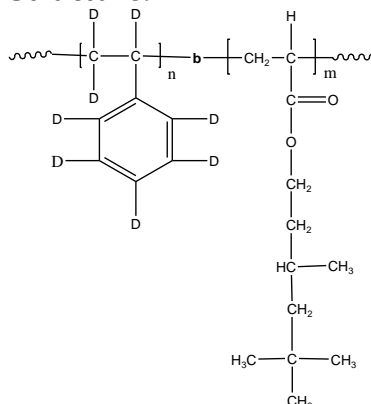


Sample Name: Deuterated**Poly(styrene(d8)-b- 3,5,5 trimethylhexyl acrylate) (protonated)****Sample #: P5984A-dPSTMHA****Structure:****Composition:**

Mn x 10 ³ dPS-b-TMHA	PDI
90.0-b-90.0	1.09
T _g for TMHA block: -40 °C	T _g for PS block: 96 °C

Synthesis Procedure:

Deuterated Poly(styrene (d8) -b-3,5,5 trimethylhexyl acrylate) is prepared by the transesterification of the deuterated poly (Styrene (d8)-b-tert.butyl acrylate) di block copolymer in presence of 3,5,5 trimethyl 1-hexanol. Esterification of tert-butyl ester to 3,5,5, 1hexyl ester is confirmed by complete disappearance of absorbance at 1360 cm⁻¹ characteristics for the tert.butyl ester.

Purification of the obtained polymer was carried out rigorously as follows to ensure the removal of the catalyst side product:

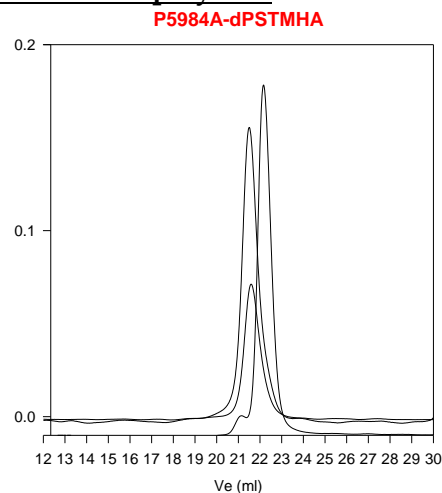
1. Dissolved the polymer in CHCl₃ and wash with de-ionized distilled water to remove the any soluble organic catalyst used in the trans esterification side product.
2. Polymer extracted from water with chloroform.
3. Polymer solution in CHCl₃ was dried over anhydrous sodium sulfate.
4. Solution filtered and than passed through a column packed with basic Al₂O₃.
5. Solution concentrated on rota-evaporator
6. Solution precipitated in cold methanol
7. Final dried under vacuum for 48h at 50°C.

Characterization:

An aliquot of the polystyrene block was terminated before addition of tert.butyl acrylate and analyzed by size exclusion chromatography (SEC) to obtain the molecular weight and polydispersity index (PDI). The final block copolymer composition and Mw/MN (PDI) is determined by SEC.

Solubility:

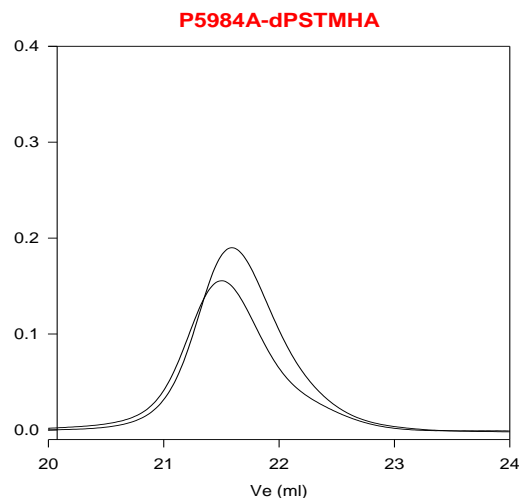
Polymer is soluble in CHCl₃, THF and toluene.

SEC of the block copolymer:

Size exclusion chromatography of deuterated (d8) polystyrene-poly(3,5,5 trimethyl hexyl acrylate)

— Deuterated Polystyrene, M_n=90000, M_w=97500, PI=1.08
— Block Copolymer PdPS(90000)-b-PtBuA(58000), PI=1.09

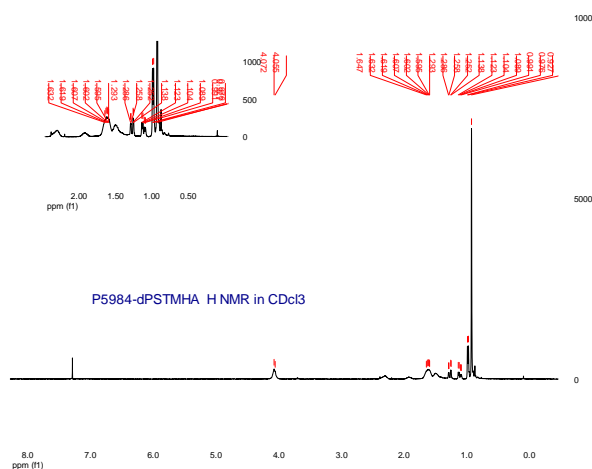
after Transesterification to PdPSTMH: (90,000-b-90,000) Pi:1.09



Size exclusion chromatography of deuterated (d8) polystyrene-poly(3,5,5 trimethyl hexyl acrylate)

— Block Copolymer PdPS(90000)-b-PtBuA(58000), PI=1.09

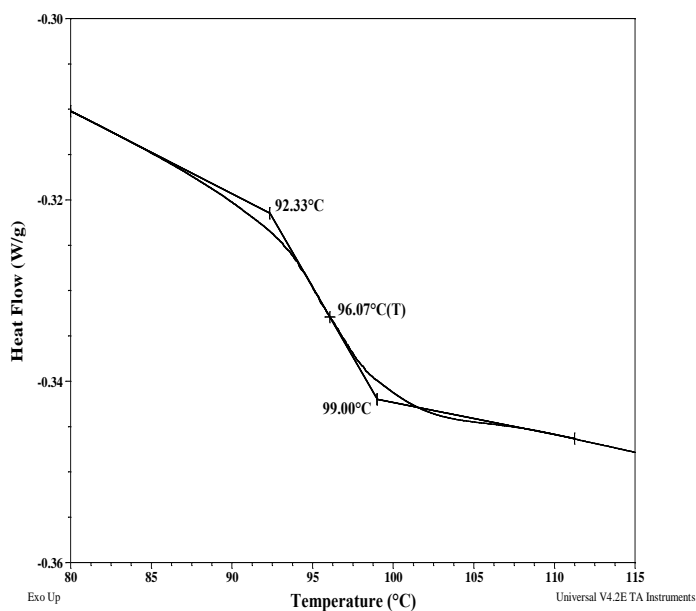
after Transesterification to PdPSTMH: (90,000-b-90,000) Pi:1.09



Thermal analysis of sample P5984A dPSTMHA

Thermal analysis of the sample was carried out using a differential scanning calorimeter (TA Q100) at a heating rate of 10°C/min. The inflection glass transition temperature (T_g) has been considered.

Thermogram for PS block:



Thermograms for TMHA block:

