Supporting Information

Preparation of Polystyrene-Polyolefin Multiblock Copolymers by Sequential Coordination and Anionic Polymerization

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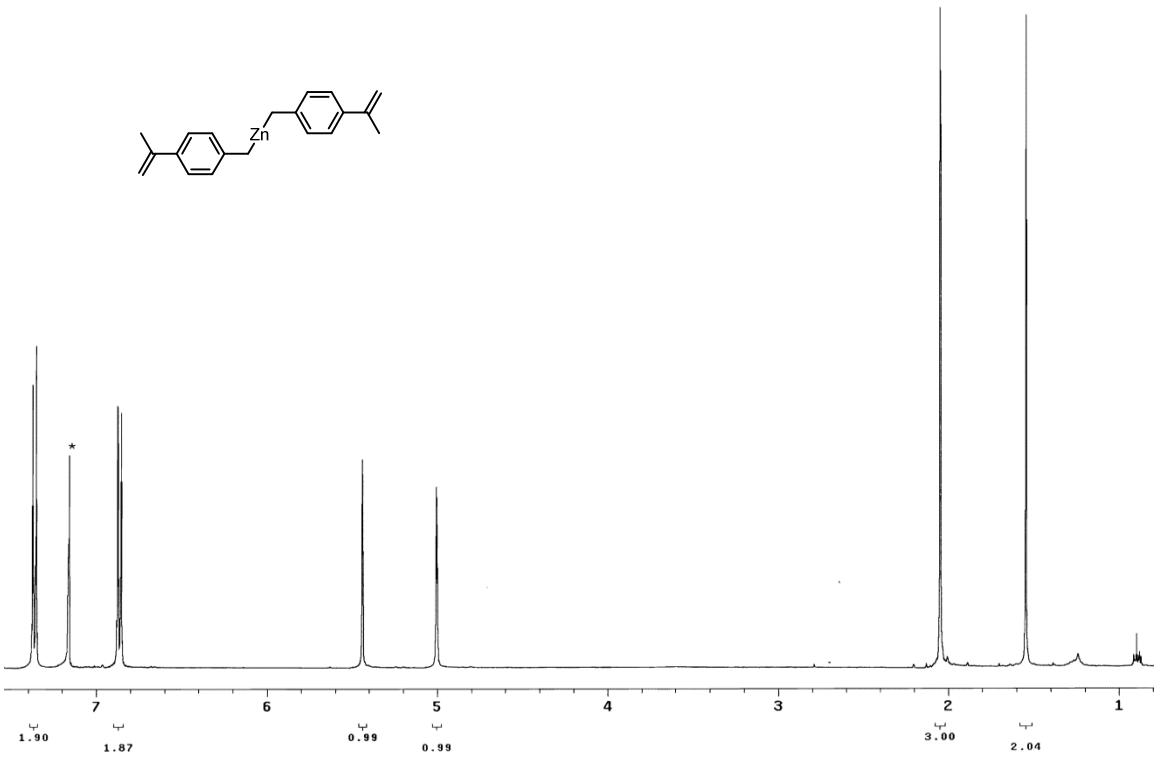
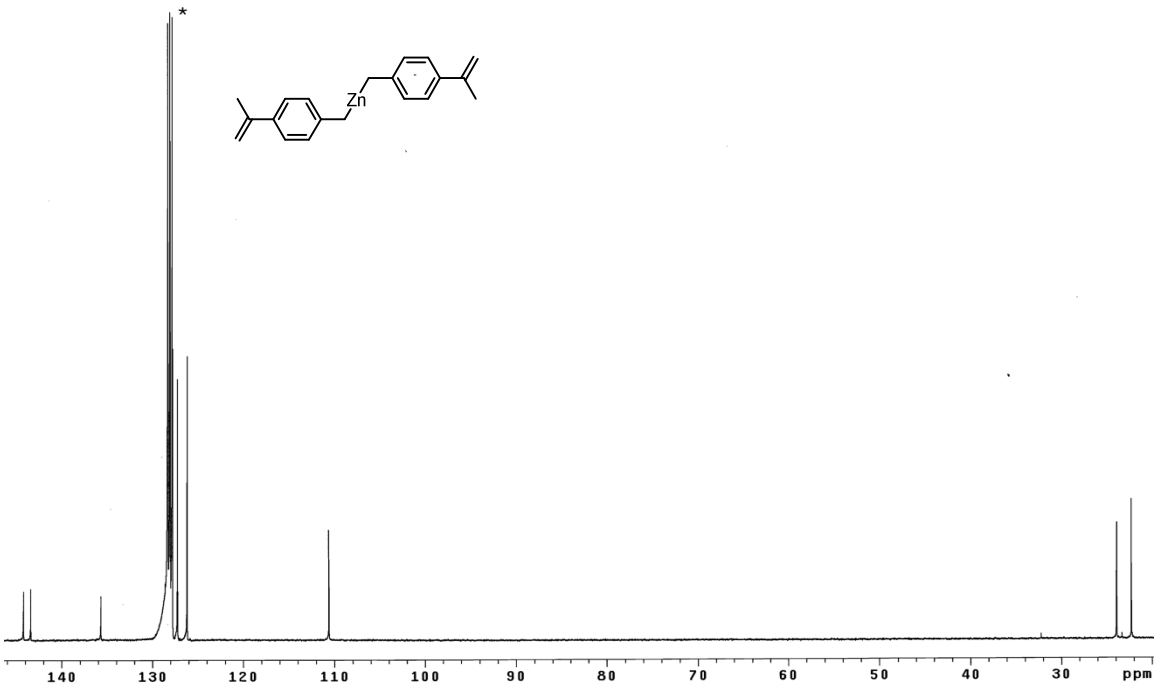
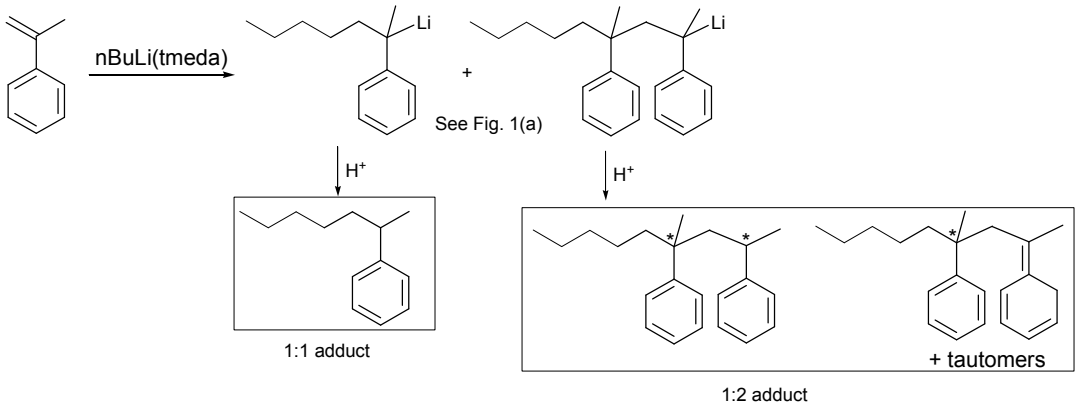
<[1]H NMR spectrum of [4-(isopropenyl)benzyl]$_2$Zn>
(The signal marked with "*" is the solvent signal)



<[13]C NMR spectrum of [4-(isopropenyl)benzyl]$_2$Zn>
(The signal marked with "*" is the solvent signal)

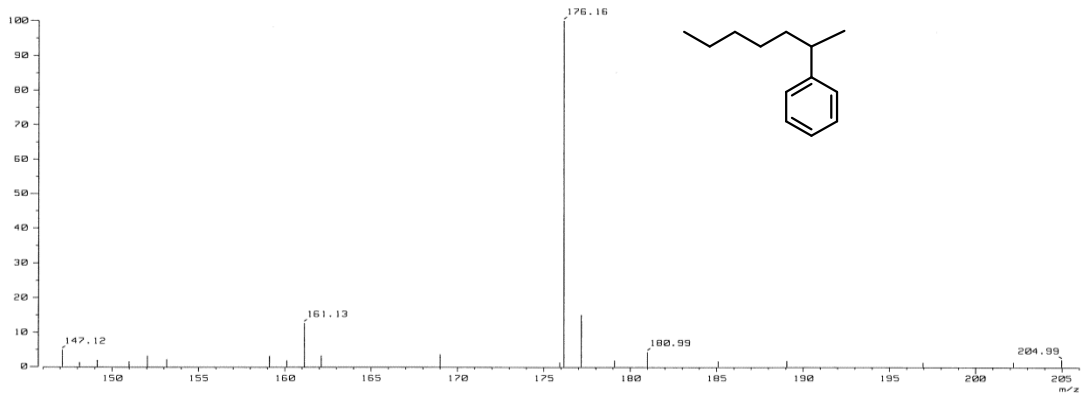




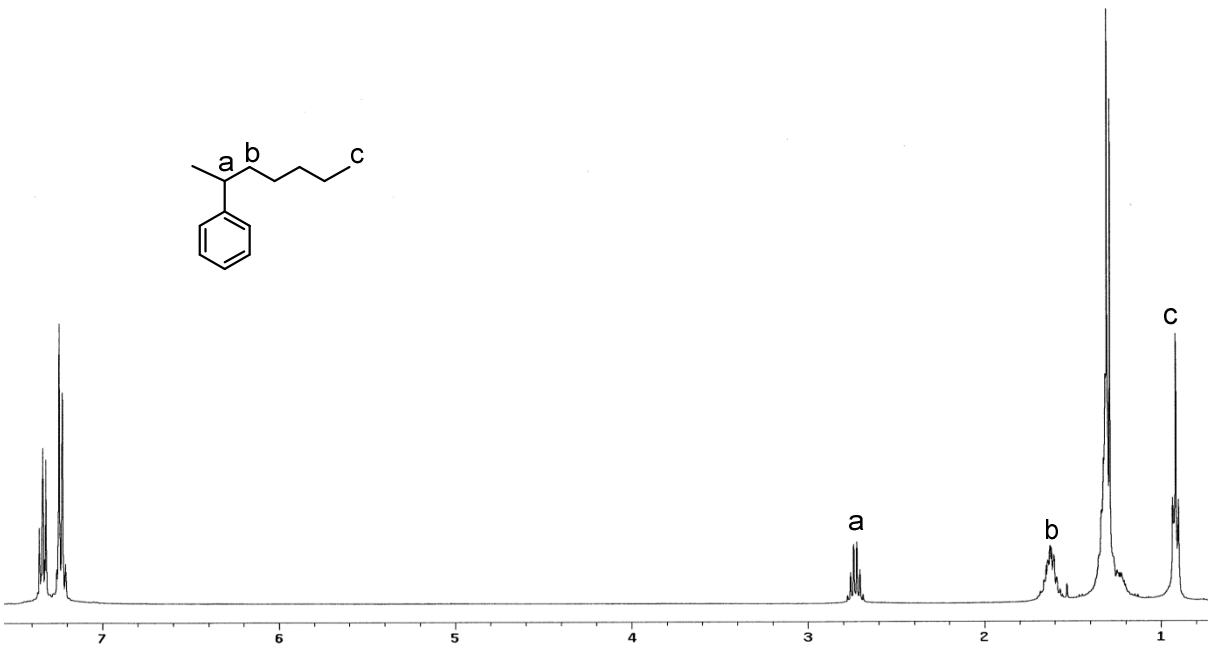
The 1:1 adduct and 1:2 adduct were separated by column chromatography on silica gel eluting with hexane

<Mass spectrum of the protonated compound of 1:1 adduct n-Bu-$CH_2C(Ph)(Me)Li$>

HRMS (EI): *m/z* calcd ($[M]^+$ $C_{13}H_{20}$) 176.1565. Found: 176.1562.

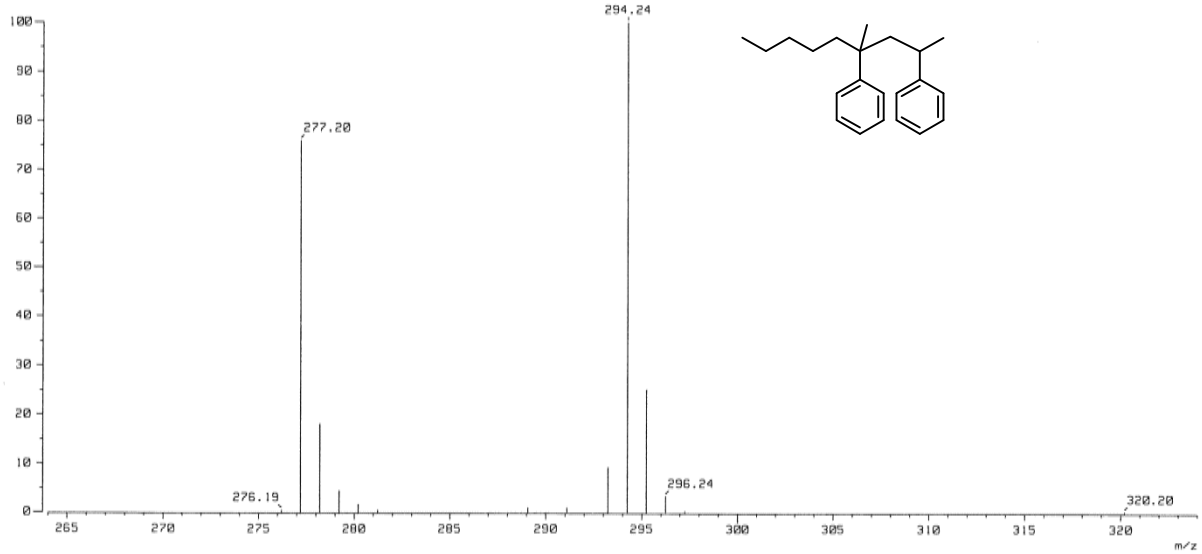


<^{1}H NMR spectrum of the protonated compound of 1:1 adduct n-Bu-$CH_2C(Ph)(Me)Li$>



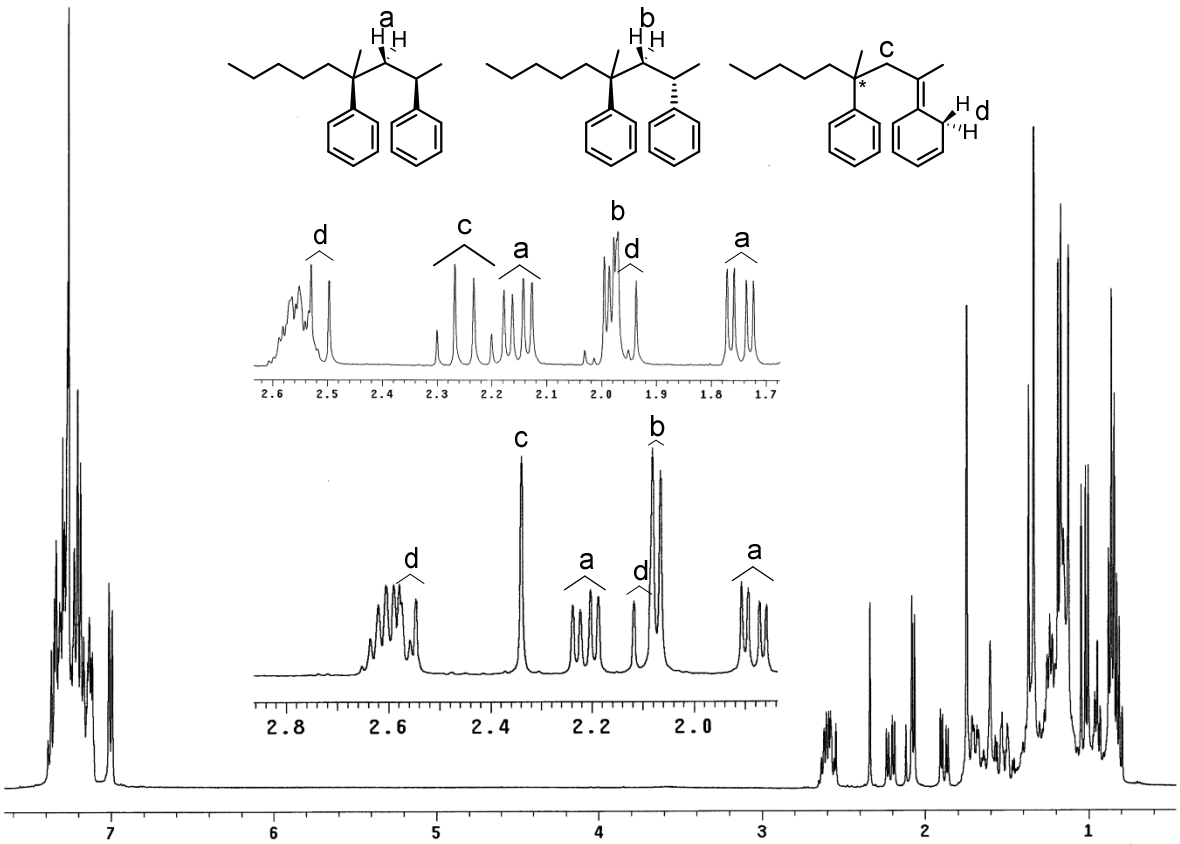
<Mass spectrum of the protonated compound of 1:2 adduct nBu-$CH_2C(Ph)(Me)$-$CH_2C(Ph)(Me)Li$>

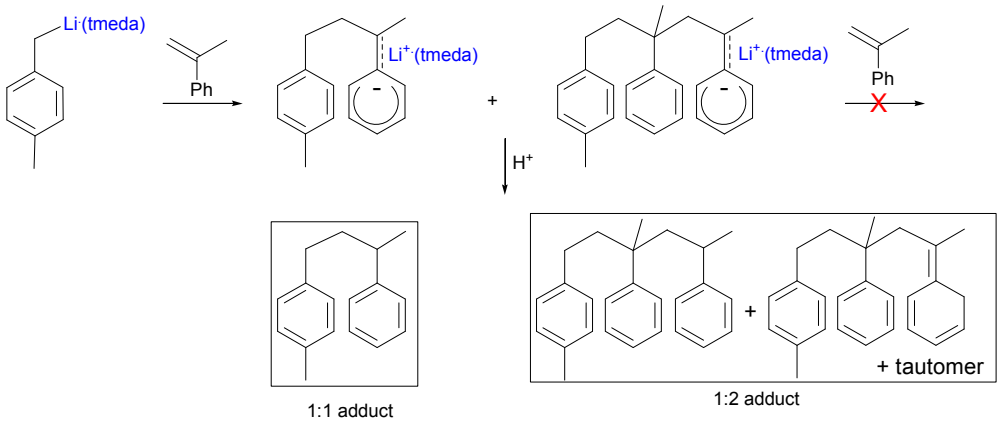
HRMS (EI): *m/z* calcd ($[M]^+$ $C_{22}H_{30}$) 294.2348. Found: 294.2350.



<^{1}H NMR spectrum of the protonated compound of 1:2 adduct nBu-$CH_2C(Ph)(Me)$-$CH_2C(Ph)(Me)Li$>

The upper spectrum was measured in C_6D_6 while the lower one measured in $CDCl_3$.



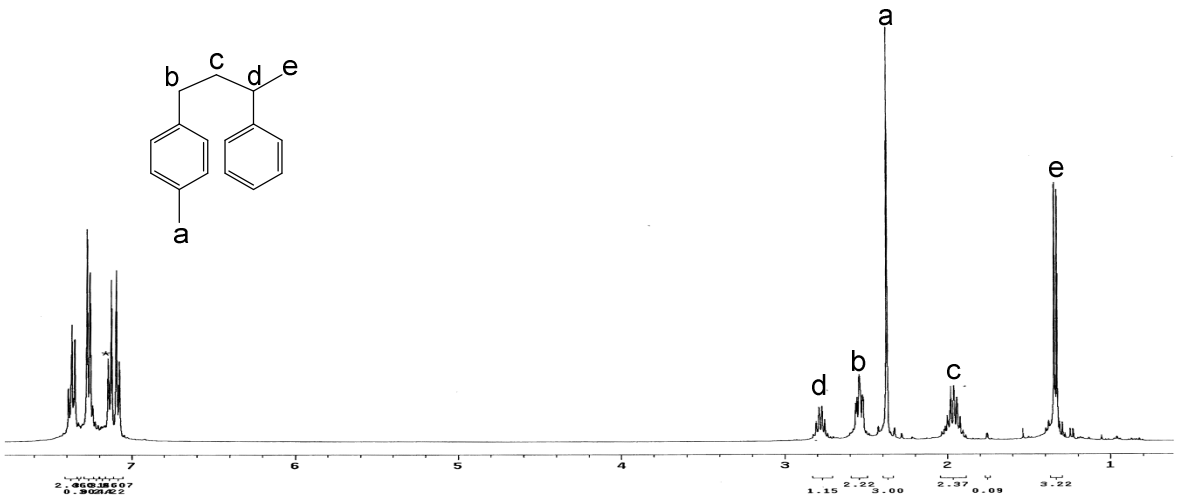


1:1 adduct

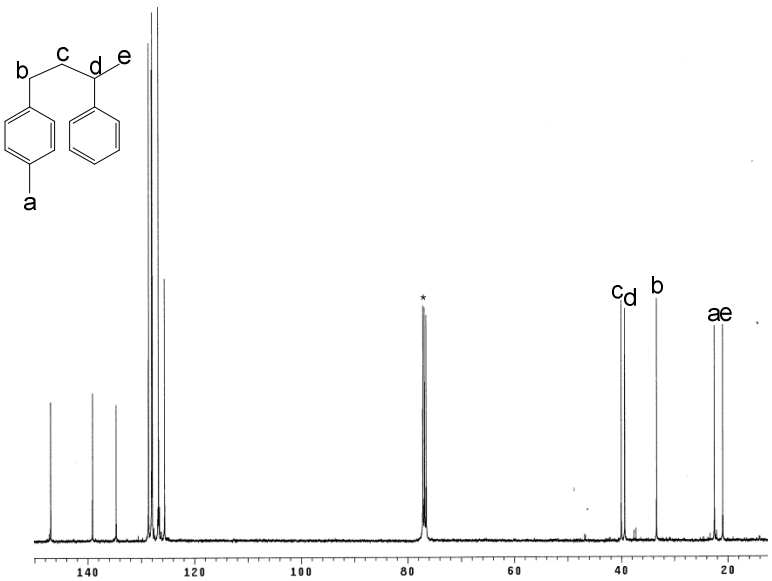
1:2 adduct

The 1:1 adduct and 1:2 adduct were separated by column chromatography on silica gel eluting with hexane

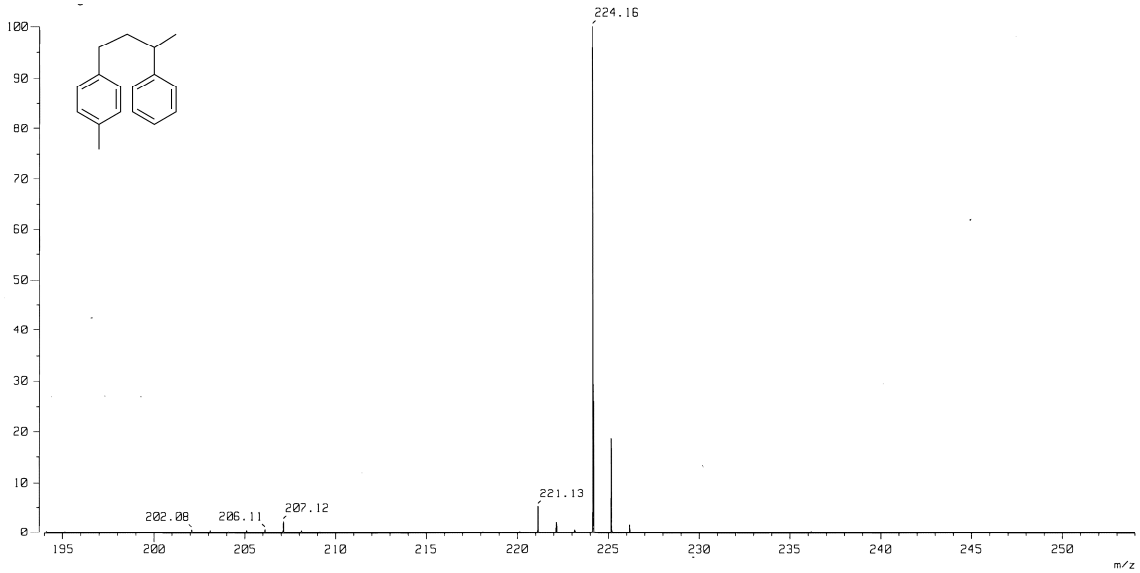
<^{1}H NMR spectrum of the protonated compound of 1:1 adduct $MeC_6H_4CH_2$-$CH_2C(Ph)(Me)Li$>



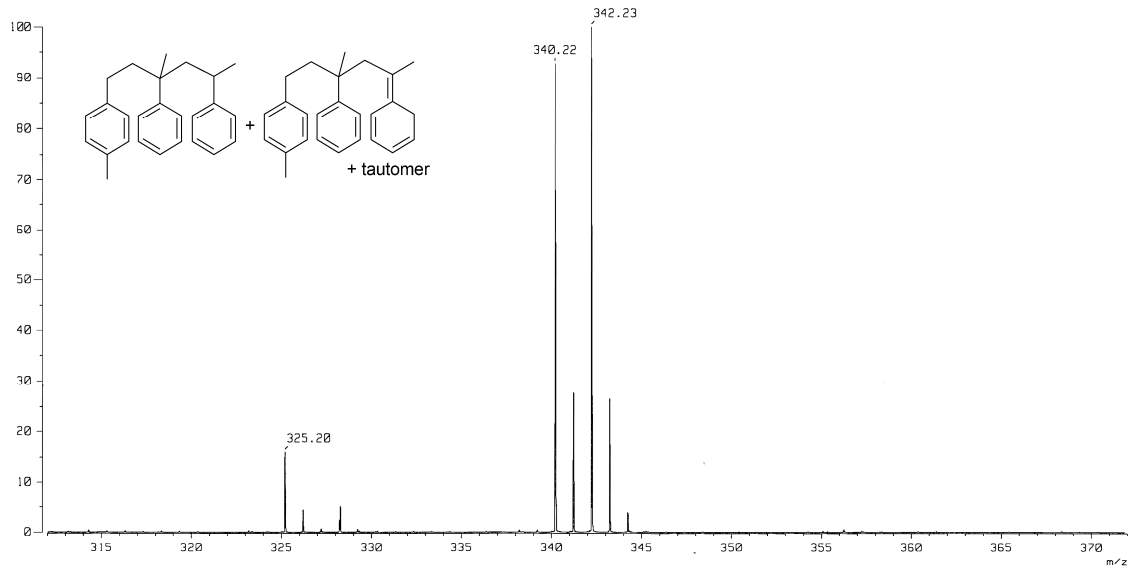
<^{13}CNMR spectrum of the protonated compound of 1:1 adduct $MeC_6H_4CH_2$-$CH_2C(Ph)(Me)Li$>



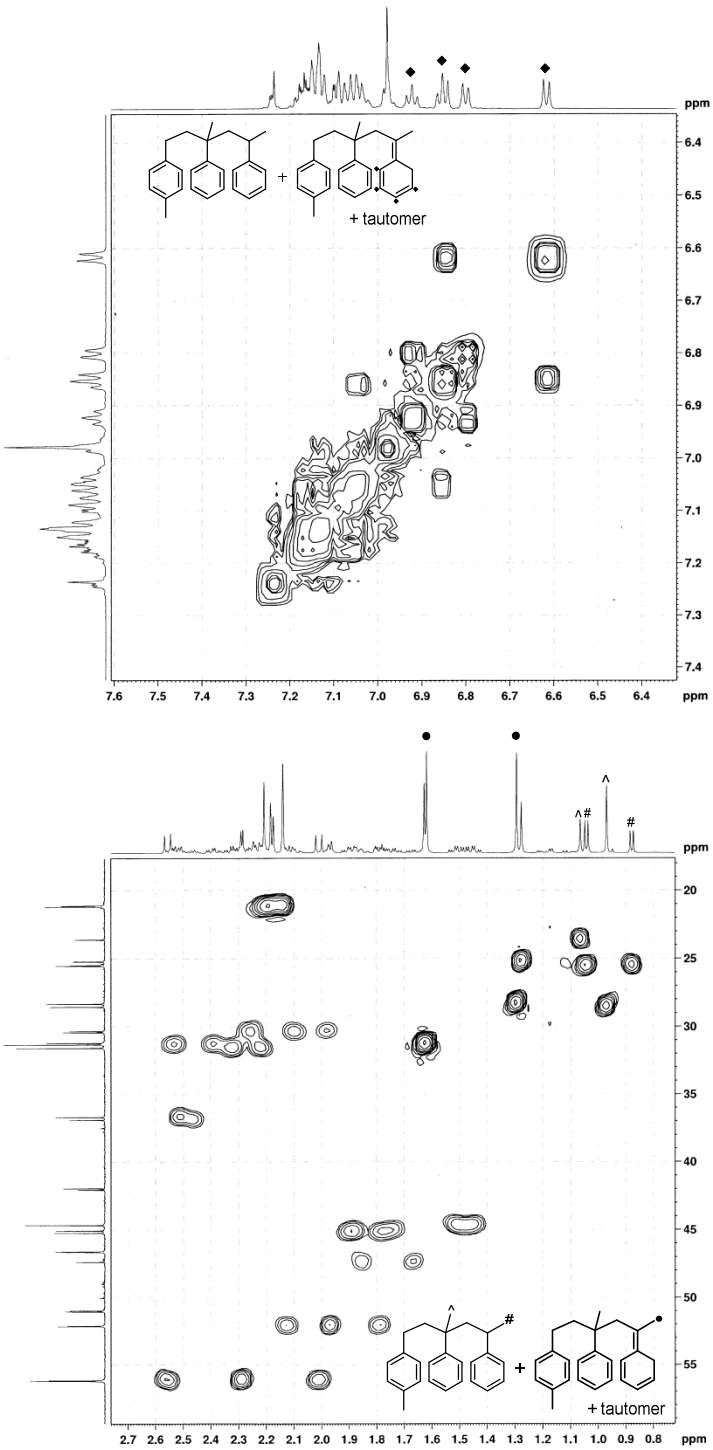
<Mass spectrum of the protonated compound of 1:1 adduct $MeC_6H_4CH_2$-$CH_2C(Ph)(Me)$>
HRMS (EI): *m/z* calcd ($[M]^+$ $C_{17}H_{20}$) 224.1565. Found: 224.1562.



<Mass spectrum of the protonated compound of 1:2 adduct $MeC_6H_4CH_2$-$CH_2C(Ph)(Me)$-$CH_2C(Ph)(Me)Li$>
HRMS (EI): *m/z* calcd ($[M]^+$ $C_{26}H_{30}$) 342.2348. Found: 342.2350.

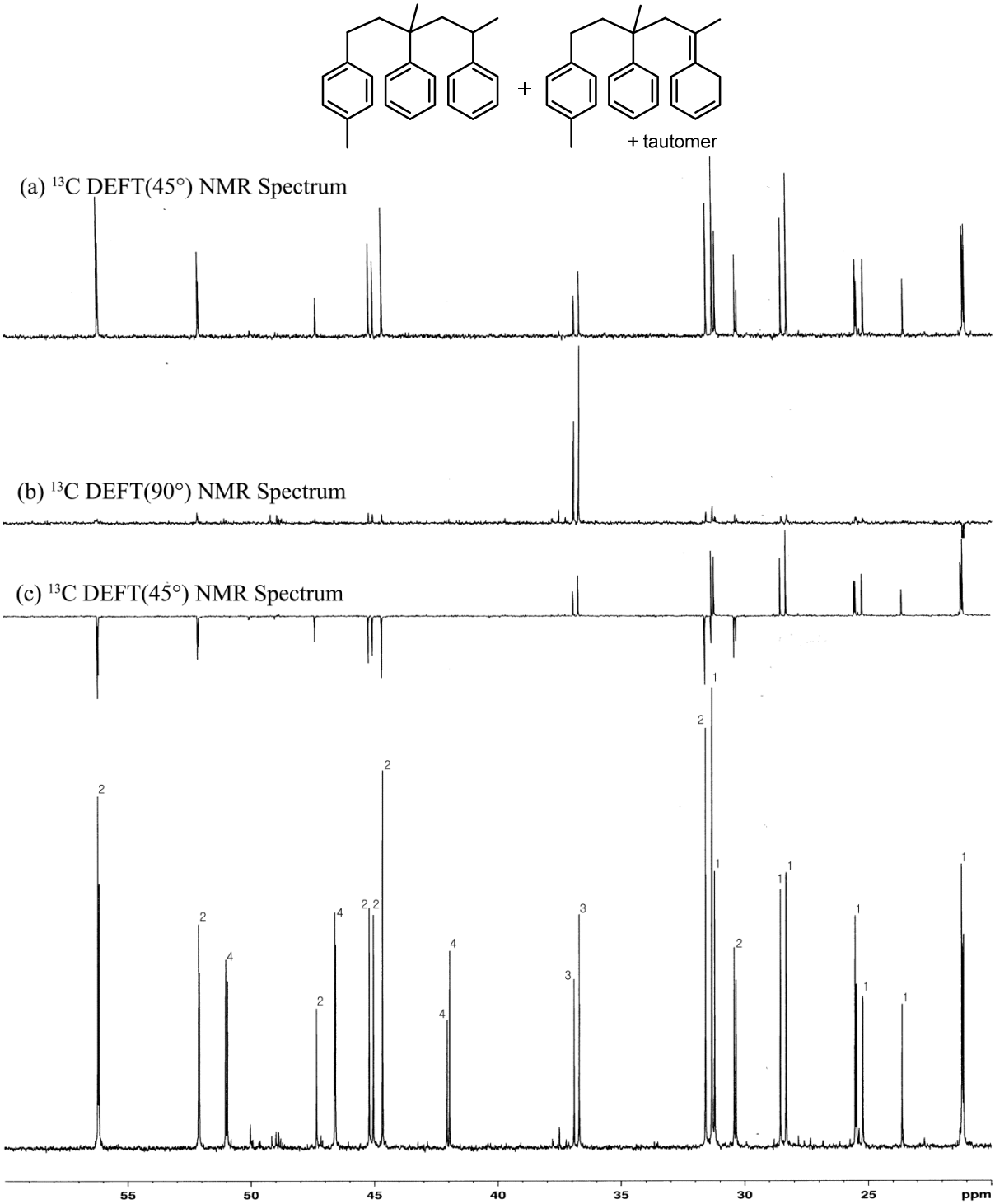


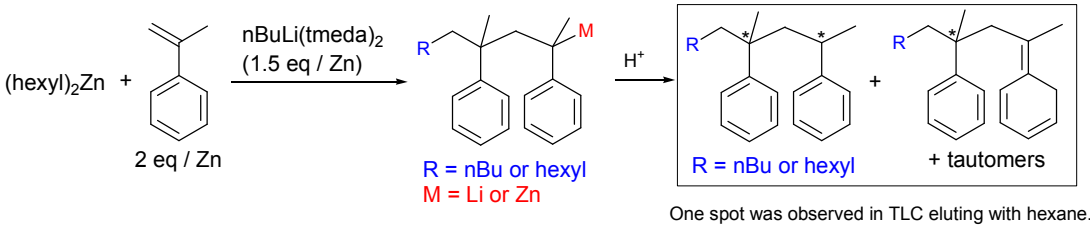
< ^{1}H–^{1}H COSY and ^{1}H–^{13}C HMQC spectra of the protonated compound of 1:2 adduct $MeC_6H_4CH_2$-$CH_2C(Ph)(Me)$-$CH_2C(Ph)(Me)Li$>



<[13]C DEFT NMR spectra of the protonated compound of 1:2 adduct $MeC_6H_4CH_2$-$CH_2C(Ph)(Me)$-$CH_2C(Ph)(Me)Li$>

"1" signals for primary carbon; "2" signals for secondary carbon; "3" signals for tertiary carbon; "4" signals for quaternary carbon



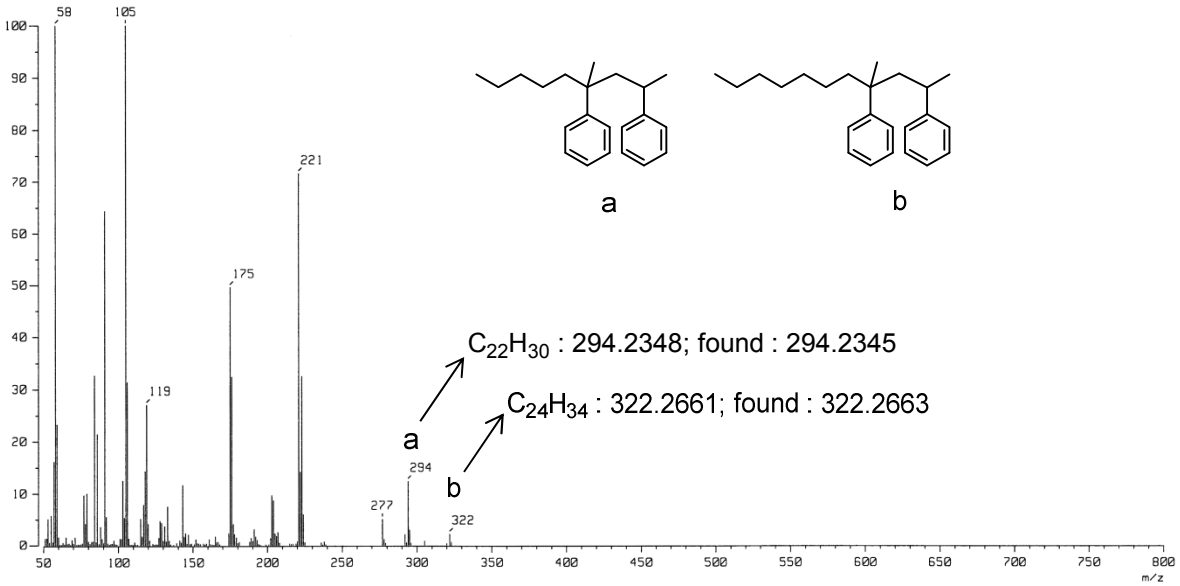


One spot was observed in TLC eluting with hexane.

<Mass spectrum of the protonated compound of 1:2 adduct nBu(or hexyl)-$CH_2C(Ph)(Me)$-$CH_2C(Ph)(Me)Li$>

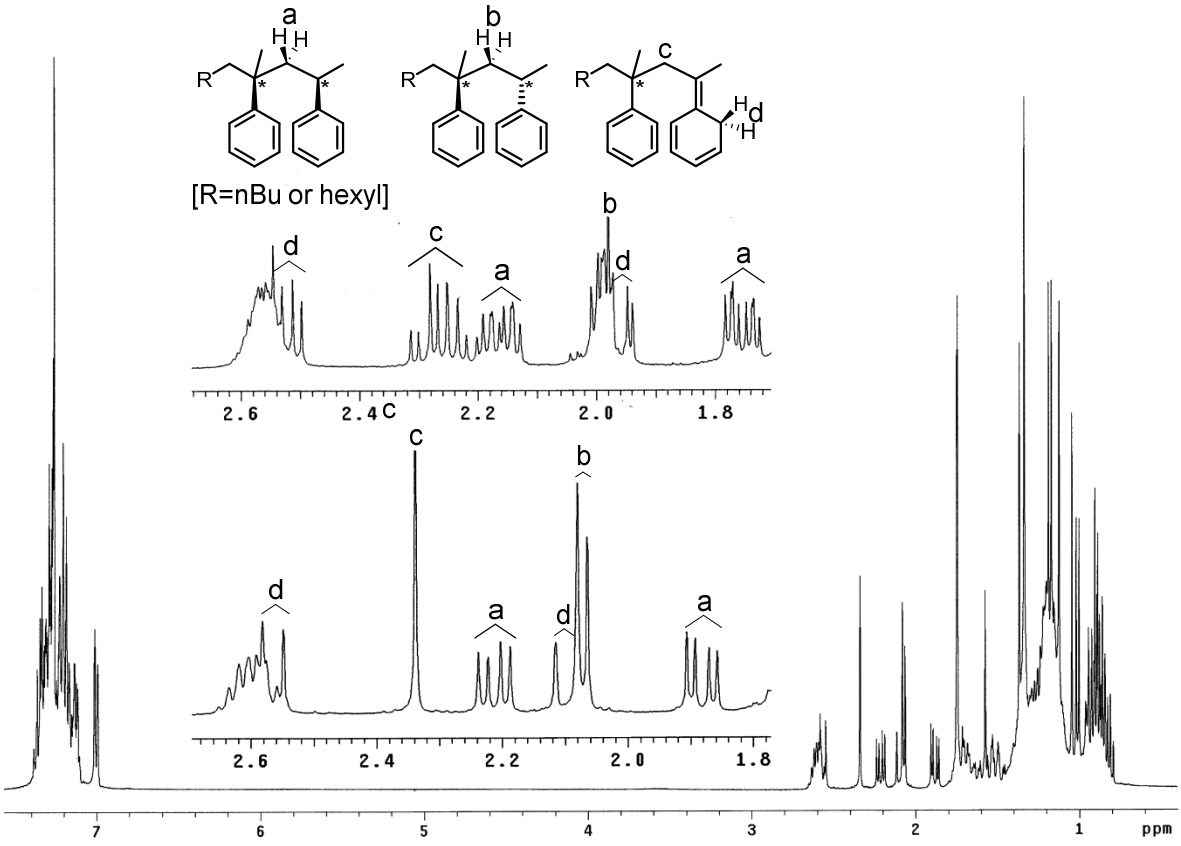
HRMS (EI): *m/z* calcd ($[M]^+$ $C_{22}H_{30}$ (nBu-$CH_2C(Ph)(Me)$-$CH_2C(Ph)(Me)$)) 294.2348. Found: 294.2345.

HRMS (EI): *m/z* calcd ($[M]^+$ $C_{24}H_{34}$ (hexyl-$CH_2C(Ph)(Me)$-$CH_2C(Ph)(Me)$)) 322.2661. Found: 322.2663.

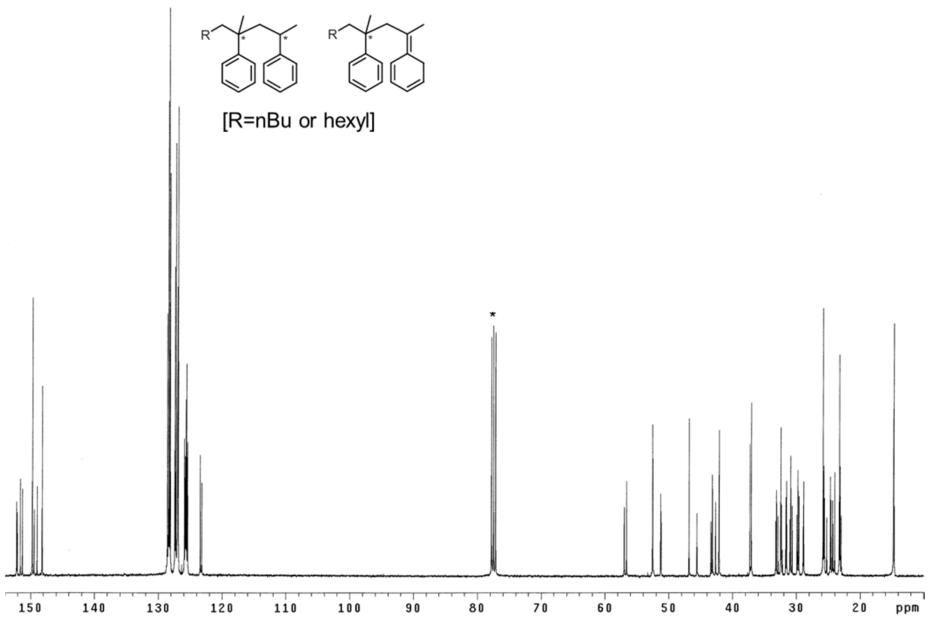


<[1]H NMR spectrum of the protonated compound of 1:2 adduct nBu(or hexyl)-$CH_2C(Ph)(Me)$-$CH_2C(Ph)(Me)Li$>

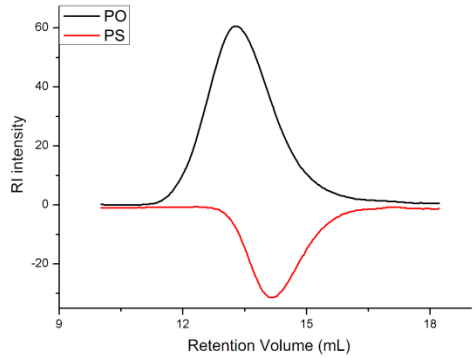
The upper spectrum was measured in C_6D_6 while the lower one measured in $CDCl_3$.



<[13]CNMR spectrum of the protonated compound of 1:2 adduct nBu(or hexyl)-$CH_2C(Ph)(Me)$-$CH_2C(Ph)(Me)Li$>

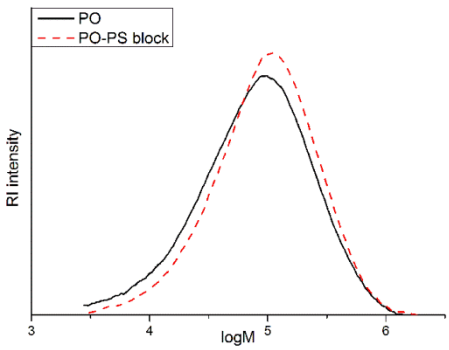


<GPC curves for PO and PS samples showing that the RI detector response is opposite>
Weight concentration is the same for each.

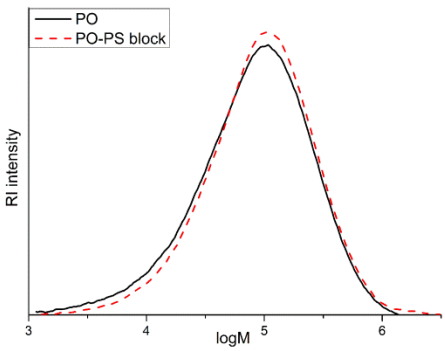


<GPC curves for samples before and after the anionic styrene polymerization>

<Entry 1 in table 2; M_w 129,000 => 143,000>



<Entry 1 in table 2; M_w 135,000 => 150,000>



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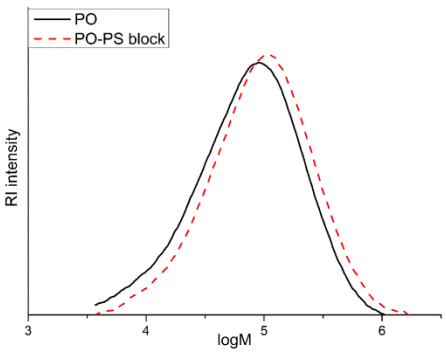

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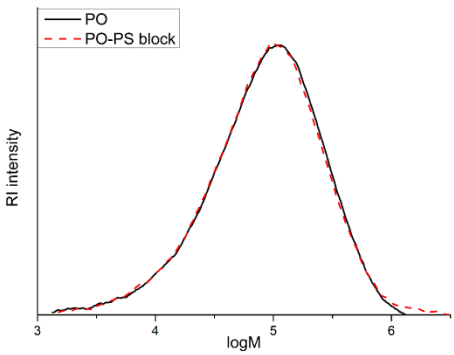
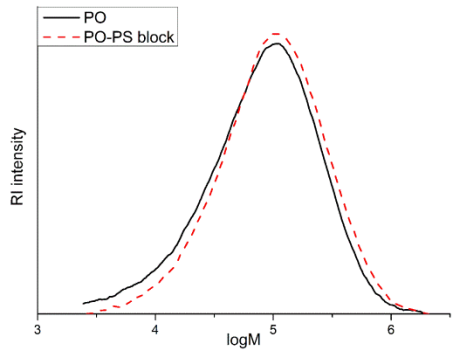
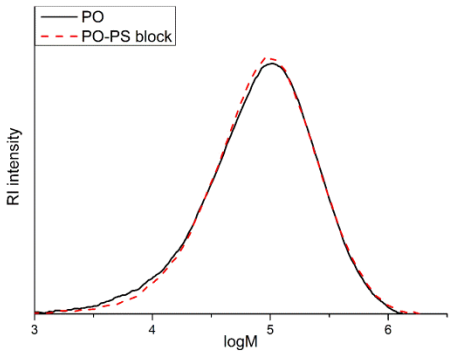


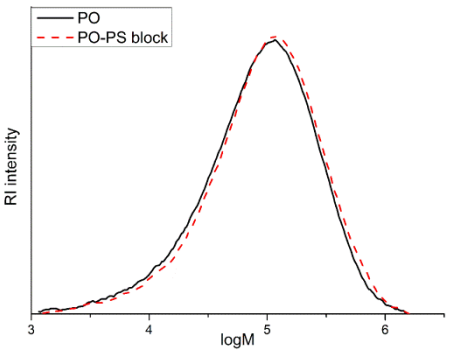
<Entry 5 in table 2; M_w 134,000 => 155,000>



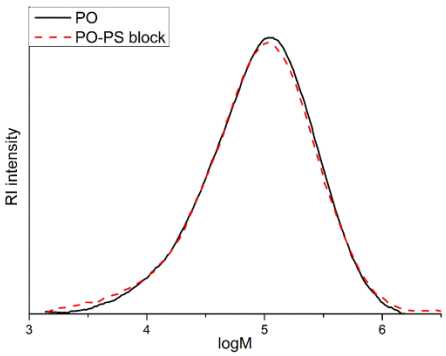
<Entry 6 in table 2; M_w 133,000 => 138,000>



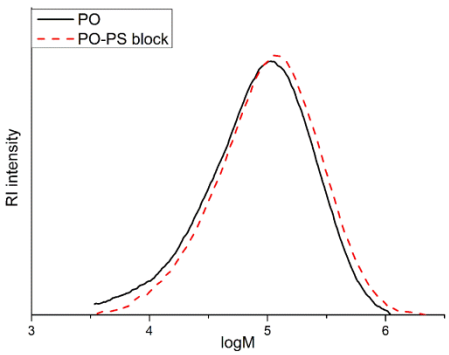
<Entry 7 in table 2; M_w 142,000 => 154,000>



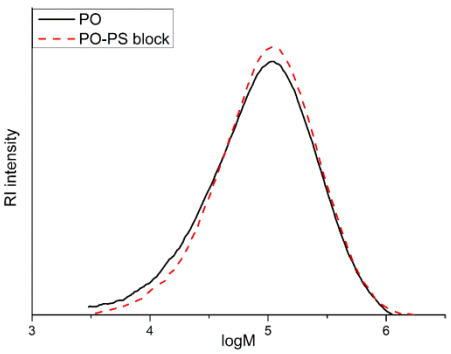
<Entry 8 in table 2; M_w 147,000 => 162,000>



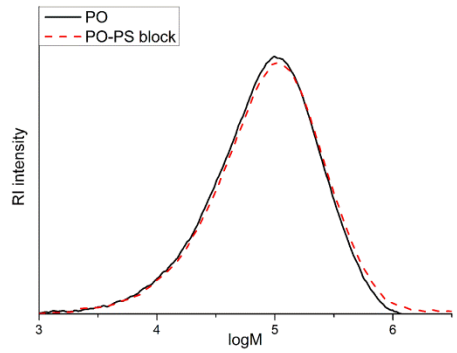
<Entry 9 in table 2; M_w 132,000 => 157,000>



<Entry 10 in table 2; M_w 136,000 => 146,000>



<Entry 11 in table 2; M_w 130,000 => 155,000>



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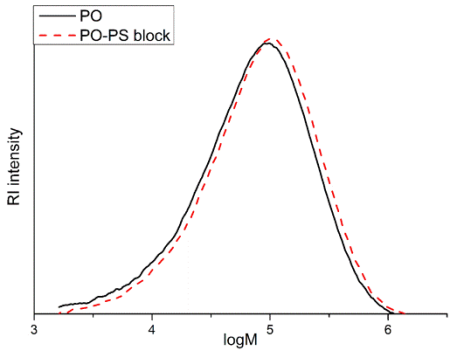

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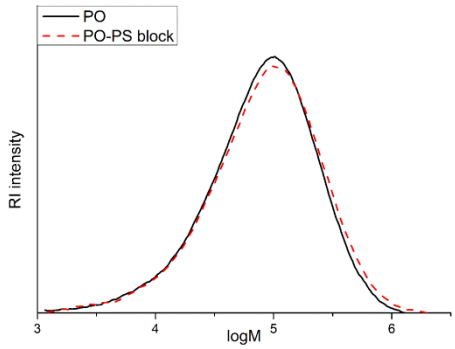
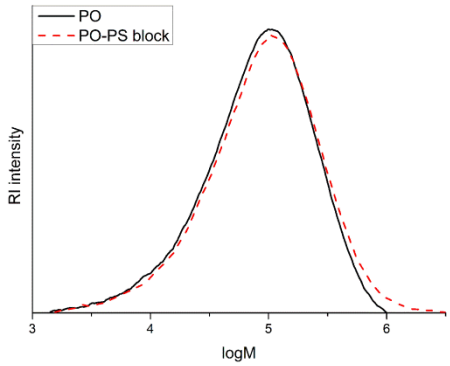
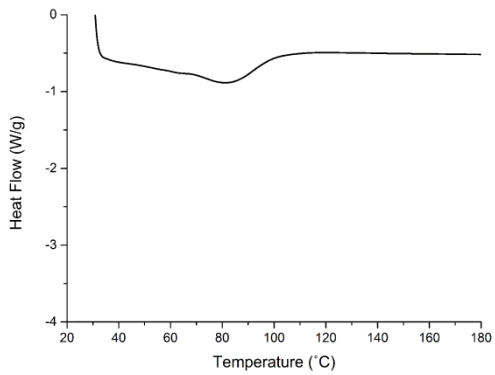


<Entry 14 in table 2; M_w 129,000 => 153,000>

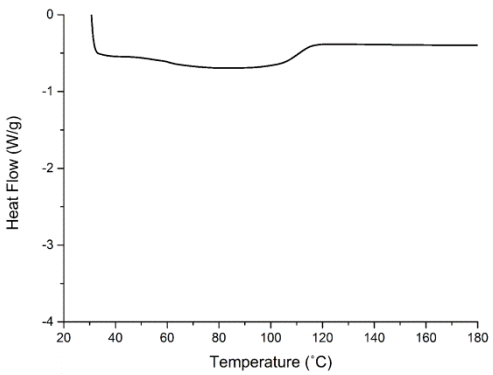


<DSC thermogram for the isolated PO-PS multiblock copolymers>

<Entry 1 in Table 2>



<Entry 1 in Table 2>



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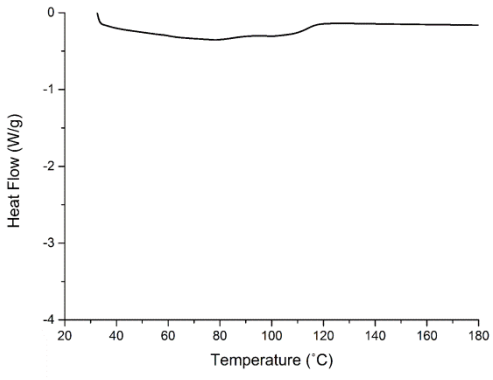

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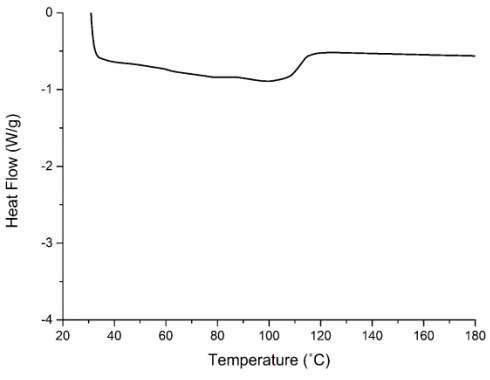

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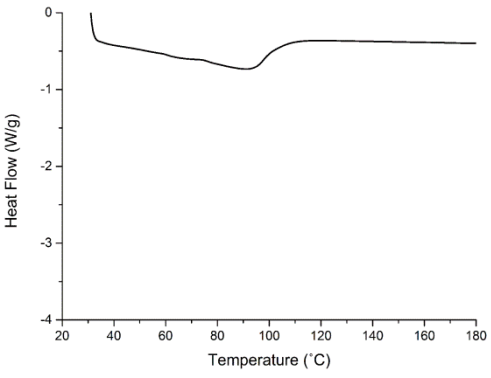

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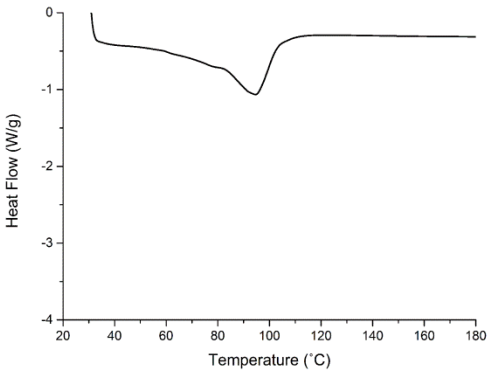

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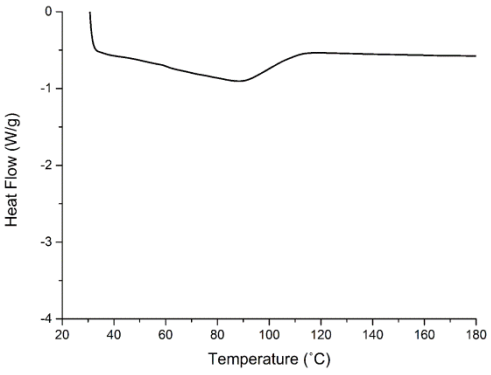

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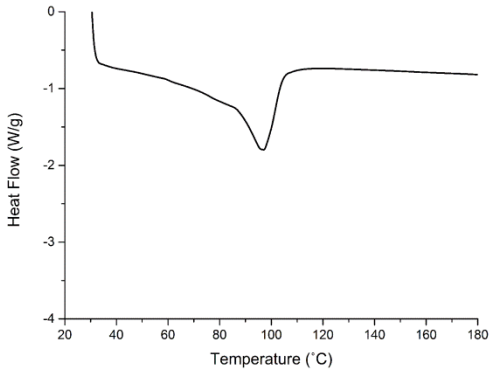

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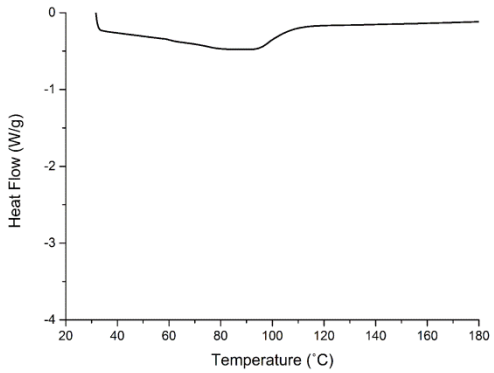

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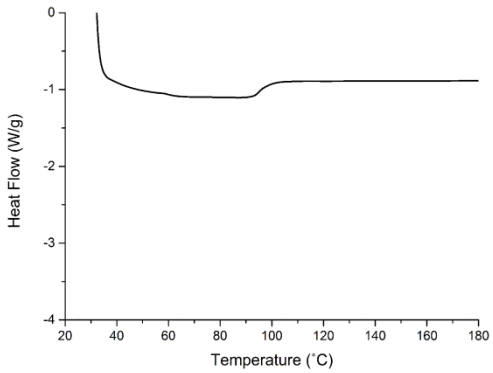

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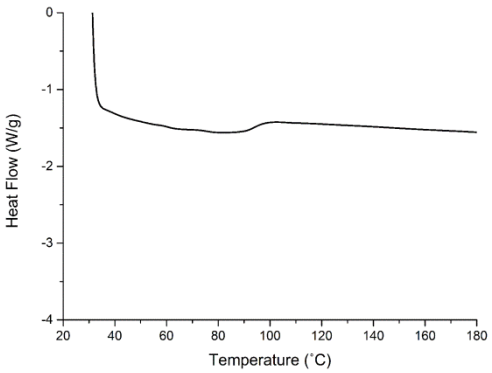

<Entry 14 in Table 2>