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Spectroscopic Ellipsometry as a Route to Thermodynamic Characterization

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S1. LCL Modeling Details

As noted in the main article, we applied the Locally Correlated Lattice (LCL) equation of state (EOS) to analyze the ellipsometric thermal expansion results and then to generate the predictions for the percent free volume of the polymer melts (Table 5 and Figure 6). The LCL EOS expression is given by

$$\frac{P}{k_B T} = \left(\frac{1}{v}\right) \ln \left[\frac{V}{V - N_m r v} \right] + \left(\frac{3}{v}\right) \ln \left[\frac{V - (N_m v/3)(r - 1)}{V} \right] - \left(\frac{3}{v}\right) \left(\frac{(2r + 1)^2}{\left(\frac{V}{N_m v}\right) - \left(\frac{1}{3}\right)(r - 1)} \right) \times \left(\frac{\exp \left[-\frac{\varepsilon}{k_B T} \right] - 1}{\left(\frac{1}{3}\right)(2r + 1) \exp \left[-\frac{\varepsilon}{k_B T} \right] + \left(\frac{V}{N_m v}\right) - r} \right) \quad (\text{S1})$$

where k_B is the Boltzmann constant and N_m is the number of molecules. There are three molecular level parameters: r , the number of segments (occupied lattice sites) per molecule; v , the volume per lattice site; and ε , the segment-segment nonbonded interaction energy. In applying this equation in practice, the pressure (P) is taken to be a function of two independent variables: temperature (T), and either the volume per molecule (V/N_m), or the specific volume ($V_{sp} = (V/N_m)/M_w$) given the molecular weight (M_w). (If an experimental molecular weight is not available, we simply assign a value of $M_w = 100$ kg/mol; any other choices, as long as they are in the polymeric regime, *e.g.* $M_w > 10$ kg/mol, will not noticeably change any per weight (intensive) properties like the specific volume, or the fractional free volume.) Eq. S1 also leads to an analytical expression for the coefficient of thermal expansion, α_v , as a function of T and V_{sp} , using the relation

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$$\alpha_V = \left(\frac{1}{V_{sp}} \right) \left(\frac{\partial V_{sp}}{\partial T} \right)_P = - \left(\frac{1}{V_{sp}} \right) \frac{\left(\frac{\partial P}{\partial T} \right)_{V_{sp}}}{\left(\frac{\partial P}{\partial V_{sp}} \right)_T} \quad (\text{S2})$$

where here we have written α_V with more detailed partial derivative notation in order to distinguish it from the other thermodynamic partial derivatives. Working in terms of independent variables, T and V_{sp} , is necessary because, as with many theoretical equations of state, V_{sp} cannot be directly expressed as a function of T and P . This also means that in practice, we solve for V_{sp} values at any given (T, P) via numerical root finding calculations.

As discussed in the main text, we only need to partially characterize the LCL model to predict the fractional free volume at ambient pressure. Therefore, in fitting each of the polymer melts we pre-set the ν parameter at a value of 8.0 mL/mol (a typical value for polymers). We then specify the following experimental values and conditions: $\alpha_V = \alpha_N$ (*i.e.* using the experimental α_N values in main article Table 5), $T = 398$ K (an average temperature of our experiments), and $P = 1$ atm. For convenience, we also set $V_{sp} = 1$ mL/g and $M_w = 100$ kg/mol, which are both typical values for polymers. Note that if we were to change either V_{sp} or M_w by a factor of ten it will not noticeably change the LCL prediction for *fractional* free volume (*e.g.* the change is $< 0.01\%$). Of course, the absolute $V_{sp}(T)$ curve for the model will not be accurate (only the relative expansion is accurate), so if, in the case of other scenarios, we also wish for accuracy in $V_{sp}(T)$, then incorporating the value of a single specific volume measurement at any chosen T would suffice for such prediction.

With the values specified, we then solve the two equations, Eqs. S1 and S2, for the two remaining unknown molecular parameters, r and ε . In accordance with the simple free volume definition in main article Eq. 3, we then calculate the fractional free volume as a function of temperature at $P = 1$ atm, $V_{free}/V = (V_{sp}(T) - V_{hc:sp})/V_{sp}(T)$, using the model's hypothetical $V_{sp}(T)$ for the specified T and $P = 1$ atm and specific hardcore volume, $V_{hc:sp} = r\nu/M_w$. As noted above, even though the model's absolute values for $V_{sp}(T)$ and $V_{hc:sp} = r\nu/M_w$ are not accurate, as long as we are consistent in the calculations and apply both of these matching model quantities together, the ratio of V_{free} to total volume, the fractional free volume, will be accurate. As it turns out in our procedure here, it is the model's ε parameter that is expected to be fairly accurate, *i.e.* ε will turn out to be almost the same value whenever a full *PVT* data set is available for fitting.

Finally, as noted in the main article (caption of Table 1), the *PVT* data that we have available for PVME are for $P \geq 10$ MPa, and so we used the LCL EOS to fit this available *PVT* data and then predicted the *PVT*-based α_V value for the PVME melt at $P = 1$ atm. In the LCL fit, we chose *PVT* data in a temperature range of 44 to 110 °C, which is close to the same range as the ellipsometry data, and chose this data in a pressure range of 10 to 20 MPa, which are the data that are the closest to atmospheric pressure. The LCL parameters resulting from this fit are: $r/M_w = 129.72$ mol/kg, $\nu = 6.7347$ mL/mol, and $\varepsilon = -1856.9$ J/mol. Based on this characterization, LCL predicts that at $P = 1$ atm and $T = 75$ °C (\sim the midpoint of the ellipsometry data range) that the α_V value should be 6.70×10^{-4} °C⁻¹; this is the *PVT*-based

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α_V value that is listed for the PVME melt in Table 2 of the main article; we expect it to be very accurate given that the fitted data are fairly close to the T, P of the prediction.

S2. A Simple Thought Experiment to Explain the Connection Between α_V and α_N

To better understand the thermal expansion of a polymer when it is under the mechanical constraint of fixed area (due to the non-expanding substrate), we imagine breaking the overall process into two separate steps. This process is presented in the diagram in Figure S1. In the first step (1→2), a temperature increase (ΔT) is applied to a substance having an original height, h_1 , and an original area of $A_1 = L_{x1} \times L_{y1}$ and volume of $V_1 = A_1 h_1$. In this step, the substance is unrestricted so it expands in all three directions to attain its equilibrium volume at the new temperature. The volume change for this step, $\Delta V(1\rightarrow 2)$, is the same as the volume change that would be calculated knowing the material's volumetric coefficient of thermal expansion, *i.e.* $\Delta V(1\rightarrow 2) \approx V_1 \alpha_V \Delta T$. In this expansion, h , and the side lengths, L_x and L_y , *all* increase, and it makes sense that $\Delta V(1\rightarrow 2) \neq A \Delta h(1\rightarrow 2)$ because it would be neglecting the contributions from changes in L_x and L_y . Note that because the *relative* expansion is the same in each Cartesian direction, if one were to measure $\alpha_N = (1/h)dh/dT$ after this first step, then it would be equal to the material's coefficient of linear expansion, $\alpha_L = \alpha_V/3$. So far, this discussion (step 1→2) has involved an unrestricted sample, that could be either in a liquid-like (melt) or glassy state.

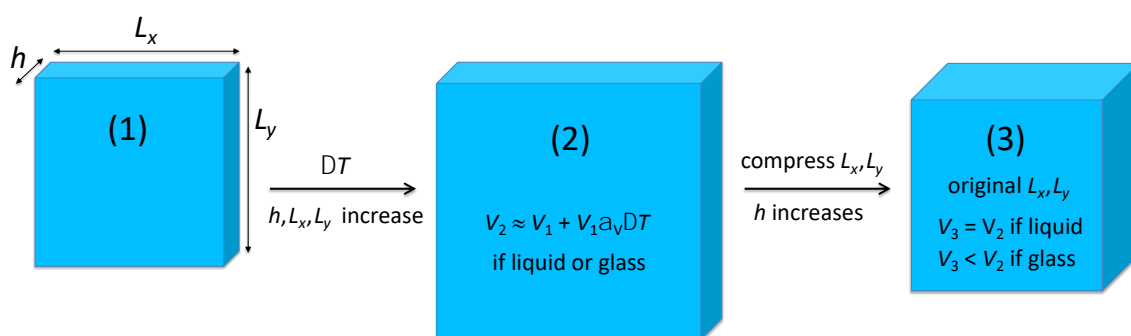


Fig. S1. Diagram of thermal expansion of a substance under the net mechanical restriction of constant area ($L_x \times L_y$), posed as a two-step process. In the first step, the temperature is increased and the sample expands freely where its lengths on all sides (h , L_x , L_y) increase while maintaining its original aspect ratio. (For simplicity we assume of course that if the sample in this first step were a low viscosity liquid, that it is not allowed to flow so freely that it takes on other arbitrary shapes.) In the second step, with T held fixed, the material's sides, L_x and L_y , are compressed until reaching their original values, while h is allowed to increase. The result of the second step will depend on whether the material is a polymer melt (liquid) or a glass. See text for discussion.

To capture the consequences of having a fixed area sample in an ellipsometry experiment, we move to the second step (2→3) of our thought experiment on the above sample: We stay at the final temperature and compress the material in the x and y directions (*i.e.* decrease L_x and L_y) to restore it to the original area, A_1 , but we still allow an unrestricted response in the material in the one remaining (normal) direction by permitting a further change in height, $\Delta h(2\rightarrow 3)$. This second step mimics the kind of process needed to measure the material's Poisson ratio, ν . (In an experiment where a material is stretched or compressed, ν is defined by the negative of the ratio of the lateral strain to the longitudinal strain.) Manipulating the sample to restore A back to its original value will cause h to

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increase further (*i.e.* $\Delta h(2 \rightarrow 3)$ is positive) as it aims to attain its preferred volume at that temperature. Here we must note an important difference between how solid (glass) and liquid films respond.

For a liquid or melt, the increase in height, $\Delta h(2 \rightarrow 3)$, will fully compensate for the compression in the other directions such that the overall volume change in the second step, $\Delta V(2 \rightarrow 3)$, will be zero. Therefore we have $\Delta V_{\text{net}} = \Delta V(1 \rightarrow 2) = A_1 \Delta h_{\text{net}} = A_1 [\Delta h(1 \rightarrow 2) + \Delta h(2 \rightarrow 3)]$. This means the net relative change in volume ($\Delta V_{\text{net}}/V_1$) will be the same as the net relative change in sample height ($\Delta h_{\text{net}}/h_1$), and so, the final apparent $\alpha_N \approx (1/h_1) \Delta h_{\text{net}}/\Delta T \approx (1/V_1) \Delta V_{\text{net}}/\Delta T$ would correspond to the same outcome as in the description of the melt (eq 1) in the main article, where we essentially concluded that $\alpha_N = \alpha_V (= 3\alpha_L)$.

On the other hand, for most solids, the volume change in this second step, $\Delta V(2 \rightarrow 3)$, will be negative. (This result is equivalently embodied in how most solids have a Poisson ratio of $\nu < 0.5$, while $\nu = 0.5$ would be required to maintain constant volume.) Even though a height change ($\Delta h(2 \rightarrow 3)$) is allowed in the second step, a solid will not change height enough to compensate for restoring the area via compression, which means that the net change, $\Delta h_{\text{net}} = [\Delta h(1 \rightarrow 2) + \Delta h(2 \rightarrow 3)]$ will fall short of what would be needed to account for the natural volume change ($\Delta V(1 \rightarrow 2)$) associated with the solid's α_V . In other words, $\Delta V_{\text{net}} = A_1 \Delta h_{\text{net}} < \Delta V(1 \rightarrow 2)$, and thus $\alpha_N \approx (1/h_1) \Delta h_{\text{net}}/\Delta T < \alpha_V$.

S3. Accounting for the temperature dependence of the refractive indices of the silicon substrate

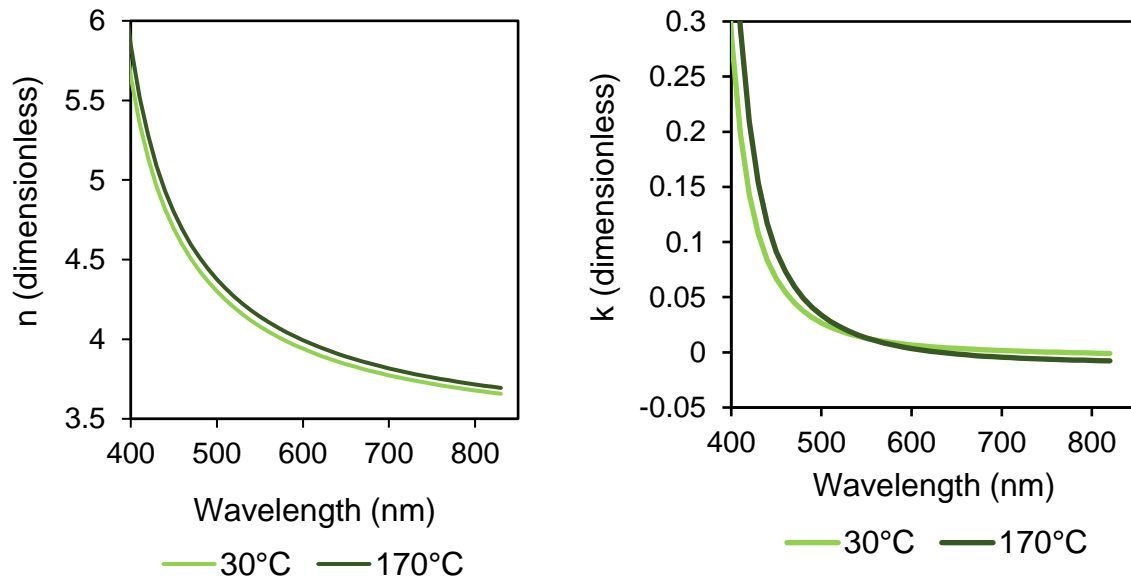


Figure S2. The temperature dependence of a) the refractive index (n) and b) extinction coefficient (k) of Si across the range of wavelengths used in our experiments. The two temperature values shown, 30 °C and 170 °C, correspond to the minimum and maximum temperatures studied. These are experimental values obtained from data in the commercial modelling software (WVASE, J.A. Woollam Co.).

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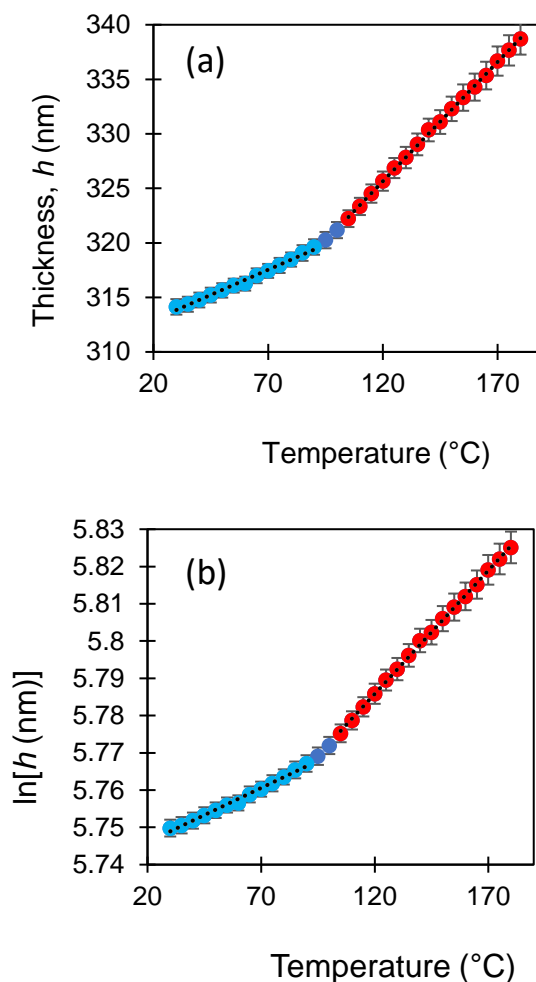


Figure S3. Thickness as a function of temperature plot for a thin film of PCHMA obtained from data analysis wherein the refractive index change of the substrate is not taken into account when fitting the model to the data. (a) Thickness on a linear axis. (b) Natural logarithm of thickness. The α_N for the glass region is $2.91 (\pm 0.080) \times 10^{-4} \text{ }^{\circ}\text{C}^{-1}$, whereas for the melt region α_N is $6.62 (\pm 0.042) \times 10^{-4} \text{ }^{\circ}\text{C}^{-1}$. The analysis of the same set of data using $\tilde{n}(T)$ is shown in Figure 3b.

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Table S1. Comparison of Coefficients of Thermal Expansion for Thin Films with and without Consideration of the Temperature-Dependent Refractive Index of Silicon

Polymer Acronym	Region	α_N found with T -dependent $\tilde{n}(\lambda)$ for Si [$\times 10^{-4} \text{ }^\circ\text{C}^{-1}$]	α_N found with $\tilde{n}(\lambda)$ for Si fixed at $T = 30 \text{ }^\circ\text{C}$ [$\times 10^{-4} \text{ }^\circ\text{C}^{-1}$]
PS	Melt	5.54	7.02
PBMA	Melt	5.54	8.45
PVME	Melt	5.63	5.96
PMMA	Melt	5.33	6.09
P α MS	Melt	4.54	8.32
PCHMA	Melt	5.49	6.62
PCHMA	Glass	1.86	2.91
TMPC	Glass	2.13	3.57