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Touching polymer chains by organic field-effect transistors

SUBJECT AREAS:
MATERIALS CHEMISTRY
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25 February 2014Accepted
7 August 2014Published
17 September 2014Correspondence and
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Organic field-effect transistors (OFETs) are used to directly “touch” the movement and dynamics of polymer chains, and then determine T_g . As a molecular-level probe, the conducting channel of OFETs exhibits several unique advantages: 1) it directly detects the motion and dynamics of polymer chain at T_g ; 2) it allows the measurement of size effects in ultrathin polymer films (even down to 6 nm), which bridges the gap in understanding effects between surface and interface. This facile and reliable determination of T_g of polymer films and the understanding of polymer chain dynamics guide a new prospect for OFETs besides their applications in organic electronics and casting new light on the fundamental understanding of the nature of polymer chain dynamics.

Organic field-effect transistors (OFETs) are a class of devices consisting of an organic semiconductor layer, a gate insulator layer and three terminals (drain, source and gate electrodes)^{1–3}. Charges inject from the source electrode into organic semiconductor layer, and then transport through the organic semiconductor layer, and flow out at the drain electrode⁴. The route of charge transport in organic semiconductor layer is named conducting channel, which exists exactly at the interface between the organic semiconductor layer and the gate insulator layer⁵ with thickness of one to several molecular layers⁶. This molecular level conducting channel is highly sensitive to out stimulus, so that OFETs could be used as an ultra sensitive sensors or actuators for pressure⁷, chemical and biological detection⁸ etc. Facchetti et al. have made a pioneer study by using OFETs for surface viscoelastic properties of polymers depending on the correlation of device mobility and micro structural and morphological alterations of semiconductor layer on polymer⁹. It opens a door for the integration of organic electronics and polymer science, e.g., to face polymer chain dynamics (e.g., the glass transition dynamics)¹⁰, one of the difficult problems of polymer sciences in this century.

The glass transition of a polymer is a reversible transition from a hard and relatively brittle state into a rubber-like state at the glass transition temperature (T_g). Therefore, T_g , corresponding to the movement and long-range transport of polymer chains, exhibiting the massive change in physical properties of a polymer, becomes a key and fundamental parameter of polymer science¹¹. Many conventional methods, including ellipsometry¹², Brillouin scattering¹³, X-ray reflectivity¹⁴, dielectric relaxation spectroscopy¹⁵ and fluorescence spectroscopy¹⁶, depending on changes of physical appearance at T_g , rather than probing the characteristics of polymer chain dynamics, all the techniques are indirect. Here, we introduce a direct way to touch polymer chain dynamics by using OFETs as molecular level probes. It is a development of Facchetti et al.'s method¹⁰ by visualizing the abrupt current change of OFETs directly at the glass transition instead of the estimation of series mobilities of OFETs as the reference addressed¹⁰.

In our experiments, OFETs are designed with bi-layer dielectrics (polymer/SiO₂). The target polymer layer (e.g., polystyrene (PS)) is sandwiched between the organic semiconductor layer (e.g., copper phthalocyanine (CuPc)) and SiO₂ gate insulator layer. CuPc was selected as the candidate due to its low cost, high thermal and chemical stability as well as excellent field-effect properties^{17,18}. The results of current–temperature characteristics of OFETs with different PS molecular weights are shown in Figure 1 (left blue curves, and different molecular weights as shown in curves of a–d). It is attractive that all curves show two distinct regions, with the drain currents initially increasing with temperature increasing, and then decreasing at higher temperatures. When extrapolating the two tendencies to their intersection to get the transition point temperature, more attractively, the temperatures at these intersection points agree very well with the T_g values of the corresponding bulk polymers, which can

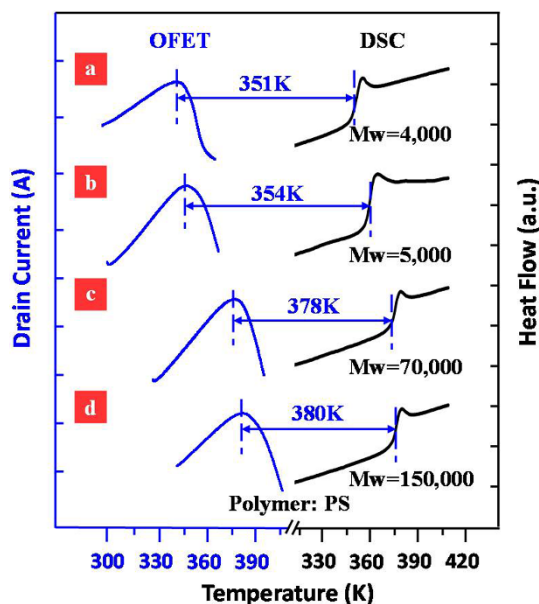


Figure 1 | Current with abrupt changes in OFETs (left-hand blue curves) and corresponding DSC scans at T_g (right-hand black curves) for PS films with different molecular weights. The currents initially increase with temperature increasing, and then decreasing at higher temperatures (left blue curves). When extrapolating the two tendencies to their intersection to get the transition point temperature, which agree very well with the T_g values of the corresponding bulk polymers by DSC (right black curves).

be confirmed by differential scanning calorimetry (DSC) results (Figure 1, right black curves, and different molecular weights as shown in curves of a–d).

Temperature-dependence Atomic force microscopy (AFM) images and in-situ X-ray diffraction (XRD) patterns of the CuPc layer in OFETs exhibit no obvious change (Figure 2 and Figure S1), indicating the morphology and microstructure of organic semiconductor layer are not responsible for the current transitions of the OFETs. Hence, the fundamental changes arising from the underlying polymer layer and the corresponding interface between organic semiconductor/polymer insulator should be responsible for such current transitions. It is worth noting that our method is different from Facchetti's^{19,20}, who correlated the device-performance trends to the evolution of organic semiconductor film morphology and microstructure, and empirically defined the glass transition temperature at which the TFT carrier mobility falls by 50%.

If we assume charge transport in organic semiconductors is pursued by hopping²¹, i.e., charges pass from one molecule to another with the assistance of phonons. With temperature increasing, the thermal vibrations of phonons will increase, which promotes charge transport and leads to an increase of current. Simultaneously, the movement and dynamics of the underlying polymer chains will be enhanced. When temperature is below T_g , the charge transport in OFETs is located in a well-defined conducting channel at the interface between organic semiconductor and polymer insulator (Figure 3a,b). However, when temperature is above T_g , the polymer transforms from a hard and relatively brittle state into a rubber-like state, i.e., the chain segments shift from a “frozen in” or cessation state (the glassy state, $T < T_g$) to a cooperative motion state (the rubbery state, $T \geq T_g$)²². Accompanied with this transformation, molecular motion and dynamics increase dramatically, typically by more than 10 orders of magnitude. This kind of cooperative motion of the polymer chains will result in the disruption of the perfect conducting channel (Figure 3c), and lower the current of the

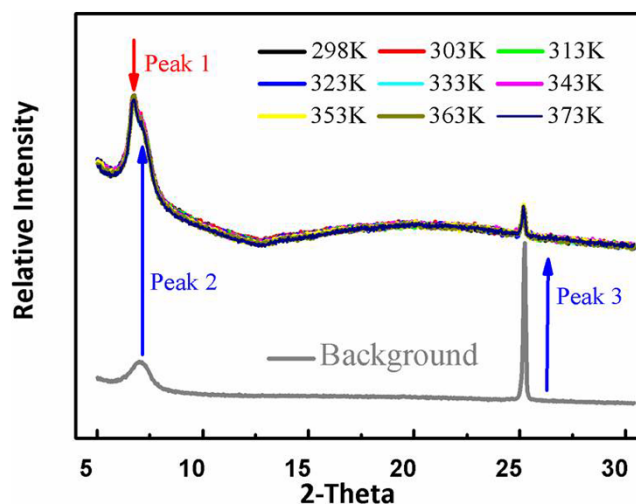


Figure 2 | In-situ XRD scans for 70-nm-thick CuPc films on PS dielectric as a function of temperature. The peak of the CuPc film (Peak 1) is at 2θ position of 6.9, corresponding to the α -phase. Additional peaks observed in the scans were from the background (Peak 2 and 3). Note that the peak position and intensity of the CuPc film are almost identical with the temperature increased to 373 K, indicating there is no obvious microstructure change in the selected temperature regime.

OFET significantly. Therefore, the current in an OFET will initially increase with temperature increasing ($T < T_g$) due to the phonon assisted charge transport, but then decrease at higher temperatures ($T \geq T_g$) because of the disruption of the perfect conducting channel by the cooperative motion of polymer chains, i.e., the current transition arises from the fundamental change in molecular motion and dynamics that occurs at T_g . This is highly according with our results as shown in Figure 1, i.e., the conducting channel of OFETs provides a direct and vivid platform to “visualize” the movement and dynamics of polymer chains and then determine the values of T_g .

In order to confirm the generality of this conclusion, other polymers, such as polylactide (PLA), polyacrylonitrile (PAN) and poly (methyl methacrylate) (PMMA), are also incorporated into OFETs to examine their current-temperature characteristics (Figure 4). Indeed, in all cases, the values of the intersection temperatures obtained from our OFETs are highly consistent with the T_g values of the corresponding bulk polymers. It confirms the generality of our method by using conducting channel of OFETs as a direct vivid platform to “touch” the movement and dynamics of polymer chains.

Moreover, another unique feature of our OFETs is the distinctive nanometer-sized confined polymer layer, which provides a facile way to examine the effects of confinement during the glass transition process by selectively tuning the thickness of polymer layer. It is generally accepted that when the thickness of polymer films decreases to a scale comparable to the cooperative length of polymer itself, the conformation of polymer molecules becomes perturbed which eventually affects the properties of the polymer due to the nanometer-sized effect^{23,24}, however, a quantitative understanding of perturbations to chain dynamics due to geometric constraints remains a challenge^{25,26}. Here, our OFETs could fill in to do something.

The results of our OFETs on the detection of polymer thickness dependence on T_g are shown in Figure 5. When PS films are relatively thin the values of T_g increase rapidly with film thickness, and then approach a constant gradually at 45–55 nm. This nanoconfined effect is probably attributed to the increasing molecular motion and dynamics with the thickness getting thinner¹¹. Since the thickness of the polymer film is comparable to, or less than, the cooperative length scale of the polymer chains, the configuration and extent

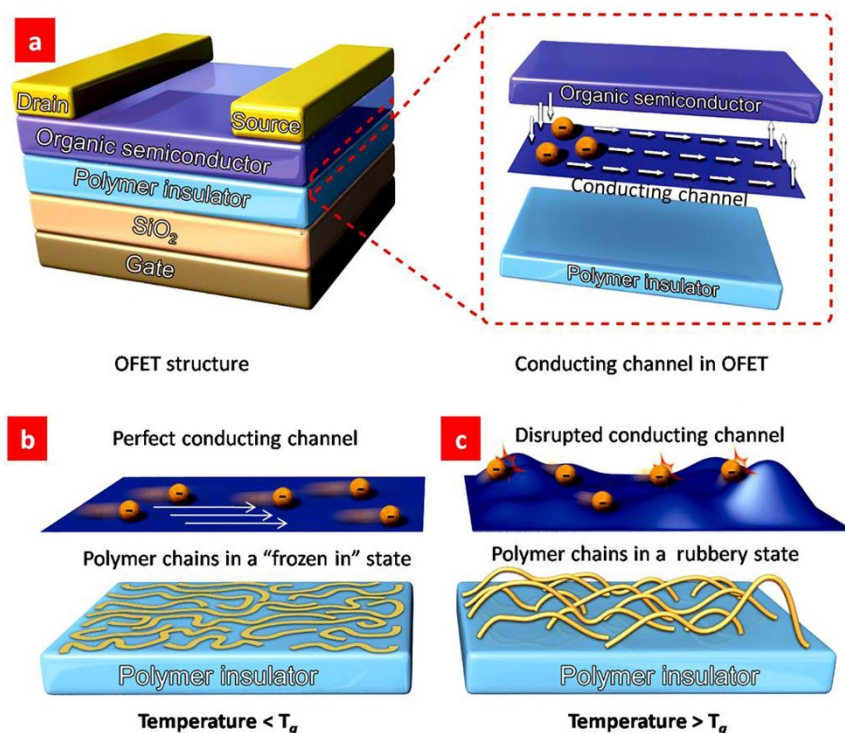


Figure 3 | OFET structure and the conducting channel in OFETs. (a), OFET structure, conducting channel is formed at the interface between polymer and organic semiconductor. (b), electron transport in a perfect conducting channel below T_g , charge transport is located in a well-defined conducting channel. (c), electron hindered in a disrupted conducting channel, above T_g , the chain segments shift from a “frozen in” or cessation state (the glassy state, $T < T_g$) to a cooperative motion state (the rubbery state, $T \geq T_g$).

of entanglement of polymer chains in the films will be different from those in the bulk. Our method offers the promise of understanding nanoconfined molecular dynamic behavior due to the advantage of easy confining film dimensions and varying the thickness. Moreover,

it is worth noting that our method could detect the transition temperature and pinpointing the location of T_g even when the film thickness is ultrathin, as thin as 6 nm (Figure S2). This makes it significantly better than other currently available techniques with signals always discontinuous or below the noise level when measuring the T_g of ultra-thin polymer films. Finally, it is attractively to be noted that the facile detection of polymer chain dynamics by OFETs opens the door for micro devices to touch polymer chain dynamics (Figure S3).

In summary, OFETs are used to directly “touch” the movement and dynamics of polymer chains, and then determine T_g . The conducting channel of OFETs exhibits several unique advantages: 1) it directly detects the dynamics of polymer chain at T_g , instead of

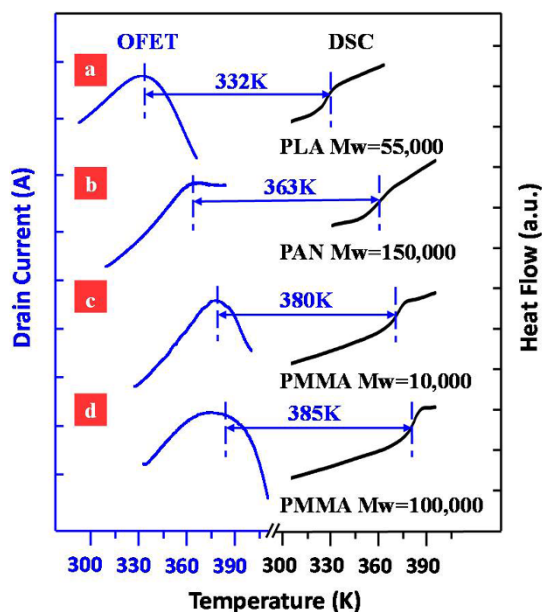


Figure 4 | Plots of drain current versus temperature for different polymers in OFETs (left-hand blue curves) and DSC scans for the corresponding polymers (right-hand black curves). (a), PLA, (b), PAN, (c,d), PMMA with different molecular mass. In all cases, the values of the intersection temperatures obtained were highly consistent with the DSC data of the corresponding bulk polymers.

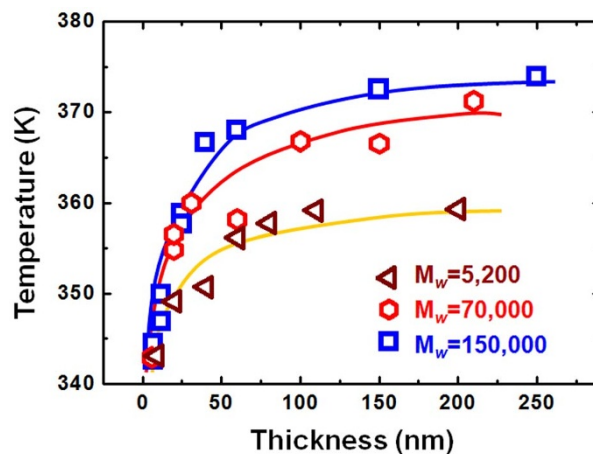


Figure 5 | Dependence of T_g values on film thickness for PS. Variation of T_g as a function of film thickness, the value of T_g increases rapidly with increasing film thickness, and then gradually approaches a constant value.



detecting changes in physical appearance as in the case of conventional techniques; 2) it allows the measurement of size effects in ultrathin polymer films (even down to 6 nm), which bridges the gap in understanding effects between surface and interface. This facile and reliable determination of T_g of polymer films and the understanding of polymer chain dynamics guide a new prospect for OFETs besides their applications in organic electronics and casting new light on the fundamental understanding of the nature of polymer chain dynamics, even the dependence of T_g on molecular mass and heating rates (Figure S4–S5) etc.

Methods

Polystyrene (PS), poly(methyl methacrylate) (PMMA), polyacrylonitrile (PAN) and polylactide (PLA) were purchased from Aldrich Chemical Co. and used as received. Details of the used polymer samples are listed in Table S1. The OFETs were characterized using a Keithley 4200 Semiconductor Parameter Analyzer equipped with a temperature controller. Temperature-dependent OFET measurements were directly performed in air with the temperature regulated at a constant heating rate. The drain current data as a function of temperature were recorded in the saturation regimes with a fixed gate voltage and drain bias of -60 and -45 V, respectively. A ramp rate of 2.5 K/min was used in order to minimize any undesirable effects, such as the different coefficients of thermal expansion in the device components. At least three measurements were recorded at each temperature and statistically averaged values were calculated. The calorimetric T_g values for the bulk polymers were obtained by differential scanning calorimetry (DSC). Atomic force microscopy (AFM) and in-situ X-ray diffraction (XRD) were employed to determine the thickness of polymer thin films and to examine the film microstructures as a function of temperature.

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Acknowledgments

The authors acknowledge the financial support from National Natural Science Foundation of China (51033006, 51222306, 51003107, 91027043, 91222203, 91233205), the China-Denmark Co-project (60911130231), TRR61 (NSFC-DFG Transregio Project), the Ministry of Science and Technology of China (2011CB808400, 2013CB933403, 2013CB933500), the Chinese Academy of Sciences.

Author contributions

W.H. and Z.W. conceived the research and designed the experiments. W.S. and H.D. fabricated the devices, performed the experiments and data analysis. All authors discussed the results and commented on the manuscript.

Additional information

Supplementary information accompanies this paper at <http://www.nature.com/scientificreports>

Competing financial interests: The authors declare no competing financial interests.

How to cite this article: Shao, W., Dong, H., Wang, Z. & Hu, W. Touching polymer chains by organic field-effect transistors. *Sci. Rep.* **4**, 6387; DOI:10.1038/srep06387 (2014).



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