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2007 J. Phys.: Condens. Matter 19 416106

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A natural length scale for the glass transition of conjugated polymer film

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Received 18 April 2007, in final form 8 August 2007

Published 10 September 2007

Online at stacks.iop.org/JPhysCM/19/416106

Abstract

A study is reported of the anomalous glass transition temperature, T_g , in thin free-standing conjugated polymer films revealed by confocal Raman scattering. Full details of the dependence of T_g on film thicknesses d ranging from less than to greater than the polymer average end-to-end distance R_{EE} are presented. In contrast to ultrathin films ($d < R_{EE}$), which always exhibit a reduction of their T_g values due to the chain confinement effect, thick films within a certain range of thicknesses distinguish themselves by presenting anomalous enhancement of two T_g values; one is interpreted as at the interface, and the other in the core. This study is strongly suggestive of a new length scale L , which lies in the range of most polymer electronic devices studied over which the physical properties of the film are greatly perturbed by the presence of free surfaces.

To fully realize the potential use of synthetic polymer films in optoelectronic device fabrication it is necessary to understand the parameters governing their electrical and thermal properties. One of the fundamental parameters is the glass-to-liquid transition temperature T_g , involving slow conformational exchange in molecular processes. This, in turn, dictates the functional limit of a specific polymer in device applications. Despite the technological significance of glass-forming polymers, the glass transition is still poorly understood. Adam and Gibbs [1] were the first who attempted to unify the two general views of a glass transition as either a real thermodynamic phase transition [2] or simply a kinetic phenomenon [3]. The authors of [1] introduced the idea of cooperative rearrangement, together with a length scale $\xi(T)$, to demonstrate such cooperativity, coupled with a thermodynamic transition, resulting in system dynamics predicted by the Williams–Landel–Ferry (WLF) equation [4].

The *layered model* is often used to describe T_g in low molecular weight free-standing films. The fundamental idea is based on the length scale of cooperative motion [5]. The authors of [5] suggest that near the interface of the film there exists a liquid-like surface layer of finite

thickness with an increased mobility, thus producing a lower T_g near the surface than the bulk value, denoted T_g^{surf} and T_g^{bulk} , respectively. The length scale for this layer is then argued to be essentially equal to $\xi(T)$, the length scale for glass transition dynamics. The effective T_g for a film of thickness d is summarized by the equation [6]

$$T_g(d) = T_g^{\text{bulk}} - \frac{2\xi(T_g) [T_g^{\text{bulk}} - T_g^{\text{surf}}]}{d}, \quad (1)$$

following a parameterization for $\xi(T)$. All the parameters in equation (1) have a well-defined physical meaning, and thus can be directly compared with other approaches. An important prediction of this model may lead to either one average T_g for the whole film (a combined bulk and boundary effect) or two distinct T_g s, respectively [5]. It shall be shown later that an ultrathin film is an example of the former, while thick film is much closer to the latter case.

The underlying origin of the preferentially increased mobility of the polymer chains at the surface layer has been the subject of much discussion [6, 7]. The first theoretical arguments regarding the issue of reduced T_g were proposed by Mayes [8]. For entropic reasons, it was suggested that chain ends are of higher concentration at the interfaces than that in the bulk, and that the polymer density in the region immediately adjacent to the interfaces should thus be reduced. This phenomenon was quantitatively predicted by the simulation conducted by Rouault and Müller *et al* [9, 10]; the increased mobility of the chain segments is a consequence of the density reduction, leading to a decreased T_g in the surface region. A possible origin for the increased mobility at the polymer–air interface was recently introduced by de Gennes [6]. It was suggested that two dominant mechanisms exist in the polymeric glass-to-liquid dynamics, namely: (i) the standard chain sliding (reptation) motions along its primitive path, which are controlled by the free volume and are independent of the chain length, and (ii) the cooperative motions, which are associated with small length scale segmental mobility. These two different modes of mobility are in constant competition. In the bulk, the cooperative motions are more efficient, while the sliding motion is inhibited due to end group hindrance. However, as the polymer film thickness reaches R_{EE} , most polymer chains will have contacts with the free interface, and the sliding motions become the dominant ones. The model is able to explain many of the features of the T_g reductions in high molecular weight free-standing film.

In this paper, we demonstrate the use of confocal Raman spectroscopy to monitor the glass transitions in free-standing poly(9,9-dioctylfluorene) films, hereafter F8, with varying thicknesses. The validity of using Raman scattering for this purpose has been recently reported on free-standing film [11–13] and supported film [14]. The measured T_g values for F8 ultrathin films ($d \sim 75$ nm) are reduced below the bulk value. Measurement on thick F8 films, however, show enhanced T_g s as well as evidence for two different T_g values. Contrary to the common belief that T_g values will inevitably be reduced in thin films, the observed T_g is increased even above the bulk value. By presenting this anomaly, which we believe is quite general to conjugated polymers, we highlight the presence of a new characteristic length (different from that for cooperative motion) which takes into account the additional constraints at the film boundaries in determining the T_g .

Probing the change in the polarized Raman intensities (RIs) of the 1605 cm^{-1} mode I_{\parallel} or I_{\perp} with varying temperature provides an empirical measure of T_g in polymer films [11, 14]. Spectra were collected with a high-throughput single-grating Renishaw Raman spectrometer, which was attached to a confocal microscope with a $50\times$ long working distance objective. The 633 nm line of a He–Ne excitation minimized the resonance Raman contribution. The conjugated polymer F8 used in this study belongs to a class of rigid-rod polymers which have attracted increasing attention for use in polymer light-emitting diodes, thin-film transistors, and solar cells [15]. The monomer unit consists of rigid planar biphenyl units, as shown

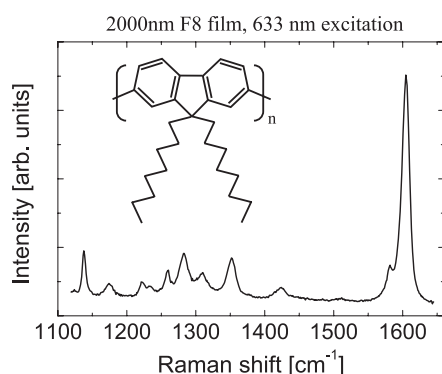


Figure 1. Raman spectrum of a thick free-standing F8 film at room temperature. The spectrum in this energy range has the aromatic in-plane stretching mode at $\sim 1605\text{ cm}^{-1}$. The inset shows explicitly the schematic structure of F8.

in the inset of figure 1. The worm-like backbone is surrounded by a cylindrical shell of disordered side chains. F8 is also known to orient well under shear, during Langmuir–Blodgett monolayer transfer in the presence of a non-homogenous flow of the molecules at the air–water interface [16].

The F8 free-standing films were prepared by spin-coating over a circular copper (Cu) mesh with a grid size of $20 \times 20\ \mu\text{m}^2$ on top of KBr substrates at speeds ranging from 50 to 3000 rpm for 40 s. The mass concentration of F8 solution is 40 mg ml^{-1} using chloroform. The molecular weight (M_w) and R_{EE} of F8 are 25 000 and 100 nm, respectively. By fast quenching from just above the solid–liquid–crystal (LC) transition temperature ($\sim 160^\circ\text{C}$), the samples were obtained initially in a glassy phase. The substrates were dissolved in distilled water and each F8 film adhering to the corresponding Cu mesh was floated off from the substrate. The nominal thicknesses of the films were measured by a Dektak profilometer. The films with Cu grid substrate were placed across a 0.5 mm diameter hole in a hot stage filled with N_2 . For bulk polymer measurement, a small amount of F8 was held directly on the sample holder of the hot stage. The heating rate was 5°C min^{-1} at a temperature interval of 1°C . Polarized spectra were recorded after a dwell time of 100 s for each temperature step. Integration times of 60 and 600 s were used for each measurement on thick and ultrathin films, respectively. Each raw spectrum was then subject to a curve-fitting routine (Grams 32, Galactic Industries, Salem, US) to obtain the Raman intensities of the 1605 cm^{-1} peaks for F8 at each point.

Figure 1 shows the spectrum in the $1150\text{--}1650\text{ cm}^{-1}$ range for F8 at room temperature. The intense Raman peaks of the aromatic C=C on-ring stretch mode at $\sim 1605\text{ cm}^{-1}$ of F8 are used for the temperature dependence studies. It has been suggested for some time that the RIs of certain molecular vibrations depend on (i) the length of conjugation, (ii) the delocalization, and (iii) the extent of π -charge transfer which dictates the electronic states of a polymer [17–20]. In particular, the RI of the phenyl mode changes with the angle of twist in sterically hindered biphenyls [21]. Thus when the two rings are coplanar, the RI is at a maximum. The polarized Raman intensities I_{\parallel} and I_{\perp} in the temperature range from 25 to 180°C are displayed in figure 2. Three phase transitions in the sample are expected upon heating: (i) a glass–solid, (ii) a solid–LC, and (iii) an LC–melt. The solid–LC and LC–melt transitions are of less interest in this study. As a result of anharmonic interactions, a general behavior is that Raman frequencies become smaller and the corresponding peak widths are broadened, when the temperature is increased. In addition, a couple of features can be seen in the temperature scans which are the

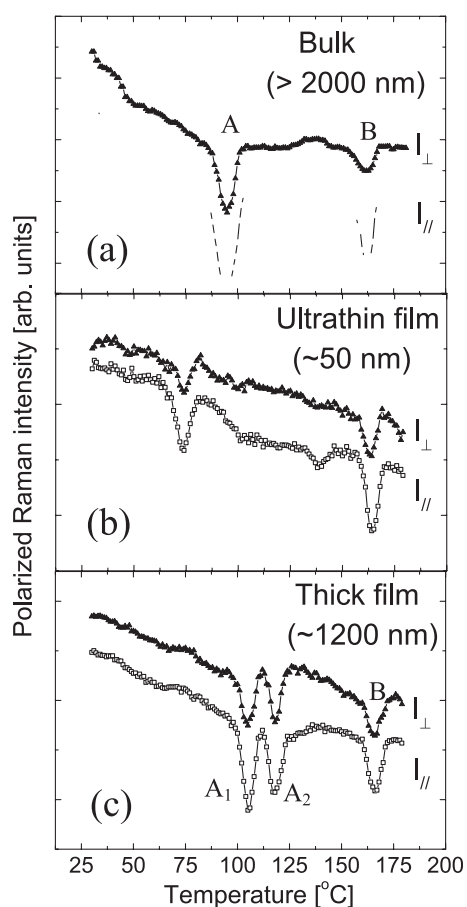


Figure 2. The temperature scans of F8. The polarized Raman intensities of the 1605 cm⁻¹ mode (a) in the bulk, (b) in an ultrathin film (~50 nm), and (c) in a thick film (~2000 nm). The heating rate is at 5 °C min⁻¹. All the data in (a)–(c) are obtained by curve fitting of the 1605 cm⁻¹ mode at different temperatures.

signatures of phase transitions. Figure 2(a) shows the expected behavior arising from changes in the self-energies of specific vibrations when they are coupled to electronic states during phase transitions, results in changing the RIs. Even though a microscopic model is not available to explain the detailed evolution in RIs in molecular liquids or polymers, their ultimate origin is very clear. The features A and B in figure 2(a) indicate the temperatures where thermal phase transitions occur. The temperatures deduced for the phase changes from figure 2(a) are roughly 95 and 160 °C, consistent with the glass–solid and solid–LC transition temperatures reported in the literature using differential scanning calorimetry [22].

The same temperature scan in an ultrathin film reveals the fact the boundary conditions in the film played a significant role in fixing the transition temperatures of the different phase. In figure 2(b), the data show clear features at the approximate temperatures where the phase transitions are expected; however, the glass transition is depressed, as indicated by the data. Comparing figures 2(c) with 2(b), we notice the thick films exhibit a much richer scenario than the ultrathin counterparts. Most notably, the T_g in thick film is (i) split into two different values, as indicated by the two features in figure 2(c), and (ii) both are shifted to higher temperatures

above the bulk value. The feature labeled as A_2 is displaced by $\sim 12^\circ\text{C}$ with respect to the feature A_1 in the Raman data. In contrast, the feature B (solid–LC transition) appears at the same temperature as in the bulk, suggesting that the main effect of the film configuration is to affect the glass transition itself.

The fact that I_{\parallel} and I_{\perp} present two different relative intensities in the glass-to-solid transition suggests that the different laser polarization modes are probing phenylene rings in two different situations. This can only happen if there are two different modes of molecular orderings in the film. It is generally accepted that conjugated polymer films, even in the melt form, are susceptible to molecular ordering induced by the surface [12, 13, 23]. Accordingly, the polarization selection rules for those phenylene rings close to the surface and in core of the film are different. As a plausible explanation for these results, the Raman temperature scan features the two different expected T_g values at the surface and in the core of the film. The transition at lower temperatures is presumably associated to the surface. This is an indirect demonstration of surface molecular ordering in conjugated polymer thin film in agreement with previous reports on aligned film and melt [12, 13]. The two deduced T_g values obtained from figure 2(c) are ~ 105.8 and $\sim 117.5^\circ\text{C}$. Despite the quite compelling evidence and the potential agreement with a standard interpretation of glass transitions in polymer thin films, the double solid-to-liquid transitions in the film are above the equivalent transition in the bulk even without distinguishing which transition is associated with the surface or bulk. This behavior is not as one would intuitively expect, namely a lower T_g of the film due to added mobility at the interfaces.

An attempt to quantitatively describe the data is given below. Figure 3 shows a comparison between the T_g values in different ranges of film thickness. The idea is to separate the length scale showing single or double T_g values. Figure 3(a) shows the extracted T_g values from the distinctive feature at a particular temperature in the polarized Raman data of the ultrathin F8 films. These films show a single lower transition temperature in the limit where d is of the order of $\sim R_{EE}$, which is the same case as ultrathin film polystyrene (PS) films [11]. A standard interpretation of T_g behavior, i.e., affected mainly by the higher chain mobility at the interfaces, can be used in this case. The difference in T_g between the value at the surface and in the core of the film is non-distinguishable, revealing a situation where only a single T_g value is observed. From equation (1), the best fit T_g^{surf} and $\xi(T_g)$ were obtained to be $23 \pm 5^\circ\text{C}$ and 5.24 nm, respectively. It is important to emphasize that the same parameters used in this layered model give essentially the same quantitative description for the PS film [5, 11]. The data in figure 3(b), focusing on a different thickness regime, clearly show the presence of a characteristic length $L \sim 2800$ nm, showing two enhanced T_g values. The data in figures 3(a) and (b) present an excellent example of a crossover produced by chain confinement under two very different situations created by competition of surface/bulk effects. For all thick F8 films considered, the extracted T_g values were collectively described by two empirical relations of the form

$$T_g(d) = \begin{cases} T_g^{\text{surf}} \left[1 - \left(\frac{L/2 - d}{\alpha_{\text{surf}}} \right)^2 \right], \\ T_g^{\text{core}} \left[1 - \left(\frac{L/2 - d}{\alpha_{\text{core}}} \right)^2 \right]. \end{cases} \quad (2)$$

This model system is constructed of enhanced T_g layers due to the molecules being entangled close to the interfaces. The confined system then exhibits a slower dynamics than that in the bulk. Equation (2) gives a quantitative description of the T_g value in the vicinity of the interfaces and core of the film. T_g^{surf} and T_g^{core} are the maximum values obtained from the two different data sets in figure 3(b); both the slope parameters, α_{surf} and α_{core} , are

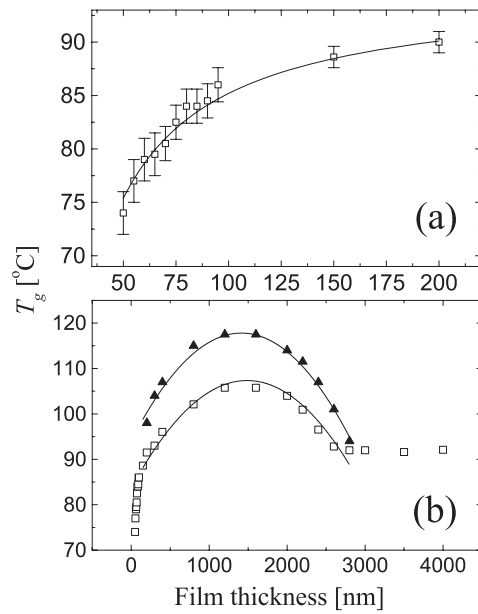


Figure 3. The summarized extracted T_g values for two different film thickness ranges. In (a), a single distinct crossover is observed below a specific film thickness. The solid line is the best fit to the data by using the layer model described in the text. In (b), there are two different sets of the T_g data labeled as A_1 and A_2 in different thickness range. The solid lines are the fit to the data by using empirical relations given in the text.

determined by curve fitting the T_g data. Equation (2) is similar to the layered model used for supported films [24], except for the quadratic dependence of T_g on d . The behavior described by equation (2) is as follows: for film thicknesses d lying within the characteristic length L , the T_g values change quadratically with increasing d . The best fits to the two sets of T_g data labeled as A_1 and A_2 in figure 3(b) were provided by $T_g^{\text{surf}} = 106 \pm 0.5$ °C and $T_g^{\text{core}} = 119 \pm 0.5$ °C, and the corresponding slope parameters are $\alpha_{\text{surf}} = 3492 \pm 100$ nm, and $\alpha_{\text{core}} = 3064 \pm 60$ nm. These are the material parameters associated with different conjugated polymers in fixing the T_g behavior. We have performed preliminarily measurements on other conjugated polymers: poly(*p*-phenylenevinylene) and its derivatives. The results suggest that the T_g anomalies are not peculiar to F8, and the interfacial effects on conjugated polymer films exhibit some degree of universality.

Finally, it is relevant to discuss the consequence for the increased T_g above the bulk value, contrary to what occurs in simpler polymers like PS [11]. The study suggests the picture of more available surface giving higher chain mobility, and thus resulting in lower T_g for thin films is not general. The presence of a free surface may not result in adding an overall mobility to the chains, depending on the polymer structure. In the case of relatively soft and non-conjugated polymers like PS, the boundary conditions at the interface impose the fewest constraints on the chains. The surface can then be used to gain additional degrees of freedom for the chains. This results in higher mobility and lower T_g . The situation in more complex polymers like F8, however, is fundamentally different. Most notably, the free boundary may act as a real constraint to the possible orientations of the monomers, as the surface is particularly susceptible to molecular alignment. In addition, π -electrons stacking are inherent in the backbone of conjugated polymers. The surface, in fact, may entangle the chains even further in the film

and restrict their mobilities by trying to satisfy the boundary conditions, thus producing an effective increase in T_g .

To summarize, these studies have provided a straightforward picture of the glass transition dynamics in confined conjugated polymer films revealed by Raman scattering. The technique covers a quantitative measurement of T_g and illustrates a very different scenario in conjugated polymers than in other non-conjugated polymers. Two essential objective observations that characterize the T_g are underlined: (i) the emergence of a natural characteristic length L over which the films exhibit two T_g values due to surface alignment effect, and (ii) a single depressed T_g value in films with $d < R_{EE}$ due to the chain confinement effect. More generally, the study defines two quantities, α_{surf} and α_{core} , to model the thermal behavior in films induced by geometric constraints, which will encourage further work on the impact of the T_g anomalies on polymer device performance.

Acknowledgments

The work on the polyfluorene investigation was carried out in the Department of Materials Science and Engineering at UCLA. The author is indebted to the generous financial support from the Air Force Office of Scientific Research, Grant number F49620-03-1-0101.

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