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SYNTHESIS AND CHARACTERIZATION OF POLYSILANES

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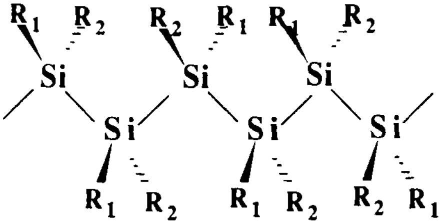
INTRODUCTION

Polysilanes are polymers with a linear Si—Si catenation in the main chain and with two organic substituents at each silicon atom:



(1)

They possess interesting physical and chemical properties and have potential commercial importance [1-3]. Molecular weights of polysilanes are often larger than $M_n = 1,000,000$ and they usually behave as thermoplastic materials which are soluble in typical organic solvents. The high catenation degree can only be matched by carbon-based chains, polygermanes, and polysulfur. Polysilanes formally resemble polyole-

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fins, but there are a number of very important differences between these two classes of polymers:

1. Poor compatibility of the inorganic backbone and organic side groups in polysilanes provides morphologies with clear mesophases [4]. Polysilanes do not form isotropic melts, but in addition to a low temperature glass transition, they exhibit a first-order transition which is associated with the melting of side groups and the partial disordering of the backbone conformation. It seems that at higher temperatures, polysilanes form columnar mesophases [5].

2. Even entirely alkyl-substituted polysilanes absorb above 300 nm with strong extinction coefficients ($\epsilon > 8000$ L/mol/cm). This absorption has been ascribed to σ-σ^* excitation. The silicon-silicon linkage is photosensitive and, depending on the wavelength and intensity of irradiation, is cleaved to various products. Silyl radicals and silylenes are typical intermediates in the photodecomposition. The photosensitivity of polysilanes leads to applications in microlithography [2, 6]. A proportion of chain scission and crosslinking depends on the structure of substituents, and both positive and negative photoresists have been prepared. Polysilanes are among the best photoresists due to very high contrast (originating in photobleaching), good etching properties (high silicon content), and the possibility of dry development (silylenes form in the presence of oxygen volatile cyclosiloxanes). One of the drawbacks of polysilanes as photoresists is relatively low sensitivity (a chemical amplification has not yet been successfully applied to the photodegradation of polysilanes).

3. UV absorption of alkyl-substituted polysilanes originates in the σ-σ^* excitation of the delocalized electrons in the backbone. This phenomenon has been thoroughly discussed theoretically and explained by similar integral orbitals on the same (β_{vic}) and neighboring (β_{gem}) silicons. Thus, from the point of view of electronic structure, polysilanes resemble polyenes more than alkanes. However, in contrast to polyacetylene, polysilanes are highly soluble, form films and fibers of good quality, and can be processed by standard techniques such as film casting, injection molding, extrusion, etc. Strong delocalization of electrons in the backbone provides materials with extremely interesting electronic properties: semiconductors, photoconductors, and nonlinear optical materials [1, 2, 7–9]. Although the current commercial application of polysilanes is limited to ceramic precursors (β-SiC fibers) [3], it seems that one of the future applications of polysilanes will be based on the combination of

optical and electronic properties, photosensitivity, and processability. The advanced materials for optoelectronics should have well-defined structures, but currently prepared polysilanes have high polydispersities and poorly controlled molecular weights. Thus, this paper will mostly deal with various preparative aspects of polysilanes directed toward improvement of structural control, but it will also describe the possibility of the control of other properties in copolysilanes of various composition.

REVIEW OF SYNTHETIC METHODS

Most recent publications in the area of polysilanes are mainly devoted to various aspects of characterization of these novel polymers. Not only absorption, emission, and fluorescence, but also thermochromism, piezochromism, spectroscopic hole burning, photoelectron spectroscopy, third harmonic generation, and a number of other techniques have been recently used [10]. Full credit for these thorough physicochemical studies should be given to the first pioneers in the field of polysilanes: Miller, West, and Ziegler, who not only provided samples of polymers, but who were able to attract leading polymer (not only) physicists and physical chemists to a wonderful world of polysilanes.

The first and still the most common preparative technique is based on the reductive coupling of disubstituted dichlorosilanes. Initially, this method was used by Kipping [11] for diphenyl derivatives and then by Burkhard [12] for dimethyl derivatives. The polymers were insoluble and impossible to characterize at that time. Soluble polysilanes were first prepared from unsymmetrically substituted dichlorosilanes [7, 13, 14]. Usually alkali metals are used, but some other reducing agents, including electrochemical coupling, have been attempted [15]. The products of condensation consist of a mixture of small cyclopolysilanes (usually cyclic tetramer, pentamer, and hexamer are formed), low molecular weight polymer (usually below $M = 10,000$), and high polymer ($M > 100,000$). A number of properties of polysilanes, especially those related to electron delocalization in the main chain, depend strongly on molecular weights. For example [2], extinction coefficients of polysilanes stabilize above $DP = 50$. Thus, polymodality of the obtained polymers limits some characterization techniques and also disables some applications. There is a current need for the preparation of well-defined polysilanes, and there are several approaches to these materials. Use of various reducing agents, inverse addition of the reducing agent (sodium dispersion) to disubstituted dichlorosilanes, use of solvents with different polarities, and low temperature reduction in the presence of ultrasound have been studied, and some of them will be discussed later in this article. There are, however, other methods which do not employ reduction of disubstituted dichlorosilanes.

Historically, the first one was the dehydrogenative coupling of hydridosilanes in the presence of transition metals. This technique usually provides low molecular weight materials ($DP < 12$) [16, 17]. There are two other routes to polysilanes based on the anionic polymerization of "masked disilenes" [18] and on anionic ring-opening polymerization [19]. These techniques may provide additional control of the microstructure of the nonsymmetrically substituted systems. The four major synthetic routes to polysilanes are summarized in Scheme 1.

The last method for the preparation of novel polysilanes is based on the modification process [20]. Various functional side groups are introduced to polymers with existing Si—Si chains. This method will be discussed in more detail later.

SONOCHEMICAL REDUCTIVE COUPLING PROCESS

Polymerization of disubstituted dichlorosilanes with alkali metals via reductive coupling has a strong character of a chain (not a step) process. Molecular weights are very high at low conversions and they are independent of the [Mt]/[Si—Cl] ratio. Thus, polymerization must proceed with some type of active sites. Several intermediates such as silylene, silyl radicals, and silyl anions have been proposed as potential chain carriers (cf. Scheme 2). The first slow step should involve electron transfer from sodium to a monomer to form a monomeric radical anion. This species should very rapidly isomerize to the monomeric radical and sodium chloride, which is insoluble in the reaction medium (1A). The identical reaction between sodium and the chloro-terminated polymer chain will provide a polymeric radical anion and eventually a polymeric radical (1B). The monomeric and the polymeric radicals can recombine in a chain growth process (1C) which involves radical intermediates exclusively. It is known, however, that silyl radicals which contain phenyl groups can be easily reduced further to silyl anions. The polysilane chain may additionally facilitate this reaction (2A). The resulting polysilyl anion will react in a nucleophilic substitution reaction (probably S_N2) with a monomer which is a stronger electrophile (contains two electron-withdrawing

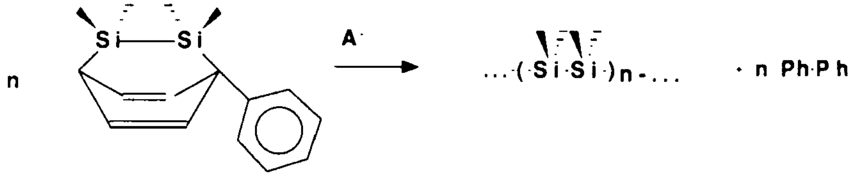
1. **Reductive Coupling**

$$n\ R_2SiCl_2 + 2n\ Mt \dashrightarrow 2MtCl + \ldots\text{-}(\text{-}R_2Si\text{-})_n\text{-}\ldots$$

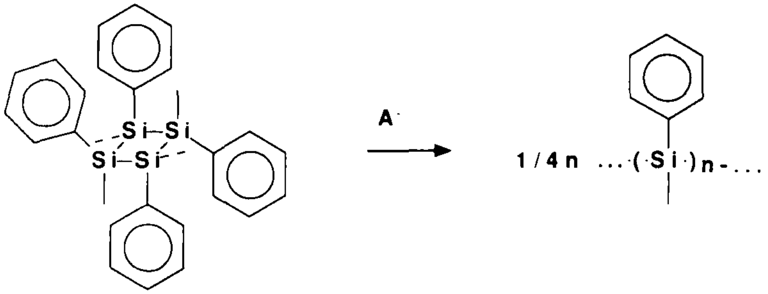
2. **Dehydrogenative Coupling**

$$n\ R_2SiH_2 + Mt^* \dashrightarrow n\ H_2 + \ldots\text{-}(\text{-}R_2Si\text{-})_n\text{-}\ldots$$

3. **Polymerization of Masked Disilenes**



4. **Anionic Ring-Opening Polymerization**



SCHEME 1.

Cl groups) than a chloro-terminated chain. This is an anionic pathway (2B).

The second electron transfer to monomeric radical would provide silylene (3A) which could be easily inserted between Si—Si linkages (3B) Silylene could dimerize to form disilene species which were isolated for compounds with bulky substituents (e.g., mesityl) [21]. Disilenes are, however, very reactive and they should rapidly polymerize if it is thermodynamically possible. Silylene could also lead to the formation of strained reactive cyclic intermediates which would be converted to polysilanes via ring-opening polymerization. However, the mechanism based

$R_2SiCl_2 + Na \dashrightarrow R_2SiCl_2^{\cdot -}, Na^+$ (1A)

$R_2SiCl_2^{\cdot -}, Na^+ \dashrightarrow R_2SiCl\cdot + NaCl$ (1A')

$\ldots\text{-}R_2SiCl + Na \dashrightarrow \ldots\text{-}R_2SiCl^{\cdot -}, Na^+$ (1B)

$\ldots\text{-}R_2SiCl^{\cdot -}, Na^+ \dashrightarrow \ldots\text{-}R_2Si\cdot + NaCl$ (1B')

$\ldots\text{-}R_2Si\cdot + R_2SiCl\cdot \dashrightarrow \ldots\text{-}R_2Si\text{-}SiR_2Cl$ (1C)

$2\ \ldots\text{-}R_2Si\cdot \dashrightarrow \ldots\text{-}R_2Si\text{-}SiR_2\text{-}\ldots$ (1C')

$2\ R_2SiCl\cdot \dashrightarrow ClR_2Si\text{-}SiR_2Cl$ (1C")

$\ldots\text{-}R_2Si\cdot + Na \dashrightarrow \ldots\text{-}R_2Si^-, Na^+$ (2A)

$\ldots\text{-}R_2Si^-, Na^+ + R_2SiCl_2 \dashrightarrow \ldots\text{-}R_2Si\text{-}SiR_2Cl$ (2B)

$R_2SiCl\cdot + Na \dashrightarrow R_2SiCl^-, Na^+$ (3A)

$R_2SiCl^-, Na^+ \dashrightarrow R_2Si: + NaCl$ (3A')

$R_2Si: + \ldots\text{-}R_2Si\text{-}SiR_2\text{-}\ldots \dashrightarrow \ldots\text{-}R_2Si\text{-}SiR_2\text{-}SiR_2\text{-}\ldots$ (3B)

SCHEME 2.

on silylene intermediates is not of primary importance, since silylene traps do not affect polymerization [22].

There are some experimental data which contradict the purely radical process. Strong solvent effects, the influence of crown ethers and cryptands on polymerization rates, and a high yield of cyclics support anionic intermediates. Cyclic polysilanes can hardly be formed via a radical process since this would require the simultaneous presence of two radicals at both chain ends, unless extensive transfer exists [the rate constant of the Cl-atom transfer for the *tert*-butylchloride is $k = 2 \times 10^6\ M^{-1}\cdot s^{-1}$, the C—Cl bond cleavage energy is 81 kcal/mol [13]; since the energy of dissociation of the Si—Cl bond (114 kcal/mol) is much higher, the rate constant of the Cl-atom transfer should be considerably lower]. The anionic chain end will, however, very efficiently "end-bite" the chloro-terminated chain end due to high anchimeric assistance in five- and six-membered rings:

$$\mathrm{Cl\text{-}SiR_2\text{-}(SiR_2)_{n\text{-}2}\text{-}SiR_2^-} \longrightarrow \overline{\left\lfloor(\mathrm{SiR_2})_{n}\right\rfloor} + \mathrm{Cl^-} \qquad (2)$$

Copolymerization studies provide additional support for the anionic mechanism. Sonochemical reductive coupling at ambient temperature is successful for methylphenyldichlorosilane but not for dialkyldichlorosilanes [23]. On the other hand, dialkyldichlorosilanes can be incorporated from 20 to 40% into polymer chains via simultaneous copolymerization. The radical mechanism would lead only to homopoly(methylphenylsilylene). Under anionic conditions the growing silyl anion can react with both electrophilic monomers and incorporate the dialkyldichlorosilane into a polymer chain.

The rate constant of the reaction of triethylsilyl radical with toluene is quite high at room temperature ($k = 1.2 \times 10^6\, M^{-1}\mathrm{s}^{-1}$) [24]. A polymer with a degree of polymerization $DP \approx 10^3$ is usually formed in less than 100 s at a monomer concentration $[M]_0 < 0.1$ mol/L in toluene as solvent ($[\text{toluene}]_0 \approx 10$ mol/L). Thus, the ratio of the rate constants of propagation to transfer should be above 10^5.

$$\mathrm{DP} < \mathrm{k_p \cdot [M]/k_{tr} \cdot [Toluene]} \qquad (3)$$

The estimated rate constant of propagation ($k_p > 10^{11}\, M^{-1}\cdot\mathrm{s}^{-1}$) would exceed the limits of a diffusion controlled process, assuming reactivity of the macromolecular radical similar to triethyl radical. Thus, a purely radical mechanism of chain growth cannot operate in the formation of polysilanes.

Nevertheless, it has been of interest to establish whether the radicals are formed as short-living intermediates in two one-electron transfer steps from chlorosilanes to anions, or the anions are formed directly in one two-electron transfer step from macromolecular chlorosilanes. The use of dichlorosilanes with a pendant alkenyl group gives the possibility of testing the presence of radical intermediates [25]. The kinetics and mechanism of intra- and intermolecular reactions between silyl radicals and alkenes depend on the electronic and steric effects in the alkene. For example, rate constants as high as $k = 1.1 \times 10^9\, M^{-1}\cdot\mathrm{s}^{-1}$ and $k = 2.2 \times 10^8\, M^{-1}\cdot\mathrm{s}^{-1}$ were reported for acrylonitrile and styrene, respective. On the other hand, the rate constant for the reaction with cyclohexene and hexene are $k = 0.9 \times 10^6\, M^{-1}\cdot\mathrm{s}^{-1}$ and $k = 4.6 \times 10^6\, M^{-1}\cdot\mathrm{s}^{-1}$ [15]. The latter rate constants are very close to the reaction of the silyl radical with toluene ($k = 1.2 \times 10^6\, M^{-1}\cdot\mathrm{s}^{-1}$). The intramolecular reaction with a 4-pentenyl substituent has also been studied and the limits of the rate constant set as $10^7\ \mathrm{s}^{-1} < k < 10^9\ \mathrm{s}^{-1}$. Thus, the intramolecular cyclization may compete with the second electron transfer which converts a radical to an anion. Anions react with primary alkenes very slowly.

Thus, under sonochemical conditions (ambient temperature), polymerization has mostly ionic character, although the intermediate radicals have been trapped as a short living species on the pathway from polymers terminated with ... $-SiR_2-Cl$ to ... $-SiR_2^-$, Mt^+ [25]. The former participates in two one-electron transfer processes, whereas the latter reacts with a monomer in a nucleophilic substitution process. The exact nature of the Si—Mt bond is still obscure and, under some conditions, it may have a covalent character.

In toluene, using sodium as a reducing agent, monomers with aryl groups react much faster than dialkylsubstituted dichlorosilanes [23]. Polymerization of dialkylsubstituted dichlorosilanes with sodium requires elevated temperatures (above 80°C), although they react readily with Na/K and K. However, methylphenyldichlorosilane does not react with potassium within 2 h under similar conditions. This apparent discrepancy has been solved by analysis of the product of the reaction of methylphenyldichlorosilane with K at longer reaction times. The resulting polymer ($M_n \approx 2000$) is *not* a polysilane [27]. See Fig. 1. It does not absorb above 300 nm, and it contains a large amount of toluene moieties, in contrast to any other polysilanes. GC/MS analysis of the first products formed in this reaction indicates the presence of Cl—Si-

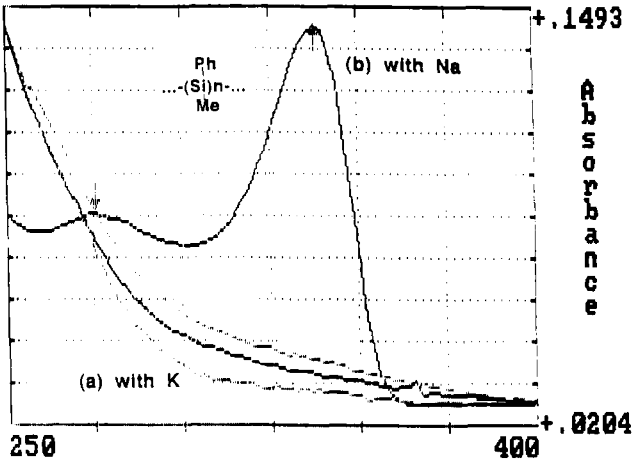


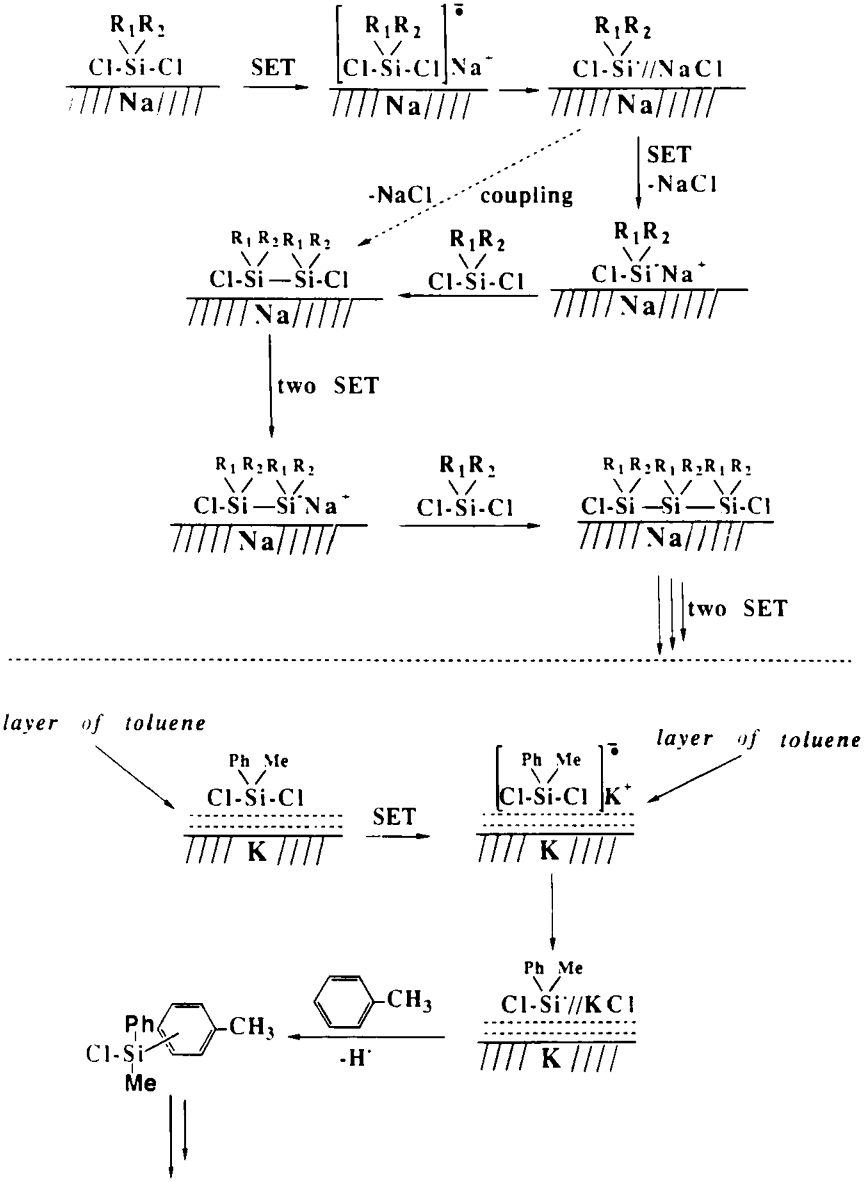
FIG. 1. UV spectra of the product of the sonochemical reductive coupling of methylphenyl dichlorosilane with sodium and with potassium in toluene at 60°C.

MePh—PhMe species formed via reaction of a monomeric radical with solvent. This result confirms the chain nature of the polymerization in which an electron transfer to a polymer chain occurs much faster than to monomer. Of course, an electron transfer to methylphenyldichlorosilane from potassium is much faster than from sodium, and an electron transfer from potassium may occur from a much longer distance than from sodium (in a way analogous to Grignard reagent formation) [26]. Therefore, the monomeric radicals may be separated from the metal surface by two or three solvent molecules and, instead of the coupling process or the second electron transfer, they diffuse to the bulk solvent and react with toluene (Scheme 3).

The reaction of silyl radicals with toluene is very fast ($k = 1.2 \times 10^6\ M^{-1}\cdot s^{-1}$) [24]. Reduction potentials of chloro-terminated oligosilanes decrease strongly with the increase of chain size due to better electron delocalization in longer oligomers. This is in good agreement with the observed slow initiation/fast propagation behavior. Thus, more reactive potassium is less selective and cannot provide oligosilanes with a chain length sufficient to participate in fast propagation. On the contrary, Si—Si catenations are interrupted by a toluene moiety which is incorporated via a radical process. Less reactive sodium is more selective, and although it reacts slower initially, it leads to oligosilanes with a length sufficient for rapid propagation (Table 1).

Reductive coupling at ambient temperatures in the presence of ultrasound leads to monomodal polymers with relatively narrow molecular weight distributions (M_w/M_n from 1.2 to 1.5) and relatively high molecular weights (M_n from 50,000 to 100,000) [23]. Two phenomena are responsible for the more selective polymerization. First, lower polymerization temperature and continuous removal of the sodium chloride from the sodium surface suppresses the formation of low molecular weight polymer (M_n from 2000 to 10,000) which might be formed via some side reactions (transfer or termination). Second, ultrasound mechanically degrades polysilanes with molecular weights above 50,000. This limit is probably set by the chain entanglement and Si—Si bond energetics. Polysilanes prepared in separate experiments could also be selectively degraded [28]. It seems that degradation in toluene in the presence of alkali metals is slightly accelerated, but no low molecular weight cyclooligosilanes are formed. On the other hand, in THF and diglyme (or in toluene in the presence of cryptands and potassium), polymer is completely degraded to cyclohexasilanes and cyclopentasilanes. The anionic intermediates have been observed spectroscopically in this degradation.

Copolymerization of various dialkyl-substituted dichlorosilanes by a



SET
-NaCl
coupling
SET
-NaCl
two SET
two SET
layer of toluene
layer of toluene
SET
-H·

SCHEME 3.

TABLE 1. Reduction Potentials for Chloropermethylpolysilanes

Compounds	$E_{1/2}$ (V)	
	R = Cl	R = Me
$R(SiMe_2)Cl$	−2.30	–
$R(SiMe_2)_3Cl$	−0.50	−0.40
$R(SiMe_2)_4Cl$	−0.47	−0.36
$R(SiMe_2)_6Cl$	−0.43	−0.24

reductive coupling process sometimes leads to block copolymers. This may be due to poor compatibility of polymers with very different substituents (e.g., small dimethyl and much larger dihexyl). In the case of similar substituents (di-*n*-butyl and di-*n*-pentyl, or di-*n*-hexyl) the copolymer composition usually corresponds to the monomer feed. The spectra of Fig. 2 represent the 20/80 statistical copolymer of di-*n*-butylsilylene and di-*n*-hexylsilylene. The expansion of the region of methyl groups from hexyl substituents allows identification of signals coming from different heptads. The distribution of various triads, pentads, and heptads is described by Bernoullian statistics, indicating similar reactivities of di-*n*-butyl-, di-*n*-pentyl-, and di-*n*-hexyldichlorosilanes [29].

RING-OPENING POLYMERIZATION

Reductive coupling of disubstituted dichlorosilanes with alkali metals is usually accompanied by the formation of cyclooligosilanes. At ambient and elevated temperatures in the presence of either light or strong reducing agents (potassium/cryptands), a polysilane can be easily degraded to cyclic oligomers [28]. Thus, polysilanes can be considered to be kinetic produces, whereas cyclic oligomers are true thermodynamic products. The majority of known cyclooligosilanes are thermodynamically stable and cannot be converted to linear polymers. Some potentially strained rings such as octaphenylcyclotetrasilane can be prepared in high yield since the repulsive interactions between two phenyl groups at each silicon atom are more important than the angular strain in the four-membered ring. Additionally, low solubility (below 1% in most organic

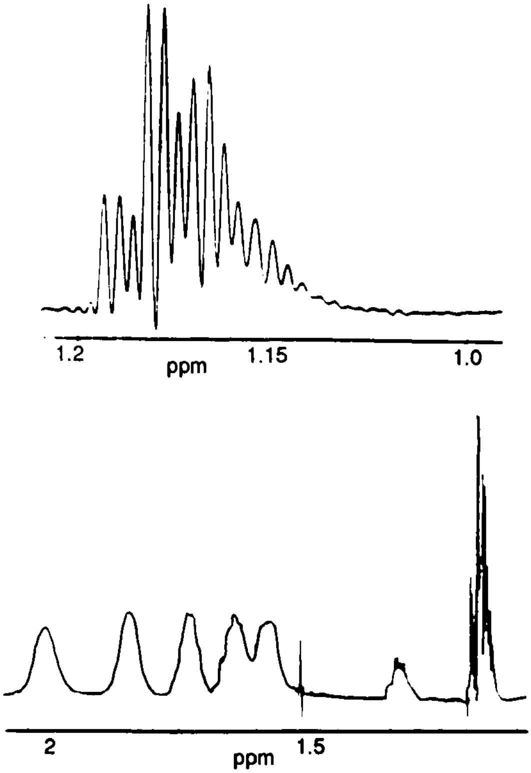
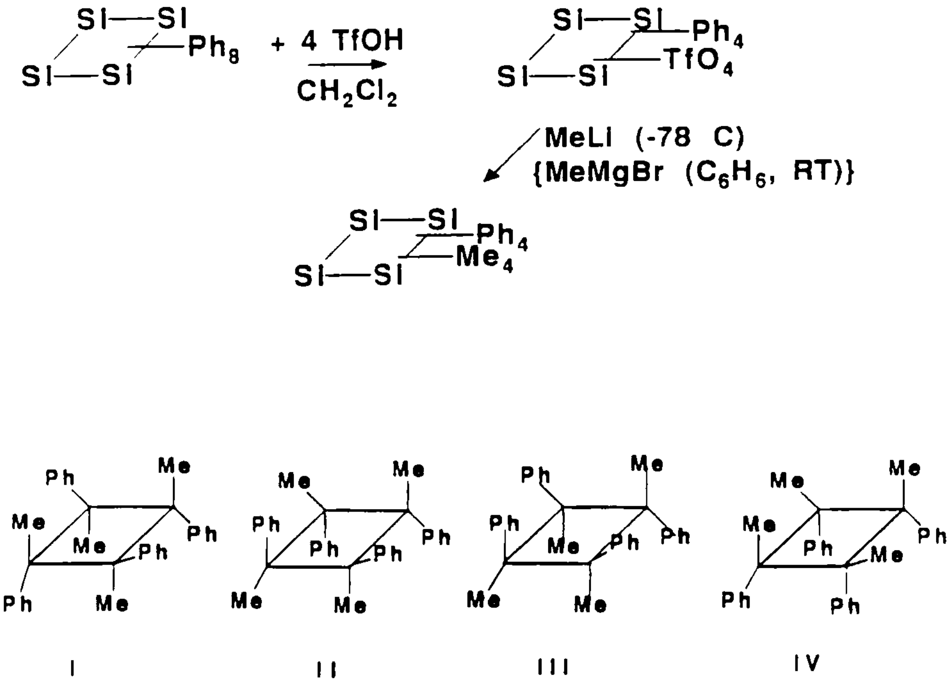


FIG. 2. ^{1}H-NMR spectrum of poly(di-*n*-hexylsilylene-*co*-di-*n*-butylsilylene) (80:20) in benzene at room temperature under enhanced resolution.

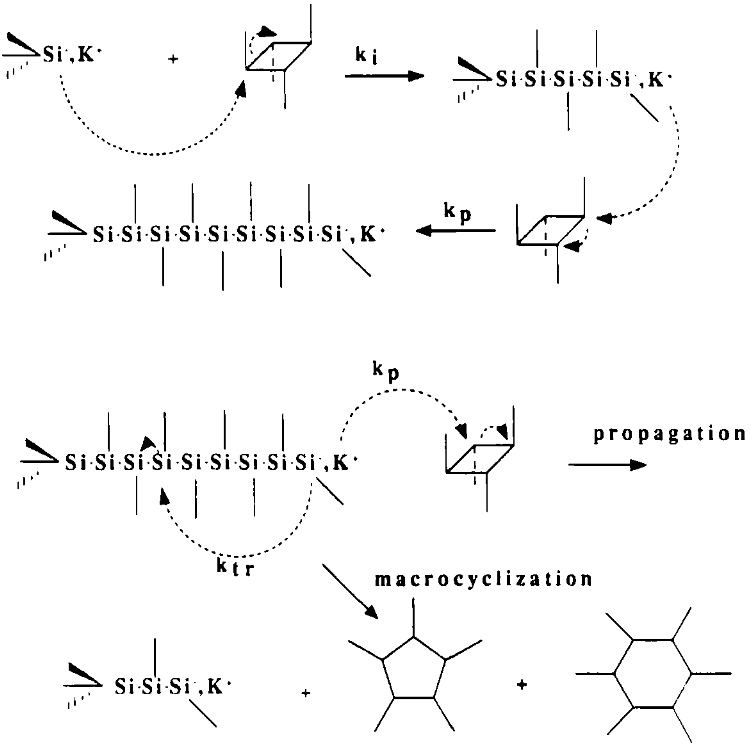
solvents) and a high melting point (mp = 323 °C) precludes polymerization of octaphenylcyclotetrasilane at higher concentrations. Probably due to similar reasons, octahexylcyclotetrasilane has not been polymerized yet. Both octaphenylcyclotetrasilane and octahexylcyclotetrasilane are formed in high yields during the reductive coupling of the corresponding dichlorosilanes. On the other hand, polymerization of methylphenyldichlorosilane yields only cyclopenta- and cyclohexasilanes; no cyclotetrasilane has been found. This indicates the potential polymerizability of 1,2,3,4-tetramethyl-1,2,3,4-tetraphenylcyclotetrasilane.

We have previously described a rapid and clean Si—Ar bond cleavage in the reaction of polysilanes with trifluoromethanesulfonic acid [30]. Reaction of octaphenylcyclotetrasilanes with four equivalents of the acid leads to 1,2,3,4-tetra(trifluoromethanesulfonyloxy)-1,2,3,4-tetraphenylcyclotetrasilane. Subsequent reaction with either methylmagnesium iodide or methyllithium yields four stereo isomers of 1,2,3,4-tetramethyl-1,2,3,4-tetraphenylcyclotetrasilane [31] (Scheme 4).

An Si—Si bond is quite labile in the presence of strong electrophiles and nucleophiles. Reaction with silyl anions leads to ring-opening and to the regeneration of the silyl anions [32]. This is the propagation step. Silyl anions may also attack the Si—Si bonds in the polysilane chain and form macrocycles and strainless cyclooligosilanes (Scheme 5). Rates of polymerization and degradation depend on solvent, temperature, and alkali metals. In pure THF with 1 mol% silyl potassium or butyllithium initiator, only cyclooligosilanes have been found after less than 2 min at room temperature. In benzene, with less than 3% THF, polymerization is completed after more than 1 h. In mixtures of 60% THF with benzene, polymerization is completed within less than 2 min, but degradation starts after 1 h. Polymers with molecular weights from 10,000 to 100,000



SCHEME 4. Synthesis of a monomer.

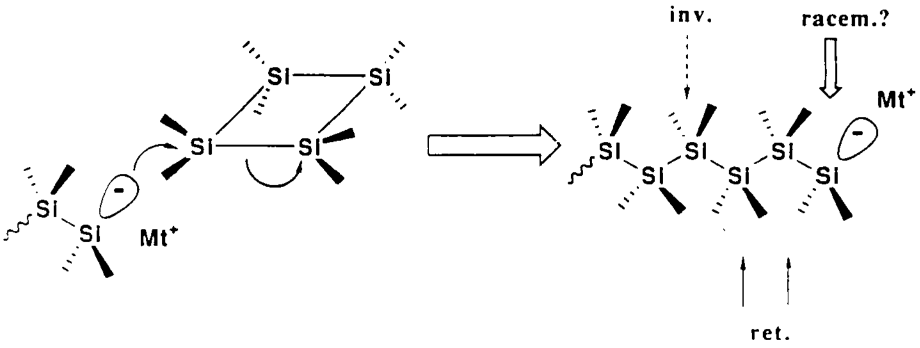


SCHEME 5.

have been prepared via the anionic ring-opening polymerization of cyclotetrasilanes.

One of the most important advantages of the ring-opening polymerization is a possible control of the microstructure (Scheme 6). Polymerization should proceed with one inversion of configuration, two retentions, and one potential racemization. This racemization may be controlled to some extent by the structure of substituents, counterion, temperature, and solvent. At present, no polysilanes with controlled tacticity have been prepared, although they may have very special properties. For example, regular alternating copolysilanes show special low energy transitions at low temperatures [33]. Stereoregular homopolysilanes may behave in a similar way.

The isolation of some of the isomers of 1,2,3,4-tetramethyl-1,2,3,4-tetraphenylcyclotetrasilanes is possible. Figure 3 shows the sample en-



SCHEME 6. Control of microstructure in ROP.

riched in one isomer (probably with all-*trans* structure). The microstructure of polymers obtained from the mixture of isomers and from the 80% enriched sample are quite different and indicate possible tacticity control (Fig. 4).

MODIFICATION OF POLY(METHYLPHENYLSILYLENE)

The severe conditions of the reductive coupling process and of the anionic polymerization allow only alkyl and aryl substituents at silicon. There are only a few polysilanes with substituents other than alkyl and aryl. However, the Si—Ph bond can be easily cleaved by strong protonic acids such as triflic acid. The rate of the dearylation is strongly influenced by the presence of an electron-withdrawing group at the neighboring Si atoms. Model studies on dearylation of α,ω-diphenylpermethyloligosilanes with triflic acid indicate that the displacement of the first phenyl group is always faster than that of the second, even for pentasilanes [34]:

$$\mathrm{Ph\text{-}(SiMe_2)_n\text{-}Ph} \xrightarrow[k]{+\mathrm{HOTf}} \mathrm{Ph\text{-}(SiMe_2)_n\text{-}OTf} \xrightarrow[k']{+\mathrm{HOTf}} \mathrm{TfO\text{-}(SiMe_2)_n\text{-}OTf} \tag{4}$$

$k/k' = 23,\ 13,\ 10,\ 7$ for $n = 2,\ 3,\ 4,\ 5$

Apparently, the reactivity of the oligosilanes increases with the chain length in contrast to the electron density on the *ipso*-C atom which can

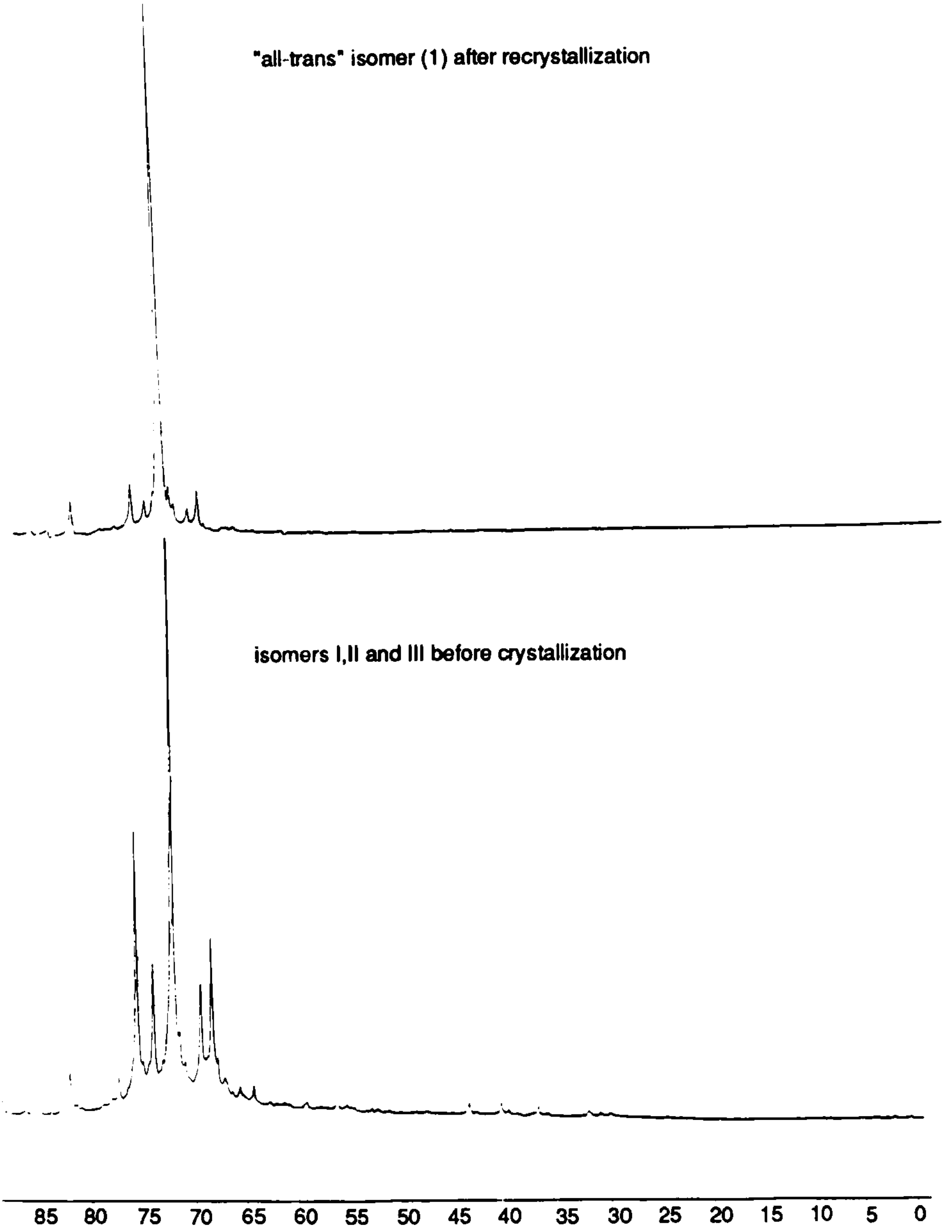


FIG. 3. ^{1}H-NMR spectrum (region of methyl groups only) of a mixture of isomeric cyclotetrasilanes before and after recrystallization from hexane.

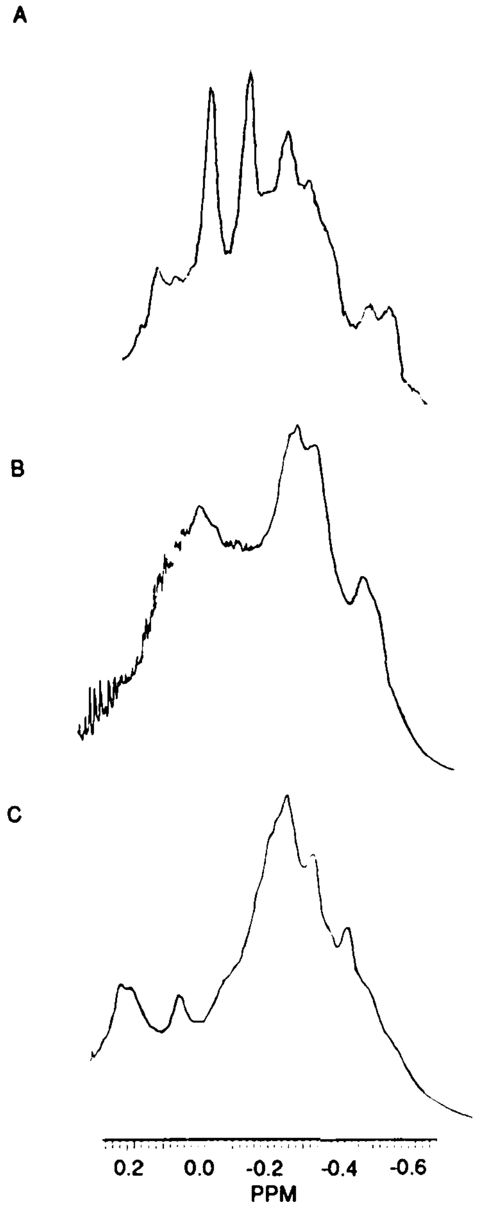
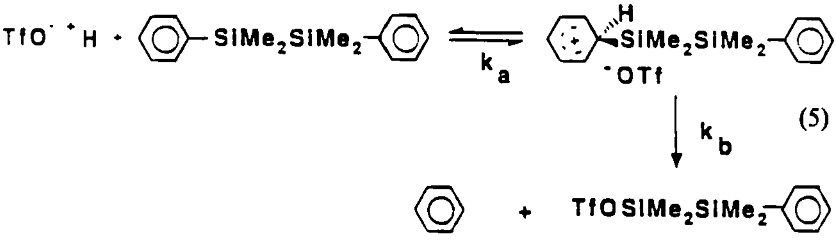


FIG. 4. ^{1}H-NMR spectrum of poly(methylphenylsilylene) obtained by ring-opening polymerization of various mixtures of cyclotetrasilanes: (A) enriched all-*cis*; (B) mixture before separation; (C) enriched all-*trans*.

be deduced from ^{13}C-NMR spectra. *Ipso*-C atoms in longer oligomers are less shielded and have lower electron densities, but are more reactive. These *ipso*-C atoms are attacked by acids in the rate-determining step.



(5)

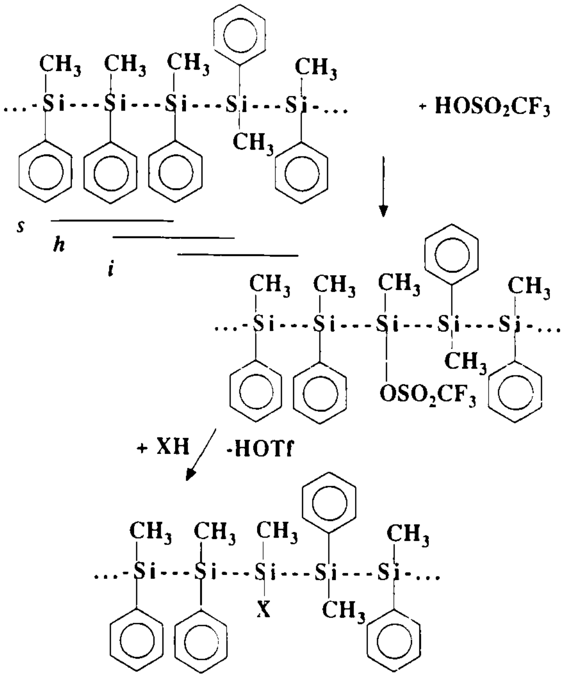
Thus, ground states cannot be responsible for the differences in reactivities. This indicates that the transition states, but not the ground states, control reactivities of polysilanes. Positive charge, in a way similar to the negative charge, can be better dissipated (stabilized) in longer oligomers. This behavior resembles polyenes more than alkanes. The strong effect of the end group transmitted through six bonds has never been reported for alkanes in which it is attenuated after three bonds.

The dearylation process applied to polysilanes containing phenyl substituents provides polymers with strong electrophilic silyl triflate moieties [35]. Silyl triflates belong to the strongest known silylating reagents. They react with ketones 10^8 times faster than silyl chlorides do. They can react with any nucleophiles such as alcohols, amines, carbanions, organometallics, etc. This opens a new synthetic avenue toward various functional polysilanes (Scheme 7).

The reactivity of silyl triflates is so high that they can initiate cationic polymerization of some alkenes and heterocyclics to form graft copolymers [36]. However, the strong electropositive character of silicon results in considerable charge density on the exocyclic groups. Table 2 shows that charge density on the endocyclic carbon atoms in the silylated tetrahydrofuranium cations is very low and insufficient for the corresponding attack by another THF molecule.

Therefore, the rates of opening of these cations are low, and long acceleration periods are found. Slow initiation prevents formation of well-defined polymers and copolymers [37].

We have used oxiranes as promoters in THF polymerization initiated by silyl triflates [38]. Initiation is very fast because the ring strain in silylated oxiranium cations facilitates the ring-opening process (Scheme 8). Oxiranes are less nucleophilic than THF and they do not homopoly-



XH: $(CH_3)_3COH$, CH_3OH, $CH_2{=}CH{=}CH_2OH$, CF_3CH_2OH

$(CH_3CH_2)_2NH$, $CH_3CH_2CH_2CH_2Li$,

also different graft copolymers such as

poly(tetrahydrofuran), (X= $...\text{-}(O\text{-}(CH_2)_4\text{-})_n\text{-}...$)

poly(N-vinylcarbazole), etc.

SCHEME 7.

merize under the reaction conditions. Thus, small amounts of oxiranes are sufficient as promoters.

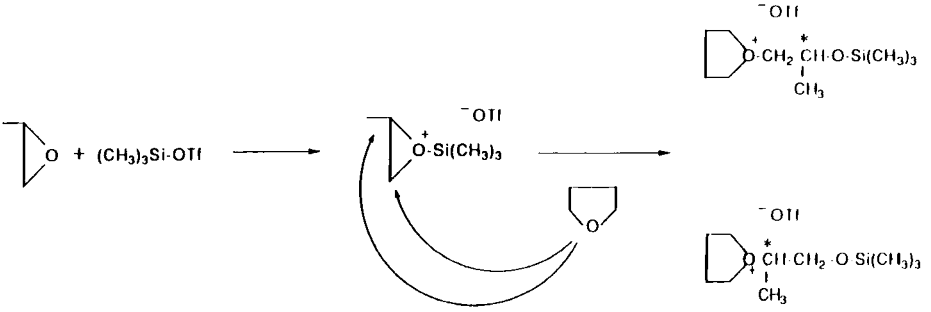
SOLID-STATE TRANSITIONS IN COPOLYSILANES

The solid state of poly(di-*n*-alkyl)silylenes has been a subject of interest since the first discovery of intriguing UV-absorption properties by Miller et al. [39]. Spincast films of polysilylenes generally show intense

TABLE 2. MNDO Calculations for Various Tetrahydrofuranium Cations

Cation	Bond length, C—O, Å	Charge	
		C_{endo}, %	Ring, %
THF	1.405	15.1	0
THF-Me$^+$	1.4722	18.5	58.8
THF-TBu$^+$	1.4720	17.8	54.5
THF-MeOMe$^+$	1.467	18.0	50.7
THF-TMS$^+$	1.446	15.7	34.3

UV-absorptions. However, the absorption behavior of poly(di-*n*-aklyl)silylenes depends strongly upon the length of the side chains. Poly(di-*n*-pentyl)silylene (PDPS) shows an intense absorption band at 315 nm, which broadens upon heating to 100°C [40]. Contrary to this, poly(di-*n*-hexyl)silylene (PDHS) shows a long wavelength absorption at 372 nm at room temperature, which transforms upon heating above 42°C to a less intense absorption at 316 nm. A similar behavior was reported for poly(di-*n*-alkyl)silylenes with longer side chains [41]. The thermochromism is usually thermally reversible. The different properties of PDPS and longer side chain homologues are attributed to changes in the backbone conformation of the polymers. The population of all-*trans* ordered segments present in the molecular backbone determines the length of the σ-conjugated chromophores [42]. The investigation of co-



SCHEME 8.

polymers with the isodimorphic [43] *n*-hexyl and *n*-pentyl units in various ratios was performed in order to give insight into the change from the 7/3 helical backbone conformation found for PDPS [44] to the all-*trans* backbone structure observed for longer side chains. The phase transitions of the copolymers were monitored by differential scanning calorimetry (DSC) as well as ^{29}Si-CP-MAS NMR and temperature-dependent solid-state UV-spectroscopy [45]. Transition temperatures and UV-absorption maxima can be controlled by the ratio of isodimorphic di-*n*-pentyl and di-*n*-hexyl units. Transition temperatures decrease from 318 K for pure poly(di-*n*-hexyl)silylene to below 270 K for ~ 1:3 copolymer, and then gradually increase up to 342 K for pure poly(di-*n*-pentyl)silylene (Fig. 5).

Entropies of phase transition decrease from $\Delta S = 11$ J/K·mol for pure poly(di-*n*-hexyl)silylene to below $\Delta S = 2$ J/K·mol for ~ 1:3 copolymer, and then remain constant and equal to ΔS for pure poly(di- *n*-pentyl)silylene. This indicates that the latter homopolymer and copolymers

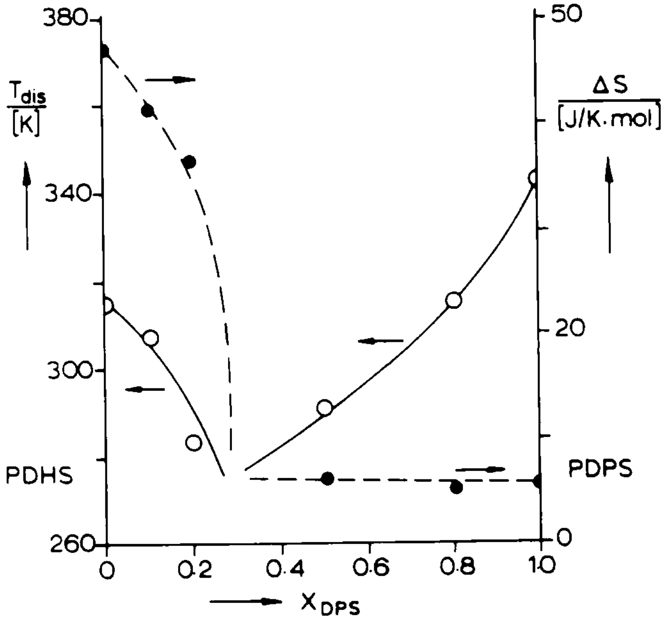


FIG. 5. Entropies and transition temperatures measured by DSC for various copolymers of PDHS and PDPS.

down to ~25% of poly(di-*n*-pentyl)silylene units form similar morphologies based on a 7/3 helix at low temperatures and on a columnar mesophase at higher temperatures.

Copolymers with a lower content of poly(di-*n*-pentyl)silylene form predominantly all-*trans* conformations at lower temperatures. This is very well confirmed by ^{29}Si-CP-MAS NMR. Pure poly(di-*n*-pentyl)silylene and copolymers down to ~25% content of poly(di-*n*-pentyl)silylene units show two signals: a broad one at −26 ppm (helix) and a sharp one at −23 ppm (mesophase). Pure poly(di-*n*-hexyl)silylene and copolymers up to ~25% content of poly(di-*n*-pentyl)silylene units show two signals: a broad one at −20 ppm (all-*trans*) and a sharp one at −23 ppm (mesophase) (Fig. 6).

Defects introduced stepwise into the highly regular structure of poly(di-*n*-hexyl)silylene apparently lead to a decrease of the crystallinity, but for copolymers containing up to 25% of di-*n*-pentyl substituents, a predominantly all-*trans* structure is maintained. However, the blue-shifted UV-absorptions reflect the loss of intramolecular order, resulting in backbone kinks and interruption of the conjugated σ-chromophores (Fig. 7).

The decrease of the disordering temperature mirrors the loss of intermolecular order of the stiff molecules. In the disordered high temperature phase, all copolymers seem to have a similar mesophase structure, with conformational disorder of the backbone and rotational motions of the side chains. A similar behavior has been observed for other inorganic–organic hybrid polymers [46]. As more di-*n*-pentyl side chains are incorporated, the packing of the all-*trans* rods becomes increasingly inefficient and short all-*trans* segments cannot sufficiently interact to preserve the planar backbone structure. Thus, a helical structure is adopted by the 25/75 *co*-PD(HS/PS). This polymer presents an energetic dilemma, similar to the case of the atactic, asymmetrically substituted poly(*n*-hexyl *n*-pentyl)silylene [47].

The control of the composition of copolysilanes allows fine tuning of the phase transitions in copolymers, their spectroscopic properties and morphologies. Thus, not only microstructure but also chain packing and supramolecular structure can be controlled by the rational synthesis of polysilanes.

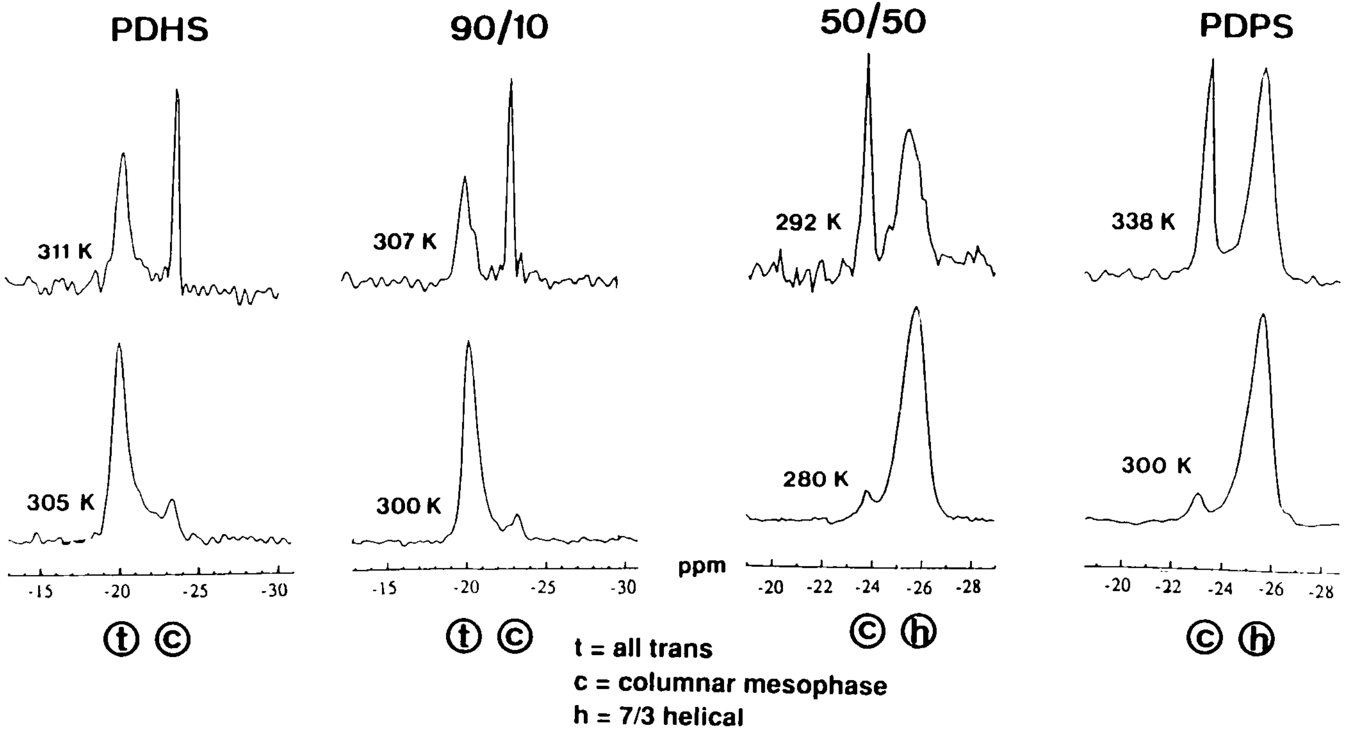


FIG. 6. ^{29}Si-CP-MAS NMR spectra of various copolymers of PDHS and PDPS recorded at variable temperatures.

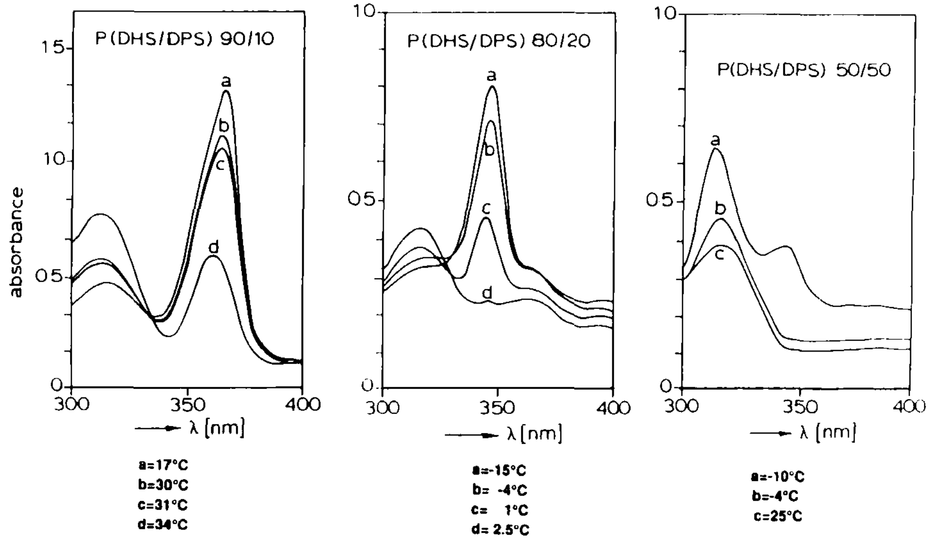


FIG. 7. UV spectra of thin films of various copolymers of PDHS and PDPS recorded at variable temperatures.

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