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Luminescent Block Copolymer Containing PEO-Like Segments for Polymer Light-Emitting Devices

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A blue light-emitting polymer, poly(distyrylbenzene-co-triethylene glycol) (PDTG), was synthesized. The ionic conductivity of PDTG at room temperature was up to $5.9 \times 10^{-7} \text{ Scm}^{-1}$. Tg was determined to be 69.5°C.

Keywords: luminescent polymer; polymer electrolyte; poly(distyrylbenzene-co-triethylene glycol)

INTRODUCTION

Poly(*p*-phenylene vinylene)(PPV)-based polymers are the main candidates for fabrication of polymer light-emitting diodes(LED)^[1] and light-emitting electrochemical cells(LEC)^[2,3]. The active layer of LEC is a mixture of luminescent polymer(e.g. PPV derivatives), ion-conducting polymer(e.g. PEO), and supporting electrolyte salt. Then the question comes out because these polymers tend to phase-separate thermodynamically. One method to solve this problem is the addition of surfactants^[4], the other one is to design new polymer that contains both ion-conducting portion and luminescent portion^[5,6]. In this paper, we report the synthesis of a new block copolymer and discuss the possibility of the application of this polymer in the light-emitting devices.

EXPERIMENTAL

1,9-Bis(4-formylphenoxy)triethylene glycol were synthesized as the followings: 14.7g(3.5mmol) of the triethylene glycol bis(tosylate), 8.4g(6.9mmol) of 4-hydroxy-benzaldehyde, and 10.0g K_2CO_3 were mixed in 150ml of DMF solution, stirred, and kept at $110^\circ C$ under N_2 overnight, which was poured into 1000ml of cold water. The precipitate was filtered and recrystallized with ethanol. 2.23g of product was obtained(yield: 60%). 1H NMR($CDCl_3$, δ), 9.9(s, 2H, -CHO), 7.8(d, 4H, ph), 7.0(d, 4H, ph), 4.3(t, 4H, $-OCH_2-$), 4.0(m, 8H, $-OCH_2-$). MS(EI), 358(2%), 148(14.3%), 104(49.7%).

Poly(distyrylbenzene-co-triethylene glycol) (PDTG) was synthesized via Wittig reaction^[7] as shown below. To a stirred mixture of 0.75g (2mmol) dialdehyde and 1.55g(2mmol) 2,5-bismethyl-1,4-xylene bis-(triphenylphosphonium chloride) in 50ml anhydrous ethanol and chloroform(1/3) was added dropwisely at room temperature a solution of 0.12g(5mmol) sodium in 10ml anhydrous ethanol. The mixture was stirred for 5h, and then a small amount of dilute hydrochloric acid and ethanol/water were added successively. The precipitate was filtered, redissolved in chloroform(10ml), and then precipitated by ethanol. The slight yellow fibrous polymer was dried in vacuum at $40^\circ C$ for 2 days.

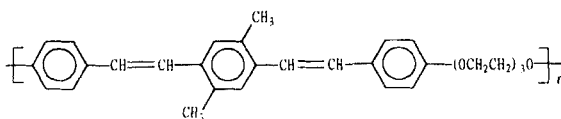


FIGURE 1 Chemical structure of PDTG.

DSC & TGA were recorded on Perkin-Elmer 7 series Thermal Analysis System. The photoluminescence and absorption spectra were obtained on the Jasco V-550 spectrometer and Perkin-Elmer LS 50B luminescence

spectrometer respectively. All fabrication of devices and all measurements were performed in air.

RESULTS AND DISCUSSION

Typical absorbance at 3006, 2921, 1688, 1603, 1509, 1454, 960 cm^{-1} can be found in the FTIR spectrum of PDTG, which is in agreement with those expected for the desired material combined with NMR results. The T_g of this type of copolymer was expecting to be increased by shortening the length of the flexible chain^[7]. T_g of the polymer was determined to be 69.5°C from DSC traces. Compared with the polymer of Benfaremo et al.^[6] with longer flexible block chain, the T_g of PDTG was increased ca. 15°C. Shortening the length of the flexible block chain works on increasing the T_g of polymer. The electrochemical measurements showed that the polymer are *p* and *n*-dopable. PDTG in solution showed strong blue photoluminescence under UV.

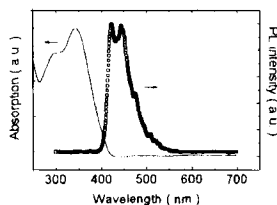


FIGURE 2 Absorption/Photoluminescence spectra of PDTG in chloroform.

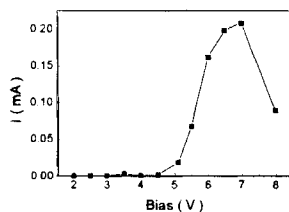


FIGURE 3 I-V characteristics of PDTG/PEO-based LED.

Fig.2 gives the absorption/photoluminescent spectra. The band gap from this absorption spectrum was determined to be 2.9eV. Although the ion-conducting chain is short, the ionic conductivity of the copolymer is satisfactory from the point of LEC fabrication. The ionic conductivity of the polymer at room temperature was up to $5.9 \times 10^{-7} \text{Scm}^{-1}$, which is comparable with the reported PEO/PPV blend^[3]. The ionic conductivity decreased sharply to be 10^{-8}Scm^{-1} as the temperature dropped to lower than 10°C.

We found in the experiments that the performance of the LED and LEC made with this polymer is not very good. We blended it with other polymer(such as PEO). The resulted polymer blend(PDTG/PEO = 1, w/w) was used as an active layer sandwiched between Al and ITO electrodes. The $I \sim V$ curve of the single-layer LED is shown in Fig.3, and the LED device emitted weak blue light. The performance of this LED degraded as the bias voltage beyond 7V. Further work on PDTG based LEC at lower temperature is under progress.

CONCLUSIONS

A polymer emitting blue light was synthesized. The ionic conductivity of the polymer at room temperature was up to $5.9 \times 10^{-7} \text{ Scm}^{-1}$. The short flexible block chain actually contributes to the increase of the T_g . This polymer shows higher thermal stability.

Acknowledgments

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