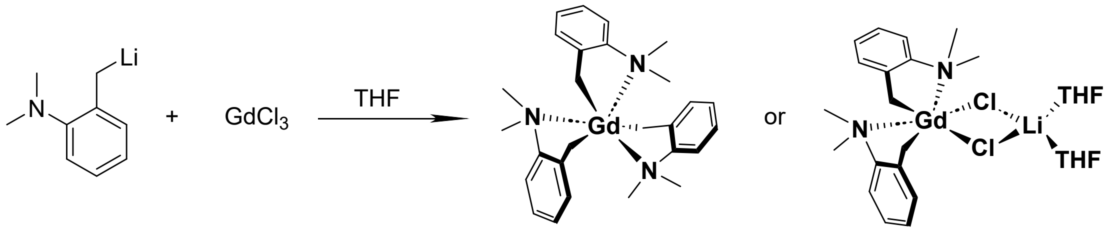
Supporting Information

Plastic-Rubber Diblock Copolymer from Copolymerization of Dimethyl-1,3-butadiene and Butadiene by Rare-earth Metal Catalyst

Jiao Zong, Benmin Hu, Shihui Li, Lei Li, Bo Liu* 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 spectrum of PBD were recorded on a Bruker AV400 (FT, 400 MHz for ^{1}H; 100 MHz for ^{13}C) spectrometer in $CDCl_3$ at 25 °C. ^{1}H and ^{13}C NMR spectrum of PDMB were recorded on a Bruker AV400 (FT, 400 MHz for ^{1}H; 100 MHz for ^{13}C) spectrometer in $C_6D_4Cl_2$ at 120 °C. The molecular weight (M_n) and molecular weight distributions (M_w/M_n) of PBD were measured by TOSOH HLC-8220 GPC at 40 °C using THF as eluent (the flow rate is 0.35 mL/min) against polystyrene standards. The molecular weight (M_n) and molecular weight distributions (M_w/M_n) of PDMB and the coplolymers were measured by means of gel permeation chromatography (GPC) on a PL-GPC220 high-temperature chromatography equipped with three PL-gel 10 μm Mixed-BLS columns at 150 °C. 1,2,4-Trichlorobenzene (TCB), containing 0.05 w/v% 2,6-di-*tert*-butyl-*p*-cresol (BHT) was employed as the solvent at a flow rate of 1.0 mL/min. The calibration was made by using polystyrene standard EasiCalPS-1. 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°.

Synthesis of Complex 1-7.
The complexes 1–5 were synthesized according to previously reported methods.[1-5]



Complex 6 Complex 7

Scheme 1. The preparation of complexes 6 and 7

Complex 6 and 7 can be easily prepared as illustrated in Scheme 1. In a nitrogen-filled glovebox, $GdCl_3$ (0.53 g, 2 mmol) was dissolved in anhydrous tetrahydrofuran (THF, 20 mL) and stirred at room temperature for 12 h. Subsequently, a THF solution (10 mL) of (2-isopropylbenzyl) lithium (0.85 g, 6 mmol) was added dropwise to the $GdCl_3$

mixture, and the reaction was allowed to proceed at 25°C for 8 h, during which the solution transitioned to a brown hue. Upon completion, lithium chloride (LiCl) byproducts were removed by filtration, and the filtrate was concentrated under reduced pressure. Light yellow crystalline product was isolated via recrystallization from a THF/hexane mixture at -20°C. The synthesis of complex 7 follows a procedure similar to that described above, with the only modification being the adjustment of the amount of (2-isopropylbenzyl) lithium to twice the molar equivalent of $GdCl_3$.

Kinetic Experiment

Polymers obtained at different polymerization times were collected, dried, weighed, and characterized using proton nuclear magnetic resonance (^{1}H NMR) spectroscopy. The molar ratio of the two monomers (f_{DMB} and f_{BD}) in the copolymer was determined based on the integral area ratio of the methyl hydrogen (H2 in Figure 2) of PMB and the vinyl hydrogen (H4 in Figure 2) of PBD. The molar fraction of DMB in the copolymer is converted to the mass fraction (w_{DMB} and w_{BD}). When the polymerization was carried out within 1 min, the isolated product was almost pure PBD according to its 1H NMR spectrum. According to the polymer yield data, BD exhibited nearly quantitative conversion (>99%). The absolute mass of DMB incorporated into the copolymer ($m_{DMB,incor}$) was determined by multiplying the total polymer yield (Y_{total}) by the mass fraction (w_{DMB}). The conversion of DMB (C_{DMB}) was then obtained by dividing this value by the initial mass of DMB charged into the reaction ($m_{DMB,init}$).

$$f_{DMB} = \frac{\frac{I_{H2}}{6}}{\frac{I_{H2}}{6} + \frac{I_{H4}}{2}} \qquad f_{BD} = 1 - f_{DMB}$$

$$w_{DMB} = \frac{f_{DMB} \times M_{DMB}}{f_{DMB} \times M_{DMB} + f_{BD} \times M_{BD}} \qquad w_{BD} = 1 - w_{DMB}$$

$$m_{DMB,incor} = Y_{total} \times w_{DMB} \qquad C_{DMB} = \frac{m_{DMB,incor}}{m_{DMB,init}} \times 100\%$$

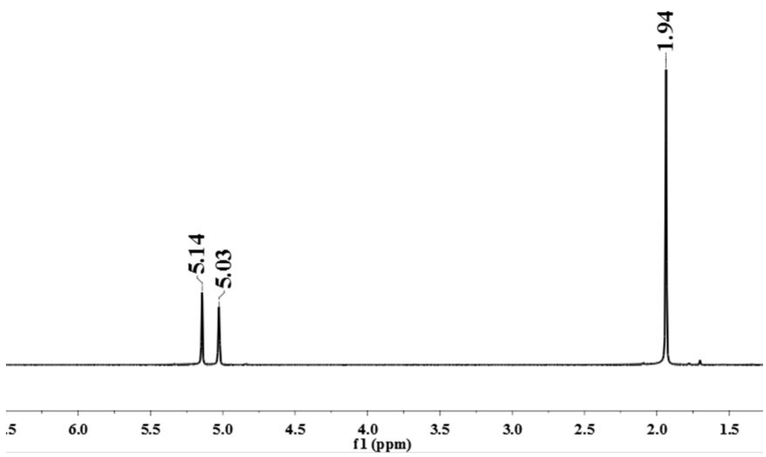
where I_{H2} and I_{H4} represent the peak areas of protons at $\delta = 1.90$ ppm and $\delta = 5.62$ ppm, respectively.

Preparation of Polymer Thin Film for TEM.

The polymer was first dissolved in $C_6D_4Cl_2$ solution (0.1 w/v%)at 120 ^{o}C 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.

1. L. Wang, D. Cui, Z. Hou, W. Li and Y. Li, *Organometallics*, 2011, **30**, 760-767.
2. D. Li, S. Li, D. Cui and X. Zhang, *Organometallics*, 2010, **29**, 2186-2193.
3. W. Gao and D. Cui, *J. Am. Chem. Soc.*, 2008, **130**, 4984-4991.
4. S. Li, D. Cui, D. Li and Z. Hou, *Organometallics*, 2009, **28**, 4814-4822.
5. Y. Pan, W. Rong, Z. Jian and D. Cui, *Macromolecules*, 2012, **45**, 1248-1253.

SFigure 1 ^{1}H NMR (400M, $CDCl_3$, 25 °C) of DMB.
SFigure 2 DSC of *cis*-1,4-PDMB (Table 1, Run 7).
SFigure 3 WAXD of *cis*-1,4-PDMB by **7**/$[Ph_3C][B(C_6F_5)_4]$/Al^iBu_3, **7**/$[Ph_3C][B(C_6F_5)_4]$/$AlEt_3$ and **7**/$[Ph_3C][B(C_6F_5)_4]$/$AlMe_3$.
SFigure 4 POM of *cis*-1,4-PDMB (Table 1, Run 7).
SFigure 5 ^{13}C NMR (400M, $CDCl_3$, 25 °C) of *cis*-1,4-PBD (Table 2, run 7).
SFigure 6 Kinetics curves (Table 3, run 4): conversion versus polymerization time.
SFigure 7 DSC of the diblock copolymer (Table 3, Run 2).
SFigure 8 DSC of the diblock copolymer (Table 3, Run 4).
SFigure 9 XRD of copolymers. (a) Table 3, run 6 (90% DMB) ; (b) Table 3, run 5 (70% DMB); (c) Table 3, run 4 (50% DMB); (d) Table 3, run 3 (40% DMB); (e) Table 3, run 2 (30% DMB).
SFigure 10 GPC curve of BD-DMB diblock copolymer (Table 3, entry 1).
SFigure 11 GPC curve of BD-DMB diblock copolymer (Table 3, entry 2).
SFigure 12 GPC curve of BD-DMB diblock copolymer (Table 3, entry 3).
SFigure 13 GPC curve of BD-DMB diblock copolymer (Table 3, entry 4).
SFigure 14 GPC curve of BD-DMB diblock copolymer (Table 3, entry 5).
SFigure 15 GPC curve of BD-DMB diblock copolymer (Table 3, entry 6).
SFigure 16 GPC curve of BD-DMB diblock copolymer (Table 3, entry 7).



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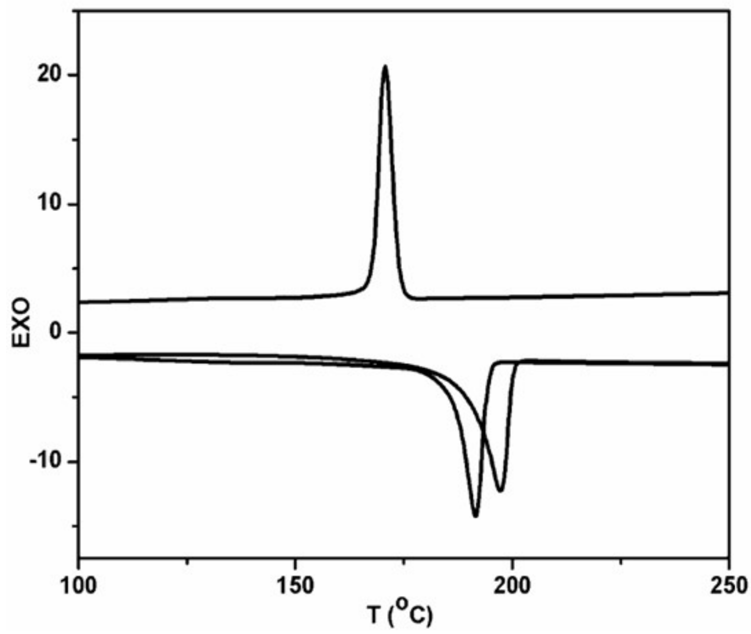
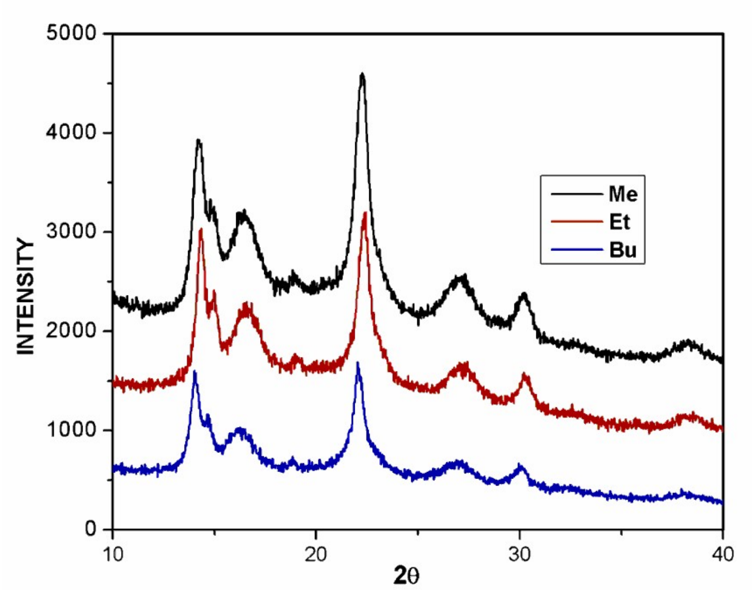
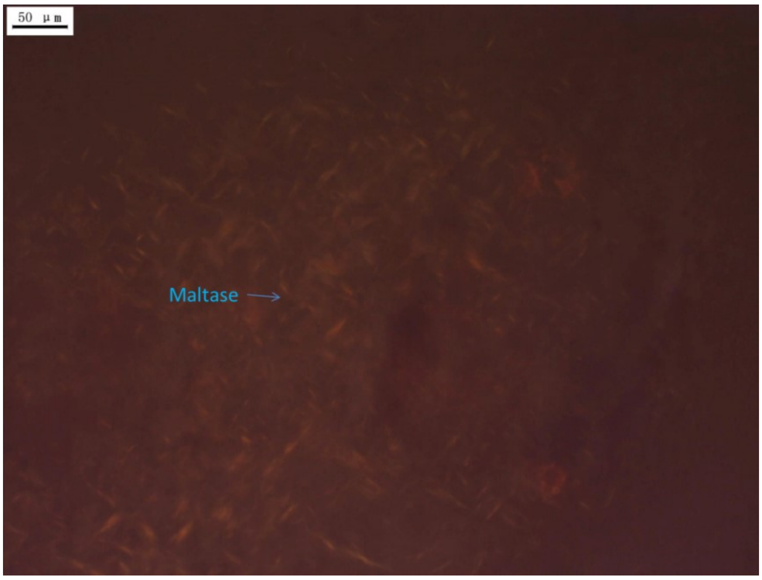


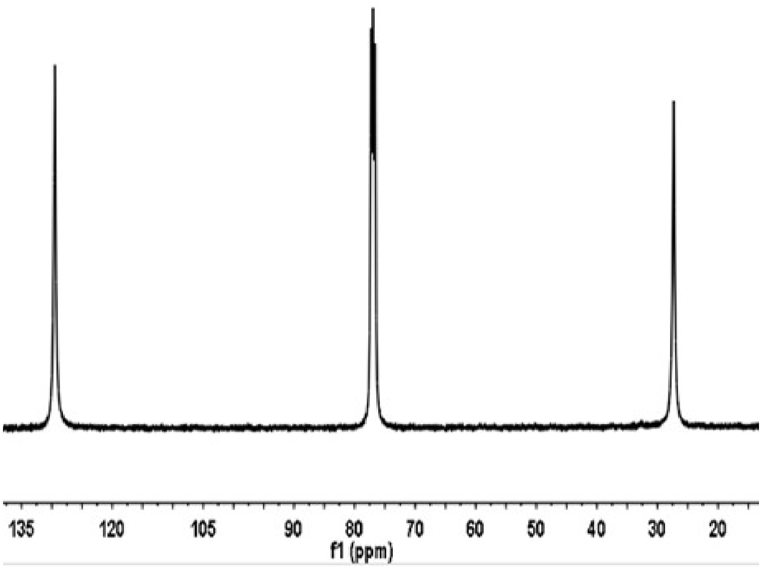
SFigure 2 DSC of *cis*-1,4-PDMB (Table 1, Run 7).



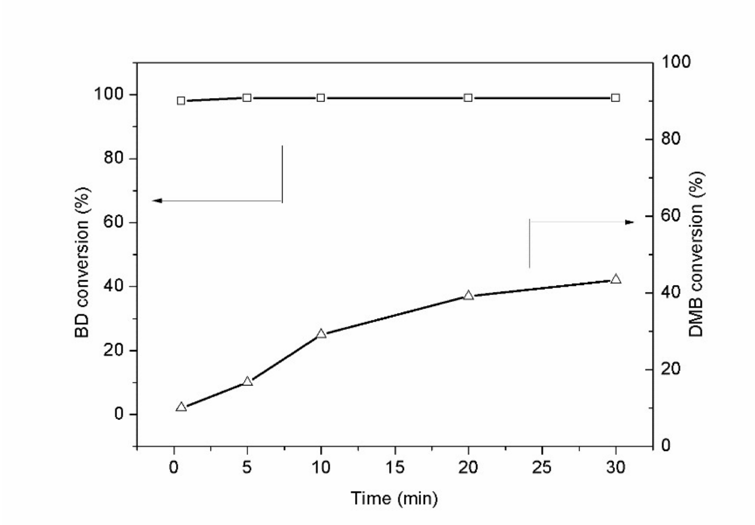
SFigure 3 WAXD of *cis*-1,4-PDMB by **7**/[Ph_3C][$B(C_6F_5)_4$]/Al^iBu_3, **7**/[Ph_3C][$B(C_6F_5)_4$]/$AlEt_3$ and **7**/[Ph_3C][$B(C_6F_5)_4$]/$AlMe_3$.



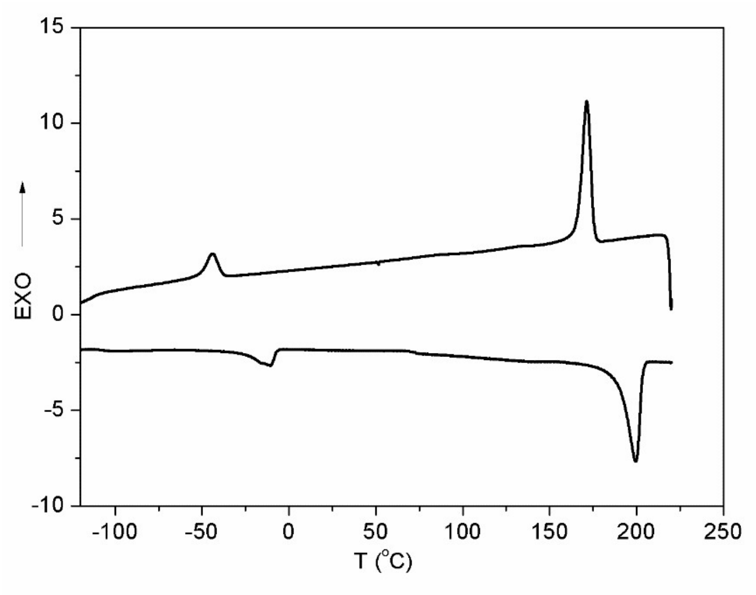
SFigure 4 POM of *cis*-1,4-PDMB (Table 1, Run 7).



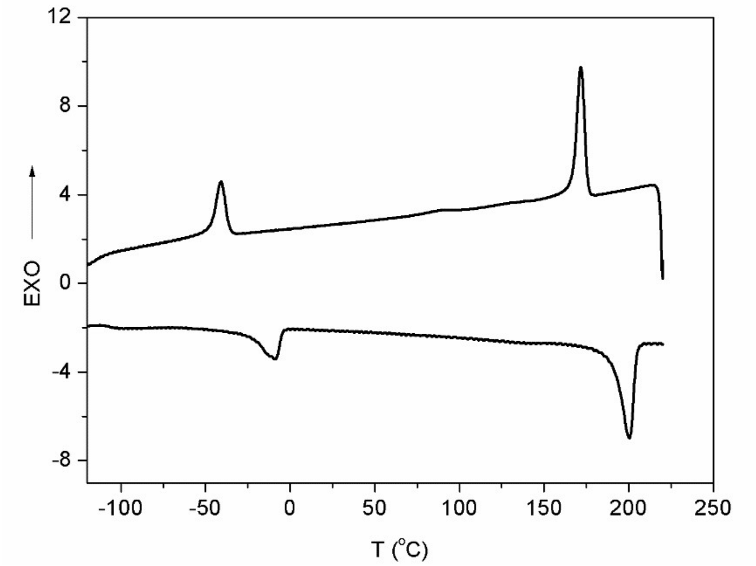
SFigure 5 ^{13}C NMR (400M, $CDCl_3$, 25 °C) of *cis*-1,4-PBD (Table 2, run 7).



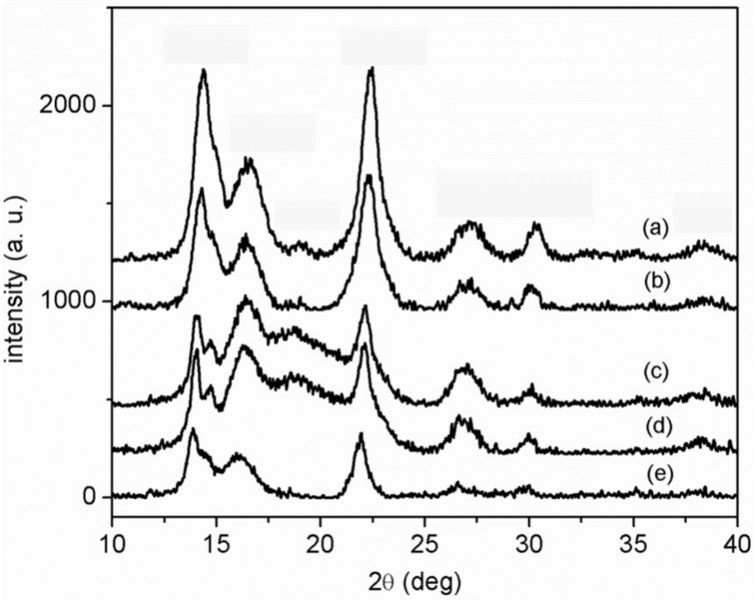
SFigure 6 Kinetics curves (Table 3, run 4): conversion versus polymerization time.



SFigure 7 DSC of the diblock copolymer (Table 3, Run 2).



SFigure 8 DSC of the diblock copolymer (Table 3, run 4).



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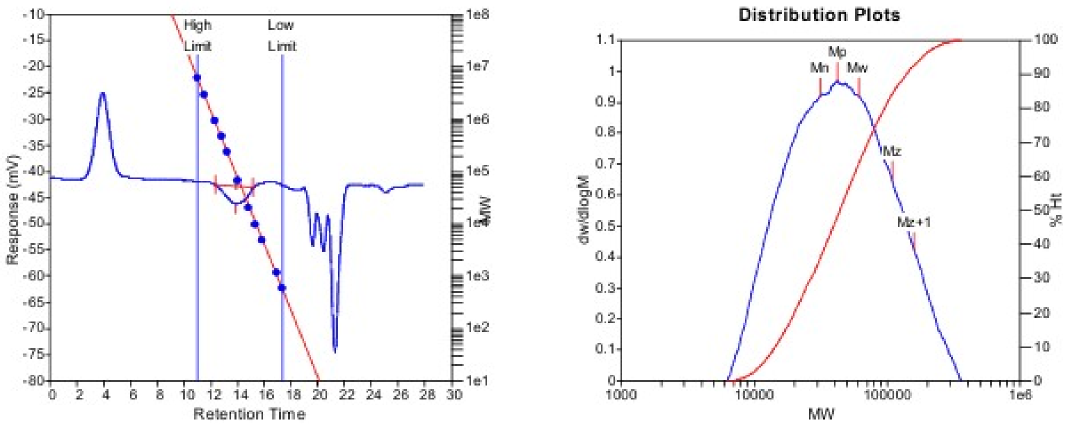
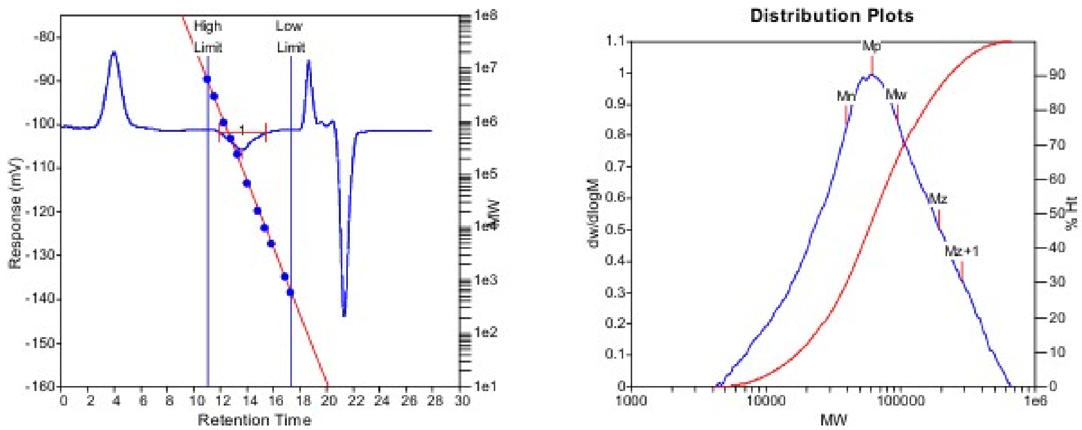
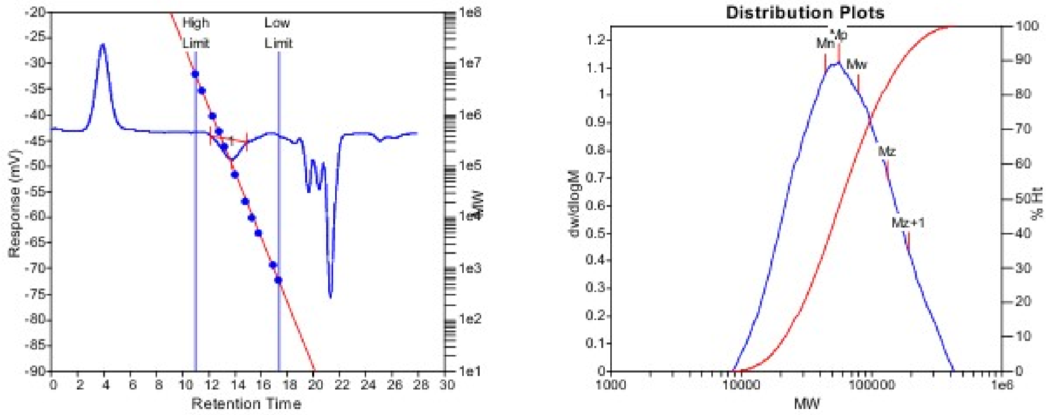


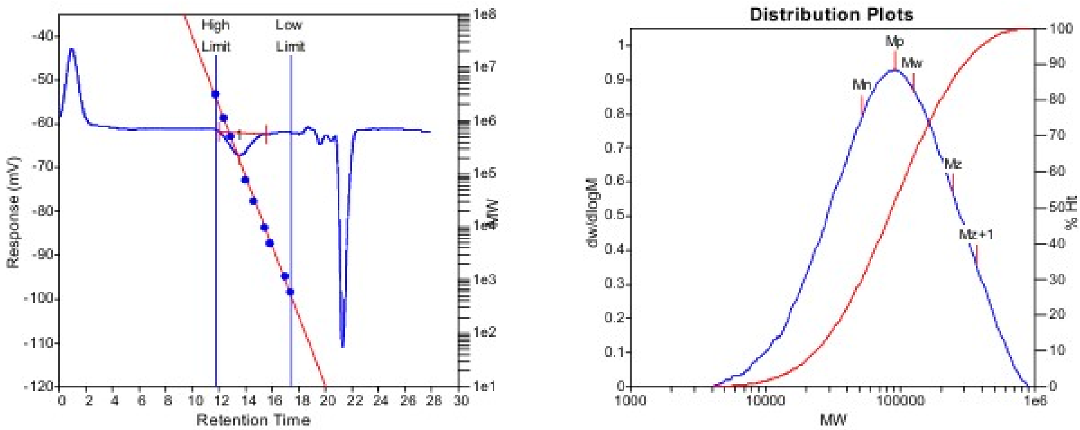
SFigure 10 GPC curve of BD-DMB diblock copolymer (Table 3, entry 1)



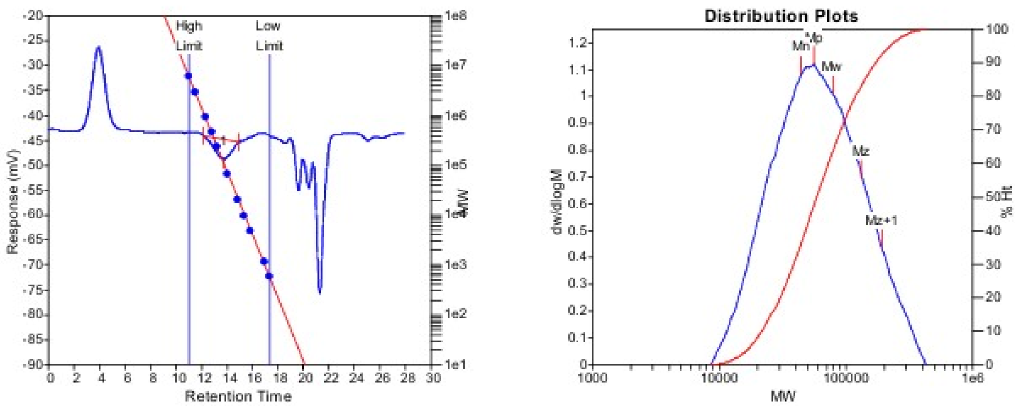
SFigure 11 GPC curve of BD-DMB diblock copolymer (Table 3, entry 2)



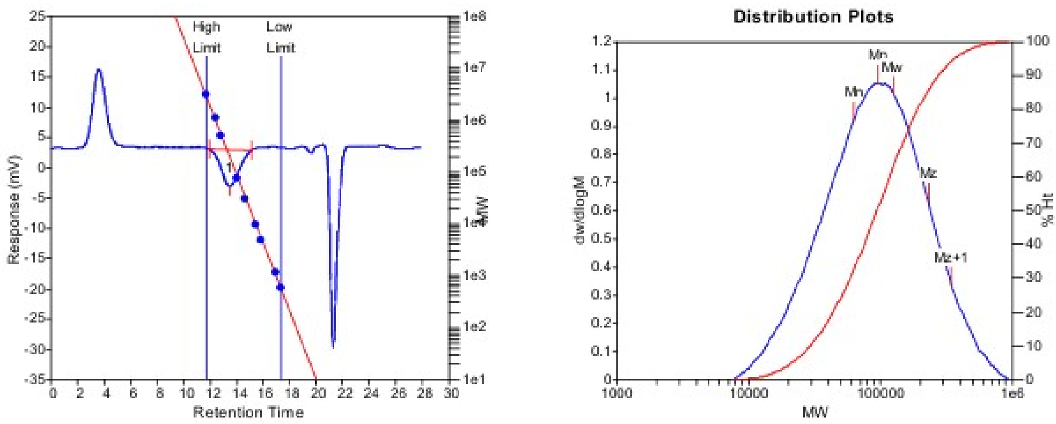
SFigure 12 GPC curve of BD-DMB diblock copolymer (Table 3, entry 3)



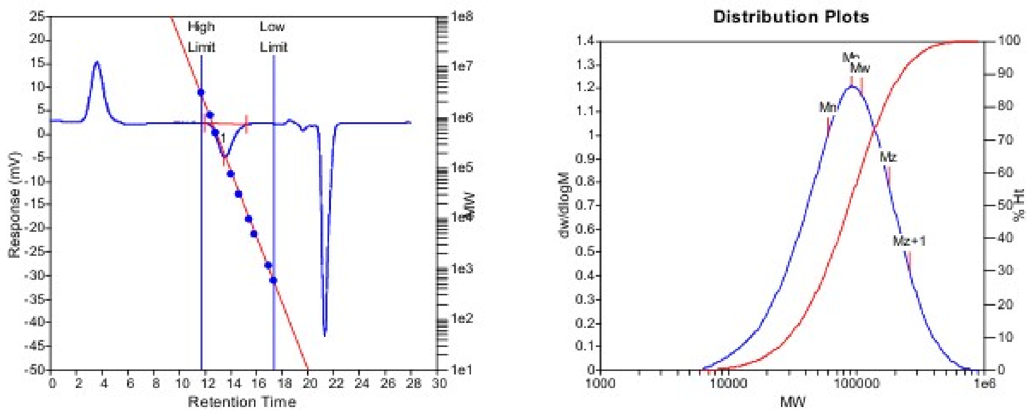
SFigure 13 GPC curve of BD-DMB diblock copolymer (Table 3, entry 4)



SFigure 14 GPC curve of BD-DMB diblock copolymer (Table 3, entry 5)



SFigure 15 GPC curve of BD-DMB diblock copolymer (Table 3, entry 6)



SFigure 16 GPC curve of BD-DMB diblock copolymer (Table 3, entry 7)