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Modification of Poly(styrene-*alt*-maleic anhydride) with 1,3,4-Oxadiazole Units for Electroluminescent Devices

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Summary: New copolymers of poly(styrene-*alt*-maleic anhydride) (PSMA) modified with 2-(4-aminophenyl)-5-(biphenyl-4-yl)-1,3,4-oxadiazole and hexylamine were prepared. The copolymers, characterized by UV-vis and FT IR spectroscopy, reached 1.22 mol % of the oxadiazole units relative to anhydride groups at the maximum (PSMA-4). Electric and optical properties of the copolymers were studied. The currents obtained depend strongly on the content of oxadiazole units in the copolymers. Currents measured in PSMA-4 were more than two orders of magnitude higher than those measured in the copolymers without oxadiazole. Using polymer blends made of poly(9,9-dihexadecylfluorene-2,7-diyl) and PSMA-4, blue light-emitting devices were fabricated and their photoluminescence and electroluminescence spectra were measured.

Keywords: electroluminescence; electron-transporting properties; oxadiazole; poly(styrene-*alt*-maleic anhydride)

Introduction

Recently, oxadiazole-containing polymers have received a great deal of interest in the field of polymeric light-emitting devices (LEDs). Low-molecular-weight oxadiazoles like 2-(biphenyl-4-yl)-5-(*tert*-butylphenyl)-1,3,4-oxadiazole (PBD) have been used as electron-transporting moieties in LEDs.[1-3] To overcome the diffusion and crystallization of low-molecular-weight oxadiazoles, polymers with attached oxadiazole moieties have been synthesized.[4,5] Recently, amphiphilic

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copolymers containing the oxadiazole rings as pendant groups were prepared by aminolysis of poly(styrene-*alt*-maleic anhydride) (PSMA) with 2-(4-aminophenyl)-5-(4-nitrophenyl)-1,3,4-oxadiazole and alkylamines (C_{10}, C_{18}).[6] The content of oxadiazole units in copolymers was found to be low (0.5 mol % relative to anhydride groups). Here we describe the modification of PSMA with 2-(4-aminophenyl)-5-(biphenyl-4-yl)-1,3,4-oxadiazole affording higher contents of the oxadiazole units in material. Electric properties of thin films were studied as well.

Experimental

Synthesis. Poly(styrene–*alt*–maleic anhydride), PSMA, (50 mol % of styrene units, M.w. 1600), was purchased from Polysciences, Inc. and used as received. 2-(4-Aminophenyl)-5-(biphenyl-4-yl)-1,3,4-oxadiazole (Oxad-NH_2) was synthesized from 4-nitrobenzohydrazide (Aldrich) and biphenyl-4-carbonyl chloride (Fluka) according to the recently published procedure.[7]

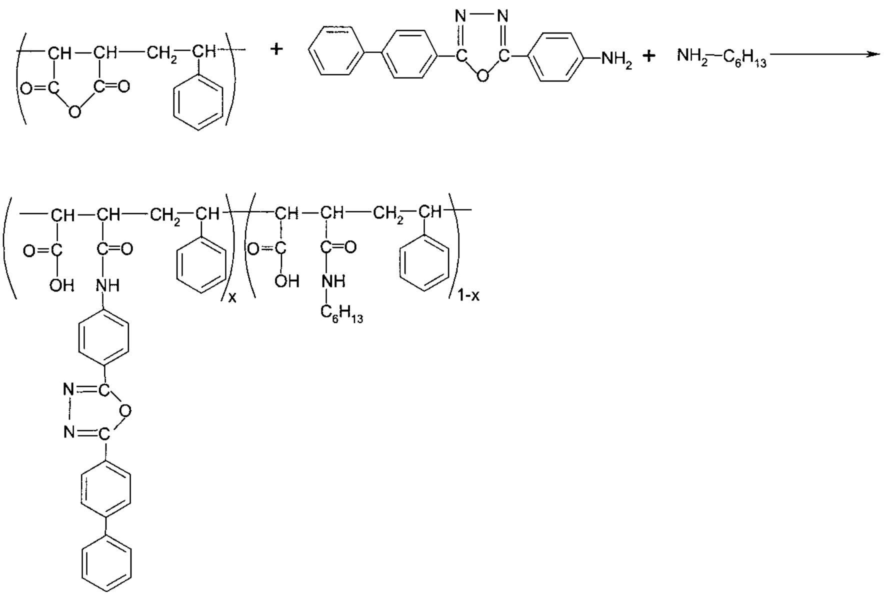

Figure 1: Modification of PSMA with Oxad-NH_2 and hexylamine

The polymer modification (Figure 1) was carried out as follows: A solution of 0.31 g (0.001 mol) of Oxad-NH_2 in *N*-methylpyrrolidone (20 ml) was added slowly (1 h) to a solution of 4.0 g of PSMA (0.02 mol of anhydride groups) in *N*-methylpyrrolidone (40 ml). The mixture was heated with stirring (Table 1, PSMA-1 – PSMA-4), then cooled to room temperature and 2.7 ml (0.02 mol) of hexylamine was added. The solution was heated to 100 °C for 5 h. After cooling, the reaction mixture was poured into ethyl acetate and the precipitate was filtered off and dried. The modified polymer was reprecipitated from methanol into ethyl acetate. PSMA-0 was prepared reacting 4.0 g of PSMA with 3.0 ml (0.022 mol) of hexylamine in *N*-methylpyrrolidone (40 ml) at 100 °C for 5 h.

Sample preparation. Thin copolymer films were prepared by spin coating from chloroform solutions, for optical studies on fused silica substrates. Polymer LEDs with a hole-injecting indium-tin-oxide (ITO) electrode and an electron-injecting aluminium electrode were fabricated. In this case the polymer layers were spin-coated on ITO substrates covered with a thin layer of poly[3,4-(ethylenedioxy)thiophene]/poly(styrenesulfonate) (PEDT:PSS). Finally, 60-80 nm thick top aluminium electrodes were vacuum-evaporated on the top of polymer films to form LEDs with typical active areas of 4 mm^2.

Electroluminescence and photoluminescence measurements. Electroluminescence (EL) and photoluminescence (PL) spectra were measured using a home-made spectrofluorometer with single photon-counting detection (SPEX, RCA C31034 photomultiplier). LEDs were supplied from a Keithley 237 source measure unit, which served for the simultaneous recording of the current flowing through the sample. PL spectra were taken perpendicular to the sample surface and the incidence angle for the excitation beam was 30° relative to the sample surface normal to minimise reabsorption. 300 W Xe lamp (Oriel) was used as the excitation source. The measured EL and PL emission spectra were corrected for the spectral response of the detection system. Current-voltage and luminance-voltage characteristics were recorded simultaneously using the Keithley 237 source measure unit and a silicon photodiode with integrated amplifier (EG&G HUV-4000B) for the detection of total light output. A voltage signal from the photodiode was recorded with a Hewlett Packard 34401A multimeter. The LED characteristics were measured in a vacuum chamber to prevent any electrode degradation. PL and absorption measurements were performed under ambient laboratory conditions.

Results and Discussion

The amidation reaction of the anhydride groups in PSMA with Oxad-NH_2 is slow. In first experiments under mild conditions, we reached very low contents of oxadiazole-modified copolymer (0.10 mol % relative to anhydride groups). Increasing the reaction time and temperature (Table 1), we reached 1.22 mol % of oxadiazole units in copolymer. This means that approximately 25 % of the feeded (5 mol %) amount of Oxad-NH_2 reacted with the anhydride copolymer. The oxadiazole content in copolymers was determined by UV-vis spectrometry in methanol (Figure 2), assuming that the molar absorption coefficient of oxadiazole structure unit in copolymer is the same as that of Oxad-NH_2 (ε_{328} = 36 500 L mol^{-1} cm^{-1}). On the other hand, the reaction of hexylamine with anhydride groups was quantitative. Analyses of FT IR spectra of PSMA-1 – PSMA-4 revealed that all anhydride group signals (1858, asym C=O; 1778, sym C=O; 1224, 922, C-O-C stretching; cm^{-1}) disappeared giving rise to those of COOH (1700, C=O stretching; 1400, O-H bending; cm^{-1}) and amide (3061, N-H stretching; 1640, C=O stretching amide I; 1563, N-H bending amide II; cm^{-1}) groups.

Table 1. Reaction of PSMA with Oxad-NH_2 and hexylamine (100 °C, 5 h)

Copolymer	Temperature °C	Reaction time h	Oxadiazole content [a)] mol %
PSMA-0 [b)]	-	-	0.00
PSMA-1	100	2	0.10
PSMA-2	135	24	0.84
PSMA-3	135	48	1.04
PSMA-4	135	72	1.22

[a)] Calculated relative to anhydride groups.
[b)] The copolymer modified with hexylamine only.

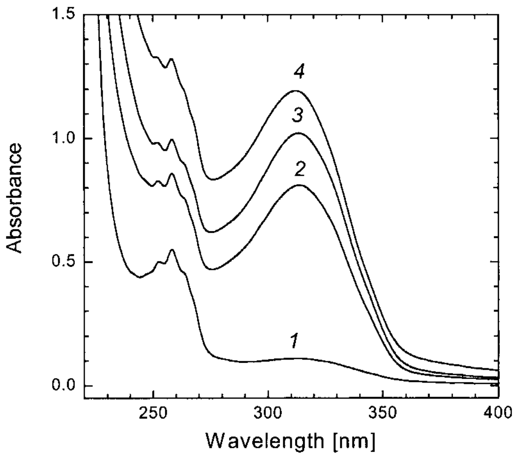

Figure 2: UV-vis spectra of PSMA copolymers modified with Oxad-NH_2 in methanol (c = 0.80 g/l, 1 cm): *1* PSMA-1, *2* PSMA-2, *3* PSMA-3, *4* PSMA-4

Electric properties of single-layer ITO/polymer/Al samples were studied. Typical dependences of the current on the applied electric field are shown in Figure 3a. It is evident that the current depends strongly on the content of oxadiazole units in the modified polymer. Significant changes in the current density were already observed in the PSMA with a low content of oxadiazole units. In comparison with PSMA-0 devices, in PSMA-1 devices (0.10 mol % of oxadiazole units) one order of magnitude higher currents and in PSMA-4 devices (1.22 mol % of oxadiazole units) more than two orders of magnitude higher currents were measured. Shapes of the electric characteristics indicate that both transport and injection properties are modified.

Recently, we have shown that the EL efficiency and time stability of polyfluorene-based LEDs were improved in blend LEDs made of poly(9,9-dihexadecylfluorene-2,7-diyl) (PFC16) and polysilane.[8] The increase in the EL efficiency was attributed to modification of the charge transport and recombination in the blend. As shown above, changes in the oxadiazole content in modified PSMA changed dramatically transport properties; therefore we tested new polymers in blends with luminescent PFC16. We succeeded in fabrication of blue light-emitting devices using a blend of PSMA-4 and PFC16. An example of electroluminescence spectrum of the ITO/PEDT:PSS/PFC16+PSMA-4/Al is shown in Figure 3b. Compared with the devices fabricated from neat PFC16, an improvement of the EL efficiency and stability was achieved and lower onset voltages were observed in the blend devices.

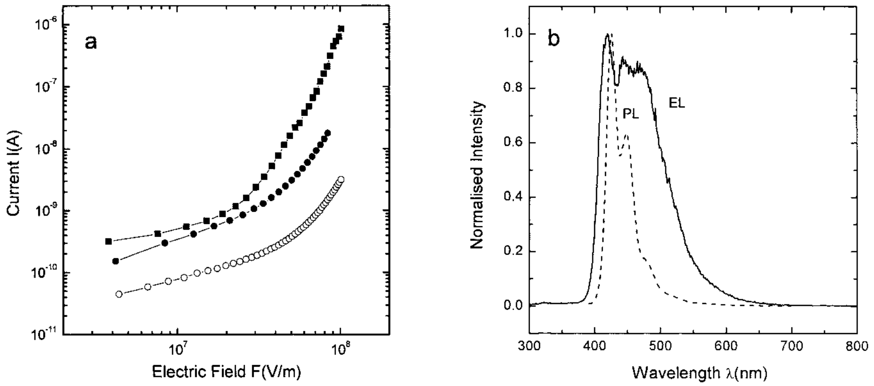

Figure 3: (a) Current-electric field characteristics for the ITO/PSMA-0/Al (open circles), ITO/PSMA-1/Al (solid circles) and ITO/PSMA-4/Al (solid squares) samples. (b) Photoluminescence and electroluminescence in the blend made of copolymer PSMA-4 and luminescent SPFC16 LED: ITO/PEDT:PSS/PFC16+PSMA-4/Al

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