Supplementary Materials for:

Gradient of Segmental Dynamics in Stereoregular Poly(methyl methacrylate) Melts Confined Between Pristine or Oxidized Graphene Sheets

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S1 Force field

The force field parameters for the model graphene-based sheets and for PMMA are provided in Table S1 and Table S2. Both PMMA and graphene force fields exclude non-bonded interactions between the first and second chemically bonded neighbors. The Lorentz–Berthelot combination rule was used for calculating the Van der Waals interactions between dissimilar atoms (including interactions between PMMA and the model graphene-based nanosheets). More details about the force fields and their references are provided in the main text.

Table S1: Force field parameters for pristine and oxidized graphene sheets.

non-bonded, $U_{\mathrm{LJ}}(r) = 4\varepsilon[(\frac{\sigma}{r})^{12} - (\frac{\sigma}{r})^{6}]$ + Coulomb	mass (g mol^{-1})	σ (nm)	ε (kJ mol^{-1})	q(e)
CGR	12.011	0.3470	0.2750	0
CEP	12.011	0.3473	0.3979	0.2
COH	12.011	0.3473	0.3979	0.265
OE	15.9994	0.3033	0.4004088	−0.4
OH	15.9994	0.3033	0.4004088	−0.683
H	1.008	0.2846	0.063597	0.418

bond stretching, Morse $U_{\mathrm{bond}} = D[1 - \exp(\beta(r - b_0))]^2$	b_0 (nm)	D (kJ mol^{-1})	β (nm^{-1})
CGR-CGR	0.1418	478.9	21.867

bond stretching, Harmonic $U_{\mathrm{bond}} = \frac{1}{2}k_{\mathrm{bond}}(r - b_0)^2$	b_0 (nm)	k_{bond} (kJ mol^{-1} nm^{-2})
CEP-CEP	0.153	292880.0
CEP-CGR	0.146	292880.0
CEP-COH	0.153	292880.0
CEP-OE	0.142	292880.0
CGR-COH	0.146	292880.0
COH-COH	0.153	292880.0
COH-OH	0.142	292880.0
H-OH	0.098	292880.0

angle bending, $U_{\mathrm{angle}} = \frac{1}{2}k_{\mathrm{angle}}(\cos\theta - \cos\theta_0)^2$	θ_0 (deg)	k_{angle} (kJ mol^{-1})
CGR-CGR-CGR	120	562.2
-CGR-[a]	120	557.9
-CEP-	109.471	470.7
-COH-	109.471	470.7
CEP-OE-CEP	104.51	446.4
COH-OH-H	104.51	446.4

dihedral angle potential, $U(\phi) = k(1 + \cos(n\phi - \phi_0))$	ϕ_0 (deg)	k (kJ mol^{-1})	n
-CGR-CGR-	180	12.56	2
-CEP-CEP-	0	0.465	3
-CEP-CGR-	180	0.349	6
-CEP-COH-	0	0.465	3
-CEP-OE-	0	1.39	3
-CGR-COH-	180	0.349	6
-COH-COH-	0	0.465	3
-COH-OH-	0	1.395	3

CGR: graphene sp^2 carbon atom. CEP: epoxide-group carbon atom. COH: hydroxyl-group carbon atom. OE: epoxide-group oxygen atom. OH: hydroxyl-group oxygen atom. H: hydroxyl-group hydrogen atom.
[a]: except CGR-CGR-CGR

Table S2: Force field parameters for PMMA.

non-bonded, $U_{\mathrm{LJ}}(r) = 4\varepsilon[(\frac{\sigma}{r})^{12} - (\frac{\sigma}{r})^{6}]$ + Coulomb	mass (g mol^{-1})	σ (nm)	ε (kJ mol^{-1})	q(e)
CX (-CH_3 and -CH_2-)	12.011	0.339967	0.457730	0.0051
CX (α carbon)	12.011	0.339967	0.457730	0.0189
CX (ester-methyl)	12.011	0.339967	0.457730	0.2801
HC	1.008	0.2649533	0.065689	0
C	12.011	0.339967	0.359824	0.7464
O	15.9994	0.2959922	0.878640	−0.5939
OS	15.999	0.3000012	0.711280	−0.4617
H1	1.008	0.2471353	0.065689	0

bond stretching, $U_{\mathrm{bond}} = \frac{1}{2}k_{\mathrm{bond}}(r - r_0)^2$	r_0 (nm)	k_{bond} (kJ mol^{-1} nm^{-2})
CX-CX	0.152	259408.0
HC-CX	0.1095	301248.0
CX-C	0.15	276144.0
C-O	0.1204	835963.2
C-OS	0.1343	344175.9
OS-CX	0.141	267776.0
CX-H1	0.1092	343088.0

angle bending, $U_{\mathrm{angle}} = \frac{1}{2}k_{\mathrm{angle}}(\theta - \theta_0)^2$	θ_0 (deg)	k_{angle} (kJ mol^{-1} rad^{-2})
HC-CX-HC	109.5	334.7
HC-CX-CX	112.6	376.6
CX-CX-CX	113.5	376.6
CX-CX-C	111.5	334.7
CX-C-O	125.4	493.7
CX-C-OS	111.0	418.4
C-OS-CX	114.0	423.4
O-C-OS	122.5	861.9
OS-CX-H1	110.0	502.1
H1-CX-H1	109.5	376.6

dihedral angle potential, $U(\phi) = \sum_{n=1}^{3} k_n(1 + \cos n\phi)$

	k_1 (kJ mol^{-1})	k_2	k_3
CX-CX-CX-CX	1.8828	0	0
CX-CX-CX-HC	0	0	0.4184
CX-CX-CX-C	0	0	0
HC-CX-CX-C	0	0	−0.12552
CX-CX-C-O	0	−1.7154	−1.2134
CX-CX-C-OS	0	−1.8828	−1.3807
O-C-OS-CX	0	−17.61464	−3.05432
H1-CX-OS-C	0	0	0.6276
CX-C-OS-CX	−2.7196	−11.506	0

CX: sp^3 carbon atom. HC: hydrogen (except ester group hydrogen). C: sp^2 carbon atom.
O: carbonyl-group oxygen. OS: ester-group oxygen. H1: ester-side-group hydrogen.

S2 Layer resolved TACF curves

The layer resolved torsional autocorrelation function (TACF) curves of the confined i-PMMA systems at $T = 550$ K are provided in Figure S1 and the curves for some of the model confined s-PMMA systems are provided in Figure S1.

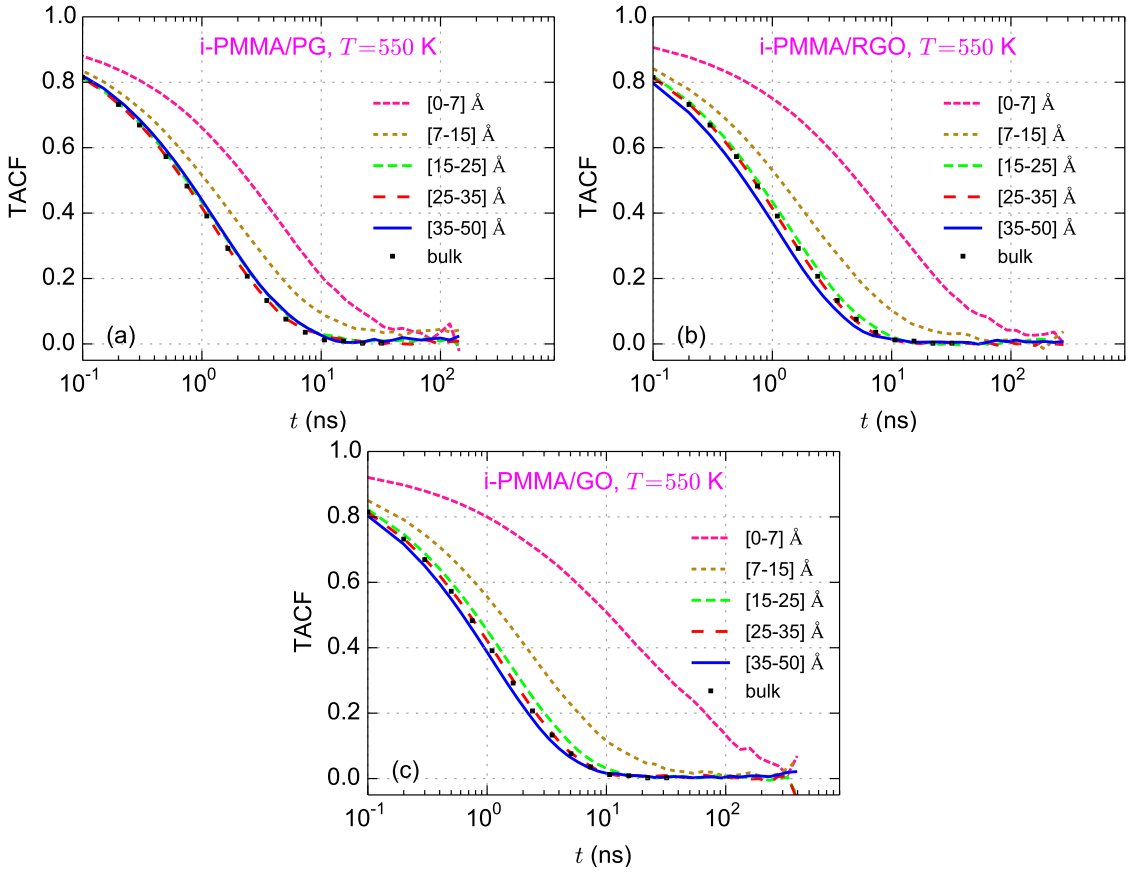

Figure S1: Layer resolved torsional autocorrelation function (TACF) curves for (a) i-PMMA/PG, (b) i-PMMA/RGO, and (c) i-PMMA/GO at $T = 550$ K.

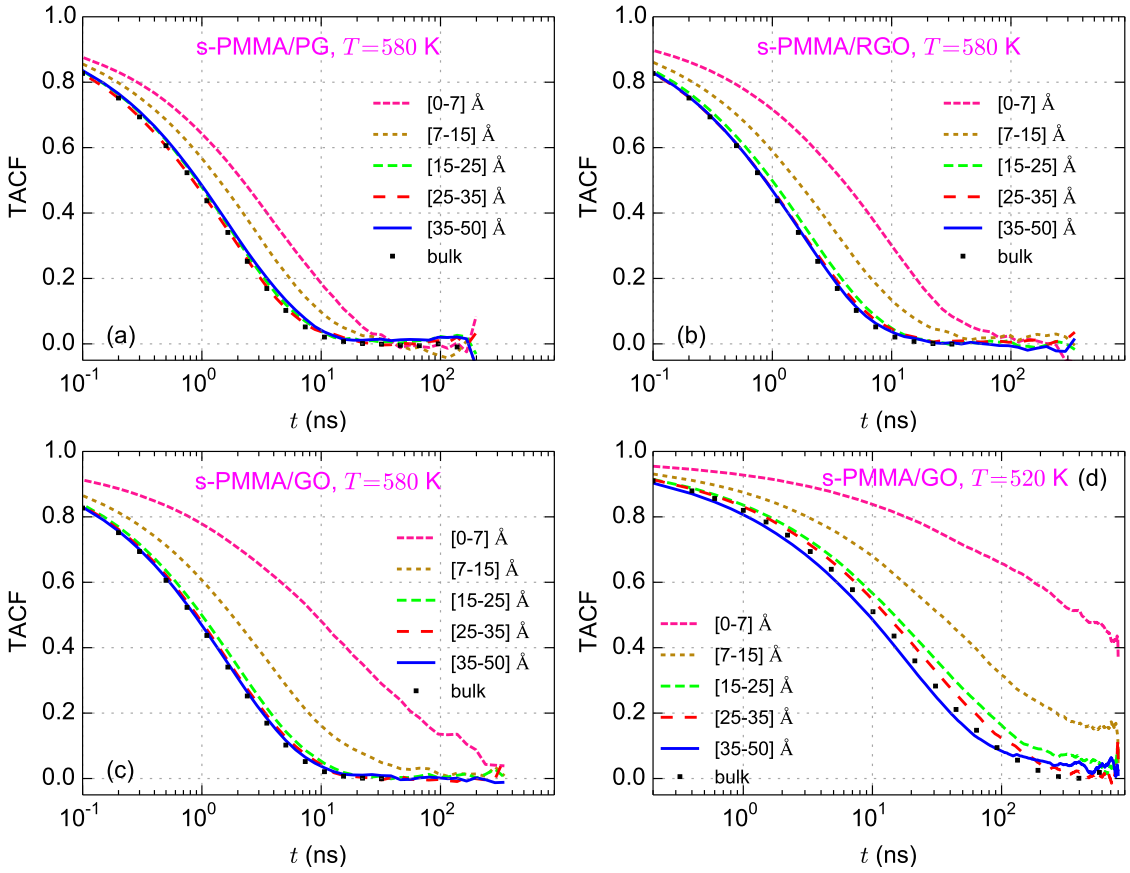

Figure S2: Layer resolved torsional autocorrelation function (TACF) curves for (a) s-PMMA/PG, (b) s-PMMA/RGO, (c) s-PMMA/GO at $T = 580$ K, and (d) s-PMMA/GO at $T = 520$ K.

S3 Relaxation times of the confined s-PMMA systems

The layer resolved relaxation times of the s-PMMA/PG, s-PMMA/RGO. and s-PMMA/GO systems at different temperatures are provided in Figure S3. The relaxation times are normalized with the respective bulk values.

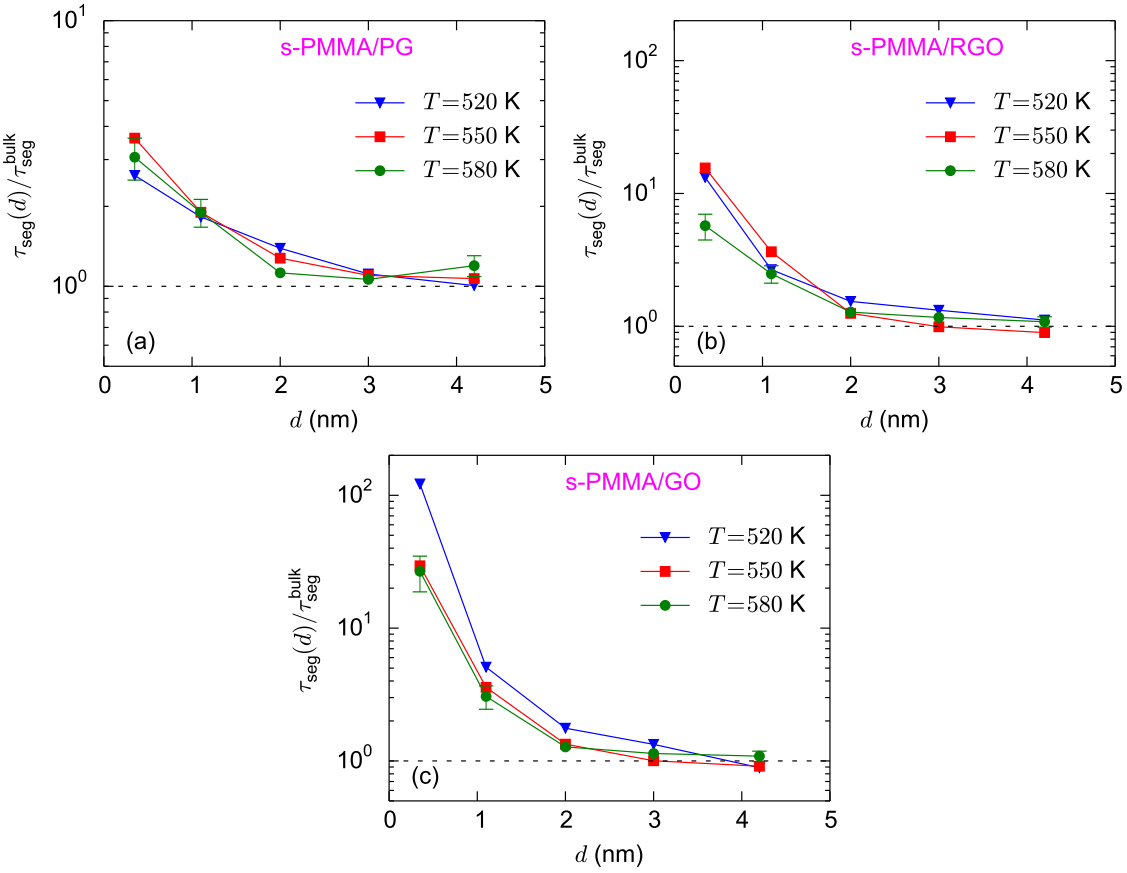

Figure S3: (a), (b), and (c) show the layer resolved values of the normalized relaxation times ($\frac{\tau_{seg}(d)}{\tau_{seg}^{bulk}}$) for the s-PMMA/PG, s-PMMA/RGO, and s-PMMA/GO interfacial systems, at different temperatures, respectively. The error bars at $T = 580$ K have been estimated based on block averaging; at lower temperatures larger error bars are expected.