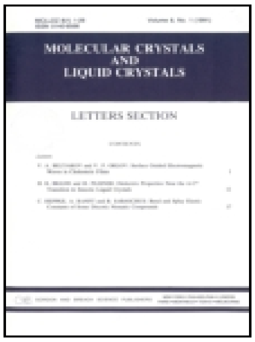


Molecular Crystals and Liquid Crystals

ISSN: 1542-1406 (Print) 1563-5287 (Online) Journal homepage: http://www.tandfonline.com/loi/gmcl20

Synthesis of Polythiophene with a Photo-Crosslinkable Side Chain

Takahito Kosaka, Toru Ube, Masa-aki Haga & Tomiki Ikeda

To cite this article: Takahito Kosaka, Toru Ube, Masa-aki Haga & Tomiki Ikeda (2015) Synthesis of Polythiophene with a Photo-Crosslinkable Side Chain, Molecular Crystals and Liquid Crystals, 617:1, 67-72, DOI: 10.1080/15421406.2015.1075826

To link to this article: http://dx.doi.org/10.1080/15421406.2015.1075826

Mol. Cryst. Liq. Cryst., Vol. 617: pp. 67–72, 2015
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2015.1075826

Synthesis of Polythiophene with a Photo-Crosslinkable Side Chain

TAKAHITO KOSAKA,[1] TORU UBE,[2] MASA-AKI HAGA,[1] AND TOMIKI IKEDA[2,*]

[1]Graduate School of Science and Engineering, Chuo University, Bunkyo-ku, Tokyo, Japan
[2]Research & Development Initiative, Chuo University, Bunkyo-ku, Tokyo, Japan

We have synthesized a photo-crosslinkable polythiophene copolymer functionalized with a cinnamate moiety to improve the stability of organic photovoltaic (OPV) cells. The active layer of OPV cells is generally bulk heterojunction (BHJ) that consists of two or more organic semiconductors. When BHJ forms a micro-phase-separated structure with a blend of two organic materials, its structure inclines to change into a macro-phase-separated one after some time. To stabilize the BHJ morphology, we used a crosslinkable polymer containing a cinnamate moiety. The copolymer film became insoluble after UV irradiation because of [2+2] dimerization of the cinnamate groups.

Keywords polythiophene; cinnamate; photo-crosslinking; nano phase separation; photovoltaic

Introduction

Recently, organic photovoltaic (OPV) cells based on conjugated polymers have attracted much attention owing to such advantages as low-cost fabrication, flexibility and light weight [1–3]. Bulk heterojunction (BHJ) devices that consist of two organic semiconductors, an electron-donor (e.g. conjugated polymer) and an electron-acceptor (e.g. fullerene derivatives), have brought a significant breakthrough in OPV cells [4–6]. However, OPV cells still have a serious problem of low stability, and they have not yet been in commercial uses. BHJ devices form micro-phase-separated structures with a blend of two organic materials, but their structures change into macro-phase-separated ones after some time due to the formation of acceptor crystals [7, 8]. In addition, it is difficult to produce multilayered structures of OPV cells because the first layer structures are destroyed by the solvent of the second layer when depositing the second layer materials on the first one. To overcome these problems, the use of crosslinkable conjugated polymers is promising. Fréchet et al. demonstrated that crosslinkable bromine-functionalized poly(3-hexylthiophene) (P3HT) is useful to improve the morphological stability of devices [8]. In this study, we show the

---

[*] Address correspondence to Tomiki Ikeda, Research & Development Initiative, Chuo University1-13-27 Kasuga, Bunkyo-ku, Tokyo 112-8551, Japan. E-mail: tikeda@tamacc.chuo-u.ac.jp

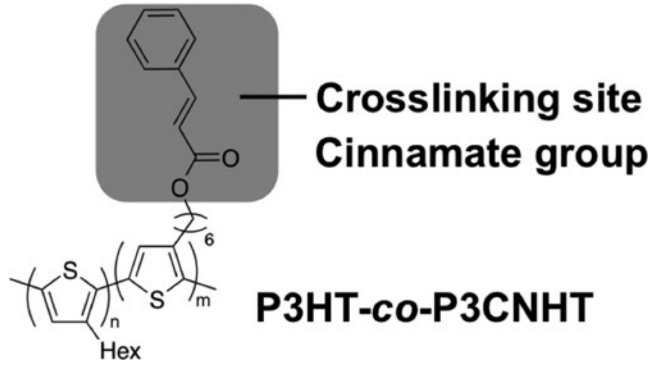


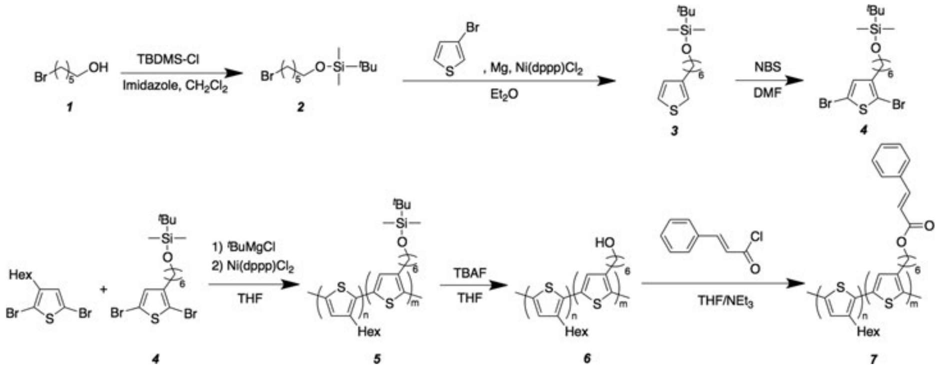
Figure 1. Chemical structure of P3HT-*co*-P3CNHT.

synthesis of a crosslinkable polythiophene copolymer functionalized with cinnamate moieties (**Figure 1**), poly[3-hexylthiophene-*co*-3-(6-cinnamoyloxy)hexylthiophene](P3HT-*co*-P3CNHT). Poly(vinyl cinnamate) has been applied in the photoresist materials to produce insoluble parts upon exposure to UV light through a photomask [9]. It is expected that the copolymer film will have a high morphological stability after photocrosslinking.

Experimental

Materials

6-Bromo-1-hexanol, 3-bromothiophene, [1, 3-bis(diphenylphosphino)propane]nickel(II) chloride (Ni(dppp)Cl_2) and cinnamoyl chloride were purchased from TCI. *tert*-butyldimethyl chlorosilane (TBDMS-Cl), 2,5-dibromo-3-hexylthiophene, tetrabutylammonium fluoride (TBAF) and *tert*-butyl magnesium chloride (^{t}BuMgCl) were obtained from Aldrich. Anhydrous diethyl ether and tetrahydrofuran (THF) were purchased from Kanto Chemical and purified by the method of Grubbs et al. [10].



Scheme 1. Synthetic routes for the monomer (***4***) and the copolymer (***7***) used in this work.

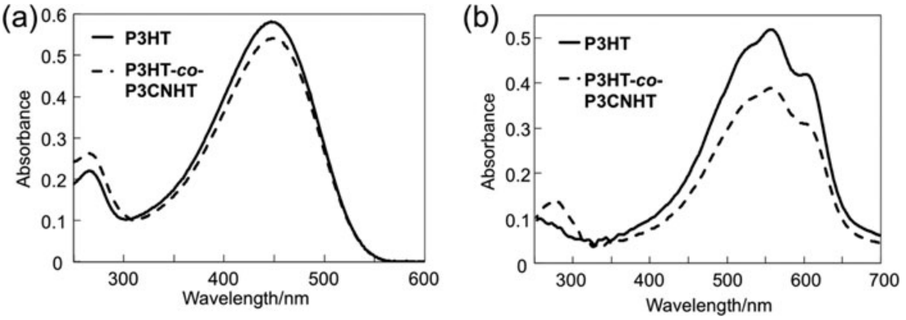


Figure 2. UV-Vis absorption spectra of P3HT (solid line) and P3HT-*co*-P3CNHT (broken line). (a) in THF solution (10 mg mL^{-1}); (b) in films.

Synthesis

The synthetic routes of a monomer (***4***) and a copolymer (***7***) are outlined in **Scheme 1**.

The synthetic routes to poly[3-hexylthiophene-*co*-3-(6-hydroxy)hexylthiophene](***6***) were reported by Grubbs et al. [11].

Poly[3-hexylthiophene-*co*-3-(6-cinnamoyloxy)hexylthiophene](P3HT-*co*-P3CNHT)(*7*). Copolymer ***6*** (71 mg) was dissolved in THF (1 mL) at room temperature, and a mixture of triethylamine (0.236 mL, 1.70 mmol) and cinnamoyl chloride (283 mg, 1.70 mmol) in THF was added to this solution. The mixture was stirred at room temperature for 2 h and precipitated into methanol, and dried under vacuum. Then the solid was dissolved in THF (1 mL), and was added a solution of triethylamine (0.250 mL, 1.80 mmol) and cinnamoyl chloride (301 mg, 1.81 mmol) in THF (1 mL). The mixture was stirred for 17 h and precipitated into methanol and dried under vacuum to give copolymer ***7*** as a black solid (42.3 mg). ^{1}H NMR (500 MHz, $CDCl_3$): δ/ppm = 7.92–7.66 (d), 7.52–7.34 (m), 6.98 (s, 1H), 6.90 (s), 6.82 (d), 6.45–6.41(d), 4.22 (t), 2.81 (t), 2.62 (t), 2.57 (t), 1.71 (q, 2H), 1.44 (q, 2H), 1.35 (m, 4H), 0.92 (t, 3H). GPC (THF, 1.0 mL/min): $M_n = 1.72 \times 10^4$, $M_w = 2.15 \times 10^4$, $M_w/M_n = 1.25$.

Measurements

The ^{1}H NMR spectra (500 MHz) were recorded on a JEOL JNM-ECX500 spectrometer and referenced internally to the solvent peaks. The molecular weight of polymers was

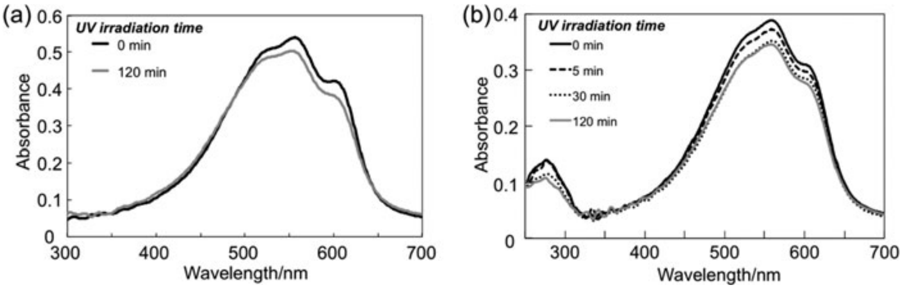


Figure 3. UV-Vis absorption spectra of (a) P3HT and (b) P3HT-*co*-P3CNHT films before and after irradiation.

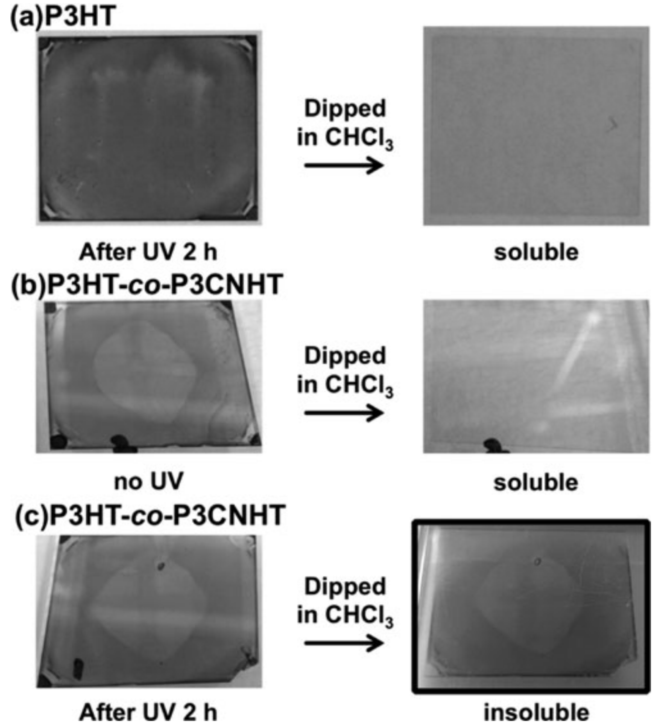


Figure 4. The effect of UV irradiation on the solubility of the films. (a) P3HT after irradiation; (b) P3HT-*co*-P3CNHT without UV irradiation; (c) P3HT-*co*-P3CNHT after UV irradiation for 2 h. Photos before (left) and after (right) immersion in chloroform.

determined by gel permeation chromatography (GPC) using a Shodex KF-803F + KF-806L column and a UV detector (elution solvent, THF; temperature 40°C; flow rate, 1.0 mL/min). Polystyrenes were used as calibrating standards. The UV-Vis spectra in solution were measured on Agilent Technologies 8543 UV-Visible Value System and spectra in films were recorded on Hitachi U-4000 spectrophotometer.

Film Preparation

The films of P3HT-*co*-P3CNHT and P3HT were prepared by spin-coating a chlorobenzene solution (10 mg mL^{-1}) onto glass substrates or quartz substrates at room temperature and the films were dried under vacuum overnight. Then the films were irradiated with UV light (313 nm, 20 mW/cm^2) from a 500 W high-pressure mercury lamp (USHIO, OPM2-502HQ) through glass filters (Tokina, U340).

Results and Discussion

*Characterization of P3HT-*co*-P3CNHT*

Grignard metathesis (GRIM) polymerization was used to obtain a copolymer with narrow molecular weight distribution [12–14]. In a typical run, we employed a mixture of monomers with a feed ratio of 2,5-dibromo3-hexylthiophene (85%) and monomer ***4*** (15%), and ^{1}H

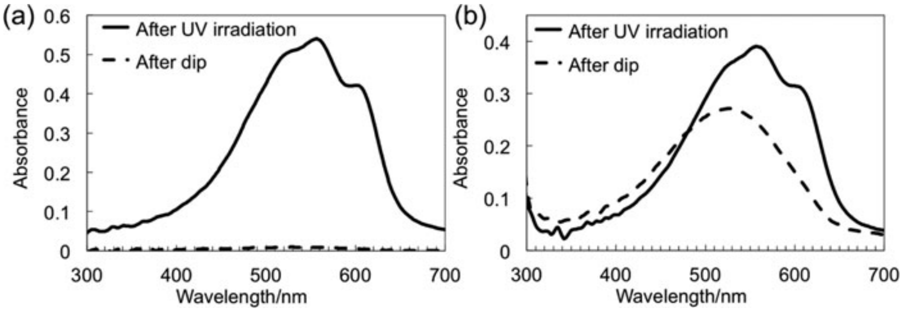


Figure 5. UV-Vis absorption spectra of the films of (a) P3HT and (b) P3HT-*co*-P3CNHT before and after immersion in chloroform.

NMR spectroscopy showed that the copolymer has a composition similar to the monomer feed ratio. The GPC curve gave a number-average molecular weight (M_n) of 1.72×10^4 and a narrow polydispersity index (M_w/M_n) of 1.25. **Figure 2a** shows UV-Vis absorption spectra of the copolymer and P3HT in THF. These spectra are almost identical, however the absorbance at 280 nm is higher in the copolymer than in P3HT because of introduction of the cinnamate groups. A similar increase of a peak was also observed in the films (**Figure 2b**).

Influence of UV Irradiation

To investigate the influence of UV irradiation, the films of P3HT and the copolymer were exposed to UV light at 313 nm. **Figure 3a** shows the UV-Vis spectra of the P3HT film before and after irradiation for 120 min, which indicates a slight decrease in a peak around 550 nm. A similar decrease in a peak was observed in the copolymer film (**Figure 3b**). As the peak around 550 nm is due to crystallization of P3HT, the decrease in the peak implies reduction in crystallinity. On the other hand, the copolymer film showed a decrease in a peak at 280 nm, which indicates that the cinnamate groups undergo [2+2] dimerization.

Solubility Test

Figure 4 shows the effect of UV irradiation on the solubility of the films in chloroform. The P3HT film without cinnamate groups was completely soluble even after UV irradiation. Similarly, the copolymer film without UV irradiation was soluble. On the other hand, the copolymer film after irradiation became insoluble. **Figure 5** shows the UV-Vis spectra of the films before and after immersion in chloroform for 24 h. In the P3HT film after irradiation, almost no absorption of the film was observed, while in the copolymer film after irradiation, absorption of the film remained after immersion in chloroform. It is suggested that the cinnamate groups of the copolymer undergo [2+2] dimerization, leading to crosslinking.

Conclusions

We have synthesized a photo-crosslinkable P3HT-*co*-P3CNHT. Indeed, the copolymer film became insoluble after UV irradiation, which indicates that the cinnamate groups of the copolymer undergo crosslinking reactions. The copolymer is useful not only to improve the stability of the materials but also to fabricate multilayers by printing processes.

References

[1] Thompson, B. C., & Fréchet, J. M. J. (2007) *Angew. Chem. Int. Ed.*, *47*, 58.
[2] Li, G., Zhu, R., & Yang, Y. (2012) *Nat. Photonics*, *6*, 153.
[3] Jørgensen, M., Norrman, K., Gevorgyan, S. A., Tromholt, T., Andreasen, B., & Krebs, F. C. (2012) *Adv. Mater.*, 24, 580.
[4] Yu, G., Gao, J., Hummelen, J. C., Wudl, F., & Heeger, A. J. (1997) *Science*, *270*, 1789.
[5] Li, G., Shrotriya, V., Huang, J., Yao, Y., Moriarty, T., Emery, K., & Yang, Y. (2005) *Nat. Mater.*, *4*, 864.
[6] Ma, W., Yang, C., Gong, X., Lee, K., & Heeger, A. J. (2005) *Adv. Funct. Mater.*, *15*, 1617.
[7] Miyanishi, S., Tajima, K., & Hashimoto, K. (2009) *Macromolecules*, *42*, 1610.
[8] Kim, B. J., Miyamoto, Y., Ma, B. & Fréchet, J. M. J. (2009) *Adv. Funct. Mater.*, *19*, 2273.
[9] Minsk, L. M., Smith, J. G., van Deusen, W. P. & Wright, J. F. (1959) *J. Appl. Polym. Sci.*, *2*, 302.
[10] Pangbor, A. B., Giardello, M. A., Grubbs, R. H., Rosen, R. K., & Timmers, F. J. (1996) *Organometallics*, *15*, 1518.
[11] Nam, C-Y., Qin, Y., Park, Y. S., Hlaing, H., Lu, X., Ocko, B. M., Black, C. T. & Grubbs, R. B. (2012) *Macromolecules*, *45*, 2338.
[12] Loewe, R. S., Khersonsky, S. M., & McCullough, R. D. (1999) *Adv. Mater.*, *11*, 250.
[13] Iovu, M. C., Sheina, E. E., Gil, R. R., & McCullough, R. D., (2005) *Macromolecules*, *38*, 8649.
[14] Lohwasser, R. H., Thelakkat, M. (2011) *Macromolecules*, *44*, 3388.