Macromolecular Research

Volume 17, Number 2 February 25, 2009

Communications

High-Speed Photorefractive Composite Sensitized by Poly(3-Hexylthiophene)

Jin-Woo Oh*, Jongwan Choi, and Nakjoong Kim*

Department of Chemistry, Hanyang University, Seoul 133-791, Korea

Received July 31,2008; Revised November 14, 2008; Accepted November 15, 2008

Introduction

Poly(3-hexylthiophene) (P3HT) has emerged as a promising material and is currently the subject of intense research[1] as it has good stability, reasonably high hole mobility in the range of 10^{-3} $cm^2V^{-1}s^{-1}$ (Ref.1) and a field effect mobility, which can be as high as 0.01-0.045 $cm^2V^{-1}s^{-1}$ in high quality self-organized samples.[2] P3HT has been used recently in the fabrication of electronic devices such as light emitting diodes,[3] solar cells,[4] and thin film field effect transistors[5] on flexible substrates. Here, P3HT is used as a sensitizer in efficient polymeric photorefractive (PR) composite.

Polymeric PR composites have numerous potential applications in real-time optical processing because they provide a medium for the recording of reversible and nonlocal grating.[6,7] The primary step in the formation of a PR grating, the photo-charge generation, is generally achieved in a charge transfer (CT) complex formed between a semiconducting polymer matrix and a sensitizer with a small amount of organic molecules, providing sensitivity in the visible and near infrared.[8-10] To date, polymeric PR composites have been sensitized with several classes of organic molecules, such as TNF,[11] TNFM,[12] TCNQ,[13] C_{60},[14] and [6, 6] PCBM;[15] but no PR composites have been sensitized with P3HT.

In this work, we report on a polymeric PR composite sensitized with P3HT. Also, we analyze the dynamic and steady-state PR properties of composite at a wavelength of λ = 632.8 nm, as a function of external electric field.

Experimental

Materials and Sample Fabrications. In this work, a photorefractive composite was prepared by doping the optically anisotropic chromophore, 2-{3-[(*E*)-2-(dibutylamino)-1-ethenyl]-5, 5-dimethyl-2- cyclohexenyliden} malononitrile (DB-IP-DC), into photoconducting polymer, poly[methyl-3-(9-carbazolyl) propylsiloxane] (PSX-Cz) sensitized by regioregular P3HT, referred to as P3HT, with the following composition: PSX-Cz/DB-IP-DC/P3HT (69/30/1 wt%). PSX-Cz provided the hole conducting matrix, DB-IP-DC was used as chromophore to confer orientational birefringence and good phase stability to the composite.[6] For reference, PSX-Cz/DB-IP-DC/2,4,7-trinitro-9-fluorenone (TNF) (69/30/1 wt%) was also prepared and is referred to as TNF. PSX-Cz and DB-IP-DC were synthesized using previously described methods.[16,17] TNF obtained from Kanto Chemistry Co. and P3HT obtained from Aldrich were used after purification. For sample preparation, the mixtures (total 100 mg) were dissolved in 400 mg of dichloromethane and the solution was filtered through a 0.2 μm membrane. The composite P3HT and TNF were cast on a patterned indium tin oxide (ITO) glass substrate, dried slowly for 12 h at ambient temperature, then heated in an oven to 90 °C for 24 h to completely remove the residual solvent. The composites were then softened on a hot plate at 100 °C, and next sandwiched between ITO glasses with Teflon film spacer of 100 μm to yield a film with a uniform thickness.[18]

Measurement. The photoconductivity of the PR samples was measured at a wavelength of 632.8 nm using a simple dc photocurrent method.[19] The current flowing through the sample was measured by the Keithley 6485 during illumination with an intensity of 20 mW/cm^2 at an applied field of 30 V/μm.

*Corresponding Authors. E-mails: daybreak0929@hanmail.net or Kimnj@hanyang.ac.kr

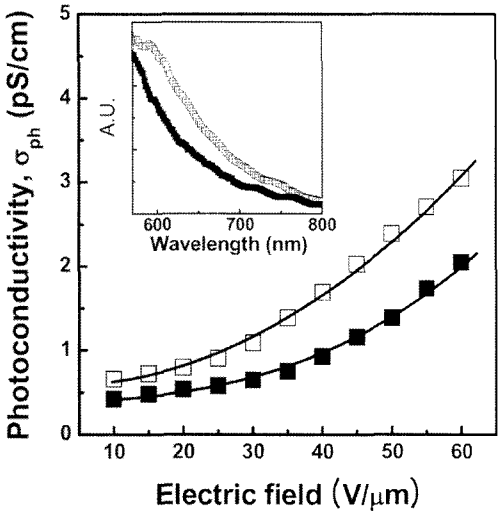

Figure 1. Field dependence of the photoconductivity at 632.8 nm in samples P3HT (open square) and TNF (closed square). Inset: Visible spectrum of PR composites P3HT (open square) and TNF (closed square).

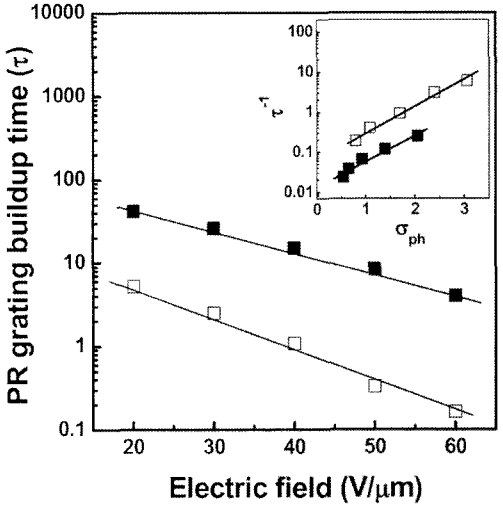

Figure 2. Field dependence of the PR grating buildup time at 632.8 nm in samples P3HT (open square) and TNF (closed square). Inset: photoconductivity dependence of the PR grating buildup speed in samples P3HT (open square) and TNF (closed square).

The photorefractive properties were characterized by a degenerate four-wave mixing (DFWM) experiment.[18] Two coherent laser beams with $\lambda = 632.8$ nm were irradiated on the sample in the tilted geometry at an incident angle of $\theta = 30°$ and 60° with respect to the sample's normal axis. The intensity of s-polarized writing beams was 30 mW/cm^2. The recorded PR grating was read by a p-polarized counter-propagating beam. An attenuated reading beam with a very weak intensity of 0.1 mW/cm^2 was used.

The grating buildup time of the PR samples was evaluated from the buildup of the beam intensity of the DFWM measurement. The time constants, τ_1 and τ_2, were calculated by fitting the evolution of the growth of the gain, $g(t)$, with the following biexponential function[20]

$$g(t) = a_1\{1-\exp(-t/\tau_1)\} + a_2\{1-\exp(-t/\tau_2)\} \quad (1)$$

Results and Discussion

Differential scanning calorimetry experiments conducted on composites P3HT and TNF yielded a broad range of glass transition temperatures between 10 and 30 °C.[21] The ability of the chromophores to reorient in the composite was further confirmed using a transient ellipsometry technique.[22]

The inset in Figure 1 shows the absorption spectra of PR composites P3HT and TNF. The absorption coefficient (α) at 632.8 nm of 100 μm thick samples was 128 and 76 cm^{-1} in P3HT and TNF, respectively. As the inset shows in Figure 1, the formation of a broad redshifted band was confirmed in a thick sample of the composite P3HT and led to a significant increase of the photoconductivity σ_{ph}.[6] As shown in Figure 1, the larger photoconductivity of sample P3HT, as compared with that of TNF, confirms that in the presence of the P3HT the photo-charge generation of carriers is significantly enhanced.

Degenerate four-wave mixing experiments were carried out to evaluate the effect of the improved photoconductivity in sample P3HT. Figure 2 shows τ_1 of samples, which were measured at five different electric fields between 20 and 60 V/μm. As was expected, an elevated external electric field caused faster grating formation in both types of samples since the charge mobility as well as the photo-charge generation efficiency increased with electric field. As shown in Figure 2, the dominant time constants (τ_1) in the sample P3HT were consistently smaller by more than an order of magnitude with respect to the ones obtained in the sample TNF. At low intensity of 30 mW/cm^2, τ_1 of sample P3HT was 163 ms in an applied field of 60 V/μm. The increment of photoconductivity from a large absorption coefficient and a fast hole mobility leads to a fast buildup of PR grating. The primary event in photorefractive effect is the formation of the space charge field (E_{sc}).[23] The magnitude of the space charge field is strongly dependent on photo-charge generation and the separation of charges.[24] The speed of PR grating buildup is governed by the number of generated charges per unit time, the speed with which the charges move through the material, and by trapping effects.[23] Overall, charge generation and transport is reflected in the value of σ_{ph}, which in the most basic picture can be written as

$$\sigma_{ph} = ne\mu = (\varphi\alpha I\tau/h\nu)e\mu \quad (2)$$

where n is the density of carriers, e is the elementary charge, μ is the hole mobility, φ is the charge generation quantum efficiency, α is the absorption coefficient, I is the optical intensity, τ is the time constant for transport, h is Plank's

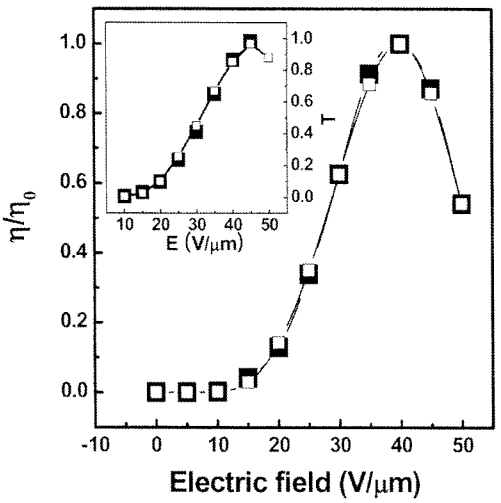

Figure 3. Field dependence of the normalized steady-state diffraction efficiency measured in samples P3HT (open square) and TNF (closed square). Inset: field dependence of the transmittance measured in samples P3HT (open square) and TNF (closed square).

constant, and v is the frequency of the light. Here we regard the value of σ_{ph} as a measure of the speed of E_{sc} formation. The PR grating buildup speed (τ^{-1}) is increased with the amount of photoconductivity, as shown inset in Figure 2. This suggests that the PR grating buildup speed is limited by σ_{ph} and therefore by E_{sc} formation.[23]

Figure 3 shows the steady-state PR properties of samples P3HT and TNF. In both types of samples, the maximum value of the diffraction efficiency was at around 40 V/μm. The maximum diffraction efficiency in sample P3HT, around 35%, was limited by absorption and scattering.[6] The inset of Figure 3 shows the transmittance of the composites, which were measured at five different electric fields between 10 and 50 V/μm. The gain coefficient was measured from two beam coupling experiment. The gain coefficient value of the sample P3HT with larger photoconductivity was higher than that of sample TNF at the same external electric field.

Conclusions

In this work, we have developed a new type PR sample with properties comparable to those of samples sensitized with organic molecules. The PR sample sensitized with P3HT has consistently shown great photoconductivity, leading to a fast grating buildup speed of 163 ms, at low intensity of 30 mW/cm^2. This sample brings the possibility of applications requiring video response rates one step closer.[23]

Acknowledgments. This work was supported by the Korea Science and Engineering Foundation (KOSEF) grant funded by the Korea government (MEST) (Grant No. R11-2007-050-01003-0) and by the Research fund of HYU (HYU-2008-T).

References

(1) Z. Chiguvare and V. Dyakonov, *Phys. Rev. B*, **70**, 235207 (2004).
(2) W. Bao, A. Dodabalapur, and A. J. Lobinger, *Appl. Phys. Lett.*, **69**, 4108 (1996).
(3) J. Shinar, *Organic Light Emitting Devices: A Survey*, American Institute of Physics, New York, 2002.
(4) C. J. Brabec, V. Dyakonov, J. Parisi, and N. S. Sariciftci, *Organic Photovoltaics: Concepts and Realization*, Springer-Verlag, Berlin, 2003, Vol. 60.
(5) C. D. Dimitrakopoulos and J. D. Mascaro, *IBM J. Res. Dev.*, **45**, 11 (2001).
(6) C. Fuentes-Hernandez, D. J. Suh, B. Kippelen, and S. R. Marder, *Appl. Phys. Lett.*, **85**, 534 (2004).
(7) S. H. Lee, W. S. Jahng, K. H. Park, N. Kim, W. -J. Joo, and D. H. Choi, *Macromol. Res.*, **11**, 431 (2003).
(8) S. J. Zilker, *Chem. Phys. Chem.*, **1**, 72 (2000).
(9) E. Mecher, F. Gallego-Gomez, H. Tillmann, H. Hörhold, J. C. Hummelen, and K. Meerholz, *Nature(London)*, **418**, 959 (2002).
(10) M. J. Cho, T. W. Lee, H. S. Kim, J. -I. Jin, and D. H. Choi, *Macromol. Res.*, **15**, 431 (2007).
(11) Z. J. Chen, F. Wang, Z. W. Huang, Q. H. Gong, Y. W. Chen, Z. J. Zhang, and H. Y. Chen, *J. Phys. D*, **31**, 2245 (1998).
(12) E. Hendrickx, J. Herlocker, J. L. Maldonadl, S. R. Marder, B. Kippelen, A. Persoons, and N. Peyghambarian. *Appl. Phys. Lett.*, **72**, 1679 (1998).
(13) K. Sutter and P. Guenter, *J. Opt. Soc. Am. B*, **7**, 2274 (1990).
(14) D. Wright, U. Gubler, Y. Roh, W. E. Moerner, M. He, and R. J. Twieg, *Appl. Phys. Lett.*, **79**, 4274 (2001).
(15) E. H. Mecher, C. Brauchel, H. H. Horhold, J. C. Hummelen, and K. Meerholz, *Phys. Chem. Chem. Phys.*, **1**, 1749 (1999).
(16) W.-J. Joo, N.-J. Kim, H. Chun, I. K. Moon, and N. Kim, *Polymer*, **42**, 9863 (2001).
(17) S. H. Cho, H. S. Lim, B. K. Jeon, J. M. Ko, J. Y. Lee, and W. G. Kim, *Macromol. Res.*, **16**, 31 (2008).
(18) H. Chun, I. K. Moon, D.-H. Shin, and N. Kim, *Chem. Mater.*, **13**, 2816 (2001).
(19) J. S. Schildkraut, *Appl. Phys. Lett.*, **58**, 340 (1991).
(20) M. A. Díaz-García, D. Wright, B. Smith, E. Glazer, and W. E. Moerner, *Chem. Mater.*, **11**, 1784 (1999).
(21) J. Y. Kwon, B. G. Kim, J. Y. Do, J.-J. Ju, and S. K. Park, *Macromol. Res.*, **15**, 533 (2007).
(22) J. A. Herlocker, K. B. Ferrio, E. Hendrickx, B. D. Guenther, S. Mery, B. Kippelen, and N. Peyghambarian, *Appl. Phys. Lett.*, **74**, 2253 (1999).
(23) D. Wright, M. A. Díaz-García, J. D. Casperson, M. DeClue, W. E. Moerner, and R. J. Twieg, *Appl. Phys. Lett.*, **73**, 1490 (1998).
(24) J.-W. Oh, C.-S. Choi, and N. Kim, *Mol. Cryst. Liq. Cryst.*, **447**, 133 (2006).