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Incorporation Of Yellow-Emitting Polyfluorene Into Silicone

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ABSTRACT

A novel yellow-emitting polyfluorene with pendant ethoxysilyl groups, PFBT-SiOEt, was prepared by Suzuki-Coupling reaction of 9,9-dihexylfluorene-2,7-bis(trimethyleneborate), 4,7-dibromo-2,1,3-benzothiazole, and 2,7-dibromo-9,9-bis(2-allyloxyethyl)-fluorene, followed by hydrosilylation reaction with dimethylethoxysilane. Solvent-free acid-catalyzed polycondensations of triethoxymethylsilane (TEMS) with silanol-terminated poly(dimethylsiloxane) (HO-PDMS-OH) were carried out in the presence of PFBT-SiOEt to obtain homogeneous silicone hybrids. UV-visible absorption and photoluminescence spectra of the hybrids suggested that the emitting polymer was homogeneously incorporated in silicone matrix retaining its optical properties.

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INTRODUCTION

Over the past decades, great efforts have been made to develop new π -conjugated polymers which are applied for organic light-emitting diodes, solar cells, field effect transistors, charge storage devices, biosensors, and actuators. We are interested in incorporation of emitting π -conjugated polymers into inorganic materials to develop a new composite material for optoelectronics applications. In previous work, we reported incorporation of hydroxy-introduced polyfluorene copolymers into silica to obtain emitting silica hybrids utilizing sol-gel technique.³

As part of our efforts to exploit a new series of hybrid material based on π -conjugated polymers, the aim of the present work is to incorporate emitting polyfluorene copolymers into silicone. Silicones have been widely used in various fields due to their elastic behavior, good thermal stability, low surface energy, and bio-compatibility. Recently, silicones have attracted considerable attention from light emitting diode (LED) manufacturers for use as encapsulants and lenses. Especially, yellow phosphor filled silicones are important materials for white LED. Since inorganic phosphor particles tend to settle out, one of the technical challenges is to ensure uniform mixing and dispersion of the binder and phosphor. Our idea is to hybridize emitting polymer with silicone to obtain a transparent luminescent material based on silicone. Since polyfluorene and silicone don't mix each other, our strategy for homogeneous mixing is simultaneous grafting of polydimethylsiloxane (PDMS) chains onto polyfluorenes and cross-linking of the introduced PDMS chains. In this study, we will report the preparation of yellow-emitting polyfluorene with pendant ethoxysilyl groups and its hybridization with silicone utilizing sol-gel technique.

Experiment:

In order to increase the compatibility between polyfluorene copolymers and PDMS, we intended to introduce ethoxysilyl functionality on the alkyl side chain. We designed yellow-emitting polyfluorene with pendant ethoxysilyl functionality, PFBT-SiOEt, as shown in Figure 1. Since ethoxysilyl functionality can participate in the sol-gel reaction with HO-PDMS-OH, grafting of PDMS chains onto polyfluorene will occur. Homogeneous hybridization is possible due to the formation of covalent bonding between emitting polymer and PDMS.

Terpolymerization of 9,9-dihexylfluorene-2,7-bis(trimethyleneborate), 7-dibromo-9,9-bis(2-allyl-oxyethyl) fluorine, and 4,7-dibromo-2,1,3-benzothia-diazole was carried out to obtain PFBT-allyl. The hydrosilylation reaction of PFBT-allyl with ethoxydimethylsilane was carried out in toluene using Karstedt's catalyst. The PFBT-SiOEt was purified by precipitation in hexane.

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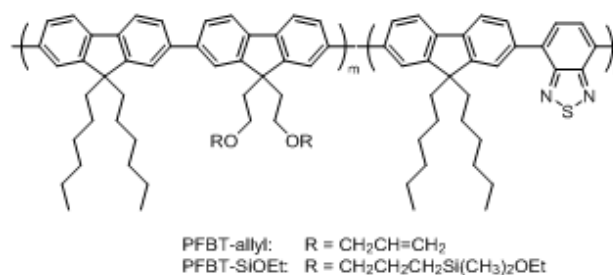


Fig. 1: Chemical structures of PFBT-allyl and PFBT-SiOEt.

Our idea for uniformly embedding polyfluorene in silicone matrix is to carry out solvent-free sol-gel reaction⁴ of HO-PDMS-OH and TEMS in the presence of polyfluorene with pendant ethoxysilyl groups. Simultaneous grafting of PDMS chain onto polyfluorene and cross-linking between the PDMS chains introduced on the polyfluorene will lead to three-dimensional network structure composed of emitting polyfluorene and PDMS. Although PFBT-SiOEt is not soluble in HO-PDMS-OH, it dissolved completely in the mixture of HO-PDMS-OH and TEMS to give a clear yellow solution. The sol-gel reaction was initiated with the addition of dibutyltin dilaurate to the reaction mixture to give silicone resin.

RESULT AND DISCUSSION

Table 1 summarizes the results of sol-gel reaction of HO-PDMS-OH and TEMS in the presence of PFBT-allyl or PFBT-SiOEt. In the case of PFBT-allyl, the organic polymer precipitated during the sol-gel process to give heterogeneous solid. Obviously, this is due to the lack of any physical or chemical interactions between PFBT-allyl and silicone. On the other hand, existence of ethoxysilyl groups was found to be effective for homogeneous hybrid formation to give a clear transparent solid (run 1 and 2), indicating that covalent bonding formation played an important role in increasing the compatibility between polyfluorene and silicone. (run 3).

Table 1: Results of Sol-Gel Reaction

run	polymer (mg)	appearance
1	PFBT-allyl (0.1)	phase separation
2	PFBT-SiOEt (0.1)	clear transparent
3	PFBT-allyl (0.5)	phase separation
4	PFBT-SiOEt (0.5)	clear transparent

Conditions: HO-PDMS-OH (MW, 400-700) = 2.0 g, TEMS = 4.8 g, (C₄H₉)₂Sn(OCOC₁₂H₂₅)₂ = 10 mg, Temp. = rt, Time 72 h.

Figure 2 shows UV-visible absorption spectra of pristine PFBT-SiOEt in THF solution and PFBT-SiOEt/silicone hybrid. There were no significant changes in the λ_{\max} between solution and silicone hybrid states, indicating no significant effect on the electronic structure of PFBT-SiOEt after hybrid formation. A slight red-shift of the absorption edge in silicone hybrid compared with that in diluted solution may be attributed to some aggregation or interaction of polymer chains.

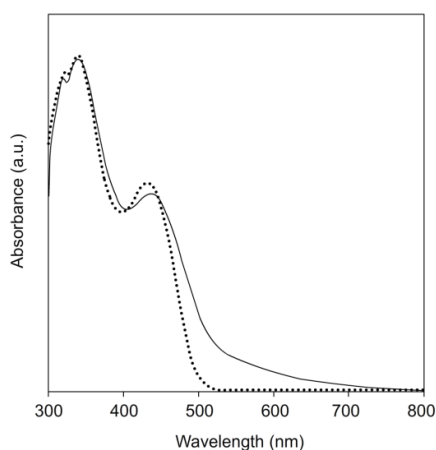


Fig. 2: UV-visible absorption spectra of PFBT-SiOEt in THF solution (dotted line) and PFBT-SiOEt/silicone hybrid (solid line).

The photoluminescence spectra of PFBT-SiOEt in THF solution and PFBT-SiOEt/silicone hybrid are shown in Figure 3. The emission of PFBT-SiOEt/silicone hybrid showed similar spectrum to that of PFBT-SiOEt in THF solution. The observed similarities in both absorption and emission spectra indicate that PFBT-SiOEt was successfully incorporated in silicone retaining its π -conjugated structure

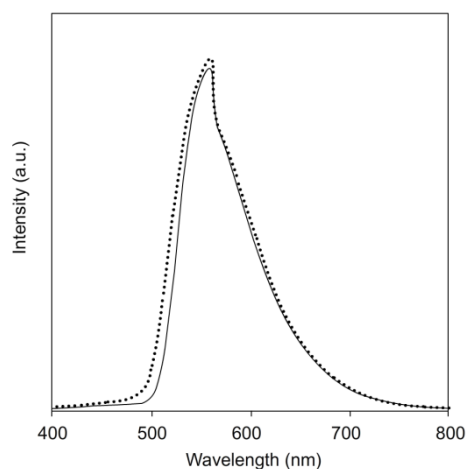


Fig. 3: Fluorescent spectra of PFBT-SiOEt in THF solution (dotted line) and PFBT-SiOEt/silicone hybrid (solid line).

Conclusion:

We have demonstrated that yellow emitting polyfluorene was successfully embedded in silicone matrix by using sol-gel reaction of TEOS and HO-PDMS-OH in the presence of PFBT-SiOEt. Since ethoxysilyl groups can participate in sol-gel reaction, simultaneous branching of PDMS chains onto polyfluorene and cross-linking between PDMS chains resulted in homogeneous hybrid retaining optical properties of the embedded emitting polymer. Transparent emitting silicone can be a new material for LED packaging.

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