College of Polymer Science and Polymer Engineering

4-8-2002

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Recommended Citation

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(Received 12 September 2001; published 25 March 2002)

Infrared visible sum frequency generation (SFG) spectroscopy has been used to study structure and melting transition temperatures of alkyl-side chain-acrylate comb polymers at air and solid interfaces. At the air interface, the SFG spectra show methyl bands and two transitions are observed: the first, near the bulk melting temperature, T_m, and the second $10-20\,°C$ higher than T_m. The shorter the alkyl side chain, the larger the difference between the two transition temperatures. In contrast, methylene bands are observed at sapphire interface with a single transition near T_m (C18).

Considerable effort has been focused on understanding whether surface phase transition temperatures are different from those in the bulk [1–12]. It is expected that surfaces will melt at a lower temperature than the bulk, and this has been experimentally observed for almost all solids studied [1,3–6]. However, small molecules that have a basic building block of linear alkyl chains such as *n*-alkanes and alcohols, exhibit surface freezing, where the surfaces show existence of ordered crystalline phases above the bulk melting temperature, T_m [7–10]. In the case of liquid crystals, smectic surface layers are observed at the vapor-nematic or vapor-liquid interfaces [2,11,12]. In this Letter, we show that when alkyl chains are chemically linked to polymer backbones the influence of interfaces on melting transitions is much stronger than that observed previously for small molecules. We observe two sharp transitions above T_m at the polymer/air interface. The first transition is associated with melting of side chains to a stable smectic-like ordered state. This ordered state persists $10-20\,°C$ above T_m beyond which a second transition to the isotropic state is observed. The presence of an additional surface phase at the polymer/air interface that does not exist in the bulk has not been observed before for small molecule *n*-alkanes, alcohols, and liquid crystals. In contrast, at the polymer/sapphire interface we observe a single transition from crystalline to disordered state near T_m (for C18). These observations have direct technological consequences to the use of long alkyl or fluorinated side chain polymers for smart adhesives, release coating, and soil resistance coating applications [13,14].

Surface sensitive IR-visible sum frequency generation (SFG) measurements have been used to study the molecular structure and melting transition temperatures of poly (*n*-alkyl acrylates) at both air and sapphire interfaces. SFG involves mixing a visible high intensity laser beam of frequency ω_1, with a tunable infrared wavelength source of frequency, ω_2. According to the dipole approximation, generation of SFG photons [at $(\omega_1 + \omega_2)$] is forbidden in the centrosymmetric bulk and is allowed at interfaces where inversion symmetry is broken [15]. The SFG is resonantly enhanced when ω_2 overlaps with the resonant frequency of a molecular vibrational mode that is both infrared and Raman active. Further, the SFG intensity is enhanced by $1-2$ orders of magnitude when the incident angles of the input beams are close to the critical angles for total internal reflection [16,17]. We have used both external and internal reflection geometries to probe the air/polymer interface, and internal reflection geometry to probe solid/polymer interface.

The SFG measurements involved overlapping visible (800 nm, 1 ps duration pulse, 1 kHz repetition rate, $100-200\;\mu J$/pulse) and tunable infrared ($1300-3800\;cm^{-1}$, FWHM = $19-24\;cm^{-1}$, 1 ps duration, 1 kHz repetition rate, $3-4\;\mu J$/pulse) beams at the polymer surfaces. The SFG measurements in internal reflection geometry were measured at incident angles of $42°$ and $12°$ with respect to the surface normal to the face of sapphire prism to study the polymer/air and polymer/sapphire interfaces, respectively. The details of the experimental protocol using internal reflection have been published elsewhere [17]. The SFG intensity from the polymer/air interface is highest near $42°$ incident angles, and it is possible to have contribution from the air interface at $12°$. To eliminate any contributions from the air interface, the data presented for the polymer/sapphire interface were measured after the polymer/air surface was exposed to brief argon plasma treatment ($1-2$ s). We have verified that this short plasma treatment destroys the order at the polymer/air interface and does not influence the polymer/solid interface [17,18]. The spectra are normalized using nonresonant signals from a ZnSe reference. The temperature measurements were done at heating rates of $0.2-0.3\,°C$/min using a Lakeshore temperature controller (relative accuracy of $0.025\,°C$, absolute temperature accuracy of $\pm 0.50\,°C$).

The comb polymers with different alkyl side chain lengths (C12–C22) (inset of Fig. 1b) were synthesized by transesterification of poly (*t*-butyl acrylate) ($M_w = 50$ K and $M_w/M_n \sim 1.12$) with an alcohol of appropriate chain length. We have used NMR to determine that the transesterification reaction proceeded to greater than 90% completion. Repeated fractionation and column chromatography were used to remove residual alcohol and were verified for purity using both NMR and mass spectroscopy. Differential scanning calorimetry performed
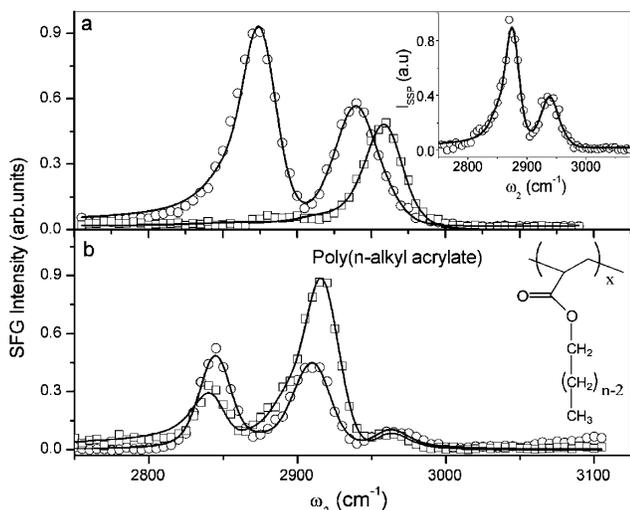
FIG. 1. (a) SFG spectra at C18 polymer/air interface in an external geometry (*Issp*, open circles, and *Ippp*, open squares). The inset shows *Issp* spectra obtained in internal reflection geometry at the C18/air interface. (b) SFG spectra at the C18/sapphire interface measured in internal reflection geometry. The chemical structure of the polymer is shown as an inset of (b). All the spectra are taken at 25 °C.

at a heating rate of 1 °C/min show one sharp melting transition summarized in Table I. Uniform films were prepared on sapphire prisms by spin coating using a 2 wt % solution of the comb polymer dissolved in toluene (300–500 nm thick) and annealed at 10–20 °C above T_m in a high vacuum oven (10^{-7}–10^{-8} torr) for 4–5 h. We discuss the results for C18 only, since similar trends were observed for C12, C16, and C22.

Figure 1a shows the *Issp* and *Ippp* intensities as a function of infrared frequency (ω_2) at the comb polymer/air interface at 25 °C (for example, *ssp* stands for *s*-polarized output, *s*-polarized visible, and *p*-polarized infrared beams). The inset shows the *Issp* spectra taken in the internal reflection geometry. The SFG spectra in internal and external reflection geometry have the same spectral features and are dominated by methyl vibrations (methyl symmetric, Fermi, and asymmetric bands at 2875, 2935, and 2960 cm^{-1}, respectively). The solid lines are fits using a Lorentzian function (with a vibration strength A_q) convoluted with the Gaussian function corresponding to the width of the infrared pulse [18]. The low asymmetric vibration strength compared to symmetric vibration strength in the *Issp* spectra ($A_{asymCH3}/A_{symCH3} \sim 0.3$)

TABLE I. Surface and bulk transition temperatures as a function of alkyl side chain length. For C12, we are currently unable to cool the sample below 15 °C to measure T_{S_1}.

| | T_{S_1} (°C) | | T_{S_2} (°C) | | |
n	Heat	Cool	Heat	Cool	T_m (°C)
12	$\cdots$	$\cdots$	19.9 ± 0.3	18.6 ± 0.3	0
16	37.1 ± 0.3	33.3 ± 1.0	50.4 ± 0.3	48.6 ± 0.7	35.2
18	49.4 ± 0.1	44.2 ± 0.3	60.7 ± 0.1	59.6 ± 0.5	48.2
22	66.4 ± 0.1	61.4	75.7 ± 0.1	74.5	65.3

indicates that the C$_3$ symmetry axis of the methyl groups in the alkyl side chains are tilted at an angle of 30°–40° with respect to the surface normal. Also, small methylene intensities ($A_{qCH3}/A_{qCH2} \sim 3.3$) indicate predominantly trans methylene chains, similar to that observed for self-assembled monolayers where the alkyl chains are oriented parallel to the surface normal [18,19]. In contrast, the SFG spectra at the polymer/sapphire interface taken in internal reflection geometry at 25 °C show predominantly methylene bands (methylene symmetric, Fermi, and asymmetric bands at 2845, 2895, and 2915 cm^{-1}, respectively) as shown in Fig. 1b. The ratio of A_{qCH3}/A_{qCH2} is 0.3 in comparison to 3.3 at the air interface. The presence of asymmetric methylene and methyl peaks in the SSP spectra indicates that the C$_3$ axis of the methyl and C$_2$ axis of the methylene groups are tilted with respect to the surface normal [18,19].

The square root of the SFG intensity is proportional to $Nf(\chi, \theta, \varphi)$, where χ, θ, φ are Euler angles describing the orientation of the molecules with respect to the laboratory coordinate system and N is the number density. Therefore, any changes in the packing or orientation of the molecules would correspondingly lead to changes in the SFG intensities. Figure 2a shows the changes in the *Ippp* intensity at the comb (C18)/air interface measured at $\omega_2 = 2960$ cm^{-1} (corresponding to methyl asymmetric vibrations) on heating and cooling (rate of 0.3 °C/min). The distinct drops in the SFG intensities indicate two sharp transitions. The first transition, T_{S_1}, at 49.4 °C is close to the bulk melting temperature for C18. A more dramatic second transition, T_{S_2}, occurs at 60.7 °C, 12.5 °C higher than T_m. Corresponding *Issp* spectra at three selected temperatures are shown in Fig. 2b. Below T_{S_1}, we find the
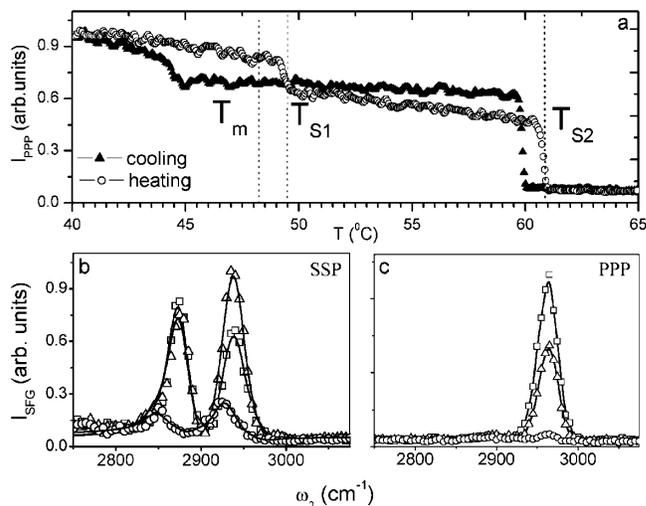

FIG. 2. (a) *Ippp* at 2960 cm^{-1}, corresponding to asymmetric methyl vibrations, as a function of temperature at heating (open circles) and cooling (filled triangles) rates of 0.3 °C/min. (b) Selected SFG spectra in *Issp* polarization at 43 °C (open square), 55 °C (open triangle), and 65 °C (open circles). (c) Selected SFG spectra in *Ippp* polarization at 40 °C (open square), 55 °C (open triangle), and 65 °C (open circles).

methyl symmetric peak is the most dominant. This feature abruptly changes at T_{S_1}, beyond which the Fermi peak is higher than the methyl symmetric. Finally, above T_{S_2} true disorder is observed where the methyl intensities in both *Issp* and *Ippp* spectra (as shown in Figs. 2b and 2c) drop close to zero and weak methylene signals are observed.

To understand the nature of the intermediate ordered state above T_m, we have analyzed the changes in the Fermi resonance at 2935 cm^{-1}. The Fermi resonance is assigned to the overtone bands of the HCH deformation modes ($2\nu_{def}$) with their intensity borrowed from the methyl symmetric CH stretching bands (ν_s) [20]. Therefore, the Fermi resonance will be higher if the difference between ν_s and $2\nu_{def}$ is small. Since infrared absorption measurements show a shift in the vibrational frequencies upon melting, we expect the magnitude of the Fermi peak to be extremely sensitive to the melting of the side chains. The *Issp* spectra obtained every 3 °C were fitted using a Lorentzian function convoluted with a Gaussian function as mentioned earlier. The ratio of A_q (Fermi)/A_q (symmetric), which we call the Fermi ratio, was plotted as a function of temperature as shown in Fig. 3a. The abrupt change in the Fermi ratio indicates that the first transition, at T_{S_1}, is associated with melting the side chains to an intermediate smectic-like surface ordered state.

To support this hypothesis, we present here two other experimental measurements. First, we have measured the changes in the Fermi ratio for carbamate comb polymers (shown in Fig. 3b) that show smectic liquid crystalline transitions in the bulk (chemical structure is provided in Ref. [18]). The carbamate polymer (with octadecyl side chains) shows a broad bulk transition from side chain crystalline to smectic liquid crystal state centered at 50 °C. In the case of carbamate polymers, the melting of side chains to a smectic surface layer is also accompanied by an increase in Fermi ratio. Second, recent SFG studies of

alkane/sapphire interface show no increase in the Fermi ratio as the temperature increases through the crystalline to rotator transition (below T_m) [21]. Since both the surface transition temperatures are above T_m, at the polymer/air interface, it is unlikely that the intermediate surface state is a crystalline rotator state, well known to exist for *n*-alkanes [22].

The surface transition temperatures as a function of the alkyl side chain length are summarized in Table I. The difference $T_{S_2} - T_{S_1}$, ΔT, increases with a decrease in the length of the alkyl side chains. Previous surface tension measurements on *n*-alkanes have shown that the differences between the surface energy of ordered methyl groups and disordered liquid surface explain surface freezing [8]. We believe that a similar hypothesis explains the presence of the smectic-like surface layer above T_m at the polymer/air interface. Also in the presence of water (polymer/water interface) we observe one transition close to T_m. This agrees with the hypothesis of surface energy as a driving force, since at the polymer/water interface there is no reason for the existence of an ordered layer above T_m [23]. In addition, the large values of ΔT for the polymer/air interface (10–20 °C), in comparison to 1–3 °C observed for alkanes and alcohols, may be explained by the restricted freedom of the alkyl side chains tethered to the polymer backbone. The surface energetics dominate over entropy for shorter chains, explaining why ΔT is larger for C12 in comparison to C22.

The melting transition at the polymer/sapphire interface is strikingly different from that at the polymer/air interface. Figure 4a shows the *Issp* intensity for the methylene symmetric (2845 cm^{-1}) vibrations as a function of temperature at the polymer/sapphire interface. The spectra in the SSP
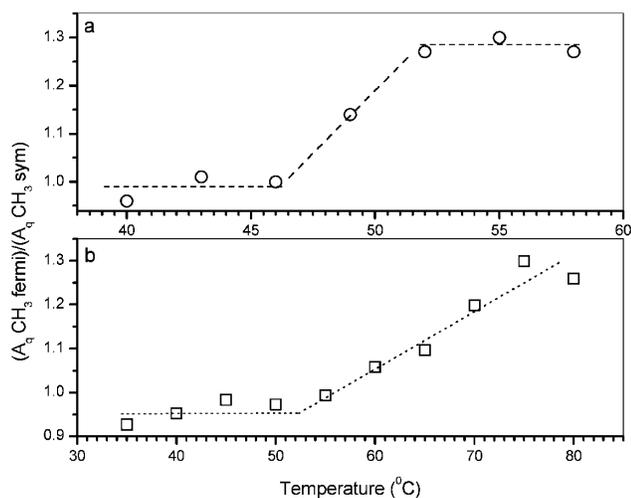
FIG. 3.   (a) Fermi ratio as a function of temperature for the acrylate combs. (b) Fermi ratio as a function of temperature for a C18 carbamate comb where the bulk shows three transitions centered at 50, 75, and 93 °C.
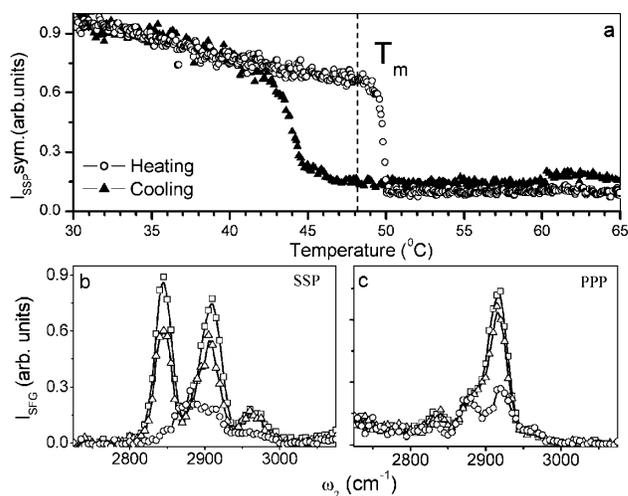
FIG. 4.   (a) *Issp* at 2845 cm^{-1}, corresponding to methylene symmetric stretch vibrations, as a function of temperature at heating (open circles) and cooling (filled triangles) rates of 0.3 °C/min at C18/sapphire interface. (b) and (c) *Issp* and *Ippp* spectra at the C18/sapphire interface taken at 30 °C (open squares), 40 °C (open triangles), and 50 °C (open circles). Solid lines in (b) and (c) are visual guides to illustrate the spectral trends.

and PPP polarization at three selected temperatures (30, 40, and 50 °C) are also shown in Figs. 4b and 4c, respectively. The qualitative differences between surface transition at solid and air interfaces (Fig. 2) are obvious. First, the symmetric signals drop sharply at 49.5 °C indicating a single transition close to T_m. A 5.5 °C hysteresis is observed on cooling, and this value is similar to the hysteresis observed in bulk melting and the first transition, T_{S_1}, at the polymer/air interface. In comparison, the second transition at T_{S_2} for the polymer/air interface shows a much smaller hysteresis (1.1 °C), indicating faster ordering kinetics. This may be explained since the order develops only at the surface, and between T_{S_1} and T_{S_2} the bulk is in the melt state. The striking differences in the transition temperatures at the solid and air interfaces support the strong role surface energy plays at the air interface in stabilizing an ordered phase above T_m. Surprisingly, at the polymer/sapphire interface, the influence of the solid surface is much weaker than that observed for small molecule liquid crystals [24]. In contrast, at the polymer/air interface, the influence of air on the transition temperatures is far greater than that observed for n-alkanes, alcohols, and liquid crystals [8–12].

In summary, we have for the first time measured structure and transition temperatures of alkyl comb polymers at both air and solid interfaces. At the polymer/air interface, methyl peaks dominate the spectra indicating predominantly trans alkyl chains normal to the surface. On heating, we find the presence of a stable intermediate smectic-like surface ordered state that persists 10–20 °C (C22 to C12) above the bulk melting temperature. In contrast, the methylene peaks dominate the SFG spectra at the polymer/sapphire interface, and upon heating we observe one sharp transition close to T_m.

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