Tightly-Bound PMMA on Silica Has Reduced Heat Capacities

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SUPPORTING INFORMATION



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S1. Additional Modeling Information

In order to understand the dependence of the heat capacity data on adsorbed amount, the models used are briefly recapped here. We first look at the mixture, two-state, and integral gradient models. In addition, the development of the gradient model with a zero intercept and a non-integral (exponential) gradient model are compared with the models used. Where possible, we have kept the equations (and numbers) the same as in the manuscript. Equations not included in the main text are preceded by S. A glossary of terms is appended to the end of this document.

Mixture Model

As described in the manuscript, the heat capacity of the composite material from the mixture model is simply the mass fraction averaged heat capacities of the bulk components or

$$C_{P(composite)} = M_P C_{PP} + M_S C_{PS}$$
(1a)

Therefore, the heat capacity of the adsorbed polymer alone is simply a constant, equal to its bulk value or, $C_{p(polymer)} = C_{pp}$. By subtracting off the contribution of the silica, we can estimate the $C_{p(polymer)}$ as:

$$(C_{P(composite)} - M_S C_{PS})/M_P = C_{P(polymer)}$$
 (1b)

The heat capacity of the polymer is then a straight line in the fits.

Two-state Model

In the two-state model, the heat capacity at a given adsorbed amount is the mass-weighted sum of the tightly-bound polymer plus that of loosely-bound polymer. For adsorbed amounts greater than $m_B^{"}$, the heat capacity of the composite becomes

$$C_{P(composite)} = M_P C_{PP} \frac{(A - m_B^{"})}{A} + f M_P C_{PP} \frac{m_B^{"}}{A} + M_S C_{PS} \text{ (for } A \ge m_B^{"}) \quad (2a)$$

For the polymer alone, subtraction of the silica contribution yields,

$$C_{P(polymer)} = \frac{\left(C_{P(composite)} - M_{S}C_{PS}\right)}{\binom{(A - m_{B}^{"})}{A} + fC_{pp}\frac{m_{B}^{"}}{A}} \quad \text{(for } A \ge m_{B}^{"}\text{)} \tag{2b}$$

where $C_{p(polymer)}$ represents the heat capacity of just the polymer in the sample (the silica contribution is subtracted out).

When the amount of polymer is less than $m_B^{"}$

$$C_{P(composite)} = f M_P C_{PP} + M_S C_{PS} \quad \text{(for } A \le m_B^{"}\text{)}$$
(3a)

where again, subtraction of the silica contribution yields, for the polymer,

$$C_{P(polymer)} = \frac{(C_{P(composite)} - M_S C_{PS})}{C_{PP} (\text{for } A \le m_B^{"})}$$
(3b)

In this model, the fraction of the bulk heat capacity, f, and the amount of the tightly-bound polymer, $m_B^{"}$ are fitted parameters. The model has a flat portion as it treats all of the tightly-bound polymer, $A \le m_B^{"}$, as having a fixed heat capacity.

Layered (Integral) Gradient Model

As described in the text, the integral gradient model is one where the initial heat capacity of the polymer closest to the surface adsorbed has a heat capacity of fC_{pp} and the polymer eventually reaches the bulk value with an exponential growth function with constant, *a* or:

$$C_{P(polymer)} = \left(\frac{1}{A}\right) \int_{0}^{A} \left[fC_{PP} + (1-f)C_{PP} \left(1 - e^{-\frac{A'}{a}}\right) \right] dt$$
$$= C_{PP} + \frac{a(1-f)C_{PP}}{A} \left(e^{-\frac{A}{a}} - 1\right)$$
(4)

Here, the term in square brackets represents the exponential dependence of the heat capacity with adsorbed amount. The heat capacity of any given "layer" is added (integration) to yield the overall heat capacity at any adsorbed amount.

(Simple) Gradient (Exponential) Model

The "simple" exponential fit is simply the exponential in the square brackets in Equation 4 above. While the integral gradient fit assigns a heat capacity to each layer of the adsorbed polymer, the simple exponential effectively treats the whole adsorbed polymer at any adsorbed amount as having a single C_p which increases with the exponential growth function or

$$\mathcal{C}_{P(polymer)} = f\mathcal{C}_{PP} + (1-f)\mathcal{C}_{PP}\left(1-e^{-\frac{A}{a}}\right) (S5)$$

While this equation is fitted in a manner similar to the layered exponential model, the fits result in different values of the parameters.

Zero-Intercept Gradient Model

The zero-intercept gradient model is the same as the layered gradient model except that it starts with the intercept (at A = 0) as $C_{p(polymer)} = 0$. This is Equation 4 without the initial C_{pp} terms and f = 0, or

$$C_{P(polymer)} = \frac{a C_{PP}}{A} \left(e^{-\frac{A}{a}} - 1 \right)$$
(S6)

The implication of this model is that the polymer nearest to the surface has zero heat capacity increasing exponentially to its bulk value, C_{pp} .

If the nearest polymer adsorbed lies very flat on the surface, it is tempting to rationalize zero heat capacity for it, however, it is unlikely that the polymer configurations on the surface would be very flat.¹ In contrast, the nearest polymer adsorbed may have AA 'more of a random coil configuration.^{1,2} Thus, the heat capacity of isolated, adsorbed polymers should be non-zero. In addition, other modes of energy storage, such as vibrational modes make the $C_{p(polymer)}$ nonzero even if the backbone motions are frozen out.³

Comprehensive Data and Modeling Results

In Figure S1, the heat capacity data at 40 °C is shown as a function of adsorbed amount along with the fits for each of the five models discussed here. Similar results were found at other temperatures. The layered gradient model fits almost all of the data better than the others. It also seems to be the most physically correct of the models proposed. For example, it seems unphysical that the polymer closest to the surface would be completely immobile, nor have any transition. On the contrary, the opposite was found from heat flow curves.^{4,5}



Figure S1. Heat capacities of the adsorbed polymer alone $C_{p(polymer)}$, (calculated by subtracting the heat capacity of the silica from total heat capacity) adsorbed on the surface at different adsorbed amounts showing predictions from the mixture (- • - •), two-state (- - -), layered gradient (---), simple exponential (•••), and zero-intercept exponential (---) models at 40° C.

S2. Fittings of the heat capacity data for polymer alone, $C_{p(polymer)}$ below bulk glass transition temperature (T_{g})

The fittings of the heat capacities of the polymers alone adsorbed on silica surface with two-state model and gradient model at temperatures the below bulk glass transition temperature, T_g (bulk), from 40 to 100 °C, are shown in Figure S2.

The heat capacities of adsorbed polymers were compared with the bulk heat capacity, dot-dashed line

on the top of the figures. In the paper, we have described the fittings of the heat capacities of polymers adsorbed on the surface at 50 °C (Figure 5), as a representative of fittings well below bulk glass transition. In this section, fittings at other temperatures below bulk T_g (40 – 100 °C) are shown.

From these figures, it is clear to see that the layered gradient model fits the data better at the smaller adsorbed amount range for all of the temperatures studied. Not all of the models are shown in these figures.







Figure S2. Heat capacities of adsorbed polymers alone at different adsorbed amounts showing the predictions from: two-state (---) and layered gradient model (—) at different temperatures starting from a) 40 °C every 10 degrees to g) 100 °C. The top line (----) shows the heat capacity of the bulk polymer (for comparison with that of adsorbed polymer).

S3. Fittings of the heat capacity data for polymer alone near the bulk glass transition temperature (T_g)

Similar fittings at other temperatures around bulk T_g are shown in Figure S3. In the paper, we have described the fittings at 120 °C in detail (Figure 5). The rest of the fittings from 110 - 140 °C are provided in this section.





Figure S3. Heat capacities of adsorbed polymers alone at different adsorbed amounts showing the predictions from: two-state (---) and layered gradient model (—) at different temperatures starting from h) 110 °C every 10 degrees to k) 140 °C. The top line (---) shows the heat capacity of the bulk polymer (for comparison with that of adsorbed polymer).

S4. Fittings of the heat capacity data for polymer alone above bulk glass transition temperature

Similar fittings at other temperatures well above bulk $T_{\rm g}$ are shown in Figure S4. In the paper, we have described the fittings at 200 °C in detail. The rest of the fittings from 170 - 200 °C are provided in this section. At all temperatures, the heat capacity of the adsorbed polymer was less than that of the bulk suggesting that adsorption of polymer on the surface adsorbed amounts.



2.5

2.0

1.5

1.0

170 °C

0



Figure S4. Heat capacities of adsorbed polymers alone at different adsorbed amounts showing the predictions from: two-state (---) and layered gradient model (—) at different temperatures starting from l) 150 °C every 10 degrees to q) 200 °C. The top line (- $\cdot - \cdot$) shows the heat capacity of the bulk polymer (for comparison with that of adsorbed polymer).

Glossary of Symbols

A total adsorbed amount of polymer in mg polymer $/m^2$ silica

a the exponential growth parameter in which the heat capacity of the adsorbed polymer approaches that of the polymer in mg/m²

 $C_{\rm pp}$ specific heat capacity of the bulk polymer in J/(g K)

 C'_{pp} specific heat capacity of the tightly-bound polymer in J/(g K) for the two-state model, = $f C_{PP}$

 $C_{p(polymer)}$ specific heat capacity of the adsorbed polymer alone in J/(g K)

 $C_{p(composite)}$ specific heat capacity of the composite material (polymer plus silica) in J/(g K)

f (in two-state model) fractional heat capacity of tightly-bound polymer

f (in layered gradient model) fractional heat capacity of the polymer adsorbed closest to the surface

 $M_{\rm p}$ mass fraction of polymer in a particular sample (total of tightly and loosely)

 $M_{\rm S}$ mass fraction of silica in a particular sample

 m_B amount of tightly bound polymer in mg/m²

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