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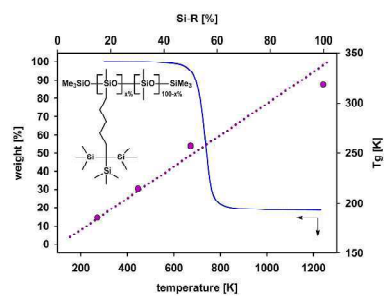
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Versatile polymeric systems based on bulky tris(trimethylsilyl)methane derivatives exhibit interesting physiochemical properties (increased chain rigidity and thermostability) and broad applicability.

Hybrid polymeric systems bearing bulky derivatives of tris(trimethylsilyl)methane.

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Abstract:

The review presents recent developments in the area of polymeric systems modified with bulky derivatives of tris(trimethylsilyl)methane (T_{Si}). These nonpolar and chemically stable moieties provide steric hindrance effect comparable to that of octahedral silsesquioxanes and severely restrict the movement of polymer segments. It leads to a significant increase of glass transition temperature a tremendous improvement of the thermostability of polymeric systems. The studies were focused on the physicochemical properties of simple, linear polymers and more elaborated hybrid systems of specific physicochemical properties. Several areas of possible application of these materials are outlined.

Keywords:

tris(trimethylsilyl)methyl, steric hindrance, polymer, hybrid material, thermal stability, applications

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1. Introduction:

A small structural modification in a side group attached to a polymer chain can lead to significant changes in its characteristic features, such as free volume¹, solubility^{2,3}, ionic conductivity⁴, or crystallinity⁵. Modification of homopolymers and copolymers with various silicon containing ligands (e.g. organosilyl groups^{6,7,8,9,10,11,12} and polyhedral silsesquioxanes (POSS)^{13,14,15} has been reported in the literature. They were shown to increase the thermooxidative stability of the studied polymeric materials, as well as improve their mechanical

properties¹⁵. POSS substituents become recently very popular in the field of polymeric materials^{13, 16}. However, sometimes quite strong associative interactions between POSS side substituents can be sometimes observed in the polymer matrix¹⁶⁻¹⁸. Another drawback for the use of POSS, built of siloxane linkages, is that they are not completely resistant to aggressive chemicals.

Derivatives of tris(trimethylsilyl)methane (referred to as "trisyl" and denoted by 'T_{Si}') occupy almost the same volume as POSS units. These overloaded carbosilane substituents can provide steric hindrance effect comparable to that exerted by tris(t-Bu)phenyl group¹⁹. Contrary to polyhedral silsesquioxanes, nonpolar tris(trimethylsilyl)methyl groups, built almost exclusively of stable Si-C bonds, are quite chemically inert. Structures based on T_{Si} ligands are well known in organometallic chemistry²⁰. Centrosymmetrical T_{Si} derivatives of metals, such as [(Me₃Si)₃C]₂Zn are exceptionally stable (chemically and thermally)²¹. Unique mechanisms of substitution at silicon atom were also reported for some trisyl derivatives²².

T_{Si}-type compounds have quite big applicative potential, e.g. they can be used as effective reducing agents²³. They have been also used for the synthesis and modification of physiochemical properties of various polymeric systems. Such T_{Si}-modified polymeric materials can exhibit quite unique characteristics. For example, a distinct sub-glass transition (β relaxation) in ladder T_{Si}-silsesquioxanes was observed as a result of a specific change in the mobility of Me₃Si groups at variable temperatures²⁴.

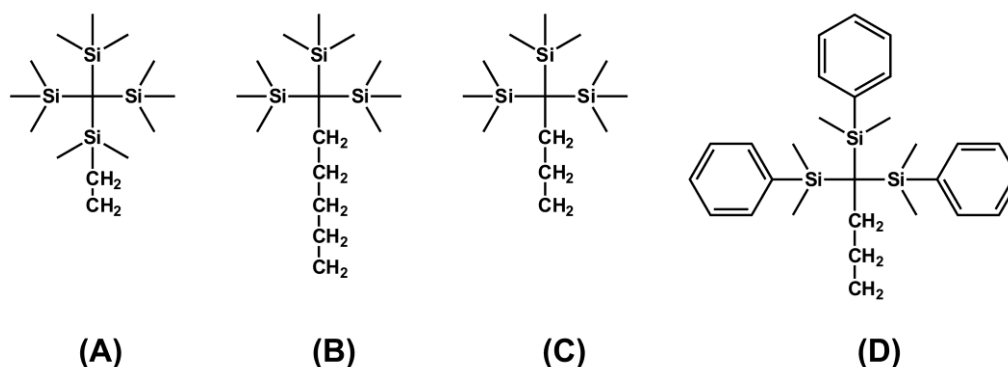
From the applicative point of view, T_{Si} moiety shielded by weakly interacting methyl groups, brings about properties pertinent to operating low intermolecular forces, such as low surface tension, good chemical and thermal stability. Applications of polymeric materials in extreme conditions can often be limited due to their poor thermal stability. Incorporation of T_{Si} in polymer matrices can improve their thermostability and provide some other specific properties. It can hinder the mobility of adjacent polymer chains to an exceptional degree. Even a very small amount of T_{Si} units can alter completely the thermal behavior of polymeric matrix, which compensates the costs of preparation. Moreover, the materials do not release environmentally harmful byproducts on their thermal decomposition. The presence of overloaded T_{Si} groups composed of nonpolar Si-C bonds is also beneficial for all materials intended for use in microelectronics.

Nevertheless, methyl groups in T_{Si} moieties can be also substituted by other reactive chemical functionalities which afford for the preparation of more elaborated hybrid systems of unique physiochemical properties. Trisyl moiety can be easily incorporated into linear to branched (dendritic) or cross-linked structures. Such materials were applied as supports for reusable catalytic systems that exhibited high reactivity and selectivity, as well as a satisfactory turnover number.

This report summarizes developments in the field of synthesis and points to attractive areas of applications of polymeric materials modified with overloaded T_{Si} groups. It presents an analysis of the data published within 1999-2011 and is the first review of the topic.

2. Properties of hybrid polymeric systems bearing sterically hindered T_{Si}-substituents.

Side substituents can change significantly the conformation and flexibility of a polymeric chain^{25, 26}. Groups of high steric hindrance can cause both a decrease of chain packing density and hinder the ease of rotation about chemical bonds in the main chain, which can have an effect on the glass transition temperature (T_g) of the modified polymer²⁷. Systematic studies involving structural modifications within the side group and the degree and regularity of substitution of the polymeric chain were carried out for T_{Si}-modified polymers to define the influence T_{Si} group (Scheme 1) can exert on the mobility of particular units of a polymer chain.

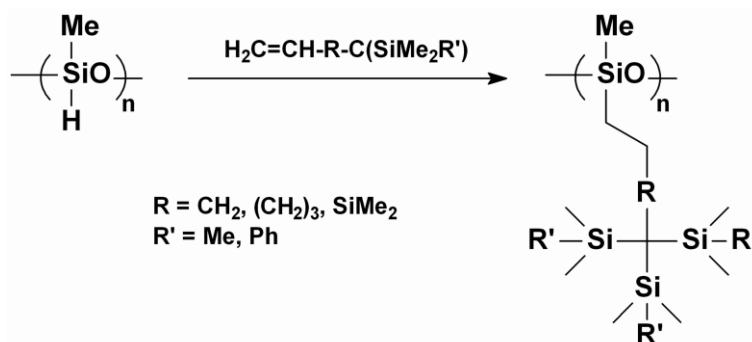


Scheme 1. Masterchart of T_{Si} -derivatives abbreviated in this review as $T_{Si}(A)$, $T_{Si}(B)$, $T_{Si}(C)$ and $T_{Si}(D)$.

2.1. T_{Si} -substituents in linear siloxane polymers and oligomers:

Polysiloxanes, due to the outstanding flexibility of Si-O-Si bonds, show low surface tension, good elasticity at low temperatures and extremely low temperature of glass transition. Consequently, they have higher diffusion and permeability coefficients than polymers (polyurethane, polyisoprene, polycyclooctene)^{28, 29, 30} typically utilized for the preparation of membranes. However, polysiloxanes are liquids of viscosity depending on their molecular weight and must be cross-linked or modified with specific side groups (e.g. POSS units¹³) in order to have good mechanical properties. Modification of polysiloxane materials with sterically demanding tris(trimethylsilyl)methyl moieties was also proven to be of great importance for their properties³¹.

Derivatives of T_{Si} groups can be introduced as side or terminal substituents. Polysiloxanes with side hydride or vinyl groups can be modified using alkenyl derivatives of T_{Si} moieties via hydrosilylation or metathesis reactions. The addition to double bond of alkenyl- T_{Si} via hydrosilylation catalysed by Pt(0)-divinyltetramethyldisiloxane complex (Karstedt's catalyst) (Scheme 2) proceeds obeying the Farmer's rule³¹. Depending on the amount of T_{Si} groups and their structure, the resulting polymers are solids or viscous liquids. It was observed that the average degree of substitution of a siloxane chain with T_{Si} units depends on the composition of the polymeric precursor and on the structure of the carbosilane group. Steric congestion prevents complete conversion of Si-H groups and homopolymers can be substituted at only about 95%mol of chain units.



Scheme 2. Modification of polysiloxanes by hydrosilylation of T_{Si} -derivatives.

Stiffening of macromolecules with a flexible backbone by side T_{Si} groups (anchor effect³²), results in an exceptionally high increase of glass transition temperature (Figure 1). The effect is augmented with the

increase of degree of substitution. The increase of T_g is often linked to better packing of polymeric chains and a decrease of the free volume in the polymer matrix. However, T_{Si} -modified siloxanes do not undergo crystallization, and are completely amorphous owing to the steric hindrance of carbosilane groups.

The influence of the size of T_{Si} substituents on the mobility of siloxane chain have been estimated using a suitable model – oligosiloxane with a small amount (~15%) of functionalized subunits randomly distributed along the main backbone. It was found that an additional increase of the glass transition temperature can be achieved on increasing the size of T_{Si} moiety [i.e. changing $T_{Si}(C)$ for $T_{Si}(D)$]. The difference is bigger than that observed on increasing the length and rigidity of the linker between T_{Si} group and the main backbone [e.g. $T_{Si}(A)$ for $T_{Si}(C)$]³¹.

The relationship between the segmental mobility of a polymer chain and the distribution of various T_{Si} -type carbosilane moieties along the siloxane backbone was studied for two homologous series of siloxane copolymers with regularly and randomly distributed T_{Si} -modified chain units³¹. In the case of polymers with smaller amount of bulky substituents (30% molar amount of T_{Si} -modified siloxane units), T_g temperature was higher if the bulky groups were distributed in an irregular manner. In samples with 50% molar amount of modified units the polymeric chains were more flexible (lower T_g) if the distribution of side bulky groups was irregular.

The effect of T_{Si} moiety adjacent to Si atoms in polymer chain was quantitatively estimated using a series of dimethylsiloxane oligomers terminated with the carbosilane units. The relaxation phenomena were studied by DSC and NMR methods with respect to the mobility of silicon atoms in the main chain³³. The measured spin–lattice relaxation times T_1 (²⁹Si NMR) of silicon atoms in siloxane chain were related to the distance between a given siloxane unit and the carbosilane moiety. It was found that the mobility of terminal siloxane units was substantially hindered, but the short range effects did not outweigh the intrinsic flexibility of siloxane bonds and the mobility of other silicon atoms was almost not affected. The results can be correlated with the change of phase transitions (increased T_g) observed for oligomers of longer siloxane chain.

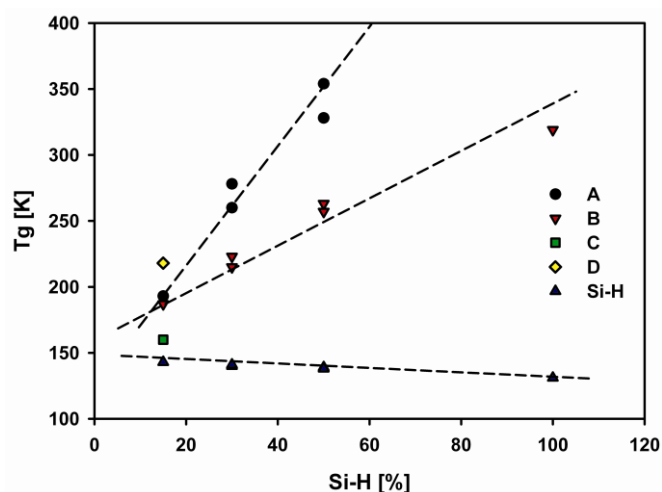


Figure 1. Relationship between T_g of oligosiloxanes (DSC measurements) and the degree of their substitution with side T_{Si} -groups (estimated by ¹H NMR, for A,B,C, D see Scheme 1) (³¹with permission from e-Polymers).

2.2 Linear polysilsesquioxanes with T_{Si}-side groups.

Polymeric silsesquioxanes bearing sterically hindered groups were obtained using T_{Si}-modified triethoxysilanes [T_{Si}(A)-Si(OEt)₃²⁴ and T_{Si}(B)-Si(OEt)₃] as their monomeric precursors. The amphiphilic structure of precursors determines the organization of oligomers during the initial stages of condensation. Some defects in the chain structure can be observed with ²⁹Si NMR, but the polymers show characteristic X-ray diffraction peaks, which indicate the presence of a defined (ladder-like) periodicity in these amorphous materials³⁴.

The rigidity of the polymeric backbone has some important consequences to the physicochemical properties of T_{Si}-silsesquioxanes. A phase transition relating to the change in the heat capacity of the polymer was recorded in DSC studies for T_{Si}(A)-polysilsesquioxane at low temperatures (310-320 K). The temperature is too low for a glass temperature transition of such a rigid system. Polysilsesquioxanes obtained with the use of less hindered T_{Si}(B)Si(OEt)₃ show a typical T_g at 396 K. It should be also stressed that glass transition of a oligo(methylsiloxane) modified (>95%) with T_{Si}(A) group was not observed before the thermal decomposition of the polymer, whereas its analogue substituted with (Me₃Si)₃C(CH₂)₅ groups undergoes devitrification at 319 K. Also, a linear oligosiloxane, modified in 50% of monomeric units with T_{Si}(A) as side groups, shows T_g at ~350 K³¹. It can be thus assumed that the phase transition observed for (T_{Si}(A)-polysilsesquioxanes does not relate to the changes of mobility in the silsesquioxane backbone, and should rather be recognized as a sub-T_g transition -β relaxation (T_β). ²⁹Si CPMAS NMR studies at temperatures corresponding to various phases proved that indeed, the transition cannot be related to the segmental movements of silsesquioxane double chain, but rather to selective specific changes in the relaxation of Me₃Si groups in T_{Si}(A) moiety (Figure 2). The heat absorbed by the system results in the increased mobility of Me₃Si groups. Such sub-T_g phenomena were detected by DMTA studies for other polymeric systems bearing very bulky substituents. Norbornyl-POSS copolymers with about 8% of molar amount of POSS-monomer showed not only a T_g at temperature higher than that observed for the parent polymer, but also α- and β-relaxation transitions¹³. T_β at 195 K was linked to the liberation of cyclohexyl groups bound to silsesquioxane cages.

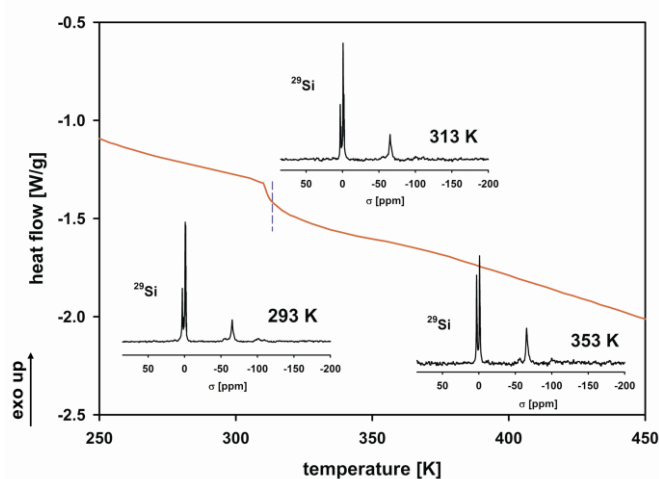


Figure 2. Correlation between relaxation in ²⁹Si CPMAS NMR and phase transition T_β recorded for (Me₃Si)₃CSiMe₂CH₂CH₂-polysilsesquioxane (²⁴with permission from Elsevier).

2.3 Linear polystyrenes with T_{Si}-side groups.

The presence of overloaded substituents can not only hinder the free rotation of bonds but also should also result in the chain separation and an increase of free volume in the polymer matrix. Such an effect was reported for polymers of rigid backbone (e.g. polyacetylenes). Poly(1-trimethylsilylpropyne) shows much higher permeability to oxygen than polypropyne, due to the presence of Me₃Si groups³⁵. Similar properties were shown by polystyrenes modified with small carbosilane substituents^{36, 37}. T_g increased to the extent dependent on the steric hindrance exerted by silyl groups (Table 1, the values in parentheses correspond to the molar percentage of silylated styrene units)^{38, 39}. Differences in polymer microstructure and packing were also observed for styryl-POSS homopolymers, that showed T_g at 610-670 K¹³, depending on the kind of POSS.

Table 1. The increase of T_g for polystyrenes modified with small carbosilane groups (based on^{38, 39}).

| | ΔT _g [K] (100%) | ΔT _g [K] (50%) | ΔT _g [K] (25%) | ΔT _g [K] (17%) |
|-----------------------------------|----------------------------|---------------------------|---------------------------|---------------------------|
| t-BuMe ₂ Si | 31 | 33 | - | 31 |
| Et ₃ Si | 18 | - | 32 | 31 |
| Me ₃ SiCH ₂ | 28 | - | - | 30 |

ΔT_g – the difference between T_g before and after modification

Polystyrenes modified with bulky T_{Si} groups can be obtained by modification of poly(4-chloromethylstyrene) and its copolymers with styrene (random distribution of functional groups). Nucleophilic substitution of the chlorine atom by T_{Si}-group can be achieved using (Me₃Si)₃CLi^{40, 41}, (H₂C=CHMe₂Si)₃CLi⁴², and (HMe₂Si)₃CLi⁴³. (Me₃Si)₃CLi and (H₂C=CHMe₂Si)₃CLi can be prepared by the metallation of T_{Si}-H by MeLi⁴⁴. (HMe₂Si)₃CLi was obtained using (HMe₂Si)₃CH and lithium diisopropylamide (LDA)⁴³. The substitution was quantitative in copolymers, but due to steric reasons homopolymers incorporated T_{Si} groups in only ~90% of all monomeric units⁴¹. It should be also noted that AIBN-initiated free radical homopolymerization of T_{Si}-functionalized styrenic monomer (4-trisilylmethyl styrene) has failed⁴⁵.

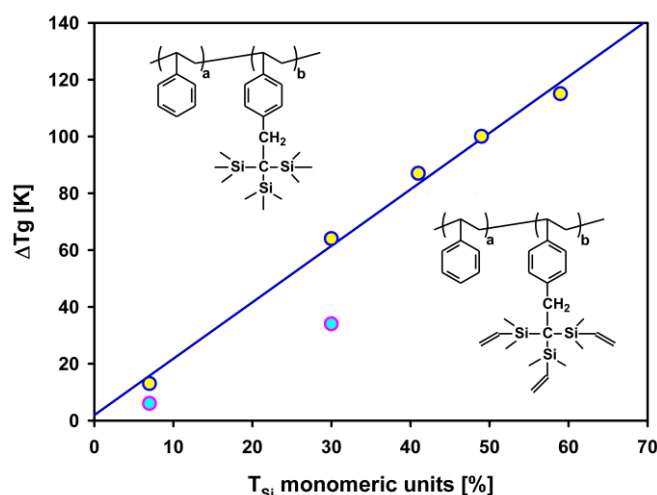


Figure 3. Relationship between T_g of polystyrenes and the degree of their substitution with T_{Si}-derivatives (⁴⁶ based on^{40, 42}).

Table 2. Increase of T_g for copolymers of 4- T_{Si} -methylstyrene and other styrenic monomers.

| comonomer | $T_{Si}Li$ | $T_{Si}M$ [mol%] | M_n | PDI | M_n-T_{Si} | PDI- T_{Si} | ΔT_g [K] | ref |
|--------------------------|------------------------|------------------|--------|-----|--------------|---------------|------------------|---------------|
| Styrene | $(H_2C=CHMe_2Si)_3CLi$ | 30 | 16000 | 1.6 | 31500 | 1.9 | 35 | ⁴² |
| styrene | $(H_2C=CHMe_2Si)_3CLi$ | 8 | 68000 | 1.9 | 45600 | 2.4 | 6 | ⁴² |
| Styrene | $(Me_3Si)_3CLi$ | 8 | 187000 | - | 200000 | - | 6 | ⁴⁰ |
| - | $(Me_3Si)_3CLi$ | 90 | 23900 | 2.5 | - | - | 170 | ⁴¹ |
| styrene | $(Me_3Si)_3CLi$ | 52 | 11200 | 2.0 | - | - | 143 | ⁴¹ |
| styrene | $(Me_3Si)_3CLi$ | 25 | 12200 | 1.8 | - | - | 96 | ⁴¹ |
| 4-methylstyrene | $(Me_3Si)_3CLi$ | 27 | 11200 | 2.0 | - | - | 89 | ⁴⁹ |
| 4-methoxystyrene | $(Me_3Si)_3CLi$ | 29 | 10400 | 2.0 | - | - | 94 | ⁴⁹ |
| α -methyl styrene | $(Me_3Si)_3CLi$ | 34 | 3300 | 2.1 | - | - | 62 | ⁴⁹ |
| - | $(HMe_2Si)_3CLi$ | >90 | 12300 | 1.7 | 12100 | 1.3 | 92 | ⁴³ |
| styrene | $(HMe_2Si)_3CLi$ | 50 | 19300 | 1.6 | 18300 | 1.7 | 79 | ⁴³ |
| styrene | $(HMe_2Si)_3CLi$ | 25 | 18900 | 1.6 | 17900 | 1.7 | 57 | ⁴³ |

$T_{Si}M$ – molar amount of trisylated chain units

M_n – molecular mass by SEC

PDI – polydispersity index by SEC

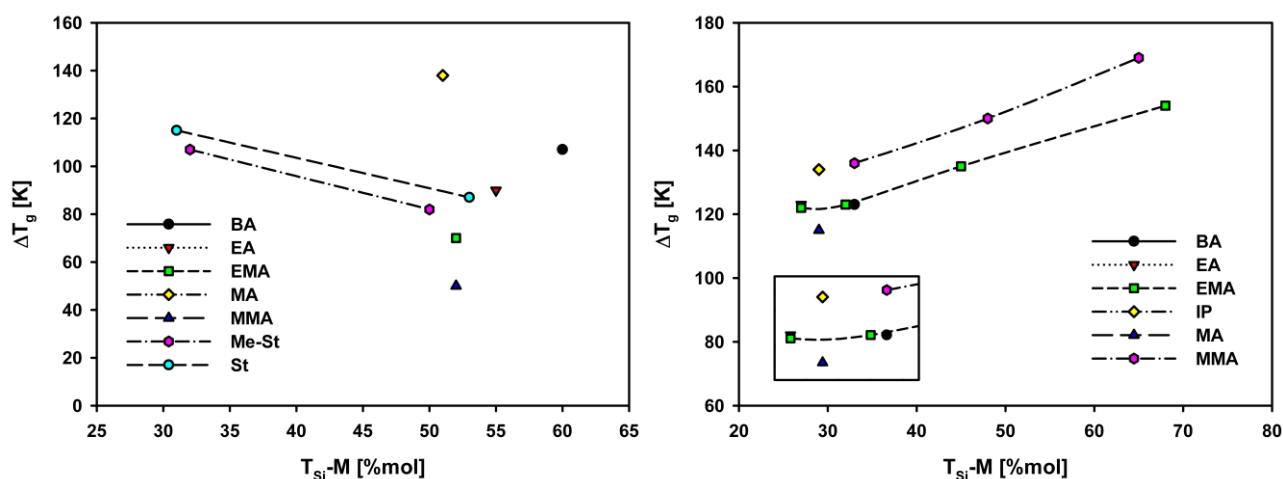
ΔT_g – the difference between T_g before and after modification with carbosilane group

Modification of styrene copolymers with T_{Si} -derivatives also leads to changes of T_g (Figure 3, Table 2). The increase of T_g (linear increase of T_g with increasing degree of substitution with T_{Si}) reflects the decrease of segmental mobility in the modified polymers and is dependent on the degree of substitution and the type of carbosilane group. Nevertheless, the relative changes are smaller than these observed for flexible oligosiloxanes.

Poly(styrene)-*co*-[2,2-bis(trimethylsilyl)ethenyl(styrenes)] can be obtained via the reaction between $(Me_3Si)_3CLi$ and polymers bearing pendant enone groups⁴⁷. Bis(silyl)ethenyl groups were attached to poly(α -methylstyrene) randomly formylated in 51% of monomeric units via Peterson olefination of $(RMe_2Si)_3CLi$ ($R=H, Me, Ph$)⁴⁸. DSC analysis after the modification showed an increase of the glass transition temperature that depended on the size of silyl group [411 K for P(α -MS-SiMe₂H), 415 K for P(α -MS-SiMe₃) and 422 K for P(α -MS-SiMe₂Ph)].

2.4. T_{Si} -modified copolymers of styrene or glycidyl methacrylate and monomers of acrylic and dienic type.

Copolymers of 4-chloromethyl styrene and monomers of acrylic or dienic type [methyl methacrylate (MMA), ethyl methacrylate (EMA), methylacrylate (MA), ethyl acrylate (EA), n-butyl acrylate (BA) and isoprene (IP)] were prepared by radical polymerization, and modified with trisyl groups using $(Me_3Si)_3CLi$ ^{45, 50}. $(Me_3Si)_3CLi$ was also used for chemical modification of epoxy groups in copolymers of glycidyl methacrylate and styrene, methylstyrene, MA, EA, BA, MMA, EMA or n-butyl methacrylate (BMA) *via* the ring opening reaction^{51, 52}.



a)

b)

Figure 4. Increase of T_g for copolymers of (a) glycidyl methacrylate (b) 4-chloromethylstyrene, and other styrenic monomers after modification with T_{Si} groups (T_{Si-M} - molar amount of trisylated chain units, ΔT_g – the difference between T_g before and after modification with T_{Si} group).

The chemical modification of the studied copolymers of random structure and introduction of side T_{Si} -type groups resulted in the formation of polymeric materials of rigid chains (Figure 4). For all styrenic copolymers the value of T_g was found to increase with the amount of trisyl groups incorporated into polymer structures. The results can be related to the effect POSS substituents exerted on polymethacrylates [ΔT_g between atactic poly(butylmethacrylate) and POSS-MA was 130 K and 200 K for, respectively, polymers modified at 10% and 50% molar amount of randomly distributed monomeric units]¹³. Surprisingly, copolymers of glycidyl methacrylate with styrene and methylstyrene modified at 50% monomeric units with bulky carbosilane groups showed their glass transitions at temperatures lower than these recorded for their less substituted precursors. T_g of other trisylated copolymers increased the more, the lower was their native T_g .

3. Thermal stability of polymeric systems modified with T_{Si} substituents.

From the applicative point of view, high thermal stability of polymeric materials is a very desirable feature. The parameter can be improved by substitution of a polymeric chain with bulky side substituents or rigid backbone segments (e.g. POSS^{13,14}) that hinder its mobility. It can retard the thermal depolymerization, especially hindering end-biting and chain transfer processes. The presence of T_{Si} groups, apart from the structural changes it can provide, can lead as well to an increase of thermal stability of the modified polymeric systems. Specific thermal stability of T_{Si} groups is reflected in the similar, well defined temperatures of decomposition of polymers modified with T_{Si} groups^{31, 53, 54}. The temperature of the maximal decomposition rate (~ 700 K) corresponds to the temperature of thermolysis of Si-C bonds⁵⁵.

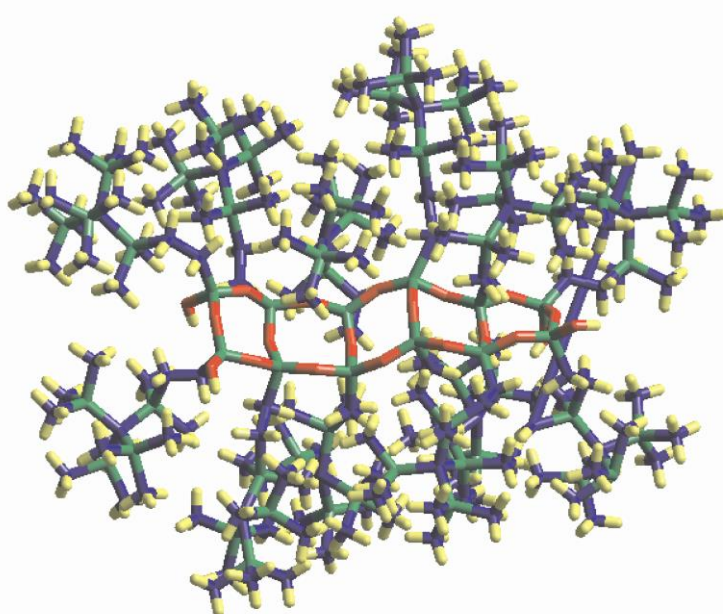


Figure 5. Structure of linear oligosilsesquioxane bearing side $T_{Si}(A)$ group.

Polymeric silsesquioxanes (Figure 5) having the main backbone of high thermal stability are good models for the studies of thermal behavior of T_{Si} groups in polymeric systems⁵³. The main double backbone composed of siloxane bonds is stable at temperatures at which thermal decomposition of T_{Si} groups occurs. 5% of weight decrease can be noted for polymeric $T_{Si}(A)$ -silsesquioxane at ~700 K in nitrogen atmosphere and at 590 K in air. FTIR and NMR analysis showed that under the inert atmosphere Me_3Si groups are lost and the polymers are converted into materials of $Si_xO_yC_z$ structure, which confirms bonds redistribution during the thermolysis. Quite interestingly, the properties of ceramic materials obtained with $T_{Si}(A)$ -silsesquioxanes in nitrogen depend on the temperature of ceramization (at ~800 K glassy solids of monolithic structure and good adhesion to metal, brittle solids at >800 K). TG-MS analysis of volatiles formed during the thermolysis in argon suggests that the decomposition proceeds via abstraction of bulky $(Me_3Si)_3CR-$ fragments⁵³. The length of central Si-C bonds within the T_{Si} group is enlarged in order to release the steric congestion within the molecule^{56,57}, but according to the reported data, it has no influence on the thermal decomposition of T_{Si} -modified polymers. Pyrolysis of $T_{Si}(A)$ -silsesquioxanes in air proceeds via standard oxidation of H-C and C-Si bonds at 600-900 K. Interestingly, photolytic degradation (high energy ArF laser light) of polysiloxanes with $T_{Si}(A)$ and $T_{Si}(B)$ moieties proceeds in a quite different way⁵⁸. The cross-linking process occurs by defragmentation of T_{Si} moieties with the formation of volatiles [Me_3SiH , $(Me_3Si)_2CH_2$, Me_4Si , CH_4 and C_2H_6], which can be used for lithographic purposes.

3.1. Linear polymers.

Linear polysiloxanes, due to the high flexibility of siloxane bonds in the main backbone, are known to undergo thermal degradation at relatively low temperatures¹⁴. It is well established that the degradation involves end-biting and chain transfer processes and leads to a complete depolymerisation by formation of volatile cyclic products³⁸.

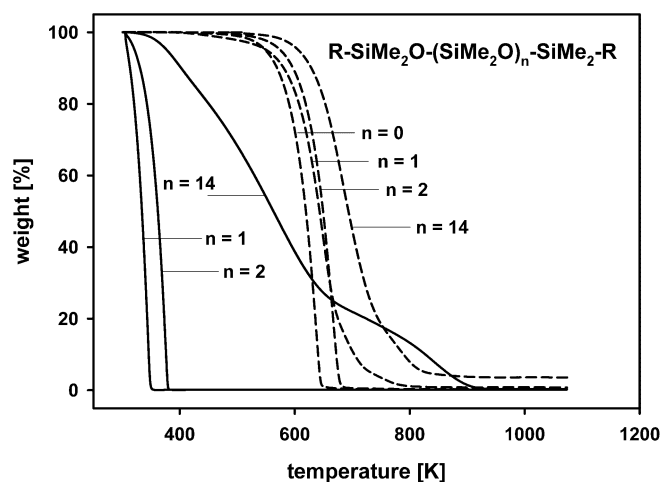


Figure 6. Thermal stability ($N_2/20$ K/min) of oligodimethylsiloxanes terminated by bulky carbosilane groups [dashed line: $R=(Me_3Si)_3CSiMe_2CH_2CH_2$] and their precursors (solid line: $R=H$) (based on ³³).

T_{Si} -type end- and side-groups can significantly increase the thermal stability of siloxane materials. Dimethylsiloxane oligomers (dimers, trimers, tetramers and hexadecamers) with bulky T_{Si} -type end groups were found to be stable up to 600 K (Figure 6)³³. The size of bulky end group [$T_{Si}(A)$ or $T_{Si}(B)$] has no significant influence on the thermal stability of the oligo(dimethylsiloxanes). The steric hindrance provided by T_{Si} groups works only for the siloxane units close to the immobilized chain end. Chain transfer processes can still occur if the polymeric chain is long enough. Consequently, the end-biting mechanism of depolymerization of dimethylsiloxane hexadecamers is hindered, but almost complete volatilization of the sample under the analysis conditions can be observed.

Modification with side T_{Si} groups (randomly or regularly distributed along the main chain) leads to a significant improvement of thermostability of polymeric systems build of siloxane bonds^{31, 53, 54}. A significant resistance to high temperatures can be observed even for poly(dimethyl-co-methyl T_{Si})siloxanes with only 15%mol of monomeric units functionalized with bulky carbosilane moieties. Thermal decomposition in the inert atmosphere occurs at temperatures close to 700 K (5% weight decrease). Depolymerisation is hindered (Figure 7a), and the ceramic residue left at 1200 K is substantial (e.g. 20% of the initial weight of a sample for polysiloxane modified with T_{Si} in 15% of monomeric units). The decomposition of oligomeric systems modified with T_{Si} -type groups under an inert atmosphere most probably involves, analogously to the decomposition of T_{Si} -silsesquioxanes⁵³, a single stage abstraction of carbosilane moieties. Consequently, the weight loss in polysiloxanes with T_{Si} units attached via linkers of different structure [$T_{Si}(A)$ or $T_{Si}(B)$] occurs at similar temperature range ³¹.

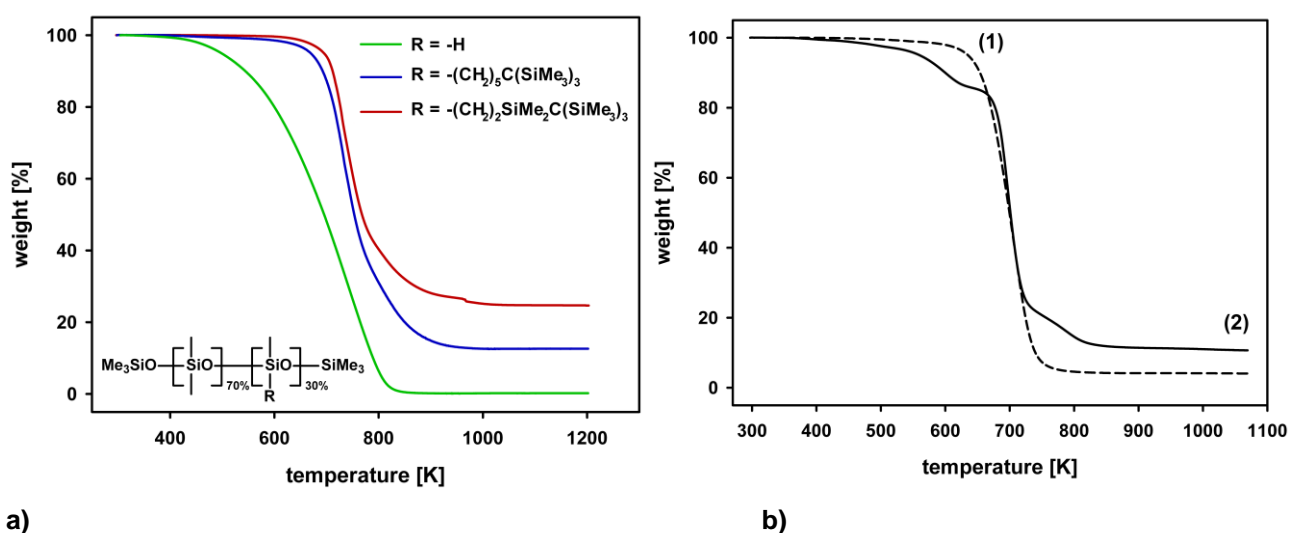


Figure 7. Thermal stability of T_{Si} -modified (30%mol of functionalized chain units) (a) siloxane copolymers ($N_2/20$ K/min) and (b) poly(chloromethylstyrene)-co-polystyrenes ($N_2/10$ K/min) before (1) and after modification with $(H_2C=CHMe_2Si)_3C$ (2) (based on literature data^{31, 42}).

However, it should be stressed that the effect a bulky group exerts on the thermostability of a polymer depends to a large extent on the type of polymer backbone. For example, any significant effect on the decomposition temperature was noted for norbornyl-POSS copolymers with ~8% of molar amount of POSS-monomer¹³. Poly(chloromethylstyrene)-co-polystyrenes of random structure and their trisylated derivatives have almost the same resistance to high temperatures, however the nature of the degradation processes is different.

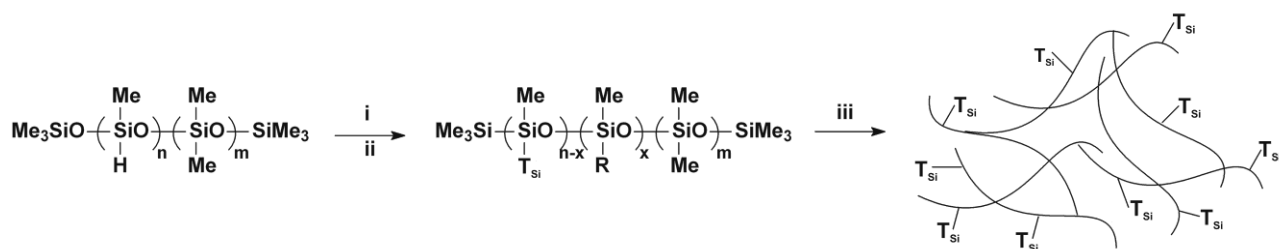
Thermal decomposition (depolymerisation)⁵⁹ of poly(chloromethylstyrene)-co-polystyrene occurs at temperatures > 670 K (Figure 7b). A small decrease of the sample weight can be typically observed above T_g of the polymer (500-620 K), due to the release of low molecular weight volatiles from the polymer matrix once it becomes more elastic. Modification of the polymer with $(H_2C=CHMe_2Si)_3C$ does not lead to any significant increase of thermostability, except that the effect of entrapment of volatiles in the polymeric matrix is eliminated⁴². It can be ascribed to the so-called “dendritic effect”, exerted in this case by bulky carbosilane groups, leading to an increase of free volume, which helps to evaporation of small molecules at temperatures lower than T_g [~400 K for 30% substitution of polymer chain with $(H_2C=CHMe_2Si)_3C$].

3.2. Cross-linked polymers.

Bulky carbosilane moieties can be used as side groups (randomly distributed) in linear polymers with cross-linkable moieties (oxiranes⁶⁰ or alkoxy silanes⁶¹) that can be transformed into polymeric networks (Scheme 3). T_{Si} type compounds $(Me_3Si)_n(R'Me_2Si)_mC(SiMe_2A)_z$ bearing acidic groups can be also used as initiators of the cross-linking process and embedded into the polymeric network⁶². It was shown that the presence of T_{Si} groups can also increase thermal stability of such cross-linked polymeric systems.

For linear polymers with oxirane moieties, and their cross-linked derivatives, T_{Si} substituents exert a stabilizing effect [higher thermal stability and better mechanical properties of cross-linked samples (including diminished contraction after crosslinking)]⁶⁰. Properties of cross-linked materials can be adjusted by the ratio of cross-links to T_{Si} groups. Increasing the molar amount of $-Me_2SiO-$ segments into the polymer backbone

diminishes the thermal stability of the studied systems. Linear polysiloxanes bearing alkoxyethyl and T_{Si} groups behave in a similar way⁶¹. However, it was noted that the increase of the molar ratio between carbosilane moieties and alkoxyethyl groups results in a lower cross-linking density, since T_{Si} moieties hinder the effective condensation of silanols at low pH. The formation of a stable network requires short thermal treatment after the preliminary cross-linking via sol-gel reaction. Poly(dimethyl-co-methyl)siloxanes bearing statistically distributed T_{Si} and alkoxyethyl groups were also cross-linked using tetralkylammonium salts and subjected to controlled thermolysis (removal of T_{Si} moieties) in order to get porous materials of high specific surface area⁵⁴.



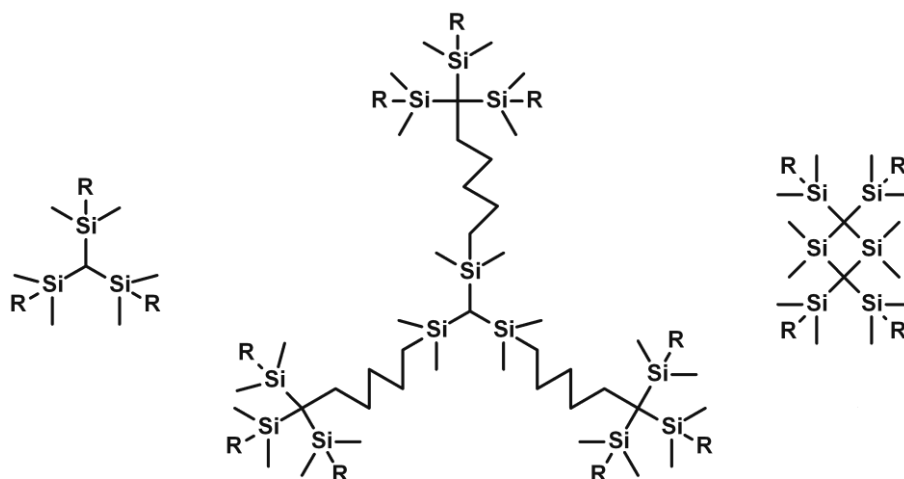
Scheme 3. Preparation of polymeric networks with T_{Si} -groups (R=epoxy or alkoxyethyl).

4. Application of hybrid T_{Si} -polymeric systems.

4.1. Branch points in polymeric structures

Bulky carbosilane moieties can be used not only as side substituents, for structural modification or improvement of thermal stability of polymeric systems. $(H_2C=CHMe_2Si)_3CH$ and $(HMe_2Si)_3CH$ were used for the preparation of tri-podal mesogenic biphenyl- and benzoate-type alkenes attached to polysiloxanes as side-chains⁶³. Such systems of increased density of rod-like side substituents showed mesomorphic properties. Polystyrenes modified with $(HMe_2Si)_3C$ groups were also used for the preparation of stable alkoxyethylated polymers^{43, 64}.

Functionalized T_{Si} -type compounds can be also applied as cores for the preparation of star-shape polymers⁶⁵ or as branching points in polymeric networks⁶². Using carbosilane cores of various morphology (Scheme 4) hybrid materials differing by the number of linear or branched polymeric arms can be prepared. For example, siloxane arms of block structure, prepared by anionic ring opening copolymerization of hexamethylcyclotrisiloxane and 2,4,6-trimethyl-2,4,6-trivinylcyclotrisiloxane, were grafted onto appropriate functionalized carbosilane cores⁶⁵.



Scheme 4. Examples of multifunctional carbosilanes that can be used in star-shape polymeric systems (based on⁶⁵)

Owing to their siloxane character, the materials have glass transition temperatures similar to that characteristic for the siloxane arms, irrespectively of the type of carbosilane core. However, a meaningful difference in the absorbed heat at glass transition (ΔC_p) was noted between a single siloxane arm and the corresponding branched structure built onto a carbosilane core. The difference becomes more pronounced on the increase of molecular weight of the siloxane arms. The enthalpy of melting and crystallization of the star-shape polymers is smaller than that recorded for the respective siloxane arms owing to their branched structure. However, these siloxane-carbosilane hybrid materials show some very peculiar physical properties. It was found that the type of carbosilane core and the length of siloxane arms strongly influences the processes of ordering of polymer matrix. The organisation of star siloxanes of long side arms is more facile at low heating rate, especially if the core is less compact. The reverse effect was observed for samples with shorter branches. For both polymers, the opposite effects were obtained at increased heating rate (Figure 8).

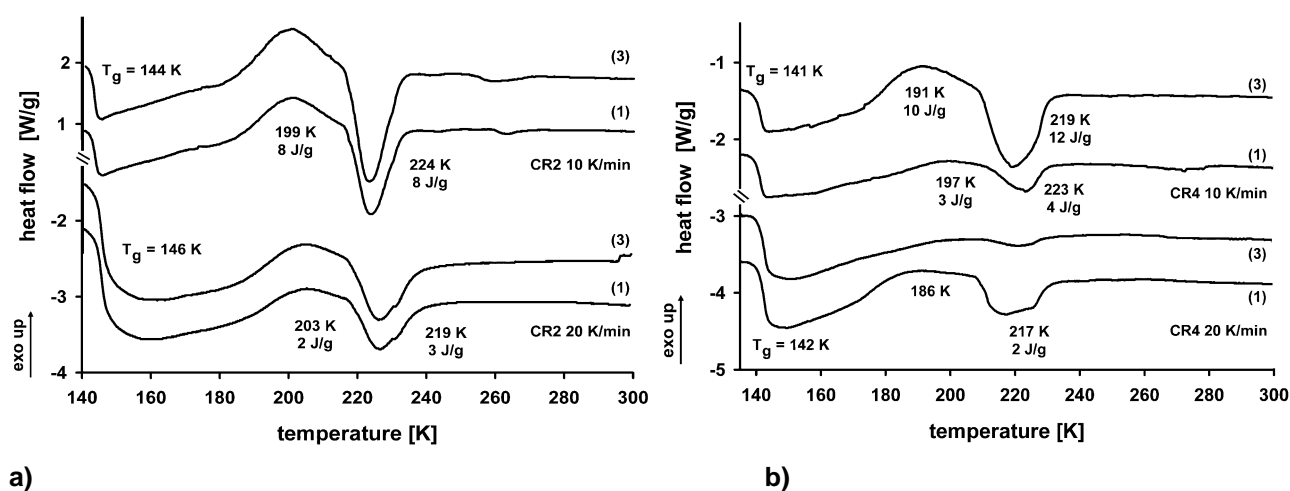


Figure 8. The organisation of polymer matrix in star-shape siloxanes with T_{Si}-type core [1,1,3,3-tetramethyl-2,2,4,4-tetrakis(dimethylsilyl)-1,3-disilacyclobutane] **(a)** CR2 - M_n of a single arm ~16000 Da, **(b)** CR4 - M_n of a single arm ~38000 Da (based on literature data⁶⁵).

4.2. Catalytic systems:

Effective removal of a catalyst from the reaction mixture is an important problem in organic and metalloorganic synthesis. The use of soluble^{66,67} or insoluble⁶⁸ polymeric supports is a frequent solution. Polystyrene, due to its chemical inertness, is often used as catalytic support^{69,70}. The hybrid materials prepared with the use of trisyl-type substituents can be also used for this purpose.

Polystyrene partially modified with $(\text{H}_2\text{C}=\text{CHMe}_2\text{Si})_3\text{C}$ have been used as a support to platinum Pt(0) by its coordination to vinyl ligands [PS- $\text{CH}_2\text{C}(\text{SiMe}_3\text{CH}=\text{CH}_2)_3$ complex] situated in the outer sphere of carbosilane molecule⁴² – analogously to the structure of Karstedt's catalyst^{71,72}. The polymeric support of such structure combines properties of classic polymeric supports and dendritic supports. Bulky $(\text{H}_2\text{C}=\text{CHMe}_2\text{Si})_3\text{C}$ groups play a role of grafted dendrons and provide the dendritic effect⁷³ which facilitates polymer swelling and diffusion of reagents and products to active catalytic sites.

The activity of the prepared polymeric supports were compared to that of commercially available heterogenic and homogenic platinum catalysts (Pt/charcoal, Pt/C_{act} i Pt/Al₂O₃, Karstedt's catalyst) and tested in a model reaction: hydrosilylation of $\text{Me}_3\text{SiCH}=\text{CH}_2$ by 1,1,2,2-tetramethyldisiloxane (Figure 9). Studies concerning the influence of immobilization of $(\text{H}_2\text{C}=\text{CHMe}_2\text{Si})_3\text{C}$ on polystyrene chains, the structure of polymer, as well as the dependence of the temperature on the catalyst activity were carried out⁴². The catalyst was found to be stable and selective and the addition of SiH to C=C proceeds almost completely according to the Farmer's rule ($[\alpha \text{ product}]/[\beta \text{ product}]=0.03$), which is comparable to the selectivity of Karstedt's catalyst. The results were reproducible, and the catalyst can be recovered from the reaction mixture and reused (turnover number $T_n=10^{74}$).

Carbosilane-siloxane polymers of star shape were also used as supports for platinum catalysts⁶⁵. Platinum was coordinated to the vinyl groups at poly(vinylmethyl-co-dimethyl)siloxane arms of block structure. Star-shape polymers of various ratio [D]/[V] in the siloxane arm were used and the activity of the catalyst was studied in the model reaction of hydrosilylation of $\text{Me}_3\text{SiCH}=\text{CH}_2$ by 1,1,2,2-tetramethyldisiloxane. It was found that the utility of the catalysts seems to be dependent on the ratio [D]/[V]. If the amount of vinyl groups was too large, the catalytic system suffered from poor solubility and low catalytic performance due to excessive inter/intra-chain coordinative cross-linking. If [D]/[V]=7 then the activity was comparable to that of Karstedt's catalyst (selectivity of SiH addition to C=C: $\alpha/\beta=0.06$).

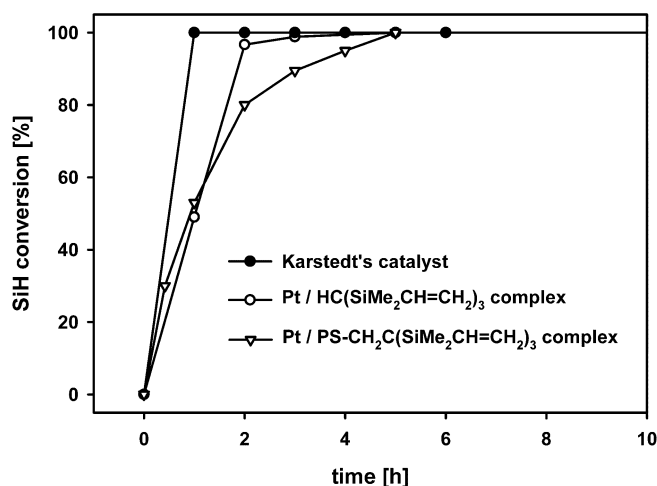


Figure 9. Comparison of the catalytic activity in a model reaction of hydrosilylation of $\text{Me}_3\text{SiCH}=\text{CH}_2$ with 1,1,2,2-tetramethyldisiloxane (based on⁶⁵).

5. Summary and perspective.

The data summarized in the review indicate that hybrid polymeric systems bearing sterically hindered T_{Si} groups show some specific and useful properties. Bulky T_{Si} groups have the advantage of being completely inert, but their derivatives with reactive substituents [e.g. $(\text{H}_2\text{C}=\text{CHMe}_2\text{Si})_3\text{C}$] can be used for specific modifications. The type and size of these carbosilane moieties, as well as its position with respect to the polymeric chain can have a significant effect on the mobility of the polymer backbone and the properties (e.g. phase transitions) of the modified polymers. In spite of low intermolecular interactions in T_{Si} -silicones their glass transition temperatures are very high. Trisyl moieties hinder chain ordering and crystallization, eliminating melting. T_{Si} -groups impart a high free volume, which also explains high solubility of the polymers. Thermal stability of linear and cross-linked polymeric systems can be also significantly increased by the presence of T_{Si} moieties.

Polymeric materials with T_{Si} groups have a significant applicative potential, exceeding the scope presented in this review (e.g. nanomaterials, lithography, membranes or protective thin layer isolating coatings). Thermostable T_{Si} -modified polymeric materials can be used as stationary phases in capillary columns. T_{Si} -silicones could also add a new dimension to membrane science. Polydimethylsiloxanes are known for their high permeability to oxygen, nitrogen and water vapour due to large free volume and high diffusion coefficient of gas into silicones. Introduction of bulky nonpolar carbosilane moieties should decrease the mobility of siloxane backbone, resulting in enhanced selectivity of diffusion. Appropriate crosslinked polysiloxanes and polysilsesquioxanes bearing side T_{Si} groups (T_{Si} -silicones) can be as well converted into microporous membranes and ceramic insulators on selective removal of templating and pore-generating trisyl moieties. Such derived carbon-rich $\text{Si}_x\text{C}_y\text{O}_z$ ceramics should have enhanced stability against crystallization and high-temperature resistance.

T_{Si} -silicones can be good example to envisage future applications in this field. They combine all the trends beneficial for low dielectric constant materials and meet the required performance criteria for microelectronics and sealing applications. They are thermally stable, exhibit low moisture uptake, are soluble in organic solvents and thus can be easily cast on various surfaces. Preliminary tests indicated that dielectric constant measured for selected poly(T_{Si} -silsesquioxanes) was found to be as low as 1.9 F/m^{24} . It makes them thus suitable as advanced polymer dielectrics for high-power electronic circuits in a miniature form of improved system performance and reliability. Precisely localized degradation/evaporation of materials containing sterically hindered carbosilanes can be achieved on irradiation with laser light. It can be a very interesting method for the preparation of very small integrated circuits. T_{Si} -silicones can be also applied as dielectric layers, non-conductive adhesives or additives in high voltage electrical insulations (cable end terminations and coatings for insulators in power lines).

In addition to their excellent thermal stability, T_{Si} -silicones are highly transparent to light, which makes them suitable for waveguide applications, lenses and encapsulants. Photonics applications require materials of low dielectric constant, low refractive index, high transparency, low intrinsic and stress-induced birefringence as well as adequate thermophysical properties. T_{Si} -silicones could thus replace phenyl-modified polysiloxane

materials, known for their increased thermal stability but less suitable for photonics due to the high refractive index.

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