Polydiphenylsilanes bearing photosensitive azocrown groups†

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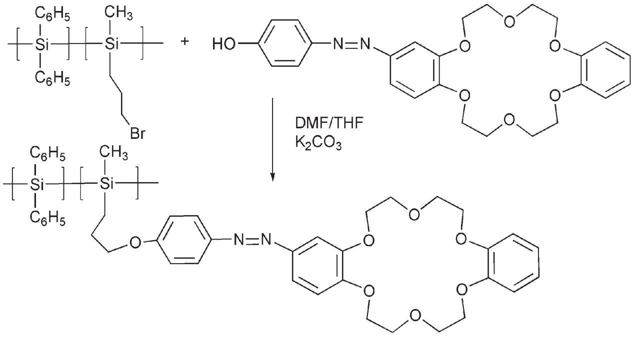
This work presents the synthesis and particularities of the reversible *trans–cis* UV light induced photoisomerization process of a polydiphenylsilane bearing (propyl-oxyphenylazo)-dibenzo-18-crown-6 side groups.

Polysilanes possess unique optical and electronic properties due to the electronic structure of the σ-electron conjugated polymer chain. Such special properties are not exhibited by crystalline Si 3D systems.[2] Over the past few years, an increasingly large number of papers described various methods of obtaining unusual polysilane structures with intriguing properties.[3] Such structures, like soluble quantum conductors (QWR)[1a,4] or polysilane–metal complexes[3a,5] find applications as organic semiconductors or NLO materials.

This paper presents the synthesis of a new poly[diphenyl-co-methyl(propyl-oxyphenylazo-dibenzo-18-crown-6)]silane, PSADF. The azocrown side segments allow the *trans–cis* isomerization induced by irradiation with a specific UV wavelength and provide the polysilane with the electrochemical sensitivity of the crown ether units.

The synthesis procedure starts from poly[diphenyl-co-methyl-(bromopropyl)]silane (PSBDF) which was obtained through the addition of allyl bromide to soluble poly[diphenyl-co-methyl(H)]silane with $M_w = 48 \times 10^3$ g mol^{-1}, $M_n = 40 \times 10^3$ g mol^{-1} (GPC analysis *vs.* polystyrene standards) and $Ph_2Si/Me(H)Si$ ratio of 3 : 1, in the presence of a catalytic amount of $H_2PtCl_6 \cdot 6H_2O$ (1% solution in isopropanol).[5c] An addition yield of 91% in the bromopropyl groups was calculated using the ^1H NMR integral for the $–SiCH_3–$ signal and elemental analysis.

At high temperature, in anhydrous solvent (DMF), PSBDF undergoes a modified Williamson reaction with (4-hydroxyphenylazo)dibenzo-18-crown-6 in the presence of anhydrous K_2CO_3 (Scheme 1). Poly[diphenyl-co-methyl(propyl-oxyphenylazo-dibenzo-18C6)] silane (PSADF) resulted as a brown solid (η = 63%) with $M_w = 87 \times 10^3$ g mol^{-1}, $M_n = 70 \times 10^3$ g mol^{-1} and mp = 232 °C. Unlike the bromopropyl-polysilane which has a low decomposition temperature, in this case the TGA analysis in air shows decomposition temperatures starting from 250–400 °C for the organosilicone backbone to 400–750 °C for the azo segment.



Scheme 1

It is known that the azobenzene derivatives undergo *trans–cis* photoisomerization in UV light with a temporary and local change of shape and polarity.[6] The process is reversible and reversion from *cis* to *trans* isomer state takes place thermally or by irradiation in the visible spectrum.[7] The photoisomerization of PSADF was performed by irradiation of the polymer solutions in DMSO with a 400 nm filtered UV light and recording the 480 nm absorption band corresponding to the n–π* transition of the azobenzene unit in *cis* conformation (Fig. 1).[8] This procedure was chosen because the azo group π−π* transitions overlap with the polysilane σ−σ* transitions. Another reason for choosing this procedure was to protect the polysilane chain against photodecomposition. UV irradiation caused an increase in the intensity of the 480 nm absorption band until a photostationary state was reached and about 65–70% of azobenzene segments were in *cis* configuration.

The *trans–cis* photoisomerization data followed a first-order kinetics with a rate constant of 8.1×10^{-3} s^{-1} at 25 °C. The isomerization process was reversed by heating at moderate temperature (70 °C). Thermal recovery needed much longer

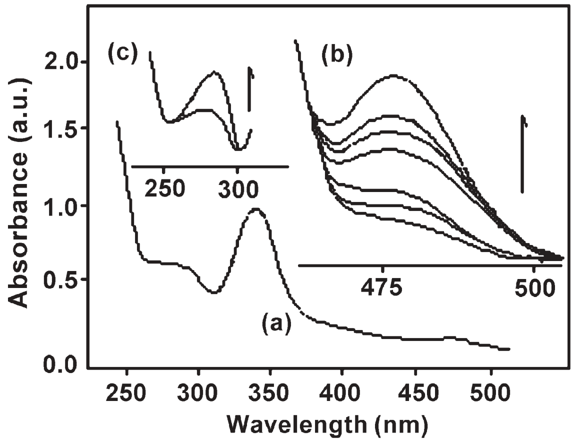


Fig. 1 (a) UV spectrum of *trans*-PSADF; (b) change of the absorption spectra of DMSO solutions of PSADF during *trans–cis* photoisomerization recorded at 0, 5, 10, 15, 20, 25, 30 min and 25 °C; (c) increasing of 280 nm peak recorded during *trans–cis* photoisomerization of PSADF.

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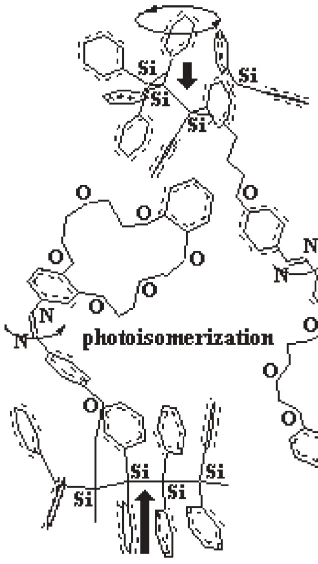

Chart 1

periods of time (about 100 min) and had first order kinetics with a rate constant of 1.80 × 10^{-4} s^{-1}, suggesting that the azobenzene segments freely isomerize.

An uncommon phenomenon was observed during the UV irradiation of the PSADF samples. The 280 nm band corresponding to the σ–π conjugation within the polysilane varied following the isomerization state of the azo-segment and reached a maximum intensity when the azobenzene units were in the *cis* conformation (Fig. 1). Due to the propylene bridge and shielding effect of the phenyl substituents, the azo-segment is isolated from the polysilane conjugated chain and therefore the electronic influences are too weak to explain this unexpected variation. In addition, if present, these electronic influences should affect especially the σ-electron delocalized system within the polysilane or the shape, position and intensity of the 332 nm band assigned to σ–σ* transitions. However, the 332 nm band remained unchanged during irradiation. Therefore the origin of this phenomenon should be explained by taking into account the conformational effect induced by the photoisomerization process, as presented in Chart 1. In polyphenylsilanes, the orbital mixing between the delocalized σ highest occupied valence band (HOVB) state of the Si-skeleton and the π highest occupied molecular orbitals (HOMO) states of the phenyl groups causes the σ–π conjugation.[9] The extent of this orbital mixing (indicated by the black arrow) depends on the phenyl π HOMO orbitals position relative to the Si skeleton which, in turn, is dictated by the position and orientation of the aromatic rings. In our case, the increase in intensity of the UV 280 nm peak proved that the movement of the azo-unit from *trans* to *cis* state induces local conformational disturbances which are responsible for repositioning the molecular planes of the phenyl groups in a more favorable position for the σ–π orbital mixing.

A variation of the extent of σ–π conjugation intensity in polysilanes strongly affects the mobility of the charge carriers,[9] and this indicates that PSADF could be used to obtain polymeric materials with optical and electronic properties controlled by photoisomerization.

Notes and references

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