Supplementary Information

Observation of Mutual Diffusion of Macromolecules in PS/PMMA Binary Film by Confocal Raman Microscopy

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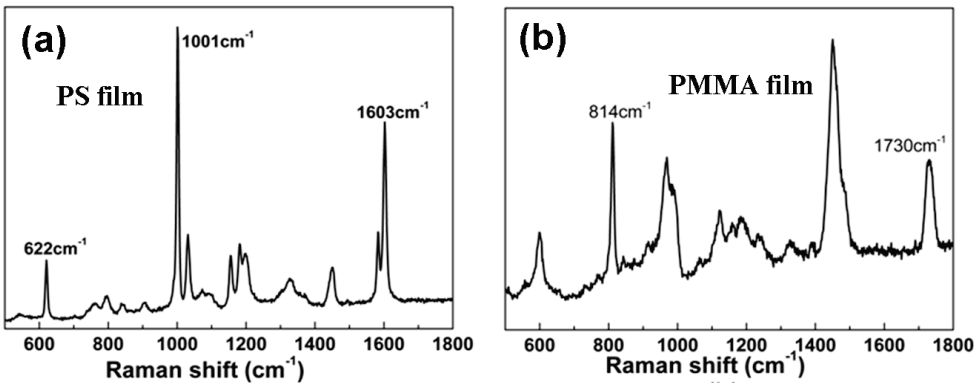

Figure S1 Raman spectra of (a) PS film and (b) PMMA film.

Table S1 Assignments of the Raman vibration spectra of PS and PMMA films

Raman shift (cm^{-1})		Mode	Assignment
PS	622	*d* (C-C)	In-plane ring deformation
	1001	*d* (C-C)+ *d* (CH)	In-plane ring deformation + out-of-plane CH deformation
	1603	ν_a (C-C)	Symmetric stretching vibration of phenyl ring
PMMA	814	ν (C=O)	Stretching vibration of C=O
	1730	ν_a (C-O-C)	Symmetric stretching vibration of C-O-C

ν, stretching (*a*, symmetric; *as*, asymmetric); ρ, rocking; δ, bending; τ, twisting; ω, wagging; *d*, deformation.

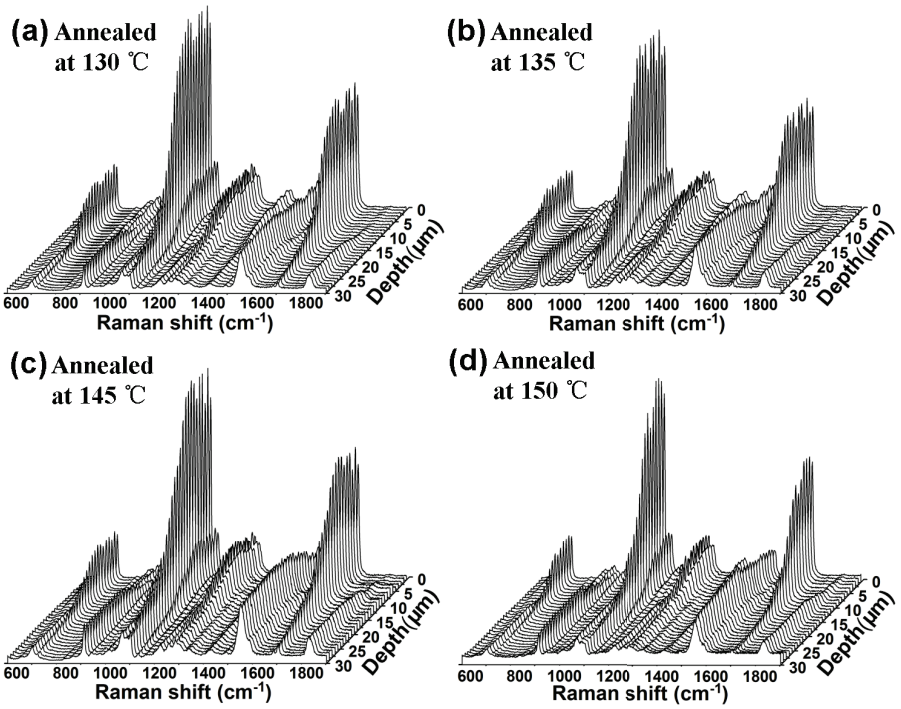

Figure S2 Raman spectra collected at different scanning depths. Annealing temperatures: (a) 130 ^{o}C, (b) 135 ^{o}C, (c) 145 ^{o}C and (d) 150 ^{o}C. The as-prepared PS/PMMA binary film is about 30 μm thick (PS ≈ 15 μm, PMMA ≈ 15 μm).

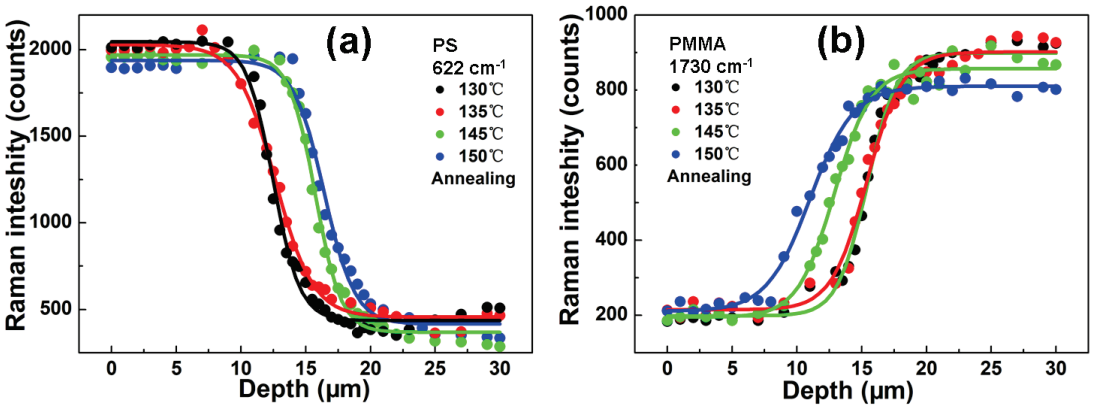

Figure S3 Depth dependence of Raman intensity of annealed PS/PMMA binary film (~30 μm thick) at (a) 622 cm^{-1} and (b) 1730 cm^{-1}.

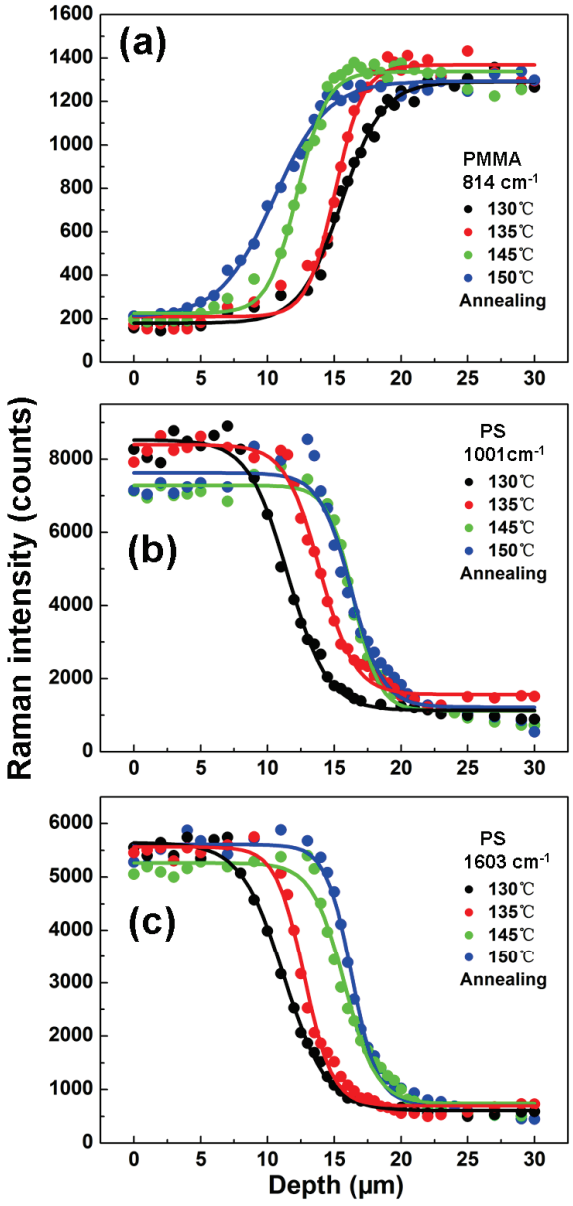

Figure S4 Depth dependence of Raman intensity of annealed PS/PMMA binary film (~30 μm thick) at (a) 814 cm^{-1}, (b) 1001 cm^{-1} and (c) 1603 cm^{-1}.

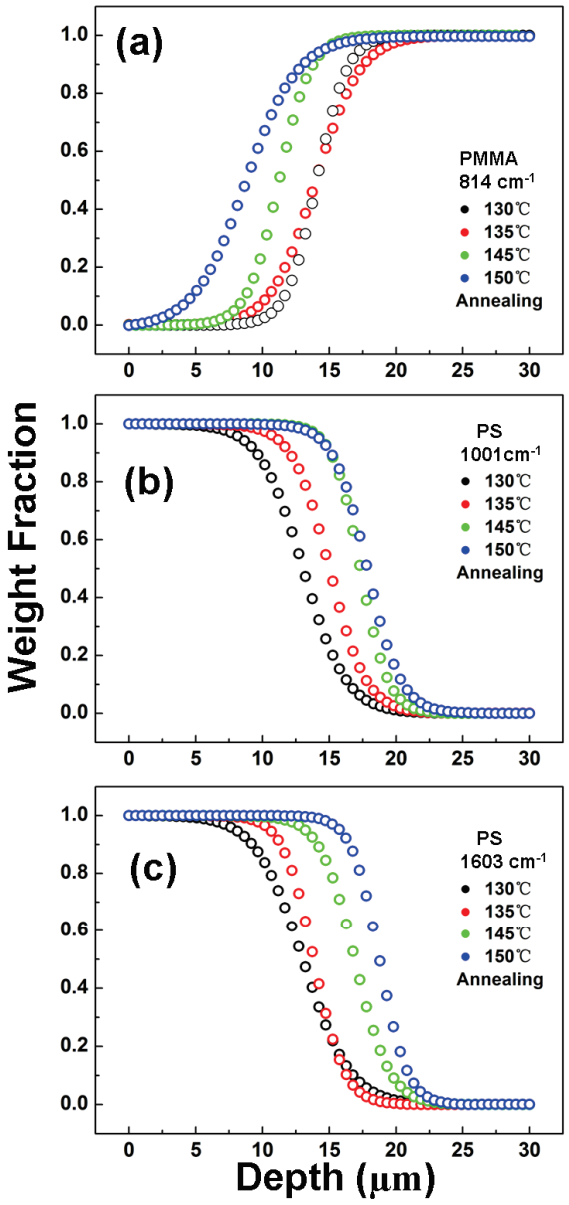

Figure S5 Weight fraction versus scanning depth of (a) PS and (b) PMMA in the annealed PS/PMMA binary film (~ 30 μm thick) at (a) 814 cm^{-1}, (b) 1001 cm^{-1} and (c) 1603 cm^{-1}.

Table S2 Tracer diffusion coefficients, D^*, corresponding to different characteristic Raman shifts estimated from Equation (5)

Annealing temperature (°C)	PS			PMMA	
	622 cm^{-1}	1603 cm^{-1}	1001 cm^{-1}	814 cm^{-1}	1730 cm^{-1}
130	1.27×10^{-14} cm^2s^{-1}	1.22×10^{-14} cm^2s^{-1}	1.34×10^{-14} cm^2s^{-1}	1.92×10^{-13} cm^2s^{-1}	1.97×10^{-13} cm^2s^{-1}
135	1.35×10^{-14} cm^2s^{-1}	1.39×10^{-14} cm^2s^{-1}	1.47×10^{-14} cm^2s^{-1}	2.30×10^{-13} cm^2s^{-1}	2.28×10^{-13} cm^2s^{-1}
145	1.52×10^{-14} cm^2s^{-1}	1.57×10^{-14} cm^2s^{-1}	1.65×10^{-14} cm^2s^{-1}	2.89×10^{-13} cm^2s^{-1}	2.93×10^{-13} cm^2s^{-1}
150	1.70×10^{-14} cm^2s^{-1}	1.79×10^{-14} cm^2s^{-1}	1.81×10^{-14} cm^2s^{-1}	3.15×10^{-13} cm^2s^{-1}	3.12×10^{-13} cm^2s^{-1}

Table S3 Transport coefficients estimated according to "slow" and "fast" theories and mutual diffusion coefficients at different Raman shifts under 130°C annealing.

Raman shift (cm^{-1})	D_T (slow theory)	$\overline{D_T}$ (slow theory)	D_T (fast theory)	$\overline{D_T}$ (fast theory)	D
622	3.16×10^{-11} cm^2s^{-1}	3.22×10^{-11} cm^2s^{-1}	6.97×10^{-11} cm^2s^{-1}	6.98×10^{-11} cm^2s^{-1}	5.34×10^{-13} cm^2s^{-1}
1001	3.19×10^{-11} cm^2s^{-1}		6.85×10^{-11} cm^2s^{-1}		5.22×10^{-13} cm^2s^{-1}
1603	3.30×10^{-11} cm^2s^{-1}		7.13×10^{-11} cm^2s^{-1}		5.48×10^{-13} cm^2s^{-1}