Supporting Information

Isoselective 3,4-(co)Polymerization of Biorenewable Myrcene Using NSN-Ligated Rare-earth Metal Precursors: Approach to New Elastomer

Bo Liu[†,‡], *Lei Li*[†,∥], *Guangping Sun*[‡], *Dongtao Liu*,[†] *Shihui Li*[*,†] *and Dongmei Cui*[*,†]

General experimental procedures.

All manipulations were performed under a dry and oxygen-free argon atmosphere using standard high-vacuum Schlenk techniques or in a glovebox. All solvents were purified via a SPS system. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV400 (FT, 400 MHz for ^{1}H; 100 MHz for ^{13}C) spectrometer. The molecular weight (M_n) was measured by TOSOH HLC-8220 GPC at 40 °C using THF as eluent (the flow rate is 0.35 mL/min) against polystyrene standards. Differential scanning calorimetry (DSC) analyses were carried out on a Q100 DSC from TA Instruments under a nitrogen atmosphere. Wide-angle X-ray diffraction (WAXD) measurements were performed using a Rigaku D/Max 2500V PC X-ray diffractometer (Cu Kα, λ = 1.5406 Å). The diffraction patterns were collected during continuous scan at a speed of 10 °/min between the angles of 5 and 50°.

Preparation of Diblock Copolymer Thin Film for TEM.

Block copolymer was first dissolved in $CHCl_3$ solution (0.1w/v%) and then directly dipped onto copper grids. The thin film was air-drying at room temperature. TEM experiments were performed on a JEOL 1011 TEM with an accelerating voltage of 100 kV in the bright-field mode.

Preparation of Diblock Copolymer Thin Film for AFM.

AFM observation was operated at the tapping mode with an SPI3800 controller (Seiko instruments Industry Co. Ltd.), performed on the block copolymer film. The film was spuncast from hot *o*- dichlorobenzene solutions (3 wt%) on hot Si substrates at 2200 rpm. The spuncast film was then annealed in high vaccum (< 10^{-7}mbar) at 70°C for 1 day. The films were subsequently imaged using a Digital Instruments Multi-mode Nanoscope. The imaging was performed in tapping mode.

Determination stereoselectivity of PMY.

The stereoselectivity (isotactic or syndiotactic) was dependent on γ-gauche effect. The measured C(0) is shielded by its γ substituents to an extent which is strongly affected by rotations around C(α)-C(β) bonds; in particular, for each γ substituent, the resonance of C shifts upfield by approximately 5 ppm when C(0)-C(α)-C(β)-C(γ) (SFig. 1) internal rotation angle is gauche, relative to the case in which it is trans. [1]

In order to distinguish *mmmm* sequence and *rrrr* sequence, a NPN-bidentate β-imidophosphonamido lutetium dialkyl complex (**2**) (chart 1), which exhibited highly 3,4-regioselectivity and syndio- stereoselectivity towards polymerization of isoprene, was used to prepare the syndiotactic 3,4 PMY.[2] Noteworthy, the resonance of *mmmm* sequence shifts downfield compared with *rrrr* sequence (SFig.2 and SFig. 3).

Preparation of low molecular weight Random Copolymer

A solution of $[Ph_3C][B(C_6F_5)_4]$ (92.0 mg, 100 μmol) in chlorobenzene (1 mL) was added to a solution of complex **1** (96.0 mg, 100 μmol) in chlorobenzene (1 mL) in a 25 mL flask under a nitrogen atmosphere. The mixture was stirred at -30 °C for a few minutes, and the mixture of isoprene (85.0 mg, 1.25 mmol) and mycrene (170 mg, 1.25 mmol) was added under vigorous stirring. The reaction was terminated after 12 h by the addition of a small amount of acidic methanol containing 2,6-di-tert-butyl-*p*-cresol (1 wt%) as an antioxidant reagent. The mixture was poured into methanol (100 mL) to precipitate the copolymer product. The copolymer was dried under vacuum at 40 °C to a constant weight (0.25 g, 100%).

Preparation of low molecular weight Diblock Copolymer

A solution of $[Ph_3C][B(C_6F_5)_4]$ (92.0 mg, 100 μmol) in chlorobenzene (1 mL) was added to a solution of complex **1** (96.0 mg, 100 μmol) in chlorobenzene (1 mL) in a 25 mL flask under a nitrogen atmosphere. The mixture was stirred at -30 °C for a few minutes, and isoprene (85.0 mg, 1.25 mmol) was added under vigorous stirring for 6 h and then mycrene (170 mg, 1.25 mmol) was added for another 6 h. The reaction was terminated with a small amount of acidic methanol containing 2,6-di-tert-butyl-*p*-cresol (1 wt%) as an antioxidant reagent. The mixture was poured into methanol (100 mL) to precipitate the copolymer product. The copolymer was dried under vacuum at 40 °C to a constant weight (0.25 g, 100%).

Reference:

1. V. Busico; and R. Cipullo, *Prog. Polym. Sci.*, 2001, **26**, 443.

2. B. Liu; L. Li; G. Sun; J. Liu; M. Wang; S. Li; and D. Cui, *Macromolecules*, 2014, **47**, 4971.

Chart 1. β-imidophosphonamido ligated Lutetium Dialkyl Complex **2**.

SFig. 1 C(0), C(α), C(β) and C(γ) in PMY.
SFig. 2 ^{1}H NMR (400M, $CDCl_3$, 25 °C) of PMY sample.
SFig 3. Overlay of ^{13}C NMR of (a) PMY prepared by **2** in toluene (b) PMY prepared by **2** in chlorobenzene (c) PMY (Table 1, run 3).
SFig. 4 ^{1}H NMR (400M, $CDCl_3$, 25 °C) of PMY sample (Table 1, Run 3).
SFig. 5 ^{13}C NMR (100M, $CDCl_3$, 25 °C) of PMY sample (Table 1, Run 3).
SFig. 6 DEPT135 (100M, $CDCl_3$, 25 °C) of PMY sample (Table 1, Run 3).
SFig. 7 HSQC map of PMY sample (Table 1, Run 3).
SFig. 8 ^{1}H NMR (400M, $CDCl_3$, 25 °C) of copolymer (Table 1, Run 12).
SFig. 9 ^{13}C NMR (100M, $CDCl_3$, 25 °C) of copolymer (Table 1, Run 12).
SFig. 10 ^{13}C NMR (100M, $CDCl_3$, 25 °C) of PMY-b-PIP sample (Table 1, Run 14).
SFig. 11 ^{13}C NMR (125M, $CDCl_3$, 25 °C) of diblock copolymer (top) and random copolymer (bottom).
SFig. 12 Photograph of PIP sample (Table 1, Run 11).
SFig. 13 Photograph of PMY sample (Table 1, Run 3).
SFig. 14 DSC chart of PMY sample (Table 1, Run 3).
SFig. 15 DSC chart of (a) (3,4-*iso*-PMY)-co-(3,4-*iso*-PIP); (b) (3,4-*iso*-PMY)-block-(3,4-*iso*-PIP); (c) (3,4-*iso*-PMY)-blend-(3,4-*iso*-PIP).
SFig. 16 TEM chart of PMY-b-PIP sample (Table 1, Run 14).
SFig. 17 AFM chart of PMY-b-PIP sample (Table 1, Run 14).
STable1 Chemical shifts of the relevant peaks in the ^{13}C NMR and ^{1}H NMR of isotactic PMY.

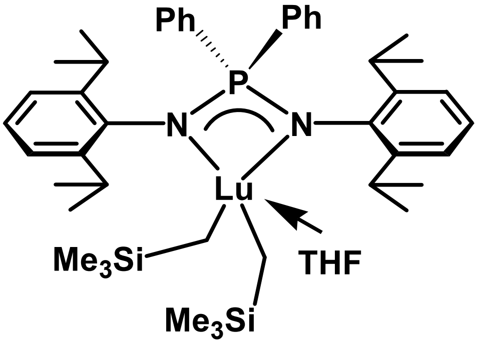
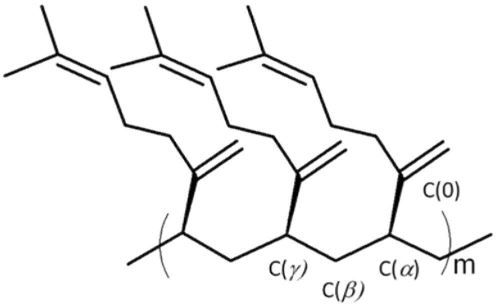
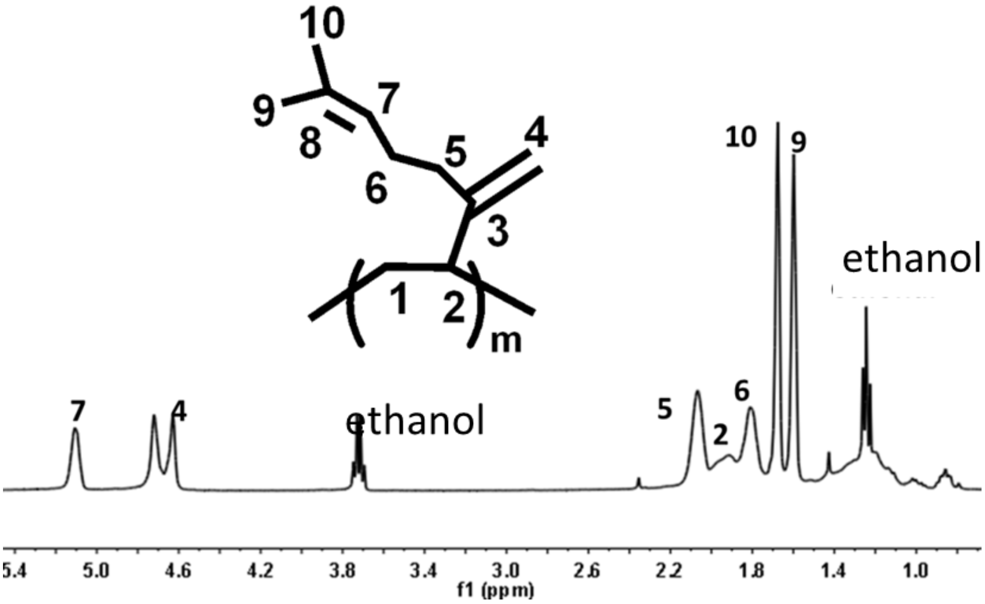


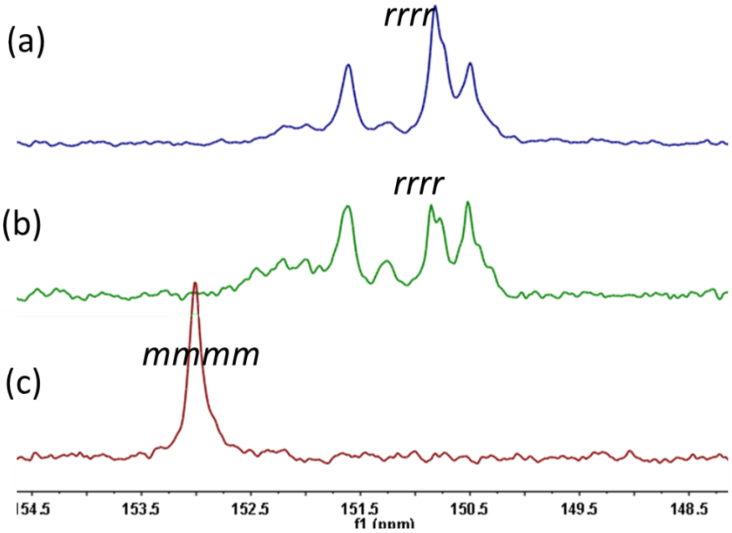
Chart 1. β-imidophosphonamido ligated Lutetium Dialkyl Complex **2**.



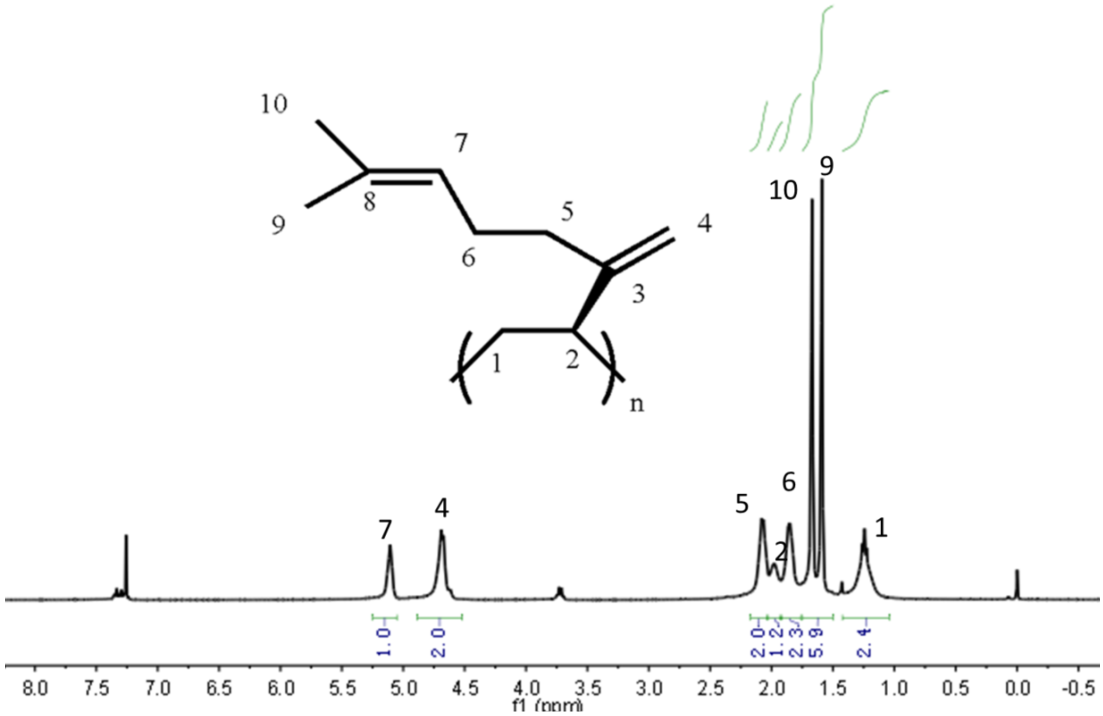
SFig. 1 C(0), C(α), C(β) and C(γ) in PMY.



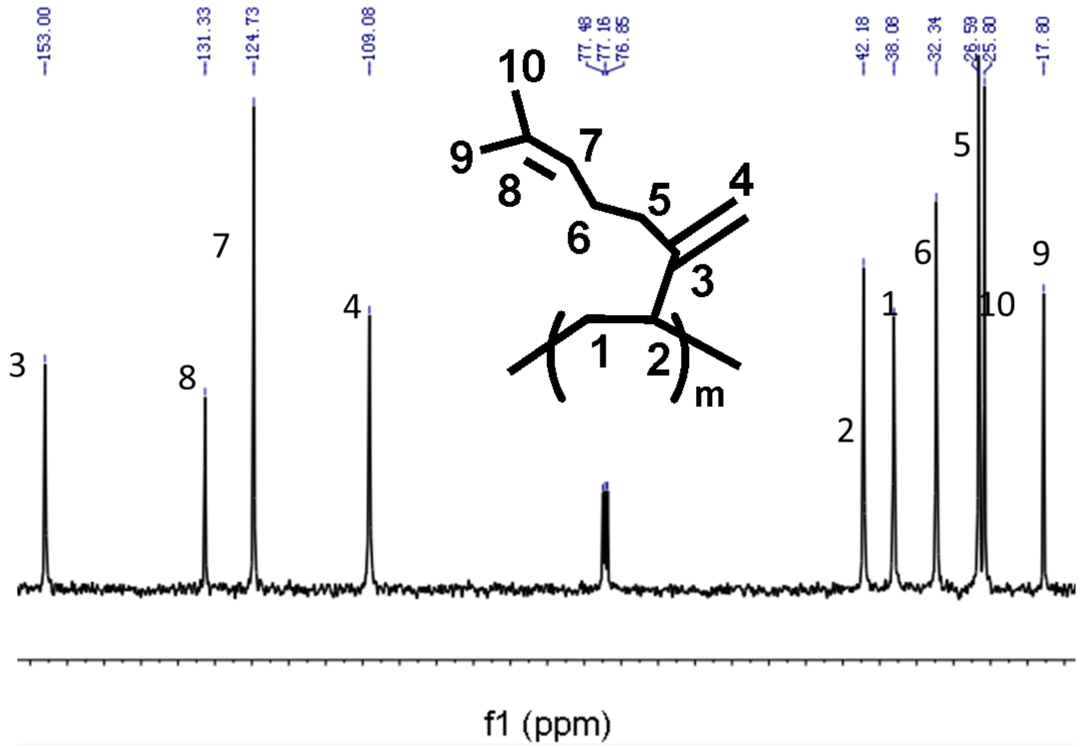
SFig. 2 ^{1}H NMR (400M, $CDCl_3$, 25 °C) of PMY sample.



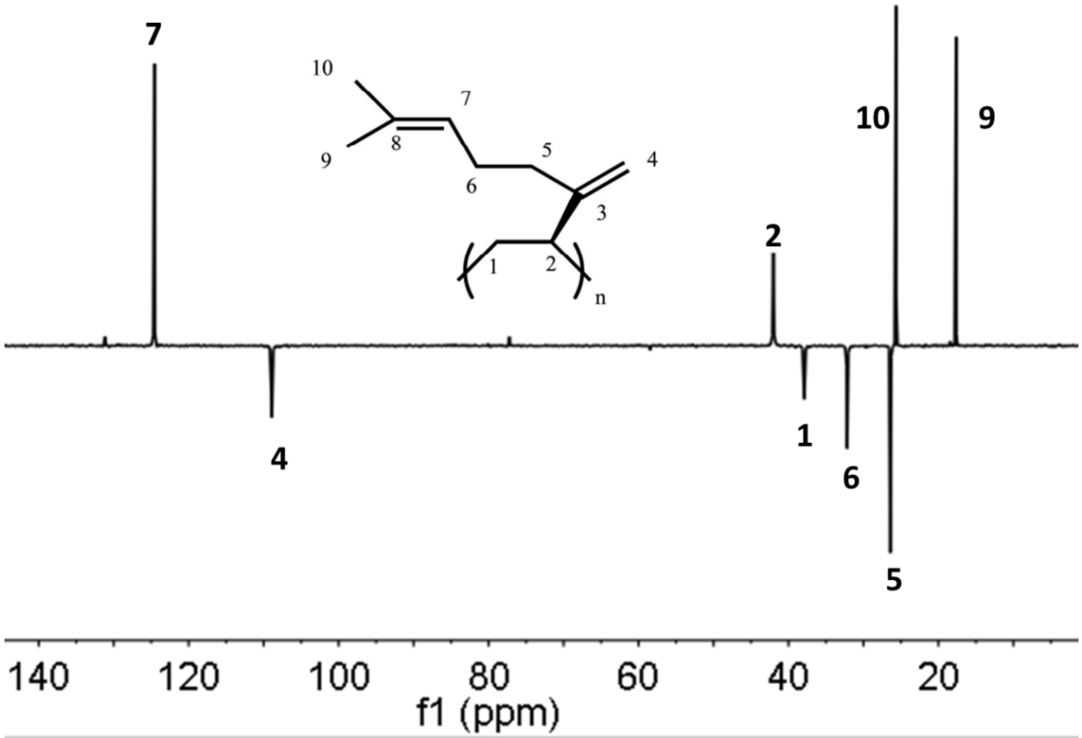
SFig 3. Overlay of ^{13}C NMR of (a) PMY prepared by **2** in toluene (b) PMY prepared by **2** in chlorobenzene (c) PMY (Table 1, run 3).



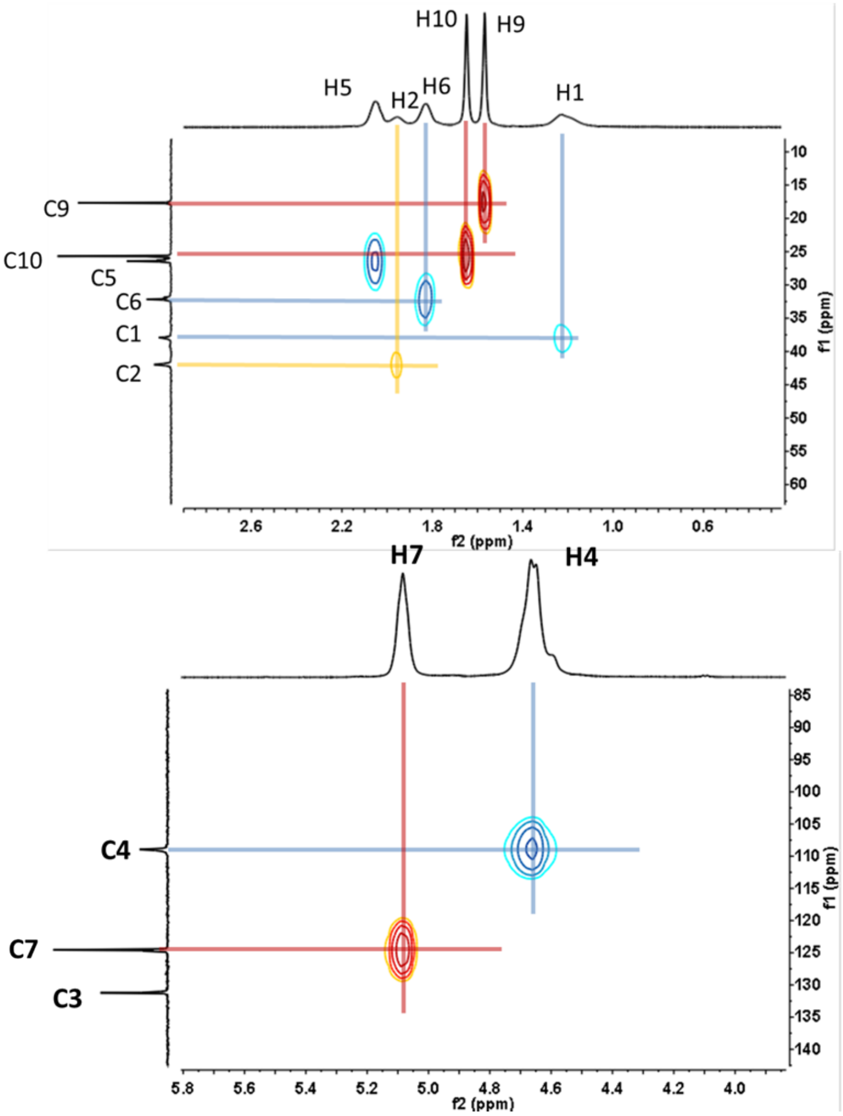
SFig. 4 ^{1}H NMR(400M, $CDCl_3$, 25 °C) of PMY sample (Table 1, Run 3).



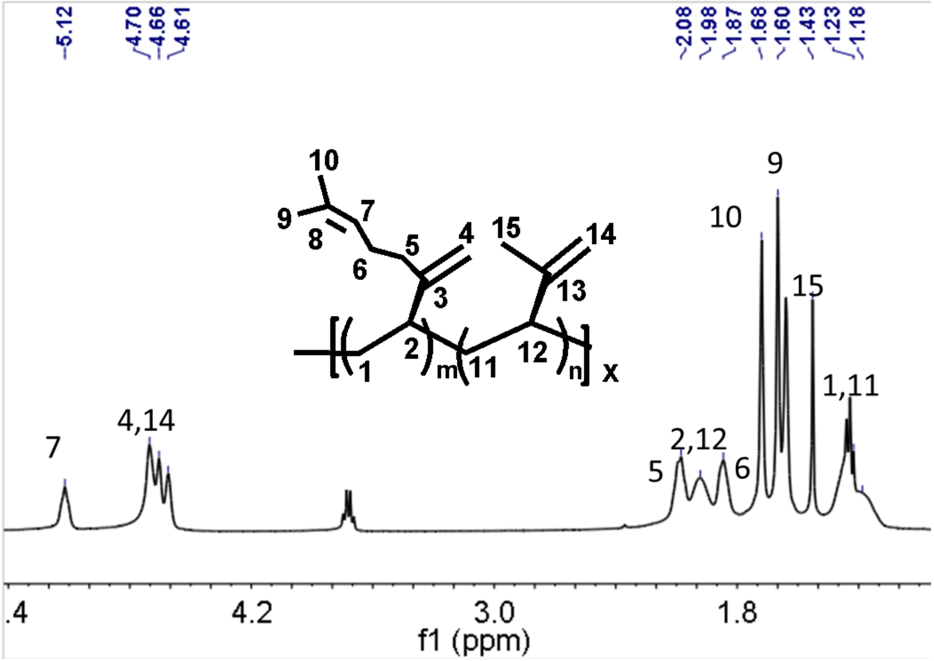
SFig. 5 ^{13}C NMR (100M, $CDCl_3$, 25 °C) of PMY sample (Table 1, Run 3).



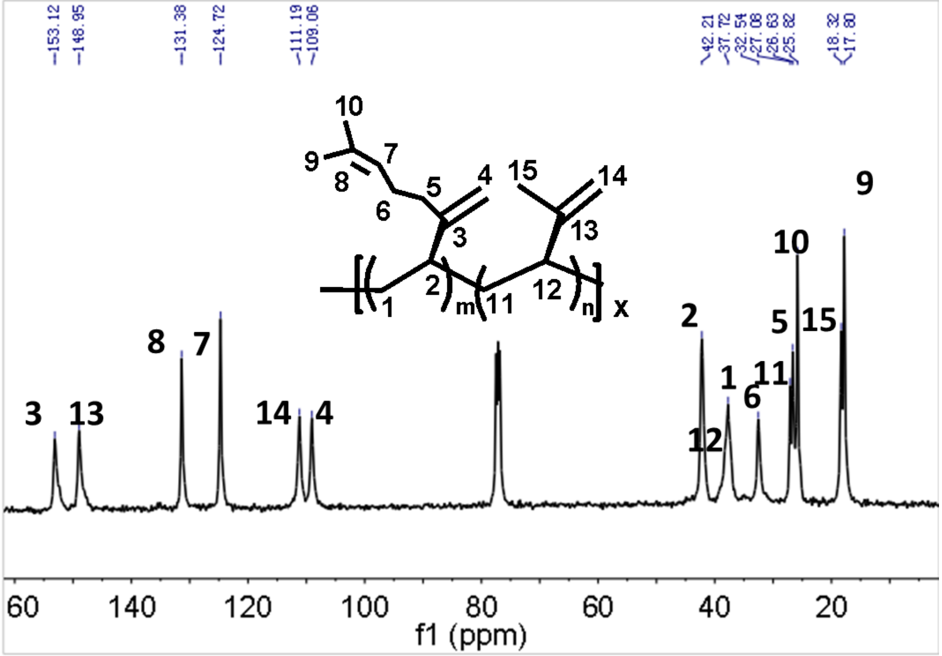
SFig. 6 DEPT135 (100M, $CDCl_3$, 25 °C) of PMY sample (Table 1, Run 3).



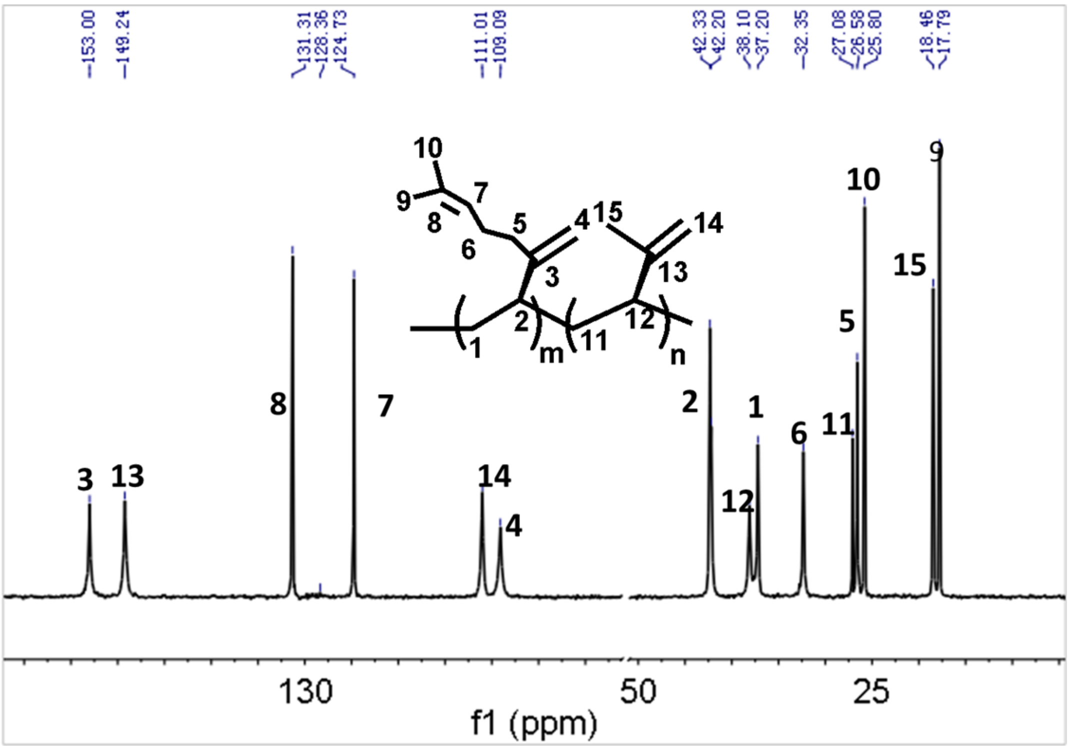
SFig. 7 HSQC map of PMY sample (Table 1, Run 3).



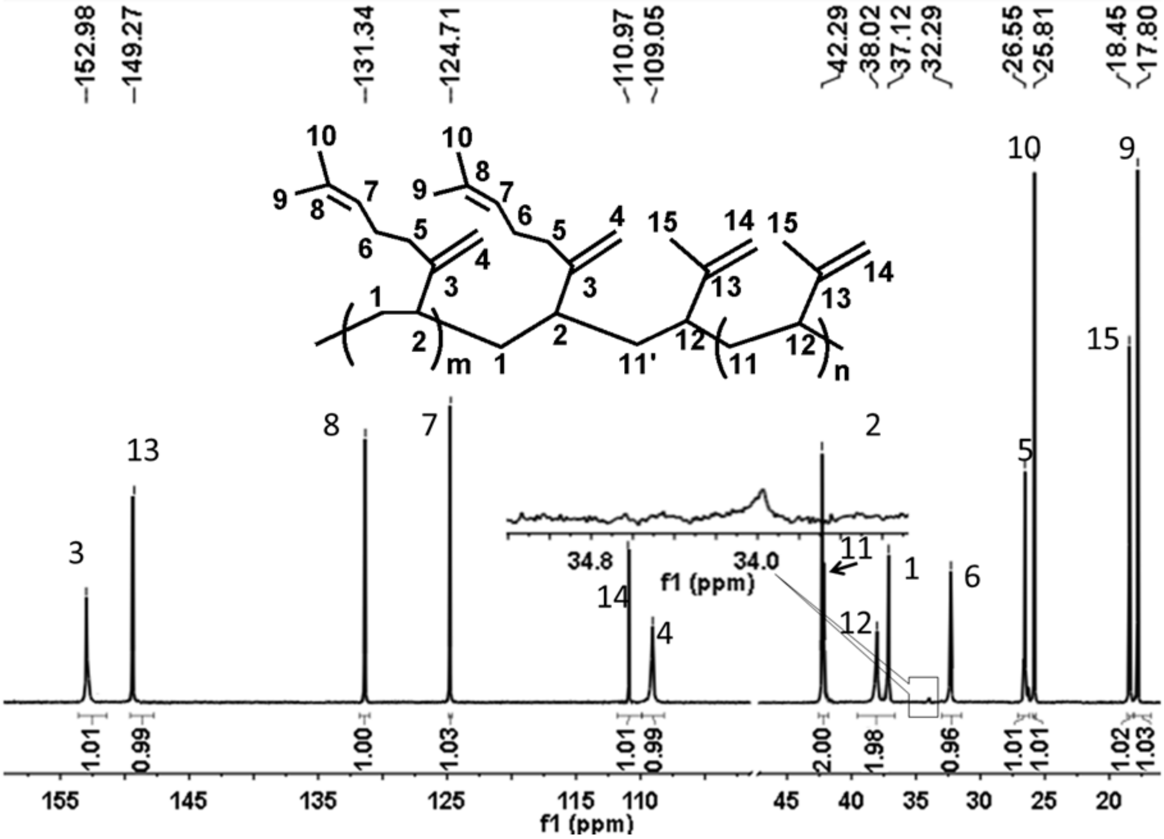
SFig. 8 ^{1}H NMR (400M, $CDCl_3$, 25 °C) of copolymer (Table 1, Run 12).

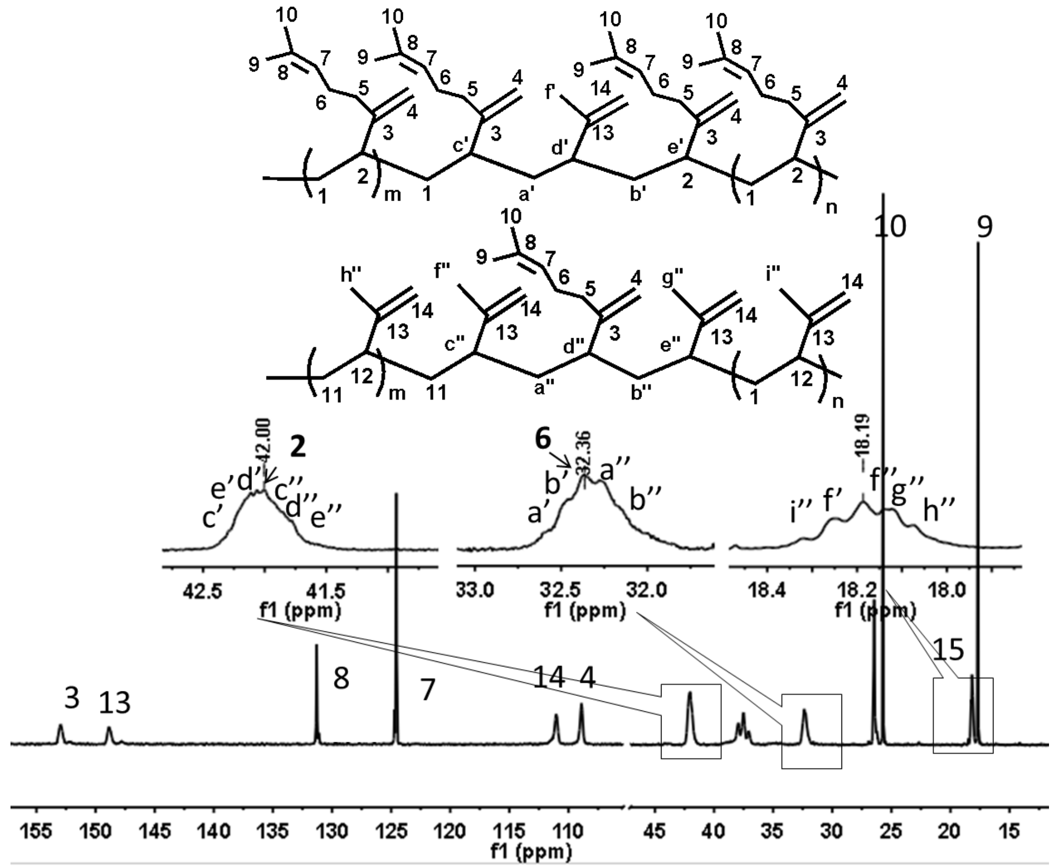


SFig. 9 ^{13}C NMR (100M, $CDCl_3$, 25 °C) of copolymer (Table 1, Run 12).

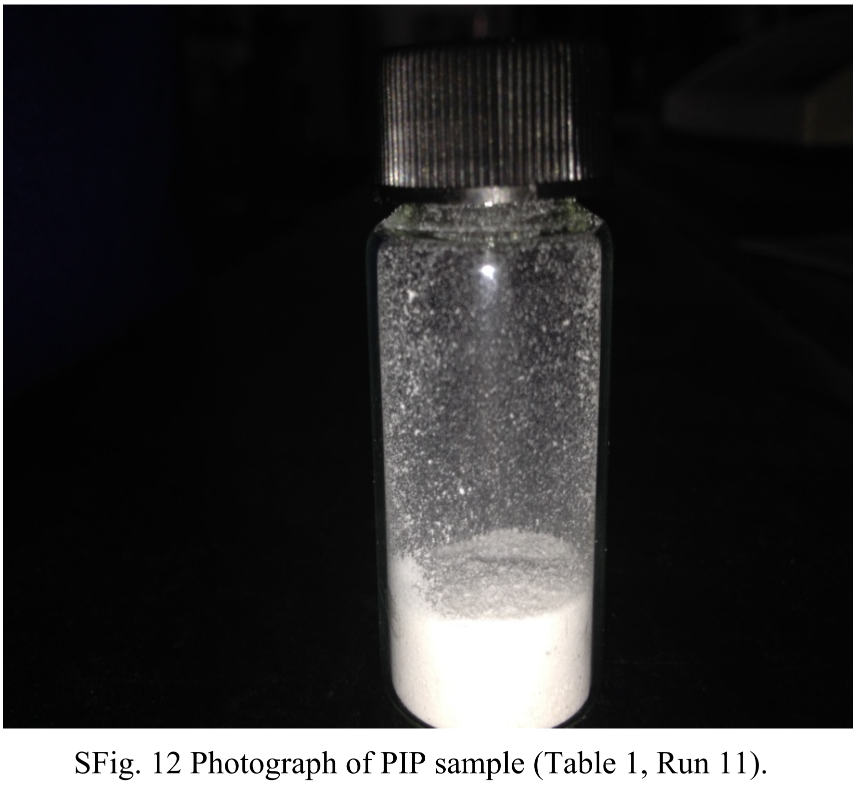


SFig. 10 ^{13}C NMR (100M, $CDCl_3$, 25 °C) of PMY-b-PIP sample (Table 1, Run 14).

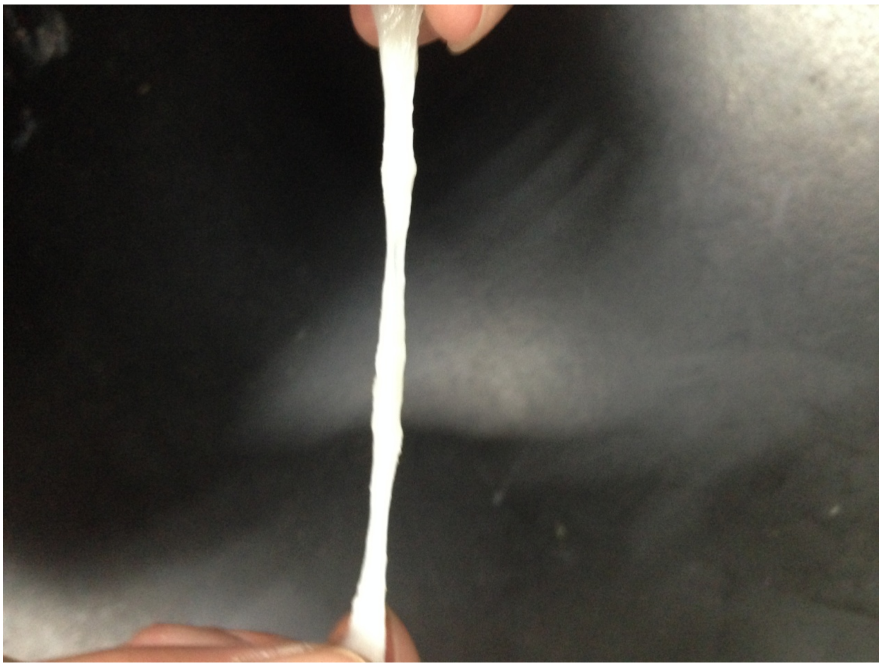




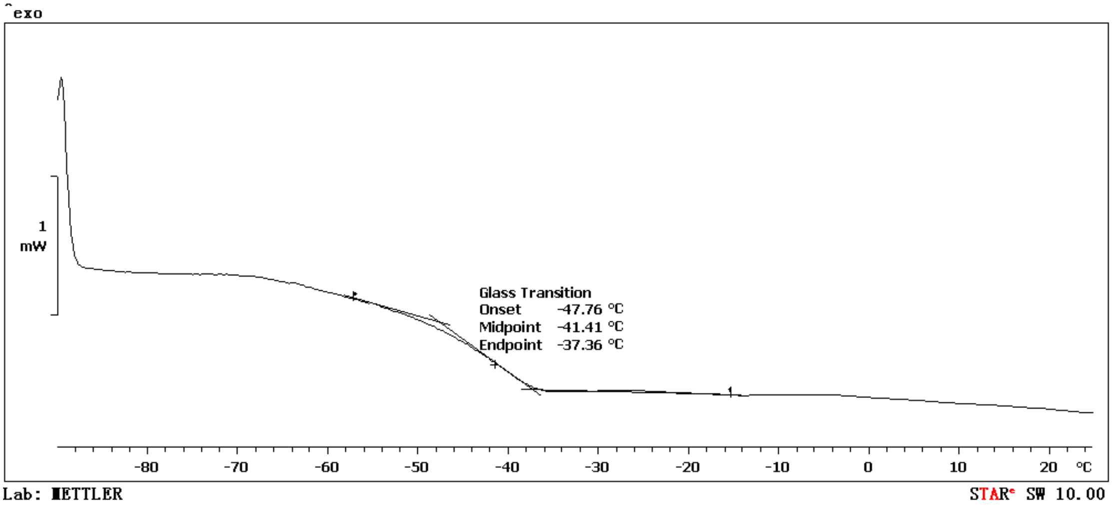
SFig. 11 ^{13}C NMR (125M, CDCl$_3$, 25 °C) of diblock copolymer (top) and random copolymer (bottom)



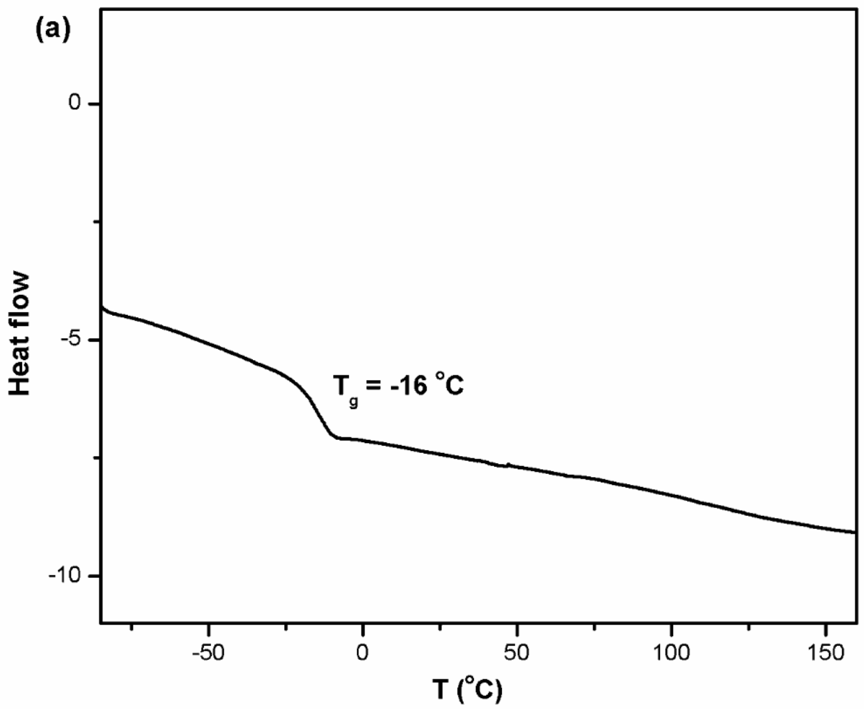
SFig. 12 Photograph of PIP sample (Table 1, Run 11).

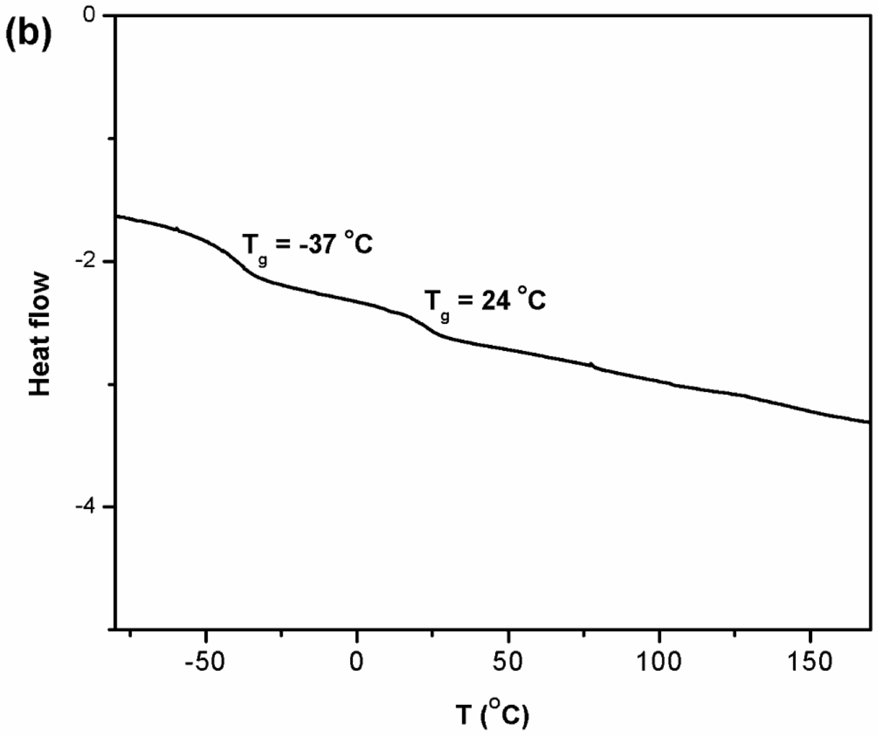


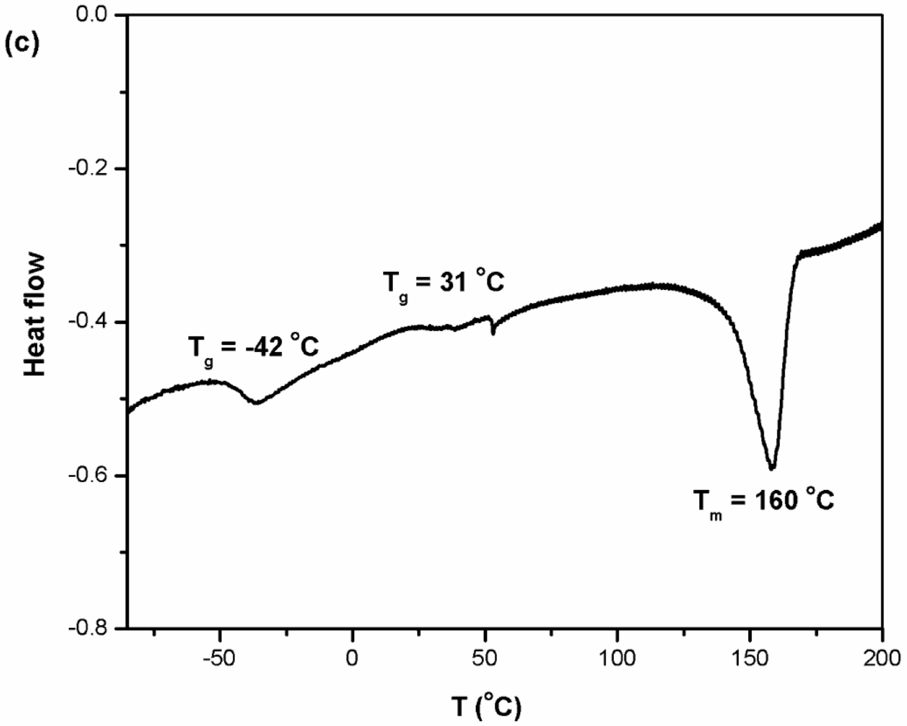
SFig. 13 Photograph of PMY sample (Table 1, Run 3).



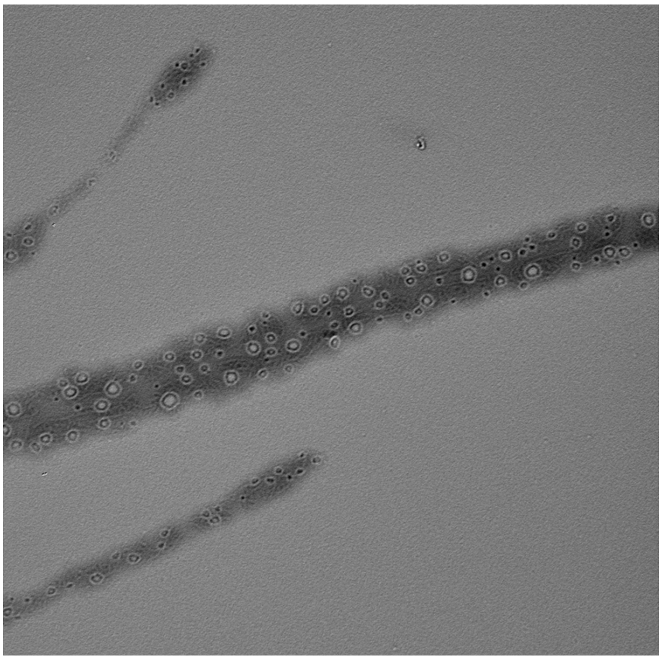
SFig. 14 DSC chart of PMY sample (Table 1, Run 3).


(a)
Heat flow
0
-5
-10
T$_g$ = -16 °C
-50
0
50
100
150
T (°C)

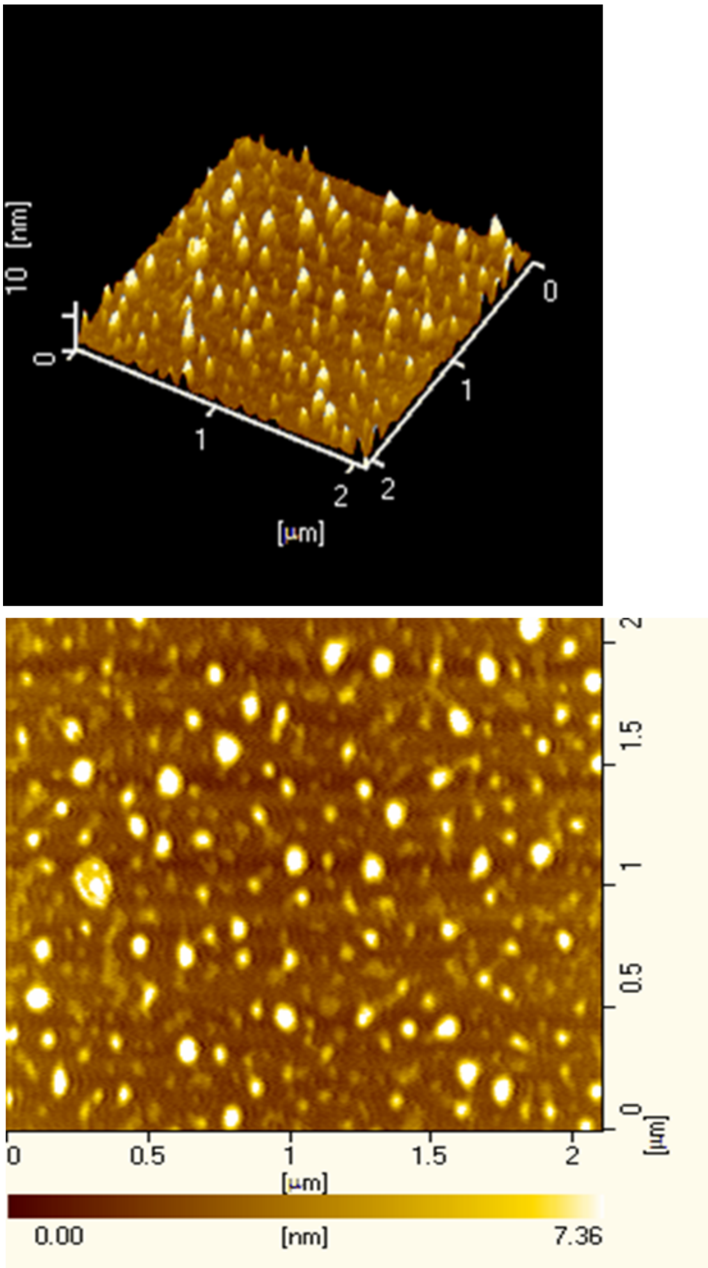

(b)
Heat flow
0
-2
-4
T$_g$ = -37 °C
T$_g$ = 24 °C
-50
0
50
100
150
T (°C)



SFig. 15 DSC chart of (a) (3,4-*iso*-PMY)-co-(3,4-*iso*-PIP); (b) (3,4-*iso*-PMY)-block-(3,4-*iso*-PIP); (c) (3,4-*iso*-PMY)-blend-(3,4-*iso*-PIP).



SFig. 16 TEM chart of PMY-b-PIP sample (Table 1, Run 14).



SFig. 17 AFM chart of PMY-b-PIP sample height(top) and phase image(bottom) (Table 1, Run 14).

STable1 Chemical shifts of the relevant peaks in the ^{13}C NMR and ^{1}H NMR of isotactic PMY

Assignments	Chemical shifts	Assignments	Chemical shifts
C1	38.1	H1	1.25
C2	42.2	H2	1.98
C3	153.0	H4	4.69
C4	109.1	H5	2.07
C5	26.6	H6	1.85
C6	32.3	H7	5.11

C7	124.7	H9	1.59
C8	131.1	H10	1.67
C9	17.8		
C10	25.8		