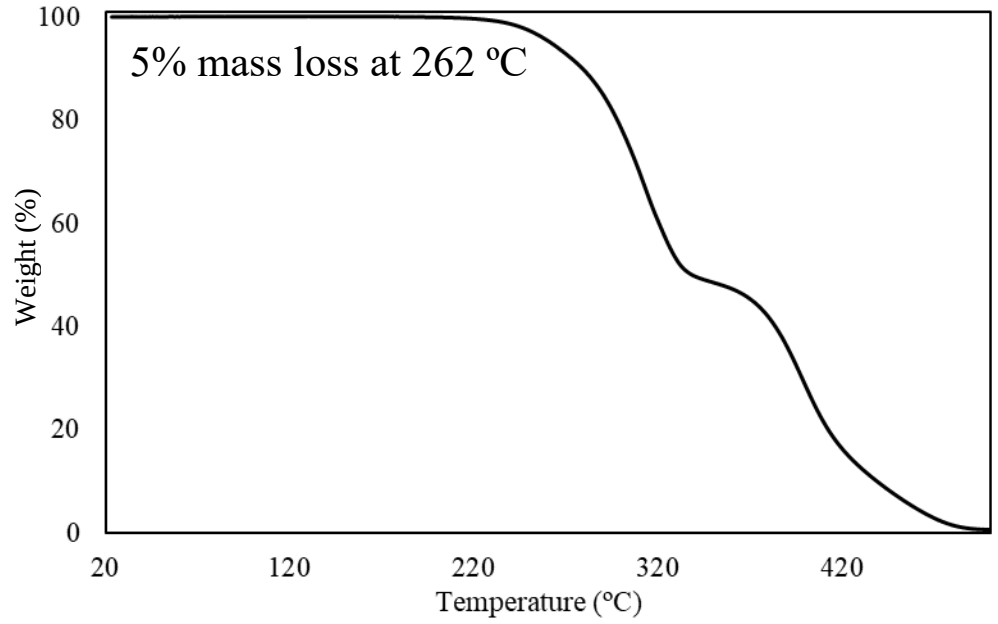

Fig. S282 TGA curve of PIP-*b*-PCL 50:50 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table S3**, entry 2.

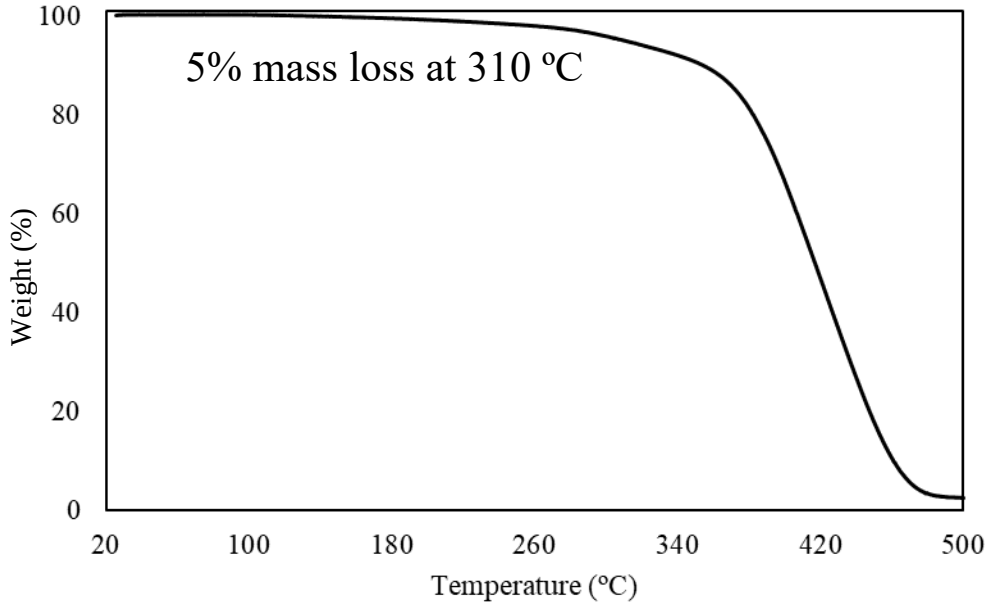

Fig. S283 TGA curve of recovered PIP 50 equivalents after hydrolysis of PIP-*b*-PCL 50:50 from **Table S3**, entry 3 (12 h).

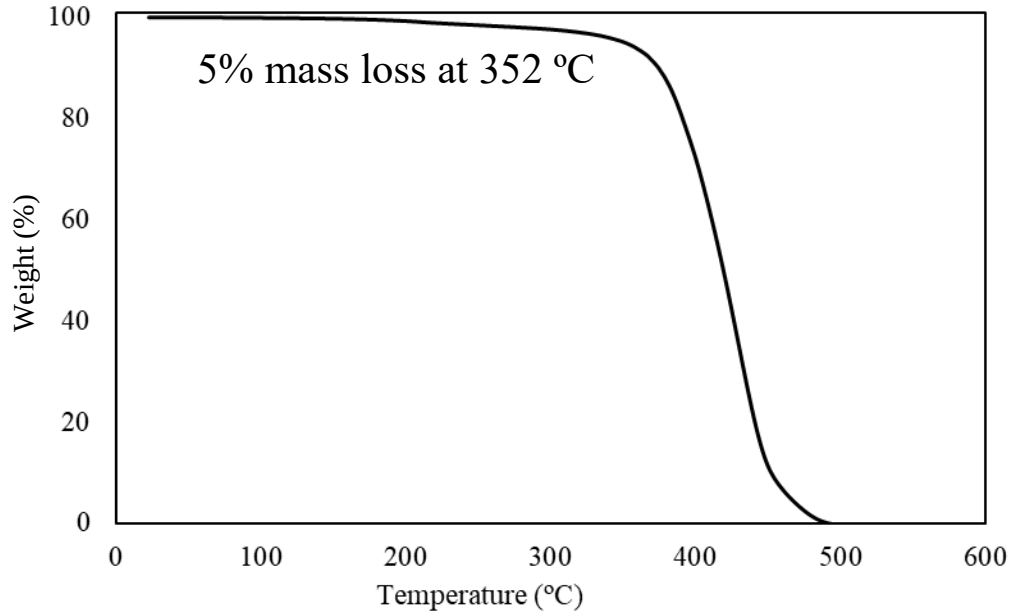

Fig. S284 TGA curve of PIP-*b*-PCL 50:50 equivalents generated by **$Y[N(SiMe_3)_2]_3$** from **Table S3**, entry 4 (6 h).

7.0 Differential Scanning Calorimetry (DSC) Characterization of Isolated Polymers

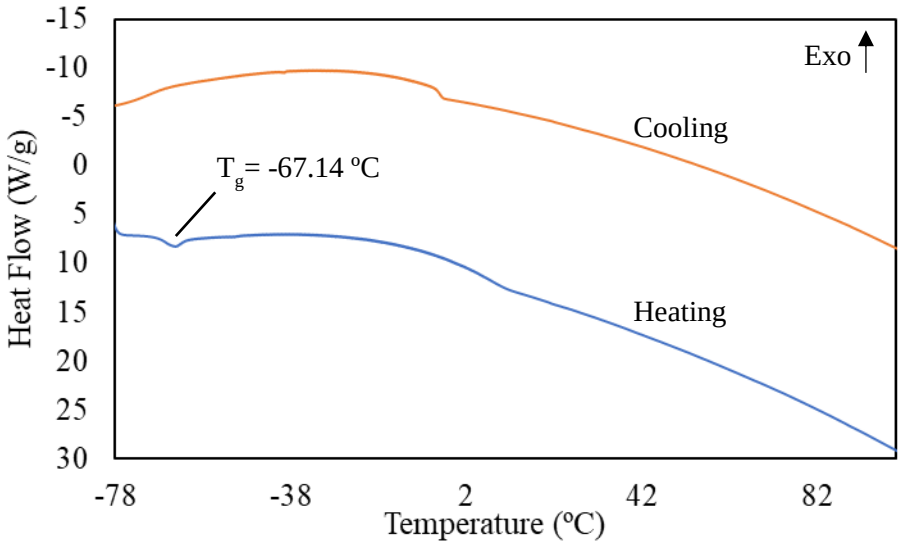

Fig. S285 DSC curve of PIP generated by **6**/[Ph_3C][$B(C_6F_5)_4$] from **Table 1**, entry 1 (12 h).

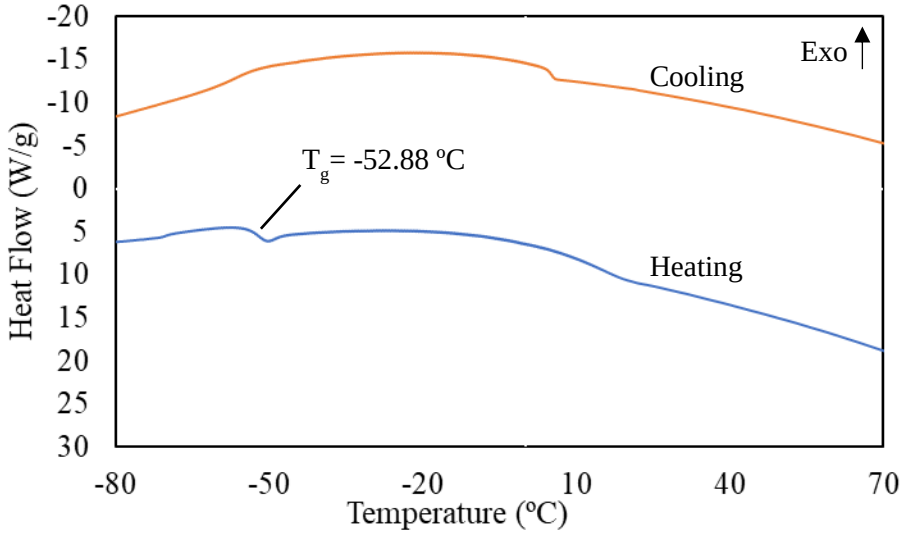

Fig. S286 DSC curve of PIP 800 equivalents generated by **8**/[Ph_3C][$B(C_6F_5)_4$] from **Table 1**, entry 3 (12 h).

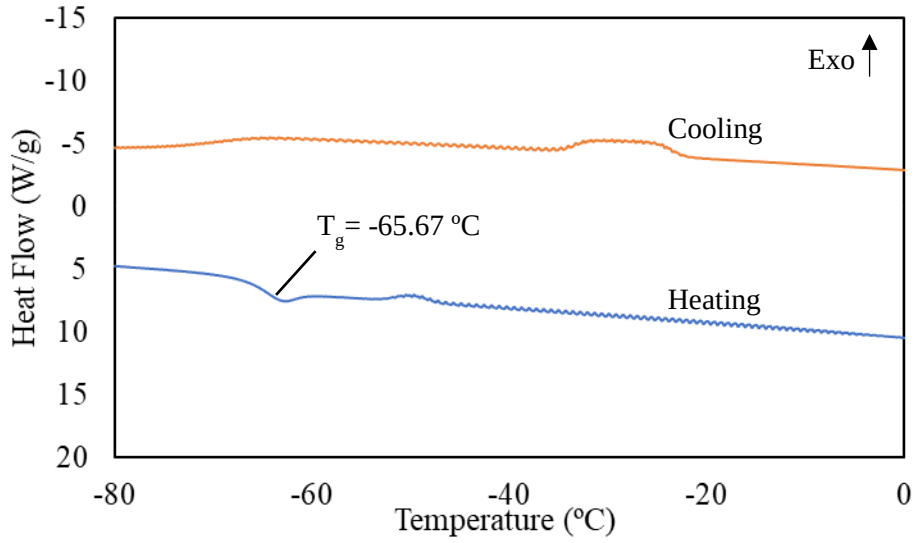

Fig. S287 DSC curve of PIP 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 1**, entry 4 (24 h).

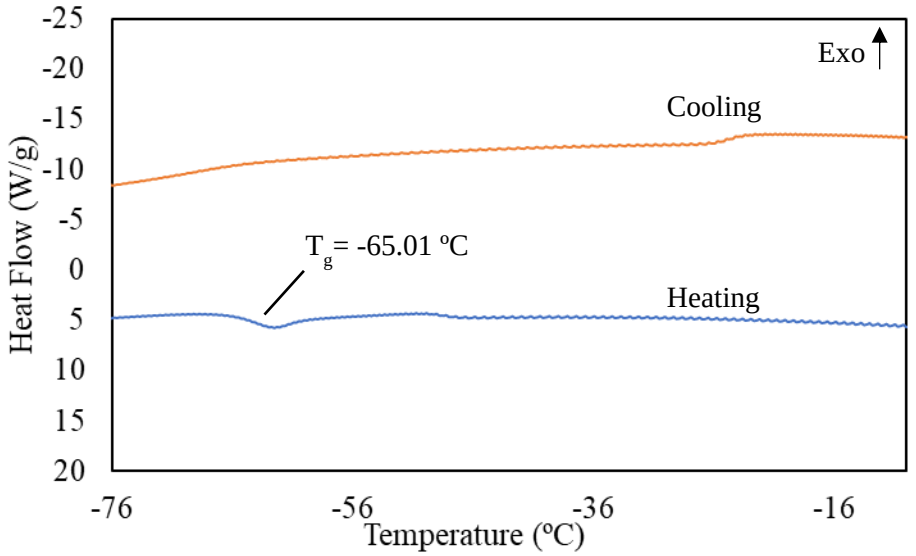

Fig. S288 DSC curve of PIP 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 1**, entry 5 (30 min).

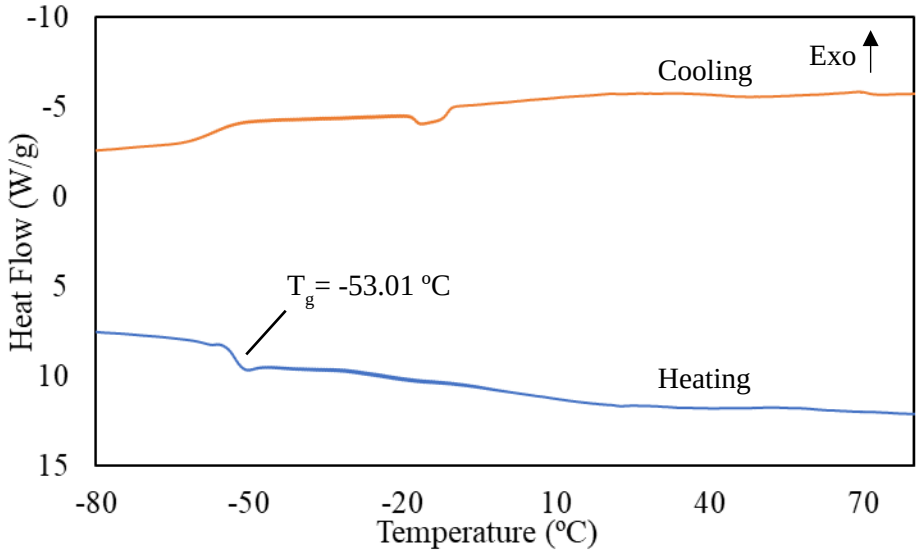

Fig. S289 DSC curve of PIP 800 equivalents generated by **8**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 1**, entry 6 (30 min).

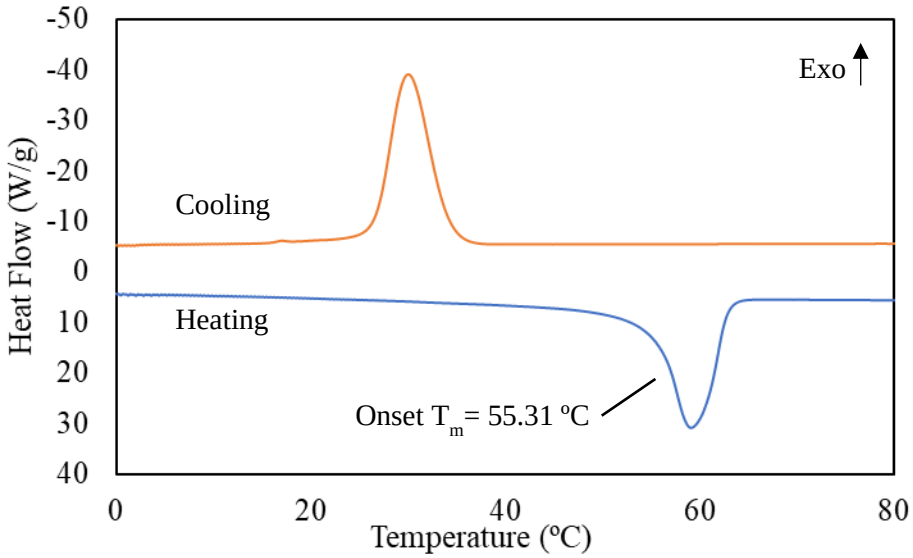

Fig. S290 DSC curve of PCL 300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 1**, entry 7 (10 min).

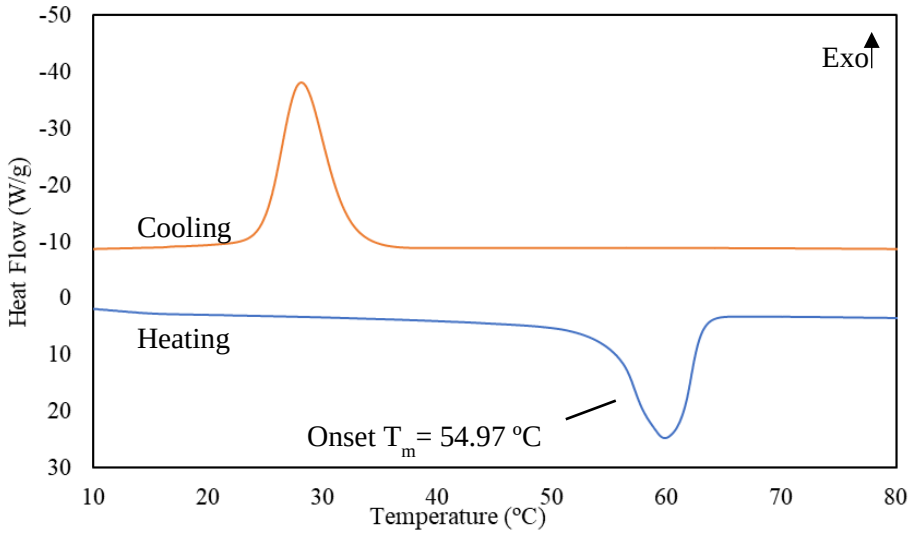

Fig. S291 DSC curve of PCL 300 equivalents generated by **8**/[Ph_3C][$B(C_6F_5)_4$] from **Table 1**, entry 8 (10 min).

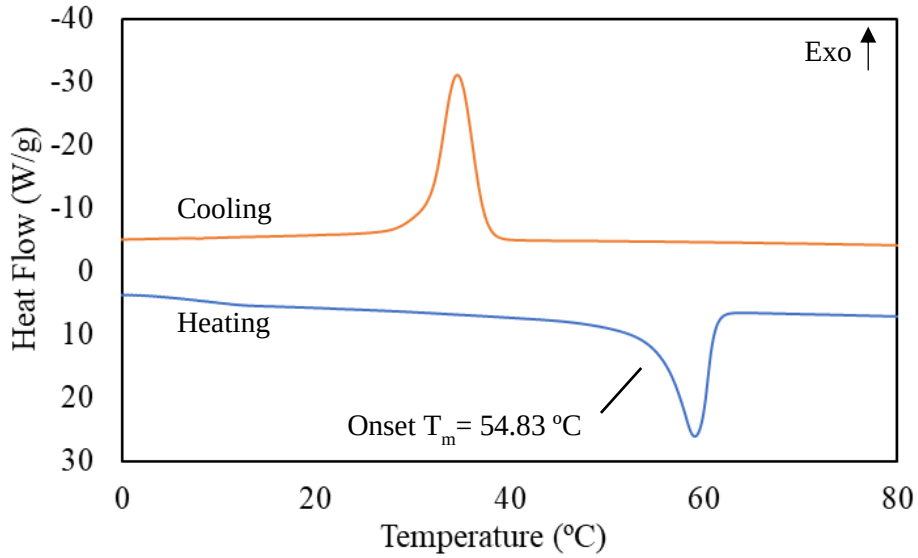

Fig. S292 DSC curve of PCL 300 equivalents generated by **6**/[Ph_3C][$B(C_6F_5)_4$] from **Table 1**, entry 9 (2 h).

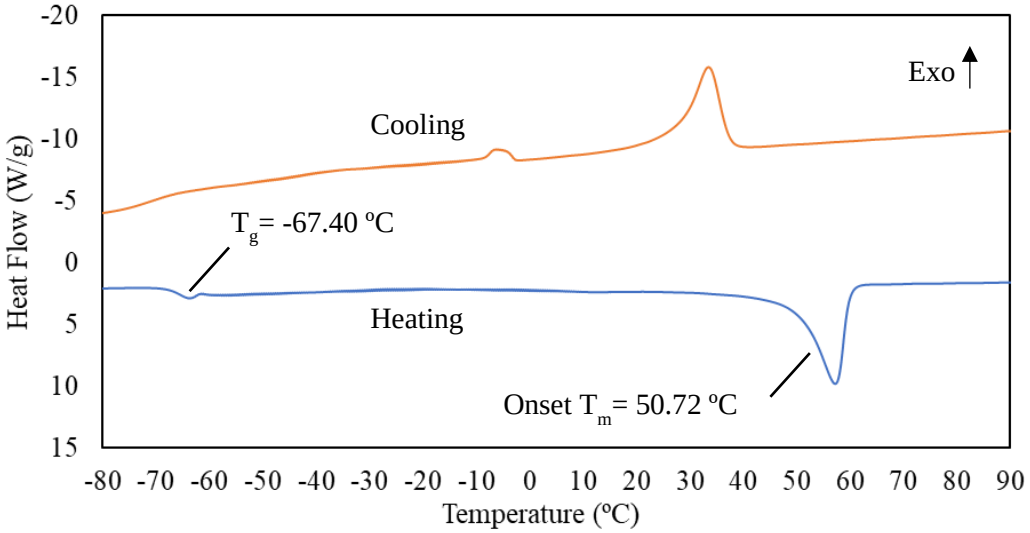

Fig. S293 DSC curve of PIP-*b*-PCL 800:300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 2**, entry 1.

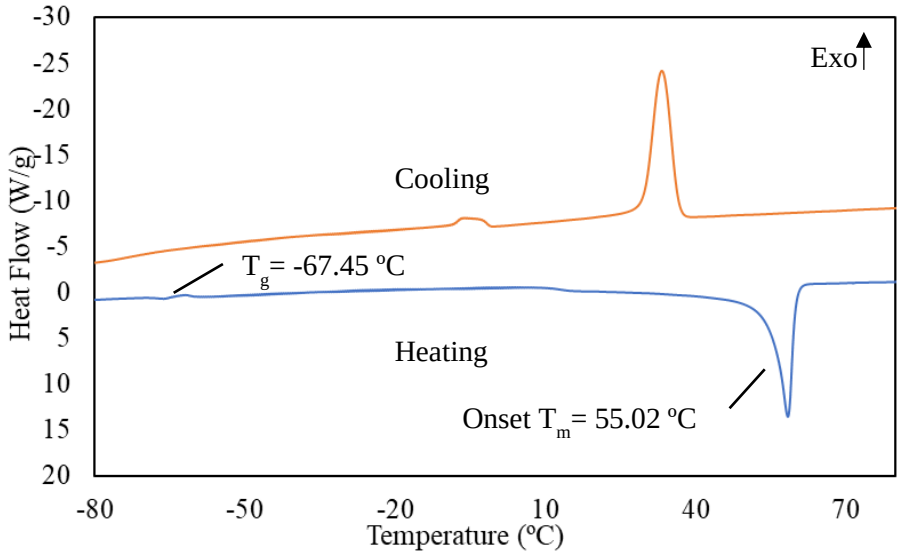

Fig. S294 DSC curve of PIP-*b*-PCL 550:550 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 2**, entry 2.

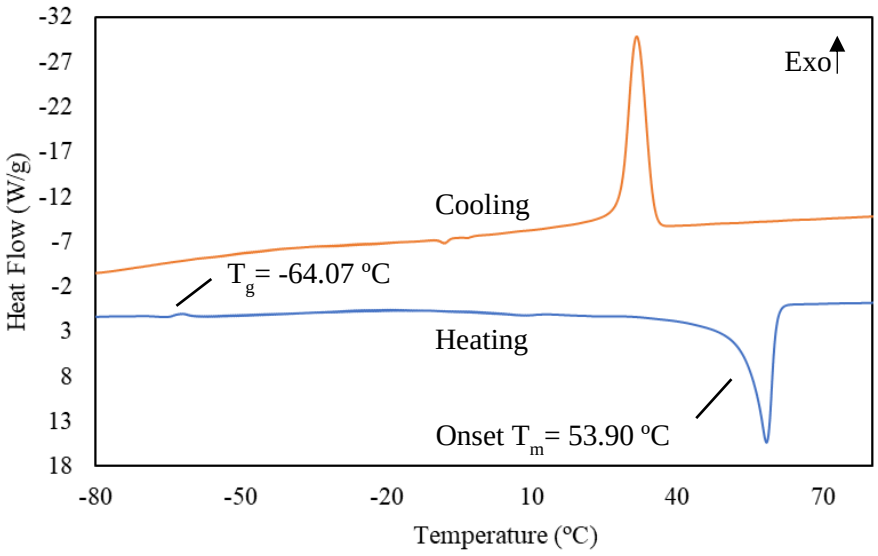

Fig. S295 DSC curve of PIP-*b*-PCL 300:800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 2**, entry 3.

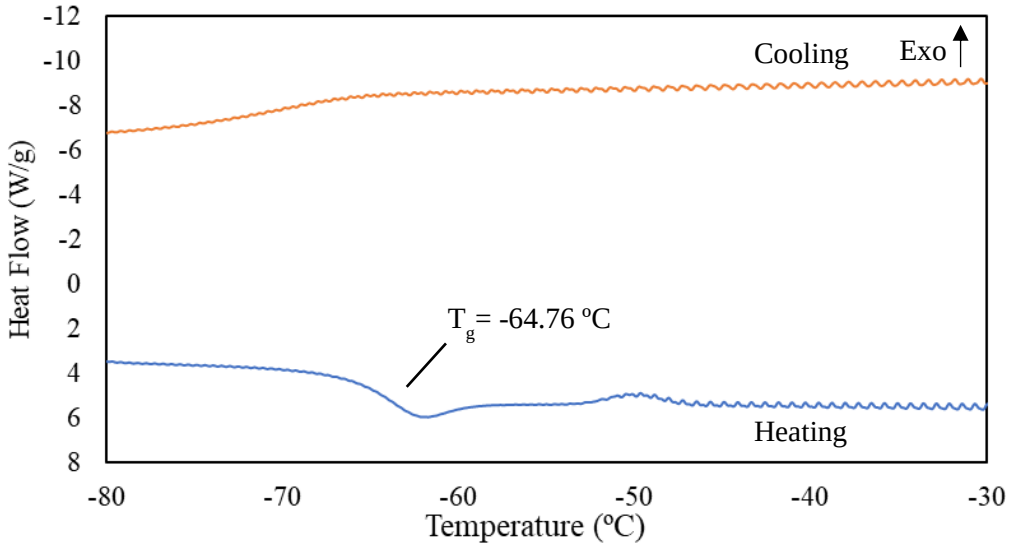

Fig. S296 DSC curve of PIP 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 3**, entry 1 (IP addition time 0 min).

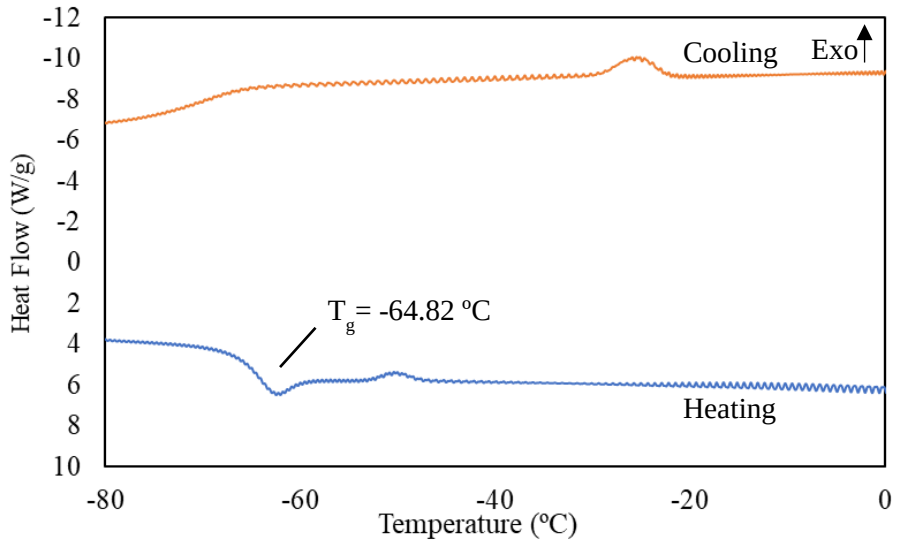

Fig. S297 DSC curve of PIP 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 3**, entry 2 (IP addition time 30 min).

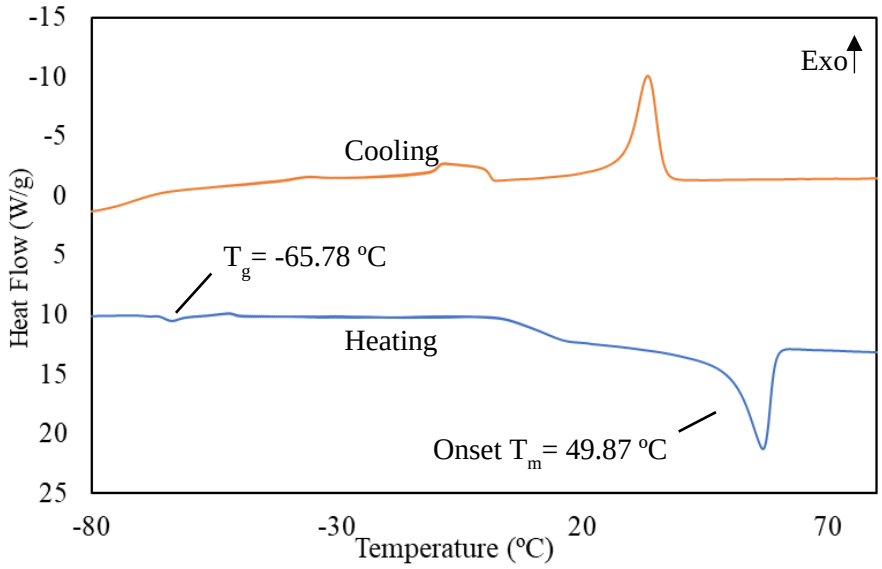

Fig. S298 DSC curve of PIP-*b*-PCL 800:300 equivalents generated by **6** and 0.5 equivalents of $[Ph_3C][B(C_6F_5)_4]$ from **Table 3**, entry 3.

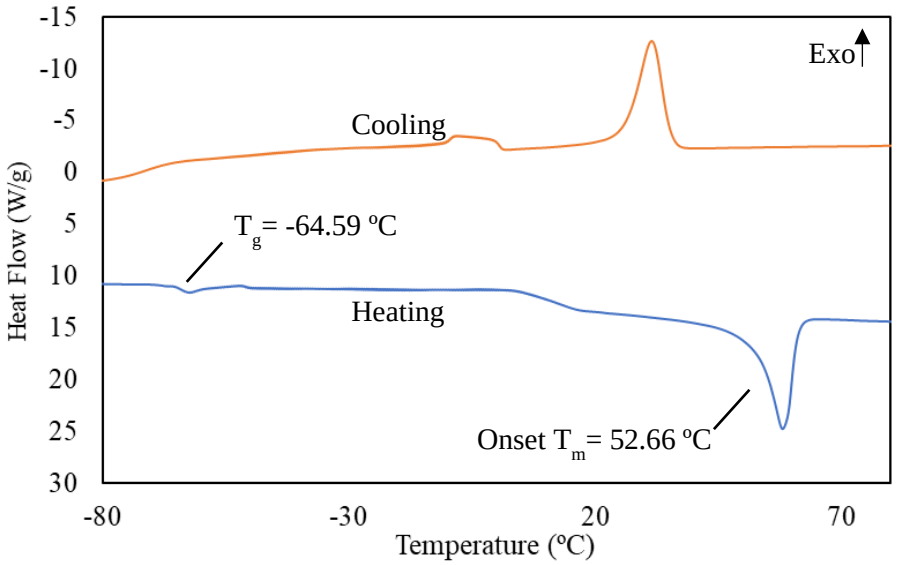

Fig. S299 DSC curve of PIP-*b*-PCL 800:300 equivalents generated by **6** and 1.5 equivalents of $[Ph_3C][B(C_6F_5)_4]$ from **Table 3**, entry 4.

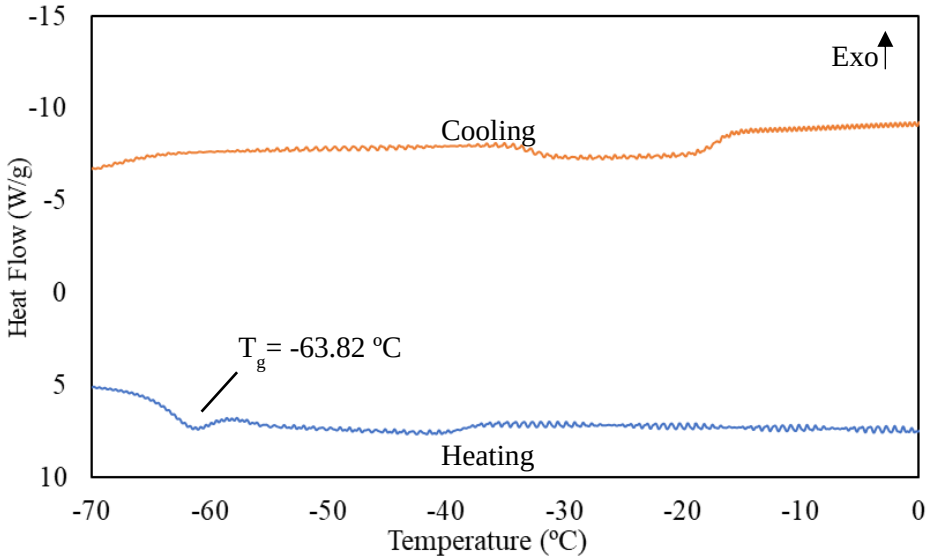

Fig. S300 DSC curve of PMyr 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 4**, entry 1 (30 min).

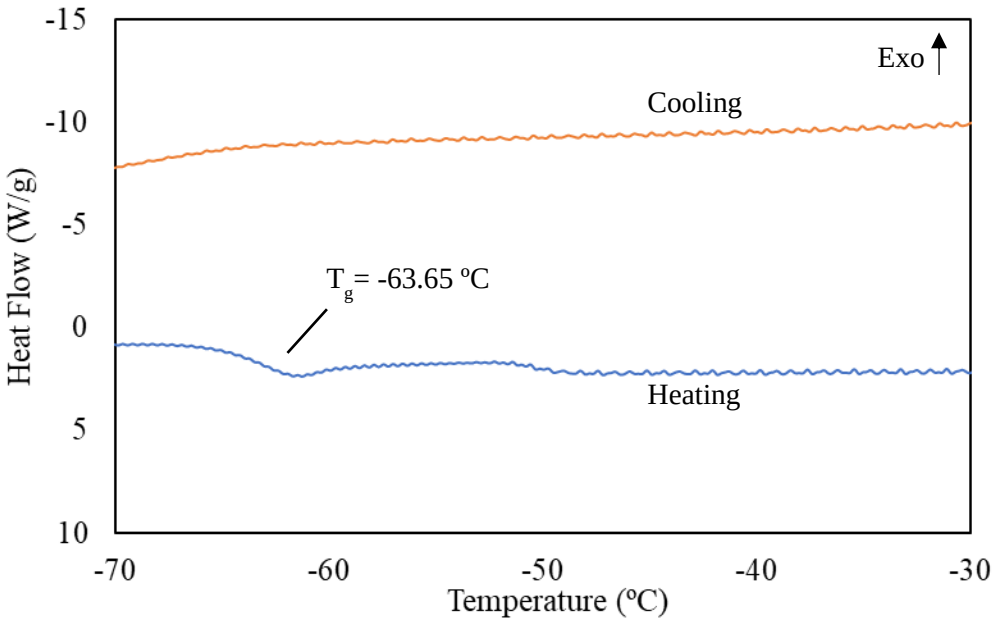

Fig. S301 DSC curve of PMyr 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 4**, entry 2 (90 min).

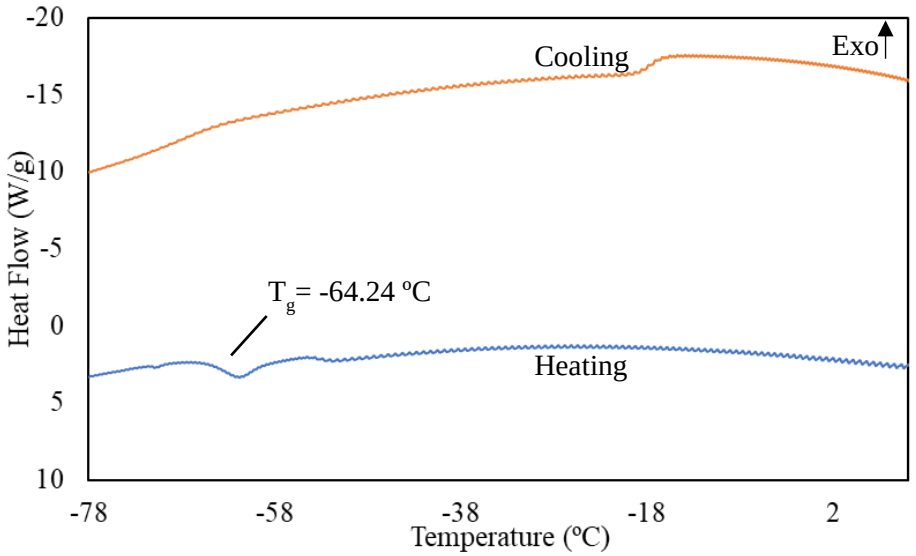

Fig. S302 DSC curve of PMyr 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 4**, entry 3 (3 h).

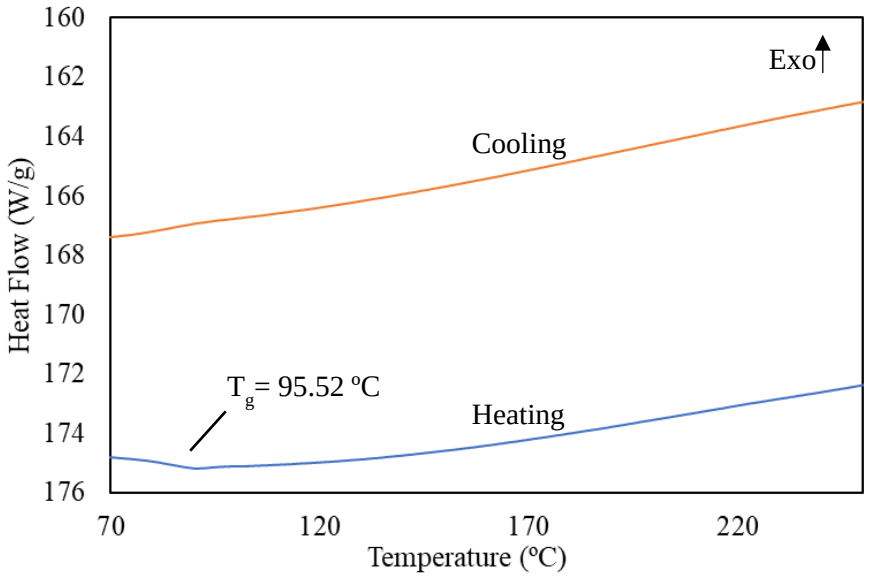

Fig. S303 DSC curve of PS 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 4**, entry 4 (30 min).

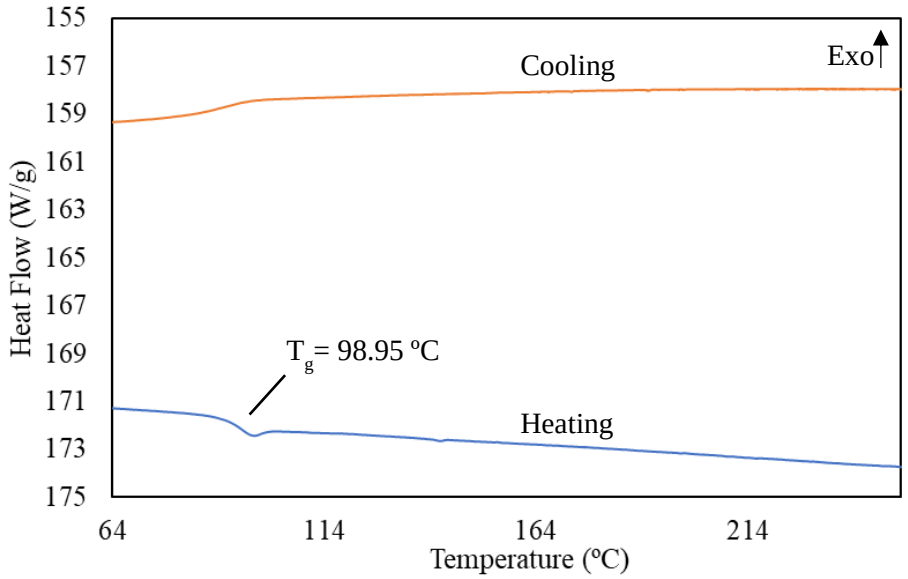

Fig. S304 DSC curve of PS 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 4**, entry 5 (20 h).

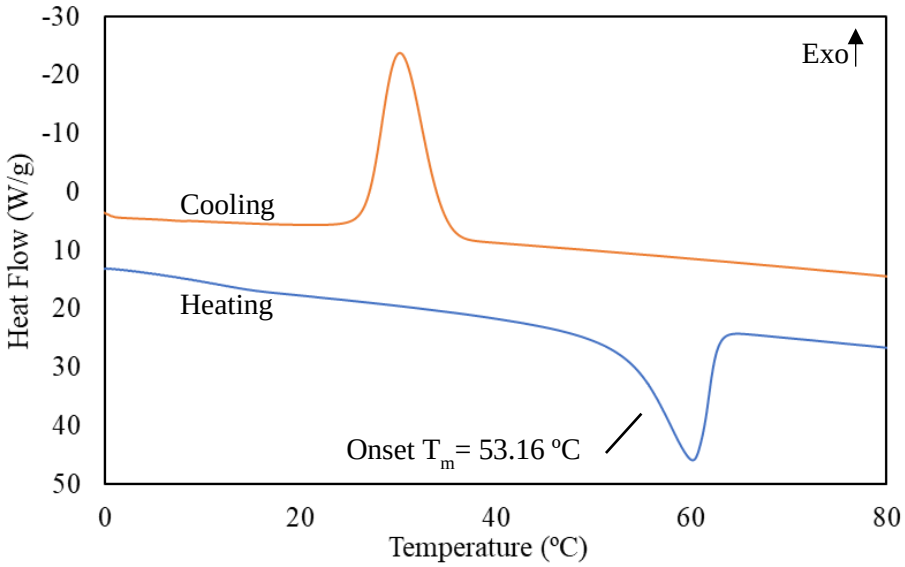

Fig. S305 DSC curve of PVL 300 equivalents generated by **6**/[Ph_3C][$B(C_6F_5)_4$] from **Table 4**, entry 6 (10 min).

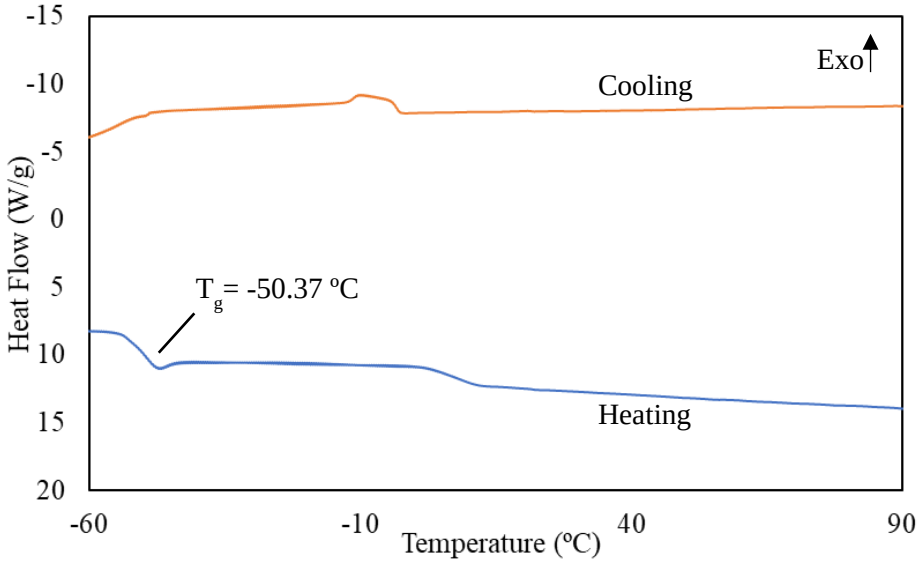

Fig. S306 DSC curve of PDL 300 equivalents generated by **6**/[Ph_3C][$B(C_6F_5)_4$] from **Table 4**, entry 7 (6 h).

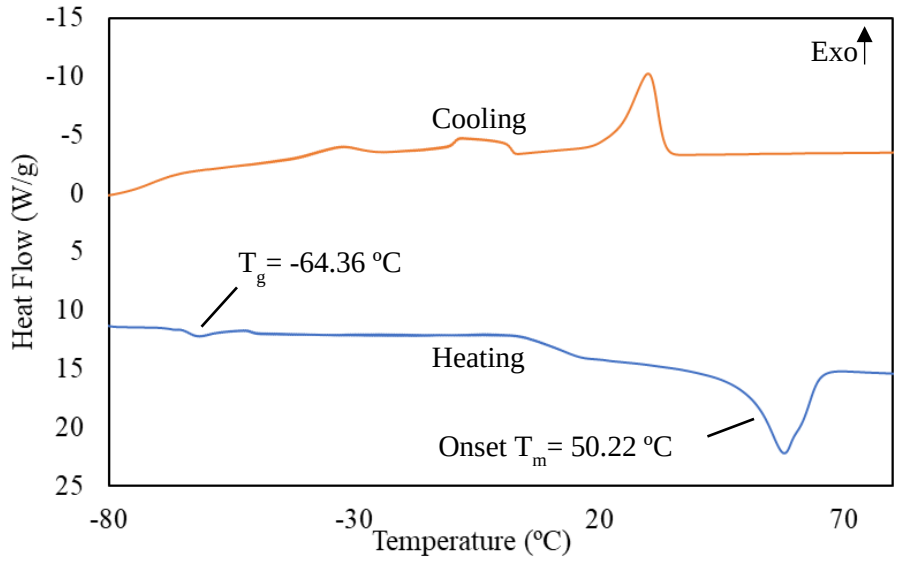

Fig. S307 DSC curve of PIP-*b*-PVL 800:300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 5**, entry 1.

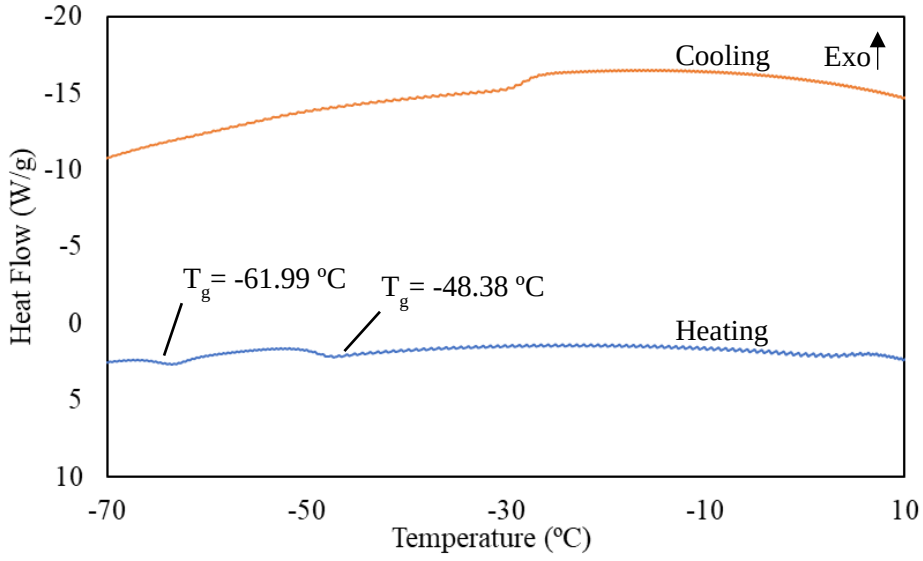

Fig. S308 DSC curve of PIP-*b*-PDL 800:300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 5**, entry 2.

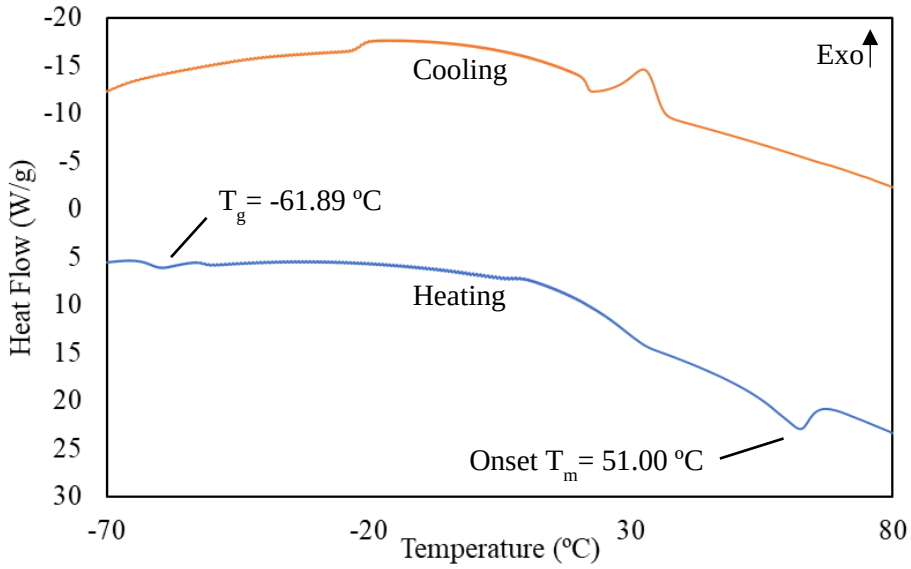

Fig. S309 DSC curve of PMyr-*b*-PCL 800:300 equivalents generated by **6**/[Ph_3C][$B(C_6F_5)_4$] from **Table 5**, entry 3.

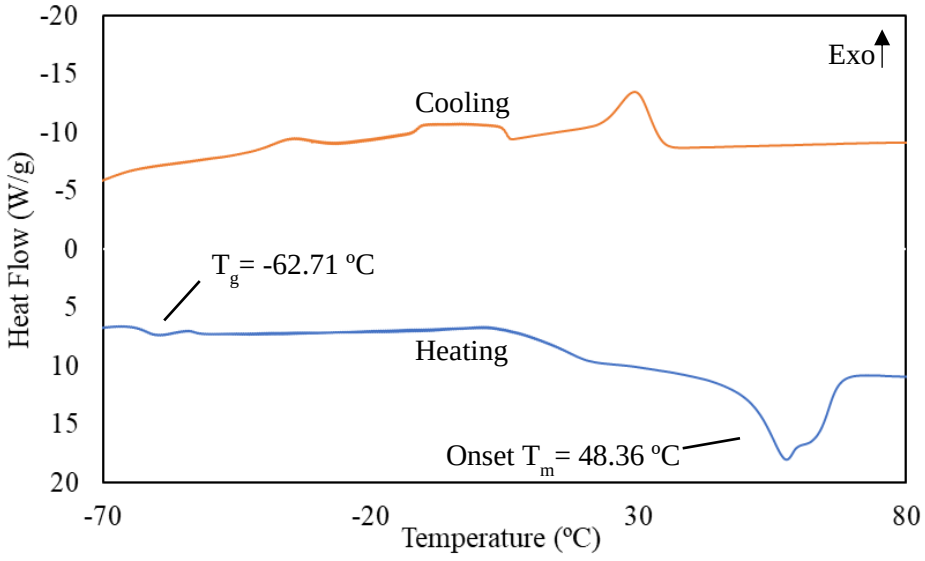

Fig. S310 DSC curve of PMyr-*b*-PVL 800:300 equivalents generated by **6**/[Ph_3C][$B(C_6F_5)_4$] from **Table 5**, entry 4.

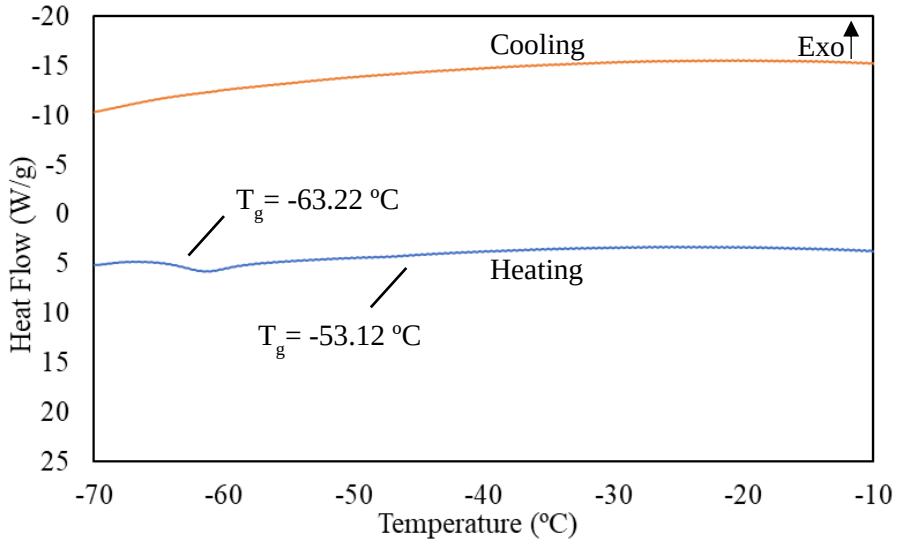

Fig. S311 DSC curve of PMyr-*b*-PDL 800:300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table 5**, entry 5.

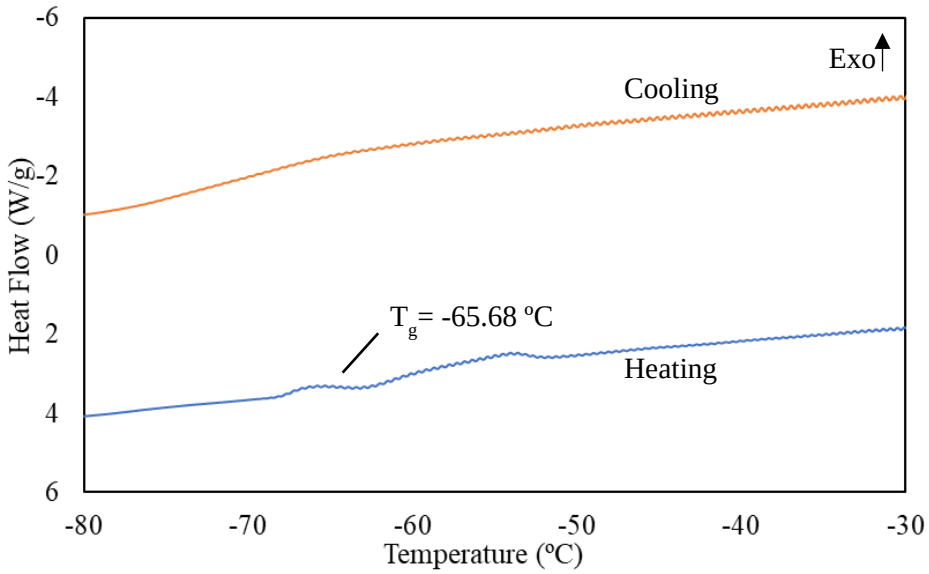

Fig. S312 DSC curve of PMyr 800 equivalents generated by **8**/$[Ph_3C][B(C_6F_5)_4]$ from **Table S1**, entry 1 (30 min).

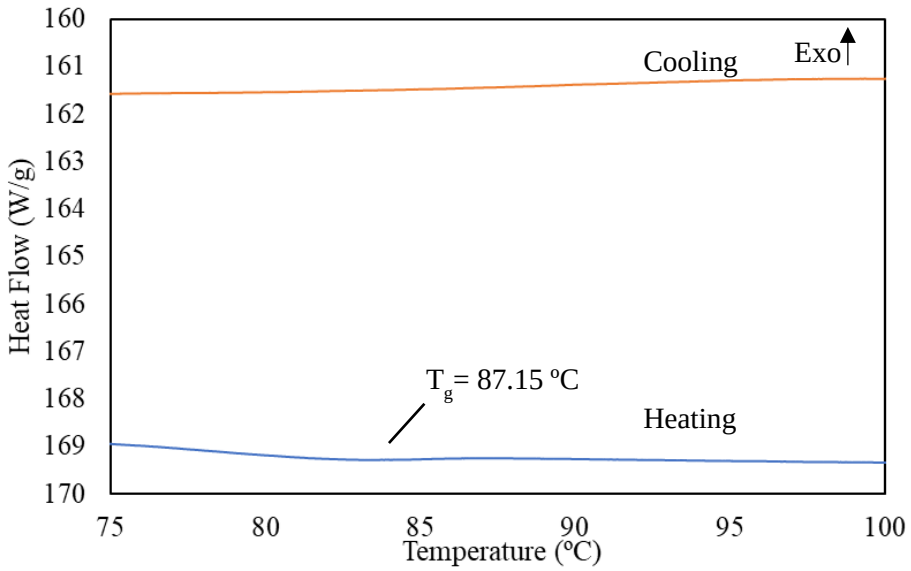

Fig. S313 DSC curve of PS 800 equivalents generated by **8**/[Ph_3C][$B(C_6F_5)_4$] from **Table S1**, entry 2 (30 min).

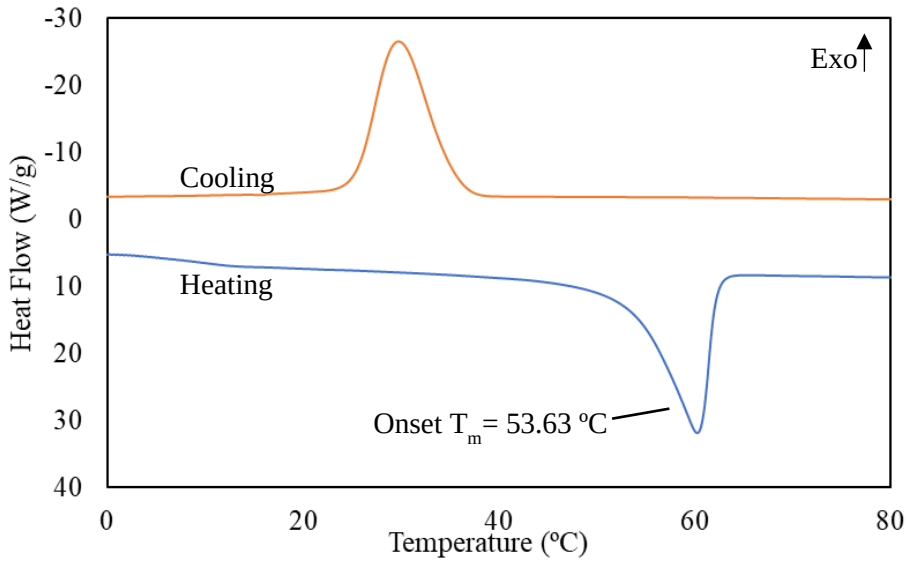

Fig. S314 DSC curve of PVL 300 equivalents generated by **8**/[Ph_3C][$B(C_6F_5)_4$] from **Table S1**, entry 3 (10 min).

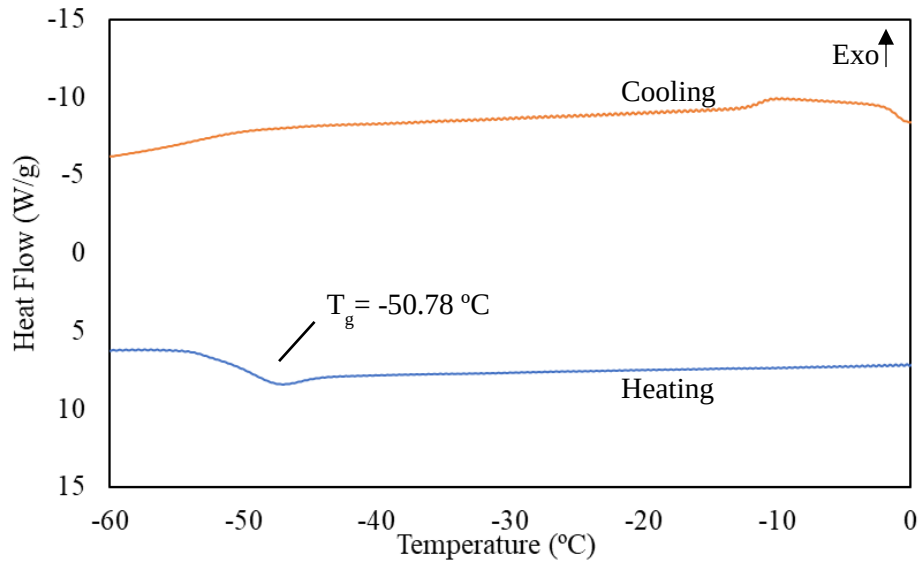

Fig. S315 DSC curve of PDL 300 equivalents generated by **8**/$[Ph_3C][B(C_6F_5)_4]$ from **Table S1**, entry 4 (6 h).

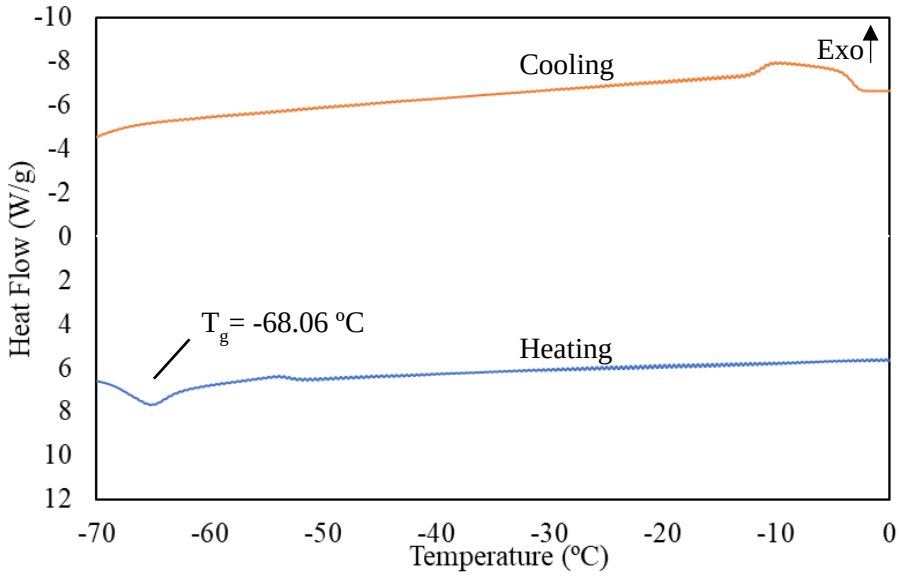

Fig. S316 DSC curve of PIP 300 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table S2**, entry 1 (12 h).

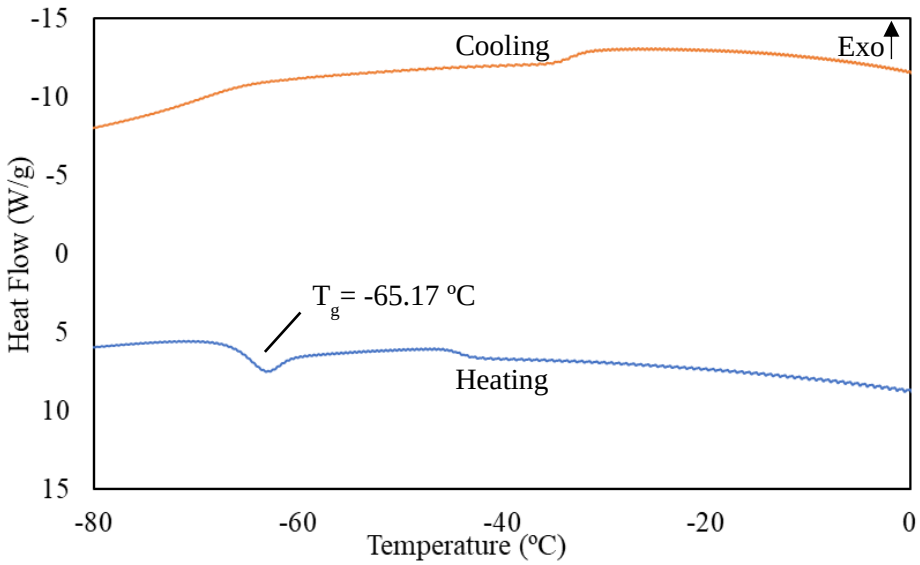

Fig. S317 DSC curve of PIP 550 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table S2**, entry 2 (12 h).

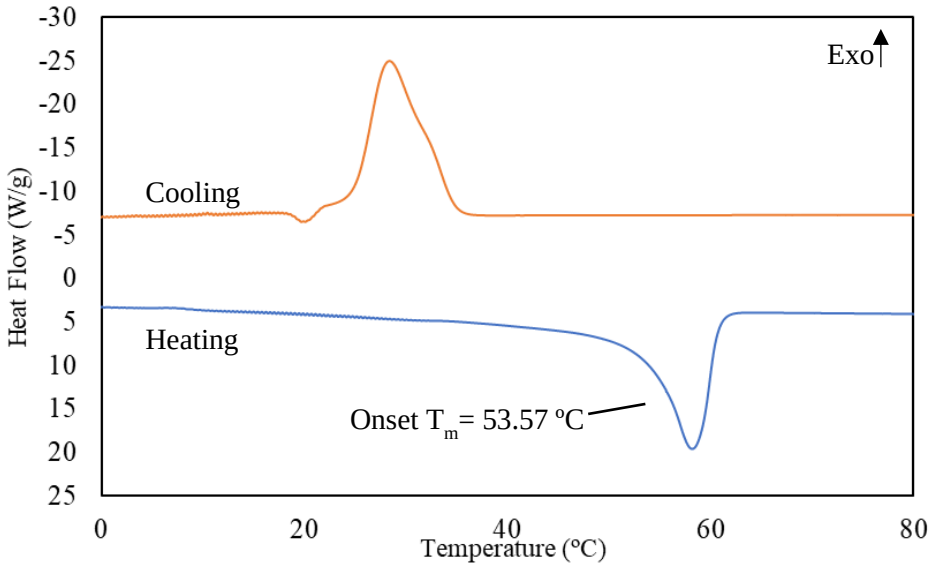

Fig. S318 DSC curve of PCL 550 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table S2**, entry 3 (2 h).

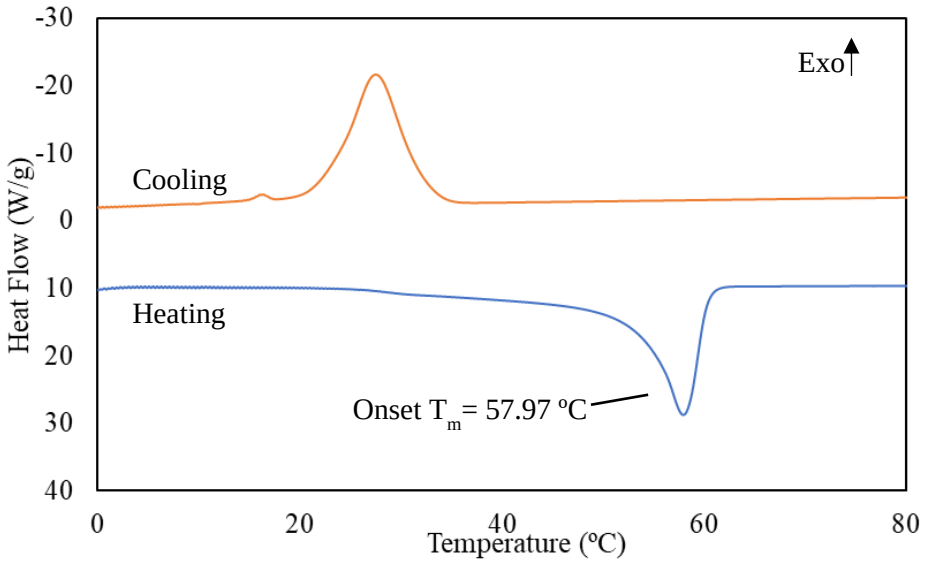

Fig. S319 DSC curve of PCL 800 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table S2**, entry 4 (2 h).

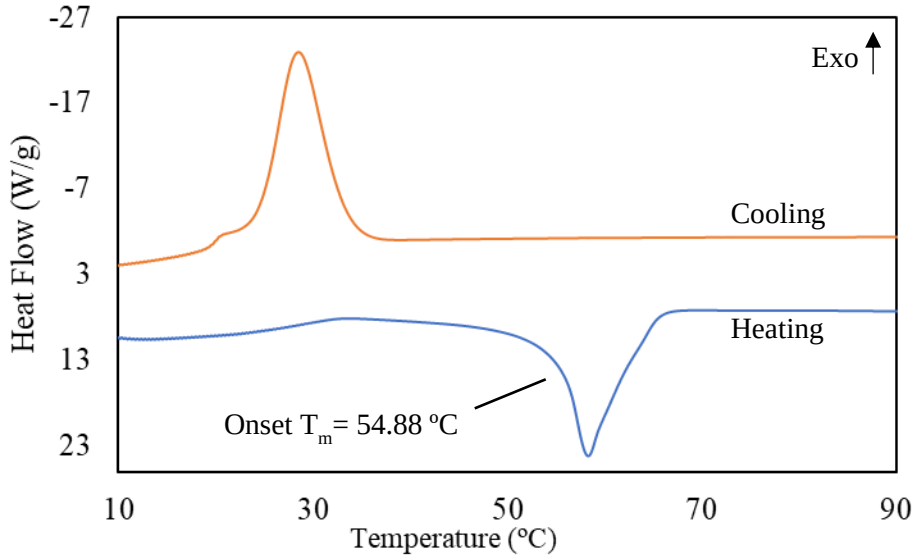

Fig. S320 DSC curve of PCL 300 equivalents generated by **6** from **Table S2**, entry 5 (No $[Ph_3C][B(C_6F_5)_4]$ added) (10 min).

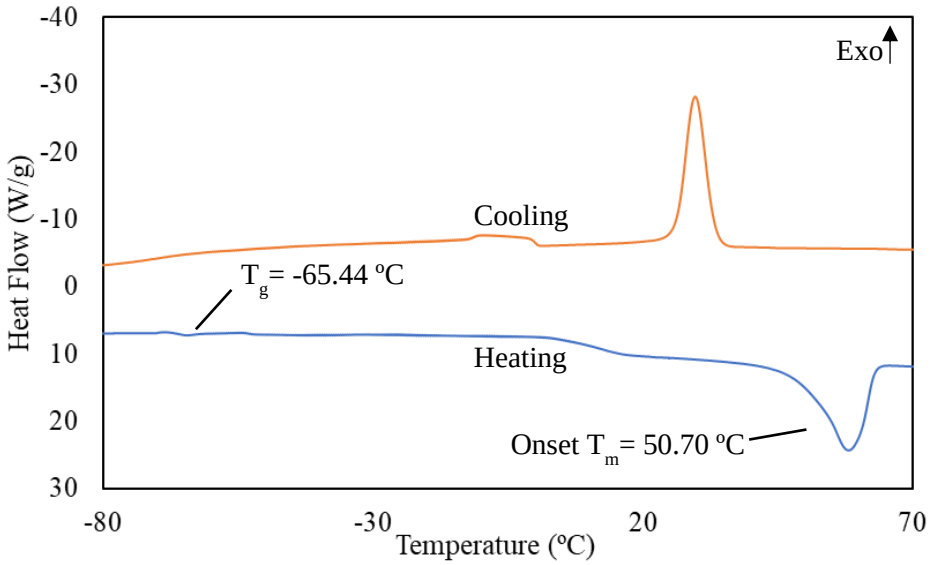

Fig. S321 DSC curve of PIP-*b*-PCL 50:50 equivalents generated by **6**/$[Ph_3C][B(C_6F_5)_4]$ from **Table S3**, entry 2.

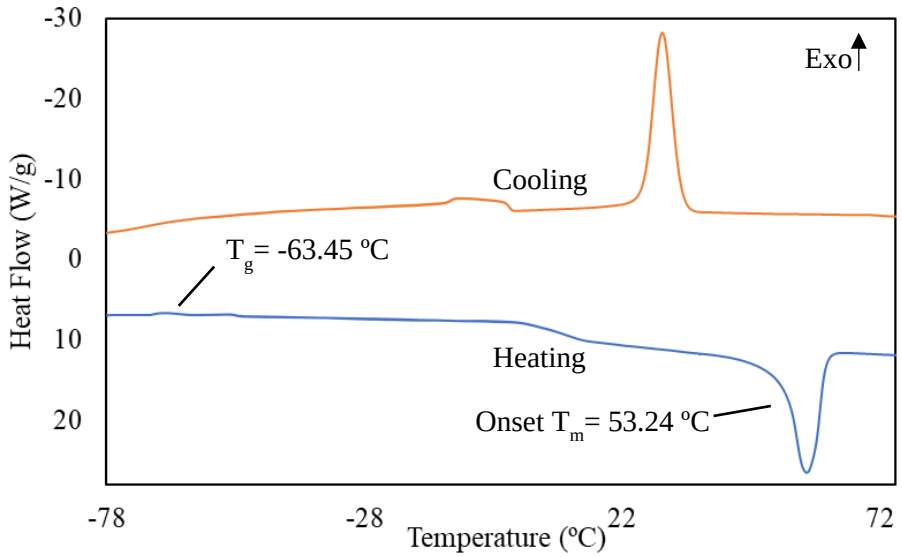

Fig. S322 DSC curve of PIP-*b*-PCL 50:50 equivalents generated by **$Y[N(SiMe_3)_2]_3$** from **Table S3**, entry 4 (6 h).