Supporting Information for

Understanding Interfacial Segregation in Polymer Blend Films with Random and Mixed Side-Chain Bottlebrush Copolymer Additives

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1. **^{1}H NMR**

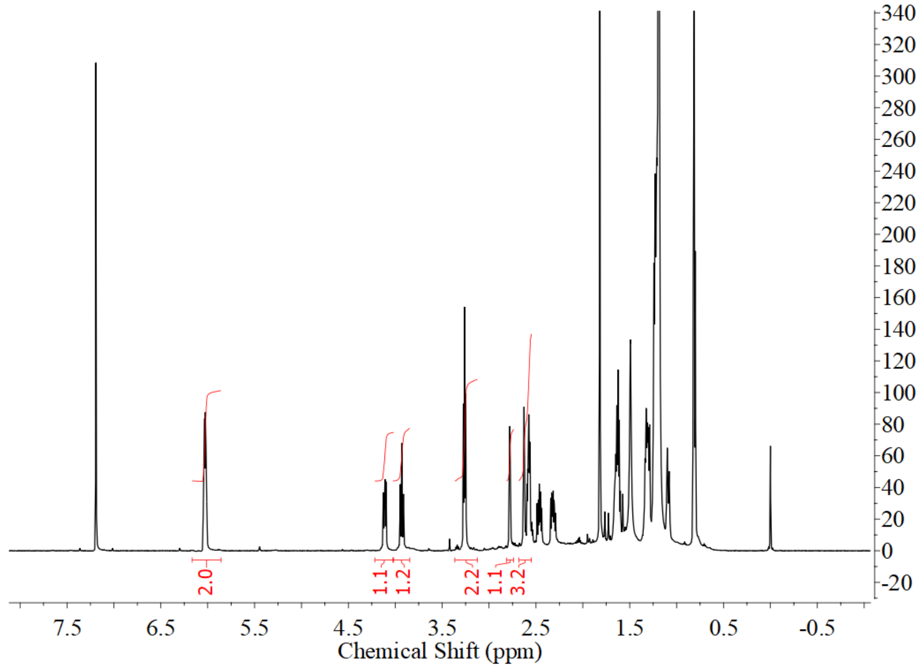


Figure S1. ^{1}H NMR spectra of NBCTA.

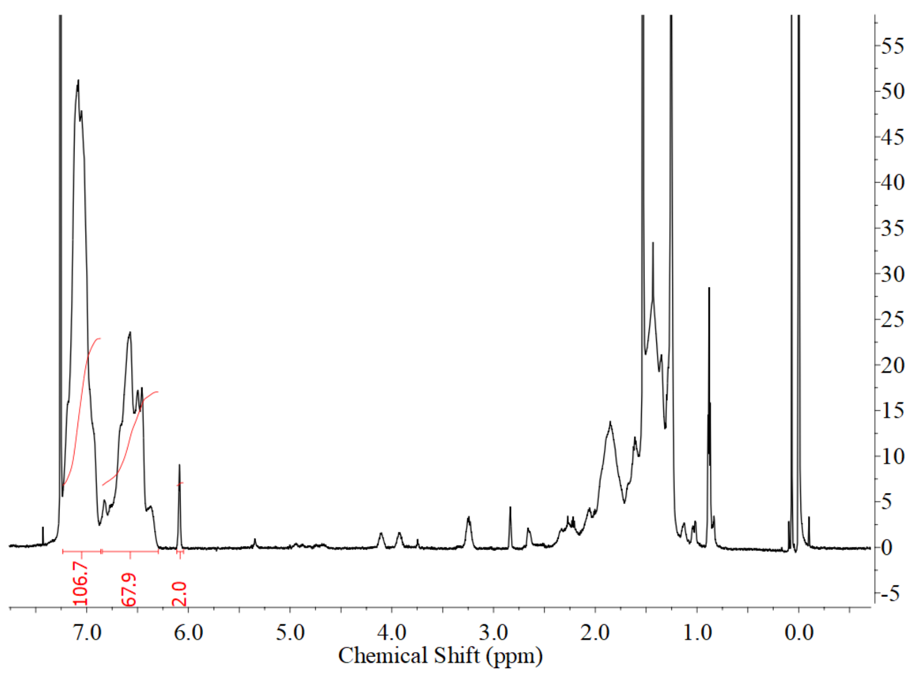


Figure S2. ^{1}H NMR spectra of NBPS macromonomer.

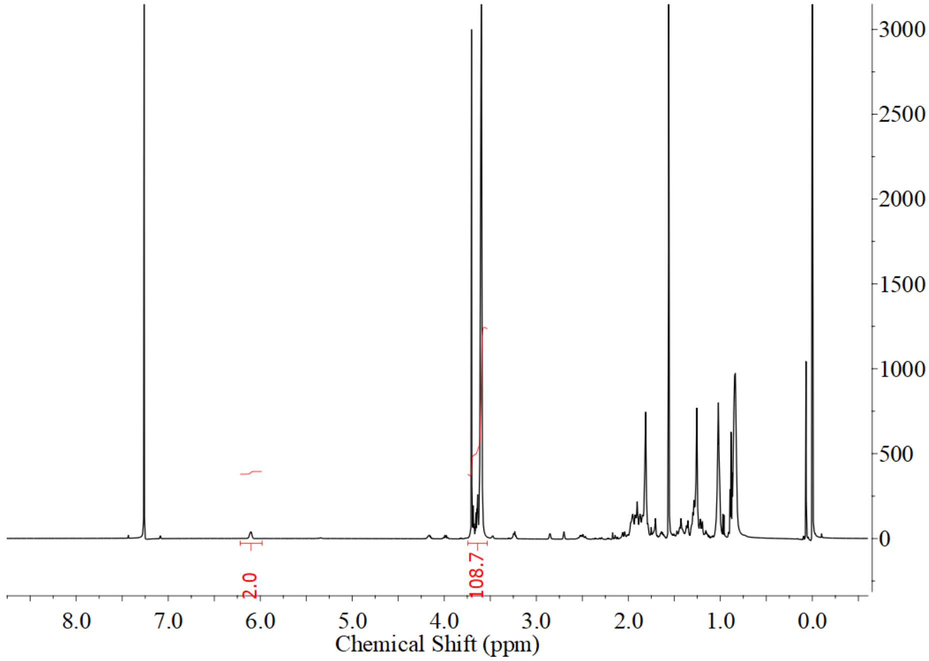


Figure S3. ^{1}H NMR spectra of NBPMMA macromonomer.

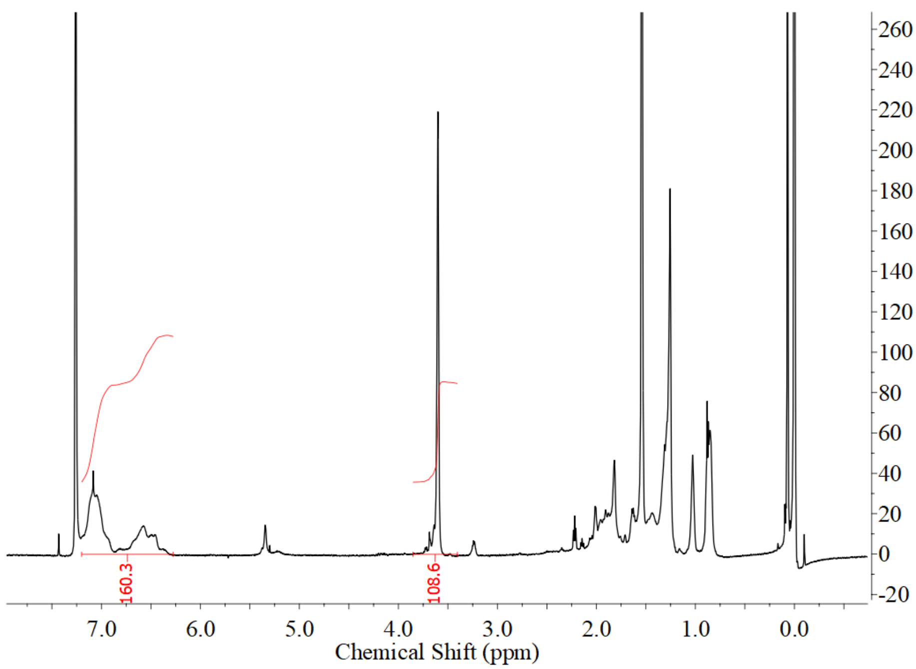


Figure S4. ^{1}H NMR spectra of BBPS-*m*-PMMA bottlebrush copolymer.

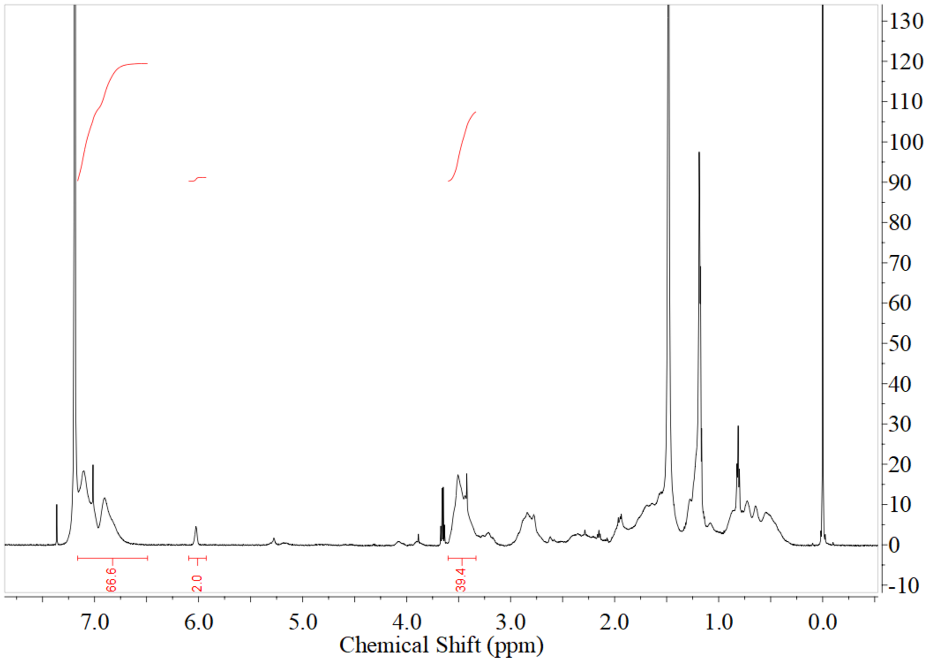


Figure S5. ^{1}H NMR spectra of NBPS-r-PMMA macromonomer

2. GPC

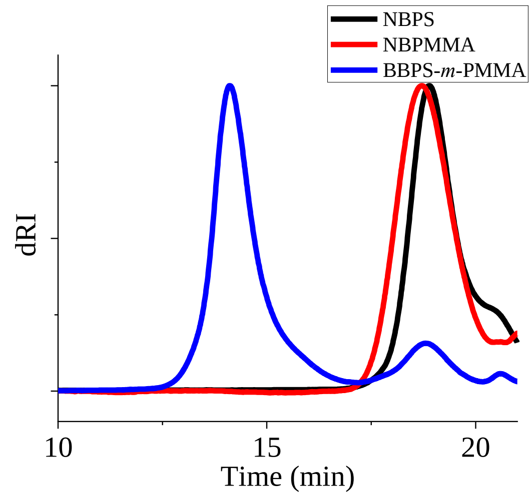


Figure S6. GPC traces of NBPS, NBPMMA macromonomers and BBPS-*m*-PMMA bottlebrush copolymer. The final macromonomer conversion was approximately 89.1 wt %, which corresponded to 10.9 wt % residual macromonomer.

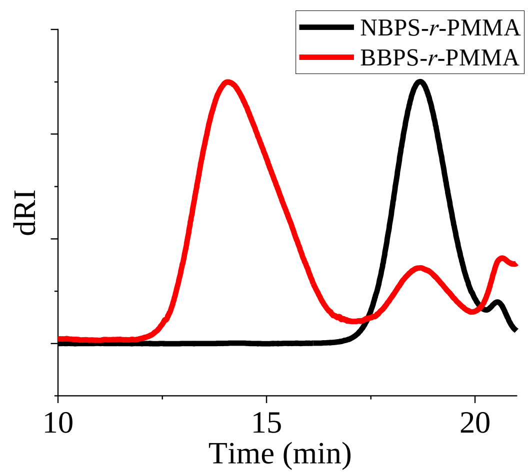


Figure S7. GPC traces of NBPS-*r*-PMMA macromonomers and BBPS-*r*-PMMA bottlebrush copolymer. The final macromonomer conversion was approximately 90.3 wt %, which corresponded to 9.7 wt % residual macromonomer.

3. Optical Microscopy

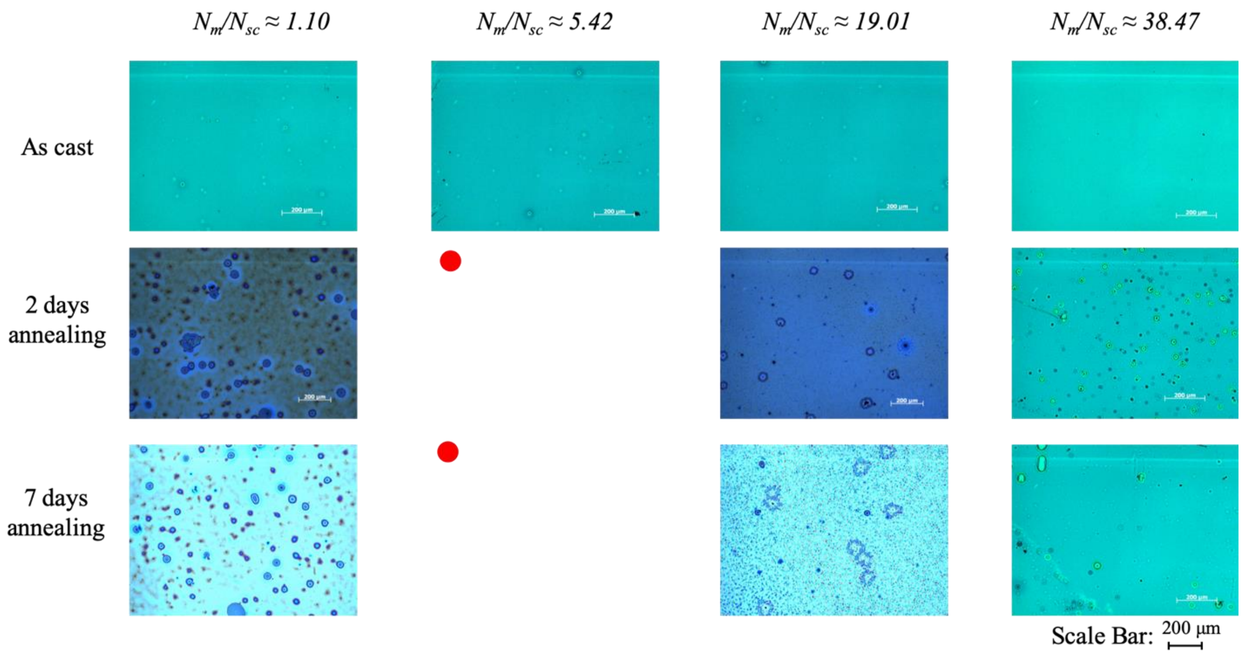


Figure S8. Optical micrographs of 10 wt% BBPS-*r*-PMMA in linear PS thin film blends.

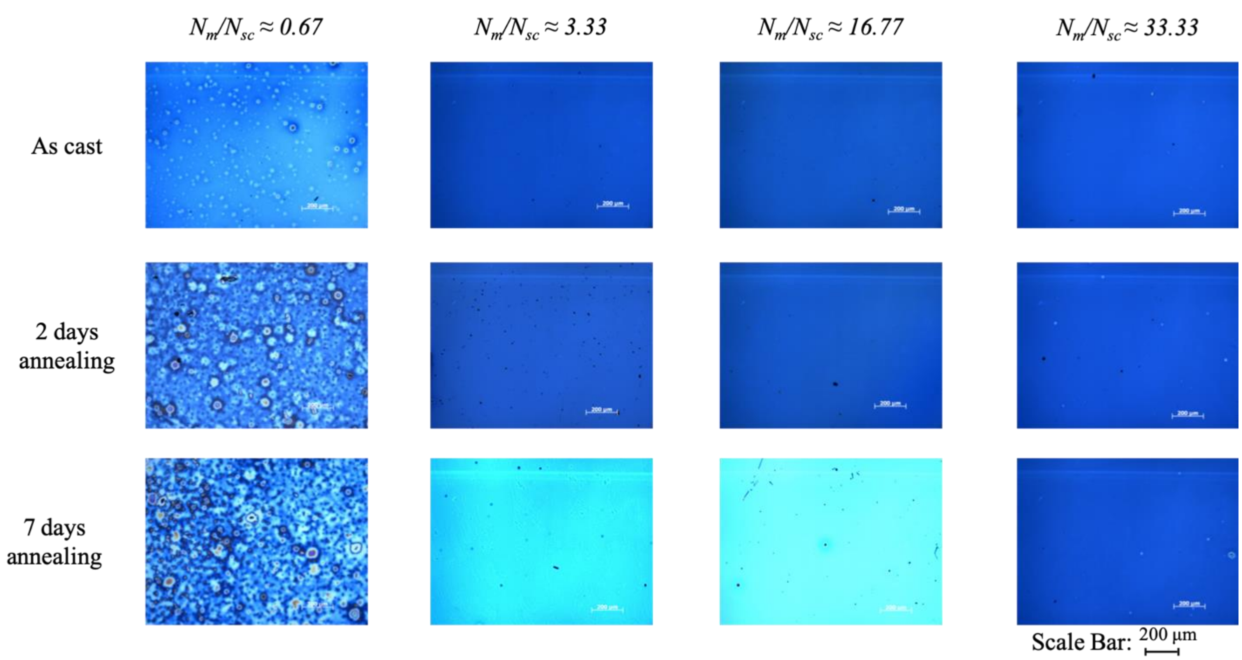


Figure S9. Optical micrographs of 10 wt % BBPS-*r*-PMMA in linear PMMA thin film blends.

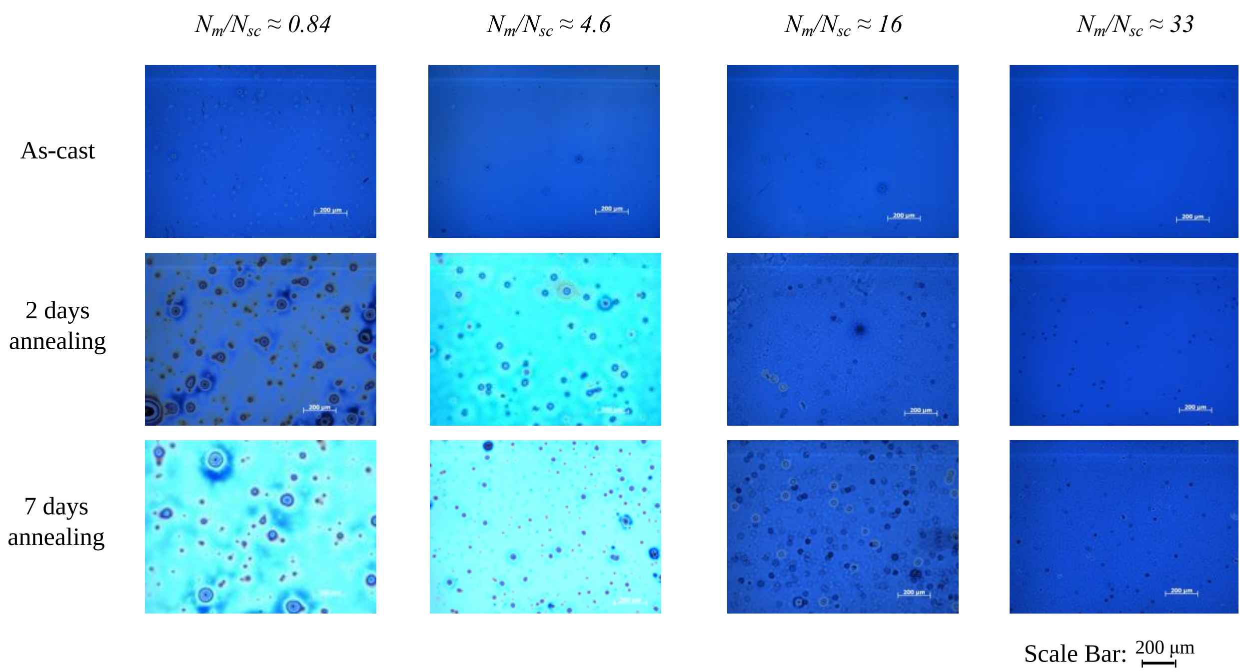


Figure S10. Optical micrographs of 10 wt % BBPS-*m*-PMMA in linear PS thin film blends.

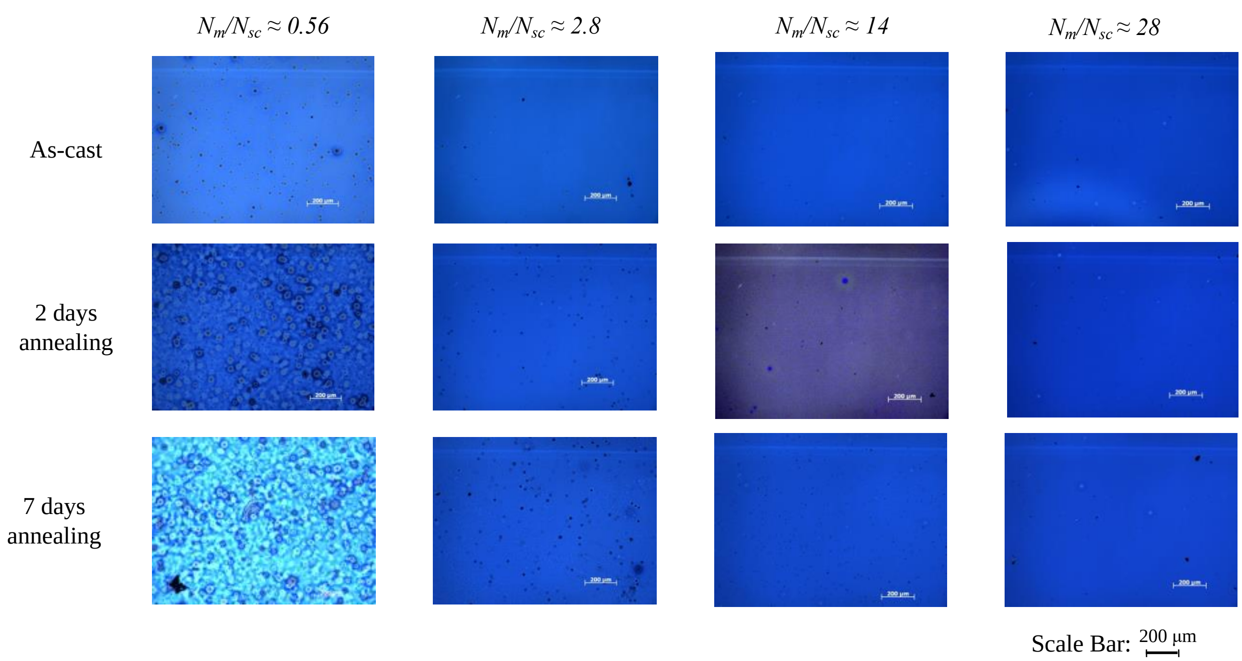


Figure S11. Optical micrographs of 10 wt % BBPS-*m*-PMMA in linear PMMA thin film blends.

4. Uncalibrated ToF-SIMS data

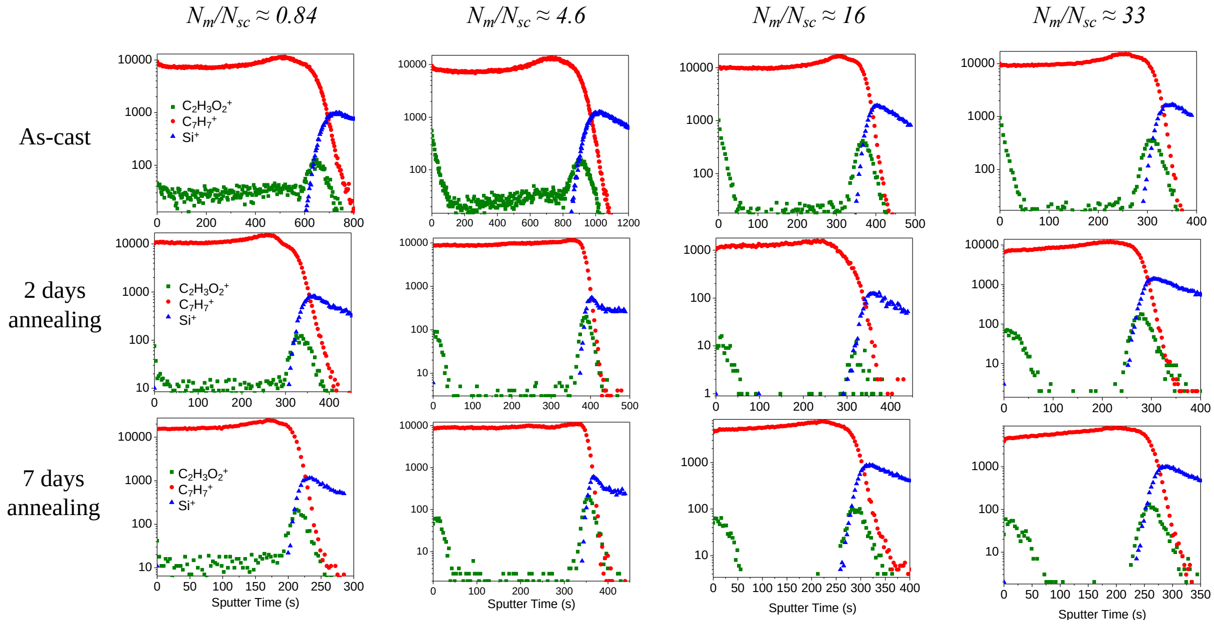


Figure S12. Uncalibrated secondary ion-intensities measured during ToF-SIMS depth profiling of 10 wt % BBPS-*m*-PMMA in linear PS blend films. $C_2H_3O_2^+$, $C_7H_7^+$, and Si^+ secondary ions are indicated in green, red, and blue, respectively.

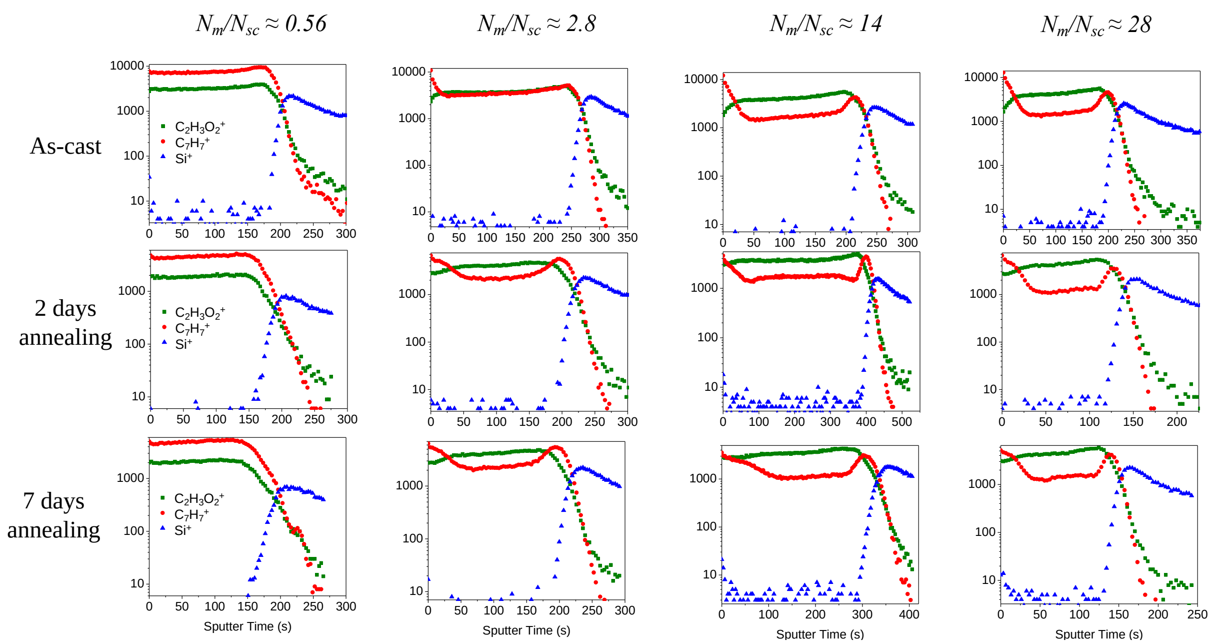


Figure S13. Uncalibrated ion-intensities measured during ToF-SIMS depth profiling of 10 wt % BBPS-*m*-PMMA in linear PMMA blend films. $C_2H_3O_2^+$, $C_7H_7^+$, and Si^+ ions are indicated in green, red, and blue, respectively.

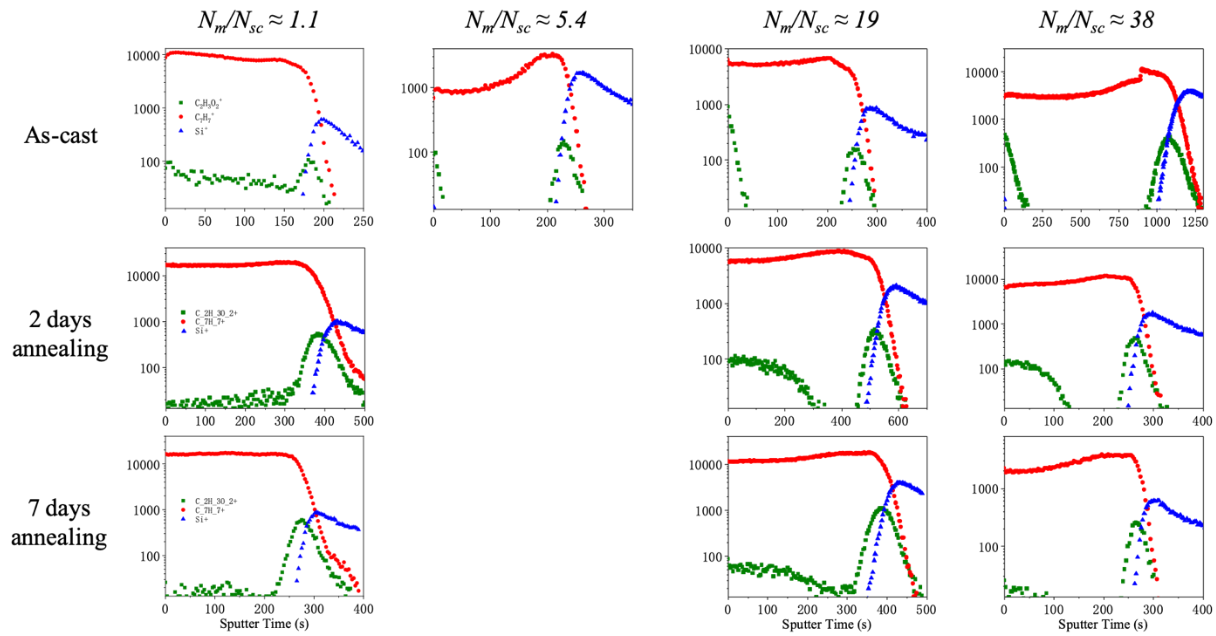


Figure S14. Uncalibrated secondary ion-intensities measured during ToF-SIMS depth profiling of 10 wt % BBPS-*r*-PMMA in linear PS blend films. $C_2H_3O_2^+$, $C_7H_7^+$, and Si^+ secondary ions are indicated in green, red, and blue, respectively.

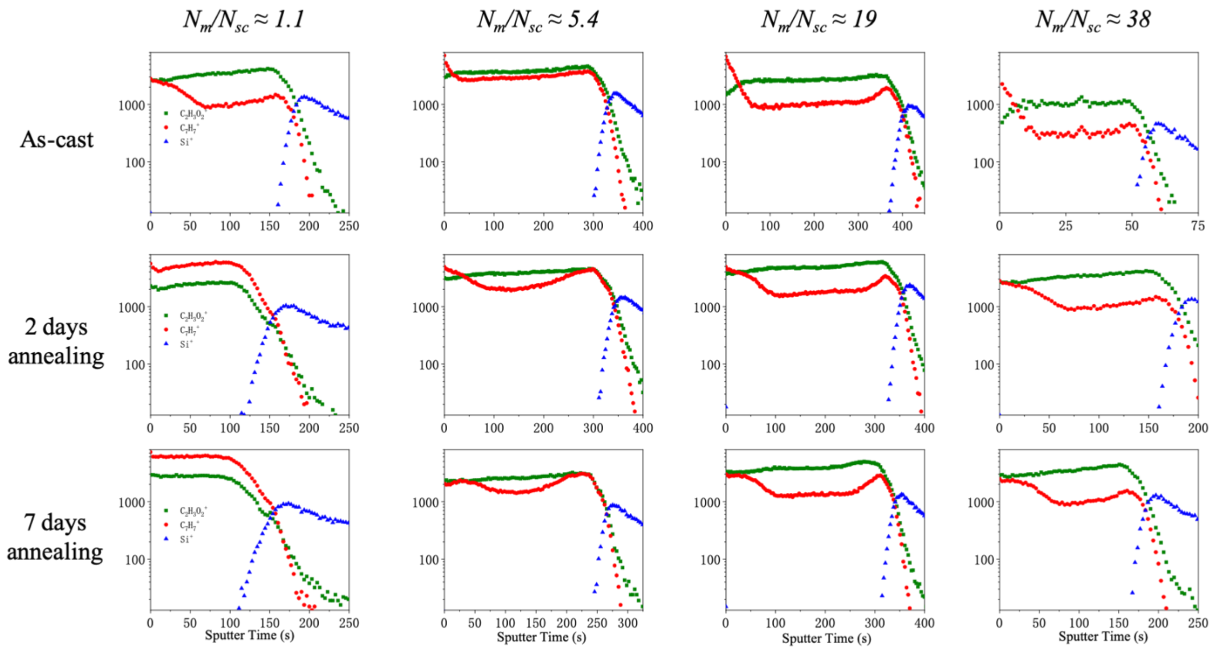


Figure S15. Uncalibrated ion-intensities measured during ToF-SIMS depth profiling of 10 wt % BBPS-*r*-PMMA in linear PMMA blend films. $C_2H_3O_2^+$, $C_7H_7^+$, and Si^+ ions are indicated in green, red, and blue, respectively.

5. Film Thickness

Table S1. Thicknesses of BBPS-*m*-PMMA in linear PS blend films.

Sample/ Thickness (nm)	$N_m/N_{sc} \approx 0.84$	$N_m/N_{sc} \approx 4.6$	$N_m/N_{sc} \approx 16$	$N_m/N_{sc} \approx 33$
As-cast	130.4	148.0	140.7	126.2
2 days annealing	169.2	205.8	136.6	118.3
7 days annealing	161.2	171.8	137.4	121.6

Table S2. Thicknesses of BBPS-*m*-PMMA in linear PMMA blend films.

Sample/ Thickness (nm)	$N_m/N_{sc} \approx 0.56$	$N_m/N_{sc} \approx 2.8$	$N_m/N_{sc} \approx 14$	$N_m/N_{sc} \approx 28$
As-cast	160.5	168.3	141.0	127.8
2 days annealing	143.3	136.4	230.0	114.2
7 days annealing	149.8	133.9	135.4	124.4

Table S3. Thicknesses of BBPS-*r*-PMMA in linear PS blend films.

Sample/ Thickness (nm)	$N_m/N_{sc} \approx 1.1$	$N_m/N_{sc} \approx 5.4$	$N_m/N_{sc} \approx 19$	$N_m/N_{sc} \approx 38$
As-cast	73.5	86.7	75.5	85.1
2 days annealing	90.2	--	127.3	73.7
7 days annealing	122.8	--	135.0	75.7

Table S4. Thicknesses of BBPS-*r*-PMMA in linear PMMA blend.

Sample/ Thickness (nm)	$N_m/N_{sc} \approx 0.67$	$N_m/N_{sc} \approx 3.3$	$N_m/N_{sc} \approx 17$	$N_m/N_{sc} \approx 33$
As-cast	93.2	77.3	123.6	82.2
2 days annealing	82.5	89.5	100.3	56.3
7 days annealing	71.8	86.5	102.2	62.2

6. Calibration and normalization of secondary ion intensities from ToF-SIMS measurements.

We calibrated and normalized the secondary ion intensity signals from ToF-SIMS measurements through analysis of a series of blends of BBPS-*r*-PMMA in PS3 and BBPS-*r*-PMMA in PMMA2. Low molecular weight polymer blends were chosen to ensure full miscibility, and no evidence of interfacial segregation was observed in the blends. For each blend, we determined the average and standard deviation of the intensity ratio of $C_2H_3O_2^+$ ions (I_{C2H3O2}) to that of $C_7H_7^+$ (I_{C7H7}) through a ToF-SIMS depth profiling measurement. These values are provided in **Table S5** for blends of NBPMMA in PS3 and **Table S6** for NBPS in PMMA2.

Table S5. Secondary ion intensity ratios I_{C2H3O2}/I_{C7H7} for BBPS-*r*-PMMA in PS3 as a function of NBPMMA composition.

PMMA wt%	PMMA/PS mass ratio	I_{C2H3O2}/I_{C7H7} [a]	σ [b]
0.00	0	0	0.0000
1.82	0.018	0.0016	0.0008
4.13	0.043	0.0050	0.0012
8.83	0.097	0.0136	0.0011
24.00	0.316	0.0514	0.0023
43.49	0.770	0.1373	0.0061

[a]the secondary ion intensity ratios represent averaged values through the depth of each blend film; [b] standard deviation of the average ion intensity ratio for each blend film.

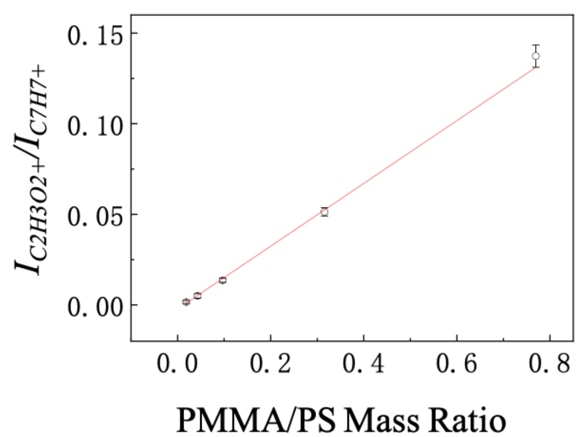


Figure S16. Secondary ion intensity ratio I_{C2H3O2}/I_{C7H7} as a function of PMMA/PS mass ratio for BBPS-*r*-PMMA in PS.

The average ion intensities vary linearly with the mass ratio of PMMA/PS in the blend film, as shown in **Figure S17** for BBPS-*r*-PMMA in PS3 and **Figure S18** for BBPS-*r*-PMMA in PMMA2. In the case of BBPS-*r*-PMMA in PS3, the slope of the trendline gives the relationship between the ion intensity ratio I_{C2H3O2}/I_{C7H7} and PMMA/PS mass ratio in the film. The PMMA content of the bottlebrush copolymers is 53 wt %, and therefore the ion intensity ratio can be used to determine the bottlebrush mass fraction for each point analyzed in the blend films.

In the case of BBPS-*r*-PMMA in PMMA2, an additional correction is necessary since PMMA2 contains a diphenylhexyl endgroup which contributes to the measured $C_7H_7^+$ intensity. As shown in **Figure S18a**, the I_{C7H7}/I_{C2H3O2} ratio is not zero even for a pure PMMA2 film. The value of I_{C7H7}/I_{C2H3O2} measured for a PS/PMMA mass ratio of zero represents the background contribution from the PMMA diphenylhexyl endgroup. This background intensity is subtracted from each measurement, resulting in a corrected I_{C7H7}/I_{C2H3O2} v.s. PS/PMMA mass ratio plot shown in **Figure S18b**. The slope of the trendline provides a relationship between the corrected ion intensity ratio I_{C7H7}/I_{C2H3O2} and the PS/PMMA mass ratio and can be used to determine the bottlebrush composition for each measurement in the film. The background contribution to I_{C7H7}/I_{C2H3O2} is determined separately for each PMMA homopolymer studied.

Table S6. Secondary ion intensity ratios I_{C7H7}/I_{C2H3O2} for BBPS-*r*-PMMA in PMMA2 as a function of NBPS composition.

NBPS wt %	PS/PMMA mass ratio	I_{C7H7}/I_{C2H3O2}[a]	σ[b]	Background-corrected I_{C7H7}/I_{C2H3O2}[c]
0	0	1.920	0.0507	0.000
0.52	0.005	2.040	0.0391	0.120

2.34	0.024	2.128	0.1534	0.208
5.08	0.054	2.289	0.0356	0.369
27.98	0.388	3.583	0.0359	1.663
44.10	0.789	5.236	0.0768	3.316

[a] the secondary ion intensity ratios are averaged values through the depth of each blend film; [b] standard deviation of the average ion intensity ratio for each blend film; [c] background corrected intensity ratios determined by substracting 1.92 from each blend analyzed.

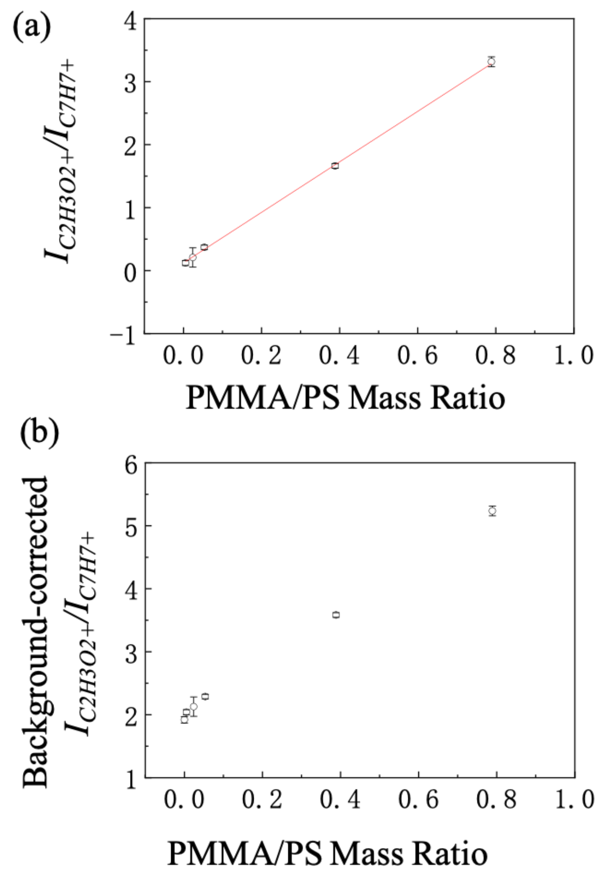


Figure S17. (a) Secondary ion intensity ratio I_{C7H7}/I_{C2H3O2} as a function of PMMA/PS mass ratio for BBPS-*r*-PMMA in PMMA2 and (b) corrected secondary ion intensity ratio I_{C7H7}/I_{C2H3O2} as a function of PMMA/PS mass ratio for NBPS in PMMA2.

7. Full Distribution of the Additives in Blends

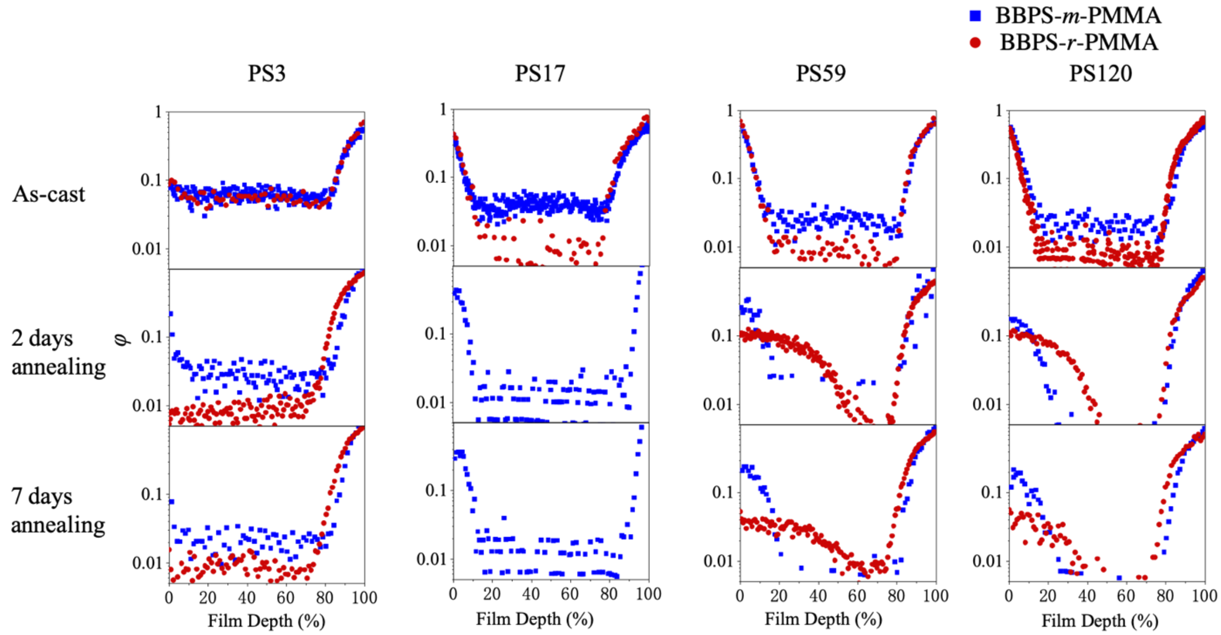


Figure S18. BBPS-*m*-PMMA and BBPS-*r*-PMMA mass composition φ as a function of film depth in blend films with linear PS. The polymer–air interface and polymer-substrate interface of the film are at 0 and 100% film depth, respectively.

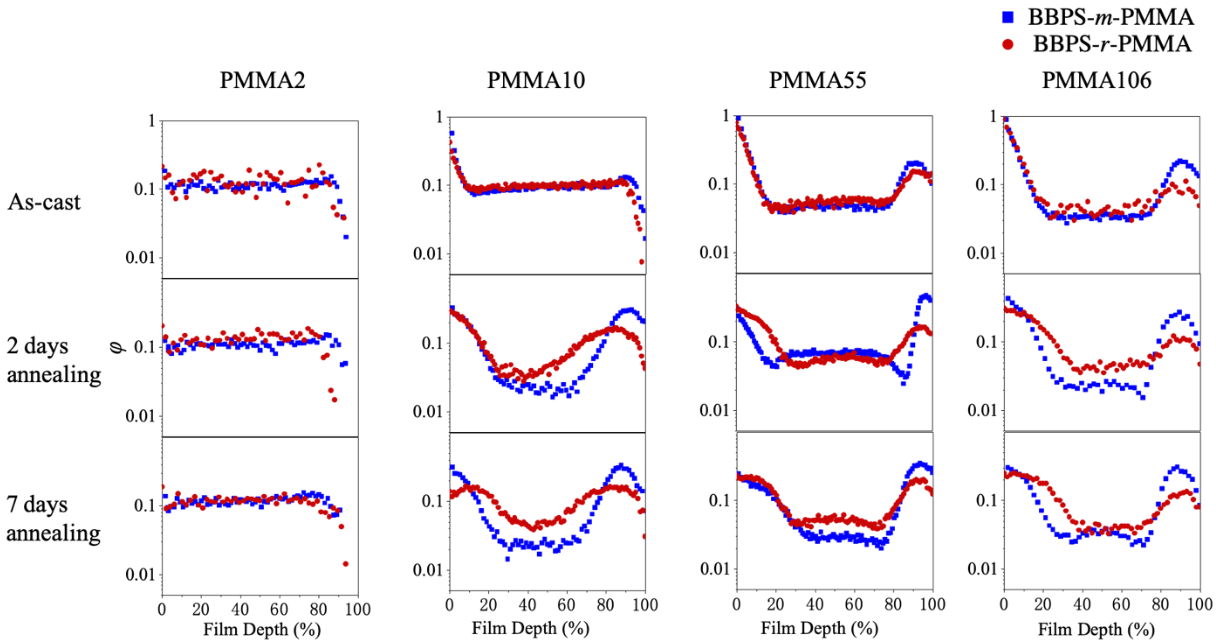


Figure S19. BBPS-*m*-PMMA and BBPS-*r*-PMMA mass composition φ as a function of film depth in blend films with linear PMMA. The polymer−air interface and polymer-substrate interface of the film are at 0 and 100% film depth, respectively.

8. Normalized Substrate Excess $Z_N{*}_{sub}$

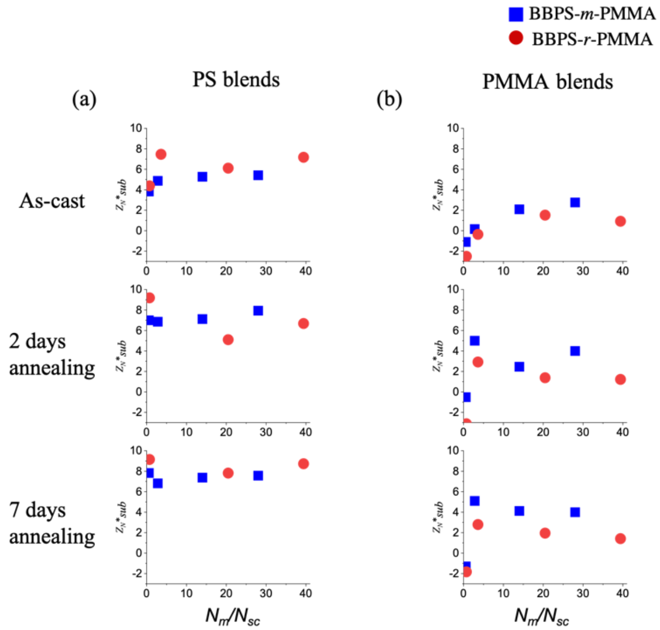


Figure S20. Normalized substrate excess $Z_N{*}_{sub}$ for (a) PS blends and (b) PMMA as a function of N_m/N_{sc} ratio.

9. Normalized Total Excess Z_N*_{tot}

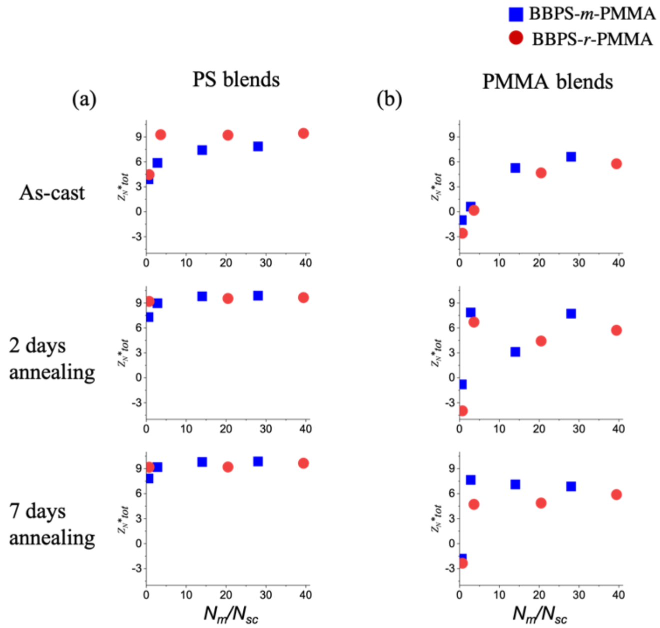


Figure S21. Normalized Total excess Z_N*_{tot} for (a) PS blends and (b) PMMA as a function of N_m/N_{sc} ratio.

10. Additive Concentration at the Middle of the Films φ^0

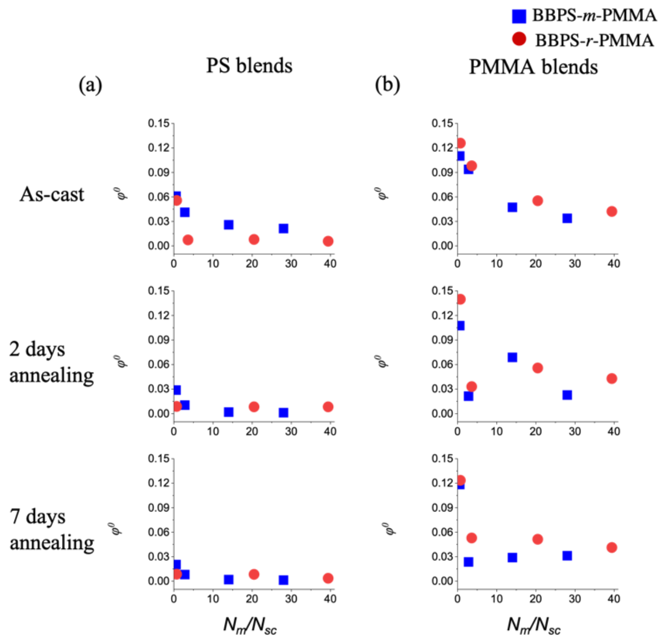
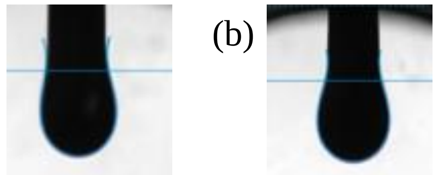


Figure S22. Bottlebrush copolymer composition in the middle of the film φ^0 for (a) PS blends and (b) PMMA as a function of N_m/N_{sc} ratio.

11. Pendant Drop



(a) BBPS-*r*-PMMA 27.05 Nm/m

(b) BBPS-*m*-PMMA 34.14 Nm/m

Figure S23. Pendant drops of melt (a) BBPS-*r*-PMMA and (b) BBPS-*m*-PMMA at 150 °C.

12. Water Contact Angle

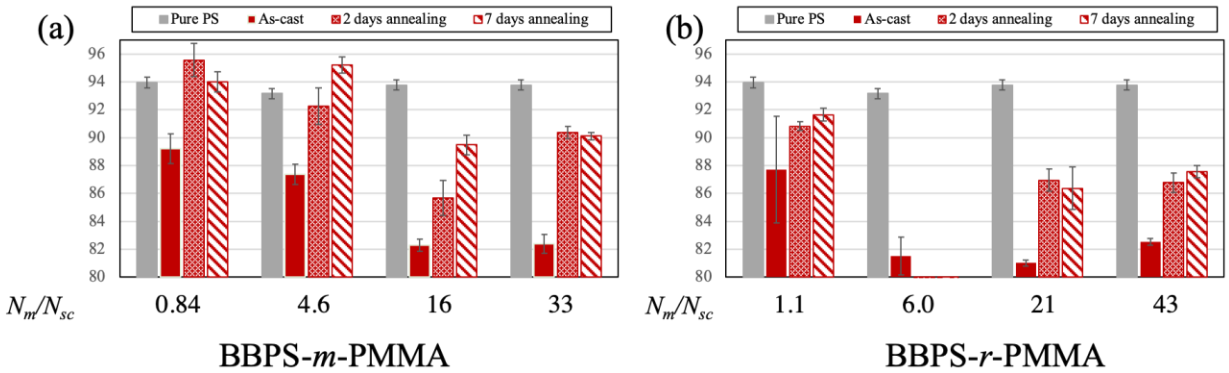


Figure S24. Water contact angle of polymer films, both in the as-cast state and thermally annealed (2 days and 7 days at 150 °C). (a) BBPS-*m*-PMMA and (b) BBPS-*m*-PMMA in linear PS. WCA for pure PS is for measurements of the pure linear homopolymer films without additives.

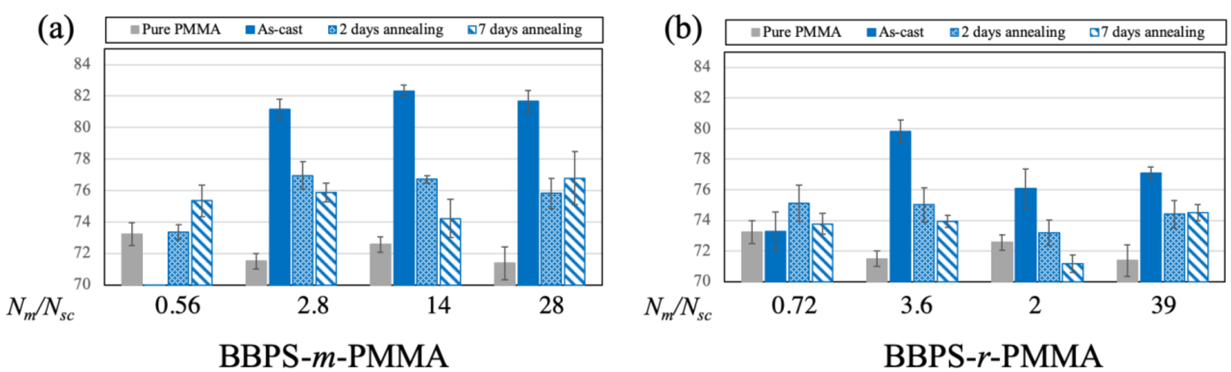


Figure S25. WCA of polymer films, both in the as-cast state and thermally annealed (2 days and 7 days at 150 °C). (a) BBPS-*m*-PMMA and (b) BBPS-*m*-PMMA in linear PMMA. WCA for pure PMMA is for measurements of the pure linear homopolymer films without additives.