

Supplementary Information

Fabricating Mesoscale Polymer Ribbons with Tunable Mechanical Properties via Evaporative Deposition and Dewetting

Cornelia Meissner, M. Saad Bhamla, Todd Emrick* and Alfred J. Crosby*

*corresponding authors

Polymer Science and Engineering Department, University of Massachusetts Amherst, Conte Center for
Polymer Research, 120 Governors Drive, Amherst, MA 01003

Experimental

Substrate Preparation

Fisher Scientific glass cover slides (24x40x0.17 mm) were washed in soap water, reverse osmosis water, and isopropanol, for 20 min each using sonication. Immediately after the cover slips were cleaned by exposure to Ozone in a UVO cleaner for 20 minutes. The glass slips were then moved to a spin coater and covered with 9 droplets of 20 mg/ml PSS in Ro water solution added through a syringe filter (Fisher brand Cat No 09-720-4 .45 micrometers 13 mm PVDF. The slides were spun at 500 rpm for 10s immediately followed by 2000 rpm for 40 s to ensure a homogenous sample thickness. The dry substrate with a PSS film of ~ 50 nm height was then taken to the laser cutter (VLS, ...) where the PSS film was removed for six line cuts with a distance of 4 mm to each other and parallel to the longer edge of the slide.

Flow Coating Set-up

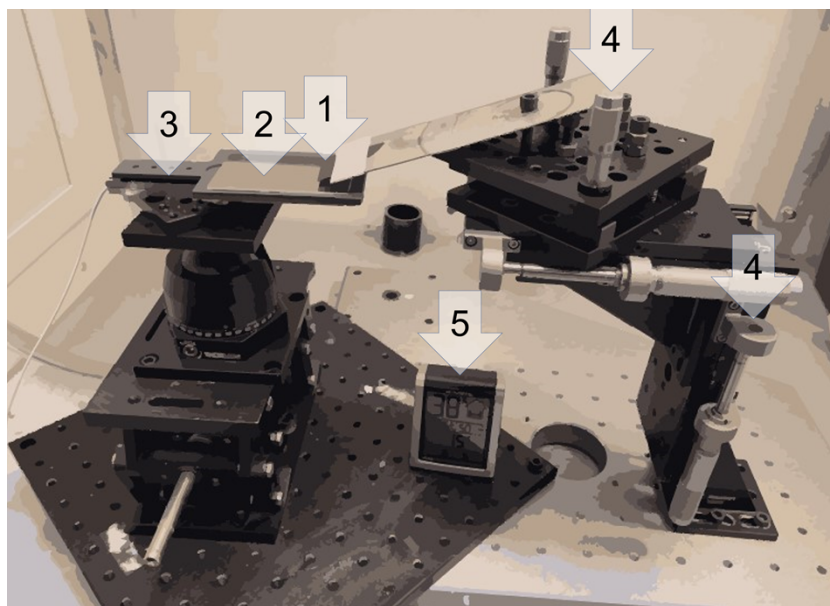


Figure SI 1

1: blade

2: slide/substrate holder

3: linear actuator/moving stage

4: micromanipulators

5: hygrometer and thermometer

Flow Coating was done on the instrument depicted above. A blade with ~ 30 degree angle is adjusted to line up about 200 micrometers above and parallel to the substrate with the micromanipulators (4). The blade (1) used in for this paper was a razor blade. The substrate is attached using a droplet of water, exploiting the capillary forces of water, on the substrate holder (2) which is affixed to a translating

stage(3). A hygrometer and thermometer (5) allows for data collection of the current humidity and temperature. The stage is subsequently moved to the left of the image away from the blade during flow coating. A similar set-up can be achieved on most modern microscope stages.

Flow Coating Experiment

3 mg/ml solutions of the polymers in distilled toluene were made at least one day (24 h) prior to flow coating to ensure complete dissolution. 5 microliters of the solution were then applied to the substrate in front of the blade by micropipette at 85% relative humidity and 20 degrees C. The solution was wicked under the blade by capillary action and the substrate was then moved 1 mm at 3 mm/s away from the injection site. Immediately after reaching the 1 mm distance a program was started to print 5 ribbons over a total of 1 mm distance at 8 s dwell time per ribbon and 250 micrometer spacing between ribbons. Following the dwell time for the last ribbon the stage was again moved at least a distance of 1 mm at 3 mm/s speed to a different location to remove excess solution from under the blade without affecting the deposited lines. Subsequently the slides were taken to the laser cutter for a second set of cuts to release one end of the filaments from the slide. These cuts were performed using the same settings described above, offset slightly from the anchoring lines.

Ribbon release

A petri dish containing 10 ml of water was set up on a microscope, the cover slide was floated on top of the solution, with the filaments exposed to the air surface. Then the slide was quickly submerged with a tap and floated onto the bottom of the petri dish where the filaments were observed. When the PSS layer comes in contact with water, it dissolves, leaving the filaments to move freely in solution except for the point at which they are anchored to the substrate by the first laser cut (pre-deposition).

Determination of ribbon thickness

The ribbon thickness and width were determined by averaging over 10 optical profilometry traces of the ribbon along the backbone with an end point weighted baseline as illustrated in Figure S4 & S5. The polybutadiene ribbons exhibit thickness variations on the order of 7nm (standard deviation) along the length of a single ribbon, as determined by taking the average and standard deviation from 10 cross-sectional profile traces using optical profilometry. This thickness variation is less than 1% variation of the total thickness (921 nm). Accordingly, since we report the average of the ribbon radius curvature along the length of the ribbon, we consider that the slight thickness variations will not have a significant impact on the measured and reported values.

For the PS-block-PBD polymers, the influence of solutal Marangoni flows² results in a distinct thickness variation along the ribbon length, as shown in the optical microscope images below (transitioning from uniform to irregular ribbon morphologies as PS content increases) see Figure S6.

Determination of helical radius

As illustrated in Figure S3 the radius was determined by measuring the diameter of coils across the helical cross-section where possible. When helices appeared to be parallel to the optical plane the diameter was measured across the side of the helix. These measurements were halved and averaged to get to the $26 \pm 4 \mu\text{m}$ ribbon radius.

Characterization

^1H (500 MHz) NMR data were collected using a Bruker Ascend TM500 spectrometer retrofitted with a Prodigy cryoprobe. Gel permeation chromatography (GPC) was recorded using an Agilent Technologies 1260 Infinity series system equipped with refractive index (RI) and ultraviolet (UV) detectors, a PL Gel 5 μm guard column, two PL Gel 5 μm analytical Mixed-C columns, and a PL Gel 5 μm analytical Mixed-D column connected in series at 40 $^\circ\text{C}$ with THF as the eluent and toluene as flow marker at a flow rate of 1 ml/min. Molecular weight and molecular weight distribution was determined using PS standards with the exception of the PMMA sample for which the calibration curve from PMMA standards was used. UV-ozone (UVO) surface treatment was conducted with Jelight Company, Inc. Model 342 UVO-Cleaner[®]. Laser cutting was carried out using a Universal Laser Systems VLS3.50 laser cutter equipped with a 30 W CO_2 (10.6 μm) laser with 4 % power, 40 % speed, and 1000 ppi pulse rate. Stage translation during evaporative deposition was carried out using a SmarAct, Inc SLC-1780s linear actuator attached to a bread board with a stage as pictured above. Optical Profilometry was performed on a Zygo NewView 7300 Optical Surface Profiler. Microscopy was performed on an inverted microscope (Axio Observer 7 Materials, Zeiss) equipped with a Hamamatsu C11440 Orca-Flash 4.0 digital camera.

Materials

Polystyrene sulfonate, polymethylmethacrylate and toluene were acquired from Sigma Aldrich. All deposited polymers PS, PBD, PS-random-PBD, and PS-block-PBD were acquired from polymersource.

Supplementary Movies

Supplementary Movie S1

PMMA ribbons with connecting inter-ribbon film after release in water. Microscope stage is being moved to induce movement of the ribbons. Scale bar 500 μm .

Supplementary Movie S2

Polybutadiene ribbon coiling into helical shape upon release in water. Scale bar 250 μm .

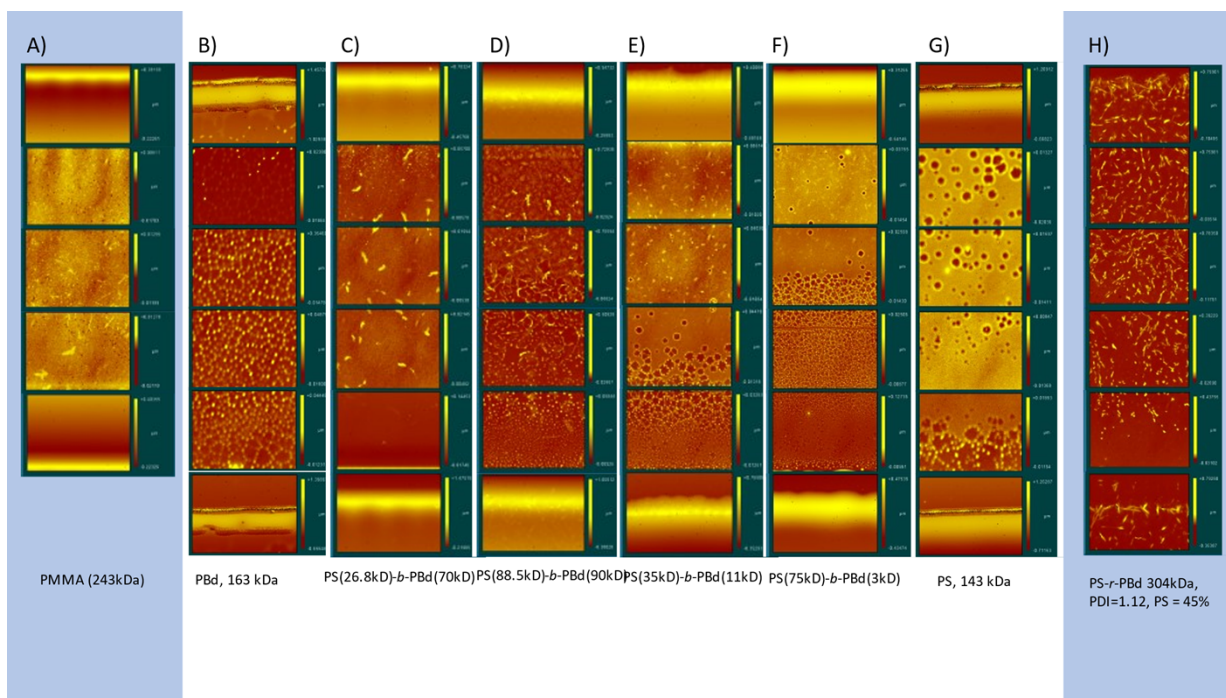


Figure SI 2 Optical profilometry traces of inter-ribbon regions showing the dewetting for block and homopolymers of polystyrene and polybutadiene, and a continuous film for PMMA.

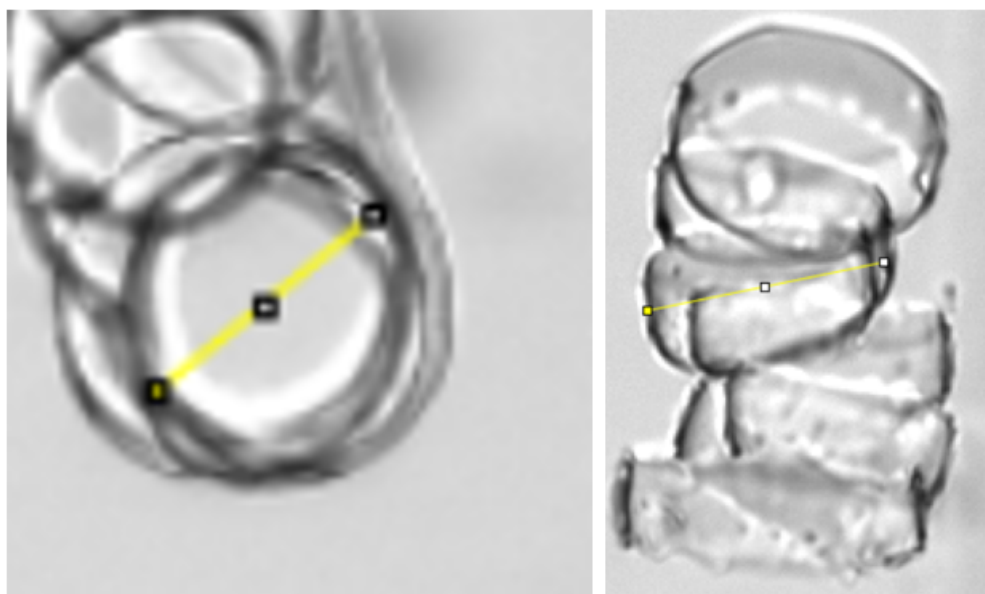


Figure SI 3 Examples of Measurements taken on the optical profilometry images to determine ribbon radius. Radius determined by measuring across helix cross-section as well as from side view of helices.

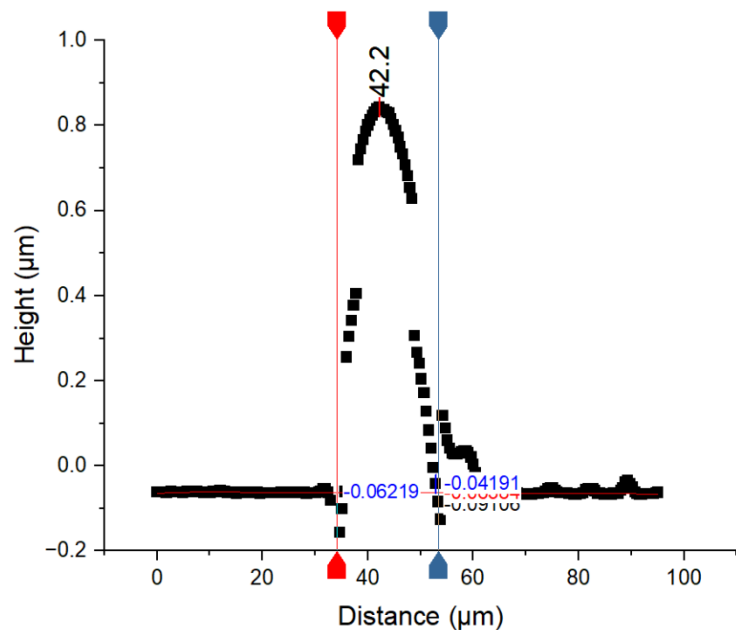


Figure SI 4 Example of ribbon cross-section as obtained by optical profilometry. Thickness and width measurements were taken with and end-points weighted baseline and

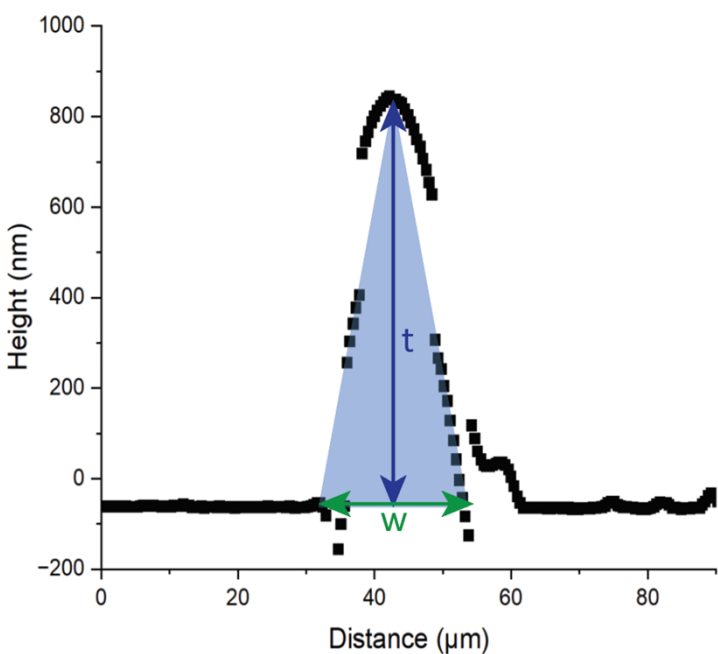


Figure SI 5. Cross-section of polymer ribbon as measured by optical profilometry. The ribbon cross-section is approximated by an isosceles triangle (blue) with the measurements of width, w , and thickness, t , describing the base and height of the triangle. Note that the y-axis dimensions are nanometers and the x-axis dimensions are micrometers.

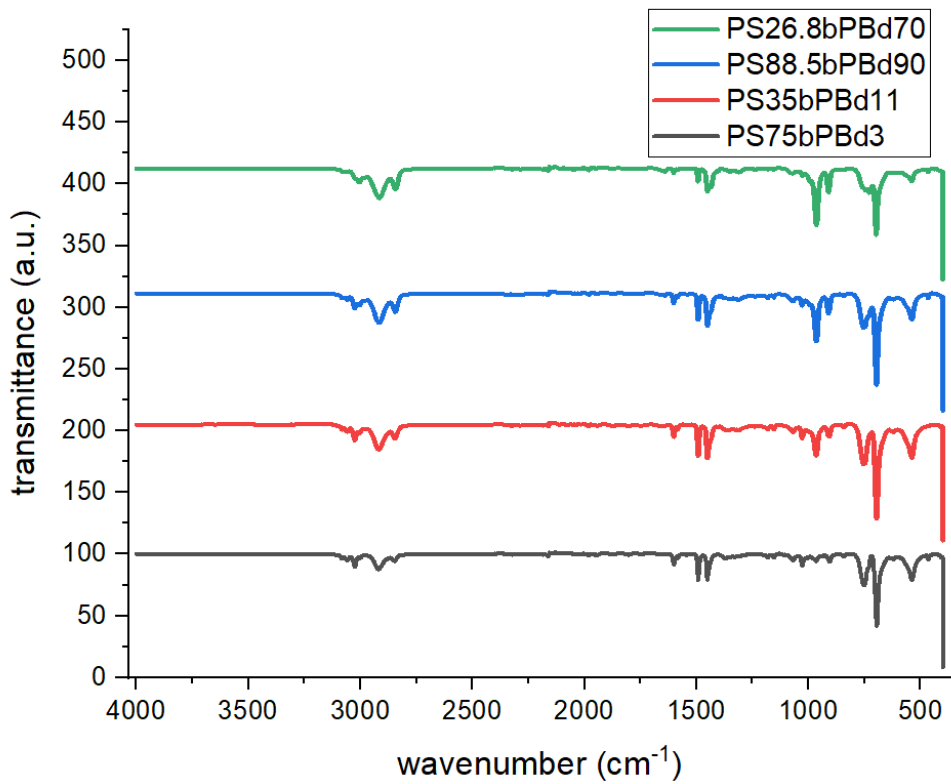


Figure SI 6 FTIR for the block polymers used in the study.

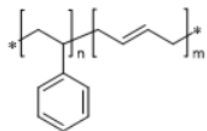


Figure SI 7 Molecular structure of the block polymers used in the study.

PS-b-PBD

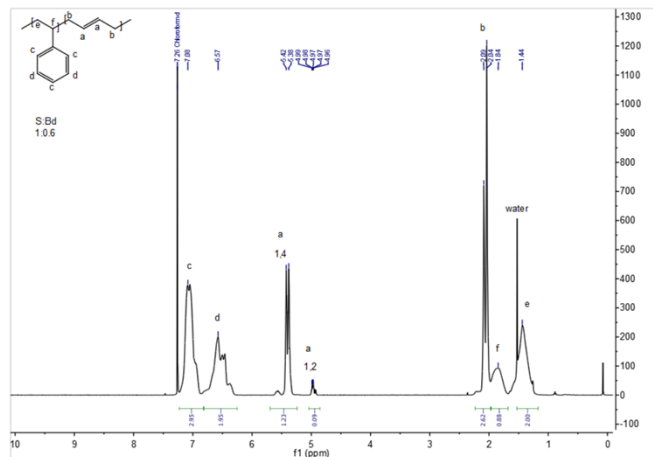


Figure SI 8 Example NMR of the block polymers used in this study. PS(35 kDa)-b-PBD (11 kDa) 1H NMR (500 MHz) in CDCl_3 .

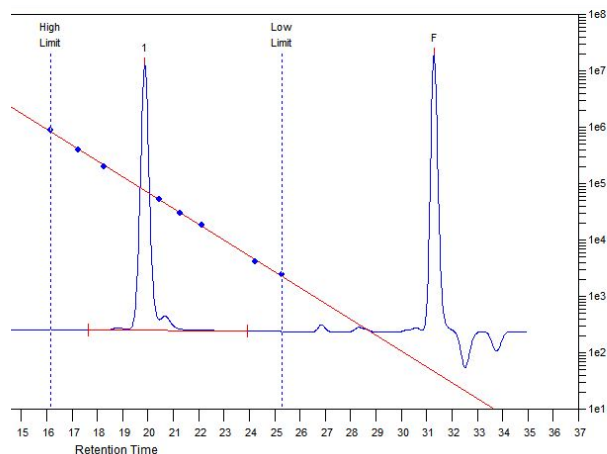


Figure SI 9 THF GPC of polymer PS(35 kDa)-b-PBD (11 kDa) from Polymersource

Mn: 71 kDa
Mw: 74 kDa
PDI 1.05

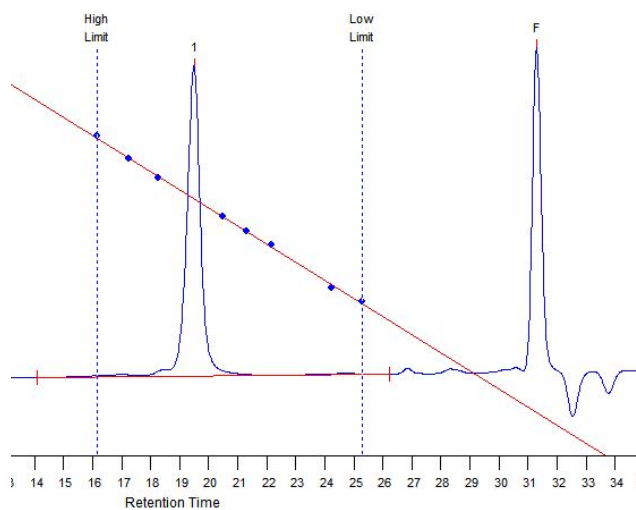


Figure SI 10 THF GPC of polymer PS(75 kDa)-b-PBD (3 kDa) from Polymersource
4 % butadiene → expected to deliver spherical morphology

Mn: 80 kDa
Mw: 117 kDa
PDI 1.45

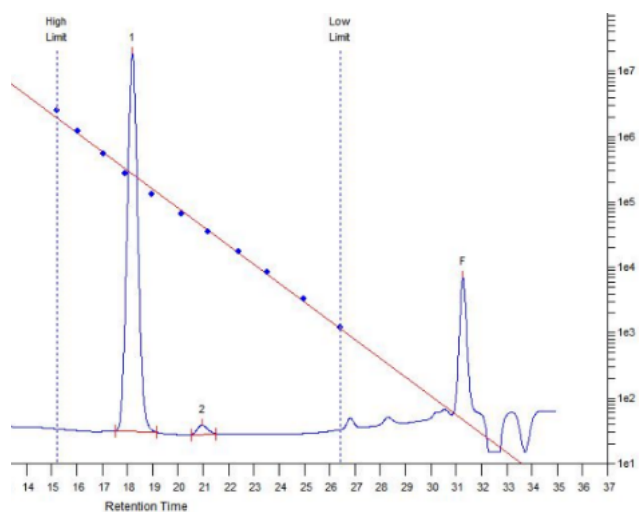


Figure SI 11 THF GPC of new polymer PS(26.8 kDa)-b-PBD (70 kDa) from Polymersource
 Mn: 268 kDa
 Mw: 273 kDa
 PDI 1.02

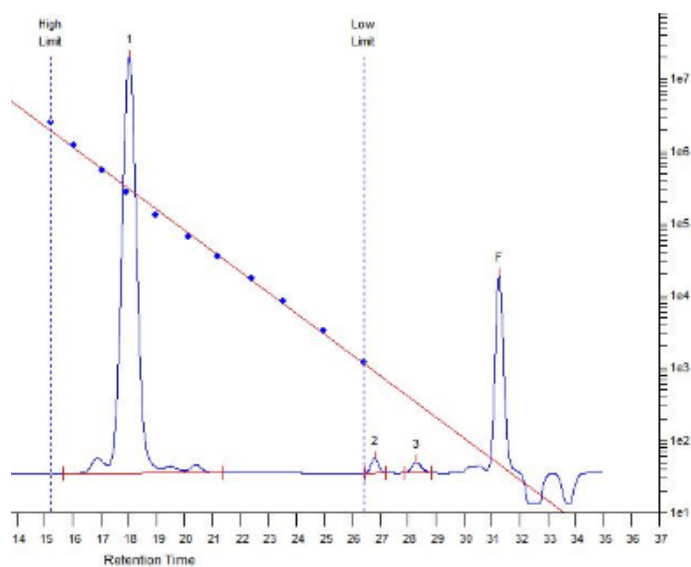


Figure SI 12 THF GPC of new polymer PS(88.5 kDa)-b-PBD (90 kDa) from Polymersource
 Mn: 276 kDa
 Mw: 307 kDa
 PDI 1.11

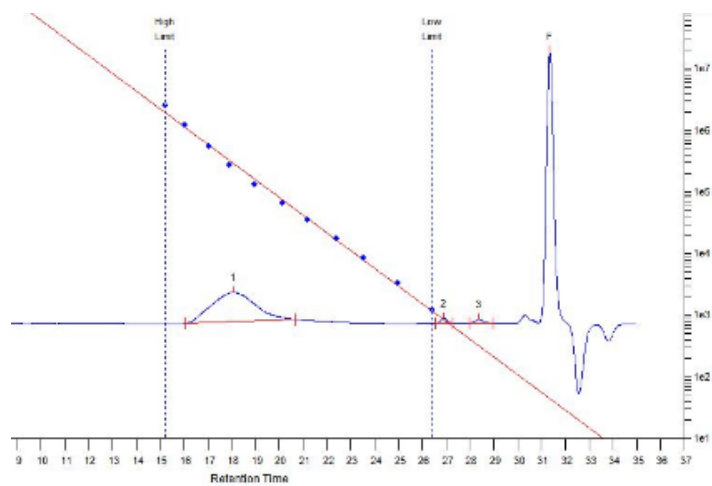


Figure SI 13 THF GPC of reference polymer PMMA (this with PMMA standards others PS standards) (90 kDa) from Polymersource

Mn: 243 kDa
 Mw: 326 kDa
 PDI 1.34