Electronic Supplementary Material (ESI) for Soft Matter.

Poly(styrene-co-butadiene) Random Copolymer Thin Films and Nanostructures on a Mica Surface: Morphology and Contact Angles of Nanodroplets

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1) Concentration Conversions.

Table SI-1: Conversions from c* to mg/ml.

	46 kg/mol (mg/ml)	**86 kg/mol (mg/ml)**	**355 kg/mol (mg/ml)**
3c*	17.34	11.13	4.17
1c*	5.81	3.71	1.39
0.1c*	0.581	0.371	0.139
0.01c*	0.0581	0.0371	0.0139
0.001c*	0.0058	0.0037	0.0014

2) Histograms Showing Polymer Aggregate Distributions.

In order to show the distribution of aggregate sizes in greater detail, a series of histograms are presented at each concentration for the lowest and highest molecular weight samples. This shows how symmetrical or asymmetrical the aggregate distributions are at varying concentrations and molecular weights. Two of the three polymer molecular weights are presented here at each concentration as this is sufficient enough to allow comparisons for molecular weight and concentration.

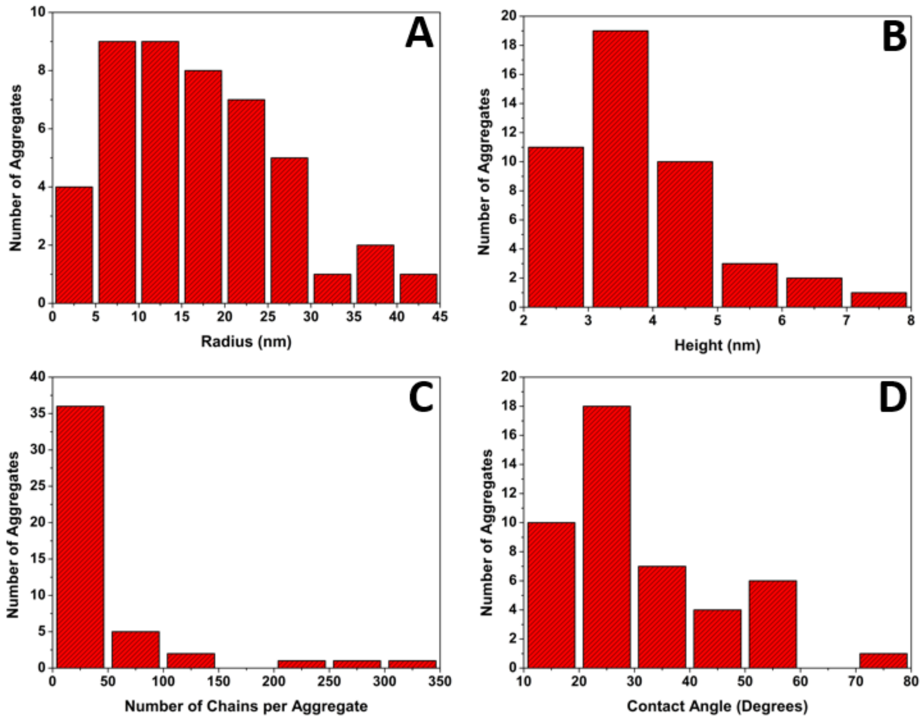

Figure SI-1: Histograms showing the distribution of aggregate morphology for the 46 kg/mol sample at a concentration of 0.001c*. (0.0058 mg/ml). (A) Radius, (B) height, (C) number of chains per aggregate, and (D) contact angle.

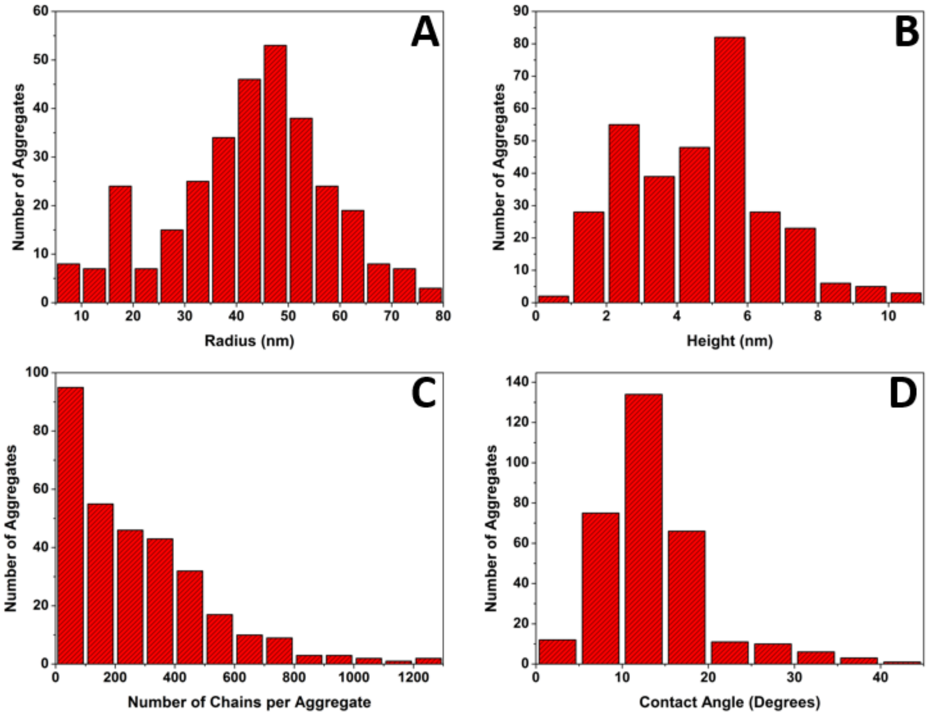

Figure SI-2: Histograms showing the distribution of aggregate morphology for the 46 kg/mol sample at a concentration of 0.01c* (0.0581 mg/ml). (A) Radius, (B) height, (C) number of chains per aggregate, and (D) contact angle.

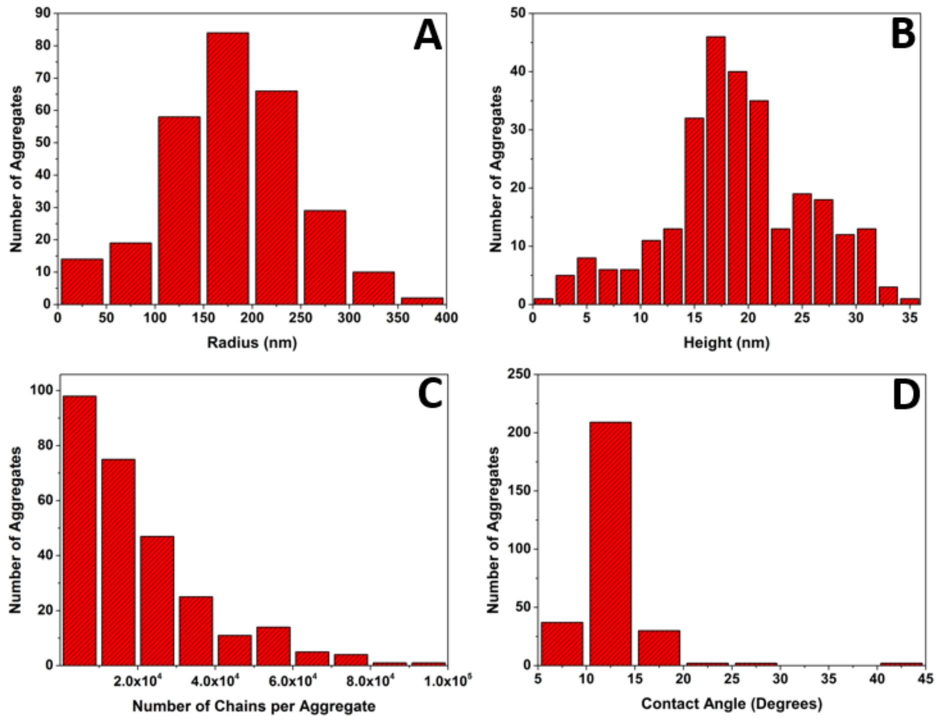

Figure SI-3: Histograms showing the distribution of aggregate morphology for the 46 kg/mol sample at a concentration of 0.1c* (0.581 mg/ml). (A) Radius, (B) height, (C) number of chains per aggregate, and (D) contact angle.

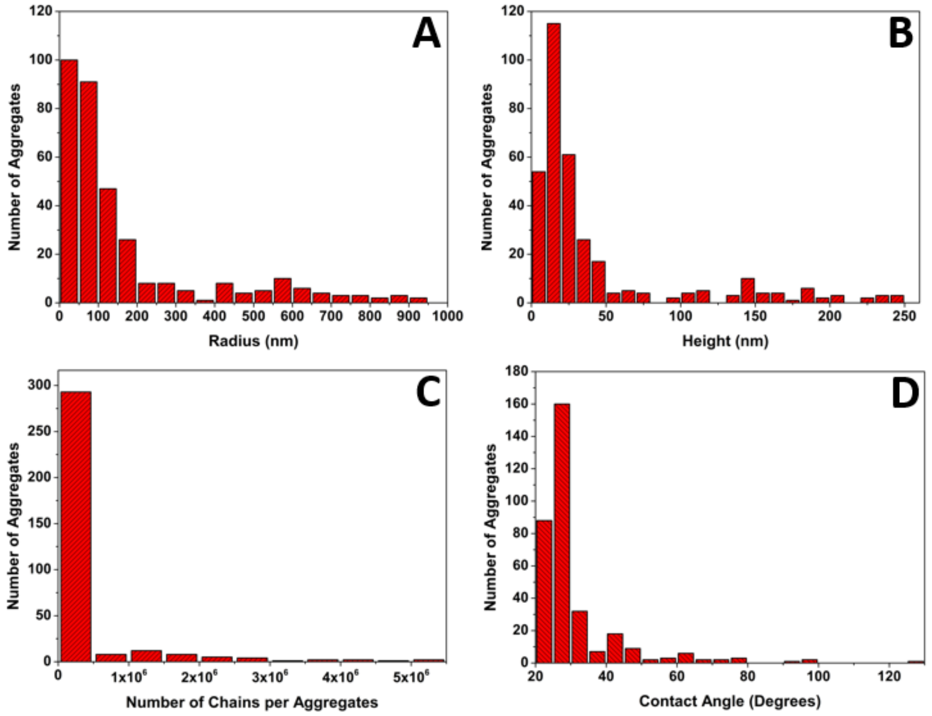

Figure SI-4: Histograms showing the distribution of aggregate morphology for the 46 kg/mol sample at a concentration of 1c* (5.81 mg/ml). (A) Radius, (B) height, (C) number of chains per aggregate, and (D) contact angle.

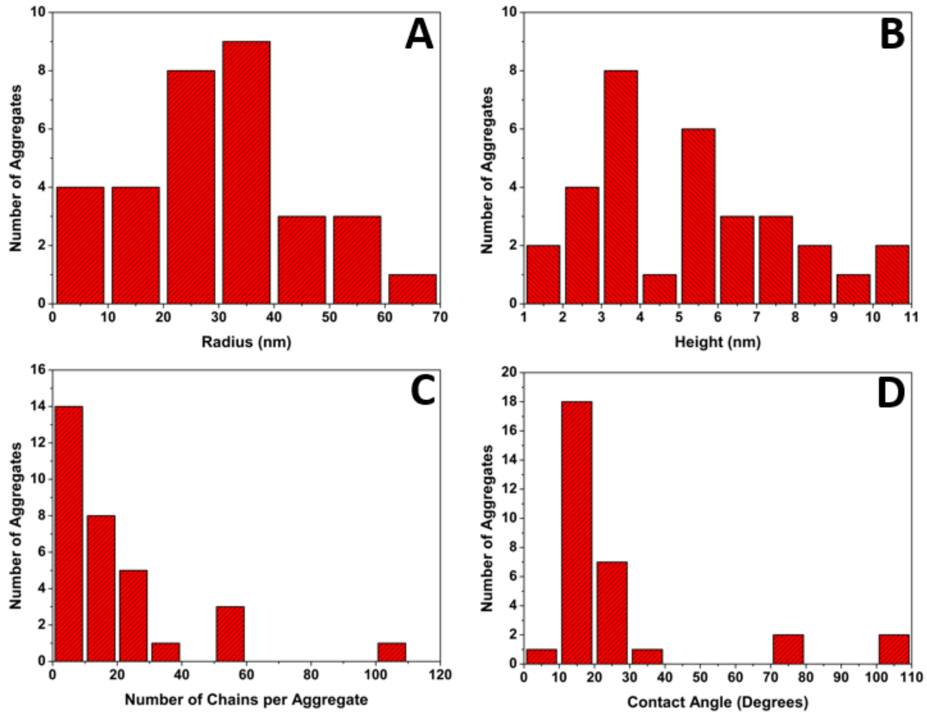

Figure SI-5: Histograms showing the distribution of aggregate morphology for the 355 kg/mol sample at a concentration of 0.001c* (0.0014 mg/ml). (A) Radius, (B) height, (C) number of chains per aggregate, and (D) contact angle.

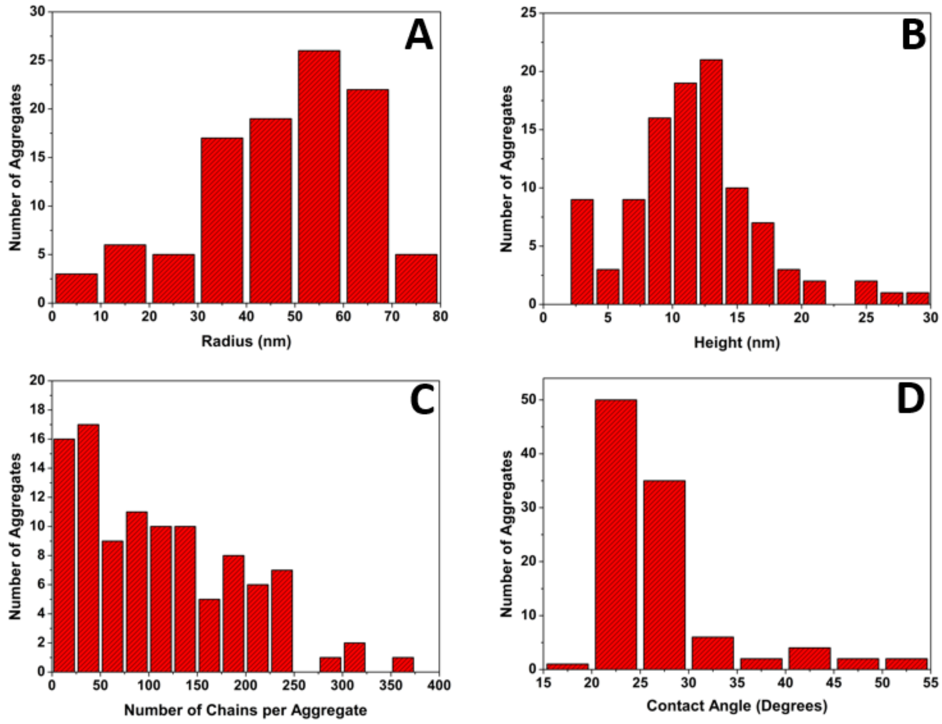

Figure SI-6: Histograms showing the distribution of aggregate morphology for the 355 kg/mol sample at a concentration of 0.01c* (0.0139 mg/ml). (A) Radius, (B) height, (C) number of chains per aggregate, and (D) contact angle.

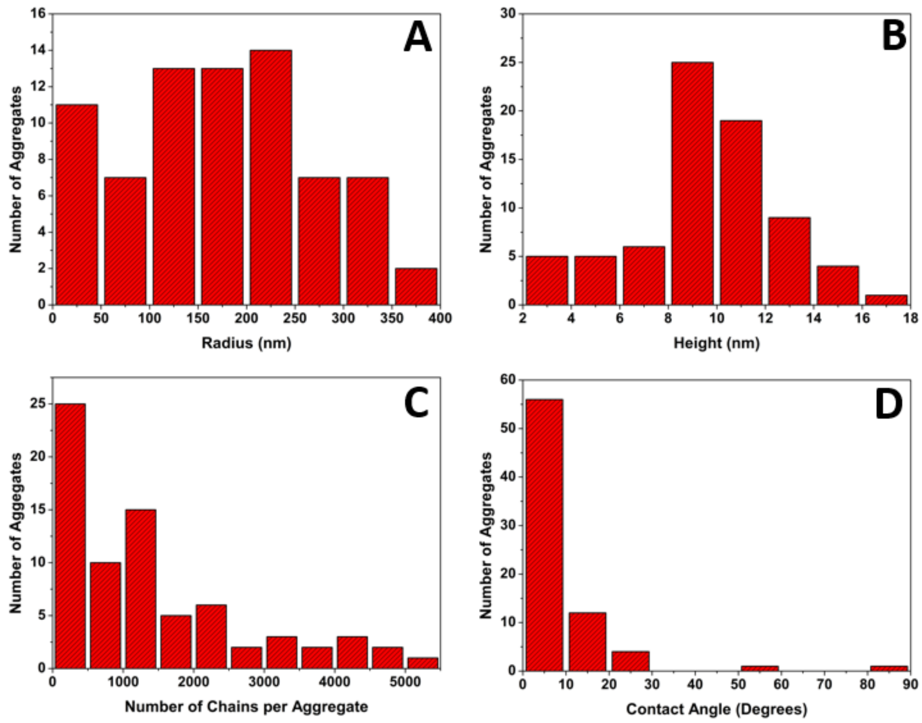

Figure SI-7: Histograms showing the distribution of aggregate morphology for the 355 kg/mol sample at a concentration of 0.1c* (0.139 mg/ml). (A) Radius, (B) height, (C) number of chains per aggregate, and (D) contact angle.

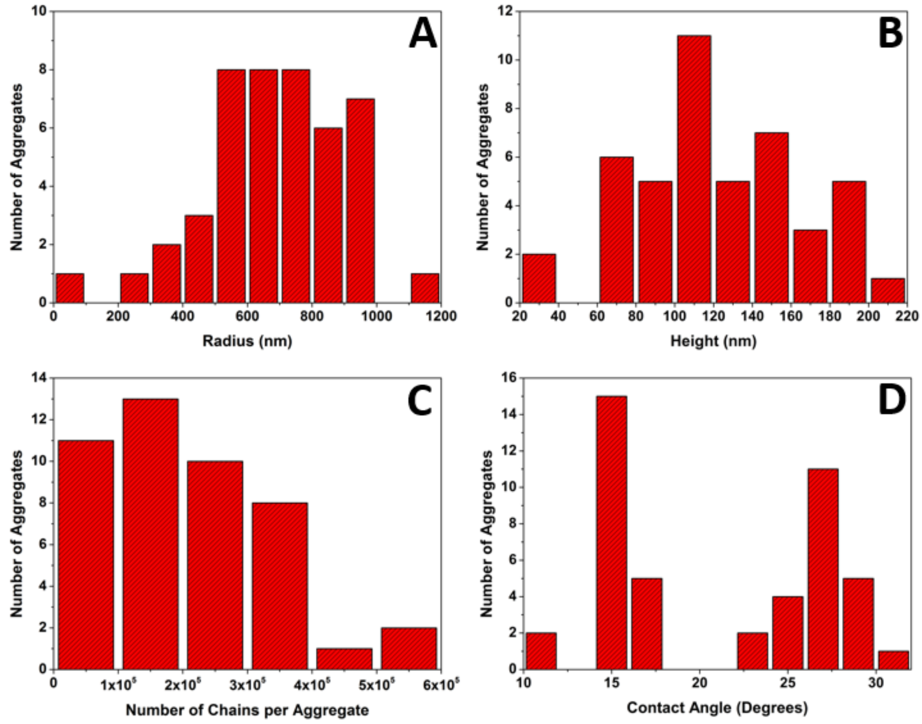

Figure SI-8: Histograms showing the distribution of aggregate morphology for the 355 kg/mol sample at a concentration of 1c* (1.39 mg/ml). (A) Radius, (B) height, (C) number of chains per aggregate, and (D) contact angle.

3) AFM Images Comparing Dewetting at Different Time Scales.

AFM images are presented for the 46 kg/mol sample at concentrations of 1c* and 0.1c*. These images compare the polymer formation on the mica surface at fixed concentrations after experiencing 16 – 72 hours drying and 15 minutes drying. Therefore, we can examine the dewetting mechanisms at different time scales.

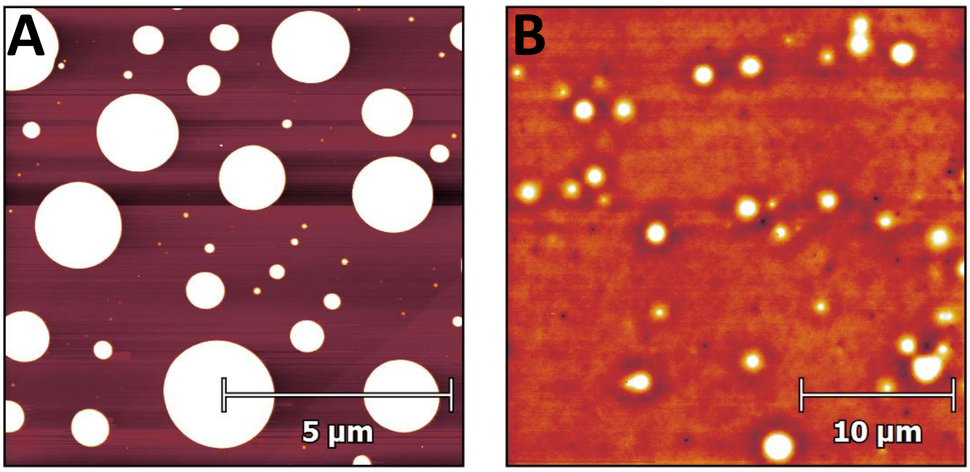

Figure SI-9: AFM images for the 46 kg/mol sample at a concentration of 1c* (5.81 mg/ml), showing the polymer formation on the mica surface after: (A) 16 - 72 hours of drying, and (B) 15 minutes of drying. Both experiments were carried out at room temperature.

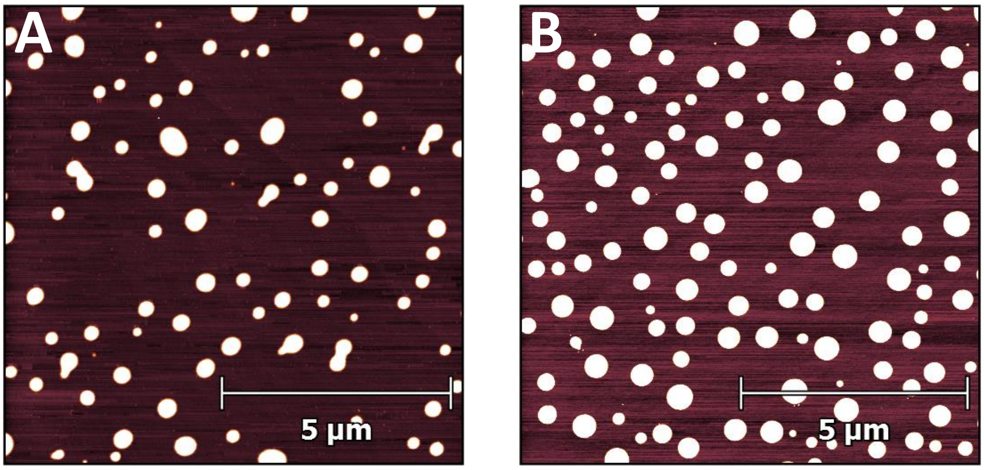

Figure SI-10: AFM images for the 46 kg/mol sample at a concentration of 0.1c* (0.581 mg/ml), showing the polymer formation on the mica surface after: (A) 16 - 72 hours of drying, and (B) 15 minutes of drying. Both experiments were carried out at room temperature.

4) Film Thickness Measurements.

In order to measure the thicknesses of the polymer films at 3c*, cross-sectional profile plots were taken across holes in the films surface. The difference in height value between the exposed mica surface and the surface of the polymer film could then be measured to provide a value for film thickness. In order to achieve a more accurate value, the measurements were taken from a flat area of the polymer surface and not close to the hole's circumference where a raised rim may be present. Measurements were taken for each hole in the film to give an average value of film thickness for each of the samples at 3c*. The measured film thickness for the profile plot in Figure SI-11 is 20 nm.

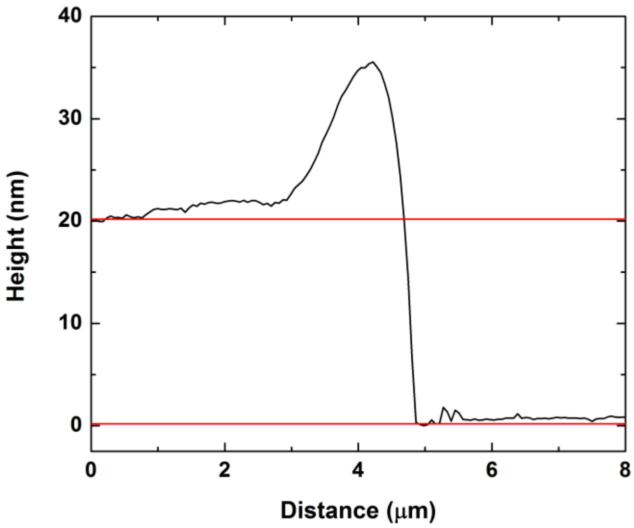

Figure SI-11: An example of a typical cross-sectional profile plot used to measure the thickness of the polymer films. This example is taken from a hole in the film of the 355 kg/mol sample at a concentration of 3c*.

5) Nanoscopic Contact Angle Measurements.

A minimum in contact angle is observed for polymer nanodroplets with radii ranging from 100 – 250 nm. Figure SI-9 shows cross-sectional profile plots for typical nanodroplets with radii ranging from 100 – 250 nm fitted to spherical caps at each molecular weight. Despite their small contact angles, these results confirm that the nanodroplets with radii ranging from 100 – 250 nm are spherical cap shaped.

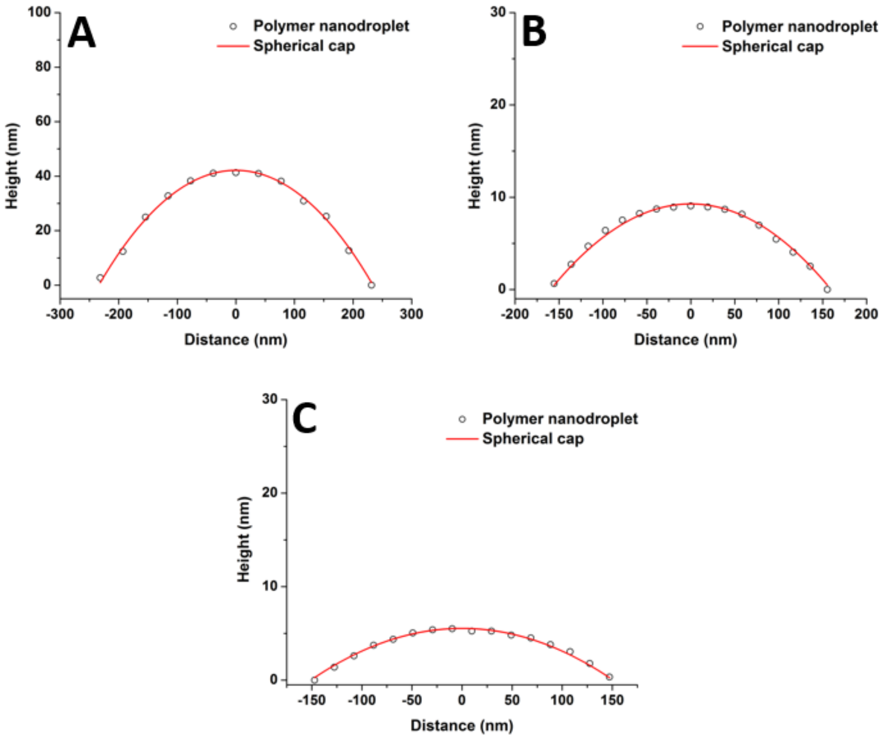

Figure SI-12: Cross-sectional profile plots of typical poly(styrene-co-butadiene) nanodroplets with radii in the range of 100 – 250 nm at each molecular weight. The cross-sections are fitted to spherical caps. (A) M_n = 46 kg/mol, (B) M_n = 86 kg/mol, and (C) M_n = 355 kg/mol

6) Macroscopic Contact Angle Measurements.

Figure SI-13 shows an annotated photograph of a typical poly(styrene-co-butadiene) random copolymer droplet on a mica surface at the macroscale. The radii of the droplets at the macroscale ranged from around 1 – 5 mm. The droplets were spherical cap shaped and the small difference in contact angle value on each side of the droplet in the image can be attributed to experimental error.

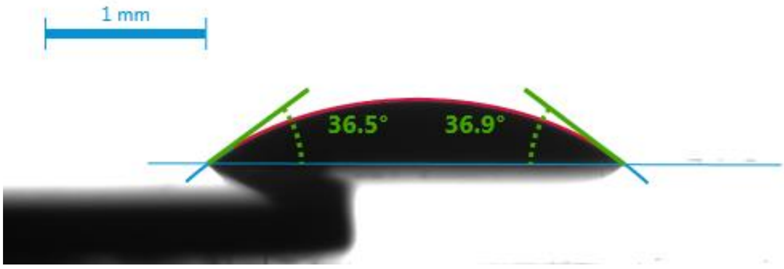

Figure SI-13: Photograph showing an example of a typical macroscopic poly(styrene-co-butadiene) droplet (M_n= 46 kg/mol) on a mica surface, annotated with contact angle values.