Electronic Supplementary Material (ESI) for Soft Matter.

Supplementary Information

Exploring a unified description of the super-Arrhenius region above and below the glass transition temperature

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In the Supplementary Information section are presented: Figure S1 that depicts the exponential characteristics of the g function, Tables S1-S4 that provide the parameters of the fitting presented in Figure 1, Figure S2/Table S5 and Figure S3/Table S6 that describe the fitting to PS nanocomposites and to PI segmental and normal modes respectively, Table S7 with the fitting parameters of iPMMA dynamics shown in Figure 5 and Tables S8-S11 for the comparison with the VFT.

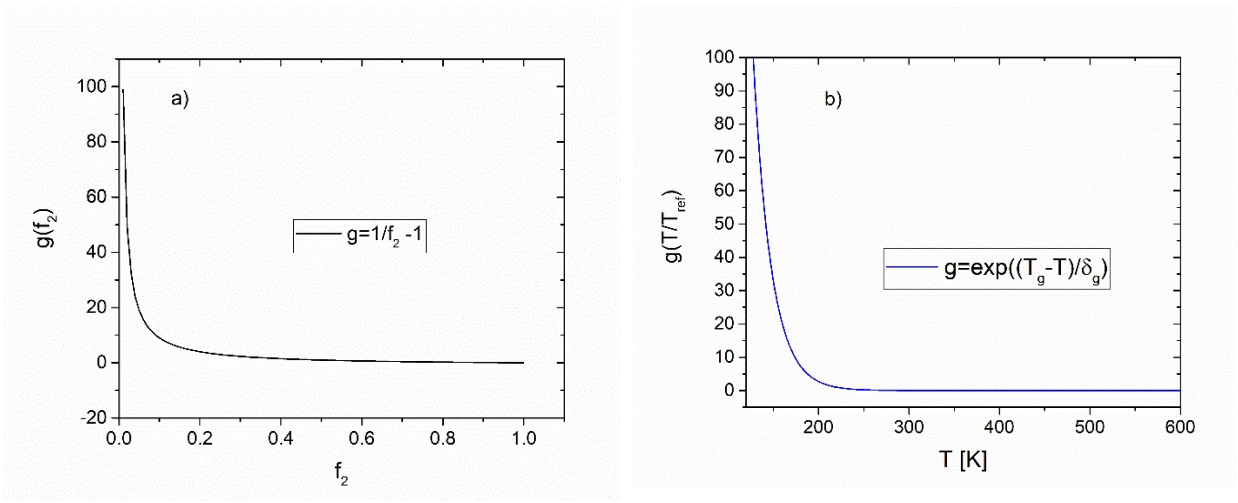

Figure S1. Plot of g, a) as a function of f_2 (fraction of mobile regions) for the region $0 \leq f_2 \leq 1$ and b) as a function of temperature for T_g =220 K and δ_g =20 K.

Table S1. Parameters for the fitting of (i) 16.5 mol% chlorobenzene/cis-decalin, (ii) 9.9 mol% 1-chloronaphthalene/cis-decalin and (iii) 8.7 mol% o-dichlorobenzene/cis-decalin. The β-relaxation is fitted with the Arrhenius equation, while the α-relaxation with the eq. 7.

	B [K]	F_o[Hz]	T_g [K]	δ_g [K]
β-relaxation (i)	2284±10	(8.9±0.1)x10^{11}		
α-relaxation (i)	2284±10	(7.0±0.1)x10^{12}	133±5	9±2
β-relaxation (ii)	3318±10	(1.6±0.1)x10^{15}		
α-relaxation (ii)	3318±10	(6.4±0.1)x10^{14}	140±5	8±2
β-relaxation (iii)	2586±10	(1.5±0.1)x10^{15}		
α-relaxation (iii)	2586±10	(4.1±0.1)x10^{13}	139±5	7±2

Table S2. Parameters for the fitting of (i) 43.4 mol% chlorobenzene/pyridine and (ii) o-terphenyl.

	B [K]	F_o[Hz]	T_g [K]	δ_g [K]
β-relaxation (i)	2673±10	(1.2±0.1)x10^{14}		
α-relaxation (i)	2673±10	(3.4±0.1)x10^{13}	128±5	6±2
β-relaxation (ii)	8898±10	(4.5±0.1)x10^{21}		
α-relaxation (ii)	8898±10	(8.7±0.1)x10^{20}	248±5	11±2

Table S3. Parameters for the fitting of (i) 36.8 mol% 1-chloronaphthalene/pyridine, (ii) 43.8 mol% toluene/pyridine and (ii) 42.5 mol% bromobenzene/pyridine.

	B [K]	F_o[Hz]	T_g [K]	δ_g [K]
β-relaxation (i)	2046±10	(4.3±0.1)x10^{11}		
α-relaxation (i)	2046±10	(1.6±0.1)x10^{11}	151±5	8±2
β-relaxation (ii)	2230±10	(1.0±0.1)x10^{12}		
α-relaxation (ii)	2230±10	(2.2±0.1)x10^{12}	130±5	5±2
β-relaxation (iii)	2257±10	(1.0±0.1)x10^{13}		
α-relaxation (iii)	2257±10	(3.7±0.1)x10^{11}	136±5	5±2

Table S4. Parameters for the fitting of (i) dimethyl phthalate and (ii) diethyl phthalate.

	B [K]	F_o[Hz]	T_g [K]	δ_g [K]

β-relaxation (i)	4932±10	(1.2±0.1)x10^{15}		
α-relaxation (i)	4932±10	(1.2±0.1x10^{16}	198±5	15±2
β-relaxation (ii)	3954±10	(1.5±0.1)x10^{14}		
α-relaxation (ii)	3954±10	(2.4±0.1)x10^{15}	188±5	16±2

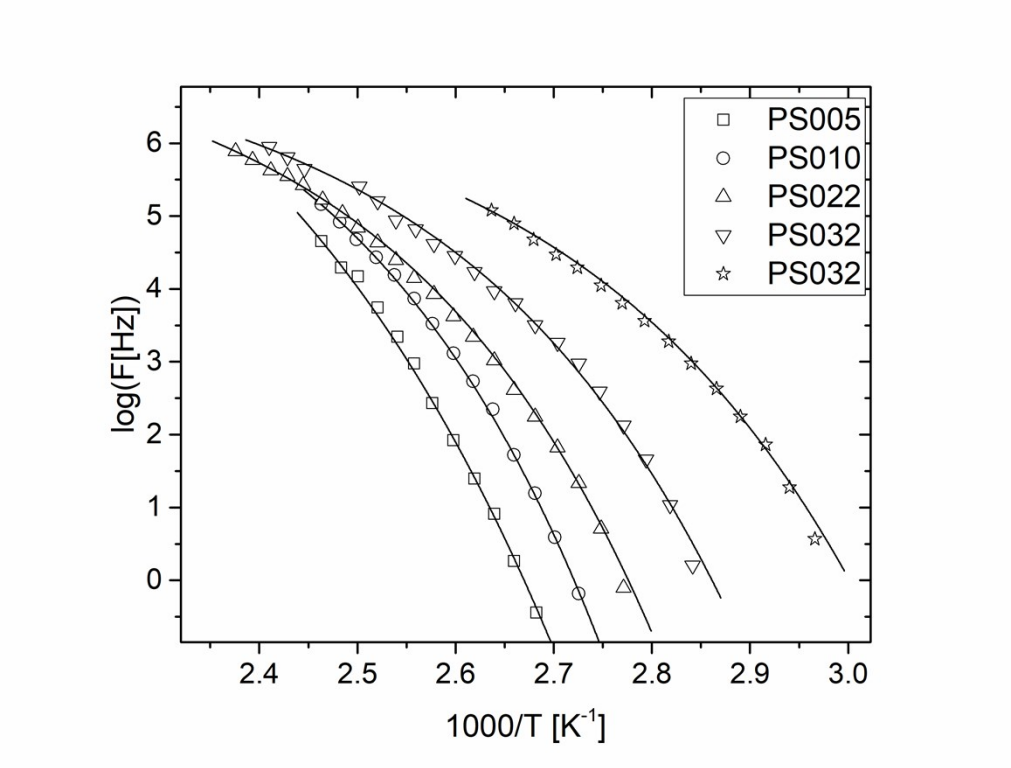

Figure S2. Frequency *F* vs inverse temperature of the *α*-mechanism, for various percentages of Phenethyl-POSS in the PS matrix. The solid lines represent fits according to eq. 7.

Table S5. Values of the fitting parameters of eq. 7 to the experimental results presented in Figure S2.

	***B* [K]**	***F*$_o$[Hz]**	***T*$_g$ [K]**	**δ_g [K]**
PS005	7279±50	(2.5±0.1)x10^{15}	367±2	40±5

PS010	7473±50	(3.8±0.1)x10^{14}	355±2	30±5
PS022	5302±50	(9.5±0.1)x10^{11}	356±2	30±5
PS032	5013±50	(4.8±0.1)x10^{11}	346±2	30±5
PS038	5548±50	(1.7±0.1)x10^{12}	323±2	28±5

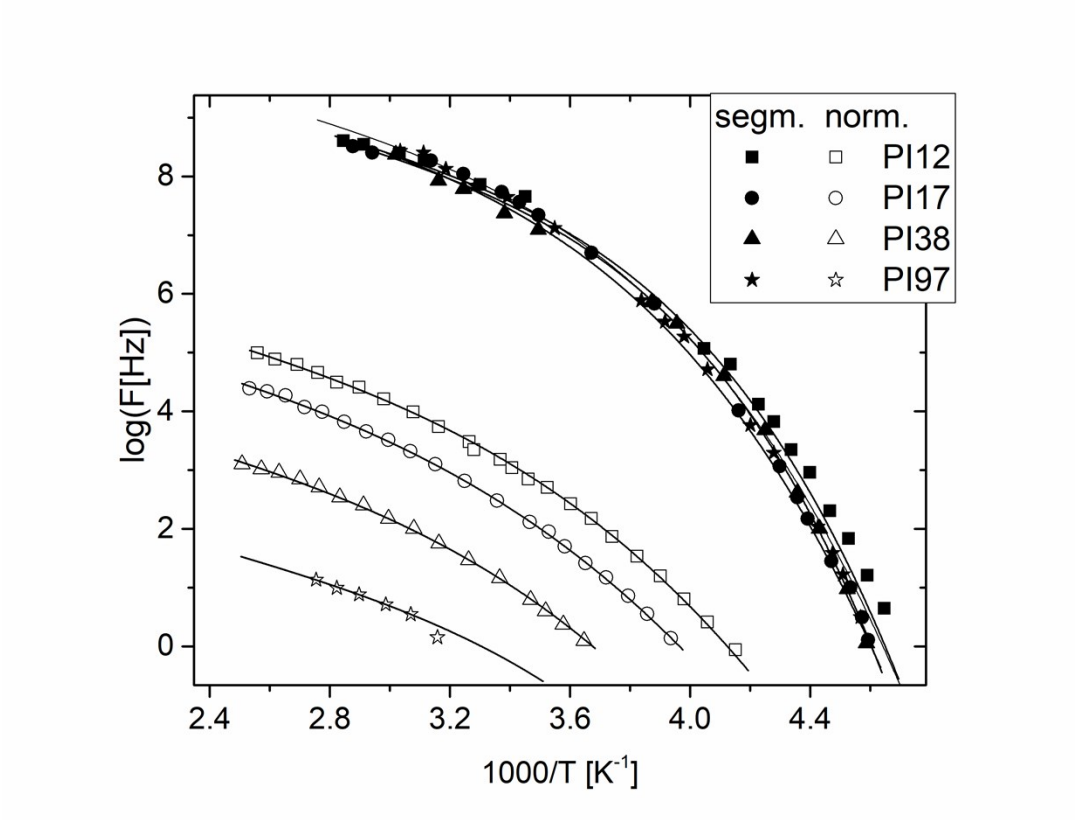

Figure S3. Frequency *F* vs inverse temperature of the segmental and normal modes of PI for various MWs.

Table S6. Values of the fitting parameters of eq. 7 to the experimental results presented in Figure S3.

	B **[K]**	***F*** $_o$**[Hz]**	***T*** $_g$ **[K]**	δ_g **[K]**

PI12segm	3245±50	(4.9±0.1)x10^{12}	213±2	30±5
PI12norm	3277±50	(5.1±0.1)x10^{8}	209±2	46±5
PI17segm	3284±50	(4.8±0.1)x10^{12}	215±2	30±5
PI17norm	3245±50	(1.3±0.1)x10^{8}	211±2	52±5
PI38segm	3310±50	(6.9±0.1)x10^{12}	215±2	35±5
PI38norm	3245±50	(5.5±0.1)x10^{6}	215±2	47±5
PI97segm	3245±50	(8.1±0.1)x10^{12}	214±2	35±5
PI97norm	3276±50	(1.3±0.1)x10^{5}	215±2	36±5

Table S7. Fitting parameters of iPMMA dynamics shown in Figure 5, in the bulk and at various film thicknesses. The common β-relaxation is fitted with the Arrhenius equation, while the α-relaxation with eq. 7.

	B [K]	**$1/\tau_o$ [s^{-1}]**	**T_g [K]**	**δ_g [K]**
β-relaxation iPMMA	8089±20	(3.4±0.1)x10^{14}		
α-relaxation bulk	8089±20	(5.5±0.1)x10^{15}	323±5	21±5
α-relaxation 137nm	8089±20	(6.1±0.1)x10^{15}	321±5	21±5
α-relaxation 68nm	8089±20	(5.5±0.1)x10^{15}	316±5	24±5
α-relaxation 36nm	8089±20	(7.3±0.1)x10^{15}	311±5	25±5
α-relaxation 20nm	8089±20	(3.9±0.1)x10^{16}	305±5	37±5

Table S8. Parameters (B, F_o, and T_o) for the VFT fitting of (i) 16.5 mol% chlorobenzene/cis-decalin, (ii) 9.9 mol% 1-chloronaphthalene/cis-decalin and (iii) 8.7 mol% o-dichlorobenzene/cis-decalin.[1] Also, a column with the ratio $\frac{T_g - \delta_g}{T_o}$ is presented, where T_g and δ_g are the model's parameters (eq. 7).

	B [K]	F_o[Hz]	T_o [K]	$\frac{T_g - \delta_g}{T_o}$
α-relax (i)	751±5	(3.6±0.1)x10^{13}	110±5	1.1
α-relax (ii)	645±5	(1.8±0.1)x10^{12}	121±5	1.1
α-relax (iii)	579±5	(1.0±0.1)x10^{13}	121±5	1.1

Table S9. Parameters (B, F_o, and T_o) for the VFT fitting of sPMMA.[2]

	B [K]	F_o[Hz]	T_o [K]	$\frac{T_g - \delta_g}{T_o}$
α-relax	816±5	(±0.1)x10^{-12}	380±5	1.0

Table S10. Parameters (B, F_o, and T_o) for the VFT fitting of PS.[3]

	B [K]	F_o[Hz]	T_o [K]	$\frac{T_g - \delta_g}{T_o}$
α-relax	475±5	(3.2±0.1)x10^{10}	334±5	1.0

Table S11. Parameters (B, F_o, and T_o) for the VFT fitting of cis PI.[4]

	B [K]	F_o[Hz]	T_o [K]	$\frac{T_g - \delta_g}{T_o}$
α-relax	758±5	(1.9±0.1)x10^{10}	179±5	1.0

References

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(3) Hao, N.; Böhning, M.; Schönhals, A. Dielectric Properties of Nanocomposites Based on Polystyrene and Polyhedral Oligomeric Phenethyl-Silsesquioxanes. *Macromolecules* **2007**, *40* (26), 9672–9679.

(4) Roland, C. M.; Schroeder, M. J.; Fontanella, J. J.; Ngai, K. L. Evolution of the Dynamics in 1,4-Polyisoprene from a Nearly Constant Loss to a Johari-Goldstein β-Relaxation to the α-Relaxation. *Macromolecules* **2004**, *37* (7), 2630–2635.