

Supplementary Material for Highlighting the interdependence between volumetric contribution of fragility and cooperativity for polymeric segmental relaxation.

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Supplementary Text

Thermodynamic scaling

Thermodynamic scaling for PETg, PVAc and PLA are presented in **Figure S1**. Nevertheless, the consistency of the scaling is much better for PVAc than for PLA and PETg. Paluch et al. have already shown for some H-bonded liquids like dipropylene glycol (DPG), such scaling cannot work⁸⁶. They explain this by a strong influence of thermodynamic conditions over the degree of H-bonds. Here, it is possible to hypothesise that for PLA and PETg, the difficulty to have a good scaling can be attributed to a high drop of isobaric fragilities with pressure as shown in **Figure 5**.

Isochoric fragility m_V two methods

The isochoric fragility m_V deduced from the isochoric expression of the relaxation times (**Equation (1)** in the main manuscript) are plotted in **Figure S2** (empty circle) as the function of the density at the glass transition normalized by the density at ambient temperature and atmospheric pressure. m_V values from **Equation (3)** in the main manuscript are also plotted in **Figure S2** (filled circle). Isochoric fragility values obtained with the two methods match well, the same behaviour of m_V increase is observed.

Determination of the parameters of the Donth's equation

T_α and δT of the Donth's equation were determined by approximating the isochronal curves of the dielectric loss with a gaussian fit (**Figure S3a**). The isochronal curves were deduced from the α -relaxation, without any contribution of the conductivity nor from β -relaxation. δT was also estimated at P_{atm} by using the imaginary part of the complex heat capacity (**Figure S3b**).

Evolution of activation volume $\Delta V^\#$ at T_g as a function of pressure

The fit of one-phase exponential decay function allowing to extrapolate the activation volume is expressed by:

$$\Delta V^\# = \Delta V_\infty^\# + A \cdot e^{-\frac{P}{P_\%}} \quad (\text{S1})$$

where $\Delta V_\infty^\#$ is the asymptotic value of activation volume at very high pressure, A is the amplitude from $\Delta V^\#(P = 0)$ up to $\Delta V_\infty^\#$, thus $\Delta V^\#_{(P=0)} = A - \Delta V_\infty^\#$ and $P_\%$ is a pressure for which the activation volume $\Delta V^\#(P)$ has reached 63% of the amplitude ranging from $\Delta V^\#_{(P=0)}$ down to $\Delta V_\infty^\#$. $3 \times P_\%$ and $5 \times P_\%$ correspond to pressures for which the activation volumes $\Delta V^\#(P)$ have reached 95% and 99% of the amplitude respectively. The fit parameters are

given in **Table S4**. One can assume that the values of $\Delta V_{\infty}^{\#}$ for the three polymers are almost reached at $P = 530$ MPa.

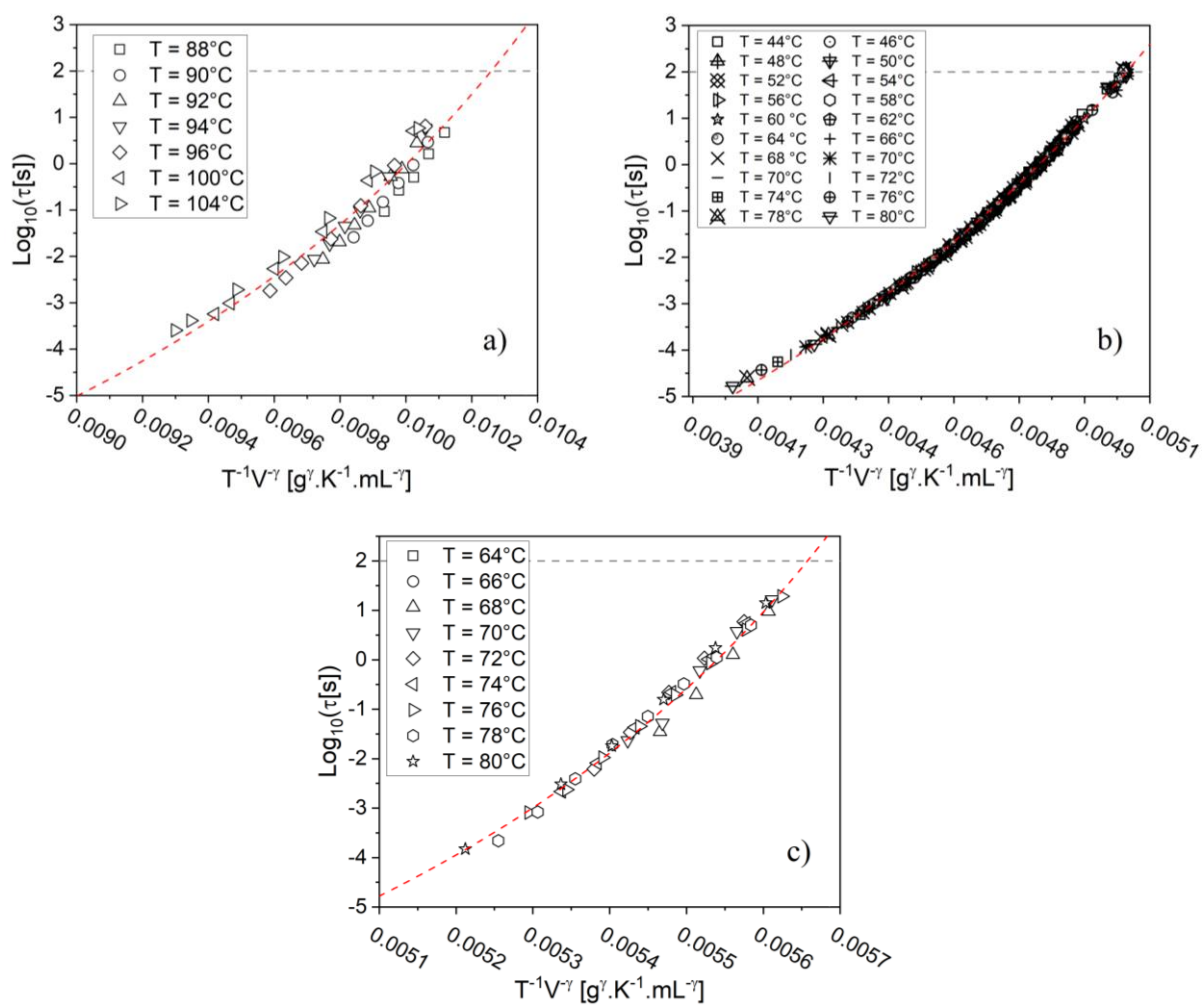


Figure S1. Relaxation times of isothermal measurements as a function of inverse product of temperature and specific volume to the power of the scaling exponent γ for a) PETg (where $\gamma = 5.975$; $\Delta\gamma = 0.178$), b) PVAc (where $\gamma = 2.477$; $\Delta\gamma = 0.029$) and c) PLA (where $\gamma = 2.737$; $\Delta\gamma = 0.042$). Red dotted lines are just guides for the eyes.

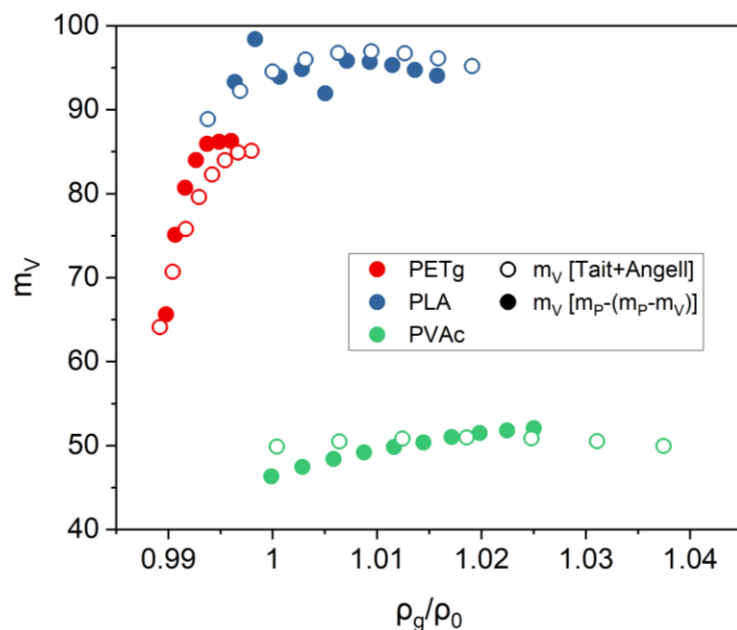


Figure S2. Isochoric fragility as a function of the density at the glass transition normalized to the density at atmospheric pressure and ambient temperature. PETg (red), PLA (blue) and PVAc (green) fragilities were calculated both according to the Angell's definition applied on isochoric relaxation times deduced by Tait's equation (empty circle), and from the difference between the isobaric fragility and the volumetric contribution (filled circles).

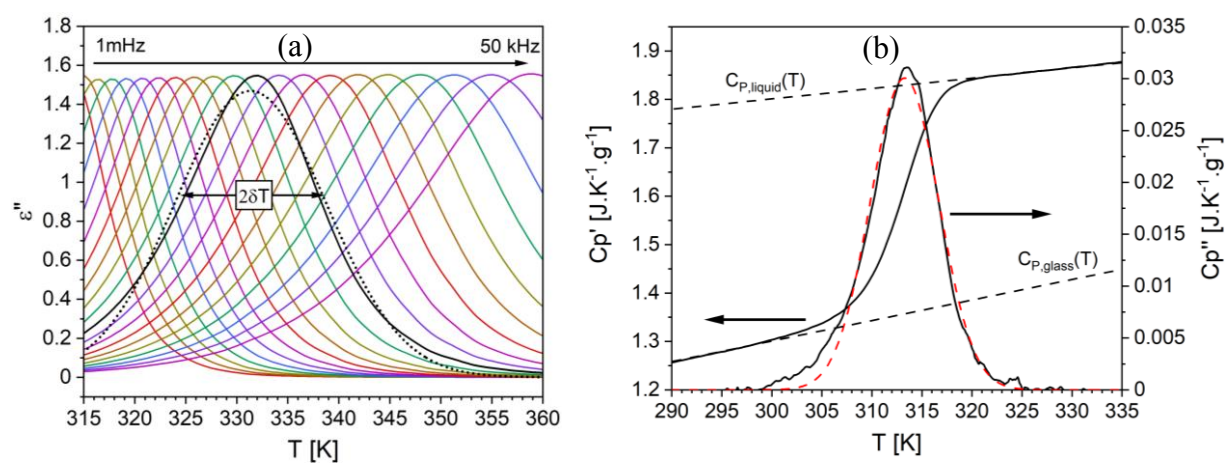


Figure S3. a) Isochronal spectra of the imaginary part of the complex permittivity ϵ'' as a function of temperature for PVAc. The black filled curve corresponds to a frequency of 134 Hz. The short dot line is its gaussian fit to calculate the mean temperature fluctuation from the standard deviation. b) The solid lines represent the real part C_p' and the imaginary part C_p'' of the complex heat capacity as the function of temperature obtained by MT-DSC, the protocol is explained by Rijal et al.¹⁰⁴. The red dashed line is the gaussian fit to determine δT . The black dashed lines are the extrapolated baselines of the specific heat capacities of the glass and the liquid-like state for PVAc.

Table S1. Fit parameters ($\log(\tau_0)$, C , $P0$), the uncertainties of C and $P0$, glass transition pressure P_g and the R-squared of the pressure VFT law of isotherms (**Equation (6)** in the main manuscript) for PETg, PLA and PVAc.

PETg							
T [K]	$\log(\tau_0[s])$	C	ΔC	$P0$ [MPa]	$\Delta P0$ [MPa]	P_g [MPa]	R^2
361.15	-2.21	90.08	2.86	413.63	12.43	40.22	0.93770
363.35	-2.61	90.05	1.50	463.86	7.29	48.90	0.98465
365.35	-2.94	100.91	1.23	556.71	6.44	56.38	0.99255
367.15	-3.21	168.59	2.09	994.48	5.82	66.11	0.99815
369.15	-3.50	105.82	2.13	708.11	7.86	75.67	0.99500
373.15	-4.01	177.54	5.20	1301.45	22.97	94.10	0.99013
377.25	-4.44	72.98	1.21	671.05	5.99	113.36	0.99651
PLA							
T [K]	$\log(\tau_0[s])$	C	ΔC	$P0$ [MPa]	$\Delta P0$ [MPa]	P_g [MPa]	R^2
337.15	-1.06	92.19	3.95	377.13	5.82	26.74	0.99662
339.15	-1.70	88.34	2.08	454.23	6.39	39.94	0.99154
341.15	-2.15	82.18	0.62	484.50	2.45	50.45	0.99954
343.15	-2.46	89.00	3.89	545.15	11.82	56.37	0.98565
345.15	-2.83	83.35	1.99	539.92	6.50	63.60	0.99433
347.15	-3.28	82.52	1.02	585.30	3.90	75.15	0.99850
349.15	-3.80	84.14	1.11	638.00	5.72	87.37	0.99613
351.15	-4.09	70.51	1.16	580.81	4.74	96.40	0.99744
353.15	-4.37	78.38	0.75	667.82	3.03	105.25	0.99912
PVAc							
T [K]	$\log(\tau_0[s])$	C	ΔC	$P0$ [MPa]	$\Delta P0$ [MPa]	P_g [MPa]	R^2
317.15	-0.83	250.00	-	2363.78	692.46	60.03	0.99661
319.15	-1.20	250.00	-	2403.02	585.11	68.70	0.99755
321.15	-1.54	250.00	-	2475.62	567.45	78.07	0.99920
323.15	-1.83	250.00	-	2654.72	450.55	90.46	0.99769
325.15	-2.16	250.00	-	2672.78	323.50	98.58	0.99868
327.15	-2.43	106.24	12.27	1234.39	130.58	108.12	0.99986
329.15	-2.72	138.89	23.88	1618.79	259.47	117.49	0.99978
331.15	-2.96	110.12	7.86	1365.98	88.94	128.37	0.99993
333.15	-3.21	129.77	21.65	1652.48	254.27	139.79	0.99971
335.15	-3.41	113.84	10.93	1542.99	135.31	152.23	0.99987
337.15	-3.63	148.35	27.85	2051.50	358.64	164.83	0.99966
339.15	-3.83	174.15	42.88	2491.52	575.89	178.37	0.99963
341.15	-4.04	142.88	33.27	2129.73	456.75	188.88	0.99956
343.15	-4.18	66.33	4.43	1098.22	63.32	193.90	0.99992
345.15	-4.36	69.31	4.23	1187.77	60.35	207.05	0.99994

347.15	-4.52	73.39	6.02	1288.73	88.30	218.85	0.99993
349.15	-4.65	72.85	4.41	1343.77	68.53	233.42	0.99996
351.15	-4.84	83.14	4.94	1537.34	76.61	244.70	0.99996
353.15	-4.98	67.03	1.32	1323.41	21.12	256.07	0.99999

Table S2. Fit parameters ($\log(\tau_\infty)$, D , T_0), the uncertainties of D and T_0 , glass transition temperature T_g , isobaric fragility m_p and the R-squared of the VFT law of isobars (**Equation (2)** in the main manuscript) for PETg, PLA and PVAc.

PETg								
P [MPa]	$\log(\tau_\infty)$ [s]	D	ΔD	T_0 [K]	ΔT_0 [K]	T_g	m_p	R^2
P_{atm}	-9.76	2.13	0.46	321.97	3.73	347.25	161.53	0.99743
10	-10.47	2.54	0.38	323.08	2.98	351.63	153.64	0.99506
20	-10.73	2.70	0.57	325.19	3.98	355.18	150.79	0.99777
30	-11.12	2.98	0.69	325.99	4.25	358.18	145.92	0.99796
40	-11.60	3.35	0.76	326.02	4.20	360.88	140.73	0.99815
50	-12.18	3.80	0.84	325.48	4.13	363.41	135.87	0.99836
60	-13.04	4.52	0.07	323.52	0.62	365.79	130.16	0.99858
70	-17.08	7.87	5.37	312.38	17.44	368.34	125.63	0.99881
PLA								
P [MPa]	$\log(\tau_\infty)$ [s]	D	ΔD	T_0 [K]	ΔT_0 [K]	T_g	m_p	R^2
P_{atm}	-14	4.60	0.06	291.37	0.48	327.76	144.12	0.99839
10	-14	4.49	0.09	295.84	0.80	331.89	147.30	0.99747
20	-14	4.41	0.15	299.19	0.80	334.98	149.79	0.99243
30	-14	4.82	0.09	297.85	0.73	336.79	138.39	0.99810
40	-14	4.91	0.11	299.30	0.86	339.18	136.07	0.99716
50	-14	5.22	0.13	298.83	1.01	341.18	128.90	0.99691
60	-14	5.09	0.09	301.86	0.66	343.60	131.70	0.99881
70	-14	5.21	0.10	302.81	0.70	345.62	129.17	0.99858
80	-14	5.33	0.11	303.64	0.74	347.55	126.64	0.99836
90	-14	5.45	0.12	304.38	0.77	349.42	124.14	0.99815
100	-14	5.58	0.12	305.04	0.80	351.22	121.67	0.99796
PVAc								
P [MPa]	$\log(\tau_\infty)$ [s]	D	ΔD	T_0 [K]	ΔT_0 [K]	T_g	m_p	R^2
P_{atm}	-14	9.80	0.12	239.36	0.83	307.27	67.76	0.99847
10	-14	9.82	0.06	241.87	0.39	310.63	68.01	0.99900
20	-14	9.77	0.05	244.11	0.30	313.19	68.10	0.99937
30	-14	9.76	0.04	246.09	0.24	315.61	68.06	0.99961
40	-14	9.76	0.04	247.86	0.24	317.93	67.90	0.99976
50	-14	9.79	0.04	249.43	0.24	320.16	67.64	0.99983
60	-14	9.84	0.05	250.83	0.32	322.31	67.60	0.99983

70	-14	9.85	0.07	252.47	0.45	324.47	67.37	0.99983
80	-14	9.89	0.09	253.84	0.53	326.54	67.01	0.99973
90	-14	9.96	0.06	255.01	0.39	328.56	66.66	0.99950
100	-14	10.03	0.05	256.16	0.30	330.55	67.76	0.99928

Table S3. Fit parameters (T_g^0 , b , Π), their uncertainties and the R-squared of the Andersson's model (**Equation (7)** in the main manuscript) for PETg, PLA and PVAc.

Polymer	T_g^0	ΔT_g^0	b	Δb	Π	$\Delta \Pi$	R^2
PETg	348.02	0.289	11.20	1.479	79.61	4.77	0.99943
PLA	329.48	0.281	7.00	1.349	177.06	9.92	0.99898
PVAc	303.85	0.044	5.50	0.194	212.73	1.83	0.99997

Table S4. Fit parameters ($\Delta V_\infty^\#$, A , P_m), their uncertainties and the R-squared of one-phase exponential decay function (**Equation (S1)**) for PETg, PLA and PVAc.

Polymer	$\Delta V_\infty^\#$ [nm ³]	$\pm \Delta V_\infty^\#$ [nm ³]	A [nm ³]	ΔA [nm ³]	P_m [MPa]	ΔP_m [MPa]	R^2
PETg	0.362	0.013	1.824	0.009	51.66	0.82	0.99997
PLA	0.354	0.069	1.090	0.025	80.94	2.80	0.98892
PVAc	0.358	0.052	0.280	0.004	106.26	3.08	0.99298