

Supplementary Material

Correlating Fragility and Heterogeneous Dynamics in Polystyrene through Single Molecule Studies

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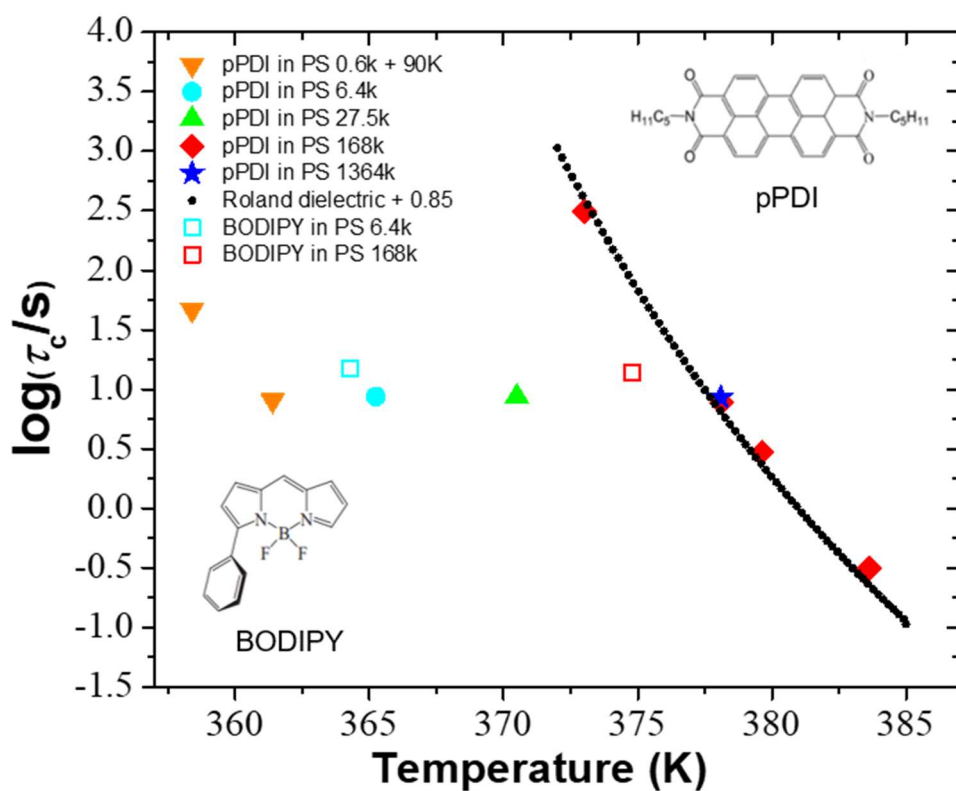


Figure S1. Temperature dependence of median τ_c values of pPDI and of BODIPY268 as a function of temperature and polystyrene molecular weight. Measurements in 0.6 kg mol⁻¹ polystyrene are plotted 100K higher than the actual measured temperature. Data collected in 168 kg mol⁻¹ polystyrene with pPDI are compared to the VFT fit of the temperature dependence reported by Roland and co-workers from dielectric spectroscopy measurements and shifted by 0.85 decades. Structures of pPDI and BODIPY are also shown.

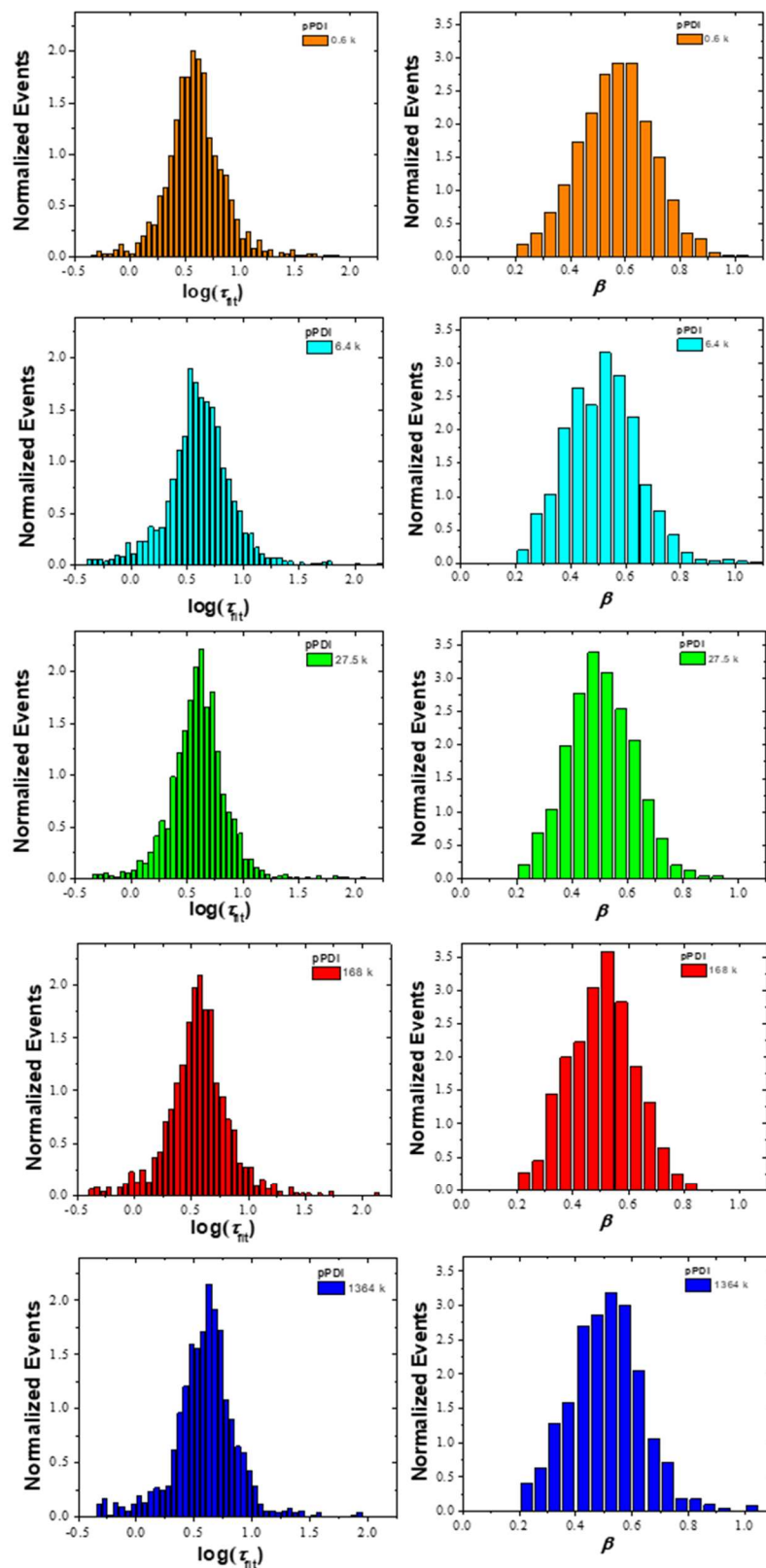


Figure S2. Single sets of τ_{fit} and β distributions of pPDI in all molecular weights of polystyrene for the longest trajectory length measurements as also presented overlaid in Fig. 2 of the main text.

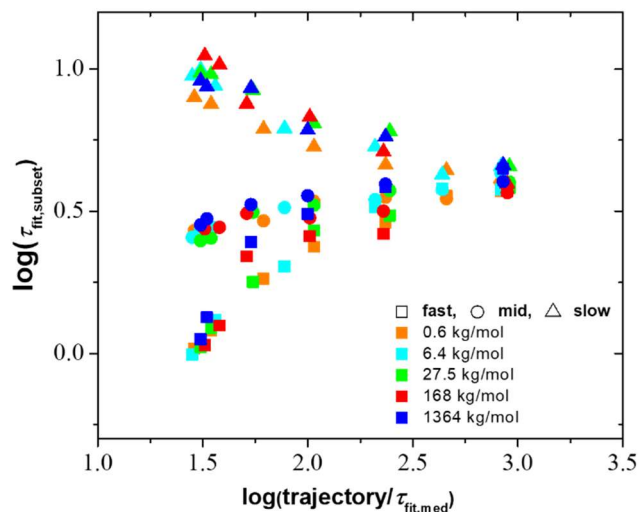


Figure S3. Median τ_{fit} values as a function of trajectory length for the 20% initially fastest (squares), initially slowest (triangles), and initially average (circles) molecule sub-ensembles of pPDI in polystyrene at each molecular weight. Data collected in polystyrene of each molecular weight were stratified into five sub-ensembles based on their τ_{fit} values at the shortest trajectory length considered. The same molecules were then analyzed at increasing trajectory length to characterize their dynamical evolution. We note that this analysis is distinct from that depicted in Fig. 3 in the main text, as here particular molecules are tracked as a function of observation time while in the other analysis all molecules are included. No systematic difference in evolution of the slow or fast sub-ensembles as a function of polystyrene molecular weight is evident.

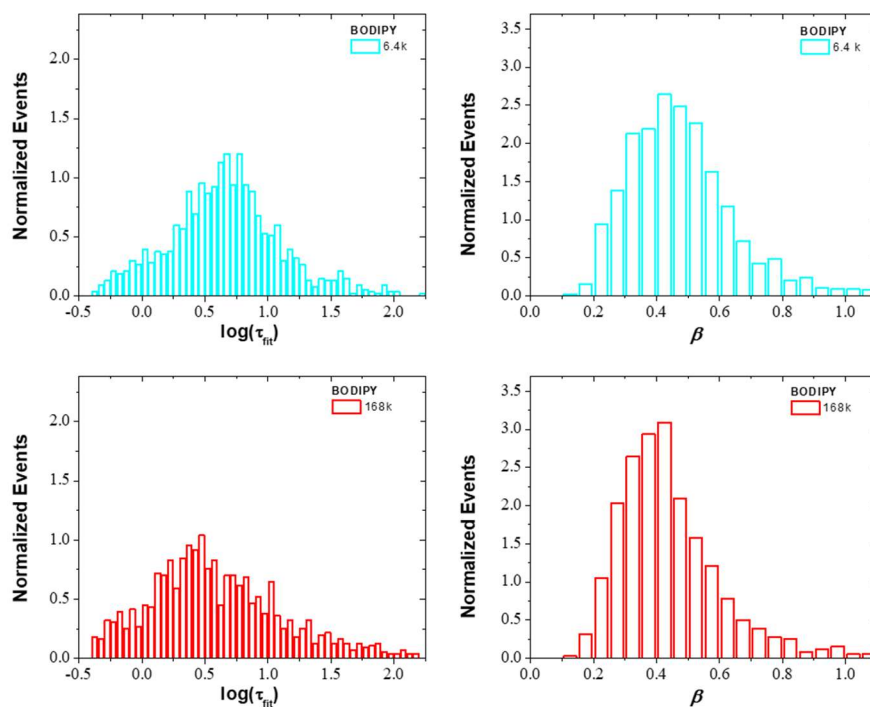


Figure S4. Single sets of τ_{fit} and β distributions of BODIPY268 in 6.4 and 168.0 kg mol⁻¹ polystyrene for the longest trajectory length measurements and as presented overlaid in Fig. 4 of the main text.

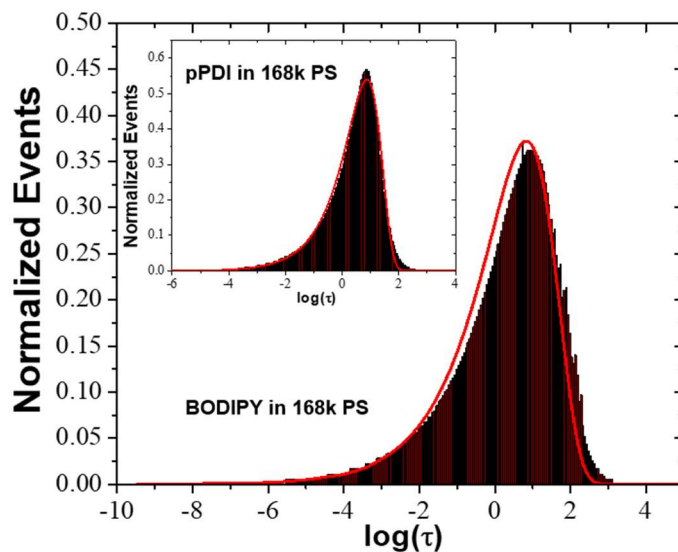


Figure S5. ILT-built distributions (columns) of 168 kg mol⁻¹ polystyrene as measured through BODIPY268 and (inset) pPDI and compared to that predicted from the ILT transform of the ACFs_{QE} (lines).

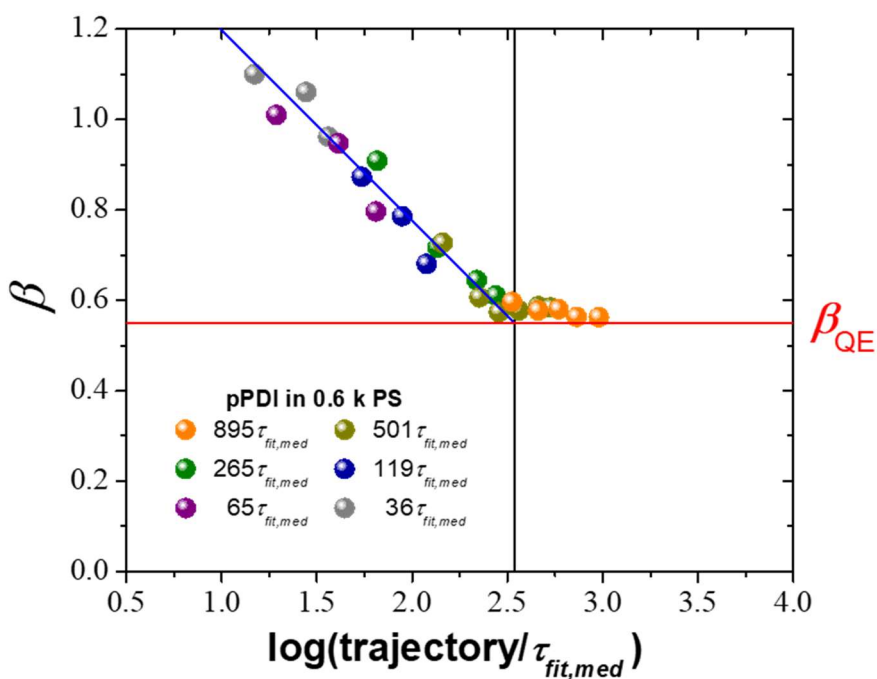


Figure S6. Median β for pPDI in 0.6 kg mol⁻¹ polystyrene as a function of trajectory length for subsets of data of particular trajectory lengths. Characteristics of fits are given in Table S3, and vertical line is drawn at the crossover time.

Molecular Weights (kg mol⁻¹)	0.6	6.4	27.5	168.0	1364.0
temperature (K)	271.4	365.3	370.5	378.1	378.1
number of molecules	1362	1657	1467	1047	1046
median τ_c (s)	7.0	8.7	8.7	7.7	8.3
median τ_{fit} (s)	3.9	4.0	4.0	3.7	4.1
median β	0.57	0.51	0.50	0.51	0.51
β_{QE}	0.55	0.50	0.48	0.49	0.49
median trajectory ($\tau_{fit,med}$)	841	839	923	901	842
median frame rate (frames/τ_{fit})	19.3	19.9	20.2	18.3	20.4
fwhm (τ_c distribution)	0.50	0.51	0.49	0.49	0.43
fwhm (τ_{fit} distribution)	0.47	0.50	0.46	0.43	0.45
fwhm (β distribution)	0.31	0.32	0.29	0.32	0.30

Table S1. Characteristics of data obtained from the longest trajectory pPDI measurements in polystyrene and presented graphically in Figure 2.

Molecular Weights (kg mol⁻¹)	6.4	168
temperature (K)	364.3	374.8
number of molecules	1699	1406
median τ_c (s)	14.9	13.9
median τ_{fit} (s)	4.50	3.30
median β	0.46	0.41
β_{QE}	0.42	0.38
median trajectory ($\tau_{fit,med}$)	747	1007
median frame rate (frames/τ_{fit})	22.7	16.5
fwhm (τ_c distribution)	0.78	0.91
fwhm (τ_{fit} distribution)	0.79	0.99
fwhm (β distribution)	0.34	0.30

Table S2. Characteristics of data obtained from the longest trajectory BODIPY268 measurements in polystyrene and presented graphically in Figure 4.

probe	pPDI			BODIPY		
polystyrene (kg mol ⁻¹)	slope	crossover time	β_{QE}	slope	crossover time	β_{QE}
0.6	-0.42 ± 0.02	2.54 ± 0.03	0.55	-	-	-
6.4	-0.41 ± 0.03	2.59 ± 0.04	0.50	-0.44 ± 0.04	2.52 ± 0.06	0.42
168.0	-0.38 ± 0.03	2.64 ± 0.05	0.49	-0.43 ± 0.02	2.63 ± 0.04	0.38

Table S3. Characteristics of decay of median β as a function of trajectory length as shown graphically in Fig. 6 and Fig. S6 and as discussed in the main text. Slope and crossover times are reported with standard error.