This article was downloaded by: [University of California, San Diego]
On: 09 August 2012, At: 14:20
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954
Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK

Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Ambipolar Carrier Transport in Terphenyl Derivative

Yukiko Takayashiki [a], Hiroaki Iino [a], Teppei Shimakawa [a] & Jun-ichi Hanna [a]

[a] Imaging Science and Engineering Laboratory, Tokyo Institute of Technology, Midori-ku, Yokohama, Japan

Version of record first published: 22 Sep 2010

To cite this article: Yukiko Takayashiki, Hiroaki Iino, Teppei Shimakawa & Jun-ichi Hanna (2008): Ambipolar Carrier Transport in Terphenyl Derivative, Molecular Crystals and Liquid Crystals, 480:1, 295-301

To link to this article: http://dx.doi.org/10.1080/15421400701826837

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.tandfonline.com/page/terms-and-conditions

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae, and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand, or costs or damages

whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Downloaded by [University of California, San Diego] at 14:20 09 August 2012

Mol. Cryst. Liq. Cryst., Vol. 480, pp. 295–301, 2008
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400701826837

Taylor & Francis
Taylor & Francis Group

Ambipolar Carrier Transport in Terphenyl Derivative

Yukiko Takayashiki, Hiroaki Iino, Teppei Shimakawa, Jun-ichi Hanna
Imaging Science and Engineering Laboratory, Tokyo Institute of Technology, Midori-ku, Yokohama, Japan

*We have investigated the liquid crystalline behavior and charge carrier transport properties in the semectic phases of a terphenyl derivative, 4-4″-bis(dodecyloxy)-3-methyl-*p*-terphenyl (12O-TPMe-O12) having methyl side chain in the terphenyl core part. In its samples highly purified by recrystallization several times, we observed the transient photocurrents indicating electronic conduction not only for holes but also electrons and determined their mobilities to be 5×10^{-4} and 0.9×10^{-2} cm^2/Vs in SmC and SmG phases, respectively. Thus, we concluded that the intrinsic nature of charge carrier transport in the terphenyl derivatives is electronic and ambipolar, where electrons and holes can be transported.*

Keywords: ambipolar; calamitic liquid crystal; electronic transport; ionic transport; mobility; terphenyl derivative

Downloaded by [University of California, San Diego] at 14:20 09 August 2012

INTRODUCTION

Since the electronic conduction was discovered in discotic and calamitic liquid crystals [1,2], the liquid crystals have called another attention as a new type of organic semiconductors that shows self-organized closely-packed molecular alignment next to the molecular crystals. The charge carrier transport in the liquid crystals exhibits very high bulk mobility far beyond those of amorphous semiconductors practically, up to 0.1–1 cm^2/Vs [3–6]. In addition, the liquid crystals, i.e., "liquid crystalline semiconductors" exhibit several unique features as

We thank Honshu Chemical Industry Co., LTD. for providing a source material for 12O-TPMe-O12. This study was partly supported by Grants-in-Aid for Scientific Research sponsored by the Ministry of Education, Culture, Sports, Science and Technology, and by NEDO international joint research grant.

Address correspondence to Jun-ichi Hanna, Imaging Science and Engineering Laboratory, Tokyo Institute of Technology, J1-2, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan. E-mail: hanna@isl.titech.ac.jp

an organic semiconductor: the carrier mobility depends on neither temperature nor electric filed; moreover, ambipolar carrier transport is often observed in some calamitic and discotic liquid crystals [7–10], while it occurs in few organic amorphous semiconductors. However, the ambipolar electronic conduction has not been concluded whether it is an inherent nature of charge carrier transport in the "liquid crystalline semiconductors" yet, because of its relatively recent discovery.

In this report, we studied the charge carrier transport in a terphenyl liquid crystal, which was hardly investigated in the point of view described above.

EXPERIMENTAL

In typical terphenyl derivatives, e.g., ω,ω'-dialkoxyterphenyls the phase transition temperature is higher than 200°C, where the liquid crystal cells fixed with a epoxy resin are not available. Because of this reason, we synthesized a terphenyl liquid crystal having the lower phase transition temperature by adding methyl group at the terphenyl core part.

Thus, 4-4″-bis(dodecyloxy)-3-methyl-*p*-terphenyl (12O-TPMe-O12), was synthesized by the Williamson synthesis shown in Figure 1(a). The resulting product was purified thoroughly by flush column chromatography and recrystallization from ethanol and successively from *n*-hexane. The phase transition temperatures were determined by differential scanning calorimetry (DSC: Shimazu 60). Its liquid crystal phases were identified by the texture observation with a polarized

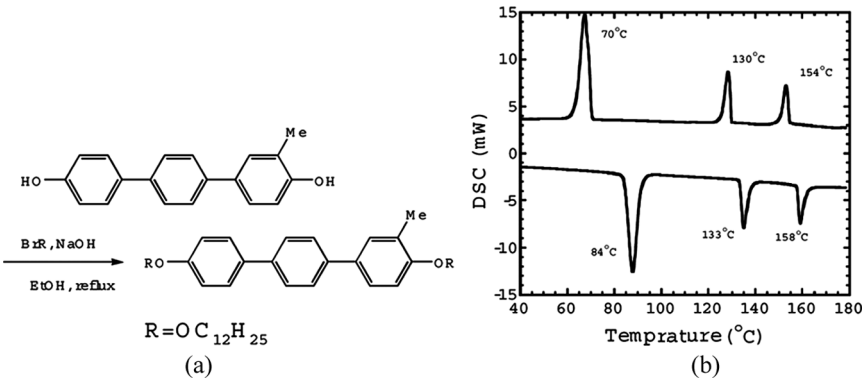

FIGURE 1 The synthetic route (a) and DSC chart (b) of 12O-TPMe-O12.

Downloaded by [University of California, San Diego] at 14:20 09 August 2012

optical microscope and x-ray diffraction analysis (Rigaku RAD-2B diffractometer with CuKα radiation).

The purified material was filled into liquid crystal cells, which were fabricated with two ITO-coated glass plates separated by silica particle spacers, using capillary action at an elevated temperature for isotropic phase. The charge carrier transport properties were characterized by using a conventional time-of-flight setup equipped with a nitrogen laser ($\lambda = 337$ nm, pulse duration $= 600$ ps) as the excitation source. The resulting transient photocurrents were recorded on a digital oscilloscope (Nicolet Pro 92). In this measurement, the one-carrier condition was well established in thicker cells about 10 μm due to a short penetration depth of 1.0 μm for 337-nm excitation light. The transit time for photo-carriers was determined from a shoulder in the transient photocurrent.

RESULT AND DISCUSSION

The terphenyl derivative, 12O-TPMe-O12, exhibited two mesophases from 84 to 158°C as shown in the DSC chart of Figure 1(b). This temperature range was about 50°C lower than those of terphenyl derivatives without a methyl side-chain compared with the range from about 130°C to 210°C [11,12]. It probes that introduction of a methyl side-chain in the terphenyl core is very effective to reduce the phase transition temperature.

Figure 2 shows the polarized optical microscopic texture and x-ray diffraction (XRD) patterns of the phase appearing a temperature range from 133°C to 158°C. The texture shows fan like patterns as

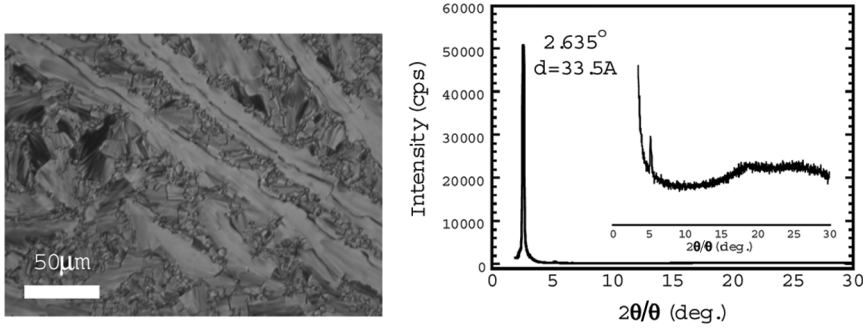

FIGURE 2 The polarized optical microscopic texture (a) and x-ray diffraction patterns (b) of 12O-TPMe-O12 at 145°C.

Downloaded by [University of California, San Diego] at 14:20 09 August 2012

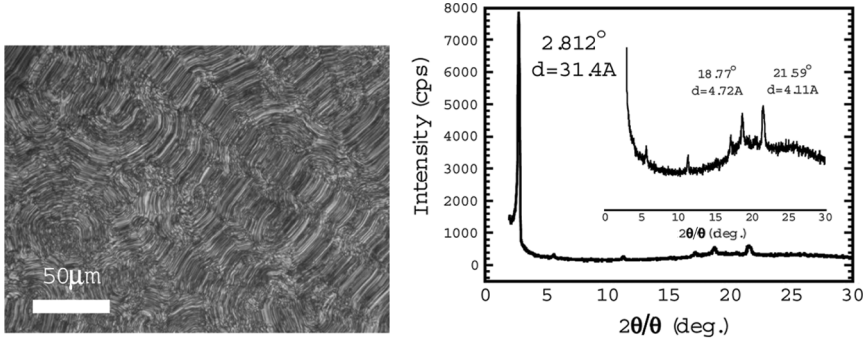

FIGURE 3 The polarized optical microscopic texture (a) and x-ray diffraction patterns (b) of 12O-TPMe-O12 at 100°C.

shown in Figure 2(a). The XRD pattern in a small angle region has clear peaks for the spacing of 33.5 Å, which corresponded to a layer spacing. However, the molecular length calculated by geometrical optimization with MM2 was about 46 Å. Thus, we conclude that the molecules of 12O-TPMe-O12 sit tilted against the smectic layer. The XRD pattern in a wide-angle region does not have any peaks, indicating that the present phase from 133°C to 158°C was SmC phase.

Figure 3 shows the texture and XRD pattern of the second phase appearing in the temperature range from 84°C to 133°C. The XRD pattern in small angle region also has peaks corresponding to the layer spacing of 31.4 Å, indicating that the molecules are tilted against the smectic layer in this phase as well. The wide angle XRD pattern has two major peaks, 18.77° and 21.59°, corresponding to the spacing of 4.72 Å and 4.11 Å, respectively. These two peaks indicate the molecular ordering in the smectic layer, i.e., the hexagonal lattice judging form a lattice constant ratio of $\sqrt{3}/2$. Therefore, the second phase is identified to be SmG phase.

In time-of-flight experiments for relatively low purity samples, we obtained well-defined non-dispersive transient photo-currents for holes, but very dispersive ones for electrons, indicating that electron transport was deteriorated by trap states attributed to chemical impurities. On the other hand, in highly purified samples after repeated recrystallization from ethanol and *n*-hexane several times, the transient photocurrents for both hole and electron exhibited well-defined shoulders as shown in Figures 4 and 5, respectively. The carrier mobilities for holes and electrons were almost same, and determined to be 5×10^{-4} and 0.9×10^{-2} cm^2/Vs in SmC and SmG

Downloaded by [University of California, San Diego] at 14:20 09 August 2012

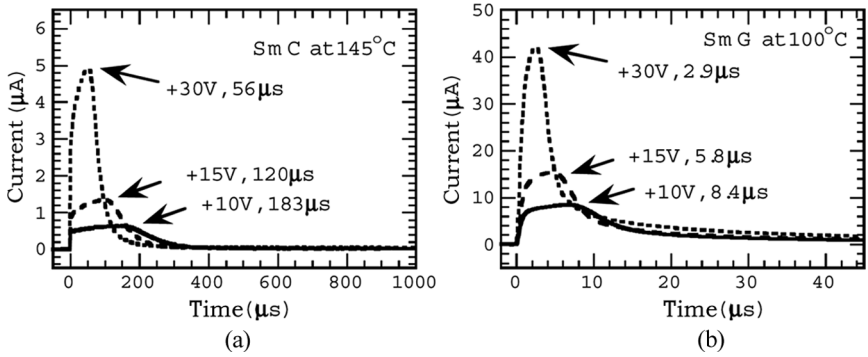

FIGURE 4 The transient photocurrent for positive carriers in the SmC phase (a) and SmG phase (b) of 12O-TPMe-O12 at 145°C and 100°C, respectively. The cell thickness was 9 μm.

phases, respectively. It is clearly shown with circles in Figures 6(a) and (b) that both mobilities depend on neither electric field nor temperature similar to the mobilities of 2-phenylnaphthalene and terthiophene derivatives reported previously. Thus, we conclude that the intrinsic carrier transport is ambipolar in the smectic mesophases of terphenyl derivatives.

In transient photocurrents for negative charge carriers, we found additional shoulders at the times of 217 μsec and 560 μsec in SmC and at the time of 5.0 ms in SmG phases as shown in Figures 5(a) and (b), respectively. They correspond to a mobility of 10^{-5} to 10^{-6} cm^2/Vs, and the mobilities exhibit Arrhenius-type of temperature dependence

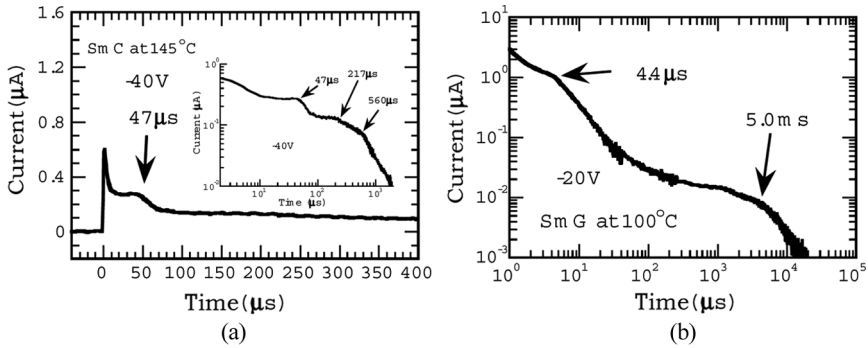

FIGURE 5 The transient photocurrent for negative carriers in the SmC phase (a) and SmG phase (b) of 12O-TPMe-O12 at 145°C and 100°C, respectively. The sample thickness was 9 μm.

Downloaded by [University of California, San Diego] at 14:20 09 August 2012

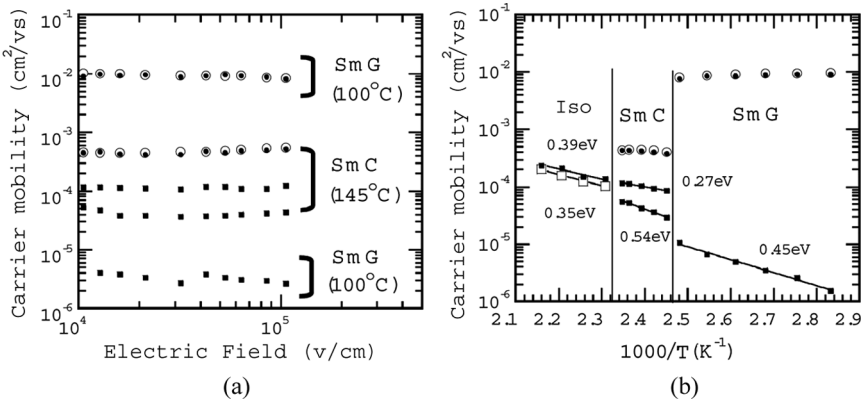

FIGURE 6 The carrier mobility in various phases of 12O-TPMe-O12 as a function of electric field (a) and temperature (b). Open and closed marks indicate positive and negative carriers, respectively. Circles and squares indicate electronic and ionic mobilities, respectively. The sample thickness was 9 μm.

with the activation energy of 0.3–0.5 eV as shown in the closed squares Figures 6(b). Judging from these behaviors, we attribute the charge carrier transport for these slow transits to the ionic conduction on the basis of our previous discussion on the second transit [9] and the multiple slow transits in the SmC phase to impurities having different ionic sizes. The mobilities for electrons and anions did not depended on the cell thickness up to 25 μm, while the relative contribution of anion photo-currents to the total photocurrents increased with an increase in the cell thickness. This fact strongly supports that the anionic conduction is caused by electron trapping in the chemical impurities in the bulk.

According to our previous result on the charge carrier transport in terthiophene derivatives, which also exhibit SmC and SmG phases, the carrier mobilities are $5 \times 10^{-4}\,cm^2/Vs$ and $1 \times 10^{-2}\,cm^2/Vs$, respectively. These values are almost same as the present mobility in each smectic phase of 12O-TPMe-O12. Taking account of the fact that the molecular distances, e.g., 4.7 Å in the SmG phase of 12O-TPMe-O12, are almost same as those of the corresponding smectic phases of terthiophene derivatives [8], the effect of heterocycles on the charge carrier mobility is not decisive.

CONCLUSION

We investigated the liquid crystalline behavior and carrier transport in a terphenyl derivative of 12O-TPMe-O12. This material exhibited

Downloaded by [University of California, San Diego] at 14:20 09 August 2012

the SmC and SmG phases at the temperature range from 133°C to 158°C and from 84°C to 133°C, respectively. In highly purified samples, the transient photo-currents exhibited well-defined non-dispersive charge transport irrespective of carrier signs, and the mobilities were determined to be 5×10^{-4} and $0.9 \times 10^{-2}\,cm^2/Vs$, respectively.

Thus, we conclude that the intrinsic nature of charge carrier transport in the terphenyls is ambipolar, even though we have to extend our study on the charge carrier transport to the other terphenyl derivatives before drawing the final conclusion on it.

REFERENCES

[1] Adam, D., Closs, F., Frey, T., Funhoff, D., Haarer, D., Ringsdorf, H., Schuhmacher, P., & Siemensmeyer, K. (1993). *Phys. Rev. Lett.*, *70*, 457.
[2] Funahashi, M. & Hanna, J. (1997). *Phys. Rev. Lett.*, *78*, 2184.
[3] Adam, D., Schuhmacher, P., Simmerer, J., Haussling, L., Siemensmeyer, K., Etzbach, K. H., Ringsdorf, H., & Haarer, D. (1994). *Nature (London)*, *371*, 141.
[4] Funahashi, M. & Hanna, J. (2005). *Adv. Mater.*, *17*, 594.
[5] Oikawa, K., Monobe, H., Takahashi, J., Tsuchiya, K., Heinrich, B., Guillon, D., & Shimizu, Y. (2005). *Chem. Comm.*, *2005*, 5337.
[6] Iino, H., Hanna, J., Bushby, R. J., Movaghar, B., Whitaker, B. J., & Cook, M. J. (2005). *Appl. Phys. Lett.*, *87*, 132102.
[7] Funahashi, M. & Hanna, J. (1997). *Appl. Phys. Lett.*, *71*, 602.
[8] Funahashi, M. & Hanna, J. (2000). *Appl. Phys. Lett.*, *76*, 2574.
[9] Iino, H., Hanna, J., & Haarer, D. (2005). *Phys. Rev. B*, *72*, 193203.
[10] Iino, H., Takayashiki, Y., Hanna, J., & Bushby, R. J. (2005). *Jpn. J. Appl. Phys.*, *44*, L1310.
[11] Andersch, J. & Tshierske, C. (1996). *Liq. Cryst.*, *21*, 51.
[12] Larios-López, L., Navarro-Rodríguez, D., Arias-Marín, E. M., Moggio, I., ReYes-Castañeda, C. V., Donnio, B., LeMoigne, J., & Guillon, D. (2003). *Liq. Cryst.*, *30*, 423.

Downloaded by [University of California, San Diego] at 14:20 09 August 2012