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PREPARATION AND DEGRADATION OF POLYSILYLENES

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Preparation and Degradation of Polysilylenes

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Mechanistic aspects of preparation and degradation of polysilylenes (polysilanes) are discussed. Reductive coupling of disubstituted dichlorosilanes 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). Ring-opening polymerization of 1,2,3,4,-tetramethyl-1,2,3,4-tetraphenylcyclotetrasilane initiated with carbanions and silyl anions provides polymers with molecular weights from 10,000 to 100,000 and gives potential possibility of the microstructure control. The dearylation of phenyl containing polysilylenes with triflic acid provides polymers with strong electrophilic silyl triflate moieties. They can react with any nucleophiles such as alcohols, amines, carbanions, organometallics, etc. and produce various functional polysilylenes. Synthesis and solid state transitions in random copolysilylenes are discussed. Thermal, mechanical, and chemical degradation of polysilylenes is described.

Key words: Polysilylenes, Polysilanes, Sonochemical Reductive Coupling, Ring-Opening Polymerization, Modification, Copolysilylenes, Copolysilanes, Degradation, Synthesis, Characterization, UV, NMR, DSC

Introduction

Compounds with a linear Si-Si catenation in the main chain and two substituents at each silicon atom belong to a general class of polysilanes or polysilylenes (a correct nomenclature, based on the structure of the silylene repeating unit; thus, a polymer with two n-hexyl substituents is poly(di-n-hexylsilylene) and a polymer with methyl and phenyl groups is poly(methylphenylsilylene)). Interesting physical and chemical properties of polysilanes such as delocalization of electrons in the main chain, photosensitivity, incompatibility of the main chain with side organic groups, processability typical for thermoplastics, as well as potential commercial applications[1,2,3] led to intensive studies of these materials. Some properties of polysilylenes depend strongly on molecular weights and well-defined polymers are required for correct characterization. It seems that the synthetic developments lag behind the current level of characterization capabilities. Therefore polysilylenes with controlled molecular weights, low polydispersities, controlled structure of segments in copolymers and designed microstructure of the asymmetrically substituted units, with various functional groups are needed as well as corresponding well- defined block and graft copolysilylenes. Determination of stability of polysilylenes and their degradation during the characterization process is also very important. Thus, this paper will deal mostly with various synthetic aspects of polysilylenes directed towards improvement of the structural control. It will also describe the possibility of control of some properties of copolysilylenes of various composition. Also a discussion of thermal, sonochemical, and chemical degradation of polysilylenes is given.

Preparation of Polysilylenes

First and still the most common preparative technique for polysilylenes is based on the reductive coupling of disubstituted dichlorosilanes. Initially, this method was used by Kipping[4] for diphenyl derivatives and then by Burkhard[5] for dimethyl derivatives. The polymers were insoluble and impossible to characterize at that time. The first soluble polysilylenes were prepared from unsymmetrically substituted dichlorosilanes [6,7,8]. Usually alkali metals are used, but some other reducing agents including electrochemical coupling has been attempted[9]. The products of condensation consist of a mixture of small cyclopolysilylenes (usually cyclic tetramer, pentamer, and hexamer are formed), low molecular weight polymer (usually $M < 10{,}000$), and high polymer ($M > 100{,}000$).

The dehydrogenative coupling of disubstituted dihydrosilanes in the presence of transition metals provides low molecular weight materials ($DP<10$), highly branched polymers can be obtained from trihydrosilanes[10,11]. There are two other routes to polysilylenes based on the anionic polymerization of "masked disilenes"[12] and on the anionic ring-opening polymerization[13]. These techniques may provide additional control of the microstructure of the nonsymmetrically substituted systems.

A last method for the preparation of novel polysilylenes is based on a modification process via silyl triflate intermediates[14]. Various functional side groups are introduced to polymers with existing Si-Si chains. The five major synthetic routes to polysilylenes are shown below:

Scheme 1

Three methods will be discussed in more detail: the reductive coupling of disubstituted dichlorosilanes with alkali metals in the presence of ultrasound, the anionic ring-opening polymerization, and the modification process.

Reductive Coupling in the Presence of Ultrasound

There are two basic mechanisms of the formation of macromolecules: chain and step growth. In the latter case functional groups in the monomer and in the polymer chain ends possess the same reactivity. The molecular weight increases slowly with conversion in these systems and formation of high polymer requires precise stoichiometric balance of reagents and nearly complete conversions (e.g. $DP_n=100$ at 99% conversion in a homogeneous polycondensation with exact stoichiometric balance). On the other hand, a monomer reacts only with the active site at the chain end in the chain growth mechanism and, under usual conditions, high polymer is formed at low conversion (e.g. DP_n=1000 at 1% conversion in most radical reactions). In these systems slow initiation is followed by rapid propagation, and eventually by termination. Polymerization of disubstituted dichlorosilanes with alkali metals via reductive coupling is a chain (not a step) process. Molecular weights are very high at low conversions and they are independent of the [Mt]/[Si-Cl] ratio. However, one must take into account the heterogeneous nature of polymerization which resembles an interfacial systems in which high polymers are formed at low conversion due to diffusion phenomena. Additional support for the chain growth mechanism comes from the electrochemical studies of various chloroterminated oligosilanes. Reductive potentials measured by polarography and cyclic voltametry for α,ω-dichloropermethylated mono- (-2 V), tri- (-0.50 V), tetra- (-0.47 V), and hexasilanes (-0.43 V) show a monotonous decrease of the reductive potential and an increase in the electron affinity[15]. Therefore, the electron transfer from the alkali metal to chloroterminated polysilylenes and oligosilanes is much faster than to the monomer (disubstituted dichlorosilane). A clear induction period gives an evidence of slow initiation and fast propagation under most polymerization conditions.

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. The mechanism based on silylene intermediates is not of primary importance, since silylene traps do not affect polymerization[16]. Some experimental data contradict the purely radical process. They include strong solvent effects, the influence of crown ethers and cryptands on polymerization rates and yields, and a high yield of cyclics which support anionic intermediates[17,18]. Cyclic polysilylenes 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. An 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.

The rate constant of the reaction of triethylsilyl radical with toluene is quite high at room temperature ($k=1.2\times10^{6}$ $\underline{M}^{-1}s^{-1}$)[19]. A polymer with a degree of polymerization $DP=10^{3}$ is usually formed in less than 100 s at a monomer concentration $[M]_o < 0.1$ mol/L in toluene ($[Toluene]_o=10$ mol/L). Thus, the ratio of the rate constants of propagation to transfer should be above 10^{5}. The rate constant of propagation estimated in this way ($k_p>10^{11}$ $\underline{M}^{-1}s^{-1}$) would exceed the limits of a diffusion controlled process, assuming reactivity of the macromolecular radical similar to triethyl radical. Therefore, a purely radical mechanism of a chain growth can not dominate in the formation of polysilylenes.

Thus, polymer must be formed in the reaction between anionic intermediates and an electrophilic monomer. The exact nature and degree of ionization of the anionic species is at present not known. A sequence of reactions involved in the entire polymerization process is given:

Scheme 2

The first slow initiation step should involve electron transfer from alkali metal (sodium) to a monomer to generate 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 and 1A'). The identical reaction between sodium and the chloro-terminated polymer chain may provide a polymeric radical anion and eventually a polymeric radical (1B and 1B'). Various silyl radicals may recombine together (1C, 1C', 1C") but this can not be a major pathway leading to high polymers taking into account the low concentration of radicals. However, silyl radicals which contain phenyl groups can easily be reduced further to silyl anions. The polysilylene 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 Cl-groups) than the chloro-terminated chain. This is the anionic pathway of the chain growth (2B). The chloroterminated chain is now at the closest proximity to the surface of the alkali metal. It accepts an electron, forms a radical anion, loses NaCl to rearrange to the radical which momentarily takes a second electron from sodium to form an anionic species. In non-polar solvents this silyl anionic species may have a strong covalent nature and the polysilylene chain associated with the huge droplet of alkali metal may resemble an electric wire plugged into a large wall. A monomer comes to the "electric contact", "squeezes" into the "plug" and a "wire" remains in essentially the same position. Silyl anions may react either with a monomer (2B) or with a chloroterminated chain end (2C). The reaction of anionic species with a monomer may be favored because of the higher electrophilicity and concentration of the monomer. However, at degrees of polymerization five or six, the anchimeric assistance (neighboring group participation) is very high and may reach values of 10^5 or even 10^6 mol/L. Under such conditions end-to-end cyclization or end-biting is possible. This results in a high yield of cyclics. Cyclooligosilanes may also be formed via back-biting reaction when the anionic species react with its own backbone. However, as it will be discussed later, this reaction occurs only in highly polar solvents. The chance of the end-biting reaction is high for six- and five-membered rings, but is very low for smaller and larger cycles. In the case of the strainless, entropy driven systems, the probability of end-to end intramolecular cyclization decreases with the ring size n:

$$P = k \cdot n^{-3/2}$$

The reaction between silyl anions and silyl chlorides may also occur bimolecularly, being strongly concentration dependent. It is possible that this condensation mechanism happens once or a few times per average chain. Nevertheless, the majority of the monomer is consumed in the reaction with the anionic chain end. Thus, above 99% of monomer units are incorporated into polymer chains via a bimolecular reaction between a monomer and a growing chain end (2B), but some (<1% ?) linkages in the macromolecules could be formed via chain coupling (condensation (2C)). This chain coupling will have a very strong effect on the final molecular weights.

In this scheme macromolecular silyl radicals play the role of transient species which very rapidly take a second electron from sodium to form silyl anions. Indeed, the lifetimes of silyl radicals must be very short since polysilylenes with pendant alkenyl groups can be prepared by the reductive coupling process. Some fraction of the double bonds is, however, consumed which confirms the presence of transient radicals[20].

In toluene, using sodium as a reducing agent, monomers with aryl groups react much faster than those with alkyl groups[21]. Polymerization of dialkylsubstituted dichlorosilanes with sodium requires elevated temperatures (above 80 °C), although they react readily at ambient temperatures either in more polar solvents (addition of glymes, THF, crown ethers, or cryptands)[22] or with stronger reducing systems (Na/K and K). Surprisingly, methylphenyldichlorosilane does not react with potassium within 2 hours under similar conditions. At longer reaction times (16 hours) low molecular weight products are formed. The apparent discrepancy (a slower reaction between a more reactive metal and a more reactive monomer) has been solved by the analysis of the product of the reaction of methylphenyldichlorosilane with K at longer reaction times. The resulting polymer (M_n=2,000) is not a polysilylene.

^{29}Si NMR and UV exclude long Si-Si catenations (no absorption above 300 nm). ^{1}H and ^{13}C NMR, as well as IR indicate a large proportion of toluene moieties, in contrast to polysilylenes which are prepared with Na. GC/MS analysis of the first products formed in this reaction indicates the presence of X-SiMePh-PhMe species (X=H, Cl), formed via reaction of a monomeric radical with the solvent molecules. The incorporation of toluene moiety occurs via a radical mechanism. An electron transfer from potassium to methylphenyldichlorosilane is faster than from sodium, and an electron transfer from potassium may occur from a much longer distance than from sodium. Therefore, the monomeric radicals may be separated from the metal surface by two or three solvent molecules, they diffuse to the bulk solvent and react with toluene , decreasing the efficiency of the coupling process or the second electron transfer. Similar reasoning was used to explain lower yield of Grignard reagent formation from Mg and alkyl iodides in comparison with less reactive alkyl chlorides[23]. Electron transfer to the chlorides occur at the magnesium surface, whereas alkyl iodides accept electrons through larger distance and could not efficiently form organomagnesium reagents but dimerize, isomerize, react with a solvent, etc.

Reduction potentials of chloro-terminated oligosilanes decrease strongly with an increase of chain length due to better electron delocalization in the longer oligomers. This is in good agreement with the observed slow initiation / fast propagation behavior. These oligosilanes must be initially formed by the coupling of radicals derived from a monomer. Silyl radicals react with toluene very rapidly. The chance of radicals coupling will be higher at the surface but much lower when separated from the alkali metal by a layer of two-three molecules of a solvent. Since the more reactive potassium donates electrons via longer distance, it is therefore less selective and can not provide oligosilanes with a chain length sufficient to participate in fast propagation. Indeed, 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 initially slower it leads to oligosilanes with a length sufficient for rapid propagation. Polymerization proceeds faster with sodium than with potassium because the overall rate of polymerization is proportional to a number of active chain ends.

Sonochemical Degradation

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)[21]. Two phenomena are responsible for the more selective polymerization. First, a lower polymerization temperature and the continuous removal of sodium chloride from the sodium surface suppresses the formation of low molecular weight polymer (M_n from 2,000 to 10,000) which might be formed via some side reactions (transfer or termination). Suppression of the formation of low molecular weight fraction is observed with a decrease of the reaction temperature in the presence of ultrasound but also in its absence. Apparently, reactions which limit chain growth have higher activation energies than propagation.

There are two limitations in the reduction of the reaction temperature: reactivity of monomers and regeneration of metal surface. For example, dialkyldichlorosilanes do not react with Na in toluene below 80 °C. Reactivity may be improved by either a shift to a more polar and better solvating media or by addition of compounds which readily solvate alkali metal cations such as cryptands and crown ethers. A catalytic amount of the additives is sufficient which indicates a rapid exchange between silyl anions and NaCl. Apparently, the size of cryptands and crown ethers in these reactions is not very important and similar results were obtained with crown-4, crown-5, and crown-6 , as well as with cryptand [2.2.2] and cryptand [2.2.1] for sodium. This may indicate that the crown serves rather to separate the silyl anion from sodium surface than to form a crowned ...-SiR_2^-, Na^+ ion pair in solution. The polymerization of more reactive arylalkyl dichlorosilanes leads to limited conversions at lower temperatures due to the occlusion of sodium particles by sodium chloride and polymer. The surface can be cleaned by ultrasound. Another possibility is to add a small amount of potassium and form a liquid Na/K alloy.

The reduction of the polydispersity of the polysilylenes in the presence of ultrasound of frequency 20 kHz has its origin in the mechanical degradation of polymers with molecular weights above 50,000. This limit is probably set by chain entanglement and Si-Si bond energetics. Polysilylenes prepared in separate experiments were selectively sonochemically degraded[24]. Low molecular weight polymers (M_n<10,000) were intact in the presence of ultrasound. Thus, selective formation of high polymer has the origin in the suppression of side reactions limiting chain growth at higher temperatures and not in the degradation of low polymer. Degradation occurs in the presence but also in the absence of alkali metals. in the presence of alkali metals, the structure of degradation products depends on the nature of the solvent. In toluene no cyclics are found, in THF polymer is degraded to cyclopentasilanes. This is the chemical degradation discussed in the next section. The molecular weight of the polysilylene degraded sonochemically depends on itsconcentration. In Figure 1 the linear correlation of the intrinsic viscosity of the degraded polysilylenes and the reciprocal concentration is shown. This indicates that degradation by shear forces occurs predominantly in chains which are entangled intermolecularly. The intercept may suggest also intramolecular entanglement. The degradation occurs when bubbles and cavities are generated by sonic waves and then implosively collapse within the entangled chains. Shorter chains do not entangle as efficiently as longer ones and they can relax in the time of the sonication event.

The efficiency of degradation decreases with temperature. In toluene at temperatures above 80 °C degradation slows down considerably. This is due to the too high vapor pressure of the solvent which prevents an efficient cavitation process. Therefore, sonochemical reactions are usually performed at temperatures at least 20 °C below the boiling point of a solvent in order to reduce its vapor pressure.

Sonochemical degradation resembles mechanical degradation by shear forces in which homolytic cleavage of Si-Si bonds occurs. The generated radicals react rapidly with the solvent and, for example, a small amount of methyl groups from the toluene-terminated chains can be detected in NMR spectra of polysilylenes degraded in toluene. Sonochemical degradation leads to a decrease of molecular weights and is not accompanied by the cycles formation, in contrast to chemical degradation. Strong reduction of polydispersity is due to the selective nature of degradation in which only the high molecular weight fraction of polymers is degraded.

Chemical Degradation

Cleavage of Si-Si bond by Nucleophiles

Action of strong nucleophiles on disilanes leads to the formation of silyl anions which are very reactive. There are a few methods for the generation of silyl anions. The first one is the reaction of disilanes with alkali metals. Reaction occurs much faster for silanes with aryl groups and its rate increases with the number of aryl groups[25]. Thus, reaction with hexaphenyldisilane is the fastest and with hexamethyldisilane the slowest. Cleavage reactions usually require nucleophilic solvents such as THF, diglyme, HMPT, or ether which can solvate alkali metal cations.

Trimethylsilyl anion can be generated by sodium and potassium alkoxides[26], especially in the presence of crown ethers. Trialkylsilyl anions can also be formed from disilanes and methyl lithium[27] or from trialkylsilanes and potassium hydride[28]. Silyl anions are very reactive and unstable species. They can participate in a number of different reactions but they can also loose an electron and form silyl radicals. For example, naphthalene abstracts an electron from the trimethylsilyl anion[29].

In preparative organosilicon chemistry the use of silyl anions has a long history and the reactions of polysilylenes are often catalyzed by small amount of hexaphenyldisilane which is a source of triphenylsilyl anions. Thus, silyl anions can rapidly attack Si-Si bond and form thermodynamic products by a scrambling process.

Degradation of Polysilylenes by Alkali Metals

Polysilylenes are usually prepared by the reductive coupling of disubstituted dichlorosilanes with alkali metals in non polar solvents such as toluene or hexane. No substantial degradation of the polymer is observed in the presence of an excess of alkali metal. Polymers with higher molecular weights are prepared in solvents of lower solvating ability. Polysilylenes can be degraded by an excess of alkali metal in THF or in diglyme. Cyclic oligomers are the only degradation products. The rate of degradation depends on the substituents at the silicon atom, solvent, alkali metal, and temperature. Qualitative degradation results are shown in Table 1.

Degradation is much faster in more polar THF than in toluene. Addition of cryptand [2.2.2] or THF to toluene increases the degradation rate. The rate of degradation strongly increases with the reactivity of the metal. Electron transfer from potassium is much easier than from sodium or from lithium. The effect of the counterion seems to be less important, since degradation initiated by sodium or lithium naphthalides proceeds nearly as fast as with potassium. On the other hand, the initial electron transfer process is strongly metal dependent. The application of the ultrasound helps to clean the metal surface by cavitational erosion but does not change the rate of degradation. Degradation is much faster for poly(phenylmethylsilylene) than for poly(di-n-hexylsilylene). This is in agreement with the general trend in the stability of silyl anions discussed in the previous section. Aryl groups on the silicon atom stabilize anionic intermediates. A counterion effect on the degradation is observed. Degradation with K^+ is faster than with Na^+ or Li^+. Moreover, lithium can not start the degradation process. Even in THF solution the first electron transfer is not possible. This may be due to surface phenomena since lithium naphthalide degrades polysilylenes efficiently. During chemical degradation cycles are formed but the molecular weight of polysilylenes does not change. This indicates a chain process with slow initiation and fast propagation.

A plausible mechanism of the degradation is shown:

Scheme 3

The first step in which a polymeric radical anion is formed should be rate limiting. It is facilitated in more polar solvents due to the energy gain by the solvation of alkali metal cations. The intermediate radical anion cleaves to a radical and an anion. The fate of the radicals is not known. They may react with a solvent, take a second electron to form a silyl anion, or recombine, although radical concentration is usually very low. The silyl anions may now start cleaving Si-Si bonds. The rate of the intramolecular reaction must be much faster than the rate of the intermolecular process due to entropic effects. The anchimeric assistance (or neighboring group participation) is the highest for the least strained five- and six-membered rings . Therefore, the degradation process leads to cyclopentasilanes and cyclohexasilanes. The back-biting process for larger or smaller rings is retarded for enthalpic reasons. The back-biting process has to be distinguished from the end-biting process which may occur during the synthesis of polysilylenes. Additional evidence for different mechanisms of end-biting and back-biting processes are provided by the structure of cyclic oligomers which are formed during the synthesis of poly(di-n-hexylsilylene). Above 80% of octa-n-hexylcyclotetrasilane ($\delta = -20.3$ ppm in ^{29}Si NMR) is formed under the reductive coupling process in a mixture of toluene and isooctane. On the other hand, the degradation leads to the formation of deca-n-hexylcyclopentasilanes ($\delta = -34.6$ ppm).

The present results clearly indicate that back-biting (or degradation) is not important in toluene in the absence of any additives. It is also not very important for poly(di-n-hexylsilylene) in THF. However, polymerization of methylphenyldichlorosilane with any alkali metal in THF will result in cyclics rather than in a linear polymer.

Degradation by Electrophiles

The Si-Si bond in polysilylenes resembles C=C bond in some chemical reactions. Thus, oxidation and halogen additions proceed under very mild conditions. Rates of reactions of disilanes with bromine decrease with the number of phenyl groups (Me_3Si-$SiMe_3$ is 300 times more reactive than $MePh_2Si$-$SiMePh_2$)[30]. This is exactly the opposite to the reaction with alkali metals. Rates of degradations are also affected by ring strain and the nature of the halide. Thus, chlorine is more reactive than bromine which is more reactive than iodine. This rate order follows the order of stability of the final silyl halides rather than the order of the halogen reactivity. This indicates a relatively late transition state which closely resembles the products. We have degraded polysilylenes by iodine and found that the cleavage of poly(methylphenylsilylene) occurs with a rate constant k=0.15 L/mol/s at 20 °C in CH_2Cl_2 solvent. Insertion of iodine leads to a decrease of molecular weight and to broader polydispersity. The α,ω-diiodopolysilylenes did not degrade by the back-biting process during a few hours. Iodosilanes are very strong silylating reagents and can be converted to a number of terminally functional polysilylenes. These telechelic materials may be further used as functional polymers and oligomers.

Thermal Degradation

Thermal decomposition of poly(methylphenylsilylene) starts at approximately 150 °C and it is accompanied by a decrease of the molecular weight of the polymer and by the formation of cyclopolysilylenes. After 24 hrs at 150 °C almost half of the polymer has been converted to cycles and the molecular weight has been reduced from M_n=85,000 to M_n=2,900. A similar decrease of the molecular weight requires 3 hours at 240 °C and 0.5 hour at 280 °C.

Figure 2 shows changes in the GPC traces for a solution of poly(methylphenylsilylene) in decaline at 150 °C. Degradation is slower than in the solid state probably due to better protection from traces of oxygen, although both reactions were run in the inert gas atmosphere: argon or nitrogen. The decrease of the molecular weight is accompanied by the formation of cyclopenta- and cyclohexasilanes.

A typical reductive coupling process is run at $T \leq 100$ °C, and therefore thermal decomposition can be neglected during the synthesis.

Copolymerization

Copolymerization of various dialkylsubstituted dichlorosilanes by the reductive coupling process may lead to products with blocky structures. 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 corresponds to the monomer feed. The NMR spectra (Figure 3) represent a 20/80 statistical copolymer of di-n-propylsilylene and di-n-hexylsilylene. The fine pattern in the methyl group region is found in the spectra recorded with an enhanced resolution.

The expansion of the region of methyl groups of the hexyl substituents allows for the identification of signals coming from different heptads in the hexyl-rich region and pentads in propyl-rich region. Figure 4 shows spectra recorded for 50/50, 80/20/ and 90/10 copolymers. The distribution of various triads, pentads, and heptads indicate similar reactivities of di-n-propyl- and di-n-hexyldichlorosilanes[29]. There is a small tendency to form blocky structures and reactivity ratios slightly larger than 1 may be deduced from the analysis of the spectra. Similar results were found with di-n-butyl- and di-n-pentylderivatives.

Ring-Opening Polymerization

Polysilylenes can be easily degraded to cyclic oligomers in the presence of strong reducing agents (potassium / cryptands). Thus, polysilylenes can be considered as kinetic products, whereas cyclic oligomers are true thermodynamic products. The majority of known cyclooligosilanes are thermodynamically stable and can not be converted into linear polymers. Some potentially strained rings such as octaphenylcyclotetrasilane can be prepared in high yield due to the repulsive interactions between two phenyl groups at each silicon atom. These interactions are more important than the angular strain in the four membered ring. Probably due to similar reasons, octa-n-hexylcyclotetrasilane has not yet been polymerized. Both octaphenylcyclotetrasilane and octa-n-hexylcyclotetrasilane 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, and no cyclotetrasilane has been found. This indicates the potential polymerizability of 1,2,3,4-tetramethyl-1,2,3,4-tetraphenylcyclotetrasilane. This monomer can be prepared by the displacement of four phenyl groups from octaphenylcyclotetrasilane with four equivalents of trifluoromethanesulfonic (triflic) acid[31]. The reaction of octaphenylcyclotetrasilane with the acid leads to 1,2,3,4-tetraphenyl-1,2,3,4-tetra(trifluoromethanesulfonyloxy)cyclotetrasilane. The subsequent reaction with either methylmagnesium iodide or methyl lithium yields four stereoisomers of 1,2,3,4-tetramethyl-1,2,3,4-tetraphenylcyclotetrasilane[31]. Attempts to introduce more than four triflate groups on the four membered ring were unsuccessful and ring cleavage was observed. However, up to four phenyl groups can be displaced without ring opening.

A Si-Si bond is quite labile in the presence of strong electrophiles and nucleophiles. The scheme below shows the anionic polymerization of the "all-trans" isomer. Reaction with silyl anions (any reactive carbanion can be used, e.g. butyl lithium) leads to ring-opening and to the regeneration of a silyl anions[32]. This is the propagation step. Silyl anions may also attack the Si-Si bonds in the polysilylene chain and form macrocycles and strainless cyclooligosilanes:

Scheme 4

The rates of polymerization and degradation depend on solvent, temperature, and alkali metals. Cyclopentasilanes have been exclusively found after less than 2 minutes at room temperature with 1 mol% of silyl potassium or butyl lithium initiator in pure THF. In benzene, with less than 3% THF, polymerization is completed in more than 1 hour. In mixtures of THF with benzene (60:40), polymerization is completed within less than 2 minutes, but degradation starts after 1 hour. Polymers with molecular weights from 10,000 to 100,000 have been prepared via an anionic ring-opening polymerization of cyclotetrasilanes. Polydispersities of these polymers are approximately $M_w/M_n=2$. This indicates some side reactions such as transfer and termination which have not yet been successfuly eliminated.

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 polysilylenes with substituents other than alkyl and aryl. However, the Si-Ph bond can be easily cleaved by strong protonic acids such as triflic acid[33,34]. Silyl triflates are among the strongest known silylating reagents. They react 10^8 times faster than silyl chlorides with ketones[35]. They react with nucleophiles such as alcohols, amines, carbanions, organometallics, etc. This approach opens a new synthetic avenue towards various functional polysilylenes:

Scheme 5

The reactivity of silyl triflates is so high that they can initiate the cationic polymerization of some alkenes and heterocyclics to form graft copolymers[36,37]. However, the strong electropositive character of silicon results in a considerable charge density on the exocyclic groups. 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.

Oxiranes, acetals, and ketones have been used as promoters in THF polymerization initiated by silyl triflates[38]. Initiation with oxiranes is the fastest due to the ring strain in silylated oxiranium cations which facilitates the ring-opening process. Oxiranes are less nucleophilic than THF and do not homopolymerize under the reaction conditions. Thus, amounts of oxiranes equimolar to silyl triflates are sufficient as promoters.

Characterization of Copolysilylenes in Solid State

Symmetrically substituted polysilylenes form highly ordered crystalline structures at ambient temperatures and transform to columnar mesophase at elevated temperatures[39]. Poly(di-n-hexylsilylene) (PDHS) forms at room temperature a planar zig-zag conformation with very extensive delocalization of sigma electrons in the all-trans bonds. This delocalization leads to UV absorption at 372 nm. At 42 °C transformation to the mesophase occurs and the maximum shifts to 316 nm[40]. The thermochromism is thermally reversible. Poly(di-n-pentylsilylene) (PDPS) shows an intense absorption band at 315 nm, which broadens upon heating to 100°C[41]. The different properties of PDPS and its longer side chain homologue are attributed to changes in the backbone conformation of the polymers. PDPS as confirmed by X-ray studies forms at ambient temperatures a 7/3 helical structure in which delocalization of electrons is much less extensive than in the all-trans structure of PDHS

The population of all-trans ordered segments present in the molecular backbone determines the length of the σ-conjugated chromophores[42]. Therefore, we prepared and studied the transitions in copolysilylenes PDHS-co-PDPS of different composition in order to correlate a change from the all-trans to the helical structure with the increasing proportion of PDPS units[43]. As discussed previously, these copolymers have random structure.

In Figure 5 UV spectra of copolymers are shown. A continuous decrease of the maximum of low energy absorption with the incorporation of a larger proportion of PDPS defects is observed (370 nm for PDHS, 360 for 90/10 copolymer, 350 for 80/20, and 345 nm for 50/50 copolymer). Also, the transition temperature is decreased from 42 °C, to 30 °C, 0 °C, and -10 °C, respectively. In the 80/20 copolymer a second weak maximum at 360 nm may correspond to a small proportion of longer PDHS sequences. The probability of finding seven consecutive DHS units decreases from 53% for 90/10 copolymer to 26% for 80/20 copolymer. For nine consecutive DHS units these probabilities decrease to 43% and 16%, respectively. Thus, a long wavelength absorption may be due to the small proportion of longer DHS sequences. Of course, this is only a rough estimate of the distribution of segments and, in addition, it is possible that DHS can force one or two isolated DPS units into the all-trans conformation. Much stronger extinction coefficients of the longer wavelength absorption has to be taken into account in any attempts to quantify these observations.

The transitions are well confirmed by the ^{29}Si-CP-MAS NMR. Pure PDPS and copolymers down to ≈ 25% content of PDPS units show two signals, a broad one at -26 ppm (helix) and a sharp one at -23 ppm (mesophase). Pure PDHS and copolymers up to ≈ 25% content of PDPS units show two signals, a broad one at -20 ppm (all-trans) and a sharp one at -23 ppm (mesophase). The broad absorptions of regular phases can be detected only with a cross polarization technique. The maximum below 350 nm for 50/50 copolymer observed at -10 °C could correspond to the short all-trans sequence but was not detected by NMR. The NMR chemical shift suggests the helical structure and a constant dihedral angle. This may indicate that in a 50/50 copolymer some deformation of the valency angle (not detected by NMR) may lead to the change in UV absorption.

The phase transitions of the copolymers were also monitored by differential scanning calorimetry (DSC). The transition temperatures decrease from 42 °C for pure PDHS to below 0 °C for the ≈1:3 copolymer, and then gradually increase up to 70 °C for pure PDPS. Entropies of phase transition decrease from ΔS=11 J/K·mol for pure PDHS to below ΔS=2 J/K·mol for the ≈1:3 copolymer, and then remain constant and equal to ΔS for pure PDPS. This indicates that PDPS and copolymers with at least ≈ 25% of PDPS 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 PDPS form predominantly all-trans conformations at lower temperatures. Defects introduced stepwise into the highly regular structure of PDHS apparently lead to a decrease of the crystallinity, but for copolymers containing up to 25% of the di-n-pentyl substituents, a predominantly all-trans structure is maintained.

A decrease in the disordering temperature reflects 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[44]. 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-pentylsilylene) and poly(n-hexyl-n-butylsilylene)[45, 46].

The control of the composition of copolysilylenes 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 a rational synthesis of polysilylenes.

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Captions for Figures:

Figure 1

Dependence of the intrinsic viscosity of poly(methylphenylsilylene) degraded sonochemically at 25 °C on the reciprocal of the polymer concentration in toluene.

Figure 2

GPC traces of poly(methylphenylsilylene) degraded thermally in decaline at 150 °C and 190 °C.

Figure 3

^{1}H NMR spectrum of poly(di-n-hexylsilylene-co-di-n-propylsilylene) [80:20] in benzene at room temerature under normal, and under enhanced resolution.

Figure 4

^{1}H NMR spectrum (region of methyl groups of hexyl moiety) of poly(di-n-hexylsilylene-co-di-n-propylsilylene) [50:50], [80:20], [90:10].

Figure 5

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

Scheme 1

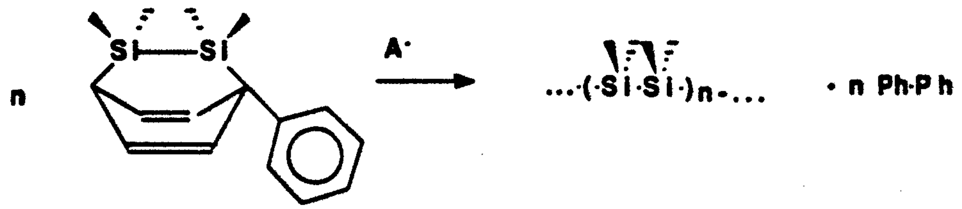
1. Reductive Coupling

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

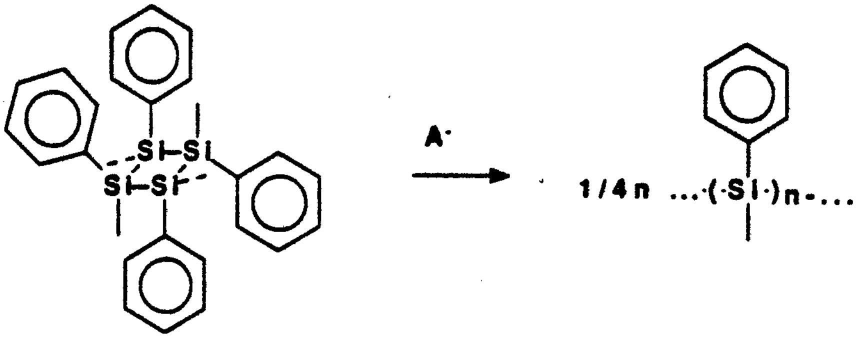
2. Dehydrogenative Coupling

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

3. Polymerization of Masked Disilenes



4. Anionic Ring-Opening Polymerization



5. Polymer Modification

$$\ldots\text{-MeSiPh-}\ldots \xrightarrow[\text{-PhH}]{\text{+HOTf}} \ldots\text{-MeSiOTf-}\ldots \xrightarrow[\text{-YOTf}]{\text{+X-Y}} \ldots\text{-MeSiX-}\ldots$$

Scheme 2

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

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

....-R_2SiCl + Na --> ....-$R_2SiCl^{\cdot -}$, Na^+ (1B)

....-$R_2SiCl^{\cdot -}$, Na^+ --> ....-$R_2Si\cdot$ + NaCl (1B')

....-$R_2Si\cdot$ + $R_2SiCl\cdot$ -->....-R_2Si-SiR_2Cl (1C)

2 ....-$R_2Si\cdot$ -->....-R_2Si-SiR_2-.... (1C')

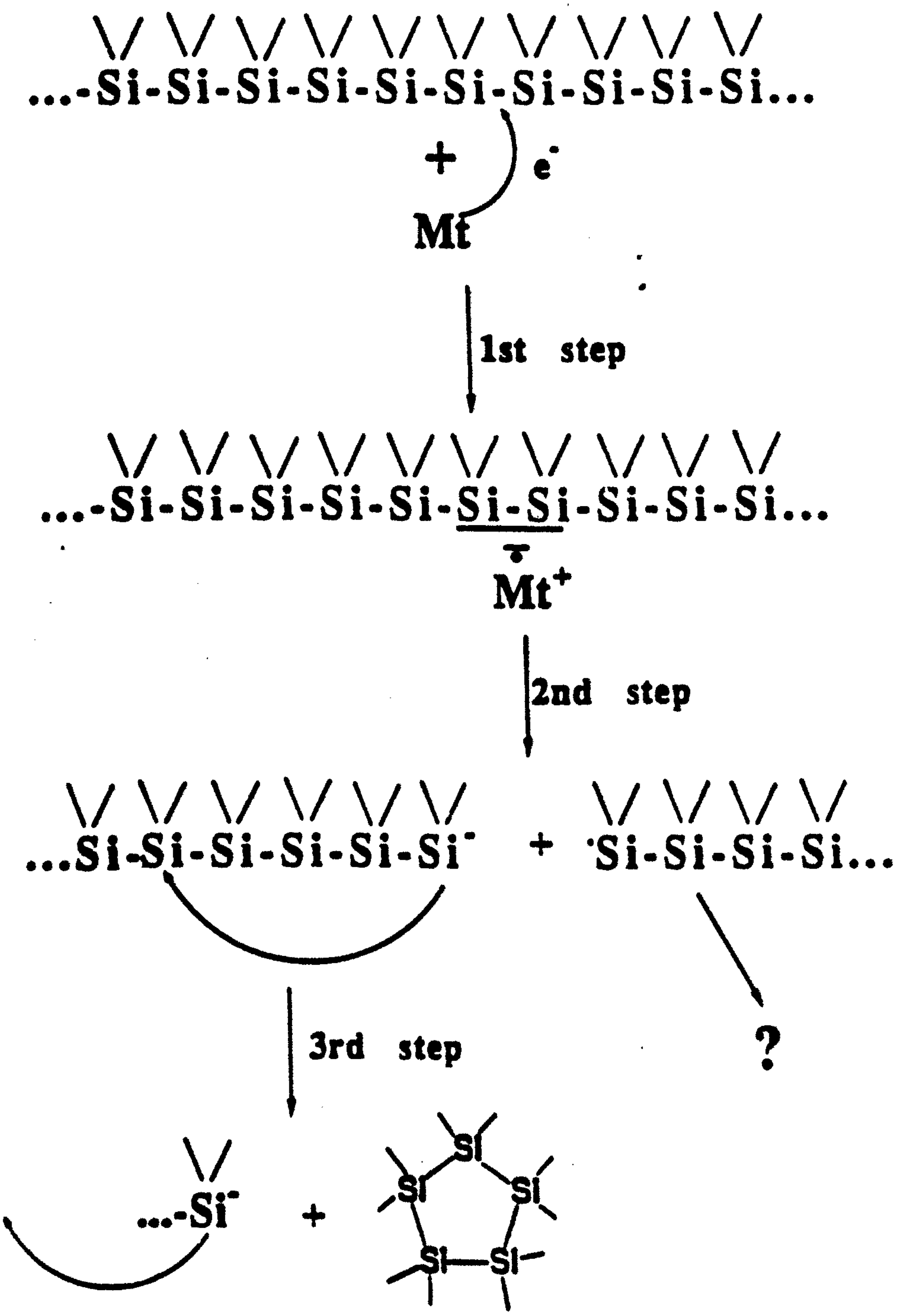
2 $R_2SiCl\cdot$ --> ClR_2Si-SiR_2Cl (1C")

....-$R_2Si\cdot$ + Na --> ....-R_2Si^-, Na^+ (2A)

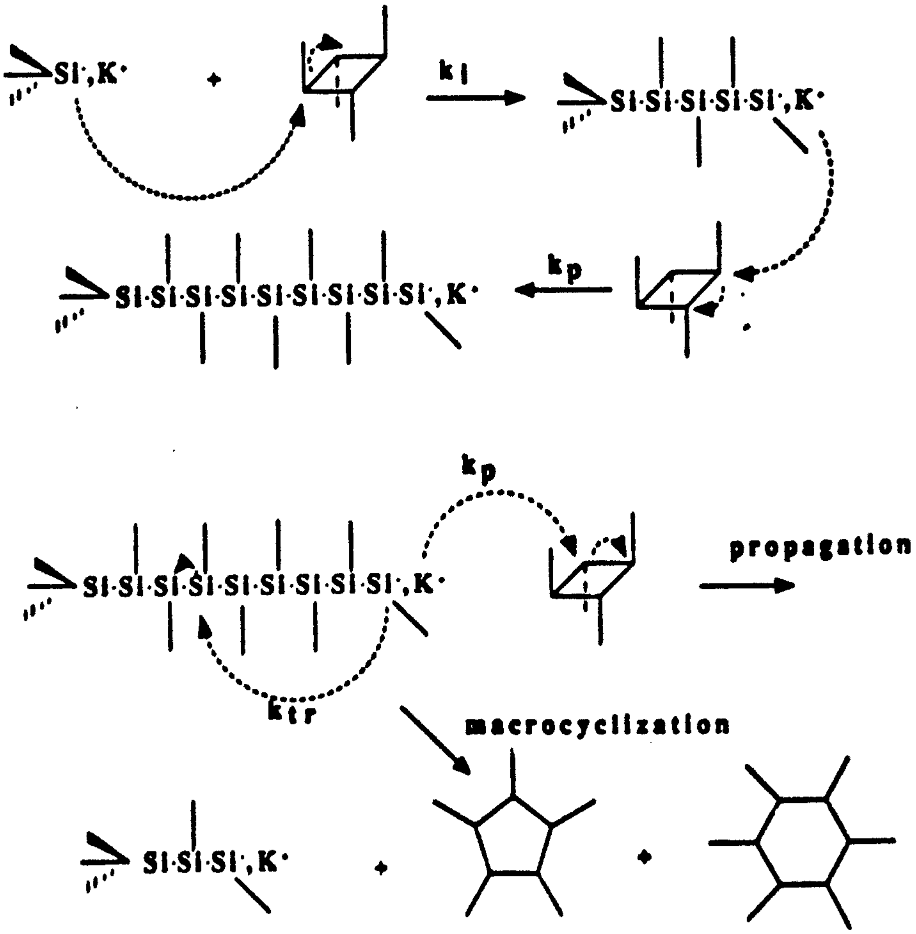
....-R_2Si^-, Na^+ + R_2SiCl_2 -->....-R_2Si-SiR_2Cl + NaCl (2B)

....-R_2Si^-, Na^+ + ...-R_2SiCl -->....-R_2Si-SiR_2-.... + NaCl (2C)

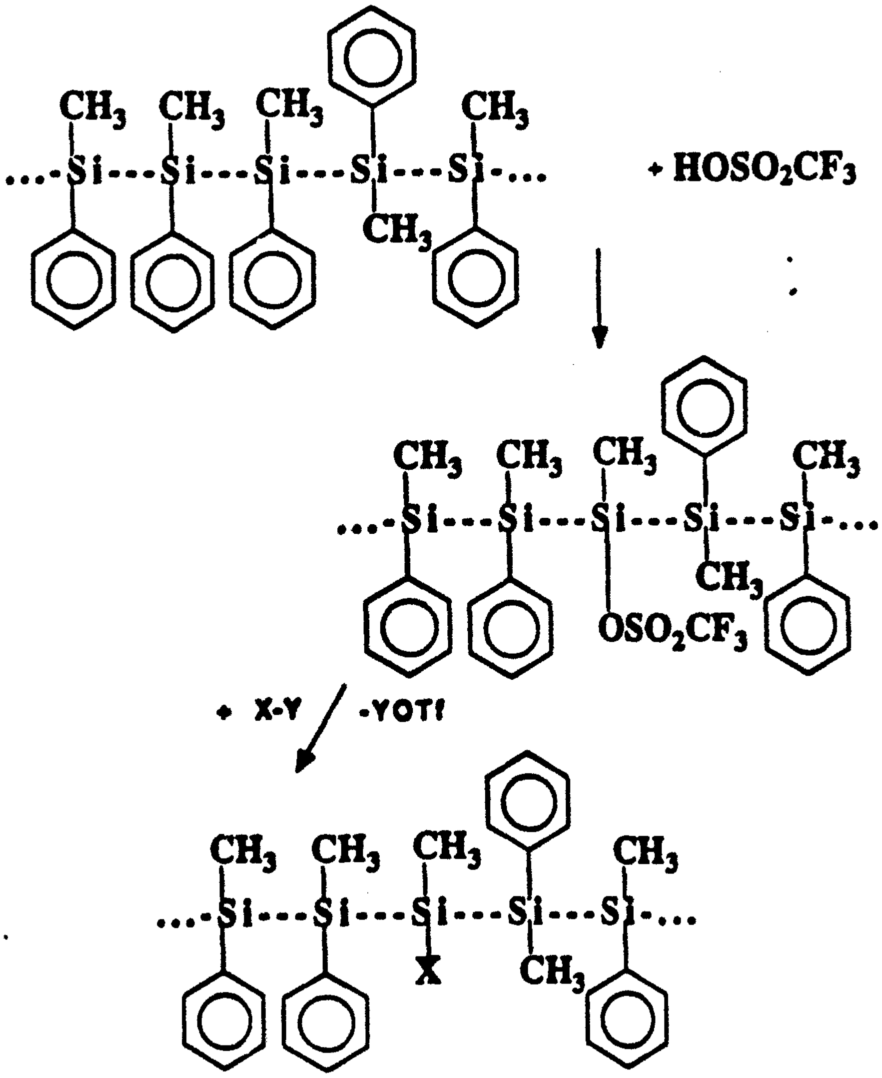
Scheme 3. Chemical Degradation of Polysilanes with Alkali Metals in Three Steps.



Scheme 4


Si·,K·
+
ki
Si·Si·Si·Si·Si·,K·
kp
Si·Si·Si·Si·Si·Si·Si·Si·Si·,K·
kp
Si·Si·Si·Si·Si·Si·Si·Si·Si·,K·
propagation
ktr
macrocyclization
Si·Si·Si·,K·
+
+

Scheme 5



X-Y: ROH, R2NH, RLi, RMgBr, etc.

also various graft copolymers: polyTHF, poly(vinyl ethers), etc

Table 1. Summary of Chemical Degradation of Polysilanes with Alkali Metals.

Solvent	Mt	$(PhMeSi)_n$	$(Hex_2Si)_n$
THF	K	v fast	slow
	Na	slow	no
	Li	no	no
	Na^+	v fast	v slow
	Li^+	v fast	v slow
Toluene	K	no	no
	Na	no	no
	#Na	slow	v slow

Li^+ or Na^+: Mt^+ $[naphthalenide]^-$

Addition of cryptand [222] or THF after polymerization

v fast < 10 min; fast < 30 min; slow > 2 hrs;

v slow > 10 hrs; no > 3 days

SONOCHEMICAL DEGRADATION OF POLY(METHYLPHENYLSILYLENE)

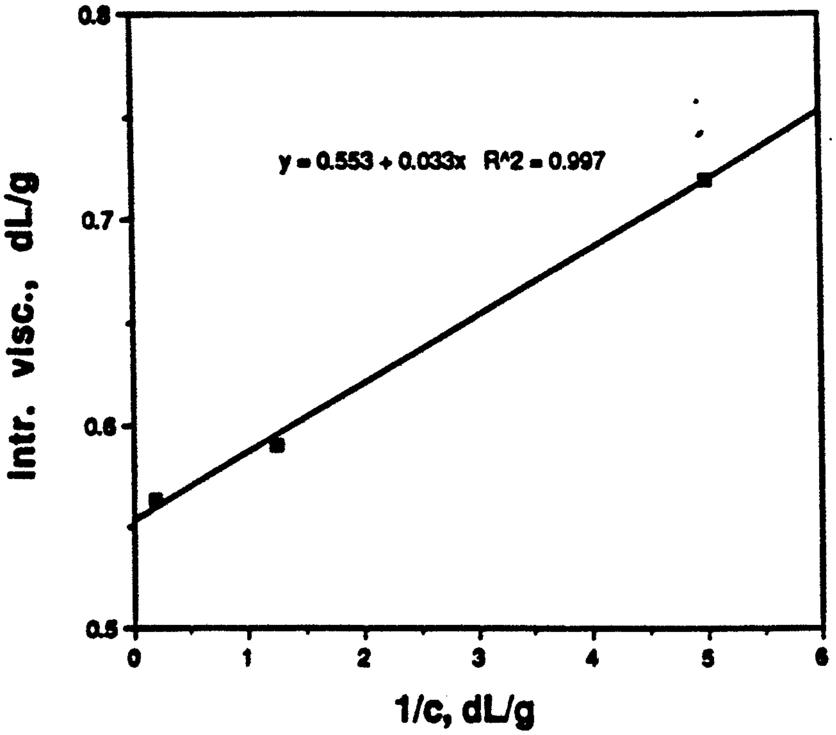
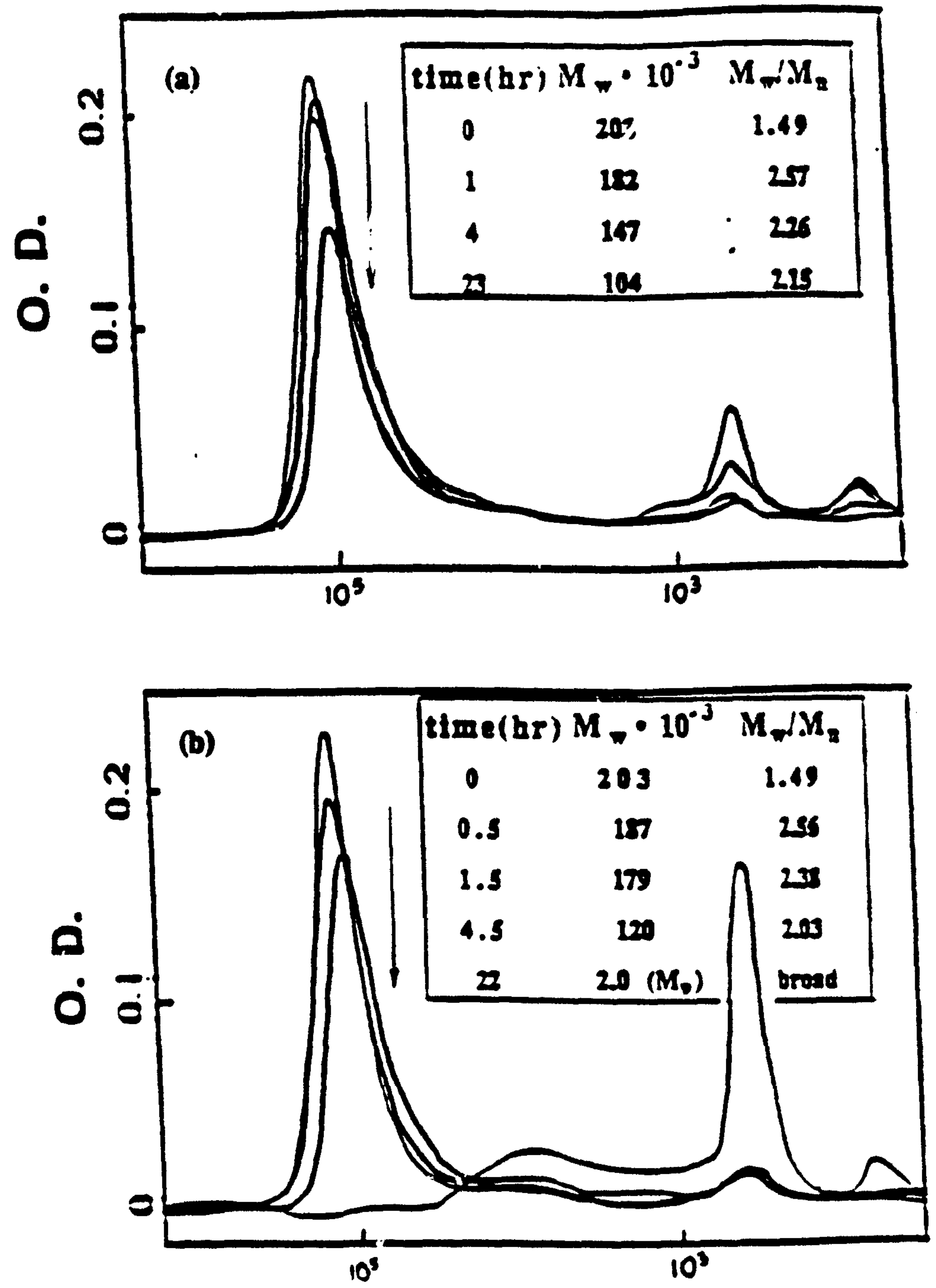


Fig.2 . GPC Traces of Thermal Degradation of in Solution at the Different Temperatures as a Function of Time: (a) 150 °C and (b) 190 °C



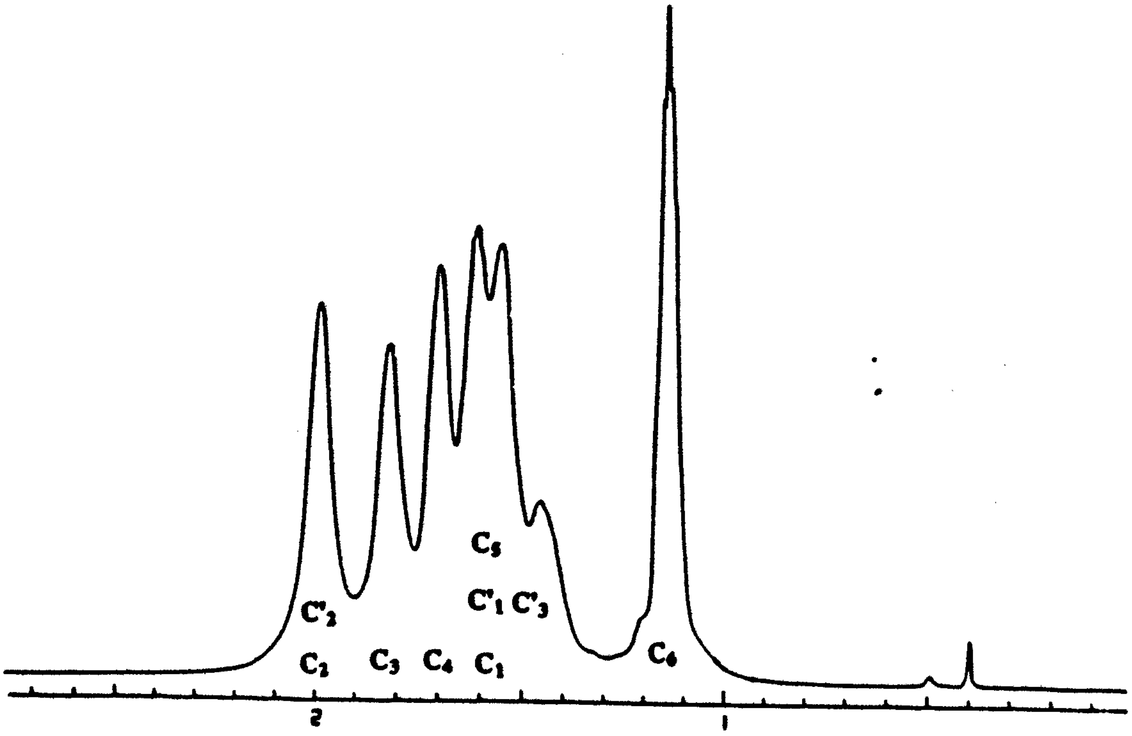
(a)

time(hr)	$M_w \cdot 10^{-3}$	M_w/M_n
0	207	1.49
1	182	2.57
4	147	2.26
23	104	2.15

(b)

time(hr)	$M_w \cdot 10^{-3}$	M_w/M_n
0	203	1.49
0.5	187	2.56
1.5	179	2.33
4.5	120	2.03
22	2.0 (M_v)	broad

620 MHz ^{1}H NMR of
poly(di-n-hexylsilylene)-co-(di-n-propylsilylene)
80 : 20



620 MHz ^{1}H NMR of
poly(di-n-hexylsilylene)-co-(di-n-propylsilylene)

Resolution More Enhanced

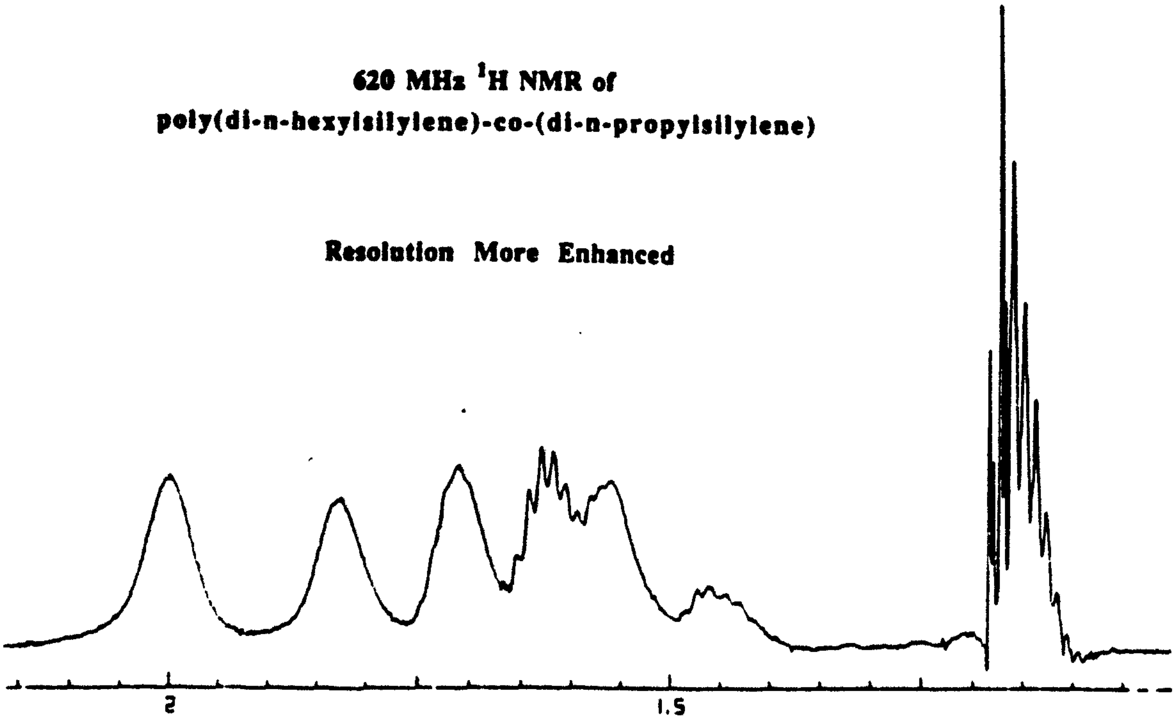


FIGURE 4

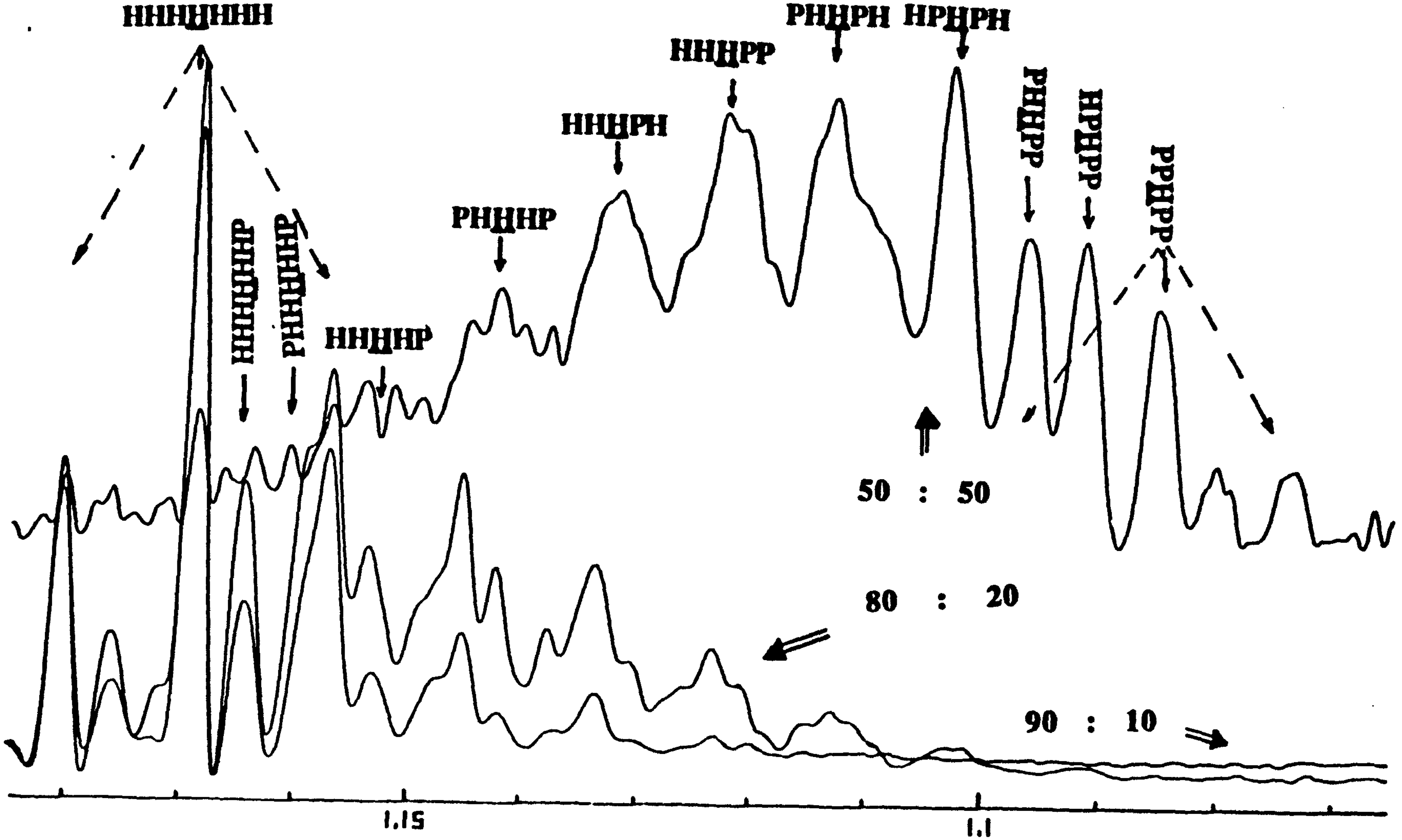

HHHHHHH
HHHHHHP
PHHHHHP
HHHHP
PHHHP
HHHPH
HHHPP
PHHPH
HPHPH
PHHPP
HPHPP
PPHPP
50 : 50
80 : 20
90 : 10
1.15
1.1

Figure 5

Temperature-dependent UV-Spectroscopy