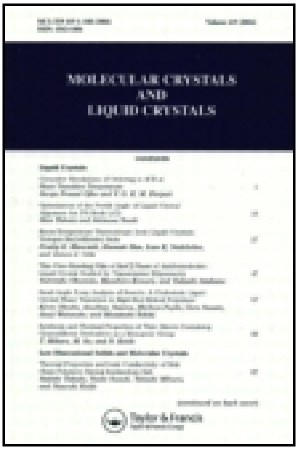

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Electro-Optical and Electrochemical Properties of Diglycidyl Ether of 4,4′-(9-Fluorenylidene)diphenol

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Diglycidyl ether of 4,4′-(9-fluorenylidene)diphenol (DGEFDP) was prepared by the reaction of 4,4′-(9-fluorenylidene)diphenol and epibromohydrin by using NaOH aqueous solution. DGEFDP film showed characteristic UV-visible absorption band at 313 nm and PL maximum values of 369 and 426 nm corresponding to the photon energy of 3.36 and 2.91 eV at 313 nm excitation. This compound exhibited deep-blue fluorescence on TLC plate. The cyclovoltamograms of DGEFDP exhibited the irreversible electrochemical behaviors between the doping and undoping peaks. The oxidation current density of DGEFDP versus the scan rate is approximately linear relationship in the range of 30 ~ 150 mV/sec. The exponent of scan rate, x value of DGEFDP, was 0.401, which means that the kinetics of the redox process is mainly controlled by the reactant diffusion process.

Keywords: cyclovoltamogram; diglycidyl ether; epibromohydrin; photoluminescence

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INTRODUCTION

Epoxy resins have excellent properties and are widely used in the areas of electric laminates, molding compounds, aerospace composites, and sport goods [1–8]. With the rapid development of the electronic/electrical industry, epoxy resins are required not only to strengthen their inherent advantages such as good chemical resistance, low shrinkage, high-grade electrical insulation, excellent adherence to many substrates including metals, but also to overcome their disadvantages such as brittleness and flammability.

Fluorene containing poly(phenylene vinylene) derivatives were good candidates as blue light-emitting organic materials for light-emitting devices for display and other purposes [9]. The diacetylene polymer via oxidative coupling of fluorene compound [10] and poly(fluorenyleneethynylene)s by alkyne metathesis of (9,9-dialkyl)fluoren-2,7-yleneethynylenes [11] were prepared and characterized. In 9,9′-spirofluorene in the polymer chains, the fluorene rings are orthogonally arranged and connected via a common tetracoordinated carbon [12]. This structural features would be expected to reduce the probability of interchain interactions and prevent the close packing of the polymer chains, resulting in good solubility of polymers [12]. We have prepared an conjugated cyclopolymer having fluorene moieties by using cyclopolymerization method [13–15] and also prepared the polyfluorenes having acetylenic functionalities in the polymer main chain via the palladium-catalyzed dehydrocoupling polymerization reaction of 2-substituted-9,9-dipropargylfluorenes [16,17]. In the interlayer system of the spirobifluorene-based conjugated polymer, the crosslinking moiety on the polymer backbone as a side branch was found to the device performance and the thermomechanical properties. The aromatic compounds with glycidyl functional groups may be thermally crosslinkable without the emitting of the low molecular gases to yield a thermally stable matrix [18].

Now we report the synthesis of difunctional fluorene epoxy resin (DGEFDP), which has the crosslinking glycidyl moieties with fluorene moieties and the characterization of its electro-optical and electrochemical properties.

EXPERIMENTAL

DGEFDP was prepared according to the following procedure. Two-necked 100 ml flask was charged with epibromohydrin (5.47 g, 40 mmol), 4,4′-(9-fluorenylidene)-diphenol (3.50 g, 10 mmol), benzyltriethylammonium chloride (0.11 g, 0.5 mmol) and 40 ml 50% NaOH aqueous solution. The reaction mixture was heated to 70°C with vigorous stirring. After 5 h, the solution was diluted with ethyl acetate and washed with water. After drying with magnesium sulfate and removal solvent, the crude mixture was purified by column chromatography on silica gel (ethyl acetate:hexane = 3:5). The resulting material was recrystallized from ethyl acetate/hexane to afford 2.47 g (57% yield) of white solid DGEFDP. ^{1}H-NMR ($CDCl_3$, 500 MHz, ppm): 7.737, 7.718 (d, 2H), 7.355–7.221 (m, 6H), 7.098, 7.081 (d, 4H), 6.755, 6.738 (d, 4H), 4.134–4.098 (dd, 2H), 3.907–3.866 (dd, 4H), 3.297–3.274 (m, 2H), 2.863–2.840 (dd, 2H), 2.701–2.683 (dd, 2H) ^{13}C-NMR ($CDCl_3$, 125 MHz, ppm): 157.18, 151.60, 139.89, 138.60, 129.15, 127.62, 127.30, 125.93, 120.07, 114.19, 68.67, 64.09, 50.04, 44.69.

FT-IR spectra were obtained with a Bruker EQUINOX 55 spectrometer using a KBr pellet. NMR spectra were recorded on a Varian 500 MHz FT-NMR spectrometer (Model: Unity INOVA) in DMSO-d_6. The optical absorption spectra were measured by a HP 8453 UV-Visible spectrophotometer. The photoluminescence spectra were obtained by Perkin Elmer luminescence spectrometer LS55 (Xenon flash tube) utilizing a lock-in amplifier system with a chopping frequency of 150 Hz. Electrochemical measurements were carried out with a Potentionstat/Galvanostat Model 273A (Princeton Applied Research). To examine electrochemical properties, polymer solution was prepared and the electrochemical measurements were performed under 0.1 M tetrabutylammonium tetrafluoroborate solution containing acetonitrile. ITO, Ag/$AgNO_3$ and platinum wire were used as a working, reference and counter electrode, respectively.

RESULTS AND DISCUSSION

We prepared a new epoxy compound with fluorene moieties, DGEFDP (Fig. 1), by the reaction of 4,4′-(9-fluorenylidene)diphenol and epibromohydrin by using NaOH aqueous solution in 57% yield.

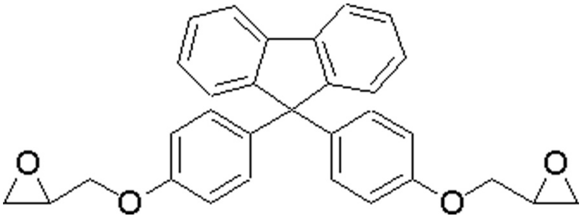

FIGURE 1 The chemical structure of DGEFDP.

The chemical structure of DGEFDP was characterized by various instrumental methods such as NMR, IR, UV-visible spectroscopies and elemental analysis. This compound was found to be thermally up to 300°C and it start to melt at 141°C and exothermic reaction started after 350°C, which means that DGEFDP has very wide processing window. The electro-optical properties of DGEFDP were measured and discussed. The UV-visible spectra and photoluminescence (PL) spectra of DGEFDP film were measured (Fig. 2). We had reported the PL spectrum of 9,9-dipropargylfluorene, it showed 432 nm PL maximum value at each excitation wavelength of UV maximum value. DGEFDP showed characteristic UV-visible absorption band at around 313 nm and PL maximum values of 369 and 426 nm corresponding to the photon energy of 3.36 and 2.91 eV at 313 nm excitation. This compound exhibited deep-blue fluorescence on TLC plate.

We also studied the electrochemical kinetic behavior of DGEFDP (Fig. 3). The cyclic voltammograms of DGEFDP were measured with the various scan rates (30 ~ 150 mV/s). The peak potentials are gradually shifted to higher potentials as the scan rate is increased. Also we have observed very stable cyclic voltammograms of DGEFDP from the consecutive scan (up to 30 cycles), which means that this material has relatively stable redox process. The oxidation of DGEFDP was occurred at 0.5 V (vs. $Ag/AgNO_3$) and it also showed the irreversible

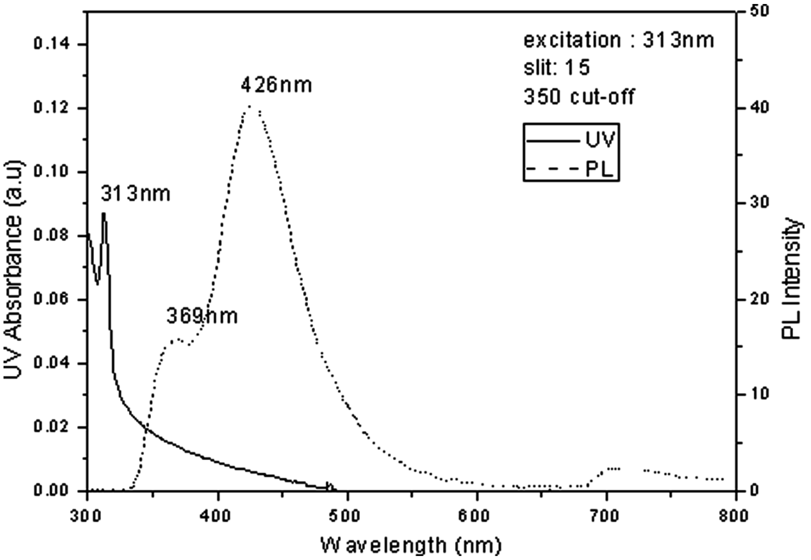

FIGURE 2 Optical absorption and photolumines spectrum of DGEFDP.

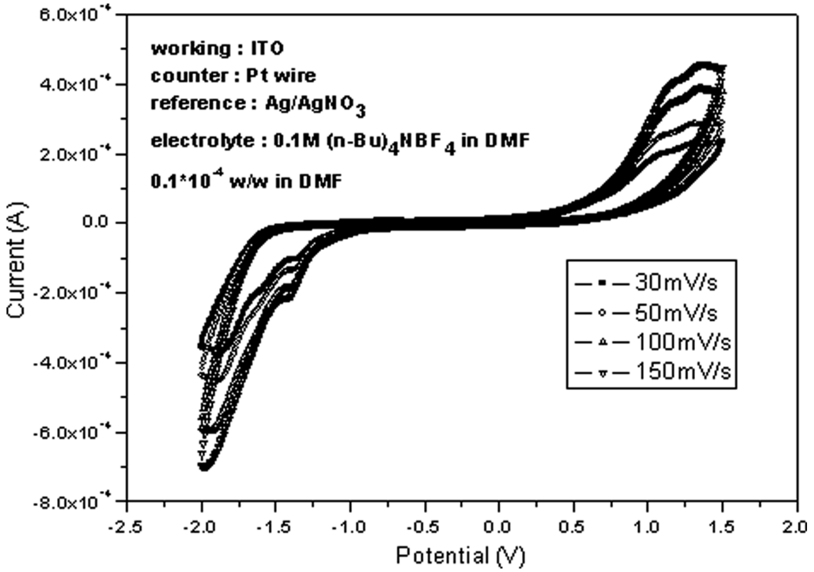

FIGURE 3 Cyclic voltammograms of DGEFDP [0.1 M $(n\text{-Bu})_4NBF_4$/DMF] with various scan rates 30 ~150 mV/sec.

reduction as shown in Figure 3. The redox current value was gradually increased as the scan rate was increased. This result suggests that the electrochemical process of DGEFDP is reproducible in the potential range of $-2.0 \sim +1.5$ V vs. $Ag/AgNO_3$.

It has been reported that the relationship between the redox peak current and the scan rate can be expressed as a power law type as follows [19,20].

$$i_{p,a} = k\ v^{x}(1)$$

$$\log i_{p,a} = \log k + x \log v(2)$$

where $i_{p,a}$ = oxidation peak current density, v = scan rate, k = proportional constant, and x = exponent of scan rate.

Assuming that electrode kinetics satisfies Eq. (1), the electrochemical redox reaction on the electrode is controlled by either the electron transfer process, where x = 1, or the reactant diffusion process, where x = 0.5 [19]. Relations satisfying Eq. (2) between the oxidation current density ($\log i_{p,a}$) and the scan rate ($\log v$) were observed. The oxidation current density of DGEFDP versus the scan rate is approximately linear relationship in the range of 30 ~ 150 mV/sec. The exponent of scan rate, x value of DGEFDP, is found to be 0.401 (Fig. 4). This value

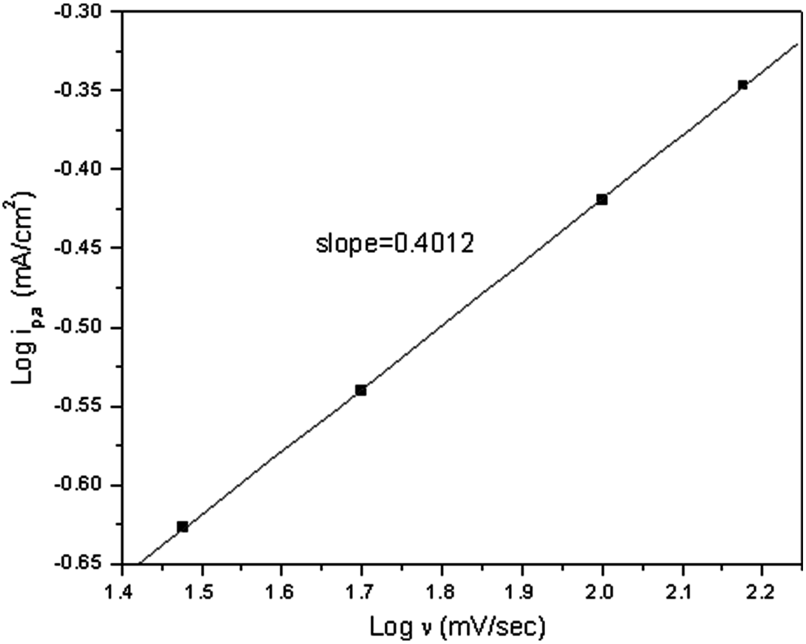

FIGURE 4 Plot of $\log i_{p,a}$ vs $\log v$ for DGEFDP.

means that the kinetics of the redox process may be mainly controlled by the reactant diffusion process [19–23].

CONCLUSIONS

In this article, we reported the synthesis of a new epoxy compound with fluorene moieties, DGEFDP, and elucidated the chemical structure of DGEFDP by NMR, IR, and UV-visible spectroscopies. The spectroscopic data confirmed that the designed ideal DGEFDP was synthesized. The cyclovoltamograms of DGEFDP exhibited the irreversible electrochemical behaviors between the doping and undoping peaks. The DGEFDP may be a candidate material for organic light-emitting diodes, chemical sensor, and functional composites for high temperature usages.

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