

Synthesis and Characterization of Fully-Functionalized Polysilanes for Photorefractive Materials

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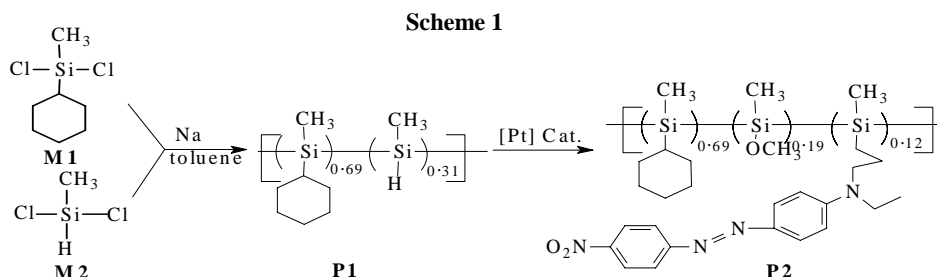
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Abstract: Hydrogen-containing polysilanes and chromophore-containing polysilanes are prepared by traditional Wurtz coupling and subsequent hydrosilylation. They are characterized by $^1\text{H-NMR}$, FT-IR, UV/VIS spectroscopies, differential scanning calorimetry (DSC) and gel permeation chromatography (GPC).

Keywords: Polysilanes, synthesis, characterization, Wurtz coupling, hydrosilylation.

Photorefractive (PR) polymers have attracted much interest since 1991¹. Furthermore, because fully-functionalized polymeric systems can overcome the shortcomings such as phase-separation and composite sublimation in composite systems they have gained especial attention.

Polysilanes can be used as novel photoconductors because of σ -electrons delocalization in the polymeric backbone². Silence³ and Nishida⁴ have studied the polysilane composite photorefractive materials and found that the response time is as fast as 39 ms, while the gain coefficient is not very satisfactory due to the chromophore's poor solubility in polysilane matrix. Our interest lies in the fully-functionalized polysilanes (in which all necessary composites are covalently connected to the polymer backbones), and the fully-functionalized polysilane photorefractive materials through chloromethylation and then etherification of polymethylphenylsilanes have been reported⁵. In this paper, a novel synthetic strategy is presented with the aim to develop fully-functionalized polysilanes with an elevated degree of chromophoric functionalization and improved processibility for PR effect.



According to **Scheme 1**, a new polyhydrosilane (**P1**) was prepared in 16% yield by standard Wurtz reductive coupling, and subsequently hydrosilylated with 4-(N-ethyl-N-allyl)-4'-nitrophenylazoaniline to afford a Dispersed Red (DR) chromophore-functionalized polysilane (**P2**) under the catalysis of dicyclopentadienedichloroplatinum. **P2** was purified by reprecipitation of its THF solution in methanol, and at this stage the remaining Si-H reacted with methanol because of the trace of platinum catalyst. The $^1\text{H-NMR}$ and IR spectra data of **P1** and **P2** are in good agreement with the expected

structures. The peak at $\delta 3.57$ ppm is assigned to Si-H proton. The mole ratio of methylcyclohexylsilylene unit and methyl(hydro)silylene unit in **P1** is about 0.69 : 0.31 by calculation from $^1\text{H-NMR}$ data, which is similar to the feeding ratio of the monomers **M1** : **M2** (2 : 1). On the other hand, after hydrosilylation the Si-H proton resonance disappeared, and two new broad peaks appeared at $\delta 4.0$ ppm and $\delta 3.3$ ppm assigned to the N-CH₂ proton resonance and Si-O-CH₃ proton resonance, respectively. From the signals for the different groups in $^1\text{H-NMR}$, the content of the chromophore (mole ratio) is calculated to be about 12%.

The Si-H absorption maximum of **P1** is present at 2083 cm^{-1} . The peaks at 540, 510 and 420 cm^{-1} are related to Si-Si stretching vibration. After hydrosilylation of **P1**, the Si-Si stretching absorption is still present, but the Si-H absorption disappeared, while phenyl skeletal breathing appeared.

P1 shows UV absorption maxima at 265 and 293 nm. **P2** shows strong λ_{max} at 456.5 nm assigned to the absorption of chromophore. The weight-averaged molecular weight of **P1** and **P2**, determined by gel permeation chromatography (GPC) based on PS standard, are 2400 and 3460, respectively.

The thermal transition behavior of polysilanes **P1** and **P2** are investigated by differential scanning calorimetry (DSC). No apparent glass transition is observed from 25°C to 300°C.

The measurement of photorefractive effect of **P2** is in due course.

Acknowledgments

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