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Luminescent Properties of a Silicone-Carbazolyl Polyfluorene Hybrid Material for Device Applications

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Summary: In the present work, bilayered hybrids obtained by hydrosilylation of polysiloxane with carbazolyl moieties (Sil-Cz) and polyfluorene (Sil-PFO) had their photophysical behavior, morphological characteristics and interaction properties studied for applications in electroluminescent devices. Fluorescence spectra of the Sil-Cz did not show emission in the excimer/aggregate region (from 400 to 500 nm). This is an unexpected behavior since most of the carbazole-based materials present excimer and aggregation. Nonetheless, this unusual observation was also predicted by geometry optimization calculations. Fluorescence spectra were taken for both compounds separately and for the bilayered system show some evidence of interaction between carbazolyl and polyfluorene moieties, giving rise to the supposition that the can form a system with tunable luminescent properties.

Keywords: carbazole; hybrid materials; polyfluorene; silicone

Introduction

Silicones form a wide class of silicon-oxide based polymers with excelent thermal and oxidative properties, low surface tension, high flexibility, high chemical stability and very high adhesion on several substrates.[1] In general, silicones are neither photoluminescent nor electroluminescent materials. Hydrosilylation is one type of reaction which occurs under mild conditions[2] that can be used to prepare photoluminescent[3] as well as electroluminescent silicones. However, electroluminescent materials have shown poor performance in devices, so far.[4] Polyfluorene and its derivatives form a promissing class of materials for both electroluminescent and photovoltaic devices.[5,6] Electroluminescence from blue to red using polyfluorene polymers and copolymers have been prepared and tested.[7–11] However, in general the eletroluminescence efficiency of the polyfluorenes can be enhanced when a hole transport layer is introduced in the device.[12] One common hole transport injector is the polycarbazole and several electroluminescent devices using polyfluorene and polycarbazole have been reported.[13]

The eletroluminescence device performance is also very sensitive to the quality of the heterojunction between the electrodes and the polymer layers.[14] The electrical properties of this heterojunction can be improved by using a conductive polymer layer in between the metalic electrode and the polymeric active layer. The PEDOT:PSS mixture is often used with very good results.[15] Therefore, for a good electroluminescent device some requirements must be fullfilled: *(i)* metalic electrodes with adequate work function; *(ii)* an intermediate layer of a conductive polymer, *(iii)* a hole injection layer and *(iv)* an active layer with high electroemission efficiency. Thus, not only a good preparation of the devices are necessary, but also strategies for new materials.

In this work we describe the synthesis and photophysical properties of a new material with potential properties for electroluminescent applications. This new material has some special characteristics

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such as: good adhesion to the ITO anode provided by the silicone chemical attachment on the electrode surface. It contains a certain amount of carbazolyl groups bonded to the silicone chain which can act potentially as a hole injector and it also contains as an active medium one polyfluorene derivative. The photoluminescence properties of this material and the role of the temperature on the photophysical properties are described.

Experimental Part

Materials

Poly(methylhydrogen)siloxane ($Me_3SiO-(SiMeHO)_{65}(OSiMe_3)$ (Sil1107) $\overline{M}_n = 4{,}062\ g\ mol^{-1}$ was supplied by Dow Corning Inc. The hydrosilylation reaction was catalyzed by the platinum divinyltetramethyldisiloxane complex (platinum catalyst, 3–3.5% platinum concentration in poly(dimethylsiloxane) terminated by dimethylvinylsilyloxy groups (Gelest (Karlsruhe). The polyfluorene poly[(9,9-dioctyl-fluorenyl-2,7-diyl)-alt-co-(9,9-di-(5-pentanyl)-fluorenyl-2′,7′-diyl)] 99% pure was purchased from ADS; the 9-vinylcarbazole was purchased from Sigma-Aldrich. The ITO over glass was purchased from SPI Supplies. All materials were used as received.

Preparation of the Fluorescent Silicones

Carbazole or polyfluorene modified-polysiloxane were prepared by hydrosilylation reaction from poly(methylhydrogensiloxane) and vinyl derivatives.[3] Carbazole modified-polysiloxane containing 0.2% m/m in carbazole (Sil-Cz) and polyfluorene modified-polysiloxane containing 1% m/m (Sil-PFO) were prepared, using a Pt-based catalyst under vigorous shaking and at controlled temperature of 30 °C in oil bath in similar procedures. The first step consists of the complex formation of the catalyst and the vinyl group (carbazole or polyfluorene), which takes place in a range of 20 min. A drop of the polysiloxane containing the dissolved Pt is added to a dilute solution of the chromophores in THF. These systems are stired for 20 min, at 30 °C. Then, the Si–H contaning polysiloxane (Sil1107) is added to these systems, to give the products of both paralel reactions: addition of the chromophore and the crosslinking process. This step in carried out in inert atmosphere (N_2 flux). These modified polysiloxanes were deposited on ITO-Glass substrates by spin-coating to give a translucid film. The total cure of the polysiloxane and its surface attachement is completed in a vacuum chamber, at 60 °C, for 72 h.

Methods

Steady-state fluorescence spectra were recorded in a range of temperatures from 20 to 410 K, with interval of 10 K, following the experimental procedure describe elsewhere.[16] Relaxation processes are evidenced on slope changes on Integrated Spectral Area x T plots.[17–19]

Because the photophysical properties are strongly dependent on the intrachain interactions, we estimated the geometry of some of the oligomers to add some insights about the photophysical behavior, using semi-empirical molecular orbital calculations carried out with the HyperChem 8.0 software.[20–22]

Results and Discussion

Polymer Characterization

Degradation and relaxation temperatures for these polysiloxanes were obtained by Thermogravimetric analysis (TGA) and Differential Scanning Calorimetry (DSC), respectively. Total degradation occurred around 913 K, while glass transition occurred at the range of 170 to 200 K and melting of the primer siloxane is at 240 K. For the crosslinked materials, this endothermic peak is not well defined in the heat flow curves.

Obtained materials were also characterized by FTIR spectroscopy. Particular changes in transmitance bands show the sucess of the reacting process, as the decrease of intenssity after reaction of the

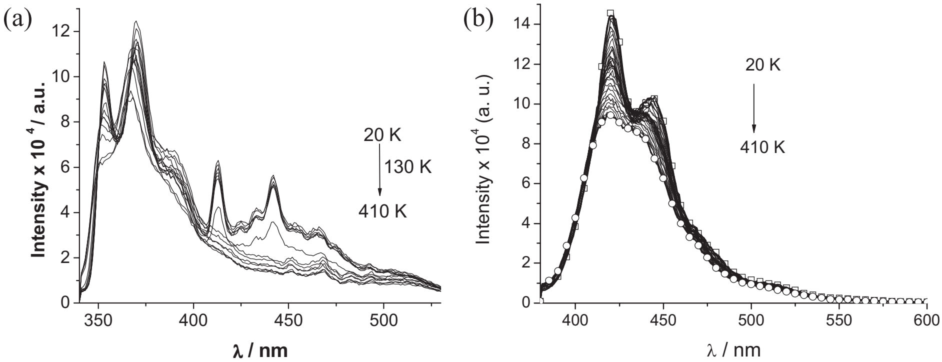
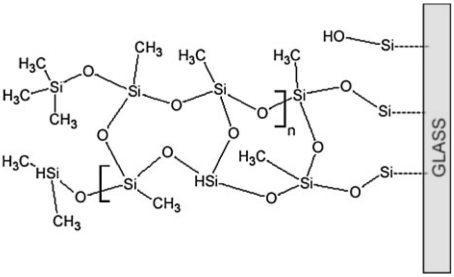


Figure 1.
Fluorescence spectra of Sil-Cz (a) $\lambda_{exc} = (330\,nm)$ and Sil-PFO (b) $\lambda_{exc} = (370\,nm)$ at several temperatures from 20 to 410 K.

band at 1261 cm^{-1}, related to tha δ C–H deformation characteristic of $Si-CH_3$ groups and of the band at 2175 cm^{-1}, due to Si-H stretch, which must be replaced for Si–O linkages in the chromophore attachment and crosslinking processes.

The undergoing reactions in these systems are: *(i)* the attachment of the chromophores to the main chain of the silicone, *(ii)* the crosslinking of the backbone[2] and *(iii)* the attachment of the polysiloxane to the ITO/Glass surface. Although the reaction takes place in an organic solvent, there is some amount of water dissolved into the polymeric material that acts as a reactant.[1] Its presence leads to the crosslinking process through nucleophilic attack to the Si–H bonds in the presence of the Pt catalyst, leading to the formation of Si–OH, with the releasing of $H_{2(g)}$, as a competitive process to hydrosilylation. This new Si–OH group can react with Si–H bonds to form Si–O–Si crosslink bonds.[2] A similar process occurs between the Si–H of the polysiloxane and the Si–OH and/or ITO–OH on the substrate surface, leading to the attachment of the polymeric film to the substrate, as shown in the cartoon.



Scheme 1.
Cartoon representing the chemical attachment of the silicone to the ITO surface.

Photophysical Properties

The emission spectra of the silicone-based polymer containing carbazolyl moieties (Sil-Cz) have two set of bands at lower temperatures; the higher intensity and higher energy band was attributed to the fluorescence, the lower intensity and low lying emission was attributed to the phosphorescence (Figure 1). No excimer band was observed neither at lower nor at higher temperatures, indicating that the carbazolyl groups cannot be overlapped.[23] This behavior is different from that observed for polyvinylcarbazole and other carbazolyl-containing polymers[22] as shown in an earlier study on a poly(methyl methacrylate)-carbazolyl based polymer (PMMA-Cz) for which excimeric and aggregates emission are present.[16] For the present material as for the former PMMA-Cz, phosphorescence is completely suppressed at temperatures higher than 130 K.

Figure 1a shows fluorescence spectra of Sil-Cz recorded at the temperature range from 20 to 410 K. The spectral pattern

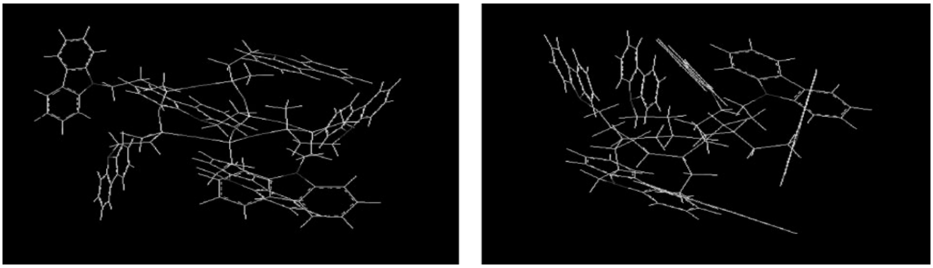


Figure 2.
Simulated structure of silicon-carbazolyl and carbon-carbazoyl based copolymers.

present a vibronic peak at 350 nm, another at 370 nm, with a shoulder at around 390 nm, very similar to those obtained for carbazole derivatives in diluted solutions. As shown, no evidence for important excimer/aggregate emission is observed, an unusual behavior for the polymeric materials containing carbazole moieties attached or doping agent, even at low concentration.

Because of the absence of the excimer/aggregate species, and in order to obtain some insights about the geometry of the Sil-Cz which prevent the excimer emission, we carried out the modeling of two structures with the same number of the carbazolyl units: one with a silicon-based structure and other with a carbon-based structure (Figure 2). As we can see, carbazolyl moieties can not form excimer species in the silicone-based polymer but they are expected to occur when present in aliphatic materials.

A reasonable explanation for these optimized geometries is that, due to the long Si–O–Si bond length, the carbazolyl moieties are not close enough to form aggregates, indicating that there is a competition between electronic attraction/repulsion forces and bond lengths/freedom of rotation. This assumption is reinforced by the data obtained from the geometry optimization of a theoretical aliphatic chain containing the carbazolyl moieties which form both excimer and ground-state aggregates.

The fluorescence spectra of the silicone-based polyfluorene are shown in Figure 1b, for several temperatures from 20 K to 410 K. The emission profile is similar to that of other polyfluorenes,[6,8,17] showing a vibronic 0–0 peak at 414 nm and a 0–1 peak at 436 nm. Although the spectral profiles are similar to those obtained for the polyfluorene films, these peaks lay in a slight higher energy, with vibronic peaks 7 nm blue-shifted.[18,19,22] Also, there is a lack of vibronic structure at higher temperatures, as expected.

The fluorescence spectra of the silicone-carbazolyl/ silicone-fluorene bilayered system are shown in Figure 3. It shows two distinct and structureless bands, one at 370 and the other at 440 nm. Although structureless, these bands lay in the same region of emission of the isolated silicone-based polymers Sil-CZ and Sil-polyfluorene (Figure 3). The lack of the vibronic structure indicates that there is a greater micro-heterogeneity around every group

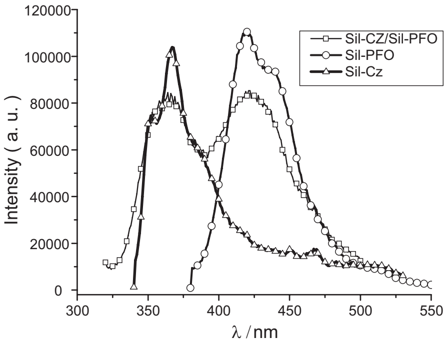


Figure 3.
Fluorescence spectra of Sil-Cz (Δ), of Sil-PFO (o) and of the Sil-Cz/Sil-PFO (□). ($\lambda_{exc} = 330$ nm).

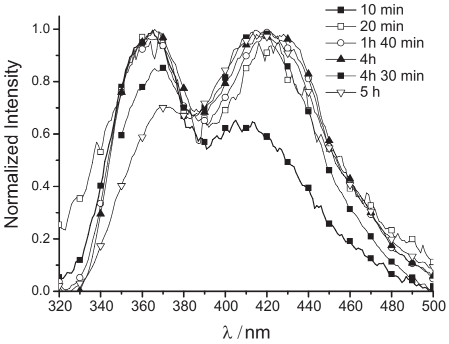


Figure 4.
Fluorescence spectra ($\lambda_{exc} = 310$ nm) obtained at a range of time, for the bilayer system of Sil-Cz/Sil-PFO on ITO (film thickness = 280 nm).

producing an inhomogeneous broadening. This micro-heterogeneity is produced by several reasons that may include a variety of the main-chain conformations and by the crosslinking of the back-bone confining some, but not all, of the moieties and by the interpenetration of both bilayers generating zones with greater density. This interpenetration also may enlarge the carbazolyl-polyfluorene distance distribution, allowing some energy transfer between those molecules which are within the Förster radium.

Evidences for the possibility of energy transfer between carbazolyl groups and polyfluorene groups were obtained following the time evolution of the reaction. As the reaction progresses and more polyfluorene is incorporated in the chain, the relative intensity of the carbazolyl groups ($\lambda_{em} = 310$ nm) decreases when compared with the polyfluorene emission ($\lambda_{em} = 560$ nm), as shown in Figure 4. Time-resolved experiments to evaluate the mechanism of the energy transfer either trivial or non-radiative processes are in progress.

Conclusion

New silicone-based luminescent hybrid polymers were obtained and had their photophysical characteristics studied. Fluorescence spectra obtained for Sil-Cz are similar to those obtained for others carbazolyl-based materials, although it does not present excimer emission. This unusual observation is also supported by optimal geometry calculations on the polysiloxane containing carbazolyl moieties attached to its chains, in which aggregation was not predicted to occur. Fluorescence spectra obtained for Sil-PFO present the same spectral profile of the isolated PFO, although the vibronic bands are 7 nm blue-shifted. This shift can be related to the effect of the attachment of the chromophore to the silicone and can be due to a minor degree of aggregation achieved at the attachment.

Fluorescence spectra taken from the bilayered system formed by a layer of Sil-Cz over a layer of Sil-PFO, both deposited on ITO, at a range of times from 10 min to 5h 30 min of reaction, showed that there is a significant change on the spectral profile with time, indicating that the progress of the reaction (crosslinking and substrate attachment) affects the photophysics of the isolated polysiloxanes, which indicates a degree of interaction between two layers that can result in good total luminescent properties.

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