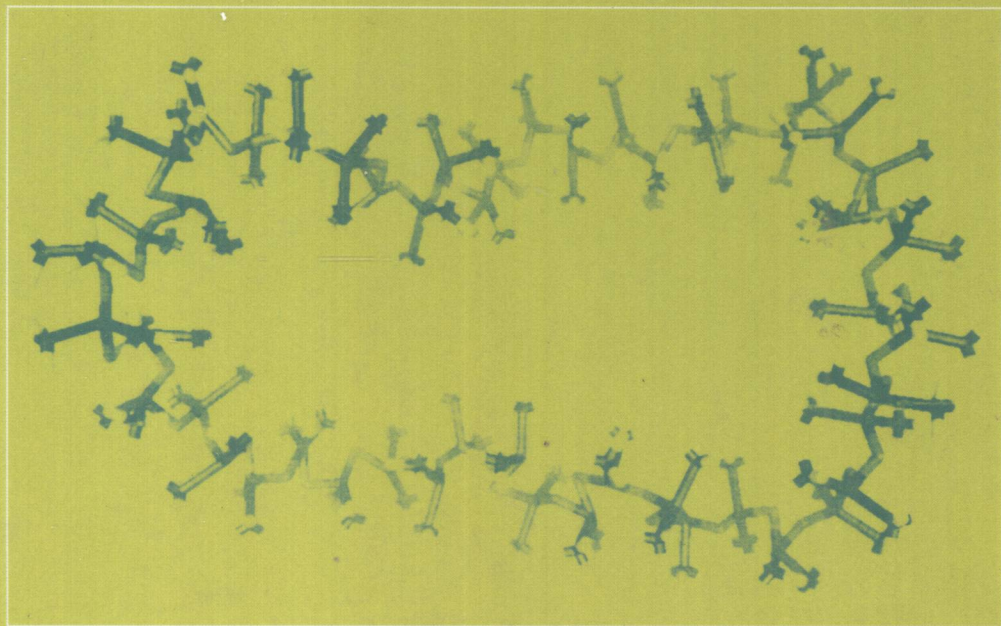


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Silicones and Silicone-Modified Materials



EDITED BY

Stephen J. Clarson, John J. Fitzgerald,
Michael J. Owen, and Steven D. Smith

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Silicones and Silicone-Modified Materials

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Silicones and Silicone-Modified Materials

Foreword

THE ACS SYMPOSIUM SERIES was first published in 1974 to provide a mechanism for publishing symposia quickly in book form. The purpose of the series is to publish timely, comprehensive books developed from ACS sponsored symposia based on current scientific research. Occasionally, books are developed from symposia sponsored by other organizations when the topic is of keen interest to the chemistry audience.

Before agreeing to publish a book, the proposed table of contents is reviewed for appropriate and comprehensive coverage and for interest to the audience. Some papers may be excluded in order to better focus the book; others may be added to provide comprehensiveness. When appropriate, overview or introductory chapters are added. Drafts of chapters are peer-reviewed prior to final acceptance or rejection, and manuscripts are prepared in camera-ready format.

As a rule, only original research papers and original review papers are included in the volumes. Verbatim reproductions of previously published papers are not accepted.

ACS BOOKS DEPARTMENT

Preface

In the early planning discussions that led to the American Chemical Society (ACS) "Silicones and Silicone Modified Materials" Symposium, we felt that although many meetings had been held during the 1980s on organosilicon chemistry, no major gathering had been held with the focus specifically on silicones. Our prediction that such a symposium was much needed was clearly proven correct by the quantity and quality of the papers presented and by the attendance and interest from the audience during the four full days of oral presentations and also at the evening poster session in Dallas, Texas.

All major technical symposia are a team effort, so it is a great pleasure to thank Kathleen Havelka and Warren Ford for their help, advice, and encouragement throughout the preparation of the symposium. Kathleen had the patience of a saint with our many requests and "past deadline" updates. Robson Story and his team were their usual efficient and helpful selves in keeping us on track with the ACS Polymer Preprints. Robert Stackman did an outstanding job with coordinated finances and expense claims and deserves our thanks. Dow Corning, Gelest, General Electric, Procter and Gamble, and Wacker kindly provided financial assistance and we thank them for helping to make it possible for many of our presenters to attend this symposium. From my own team at the University of Cincinnati, we thank Mark Van Dyke, Rob Johnston, Jennifer Kearney, Susan Junk, and Melissa Scholle, who each gave invaluable assistance with all the various correspondence in both paper and electronic form for both the symposium and this book.

Anne Wilson of the ACS Books Department has been of terrific help at every stage of the commissioning and preparation of this book. We are fortunate to have the ACS Polymer Preprints for the meeting available for the presenters who were unable to contribute to this ACS Symposium book. We trust, however, that the various chapters from the symposium that are included here are of interest to the global silicones community. For those colleagues not able to join us in Dallas in the Spring of 1998, we are delighted that the ACS has kindly welcomed us back for the Spring Meeting in 2001 in San Diego for what we hope will be another lively gathering of our colleagues from the worldwide silicones community.

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Chapter 1

Overview of Siloxane Polymers

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This review provides coverage of a variety of polysiloxane homopolymers and copolymers, and some related materials. Specific systems include (i) linear siloxane polymers $[-\text{SiRR}'\text{O}-]$ (with various alkyl and aryl R and R' side groups), (ii) sesquisiloxane polymers possibly having a ladder structure, (iii) siloxane-silarylene polymers $[-\text{Si}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_2(\text{C}_6\text{H}_4)_m-]$ (where the phenylenes are either *meta* or *para*), (iv) silalkylene polymers $[-\text{Si}(\text{CH}_3)_2(\text{CH}_2)_m-]$, (v) polysiloxanes of enhanced crystallizability through modifications of chemical and stereochemical structures, (vi) elastomers from water-based emulsions, and (vii) random and block copolymers, and blends of some of the above. Topics of particular importance are preparative techniques, end-linking reactions, and the characterization of the resulting polymers in terms of their structures, flexibilities, transition temperatures, permeabilities, and surface and interfacial properties. Applications of these materials include their uses as high-performance fluids, elastomers, coatings, surface modifiers, separation membranes, soft contact lens, body implants, and controlled-release systems. Also of interest is the use of sol-gel hydrolysis-condensation techniques to convert organosilanes to novel reinforcing fillers within elastomers, and to ceramics modified by the presence of elastomeric domains for the improvement of impact strengths.

Of the semi-inorganic polymers, the siloxane or "silicone" polymers have been studied the most, and are also of the greatest commercial importance (1-13). The present review provides an overview of some of these polysiloxanes and related materials, emphasizing their structures, most important and interesting physical properties, and a variety of their applications.

Siloxane-Type Polymers

Preparation. Polymers of the type $[-\text{SiRR}'\text{O}-]_x$ are generally prepared by a ring-opening polymerization of a trimer or tetramer (14-19) where R and R' can be alkyl or aryl and x is the degree of polymerization. In this reaction, macrocyclic species are

generally formed to the extent of 10-15 wt %. The lower molecular weight ones are generally stripped from the polymer before it is used in a commercial application. Their presence is also of interest from a more fundamental point of view, in two respects. First, the extent to which they occur can be used as a measure of chain flexibility (20). Second, the separated species can be used to test theoretical predictions of the differences between otherwise identical cyclic and linear molecules (21). In some cases, an end blocker such as $\text{YR'SiR}_2\text{OSiR}_2\text{R'Y}$ is used to give reactive $-\text{OSiR}_2\text{R'Y}$ chain ends (22). Polymerization of non-symmetrical cyclics gives stereochemically variable polymers $[-\text{SiRR'O-}]$ analogous to the totally organic vinyl and vinylidene polymers $[-\text{CRR'CH}_2-]$. In principle, it should be possible to prepare them in the same stereoregular forms (isotactic and syndiotactic) which have been achieved in the case of some of their organic counterparts. Work of this type is showing great promise (23-25).

Polymerization of mixtures of monomers can of course be used to obtain random copolymers. They are generally highly irregular, but now in the chemical rather than stereochemical sense. Correspondingly, they generally show little if any crystallizability.

Some topics involving polymerizations and related chemical reactions which were covered at the "Silicones and Silicone Modified Materials" symposium are conversions from silicon itself to semi-inorganics (contribution by Lewis), ring-opening polymerizations (contributions by Chojnowski, Soum, Kress, Jallouli, and Komuro), atom-transfer radical polymerizations (Matyjaszewski), hydrosilation polymerizations (Kaganove, Tronc, Narayan-Sarathy), polymerizations with controlled stereochemistry (Kawakami), condensation polymerizations (Fu), and polysilane syntheses (Newton) (26).

Homopolymers.

Flexibility. The most important siloxane polymer is poly(dimethylsiloxane) (PDMS) $[-\text{Si}(\text{CH}_3)_2\text{O-}]$ (6,9,11). It is also one of the most flexible chain molecules known, both in the dynamic sense and in the equilibrium sense (20,27-31). Dynamic flexibility refers to a molecule's ability to change spatial arrangements by rotations around its skeletal bonds. The more flexible a chain is in this sense, the more it can be cooled before the chains lose their flexibility and mobility and become glassy. Chains with high dynamic flexibility thus generally have very low glass transition temperatures T_g . Since exposing a polymer to a temperature below its T_g generally causes it to become brittle, low values of T_g can be very advantageous, particularly in the case of fluids and elastomers.

The T_g of PDMS, $\sim -125^\circ\text{C}$, is the lowest recorded for any common polymer. Two reasons for this extraordinary dynamic flexibility are the unusually long Si-O skeletal bond, and the fact that the oxygen skeletal atoms are not only unencumbered by side groups, they are as small as an atom can be and still have the multi-valency needed to continue a chain structure. Also, the Si-O-Si bond angle of $\sim 143^\circ$ is much more open than the usual tetrahedral bonding occurring at $\sim 110^\circ$. In addition, this bond angle has tremendous deformability. These characteristics also increase the chain's equilibrium flexibility, which is the ability of a chain to be compact when in the form of a random coil. This type of flexibility can have a profound effect on the melting point T_m of a polymer. In this case, it is the origin of the very low T_m (-40°C) of PDMS.

In this regard, crystallization is very important in the case of elastomers, since crystallites can act as reinforcing agents, particularly if they are strain induced. For this reason, it is of interest to make siloxane-type backbones with increased stiffness, in an attempt to increase the T_m of the polymer. Examples of ways to make a polymer more rigid is to combine two chains into a ladder structure, insert rigid units such as p-phenylene groups into the chain backbone, or add bulky side groups to the backbone.

Insertion of a silphenylene group $[-\text{Si}(\text{CH}_3)_2\text{C}_6\text{H}_4-]$ into the backbone of the PDMS repeat unit yields either the siloxane meta and para silphenylene polymers (32-38). The T_g of the former polymer is increased to -48°C , but no crystallinity has been

observed to date (36,37). Since the repeat unit is symmetric, it should be possible to induce crystallinity by stretching. As expected, the *p*-silphenylene group has a larger rigidifying effect, increasing T_g to -18°C , and giving rise to crystallinity with a T_m of 148°C . The resulting polymer is thus a thermoplastic siloxane. Silarylene polymers having more than one phenylene group in the repeat unit could be of considerable interest because of the various meta, para combinations that could presumably be synthesized. It is intriguing that even some flexible siloxane polymers form mesomorphic (liquid-crystalline) phases (39,40).

Unusual polysiloxane structures that were covered at the symposium are stiffened chains (Van Dyke, Zhang, Lauter), cyclics (Semlyen, Dagger), ladders and cages (41) (Crivello, Lichtenham, Feher, Rebroy, Carpenter, Rahimian, Haddad), hyperbranched structures (Möller, Herzig, Muzafarov, Vasilenko), dendrimers (42,43) (Dvornic, Owen, Vasilenko, Sheiko, Rebroy), and sheets and tubes (Kenney, Katsoulis) (26).

Permeability. Siloxane polymers have much higher permeability to gases than most other elastomeric materials (44). They have therefore long been of interest for use as gas separation membranes, the goal being to vary the basic siloxane structure to improve selectivity without decreasing permeability. Some of the polymers which have been investigated in a major project (45) of this type were: $[-\text{Si}(\text{CH}_3)\text{RO}-]$, $[-\text{Si}(\text{CH}_3)\text{XO}-]$, $[-\text{Si}(\text{C}_6\text{H}_5)\text{RO}-]$, $[-\text{Si}(\text{CH}_3)_2(\text{CH}_2)_m-]$, $[\text{Si}(\text{CH}_3)_2(\text{CH}_2)_m\text{Si}(\text{CH}_3)_2\text{O}-]$, and $[\text{Si}(\text{CH}_3)_2(\text{C}_6\text{H}_4)_m\text{Si}(\text{CH}_3)_2\text{O}-]$, where R is typically an *n*-alkyl group and X is an *n*-propyl group made polar by substitution of atoms such as Cl or N. Unfortunately, structural changes that increase the selectivity are generally found to decrease the permeability, and vice versa.

Another type of membrane designed as an artificial skin coating for burns also exploits the high permeability of siloxane polymers (46). The inner layer of the membrane consists primarily of protein and serves as a template for the regenerative growth of new tissue. The outer layer is a sheet of silicone polymer which not only provides mechanical support, but also permits outward escape of excess moisture while preventing ingress of harmful bacteria.

Soft contact lens prepared from PDMS provide a final example. The oxygen required by the eye for its metabolic processes must be obtained by inward diffusion from the air rather than through blood vessels. PDMS is ideal for such lenses (46) because of its high oxygen permeability, but it is too hydrophobic to be adequately wetted by the tears covering the eye. This prevents the lens from feeling right, and can also cause very serious adhesion of the lens to the eye itself. One way to remedy this is to graft a thin layer of a hydrophilic polymer to the inner surface of the lens. Because of the thinness of the coating the high permeability of the PDMS is essentially unaffected.

Some Unusual Properties of Poly(Dimethylsiloxane). Atypically low values are exhibited for the characteristic pressure (47) (a corrected internal pressure, which is much used in the study of liquids), the bulk viscosity η , and the temperature coefficient of η . Also, entropies of dilution and excess volumes on mixing PDMS with solvents are much lower than can be accounted for by the Flory Equation of State Theory (47). Finally, as has already been mentioned, PDMS has a surprisingly high permeability.

Although the molecular origin of these unusual properties is still not known definitively, a number of suggestions have been put forward. One involves low intermolecular interactions, and another the very high rotational and oscillatory freedom of the methyl side groups on the polymer. Still others focus on the chain's very irregular cross section (very large at the substituted Si atom and very small at the unsubstituted O atom (47)), or packing problems associated with the alternating large and more normal bond angles.

Surface and Interfacial Properties. The polysiloxanes generally have very low surface energies (48,49), and considerable research is underway to measure and control surface and interfacial properties in general. For example, adding fluorine atoms to the side chains on a polysiloxane backbone should have a marked effect in this regard (50).

Unusual properties of polysiloxanes that were covered at the symposium are solubility parameters (Rigby), photoluminescence (Pernisz), formation of mesophases (51-53) (Godovsky), films (Takahara, Inagaki), and surfaces (Wynne, Owen, Kowalewski, Jukarainen) (26).

Reactive Homopolymers.

Types of Reactions. In the typical ring-opening polymerization, reactive hydroxyl groups are automatically placed at the ends of the chains. Substitution reactions carried out on these chain ends can then be used to convert them into other functional groups, and these functionalized polymers can undergo a variety of subsequent reactions. Hydroxyl-terminated chains, for example, can undergo condensation reactions with alkoxysilanes (54). A difunctional alkoxysilane leads to chain extension, and a tri- or tetrafunctional one to network formation. Corresponding addition reactions with di- or triisocyanates represent other possibilities. Similarly, hydrogen-terminated chains can be reacted with molecules having active hydrogen atoms (54). A pair of vinyl or other unsaturated groups could also be joined by their direct reactions with free radicals. Similar end groups can be placed on siloxane chains by the use of an end blocker during polymerization (22). Reactive groups such as vinyls can of course be introduced as side chains by random copolymerizations involving, for example, methylvinylsiloxane trimers or tetramers.

Topics involving functionalized polymers that were covered at the symposium include fluorosilicones (48,50,55) (Narayan-Saratahy), amino acid functionalizations (Matisons), grafts (Priou), hydrosilation reactions (Hu), chain-end functionalizations (Fu, Brzezinska, Miranda), and siloxanes as branches (Kishimoto) (26).

Block Copolymers. One of the most important uses of end-functionalized polymers is the preparation of block copolymers, in part because of the tendency of such copolymers to undergo phase separation into novel morphologies (22,56). The reactions are identical to the chain extensions already mentioned except that the sequences being joined are chemically different. In the case of the $-\text{OSiR}_2\text{R}'\text{Y}$ chain ends, R' is typically $(\text{CH}_2)_{3.5}$ and Y can be NH_2 , OH , COOH , $\text{CH}=\text{CH}_2$, etc. The siloxane sequences containing these ends have been joined to other polymeric sequences such as carbonates, ureas, urethanes, amides, and imides.

Phase separations, blends, and related subjects (57-64) covered at the symposium involved binodal and spinodal phase separations (Viers), block copolymers (Weber, McGrath, Yilgor, Gravier), blends (Talmon, Krencieski, Singh, Yilgor, Pearce), and interpenetrating networks (65) (Boileau, Wengrovius) (26).

Elastomeric Networks. The networks formed by reacting functionally-terminated siloxane chains with an end linker of functionality three or greater have been extensively used to study molecular aspects of rubberlike elasticity (32,66,67). They are "model", "ideal", or "tailor-made" networks in that a great deal is known about their structures by virtue of the very specific chemical reactions used to synthesize them. For example, in the case of a stoichiometric balance between chain ends and functional groups on the end linker, the critically important molecular weight M_c between cross links is equal to the molecular weight of the chains prior to their end linking. Also, the functionality of the cross links (number of chains emanating from one of them) is simply the functionality of the end-linking agent. Finally, the molecular weight distribution of the network chains is the same as that of the starting polymer, and there should be few if any dangling-chain irregularities.

Since these networks have a known degree of cross linking (as inversely measured by M_c), they can be used to test the molecular theories of rubberlike elasticity,

particularly with regard to the possible effects of inter-chain entanglements (32,66). Intentionally imperfect networks can also be prepared, by unbalancing the stoichiometry, or by using chains with reactive groups at only one of their ends.

One of the most interesting types of model networks is the bimodal, which consists of very short chains intimately end linked with the much longer chains that are representative of elastomeric materials (32,66,68-72). These materials have unusually good elastomeric properties, specifically large values of both the ultimate strength and maximum extensibility. Possibly the short chains contribute primarily to the former, and the long chains primarily to the latter. Also, not only do short chains improve the ultimate properties of elastomers, but long chains improve the impact resistance of the much more heavily cross-linked thermosets.

Some topics involving additives, curing, and reinforcement of elastomers by fillers that were covered at the symposium are: additives (Perry), curing (Tsiang, Singh, Chu, Priou, Wu, Taylor), reinforcement (Osaheni, Okel, Cosgrove, Cohen-Addad, Matejka), and water-based elastomers (Liles, Bowens) (26).

Cyclic Trapping. If relatively large PDMS cyclics (21,73) are present when linear PDMS chains are end linked, then some of them will be permanently trapped by one or more network chains threading through them (32,74-76). Interpretation of the fraction trapped as a function of ring size, using rotational isomeric theory and Monte Carlo simulations, provides very useful information on the spatial configurations of cyclic molecules, and the mobilities of the end-linking chains.

Copolymers.

Random. These materials may be prepared by the copolymerization of a mixture of monomers rather than the homopolymerization of a single type of monomer (15). One reason for doing this is to introduce functional species, such as vinyls or hydrogens, along the chain backbone to facilitate cross linking. Another is the introduction of sufficient chain irregularity to make the polymer inherently non-crystallizable.

Block. As already mentioned, the sequential coupling of functionally-terminated chains of different chemical structure can be used to make block copolymers, including those in which one or more of the blocks is a polysiloxane (77-79). If the blocks are relatively long, separation into a two-phase system almost invariably occurs. Frequently, one type of block will be in a continuous phase and the other will be dispersed in it in domains having an average size the order of a few hundred angstroms. Such materials can have unique mechanical properties not available from either species when present simply in homopolymeric form. Sometimes, similar properties can be obtained by the simple blending of two or more polymers (57).

Applications.

Medical. There are numerous medical applications of siloxane polymers (46). Prostheses, artificial organs, facial reconstruction, and catheters, for example, take advantage of the inertness, stability, and pliability of the polysiloxanes. Artificial skin, contact lenses, and drug delivery systems utilize their high permeability as well.

Non-Medical. Illustrative non-medical applications are high-performance elastomers, membranes, electrical insulators, water repellents, anti-foaming agents, mold-release agents, adhesives, protective coatings, release control agents for agricultural chemicals, encapsulation media, and hydraulic, heat-transfer, and dielectric fluids (46). They are based on the same properties of polysiloxanes just mentioned and also their ability to modify surfaces and interfaces (for example as water repellents, anti-foaming agents, and mold-release agents).