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# CROSSLINKABLE SILYLDIHYDROARYLENES

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# CROSSLINKABLE SILYLDIHYDROARYLENES

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## ABSTRACT

Crosslinkable silyldihydroarylenes were synthesized starting from 1,4-(dimethylhydrosilyl)dihydronaphthalene and 9,10-(dimethylhydrosilyl) dihydro-anthracene via catalytic addition of the Si-H reactive groups to the unsaturated bond of triethoxyvinylsilane. Subsequent condensation of the alkoxyl groups leads to bridged polysilsequioxanes which could be used to generate protective layers. IR, and $^1$H-NMR spectral analyses were performed in order to determine the chemical structure of the bis(triethoxysilylethylene)dihydroarylenes. During crosslinking swelling measurements were performed in order to determine the optimal conditions of the process.

*Key Words*: Polymer; Polysilsesquioxane; Carbosiloxane; Naphthalene; Anthracene

## INTRODUCTION

The physical and chemical properties of inorganic polymers can be greatly improved by the introduction of organic groups into the inorganic framework [1]. These properties are influenced by each of the components and their domain size. The demand for improved standards of performance has stimulated research in the area of nanocomposites, hybrid materials with domains on the nanometer scale [2]. Further reduction in domain size accesses the molecular level. This may be accomplished by incorporating

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the polymerizable inorganic group and an organic constituent in the same molecule. The resulting hybrid material morphology could be modulated by the organic/inorganic segments ratio [3]. For this purpose, highly crosslinked hybrid organic–inorganic materials have been prepared from molecular building blocks that contain a variable organic fragment attached to two or more trifunctional silyl groups by nonhydrolizable carbon-silicon bonds. Sol-gel polymerization of such poly(trialkoxysilyl) monomers inherently leads to network materials, bridged polysilsesquioxane. The polymer-bridged polysilsesquioxanes represent one extreme for which the inorganic component is small compared to the organic one [4]. To obtain a greater degree of control over morphology it is suitable to use bis or tris(trialkoxysilanes) as the molecular building blocks for the hybrid materials [5–11] and a rigid molecular spacer which could introduce porosity in the resulting material.

This work is an attempt to obtain crosslinkable silyldihydroarylene polymers which could be used to obtain bridged polysilsesquioxanes as thin layers at direct exposure to ambient moisture. In order to determine the optimal crosslinking conditions, swelling measurements at various intervals of time were also presented.

## EXPERIMENTAL

### Materials

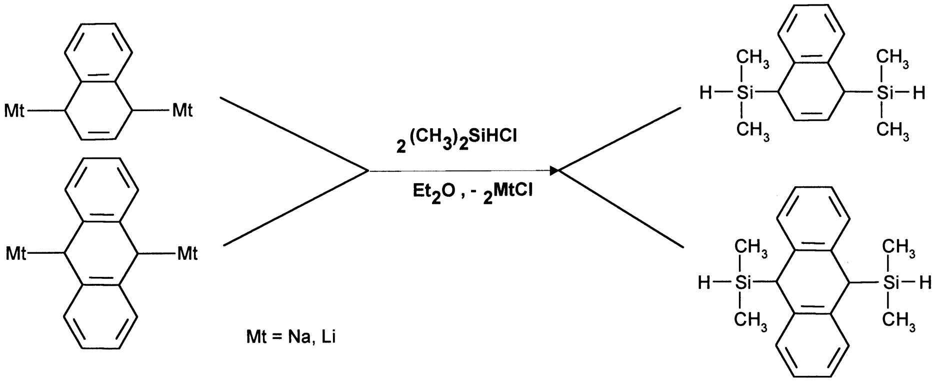
Methyldichlorosilane (98.5% purity) and vinyltriethoxysilane (>98% purity) were supplied by Merck. Naphthalene, anthracene (98.5% purity), hexachloroplatinic acid, $H_2PtCl_2 \cdot 6H_2O$ solution in isopropyl alcohol (HCPA) and dibutyltin dilaurate (pract., >97%) were obtained from Fluka Ag. Methyldichlorosilane was freshly distilled before use.

### Apparatus

$^1$H-NMR spectra were obtained on a JEOL 80 MHz spectrophotometer using $CDCl_3$ as the solvent and tetramethylsilane as the internal standard. IR spectra were recorded on a Perkin-Elmer spectrophotometer in the 400–4000 $cm^{-1}$ region using KBr pellets.

### Synthesis of Dimethylhydrosilyldihydroarylenes

Dimethylhydrosilyldihydroarylenes were synthesized through the coupling reaction of dilithium-dihydroarylenes with methyldichlorosilane in solvent diethyl ether or THF at room temperature following the general procedure described elsewhere [12, 13]. A reaction flask equipped with a



***Reaction Scheme 1.*** Synthesis of dimethylhydrosilyldihydroarylenes.

stirring bar, a reflux condenser, an argon inlet and a dropping funnel was carefully dried and then charged with 0.20 mol dilithium-dihydroarylene dissolved in 50 mL anhydrous diethyl ether. This solution was titrated at room temperature, under vigorous stirring with a 50% wt. methyldichlorosilane solution in diethyl ether until total change of color (Reaction Scheme 1). A white, solid LiCl precipitate separated during this reaction and was filtered under argon atmosphere. Finally, the excess of methyldichlorosilane and the solvent were stripped off.

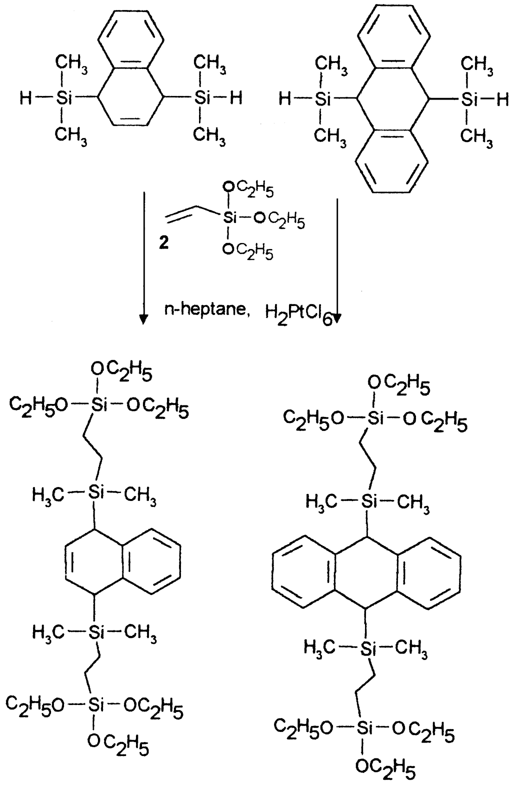
1,4-Bis(dimethylhydrosilyl)dihydronaphthalene – dark yellow liquid product, 8 g, yield: 35%.

9,10-Bis(dimethylhydrosilyl)dihydroanthracene – dark blue liquid product, 10 g, yield: 43%.

### Synthesis of *bis*[(2-Triethoxysilylethylene)-dimethylsilyl]dihydroarylene (TESHA)

A mixture of 0.024 mol dimethylhydrosilyldihydroarylene and 0.05 mol vinyltriethoxysilane in 50 mL anhydrous n-heptane were charged under dry inert atmosphere in a 250 mL three-necked round-bottomed flask fitted with a reflux condenser, a dropping funnel and a mechanical stirrer. This mixture was heated to gentle reflux and then a 0.01 N solution of hexachloroplatinic acid in isopropyl alcohol ($5 \cdot 10^{-6}$ g $H_2PtCl_6$/mol compound with vinyl groups) was added. The reaction proceeds smoothly within 30–60 minutes. (Reaction Scheme 2). The solvent n-heptane and vinyltriethoxysilane in excess were distilled under vacuum from the system. The remaining product was washed with isopropyl alcohol to remove the unreacted silylarylene.

1,4-Bis[(2-triethoxysilylethylene)dimethylsilyl]dihydronaphthalene (TESHA1): light brown liquid, 10 g, yield: 80%.



***Reaction Scheme 2.*** TESHA1 and TESHA2 synthesis reaction.

9,10-Bis[(2-triethoxysilylethylene)dimethylsilyl]dihydroanthracene (TESHA2): brown liquid, 9.5 g, yield: 70%.

## Swelling Measurement

To obtain the crosslinked material, samples of triethoxysilyl-ethylene-dihydroarylenes were exposed to ambient moisture in the absence or in the presence of various amounts of dibutyltin dilaurate (DBTL) catalyst, at various temperatures.

After crosslinking for certain time, samples of the solid material were removed, swollen in toluene for 24 hours and weighted ($m_1$). After that, the samples were washed with toluene, dried under vacuum for 24 hours at room temperature and weighed again ($m_2$). Swelling ($S$) was calculated as:

$$S = \frac{m_1 - m_2}{m_2}$$

## RESULTS AND DISCUSSION

Bridged polysilsesquioxanes were prepared through the hydrolytic condensation reaction of bis(trialcoxysilyl)arylene monomers (TESHA) derived from naphthalene and anthracene (Fig. 1). These monomers were prepared via addition of Si-H functional silyldihydronaphthalene or silyldihydroanthracene to vinyltriethoxysilane using conventional Speier catalyst [14] (Reaction Scheme 2).

Spectral analyses of TESHA's were performed in order to determine their structural characteristics [15].

The $^1$H-NMR spectrum of the TESHA1 (Fig. 2) shows characteristic chemical shifts ($CDCl_3$) at: $\delta = 0.25$ ppm, s (Si-$\mathbf{CH}_3$); $\delta = 0.37$ ppm, s (Si-$\mathbf{CH}_2$-$\mathbf{CH}_2$-Si); $\delta = 1.15$ and 3.62 ppm (Si-O-$\mathbf{CH}_2$-$\mathbf{CH}_3$); $\delta = 2.45$, s (Si-$\mathbf{CH}$-); $\delta = 5.64$, t (-$C_6\mathbf{H}_2$-); $\delta = 7.02-7.81$, m (-$C_6\mathbf{H}_4$-).

Characteristic IR absorption bands for TESHA1: 700–850 $cm^{-1}$ (-CH-naphthalene); 1080–1100 $cm^{-1}$ (Si-O-$C_2H_5$); 1100–1170 $cm^{-1}$ (Si-$CH_2$-$CH_2$-Si) ; 1250 $cm^{-1}$(Si-$CH_3$); 2900–3000 $cm^{-1}$ (CH arom).

The $^1$H-NMR spectrum of the TESHA2 shows characteristic chemical shifts ($CDCl_3$) at: $\delta$ 0.50 ppm, s (Si-$\mathbf{CH}_3$ ); $\delta = 0.37$ ppm, s (Si-$\mathbf{CH}_2$-$\mathbf{CH}_2$-Si); $\delta = 1.15$ and 3.62 ppm, (Si-O-$\mathbf{CH}_2$-$\mathbf{CH}_3$); $\delta$ 2.43 ppm, s (-Si-$\mathbf{CH}$-); $\delta = 5.62$, t (-$C_6\mathbf{H}_2$-); $\delta$ 7.33–7.85, m (-$C_6\mathbf{H}_4$-).

The IR spectrum of the TESHA2 (Fig. 3) shows specific absorption bands at: 700–900 $cm^{-1}$(-CH-anthracene); 1070–1090 $cm^{-1}$ (Si-O-$C_2H_5$); 1100–1160 $cm^{-1}$ (Si-$CH_2$-$CH_2$-Si); 1260 $cm^{-1}$ (Si-$CH_3$); 2950–3100 $cm^{-1}$ (CH arom).

The spectral analysis confirmed the appearance of the characteristic signals of the ethylene bridge resulted from the addition process. Therefore in the $^1$H-NMR spectrum these appeared in the 0.36–0.38 ppm region. IR

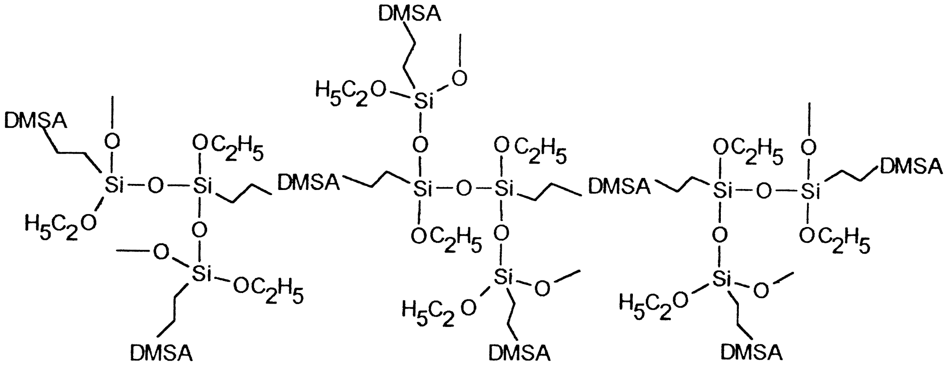


*Figure 1.* Bridged dihydroarylenecarbosiloxane DMSA = dimethylsilyldihydroarylene.

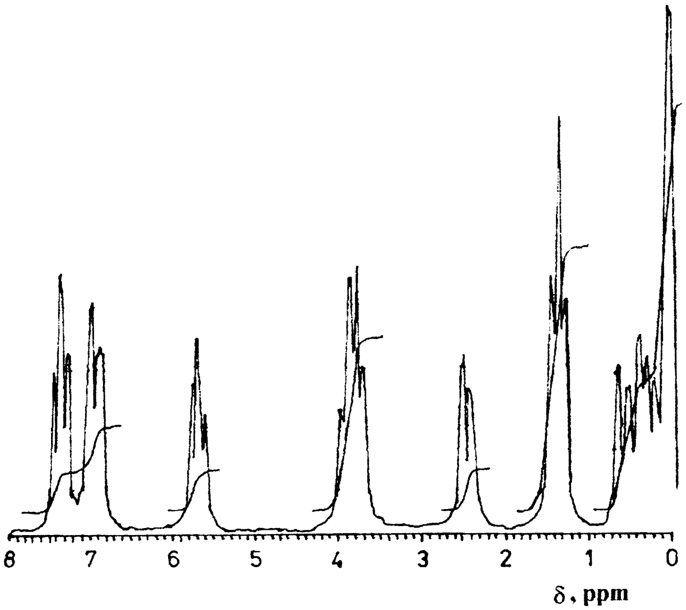


*Figure 2.* $^1$H-NMR spectrum of TESHA1.

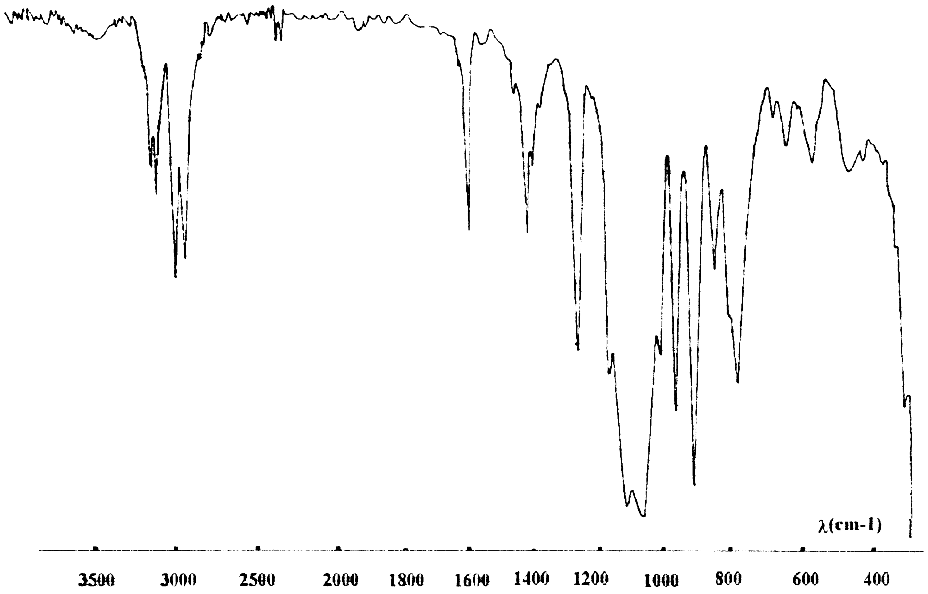


*Figure 3.* IR spectrum of TESHA2.

spectral data show a characteristic peak in the 1070–1170 $cm^{-1}$ region resulted through overlapping of (Si-$CH_2$-$CH_2$-Si) and (Si-O-$C_2H_5$) absorption bands.

The crosslinking mechanism proceeds via two elementary steps, which are the hydrolysis of the ethoxysilane groups and the condensation of the resulting silanols. Therefore the properties of the obtained polymers depend on specific parameters such as reaction time, catalyst, temperature, and moisture presence.

Qualitative experiments were made varying these parameters in order to obtain information on the optimal crosslinking conditions.

### Ambient Exposure Without Catalyst

Crosslinking was observed for samples exposed to ambient atmosphere at different temperatures. Results are presented in Table 1.

In this case, the crosslinking reaction was present as a result of the diffusion of water from the ambient atmosphere within various periods of time which became shorter when increasing the temperature. A slight influence of the nature of the arylene segment was observed. Therefore in the case of the anthracene polymer the gelation time was longer and became almost constant over 50°C.

In order to reduce the crosslinking time, small amounts of water (~2% vol.) were added, under stirring, directly into the liquid samples. In this case, the crosslinked polymer changed its color to light brown and became very sticky. We assumed that the presence of water into the liquid sample initiate parallel and incomplete hydrolysis and condensation reactions which lead to a great dimensional dispersity of the obtained polymer chains.

To increase the rate of the crosslinking process, dibutyltin dilaurate (DBTL) was used as a well known catalyst for condensation processes of

***Table 1.*** Crosslinking Time vs. Temperature

| Oligomer | Temperature (°C) | Crosslinking Time Ambient Moisture, (D) | Crosslinking Time Water Added, (D) |
|---|---|---|---|
| TESHA1 | Room temperature | 4 | 2 |
| | 50 | 3 | 1 |
| | 70 | 2 | 0.5 |
| TESHA2 | Room temperature | 7 | 3 |
| | 50 | 5 | 2 |
| | 70 | 5 | 2 |

alcoxysilanes in industrial applications. All experiments were made at ambient moisture exposure.

## Influence of the Crosslinking Temperature

As shown in Table 1, a strong influence of the temperature on the crosslinking time could be noticed only below 50°C. At higher temperatures (70°C) both copolymers seem to arrive at constant crosslinking time values which could not be modified with further increase of temperature or DBTL concentration. In every case, swelling reached a plateau in various intervals of time depending on the temperature and catalyst concentration. In the dihydronaphthalene case, constant values of swelling were reached after 24 hours at 70°C and 30 hours at room temperature ([DBTL] = 0.5%, Fig. 4). In the dihydroanthracene case, this plateau was reached after 30 hours at 70°C and 40 hours at room temperature ([DBTL] = 0.5%, Fig. 5).

## Influence of the Dibutyltin Dilaurate

In the domain of low DBTL concentrations it is possible to observe (Table 2) a strong temperature dependence on the gelation time.

Increasing of the DBTL concentration leads to a shortening of the crosslinking time for both copolymers. The same effect could be obtained using higher temperatures. At room temperature, the crosslinking time de-

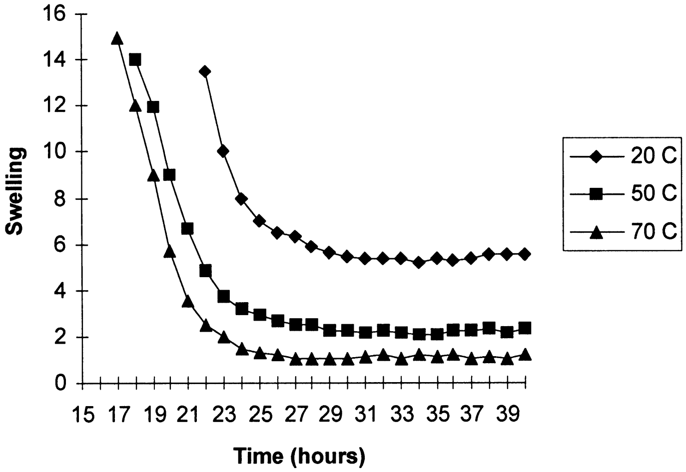


*Figure 4.* Swelling vs. crosslinking time of dihydronaphthalene copolymer at 0.5% DBTL and various temperatures.

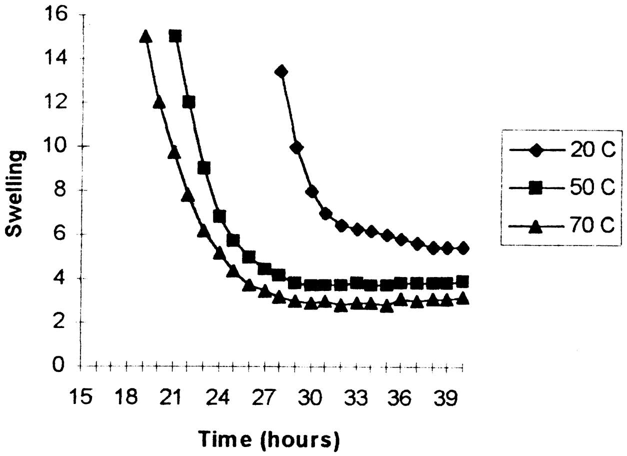


*Figure 5.* Swelling vs. crosslinking time of dihydroanthracene copolymer at 0.5% DBTL and various temperatures.

*Table 2.* Crosslinking Time vs. Concentration of Dibutyltin Dilaurate and Temperature

| Arylene | Catalyst Concentration, %Wt | 0.5 | 1 | 1.5 |
|---|---|---|---|---|
| TESHA1 | Room temperature | 22 h | 16 h | 15 h |
| | 50°C | 18 h | 14 h | 13 h |
| | 70°C | 17 h | 13 h | 13 h |
| TESHA2 | Room temperature | 28 h | 24 h | 22 h |
| | 50°C | 21 h | 20 h | 20 h |
| | 70°C | 19 h | 19 h | 19 h |

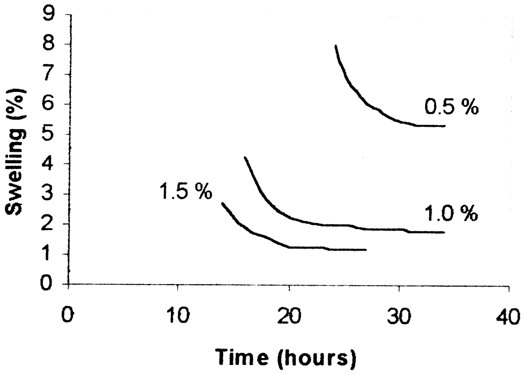


*Figure 6.* Swelling vs. crosslinking time for dihydronaphthalene copolymer at room temperature and various DBTL concentrations.

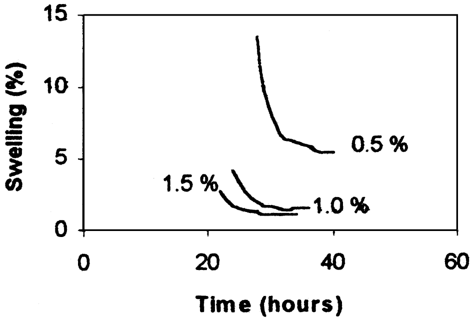


*Figure 7.* Swelling vs. crosslinking time for dihydroanthracene copolymer at room temperature and various DBTL concentrations.

pendence on the DBTL concentration (Figs. 6 and 7) shows an optimum at 1.5% DBTL.

## CONCLUSION

Crosslinkable polysilsesquioxanes with naphthalene or anthracene segments were synthesized via addition of triethoxyvinylsilane to Si-H functional dihydroarylenecarbosilanes.

Through exposure at ambient moisture and various amounts of dibutyltin dilaurate as condensation catalyst, a crosslinking study of the alcoxy functionalized carbosilane monomers at different temperatures was made.

Both materials could be used as precursors for thermoresistant polymer protective coatings.

## REFERENCES

1. Schmit, H. Multifunctional Inorganic-Organic Composite Sol-Gel Coatings for Glass Surfaces **1994**, *178*, 302.
2. Novak, B.M. Nanostructured Organic-Inorganic Hybrid Materials Synthesized 'Through Simultaneous Processes. ACS Symposium Series **1995**, *585*, 86.
3. Wei, Y.; Yeh, J.-M.; Jin, D.; Jia, X.; Wang, J. Composites of Electronically Conductive Polyaniline with Polyacrylate-Silica Hybrid Sol-Gel Materials. Chem. Mater. **1995**, *7*, 969.
4. Shea, K.J.; Loy, D.A.; Webster, O.W. Aryl-Bridged Polysilsesquioxanes-New Microporous Materials. Chem. Mater. **1989**, *1*, 572.
5. Keller, T.M. High-Temperature Copolymers from Inorganic-Organic Hybrid Polymer and Multi-Ethynylbenzene. ACS Symposium Series **1995**, *599*, 267.
6. Shea, K.J.; Loy, D.A.; Webster, O.W. Arylsilsesquioxane Gels and Related Materials. New Hybrids of Organic and Inorganic Networks. J. Am. Chem. Soc. **1992**, *114*, 6700.

7. Corriu, R.J.P.; Moreau, J.J.E.; Thepot, P.; Man, M.W.C.; Chorro, C.; Lere-Porte, J.P.; Sauvajol, J.L. Trialkoxysilyl Mono-, Bi-, and Terthiophenes as Molecular Precursors of Hybrid Organic-Inorganic Materials. Chem. Mater. **1994**, *6*, 640.
8. Rehahn, M.; Organic/inorganic Hybrid Polymers. Acta Polymerica **1998**, *49* (5), 201.
9. Barrie, P.J.; Carr, S.W.; Ou, D.L.; Sullivan, A.C. Formation and Characterization of Novel Organo-Disilicate Glasses. Chem. Mater. **1995**, *7*, 265.
10. Loy, D.A.; Buss, R.J.; Assink, R.A.; Shea, K.J.; Oviatt, H. Alkylene-Bridged Polysilsesquioxane Aerogels, Highly Porous Hybrid Organic-Inorganic Materials. Journal of Non-Crystalline Solids **1995**, *186*, 44.
11. Jamison, G.M.; Loy, D.A.; Shea, K.J. Bridged Polygermsesquioxanes. Organically Modified Germanium Oxide Materials. Chem. Mater. **1993**, *5*, 1193.
12. Sacarescu, L.; Luchian, N.; Marcu, M.; Sacarescu, G.; Ardeleanu, R. Hydrosilnaphthalene-Siloxane Copolymers. Journ. Mac. Sci., Pure & Appl. Chem. **1997**, *A34* (4), 735.
13. Sacarescu, G.; Sacarescu, L.R.; Ardeleanu, M.; Marcu, N. Voiculescu, Polysilaanthracene Synthesis. Eur. Polym. J. **2000**, *36*, 2089.
14. Speier, J.L.; Webster J.A.; Barnes, G.H. The Addition of Silicon Hydrides to Olefinic Double Bonds. Part II. The Use of Group VIII Metal Catalysts. J. Am. Chem. Soc. **1957**, *79*, 974.
15. Smith, A.L. *The Analytical Chemistry of Silicones*; John Wiley & Sons, Inc.: New York, 1991; 305–362.

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