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# Hybridization of Polyfluorene with Silicone Resin

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**ABSTRACT**

Novel polyfluorene carrying 2,1,3-naphthoselenadiazole unit with pendant ethoxysilyl groups,poly[2,7-(9,9-dihexylfluorene)-2,7-(9,9-bis(2-(3-ethoxydimethylsilyl)propoxyfluorene))-co-2,7-(9,9-dihexylfluorene)-4,7-(2,1,3-naphthoselenadiazole)] (PFNSeD-SiOEt), was prepared. Sol-gel reaction of tetraethoxysilane (TEOS) and silanol-terminated polydimethylsiloxane (HO-PDMS-OH) was carried out in the presence of PFNSeD-SiOEt to give PFNSeD-SiOEt/silicone hybrid. Fluorescent spectrum of the silicone hybrid revealed that emitting polymer was successfully dispersed homogeneously in the silicone matrix without aggregation.



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## INTRODUCTION

Conjugated polymers are attractive materials for application in electronic and optoelectronic devices. Among them, polyfluorene derivatives have been received great attention due to their charge transport properties, high emission quantum yield, reasonable thermal and chemical stabilities, and tunable emissions that depend on the chemical structure. We have successfully incorporated emitting organic polymers into silica to obtain organic/inorganic emitting materials (Kubo *et al*., 2005; Shoyama *et al*., 2006; Miyao *et al*., 2010).

As part of our efforts to exploit a new series of hybrid material based on π–conjugated polymers, we are interested in incorporation of emitting fluorene polymer into silicone. Silicones have been widely used in various fields due to their elastic behavior, good thermal stability, low surface energy, and bio-compatibility. Especially, silicones have attracted considerable attention from light emitting diode (LED) manufacturers for use as encapsulants and lenses. 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. Hybridization of emitting polymer with silicone will provide a transparent luminescent material for LED material. Recently, we prepared a novel yellow-emitting polyfluorene with pendant ethoxysilyl groups. However, SEM and TEM observation were not effective to confirm the complete mixing of the two components due to the very small amount of fluorene polymer in the silicone hybrid.

In this study, in order to check the homogeneous mixing, the hybridization of polyfluorene which incorporates naphthoselenadiazole (NSeD) moiety was investigate. Polyfluorenes which consists of naphthoselenadiazole units is reported to exhibit different emission spectrum between solution and solid states. Therefore, this copolymer can be used as an indicator to check the aggregation of macromolecules in silicone matrix by observing the emission spectrum.

## RESULT AND DISCUSSION

The synthetic pathway of PFNSeD-SiOEt was shown in Figure 1. Firstly, PFNSeD-allyl was prepared by Suzuki coupling reaction between 9,9-dihexylfluorene-2,7-bis (trimethyleneborate), 2,7-dibromo-9, 9-bis(2-allyloxyethyl)fluorene, and 4,7-dibromo-2,1,3-naphthoselenadiazole. Secondly, the pendant allyl group was converted to ethoxysilyl group by hydrosilylation with dimethylethoxysilane in the presence of Karstedtcatalystto obtain PFNSeD-SiOEt.

Hybridization of PFNSeD-SiOEt with silicone was carried out by solvent-free hydrolysis and polycondensation reaction (Alexandru *et al*., 2010) (Sol-Gel reaction) of tetraethoxysilane (TEOS) with silanol-terminated poly(dimethylsiloxane) (HO-PDMS-OH, MW = 400-700) in the presence of PFNSeD-SiOEt using dibutyltin dilaurate as a catalyst. The procedure is shown in Figure 2.

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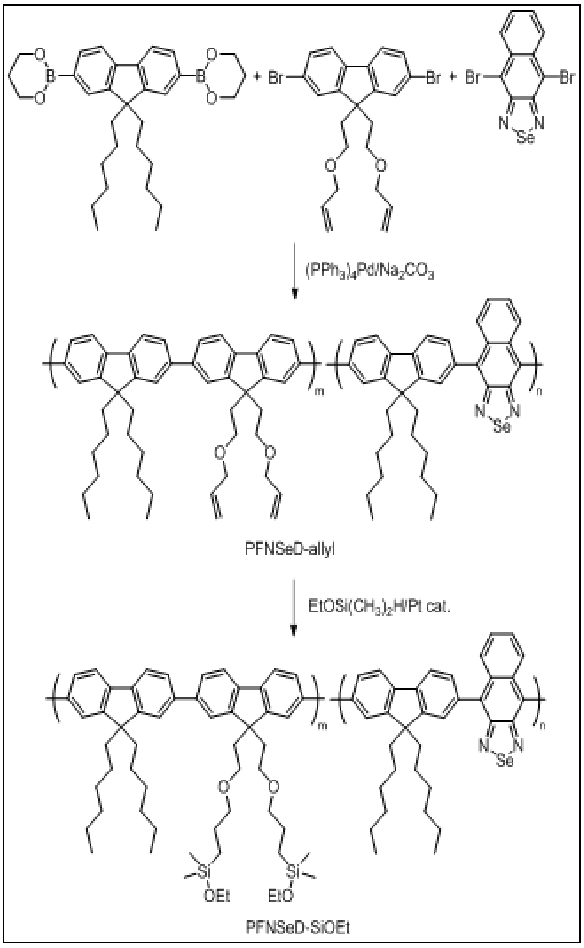


**Fig. 1:** Synthetic pathway of PFNSeD-SiOEt.

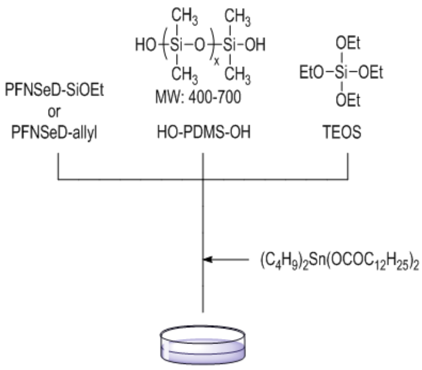


**Fig. 2:** Procedure of Hybridization.

For comparison, sol-gel reaction of TEOS and HO-PDMS-OH was carried out in the presence of PFNSeD-allyl instead of PFNSeD-SiOEt. 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 PFNSeD-allyl and PFNSeD-SiOEtare not soluble in HO-PDMS-OH, they dissolved completely in the mixture of HO-PDMS-OH and TEOS to give a clear yellow solution. In the case of using PFNSeD-SiOEt as an emitting polymer, the resulting hybrid was a clear transparent homogeneous solid. On the other hand, aggregation of polymer was observed when sol-gel reaction was carried out in the presence of PFNSeD-allyl. Obviously, this phase separation is because of the lack of any physical or chemical interactions between PFNSeD-allyl and silicone.

Figure 3 shows photoluminescent spectra of PFNSeD-SiOEt in THF solution, in solid stae (thin film), and PFNSeD-allyl/silicone. The spectra of PFNSeD-SiOEt in THF solution and PFNSeD-SiOEt/silicone exhibited similar emission profile. Both spectra consisted of two emission peaks at shorter wavelength (440 nm) and at longer wavelength (690 nm). The former emission is from fluorene moiety, and the latter is from naphthoselenadiazole moiety. The emission from solid PFNSeD-SiOEtexhibited only one emission peak at 690 nm. This is because of energy and/or electron transfer between chains in the solid state (Yang *et al*., 2004). This means that emitting PFNSeD-SiOEt molecules were immobilized in silicone matrix without aggregation. In other words, PFNSeD-SiOEt/Silicone is a homogeneous hybrid. Actually, the fluorescent color from PFNSeD-SiOEt/Silicone was purple which arise from the mixture of blue and red. While, red fluorescence was observed from PFNSeD-allyl/silicone due to the aggregation of polymers.

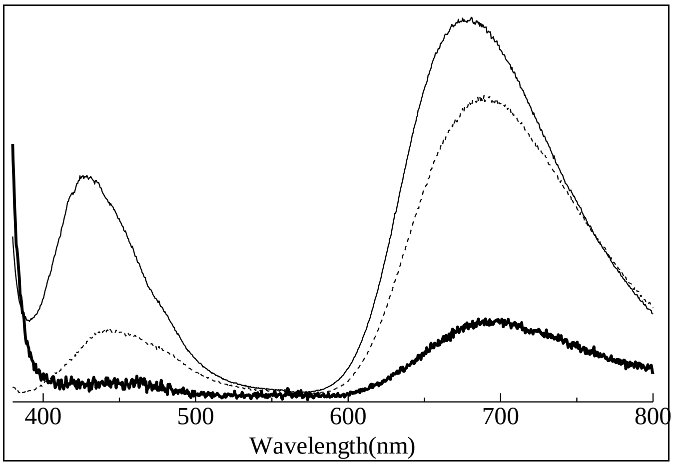


**Fig. 3:** Photoluminescent spectra of PFNSeD-SiOEt in THF solution (dashed line), in solid state (thin film) (thick line), and PFNSeD-SiOEt/silicone (solid line).

*Conclusion:*

We have demonstrated that emitting polyfluorene was successfully embedded in silicone matrix by usgging sol-gel reaction of TEOS and HO-PDMS-OH in the presence of ethoxysilyl-functionalized polyfluorene. Since ethoxysilyl groups can participate in sol-gel reaction, simultaneous branching of PDMS chains onto polyfluorene and cross-linking between PDMS chains led to homogeneous hybrid formation. Emission spectra from the silicone hybrid indicated homogeneous mixing of emitting polymer and PDMS.

## REFERENCES

Alexandru, M., M. Cazacu, A. Nistor, V.E. Musteata, I. Stoica, C. Grigoras and B.C. Simionescu, 2010. "Polydimethylsiloxane/Silica/Titania Composites Prepared by Solvent-Free Sol-Gel Technique", *Journal of Sol-Gel Science Technology*, 56: 310-319.

Kubo, M., C. C. Takimoto, Y. Minami, T. Uno, T. Itoh and M. Shoyama, 2005. "Incorporation of π-Conjugated Polymer into Silica: Preparation of Poly[2-methoxy- 5-(2-ethylhexyloxy)-1,4-phenylenevinylene]/ Silica and Poly(3-hexylthiophene)/Silica Composites," *Macromolecules*, 38: 7314-7320.

Miyao, A., Y. Mori, T. Uno, T. Itoh, T. Yamasaki, A. Koshio and M. Kubo, 2010. "Incorporation of Fluorene-Based Emitting Polymers into Silica", *Journal of Polymer Science: Part A: Polymer Chemistry*, 48: 5322-5328.

Shoyama, M., K. Inoue, T. Uno, T. Itoh and M. Kubo, 2006. "Emission from Silica Hybrid Containing RGB Fluorescent Conjugated Polymers", *Polymer Bulletin*, 57: 865-871.

Yang, J., C. Jiang, Y. Zhang, R. Yang, W. Yang, Q. Hou and Y. Cao, 2004. "High-Efficiency Saturated Red Emitting Polymers Derived from Fluorene and Naphthoselenadiazole", *Macromolecules*, 37: 1211-1218.