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Thermodynamic Study of a Novel Surface Ordered Phase above the Bulk Melting Temperature in Alkyl Side Chain Acrylate Polymers

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Surfaces of most liquids in contact with air have higher entropy and lower melting temperature T_s than the bulk.[1] However, materials consisting of linear alkyl chains such as n-alkanes and alcohols exhibit surface freezing, where the surfaces remain ordered 1−3 K above the bulk melting temperature (T_m).[2−4] Interestingly, chemical attachment of linear alkanes to a polymeric backbone (poly(n-alkyl acrylates)) dramatically increases the temperature window where the ordered phase exists ($\Delta T = (T_s - T_m) \approx 9-20$ K). In fact, surface sensitive infrared-visible sum frequency generation spectroscopy and X-ray scattering show the presence of two distinct surface transitions.[5,6] One (T_{s1}) associated with crystalline to smectic-like phase and the other (T_{s2}) from smectic-like to disordered liquid phase. Why these side chain polymers show enhanced temperature range of surface order in comparison to small molecule alkanes and alcohols is not understood. Intuitively, this could be attributed to lower entropy due to chemical attachment of the side chains to the polymer backbone (loss of positional entropy). Here, we report the first surface tension measurements of side chain acrylate polymers as a function of temperature to measure the thermodynamic parameters of this ordered surface phase. Surprisingly, it is not the positional entropy but partial crystallinity that controls the magnitude of ΔT. These results offer interesting possibilities to control the surface properties by altering the linker groups that attach these hydrocarbon chains to the polymer backbone for applications in the areas of smart adhesives and release coatings.[7,8]

Table 1. Transition Temperatures, ΔT, and $\Delta\gamma$ for Poly(n-alkyl acrylates)

polymer (length, n)	T_m heat, K	T_f cool, K	T_{s2}, K	ΔT heat, K	$\Delta\gamma$ heat, mNm^{-1}
16	308.2	304.7	320.0	11.8	4.6
18	320.7	317.2	329.8	9.1	5.1
22	336.5	333.5	336.5	7.5	6.6

Poly(n-alkyl acrylates) were obtained from Landec Corporation and were used as received. The polydispersity of these polymers were broad (10−20) due to melt polymerization process. Measurements on narrower polydisperse samples (≈3) showed similar results. Also the results were consistent with poly(n-alkyl acrylates) prepared by transesterification of poly(*tert*-butyl acrylate) having polydispersity of 1.12 with an alcohol of an appropriate chain length.[5] Differential scanning calorimetry (DSC) performed at a heating rate of 0.5 K/min showed a sharp melting transition and diffuse freezing transition for side chain length, $n = 16$, 18, and 22 (see Supporting Information). The bulk transition temperatures (T_m and T_f), enthalpy (in this paper enthalpy is assumed to be equivalent to energy because of negligible contribution of pdV, $\Delta\epsilon_b$), and entropy ΔS_b of melting are shown in Tables 1 and 2. The suffix b corresponds to bulk. $\Delta\epsilon_b$ and ΔS_b are reported for the heating cycle rather than the cooling cycle because of the sharp melting transition. The surface tension was measured with a thin platinum wire of nominal diameter 0.5 mm attached to Wilhelmy Cahn 2000 microbalance. The actual diameter of the wire (0.53 mm) was calibrated using heptane. The error in absolute surface tension measurements is ± 0.5 mN m^{-1}. The cell temperature was changed in steps of 0.2 K at the rate of 0.1 K/min and the data recorded after 10 min to ensure thermal equilibrium. Platinum probe and the sample were

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Table 2. Changes in Entropy and Energy during Heating Cycle for Poly(*n*-alkyl acrylates)[a]

polymer	ΔS_b	$\Delta(\mathrm{d}\gamma/\mathrm{d}T)$	$(\mathrm{d}\gamma/\mathrm{d}T)_{T<T_{s2}}$	$\Delta\epsilon_b$	$\Delta\epsilon_s$
16	0.51	0.59	0.46	160	190
18	0.64	0.68	0.57	210	220
22	0.88	0.98	0.89	300	340

[a] $\Delta\epsilon_s$ (mJ m^{-2}) is calculated as described in the text. $\Delta\epsilon_b$ in units of mJ m^{-2} and ΔS_b in units of mJ m^{-2} K^{-1} are calculated from the corresponding DSC values by assuming 20.4 Å^2/side chain.[6] $\Delta(\mathrm{d}\gamma/\mathrm{d}T)$ and $(\mathrm{d}\gamma/\mathrm{d}T)_{T<T_{s2}}$ have units of mN m^{-1} K^{-1}.

enclosed in a temperature-regulated cell to ensure that the probe and the polymer melt were at the same temperature. The temperature was regulated with a relative accuracy of 0.025 K. The absolute temperature was calibrated using the melting point of different chain length alkanes.

Measurements of surface tension, γ, during the heating and cooling cycles for $n = 16$, 18, and 22 are shown in Figure 1. The T_m and bulk freezing temperatures (T_f) measured using DSC are shown as dotted lines in Figure 1. The bulk T_f values are lower than those determined from surface tension due to the presence of the platinum wire as a potential nucleation site. Henceforth, we have used only the data from the heating cycle in the rest of the paper. Since $\mathrm{d}\gamma/\mathrm{d}T = -(S_s\text{-}S_b)$ (where S_s and S_b are the entropy of the surface and the bulk, respectively), the increase in γ with increase in temperature below T_{s2} indicates that the surface molecules have lower entropy than in the bulk. This is opposite of what has been reported for polymer melts.[9] The abrupt change in $\mathrm{d}\gamma/\mathrm{d}T$ at T_{s2} indicates a first-order transition from an ordered to a disordered surface layer.[2] There is also a small hysteresis at T_{s2} in cooling and heating cycle. As no bulk transition is expected at T_{s2}, the difference in $\mathrm{d}\gamma/\mathrm{d}T$ before and after T_{s2} ($\Delta(\mathrm{d}\gamma/\mathrm{d}T)$) is the difference in entropy between disordered and ordered surface layer (Table 2). Surprisingly, there is no change in the slope near the expected transition at T_{s1}, suggesting that the excess surface energy per unit area and entropy is similar for the surface crystalline and smectic-like surface phases. The significance of this result will be discussed in a future publication and here we concentrate on the transition observed at T_{s2}.

The difference in energy between the ordered and disordered surface layer (change in excess surface energy, $\Delta\epsilon_s$) can be calculated as follows:[10]

$$\Delta\epsilon_s = \Delta\gamma - [T_{s2}(\mathrm{d}\gamma/\mathrm{dT})_{T>T_{s2}} - \mathrm{T_m}(\mathrm{d}\gamma/\mathrm{dT})_{T<T_{s2}}] \quad (1)$$

where $\Delta\gamma = (\gamma_{T_{s2}} - \gamma_{T_m})$. We assume that the difference in heat capacity between the surface and the bulk is negligible. On plugging the appropriate quantities from Tables 1 and *2* for poly(behenyl acrylate), $\Delta\epsilon_s$ is found to be 340 mJm^{-2}, which is in good agreement with $\Delta\epsilon_b$ (Table 2). Data also show a good match between $\Delta(\mathrm{d}\gamma/\mathrm{d}T)$ and ΔS_b (Table 2). The values of ΔT for poly(*n*-alkyl acrylates) increase with decreasing side chain length even though $\Delta\gamma$ decreases with decrease in side chain length (Table 1). This can be attributed to the relative large drop in $(\mathrm{d}\gamma/\mathrm{d}T)_{T<T_{s2}}$ compared to the drop in $\Delta\gamma$ with decrease in side chain length, leading to the increase in $(\Delta\gamma/(\mathrm{d}\gamma/\mathrm{d}T)_{T<T_{s2}})$.

When compared to docosane ($\Delta\gamma \approx 3.8$ mN m^{-1} and $(\mathrm{d}\gamma/\mathrm{d}T)_{T<T_s} = 1.20$ mN m^{-1} K^{-1}),[3] $\Delta\gamma$ is higher and $(\mathrm{d}\gamma/\mathrm{d}T)_{T<T_{s2}}$ is lower for poly(behenyl acrylate), leading to approximately thrice the value of ΔT for poly(behenyl acrylate) than ΔT for docosane. Assuming the dominant missing interaction for the top methyl groups on the surface with the bulk is given by van der Waals interactions, then the excess free energy at T_m varies as $1/d^2$, where d is the layer spacing.[2] The layer spacing in poly(*n*-alkyl acrylates) is larger than the corresponding alkane because of the additional length of the bridging group.[6] This suggests a lower surface tension at T_m and hence higher $\Delta\gamma$ for poly(*n*-alkyl acrylates).

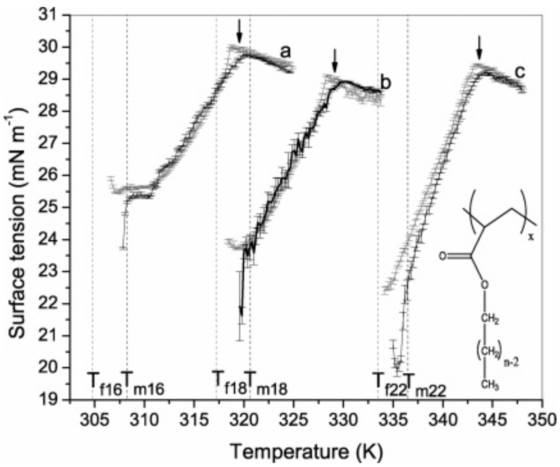

Figure 1. Temperature dependence of surface tension for poly(*n*-alkyl acrylates): (a) poly(hexadecyl acrylate) ($n = 16$), (b) poly(octadecyl acrylate) ($n = 18$), and (c) poly(behenyl acrylate) ($n = 22$). The chemical structure of poly(*n*-alkyl acrylates) is shown in the inset. The gray and black symbols are for cooling and heating cycles, respectively. The arrows indicate the surface transition temperature, T_{s2}.

Table 3. Values of *x*, ΔS_{pos} (mN m^{-1} K^{-1}) and Differences in ($\mathrm{d}\gamma/\mathrm{d}T$) between Alkanes (Ocko et al.[3]) and Correponding Poly(*n*-alkyl acrylates) (mN m^{-1} K^{-1})

polymer	x	ΔS_{pos}	$(\mathrm{d}\gamma/\mathrm{d}T)_{alk} - (\mathrm{d}\gamma/\mathrm{d}T)_{poly}$
16	0.47	0.07	0.35
18	0.54	0.08	0.34
22	0.66	0.09	0.31

The reasons for smaller values of $(\mathrm{d}\gamma/\mathrm{d}T)_{T<T_{s2}}$ for poly(*n*-alkyl acrylates) in comparison to alkanes is puzzling. The difference in $\Delta\epsilon_s$ between poly(*n*-alkyl acrylates) and alkanes can be attributed to partial crystallinity. This can be due to only a fraction of side chains crystallizing or only a fraction of methylene units within the side chain participating in the crystallinity. On the basis of our grazing incidence X-ray diffraction results[6] we believe that this is predominantly due to partial crystallinity within the side chains. The same conclusion was also reached for bulk crystallization by Jordan et al.[11] This partial involvement of side chain in surface ordered phase implies that $(\mathrm{d}\gamma/\mathrm{d}T)_{T<T_{s2}}$ for poly(*n*-alkyl acrylates) is lower than alkanes. Let us define x as the fraction of methylene units that crystallize and equal to $\Delta\epsilon_{b,acrylate}/\Delta\epsilon_{b,alkane}$.[12] One can then write

$$\mathrm{T}_{\mathrm{m},acrylate} = \left(\frac{x\Delta\epsilon_{b,alkane}}{x(\Delta \mathrm{S}_{b,alkane} - \Delta \mathrm{S}_{pos})}\right) \quad (2)$$

ΔS_{pos} is the additional change in entropy in alkanes due to positional freedom above T_s.

On substituting T_m for poly(*n*-alkyl acrylates) from Table 1, $\Delta\epsilon_{b,alkanes}$ and $\Delta S_{b,alkanes}$ from Ocko et al.,[3] and $\Delta\epsilon_{b,acrylate}$ from Table 2, we calculate x and ΔS_{pos} as a function of chain length (Table 3). The values of ΔS_{pos} are small compared to the difference between $(\mathrm{d}\gamma/\mathrm{d}T)_{T<T_{s2}}$ for poly(*n*-alkyl acrylates) and corresponding

alkanes. Surprisingly, this indicates that the dominant factor in reducing $(\mathrm{d}\gamma/\mathrm{d}T)_{T<T_{s2}}$ for poly(*n*-alkyl acrylates) is partial side chain crystallinity. Furthermore, the decrease in $(\mathrm{d}\gamma/\mathrm{d}T)_{T<T_{s2}}$ with decrease in chain length is also attributed to decrease in ratio x.

In summary, we present the first surface tension data as a function of temperature for poly(*n*-alkyl acrylates). The sharp change in slope of surface tension above T_m is associated with the presence of ordered alkyl side chains at the air surface. The temperature window where the ordered phase exist is much higher than small molecule alkanes and is primarily due to partial crystallinity within the side chains. The consequences of these results have important implications in similar systems containing chemically attached hydrophobic side chains such as surfactants, dendrimers and biomolecules.

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Supporting Information Available: A figure showing DSC melting and crystallization plots for poly(*n*-alkyl acrylates). This material is available free of charge via the Internet at http://pubs.acs.org.

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