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Conformation-Sensitive Surface Dynamics in Thin Poly(ethylene terephthalate) Film

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ABSTRACT:

In this paper, the surface average conformation of poly(ethylene terephthalate) (PET) films was modulated by adjusting the water content in corresponding trifluoroacetic acid (TFA) spin-coating solutions, which was confirmed by surface-sensitive sum frequency generation (SFG) vibrational spectroscopy. Molecular dynamics simulation results showed that the added water molecules partly disrupt the hydrogen bond network between TFA molecules and PET chains and make it possible to preserve the statistical average bulk-like spherical conformation at film surface during the formation of PET film. Slower surface crystallization kinetics, higher surface glass transition temperature ($T_g^{surface}$) and suppressed T_g -confinement effect were observed when the surface average conformation changed from oriented oblate ellipsoidal conformation to isotropic spherical conformation, showing that surface dynamics is very sensitive to chain conformation.

1. INTRODUCTION

Extensive experimental and simulation results in the past two decades have verified that when compared to polymer chains in the bulk, polymer chains near a free surface exhibit more enhanced mobility of chain segments.¹⁻¹⁰ Faster relaxation dynamics,⁴⁻⁸ larger diffusion coefficient⁹ and lower viscosity¹⁰ can be observed at the free surface. The activation of polymer motion at the surface will affect the dynamics of the whole film and plays an increasingly significant role as the film thickness decreases.¹¹ Hence, there is immense interest in exploring the essential attributes of polymer chains at the free surface, which can help to gain a deeper understanding of confinement effects and develop strategies to modulate the unique physical properties of polymer nanoconfinement materials.

Many studies¹²⁻¹⁵ have focused on differences between polymer chain near a free surface and bulk polymer chain on some phenomenological characteristics (e.g. packing density, free volume and entanglement). Simulations³ and positron annihilation lifetime spectra¹² have shown that the packing density at the surface is much lower than bulk, exhibited a higher free volume to accelerate the motion of polymer chain. Brown and Russell¹⁴ suggested that the entanglement density of polymer chain near a surface is markedly reduced. These characteristics have been widely used to explain the observed enhanced segmental dynamics at the surface and describe many size-dependent behaviors. From another perspective, it is reported that the enhanced segmental mobility at the surface may be related to the local conformation of the chains at the surface. In the bulk, polymer chains adopt a random-walk conformation and the

volume pervaded by a polymer chain is ellipsoidal. Such ellipsoids can orient in all directions and sweep out a spherical volume on average.¹⁴ However, according to Silberberg,^{16,17} an interface (e.g., polymer/air interface) can be considered a reflecting plane that reverses the trajectory of the chains that would have crossed the plane into the polymer. As a result of this process, the radius of gyration (R_g) normal to the plane is compressed, while the R_g parallel to the plane is unperturbed or slightly extended. Hence, the local conformation near a surface is presented as an oblate ellipsoid (or described as “pancake-like”¹⁸), which has been confirmed by a series of theoretical calculations,^{14,15} simulations¹⁹ and experiments.^{20,21} Moreover, the rotation of such ellipsoidal conformation is restricted due to the major axis of the ellipsoid prefer to parallel to the surface, resulting in an anisotropic stacking. Considering that the difference between surface and bulk average chain conformation will cause variations in the entanglement and packing behaviors at the surface,¹⁴ the chain conformation difference could be an underlying driver for changes in the surface segmental dynamics and offer a new sight to free surface effect. Nevertheless, studies on the relationship between surface chain conformation and its dynamics are scarce because of the technical difficulty in controlling and detecting the conformation of surface chains.

Sum frequency generation (SFG) vibrational spectroscopy is a powerful technique that is able to gain information about the molecular level structure of a polymer at a surface or interface,²²⁻²⁴ where centrosymmetry is broken to able to generate SFG signal in a second-order nonlinear optical process. From SFG spectra, the molecules orientation and conformation can be obtained. By using this technique, Tanaka²⁵ and

Dhinojwala²⁶ determined that the main chain of polystyrene (PS) is most likely aligned parallel to the polymer/substrate and polymer/air interfacial planes during the spin-coating process used to prepare the films. Nevertheless, the coil conformation, present in polymer solution will be partly retained in the films²⁷⁻³⁰ due to rapid evaporation of the solvent during spin-coating. Tsui *et al.*³¹ and Reiter *et al.*³² found that PS films with different chain conformations can be produced by spin-casting from decalin solutions at different temperatures near the theta temperature and different solvents to adjust the solvent quality. Lu *et al.*³³ found that surface molecular conformation of polymer films can be described by correlating the SFG resonant signals of the rigid side chromophoric groups to the introduced surface chain arc included angle, which are affected by adding different content of poor solvent before film preparation. Here, in this paper, deionized water was used as a poor solvent to add to the poly(ethylene terephthalate) (PET) trifluoroacetic acid (TFA) solutions used in spin-coating and PET films with different surface chain conformations were prepared, that could be detected by SFG. Stepwise crystallization and glass transition behavior of PET films were investigated to extract information about the surface dynamics.^{6,34,35} Our results provide direct evidence that when the surface polymer chain conformation changed from an oriented oblate ellipsoid to an isotropic sphere, slower surface crystallization kinetics, higher $T_g^{surface}$ (T_g of surface crystallization layer) and suppressed T_g -confinement effect were observed. Results from SFG and molecular dynamics (MD) simulations also showed that the addition of water can disrupt the hydrogen bond network (solvation effect) between the TFA molecules and PET chains, making it possible for the chains to maintain their

conformation as the film transitions from solution state to the solid state during spin-coating.

2. EXPERIMENTAL SECTION

2.1 Materials and Film Preparation. Poly(ethylene terephthalate) (PET, the chemical structure is shown in [Figure 1a](#)) [*Polymer Source* Ltd., Canada, $M_w = 30$ kg/mol, $M_w/M_n = 1.87$] was dried under vacuum at 353 K for 48 h prior to solution preparation. Amorphous ultrathin PET films were spin-coated from solutions of PET in a mixture of trifluoroacetic acid (TFA) and poor solvent (e.g. water, chloroform, ethanol, etc.) (vol%) on piranha solution-cleaned (100) silicon wafers or fused silica substrates. Before measurement, the PET films were kept under a high vacuum (pressure $< 10^{-6}$ mbar) at room temperature for 48 h to remove any residual solvent, which is confirmed by polarization modulation infrared reflection absorption spectroscopy (PM-IRRAS) (see [Figure S1](#)). No detectable IR signals attributed to solvent can be observed. Moreover, the T_g of PET thick films (> 300 nm) prepared from solutions with different water content keeps constant about 348 K, eliminating the case that solvents exist as plasticizers. Both observations revealed that the PET films do not contain appreciable amounts of water.

2.2 Characterization. A custom-designed SFG spectrometer (EKSPLA, Lithuania) was used to detect the molecular structure information of polymer near the free surface. During measurement, the incident angles of a 532 nm visible laser beam and a tunable infrared (IR) laser beam were fixed at 70° and 50° respectively to generate sum

frequency (SF) signals ($\omega_{\text{SF}} = \omega_{\text{IR}} + \omega_{\text{vis}}$) in a second-order nonlinear optical process.^{36,37}

At where medium is isotropic, the susceptibility for this process is equal to zero, and no SF signal can be generated. However, at where the macroscopic centrosymmetry is broken^{38,39}, such as a surface or an interface, the susceptibility is not zero and the two input visible and infrared laser beams can superimpose to produce a third beam (SF signal). Hence, SFG is an interface-specific technique with molecule level (about 1~2 nm) interfacial sensitivity. The *ssp* (SF/*s*, visible/*s*, and IR/*p*) and *ppp* (SF/*p*, visible/*p*, and IR/*p*) polarization SF signals were collected by a monochromatic spectrograph. *s* represents the polarization direction normal to the surface, while *p* represents the polarization direction parallel to the surface. Molecular dynamics (MD) simulations were performed using the GROMACS-5.0.7 package with a time step of 2 fs.⁴⁰ The GROMACS topologies of PET were generated using the PRODRG server,⁴¹ the topologies of TFA and CHCl₃ were obtained from the Automated Topology Builder server and the topologies of H₂O was presented by the TIP3P water model.⁴² The force field parameters for TFA and CHCl₃, as well as PET, were derived from the GROMOS96 force field.⁴³ The Particle mesh Ewald algorithm⁴⁴ was employed to calculate the long-range electrostatic interaction, and the cutoff was set to be 13.0 Å. The Lennard-Jones (LJ) potentials of cross interaction between PET and different solvent molecules were obtained by the Lorentz-Berthelot rule.⁴⁵ Periodic boundary conditions (PBC) were applied in all directions. After energy minimization and pre-equilibration of the system, the procedure runs at the constant temperature (298K) and pressure (1bar) conditions controlled by the Berendsen algorithm.⁴⁶ Each simulation

was conducted in a 50 ns NPT ensemble, where the last 30 ns or 40 ns were used for analysis. In this simulation period, the average R_g of PET chains fluctuated slightly around a mean value (see Figure S2), which indicates that the simulation has reached equilibrium. The starting conformation for the simulations of PET chain was constructed by visual molecular dynamics (VMD)⁴⁷ and PET chain length of 10 constitutional units was employed. This model is long enough while also allows a high computational efficiency. The concentration of PET was fixed to 0.24 wt%, which is the same as the experimental condition used to get 24 nm PET films. In the simulations, the numbers of H-bond between TFA molecules and PET chains or H₂O molecules and PET chains in different solvent systems (TFA, TFA / H₂O, and TFA / CHCl₃) were measured to show the effect of the addition of poor solvents. The cold crystallization and glass transition behaviors of PET film were detected *in situ* by ellipsometer (EP³SW, Accurion GmbH Co., Germany) at a fixed incident angle of 60° and a wavelength of 658 nm with 2 K/min heating rate. During heating, the ellipsometric angle (Δ) was continuously monitored as a function of temperature (T) to sensitively reflect the variations of PET film in thickness and density during cold crystallization process and glass transition. For the employed PET film, Δ is almost inversely proportional to the film thickness (see Figure S3a). The turning point of the thermal expansion coefficient near 337 K is considered as the glass transition temperature and the two abrupt drops of film thickness (or two abrupt rises of Δ) are considered as the surface and bulk crystallization process, respectively, as demonstrated in our previous works.^{35,48} From Figure S3, the glass transition temperature (T_g), the crystallization temperatures of free

surface and bulk layer ($T_c^{surface}$ and T_c^{bulk}) were easily obtained from the curve of Δ vs T and its temperature derivative ($d\Delta/dT$) vs T curve (the $d\Delta/dT$ vs. T curve was smoothed by a Savitzky-Golay algorithm of the second polynomial order using a 5-point window). The surface topography of the PET films was probed by peak force tapping mode in a Multimode-8 AFM (Bruker Co., USA). In the measurement of surface crystallization temperature ($T_c^{surface}$) by AFM, about 10 PET films, prepared from PET TFA solutions with different poor solvent contents (e.g. add 1.1 vol% water as poor solvent), were placed on a hot stage and heated at 2 K/min. When the temperature reached a certain value, one film was quickly quenched to room temperature to probe the surface crystallization morphologies by Peak force quantitative nanomechanical (PF-QNM) technique. The area fraction of the crystallization domains was evaluated by the Nanoscope Analysis 1.40 software as reported before.^{34,35,49}

3. RESULTS AND DISCUSSION

3.1 Modulation and characterization of chain conformation on the PET film surface

Information on the molecular structure of the polymer near the free surface was obtained using a custom-designed SFG spectrometer. [Figure 1b](#) shows the SFG spectra for PET films prepared from solutions with different addition of water. The pronounced peak at 1720 cm^{-1} in the *ssp* spectra is attributed to the stretching vibration of the ester carbonyl group ($-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{O}-$).^{50,51} The SFG signal has been verified to originate from the

free surface and not from the PET/substrate interface or bulk.⁵¹ The strong peak observed in the *ssp* spectra shows that the stretching vibration of the ester carbonyl group can be detected in the direction normal to the free surface, while the absence of a resolvable signal in the *ppp* spectra shows that there is no stretching vibration detected parallel to the surface (Figure 1b, 0 vol% water), which was similar to the symmetric C-H stretching of the ester methyl groups on polymethyl methacrylate (PMMA) surface in the same geometry and calculation showed that the ester methyl groups were oriented toward the surface normal.⁵² Hence, it is indicated that ester carbonyl groups on the PET surface are oriented normal to the surface (see Figure 1c), the same as the result reported by Chen *et al.*⁵¹ As we know, the fragment of PET main chain (see Figure 1a) lies essentially in a common plane and the carbon-oxygen double bond in carbonyl group is collinear and can't rotate freely. Taking steric hindrance and minimum energy principle into consideration, the carbonyl group is approximately perpendicular to fragment and the carbonyl groups only can stay in the plane perpendicular to the main chain. Then, the polymer main chain is aligned parallel to the free surface plane,^{51,52} inferring an oriented oblate ellipsoid conformation. Such an oblate ellipsoid conformation at a surface (or an interface) was theoretically predicted by Silberberg^{16,17} and Brown *et al.*,¹⁴ confirmed by computer simulation^{19,53} and some experimental observations^{15,54} and calculated by Lu using the chain arc model.³³ The free surface can be considered as a reflecting plane, the chain trajectory that would have occurred across the plane is reflected back into the polymer. While the reflecting back part leads to an increase in density, which tends to push polymer towards the surface.⁵³

The superposition of these two opposite effects make the case that there are few chains whose center of mass is situated near or at the surface. Those chains are compressed along the surface normal direction as oblate ellipsoid and the polymer backbones are aligned parallel with the surface plane.

Figure 1. (a) The chemical structure of PET. (b) The surface *ssp* SFG spectra of 24 nm PET films prepared from TFA / H_2O solutions with different additions of H_2O . The inset shows the surface *ppp* SFG spectra. (c) Carbonyl group orientation inferred from the SFG spectra in panel b. (d) The surface *ssp* SFG spectra of 24 nm PET films prepared from TFA solution followed by annealing at room temperature under saturated H_2O vapor for 7 days; TFA / CHCl_3 (10 vol%) solution and TFA / $\text{CH}_3\text{CH}_2\text{OH}$ (1.5 vol%) solution. The inset shows the film geometry for detecting SFG signals from free surface.

The fact that the height of the peak at 1720 cm^{-1} in the *ssp* SFG spectra was increasingly suppressed with increasing H_2O and still no signal was observed in the *ppp*

SFG spectra (the inset in [Figure 1b](#)) suggest that the normal orientation of the ester carbonyl groups at the surface was suppressed with addition of H₂O, towards random orientation as shown in [Figure 1c](#). Based on the principle of SFG, SFG signal is only sensitive to the polymer conformation changes along the direction of surface normal.³³ Hence, such variation in the SFG signal and carbonyl groups orientation indicate that the polymer backbones are gradually adopting an isotropic spherical conformation similar to the random coil conformation. We should also point out that surface SFG signals can only infer comparative and average chain conformations at the surface, but not exact conformations, such as the trend of average conformation from oriented oblate ellipsoidal conformation to isotropic spherical conformation. To further explore the effect of water on surface chain conformation, PET film was first prepared from pure TFA solution without any water and then annealed with saturated water vapor at room temperature. It is shown that the SFG signal was not affected by annealing in the presence of water vapor ([Figure 1d](#)). Therefore, only H₂O added to the casting solution had an effect on the surface conformation. Other poor solvents, such as chloroform (CHCl₃) and ethanol (CH₃CH₂OH), were also added to the PET TFA solutions. The SFG signal of the PET surface was similarly suppressed by the addition of 1.5 vol% ethanol, but the addition of 10 vol% chloroform produced no effect ([Figure 1d](#)). This observation shows that not all poor solvents can modulate the surface conformation of a spin-coated film.

Figure 2. (a) The hydrogen bond number between solvent and PET chains versus time in different solvent systems. (b) Snapshots of the PET chain and nearby solvent molecules which are able to form H-bond with PET. The H-bonds were marked by green dotted line.

To examine the origin of different surface conformations produced by different poor solvents, MD simulation was utilized to investigate the interaction between the solvent and PET chain in various solvent systems (TFA, TFA / H₂O, and TFA / CHCl₃). In the simulation, the concentration of PET was fixed at 0.24 wt%, which is the same as that used to obtain the 24 nm PET films in experiment. The carbonyl groups in PET chains can provide reactive sites for forming hydrogen bonds with the poor solvent. According to the statistical results, the number of H-bonds between PET and solvent molecules (e.g., TFA and H₂O) in different solvent systems were shown in Figure 2a. It was found that the H-bond number between the TFA and PET chains in TFA / CHCl₃ (CHCl₃: 10 vol%) solvent system is the same as that in pure TFA, but reduced in TFA / H₂O (H₂O: 1.5 vol%) system. In addition, the H-bonds between H₂O and PET chains

were observed in TFA / H₂O system and it is worth noting that the summation number of the H-bond formed by TFA and H₂O is equal to the H-bond number between the TFA and PET chains in pure TFA system. The H-bonds were presented clearly in the snapshots of the PET chain in TFA and TFA / H₂O systems (green dotted lines in [Figure 2b](#)). In the TFA solvent system, the TFA molecules are neatly arranged along the polymer to show perfect solvation, the R_g of this chain is computed about 2.70 nm (expanded by about 4% than R_g^{bulk} , R_g^{bulk} is about 2.60 nm based on Ref.⁵⁵). Upon adding water in the system, certain amount of TFA molecules are replaced by H₂O molecules to form H-bonds with PET chains and the R_g is about 2.36 nm (collapsed by about 9 % than R_g^{bulk}). These observations indicate that the solvation around the PET chain was partly broken by the addition of H₂O, but the addition of CHCl₃ can't break the solvation due to the lack of ability to form H-bond, even though the R_g of PET chain also suppressed (R_g is about 2.29 nm when adding 10 vol% chloroform, collapsed by about 12 % than R_g^{bulk}). As a result, the sites where TFA molecules replaced by H₂O molecules are undissolved and the chain conformation may be partly fixed. Within a certain range, more water may lead to more stable conformation. Such effect leads to maintain the random coil conformation of PET as it transitions from a solution to a solid film surface during spin-coating. However, the solvation remained intact after adding CHCl₃, the polymer chain still adopts a comfortable conformation (oblate ellipsoid) during spin-coating. Other poor solvents (e.g., methanol, n-hexane and dichloromethane) were employed to add to the PET solution, it is found that only the poor solvents which have larger polar fraction and able to form H-bond with PET chains

can modulate the surface conformation (see Table S1).

Figure 3. Surface topography of 24 nm PET films prepared from TFA, TFA/ H₂O (H₂O: 1.5 vol%) and TFA / CHCl₃ (CHCl₃: 10 vol%) solutions, respectively. The inset is the evolution of height at the position marked by white line.

Figure 3 shows the AFM topographic images of PET films prepared from different solvent systems. There is no difference in surface topography and all display an amorphous morphology with small roughness.^{6,34} These observations support the idea that the chain conformation may be the only difference at the surface of PET films prepared from different solvent systems. It is worth noting that the chain conformation in the bulk layer underneath the surface region may also vary with the content of water in the solution.^{31,33} Although the actual variation is still unknown due to lack of detection methods, we believe that the extent of conformation variation in the bulk layer is much less than that in the surface layer, due to the following three reasons: (i) surface chains prefer to adopt an oblate ellipsoid conformation, bulk chains prefer to adopt a spherical conformation. The polymer chains in the bulk layer can orient freely and sweep out an average spherical volume similar to the bulk-like conformation, while the

rotation of surface chain is seriously hindered;^{14,15,53} (ii) MD simulation showed that the chain size in solution decreased only by about 9 % when 1.1 vol% water was added; (iii) because of the quite low molecular weight ($M_w = 30$ kg/mol), the stretch caused by centrifugal force during spin-coating process on bulk chain can be ignored.⁵⁶ Our primary focus in this study is on the relationship between surface average conformation and surface dynamics.

3.2 The effect of chain conformation on surface crystallization kinetics of PET film

Cold crystallization and glass transition behavior were detected *in situ* by variable-temperature ellipsometry and AFM. Figure 4a shows the evolution of the ellipsometric angle delta (Δ) and its differential ($d\Delta/dT$) with temperature in 24 nm PET films with different surface average chain conformations (0 vol% water is related to oblate ellipsoids, 1.1 vol% water is related to isotropic spheres). Three transitions are evident for the film with 0 vol% water added during heating. The first transition, occurring at 338.5 K, appeared at the turning point in the linear correlation plot of Δ vs. T and is normally assigned to glass transition. The second and third transition appeared as an abrupt rise in Δ and a peak in $d\Delta/dT$, which belongs to surface and bulk crystallization, respectively (see Figure 4a).^{6,34} The two crystallization processes are mutually independent, and the surface and bulk-like crystallization temperatures ($T_c^{surface} = 368$ K and $T_c^{bulk} = 388$ K) could be precisely identified by the peak in $d\Delta/dT$.^{57,58} When water content increases to 1.1 vol%, the surface crystallization process shifts to a higher temperature and merges together with the bulk crystallization process. Fortunately, in

the evolution of $d\Delta/dT$, two partly overlapping peaks can be differentiated, and $T_c^{surface} = 378$ K and $T_c^{bulk} = 388$ K. It is interesting that $T_c^{surface}$ increases gradually from 368 K to 378 K with increasing water content until 1.1 vol%, showing the suppression of surface dynamics (Figure 4b). When the

Figure 4. (a) Temperature dependence of ellipsometric angle (Δ) and its temperature derivative for 24 nm PET films prepared from solutions with 0 vol% or 1.1 vol% added water (heating rate: 2 K/min). (b) $d\Delta/dT$ plotted as a function of temperature (T) for 24 nm PET films with various surface chain conformations. Surface chain conformation is tuned by increasing the water contents in the casting solutions from 0 vol% to 1.5 vol%.

water content is increased to 1.5 vol%, both $T_c^{surface}$ and T_c^{bulk} remain constant. $T_c^{surface}$ can also be determined by monitoring the surface crystallization morphology evolution with temperature by AFM. About 10 pieces of 24 nm PET films, which were prepared from solutions with 1.1 vol% added water, were placed on a hot stage and heated at 2 K/min. When the temperature reached a certain value, one film was quickly quenched to room temperature to probe the surface crystallization

Figure 5. Surface crystallization behavior of 24 nm PET film prepared from PET solutions in a mixture of trifluoroacetic acid and water (1.1 vol%). (a) AFM topographic images exhibit the growth of surface crystals that were heated to various temperatures at a heating rate of 2 K/min (scale: 20 $\mu\text{m} \times 20 \mu\text{m}$, inset image: 5 $\mu\text{m} \times 5 \mu\text{m}$). (b) Evolution of the fraction of surface crystallization as a function of temperature.

morphologies. The evolution of surface crystallization morphologies in 24 nm PET film with temperature is shown in Figure 5a. At 373 K, dendritic crystals began to emerge, and the surface was almost covered by crystals at 380 K. By using the Nanoscope Analysis 1.40 software, the fraction of surface crystallization region was estimated, and plotted as a function of temperature in Figure 5b. Then, T_c^{surface} was identified to be 377 K for the 1.1 vol% water films. For the 0 vol% water films, T_c^{surface} was 369 K.³⁴ These values were similar to those obtained by ellipsometry.

When the film is about 10 nm thick, the whole film is made of the surface

crystallization layer which has been found to have a thickness of 10 nm. Accordingly, we also found that the $d\Delta/dT$ measurement of this film only shows surface crystallization, but no bulk crystallization (Figure S4). Moreover, almost the same $T_c^{surface}$ was observed for the 10 nm and 38 nm films, indicating that the substrate effect on the crystallization behavior can be ignored.³⁴ On the other hand, for film thick as 160 nm, only bulk crystallization can be observed because the decrease in thickness caused by surface crystallization is concealed by the expansion of the thick bulk layer.⁴⁹ Here, we examined the crystallization behavior of 10 nm and 160 nm PET films with different surface chain conformations to evaluate the effect of chain conformation on $T_c^{surface}$ and T_c^{bulk} , respectively (see Figure S5). The aforementioned results of $T_c^{surface}$, T_c^{bulk} and I_{1720} (SFG intensity at 1720 cm^{-1}) as functions of water content are all summarized in Figure 6. I_{1720} can initially be seen decreasing with water content, which indicates the surface average conformation transitions from the oriented oblate ellipsoid to the isotropic sphere and then remains unchanged. Concomitant with this variation in surface conformation, $T_c^{surface}$ increases at a similar rate. Hence, we believe that surface conformation plays a dominant role in surface dynamics. Moreover, when chloroform was employed as a poor solvent, $T_c^{surface}$ was always unchanged even the addition of chloroform was increased to 80 vol% (see Figure S6) because chloroform molecules can not perturb the H-bond network between TFA and PET chains and can not modulate the surface conformation of PET films (see Figure 2a and Figure 1d). In addition, T_c^{bulk} remained unchanged regardless of how much water or chloroform was added (Figure 6 and Figure S6). It is seems that bulk dynamics is less sensitive to chain conformation

since bulk chains do not contact with the free surface. It also can be supposed that the entanglement of bulk chains may change a little when adding poor solvents to solution because the concentration of PET solution is very low so that the interpenetration of polymer chains is limited.^{29,30}

Figure 6. $T_c^{surface}$, T_c^{bulk} and I_{1720} of PET films prepared from solutions with different water contents. (■□) T_c^{bulk} obtained by ellipsometry on 24 nm and 160 nm PET films, (●○) $T_c^{surface}$ obtained by ellipsometry on 24 nm and 10 nm PET films, (▲) $T_c^{surface}$ obtained by AFM on 24 nm films, (▽) I_{1720} obtained by SFG on the surface of 24 nm PET films.

3.3 The effect of surface chain conformation on glass transition of thin PET film

The glass transition temperature (T_g) was obtained at the turning point of the thermal expansion behavior as observed in a Δ vs. T curve. Figure S7 presents a representative set of Δ vs. T curves showing that films with different added water contents and hence different surface conformations exhibit different T_g 's. Moreover, Figure 7 shows the thickness dependence of the average T_g of thin PET films with

different surface chain conformations. With decreasing PET film thickness, a reduction in T_g can be observed, which is known as the T_g -confinement effect.^{59,60} For

Figure 7. Thickness-dependent T_g of PET films prepared from casting solutions with various water content. The dashed lines are the best fits of the $T_g^{film} \sim h$ data using Eq. (1), $T_g^{bulk} = 348.5$ K, and $A = 11$ nm. The inset shows $T_g^{surface}$ increases as a function of water content in the PET casting solution.

PET films with oriented ellipsoid surface chain conformation (0 vol% water), a reduction in T_g of up to 15 K for the 10 nm film can be observed. When the surface conformation approaches isotropic spherical conformation (1.1 vol% water), the reduction in T_g is diminished to 3.5 K. This indicates that the T_g -confinement effect can be tuned by adjusting the surface chain conformation. Compared to the other reported methods to tune or eliminate T_g -confinement effect, such as capping a layer on the surface to eliminate free surface,^{6,60-62} adding plasticizer to reduce the difference between surface and bulk dynamics,⁶³ enhancing the interaction between polymer and substrate to suppress surface dynamics remotely⁶⁴ and changing the chain topology (e.g.

cyclic⁵⁹ and star⁶⁵), the method based on modulating surface chain conformation does not change the structure of polymer film, not modify the chain topology and not take additive in the film system, shows a lot of advantages. It is shown that the thickness of surface crystallization layer is independent of the surface chain conformation (see Figure S8) and film thickness. Moreover, Figure 6 shows that the segmental dynamics of the surface crystallization layer changes with surface conformation, but not that of bulk layer. Hence, consider a two-layer model⁶⁶ that has a surface crystallization layer (which was ultimately turned from the surface mobile layer with enhanced segment dynamics⁴⁸) with $T_g = T_g^{surface}$ and thickness A , and the remainder of the film has the same T_g value as the bulk value (T_g^{bulk}). The average T_g of the film (T_g^{film}) can be written as follows:

$$T_g^{film} = T_g^{bulk} + A(T_g^{surface} - T_g^{bulk}) / h \quad (1)$$

where h is the film thickness, T_g^{bulk} is approximately 348.5 K, and A is approximately 11 nm, which is similar to the reported values reported before^{34,67}. The best fit results were plotted as dashed lines in Figure 7. From the fit, $T_g^{surface}$ was inferred and plotted vs. water content in the inset. By increasing the water content in the PET solution from 0 vol% to 1.1 vol%, $T_g^{surface}$ increased from 332.5 K to 344 K, and remained constant when the water content was increased to above 1.1 vol%. This observation shows the same trend with water content as $T_c^{surface}$, reaffirming the sensitivity of surface dynamics to chain conformation.

Figure 8. (a) SFG spectra from the surface of 24 nm PET films prepared by adding 1.1 vol% water before and after annealing at 564 K for 15 s to permit chain relaxation. (b) Ellipsometric angle Δ and $d\Delta/dT$ plotted as functions of temperature (T) of 24 nm PET films before and after annealing at a heating rate of 2 K/min.

The isotropic spherical conformation at the surface of PET film prepared by adding 1.1 vol% water is not an equilibrium conformation. When the film was annealed at 554 K, above the melting temperature, the polymer chain relaxes to its equilibrium conformation. Figure 8a shows the *ssp* SFG spectra from the surface of a 24 nm PET film prepared by adding 1.1 vol% water before and after annealing at 564 K for 15 s. It indicates that the surface conformation almost recovers from that of isotropic spherical conformation to oriented oblate ellipsoid after annealing. At the same time, the T_g changes from 346 K to 338.5 K and T_c^{surface} reduces from 379 K to 370 K (see Figure 8b), showing acceleration of surface dynamics upon annealing. On the other hand, T_c^{bulk} remains constant. This result further confirms the sensitivity of surface dynamics on chain conformation.

Variations in the surface chain conformation may be sensitive to the entanglement at the surface. When the surface chain conformation changes from oblate ellipsoid to isotropic spherical conformation, the interpenetration between surface chains may be enhanced²¹ in consideration of R_g only collapsed about 9 % than R_g^{bulk} when adding 1.1 vol% water in PET solution. Then, entanglement may be enhanced to suppress surface dynamics. More importantly, the variations in the surface chain conformation will affect the number of contacts between the polymer chain and the free surface. de Gennes⁶⁸ proposed the chain motion near a surface to be a sliding one, which based on collective motions of a “loop” (which does not involve the chain ends) along the chain. In the sliding motion, the contact sites between polymer chain and free surface are very important, corresponding to high free volume and separate the chain into some “loops”. The high free volume can be transferred along the “loops” to enhance chain mobility. When the surface chain conformation changes from an oblate ellipsoid to a bulk-like random coil, the average number of contact sites in each polymer chain is reduced. As a result, the dynamics of the surface chain are suppressed.

4. CONCLUSIONS

In conclusion, polymer surface chain conformation was modulated by preparing PET films from casting solutions with different addition of water. MD simulations showed that the H-bond network between TFA and PET chains is partly disrupted by the water molecules added, some sites of the chain are dissolved, and the chain conformation may be more stable. Then the average chain conformation which is

preserved upon transition to solid film surface is more spherical. By increasing the water content in the PET solution from 0 vol% to 1.1 vol%, the surface average chain conformation could be tuned from an oriented oblate ellipsoid to an isotropic spherical conformation. At the same time, both $T_c^{surface}$ and $T_g^{surface}$ increased, and the T_g -confinement effect was suppressed. We contemplate that variations in the surface average chain conformation from ellipsoidal to spherical, may cause the number of contact sites between the polymer chains and the free surface to decrease and the entanglement to increase, and thereby suppress the surface chain dynamics. When the water content was increased to above 1.1 vol%, $T_c^{surface}$, $T_g^{surface}$ and T_g -confinement no longer changed. Concomitantly, the surface average conformation also did not change. These results provide direct evidence that chain conformation plays a dominant role in the surface dynamics.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macromol.XXXXXXX. Elimination of residual water from the PET, the evolution of R_g with simulation time, the method of ellipsometry to detect crystallization behaviors, the effects of different poor solvents, the crystallization behaviors of different thickness PET films, the effect of surface conformation on the crystallization behavior of 10 nm and 160 nm PET films, the effect of chloroform on surface crystallization, T_g measurement from delta versus T curve, the calculation of surface crystallization layer thickness on PET films. Table S1 and Figures S1-S8 (PDF)

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The authors declare no competing financial interest.

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Supporting Information for:

Conformation-Sensitive Surface Dynamics in Thin Poly(ethylene terephthalate) Film

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1. Elimination of residual water from the PET

In order to eliminate the influence of residual water, which can exert a significant effect on the chain conformation and dynamics at the surface, the as-spun PET films were annealed at high vacuum (pressure $< 10^{-6}$ mbar) for 48 h at room temperature after preparing on Au substrate from solution with different addition of water. Furthermore, PET films were detected by polarization modulation infrared reflection absorption spectroscopy (PM-IRRAS) to confirm whether the residual water was removed completely or not, as shown in Figure S1. No detectable IR signals can be observed in the region from 3200 cm^{-1} to 3600 cm^{-1} , which revealed that the PET films do not contain appreciable amounts of water. Moreover, the T_g of PET thick films ($> 300\text{ nm}$) prepared from solutions with different water content keeps constant about 348 K , eliminating the case that solvents exist as plasticizers. Both observations revealed that the PET films do not contain appreciable amounts of water.

Figure S1. PM-IRRAS spectra from 24 nm PET films prepared from solutions with various addition of water on Au substrate.

2. The evolution of R_g with simulation time

The R_g of PET chain as a function of simulation time in TFA and TFA / H₂O systems were shown in Figure S2. It is found that the value of R_g reaches almost constant in the last 30 ns simulation (a total of 50 ns). Moreover, the number of H-bond in different solvent systems also kept constant in the last 40 ns (see Figure 2a). Based on these results, it is believed that the simulation reaches equilibrium.

Figure S2. Average R_g of PET chains as a function of simulation time in TFA and TFA / H₂O systems.

3. The method of ellipsometry to detect crystallization behaviors

Using ellipsometry, the *in-situ* evolution of film thickness can be easily obtained with the increasing of temperature at a heating rate of 2 K/min (see Figure S3a, refractive index $n = 1.571$). At the beginning of heating, the film thickness increases and the glass transition occurs at the turning point of the thermal expansion behavior changes. Continue to heat up, two abrupt drops of film thickness can be observed. It is demonstrated in our previous works^{1,2} that the two abrupt drops belong to surface and bulk crystallization, respectively. The differential results of dh/dT and $d\Delta/dT$ were

shown in Figure S3b, from which $T_c^{surface}$ and T_c^{bulk} can be easily obtained.

Figure S3. Temperature dependence of (a) film thickness (h) and ellipsometric angle (Δ) (b) dh/dT and $d\Delta/dT$ for 18 nm PET film (heating rate: 2 K/min).

4. The effects of different poor solvents

The surface chain conformation of PET films prepared from solutions with different addition of water was investigated by SFG and MD. Stepwise crystallization and glass transition behavior of PET films were investigated to extract information about the surface dynamics. The results are summarized in Table S1.

Table S1. Solubility properties of a series of poor solvents for PET and their effect on surface conformation and surface dynamics

Poor Solvent	bp (K)	δ (cal ^{1/2} ·cm ^{-3/2})	P	Whether it can form H-bond with PET	Surface conformation	Whether it affects surface dynamics
n-Hexane	342	7.3	0	No	Oblate ellipsoid	No
Chloroform	334.7	9.3	0.017	No	Oblate ellipsoid	No
Dichloromethane	312.7	9.7	0.120	No	Oblate ellipsoid	No
Tetrahydrofuran	337.5	9.9	0	No	Oblate ellipsoid	No
Ethanol	351.3	12.7	0.268	Yes	Isotropic sphere	Yes
Methanol	338	14.5	0.388	Yes	Isotropic sphere	Yes
Water	373	23.2	0.819	Yes	Isotropic sphere	Yes

bp is the boiling point, δ is the solubility parameter of solvent, P is the polar fraction of solvent, the solubility parameter of PET is about 10.7 cal^{1/2}·cm^{-3/2}. The data come from Polymer Handbook, 4th ed.

It is shown that different poor solvents exhibit different effect on surface conformation and subsequently whether the surface dynamics are altered. It is found that only the poor solvents (e.g. ethanol, methanol, water) which have larger polar fraction and are able to form H-bond with PET chain can modulate the surface conformation and affect the surface dynamics. While the other poor solvents (e.g. n-hexane, chloroform, dichloromethane and tetrahydrofuran) plays no effect on surface conformation and surface dynamics.

5. The crystallization behaviors of different thickness PET films

The crystallization behaviors of different thickness PET films were shown in [Figure S4](#). It is found that the stepwise crystallization behavior can be observed on 38 nm, 24 nm and 18 nm PET films. But, compared to the peak of surface crystallization, the peak of bulk crystallization becomes smaller and smaller with the decreasing of film thickness. When thickness is decreased to 10 nm, only surface crystallization

Figure S4. $d\Delta/dT$ plotted as a function of temperature (T) of different thickness PET films prepared without water.

process can be observed. When thickness is increased to 160 nm, the volume fraction of surface layer is too small that the decrease in thickness caused by surface crystallization may be concealed by the expansion of thick bulk layer, only bulk crystallization can be observed.

6. The effect of surface conformation on the crystallization behavior of 10 nm and 160 nm PET films

Due to the same $T_c^{surface}$ was observed at 10 nm and 38 nm film (Figure S4), the interfacial effect on crystallization behavior may be negligible. For 10 nm PET films, only surface crystallization process could be observed. And for 160 nm PET films, only bulk crystallization process could be noted. Then, the crystallization behavior of 10 nm and 160 nm PET films with different surface chain conformation were examined to evaluate the effect of chain conformation on $T_c^{surface}$ and T_c^{bulk}

Figure S5. $d\Delta/dT$ plotted as a function of temperature (T) of (a) 10 nm and (b) 160 nm PET films with various surface chain conformations to obtain the evolution of $T_c^{surface}$ and T_c^{bulk} . Surface chain conformation was tuned from oblate ellipsoid to bulk-like spherical conformation by increasing the addition of water from 0 vol% to

1.1 vol%, which is detected by SFG. Continue to increase the water content to 1.8 vol%, surface conformation shows no more change.

respectively, as shown in Figure S5. It is shown that the $T_c^{surface}$ on 10 nm PET increases as the surface chain conformation was tuned from oblate ellipsoid to bulk-like spherical conformation, while T_c^{bulk} remains constant. Such observation is the same as the evolution of $T_c^{surface}$ and T_c^{bulk} obtained from 24 nm PET films.

7. The effect of chloroform on surface crystallization

Figure S6. $d\Delta/dT$ plotted as a function of temperature (T) to obtain the evolution of $T_c^{surface}$ and T_c^{bulk} of 24 nm PET films prepared from a mixed solution, where the volume fraction of chloroform in TFA and chloroform solvent system was tuned from 0 vol% to 80 vol% to adjust the solvent quality.

Chloroform was employed as another poor solvent to compare with the effect of water on surface crystallization. The volume fraction of chloroform in TFA and

chloroform solvent system was tuned from 0 vol% to 80 vol% to adjust the solvent quality before preparing the PET film. However, unlike the situation produced when water was used as poor solvent, changing the volume fraction of chloroform plays no effect on the crystallization behavior, as shown in Figure S6. It could be explained that the addition of chloroform can't perturb the H-bond network between TFA and PET chains and can't modulate the chain conformation at surface, while the addition of water works, which is shown in Figures 2a and 1b.

8. T_g measurement from delta versus T curve

Figure S7 is a representative example to show how to obtain the T_g . T_g was obtained at the turning point in the linear correlation plot of Δ vs. T curve. With the surface average conformation changes from oblate ellipsoid to the isotropic spherical conformation, the T_g of 24 nm PET film gradually increases.

Figure S7. Ellipsometric angle Δ plotted as a function of temperature (T) of 24 nm PET films with different surface chain conformation at a heating rate of 2 K/min.

9. The calculation of surface crystallization layer thickness on PET films

The stepwise crystallization behavior of PET film can be observed in the evolution of ellipsometric angle Δ with temperature at a heating rate 2 K/min.^{1,3} The two rises of Δ , which are separated by a discernible plateau (water content: 0 vol% in [Figure S8](#)), indicate two independent crystallization processes. It is reported¹ that the first crystallization process belongs to the crystallization of surface layer and the second belongs to the crystallization. In a model system, the PET film can be divided into surface enhanced crystallization dynamics layer and the bulk-like layer. Then the thickness of surface crystallization layer (A) can be calculated from the ellipsometry data. According to our previous work,² A could be obtained as follows:

$$A = \frac{X_t^{bulk} d\Delta_{surf}}{X_t^{bulk} d\Delta_{surf} + X_t^{surf} d\Delta_{bulk}} \times h$$

where $d\Delta_{surf}$ and $d\Delta_{bulk}$ are the variations in Δ caused by surface and bulk crystallization processes, respectively; X_t^{surf} and X_t^{bulk} are the crystallinity degree of surface and bulk layer, respectively; h is the film thickness. X_t^{surf} can be reasonably assumed to be close to X_t^{bulk} for thin PET films (<30 nm) and then the value of A can be calculated from the evolution of ellipsometric angle Δ with temperature (see [Figure S8](#)). It is found that when increasing the addition of water from 0 vol% to 0.75 vol%, the value of $d\Delta_{bulk} / (d\Delta_{surf} + d\Delta_{bulk})$ (about 0.46) almost remains constant (see the red line in [Figure S8](#)). This indicates that A remains constant and the value is about 11 ± 0.2 nm, the same as our previous work.³ And it is reasonable to speculate that A is still unchanged when increasing the addition of water to 1.1 vol% or more. Moreover, it has been proven that A is film thickness independent.²

Figure S8. Normalized ellipsometric angle Δ as a function of temperature (T) of PET films prepared from solution with different addition of water at a heating rate of 2 K/min. The variations in Δ caused by surface crystallization are the same in these PET films.

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