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Elastic Moduli of Organic Electronic Materials by the Buckling Method

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ABSTRACT: Mechanical moduli of common organic electronic materials are measured by the buckling method. The organic layers were prepared on the elastomer polydimethylsiloxane (PDMS) substrate by transfer, direct spin-coating, or thermal evaporation. When a small (~2%) compressive strain is applied to organic/PDMS film samples, the layer becomes buckled with a characteristic wavelength. Fitting the experimentally measured data of buckling wavelength as a function of layer thickness with a model equation yields the mechanical modulus of the organic layer. The measured values compare well with those from theoretical predictions for materials such as poly(3-hexylthiophene) (P3HT) and its blend with [6,6]-phenyl C_{61}-butyric acid methyl ether (PCBM). The modulus of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) is similar to that of pure PSS, which is contrary to the common expectation that the ionic interaction between PEDOT and PSS chains may lead to a modulus value 2−3 times larger than that of the constituent polymers. The similarity is likely due to a very small amount of PEDOT added and the oligomeric nature of PEDOT. Thermally evaporated pentacene film has a modulus value of ~15 GPa, which is an order of magnitude larger than those of other polymeric materials investigated here, and reveals delamination bukling behavior when the magnitude of compression is relatively large. The residual solvent in polyaniline (PANI) plays the role of plasticizer and leads to a very small modulus. The measured mechanical moduli of common organic electronic materials would be valuable for designing and implementing flexible and/or stretchable organic electronics.

Introduction

Organic electronic materials, in either oligomeric or polymeric forms, have been used in various electronic devices[1] as an active semiconductor or conducting layers, as in thin film transistors,[2] light-emitting diodes,[3] and photovoltaics.[4] Some of these applications have now reached the stage of commercialization. The unique advantages of organic electronic materials include easy processability, low cost, and inherent flexible nature of materials, among others. In particular, the mechanical flexibility of organic materials may facilitate the implementation of flexible or even stretchable electronics. It is noted that, for the flexible electronics applications, the mechanical properties of materials involved should be known, which would help design and analyze the mechanical behavior of final product, during processing as well as in active service. For example, one can get high bendability of flexible electronic devices if they are positioned at or near the mechanical neutral plane, which is in turn determined by the thicknesses and moduli of constituent material layers.

One of the recent additions to the mechanical metrology of thin film materials is the buckling-based method.[5−10] The buckling phenomenon has long been studied in structural mechanics field,[11] where the buckling should be avoided because it means disastrous collapse of structures. Since the seminary work of Whitesides' group on the controlled buckling,[12] however, the renewed interests on the buckling phenomenon range from mechanics,[13] tunable optics,[14] metrology,[5−10] to stretchable electronics.[15] In the buckling-based metrology, a thin film of material is prepared on soft, compliant elastomeric substrate such as polydimethylsiloxane (PDMS). The film buckles to form a wavy, wrinkled surface when the sample is compressively strained, and the applied compressive strain is larger than the critical buckling strain of a given system. By applying the well-known buckling formulas together with the measured buckling wavelength and other relevant material properties, one can extract the mechanical modulus of the film material. This method has been successfully demonstrated in the measurement of the moduli of thin polymer films,[5,8] polyelectrolyte multilayers (PEM),[7,10] and those of gradient substrates.[9] One of the inherent advantages of this method is that it is very well suited for thin film materials, for which it is not easy or possible to prepare bulk form of samples for the measurement of their mechanical moduli.

In this work, we measured Young's modui of common organic electronic materials by the buckling method. The organic materials investigated here include poly(3-hexylthiophene) (P3HT), a blend of P3HT with a fullerene derative of [6,6]-phenyl C_{61}-butyric acid methyl ether (PCBM), poly(3,4-ethylenedioxythiophene):polystyrenesulfonate (PEDOT:PSS), emeraldine base polyaniline (PANI), and pentacene. P3HT has been used in a variety of applications including transistors, organic light-emitting diodes (OLED), and sensors. P3HT/PCBM composite material finds its application as an active material in plastic photovoltaic devices, called bulk heterojunction (BHJ) organic solar cell, because one can greatly increase the junction area and thus light-harvesting efficiency by using the composite form.[16] PEDOT:PSS and PANI are conducting polymers and thus used for electrodes, electromagnetic shielding device, anticorrosion, and charge injection layer in organic electronic devices, etc. Finally, pentacene is the choice of material as an active semiconductor in organic thin film transistor due to its high mobility. In spite of widespread applications of these materials in various organic electronic devices, few literature results could be found on their mechanical properties. For comparison, the moduli were also calculated based on theoretical correlations proposed in the literature. The experimentally measured modulus values were found to be in reasonable agreement with the calculated values.

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Experimental Section

PDMS (Sylgard 184, Dow Corning) was prepared by mixing the base resin and the curing agent in 10:1 (by weight) ratio, as recommended by the supplier. This mixture was vigorously agitated and poured into a Petri dish. The mixture was cured at 60 °C for > 4 h in oven, after removing the entrapped air during mixing at room ambient for 1−2 h. The cured PDMS was cut into small rectangular slabs (~2 cm × 5 cm). The air-side surface of cured PDMS elastomer was used for buckling experiments.

Film transfer, direct spin-coating, or thermal evaporation was used as film preparation methods for buckling experiments. Regioregular poly(3-hexylthiophene) (*rr*-P3HT; Rieke Specialty Polymers) was dissolved in chlorobenzene. The solvent used here, chlorobenzene, swells PDMS significantly, which makes it impossible to spin the layer directly on PDMS. Thus, the P3HT layer was spun on a glass substrate that had been vapor-deposited with a fluorinated self-assembled monolayer (SAM) material, tridecafluoro-1,1,2,2-tetrahydrooctyltrichlorosilane (FOTCS). The film thickness of P3HT was controlled by varying both the solution concentration (2−10 wt %) and the spin speed. After the spin, the sample was annealed at 100 °C for 3 h to completely drive out the solvent. A flat slab of PDMS that is laminated on another glass slide was then made contact onto P3HT layer and detached instantaneously. This fast pick-up[17] was very successful and resulted in the transfer of the P3HT layer to PDMS slab. We note that it was impossible to pick up the P3HT layer onto PDMS from the glass substrate without the fluorinated SAM treatment. The P3HT layer that was spun on bare glass substrate easily passed the Scotch tape test, which means very strong adhesion with the substrate. A similar process was used for the preparation of composite layer of P3HT/PCBM. A 2.5 wt % solution of PCBM (Nano-C) in chlorobenzene was mixed with 3.2 wt % P3HT/chlorobenzene solution, which led to the composition of P3HT:PCBM = 1:0.8. The composite layer was formed on SAM-treated glass substrate by spinning. The annealing of this composite layer is known to enhance the cell efficiency in bulk heterojunction organic solar cell applications.[18,19] The change in mechanical property of this composite upon annealing, however, is not yet known. To check this possibility, we prepared the P3HT/PCBM composite films into two groups: one group that underwent thermal annealing at 100 °C for 3 h and the other that did not.

The hydrophilic materials such as PEDOT:PSS (Baytron P VPA14083) and PANI (Sigma-Aldrich) were directly spun on PDMS substrate. The PEDOT:PSS was used as-received, while the PANI was dissolved in 1-methyl-2-pyrrolidone (NMP) at a concentration of 0.4 wt %. For the spin-coating of these hydrophilic solutions on hydrophobic PDMS, the PDMS surface was treated with oxygen plasma (O_2 10 sccm, 200 mTorr, 100 W, 30 s; PVTronics) to make its surface hydrophilic. The oxygen plasma is known to convert the surface of PDMS into stiff, silica-like layer.[20] It is also known that the converted silica layer recovers its original hydrophobic state in 1−3 days.[21,22] Therefore, the sample was allowed to recover its original state by leaving the sample undisturbed for more than 7 days after the spin-coating of polymers on O_2 plasma-treated PDMS.[23] The film thickness was controlled by varying the solution concentration and spin speed. Pentacene (Sigma-Aldrich) was directly deposited on PDMS by thermal evaporation.

The film thicknesses were measured using surface profiler (KLA Tencor), except for evaporated pentacene, for which the thickness was monitored and controlled by film thickness monitor (STM-100/MF, Sycon Instruments).

For buckling experiments, the organic layer/PDMS sample was loaded onto a homemade compression stage. The sample was compressed, typically up to ~2%, under an optical microscope (Olympus BX60) equipped with a digital camera. Care was taken to maintain the compressive strain for buckling as small as possible because the buckling wavelength has been shown to decrease at large compression.[13] Poor adhesion of these organic materials with PDMS also limits the level of applicable compressive strain. The buckling wavelength was determined from captured microscope images, by measuring the horizontal distance of many waves (typically 10−30) and dividing it by the number of waves within. This method leads to a more accurate buckling wavelength than the value obtained by measuring the length of single wave due to the averaging effect. Also, atomic force microscopy (AFM; DI3100, Veeco) was used to measure the buckling wavelength, based on sectional profile, when the wavelength is too small to be measured by optical microscopy. As in the case of OM image analysis, 10−30 waves in AFM images were averaged to determine the buckling wavelength.

With the experimentally measured values of buckling wavelength and film thickness, the mechanical modulus of film material can be calculated using the following equation:

$$\overline{E}_{\mathrm{f}} = 3\overline{E}_{\mathrm{s}}\left(\frac{\lambda}{2\pi h}\right)^3 \qquad (1)$$

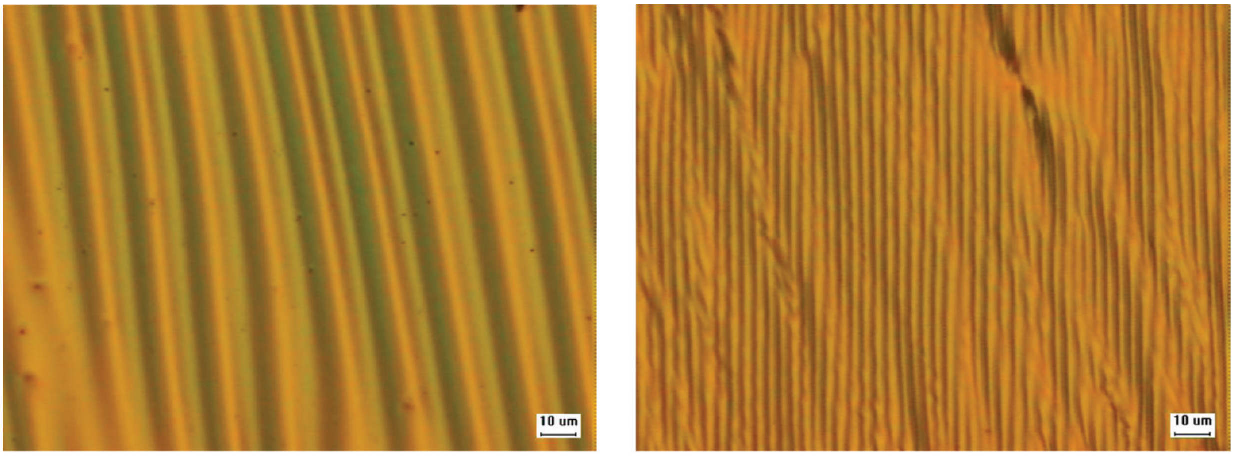
Here, $\overline{E}$s are the plane-strain moduli ($\overline{E} = E/(1 - \nu^2)$), ν the Poisson ratio, h the film thickness, and λ the buckling wavelength. The subscripts s and f represent substrate and film, respectively. The buckling wavelength was plotted as a function of film thickness to fit the data to a line that goes through the origin. Then, the slope of the fitted line is used to calculate the mechanical modulus of film material. For the substrate PDMS, 2 MPa and 0.5 are used for Young's modulus and Poisson ratio, respectively. For the Poisson ratio of film materials, 0.35 is used, which was later checked and confirmed with the values from theoretical calculation. Note that the variation in the moduli of film materials was within ~5% for the Poisson ratio values of 0.3−0.4, which means that the extracted modulus is not very sensitive to a change in the value of Poisson ratio.

Results and Discussion

Figure 1 shows representative optical microscope (OM) images of buckled films of P3HT and P3HT/PCBM. The wavelength vs thickness data were fitted to a line that passes through the origin, where its slope is used to extract the modulus of film materials.[24] The Young's modulus of P3HT is extracted to be ~1.3 GPa, which is comparable to the values of ~0.7 GPa in the literature.[25,26] and to the theoretically calculated value of ~2.1 GPa.[32] A notable increase in mechanical modulus, ~6.2 GPa, was found for the P3HT/PCBM blend film,[24] which is ~5 times larger than that of pure P3HT. This increase is due to the filler effect of PCBM nanoparticles that are dispersed in P3HT matrix polymer.

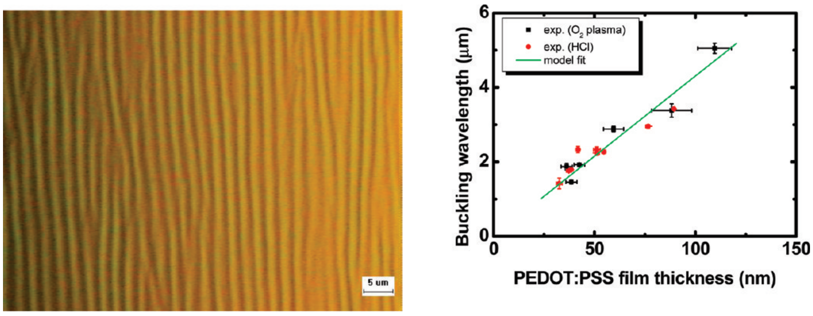
As mentioned in the Experimental Section, we performed the exactly same buckling experiments for both annealed and nonannealed P3HT/PCBM composite layers. It is well-known that the nanoscale morphology of the P3HT/PCBM composite affects the cell performance of bulk heterojunction (BHJ) plastic photovoltaics.[18,19] The phase separation and thus the formation of bicontinuous crystalline domain of each constituent by thermal annealing, i.e., P3HT and PCBM, are believed to be the reasons for the enhanced solar cell efficiency. Therefore, it should be interesting to check if there is any difference in mechanical properties between annealed and nonannealed blend layers. Although the data are not shown here, there was no noticeable difference in the mechanical moduli of annealed and nonannealed P3HT/PCBM composite samples.

The buckled OM image and wavelength vs thickness plot for the PEDOT:PSS[27,28] layer are shown in Figure 2. From the linear fit to the experimental data, the modulus of PEDOT:PSS is estimated as ~2.3 GPa. The theoretical prediction of each constituent polymer, i.e., PEDOT and PSS, is ~3.5 GPa.[29] Thus,



(a) (b)

Figure 1. Representative optical microscopy images of buckled films on elastomeric substrate PDMS: (a) regioregular (rr) P3HT and (b) P3HT/PCBM composite layer.

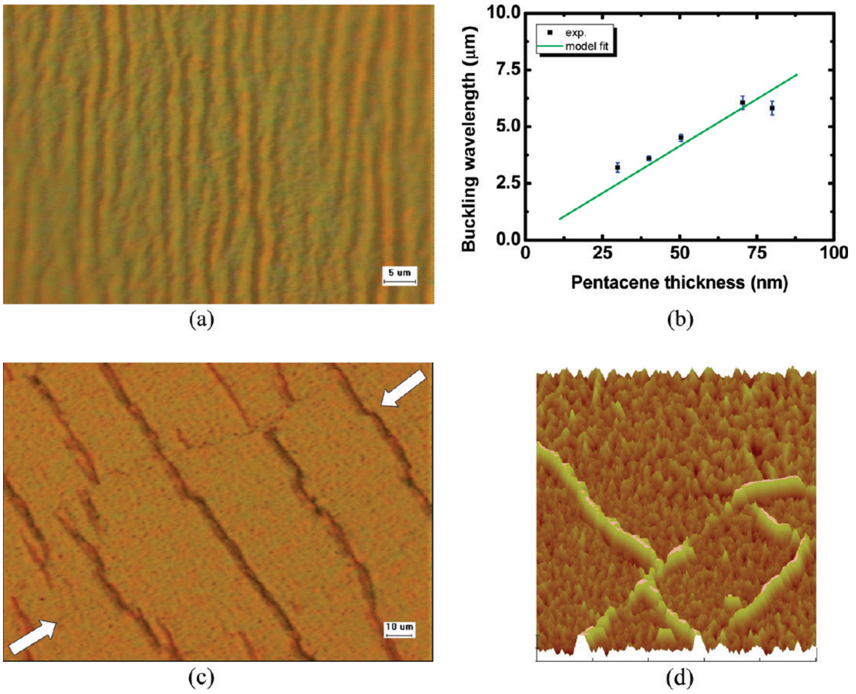


(a) (b)

Figure 2. (a) Optical microscopy image of buckled PEDOT:PSS film on elastomeric PDMS and (b) experimental data of buckling wavelength as a function of film thickness.

the PEDOT:PSS film has essentially the same modulus as those of constituent polymers. The application of composite theory, successfully applied for P3HT/PCBM blend used in this work,[29] however, turned out to be unsuccessful. This failure means that the addition of oligomeric PEDOT to PSS matrix has a negligible effect on the mechanical modulus, which is quite contrary to the case of polyelectrolyte multilayer (PEM). In the study of PEMs, it was found that the strong ionic bonding (also called as ionic or electrostatic cross-linking) between the layers leads to a modulus 2−3 times larger than that of parent homopolymers.[30,31] In the case of PEDOT:PSS, the oligomeric (6−18 repeating units) nature of PEDOT may prevent the blend system from cross-linking; rather, the added PEDOT molecules are simply stitched along the parts of long chain of PSS polymer. Also, the PEDOT:PSS material used in this work was designed to be used for OLED application, where the smoothening of ITO electrode surface by PEDOT:PSS layer is one of the utmost requirements, in addition to hole transporting layer. These requirements can be met by formulating the blend with a very small amount of PEDOT (PEDOT:PSS = 1:6 by weight in the present cases), which was attributed to the absence of interpenetration and ionic stitching of polyelectrolyte chains leading to an entangled and cross-linked network. The modulus of PEDOT:PSS materials was measured using tensile test and was shown to be 2.5−3.0 GPa in the literature.[32] This finding confirms again the negligible effect of ionic interaction between oligomeric PEDOT molecules and long chain PSS molecules in the blend.

Although we used PDMS substrates that were left for a week to recover its initial hydrophobic surface after the very mild O_2-plasma treatment, as described earlier in the Experimental Section, there might be a concern about the interfering effect of oxidized, silica-like (SiO_x) skin layer on PDMS on the results of buckling experiments. If there would be a silica layer on PDMS, which is much stiffer than bulk PDMS, this would affect the buckling behavior of overlying organic layers, and we have to include the effect of this skin layer in analyzing the experimental results. Even if there would not be a continuous, uniform layer of SiO_x on PDMS (the hydrophobic recovery is conjectured to occur by out-diffusion of uncured PDMS molecules from the bulk, through the micro/nanocracks in SiO_x layer[22]), this might have an adverse effect on the buckling of organic materials. To check these possible adverse effects, if any, of the modified SiO_x layer on the buckling experiments, we used acid treatment of PDMS surface to endow surface hydroxyl groups (−OH) on PDMS without significantly altering the mechanical properties of PDMS.[33] In this approach, the flat slabs of cured PDMS were immersed in 10 vol % aqueous HCl solution for 16 h, rinsed with deionized water, and dried for 1 h at room ambient. This acid treatment of PDMS induces the cleavage of Si−O bonds along the PDMS backbones, which leads to the formation of hydroxyl groups on the surface.[34,35] The hydrophobic nature of PDMS confines this acid-induced cleavage to only the surface region of PDMS. The water-based, hydrophilic PEDOT:PSS solution can now be directly spun on this acid-treated PDMS slabs for the buckling



(a) (b)

(c) (d)

Figure 3. (a) Optical micrograph image of buckled pentacene film on PDMS, (b) Young's modulus of pentacene film by fitting the experimental data with model equation, (c) the delaminated surface of pentacene film after applying and releasing high strain (~10%), and (d) 3-dimensional atomic force microscopy image (50 μm × 50 μm, z-scale = 200 nm) of delaminated pentacene film on PDMS, such as shown in (c).

Table 1. Comparison of Modulus Values of Common Organic Semiconductor Materials, Measured by the Buckling Method, Predicted from Theoretical Correlations and Literature Values

	Young's modulus (GPa)		
materials	buckling expt	theory	lit. value
rr-P3HT	1.33 (±0.01)	2.18 (±0.26)	~0.7[25,26]
P3HT/PCBM	6.02 (±0.03)	7.3 (±0.88)	
PEDOT		3.79 (±0.45)	
PSS		4.23 (±0.50)	
PEDOT:PSS	2.26 (±0.05)		2.5−3[32]
PANI[29]	~0.03	1.53 (±0.18) to 2.0 (±0.24)	0.2−2[29]
pentacene	16.09 (±2.83)		

experiments, and the resulting data are included in Figure 2b (filled red circles). The modulus values, extracted from buckling experiments performed on both O_2-plasma PDMS and HCl-treated PDMS, 2.41 ± 0.20 and 2.26 ± 0.05 GPa, respectively, are essentially the same within experimental uncertainties, which clears out any concerns about the interfering effect of skin layer on PDMS used in this work.

The modulus of pentacene film is found to be ~15 GPa, as shown in Figure 3a,b. This large value of modulus is due to the polycrystalline nature of pentacene. This stiff nature of pentacene film, together with poor adhesion on PDMS, led to delamination buckling when a large compressive strain (~10%) is applied. Once the delamination occurs, the surface of pentacene film between delamination buckles becomes flat, i.e., no surface undulation, because the compressive strain is mainly absorbed in the formation of delamination buckles, as shown in Figure 3c,d.

Table 1 summarizes and compares the modulus values from buckling experiments, theoretical predictions, and literature values. The experimental results based on buckling phenomenon compares well with theoretical values, except for PEDOT:PSS, where the ionic bonding leads to totally different situation.

Conclusions

The buckling-based measurements of mechanical moduli of various organic semiconductor materials are presented in this work. Because of limitations in preparing bulk samples of these materials for conventional tensile test, the buckling method is very well suited for the determination of mechanical properties of these materials.

The measured modus value for P3HT is in reasonable agreement with that from theoretical prediction. For the P3HT/PCBM composite layer, the mechanical modulus was ~5 times larger than that of pure P3HT due to the filler effect of PCBM nanoparticles. The mechanical modulus of PEDOT:PSS was found to be similar to the theoretical value of pure PSS. Although the strong ionic interaction between constituent polymers may lead to a modulus 2−3 times larger than that of parent polymers, as observed in polyelectrolyte multilayer system, a very small amount of PEDOT and its oligomeric nature are responsible for the experimentally observed behavior, i.e., negligible effect of PEDOT addition on long PSS polymer chain. The evaporated pentacene film showed an order of magnitude larger modulus compared to other polymeric semiconductor materials. This stiff nature of pentacene may lead to film delamination unless proper cautions (no large strain applied unintentionally) are taken during/after processing. The mechanical modulus values of common organic semiconductor materials, determined by the buckling method in this work, would be valuable in designing and implementing mechanically flexible and/or stretchable organic electronics.

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Supporting Information Available: Details for the theoretical estimation of mechanical properties of organic materials, modulus of P3HT/PCBM blend from composite theory, and experimental data on the buckling of PANI. This material is available free of charge via Internet at http://pubs.acs.org.

References and Notes

(1) Forrest, S. R. *Nature* **2004**, *428*, 911–918.
(2) Bao, Z.; Locklin, J. *Organic Field-Effect Transistors*; CRC Press: New York, 2007.
(3) Vaeth, K. M. *Inform. Display* **2003**, *19*, 12–17.
(4) Poortmans, J.; Arkhipov, V. *Thin Film Solar Cells*; Wiley: New York, 2006.
(5) Stafford, C. M.; Harrison, C.; Beers, K. L.; Karim, A.; Amis, E. J.; Vanlandingham, M. R.; Kim, H.-C.; Volksen, W.; Miller, R. D.; Simonyi, E. E. *Nat. Mater.* **2004**, *3*, 545–550.
(6) Stafford, C. M.; Guo, S.; Harrison, C.; Chiang, M. Y. M. *Rev. Sci. Instrum.* **2005**, *76*, 062207.
(7) Nolte, A. J.; Rubner, M. F.; Cohen, R. E. *Macromolecules* **2005**, *38*, 5367–5370.
(8) Stafford, C. M.; Vogt, B. D.; Harrison, C.; Julthongpiput, D.; Huang, R. *Macromolecules* **2006**, *39*, 5095–5099.
(9) Wilder, E. A.; Guo, S.; Lin-Gibson, S.; Fasolka, M. J.; Stafford, C. M. *Macromolecules* **2006**, *39*, 4138–4143.
(10) Nolte, A. J.; Cohen, R. E.; Rubner, M. F. *Macromolecules* **2006**, *39*, 4841–4847.
(11) Allen, H. G. *Analysis and Design of Structural Sandwich Panels*; Pergamon Press: London, 1969.
(12) Bowden, N.; Brittain, S.; Evans, A. G.; Hutchinson, J. W.; Whitesides, G. W. *Nature* **1998**, *393*, 146–149.
(13) Jiang, H.; Khang, D.-Y.; Song, Z.; Sun, Y.; Huang, Y.; Rogers, J. A. *Proc. Natl. Acad. Sci. U.S.A.* **2007**, *104*, 15607–15612.
(14) Harrison, C.; Stafford, C. M.; Zhang, W.; Karim, A. *Appl. Phys. Lett.* **2004**, *85*, 4016–4018.
(15) Khang, D.-Y.; Jiang, H.; Huang, Y.; Rogers, J. A. *Science* **2006**, *311*, 208–212.
(16) Yu, G.; Gao, J.; Hummelen, J. C.; Wudl, F.; heeger, A. J. *Science* **1995**, *270*, 1789–1791.
(17) Meitl, M. A.; Zhu, Z.-T.; Kumar, V.; Lee, K. J.; Feng, X.; Huang, Y. Y.; Adesida, I.; Nuzzo, R. G.; Rogers, J. A. *Nat. Mater.* **2006**, *5*, 33–38.
(18) Hoppe, H.; Sariciftci, N. S. *J. Mater. Chem.* **2006**, *16*, 45–61.
(19) Campoy-Quiles, M.; Ferenczi, T.; Agnostinelli, T.; Etchegoin, P. G.; Kim, Y.; Anthopoulos, T. D.; Stavrinou, P. N.; Bradley, D. D.; Nelson, J. *Nat. Mater.* **2008**, *7*, 158–164.
(20) Bowden, N.; Huck, W. T. S.; Kenis, P.; Whitesides, G. W. *Appl. Phys. Lett.* **1999**, *75*, 2557–2559.
(21) Bodas, D.; Khan-Malek, C. *Sens. Actuators, B* **2007**, *123*, 368–373.
(22) Hillborg, H.; Ankner, J. F.; Gedde, U. W.; Smith, G. D.; Yasuda, H. K.; Wikstrom, K. *Polymer* **2000**, *41*, 6851–6863.
(23) Neither the O_2 plasma treated PDMS nor the recovered PDMS for 7 days showed any buckling when compressed under OM and AFM, which means that our plasma treatment condition is so mild that it does not affect the buckling behavior of the coated film.
(24) Khang, D.-Y.; Rogers, J. A.; Lee, H. H. *Adv. Funct. Mater.* **2008**, *18*, 1–11.
(25) Kuila, B. K.; Nandi, A. K. *J. Phys. Chem. B* **2006**, *110*, 1621–1631.
(26) Miyauchi, S.; Kondo, T.; Oshima, K.; Yamaguchi, T.; Shimomura, M.; Mimoto, H. *J. Appl. Polym. Sci.* **2002**, *85*, 1429–1433.
(27) Groendaal, L. B.; Jonar, F.; Freitag, D.; Pielartzik, H.; Reynolds, J. R. *Adv. Funct. Mater.* **2000**, *12*, 481–494.
(28) Kirchmeyer, S.; Reuter, K.; Simpson, J. C. In *Conjugated Polymers: Theory, Synthesis, Properties, and Characterization*, 3rd ed.; CRC Press: New York, 2007.
(29) See Supporting Information.
(30) Mermut, O.; Lefebvere, J.; Gray, D. G.; Barrett, C. J. *Macromolecules* **2003**, *36*, 8819–8824.
(31) Pavoor, P. V.; Bellare, A.; Strom, A.; Yang, D.; Cohen, R. E. *Macromolecules* **2004**, *37*, 4865–4871.
(32) Lang, U.; Dual, J. *Key Eng. Mater.* **2007**, *345−346*, 1189–1192.
(33) Huang, H.; Chung, J. Y.; Nolte, A. J.; Stafford, C. M. *Chem. Mater.* **2007**, *19*, 6555–6560.
(34) Perutz, S.; Kramer, E. J.; Baney, J.; Hui, C. Y. *Macromolecules* **1997**, *30*, 7964–7969.
(35) Perutz, S.; Wang, J.; Kramer, E. J.; Ober, C. K.; Ellis, K. *Macromolecules* **1998**, *31*, 4272–4276.