Supplementary Information: A Monte Carlo Simulation of Tracer Diffusion in Amorphous Polymers

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Part I: Tracer Diffusivities of IMC and DLM for Different Decoupling Scenarios

Figs. S1 and S2 present, respectively, tracer diffusivities of IMC and DLM in the polymers of this study under the three scenarios corresponding to waiting time–rotational time relation: 1) volume-based interpretation of decoupling $\xi = \tilde{V}_D/(\tilde{V}_D + \tilde{V}_{0,P})$, 2) decoupling related to the stretching exponent of rotational correlation function $\xi = \beta_{KWW}$, and 3) the fragility-dependent interpretation $\xi = 1.1 - 0.005m$. In all cases, the volume-based interpretation delivers the strongest temperature dependence and the smallest diffusivities.

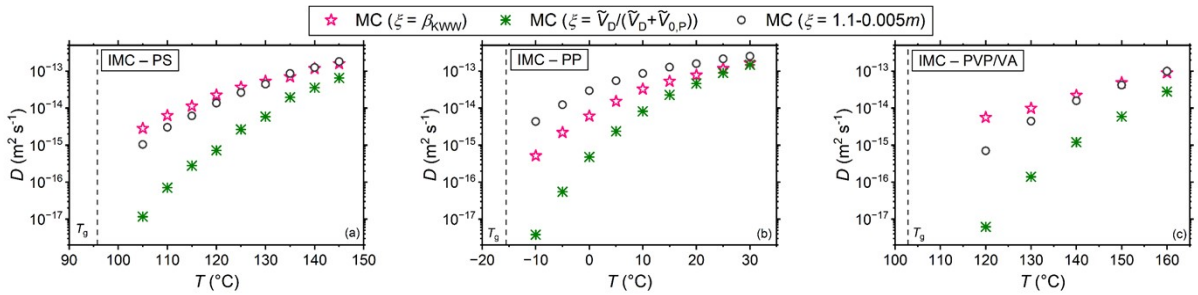

Fig. S1 Tracer diffusivities of IMC in (a) PS, (b) PP, and (c) PVP/VA.

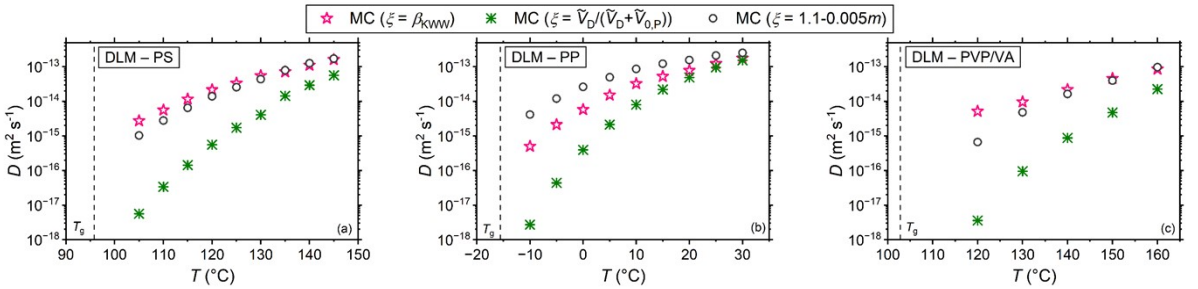

Fig. S2 Tracer diffusivities of DLM in (a) PS, (b) PP, and (c) PVP/VA.

Part II: Values of the Decoupling Exponent ξ

The estimated ξ values used in this study are summarized in Table S1. The volume-based correlation treats ξ as a binary parameter, whereas the other two approaches consider ξ at infinite dilution to be a pure polymer property.

Table S1 Values of ξ used for the tracer diffusivity simulations of this work.

	adjusted ξ [a]	$\xi = \tilde{V}_D/(\tilde{V}_D + \tilde{V}_P)$	$\xi = 1.1 - 0.005m$ [b]	$\xi = \beta_{KWW}$ [a]
TET–PS	0.305 to 0.630	0.642		
BPEA–PS	0.755 to 0.820	0.764		
TTI–PS	0.500 to 0.782	0.678		
RUB–PS	0.991 to 1.229	0.814	0.434	0.368 to 0.472 [c]
IMI–PS		0.642		
DLM–PS		0.770		
IMC–PS		0.724		
IMI–PP		0.815		
DLM–PP		0.892	0.336	0.500 to 0.731 [d]
IMC–PP		0.866		
IMI–PVP/VA		0.692		
DLM–PVP/VA		0.808	0.470	0.333 to 0.500 [e]
IMC–PVP/VA		0.767		

[a] Because ξ becomes temperature-dependent a range is reported.
[b] The fragility indices m can be found in a previous work.[1]
[c] For detailed values see Table S2
[d] For detailed values see Table S3
[e] For detailed values see Table S4

Part III: Parameters of the Stretched Exponential Functions

Tables S2 to S4 list τ_{KWW} and β_{KWW} obtained from dielectric spectra,[1–3] for PP, PS, and PVP/VA, respectively. These were used to obtain the waiting time distributions according to eqn (8) of the main manuscript.

Table S2 Stretched exponential parameters of PS.

T (K)	τ_{KWW} (s)	β_{KWW} (–)
378	2.99×10^{-1}	0.3679
383	2.80×10^{-2}	0.3799
388	4.05×10^{-3}	0.3843
393	8.26×10^{-4}	0.3850
398	2.01×10^{-4}	0.4010
403	6.19×10^{-5}	0.3980
408	1.67×10^{-5}	0.4622
413	6.55×10^{-6}	0.4624
418	3.04×10^{-6}	0.4724

Table S3 Stretched exponential parameters of PP.

T (K)	τ_{KWW} (s)	β_{KWW} (–)
263	9.90×10^{-2}	0.5001
268	4.64×10^{-3}	0.5134
273	4.35×10^{-4}	0.5402
278	7.03×10^{-5}	0.5585
283	1.63×10^{-5}	0.5770
288	5.83×10^{-6}	0.6228
293	2.65×10^{-6}	0.6768
298	1.29×10^{-6}	0.6919
303	7.73×10^{-7}	0.7308

Table S4 Stretched exponential parameters of PVP/VA.

T (K)	τ_{KWW} (s)	β_{KWW} (–)
393	1.72×10^{-1}	0.3332
403	5.06×10^{-3}	0.3931
413	3.56×10^{-4}	0.4277
423	4.91×10^{-5}	0.4501
433	8.35×10^{-6}	0.4999

Part IV: Lennard–Jones Diameters

The Lennard–Jones diameters σ of the species used for obtaining jump lengths according to eqn (16) are presented in Table S5.

Table S5 Lennard–Jones diameters of the investigated species.

substance	σ (Å)
deltamethrin	10.50
imidacloprid	8.53
indomethacin	9.88
rubrene	11.46
BPEA	10.38
tetracene	8.52
TTI	8.99
propylene	5.19
styrene	7.01
vinylpyrrolidone	7.04
vinyl acetate	6.50

References:

1 A. Mansuri, M. Völkel, D. Mihiranga, T. Feuerbach, J. Winck, A. W. P. Vermeer, W. Hoheisel and M. Thommes, *Eur. J. Pharm. Biopharm.*, 2023, **190**, 107–120.

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