Competition between substrate-mediated $\pi$-$\pi$ stacking and surface-mediated $T_g$ depression in ultrathin conjugated polymer films

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Abstract. We report surface and interface effects in dynamics and chain conformation in the thin film of conjugated polymer PCDTBT. To probe dynamic anomalies, we measure the glass transition temperature ($T_g$) of PCDTBT films as a function of thickness, and find that there is a significant depression in $T_g$ for films less than 100 nm thick; a result qualitatively similar to that observed in many other polymer film systems. However, for films less than 40 nm, the $T_g$ converges to a constant value of 20 K below its bulk value. Grazing incidence X-ray diffraction shows depth-dependent molecular organization that is associated with the unusual thickness-dependent dynamics.

1 Introduction

Polymers have demonstrated deviations from their bulk physical properties when they are in confinement [1–4]. Such phenomena are very striking in thin polymer films, for which the glass transition temperature ($T_g$) [1–4] and viscosity [5,6] are widely observed to deviate significantly from bulk values when a film is created having a thickness below some critical value. Whilst the enhanced dynamics of polymer chains at a free surface will always reduce $T_g$ [7], strong polymer-substrate interactions can often increase $T_g$ [1,8]. Such effects can be quantified using models [1,9,10] that describe a thin-film consisting of a number of separate layers in which the polymer molecules have different chain mobility. Despite this growing understanding of the structure of thin films of saturated polymers, less is known regarding the deviation of bulk properties of conjugated polymers when they are formed into thin films, although one study has observed a deviation in $T_g$ in two fluorene-based conjugated polymers [11]. Conjugated polymers usually have greater chain stiffness than conventional saturated polymers (for example polystyrene) that has served as a model system to study $T_g$ deviation in thin films. Although some conjugated polymers are non-crystalline, an intermediate level of order is usually present resulting from $\pi$-$\pi$ stacking between polymer backbones. Despite the importance of this class of device applicable material, the effect of a substrate or an interface on such states of intermediate order is not however well understood.

In this work, we explore the changes in $T_g$ and molecular organization of thin films of a conjugated polymer poly[N-9′-heptadecanyl-2,7-carbazole-alt-5,5-(4′, 7′-di-2-thienyl-2′, 1′, 3′-benzothiadiazole)] (PCDTBT). PCDTBT is one of a relatively new class of low-energy-gap polymers that have been used to fabricate photovoltaic devices and field effect transistors [12,13]. Our measurements suggest the existence of a series of distinct depth-dependent morphological phases within the film, with a $\pi$-$\pi$ stacked layer having increased coherence length existing close to the substrate and lamellar-type order towards the film surface. We speculate that such structural heterogeneity may directly affect the electronic properties of conjugated polymer thin films; a conclusion that has relevance for the operation of organic-electronic devices [14,15].

2 Experimental methods

The polymer PCDTBT was synthesized according to our previous report [16], and had an $M_w$ of 29.3 kDa and a polydispersity of 1.57 as measured by GPC. Figure 1
shows the molecular structure of PCDTBT. GPC was performed in 1,2,4-trichlorobenzene (TCB) at a temperature of 100 °C. The GPC curves were obtained by the RI-detection method, with a series of narrow polystyrene standards used to calibrate the instrument. To prepare thin films, PCDTBT was dissolved in chlorobenzene (CB) at a range of different concentrations (from 1.3 to 40 mg/ml) and deposited on a Si/SiO$_2$ substrate by spin-casting to create films having thickness between 12 and 200 nm. In each case a fixed spin speed was used (1000 rpm) to reduce the varying effects of the centrifugal force on intermolecular interactions during spin casting. Spectroscopic ellipsometry was used to determine film thickness, with a Cauchy model used to fit these measurements over the wavelength range in which the film is optically transparent.

To determine $T_g$, PCDTBT films were heated from 25 to 200 °C under a N$_2$ atmosphere and then cooled to 25 °C at a rate of 2 °C/min. The thickness-dependent $T_g$ of PCDTBT films was measured using ellipsometry during a cooling cycle. Grazing-incidence wide-angle X-ray scattering (GIWAXS) measurements were carried out at the I-16 beamline, Diamond Light Source (UK). Samples were mounted in a custom-built experimental chamber (filled with helium to reduce scatter) featuring an internal beam-stop and blade held above the sample as described previously [13]. PCDTBT samples for GIWAXS measurement were either studied as-cast, or were annealed ex situ by heating to 200 °C and then returned to room temperature at a rate of 2 °C/min. This process replicates the thermal protocol used to study films using ellipsometry to determine the $T_g$. All films were prepared on clean Si/SiO$_2$ wafers. A series of GIWAXS scattering patterns were recorded at different grazing incidence angles with a step of 0.02°, using 12 keV energy X-rays and a Pilatus 2M detector to record images with a 30 second exposure time.

3 Results and discussion

Our previous work has demonstrated that any residual CB casting solvent trapped in a PCDTBT film during spin-casting evaporates rapidly during the initial heating cycle once the film reaches a temperature of 135 °C (the boiling point of CB) [13]. This process removes all casting solvent from the film, and thus on cooling we can use the change in the gradient of $\Psi$ to extract the $T_g$. We have confidence in this procedure, as the coincidence and reproducibility of the change in $\Psi$ as a function of temperature observed on the first cooling cycle and second heating cycle are excellent. We do not expect degradation of PCDTBT to occur in our measurements as all heating/cooling cycles were performed under a N$_2$ atmosphere at temperatures well below the degradation temperature [17] of PCDTBT (> 450 °C).

Figure 2a summarizes recorded values of $\Psi$ (at 650 nm) determined using ellipsometry for films having different thickness as a function of temperature. Interestingly as the film thickness is reduced below 40 nm, the difference in the slope of the glassy and rubbery regime reduces, indicative of a reduced strength of the $T_g$ transition in such thin films. This behavior is qualitatively similar with that observed in saturated PS films [18]. It is also notable that the width of the $T_g$ transition apparently reduces as the $T_g$ of PCDTBT thin film is reduced; a conclusion evidenced from the temperatures at which the expansion of the film (as measured by $\Psi$ at 650 nm) deviates from linearity.

Figure 2b shows that as the PCDTBT film thickness reduces, $T_g$ is reduced from 130 °C at 100 nm to around 110 °C at 40 nm. This relatively small depression in $T_g$ (20 °C) is smaller than that has been observed in polystyrene, where a $T_g$ reduction up to 40 °C has been observed [1]. Interestingly, the depression in $T_g$ in PS only occurs when the film thickness is less than 50 nm [1], whilst in PCDTBT this effect occurs once the film is reduced below 100 nm; a result in accord with another study on two fluorene-based conjugated polymers [11]. The most striking feature presented in fig. 2b is that the $T_g$ of the PCDTBT film converges to a value of approximately 110 °C (vide infra) at a film thickness of 40 nm and does not undergo additional reduction as the film is further thinned, whereas in PS films the $T_g$ continues to decrease even when the film thickness is reduced below 40 nm.

We can understand the differences between the onset thickness of $T_g$ depression in PCDTBT and PS on the basis of chain stiffness; previous work [19] on polycarbonate (having a chain stiffness greater than PS) has found the onset thickness for $T_g$ deviation starts at 142 nm, a value much larger than the critical thickness of PS. Ellis et al. [20] also found that modification of the PS monomer unit can substantially change the $T_g$ deviation behavior, and concluded that chain stiffness is responsible for increased onset thickness of the depressed-$T_g$ surface layer via its influence on the cooperative segmental size of the polymers. We conclude therefore that PCDTBT has a higher chain stiffness than PS, resulting in a comparatively larger cooperative segmental size and a higher onset thickness for $T_g$ deviation.

We can quantify the $T_g$ depression behavior in films having a thickness between 100 and 40 nm using a phenomenological two-layer model [1] as expressed using eq. (1). Here the parameter $\gamma$ empirically describes the thickness of the surface layer with $\delta$ being a fitting constant and $h$ the entire thickness of the film,

$$T_g = T_g^{bulk} \left[ 1 - \left( \frac{\gamma}{h} \right)^\delta \right].$$  (1)
We find that this model provides a good fit to the experimental data within the $T_g$ depression region. From our best fit ($\chi^2 = 4.6$), we obtain the bulk values $T_g^\text{bulk} = 131 \, ^\circ\text{C}$, $\gamma = 19.3 \, \text{nm}$ and $\delta = 2.1$. The value of $T_g^\text{bulk}$ determined here agrees well with a previous measurement of the bulk $T_g$ of PCDTBT of 130$^\circ$C determined using differential scanning calorimetry [17].

In direct contrast to polymers having a saturated molecular backbone, PCDTBT molecules undergo $\pi$-$\pi$ stacking in a solid thin film after spin casting from solution. We have used grazing-incidence wide-angle X-ray scattering (GIWAXS) to study the $\pi$-$\pi$ stacking in PCDTBT following our previously reported methodology [13]. The data shown in fig. 3a was recorded from an as-cast (annealed) PCDTBT film. Here, $\pi$-$\pi$ stacking is evidenced via a scattering “crescent” observed at $q = 1.57 \, \text{Å}^{-1}$ in the 2D X-ray scattering image [13,21]. The fact that this peak is primarily in the out-of-plane direction indicates that the conjugated backbones adopt a face-on orientation and lay parallel to the silicon substrate. The innermost diffraction ring at a $q = 0.31 \, \text{Å}^{-1}$ (partly blocked in the out-of-plane direction by the flare after the beam stop) is attributed to 1st-order scattering from side-chain ordering, and is associated with the distance (ca. 20 Å) between bi-layer ordered lamella of PCDTBT backbones separated by the two alkyl side-chain lengths [13, 21,22].

The data presented in fig. 3b was recorded from a PCDTBT film that had been subject to the same heating and cooling cycles used in the ellipsometry measurements used to determine $T_g$. Here, a new diffraction peak at $q = 0.63 \, \text{Å}^{-1}$ appears in the out-of-plane direction of the 2D image: a feature recently assigned as the 2nd-order diffraction of the bi-layer lamella spacing [22]. Such a structure is observed if a PCDTBT film is annealed above its bulk $T_g$ and originates from PCDTBT molecules adopting a lamellar structure with an edge-on orientation [22]. Our X-ray scattering measurements presented here confirm therefore that the molecular structure in PCDTBT films upon thermal treatment above the bulk $T_g$ is characterized by an admixture of face-on stacking and edge-on lamellar stacking.

We have used GIWAXS measurements performed as a function of grazing-incidence angle ($\alpha$) to probe the structure as a function of depth below the film surface [23]. This permits us to determine $\pi$-$\pi$ stacking coherence length using $L = 2\pi/\Delta q$, where $\Delta q$ is the full width at half-maximum of the scattering crescent observed at $q = 1.57 \, \text{Å}^{-1}$. Here, $\Delta q$ is determined from a Gaussian multi-peak fit to the raw scattering data in the out-of-plane direction, a selection of which is shown in fig. 3c. We summarize the $\pi$-$\pi$ stacking coherence length determined at different incidence angles in fig. 3d, with data plotted for two films having a thickness of 30 and 50 nm.

To understand the significance of such data, it is necessary to relate grazing-incidence angles ($\alpha$) to the regions in the film at which X-ray scattering is being generated. For grazing-incidence angles less than the critical angle for total reflection from the polymer ($\alpha_e^\text{pol}$), we can straightforwardly calculate the penetration depth of the X-rays at grazing-incidence angles $\alpha < \alpha_e^\text{pol}$ using the methodology outlined in Appendix A. Here, the X-ray scattering process is confined to a depth $< 15 \, \text{nm}$ from the surface. We find that close to the film surface ($\alpha = 0.03^\circ$) the $\pi$-$\pi$ stacking coherence length is approximately (7.0 ± 0.5) Å (see fig. 3d). For incidence angles $\alpha^\text{pol} < \alpha < \alpha_e^\text{Si}$ (where $\alpha_e^\text{Si}$ is the critical angle of the Si substrate), a standing wave forms in the film as a result of interference between the incident X-ray beam and the beam reflected from the polymer-substrate interface [24]. We calculate the structure of this standing wave as outlined in Appendix A (and shown in figs. 4 and 5). For this range of angles,
Fig. 3. Heterogeneous vertical structure in PCDTBT thin films. 2D grazing incidence X-ray images of a 50 nm thick film at \( \alpha = 0.11^\circ \) in an as-cast state (a) and after the heating/cooling cycle for \( T_g \) measurement (b). Panel (c) shows the raw scattering data for a 50 nm thick film at three different grazing incidence angles in the out-of-plane direction. Panel (d) shows the \( \pi-\pi \) stacking coherence length as a function of grazing incidence angle, together with the relative intensity changes of peaks at \( q = 0.63 \) and 1.57 Å\(^{-1}\).
reduced π-π stacking, a bulk intermediate layer and an interface layer with pronounced π-π stacking that is stabilized by interaction with the substrate. As the film is progressively thinned, a reduction occurs in the thickness of the bulk layer. As the total film thickness falls below 40 nm, this bulk layer vanishes entirely, resulting in a film consisting of a lamellar-ordered surface-layer positioned on a substrate layer having pronounced π-π stacking.

Here, a competition arises between the substrate-directed π-π stacked layer (having increased $T_g$) and a lamella-ordered layer located at the film surface having reduced π-π stacking and thus depressed $T_g$. This results in the apparent convergence of $T_g$ to 110 $^\circ$C even in the thinnest films studied. Without the existence of the π-π stacking driven by the presence of the substrate interface, we anticipate that the $T_g$ would not converge as observed but would undergo further reduction as the film is thinned. Indeed, the ellipsometry data presented in fig. 2a suggests that the width of the $T_g$ transition reduces as the total thickness of the PCDTBT film is reduced, an observation consistent with a relative increase in the volume fraction of the π-π stacked layer and a general reduction in conformational heterogeneity.

We believe the observation of the heterogeneous molecular structure in conjugated-polymer thin films has significant relevance for their application in organic electronic devices. It is known that coherence length in a conjugated polymer phase can substantially increase the efficiency of bulk heterojunction solar cells [25]. However, our measurements demonstrate a variation in coherence length that is driven by proximity to an interface and a free surface. This effect will be particularly important in devices such as bottom-gate field effect transistors (FET) that utilize a SiO$_2$ gate dielectric. Here, charge transport occurs through a channel having a width of a few nanometers positioned in close proximity to the gate insulator. π-π stacking in this layer driven by interactions with the substrate will be particularly important in generating a molecular system having high charge-carrier mobility. Clearly, the degree of π-π stacking driven by interactions with the substrate will be dependent on the nature of the substrate, and on the propensity of the (macro)-molecules under study to undergo π-π stacking. Nevertheless the ability to control and drive this process has wider important implications for the efficient operation of organic-based light-emitting diodes or photovoltaic devices, as molecular-scale order is likely to increase charge-carrier mobility and thus increase the rate at which charges can be injected or extracted. Developing methods to control nanoscale order close to an interface by—for example—controlling surface energy may present a useful means to optimize such electronic properties.

### 4 Conclusions

In conclusion, we have quantified depth-dependent morphological structure within a PCDTBT conjugated-polymer thin film using spectroscopic ellipsometry and grazing-incidence X-ray scattering. Our results indicate a thickness-dependent glass transition temperature that results from a competition between π-π stacking driven by proximity to the substrate and lamellar structure with reduced π-π stacking near the film’s free surface. Our work provides insight into heterogeneity in molecular morphology and in particular provides a methodology to explore the effect of different device-applicable substrate materials and interfaces on controlling electronic functionality.

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### Appendix A. X-ray penetration depth at different grazing-incidence angle

**X-ray electric-field depth intensity**

![Fig. 4.](image)

The incidence (A), reflection (B) and transmission (T) of X-ray in a three-layer system. The refractive index $n$ of an electromagnetic medium for X-ray is $n = 1 – \delta – i\beta$, with $\delta$ the refractive index decrement and $\beta$ the absorption index. The real and complex parts of the refractive index are assumed to be constant throughout the film. Both medium 1 (air) and substrate are considered infinite and lossless media. At 12 keV, the refractive index of the polymer layer is $n = 1–2 \times 10^{-6} – (2.0 \times 10^{-5})$, and $n = 1–3.36 \times 10^{-5} – (4.4 \times 10^{-6})$ for Si.

When the grazing-incidence angle of the X-ray beam is below the critical angle ($\alpha_c$) of the thin film, the electric field intensity in the film is evanescent in nature and decays exponentially as a function of depth. For angles $\alpha < \alpha_c$, we can quantify the penetration depth ($l$) of the X-rays into the film using eq. (A.1) [26,27].

$$l = \frac{\sqrt{2} \lambda}{4\pi} \sqrt{\left((\alpha^2 - \alpha_c^2)^2 + (\lambda\mu\rho/4\pi)^2\right)^{-1/2} + \alpha_c^2} + \alpha^2.$$  

(A.1)

Here, $\lambda$ is the wavelength of synchrotron X-ray, $\mu\rho$ is the mass absorption coefficient of the film and $\rho$ its density, assumed to be 1300 kg m$^{-3}$; $\alpha_c = 0.115\lambda$. The critical angle is calculated using $\alpha_c = \sqrt{2(\ln N_A^g - Z\sqrt{\pi/2})} / N_A^g$, where $\lambda$ is the wavelength of the incident X-rays (1.033Å), $r_e$ is the classical electron radius ($2.814 \times 10^{-14}$ nm), $N_A^g$ is Avogadro’s number, $Z$ the averaged atomic number and $A$ the averaged atomic mass. For incidence angles between the
critical angle of the polymer ($\alpha_{\text{pol}}^c$) and the Si substrate ($\alpha_{\text{Si}}^c = 0.15^\circ$ for 12 keV X-rays) the X-ray beam penetrates into the bulk of the film, with a standing wave being formed as a result of interference between the incident beam and the beam reflected from the polymer-substrate interface [24]. The calculation of the electromagnetic field intensity distribution as a function of depth using a transfer matrix reflectivity model [28] indicates that the field maximum of the standing wave locates close to the centre of the film (for a 30 nm thick film) or near the interface with the Si substrate (for a 50 nm thick film) (see fig. 5). For $\alpha > \alpha_{\text{Si}}^c$, the X-ray beam penetrates the entire depth of the PCDTBT film and enters the Si/SiO$_x$ substrate, probing an averaged structure of the whole film.

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Fig. 5. X-ray electric-field intensity as a function of depth at different incidence angles in films with a thickness of (a) 30 nm and (b) 50 nm. The curves are offset for clarity.