

Synthesis and Photoresponse Properties of Tricyanovinylized Polysilane

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Summary: To broaden its photoresponse window, the new polysilane **2** with a pendant (tricyanovinyl)aniline group has been prepared by a facile post-tricyanovinylation reaction of the *N,N*-dialkylaniline-substituted polysilane precursor **1**. A steady-state photoconductivity study showed that polysilane **2** has an extended photoresponse region from the traditional ultraviolet to the visible region compared with polysilane **1**.

Introduction

Polysilanes, polymers with Si–Si catenation in the main chain, may be used as photoresists, photoconducting materials, and Si–C ceramic precursors.¹ Furthermore, because of their considerably high hole-drift mobility, on the order of 10^{-4} cm V⁻¹ s⁻¹, which originates from the strong σ -electron delocalization along the silicon backbone,² polysilanes have also been proposed to be used as hole-transfer materials in organic photo-receptors and photocopier applications.³

However, most polysilanes show very low photocarrier generation efficiency. For example, poly(methylphenylsilane) was reported to have a saturation photocarrier generation efficiency of about 1.0%.⁴ Thus, there is a great obstacle to their use as photoconductors. When C₆₀ was doped into polysilanes, the photocarrier generation efficiency was improved in the visible region, but it was still poor.⁴ Kakimoto et al.⁵ reported that the introduction of oligothiophene segments into a polysilane main chain successfully extended its photoconductivity in a wide wavelength region, from the UV to the visible. More recently, some polysilanes containing

coumarin 6 (C6) or rhodamine 6G (R6G) were found to exhibit excellent wavelength-selective photoconductivity in the blue/red regions.⁶ These results strongly suggest that attaching an electron pull–push chromophore into a polysilane backbone should extend the photosensitive region from the UV to the visible region. Meanwhile, the functional polymer system with an attached chromophore could diminish the possibilities of phase separation and diffusion that usually occur in the host–guest polymers. Herein, a facile post-functionalization reaction is used to successfully introduce a strong electron-attracting tricyanovinyl group into a polysilane side chain. The wavelength-dependent photosensitivity of this polymer over a wide wavelength range is studied.

Experimental Section

Tetracyanoethylene (TCNE) was purified twice by sublimation. Poly(styrenesulfonate)/poly(2,3-dihydrothieno[3,4-*b*]-1,4-dioxin) (PEDOT; 1.3 wt % dispersion in water) was purchased from Aldrich. Tetrahydrofuran (THF) was dried over Na–K alloy. *N*-Methylpyrrolidinone (NMP) was distilled from CaH₂. ¹H NMR spectra of the polymers were obtained with a Varian Mercury 300 spectrometer using the residue proton of CDCl₃ as an internal standard. FT-IR spectra were recorded on a Testscan Shimadzu FT-IR 3000 series spectrometer in the region of 4000–400 cm⁻¹ on KBr pellets. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were performed using a Rigaku Thermoflex DSC8131 and TG8110, respectively, at a scan rate of 10 °C/min under a nitrogen atmosphere. UV–visible spectra were measured with a Shimadzu 160A spectrometer. Molecular weights of the polymers were determined in THF using a Waters 2960D separation module containing a Styragel HR1 THF column and a Waters 2410 refractive index detector with a calibration curve for polystyrene standards.

Synthesis of Polysilane 1.⁷ To a sodium dispersion (1.3 g, 0.10 mol) in 20 mL of dry toluene was added dropwise a mixture of methylphenyldichlorosilane (3.9 g, 20.6 mmol) and *N*-(3-(methylchlorosilyl)propyl)-*N*-ethylaniline⁷ (1.42 g, 5.04 mmol) in 5 mL of dry toluene at a rate sufficient to maintain vigorous reflux. The mixture was heated at reflux for an additional 5 h and cooled to room temperature. Then an excess of ethanol was added until no more gas was evolved. The mixture was filtered, and the residue was washed with dry toluene (2 × 5 mL) and diethyl ether (2 × 5 mL). The filtrates were collected, and the solvent was removed under reduced pressure. The colorless oily residue was redissolved in 5 mL of THF, and 20 mL of methanol was added. After removal of volatiles under vacuum at 45 °C, 1.2 g (34%) of white,

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crystalline polysilane **1** was obtained. $^1\text{H NMR}$ (CDCl_3 , δ): 7.8–6.2 (Ar H), 3.4–2.9 (NCH_2), 1.7 (NCCH_2), 1.2–0.9 (CCH_3 , SiCH_2), 0.4 to –1.0 (SiCH_3). FT-IR (KBr, cm^{-1}): 3442, 2920, 2897, 1491, 1450, 1420, 1344, 1194, 752, 698, 462. Anal. Calcd for $(\text{C}_{8.0}\text{H}_{10.2}\text{N}_{0.2}\text{Si})_n$: C, 70.07; H, 7.45; N, 2.04. Found: C, 69.56; H, 7.69; N, 1.89.

Synthesis of Polysilane 2 by Tricyanovinylolation. A solution of 0.50 g of **1** (0.73 mmol of aniline subunits) and 0.12 g (0.94 mmol) of TCNE in 5 mL of NMP was stirred at 100 °C for 18 h. After the mixture was cooled, an excess of anhydrous K_2CO_3 was added. The mixture was filtered, and the filtrate was added to 100 mL of methanol. The resulting solid polymeric product was purified by addition of its THF solution into methanol. This process was repeated to give 0.46 g (82%) of **2**. $^1\text{H NMR}$ (CDCl_3 , δ): 8.0 (Ar H), 7.8–6.2 (Ar H), 3.4–2.9 (NCH_2), 1.7 (NCCH_2), 1.2–0.9 (CCH_3 , SiCH_2), 0.4 to –1.0 (SiCH_3). FT-IR (KBr, cm^{-1}): 3442, 2920, 2897, 2212, 1606, 1491, 1450, 1420, 1344, 1194, 752, 698, 463. Anal. Calcd for $(\text{C}_{8.9}\text{H}_{10.02}\text{N}_{0.74}\text{Si})_n$: C, 68.82; H, 6.46; N, 6.68. Found: C, 69.03; H, 6.39; N, 6.53.

Photoconductivity Experiments. The films for photoconductivity measurements were prepared by spin-coating their THF solution onto the ITO (indium tin oxide) glass substrate spin-coated with 70 nm PEDOT. The film thickness was measured to be about 150 nm using Tencor 500 surface profiler equipment. Finally, 100 nm of Al was thermally evaporated onto the film as the cathode. Steady-state photoconductivity measurements were carried out using an electrometer with a standard calibrated silicon photodiode. Monochromatic light from a 100 W Xe lamp through a monochromator was used as a light source for irradiation.

Results and Discussion

Tricyanovinyl compounds have been widely used as chromophores in nonlinear optical studies (including small molecules⁸ and polymer⁹ systems), due to their strong electron-withdrawing ability. However, this chromophore has not been introduced into polysilane systems, in part because such pull–push molecules are easily decomposed during the harsh Wurtz coupling reaction, usually used to prepare high-molecular-weight polysilanes.^{1c,d} A postfunctional strategy constitutes an alternative access to chromophore-functionalized polysilanes. Indeed, our recent review paper has summarized some postfunctionalization methods proposed by our group for introducing chromophores into polysilanes for nonlinear optical studies. Post-tricyanovinylolation was highlighted as one of the most important methods.¹⁰ Treatment of polysilane **1**, readily prepared by our previous procedure,⁷ with TCNE in NMP at 100 °C afforded the violet-red polymer **2** in good yield (Scheme 1). After completion of the reaction, an expected change in $^1\text{H NMR}$ spectrum appeared as an emerging peak at 8.0 ppm, corresponding to the aromatic proton ortho to the tricyanovinyl group, indicating that the tricyanovinyl group was attached at the position para to the amino functional group. The content of tricyanovinylaniline subunits in polysilane **2** was calculated to be about 0.18 by integration of its $^1\text{H NMR}$ spectrum. The FT-IR spectrum also provided strong evidence for

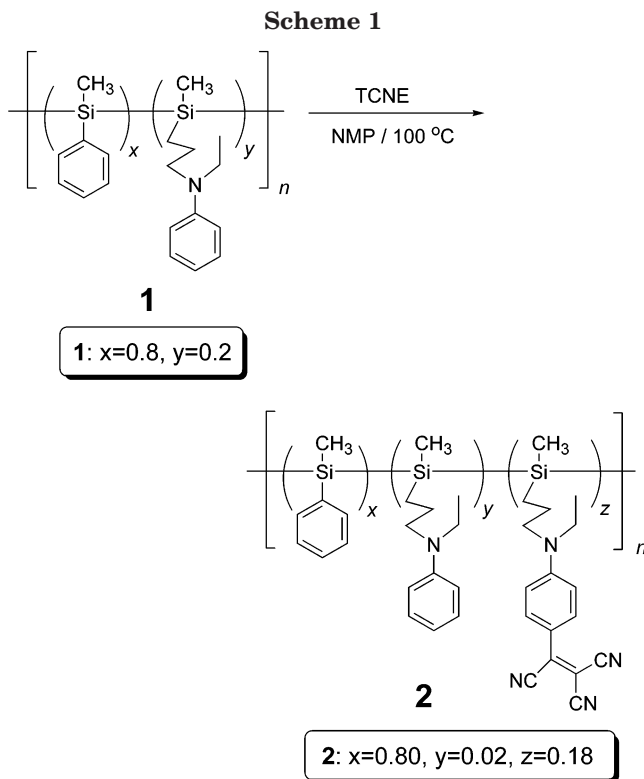


Table 1. Physical Properties of Polysilanes 1 and 2

	M_w^a	PDI	λ_{max} (nm)	T_g (°C)	T_d (°C) ^b
1	13 300	1.22	330	96	334
2	10 300	3.77	330, 525	11	267

^a The molecular weights were determined by gel permeation chromatography in THF with polystyrene as standard. ^b The decomposition temperatures were measured by thermal gravimetric analysis and are referenced to the onset decomposition temperature.

the successful introduction of tricyanovinyl groups into polysilane **2**. In contrast to **1**, polysilane **2** shows two new peaks at 2212 and 1623 cm^{-1} due to the $\text{C}\equiv\text{N}$ vibration and to the $\text{C}=\text{C}$ vibration in the tricyanovinyl group, respectively. On the other hand, the medium absorption at ca. 463 cm^{-1} corresponding to the Si–Si skeleton remained unchanged in location and strength after tricyanovinylolation, demonstrating that the polysilane main chain remains intact during this postpolymerization procedure. This can also be confirmed by the molecular weight measurements.

Molecular weights of **1** and **2** were determined by gel permeation chromatography (GPC) with monodisperse polystyrene (PS) as a relative standard (Table 1). Both **1** and **2** have comparably high molecular weights, 13 300 and 10 300 Da, respectively, demonstrating that only limited chain scissions of the polysilane backbone occurred in the post-functionalization. Polysilanes **1** and **2** are soluble in 1,2-dichloroethane, chloroform, THF, DMSO and NMP. High-optical-quality thin films can be obtained by a spin-coating technique.

The thermal properties of **1** and **2** were evaluated by means of differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). Table 1 lists their glass transition temperatures (T_g) and onset decomposition temperatures (T_d). After tricyanovinylolation, polysilane **2** shows a lower glass transition temperature

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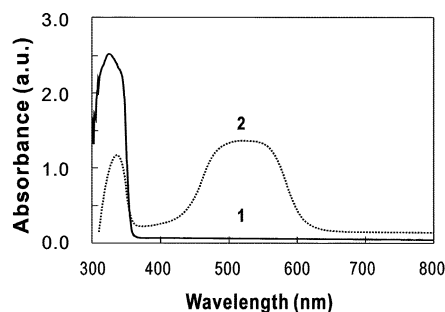


Figure 1. Electronic absorption spectra of **1** and **2** as thin films at room temperature.

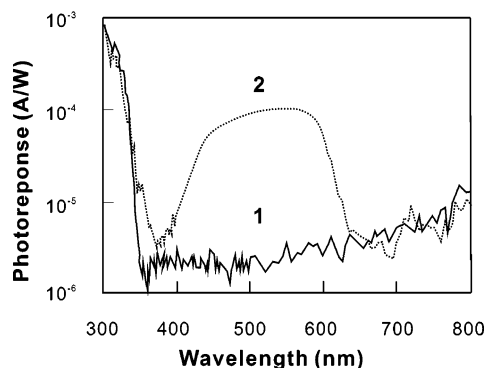


Figure 2. Wavelength dependence of the photocurrents of **1** and **2**.

than its precursor **1**. Both polysilane **1** and **2** exhibited good thermal stability up to 267 °C, which was revealed by TGA. Comparing precursor **1** with derived **2**, it can be seen that the introduction of tricyanovinyl groups not only decreases the glass transition temperature of **2** but also reduces its thermal stability.

Because of the strong σ -electron delocalization along polysilane backbones, these polymers usually exhibit strong absorption in the UV and near-UV regions. The absorption spectra of **1** and **2** in THF show that polysilane **1** has a strong absorption (λ_{max}) at ca. 330 nm, corresponding to the σ -electron delocalization in the polysilane backbone. After post-functionalization, polysilane **2** maintains this strong absorption band, demonstrating that the post-functionalization reaction has little effect on the polymer skeleton. In addition to this characteristic absorption peak of the polysilane, a new, strong, sharp absorption band emerges at 525 nm, ascribable to the intramolecular charge transfer of the (tricyanovinyl)aniline chromophore, indicating again the successful introduction of the tricyanovinyl-type chromophore into polysilane.

The electronic absorption spectra of thin films of **1** and **2** are illustrated in Figure 1. The solid films show absorption characteristics similar to those for the polysilanes in THF solution, except for a broader profile.

To gain insight into the effect of the (tricyanovinyl)aniline side chain on the photoresponse, the steady-state photoconductivity spectra of polysilane films of **1** and **2** were obtained at room temperature (Figure 2). The photoconductivity spectra of **1** and **2** have a profile similar to that for their electronic absorption spectra in films (Figure 1), except that the peaks are even broader. Polysilane **1** has a very high photoconductivity at a region from 300 to 350 nm, resulting from the σ -electron delocalization along the main chain, and

almost no photoresponse in the visible region. After the introduction of the (tricyanovinyl)aniline groups, polysilane **2** not only maintains high photoconductivity in this region but also shows a new, comparably high photoconductivity region at 400–650 nm corresponding to the electric charges effectively generated inside the (tricyanovinyl)aniline chromophore units. Since the polysilane backbone and the (tricyanovinyl)aniline side chain are connected only by a simple alkyl chain, a conjugated interaction is not possible between these two parts. If only the electronic levels and interaction of these two parts are taken into account, the (tricyanovinyl)aniline pendant and the polysilane backbone can be studied separately. It is reported that tricyanodimethylaniline and polysilanes have nearly equal lowest unoccupied molecular orbital (LUMO) levels (about 5.5–5.6 eV) but have a large difference in the highest occupied molecular orbital (HOMO) levels, which are about 3.8–3.9 and 1.0–1.5 eV, respectively.^{6,11} At a certain working wavelength (e.g., 400–650 nm in our case), therefore, polysilanes work as a potential barrier of the electronic-hole pair generated in (tricyanovinyl)aniline rather than hole transport materials. Photocarriers move among the (tricyanovinyl)aniline chromophore predominantly by hopping with the aid of applied electric fields.⁶ If we combine these two parts of the photoresponse properties, as seen from Figure 2, there is only a very narrow wavelength window (350–400 nm) showing a relatively low photoresponse in the region of 300–650 nm. This implies that almost all of the incident light from 300 to 650 nm can be absorbed and the resulting excimers can be responsible for the high photocurrent response in this region. Therefore, the introduction of (tricyanovinyl)aniline groups brings about a broader photoresponse region from the UV to visible. Despite the unsuitability of the energy levels of polysilane and tricyanovinylaniline in our present system, this still gives us a convenient route to extend the photoresponse region of a polysilane. The optimization of energy levels in both the polysilane and the chromophore to efficiently transfer generated holes from the chromophore to the polysilane will enable us to obtain a more efficient and high-speed photosensor.

Conclusion

In summary, tricyanovinyl groups have been successfully used to introduce tricyanovinyl groups into a polysilane. Our results show that this post-functionalization reaction has little influence on the polysilane main chain. A steady-state photocurrent study showed that the introduction of tricyanovinyl groups leads to an increase of the photoresponse window from 300–350 nm to 300–650 nm. Therefore, the introduction of a chromophore into polysilane side chains provides a new opportunity to extend the photoconductivity from the UV region to the visible region.

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