Novel Copolymers for Electroluminescent Devices

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ABSTRACT: Two novel luminescent block copolymers (CE–PPV and CE–DMPPV), containing alternating distyrylbenzene [poly(phenylene vinylene) model oligomer] as light-emitting units and crown-ether segments as ionic conductive and spacer units were synthesized by use of a Wittig reaction between the dialdehyde monomer and 1,4-xylylene-bis(triphenylphosphonium bromide) or 1,4-bis(triphenylphosphoniomethyl)-2,5-dimethoxybenzene dichloride. The synthesized polymers were characterized with FTIR, ^{1}H-NMR, UV–Vis, differential scanning calorimetry, and gel permeation chromatography. The number-average molecular weights were 6896 with a polydispersity index of 1.75 for CE–PPV, and 9301 with a polydispersity index of 2.474 for CE–DMPPV, respectively. The decomposition temperatures and the glass-transition temperatures were in the range of 395–411°C and 75–77°C, respectively. The electrochemical properties of the copolymers were evaluated and the highest occupied molecular orbital and the lowest unoccupied molecular orbit energy levels of the copolymers were estimated by cyclic voltammetry. Efficient light-emitting diodes were successfully fabricated. The synthesis, characterization, and electroluminescent properties of the polymers are reported in this study.© 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 3316–3321, 2002

Key words: block copolymers; electrochemistry; luminescence; conjugated polymers; light-emitting diodes (LED)

INTRODUCTION

Since the discovery of electroluminescence in poly(*p*-phenylene vinylene) (PPV),[1] the research devoted to the synthesis of the conjugated polymers and the fabrication of the related electroluminescent (EL) devices has made significant progress over recent years.[2,3] Among the numerous conjugated polymers that have been investigated for use as the emissive layer in EL devices, PPV and its derivatives are the most intensively studied polymer systems because of their high luminescence and easy modification of the chemical structure for tailor-made applications using their electronic properties in many different fields.[4,5] In particular, the synthesis of PPV copolymers with alternating emissive units, distyrylbenzene, and flexible spacers on the main chain has been afforded considerable attention, given that the well-defined short conjugated distyrylbenzene segment exhibits a higher fluorescent quantum yield than that of the related fully conjugated PPV-based polymers, and the nonconjugated spacer confers to the polymer good solubility, film-forming property, and/or other functionality.[6–10] However, to the best of our knowledge, there are still no reports on those PPV-based polymers with crown-ether segments as spacers.

On the basis of the preceding considerations, two novel PPV-based block copolymers containing alternating distyrylbenzene as emissive units and crown ether as spacers have been designed and synthesized for the first time. It is expected that these polymers not only demonstrate high EL efficiency, good processability, and film-forming properties but also possess ionic conductivity, which would make the polymers good candidates for fabricating novel light-emitting electrochemical cells (LECs). The light-emitting diode (LED) devices based on the two copolymers have been fabricated, and the EL characteristics of the devices were evaluated in this study.

EXPERIMENTAL

Materials

The synthetic routes of monomer and polymers are illustrated in Scheme 1.

3,4-Dihydroxybenzaldehyde and 1,4-xylylenebis (triphenylphosphonium bromide) (98%) was purchased from Aldrich (Milwaukee, WI). 1,8-Dichloro-3,6-dioxaoctane was synthesized according to the method proposed by Pederson.[11] 1,4-Bis(triphenylphosphoniomethyl)-2,5-dimethoxybenzene dichloride and diformyl-dibenzo-24-*crown*-8 (**1**) were synthesized
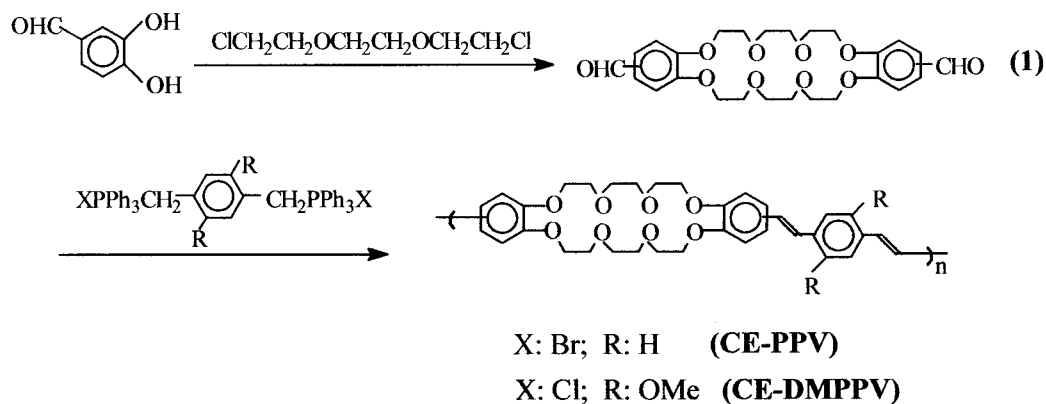
Scheme 1 The synthetic route of polymers.

following the published procedure.[12] The other reagents and solvents were commercially available and used without further purification.

General polymerization procedure

To a stirred solution of an equimolar amount of a dialdehyde monomer (**1**) (0.002 mol) and the related phosphonium salt (0.002 mol) in 40 mL of anhydrous ethanol and chloroform (1/1), a solution of 10 mL of sodium ethoxide (freshly prepared by the dissolution of approximately 0.005 mol of cleaned sodium metal in 10 mL of anhydrous ethanol) was added dropwise at ambient temperature under a nitrogen atmosphere. The mixture was stirred for 24 h after the addition, and then neutralized to pH 6–8 with 2% hydrochloric acid. The solids were collected at the end of the condensation reaction, and thoroughly washed with ethanol/water (3/1) to remove the by-products triphenylphosphine oxide and NaCl. It was subsequently isomerized into an all-*trans* configuration by refluxing 6 h in chloroform with a catalytic amount of iodine in the absence of light and under nitrogen. The crude product was precipitated in methanol, and the obtained polymer was dried in a vacuum oven at 40°C for 1 week.

Yield: 51% for CE–PPV. ANAL. calcd for $C_{34}H_{38}O_8$: C, 71.08%; H, 6.62%. Found: C, 69.12%; H, 6.51%.

Yield: 34% for CE–DMPPV. ANAL. calcd for $C_{36}H_{42}O_{10}$: C, 68.14%; H, 6.62%. Found: C, 64.99%; H, 6.64%.

Characterization and instrumentation

^{1}H-NMR spectra were obtained from UNITY-200 spectrometer (Varian Inc., Sweden) in $CDCl_3$ with TMS as an internal standard. FTIR characterization was performed on a Nicolet 560 spectrometer (Nicolet Instruments, Madison, WI), using KBr discs containing the polymer samples. Gel permeation chromatography (GPC) measurement was performed on a PL-GPC210 instrument by using THF as eluent, calibrated with polystyrene standards (MW of PS: 500–8,500,000; Polymer Laboratories, Shropshire, UK; EasiCal). Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) for polymers were carried out under nitrogen, at a heating rate of 10°C/min, by use of the TA MDSC-2910 and TGA-2050 instruments (TA Instruments, New Castle, DE). Cyclic voltammograms of the polymer film were recorded on EG and G PARC Model 283 potentiostat/galvanostat, by use of a Pt disk as the working electrode (0.785 mm^2), a Pt wire as a counter electrode, and an Ag wire as a quasi-reference electrode. Tetrabutylammonium hexafluorophosphate (Bu$_4$PF$_6$, 0.1M) dissolved in 1,2-dichloroethane was employed as the supporting electrolyte and the entire system was degassed with nitrogen for 15 min. Ultraviolet–visible (UV–Vis) absorption spectra for both the chloroform solution and film were taken from the Perkin–Elmer Lambda Bio 40 spectrophotometer (Perkin Elmer Cetus Instruments, Norwalk, CT). Photoluminescence (PL) spectra of polymer in chloroform solutions and net films were measured using Perkin–Elmer LS 50B and a Hitachi 850 fluorimeters (Hitachi, Tokyo, Japan), respectively. EL analyses were performed at room temperature under an air atmosphere with an Acton Research SP 300i system linked with CCD.

Preparation of the LEDs

The LEDs, with the configuration of indium tin oxide (ITO)/poly(3,4-ethylenedioxythiophene) (PEDOT)/CE–PPV/Ca (Al) or (ITO)/PEDOT/CE–DMPPV/Ca (Al), were prepared by spin-coating an aqueous solution of PEDOT–PSS on a glass/ITO substrate (thickness ~ 60 nm), then spin-coating a chloroform solution of the related polymer on the surface of the PEDOT layer, followed by the thermal evaporation of the Ca (40 nm) at 0.00267 Pa. At last, a layer of Al (~ 100 nm) was deposited on the surface to protect the reactive Ca. The area of emissive layer is about 0.25 cm^2.

RESULTS AND DISCUSSION

Synthesis and structure characterization of copolymers

As shown in Scheme 1, monomer diformal-dibenzo-24-*crown*-8 (**1**) was synthesized previously through a reaction between 3,4-dihydroxybenzaldehyde and 1,8-dichloro-3,6-dioxaoctane in the presence of base NaOH. To prepare the dialdehyde monomer (**1**), some systems have been tried, such as NaOH/1,8-dichloro-3,6-dioxaoctane/*n*-butanol, NaOH/1,8-dichloro-3,6-dioxaoctane/ethylene glycol monomethyl ether, K_2CO_3/triethylene glycol ditolsylate/DMF, and so forth. However, the yields for all these systems were not enough high. To ensure high yield, the reaction conditions must be carefully controlled. The polymers were obtained by Wittig condensation polymerization of equimolar quantities of monomer (**1**) and the relative phosphonium salt, and were subsequently isomerized to an all-*trans* configuration by refluxing the chloroform solutions with a catalytic amount of iodine in the absence of light and under nitrogen.

Calculated and found elemental analysis results indicate the presence of some impurities in the polymers. It is essential to further improve the purity of the polymers to improve the quantum yield of the polymers. The synthesized polymers are easily soluble in chloroform, methylene dichloride, and DMF. High quality polymer films can be obtained by spin coating from chloroform solution after filtration. The number-average and weight-average molecular weights for CE–PPV are 6898 and 12,071, respectively, whereas those for CE–DMPPV are 9301 and 23,010, respectively, relative to polystyrene standards.

The structures of copolymers were confirmed by FTIR, ^{1}H-NMR, and elemental analysis. Figure 1 presents the FTIR spectra of dialdehyde monomer and
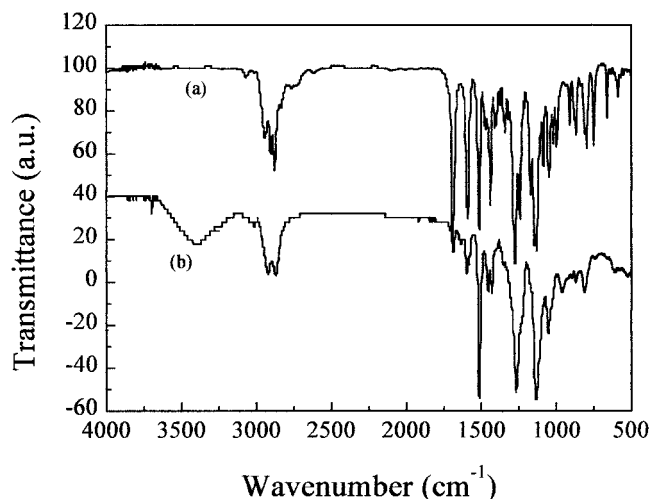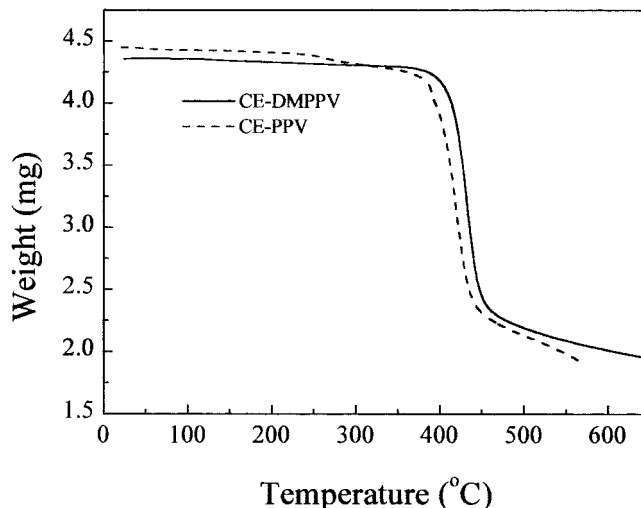
Figure 2   TGA curves of CE–PPV and CE–DMPPV.

CE–PPV. In the spectrum of the copolymer, the peak at about 1700 cm^{-1} corresponding to the stretching mode of CH=O of monomer (**1**) drastically decreases and a new peak at about 960 cm^{-1} appears, which implies the formation of a *trans*-vinylene group. The FTIR spectrum of CE–DMPPV is similar to that of CE–PPV. In ^{1}H-NMR spectra, a peak at 9.82 ppm, assigned to the chemical shift of aldehyde protons of monomer (**1**), nearly disappears, whereas new peaks, assigned to the two protons linking to the vinylene group, appear at about 7.00–7.05 ppm in the corresponding copolymers. The results of elemental analyses are also in agreement with the desired chemical composition of the polymers.

The TGA curves of the two polymers are shown in Figure 2. The two polymers exhibit excellent thermal stability. They are thermally stable up to 395–411°C. DSC curves display glass transitions at about 77 and 74.7°C for CE–PPV and CE–DMPPV, respectively.

Optical properties

Figure 3 displays the UV–Vis absorption and PL spectra of CE–PPV. PL spectra were recorded with an excitation wavelength corresponding to the absorption maximum wavelength. The absorption peaks of polymer solution appear at about 351, 317, 276 nm, respectively. Compared with the solution case, the absorption maximum of polymer film at 361 nm shows a 10-nm red shift, suggesting that an aggregate has been formed in the film state. The absorption edge of CE–PPV film appears at about 427 nm, which corresponds to a highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbit (LUMO) bandgap (Eg) of about 2.90 eV. There are two peaks in the PL spectrum of the polymer solution, located at 420 and 440 nm, respectively. Similar to the

**Figure 1**   FTIR spectra of (a) monomer (**1**); (b) polymer CE–PPV.

polymer solution, there are also two peaks: a maximum peak at about 463 nm and a shoulder at about 500 nm, in the PL spectrum of casting film. Just like UV–Vis, the PL maximum peak of the polymer film also demonstrates an approximately 20-nm bathochromic shift with respect to the solution.

For CE–DMPPV, the maximum absorption peak of the chloroform solution appears at 383 nm, with a shoulder at the low wavelength side (317 nm), and there are two peaks in the PL spectrum, located at 452 and 477 nm, respectively. It is obvious that CE–DMPPV emits longer-wavelength light than that of CE–PPV. From the edge absorption of the thin film sample, the Eg is estimated to be 2.78 eV, which is 0.2 eV lower than that of CE–PPV. It is evident that the introduction of two methyloxy groups into 2- and 5-positions of the middle phenyl ring in PPV segments can significantly decrease the Eg of the polymer, which is attributed to the weak electron-donating characteristic of the methoxy group that provides electrons to take part in the conjugation, and its electronic contribution prevails over its steric contribution.
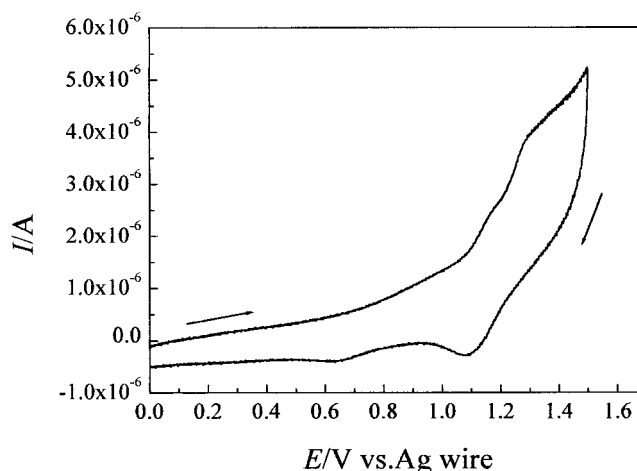
The relative PL quantum yields of the polymers in dilute chloroform solutions were examined to be 46.65% for CE–PPV and 42.39% for CE–DMPPV, from the corrected spectrum against a 1,6-diphenyl-1,3,5-hexatriene solution in cyclohexane as standard (assume 80% quantum yield at 350 nm excitation).

Electrochemical properties

A typical cyclic voltammogram (CV) corresponding to the oxidation of CE–PPV is shown in Figure 4. The polymer film demonstrates an irreversible p-doping process when an anodic scan is performed. The anodic peak occurs at 1.5 V (versus Ag/Ag^+) and the onset ($E_{ox,on}$) at 1.03 V (versus Ag/Ag^+). Because of the broad bandgap of the copolymer, it is difficult to ob-
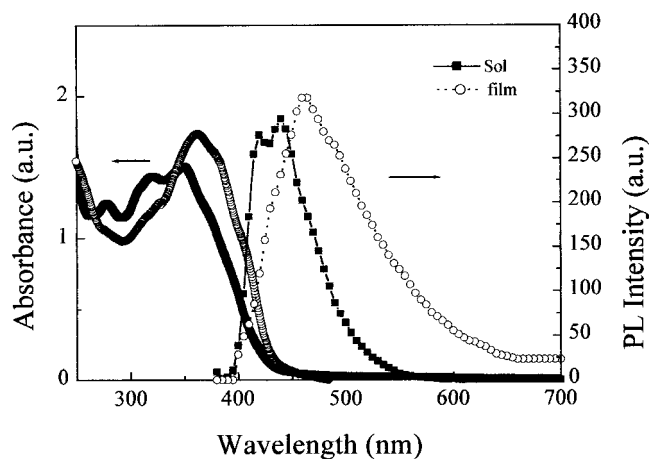
Figure 4 Cyclic voltammogram of CE–PPV in $C_2H_4Cl_2$ with $0.1M$ Bu_4PF_6 as supporting electrolyte. Scan rate: 20 mV/s.

tain the reduction onset from the CV directly. The HOMO and LUMO values are calculated to be -5.71 eV and -2.81 eV, by assuming the energy level of ferrocene/ferrocenium (E_{FOC}) at -4.8 V ($E_{FOC} = 0.12$ V versus Ag/Ag^+).[13] Moreover, according to the following equation,[14]

$$Eg/e = E_{ox} - E_{red},$$

we can estimate the reduction onset at about -1.87 V versus Ag wire. The onset potential datum indicates that the copolymer is a typical p-type material. According to the same method, E_{ox} and E_{red} of CE–DMPPV were estimated to be 0.96 and -0.82 V, respectively, whereas the HOMO and LUMO were -5.64 and 2.86 eV, respectively.

Electroluminescent characteristics of LEDs

Figure 5 shows the current–voltage and current–brightness characteristics of the LED devices based on CE–PPV and CE–DMPPV, respectively. The device made from CE–PPV shows a turn-on voltage at about 4.5 V, both for current and for light emission under forward bias (positive at ITO electrode) [Fig. 5(a)]. The maximum current and brightness values obtained were 121 mA/cm² and 54 cd/m², respectively, under forward bias of 11 V. Nevertheless, by further increasing the applied voltage, the light intensity of the device did not increase but declined. The reason, as we consider, may be that, once voltage increases to a certain extent, many excitons get to the counterelectrode before recombination, and consequently are quenched, thus causing a decline of the light intensity because of a decrease in probability of recombination of the carriers. No light emission and current were observed under the reversed bias for the device. The

Figure 3 UV–Vis and PL spectra of CE–PPV in a chloroform solution and a net film.

onset voltage of the device made from CE–DMPPV was about 5 V [Fig. 5(b)]. The maximum brightness was 63.5 cd/m² under a forward bias of 18 V.

Figure 6 represents the EL spectrum of the device based on CE–PPV. For convenience of comparison, the PL spectrum of polymer film is given in the figure at the same time. The emission maximum of the EL spectrum appears at a wavelength of around 463 nm, corresponding to blue light emission. We note that the EL spectrum is similar to its PL spectrum, indicating that they have similar relaxation processes. Compared with CE–PPV, the EL emission maximum of CE–DMPPV demonstrates a 27-nm red shift, located at around 490 nm, which lies in the greenish-blue light region.

It is well known that a serious phase separation occurred in those LEC devices using a blend of fully conjugated luminescent polymer with electrolyte, poly(ethylene oxide) or crown ether, and lithium tri-
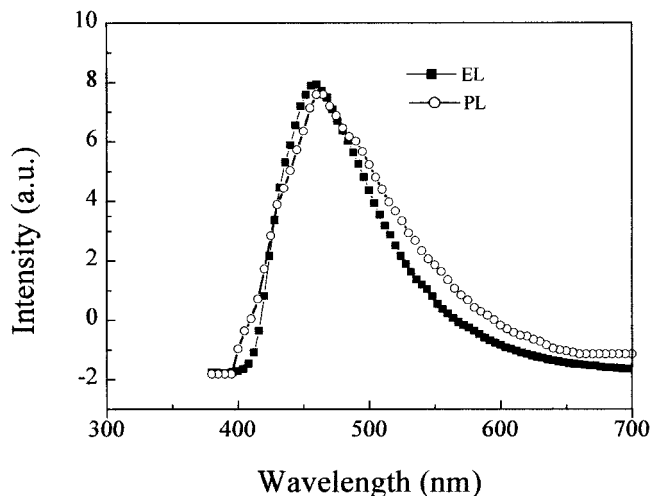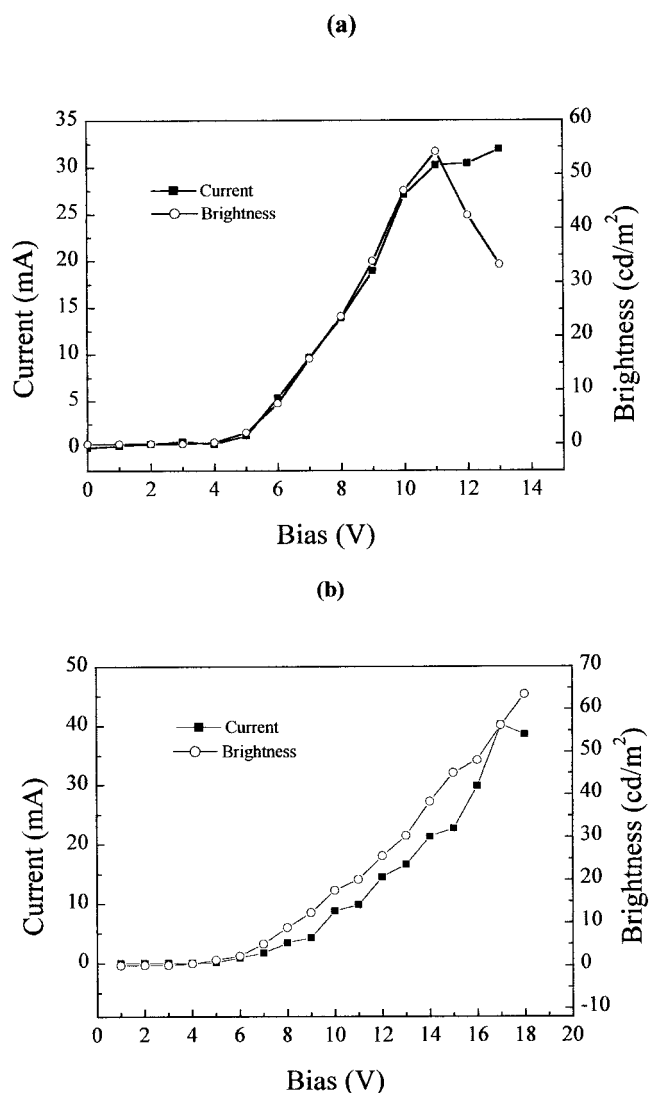

Figure 6 PL and EL spectra of CE–PPV.

flate as emitter, because of the different chemical structures of the conjugated polymer and the electrolyte. In our previous work,[12,15–18] some copolymers, which embedded PEO short segments in the polymer main chain, have proved to be good emitters for LEC devices in which the phase separation problem is overcome because of the good compatibility of polymers with PEO. In CE–PPV and CE–DMPPV, the crown-ether segment is also expected to play the same role as the PEO short segment in those polymers. It has been proved that a blend of CE–PPV or CE–DMPPV with PEO and lithium triflate is the ideal emitter for LECs. Moreover, a blend of these polymers with lithium triflate could be directly used to prepare LECs in the absence of an additional electrolyte, in that the crown-ether segment has provided the polymers with ionic conductivity. The details about LECs will be published in a future study.

CONCLUSIONS

Two novel luminescent block polymers containing alternating distyrylbenzene as light-emitting units and crown-ether segments as ionic conductive and spacer units have been synthesized and characterized. The resulting polymers exhibit excellent thermal stability. The introduction of crown ether into the polymer main chains not only enhanced the processability of polymers and improved the compatibility of luminescent polymers with electrolyte, but also provided the polymers with ionic conductivity. LEDs with the configuration of ITO/PEDOT/polymer/Ca (Al) were fabricated, and the possibility of the polymers' application in LEC devices was discussed.

Figure 5 The current-voltage and bright-voltage characteristics of LEDs based on (a) CE–PPV and (b) CE–DMPPV.

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