

Electronic Supplementary Information (ESI) for “Combined Description of Pressure-Volume-Temperature and Dielectric Relaxation of Several Polymeric and Low-Molecular-Weight Organic Glass-Formers using SL-TS2 Approach”

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Free Energy Minimization

To find thermodynamic equilibrium, we need to minimize G with respect to ψ and ν , leading to the following equations,

$$\begin{aligned}
& \dot{T} \left[\ln \frac{\psi}{1-\psi} + \ln \frac{r_S}{r_L} + \frac{r_L - r_S}{\langle r \rangle} + (r_L - r_S) \left(\frac{1}{\nu} - 1 \right) \ln \frac{1}{1-\nu} \right] \\
& + \frac{\nu}{\langle r \rangle^2} \left\{ (r_L - r_S) \psi^2 r_S^2 - 2\psi r_S^2 r_L \right\} \\
& + 2\alpha_{LS} \frac{\nu}{\langle r \rangle^2} \left\{ (r_L - r_S) \psi (1-\psi) r_S r_L - r_S r_L [(1-\psi) r_L - \psi r_S] \right\} \\
& + \alpha_{LL} \frac{\nu}{\langle r \rangle^2} \left\{ (r_L - r_S) (1-\psi)^2 r_L^2 + 2(1-\psi) r_L^2 r_S \right\} - \frac{\dot{P}}{\nu} (r_L - r_S) = 0
\end{aligned} \tag{S1a}$$

$$\begin{aligned}
& \dot{T} \left[\ln(1-\nu) + \nu \left\{ 1 - \frac{1}{\langle r \rangle} \right\} \right] + \\
& \nu^2 \left[\left(\frac{\psi r_S}{\langle r \rangle} \right)^2 + 2\alpha_{LS} \left(\frac{\psi r_S}{\langle r \rangle} \right) \left(\frac{\{1-\psi\} r_L}{\langle r \rangle} \right) + \alpha_{LL} \left(\frac{\{1-\psi\} r_L}{\langle r \rangle} \right)^2 \right] + \dot{P} = 0
\end{aligned} \tag{S1b}$$

Here, $\dot{T} = \frac{k_B T}{\varepsilon^*}$, and $\dot{P} = \frac{P v_0}{\varepsilon^*}$. We can re-write equations (S1a) – (S1b) in the following

form,

$$\ln \frac{\psi}{1-\psi} + \Delta \dot{S} - \frac{\Delta \dot{U} + \dot{P} \Delta \dot{V}}{\dot{T}} = 0 \tag{S2a}$$

$$\dot{T} \left[\ln(1-\nu) + \nu \left\{ 1 - \frac{1}{\langle r \rangle} \right\} \right] + \nu^2 J + \dot{P} = 0 \tag{S2b}$$

where,

$$\Delta \dot{S} = \ln \frac{r_S}{r_L} + \frac{r_L - r_S}{\langle r \rangle} + (r_L - r_S) \left(\frac{1}{\nu} - 1 \right) \ln \frac{1}{1 - \nu} \quad (\text{S3a})$$

$$\begin{aligned} -\Delta \dot{U} = & \frac{\nu}{\langle r \rangle^2} \left\{ (r_L - r_S) \psi^2 r_S^2 - 2\psi r_S^2 r_L \right\} \\ & + 2\alpha_{LS} \frac{\nu}{\langle r \rangle^2} \left\{ (r_L - r_S) \psi (1 - \psi) r_S r_L - r_S r_L [(1 - \psi) r_L - \psi r_S] \right\} \\ & + \alpha_{LL} \frac{\nu}{\langle r \rangle^2} \left\{ (r_L - r_S) (1 - \psi)^2 r_L^2 + 2(1 - \psi) r_L^2 r_S \right\} \end{aligned} \quad (\text{S3b})$$

$$\Delta \dot{V} = \frac{(r_L - r_S)}{\nu} \quad (\text{S3c})$$

$$J = \left(\frac{\psi r_S}{\langle r \rangle} \right)^2 + 2\alpha_{LS} \left(\frac{\psi r_S}{\langle r \rangle} \right) \left(\frac{\{1 - \psi\} r_L}{\langle r \rangle} \right) + \alpha_{LL} \left(\frac{\{1 - \psi\} r_L}{\langle r \rangle} \right)^2 \quad (\text{S3d})$$

Solutions of equations (S2a)–(S2b) describe the equilibrium values of ψ and ν for any given T and P.

Equations of evolution for non-equilibrium case (isobaric cooling from equilibrium melt)

To describe the non-equilibrium behavior of ν and ψ during, e.g., cooling from high-temperature equilibrium phase, we used a simple “relaxation time approximation”, stipulating¹ that the relaxation time for ψ is the JG β -relaxation and the relaxation time for ν is the (often much slower) α -relaxation,

$$\frac{d\psi}{dt} = \frac{\psi^* - \psi}{\tau_\beta} \quad (\text{S4a})$$

$$\frac{dv}{dt} = \frac{v^* - v}{\tau_\alpha} \quad (\text{S4b})$$

Here, we define ψ^* and v^* in the following way. First, we solve equations (S2a)—(S2b) to obtain the equilibrium values, $\psi_{eq}(T, P)$ and $v_{eq}(T, P)$. Next, we set $v^* = v_{eq}(T, P)$ and update v using equation (S4b). Finally, we re-calculate ψ^* by solving equation (S2a) with the new value of v . Note that this approach is similar in spirit to well-known Tool-Narayanaswami-Moynihan (TNM)²⁻⁴ and Kovacs–Aklonis–Hutchinson–Ramos (KAHR)⁵ models.

To simplify the non-equilibrium modeling even further, we consider the following assumption. Let us define T_g ($\geq T_x$) as the temperature below which the temperature change becomes faster than the α -relaxation, i.e., $T_g^{-1} |q| \tau_\alpha(T_g) \cong 1$ (where $q = \frac{dT}{dt}$ is the cooling rate). In this case, for $T > T_g$, both ψ and v equilibrate fully, while for $T < T_g$, $v = v_{eq}(T_g)$ does not change, while $\psi = \psi^*(T; v)$ still continues to increase as the temperature is decreased, but significantly slower than in the equilibrium limit. For more details, see ref.⁶ and the main text.

Derivation of the Casalini-Roland Scaling

The specific volume of a material can be expressed in terms of v and ψ as,

$$v_{sp} = v_{sp,0} \frac{\langle r \rangle}{r_S V} = v_{sp,0} \frac{r_S \psi + r_L (1 - \psi)}{r_S V} \quad (\text{S5})$$

where $v_{sp,0}$ can depend on pressure but not on temperature. The scaling relationships proposed by Casalini, Roland, and co-workers suggest that,⁷⁻⁹

$$\tau_{\alpha}(T, P) = f \left[T \left(v_{sp}(T, P) \right)^{\gamma} \right] \quad (S6)$$

where γ is a material-dependent constant, independent of T and P . This scaling means that the state of the material depends not on T and P independently, but on a combined state variable $X = T \left(v_{sp}(T, P) \right)^{\gamma}$. On the other hand, in refs.^{1,6} we demonstrated that in the limit of sufficiently low pressures, equations 6a and 6b can be re-written as,

$$\tau_{\beta}(T, P) = \tau_{\infty} \exp \left[\frac{E_L(P)}{RT_X(P)} (1 + Z) \right] \quad (S7a)$$

$$\begin{aligned} \tau_{\alpha}(T, P) &= \tau_{\infty} \exp \left[\frac{E_L(P)}{RT} + \frac{E_S(P) - E_L(P)}{RT} \psi(T, P) \right] \\ &= \tau_{\infty} \exp \left[\frac{E_L(P)}{RT_X(P)} (1 + Z) + \frac{E_S(P) - E_L(P)}{RT_X(P)} (1 + Z) \psi(Z) \right] \end{aligned} \quad (S7b)$$

Here, $Z = \frac{T}{T_X(P)} - 1$ is a different “state variable” that also combines the effects of temperature and pressure. As discussed in ref. ¹, the solid fraction $\psi(T, P) \equiv \psi(Z)$ for the equilibrium case (above the glass transition); also, for constant-cooling-rate experiments performed at different

pressures, a similar relationship holds as well, $\psi(T, P; q) \equiv \psi\left(\frac{T}{T_g(P)}; q\right)$ (the ratio T_g/T_x is slightly cooling-rate dependent, but pressure-independent for any given cooling rate q).

Going back to the (τ TV) scaling relationships, we can substitute equation (S5) into equation (S6) to obtain,

$$\tau_\alpha(T, P) = f\left[T(v_{sp}(T, P))^\gamma\right] = f\left[\frac{T_x(P)}{1+Z} \left(v_{sp,0}(P) \frac{r_s \psi(Z) + r_L \{1 - \psi(Z)\}}{r_s v(Z)}\right)^\gamma\right]$$

(S8)

To satisfy the scaling, we need to eliminate the explicit pressure dependence in equation (S8), leading to the equations (5a) and (5b) of the main text.

Experimental Data and their Scaling Analysis

Experimental data for o-terphenyl (OTP),¹⁰⁻¹² phenylphthalein-dimethylether (PDE),^{13,14} and polychlorinated biphenyl (PCB62)^{15,16} are summarized in Figure S1 (specific volume) and S2 (dielectric relaxation time) for multiple pressures and temperatures. The data for OTP were collected using isobaric measurements (as a function of temperature for constant pressure), while the data for PDE and PCB62 were collected using isothermal measurements (as a function of pressure for constant temperature).

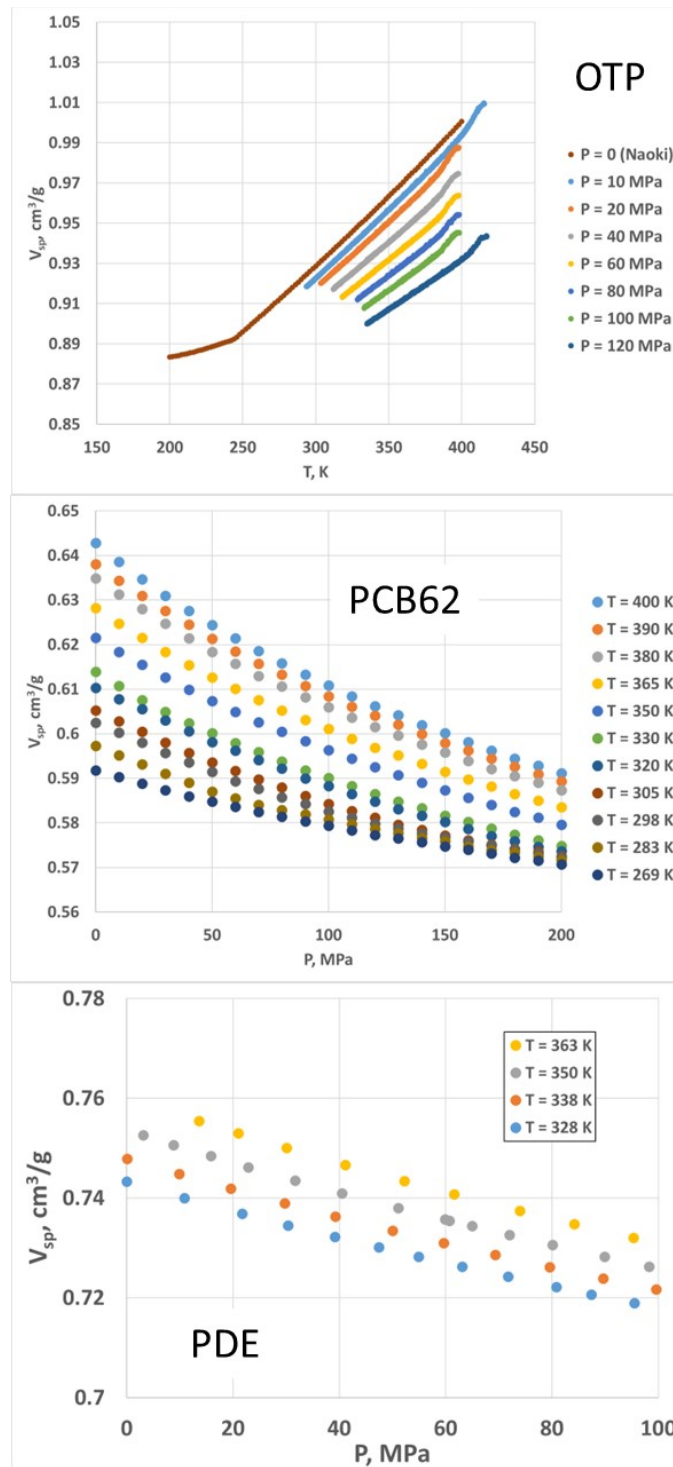


Figure S 1. Specific volume data for OTP (top; isothermal), PCB62 (middle; isobaric), and PDE (bottom; isobaric).

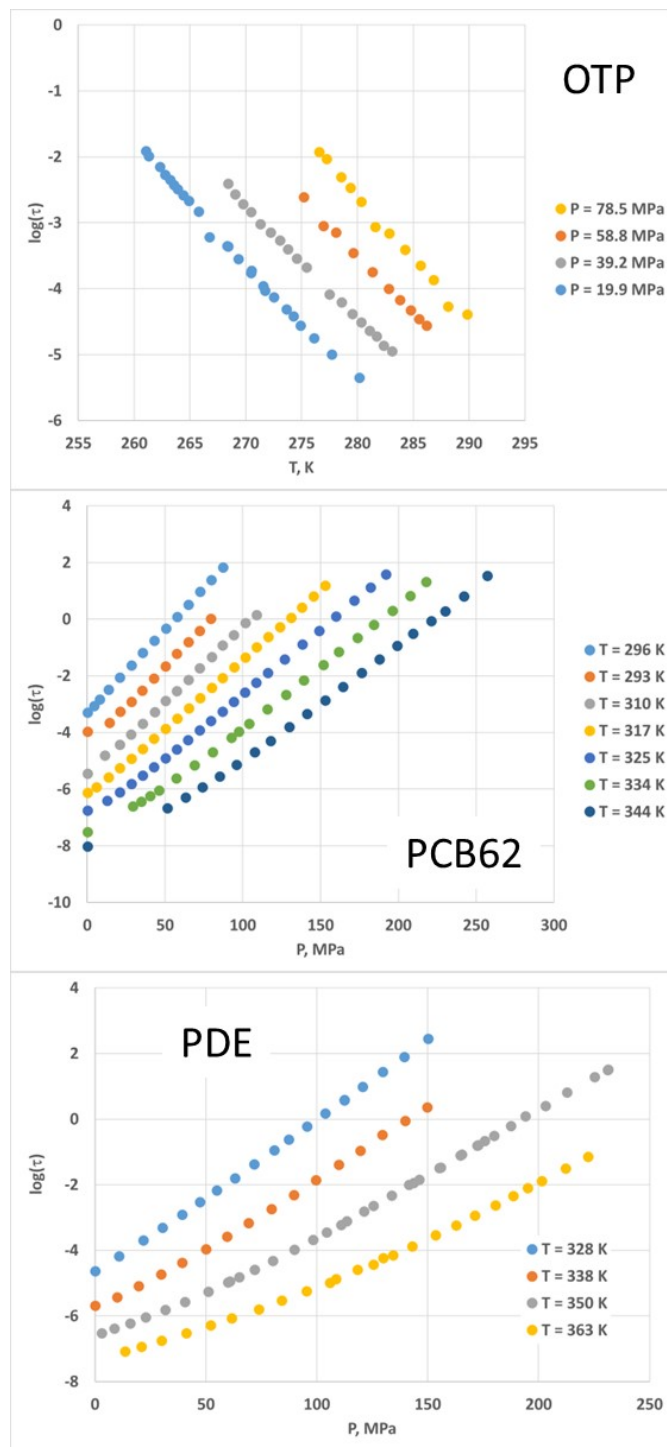


Figure S 2. Dielectric relaxation time data for OTP (top; isothermal), PCB62 (middle; isobaric), and PDE (bottom; isobaric).

The Scaling Exponent

In Table S1, the scaling exponent γ regressed using our current approach is compared to the earlier analysis of Casalini and Roland¹⁷ for PDE, OTP, and PCB62. The row called “ γ (Casalini-Roland)” corresponds to their estimate of γ using thermodynamic relationships, while the row “ γ (exp)” is the result of direct scaling analysis similar to ours. As expected, our regression is within the error bars from “ γ (exp)” and very close to “ γ (Casalini-Roland)”.

Table S 1. The scaling exponent from current work and earlier analysis of Casalini and Roland.

Parameter	PDE	PCB	OTP
γ (current work)	4.6 ± 0.3	8.5 ± 0.7	4.05 ± 0.25
γ (Casalini-Roland)	4.5 ± 0.3	8.1 ± 0.86	4.05 ± 0.3
γ (exp)	4.5	8.5	4.0

Relationship between SL-TS2 Model Parameters and Experimental Characteristics of the Material

Here, we describe in detail how the parameters of the SL-TS2 model are related to the measured characteristics of the material. We illustrate it on the example of ortho-terphenyl (OTP). As a reminder, the modeling refers to the case of ambient pressure ($P = 0$) – the data for higher pressure are captured by the scaling relationships (equations 5a and 5b of the main text)

The model parameters and the experimental parameters used to characterize the specific volume and the relaxation time (as functions of temperature under atmospheric pressure) are summarized in Table S2 below.

Table S 2. SL-TS2 parameters and the experimentally determined parameters used to characterize the specific volume and relaxation time of glass-formers as functions of temperature. The highlighted rows correspond to the SL-TS2 parameters that are identical to the experimentally determined ones.

SL-TS2		Experimental	
Parameter	Units	Parameter	Units
T_g	K	T_g	K
$\log(\tau_\infty)$		$\log(\tau_\infty)$	
E_L	kJ/mol	E_a	kJ/mol
E_S	kJ/mol	T_A	K
T^*	K	D	K
V_{sp0}	cm ³ /g	T_0	K
α_{LL}		$V_{sp,g}$	cm ³ /g
\bar{r}		κ_L	K ⁻¹
ξ		κ_G	K ⁻¹

The SL-TS2 model parameters are:

- Glass transition temperature, T_g ;
- Logarithm of the high-temperature relaxation time limit, $\log(\tau_\infty)$;
- Arrhenius activation energy in the liquid state, E_L ;
- Arrhenius activation energy in the solid state, E_S ;
- Sanchez-Lacombe characteristic temperature, T^* ;
- Zero-temperature specific volume of the solid state, V_{sp0} ;
- Ratio of cohesive energies of liquid and solid states, α_{LL} ;
- Average “size” of the CRR in terms of Sanchez-Lacombe lattice units,

$$\bar{r} = 0.5(r_L + r_S)$$

- Relative volume difference between the liquid and solid states,

$$\xi = \frac{0.5(r_L - r_S)}{r}$$

The parameters derived from experimental measurements are as follows,

- Glass transition temperature, T_g ;
- Logarithm of the high-temperature relaxation time limit, $\log(\tau_\infty)$;
- Arrhenius activation energy at high temperatures, E_a ;
- Temperature corresponding to the transition from VFT-like behavior to Arrhenius-like behavior, T_A ;
- VFT energy parameter, D ;
- VFT “divergence” temperature, T_0 ;
- Specific volume at $T = T_g$, $V_{sp,g}$;
- Coefficient of volumetric thermal expansion in the glassy state, κ_G ;
- Coefficient of volumetric thermal expansion in the liquid state, κ_L .

Mathematically, the “experimental” parameters correspond to the fitting of the experimental data using the following approximate expressions:

(Relaxation time):

$$\log \{\tau_{\text{exp}}(T)\} = \begin{cases} \log \tau_\infty + \frac{E_L}{RT}, T > T_A \\ \log \tau_\infty + \frac{E_L}{RT_A} + \frac{D}{T - T_0} - \frac{D}{T_A - T_0}, T_0 < T < T_A \end{cases}$$

(S9)

(Specific volume):

$$v_{sp}(T) = \begin{cases} v_{sp,g} \exp \left\{ \kappa_L (T - T_g) \right\} & T > T_g \\ v_{sp,g} \exp \left\{ \kappa_G (T - T_g) \right\} & T < T_g \end{cases}$$

(S10)

Equation (S9) uses the description of relaxation time where the VFT model is used for $T < T_A$, and the Arrhenius model is used for $T > T_A$. Equation (S10) uses simple one-parameter exponential equation of state for specific volume above and below $T = T_g$; obviously, more complex expressions like Tate equation can be used.

The first three parameters in SL-TS2 and “experimental” sets are identical. To determine the remaining six SL-TS2 parameters, we need to minimize the “objective function” defined as,

$$Obj = \left\langle \left| \log \left\{ \tau_{exp}(T) \right\} - \log \left\{ \tau_{fit}(T) \right\} \right| \right\rangle + \left\langle \left| \log \left\{ V_{sp,exp}(T) \right\} - \log \left\{ V_{sp,fit}(T) \right\} \right| \right\rangle$$

(S11)

Here, $\langle \dots \rangle$ means averaging, and $|\dots|$ means absolute value. The minimization of the objective function is performed using a large number ($N = 1000$) of calculations where the six SL-TS2 parameters are varied within a specific region in the parameter space, following an initial trial and error process to find the starting point.

Before the start of the optimization, we introduce one additional transformation, defining the following parameters,

$$\Delta\mathcal{F}_X = \ln \frac{1-\xi}{1+\xi} + 2\xi + 2\bar{r}\xi \left(\frac{1}{\nu_X} - 1 \right) \ln \frac{1}{1-\nu_X} \quad (\text{S12a})$$

$$\begin{aligned} \Delta\mathcal{G}_X &= \nu_X \bar{r} (1-\xi)^2 \left\{ 1 - \frac{1}{2}\xi \right\} \\ &\quad + \sqrt{\alpha_{LL}} \nu_X \bar{r} (1-\xi)(1+\xi)\xi \\ &\quad - \alpha_{LL} \nu_X \bar{r} (1+\xi)^2 \left\{ \left(1 - \frac{1}{2}\xi \right) \right\} \end{aligned} \quad (\text{S12b})$$

$$\mathcal{F}_X = \frac{\Delta\mathcal{G}_X}{\Delta\mathcal{F}_X} \quad (\text{S12c})$$

The occupancy at the transition, ν_X , is the solution of equation,

$$\mathcal{F}_X \left(\ln(1-\nu_X) + \nu_X \left\{ 1 - \frac{1}{r} \right\} \right) + \nu_X^2 J_X = 0 \quad (\text{S13})$$

$$\text{With } J_X = \frac{1}{4} \left(\left[(1-\xi) \right]^2 + 2\sqrt{\alpha_{LL}} (1-\xi)(1+\xi) + \alpha_{LL} \left[(1+\xi) \right]^2 \right).$$

We will now vary $\Delta\mathcal{F}_X$ and \mathcal{F}_X as independent parameters and compute \bar{r} and α_{LL} afterwards from equations (S12a--c) The meaning of $\Delta\mathcal{F}_X$ and \mathcal{F}_X is fairly intuitive: \mathcal{F}_X is the “reduced” temperature at which the solid and liquid elements are present in equal numbers, and

ΔS_x^\ddagger is the slope of the dependence of $\ln \frac{\psi}{1-\psi}$ on $\frac{1}{T}$ at this temperature – and thus directly related to the fragility of the material.

The specific volume and the relaxation time are expressed in terms of ψ and ν as,

$$v_{sp} = v_{sp,0} \frac{\langle r \rangle}{r_s \nu} = v_{sp,0} \frac{r_s \psi + r_L (1-\psi)}{r_s \nu}$$

$$\log \{ \tau_\alpha (T) \} = \log \{ \tau_\infty \} + \frac{1}{\ln(10)} \left[\frac{E_L}{RT} + \frac{E_S - E_L}{RT} \psi \right]$$

As a starting point, we determine the temperature, T_A , above which the temperature dependence of the relaxation time becomes Arrhenius-like. Per Bicerano,¹⁸ at least for polymers, $T_A/T_g \approx 1.2$; however, this is only a rough guidance that needs to be tested for each specific material. For OTP, we plot the dependence of $\log(\tau)$ on $1000/T$ (Arrhenius plot) and fit the lower portion, between 0 and $1000/T_A$, to a simple linear function while varying T_A and monitoring the fit parameters – see Figure S3 and Table S3 below.

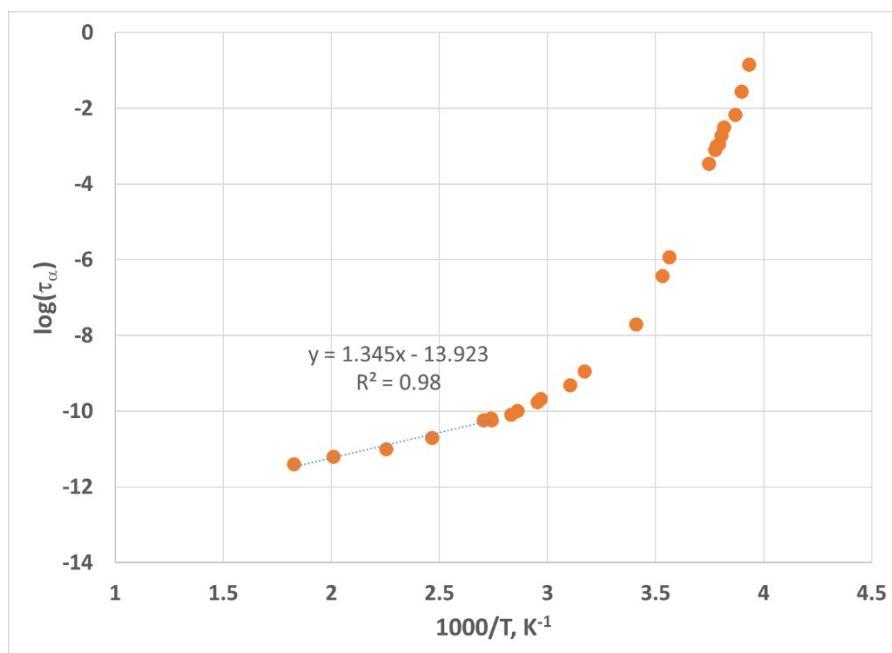


Figure S 3. Arrhenius plot for OTP. The trendline corresponds to the linear fit to the data, assuming $T_A = 365$ K and restricting the fit to points having $T > T_A$.

Table S 3 Coefficient of determination (R^2), $\log(\tau_\infty)$, and the liquid-state activation energy, E_L as a function of chosen T_A .

T_A , K	R^2	$\log(\tau_\infty)$	E_L , kJ/mol
315.5	0.9416	-14.73	32.47
337.1	0.9743	-14.23	28.44
349.5	0.9836	-14.01	26.51
365	0.98	-13.92	25.74

Based on this analysis, we can estimate that $T_A = 330 \pm 15$ K, $\log(\tau_\infty) = -14.2 \pm 0.3$, and $E_L = 27 \pm 3$ kJ/mol. (Note that T_A is not an SL-TS2 model parameter but $\log(\tau_\infty)$ and E_L are). The remaining six SL-TS2 parameters are now determined by running multiple calculations aiming to minimize the objective function (equation (S11)). The results are given in Table S4.

Table S 4. Calculated SL-TS2 parameters (with estimated errors) for OTP.

SL-TS2 for OTP		
Parameter	Units	Value
T_g	K	248 ± 2
$\log(\tau_\infty)$		-14.2 ± 0.3
E_L	kJ/mol	27 ± 3
E_S	kJ/mol	140 ± 5
T^*	K	658 ± 5
V_{sp0}	cm ³ /g	0.839 ± 0.002
T_X	K	238 ± 2
ΔS_X^\ddagger		2.25 ± 0.25
ξ		0.022 ± 0.004

Finally, we need to calculate \bar{r} and α_{LL} , as discussed above. By numerically solving equations (S12a--c), we obtain: $\alpha_{LL} = 0.958 \pm 0.003$, and $\bar{r} = 486 \pm 50$. Note that bounds on α_{LL} are very tight – even small variations in α_{LL} would lead to significant changes in $T_X (= T^* \frac{\bar{r}}{T_X})$.

Note that in general, the “Arrhenius” temperature, T_A , is not experimentally accessible; even where it is (in the case of OTP), there is a considerable uncertainty about its exact value (estimates range from ~ 335 K (current paper) to ~ 400 K¹¹ to ~ 450 K¹⁹, depending on the chosen criterion). If a glass-former has high glass transition temperature and/or low decomposition temperature, T_A becomes experimentally inaccessible, and the errors in the determination of E_L and $\log(\tau_\infty)$ become significantly larger (roughly, ± 10 kJ/mol and ± 1.0 , respectively). However, the errors in the determination of all the other parameters would not be affected significantly. More detailed discussion of the topic will be done in future publications.

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