

NEW POSSIBILITIES FOR THE SYNTHESIS OF REACTIVE FUNCTIONAL AMINOPOLYSILANES USING AZIDE PATHWAY

ANDREI DASCĂLU¹, RODINEL ARDELEANU¹ and
BOGDAN C. SIMIONESCU, member of the Romanian Academy^{1,2}

¹“Petru Poni” Institute of Macromolecular Chemistry, Centre of Advanced Research
in Bionanoconjugates and Biopolymers, Aleea Gr. Ghica Voda 41A, Iași 700487 Romania

²“Gheorghe Asachi” Technical University of Iași,
Department of Natural and Synthetic Polymers, 700050 Iași, Romania
Corresponding author: Andrei Dascălu, idascalu@icmpp.ro

Two new reaction frameworks with high stereospecificity and high yields are described. Azidopolysilanes offers multiple options for obtaining aminopolysilanes, either by reducing the azido group using the Staudinger technique or by Huisgen 1,3 cycloaddition reaction with ethynylaniline. The obtained aminopolysilanes were structurally characterized by ¹H-NMR, FT-IR, elemental analysis. The optical properties were determined by fluorescence spectroscopy.

Key words: functional polysilanes, azides, Huisgen 1,3-cycloaddition, Staudinger reduction.

1. INTRODUCTION

Polysilanes have attracted considerable interest during the last decades because of their interesting electronic and photophysical properties and their potential applications in new materials such as ceramic precursors [13, 14], electric conductors [9], in photoconductivity [8], in microlithography [6] and in nonlinear optical devices [11]. Their unique optoelectronic properties are attributed to the σ conjugation occurring along the silicon main chain, hence they are extremely sensitive to the polymer conformation and to the substituents attached to the polymer backbone [7].

Polysilanes containing functional groups have been prepared either by polymerization of monomers already bearing the desired functionalities or by substitution reactions of the parent polysilanes, usually those with Si-H bonds [3].

The increasing need for materials with tightly controlled structures caused the introduction of synthetic organic concepts into materials science; one important example is represented by the Click Chemistry [2, 10].

In this paper, we report the rapid synthesis of amino polysilanes via click chemistry reactions and by the reduction of polysilane azides.

2. EXPERIMENTAL SECTION

2.1. SYNTHESIS OF POLY(DIPHENYL-CO-METHYL-H)SILANE (PDFMS)

In a 1L flask with four necks equipped with a condenser and a magnetic stirrer, 30 g of silica powder grain of 0.06 mm were introduced under argon atmosphere and vacuum dried at 150°C. Once the silicon was dry, 15 g of freshly cut Na were placed inside and heated while stirring vigorously until the sodium is melted and mixed intimately with the silica powder. Under argon atmosphere, 300 ml dry THF were added over the mixture. 7.33 mL methyl(H) dichlorosilane (MDCS) and 44.5 mL diphenyldichlorosilane (DFDCS) were then added dropwise using a funnel at room temperature to prevent foaming. The reaction mixture was stirred rapidly at room temperature for 6–10 h. Termination was achieved by the slow addition of methanol to ensure complete extinction (aprox. 50 mL). The solvent mixture was then distilled to dryness and the residue was dissolved in 150 mL of hot toluene and filtered in order to separate the dry mixture of salt and silica. The solvent layer was kept and the aqueous layer was washed 3–4 times with the organic solvent to dissolve any polymer traces left in the water. The solvent extracts were combined, dried for 2 h over anhydrous magnesium sulfate, filtered, and the solvent removed under vacuum. Removal of the cyclosilane fraction was achieved through repeated precipitations of the product by slowly adding a THF solution of the crude polymer dropwise to rapidly stirred propane-2-ol. Yield: 51.5%.

Anal. Calcd (%) for $C_{61}H_{54}Si_6$: C, 76.72; H, 5.70; Si, 17.60. Found: C, 75.16; H, 7.68; Si, 17.16.

IR (KBr) cm^{-1} : 3070, 3044 C-Har; 2980, 2860 C-H; 2080, Si-H; 1455, Si-C₆H₅; 1250, Si-CH₃; 1100, Si-Si; 880, Si-CH₃; 750, 705 Si-C; 460, Si-Si.

UV-vis: λ_{max} 330 nm, ϵ 12 500 $cm^{-1} dm^3 mol^{-1}$.

¹H-NMR (400 MHz, (CDCl₃): 7.25 (broad, 50H, C₆H₅); 4.25 (sharp, 1H, Si-H); 0.15 (broad, 3H, CH₃).

2.2. SYNTHESIS OF PDFMS-AZIDOPROPYL

In a typical procedure 1.24 g NaN₃ (0.19 moles) were dissolved in 25 mL anhydrous DMSO. After addition of polysilane propyl bromide (1.32 g, 0.38 moles) to the azide solution, the reaction was protected from light with aluminium foil, and stirred at 50°C for 7 days, until the complete transformation occurred, indicated by the color shift from purple to dark red. The reaction mixture was diluted with water (50 mL) and extracted two times with ethylether (50 mL). Washing of the ether phase followed by drying (Na₂SO₄) and solvent evaporation led to a high purity azide derivative (91% yield).

Anal. Calcd (%) for $C_{64}H_{59}Si_6N_3$: C, 74.06; H, 5.70; Si, 16.20; N, 4.05. Found: C, 74.16; H, 5.60; Si, 16.25; N, 4.0.

IR (KBr): cm^{-1} 3044 (C-H), 3000, 3070 C-Har; 2980, 2860 C-H; 2100, N₃ asim; 1455, Si-C₆H₅; 1340, N₃ sim, 1250, Si-CH₃; 1100, Si-Si; 880, Si-CH₃; 750, 705 Si-C; 460, Si-Si.

2.3. SYNTHESIS OF PDFMS-AMINOPROPYL

2.2 g (2.12 mmol) PDFMS-azidopropyl were dissolved in 10 mL DMSO, followed by the addition of 0.656 g (2.5 mmol) triphenylphosphine and stirred for 12 h at room temperature. In the next step, 10 mL of distilled water were added and the reaction mixture was stirred for another 12h at room temperature. The reaction mass was extracted twice with 25 mL of ethyl ether. The two organic phases were combined, washed with water and dried with magnesium sulfate. Finally, the ethyl ether was removed by distillation under vacuum. A viscous yellowish product was obtained (77% yield).

Anal. Calcd (%) for $C_{64}H_{61}Si_6N$: C, 75.96; H, 6.03; Si, 16.62. Found: C, 76.23; H, 5.87; Si, 16.85; N, 1.2; IR (KBr): cm^{-1} , 3425, 3385, N-H; 3044, C-H; 3000, 3070 C-Har; 2980, 2860, C-H; 1630, N-H; 1455, Si-C₆H₅; 1250, Si-CH₃; 1100, Si-Si; 880, Si-CH₃; 750, 705 Si-C; 460, Si-Si.

¹H-NMR (400 MHz, CDCl₃): 7.25 (broad, 50H, C₆H₅); 4.65 (s, 2H), 2.70 (br s, 2H, Si-CH₂-CH₂-CH₂-), 1.65(broad, 2H, Si-CH₂-CH₂-CH₂-), 0.65(broad, 2H, Si-CH₂-CH₂-CH₂-) 0.15 (broad, 3H, Si-CH₃).

2.4. SYNTHESIS OF PDFMS-PROPYL-TRIAZOLYL-ANILINE

1.75 g (1 mmol) polysilane azide and 0.117 g 4-ethynylaniline (1 mmol) were dissolved in dried DMSO (15 mL), and mixed with 0.594 g TMEDA (3 mmol) and 0.075 g (3 mmol) copper bromide. The reaction mixture was stirred continuously for 12 h at 70 °C. The brown product was precipitated in water, filtered, washed with ethanol and recrystallized from DMSO (84 % yield).

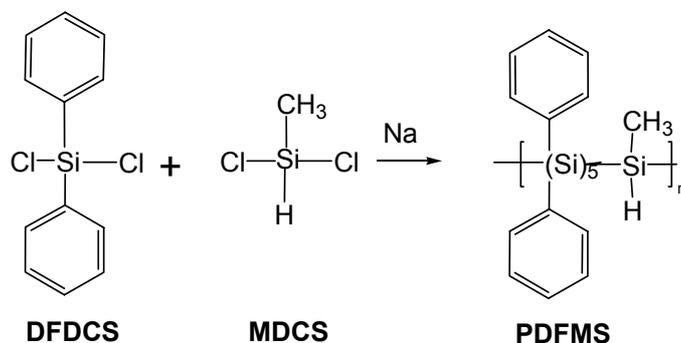
Anal. Calcd (%) for $C_{72}H_{65}N_4Si_6$: C, 74.93; H, 5.64; N, 4.85; Si, 14.57; Found: C, 75.10; H, 5.60; N, 4.77; Si, 14.53.

IR (KBr): cm^{-1} , 3425, 3385, N-H; 3044, C-H; 3000, 3070, C-Har; 2980, 2860, C-H; 1630, N-H; 1455, Si-C₆H₅; 1250, Si-CH₃; 1100, Si-Si; 880, Si-CH₃; 750, 705 Si-C; 460, Si-Si.

¹H-NMR (400 MHz, CDCl₃): 8.23-6.81(broad, 55H, H_{ar}); 4.93 (s, 2H), 2.70 (br s, 2H, Si-CH₂-CH₂-CH₂-), 1.95(broad, 2H, Si-CH₂-CH₂-CH₂-), 0.83(broad, 2H, Si-CH₂-CH₂-CH₂-) 0.15 (broad, 3H, Si-CH₃).

3. RESULTS AND DISCUSSIONS

Poly(diphenyl-co-methyl-H)silanes (PDFMS) were obtained by reacting the sodium deposited on silicon powder with a mixture of diphenyldichlorosilane and dichloromethyl-H-silane in tetrahydrofurane as solvent, by known Wurtz reaction (Scheme 1). The novelty is that the reaction takes place at room temperature in solvent with high complexing capacity, aiming at the preservation of the reactive Si-H bond.



Scheme 1. Schematic representation of the PDFMS synthesis procedure.

Important parameters of the unfolding reaction are the reaction temperature, the degree of sodium dispersion and the reaction time [4, 5, 12]. It is necessary to maintain a lower temperature reaction for 3–4 h, in order to avoid secondary reactions such as cyclization, Si-Si bond breaking and loss of reactive Si-H functions.

The degree of dispersion of sodium, either in the form of dispersion in toluene at reflux or in the form of films deposited on inert supports (SiO₂, K alloy, etc.) is crucial for the final performance of the reaction. A high degree of dispersion is the guarantee of a maximum yield of the reaction.

The Si-H bond was evidenced using FT-IR spectral analysis (Fig. 1) where the specific vibration band is observed at 2088 cm⁻¹.

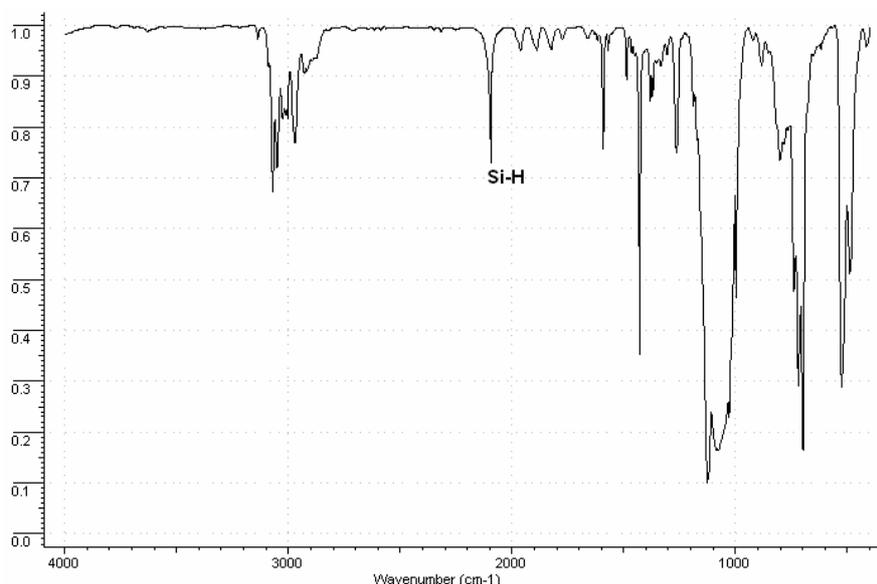


Fig. 1. FT-IR spectrum of PDFMS.

Quantitative determination of the Si-H bond, and the monomers copolymerization ratio were determined using the spectrophotometric analysis Si-C₆H₅/Si-CH₃ ¹H-NMR[14] by analyzing the signals at 7.25 ppm (Si-C₆H₅), 4.25 ppm (Si-H) and 0.15 ppm (Si-CH₃) (Fig. 2).

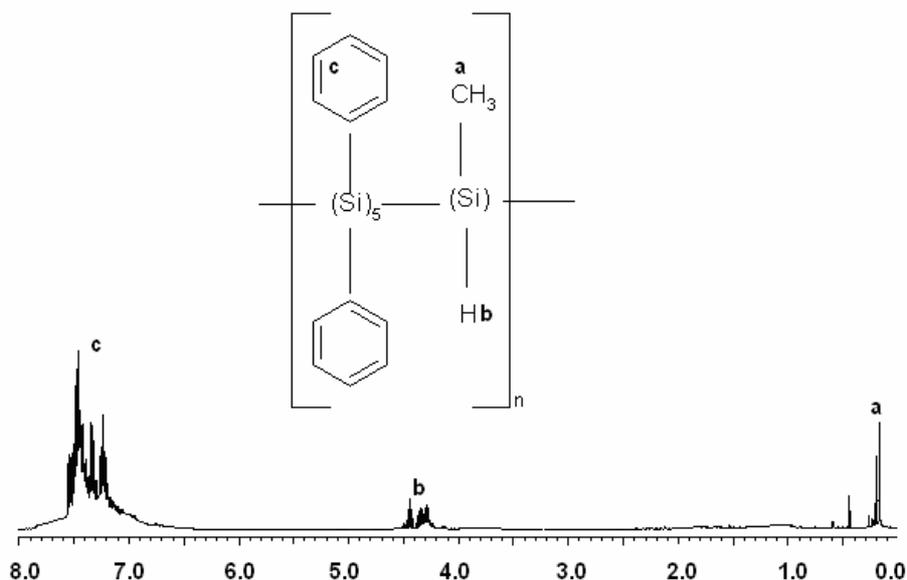
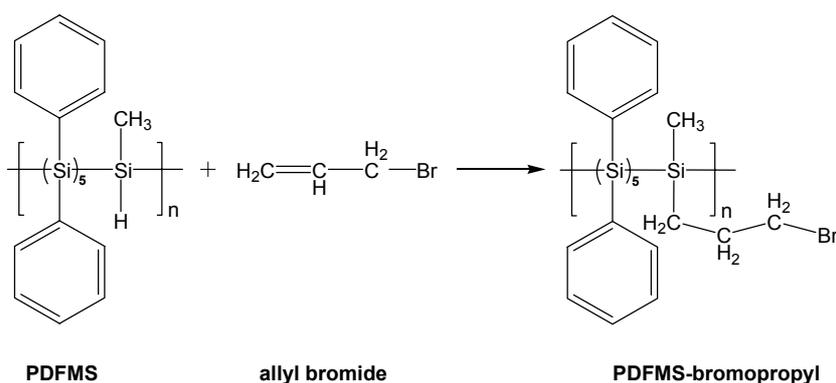


Fig. 2. ¹H-NMR PDFMS spectrum.

The synthesis procedure of poly[diphenyl-co-methyl-(bromopropyl)]silanes (PDFMS-bromopropyl) involves the addition of allyl bromide (Scheme 2) to soluble poly[diphenyl-co-methyl(H)]silanes with and Ph₂Si/Me(H)Si ratio of 5 : 1, in the presence of a catalytic amount of H₂PtCl₆/6H₂O (1% solution in isopropanol).



Scheme 2. Schematic representation of the PDFMS-bromopropyl synthesis procedure.

The response time was determined by monitoring the reaction through FT-IR spectral analysis - vibration band of Si-H bond at 2088 cm^{-1} (Fig. 3).

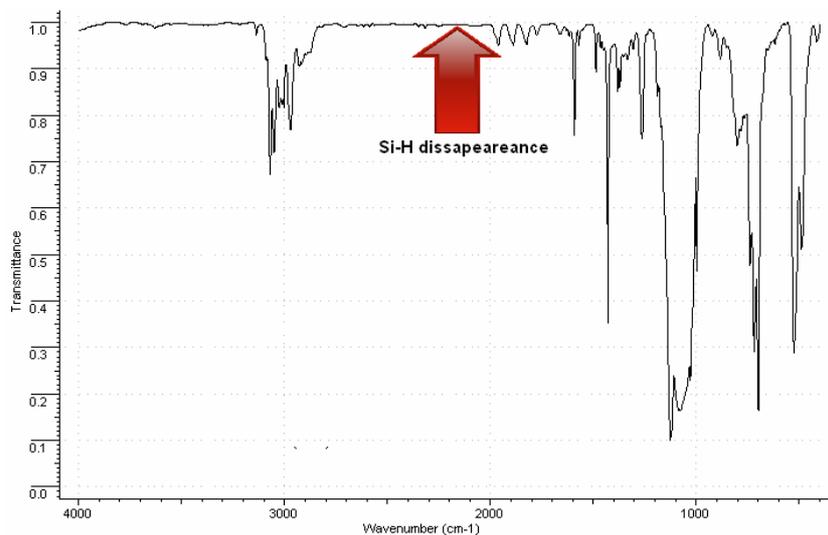


Fig. 3. FT-IR spectrum of PDFMS-bromopropyl.

An addition yield of 91% in the bromopropyl groups was calculated using the $^1\text{H-NMR}$ integral for the $-\text{SiCH}_3$ signal and elemental analysis (Fig. 4).

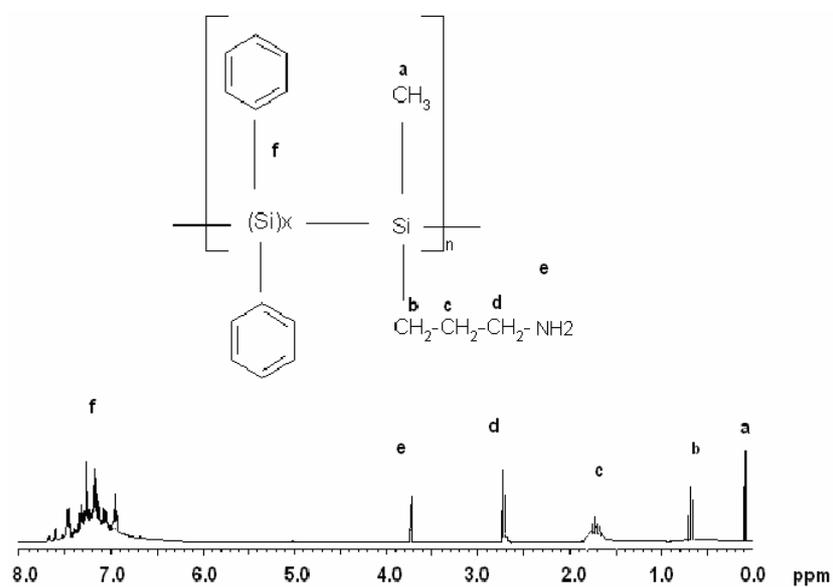
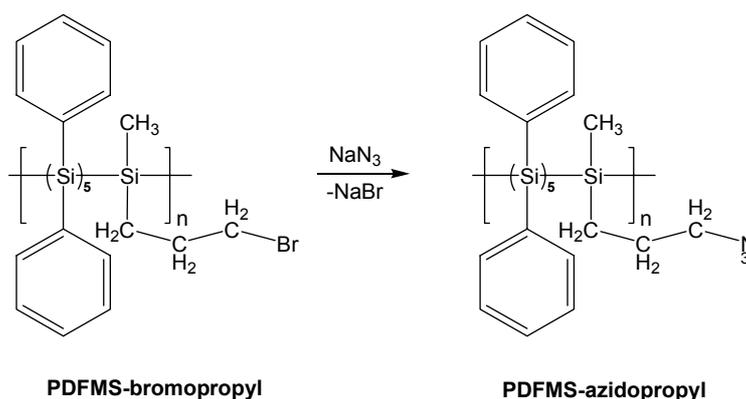


Fig. 4. $^1\text{H-NMR}$ spectrum PDFMS-aminopropyl.

PDFMS-azidopropyl was obtained by the azidopropyl-replacement reaction between sodium azide and the bromopropyl-PDFMS derivative. The reaction was performed in mixed solvents (dimethylsulfoxide + tetrahydrofuran) (DMSO + THF) at approximately 50°C, for 72 hours (Scheme 3). The use of a mixture of solvents is necessary because the reaction partners have different polarities. After the reaction is ended, the reaction mass is diluted with water 1:1 and is extracted twice with diethyl ether.



Scheme 3. Schematic representation of the PDFMS-azidopropyl synthesis procedure.

The final product is obtained by distillation of solvent under vacuum. FT-IR spectral analysis enables qualitative assessment of the degree of substitution of the halogen with the azido group by appearance of the vibration band at 2100 cm^{-1} due to azido groups (Fig. 5).

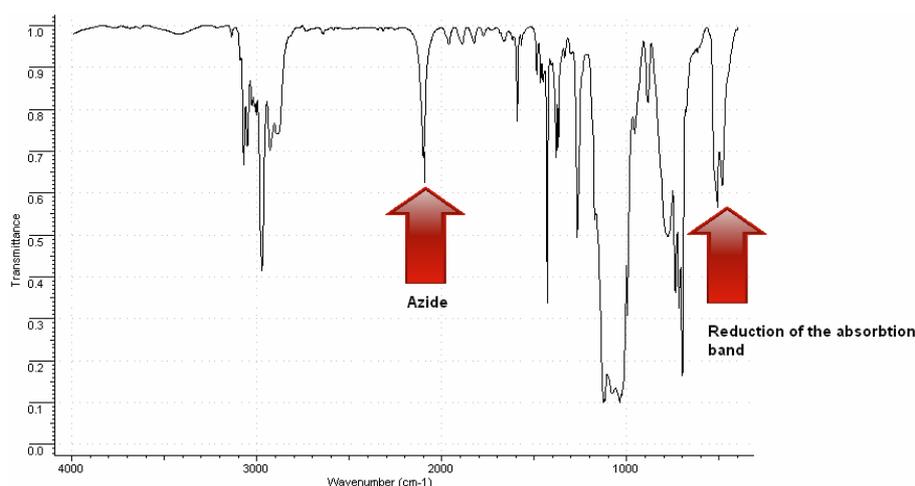
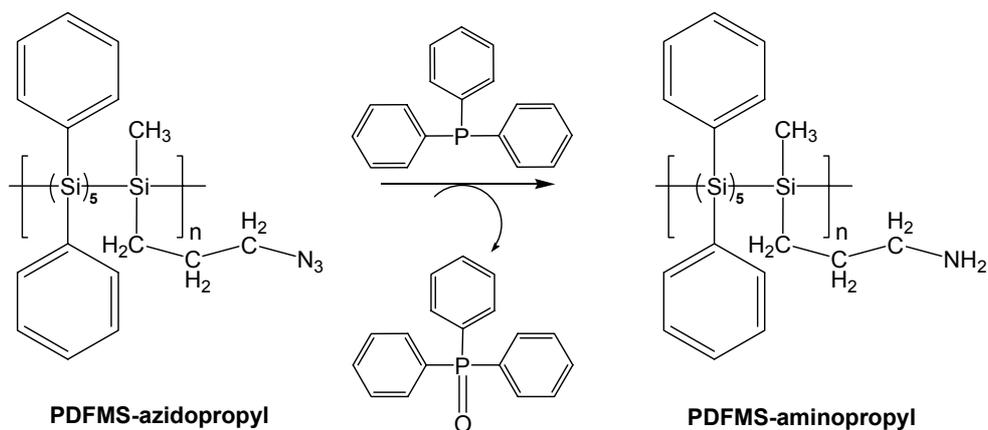


Fig. 5. FT-IR spectrum of PDFMS-azidopropyl.

Reducing the azidic groups to amines can be achieved through a varied set of methods. But the specific features of the silane bond requires a careful selection of the available methods [1]. Following experimentations made, it was concluded that the adequate method for reducing the azido group is the Staudinger method. Using this method the silane chain length or structure of the atom substituents for silica are not affected (Scheme 4).



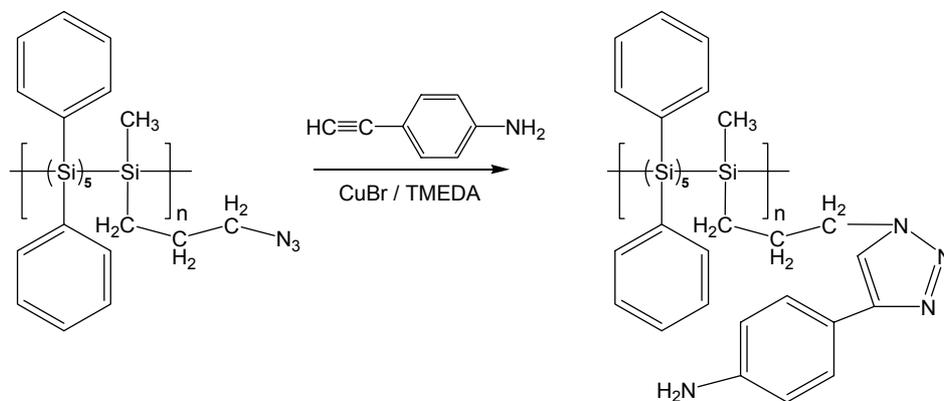
Scheme 4. Schematic representation of the PDFMS-aminopropyl synthesis procedure.

Synthesis was performed in anhydrous THF at a room temperature for 24 h. The reaction was monitored through the vibration band of the azido group at 2100 cm^{-1} in the FT-IR spectra.

A second method of obtaining aminofunctional polysilanes is the 1,3-Huisgen cycloaddition of poly(azidopropyl) silane and 4-ethynyl-aniline in the presence of a catalyst (Scheme 5). The important parameter of the synthesis is the catalytic system which requires no water and protects the Si-Si structure. An effective catalytic system was found to be CuBr / TMEDA (tetramethylethylenediamine) in THF [10].

The synthesis was performed in anhydrous THF at a temperature of 50°C for 48 h in the presence of the catalyst. The reaction was monitored through the disappearance of the azido group vibration band at 2100 cm^{-1} in the FT-IR spectra. The structure is confirmed by the presence of the triazole proton at 7.6 ppm in the $^1\text{H-NMR}$ spectrum (Fig. 6).

Fluorescence spectroscopy measurements revealed that the PDFMS-propyl-triazoly-aniline exhibits an emission band at 405 nm (Fig. 7).



PDFMS-azidopropyl

PDFMS-propyl-triazolyl-aniline

Scheme 5. Schematic representation of the PDFMS-propyl-triazolyl-aniline synthesis procedure.

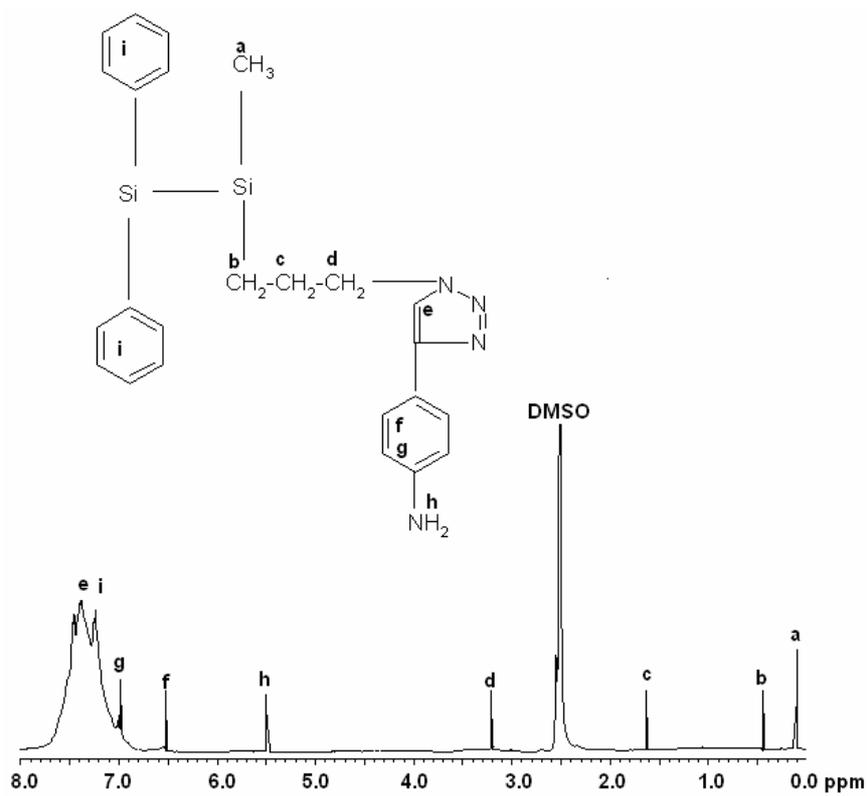


Fig. 6. $^1\text{H-NMR}$ spectrum PDFMS-propyl-triazolyl-aniline.

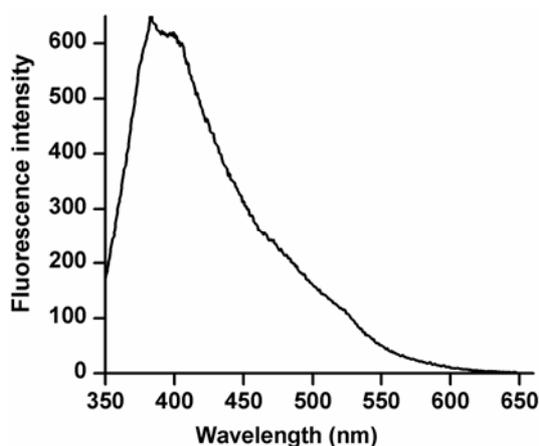


Fig. 7. Fluorescence spectrum of PDFMS-propyl-triazolyl-aniline.

4. CONCLUSIONS

Organo-functional polysilanes are a class of compounds with numerous applications such as semiconductors, nonlinear optic devices and composite materials. Despite their interesting properties, the functionalization alternatives of the silane chain are limited. To this day a relative small number of polysilane functionalization methods have been developed. We have successfully developed a reliable polysilane functionalization technique either by reducing the azidic group using the Staudinger technique or by Huisgen *1,3* cycloaddition reaction with ethynylaniline.

Acknowledgements. Paper dedicated to the 65th anniversary of “Petru Poni” Institute of Macromolecular Chemistry of Romanian Academy, Iași, Romania.

REFERENCES

1. HALLAND N., BRAUNTON A., BACHMANN S., MARIGO M., JORGENSEN K.A., *Direct Organocatalytic Asymmetric α -Chlorination of Aldehydes*, *J. Am. Chem. Soc.*, 2004, **126**, 15, 4790–4791.
2. HAWKER C.J., WOOLEY K.L., *The Convergence of Synthetic Organic and Polymer Chemistries*, *Science*, 2005, **309**, 5738, 1200–1205.
3. HAYASE S., *Polysilanes with functional groups*, *Endeavour*, 1995, **19**, 3, 125–131.
4. HOLDER S.J., ACHILLEOS M., JONES R.G., *Room-Temperature, High-Yield Route to Poly(*n*-alkylmethylsilane)s and Poly(*di-n*-hexylsilane)*, *Macromolecules*, 2005, **38**, 5, 1633–1639.
5. JONES R.G., HOLDER S.J., *High-yield controlled syntheses of polysilanes by the Wurtz-type reductive coupling reaction*, *Polym. Int.*, 2006, **55**, 7, 711–718.
6. KABETA K., WAKAMATSU S., IMAI T., *Polysilane Synthesis by Catalytic Disproportionation of Alkoxydisilanes with Organolithium Reagents*, *Chem. Lett.*, 1995, **24**, 2, 119–120.

7. KAMETA N., HIRAMUATSU H., SANJI T., SAKURAI H., *Network Polysilanes with Amino Groups: Synthesis from By-Products in the Industrially Operated Direct Synthesis of Chloromethylsilanes and their Photophysical Properties*, J. Inorg. Organomet. Polym Mater., 2007, **17**, 4, 589–594.
8. KOE J.R., MOTONOGA M., FUJIKI M., WEST R., *Synthesis and Spectroscopic Characterization of Heteroatom Polysilylenes: Poly(dialkoxysilylene)s and Evidence for Silicon σ -Oxygen n Mixing Interaction*, Macromolecules, 2001, 34, 4, 706–712.
9. KOE J.R., FUJIKI M., *Heteroatom Polysilylenes*, Silicon Chemistry, 2002, **1**, 2, 77–87.
10. LI C., FINN M.G., *Click chemistry in materials synthesis. II. Acid-swappable crosslinked polymers made by copper-catalyzed azide-alkyne cycloaddition*, J. Polym. Sci. Part A: Polym. Chem., 2006, **44**, 19, 5513–5518.
11. MORITOMO Y., TOKURA Y., TACHINABA H., KAWABATA Y., MILLER R.D., *Excited states of one-dimensional excitons in polysilanes as investigated by two-photon spectroscopy*, Phys. Rev. B, 1991, **43**, 18, 14746–14749.
12. SACARESCU G., SACARESCU L., ARDELEANU R., KURCOK P., JEDLINSKI Z., *Si-H Functional Polysilanes via a Homogeneous Reductive Coupling Reaction*, Macromol. Rapid Commun., 2001, **22**, 6, 405–408.
13. SAKURAI H., *Advanced Technology of Organosilicon Polymers*, CMC Co LTD, Tokyo, 1996.
14. SAKURAI H., HONBRI R., SANJI T., *Stereoselective Anionic Polymerization of Amino-Substituted Masked Disilenes*, Organometallics, 2005, **24**, 17, 4119–4121.
15. VAULTIER M., KNOUZI N., CARRIE R., *Reduction d'azides en amines primaires par une methode generale utilisant la reaction de Staudinger*, Tetrahedron Letters, 1983, **24**, 8, 763–764.

Received April 10, 2014