

# HYPERBRANCHED POLYDIALLYLSILANES - REITERATIVE DENSIFYING OF MOLECULAR STRUCTURE

Olga B. Gorbatshevich<sup>1</sup>, Aziz M. Muzafarov<sup>1</sup>, Vladimir G. Krassowski<sup>1</sup>,  
Georgios Pistolis<sup>2</sup>, Angelos Malliaris<sup>2</sup>

(1) Laboratory of Organoelement Polymers Synthesis, Institute of Synthetic Polymer Materials of Academy of Sciences of Russia, Profsoyuznaya 70, Moscow 117393, Russia, Fax: 007-095-420-22-29, aziz@ispm.ru,

(2) Molecular Electronic Spectroscopy Lab, Institute of Physical Chemistry, NRC «Demokritos», Agia Paraskevi Attiki, 15310 Athens, Greece

## Introduction

Hyperbranched polymers which are in close relation to correspondent dendrimers attract much attention as available analogs that could be used in some applications. Main differences between regular and irregular dendritic systems were clearly formalized using differences in polymers composition<sup>1</sup>. At the same time it's clear that the differences in the set of structural units could be easily eliminated by one-two step synthetic operations. This makes the non-formal valuation of the similarity and the differences between two systems actual enough. As a flexible synthetic media - chemistry of polyallylcarbosilane's was chosen. It has been shown earlier that full conversion of allylic groups in hydrosilylation process could be achieved<sup>2</sup>. The process of hyperbranched polyallylcarbosilane structure densifying was realized using the reiterative approach to molecular structure formation. In order to be able accurately estimate densification results fluorescent dye molecule has been introduced in molecular structure. This work focused on chemical transformation of starting polymer structure performing.

## Experiment

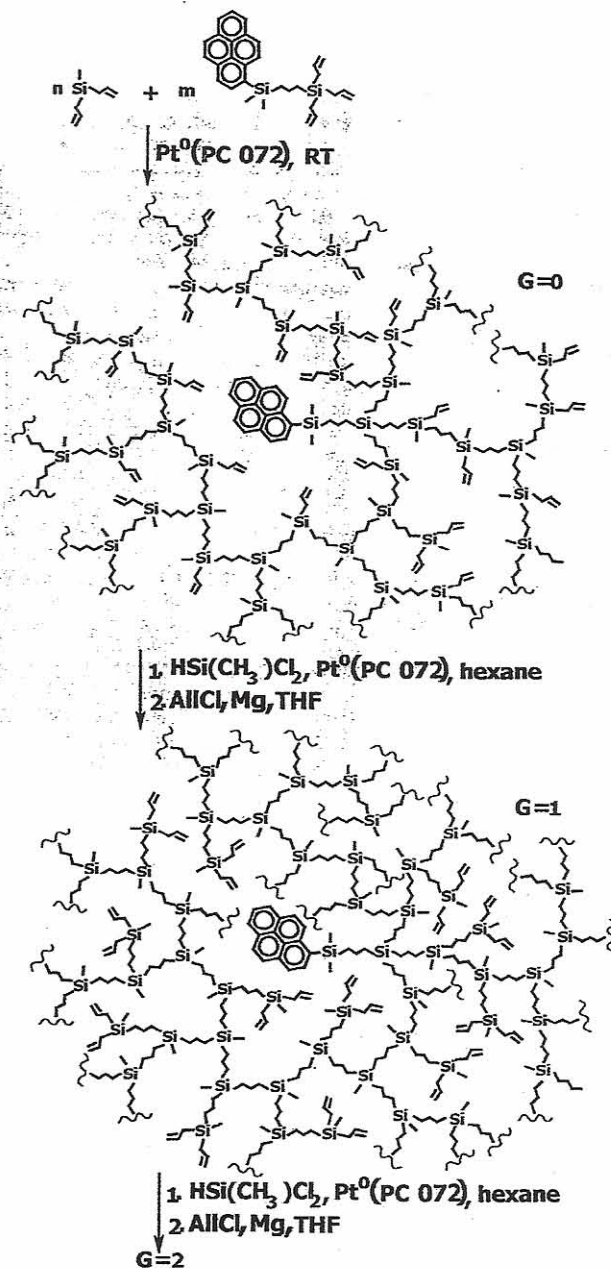
**Synthesis** The pyrene bearing regulator of the chain growth, viz. 1-(triallylsilyl)-3-(dimethylpyrenylsilyl)propane (I), was prepared following an already published procedure<sup>3</sup>. b) The pyrene bearing polymethyldiallylsilane (II) was synthesized in a way analogous to that of the synthesis of the non-pyrene containing corresponding hyperbranched polymer<sup>4</sup>. Thus, to a one-necked round bottom flask filled with an inert gas (argon), 0.13 g (0.0003 mol) of 1-(triallylsilyl)-3-(dimethylpyrenylsilyl)propane and 7.63 g (0.06 mol) of methyldiallylsilane were placed. The mixture was stirred up to complete homogenization and PC072 catalyst was added (1  $\mu$ L of the catalyst per 1 mL of the reaction mixture). The completion of the reaction was confirmed by the total disappearance of the IR absorption band of Si-H bonds at 2130  $\text{cm}^{-1}$ . The thus obtained polymer was precipitated from a benzene solution by ethanol to remove the low-weight fraction and the catalyst.

**Measurements** <sup>1</sup>H NMR spectra of the samples were recorded using WM-250 spectrometer in CDCl<sub>3</sub> solution. GPC analysis was performed in THF in a Knauer set up equipped with Ultrastaygel 8x300 mm column (Waters) having pore size 10<sup>3</sup> Å, the detectors being, RI Waters R-410 and Knauer UV spectrometer. IR absorption spectra were recorded on a Bruker Equinox 55/S FTIR-spectrometer. The fluorescence instrumentation and methods employed in the present study have been described in previous publications<sup>5</sup> and need not be repeated here.

## Results and discussion

The method of hyperbranched polymethyldiallylsilane preparation was realized using initial core (B3-type) containing fluorescent dye molecule. By this approach introduction only single labeled molecule per hyperbranched macromolecule could be reached. At the same moment the competitive character of hyperbranched structure formation did not guarantee marking of each macromolecule. However, having in mind that the goal of this work is estimation of molecular structure densifying and will not concerned bulk properties it's only important to have high enough concentration of labeled macromolecules to study with various physical approaches. General scheme of the hyperbranched polymers synthesis and further densifying of its structure shown on the Scheme 1. After the first step of the process typical hyperbranched polymethyldiallylsilane was prepared as transparent liquid with slightly green-

yellowish color caused by Py-fragments. The comparison of fluorescent spectra of precipitated polymer with initial core (regulator) compound ones shows that even in bulk Py-dye fragments did not form eximers in spite of strong band observed for core molecule in fluorescent spectra (Fig.1). This fact indicate that even initial hyperbranched polymers structure already rather crowded. Further treatment should even increase the steric hindrance of polymer structure. The next couple of chemical operation: hydrosilylation and Grignard reaction lead to conversion any linear units in molecular structure. It contents now the dendritic and terminal units only, besides labeled core of course. It's important to note that operation of reiterative growth was done with full conversion at each of two stages.



Scheme 1 Densification of hyperbranched polymethyldiallylcarbosilane using reiterative growth method

This fact clearly monitored by  $^1\text{H}$  NMR spectra data shown at Fig. 2 a, b and c. Fig 2a clearly shows signal of Allylic groups protons and triplet of Methyl groups protons indicative for linear, terminal and dendritic terminal units.

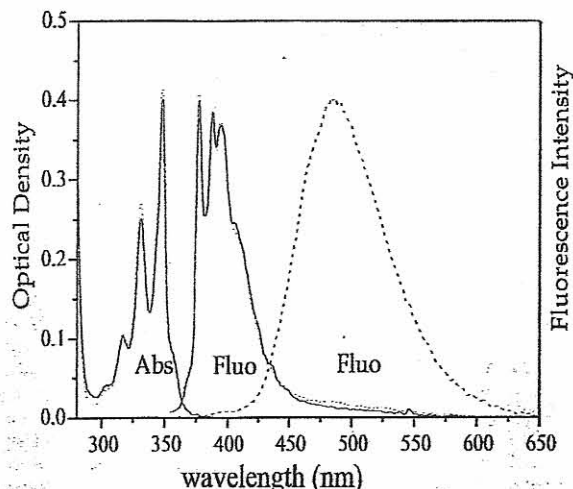


Figure 1 Adsorption/Fluorescence spectra of low MW (dotted line) and high MW (solid line) fractions of polymethyldiallylsilane in bulk; (dashed line): fluorescence spectrum of regulator

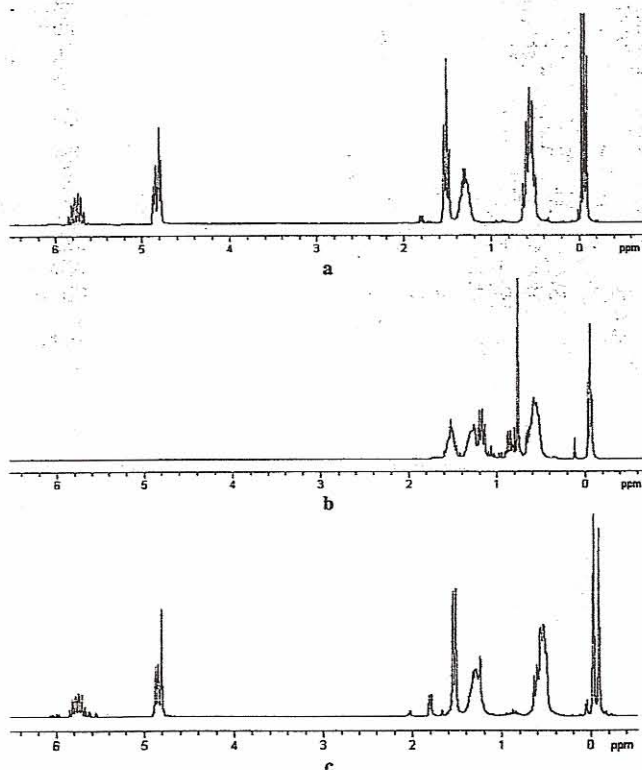


Figure 2.  $^1\text{H}$  NMR spectra: a) Initial hyperbranched polymethyldiallylsilane; b) after hydrosilylation reaction; c) after hydrosilylation and Grignard reactions

The next Fig.2b demonstrates disappearance of allylic double bond protons and presence of two different type of methyl groups protons signals: for terminal and dendritic units only Fig.2c shows appearance of allylic protons multiples after Grignard reaction, disappearance of methyl groups protons signal correspondent to methyldichlorosilyl units and doublet of methyl groups protons instead triplet

in starting hyperbranched polymer (Fig. 2a). These changes indicate only two types of methyl groups presence: at terminated units and at dendritic units. Thus, at list structural unit composition became the same with those of correspondent dendrimer.

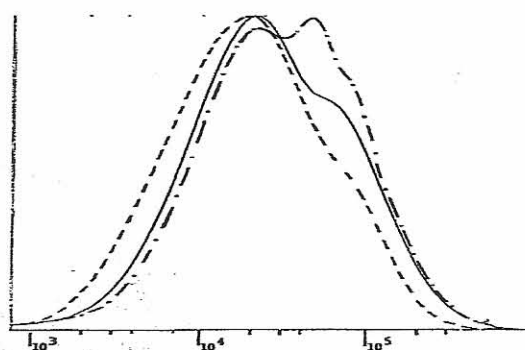


Figure 3 GPC curves of hyperbranched polymethyldiallylsilanes: Initial hyperbranched polymer (dotted line); after first treatment (solid line); after second treatment (dashed line)

The data of GPC analysis for all three samples: initial hyperbranched polymer and two it's modifications prepared by reiterative method discussed above are shown at Fig.3. Even taking into account that GPC data of hyperbranched polymers obtained against Polystyrene standards could not be used directly, one could find that hydrodynamic radius all three samples very close. At the same time each synthetic iteration increase molecular mass exactly in twice, which means that sample G2 has four times larger molecular weight in comparison with initial polymer. Two last conclusions related to the same objects allow to discuss densifying of hyperbranched polymer structure after modification of it's molecular structure using reiterative method.

#### Conclusion

Three samples of hyperbranched polymethyldiallylsilane containing fluorescent dye unit per molecule possesses identical chemical composition and type of molecular organization have been synthesized. The data of preliminary characterization using GPC and NMR data allow to come to conclusion molecular structure densifying concerned. Fine experiments of fluorescence quenching experiments together with SAXS measurements going to be used for further investigation of presented objects.

#### Acknowledgments

Authors thank NATO Scientific Office (Grant CRG.LG974186) Young Scientist Commission of Academy Sciences of Russia for financial support

#### References

1. (a) Hawker, C.J.; Lee, R.; Frechet, J.M.J. *J. Am. Chem. Soc.* 1991, 113, 4583; Holter D.; (b) Burgath A.; Frey H. *Acta Polymerica* 1997, 48, 30
2. Muzafarov, A.M.; Gorbatshev, O.B.; Rebrov, E.A.; Ignat'eva, G.M.; Chenskaya, T.B.; Myakushev, V.D.; Bulkin, A.F.; Papkov, V.S. *Polymer Science* 1993, 35, 1575.
3. Krasovskii, V. G.; Ignat'va, G. M.; Myakushev, V. D.; Sadovskii, N. A.; Strelkova, T. V.; Muzafarov, A. M. *Polymer Science* 1996, 38, 1070.
4. Drohmann, Ch.; Moller, M.; Gorbatshev, O.B.; Muzafarov, A. M. *J. Polym. Science Part A: Polymer Chemistry* 2000, 38, 741.
5. (a) Pistolis, G.; Malliaris, A. *Chem. Phys.* 1998, 226, 83. (b) Pistolis, G.; Malliaris, A. *J. Phys. Chem.* 1998, 102, 1095.