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Optical properties and improvement of electroluminescent properties in conducting block copolymers with Si atoms in main chains

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The use of π -conjugated conducting polymers as functional materials has attracted much attention from the point of view of basic science and applications, because of their high processability, stability, and promising electrical and optical properties[1]. Utilizing conducting polymers with relatively large band gaps, polymer blue light-emitting diodes (LEDs) could be realized.

On the other hand, copolymers with a π -conjugated segment and silicon (Si) atom in each monomer unit of polymer main chains are expected to possess unique characteristics and functionalities. Recently, copolymers such as poly(disilanyleneoligophenylene)s[2] and poly(disilanyleneoligothienylene)s[3] were synthesized and demonstrated the solubility in common solvents and the blue-to-red electroluminescent (EL) properties, since Si in main chains interrupts the π -conjugated chain and limits the π -conjugation length. Copolymers synthesized by the modified synthetic process should also have other π -conjugated segments and the possibility of exhibiting unique luminescent properties. Indeed, Kim *et al.* reported on their success in the synthesis of copolymers with Si atoms in main chains, and demonstrated color tuning of the emission to reduce the lowest unoccupied molecular orbital (LUMO) level[4]. In the case of the polymer LEDs utilizing such copolymers, suppression of the operating voltage to obtain blue emission might be realized. In addition, these copolymers promise to improve the thermal stability and possess high carrier mobility.

In this study, we report on the optical properties, such as photoluminescence (PL), spectral narrowing of PL, and the EL properties of conducting polymers with Si atoms in main chains, and methods for improvement of EL properties are also suggested.

Four kinds of conducting polymers, poly(diphenylsilylene-di-*p*-phenylene vinylene-*p*-phenylene) (SiPhPPV), poly(hexylmethylsilylene-*p*-phenylene vinylene-9,9-dihexylfluorene vinylene-*p*-phenylene) (SiHMFPPV), poly(diphenylsilylene-*p*-phenylene vinylene-9,9-dihexylfluorene vinylene-*p*-phenylene) (SiPhFPV), and poly(diphenylsilylene-*p*-phenylene vinylene-thienylene vinylene-*p*-phenylene) (SiPhTPPV), were synthesized and demonstrated the solubility in common solvents and the blue-to-red electroluminescent (EL) properties, since Si in main chains interrupts the π -conjugated chain and limits the π -conjugation length. Copolymers synthesized by the modified synthetic process should also have other π -conjugated segments and the possibility of exhibiting unique luminescent properties. Indeed, Kim *et al.* reported on their success in the synthesis of copolymers with Si atoms in main chains, and demonstrated color tuning of the emission to reduce the lowest unoccupied molecular orbital (LUMO) level[4]. In the case of the polymer LEDs utilizing such copolymers, suppression of the operating voltage to obtain blue emission might be realized. In addition, these copolymers promise to improve the thermal stability and possess high carrier mobility.

lene-*p*-phenylene) (SiPhThV), the molecular structures of which are shown in Fig. 1, were studied in the present work.

These polymers were synthesized and purified by the method already described[4,5]. In these polymers, π -conjugations are regularly interrupted along the backbone by Si atoms, resulting in isolated chromophores that emit blue or red lights in color. These polymers are soluble in common organic solvents such as chloroform and toluene.

When the SiPhPPV, SiHMFVPV, SiPhFPV, and SiPhThV films were excited by light from a Xe lamp, the wavelengths of which correspond to the absorption peaks, strong PL was observed. The PL spectra are shown in Fig. 2. The emission colors were, therefore, blue for SiPhPPV and SiHMFVPV, bluish green for SiPhFPV, and red for SiPhThV, respectively.

PL quantum efficiencies of the polymer films are evaluated when the laser line at 363.7 nm of an Ar⁺ laser was adopted as excitation sources. It should be noted that SiPhPPV demonstrated the highest efficiency, 26.4 % (photon/photon), in these polymers in spite of the shortest peak wavelength of the emission. The efficiency is comparable with the previously reported efficiency of blue luminescent conducting polymers[6,7].

When the excitation intensity of the nitrogen laser pulse at 337.1 nm was increased, the emission spectra of the SiPhPPV film changed as shown in Fig. 3. It is seen that the broad PL spectrum of SiPhPPV obtained at low excitation intensities in Fig. 2 changes at high excitation intensities to a much narrower and stronger emission band peaked at 444 nm with the spectral width of 5 nm. The emission spectral narrowing is accompanied by a nonlinear amplification as illustrated in the inset of Fig. 3. The spectrally narrowed emission is interpreted as being caused by the amplified spontaneous emission[6] enhanced by the optical waveguiding in the SiPhPPV film.

In the case of LEDs utilizing SiPhPPV, SiHMFVPV, SiPhFPV, and SiPhThV as emission layers, that is, with a structure of indium-tin-oxide(ITO)/ polymer/ aluminum(Al), strong EL was observed. The emission intensity starts to increase at around 12 V. The emission peak wavelengths of polymers coincide with those of PL. Although some alternating copolymers have

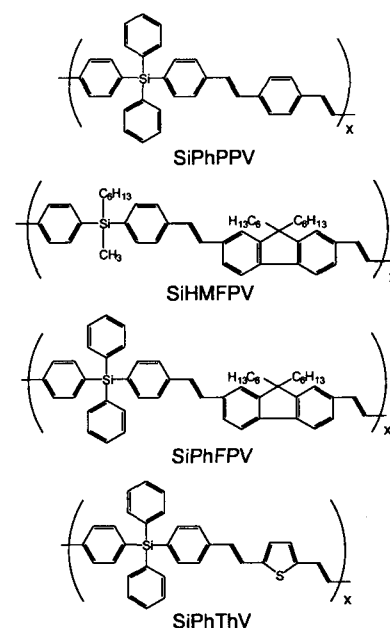


Fig. 1: Molecular structures of conducting polymers with Si atoms in the main chains.

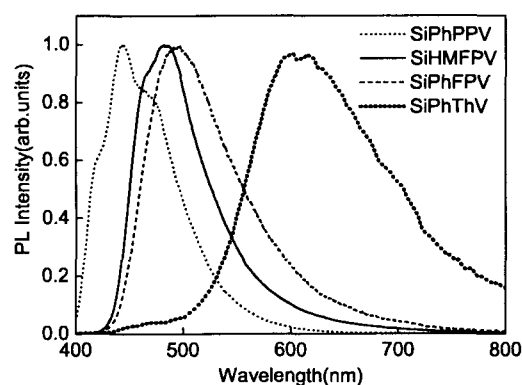


Fig. 2: PL spectra of conducting polymers with Si atoms.

already been known as EL materials, such blue luminescent alternating copolymers with high quantum efficiencies[7] have hardly been reported. It should be emphasized that copolymers, such as SiPhPPV, could be candidates of blue luminescent materials for organic blue LEDs and blue lasers.

Improvement of emission efficiency is one of the most inevitable points in polymer LEDs for realization of the flat panel displays. In this study, two attempts to achieve higher efficiency were carried out. One of them was surface treatment effects of ITO by two silyl coupling materials, *N*-(2-aminoethyl-3-aminopropyl)trimethoxy silane (TMS) and 1,1,1,3,3,3-hexamethyldisilazane (HMDS). The other was efficiency improvement by the annealing process after fabrication of LEDs.

Both LEDs of surface modification by a silyl coupling layer on ITO surfaces pretreated by oxygen plasma demonstrated 1.5-2 times higher emission intensity at the same current than that with unmodified ITO. Since the current-voltage characteristics and the turn-on voltages of all LEDs were almost the same, it should be noted that the emission efficiency changed markedly. By using the silyl coupling layer, such as TMS, tight adhesion between the substrate surface and spin-coated polymer film might be obtained.

Indium atom diffusion from ITO in the polymer emission layer is one of the most serious problems in organic LEDs that has been reported by several groups previously[8]. However, the coating of silyl coupling layer could prevent the indium contamination from the ITO electrode. The surface treatments by TMS and HMDS were available and effective to improve the EL efficiency for normal EL materials such as PPV derivatives as well as copolymers with the Si atom. The EL enhancement factors were slightly different for each conducting polymer.

The annealing process was carried out after deposition of the Al cathode onto polymer films. The fabricated LEDs were loaded into a quartz tube and annealed by an electric furnace in vacuum at various temperatures for 1 h. Figure 4 shows current density EL intensity characteristics of EL devices annealed with various annealing temperatures after Al deposition. Comparing the light intensity at the same current density, LED annealed at 100 °C achieved twice stronger intensity than an unannealed one. However, in the case of LEDs annealed at 140 or 180 °C, the emission intensity was quenched markedly. Such annealing effects could not be observed in the annealing process before deposition of the Al cathode onto polymer films. The thermal treatment might be effective for EL devices of any conducting polymer LEDs

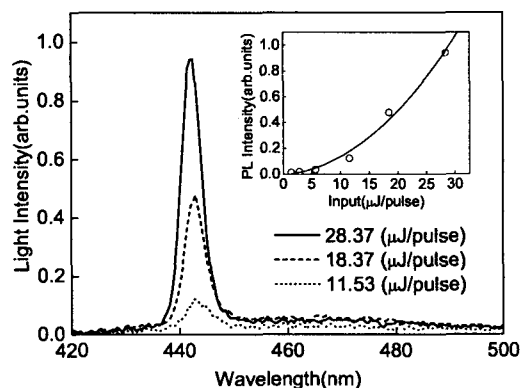


Fig. 3: Optical emission spectra at different excitation pulse energies in SiPhPPV thin film. Inset shows the emission peak intensity dependence on the excitation intensity in SiPhPPV thin film.

with the Al cathode. In the case of polymer LEDs with a magnesium-silver alloy cathode, such improvement of EL efficiency could not be found.

As previously reported, Al diffusion into the polymer film at the interface between the polymer layer and the Al cathode has been known[9]. Thermal treatment after Al deposition promotes adhesion between the polymer layer and the Al cathode and formation of the chemical bond such as the C-Al or C-O-Al covalent bonds[10], resulting in an efficient electron injection interface due to the interfacial adhesion. Thermal treatment over optimum temperature might enhance interchain interaction of polymers or degenerate the polymer film, resulting in the low emission efficiency.

In conclusions, the optical properties of conducting polymers with Si atoms in main chain, such as optical absorption, PL, and EL were studied. The strong PL with high quantum efficiency was clarified in the films, and the spectral narrowing was observed by pulse excitation of a nitrogen laser. The intense blue or red EL was demonstrated and the emission efficiency was improved by the electrode surface modification and the annealing process.

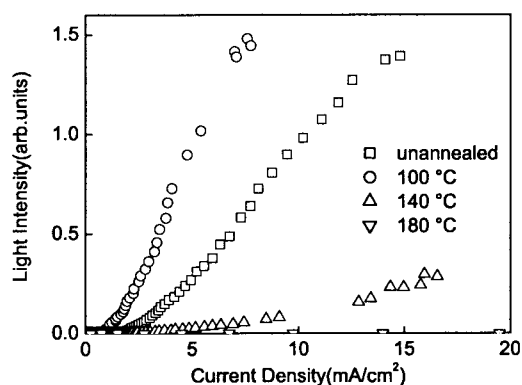


Fig. 4: Current density EL intensity characteristics of SiPhPPV LEDs annealed with various annealing temperatures after Al deposition.

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