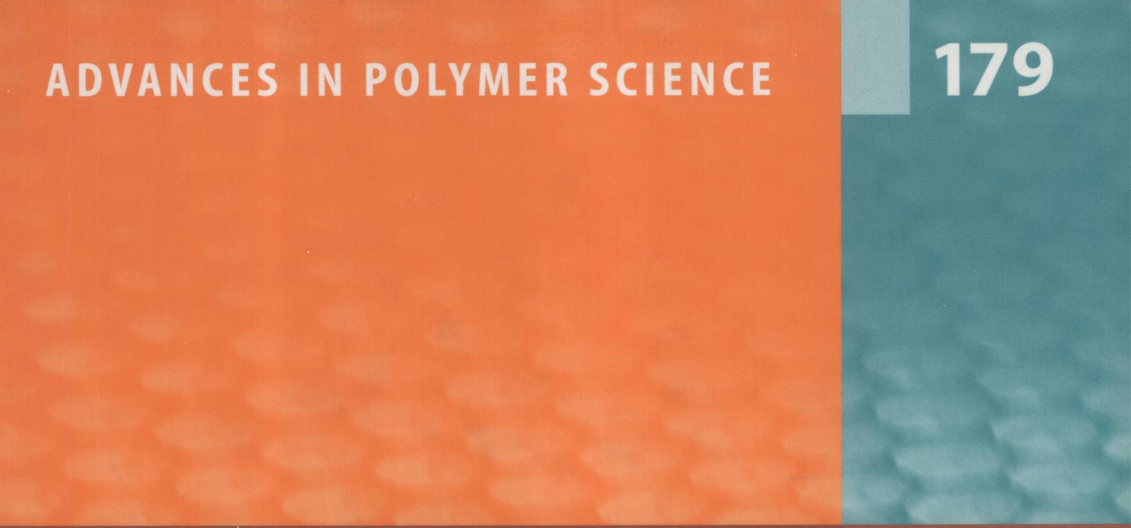
ADVANCES IN POLYMER SCIENCE

179



Inorganic Polymeric Nanocomposites and Membranes

Springer

Inorganic Polymeric Nanocomposites and Membranes

With contributions by
O. Becker · B. Boutevin · F. Guida-Pietrasanta · N. Hasegawa
M. Klapper · P. V. Kostoglodov · D. Likhatchev · K. Müllen
M. Kato · A. L. Rusanov · G. P. Simon · A. Usuki

Springer

This series presents critical reviews of the present and future trends in polymer and biopolymer science including chemistry, physical chemistry, physics and material science. It is adressed to all scientists at universities and in industry who wish to keep abreast of advances in the topics covered.

As a rule, contributions are specially commissioned. The editors and publishers will, however, always be pleased to receive suggestions and supplementary information. Papers are accepted for "Advances in Polymer Science" in English.

In references Advances in Polymer Science is abbreviated *Adv Polym Sci* and is cited as a journal.

The electronic content of *Adv Polym Sci* may found at springerlink.com

Library of Congress Control Number: 20045921922

ISSN 0065-3195
ISBN-10 3-540-25325-4 **Springer Berlin Heidelberg New York**
ISBN-13 978-3-540-25325-9 **Springer Berlin Heidelberg New York**
DOI 10.1007/b101390

Springer is a part of Springer Science+Business Media
springeronline.com

Printed in Germany

Cover design: *Design & Production* GmbH, Heidelberg
Typesetting and Production: LE-TEX Jelonek, Schmidt & Vöckler GbR, Leipzig

Printed on acid-free paper 02/3141 YL – 5 4 3 2 1 0

179
Advances in Polymer Science

Advances in Polymer Science

Recently Published and Forthcoming Volumes

Intrinsic Molecular Mobility and Toughness of Polymers II
Volume Editor: Kausch H.H.
Vol. 188, 2005

Intrinsic Molecular Mobility and Toughness of Polymers I
Volume Editor: Kausch H.H.
Vol. 187, 2005

Polysaccharides I
Structure, Characterisation and Use
Volume Editor: Heinze T.T.
Vol. 186, 2005

Advanced Computer Simulation Approaches for Soft Matter Science II
Volume Editors: Holm C., Kremer K.
Vol. 185, 2005

Crosslinking in Materials Science
Vol. 184, 2005

Phase Behavior of Polymer Blends
Volume Editor: Freed K.
Vol. 183, 2005

Polymer Analysis · Polymer Theory
Vol. 182, 2005

Interphases and Mesophases in Polymer Crystallization II
Volume Editor: Allegra G.
Vol. 181, 2005

Interphases and Mesophases in Polymer Crystallization I
Volume Editor: Allegra G.
Vol. 180, 2005

Inorganic Polymeric Nanocomposites and Membranes
Vol. 179, 2005

Polymeric and Inorganic Fibres
Vol. 178, 2005

Poly(arylene ethynylene)s
From Synthesis to Application
Volume Editor: Weder C.
Vol. 177, 2005

Metathesis Polymerization
Volume Editor: Buchmeiser M.R.
Vol. 176, 2005

Polymer Particles
Volume Editor: Okubo M.
Vol. 175, 2005

Neutron Spin Echo in Polymer Systems
Authors: Richter D.,
Monkenbusch M., Arbe A., Colmenero J.
Vol. 174, 2005

Advanced Computer Simulation Approaches for Soft Matter Sciences I
Volume Editors: Holm C., Kremer K.
Vol. 173, 2005

Microlithography · Molecular Imprinting
Vol. 172, 2005

Polymer Synthesis
Vol. 171, 2004

NMR · 3D Analysis · Photopolymerization
Vol. 170, 2004

Long-Term Properties of Polyolefins
Volume Editor: Albertsson A.-C.
Vol. 169, 2004

Polymers and Light
Volume Editor: Lippert T.K.
Vol 168, 2004

New Synthetic Methods
Vol. 167, 2004

Editorial Board

Prof. Akihiro Abe
Department of Industrial Chemistry
Tokyo Institute of Polytechnics
1583 Iiyama, Atsugi-shi 243-02, Japan
aabe@chem.t-kougei.ac.jp

Prof. A.-C. Albertsson
Department of Polymer Technology
The Royal Institute of Technology
S-10044 Stockholm, Sweden
aila@polymer.kth.se

Prof. Ruth Duncan
Welsh School of Pharmacy
Cardiff University
Redwood Building
King Edward VII Avenue
Cardiff CF 10 3XF
United Kingdom
duncan@cf.ac.uk

Prof. Karel Dušek
Institute of Macromolecular Chemistry
Academy of Sciences of the
Czech Republic
Heyrovský Sq. 2
16206 Prague 6, Czech Republic
dusek@imc.cas.cz

Prof. Dr. W. H. de Jeu
FOM-Institute AMOLF
Kruislaan 407
1098 SJ Amsterdam, The Netherlands
dejeu@amolf.nl
and
Dutch Polymer Institute
Eindhoven University of Technology
PO Box 513
5600 MB Eindhoven, The Netherlands

Prof. Jean-François Joanny
Physicochimie Curie
Institut Curie section recherche
26 rue d'Ulm
75248 Paris cedex 05, France
jean-francois.joanny@curie.fr

Prof. Hans-Henning Kausch
EPFL SB ISIC GGEC
J2 492 Bâtiment CH
Station 6
CH-1015 Lausanne, Switzerland
kausch.cully@bluewin.ch

Prof. S. Kobayashi
Department of Materials Chemistry
Graduate School of Engineering
Kyoto University
Kyoto 615-8510, Japan
kobayasi@mat.polym.kyoto-u.ac.jp

Prof. Kwang-Sup Lee
Department of Polymer Science & Engineering
Hannam University
133 Ojung-Dong
Daejeon 306-791,Korea
kslee@mail.hannam.ac.kr

Advances in Polymer Science Also Available Electronically

For all customers who have a standing order to Advances in Polymer Science, we offer the electronic version via SpringerLink free of charge. Please contact your librarian who can receive a password or free access to the full articles by registering at:

springerlink.com

If you do not have a subscription, you can still view the tables of contents of the volumes and the abstract of each article by going to the SpringerLink Homepage, clicking on "Browse by Online Libraries", then "Chemical Sciences", and finally choose Advances in Polymer Science.

You will find information about the

- Editorial Board
- Aims and Scope
- Instructions for Authors
- Sample Contribution

at springeronline.com using the search function.

Contents

Adv Polym Sci (2005) 179: 1–27
DOI 10.1007/b104479

Polysilalkylene or Silarylene Siloxanes Said Hybrid Silicones

F. Guida-Pietrasanta (✉) · B. Boutevin

Laboratoire de Chimie Macromoléculaire, UMR 5076 CNRS,
Ecole Nationale Supérieure de Chimie de Montpellier, 8 Rue de l'Ecole Normale,
34296 Montpellier Cedex 5, France
francine.guida-pietrasanta@enscm.fr, bernard.boutevin@enscm.fr

Abstract This paper reviews different methods of synthesis of polysilalkylene or silarylene siloxanes that are sometimes called "hybrid" silicones. This special type of silicone has been developed to avoid the drawback of the depolymerization of classical polysiloxanes in certain conditions and to obtain elastomers with enhanced thermal and fuel resistance properties. These silicones have been prepared through two main routes: the polycondensation of α,ω-bis silanol monomers (prepared either via an organometallic route or via hydrosilylation of α,ω-dienes) and the polyhydrosilylation of α,ω-dienes with dihydrodisiloxanes or oligosiloxanes.

Keywords Fluorinated polysiloxanes · Hydrosilylation · Polycarbosiloxanes · Polycondensation · Polysilalkylene siloxanes · Polysilarylene siloxanes

Abbreviations

BPA	bisphenol A
DMS	dimethylsiloxane
HSCTs	high speed civil transports
PDMS	polydimethylsiloxane
PI/PS	poly(imidesiloxanes)
Pt-DVTMDS	platinum-divinyl-1,3 tetramethyldisiloxane
PTFPMS	polytrifluoropropylmethylsiloxane

$ScCO_2$	supercritical carbon dioxide
TMG/CF_3CO_2H	tetramethylguanidine/trifluoroacetic acid
TMPS-DMS	tetramethyl-p-silphenylenesiloxane-dimethylsiloxane

1
Introduction

Classical polysiloxanes – $[(R)(R')SiO]_n$ – have been extensively studied and some of them were already commercialized as early as the 1940s. Their various properties allowed applications in such various fields as aeronautics, biomedical, cosmetics, waterproof surface treatment, sealants, unmolding agents, etc. What is particularly interesting with silicones is the great flexibility of their backbones, due to the OSiO chainings, which induces a very low glass transition temperature (T_g), and also their low surface tension which makes them hydrophobic. These two properties account for their wide range of applications despite their high cost.

They also exhibit a rather good thermal stability, but in certain conditions (in acid or base medium or at high temperature) they may depolymerize due to chain scission of some SiOSi moieties through a six centers mechanism [1] (cf. Fig. 1), and give rise to cycles and shorter linear chains.

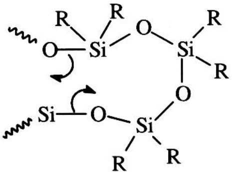
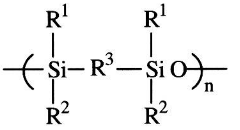


Fig. 1

This intramolecular cycloreversion may occur from at least 4 SiO bonds [2].

So, several researchers have shown interest in another type of polysiloxane: polysilalkylenesiloxanes or hybrid silicones alternating SiO and SiC bonds in their backbones and having the following general formula:



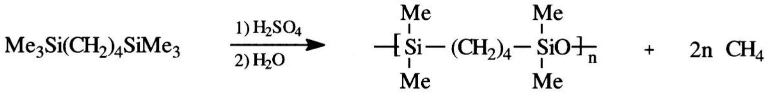
$$\left(\underset{R^2}{\overset{R^1}{Si}} - R^3 - \underset{R^2}{\overset{R^1}{Si}}\,O \right)_n$$

Fig. 2

where R^3 may be an alkyl, aryl, alkyl aryl or fluoroalkyl chain.

Several synthetic routes have been described in the literature to obtain these polysiloxanes. They will be examined hereafter.

One of the first examples of hybrid silicone was published in 1955 [3] by Sommer and Ansul, who reported the obtention of hybrid "paraffin-siloxanes" containing the 1,6-disilahexane group which was synthesized as follows:



$$Me_3Si(CH_2)_4SiMe_3 \xrightarrow[2)\,H_2O]{1)\,H_2SO_4} -\!\!\left[\overset{Me}{\underset{Me}{Si}}-(CH_2)_4-\overset{Me}{\underset{Me}{Si}}O\right]_n\!\!- \;+\; 2n\,CH_4$$

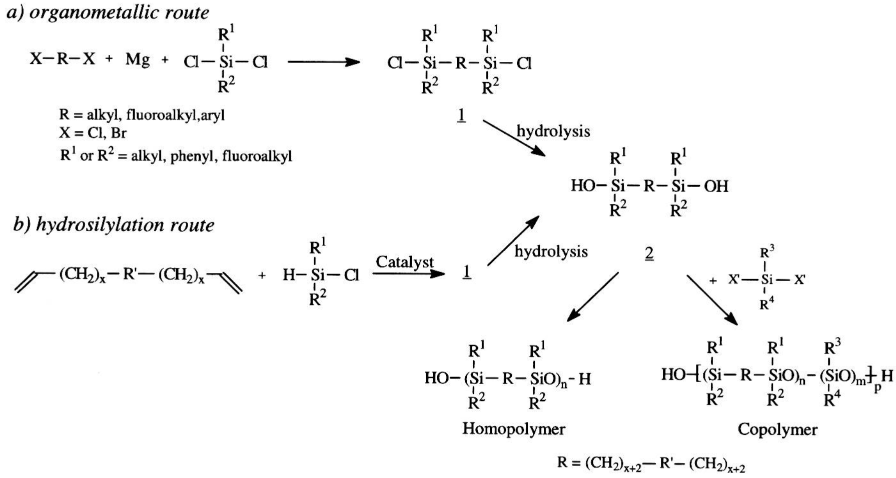
Scheme 1

This hybrid silicone was presented as a compound having an intermediate structure between linear methylpolysiloxanes and paraffin hydrocarbons.

Then, during the years 1960–1970 many other examples of hybrid silicones were described, particularly silphenylene-siloxanes that are hybrid silicones containing phenyl groups in the backbone of the siloxane chain, and also fluorinated hybrid silicones with or without aromatic groups in the backbone or as side chains.

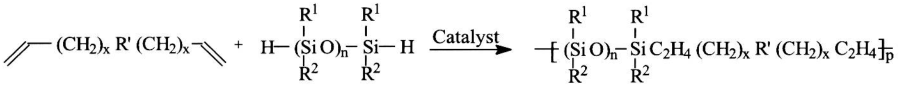
These silicones are generally obtained using two main pathways:

1. From bis-silanol monomers, themselves prepared either via an organometallic route or via hydrosilylation of α,ω-dienes. The bis-silanol monomers are then polymerized to give hybrid homopolymers or condensed with difunctional silanes to give copolymers (cf. Scheme 2).



Scheme 2

2. Through polyaddition of α,ω-dienes with α,ω-dihydro di or oligosiloxanes, in other words by polyhydrosilylation (cf. Scheme 3).



Scheme 3

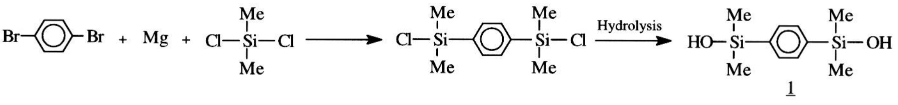
This review concerns silalkylene siloxanes fluorinated or non fluorinated, aromatic or nonaromatic, but we have voluntarily excluded polysilanes, i.e. polymers that contain silicon but without any SiOSi bonds.

2
Synthesis of Hybrid Silicones Starting from Bis-Silanol Monomers

2.1
From Bis-Silanol Monomers Obtained via an Organometallic Route

2.1.1
Aryl and/or Alkyl Backbone

One of the first hybrid bis-silanols that was used in the synthesis of hybrid silicones, and reported by Merker and Scott in 1964 [4], was bis-hydroxy(tetramethyl-p-silphenylene siloxane) 1. It was obtained via a magnesium route according to Scheme 4:



Scheme 4

Then, after polycondensation, it led to the corresponding homopolysilphenylene siloxane (cf. Fig. 3):

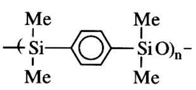
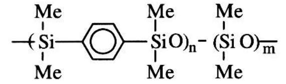


Fig. 3

In reference [4] some previous attempts to synthesize bis-silanol 1 are cited but the results were not reproducible.

The hybrid homosilphenylenepolysiloxane presents a better thermal stability than polydimethylsiloxane (PDMS). It is solid (melting point = 148 °C instead of – 40 °C for PDMS).

Bis-silanol 1 has been used in different syntheses of random, alternated or block copolymers. Merker et al. [5] described random and block copolymers of the following structure:



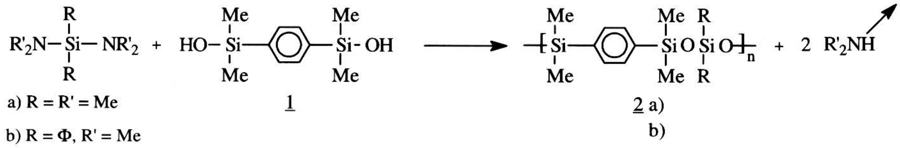
$$-\!\left(\mathrm{Si(Me)_2}-C_6H_4-\mathrm{Si(Me)_2O}\right)_n-\left(\mathrm{Si(Me)_2O}\right)_m-$$

Fig. 4

These polymers were elastic at temperatures above their melting points (which may be up to 148 °C depending on the amount of oxysilphenylene component).

Alternating copolymers were supposed to exhibit the lower crystallinity and the higher thermal stability, but the authors were not able to obtain such polymers as their synthesis method (condensation of 1 with dimethyldichlorosilane) did not lead to alternance.

One year later, Curry and Byrd [6] obtained alternating copolymers by condensing diol 1 with diaminosilanes (cf. Scheme 5):



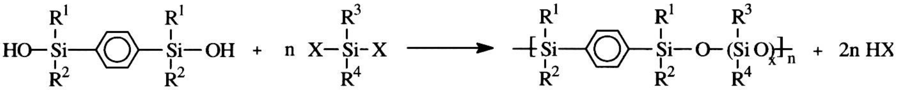
Scheme 5

This same reaction has been reproduced some years later by Burks et al. [7] and amorphous copolymers 2a and 2b were prepared, and studied as thermostable elastomers for the aeronautic industry. Copolymer 2a or poly[1,4-bis(oxydimethylsilyl)benzene dimethylsilane] exhibited a glass transition temperature $T_g = -63$ °C and a very good stability at high temperature. Copolymer 2b or poly[1,4-bis(oxydimethylsilyl)benzene diphenylsilane] exhibited a $T_g = 0$ °C and a higher stability at high temperature.

They were crosslinked at room temperature with $Si(OEt)_4$ and dibutyltin diacetate to give thermostable elastomers.

Since the beginning of the 1980s and during the 1990s, Dvornic and Lenz and their co-workers have published numerous articles on the synthesis of silarylene siloxanes and the study of their thermal properties [8–18]:

The synthesis was achieved according to Scheme 6:



Scheme 6

In reference [15], the authors compare four different ways to obtain these hybrid silarylene-siloxane copolymers:

1. $X = Cl$
2. $X = OCOCH_3$
3. $X = NMe_2$
4. $X = N(\Phi)CON <$ (ureido)

They conclude that the copolymers with higher molecular weights are obtained with ureidosilanes, while those with the lower molecular weights are obtained with chloro and acetoxy silanes, because in both these cases, degradation side reactions occur with the acids formed (HCl and CH_3COOH).

In the various publications [8–18], the nature of R^1 to R^4 were different: methyl, ethyl, vinyl, alkyl, phenyl, cyanoethyl, cyanopropyl, hydrogen and, more recently, fluoroalkyl [17].

The relations between the nature of the polymers and the glass transition temperatures have been studied [16], as well as their thermal stability [13, 14]. The authors have shown that the presence of an aromatic unit in the main chain increases the T_g, as well as the presence of bulky side groups (phenyl, cyanoalkyl, fluoroalkyl). On the contrary, the presence of vinyl or allyl side groups decreases the T_g.

Concerning thermal stability, the best resistance to thermal degradation is obtained with exactly alternating copolymers ($x = 1$ in Scheme 6).

In nitrogen, resistance to pure thermal degradation decreases depending on the type of the side groups R^3 and R^4 (when $R^1 = R^2 = CH_3$) in the following order:

$$CH = CH_2 > C_6H_5 > CH_3 > H > C_2H_4CF_3 > C_2H_4C_6F_{13}$$

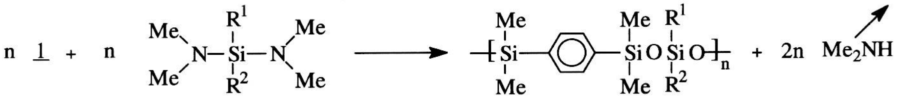
So, the highest stability is observed with the vinyl group.

The synthesis and the properties of silphenylene-siloxanes have been summarized in a chapter of a monograph on silicon polymers [18]:

- DSC (Differential Scanning Calorimetry) measurements showed that the T_g increased when the size of the side groups increased.
- Thermal stability of these polymers is very high: in TGA (Thermal Gravimetric Analysis), they show decomposition not until 480 to 545 °C.

- The average molecular weights of the polymers range from 70 000 to 340 000.

More recently, in 1998 and 1999, McKnight et al. [19–21] reported some vinyl-substituted silphenylene siloxane copolymers with exactly alternating structures and varying vinyl content that were synthesized through disilanol diaminosilane polycondensation, as follows:



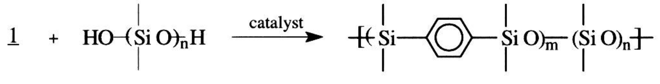
$R^1 = R^2 = CH_3, CH{=}CH_2$, mixt.$CH_3/CH{=}CH_2$

Scheme 7

The copolymers were described as thermally stable, high-temperature elastomers.

It was said that "they had low T_gs (ranging from – 26 to – 86 °C) and exhibited the highest degree of thermal and oxidation stability that has been observed so far for any elastomers". Additionally they were supposed to be promising candidates for potential applications as flame-retardant elastomers, one of the critical needs in many industrial branches such as the aircraft and automotive industry.

A few years earlier, in 1991, Williams et al. [22] had performed the structural analysis of poly(tetramethyl-p-silphenylene siloxane)-poly(dimethylsiloxane) copolymers (TMPS-DMS copolymers) by ^{29}Si NMR. These copolymers were obtained by the condensation of bis-hydroxy(tetramethyl-p-silphenylene siloxane) 1 with α,ω-dihydroxy polydimethyl oligosiloxanes, in the presence of a guanidinium catalyst (cf. Scheme 8):



TMPS -DMS copolymers

Scheme 8

This NMR analysis is particularly useful as the block TMPS-DMS copolymers exhibit a wide range of properties depending upon the composition and average sequence lengths of the soft dimethylsiloxane segments and the hard crystalline silphenylene blocks.

In the years 1988 and 1989, in our laboratory [23, 24] the same bis-hydroxy (tetramethyl-p-silphenylene siloxane) 1 had been used in polycondensation with chlorosilanes fluorinated or nonfluorinated, type $Cl_2Si(Me)R^i$ with $R^i = H$, $CH=CH_2$, R_F and $R_F = C_3H_6OC_2H_4C_nF_{2n+1}$, $C_2H_4C_6F_5$, $C_3H_6OCF_2CFHCF_3$, $C_2H_4SC_2H_4C_nF_{2n+1}$, $C_3H_6SC_3H_6OC_2H_4C_nF_{2n+1}$ and silicones with the following general formula were obtained:

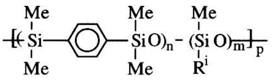


Fig. 5

Silicones containing, at the same time, $R^i = R_F$, $R^i = H$ and $R^i =$ vinyl, are fluorinated silicones with low viscosities, easily crosslinkable by addition of Pt catalyst and that give access to "pumpable" fluorinated silicones.

Later, in 1997, we also described a hybrid silalkylene (C_6H_{12}) polysiloxane obtained by polycondensation of the corresponding hybrid bisilanol bearing methyl and phenyl pendant groups and showed that it also exhibited a good thermal stability [25]. Its $T_g = -52$ °C was higher than that of PDMS, but its degradation temperature in nitrogen was about 100 °C higher than for PDMS and was also higher in air.

Stern et al. [26] had published, in 1987, an article where they studied the structure-permeability relations of various silicon polymers and which gave, among others, the T_g of several hybrid silicones $-[(Me)_2Si-R-Si(Me)_2O]_x-$, where $R = -C_2H_4-, -C_6H_{12}-, -C_8H_{16}-$ (T_gs around -90 °C), $R = m\text{-}C_6H_4-$ ($T_g = -48$ °C) and $R = p\text{-}C_6H_4-$ ($T_g = -18$ °C), but nothing was said about their synthesis.

In fact, in 1997, the synthesis of poly(tetramethyl-m-silphenylene siloxane) was reported by Mark et al. [27] as follows:

Scheme 9

The T_g was then evaluated as -52 °C which is close to the value of -48 °C given by Stern et al. and no melting temperature was detected, contrary to the equivalent p-silphenylene polymer. TGA measurements revealed very good high temperature properties with the onset temperatures for degradation being 415 °C under nitrogen and 495 °C in air.

Finally, silarylene-siloxane-diacetylene polymers were reported by Homrighausen and Keller in 2000 [28], as precursors to high temperature elastomers. They were obtained as follows: