Supporting Information

Molecular Simulation of Tracer and Self-Diffusion in Entangled Polymers

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1 Summary of Systems Investigated

The systems investigated in this paper are tabulated.

MD	BFM	SS
50×500	100×1080	5×20
100×500	200×540	10×20
200×250	225×480	20×20
	250×432	35×20
		50×20
		100×20
		150×20

Table 1: **Monodisperse Melts for Self-Diffusion Studies**: Systems ($N \times n$), where $N = N_p = N_m$ is the number of beads per chain, and n is the total number of chains in the ensemble.

$N_p \times n_p$	$N_m \times n_m$	BB	CM
75 × 49	30 × 1111	x	x
75 × 49	75 × 444		x
75 × 49	150 × 222	x	x
75 × 49	225 × 148	x	x
75 × 144	300 × 324	x	x
100 × 108	100 × 972		x
150 × 52	10 × 7085	x	
150 × 52	30 × 2361	x	
150 × 52	75 × 944	x	x
150 × 72	150 × 648		x
150 × 72	300 × 324	x	x
200 × 54	200 × 486		x
225 × 48	300 × 324	x	x
250 × 43	250 × 388		x
100 × 108	300 × 324		x
200 × 54	300 × 324		x
250 × 52	300 × 393		x

Table 2: **BFM Simulations of Binary Blends, and Clamped Matrix Chains**: Systems used to study probe and tracer diffusion with monomer number fraction of the probe $f_p = n_p N_p/(n_p N_p + n_m N_m) = 0.10$. The first two columns show the length and number of the probe and matrix chains, respectively. An "x" in the third or last columns indicates a simulation of binary blends with CR or with clamped matrix chains, respectively.

MD binary blends		SS binary blends		SS no-CR
$N_p \times n_p$	$N_m \times n_m$	$N_p \times n_p$	$N_m \times n_m$	$N_p \times n_p$
50×300	1000×85	5×60	100×17	5×60
100×150	1000×85	10×30	100×17	10×30
200×75	1000×85	20×15	100×17	20×15
		35×12	100×34	35×12
		50×12	100×34	50×12
				100×17

Table 3: **MD and Slip Spring Simulations**: Systems ($N \times n$), where N is chain length and n is the number of chains. The subscripts "p" and "m" indicate "probe" and "matrix chains", respectively. The last column corresponds to SS simulations in which CR is switched off.

2 Tabulated Self and Tracer Diffusion Data

Tables 4-7 summarize the diffusion coefficients obtained from the BFM, MD, and SS models. A brief description of simulation and parameter settings are provided in the captions to the tables. The number of beads and the diffusion coefficients obtained from the SS simulations are rescaled and expressed in terms of MD units.

N	n	D_s ($\times 10^{-6}$)	Ref. Num.
30	3240	245 ± 3	4
32	125	257	3
40	100	175	3
50	80	115	3
75	1296	51.6 ± 1	4
80	50	41.8	3
100	1080	29.4 ± 0.4	this work
150	648	11.2 ± 0.4	4
160	25	9.62	3
200	540	5.9 ± 0.2	this work
225	480	4.4 ± 0.1	this work
250	432	3.3 ± 0.1	this work
300	45	2.71	3
300	360	2.15 ± 0.23	2
315	908	1.84 ± 0.07	1

Table 4: **BFM Monodisperse**: Systems with $N = N_m = N_p$ simulated here, and in the literature as indicated by the reference number (as listed at the end of SI) in the last column. n is the number of chains used in the simulation.

N_p	N_m	D ($\times 10^{-6}$)	$\hat{D}$ ($\times 10^{-6}$)
75	30	91.9 ± 1.5	33.8 ± 2.8
75	75	51.6 ± 1.0	28.8 ± 1.9
75	150	39.1 ± 1.3	29.5 ± 2.2
75	225	31.1 ± 1.6	28.3 ± 2.3
75	300	36.2 ± 2.5	29.5 ± 0.9
100	100		15.1 ± 0.7
150	10	57.2 ± 0.3	
150	30	37.9 ± 0.5	
150	75	23.4 ± 0.5	6.5 ± 0.6
150	150	11.2 ± 0.4	6.2 ± 0.4
150	300	8.0 ± 0.2	6.9 ± 0.3
200	200		3.0 ± 0.2
225	225		2.3 ± 0.2
225	300	3.3 ± 0.1	2.4 ± 0.1
250	250		1.9 ± 0.2
300	10	25.1 ± 0.5	
300	30	16.0 ± 0.2	
300	75	8.3 ± 0.2	
300	150	4.4 ± 0.3	
300	300	2.2 ± 0.2	1.4 ± 0.1
100	300		15.6 ± 0.7
200	300		3.7 ± 0.3
250	300		1.9 ± 0.2

Table 5: **BFM Blends**: Systems used to study probe and tracer diffusion with $\phi_p = 0.05$. The last column shows results from clamped matrix simulations, which is used to estimate D_∞. The $N_p = 300$ probe diffusion diffusivities were previously reported in ref. 4.

N_p	D_s ($\times 10^{-4}$)	$D_p \times 10^{-4}$
5	149.9 ± 7.4	
10	72.6 ± 3.6	
25	24.9 ± 1.3	
50	10.2 ± 0.5	7.1 ± 0.4
100	3.6 ± 0.2	2.0 ± 0.2
200	0.9 ± 0.1	0.6 ± 0.1

Table 6: **MD Simulations**: Self and probe diffusion coefficients of probe chains, D_s and $D_p(N_p, N_m = 1000)$, obtained from MD simulations. D_s is calculated by averaging over all chains in the monodisperse melt, while D_p is obtained from the 15% probe chains blended in long chain matrices of chain length $N_m = 1000$.

N_p	D_s ($\times 10^{-6}$)	$D_p \times 10^{-6}$	$\tilde{D} \times 10^{-6}$
50	9480.0 ± 300.0	7650.0 ± 300.0	7590.0 ± 300.0
100	3490.0 ± 100.0	2410.0 ± 100.0	2310.0 ± 100.0
200	810.4 ± 21.0	524.0 ± 12.0	459.0 ± 13.0
350	187.6 ± 7.0	133.0 ± 5.0	113.0 ± 5.0
500	71.1 ± 3.1	56.9 ± 2.8	48.8 ± 3.0
1000	12.1 ± 0.6	12.1 ± 1.1	9.7 ± 1.1
1500	4.5 ± 0.4		4.2 ± 0.8

Table 7: **SS Simulations**: Diffusion coefficients of probe chains in monodisperse melts, D_s, binary blends consisting of 15% probe chains in a matrix of long chains, D_p, and in permanent networks in which CR is switched off, $\tilde{D}$, obtained from single-chain slip-spring model simulations. The numbers of beads, length and time scales have all been mapped to those used in the MD simulations. The matrix chain length in the binary blends is mapped to $N_m = 1000$ of the flexible KG bead-spring chains.

3 Comparison with MCSS and PCN Simulations

In figure 1, we overlay the MCSS (multichain slip spring) and PCN (primitive chain network) calculations of Masubuchi and Uneyama on Figure 4 from the paper.[5] As seen from the plot, the range of the SS simulations performed in this work is similar to the MCSS calculations (dashed red lines), and the agreement between these two sets of calculations is excellent within reported error bars. The PCN series lies slightly above the SS and MCSS simulations, and perhaps shows some early signs of transitioning to a pure reptation ($D_s \sim Z^{-2}$) regime.

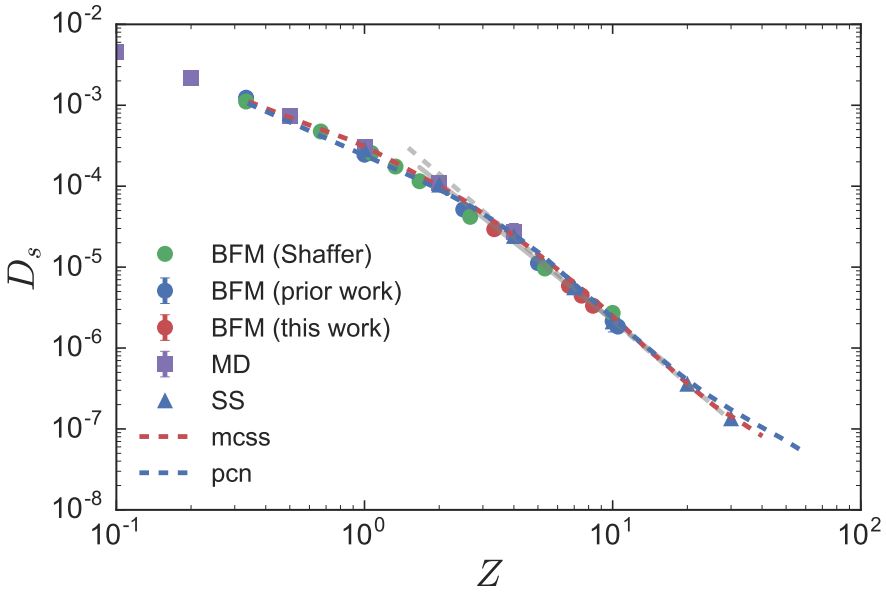

Figure 1: Figure 4 from the manuscript overlaid with data from Masubuchi's MCSS (dashed red) and PCN (dashed blue) simulations.

4 Tracer Diffusivity from Clamped Matrix Simulations

In the BFM simulations, we estimate tracer diffusivity using $D_\infty(N_p) \approx \langle \hat{D}(N_p) \rangle$. The validity of this assumption hinges on the independence of $\hat{D}$ and matrix molar mass. We tested this insensitivity by performing a suite of CM simulations (results are shown in tables 4 and 5) at different values of N_p and N_m. For example, at N_p = 75, we performed five different simulations at N_m = 30, 75, 150, 225, and 300. The average across these five simulations, $\langle \hat{D} \rangle = 2.90 \pm 0.20 \times 10^{-5}$, was used to normalize $\hat{D}(N_p = 75, N_m)$. Similar calculations were performed for all the different probes. Figure 2 plots the normalized CM probe diffusivity for all the samples studied with CM simulations. Normalization by $\langle \hat{D} \rangle$ enables us to plot data at different N_p on the same plot. The data are clustered around the expected value of unity over the entire range of molecular weights studied. It demonstrates that $\hat{D}(N_p, N_m)$ is insensitive to N_m over the range of molecular weights studied here. This generality gives us the confidence to extrapolate $\hat{D}$ to the $N_m \gg N_p$ regime, and hence to estimate D_∞.

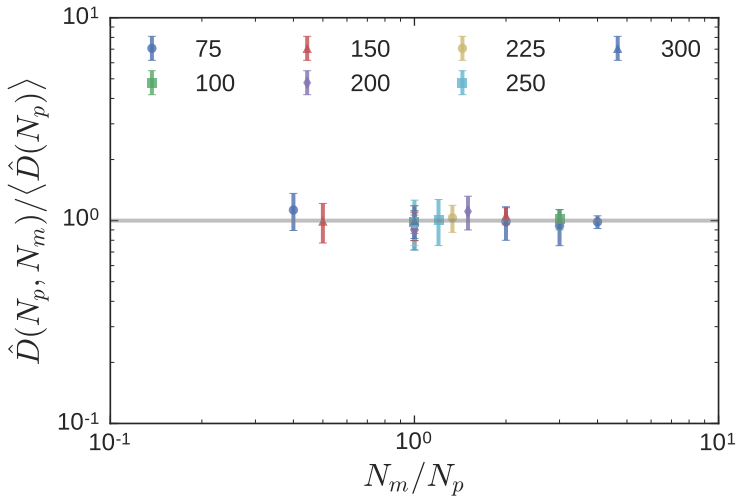

Figure 2: Normalized probe diffusivity from CM simulations for N_p between 75 and 300, and range of N_m as shown in table 5. The value of the probe diffusivity $\hat{D}(N_p, N_m)$ at a particular N_p is normalized by the averaging over different N_m simulated $\langle \hat{D}(N_p) \rangle$. It shows that probe diffusivity from CM simulations is insensitive to N_m.

References

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