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Synthesis of a Novel Blue- light- emitting Polymer Material Bearing Coumarin Pendants

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Abstract: A novel blue luminescent polymer bearing coumarin pendants was prepared. Its luminescent properties were determined indicating that it had strong blue fluorescent properties and good film formation ability. This novel polymer can be used as a blue organic electroluminescent material (OELM) in organic electroluminescent devices.

Keywords: Synthesis, coumarin, fluorescence, polymer, blue organic electroluminescent material.

Since the pioneering work of C. W. Tang *et al*[1]., which demonstrated efficient electroluminescent (EL) devices based on organic materials, many efforts have been devoted to explore new EL materials for display applications. Two distinct classes of the organic materials, namely small organic molecules and conjugated polymers have been developed for this purpose. Semiconducting (conjugated) polymers have served for photon applications; they have high fluorescence efficiencies (>60%), emit at wavelengths that span the entire visible spectrum. They are mechanically flexible, and can be deposited as uniform thin films by casting from solution. Since the fabrication of the first polymer light emitting diode (LED) in 1990[2], there has been extensive research on polymer LEDs and many improvements have been made[3-7]. Although much progress has been achieved on organic electroluminescence device (OELD), there are still some defects, such as: both the efficiency and stability of blue and red OELDs are not good. The design and synthesis of new blue and red OELMs with better device structures were the key problems.

Coumarin and its derivatives have excellent fluorescent property with high photoluminescence (PL) quantum efficiency. They are widely used as fluorescence dyes or laser dyes. Coumarin and most of its derivatives are strongly fluorescent in liquid solutions, but they are easily quenching in solid state, so coumarin and its derivatives as electroluminescent materials always need doped in polymer host. However this fabrication method could not prevent the crystallization of coumarin molecule, which affects the device's lifetime. We introduce coumarin to the side chains of the polymer. By this method the phenomena of fluorescent quench and the instability of the OELDs, which caused by the crystallization of coumarin, were avoided.

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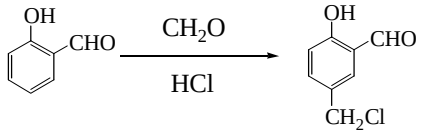
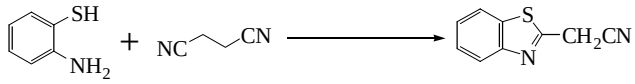
We designed and synthesized coumarin-CPA according to **Scheme**. It was shown that it can emit pure blue light, and has a good film formation. Its photoluminescence properties were studied as shown in **Table 1**. Its strong PL showed that it could be used as a blue OELM.

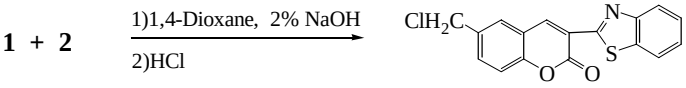
Scheme Synthesis of coumarin-CPA



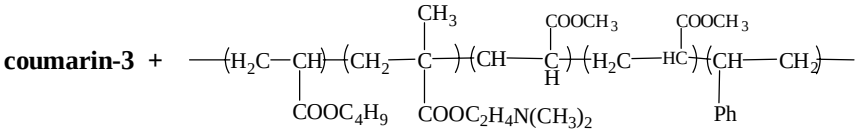
1



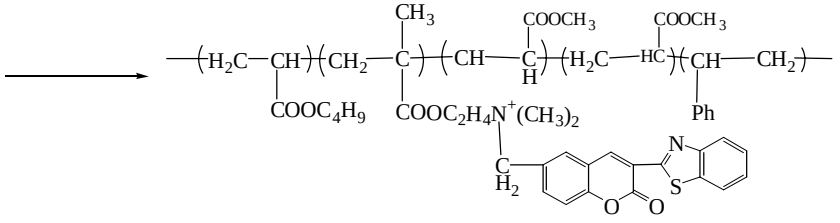
2



coumarin-3



CPA



coumarin-CPA

Experimental

2-Aminothiophenol was purchased from Aldrich Chemical Co. and used without further purification. The solvents were dried and distilled. The copolymer of PMMA (CPA),

which had the characteristics of Mn=5493, Mw=14038, Mp=10686, σ =2.555, cont.10-15% hydroxyl and 10% dimethylamine, was supplied by Prof. De Ben CHEN of Department of Chemistry, Sichuan University. **1**, **2** were synthesized according to literatures[8,9]. 3.5 g (20 mmol) **2**, 3.4 g (20 mmol) **1**, 30 mL anhydrous 1,4-dioxane were mixed. At 35°C, 2 mL 4% sodium hydroxide solution was added and stirred for 5 minutes. Then 35% 30 mL hydrochloric acid were added and refluxed for 1 h. After cooling to room temperature, to the mixture 100 mL water was added. The mixture was filtered and washed with water until pH was 6-7. 3.2 g yellow powder crude product was obtained after drying. It was purified by column chromatography on silica gel, eluting with: chloroform : benzene : THF (2:2:1). 2.2 g (33.5%) coumarin-3 as yellow crystals was obtained, mp 239-240°C. Elemental analysis calcd for $C_{17}H_{10}ClNO_2S$: C, 62.29; H, 3.07. Cl, 10.82; N, 4.27; O, 9.76; S, 9.78; Found: C, 62.24; H, 3.10; Cl, 10.89; N, 4.31; O, 9.73; S, 9.73.

1 g CPA and l00 mg coumarin-3 were dissolved in 50 mL anhydrous THF. 100 mg anhydrous sodium carbonate was added, stirred and refluxed for 33 h until TLC analysis showed that the fluorescence of coumarin-CPA did not increase any more. The mixture was filtered. The solvent was removed. The residue was dissolved in benzene, and petroleum ether was added to precipitate brown-yellow product. This process was repeated until TLC analysis showed that the fluorescence in filtrate disappeared. coumarin–CPA was dried in vacuum. 0.4 g brown-yellow final product was obtained. IR (KBr, cm^{-1}): υ (cm^{-1}): 3560~3300 (br: O-H), 3027 (ph-H), 2959 (C-H), 2400~F2800 (NC), 1725 (C=O), 1458 (C-H), 1165 (C-O), 763, 701 (δ ph-H).

Results and Discussion

The coumarin-3 has a plane structure, which causes a strong intermolecular interaction, thus fluorescence was quenched in solid state. We introduced coumarin-3 to the amino ester side chains of CPA, which is a copolymer of butyl acrylate, methyl acrylate, dimethylaminoethyl methylacrylate, hydroxyethyl arcylate and styrene. Thus, the containment of coumarin can be controlled; the fluorescence quench can be avoided. Morever, the coumarin-CPA contains many hydrophilic groups such as hydroxyl, ester and amine group, which can improve the adhesive to the glass or indium-tin oxide (ITO). Because PL has almost the same mechanism to EL, we investigated the fluorescent properties of the cumarin-3 and coumarin-CPA with their EL spectra.

Table 1 Photoluminescence property of coumarin-3 and coumarin-CPA
(λ_1:in chloroform solution ; λ_2:Solid state)

	coumarin-3		coumarin-CPA	
	λ_1	λ_2	λ_1	λ_2
λ_{Exmax}(nm)	432	418	380	370
λ_{Emmax}(nm)	525	450	446	456

We can draw the conclusion that coumarin-CPA has good PL properties in both

solution and solid states. The light emission lies in blue region, so it can be used as blue OELM. When the solution of coumarin-CPA was cast, it could form a quite smooth and good film.

In summary, this novel polymer material bearing coumarin pendants has good fluorescence and film-forming ability. It can be used to fabricate OELDs by spining.

Acknowledgment

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