Polymer Light-Emitting Diodes Using Poly(9,9-dioctylfluorene) Gel by Thermal Printing Method

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1. Introduction
Organic devices utilizing conducting polymers have attracted considerable interest because of their advantages in large-area device fabrication. It is important to control the spatial geometry of the light source. Various methods such as ink-jet printing, solvent-assisted micromolding, maskless dye-diffusion technique and friction-transfer technique have been developed.

Fluorene-type polymer has emerged as an important class of conducting polymers due to their efficient emission and high stabilities. [1] Fluorene-type polymer also has the potential to be in full color emission via energy transfer to longer wavelength emitters in blends with other fluorescent and phosphorescent dyes. The characteristics of polymer photonic devices fabricated by wet processing are strongly dependent on the self-organized structure as the polymer solution passes from the liquid phase to the solid phase. Poly(9,9-dioctylfluorene) (F8) which have a blue emission exhibits various morphological behaviors. [2-3] There are intermediate phases such as glass phase and liquid crystal phase between the liquid and solid state. Thermotropic liquid phase at the high temperatures and lyotropic liquid crystal phase in the solution were observed for some conducting polymers. A polymer gel is an intermediate phase between a polymer solution and a solid state phase.

Generally, the common organic solvents such as chloroform, chlorobenzene and toluene in which the conducting polymers were readily soluble without any gel formation, were used for the fabrication of a thin film. In this study, F8 gel was found to be formed when the content of F8 was more than a certain concentrations in solutions such as 1,2,4-trichlorobenzene, 1,2-dichlorobenzene and 2-chloro-1,4-dimethylbenzene. The time that changes from the F8 sol into the gel tends to become fastest for 1,2,4-trichlorobenzene. In the case of 1,2,4-trichlorobenzene, the change from F8 sol to F8 gel occurs when the content of F8 was approximately more than 0.5 wt% for solution, corresponding to 600 molecules of 1,2,4-trichlorobenzene per 9,9-dioctylfluorene repeating unit.

2. Experimental
The substrate was degreased with solvents and cleaned in a UV ozone chamber. First, a poly(ethylene dioxythiophene) : poly(styrene sulfonic acid) (PEDOT: PSS) hole injection layer was spin-coated on the ITO -coated glass substrate at 45 nm thickness. 1,2,4-trichlorobenzene with high boiling point was used as a solvent. A phosphorescence material tris(1-phenylisoquinoline) iridium (III) (Ir(piq)3) as a doped dye was used. The doping concentration of Ir(piq)3 was 6 wt% relative to F8. The cathode consisted of CsF (3nm)/Mg:Ag/Ag was deposited in vacuum at a chamber base pressure of about 10^-4 Pa. Finally, the device was covered with a glass plate and encapsulated by epoxy resin in an argon gas atmosphere to prevent oxidation of the cathode and the organic layer. The active area was 4 mm².

3. Results and discussion
F8 gel was formed when the content of F8 was more than a certain concentrations in solutions such as 1,2,4-trichlorobenzene, 1,2-dichlorobenzene and 2-chloro-1,4-dimethylbenzene. The time that changes from the F8 sol into the gel tends to become fastest for 1,2,4-trichlorobenzene. In the case of 1,2,4-trichlorobenzene, the change from F8 sol to F8 gel occurs when the content of F8 was approximately more than 0.5 wt% for solution, corresponding to 600 molecules of 1,2,4-trichlorobenzene per 9,9-dioctylfluorene repeating unit.

![Fig. 1. Absorption and PL spectra of F8 sol and gel. The inset shows the change of intensities of absorption peaks at 438 nm and 394 nm after annealing the F8 gel and cooling back to room temperature.](image-url)

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This result indicates that the polymer chains of F8 gel with lower energy band gap are highly conjugated and ordered, compared with the F8 sol. An absorption spectrum of F8 gel with a peak at 438 nm is almost identical to the formation of β phase, because other studies of F8 films prepared by various methods such as solvent vapor treatment and heat treatment have shown that this peak originates from the β phase with planarized conformation.[3] In β phase, the torsion angle between neighboring 9,9-dioctylfluorene units is 180° as shown in Fig. 2(d). The change of intensities of absorption peaks at 438 nm and 394 nm after annealing the F8 gel and cooling back to room temperature are shown in the inset of Fig. 1. The peak intensity at 438 nm decreases with increasing the annealing temperature. The peak at 438 nm vanishes after annealing F8 gel at more than 80 °C, which is consistent of a glass transition temperature of F8. That is, these results suggest that the change from the F8 sol to gel results from the occurrence of β phase.

By annealing the F8 gel at more than 80 °C, F8 gel is transformed into F8 sol. The transition between the F8 sol and gel is reversible as shown in Fig. 2(a)(b). The F8 film was fabricated by the schematic procedure of thermal printing method using F8 gel as shown in Fig. 2(e). At room temperature, a gel state was kept because the solvent with high boiling point was used for high heat treatment. F8 gel, which is self-organized and soft, can be filled in the cases with various shapes. In this study, a syringe in which the F8 gel was contained was moved on the patterned ITO-coated substrate annealing at the moderate temperature. The thickness of F8 film can be controlled by the concentration of F8 for solvent and transfer speed of F8 gel. In this study, the F8 films were fabricated from the 1.5 wt% F8 gel.

The characteristics of PLEDs are strongly dependent of the film-formation condition. It is well-known that the morphology and optical properties of F8 films fabricated by spin-coating change after thermal treatment. In the case of thermal printing method, by controlling the substrate temperature, the properties of F8 films can be expected to be changed. For the thin film by the thermal printing method at the substrate temperature of 80 °C, the maximum peaks and shoulders of EL spectrum are located at approximately 440, 466, 498 and 530 nm as shown in Fig. 3. The spectrum indicates a pure blue emission from F8 layer with CIE coordinates of (0.16, 0.16). For a F8 film at 90 °C, the maximum peaks and shoulders of EL spectrum are located at approximately 436, 460, 490 and 525 nm. The EL spectrum of blue PLED at 80 °C blue-shifts, compared with that at 90°C. The emission on the low-energy sides increases with the annealing substrate temperature. It showed that the CIE coordinates moved from (0.16, 0.16) to (0.25, 0.33). This phenomenon is related with the crystallization of F8 films. The luminance of a PLED by thermal printing method at 80°C is approximately 560 cd/m² at a current density of 0.1 A/cm².

The dye doping method is practically important because it is easy to improve performance such as color tunability. In this case, F8 gel is formed from a F8 sol contained with solvent and F8. Therefore, F8 gel doped with dyes can be made from the solvent contained F8 and dyes. For a PLED using F8 gel doped with red emissive phosphor Ir(piq)₃, the peak wavelength of 620 nm with a slight shoulder and the red light emission form Ir(piq)₃ was observed.

![Fig. 2. Fabrication process by a thermal printing method using F8 gel. Photographs of (a) F8 sol and (b) gel, chemical structures of (c) F8 and (d) a F8 chain in the β phases conformation, (e) scheme of fabrication process using F8 gel.](image)

![Fig. 3. EL spectra of blue PLEDs with various annealing substrate temperatures and a red PLED.](image)

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### References