

# Modifications of hydrosiloxane polymers for coating applications

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## Summaries

### Modifications of hydrosiloxane polymers for coating applications

An alternative approach to the formation of resins by hydrolysis-condensation reactions has been developed and evaluated. It combines the use of inexpensive polysiloxanes and transition metal catalysts to easily modify polymers in a one-pot reaction. Polyhydridomethylsiloxane (PHMS) serves as the base polymer, and it can be cured or modified by dehydrocoupling or a combination of hydrosilylation-dehydrocoupling reactions, both catalysed by transition metal catalysts (Pt and Ru). The modified polymers are linear and contain very high mol% of Si-OH and combinations of Si-OH and Si-OR pendant groups. These groups assist the bonding to surfaces when the modified polymers are deposited as coatings. They then cure by condensation and hydrolysis-condensation reactions, catalysed by both acids and bases. The modified polymers are used for low-temperature paint-like applications, especially where ambient curing is desirable. This article discusses modifications of PHMS for coating applications and describes potential coating applications and typical coating strategies.

### Modifications des hydrosiloxanpolymères pour être utilisées en revêtements

Un moyen alternatif d'aborder la production des résines par des réactions d'hydrolyse-condensation a été mis au point et évalué. La tentative unit l'emploi de polysiloxanes peu chers aux catalyseurs de métaux transitoires à l'intention de modifier facilement des polymères par une réaction dans un récipient. Polyhydridométhylsiloxane (PHMS) sert de polymère de base et il peut être durcis ou modifié par les réactions de déhydrocouplage ou une combinaison de déhydrocouplage et de déhydrocouplage tous les deux catalysés par des métaux transitoires (Pt et Ru). Les polymères modifiés sont linéaires et contiennent un pourcentage très élevé de groupements pendants de Si-OH et de combinaisons de Si-OH et de Si-OR. Ces groupements facilitent l'adhérence aux surfaces lorsque les polymères modifiés sont déposés en tant que revêtements. Là, ils durcissent par des réactions de condensation ou d'hydrolyse-condensation, catalysées à la fois par des acides ou des bases. On utilise les polymères modifiés en produits semblables aux peintures pour des applications aux températures relativement basses, surtout lorsque le durcissement à température ambiante est souhaitable. Cet article discute les modifications de PHMS pour produits de peintures et il décrit les produits de peinture éventuels et des stratégies typiques à l'égard des produits de peintures.

### Veränderung von Hydrosiloxanpolymeren für Beschichtungsstoffanwendung

Ein alternative Ansatz zu der Herstellung von Harzen durch Hydrolyse-Kondensationsreaktionen wurde entwickelt und bewertet. Es kombiniert den Gebrauch der preisgünstigen Polysiloxane und Übergangsmetallkatalysatoren um Polymere mittels einer Einzigfahreaktion leicht zu modifizieren. Polyhydridomethylsiloxan (PHMS) steht also Grundpolymer und es läßt sich aushärten oder modifizieren durch Dehydrokopplung oder durch eine Kombination der Hydrosilylations-Dehydrokopplungsreaktionen, beide katalysiert von Übergangsmetallen (Pt und Ru). Die modifizierten Polymere sind linear und srhalten ein en Hochmolekularprozentsatz von Si-OH und Kombinationender Si-OH und Si-OR Anhängerggruppen. Diese Gruppen helfen dem Abbinden an Oberflächen wenn die modifizierte n Polymere also Beschichtungen hingeleget werde. Dann sie härten durch Kondensations- und Hydrolyses-Kondensationsreaktionen katalysiert durch beide Säuren und Basen aus. Die modifizierten Polymere werden zu niedrigtemperaturen Beschichtungsstoffs angewandt, vor allem wo Aushärtung bei Umgehenstemperatur ist wünschenswert. Dieser Beitrag diskutiert Modifikationen der PHMS für Beschichtungsstoffanwendungen und auch beschreibt eventuelle Beschichtungsstoffanwendungen und auch typische Beschichtungsstoffstatiken.

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## Introduction

SRI International is developing a new concept for a broad range of coating applications based on novel polysiloxane technology. This effort is part of a growing interest in developing organo-silicon and silicate-based coatings with enhanced performance.<sup>1</sup> The approach combines the use of inexpensive polysiloxanes and transition metal catalysis for easily modifying polymers in a one-pot reaction.<sup>2</sup> The modifications are planned to reduce deficiencies in and significantly improve coating processes and performance characteristics.<sup>3</sup> This is a low-cost alternative route to T-polymers, silsesquioxanes, and MQ siloxane-based resins. (MQ resin is a "commercial" definition for a silicon resin, which is composed on reacting tri-organic mono-chlorosilane with tetrachlorosilane:  $mR_3SiCl + nSiCl_4 + H_2O \rightarrow (R_3SiO_{0.5})_m(SiO_2)_n + HCl$ . The M stands for mono, ie, a silicon atom with a single Si-O bond. The Q stands for quaternary, ie, a silicon atom with 4 Si-O bonds. Since both exist in this resin, it is called MQ resin.) The synthesis is very versatile, and the polymers evolved have a distinctive structure (primarily linear) and rheological characteristics compared with the branched or cage-like products, usually obtained by hydrolysis-condensation reactions.<sup>4</sup>

The synthesis route aims at developing advanced coatings with combinations of mechanical, chemical, thermal, or electronic functions. Their foreseeable performance characteristics include

- Corrosion resistance
- High temperature stability
- Oxidation protection at elevated temperature
- Surface hardening
- Optical modification and enhancement of transparent materials

- Development of hydrophobic non-wetting or inert surfaces
- Development of hydrophilic lubricating coatings
- Surface sealing
- Low-k properties – Materials with low coefficient of conductivity (high electric resistivity) and low electrical capacity. These are materials that are very good for electric insulation.
- Strengthening of glass and ceramics
- Joints and interfaces between materials.

Four major coating systems are being evaluated for processing the newly developed polymers as ceramic and cured polymer coatings: (1) thin films for high temperature, (2) ceramic paints, (3) thin films and thick varnishes for temperatures below 400°C, and (4) non-ceramic paints.

Table 1 lists potential applications for low and high temperature conditions based on these four coating approaches.

## Background

SRI has developed polymeric materials with controlled structures that can be processed like conventional polymers and converted on pyrolysis to ceramic materials. Also the polymers can be used as polymeric materials with unique properties without being converted into ceramic products. Most of SRI's research has been concentrated on developing syntheses for polysilazanes, polysiloxazanes, and polysiloxanes-intermediates to  $Si_3N_4$ ,  $Si_2ON_2$ ,  $SiO_2$ , and SiC-with excellent processability due to their polymeric nature and efficient pyrolytic conversion.<sup>5</sup>

The synthesis method enables preparation of intermediates for many ceramic compositions. Also it enables synthesis of polymers with a wide range of viscosities that convert in high yields to ceramics.

The process is very practical for modifying and cross-linking such polymers. It is based mainly on patented catalytic reactions that are extremely efficient. The core of the chemistry is transition metal catalyzed dehydrocoupling reactions between compounds containing Si-H bonds and compounds containing O-H or N-H bonds. Also it includes hydrosilylation reactions catalysed by the same or a different catalyst. The core synthesis technology is illustrated in Figure 1. Currently, homogeneous, ruthenium and platinum catalysts are used at levels of 10 to 500 ppm relative to the pre-modified polymer.

The method enables production of polymers that can be fully converted into an inorganic network (amorphous ceramics) at temperatures as low as 200°C.<sup>6</sup> In contrast, SRI is also developing polymers that retain their organic functional groups above 400°C.<sup>7</sup> The latter capability is promising for the development of relatively high temperature thick coatings and polymeric composite materials.

## Results and Discussion

The catalytic modification and curing techniques serve as the core for the coating applications currently under development. The authors' method uses inexpensive polyhydridomethylsiloxane, a by-product in the silicone industry. Polyhydridomethylsiloxane (PHMS) and its modifications are used for various clear and filled coating applications. This article concentrates on the synthesis techniques for modifying polyhydridomethylsiloxanes to alter their physical and chemical characteristics. Mostly modified polymers are currently used, because PHMS alone does not wet most surfaces and does not cure well at room temperature.

The transition-metal catalysed curability of PHMS is insufficient at ambient tem-

**Table 1. Potential coating applications based on various processing strategies**

<i>Thin ceramic films for high temperatures (up to 1300°C)</i>	<i>Ceramic painted coatings (filled polymer) for high temperatures (up to 1500°C)</i>	<i>Medium thickness transparent coatings for 'low temperatures' (up to 400°C)</i>	<i>Thick filled-polymer coatings for 'low temperatures' (up to 400°C)</i>
Oxidation and corrosion resistance	Oxidation and corrosion resistance	Oxidation and corrosion resistance	Oxidation and corrosion resistance
Glass and ceramic strengthening	Electronic functional	Personal care and consumer	Nonconductive
Low K, nonconductive	Gradient coatings	Low K, nonconductive	Durable paints
Optical coatings	Filters	Surface hardening	Waterproofing
		Optical coatings	Soil resistance
		Waterproofing	Biomedical
		Soil resistance	Lubricating
		Hydrophilic	Membrane
		Biomedical	Sealants
		Lubricating	Low K
		Sealants	

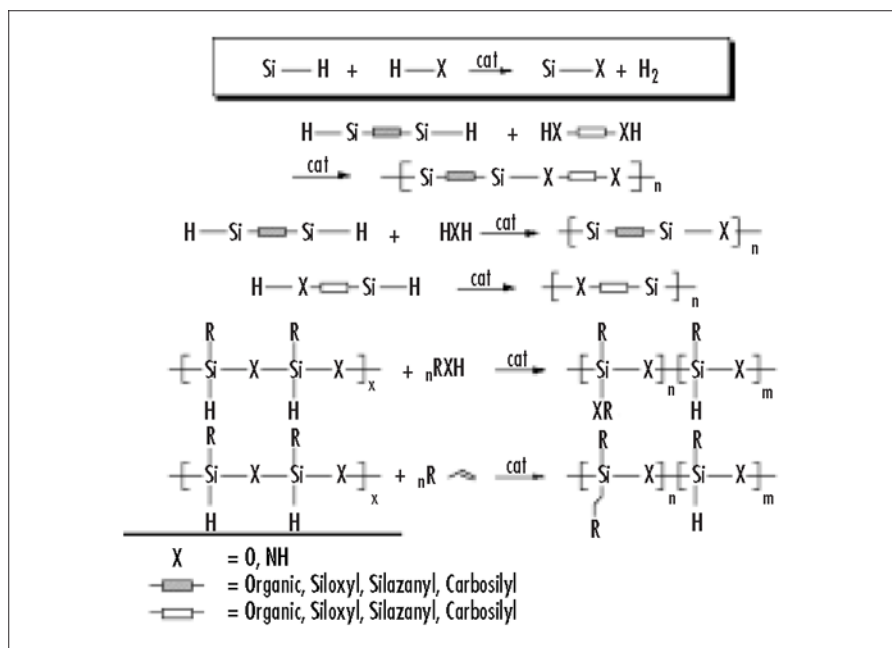


Figure 1. Typical scheme of dehydrocoupling.

perature. Although, it is activated at this temperature, the degree of cure remains low because of steric hindrance and moisture permeability. Consequently, the coatings remain too soft to be considered as protective layers.

### Polyhydridomethylsiloxane (PHMS)

Polyhydridomethylsiloxane is a linear polymer formed by hydrolysing methylchlorosilane, a by-product of the silicone industry. The polymer can be produced directly or by ring-opening polymerization of the cyclomers produced by the same reaction. PHMS is available as a low molecular weight polymer (MW in the range of 2000 to 4000) with viscosity of 20 to 50 cps. PHMS is very stable before catalytic activation in the absence of a cross-linking catalyst. Also lack of cross-linking would result in very low conversion yields of the polymer to its derived ceramic product on pyrolysis. However, the base polymer is still very useful for paint applications when heat treatment above 100°C is acceptable.

Although the polymer is very hydrophobic and does not wet surfaces well, certain powder fillers form slurries with the base PHMS to increase surface wetting. Flake aluminum and titanium dioxide fine particles are good fillers that improve surface wetting. Wetting characteristics can also be improved or tailored to specific substrates by modifying the polymer with hydroxy, alkoxy, or other polymer functional groups.

### Modifications of polyhydridomethylsiloxane

PHMS is dehydrocoupled with water or alcohols in the presence of a transition metal catalyst to form a polymer that easily wets inorganic surfaces. Levels in the range of 10 to 500 ppm of triruthenium dodecacarbonyl,  $\text{Ru}_3(\text{CO})_{12}$ , and various homogeneous platinum catalysts can activate the dehydrocoupling reaction. PHMS can also be hydrosilylated, using the same types of transition metal catalysts (Pt compounds in particular).<sup>7</sup>

Figure 2 shows the types of modified polymers that have been synthesised to meet specific applications needs. All

these modifications were made by a one-pot-reaction, usually without the use of excessive solvent(s), purification, or other costly processing operations. These polymers can be considered as 'the inorganic analogues of polyacrylates' because of the broad range of versatile grafting possibilities.

### Hydroxyl-modified polyhydridomethylsiloxanes (PHMS-OH)

In contrast to partial hydrolysis-condensation of  $\text{MeSi}(\text{OR})_3$ , which provides a branched or crosslinked product with various distributions of T (tri-substituted) and D (di-substituted) siloxane units,<sup>4</sup> the dehydrocoupling reaction allows the formation of linear (D) siloxanes that have over 90 mol% Si-OH groups.

Siloxanes containing multiple Si-OH groups tend to condense rapidly and form insoluble gels. However, the authors have found conditions under which PHMS can react with water in an appropriate solvent and catalyst to form a fully hydroxylated polymer. This polymer remains stable in appropriate solutions and conditions for a long period. Although the product, PHMS-OH, is still a low viscosity polymer (about 80 to 100 cps), it becomes very sticky to the touch, in contrast to the slippery nature of the original PHMS. Contrary to PHMS, the modified polymer wets inorganic surfaces very well (metals, glass, ceramics).

Before modification, PHMS is very soluble in apolar solvents such as hydrocarbons and aromatics, but insoluble in methanol or alcohol/water mixtures. After the initial dehydrocoupling reaction with water in alcohol, the mixture

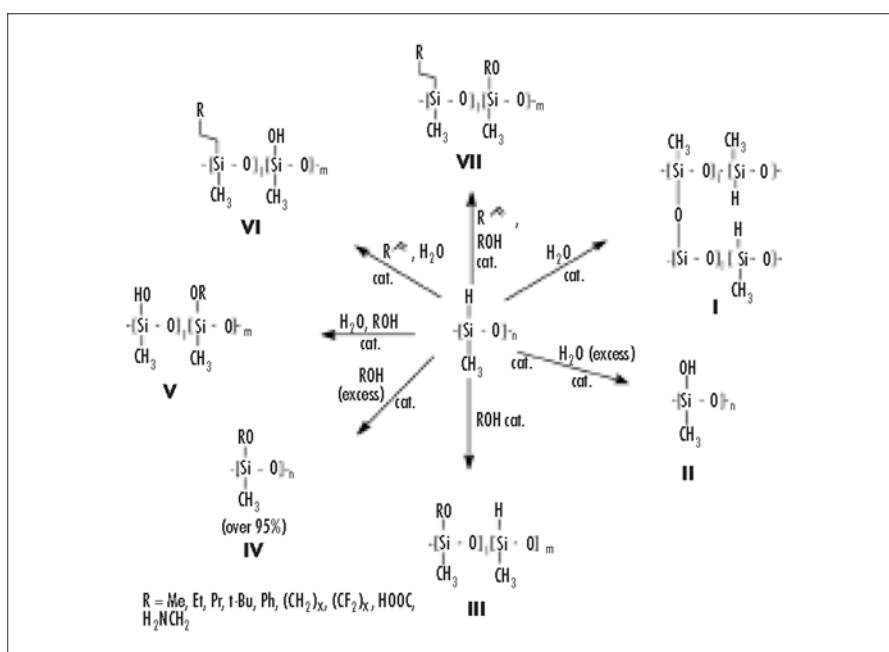


Figure 2. Transition metal catalyzed modifications of PHMS

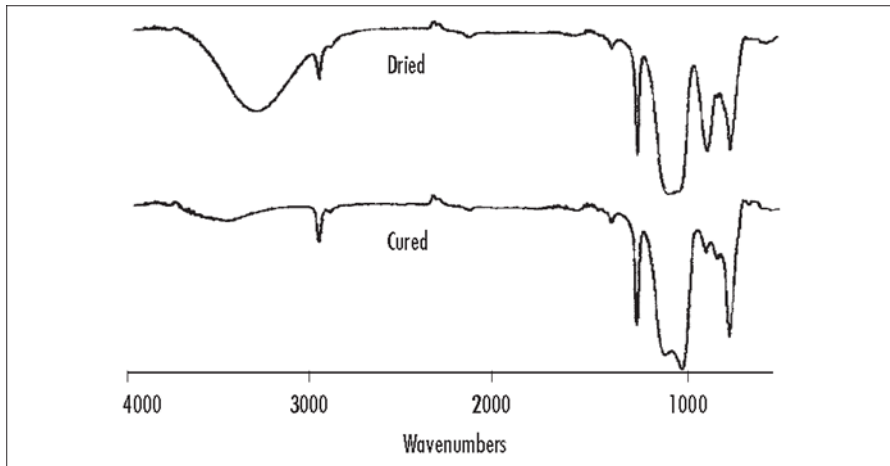


Figure 3. FT-IR of PHMS-OH before and after curing

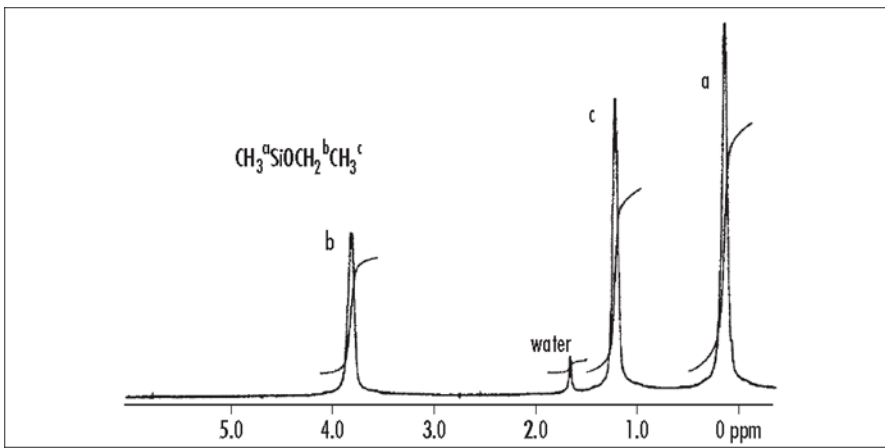


Figure 4. The  $^1\text{H}$  NMR spectrum of a fully ethoxylated PHMS

becomes biphasic. During the reaction, an emulsion is formed, and near the end of the reaction, the polymer derivative becomes soluble in the alcohol. The final PHMS-OH product is very soluble in a mixture of ethanol and water, but loses its solubility in hydrocarbon and aromatic solvents. Thus, the polymer is converted from a completely hydrophobic material to a relatively hydrophilic material. The hydroxylated polymer also bonds to surfaces through surface hydroxyl groups. In the absence of solvent, the polymer self-cures by a condensation reaction that can be enhanced thermally or by a variety of condensation catalysts (such as a base).

The Fourier transform infrared (FTIR) spectrum, shown in Figure 3, reveals that the low viscosity product has lost all the original Si-H bonds ( $2160\text{cm}^{-1}$ ) and that a large, very broad Si-OH band is formed [ $3300$  (vbr) and  $887\text{cm}^{-1}$ ]. This large band indicates significant hydrogen bonding. Calibration of this band indicates that the fraction of Si-OH is close to 100%. This band disappears slowly if the polymer is set in the absence of solvent. It is rapidly eliminated when the

polymer is heat cured by condensing the Si-OH groups to Si-O-Si bonds.

#### Alkoxy-modified polyhydrido-methylsiloxanes (PHMS-OR)

PHMS can be also modified by alkoxylation by dehydrocoupling a broad range of alcohols. This reaction also opens the potential for coupling the Si-H containing polymer with organic materials such as polyols containing multiple hydroxy groups. Figure 4 shows a  $^1\text{H}$  NMR spectrum of close to 100% modified ethoxylated PHMS. This polymer is still a low viscosity product in the range of 100 cps. Figure 5 shows the  $^1\text{H}$  NMR of 87% t-butoxy-PHMS, demonstrating the ability to easily substitute bulky alcohols. Dehydrocoupling with t-butanol is inhibited only after conversion of 80% of the Si-H bonds.

The alkoxy-substituted polymers are only slightly reactive in the presence of moisture under the pH conditions generated 'in situ' during the synthesis. In contrast to the Si-OH modified polymers, they are stable in the absence of solvent and even on slight exposure to moist air. They cure well after the solvent is removed and acid or base catalysts are added.

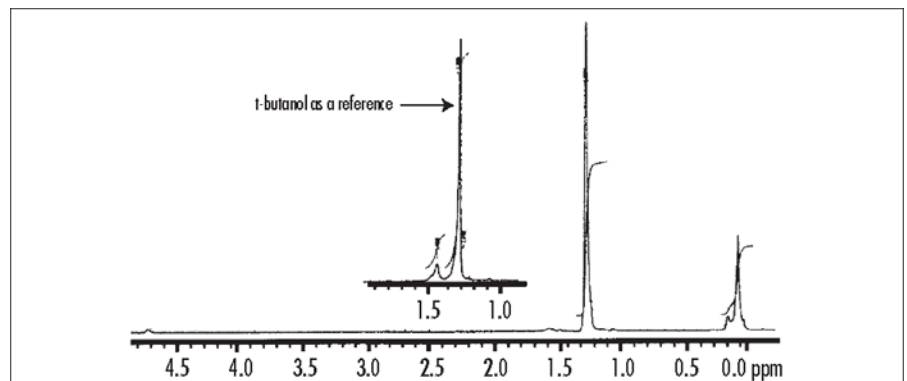


Figure 5. The  $^1\text{H}$  NMR spectrum of 87% modified t-BuO-PHMS

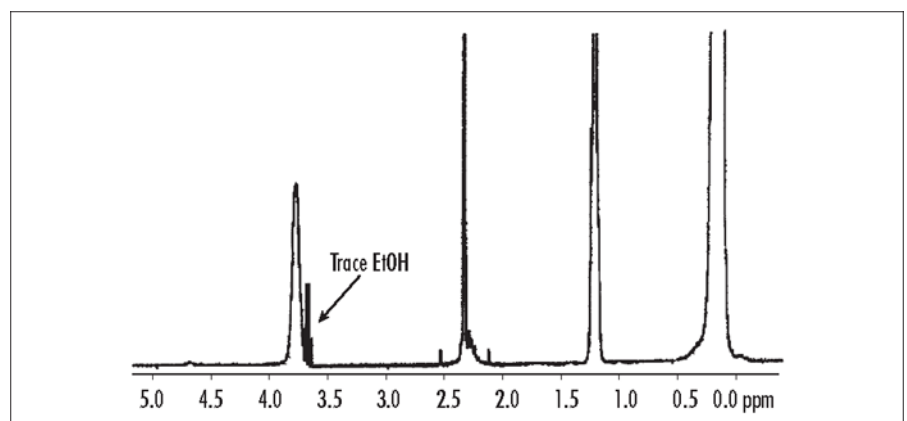


Figure 6. An  $^1\text{H}$  NMR of 20% ethoxylated PHMS-OH

*Alkoxy, hydroxy-modified polyhydromethylsiloxanes (RO-PHMS-OH)*

A combination of the two modifications described above was found to be very useful for a broad range of applications, including binders and coatings, and can be formed by reacting partially alkoxy-ated polymer with water. An  $H^1$  NMR of 20% ethoxylated PHMS-OH is shown in Figure 6.

Other examples for such substitutions include modification with methanol, benzyl alcohol, 2,2,2-trifluoro-ethanol, methoxy-ethanol, t-butanol, isopropanol, octanol, and cyclohexanol. The polymers derived are more stable to self-condensation in the absence of water than the PHMS-OH and can be activated easily by using various condensation catalysts.

*Alkyl, hydroxy-modified polyhydromethylsiloxanes (R-PHMS-OH)*

Another type of modification is under evaluation, in which hydrosilylation followed by dehydrocoupling reactions are coupled in a one-pot reaction. These polymers can be alkyl-, hydroxy-modified polymers (R-PHMS-OH), alkyl-, alkoxy-modified polymers (R-PHMS-OR), or alkyl-, alkoxy-, hydroxy-modified polymers (R-, RO-PHMS-OH). An example of such a polymer is 20% styryl modified PHMS-OH. The NMR spectrum of a styryl modified PHMS (before dehydrocoupling) and an IR spectrum of the hydroxylated product are shown in Figures 7 and 8, respectively.

Typically, the substitution during the hydrosilylation favours the formation of  $\alpha$ -Si-C bonds because of steric hindrance effects. However, in the styryl case, the ratio between  $\alpha$  and  $\beta$  substitutions is almost 1:1. Other evaluated substitutions are long alkyl chains such as octyl, hexyl, fluorinated alkyls, and alkyls with other functionalities.

An example of alkylated-alkoxyated combined product (R-, RO-PHMS-OH) is 10% styryl-, 10% ethoxy PHMS-OH. Its  $H^1$ -NMR spectrum is shown in Figure 9.

Using this approach, the authors have been able to obtain substituting groups that can provide crosslinking with other epoxy and urethane reagents. Examples are aminopropyl- and glycidyl-modified PHMS-OH. The NMR spectrum in Figure 10 represents a 10% aminopropyl product and 90% ethoxy groups. Currently, the synthesised glycidyl-modified polymers seem to have various levels of

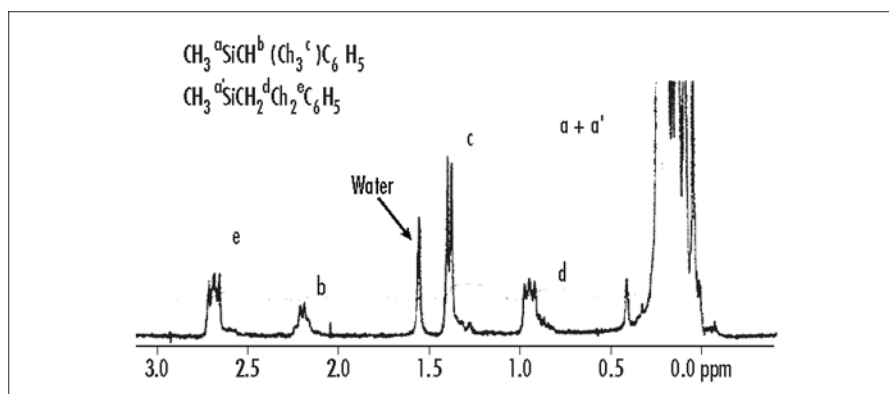


Figure 7.  $H^1$  NMR of 20% styryl-PHMS

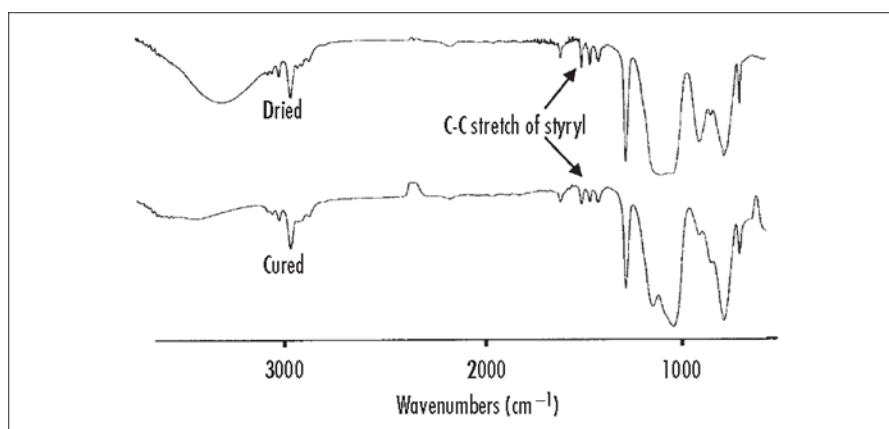


Figure 8. FTIR of 20% styryl-PHMS-OH

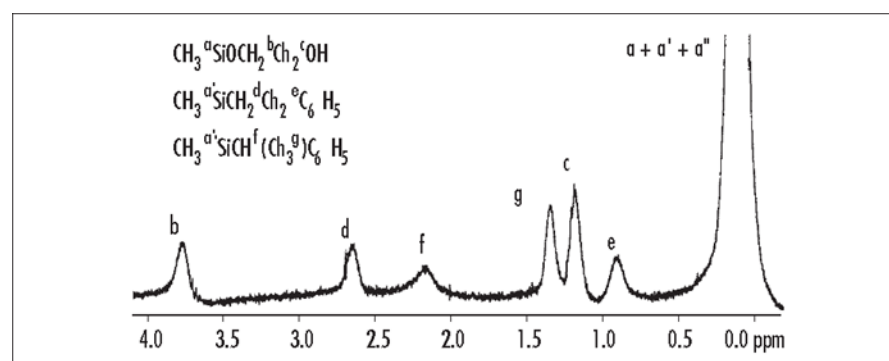


Figure 9.  $H^1$  NMR of 10% styryl, 10% ethoxy PHMS-OH

opened oxirane groups. Studies to reduce the level of the epoxy functional group are under way.

### Coating applications

SRI's approach provides a wide range of choices for changing the physical and the chemical properties of the polymeric coatings by

- Tailoring the composition and structure of the inorganic backbone network
- Changing the organic substituents, as discussed in this article
- Choosing the cross-linking reagents
- Varying the environmental conditions during the curing and pyrolysis (if used) steps.

Currently, several of the curing processes involve heat and moisture (the water serves as the curing agent). Therefore, it is possible to develop a steam curing process. Some of the active systems do not require heat and are processed at room temperature. Information about formulations, processing, and final properties of such systems can not be published at this stage. Examples of thin high-temperature, non-wetting, and corrosion resistance coatings have been reported in the patent literature.<sup>3</sup> Also a novel coating approach for strengthening glass articles has been published.<sup>8</sup>

Both clear coatings and filled (pigmented) formulations and coating processes are being studied. The systems for the



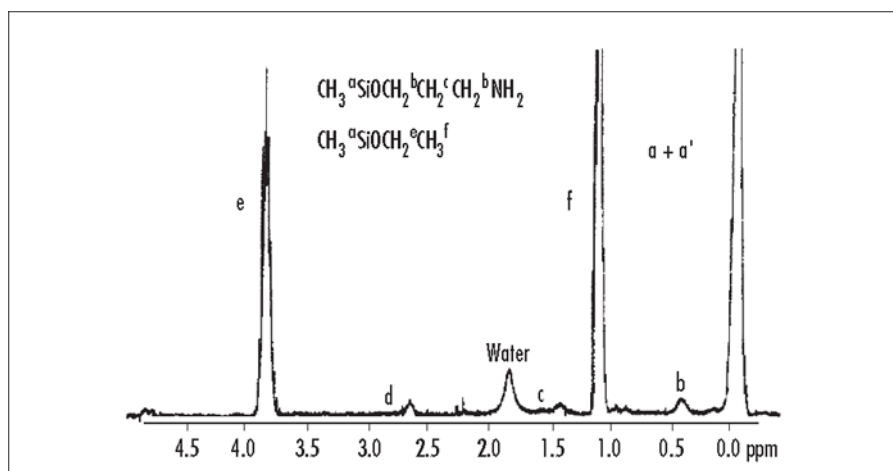


Figure 10.  $^1\text{H}$  NMR of 10% aminopropyl-, 90% ethoxy-PHMS-OH

various coating applications are discussed below.

#### Thin films for high temperature

The polymers serve as pre-ceramic polymers, which convert to silica in very high yield (up to 95 wt%) by heat treatment above 450°C. In attempts to maintain transparency, such coatings are processed from relatively low concentration solutions (5 to 20 wt%). They are not filled with powders and can be deposited with high integrity only as thin films (~1  $\mu\text{m}$  per layer).

#### Ceramic paints

The polymers are used as pre-ceramic binders, forming slurries with reactive and inert fillers. These paints are deposited with thicknesses of 10 to 50  $\mu\text{m}$  per layer and pyrolysed. Metallic reactive fillers are used to compensate for the polymer shrinkage that occurs during the pyrolysis, because they expand upon oxidation.

#### Thin films and thick 'varnishes' for temperatures below 400°C

These non-filled coatings retain a small or medium fraction of organic substituents (bonded to the inorganic skeleton). They are thermally stable up to 400°C in air, primarily due to high cross-linking density. Such coatings can be deposited as transparent 'varnishes' having thickness of up to 50  $\mu\text{m}$  (2 mils) without cracking. The maximum affordable thickness depends on the maximum operating temperature and the characteristics of the substrate.

#### Nonceramic paints

Modified polysiloxanes based on SRI's technology serve as binders, mixed with inorganic powders, pigments, and other additives to form paint slurries. The slurries are deposited by conventional paint-

ing techniques with thicknesses of 50 to 200  $\mu\text{m}$  (2 to 4 mils) per layer. They can be then cured at ambient temperature or baked at relatively low temperature, converting into hard protective coatings.

The characteristics of the various coatings, currently under development using different polymers, formulations, and processing approaches based on the above technology include

- Hard corrosion-resistant coatings (with thickness in the range of 50 to 100  $\mu\text{m}$ )
- High thermal stability (up to 400°C without fillers and higher with appropriate additives)
- Thick protective coatings for metals and ceramic that are stable between 500° to 1400°C (depending on the substrate's surface properties and thermal expansion coefficient)
- Good flexibility of 10- to 50- $\mu\text{m}$ -thick clear coatings that allows complete bending of metal sheets (<1 mm thick) without rupturing
- Good flexibility as thin coatings on plastic materials
- Sufficient hardness (up to 9H); a good candidate for transparent plastic coatings and paint replacement
- Good adhesion to various surfaces (for example 5B on steel)
- Non-wetting coatings, stable up to 400°C in air; non-wetting characteristics are observed for either water or for both water- and organic-based liquids, depending on the surface composition
- Enhanced visibility and degradation resistance of transparent plastic materials.

More information about the coating processing and their characteristics will become available and be presented in the future.

## Conclusions

A broad range of synthetic modifications of polyhydridomethylsiloxane has been produced to demonstrate the versatility of PHMS, using combinations of transition-metal catalysed dehydrocoupling and hydrosilylation-dehydrocoupling. These reactions are performed as one-pot reactions using 10 to 500 ppm of catalysts. Some modifications described in this article have been evaluated as improved polymers for coating applications.

The modified polymers can be significantly stable towards condensation reactions, that would result in the polymer setting, in spite of the high level of Si-OH groups, even when present in relatively concentrated solutions. The steric conformations and natural pH level of the polymers are probably the main reasons for the stability. They can be cured at room temperature and, therefore, are suitable for ambient temperature coating applications.

Overall, the authors anticipate that several coating applications will emerge from these modified polysiloxane and pre-ceramic polymers. Many of these applications are related to low-cost commercial and industrial products or needs. Coatings formulated with these polymers and their performance are under development and will be presented in future publications.

## Acknowledgements

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