

5-30-2003

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Recommended Citation

Gautam, Keshav S.; Kumar, Satyendra; Wermeille, Didier; Robinson, Doug; and Dhinojwala, Ali, "Observation of Novel Liquid-Crystalline Phase Above the Bulk-Melting Temperature" (2003). *College of Polymer Science and Polymer Engineering*. 25.

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Observation of Novel Liquid-Crystalline Phase above the Bulk-Melting Temperature

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(Received 15 November 2002; published 27 May 2003)

In this paper, we show that a noncrystalline but ordered smectic-like phase exists above the bulk-melting temperature (T_m) at poly(*n*-alkyl acrylates)-air interface. The surface ordered phase is one monolayer thick and undergoes a sharp transition from order to disorder 10 °C above T_m for $n = 22$. The presence of a surface phase that does not exist in the bulk has important implications in the design of thermally responsive adhesives.

DOI: 10.1103/PhysRevLett.90.215501

PACS numbers: 61.41.+e, 61.10.Eq, 61.10.Kw, 61.30.Hn

It has been known for some time that the surfaces melt before the bulk-melting temperatures (T_m) [1,2]. Exceptions include small molecule alkanes and alcohols [3–5], where a crystalline layer is formed (1–3) °C before the bulk crystallization temperature. It has been shown recently that, when short alkyl chains are chemically linked to a flexible polymer backbone, the surface order-to-disorder transition takes place in two steps [6]. These measurements were done using surface sensitive sum-frequency generation (SFG) spectroscopy where the SFG intensity is proportional to the orientation of alkyl side chains. The first transition is at (1–2) °C above T_m , followed by a second transition at (10–20) °C above T_m (depending on the size of the side chain). This result is reminiscent of a two-step transition from a crystalline order to isotropic liquid state via a hexatic smectic liquid-crystalline phase predicted for 2D melting [7]. Although the SFG measurements were intriguing, they were unable to establish the nature of these transitions at comb polymer-air interfaces.

Here, we unequivocally present evidence that the first transition is associated with the melting of surface alkyl chains to an ordered monolayer (1–2) °C above T_m . The evidence is based on results of grazing incidence x-ray diffraction (GIXD), x-ray reflectometry (XR), and SFG measurements. The ordered monolayer, consisting of predominantly all trans-alkyl chains, undergoes a second transition 10 °C above T_m for $n = 22$. Interestingly, both these transitions occur above bulk T_m , unlike the predictions from 2D melting. Comb polymers containing hydrophobic side chains are commonly coated on the backside of an adhesive tape so that the tape can be peeled off the roll easily. Understanding the surface structure and transition temperatures is relevant in the development of thermally surface-responsive materials [8–11].

The poly(*n*-alkyl acrylate) comb polymers of different alkyl side chain lengths were synthesized by transesterification of poly(*t*-butyl acrylate) with an alcohol of ap-

propriate chain length. Here, we primarily discuss the results for the comb polymer with twenty-one methylene and one-methyl unit side chains ($n = 22$). The bulk-melting and crystallization temperatures are 64.9 °C and 60.8 °C measured using differential scanning calorimetry (DSC) at heating and cooling rates of 0.3 °C/min. Below T_m , wide-angle x-ray diffraction measurements show two peaks: the first one associated with lateral crystalline packing of alkyl side chains with d spacing of 4.2 Å, and the second peak due to longitudinal two-layer packing of alkyl side chains at 44 Å [12]. The samples for surface measurements were prepared by spin coating a 2–4 wt % polymer solution in toluene on glass substrates followed by annealing at (10–20) °C above T_m in a vacuum oven for 4–5 h.

The GIXD and XR measurements were performed at the Advanced Photon Source (MuCAT sector) at the Argonne National Laboratory using a synchrotron x-ray beam of $\lambda = 0.7684$ Å. The glancing angle scattering geometry is shown in Fig. 1(a). The wave vectors for the incident, reflected, and scattered waves are represented as k_i , k_r , and k_f , respectively. The scattered diffraction beam was imaged using an image plate detector (resolution of 150 $\mu\text{m}/\text{pixel}$). For incident angle $\alpha_i < \alpha_c$ (critical angle for total reflection) the scattering depth, from where the diffraction pattern originates, is 40–80 Å and the scattering from the bulk is suppressed in this geometry [2]. XR measurements were performed in the specular condition, $\alpha_i = \alpha_r$, where the x-ray intensity is monitored as a function of α . Uniform layers with thickness D result in the periodic variation in the intensity of the reflected beam, also known as Kiessig fringes. The period of the modulation gives the layer thickness, $\Delta q_z = 2\pi/D$.

Figure 1(b) shows the GIXD results at 60 °C (below T_m) at an incident angle of $\alpha_i = 0.5\alpha_c$. The presence of a crystalline surface layer is evident from the two bright equatorial bands. An expanded view of this region is shown in Fig. 1(c). The disappearance of this band

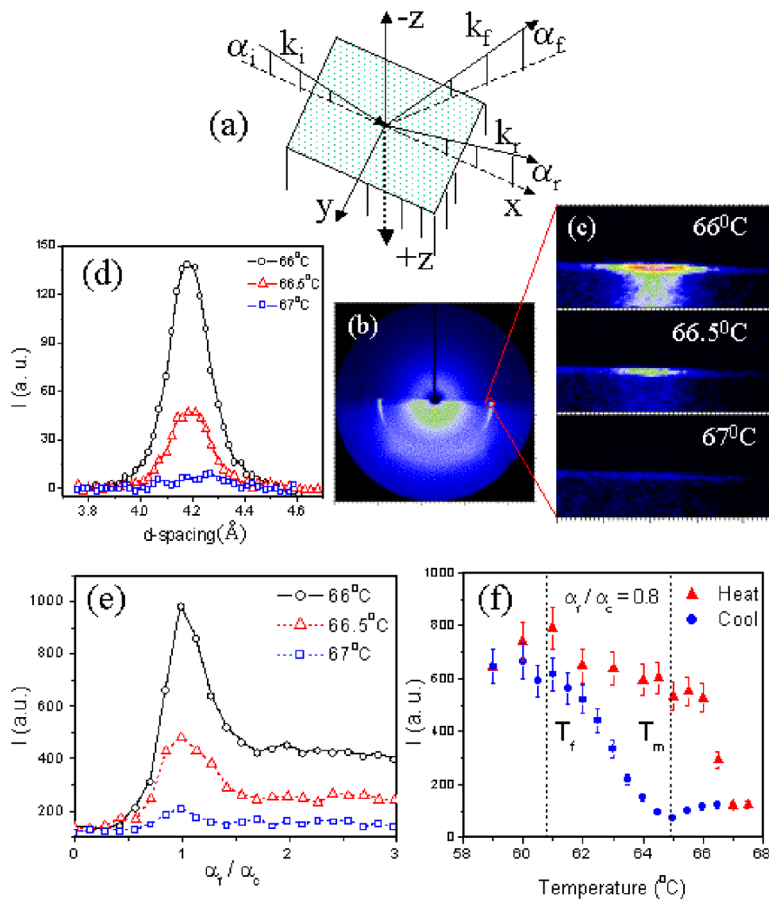


FIG. 1 (color online). (a) Schematic geometry of the GIXD experimental setup. (b) Image of the diffraction patterns on the plate detector at 60 °C. Since the x-ray beam is cut into half during the alignment procedure for grazing incidence measurements, only half of the plate detector is illuminated. (c) Expanded views of the diffraction patterns obtained above the bulk-melting temperature T_m (64.9 °C). (d) X-ray intensity as a function of d spacings obtained from the diffraction patterns shown in Fig. 2(c). (e) X-ray intensity as a function of α_f/α_c obtained from the diffraction patterns in Fig. 2(c). (f) X-ray intensity as a function of temperature at a fixed value of $\alpha_f/\alpha_c = 0.8$ in the heating (triangles) and cooling (circles) cycles. The dashed lines are bulk transition temperatures measured using DSC at a heating and a cooling rate of 0.3 °C/min.

at 66.5 °C (1.6 °C above bulk melting) indicates melting of surface alkyl chains. The in-plane orientation is determined from the position of the diffracted peak in the radial direction. The diffraction from a silicon powder was used to calibrate the distance from the sample and the position of the center of the beam. The x-ray intensity as a function of calculated d spacings is plotted in Fig. 1(d). Since the region next to the equator is most sensitive to the interface, we have plotted only the intensity very close to the equator in Fig. 1(d) (corresponding to $\alpha_f \sim 0$). The position of the peak corresponds to a lattice spacing of 4.2 Å. Assuming hexagonal packing, this corresponds to a side chain-chain spacing of 4.85 Å and the area per side chain of 20.4 Å²/chain. These numbers are consistent with the orientation of side chains parallel to the surface normal [6]. The in-plane lattice spacing is similar to its value in the bulk, indicating that the chain packing at the surface is similar to that in the bulk. Upon heating, the peak intensity decreases sharply indicating melting of the surface chains.

The melting transition can be quantified by plotting the GIXD intensity as a function of α_f/α_c as shown in Fig. 1(e). The presence of a peak at $\alpha_f/\alpha_c = 1$ is consistent with the theoretical prediction based on distorted wave born approximation [13]. In this geometry, the scattering depth is a function of both α_f/α_c and α_i/α_c . For $\alpha_i/\alpha_c = 0.5$ and $\alpha_f/\alpha_c < 1$ the scattering depth is ~ 40 Å for this hydrocarbon system. The sharp peak in Fig. 1(e) is superimposed on top of a second broad peak that has a maximum intensity centered close to $\alpha_f = 0$. This indicates that the crystallized alkyl chains are oriented normal to the surface and has been discussed in detail for alkanes and alcohols in Refs. [4,5]. The orientation of the alkyl chain normal to the surface is also consistent with the SFG measurements [6]. Interestingly, the intensity of the broadband peak does not drop off as rapidly as expected based on the length of the alkyl side chain. This indicates that not all methylene units are crystalline. To monitor the changes in the surface structure as a function of temperature we plot the GIXD

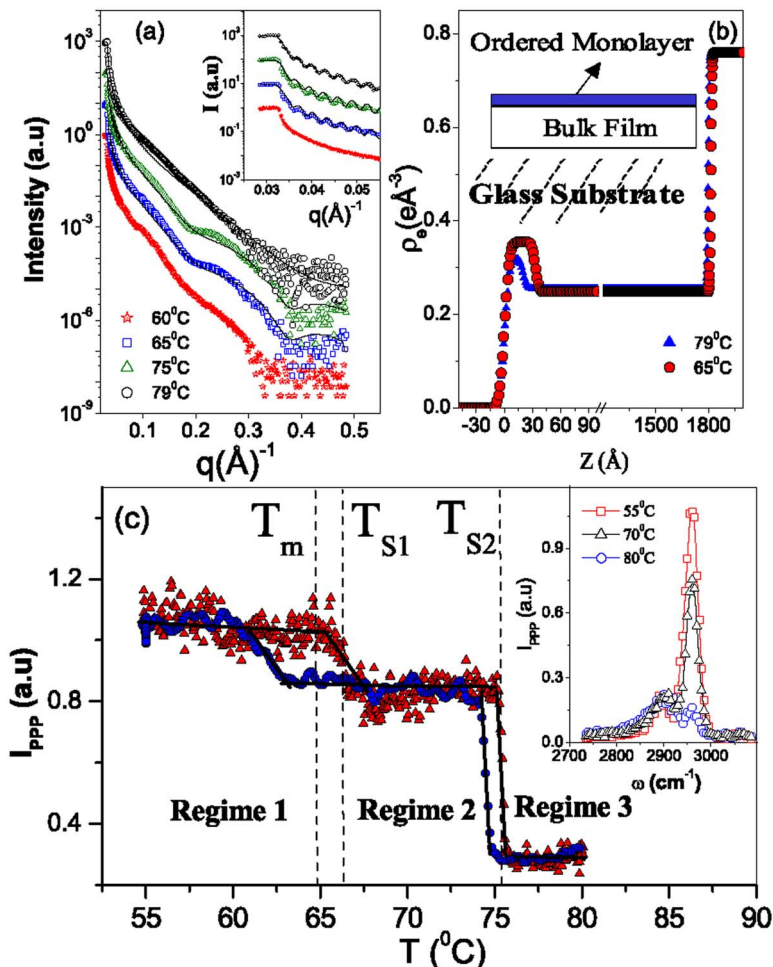


FIG. 2 (color online). (a) X-ray intensity plotted as a function of q_z (\AA^{-1}) for four different temperatures. These measurements were done in the cooling cycle. The solid lines are fits to the data points using a two-layer model on a glass substrate. Fits for 60 $^{\circ}\text{C}$ data are not provided due to increased roughness of the film after the bulk crystallizes. The inset is the same graph over a narrow q_z range indicating fringes corresponding to the thickness of the film. (b) Density profiles in $e\text{\AA}^{-3}$ plotted as a function of film thickness (\AA) in the direction normal to the sample surface obtained using a two-layer model, shown in the inset, at 79 $^{\circ}\text{C}$ (triangle) and 65 $^{\circ}\text{C}$ (circle). (c) SFG intensity of the methyl asymmetric peak at 2960 cm^{-1} plotted as a function of temperature in the PPP polarization. The dotted lines indicate the bulk transition (T_m) and the two surface transitions, T_{S1} and T_{S2} , respectively. The inset in (c) is the I_{PPP} (p -polarized SFG, p -polarized visible, and p -polarized infrared) SFG spectra at 55, 70, and 80 $^{\circ}\text{C}$.

intensity at a fixed value of $\alpha_f/\alpha_c = 0.8$ as shown in Fig. 1(f). Upon heating, the intensity drops rapidly at 66.5 $^{\circ}\text{C}$ (T_{S1}) corresponding to the melting of surface chains. Upon cooling, we observe a significant hysteresis suggesting slow nucleation kinetics at the surface. The dashed lines show the bulk transition temperatures on heating and cooling rates of 0.3 $^{\circ}\text{C}/\text{min}$. The rare presence of an ordered crystalline layer on top of an isotropic bulk is similar to that observed [3–5] recently for small molecule alkanes and alcohols.

The GIXD analysis indicates that the long-range crystalline order is lost above 67 $^{\circ}\text{C}$. However, the XR measurements indicate a presence of a higher density surface layer existing above 67 $^{\circ}\text{C}$. The specular XR intensities at four representative temperatures are shown in Fig. 2(a) as a function of momentum transfer, q_z , after

off-specular corrections. The expanded region corresponding to short q_z is also shown as an inset. The data presented in Fig. 2(a) were taken in the cooling cycle. The Kiessig fringes at short q_z correspond to the thickness of the comb polymer film on the glass substrate (data at 79 $^{\circ}\text{C}$). Upon cooling to 75 $^{\circ}\text{C}$, two sets of fringes are observed: one with a small period corresponding to the thickness of the film and the other with a larger period corresponding to the higher density monolayer on top of a lower density isotropic melt. The two sets of fringes persist on cooling, as observed at 65 $^{\circ}\text{C}$, until the surface and the bulk side chains crystallizes. At 60 $^{\circ}\text{C}$, the bulk crystallizes, and due to an increase in roughness, the short- and the long-range Kiessig fringes disappear. This is also consistent with the complete recovery of a strong x-ray diffraction peak in

the GIXD measurements below 60 °C in the cooling cycle.

The solid lines in Fig. 2(a) represent the fits using a two-layer model consisting of an ordered monolayer of higher density on top of a disordered melt as shown in the inset in Fig. 2(b). The density profiles obtained from the fits are shown in Fig. 2(b). Complicated models using more than a two-layer geometry give better fits; however, the conclusions reached using a simple model are not affected. Between T_{S1} and T_{S2} , two layers are observed corresponding to a dense surface layer 33 Å thick on top of an isotropic bulk. This correlates very well with a monolayer of a predominantly trans-alkyl side chain attached to a polymer backbone by an acrylate linkage and oriented normally to the air-film interface. The density values that we obtained are consistent with those expected for hydrocarbons [4]. A similar observation of an ordered monolayer is also observed for side chains that are 18 carbons long. For $n = 18$, the x-ray reflectivity data reveal a 28 Å all-trans-alkyl side chain oriented with its chain axis parallel to the surface normal. The presence of a liquid-crystalline monolayer on top of an isotropic liquid melt is consistent with GIXD and our previously reported SFG measurements [6].

We finally present the SFG data to understand the second transition associated with disordering of the smectic-like surface layer. The details of the SFG measurements are provided elsewhere [6]. In the limit of the dipole approximation, the generation of the SFG signals is forbidden in the bulk and allowed only at the interface. Further, the SFG intensity is sensitive to the orientation and the number of molecules present at the interface [14]. We have previously shown that below T_m , the SFG spectra show strong methyl vibration bands indicating ordered methyl groups at the surface and predominantly all-trans alkyl chains [6]. Here, we discuss only the transition temperatures measured by monitoring the SFG intensity of terminal methyl groups. In Fig. 2(c), the SFG signal at 2960 cm^{-1} , associated with asymmetric methyl stretching vibration, is shown as a function of temperature at a heating and cooling rate of 0.3 °C/min. The first transition is associated with melting of the surface chains and is consistent with the GIXD results in Fig. 1. Upon further heating we continue to observe strong methyl SFG signals indicating the presence of ordered alkyl side chains at the surface and consistent with XR results above T_m . Finally, at $T_m + 10$ °C a sharp drop in the SFG intensity indicates a transition from a smectic-like state to a disordered surface layer with a 1 °C hysteresis upon cooling.

A stable smectic-like monolayer above T_m is unlike a prewetting nematic or smectic layer known to form at both the air and the solid interfaces for liquid crystals above the nematic-isotropic transition temperatures

[15,16]. For liquid crystals, this surface layer acts as a precursor to the nematic or smectic order that develops and grows into the bulk. For comb polymers, the observation of an ordered smectic-like monolayer is different, since no such liquid-crystalline phases exist in the bulk. This is also different from the surface freezing, where a crystalline surface layer exists on top of a disordered melt, observed recently for small molecule n -alkanes and alcohols. For n -alkanes and alcohols this crystalline layer melts to a disordered surface layer at $T_m + (1-3)$ °C [3-5]. The presence of this unique surface phase has important implications in understanding surface properties of many similar systems containing chemically attached alkyl linkages such as surfactants, dendrimers, and biomolecules.

We acknowledge the NSF-DMR-9984996 (A. D.) and Petroleum Research Funds for their financial support. We thank Andrea Kasko, Casey Shaffer, and Sergey Mamedov for help with DSC, synthesis, and temperature calibrations, respectively.

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