Supplementary Information for

The dynamics of freestanding films: predictions for poly(2-chlorostyrene) based on bulk pressure dependence and thoughtful sample averaging

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LCL Equation of State Application to Bulk Poly(2-chlorostyrene): *PVT* Data Fitting for Free Volume Analysis and Modeling of the Local Density Profile

In order to obtain free volume values, $V_{\text{free}}(T,P) = V(T,P) - V_{\text{hc}}$, for application in the Cooperative Free Volume (CFV) rate model's $\tau(T,V_{\text{free}})$ expression, we first analyze the system's pressure, volume, temperature (*PVT*) data using the Locally Correlated Lattice (LCL) equation of state (EOS)[1] to obtain V_{hc}, the system's limiting volume at close packing. The LCL EOS expression is given by

$$\frac{P}{k_{\text{B}}T} = \left(\frac{1}{v}\right)\ln\left[\frac{V}{V - N_{\text{m}}rv}\right] + \left(\frac{3}{v}\right)\ln\left[\frac{V - (N_{\text{m}}v/3)(r-1)}{V}\right]$$
$$-\left(\frac{3}{v}\right)\left(\frac{(2r+1)^2}{(V/N_{\text{m}}v) - (1/3)(r-1)}\right) \times \left(\frac{\exp[-\varepsilon/k_{\text{B}}T] - 1}{(1/3)(2r+1)\exp[-\varepsilon/k_{\text{B}}T] + (V/N_{\text{m}}v) - r}\right) \tag{S1}$$

k_{B} is the Boltzmann constant and N_{m} is the number of molecules. In practice, the pressure (P) is calculated as a function of two independent variables: temperature (T), and either the volume per molecule (V/N_{m}), or the volume per mass ($V/(N_{\text{m}}M_{\text{w}})$) given the molecular weight (M_{w}).) The molecular parameters are: r, the number of segments (occupied lattice sites) per molecule, v, the volume per lattice site, and ε, the segment-segment nonbonded interaction energy. The r,v,ε values are obtained by fitting Eqn S1 to *PVT* data, and this then leads to the characteristic volume at close-packing, which is given by $V_{\text{hc}} = N_{\text{m}}rv$, or equivalently in volume per gram, $V_{\text{hc}} = rv/M_{\text{w}}$ where M_{w} is the molecular weight in g/mol and where v is in volume per mol.

We use PVT data for P2ClS (M_w = 58,000 g/mol) from Roland et al.[2] and fit in a range of T = 403 to 463K and P = 0 to 100 MPa, and obtain fitted parameter values of r = 5361, v = 7.930 mL/mol, and $\varepsilon = -2244$ J/mol; this leads to V_{hc} = 0.7330 mL/g. In our procedure (see for example refs [3–6]), when we apply this value of V_{hc} to calculate free volumes, $V_{\mathrm{free}}(T,P) = V(T,P) - V_{\mathrm{hc}}$, at each T,P point (e.g. at a chosen dynamics T,P data point), we use the LCL EOS $V(T,P)$ value calculated at that T,P. At T,P values in or near the fitting range, the difference between the theoretical LCL volume and the actual experimental volume (if available) would of course be very small and so the caution is irrelevant, but when working outside the fitting range (where LCL volumes may start to differ somewhat from experiment), it is best to stay consistent, using the model's theoretical $V(T,P)$ together with its corresponding model V_{hc}.

The LCL EOS, in combination with the square gradient approximation,[7–9] was also applied to calculate the local density profile for the P2ClS free surface based on the above characterization of the P2ClS PVT behavior. Here the Helmholtz free energy density at a given position, z, near the free surface is given by $a(\rho(z)) = a_0(\rho(z)) + \kappa(\nabla\rho(z))^2$. $a_0(\rho(z))$ is the homogenous contribution, and $\kappa(\nabla\rho(z))^2$ is the gradient term (with parameter κ) that accounts for the inhomogeneous contribution coming from the locally varying density. The LCL EOS is used to calculate $a_0(\rho(z))$ for the given ρ value. Given a value for the parameter κ, the surface tension, σ, and local density profile, $\rho(z)$, can then be calculated by integrations carried out over the variable, ρ; see for example the details described in refs [7–9].

Here for P2ClS, we first fit the value of κ such that it leads to agreement with the experimental surface tension, and once this κ value is obtained we then use it to calculate the corresponding P2ClS density profile, as shown for example in Fig. 3 in the main article (for T = 425 K). The experimental surface tension for P2ClS was approximated based on values for polymer critical surface tension that have been tabulated in Lee.[10] The value for P2ClS (42 mN/m) is found to be somewhat higher than that for PS (36 mN/m), an observation that correlates with the former having a somewhat higher cohesive energy and T_g value. The critical surface tension (measured using solvent contact angles) is typically similar to, but still distinct from, the surface tension measured on the melt e.g. by the pendant drop technique. Therefore we obtained an estimate of latter for P2ClS by taking the available experimental PS surface tension (30.6 mN/m at $T = 433\text{K}$)[11] and scaling it by the ratio of the P2ClS to PS critical surface tension (42/36) which thus gives the approximate P2ClS surface tension of about 35.7 mN/m at 433K which is the value that was used to obtain κ.

References

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