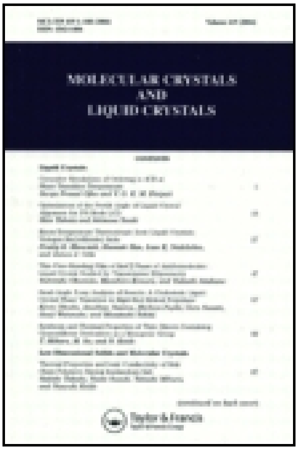

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Synthesis and Electroluminescent Properties of Polyurethane with Stilbene Dye Pendant

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Synthesis and Electroluminescent Properties of Polyurethane with Stilbene Dye Pendant

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A polyurethane (PU) derivative with a stilbene side chain was prepared from 4-cyano-4'-[N,N- bis (2-hydroxyethyl) amino] stilbene and 2,4-tolylene diisocyanate (2,4-TDI). The stilbene dye was synthesized by Wittig reaction of 4 – [N,N-bis (2-hydroxyethyl) amino] benzaldehye with (4-cyanobenzyl) triphenyl phosphonium chloride. The molecular structures were confirmed by elemental analysis, FT-IR and 1H-NMR spectroscopy and the thermal properties were investigated by DSC. The PU derivative exhibits strong photoluminescence (PL) in the green spectral region peaking at 510 nm. Single-layer electroluminescent devices with ITO and MgAg as electrodes were fabricated via spin-coating from PU solution.

Keywords: Polyurethane (PU) derivative; Stilbene; Electroluminescence

INTRODUCTION

Since the first demonstration of electroluminescene (EL) from a fully π-conjugated polymer,[1] polymeric materials have attracted considerable attention as emissive layers in light-emitting diode structures. A variety of polymer systems, such as fully π-conjugated polymers,[2] polymers with chromophores attached to the main chain or to side chains,[3] and molecularly doped dye-polymer[4] composites have been used. In this paper, we report the synthesis and EL properies of a new EL polymer with a urethane linkage

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group.

EXPERIMENTAL

Synthesis of EL polymer

The synthsis scheme of the stilbene dye is illustrated in Figure 1. The Stilbene dye (1) was synthesized by Wittig reaction of 4- [N,N-bis(2-hydroxyethyl) amino]benzaldehye with (4-cyanobenzyl)triphenyl phosphonium chloride, and confirmed with ^{1}H-NMR (DMSO-d_6): δ 6.70-7.92 (10H, aromatic H and stilbene H), 4.80 (2H, hydroxyl H), 3.60 (8H, aliphatic protons). FT-IR (KBr) bands at 3426 (O-H stretching), 2926 and 2886 (CH_2 stretching), 2223 (C-N stretching) cm^{-1} were confirmed. Elemental analysis results are as follows: calcd., C 74.00%, H 6.54%, N 9.08% ; obsd., C 73.18% H 6.44%, N 8.73%. The melting point is 183 °C.

A solution of compound **1** in N,N-dimethylformamide (DMF) and a solution of 2,4-TDI in DMF ([NCO]/[OH]=1.05) were mixed and refluxed under stirring for 6 hrs at 110°C in a nitrogen atmosphere. Then the solution was cooled to room temperature and poured into vigorously stirred water. The precipitated PU was separated by filtration and washed with water several times. The PU was purified by reprecipitation from methanol/water. FT-IR (KBr) bands at 3420 (N-H stretching), 2926 and 2886 (CH_2 stretching), 2223 (C-N stretching), 1710 (C=O stretching) cm^{-1} were confirmed. Elemental analysis results are as follows: calcd., C 69.70%, H 5.43%, N 11.61% ; obsd., C 69.02% H 5.76%, N 11.61%. The glass-transition temperature of the polymer was found to be 120 °C from a DSC analysis.

Fabrication and Evaluation of EL Devices

PU films with a thickness of approximately 130 nm were fabricated on ITO-coated glass substrates via spin-coating from a 3.0 wt% THF solution. The film thickness was determined using a dual-beam interference microscope.

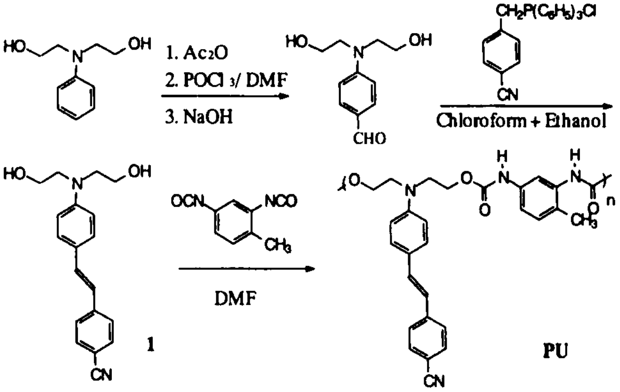

FIGURE 1 Synthetic route of PU

The surface of the films appeared homogeneous from an optical microscope image. On top of the polymer layer MgAg (weight ratio 10:1) alloy electrodes with a thickness of approximately 200 nm were fabricated via vapor deposition. The size of the emitting area was 2×2 mm and 8 devices were prepared on the same substrate in a single process under identical conditions. A source-measure unit (Keithley 238) and luminance meter (Topcon BM-5A) were employed for L-J-V measurements.

RESULTS AND DISCUSSION

In comparison between the IR Spectrum of the PU polymer and that of the compound 1, a C=O stretching band at approximately 1710 cm^{-1} was observed in the polymer, which is characteristic of an urethane group. The DSC thermogram of compound 1 shows an endothermic peak at 183.0℃ which is attributed to melting of the material. The thermogram of PU exhibits a shoulder at 120.0℃. PU is soluble in common organic solvents, and thin films obtained through spin-coating appeared homogeneous. Figure 2 shows the PL and EL spectra of a single-layer device. The PL spectrum peaks at

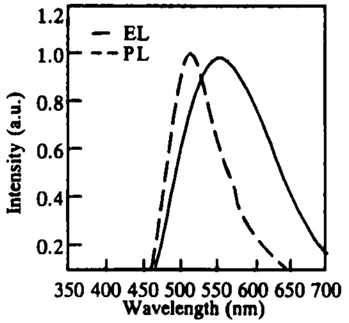

FIGURE 2. The EL spectrum for the single -layer device and PL spectrum of the PU thin film.

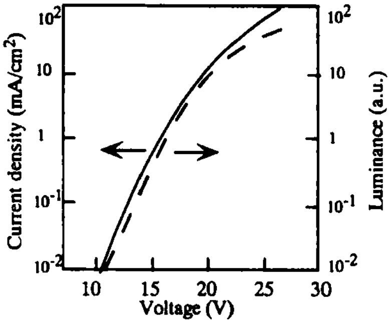

FIGURE 3. Luminance-current density -voltage curves in a PU single layer diode.

510 nm whereas the EL peak is red shifted by 40 nm and the EL band is broader. Figure 3 shows the current density and the luminance of a device versus applied voltage. Luminance revealed increase in the current density over 14 mA/cm^2 as the current density increased. In result, a luminance of approximately 50 cd/m^2 was observed at the maximum current density of 100 mA/cm^2, in which the quantum efficiency was calculated to be 0.015%.

In conclusion, a PU bearing stilbene dye was prepared from compound 1 and 2,4-TDI, and the EL properties were investigated. Investigation on the difference between the PL and EL peak wavelength, as well as the improvement of the performance of EL devices are under way.

Acknowledgments

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