STARS

Faculty Bibliography 2010s

Faculty Bibliography

1-1-2012

Near-infrared photoresponse sensitization of solvent additive processed poly(3-hexylthiophene)/fullerene solar cells by a low band gap polymer

Zhongjian Hu
University of Central Florida

Simon Tang
University of Central Florida

Anne Ahlvers
University of Central Florida

Saiful I. Khondaker
University of Central Florida

Andre J. Gesquiere
University of Central Florida

Find similar works at: https://stars.library.ucf.edu/facultybib2010
University of Central Florida Libraries http://library.ucf.edu

Recommended Citation

Showcase of Text, Archives, Research & Scholarship

Near-infrared photoresponse sensitization of solvent additive processed poly(3-hexylthiophene)/fullerene solar cells by a low band gap polymer

Zhongjian Hu, Simon Tang, Anne Ahlvers, Saiful I. Khondaker, and Andre J. Gesquiere

View Online   Export Citation

ARTICLES YOU MAY BE INTERESTED IN

Near-infrared photoresponse sensitization of solvent additive processed poly(3-hexylthiophene)/fullerene solar cells by a low band gap polymer

Zhongjian Hu,[1] Simon Tang,[1] Anne Ahlvers,[1,2] Saiful I. Khondaker,[3] and Andre J. Gesquiere[1,a]

[1]NanoScience Technology Center, Department of Chemistry and CREOL, The College of Optics and Photonics, University of Central Florida, 12424 Research Parkway Suite 400, Orlando, Florida 32826, USA
[2]Department of Physics, Truman State University, 100 E Normal St., Kirksville, Missouri 63501, USA
[3]NanoScience Technology Center, Department of Physics, University of Central Florida, 12424 Research Parkway Suite 400, Orlando, Florida 32826, USA

With the aim of extending the photoresponse of the poly(3-hexylthiophene)/[6,6]-phenyl-C61-butyric acid methyl ester photovoltaic system into the near-infrared region, a low band gap polymer poly[2,1,3-benzothiadiazole-4,7-diyl[4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b′]dithiophene-2,6-diyl]] was incorporated to make ternary blend solar cells. Solvent additive 1,8-diiodooctane (DIO) was applied to optimize the phase separation in a one-step active layer preparation. Devices fabricated with DIO additive demonstrate an improvement of device power conversion efficiency by 17%, which can be attributed to favorable microscopic structure of the ternary blend with 1:1:0.2 composition processed with DIO and extended absorption on the red side of the visible spectrum up to 900 nm. © 2012 American Institute of Physics. [http://dx.doi.org/10.1063/1.4742143]

Since the first few reports of poly(3-hexylthiophene)/[6,6]-phenyl-C61-butyric acid methyl ester (P3HT/PC$_{60}$BM) solar cells with power conversion efficiency (PCE) of more than 4%,[1,2] great research effort has been devoted to the optimization of morphology, charge transport, device architecture, as well as improving the understanding of active layer photophysics.[3–7] It has been estimated that P3HT, with a band gap of 1.9 eV, can only absorb ~27% of the solar photons, which strongly limits further device performance improvement of pure P3HT/PC$_{60}$BM devices.[8,9] Although the fabrication of tandem solar cells represents a promising approach to harvest more solar photons in a broad wavelength range,[10] the wide applicability of this complicated multilayer structure has been hampered by difficulties in controlling the photocurrent balance between the front and back cells and by attenuation of light that can be absorbed by the back cell due to the presence of the front cell.[11] In contrast to the tandem solar cell architecture, devices incorporating ternary blended active layers formed by incorporation of near-infrared (NIR) sensitizers into the binary P3HT/PC$_{60}$BM structure offer a more simple and versatile alternative approach in realizing a broad solar photon capture range.[12–15] To realize effective sensitization in P3HT/PC$_{60}$BM cells, the sensitizer should not only exhibit a complementary absorption to this material system but also have energy levels intermediate relative to those of P3HT and PC$_{60}$BM to facilitate charge transfer.[12,13] Recently, researchers have shown incorporation of small far-red-absorbing dyes in the prototypical P3HT/PC$_{60}$BM cells[12,13,15]; however, less attention has been given to the development of ternary blended solar cells incorporating low band gap (LBG) polymers.[14,16,17]

In this letter, we report the photoresponse sensitization of P3HT/PC$_{60}$BM solar cells with the LBG polymer poly[2,1,3-benzothiadiazole-4,7-diyl[4,4-bis(2-ethylhexyl)-4H-cyclopenta-[2,1-b:3,4-b′]dithiophene-2,6-diyl]] (PCPDTBT) in the presence of a solvent additive, 1,8-diiodooctane (DIO). Compared to the optimized control devices P3HT/PC$_{60}$BM, the P3HT:PC$_{60}$BM:PCPDTBT active layer with 1:1:0.2 composition (wt. ratio) and processed with DIO yields an improvement of 17% in PCE. The devices yield a short-circuit current density (J$_{sc}$) of 12.67 mA/cm^2, while the open-circuit voltage (V$_{oc}$) and fill factor (FF) remain similar to the control device at 0.55 V and 0.48, respectively. We show that the accumulation of favorable microscopic structure of the ternary blend with 1:1:0.2 composition processed with DIO, together with extended absorption on the red side of the visible spectrum are responsible for the observed device performance improvement.

Figure 1 shows the chemical structures of PCPDTBT and the energy level diagram of device components. As can be seen, PCPDTBT exhibits intermediate energy levels with respect to P3HT and PC$_{60}$BM. P3HT and PCPDTBT were purchased from Rieke Metals and 1-material, respectively. PC$_{60}$BM, 1,2-dichlorobenzene (DCB) and DIO were obtained from Sigma Aldrich and used as received. To prepare devices without DIO additive, the blended solutions of P3HT, PCPDTBT, and PC$_{60}$BM with different weight ratios were spin cast from DCB on top of a 40 nm thick poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) layer (PEDOT:PSS, Clevios P VP AI 4083, HC Starck) that was deposited on an ITO-coated glass substrate. Devices with DIO additive were prepared in the same way, but with addition of 3 vol. % DIO to DCB. The active layer thickness is around 210 nm as measured with atomic force microscopy (AFM, Digital Instruments Dimension 3100). The Ca (25 nm) and Al (80 nm) cathode was thermally deposited sequentially at a rate of ~0.6 Å/s. The active area of the devices is 0.066 cm^2. Device performance was characterized under simulated AM 1.5 G solar irradiation at 100 mW/cm^2 calibrated with a standard monocrystalline
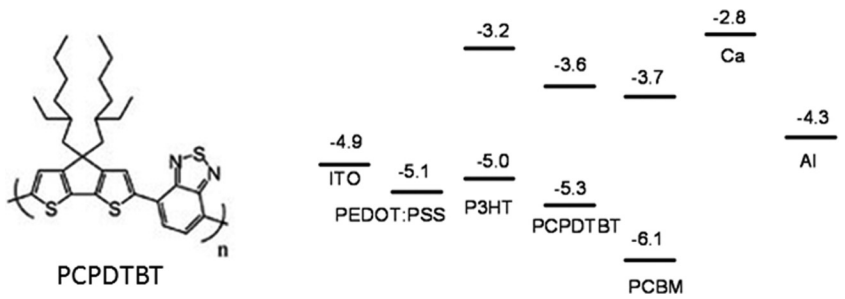
a)Electronic mail: andre@ucf.edu.

FIG. 1. Chemical structure of PCPDTBT (left) and energy level diagram of the PCPDTBT blended P3HT/PC$_{60}$BM solar cells (right).
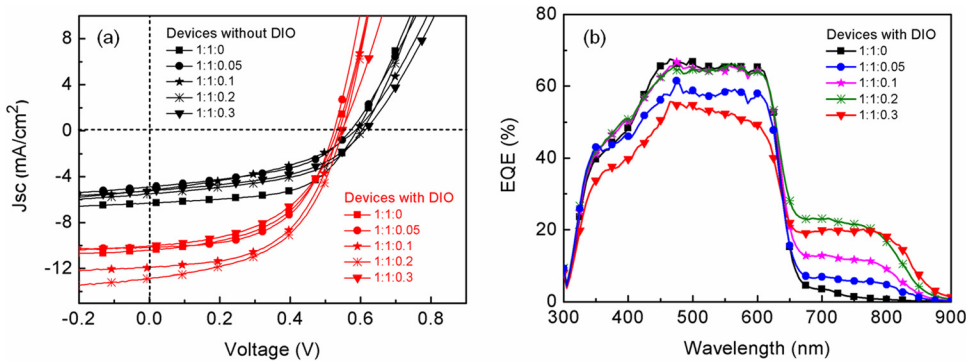

FIG. 2. (a) J-V characteristics of solar cells with different PCPDTBT concentrations processed without (black) and with (red) DIO solvent additive. (b) EQE curves of solar cells incorporating DIO and different PCPDTBT concentrations. The weight ratios of P3HT:PC$_{60}$BM:PCPDTBT are indicated in the panels.

silicon reference solar cell (Newport, 91150 V) with KG-5 visible color filter certificated by NIST (National Institute for Standards and Technology) to the ISO-17025 standard that is traceable to the National Renewable Energy Laboratory (NREL). External quantum efficiency (EQE) data was taken using the QE/IPCE Measurement kit (QE-PV-SI) from Newport.

The photocurrent density-voltage (J-V) characteristics of the devices studied herein are displayed in Figure 2(a). Figures of merit of the devices processed without and with DIO were extracted from these data and are summarized in Table I.

For the reference P3HT/PC$_{60}$BM solar cell, the incorporation of solvent additive DIO increases J$_{sc}$ from 6.36 mA/cm^2 to 10.55 mA/cm^2 with a slight drop in V$_{oc}$ and FF, resulting in an increase of PCE from 2.17% to 2.84%.

Ternary blended solar cells processed in the absence of DIO exhibit lower efficiency than the corresponding reference P3HT/PC$_{60}$BM solar cell (see Table I). Upon incorpora-

TABLE I. Device performance of solar cells with different PCPDTBT contents processed without and with DIO solvent additive.

P3HT:PC$_{60}$BM:PCPDTBT (wt. ratio)	Processed with 3 vol. % DIO	J$_{sc}$ (mA/cm^2)	V$_{oc}$ (V)	FF	PCE (%)
1:1:0	No	6.36	0.59	0.58	2.17
	Yes	10.55	0.55	0.49	2.84
1:1:0.05	No	4.60	0.58	0.49	1.32
	Yes	10.21	0.53	0.52	2.78
1:1:0.1	No	5.12	0.59	0.44	1.32
	Yes	11.84	0.53	0.50	3.13
1:1:0.2	No	5.55	0.58	0.52	1.57
	Yes	12.67	0.55	0.48	3.33
1:1:0.3	No	5.48	0.61	0.46	1.52
	Yes	10.03	0.55	0.50	2.75

tion of PCPDTBT, the short-circuit current, fill factor and device PCE are all lowered with respect to that of the reference P3HT/PC$_{60}$BM solar cell. This can be ascribed to the non-optimized film morphology due to the presence of PCPDTBT in the active layer, as discussed for the absorption data (Figure 3(a)) and the AFM data hereafter (Figure 4).

With regard to solar cells prepared with DIO, the device with the lowest PCPDTBT concentration (1:1:0.05 for P3HT:PC$_{60}$BM:PCPDTBT) exhibits similar device performance as the reference cell. For the 1:1:0.2 PCPDTBT sensitized solar cell the device exhibits a 20% increase in J$_{sc}$, i.e., from 10.55 mA/cm^2 observed for the P3HT/PC$_{60}$BM optimized control solar cell to 12.67 mA/cm^2 for the 1:1:0.2 ternary blended solar cell. Meanwhile V$_{oc}$ and FF remain similar to the optimized reference cell, leading to an efficiency of 3.33% for the 1:1:0.2 PCPDTBT sensitized solar cell compared to 2.84% for the reference P3HT/PC$_{60}$BM solar cell incorporating DIO. Note that there is a small decrease of V$_{oc}$ for the DIO processed devices relative to the devices without DIO, which is due to the increase in energy of the highest occupied molecular orbital (HOMO) energy level of crystalline P3HT structures.[12,18,19]

The EQE data displayed in Figure 2(b) for the devices fabricated with DIO additive indicate the origin of the observed 20% increase in J$_{sc}$ and 17% increase in PCE for the 1:1:0.2 ternary blended solar cell. At the blending ratio of 1:1:0.2, the EQE at 700 nm reaches 23% due to the PCPDTBT sensitization of the NIR photoresponse in these ternary blended devices. Meanwhile the EQE contribution from P3HT/PC$_{60}$BM absorption (ranging from 300 nm to 650 nm) remains unchanged. The solar cell photocurrent density (J$_{sc}$) can be calculated by integrating the EQE spectra with the AM 1.5 G solar spectrum using Eq. (1)

$$J_{sc} = \frac{q}{hc} \int_{\lambda_1}^{\lambda_2} EQE(\lambda) \cdot P_{in}(\lambda) \cdot \lambda d\lambda, \qquad (1)$$
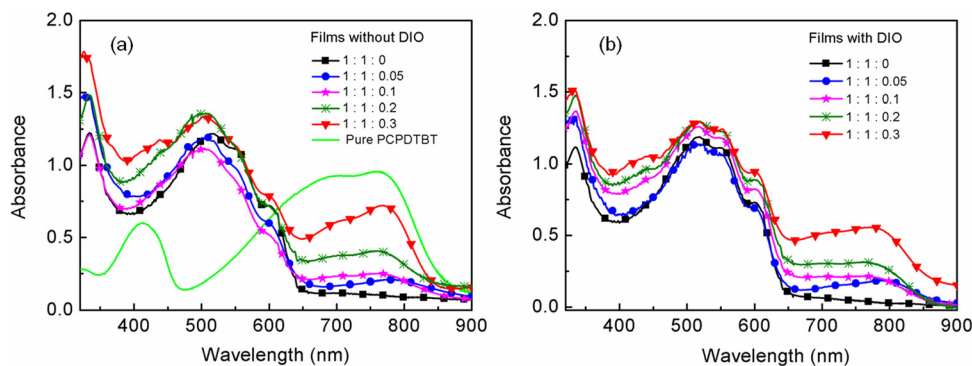
FIG. 3. Absorption spectra of films prepared without (a) and with solvent additive DIO (b). The weight ratios of P3HT:PC$_{60}$BM:PCPDTBT are indicated. Absorption spectrum of a pure PCPDTBT film spin cast from dichlorobenzene is included in (a).

where q is the elementary charge, *h* Plank's constant, c the speed of light, λ_1 and λ_2 are wavelength limits of EQE spectrum, EQE(λ) the external quantum efficiency as a function of wavelength (λ), P$_{in}$(λ) spectral irradiance under standard AM 1.5 G solar illumination.[20] According to Eq. (1), the J$_{sc}$ values for the control device and the 1:1:0.2 ternary blended device are estimated to be 10.22 mA/cm^2 and 12.57 mA/cm^2, respectively. These results match well with the J-V results shown above.

The role of the active layer absorption profiles in these device characteristics was studied first. Figure 3 presents the absorption spectra of P3HT/PC$_{60}$BM films with different PCPDTBT concentrations and a pure PCPDTBT film processed without and with DIO. With increasing PCPDTBT concentration (up to weight ratios for P3HT:PC$_{60}$BM:PCPDTBT of 1:1:0.3), the ternary blend exhibits an increasing absorbance in the range of 650 nm to 900 nm due to PCPDTBT absorption, supporting the observations made from the EQE data. The resulting broad absorption wavelength range from 300 nm to 900 nm of the ternary blend films was expected to generate higher photocurrent output than the P3HT/PC$_{60}$BM control device, although this is only the case for the 1:1:0.1 and 1:1:0.2 ternary blended devices due to the effects of active layer morphology at lower blending ratios. The absorption data also hint at morphological effects in the active layer as a function of composition and processing that play a role in the observations made for the J-V data. For films processed without DIO additive, direct addition of PCPDTBT leads to a pronounced blue shift of the P3HT absorption maximum from

515 nm for the control P3HT/PC$_{60}$BM film to about 505 nm for all the PCPDTBT incorporated films (Figure 3(a)). In addition, the vibronic shoulders of the P3HT absorption at 550 nm and 600 nm that are due to the interchain interactions become less defined in the presence of PCPDTBT, although peak positions do not shift in those cases. These observations indicate a disruption of the P3HT ordered structure by PCPDTBT, which can be verified by the AFM data shown hereafter. In comparison, the introduction of DIO can recover the crystalline structure of P3HT as can be observed from absorption profiles of films with DIO shown in Figure 3(b), which is attributed to microscopic phase separation in the presence of DIO.[21] The P3HT absorption maximum and vibronic characteristics are not significantly affected by the addition of PCPDTBT in the presence of DIO.

The active layer morphology was studied further by AFM. Figure 4 presents AFM topography and phase images of the reference P3HT/PC$_{60}$BM solar cells and the PCPDTBT ternary blended devices (1:1:0.2 and 1:1:0.3 P3HT:PC$_{60}$BM:PCPDTBT ratios). As clearly shown in Figures 4(a),(f), and 4(b),(g), direct incorporation of PCPDTBT (i.e., without adding DIO) with a ratio of 1:1:0.2 induces a relatively smoother surface and disrupted phase separation compared to the reference P3HT/PC$_{60}$BM cell, which are indicative of a decrease of P3HT crystallinity since a rough surface of P3HT/PC$_{60}$BM is usually attributed to P3HT crystallization into ordered structures.[1,22] This result is in accordance with the blue shift of the absorption maximum of P3HT due to the presence of PCPDTBT. For the reference
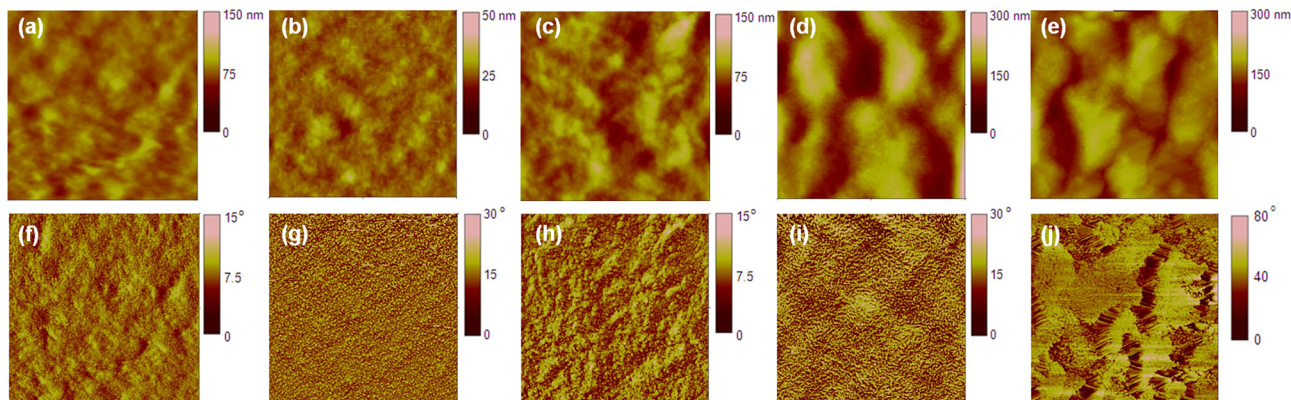

FIG. 4. AFM topography images of (a) P3HT/PC$_{60}$BM cell without DIO, (b) P3HT:PC$_{60}$BM:PCPDTBT = 1:1:0.2 cell without DIO, (c) P3HT/PC$_{60}$BM cell with DIO, (d) P3HT:PC$_{60}$BM:PCPDTBT = 1:1:0.2 cell with DIO, (e) P3HT:PC$_{60}$BM:PCPDTBT = 1:1:0.3 cell with DIO. Corresponding AFM phase images (f)-(j) are shown below each topography image. The scan size for all the images is 5 × 5 μm^2.

P3HT/PC$_{60}$BM cells, the addition of DIO induces a slightly rougher surface and a finer phase separation of the active layer (Figures 4(c) and 4(h)), which is favorable for photoinduced charge separation and subsequent charge transport. With the incorporation of DIO in the 1:1:0.2 PCPDTBT incorporated cell, a rough surface topography is also observed accompanied with fine phase separation and fibrillar structure as shown in Figures 4(d) and 4(i). This favorable microscopic structure of the ternary blend together with the complementary absorption and appropriate energy levels of PCPDTBT is responsible for the observed device performance improvement. When the PCPDTBT content increases up to 1:1:0.3, macrosize phase separation can be observed (Figures 4(e) and 4(j)), which is assumed to be responsible for the observed drop in device performance for this active layer composition.

In summary, we have demonstrated optimization of ternary blended active layers for OPVs using the additive DIO. The solvent additive DIO serves to optimize the microscopic structure of the active layer. With this approach the incorporation of PCPDTBT in P3HT/PC$_{60}$BM cells with a weight ratio of 1:1:0.2 for P3HT:PC$_{60}$BM:PCPDTBT lead to a 20% increase in short-circuit current density and a 17% increase in device performance in the presence of DIO additive, compared to the optimized reference P3HT/PC$_{60}$BM device. Our results indicate that with the proper control of the morphology of ternary blended materials, NIR absorbing conjugated polymers can be effectively used to efficiently extend the photon capture range of polymer solar cells.

[1]G. Li, V. Shrotriya, J. S. Huang, Y. Yao, T. Moriarty, K. Emery, and Y. Yang, Nat. Mater. **4**(11), 864 (2005).
[2]W. L. Ma, C. Y. Yang, X. Gong, K. Lee, and A. J. Heeger, Adv. Funct. Mater. **15**(10), 1617 (2005).
[3]L. M. Chen, Z. Xu, Z. R. Hong, and Y. Yang, J. Mater. Chem. **20**(13), 2575 (2010).
[4]B. C. Thompson and J. M. J. Frechet, Angew. Chem. Int. Ed. **47**(1), 58 (2008).
[5]V. D. Mihailetchi, H. X. Xie, B. de Boer, L. J. A. Koster, and P. W. M. Blom, Adv. Funct. Mater. **16**(5), 699 (2006).
[6]L. M. Chen, Z. R. Hong, G. Li, and Y. Yang, Adv. Mater. **21**(14–15), 1434 (2009).
[7]T. M. Clarke and J. R. Durrant, Chem. Rev. **110**(11), 6736 (2010).
[8]C. J. Brabec, S. Gowrisanker, J. J. M. Halls, D. Laird, S. J. Jia, and S. P. Williams, Adv. Mater. **22**(34), 3839 (2010).
[9]G. Dennler, M. C. Scharber, and C. J. Brabec, Adv. Mater. **21**(13), 1323 (2009).
[10]J. Y. Kim, K. Lee, N. E. Coates, D. Moses, T. Q. Nguyen, M. Dante, and A. J. Heeger, Science **317**(5835), 222 (2007).
[11]F. Meillaud, A. Shah, C. Droz, E. Vallat-Sauvain, and C. Miazza, Sol. Energy Mater. Sol. C **90**(18–19), 2952 (2006).
[12]J. Peet, A. B. Tamayo, X. D. Dang, J. H. Seo, and T. Q. Nguyen, Appl Phys. Lett. **93**(16), 163306 (2008).
[13]J. H. Huang, M. Velusamy, K. C. Ho, J. T. Lin, and C. W. Chu, J. Mater. Chem. **20**(14), 2820 (2010).
[14]M. Koppe, H. J. Egelhaaf, G. Dennler, M. C. Scharber, C. J. Brabec, P. Schilinsky, and C. N. Hoth, Adv. Funct. Mater. **20**(2), 338 (2010).
[15]S. Honda, T. Nogami, H. Ohkita, H. Benten, and S. Ito, ACS Appl. Mater. Interfaces **1**(4), 804 (2009).
[16]S. J. Park, J. M. Cho, W. B. Byun, J. C. Lee, W. S. Shin, I. N. Kang, S. J. Moon, and S. K. Lee, J. Polym. Sci. Pol. Chem. **49**(20), 4416 (2011).
[17]C. H. Chen, C. H. Hsieh, M. Dubosc, Y. J. Cheng, and C. S. Su, Macromolecules **43**(2), 697 (2010).
[18]W. C. Tsoi, S. J. Spencer, L. Yang, A. M. Ballantyne, P. G. Nicholson, A. Turnbull, A. G. Shard, C. E. Murphy, D. D. C. Bradley, J. Nelson, and J. S. Kim, Macromolecules **44**(8), 2944 (2011).
[19]K. Vandewal, A. Gadisa, W. D. Oosterbaan, S. Bertho, F. Banishoeib, I. Van Severen, L. Lutsen, T. J. Cleij, D. Vanderzande, and J. V. Manca, Adv. Funct. Mater. **18**(14), 2064 (2008).
[20]West Conshoken American Society for Testing and Materials (ASTM) Standard G159, PA, USA.
[21]X. Bai and S. Holdcroft, Macromolecules **26**(17), 4457 (1993).
[22]G. Li, V. Shrotriya, Y. Yao, J. S. Huang, and Y. Yang, J. Mater. Chem. **17**(30), 3126 (2007).