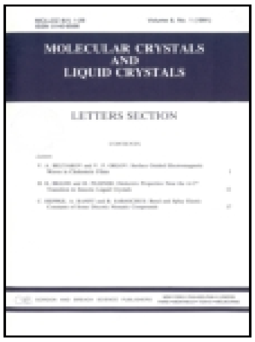

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Molecular Crystals and Liquid Crystals

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

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To cite this article: Chiho Katagiri & Ken-ichi Nakayama (2016) Comparison of the carrier mobilities of annealed P3HT films by using charge carrier extraction by linearly increasing voltage and space-charge limited current, Molecular Crystals and Liquid Crystals, 629:1, 193-199, DOI: 10.1080/15421406.2015.1094865

To link to this article: http://dx.doi.org/10.1080/15421406.2015.1094865

MOLECULAR CRYSTALS AND LIQUID CRYSTALS
2016, VOL. 629, 193–199
http://dx.doi.org/10.1080/15421406.2015.1094865

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Comparison of the carrier mobilities of annealed P3HT films by using charge carrier extraction by linearly increasing voltage and space-charge limited current

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ABSTRACT
Vertical mobilities of poly-3-hexythiophene (P3HT) thin films annealed with various temperatures were estimated by using charge carrier extraction by linearly increasing voltage (CELIV) method, and were compared with those estimated from a conventional space-charge limited current (SCLC) method. Both methods revealed that the mobilities were improved with increasing annealing temperature because of enhanced crystallinity of the P3HT film. In high annealing temperature more than 150°C, SCLC method could not be applicable due to deviation from theoretical analysis; in contrast, CELIV method was valid for all annealing conditions.

KEYWORDS
Charge carrier mobility; poly-3-hexythiophene; charge carrier extraction by linearly increasing voltage; space-charge limited current

Introduction

The bulk heterojunction organic photovoltaics (OPVs) based on blends of conjugated polymers and fullerene derivatives have achieved high power conversion efficiency [1,2]. Although these developments are produced by introducing new materials and device structure, investigation of mechanism of charge properties, such as charge carrier mobility and recombination dynamics, is also required for further improvement of OPVs performance. One of key issues is charge extraction efficiency that is governed mainly by charge carrier mobility of hole and electron. There have been various methods for carrier mobility measurement, for example, time-of-flight (TOF) and space-charge limited current (SCLC) method. The TOF method requires a thick film more than 1 μm, which is unsuitable for evaluating mobility of practical OPV cells. The SCLC method is applicable to practical thin films; however, it tends to be affected by film preparation and/or combination of electrode and organic materials, because this method requires ohmic contact at the electrode interface [3–5]. Recently, the charge carrier extraction by linearly increasing voltage (CELIV) method [6–8] has been proposed, where the mobility is estimated from the transient current waves derived from extraction of equilibrium free carriers. The advantages of CELIV are that this method can be applied to actual

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This paper was originally submitted to *Molecular Crystals and Liquid Crystals,* Volumes 620–622, Proceedings of the KJF International Conference on Organic Materials for Electronics and Photonics 2014.

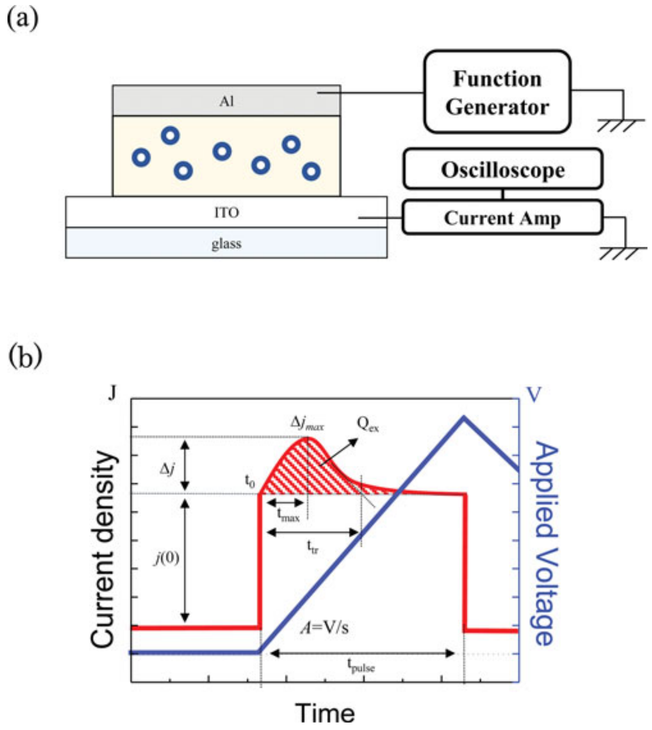

Figure 1. (a) Device structure and CELIV measurement system. (b) Typical transient waves in CELIV measurement; applied voltage wave (blue line) and CELIV current wave (red line). Analytical parameters are also indicated.

devices which have organic thin films (several hundreds nanometer) and estimate mobility and equilibrium carrier concentration concurrently.

In this paper, we investigated vertical carrier mobility of a poly-3-hexythiophene (P3HT) thin film annealed with various temperatures using the CELIV method, and compared it with that estimated from the conventional SCLC method. Lateral mobility of a P3HT film has been extensively studied by using OFET devices, and it is well known that the mobility is improved by thermal annealing and crystallization of the film [9,10]. However, there have been few reports on the vertical mobility [11], although P3HT has been widely used for OPVs. We demonstrate high usability of the CELIV method to estimate the vertical mobility in comparison with the SCLC method.

Experimental

A single-layered device for CELIV and SCLC measurements was fabricated by spin-coating a P3HT thin film on an indium thin oxide (ITO) glass substrate (Fig. 1(a)). An ITO glass substrate was first cleaned by ultra-sonication sequentially in acetone and 2-propanol each of 10 min, and UV-ozone treatment for 24 minutes. A chloroform solution of P3HT (20 mg/ml) was then spin-cast at 1000 rpm, yielding a 280 nm-thick thin film. The device was annealed at 100, 150 and 180°C for 10 and 30 min in air. An Al electrode (100 nm) was deposited on top of the P3HT film. The active area was 0.04 cm^2. The thin-film structure was characterized by X-ray diffractometry (XRD, Rigaku, SmartLab) with out-of-plane configuration.

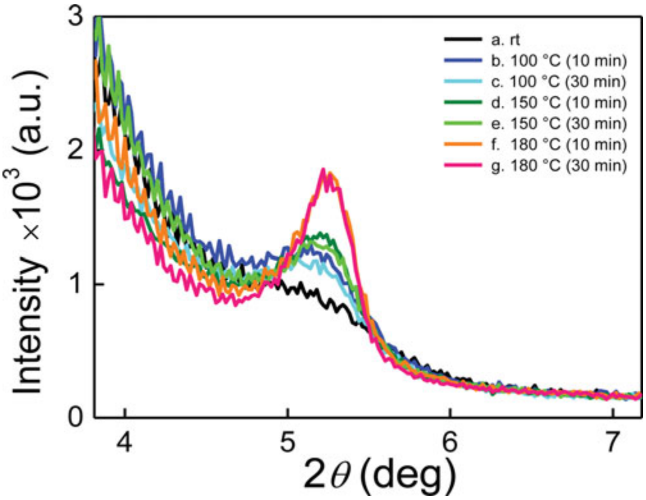

Figure 2. X-ray diffraction patterns of the P3HT thin films with various annealing temperatures and time.

The applied voltage and CELIV transient current is shown in Fig. 1(b). A triangular-shaped voltage pulse with a voltage rise speed A was applied to the ITO electrode. Beforehand, a forward bias at 0.5 V was applied to cancel internal built-in potential arising from the difference of work function between the two electrodes. The CELIV signal $j(t)$ is composed of a rectangular-shaped transient current corresponding to the capacitive displacement current $j(0) = A \times \varepsilon\varepsilon_0/d$ and the transient current due to extracted carriers. The transient current Δj was calculated by subtracting $j(0)$ and injection current from the counter electrode from $j(t)$, where ε and ε_0 are the relative and vacuum permittivities, and d is thickness of the organic film. The Δj is derived from drift current of equilibrium charge carriers, and indicates a peak at Δj_{max}. The voltage rise speed A was set to be 50 kV/s. The carrier transit time (t_{tr}) was estimated from an intersection point between extrapolated line in transient current decay and capacitive displacement current as shown in Fig. 1(b).

The measurement was performed in a vacuum prober (Oyama, ALT80K). A triangular-shaped voltage was applied by using a waveform generator (Agilent 33511B), and electrical current through the device was monitored by an oscilloscope (Agilent, DSO-X 2004A) with a high-speed current amplifier (Keithley, 428). The current-voltage characteristics for SCLC measurement were measured by a semiconductor parameter analyzer (Agilent Technologies, 4155C).

Results and discussion

Thin-film structures of the P3HT film annealed at various temperatures were investigated by out-of-plane XRD measurements (Fig. 2). All the films showed one peak or shoulder at $2\theta = 5.25 \pm 0.05°$ corresponding to lattice spacing $d = 1.68 \pm 0.02$ nm, which is assigned to lamellar structure with edge-on orientation of P3HT molecules [12]. This peak was enhanced by increasing annealing temperature, and the half maximum full-width (FWHM) was decreased from 0.68 at 100°C to 0.42 at 180°C. These results show that crystallinity of P3HT film was enhanced with increasing temperature. However, longer annealing time of 30 min at 180°C gave a rather larger FWHM value of 0.53, indicating decrease of crystallinity.

Figure 3 shows transient current signals of CELIV measurements with various annealing temperature and time. The transient current for all the samples showed clear peak and decay,

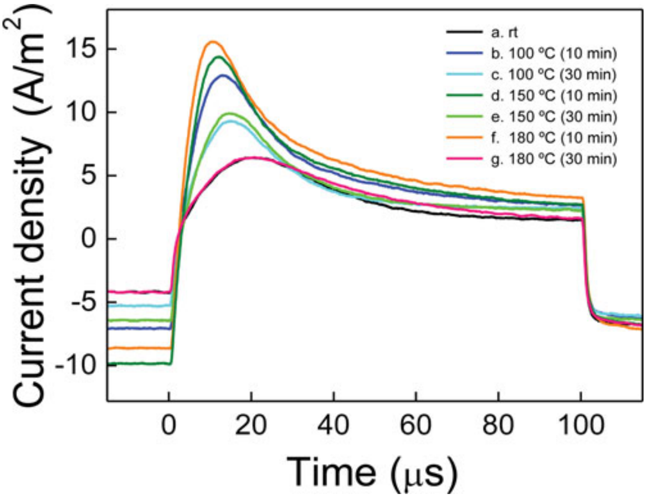

Figure 3. CELIV transient currents for ITO/P3HT(280 nm)/Al devices with various annealing temperatures and time.

converging on displacement current component $j(0)$. The current peak became sharper with increased annealing temperature when the annealing time was 10 min. However, the peak became rather broader with increasing annealing time. Charge carrier mobility by CELIV (μ_{CELIV}) was estimated according to the following equation [8].

$$t_{tr} = d\sqrt{2/\mu A} \tag{Eq. 1}$$

Also, this method gives information on equilibrium carrier concentration. The carrier concentration n was calculated by integrating the transient current Δj using following equation [13].

$$n_{ex} = \frac{\int_0^{t_{pulse}} \Delta jdt}{ed} \tag{Eq. 2}$$

Table 1 summarizes estimated charge carrier mobilities, carrier concentrations and related parameters. The vertical carrier mobilities of annealed P3HT films were successfully measured by the CELIV method. The CELIV mobility of the P3HT film without annealing was estimated at 1.25×10^{-5} cm^2/Vs. The mobility was increased by annealing and a value of 3.58×10^{-5} cm^2/Vs was observed at 180°C for 10 min, which was attributed to increasing

Table 1. The estimated parameters from the CELIV measurements for the P3HT devices with various annealing temperatures and time.

	annealing condition		μ_{CELIV}	Q_{ex}	n_{ex}
	[°C]	[min]	[cm^2/Vs]	[C]	[cm^{-3}]
a	rt		1.25×10^{-5}	6.67×10^{-10}	3.72×10^{15}
b	100	10	2.81×10^{-5}	1.04×10^{-9}	5.80×10^{15}
c	100	30	2.55×10^{-5}	6.44×10^{-10}	3.59×10^{15}
d	150	10	3.39×10^{-5}	1.20×10^{-9}	6.69×10^{15}
e	150	30	2.75×10^{-5}	7.66×10^{-10}	4.27×10^{15}
f	180	10	3.58×10^{-5}	1.28×10^{-9}	7.11×10^{15}
g	180	30	8.74×10^{-6}	7.39×10^{-10}	4.12×10^{15}

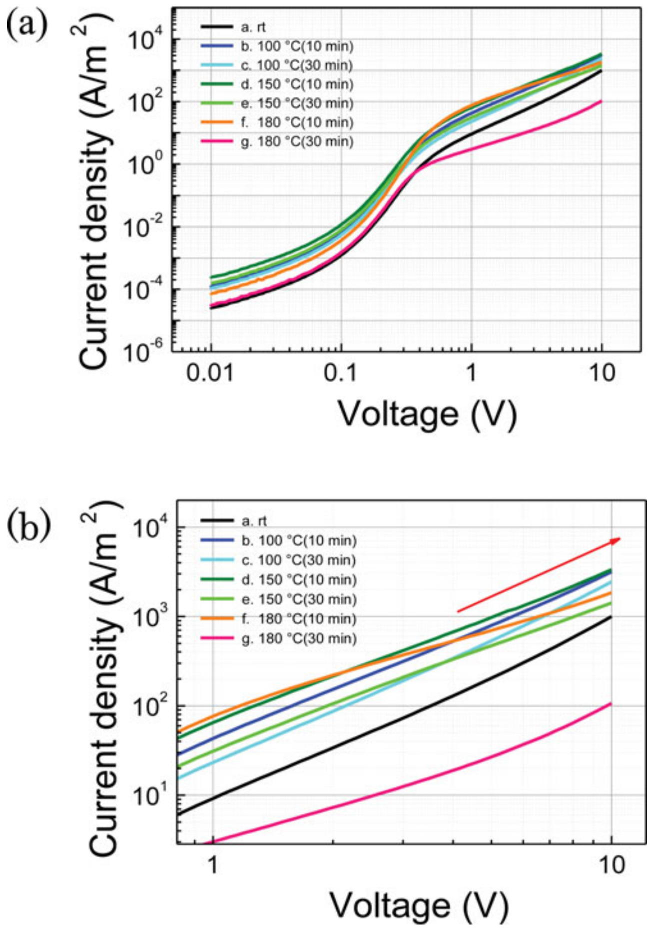

Figure 4. (a) *J-V* curves and (b) *J-*V^2 plots for ITO/P3HT(280 nm)/Al devices with various annealing temperatures and time.

crystallinity upon thermal annealing. The mobility for 30 min annealing was lower than that for 10 min annealing, while the crystallinity of P3HT film was improved as shown in Table 1. In addition, the mobility at 180°C for 30 min indicated especially low value. These results suggest that the number of carrier traps in the P3HT films was increased by annealing for long time in air.

The mobility of the P3HT films was also estimated by conventional SCLC. Note that SCLC measurements can be performed by using the same devices (ITO/P3HT/Al) with that for CELIV measurement. Fig. 4(a) shows the double logarithmic plot of current density versus voltage (log J – log V plots) for SCLC with various annealing temperature and time. The mobility is estimated using equation of trap-free SCLC (TF-SCLC) model [14].

$$J = \frac{9}{8}\varepsilon\varepsilon_0\mu\frac{V^2}{d^3} \qquad \text{(Eq. 3)}$$

According to this model, a log J – log V plot gives a slope n = 2, indicating a relationship of $J \propto V^2$. If there are carrier traps in the film, rapid increase of current density shown in Fig. 4(a) is observed with $n > 2$ [15]. However, in high voltage region, injected carriers fill the traps, and consequently, TF-SCLC model becomes valid. We carefully chose n = 2 region in the log

Table 2. The estimated parameters from the SCLC measurements for the P3HT devices with various annealing temperatures and time.

	annealing condition			μ_{SCLC}
	[°C]	[min]	n	[cm^2/Vs]
a	rt		2	6.23×10^{-5}
b	100	10	2	2.26×10^{-4}
c	100	30	2	1.62×10^{-4}
d	150	10	1.9	2.34×10^{-4}
e	150	30	1.6	–
f	180	10	1.3	–
g	180	30	1.3∼2.4	–

J – log V plot and estimated SCLC mobilities (μ_{SCLC}) as shown in Fig. 4(b). The estimated mobilities are summarized in Table 2. For 10 min annealed devices, the observed current and estimated mobility were improved with an increase in annealing temperature. However, the P3HT films annealed at 150 and 180°C for 30 min indicated $n < 2$ slope as shown in Fig. 4(b). Since SCLC models taking account of shallow traps gives $n > 2$, the observed log J – log V plot is difficult to be explained by any SCLC models. This might be because high-temperature annealing affects contact interface at the ITO electrode, and obstruct ohmic contact. Generally, SCLC is easily influenced by preparation condition of devices, in particular, electrode interface. In contrast, the CELIV mobility could be estimated in all annealing conditions, indicating high usefulness of CELIV method in comparison with SCLC method.

Figure 5 indicates comparison between mobilities estimated from CELIV and SCLC methods for various annealing temperature. Both measurement methods showed similar tendency; increasing mobility for increasing annealing temperature due to crystallization of the P3HT film. The difference between CELIV and SCLC mobility is explained by two aspects; electric field dependence of mobility, and carrier trapping in the films. It is commonly known as Poole-Frenkel effect that mobility of organic semiconductor increases with increasing electric field. The electric field for the SCLC measurement is estimated to be 3.4×10^5 V/cm from the applied voltage and film thickness. The electric-field for the CELIV measurement is calculated from an equation of $E = A \times t_{max} / d$ [16] to be 1.7×10^4 V/cm, which is much lower

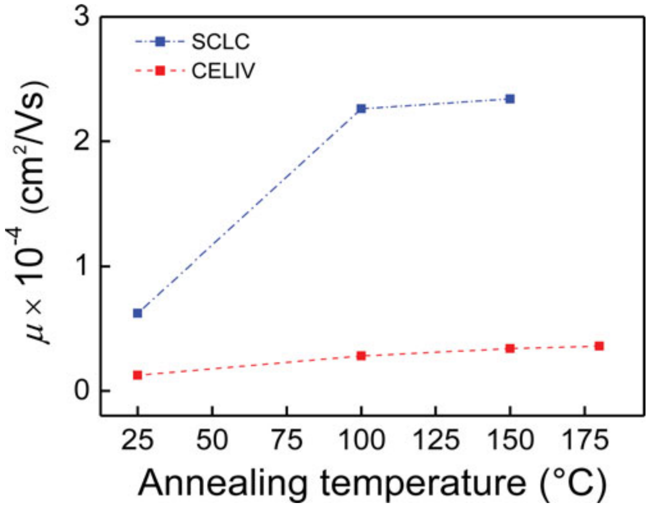

Figure 5. Comparison of charge carrier mobility between SCLC and CELIV measurements.

than that for the SCLC measurement. This is one reason why the SCLC mobilities are higher than the CELIV mobilities. The other aspect is carrier trapping and filling effect. The higher electric field in the SCLC measurement gives higher current density. Higher carrier density causes trap filling in the film, reducing the shallow trap effect. This enhances the difference between CELIV and SCLC mobilities.

Conclusion

The influence of thermal annealing on vertical carrier mobility of the P3HT films was examined by using CELIV and SCLC methods. Both mobilities increased with an increase in annealing temperature. However, SCLC method was not applicable for high temperature region due to deviation from theoretical relationship, because ohmic contact required for SCLC measurement is easily affected by preparation condition. In contrast, the CELIV mobility could be estimated in all annealing conditions. Therefore, the CELIV method can be more widely applied in comparison with SCLC method.

Acknowledgment

This research was supported by CREST program by Japan Science and Technology Agency (JST) and Grant-in-Aid for Scientific Research from the Japan Society for the Promotion of Science (JSPS).

References

[1] Li, G., Shrotriya, V., Huang, J. S., Yao, Y., Moriarty, T., Emery, K., & Yang, Y. (2005). *Nat. Mater.*, *4*, 864.

[2] Brabec, C. J., Gowrisanker, S., Halls, J. J. M., Laird, D., Jia, S. J., & Williams, S. P. (2010). *Adv. Mater.*, *22*, 3839.

[3] Wang, Z. B., Helander, M. G., Greiner, M. T., Qiu, J., & Lu, Z. H. (2009). *Phys. Rev. B*, *80*.

[4] Koo, Y. M., Choi, S. J., Chu, T. Y., Song, O. K., Shin, W. J., Lee, J. Y., Kim, J. C., & Yoon, T. H. (2008). *J. Appl. Phys.*, *104*.

[5] Matsushima, T., Kinoshita, Y., & Murata, H. (2007). *Applied Physics Letters*, *91*, 253504.

[6] Juska, G., Arlauskas, K., Viliunas, M., & Kocka, J. (2000). *Phys. Rev. Lett.*, *84*, 4946.

[7] Juska, G., Nekrasas, N., Valentinavicius, V., Meredith, P., & Pivrikas, A. (2011). *Phys. Rev. B*, *84*.

[8] Juska, G., Arlauskas, K., Viliunas, M., Genevicius, K., Osterbacka, R., & Stubb, H. (2000). *Phys. Rev. B*, *62*, R16235.

[9] Zen, A., Pflaum, J., Hirschmann, S., Zhuang, W., Jaiser, F., Asawapirom, U., Rabe, J. P., Scherf, U., & Neher, D. (2004). *Adv. Funct. Mater.*, *14*, 757.

[10] Cho, S., Lee, K., Yuen, J., Wang, G. M., Moses, D., Heeger, A. J., Surin, M., & Lazzaroni, R. (2006). *J. Appl. Phys.*, *100*.

[11] Park, J. H., Kim, J. S., Lee, J. H., Lee, W. H., & Cho, K. (2009). *J. Phys. Chem. C*, *113*, 17579.

[12] Erb, T., Zhokhavets, U., Gobsch, G., Raleva, S., Stuhn, B., Schilinsky, P., Waldauf, C., & Brabec, C. J. (2005). *Adv. Funct. Mater.*, *15*, 1193.

[13] Pivrikas, A., Sariciftci, N. S., Juska, G., & Osterbacka, R. (2007). *Prog. Photovoltaics*, *15*, 677.

[14] Brutting, W., Berleb, S., & Muckl, A. G. (2001). *Org. Electron.*, *2*, 1.

[15] Nicolai, H. T., Kuik, M., Wetzelaer, G. A. H., de Boer, B., Campbell, C., Risko, C., Bredas, J. L., & Blom, P. W. M. (2012). *Nat. Mater.*, *11*, 882.

[16] Mozer, A. J., Sariciftci, N. S., Pivrikas, A., Osterbacka, R., Juska, G., Brassat, L., & Bassler, H. (2005). *Phys. Rev. B*, *71*.