Liquid Crystalline Oxadiazole with Electron Transporting Capability

Hiroaki Tokuhisa, Masanao Era, and Tetsuo Tsutsui
Department of Materials Science and Technology, Graduate School of Engineering Sciences, Kyushu University, Kasuga, Fukuoka 816

(Received November 28, 1996)

In a thin film of an oxadiazole-based liquid crystal, 2,5-bis(4-octadecyloxybenzilidene-4-aminophenyl)-1,3,4-oxadiazole **1**, fairly high electron mobility enhanced by molecular orientation was observed; electron mobility in the glassy liquid crystalline film of oxadiazole **1** was 3.6 x 10^{-5} cm^{2}V^{-1}s^{-1} at an electric field of 2x10^5 Vcm^{-1} at room temperature, and the value was about ten times that in the isotropic glassy film of oxadiazole **1**.

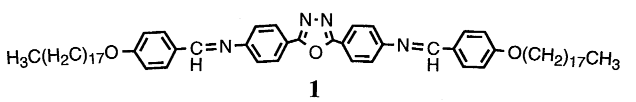
Since the demonstration of highly efficient organic LED's, research activity on organic-based electronic devices has been much increasing. In this research area, development of electron conductor with high carrier-transporting capability is one of key points to construct high performance organic-based electronic devices, because organic electron-conductors with high carrier mobility are few in comparison with organic hole-conductors.

Liquid crystalline materials with carrier-transporting chromophore are promising as high carrier mobility materials.[1-4] Some liquid crystalline materials give uniform films with high-degree of molecular orientation which promotes large overlap of wavefunctions of the carrier-transporting chromophore. Thus, high carrier mobility is expected to be attained in thin films of the liquid crystalline materials. In fact, a liquid crystalline film of a discotic liquid crystal, 2,3,6,7,10,11-hexahexylthio-triphenylene, has been reported to exhibit extremely high hole-mobility in a columnar phase.[1]

Recently, we demonstrated that oxadiazoles possess high potential of electron transport from the conventional time-of-flight (TOF) measurement in molecularly doped polymer.[5] In particular, 2,5-bis(4-naphthyl)-1,3,4-oxadiazole (BND) was found to be one of the best organic electron conductors; the electron drift mobility of 50 wt% BND doped in polycarbonate was 2.2x10^{-5} cm^{2}V^{-1}s^{-1} at an electric field of 7.5x10^5 Vcm^{-1} at room temperature. For the development of high performance electron-transporting materials, therefore, we have prepared liquid crystals with oxadiazole chromophore as a mesogenic unit. Here, we report briefly about phase transition behavior of the oxadiazole-based liquid crystal, and electron mobility and molecular orientation in the liquid crystalline film.

An oxadiazole-based liquid crystal, 2,5-bis(4-octadecyloxy-benzylidene-4-aminophenyl)-1,3,4-oxadiazole **1**, was synthesized by the condensation of 2,5-bis(4-aminophenyl)-1,3,4-oxadiazole and 4-octadecyloxybenzaldehyde. The chemical structure of oxadiazole **1** is shown in Figure 1. Phase transition of oxadiazole **1** was examined by the differential scanning calorimetry (DSC) measurement.

The DSC curves of oxadiazole **1** is shown in Figure 2. The curve (a), which is a first heating scan from crystal of oxadiazole **1**, exhibits three endothermic peaks, corresponding to the phase transitions from the crystalline phase to a mesophase (mesophase A) at 348 K, from the mesophase A to another mesophase (mesophase B) at 411 K, and from the mesophase B to an isotropic phase at 482 K. The mesophases A and B were assumed to be smectic and nematic liquid crystalline phases from optical polarized microscope observation, respectively. At this stage, however, we have no additional experimental evidence to assign the mesophases. Then, the mesophase at lower temperature is referred as the mesophase A and the mesophase at higher temperature as the mesophase B in this letter.



1

Figure 1. Molecular structures of liquid crystalline oxadiazole **1**.

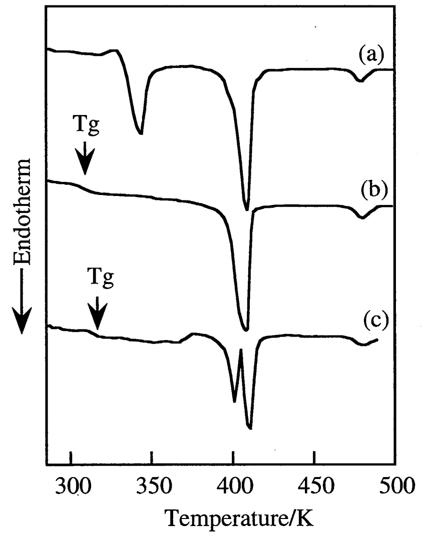


Figure 2. DSC curves of oxadiazole **1**; (a): a first trace of crystal of oxadiazole **1**, (b): a trace after quenching from mesophase B, (c): a trace after quenching from isotropic phase.

On the other hand, quenched oxadiazole **1** formed a glassy liquid crystal of the mesophase A. The curve (b) in Figure 2 shows the DSC heating trace of oxadiazole **1** quenched from the mesophase B. The DSC curve exhibits glass transition at around 307 K and two endothermic peaks at 411 K and at 482 K which are assigned to the transition temperatures from the mesophase A to the mesophase B and from the mesophase B to an isotropic transition of oxadiazole **1**, respectively. It shall be noted that the phase transition peak from crystalline phase to the mesophase A disappeared in the curve. The results clearly reveal that the quenched oxadiazole **1** formed a glassy liquid-crystal of the mesophase A below the glass transition temperature Tg of 307 K. Oxadiazole **1** formed an isotropic glass with the glass transition temperature Tg of 316 K, when it was quenched from an isotropic phase. The curve (c) shows the DSC curve of oxadiazole **1** quenched from an isotropic phase.

Electron mobility in oxadiazole **1** was evaluated with a conventional TOF measurement. The TOF measurements were carried out according to reference 5. In the TOF measurement, we employed a two-layer-type sample with a perylene derivative

(PV) as a carrier generation layer; indium-tin-oxide (ITO)/PV carrier generation layer/oxadiazole **1**/ITO. Thickness of oxadiazole **1** was 17μm. For generating carriers only within the PV layer, a dye laser tuned at 504 nm was used as an excitation light source. The dye laser was irradiated to the ITO electrodes which were charged negatively. The TOF measurements were performed on the three types of oxadiazole **1** films: polycrystalline film, glassy liquid crystalline film, and isotropic glassy film.

The polycrystalline film of oxadiazole **1** looked intransparent and light-scattered. In the film, very small photocurrent signal was observed. From this photocurrent signal, transit time t_T could not be determined. Small photocurrent signal in the polycrystalline film may be due to deep traps which were formed at boundary of the polycrystalline textures.

Owing to the formation of glassy films, on the other hand, the quenched films were uniform even at room temperature. Further, the photocurrent signals in the glassy liquid crystalline and isotropic glassy films were much large compared with that of the polycrystalline film. Figure 3 shows the transient photocurrent profiles due to electron transport of oxadiazole **1** at an electric field of 2.0 x 10^5 Vcm^{-1} at room temperature: a glassy liquid crystalline film (I) and an isotropic glassy film (II). The values of transit time t_T in the glassy films were determined by using double logarithmic plot according to the Scher-Montroll theory (insets in Figure 3).[6] Well-defined inflection points are observed in the plots. From the inflection points, the values of t_T in the films were determined. Mobility μ was calculated according to the equation $\mu = L/t_TF$, where L is film thickness and F applied field. The values of electron mobility in the glassy liquid crystalline film and the isotropic glassy film of oxadiazole **1** were 3.6 x 10^{-5} $cm^2V^{-1}s^{-1}$ and 2.1x$10^{-6}$$cm^2V^{-1}s^{-1}$ at an electric field of 2x10^5 Vcm^{-1} at room temperature, respectively. The value in the glassy liquid crystalline film is more than ten times that in the isotropic glassy film. Because oxadiazole molecules is assumed to form random orientation in the isotropic glassy film, large enhancement of electron mobility in the glassy liquid crystalline film is supposed to be caused by regular molecular orientation in the glassy liquid crystalline phase.

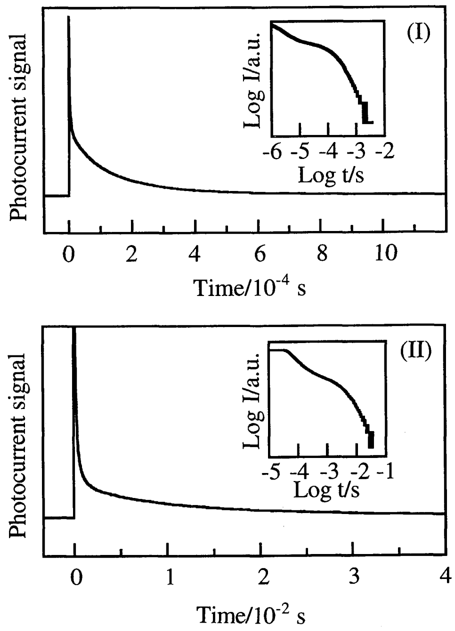


Figure 3. Transient photocurrent profiles due to electron transport of oxadiazole **1** at an electric field of 2.0x$10^5$$Vcm^{-1}$ at room temperatures: (I); glassy liquid crystalline film and (II); isotropic glassy film. Insets show double logarithmic plot of each profile.

Lastly, we evaluated molecular orientation in the glassy liquid crystalline film by the linear dichroism. When incident angle of polarized light to the film surface was increased from 0 degree to 45 degrees, dichroic ratio Ap/As of the glassy film of oxadiazole **1** decreased from 0.97 to 0.80, where Ap and As were absorbances at absorption peak wavelength due to the transition moment along long molecular axis of oxadiazole **1** for p- and s-polarized light beams, respectively. The result demonstrates that long axis of oxadiazole **1** molecule was laid almost parallel to the film plane. The parallel molecular orientation suggests that electron-transporting oxadiazole-chromophore is stacked normal to the film plane, in other words, an electron-transporting pathway is formed along the film normal. The molecular orientation is most likely to provide the fairly high electron mobility in the glassy liquid crystalline film of oxadiazole **1**.

In conclusion, we successfully demonstrated that the oxadiazole-based liquid crystal, **1** possesses electron transporting capability and that electron mobility of oxadiazole **1** in the glassy liquid crystalline film is much enhanced in comparison with that in the isotropic glassy film. The large enhancement of electron mobility is most likely to be due to the regulated molecular orientation in the glassy liquid crystalline film.

References

1 D.Adam, P.Schumacher, J.Simmerer, L.Haessling, K.Siemensmeyer, K.H.Etzbach, H.Ringsdorf, and D.Haarer, *Nature,* **371**, 141 (1994).
2 K.Okamoto, S.Nakajima, A.Itaya, and S.Kusabayashi, *Bull. Chem. Soc. Jpn.*, **56**, 3545 (1983).
3 Y.Shimizu, A.Ishikawa, and S.Kusabayashi, *Chem. Lett.,* **1986** 1041.
4 N.Boden, R.J.Bushby, J.Clements, M.V.Jesudason, P.F.Knowles, and G.Williams, *Chem. Phys. Lett.,* **152**, 94 (1988).
5 H.Tokuhisa, M.Era, T.Tsutsui, and S.Saito, *Appl. Phys. Lett.,* **66**, 3433 (1995).
6 H.D.Scher, and E.W.Montroll, *Phys.Rev.*, **B12**, 2445 (1975).