Novel liquid-crystalline and amorphous materials containing oxadiazole and amine moieties for electroluminescent devices

Hiroyuki Mochizuki,[a] Takahiro Hasui,[a] Masuki Kawamoto,[a] Takeshi Shiono,[a] Tomiki Ikeda,*[a] Chihaya Adachi,[b] Yoshio Taniguchi[b] and Yasuhiko Shirota[c]

[a] *Chemical Resources Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan. E-mail: tikeda@res.titech.ac.jp*

[b] *Department of Functional Polymer Science, Faculty of Textile Science and Technology, Shinshu University, Ueda, Nagano 386-8567, Japan*

[c] *Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamadaoka, Suita, Osaka 565-0871, Japan*

Received (in Cambridge, UK) 12th July 2000, Accepted 10th August 2000
First published as an Advance Article on the web 13th September 2000

Three 1,3,4-oxadiazole derivatives with an amine and an alkyl tail were designed and synthesized as novel electroluminescent materials; it was found that the length of alkyl tail and the structure of the amine strongly affect the phase structure of the oxadiazole derivatives.

Functional organic materials have been the subject of recent research work in relation to their optical and electronic properties as well as their industrial applications in many fields such as electroluminescent (EL) devices, transistors, batteries, sensors, photoreceptors and displays.[1] However, practical products made of organic compounds are solely photoreceptors and displays. Thus, the advantages of organic compounds are not sufficiently utilized in practical materials and devices.

Liquid-crystalline (LC) phases and amorphous states of organic materials have been known to show unique morphology. LC materials are quite attractive in terms of possessing both self-organizing capability and fluidity. On the other hand, amorphous materials are promising in terms of their excellent processability, flexibility, transparency, non-existence of grain boundaries and isotropic properties. Recently, much attention has been paid to low-molecular-weight materials which form stable amorphous glasses above rt.[2] It is of interest and of significance to develop photo- and electroactive amorphous molecular materials, which consist of π-electron systems and have glass transition temperature (T_g) higher than rt, for use in electronic devices.

In 1990, it was found that 2-(biphenyl-4-yl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (PBD) functioned very well as an excellent electron transport material (ETM) in an organic multilayer EL diode.[3] After this report, many researchers began to use various kinds of oxadiazole molecules to obtain high EL performances. Furthermore, in recent studies of polymer light-emitting diodes, the oxadiazole moieties were demonstrated to possess high potential for electron transport.[4]

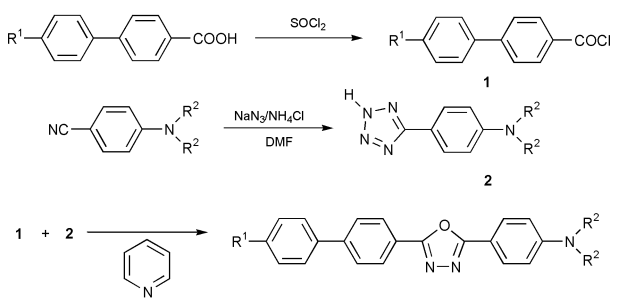
Introduction of the oxadiazole moieties to polymer main chains and to mesogens of LC compounds is expected to tune EL efficiencies and electron transport properties. EL polymers with *p*–*n* diblock structures were reported, in which thiophene and 1,3,4-oxadiazole moieties connected alternately to form fully conjugated rigid-rod polymers: one has been successfully used to fabricate single layer EL devices showing blue emission.[5] Likewise, LC compounds containing oxadiazole moieties were reported to exhibit a high electron transport capability and blue EL emission.[6]

In this study, we report the synthesis and properties of a novel class of oxadiazole derivatives for photo- and electroactive materials, emphasizing that the length and structure of the introduced moieties strongly affect the phase structure of the oxadiazole derivatives.

The oxadiazole derivatives in this study were prepared starting from 4-(4-*n*-alkylphenyl)benzoic acid by the synthetic route shown in Scheme 1. 4-(4-*n*-Alkylphenyl)benzoic acid was reacted with an excess of thionyl chloride. The resulting 4-(4-*n*-alkylphenyl)benzoyl chloride was reacted with aminophenyltetrazole derivatives in dry pyridine at 135 °C, yielding the products: 2-(4′-propylbiphenyl-4-yl)-5-(4-*N*,*N*-dimethylaminophenyl)-1,3,4-oxadiazole (**3-OXD-Me**), 2-(4′-heptylbiphenyl-4-yl)-5-(4-*N*,*N*-dimethylaminophenyl)-1,3,4-oxadiazole (**7-OXD-Me**) and 2-(4′-heptylbiphenyl-4-yl)-5-(4-*N*,*N*-diphenylaminophenyl)-1,3,4-oxadiazole (**7-OXD-Ph**).[7] These products were purified by column chromatography on silica gel, followed by recrystallization from toluene–ethanol. The overall yields were about 55%. The oxadiazole derivatives were characterized as obtained by FT-IR, ^{1}H NMR and elemental analysis.

Thermotropic and LC behaviors were evaluated by means of DSC (heating and cooling rate: 2 °C min^{-1}) and polarizing microscopy. Fig. 1 shows DSC thermograms of **3-OXD-Me** and **7-OXD-Me** on the third cooling. It was found that **3-OXD-Me** showed only a sharp exothermic peak corresponding to a melting point (T_m) at 174 °C. By contrast, **7-OXD-Me** exhibited two exothermic peaks at 143 and 138 °C. It seems that the peak at 143 °C is due to isotropic (I)-nematic (N) phase transition and another peak at 138 °C is due to N-crystal phase transition. Fig. 2 shows the textures observed with a polarizing microscope at 140 and 100 °C, respectively. Referring to the Schlieren texture, the phase could be assigned to an N phase at 140 °C, and then a typical crystal texture was observed at 100 °C. As **7-OXD-Me** showed no LC phase on heating but an N phase on cooling, it seems to be a monotropic LC material.

DSC thermograms of **7-OXD-Ph** on the first and the second heating are shown in Fig. 3. When the crystalline sample of **7-OXD-Ph** obtained by recrystallization from ethanol–toluene was heated, **7-OXD-Ph** exhibited T_m at 166 °C to give an I phase. **7-OXD-Ph** in the I phase was then cooled by standing in



3-OXD-Me: R^1, -(CH$_2$)$_2$CH$_3$; R^2, -CH$_3$
7-OXD-Me: R^1, -(CH$_2$)$_6$CH$_3$; R^2, -CH$_3$
7-OXD-Ph: R^1, -(CH$_2$)$_6$CH$_3$; R^2, -C$_6$H$_5$

Scheme 1 Synthetic route for compounds used in this study with abbreviations.

DOI: 10.1039/b005550f

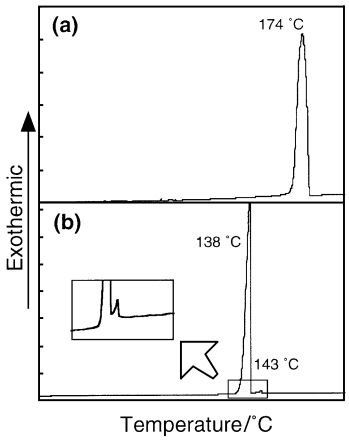


Fig. 1 DSC thermograms on the third cooling. (a), **3-OXD-Me**; (b), **7-OXD-Me**.

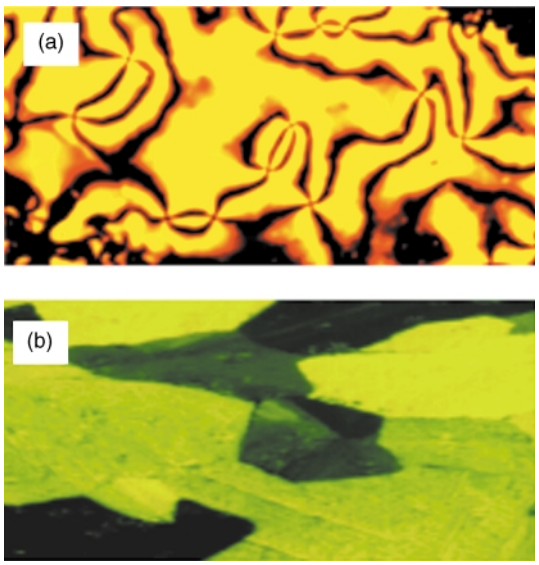


Fig. 2 Polarizing optical micrographs of the texture of **7-OXD-Me**. (a), at 140 °C (N phase); (b), 100 °C (crystalline phase).

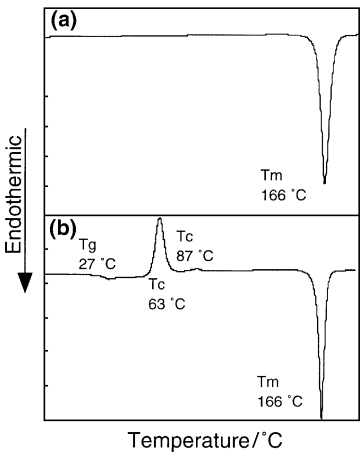


Fig. 3 DSC thermograms of **7-OXD-Ph**. (a), on the first heating; (b), on the second heating.

air, and it formed spontaneously the supercooled liquid state, which changed into the amorphous glassy state. On the second heating, T_g was observed at 27 °C, and then the first exothermic peak owing to crystallization appeared at around 60 °C. Subsequently, another crystallization occurred at 87 °C and the crystal melted at 166 °C. These phenomena of crystallization from the melt were confirmed with a polarizing microscope, however, the structure of each crystal was beyond identification.

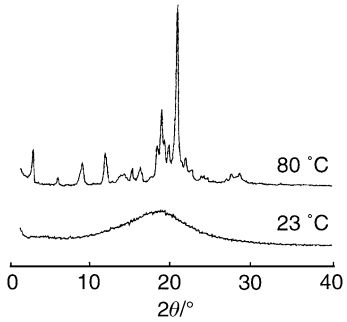


Fig. 4 X-Ray diffraction patterns of **7-OXD-Ph** at 23 and 80 °C.

The formation of an amorphous glass was evidenced in the X-ray diffraction patterns of **7-OXD-Ph** at rt (23 °C) and 80 °C, as exhibited in Fig. 4. **7-OXD-Ph** showed no sharp signals but only broad halos, when cooled from an I state to 23 °C, indicating that **7-OXD-Ph** is in an amorphous state. On the other hand, several sharp signals appeared at 80 °C, suggesting that **7-OXD-Ph** is in a crystalline state. **7-OXD-Ph** did not show an LC phase but an amorphous state; steric hindrance between two clusters of benzene rings of **7-OXD-Ph** may contribute to formation of the amorphous glass.

All materials investigated in this work emitted strong blue fluorescence with high quantum yields (0.81–0.91); emission peaks of **3-OXD-Me** and **7-OXD-Me** were 420 nm, and that of **7-OXD-Ph** was 436 nm. It is assumed that these compounds show an excellent EL performance. The present study will enable us to perform molecular design of various compounds based on oxadiazole for developing photo- and electroactive materials. These materials are expected to find potential application as functional materials, *e.g.* charge transport and luminescent materials for photoreceptors and electroluminescent devices.

In summary, 1,3,4-oxadiazole derivatives with amine and alkyl tails were designed and prepared as novel EL materials: the phase structures and optical properties of the oxadiazole derivatives were investigated in this study. We found that the length of the alkyl tail and the structure of the amine strongly affected the phase structure of the oxadiazole derivatives.

Notes and references

1 C. W. Tang and S. A. VanSlyke, *Appl. Phys. Lett.*, 1987, **51**, 913; J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackay, R. H. Friends, P. L. Burn and A. B. Holmes, *Nature*, 1990, **347**, 539; A. J. Epstei, *MRS Bulletin*, June 1997, 16; G. P. Wiederrecht, A. B. Yoon and M. R. Wasielewski, *Science*, 1995, **270**, 1794; T. Ikeda and O. Tsutsumi, *Science*, 1995, **268**, 1873.
2 Y. Shirota, T. Kabata and N. Noma, *Chem. Lett.*, 1989, 1145; A. Higuchi, H. Inada, T. Kabata and Y. Shirota, *Adv. Mater.*, 1991, **3**, 549; H. Inada and Y. Shirota, *J. Mater. Chem.*, 1993, **3**, 319; W. Ishikawa, K. Noguchi, K. Kuwabara and Y. Shirota, *Adv. Mater.*, 1993, **5**, 559; K. Katsuma and Y. Shirota, *Adv. Mater.*, 1998, **10**, 223.
3 C. Adachi, T. Tsutsui and S. Saito, *Appl. Phys. Lett.*, 1990, **56**, 799; C. Adachi, T. Tsutsui and S. Saito, *Appl. Phys. Lett.*, 1990, **57**, 513.
4 C. Hosokawa, N. Kawasaki, S. Sakamoto and T. Kuzumoto, *Appl. Phys. Lett.*, 1992, **62**, 2503; Q. Pei and Y. Yang, *Chem. Mater.*, 1995, **7**, 1568.
5 W. Huang, H. Meng, W. Yu, J. Gao and A. J. Heeger, *Adv. Mater.*, 1998, **10**, 593.
6 H. Tokuhisa, M. Era and T. Tsutsui, *Appl. Phys. Lett.*, 1998, **72**, 2639.
7 N. Tamoto, C. Adachi and K. Nagai, *Chem. Mater.*, 1997, **9**, 1077.