ORGANIC POLYMER LEDS WITH MOBILE AND IMMOBILE IONS

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Abstract: The syntheses of partially conjugated alkoxy substituted Poly(p-phenylenevinylene) (PPV) materials with tertiary amines and cationic species covalently bound to the polymer backbone are described. The amine/cationic species are introduced via a polymer analogous reaction of a functional alcohol and the chloro-precursor polymer. Single layer, polymer light emitting diodes (PolyLEDs) , prepared with the modified polymer materials show a strong 'burn-in' effect, leading to very high electroluminescence (EL) quantum efficiencies especially with higher workfunction cathodes.

Introduction

After the introduction of polymers as the active, light emitting layer in light emitting diodes (LEDs) (Ref. 1) a growing interest has developed in this field (Ref. 2). Often mentioned attractive properties of polymeric materials, such as good processibility and mechanical stability are obvious advantages over low molecular weight materials. Another interesting possibility, unique to the macromolecular systems, is the fact that multiple functionality's can be easily combined in one single polymer molecule. Recently a polymer light emitting cell (LEC) was introduced, in which a mixture of a (photo)luminescent polymer, low molecular weight salt and poly(ethylene oxide) is the active layer of the device (Ref. 3). If (molecular) mixing of certain species in an organic film is needed, it is often advantageous to couple them to a polymeric backbone, in stead of applying them as an additive. Especially if demixing, crystallization or phase separation may occur, or if there are large differences in properties such as solubility, melting points, etc. attaching the additives to a polymeric backbone can facilitate the processing of such complex mixtures.

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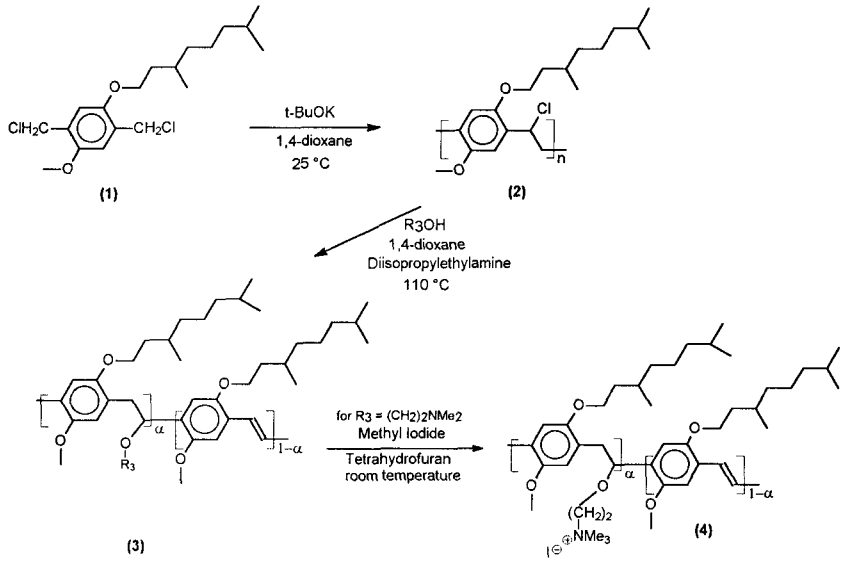
Here, we present materials with cationic species covalently bound to the polymer backbone. The ionic species are introduced via a polymer analogous reaction according to scheme 1.



Scheme 1. Route to modified polymers

Experimental

General. All reactions were carried out under a nitrogen atmosphere in standard glassware, which was dried in an oven at 150 °C before use. Solvents were purified before use by distillation.

Polymer Synthesis. In a typical experiment, a 500 ml three-necked flask with magnetic stirring bar, was filled with 6 mmol of monomer (1) dissolved in 400 ml of dry dioxane. The solution was heated to 30°C and a solution containing 6 mmol potassium *tert*-butoxide (*t*BuOK) in 100 ml of dry dioxane was added slowly with stirring. The polymer which was formed, is the non-conjugated chloro-precursor (2). To obtain the modified polymer (3), 0.2 mol of 3-dimethylamino-1-ethanol (or of another functional alcohol) was added to the solution. Also 5 ml of diisopropylethylamine was added as a base. The solution was heated under nitrogen at 110°C for 20 hours. Polymer (3) is obtained with 10 % of dimethylaminoethoxy-substituents on the backbone. After cooling, the polymer was precipitated in methanol, filtered, washed with methanol and dried under vacuum.

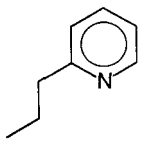
Alkylation. After dissolving polymer (3) in THF, 2 g of methyl iodide was added, and the solution was stirred for 1 h at room temperature in the dark. Precipitation in hexane gives polymer (4).

Devices. 'Standard' devices were prepared on ITO-covered glass substrates by spincoating of a polymer solution. Polymer layers were 100-150 nm thick. Cathode materials were deposited using standard thermal evaporation techniques.

Results and Discussion

In a previous paper the synthesis of partially conjugated alkoxy-PPV was described (Ref. 4). According to this procedure, initially the chloro-precursor polymer is formed, which is heated in the presence of methanol. During this thermal dehydrochlorination reaction, part of the chlorine atoms on the backbone are substituted by the alcohol, leading to a partly conjugated polymer material. This polymer analogous reaction works also for other (primary) alcohols, and is therefor a versatile way to prepare PPV-materials with special functionality's. A broad range of functional groups can be introduced in the polymer in this way. Here we focus on the introduction of the tertiary amine functionality. In Table 1, a list of the polymers described here is given.

Table 1. List of modified polymers (3)

R_3	Polymer number	α	other
	3(a)	0.08	n=2
	3(b)	0.03	n=3
	3(c)	0.07	n=3
	3(d)	0.18	n=3
	3(e)	0.07	n=6
	3(f)	0.05	n=11
	3(g)	0.08	
Me	3(h)	0.10	

Single-layer devices were prepared with the modified polymers (4a-g), using (one of) three different electrode materials: Ca, In and Au. External quantum efficiencies for two of the modified polymers (3/4(a) and of a reference material, modified with methoxy groups (3h), is shown in table 2.

Table 2. Maximum external quantum efficiency of LEDs with different cathodes

polymer	Maximum External EL Efficiency (% photons/electron)		
	Ca	In	Au
3(a)	1.1	1.1*	0.25*
4(a)	1.2	1.3*	1.1*
3(h)	1.1	0.16	<0.01

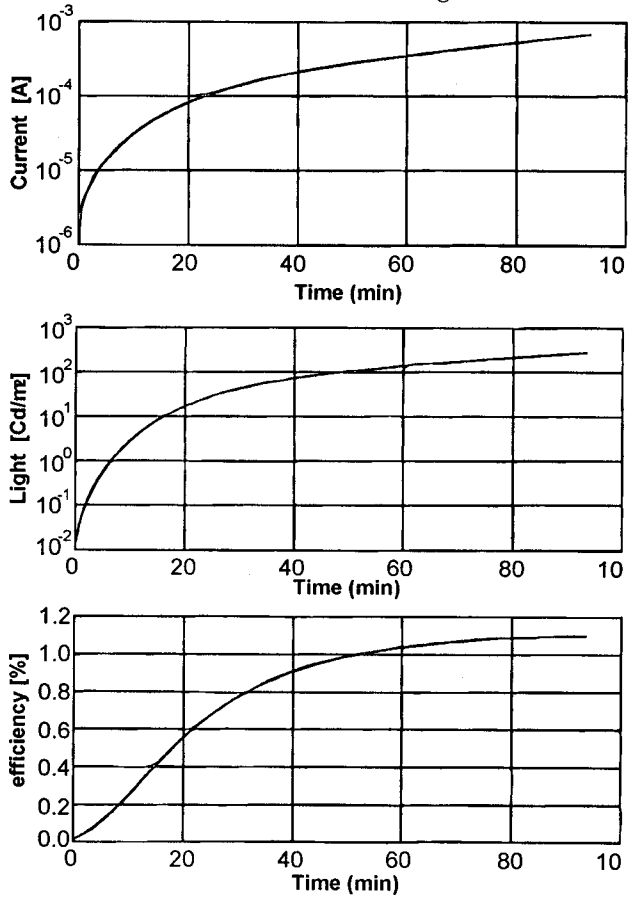
* after 'burn-in'

As expected, devices prepared with the reference polymer 3(h) show electroluminescence yield which is strongly dependent on the cathode material (Ref. 5). This is generally interpreted as a consequence of the difference in work function of the cathode, leading to a larger barrier for the injection of electrons. However, the workfunction of the metal is defined, and measured in vacuum with ultraclean surfaces. This is not the case in a polymer LED, which means that large deviations can occur in the actual situation. The presence of a polymer layer on the electrode surface may influence its 'workfunction' to a large extent. An analogous situation is found in electrochemistry, where it is a well known fact that the redox potential of a metal is strongly dependent on the presence or absence of certain ligands or ions, eg.

Ag^+	+ e^- <--->	Ag		+ 0.799 V (vs. stand. hydrogen)
$Ag(NH_3)_2^+$	+ e^- <--->	Ag + 2 NH_3		+ 0.373 V
AgI	+ e^- <--->	Ag + I^-		- 0.152 V

In our modified materials, we have introduced moieties that can act much in the same way, thus changing the actual 'workfunction'/redox potential of the cathode material.

Figure 1. Characteristics of freshly prepared device (polymer 4(a), 3x3 mm) with gold cathode driven at constant voltage



This is reflected in the behavior of the LEDs prepared with the modified polymer materials 3/4(a-g). Initially their behavior is much like the reference material 4(h), but they show a strong 'burn-in' effect, especially with higher workfunction cathodes. Figure 1 shows the time dependency of the device characteristics for a freshly prepared LED (size 3x3 mm) of polymer 4(a), with a gold cathode, driven at a constant voltage. A strong increase of current, light output and EL quantum efficiency is observed. In case of the polymers (4) the diffusion of the mobile anions away from the interface with the cathode compensates for the injected charge, leading to higher currents at constant voltage. The enhanced field at the interface facilitates charge injection. As a consequence, the efficiency can increase over several orders of magnitude (Ref. 6). No changes were found in the UV/VIS absorption spectrum of the polymer layer however, suggesting that apparent changes in the material are localized on the interface with the electrode(s).
The substitution of calcium as a cathode material with indium or gold has a strong influence on the (ambient) lifetime performance of the (non-encapsulated) device, and especially shelf life is drastically improved if the use of air sensitive metals can be avoided. After six months storage in air the devices did not show any degradation.

Conclusions

The introduction of functional groups in PPV can be easily achieved by a polymer analogous reaction on the chloro-precursor. Modification of the material with tertiary amine or cationic moieties leads to materials with distinctly better performance when used as the active layer in a single layer polymer LED with air stable electrodes.

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