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Some Interesting Things about Polysiloxanes

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ABSTRACT
Poly(dimethylsiloxane) [$-Si(CH_3)_2O-$] is by far the most studied of the polysiloxanes and is known to exhibit some intriguing physical properties, in particular very high permeability to gases. Simulations are underway in an attempt to understand some of these peculiarities. In addition, other symmetrically substituted polysiloxanes exhibit mesophases that are not understood at all. In the case of cross-linked polysiloxanes, there have been many important developments, including (i) elastomers undergoing strain-induced crystallization through control of chain stiffness or stereochemical structure, (ii) model elastomers (including dangling-chain networks), (iii) possible thermoplastic elastomers, (iv) bimodal network chain-length distributions, and (v) cross linking in solution. Interesting elastomeric composites include those with (i) in-situ-generated ceramiclike particles, (ii) ellipsoidal fillers, (iii) claylike-layered fillers, (iv) polyhedral oligomeric silsesquioxane (POSS) particles, (v) porous fillers, (vi) controlled particle−elastomer interfaces, and (vii) elastomeric domains generated within ceramic phases. Also of interest are some new techniques that have been used to characterize polysiloxane networks.

Introduction

Polysiloxanes, which contain [SiRR′O] repeat units, are unique among inorganic and semi-inorganic polymers. They have been the most studied members of this class by far and are the most important with regard to commercial applications. Thus, it is not surprising that a large number of reviews exist describing the synthesis, properties, and applications of these materials, with some of them very recent.[1,2] The purpose of the present article, however, is not to give a comprehensive overview of these polymers but rather to focus on some novel and interesting aspects of polysiloxane science and engineering, including properties that have been reported and interpreted, work in progress, and some important unsolved problems.

The Polysiloxane Chains Themselves

Chain Structure. The Si−O backbone of this class of polymers endows it with a variety of intriguing properties. For example, the strength of this bond gives the siloxane polymers considerable thermal stability, which is very important for their use in high-temperature applications (for example, as heat-transfer agents and high-performance elastomers).[2] The nature of the bonding and the chemical characteristics of typical side groups give the chains a very low surface free energy and, therefore, highly unusual and desirable surface properties. For example, polysiloxanes are often used as mold-release agents, waterproof coatings, and biomedical materials.

Additional structural information is presented in the sketch of poly(dimethylsiloxane) (PDMS) shown in Figure 1. First, the Si−O bond length is 1.64 Å, which is significantly longer than that for the C−C bond (1.53 Å). Also, the Si−O−Si bond angle is approximately 143°, which is much larger than the usual tetrahedral value (∼110°). In addition, this bond angle is so flexible that it can readily pass through the linear 180° state.[2] Finally, the torsional potential about Si−O bonds is significantly lower than that about C−C bonds. All of these features, in concert, make the PDMS chain one of the most flexible chains known. This gives PDMS and most other polysiloxanes very low transition temperatures, as will be described below. Also of interest is the fact the oxygen skeletal atoms are unencumbered by side groups; they are as small as an atom can be and still have the divalency needed to continue a chain structure. This gives the chain a very irregular cross section. As will also be discussed below, this could influence the way the chains pack in the bulk, amorphous state which, in turn, gives the chains very unusual equation-of-state properties. Finally, because the bond angles alternate, the low-energy planar all-trans form of the chain approximates a series of closed polygons. As a result, siloxane chains exhibit a number of interesting properties.[2]

These structural features increase the *equilibrium* flexibility of the chain, which is the ability of a chain to take on a compact shape when in the form of a random coil, and this affects the melting point T_m. Equilibrium flexibility is generally measured, inversely, by the mean-square end−end distance of the chain as unperturbed by complicating excluded-volume effects.[3] They also increase the *dynamic* flexibility of the chain, which affects its glass transition temperature T_g (below which the polymer can become glassy and brittle).

Conformations and Spatial Configurations. The first member of this series, PDMS, $[-Si(CH_3)_2O-]_x$, has been studied more extensively with regard to its configuration-dependent properties than any other chain molecule.[3] Trans states are of lower energy than gauche states (rotational angles $\phi = \pm 120°$) in this chain, because of the favorable interactions between methyl groups. Also important is the fact that conformations involving the unlike $g^{\pm}g^{\mp}$ pairs about skeletal bond pairs give rise to “pentane-type interferences”[3] and are therefore excluded or suppressed. These are the most important features of the roatational isomeric state model of these chains, which has successfully been used to interpret experimental

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Jim Mark has been working on various aspects of polysiloxane science and technology for 4 decades now but admits that he still has a lot to learn about this challenging area. The present Account of some of these materials is based on a presentation related to his receiving the 2004 ACS Kipping Award in Silicon Chemistry. Using this occasion to review such polymers seemed particularly appropriate, because this is the first Kipping Award recognizing contributions in silicon polymer chemistry.

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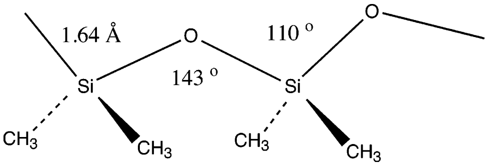

FIGURE 1. Sketch of a portion of a PDMS chain, showing some structural information relevant to its high flexibility. Closed figure after 360/(143 − 110) = 11 repeat units.

values of various configuration-dependent properties of PDMS and other polysiloxanes.

Much experimental and theoretical work has also been reported on the cyclization of dimethylsiloxane chains and on the study of the properties of these cyclics.[2] At least in the limit of large chain length, the agreement between theory and experiment is excellent and, thus, is in strong support of the rotational isomeric state model for PDMS.

Stereochemically-Variable Polysiloxanes. In these unsymmetrically disubstituted chains, such as poly(methylphenylsiloxane), the substituents of one type can be on the same side of the all-trans chain, on opposite sides or on either side in a random arrangement. These are the isotactic, syndiotactic, and atactic forms best known with regard to vinyl polymers. So far, it has not been possible, however, to find catalysts that parallel the Zeigler−Natta catalysts used to prepare isotactic poly(α-olefin) polymers. There has been very promising work based on ring-opening polymerization of cyclics of isotactic stereochemistry using catalysts that prevent scrambling of the cyclic stereochemistry during polymerization. This has yielded poly[(methyl(3,3,3-trifluoropropyl)siloxane] samples ranging from the usual noncrystallizable (atactic) form to materials that undergo strain-induced crystallization to thermoplastics (that are crystalline at ambient temperatures).[4]

Some Unusual Side Groups. Including fluoro groups in the side chains of a polysiloxane can improve solvent resistance and modify surface properties.[2,5] Most interest has focused on replacing some hydrogens with fluorines in *n*-alkyl groups, for example, the three fluorines in the trifluoropropyl group $(CH_2)_2CF_3$ mentioned above. In addition, one, two, or three fluorines have also been substituted into the phenyl groups of poly(methylphenylsiloxane).[6] Homopolymers and copolymers having *p*-tolylsiloxane groups have been of particular interest with regard to their formation of liquid-crystalline phases.[7] Also, if the side groups are sufficiently hydrophilic, the polysiloxane can even become water soluble.[8] A final example is the use of optically active groups as side chains, the simplest example being the *secondary* butyl group $-CH(CH_3)(C_2H_5)$. Such polymers could be studied using any of the numerous techniques developed to characterize optically active polymers such as the proteins.

Poly(dimethylsilmethylene). This polymer $[-Si(CH_3)_2-CH_2-]_x$ can be thought of either as a hydrocarbon analogue of PDMS (in which O atoms are replaced by CH_2 groups) or as a silicon analogue to polyisobutylene $[-C(CH_3)_2CH_2-]_x$ (in which a Si atom replaces one of the two skeletal C atoms in the repeat unit).[2] The polymer is shown schematically in Figure 2. The Si−C bonds are 1.90 Å long and, in contrast to siloxane chains, the two types of skeletal bond angles are essentially approximately tetrahedral. Most interesting is the fact that, because CH_2 and CH_3 groups have very similar sizes and interactions, this chain molecule should have some characteristics of the idealized "freely-rotating" chain.[3] This conclusion is supported by experimental evidence, which indicates that the unperturbed dimensions of the polymer are relatively small and that both its unperturbed dimensions and dipole moments are essentially independent of the temperature.

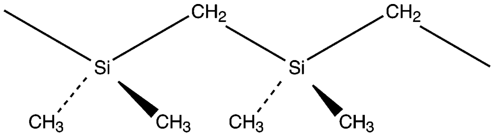

FIGURE 2. Poly(dimethylsilmethylene) chain.

Equilibrium Flexibility of the Polymer Chains. The equilibrium type of flexibility mentioned above has a profound effect on T_m of a polymer, because T_m is inversely proportional to the entropy of fusion. High flexibility in this equilibrium sense means high conformational randomness in the amorphous state and, thus, a high entropy of fusion and low melting point. This entropy can be reduced by a stretching process, in what is called "strain-induced crystallization". The crystallites thus generated can be very important because they may provide considerable reinforcement for a network. However, most polysiloxane elastomers have melting points that are unfortunately too low to benefit from this effect. For this reason, there is considerable interest in inserting a *m*-silphenylene unit $[-Si(CH_3)_2C_6H_4-]$ into polysiloxane backbones.[9] The T_g of the former polymer is increased to −48 °C (relative to −125 °C for PDMS), but no crystallinity has been detected to date. Because the repeat unit is symmetric, it should be possible to induce crystallinity by stretching. The explanation here is that the chains are prevented from completely disordering themselves by being held elongated by the stretching force rather than by the structural features of the chains. As expected, the *p*-silphenylene group has a larger stiffening effect, increasing the 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. Cyclohexylene (C_6H_{10}) groups can switch between boat and chair forms and should thus be less stiff than phenylene groups. Both *meta* and *para* groups could be of interest in this regard.

Crystallinity Simulations. There has been success in simulating the crystallinity of some polysiloxanes. This work was based on a model for simulating chain ordering in copolymers composed of two comonomers, at least one of which is crystallizable. Monte Carlo techniques are first used to generate chains with sequences that are representative of those occurring in the polymers of interest. In the case of chemical copolymers, the generation is based on standard copolymerization equations containing the usual reactivity ratios. In the case of stereochemical copolymers, the generation is based on replication probabilities (*meso* rather than *racemic* placements). Typically, the generated chains are placed in parallel, two-dimensional arrangements. Neighboring chains are then searched for by like-sequence matches that could lead to the formation of crystallites to estimate the extent of crystallinity.[1,10]

An example in the polysiloxane chemical copolymer area involved modeling random and semiblocky poly(diphenylsiloxane-*co*-dimethylsiloxane) copolymers. In this example, the chains were placed alongside one another in a two-dimensional array, with black squares representing dimethylsiloxane (DMS) units and white squares representing diphenylsiloxane (DPS) units.[11] "Like" squares neighboring each other in the same row were then viewed as coalescing into blocks, the lengths of which were compared with the known minimum length required to form a crystallinte. It was thus possible to identify crystallizable DPS regions as distinct from noncrystallizable DMS components or units of the crystallizable DPS component that were not long enough to crystallize.[11] A value of the degree of crystallinity of a simulated sample was then determined by counting the units involved in the matching sequences relative to the total number of units of all of the chains. The crystallites thus identified presumably act as cross-linking sites and reinforcing domains, providing the additional toughness that the semiblocky copolymers have over their random counterparts.

An example of such modeling of a stereochemically variable polysiloxane focused on poly[methyl(3,3,3-trifluoropropyl)siloxane],[12] a polymer often studied with regard to the already mentioned new synthetic techniques for controlling stereoregularity and thus crystallizability.[4]

Liquid-Crystalline Polysiloxanes. It is intriguing that even some flexible siloxane polymers form mesomorphic (liquid-crystalline) phases.[13] In the case of the symmetric chains [SiR_2O] with $(CH_2)_mCH_3$ R side chains, mesophases are observed for $m = 1-5$ and the driving force is obviously not chain-stiffness, because these are very flexible polymers. For PDMS ($m = 0$), the mesophase formation is apparently suppressed by crystallization of the backbone and, for $m > 5$, by crystallization of the side chains. In addition, some polysiloxanes form liquid-crystalline phases because of the presence of relatively stiff side chains. They have been often studied, particularly with regard to the effect of deformation of the elastomeric polysiloxane phase on the mesomorphic behavior exhibited by the side chains.

Dynamic Flexibility. Dynamic flexibility refers to the ability of a molecule 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 the bulk material becomes glassy. Chains with high dynamic flexibility thus generally have very low glass transition temperatures T_g.[14,15] Because exposing a polymer to a temperature below its T_g generally causes it to become brittle, low values of T_g can be advantageous, particularly in the case of fluids and elastomers. Structural changes that increase the equilibrium stiffness of a chain generally also increase its dynamic stiffness and thus increase T_g. Conversely, the very high flexibility of PDMS is the origin of its low T_m (−40 °C) as well as its very low T_g (−125 °C).[14,15]

Permeability. Siloxane polymers have a much higher permeability to gases than most other elastomeric materials. For this reason, they have long been of interest for gas separation membranes, with the goal being to vary the basic siloxane structure to improve selectivity without decreasing permeability. A related application is in controlled drug delivery.[16] In addition to numerous experiments, there have been several simulations dealing with the permeability of polysiloxane membranes. Some ongoing research in this area is described below.

Some Environmental Aspects. Polysiloxanes are remarkably degradable in soils, if claylike materials are present to act as catalysts. There is also interest in synthesizing polysiloxanes in environmenally friendly carbon dioxide. Recycling of polymers has also become an important environmental issue. Becaused of its high cost, such studies include polysiloxanes, including ones that are heavily filled with silica.[17]

Thermodynamics. Of particular interest in this area are the thermodynamics of mixing and phase diagrams showing miscibility and phase separation among various polysiloxanes, including cyclics.[2] Related to phase separation is the segregation of siloxanes to surfaces in multiphase systems because of their low surface energies. As a result, a blend or block copolymer having only a small overall percent of siloxane can have surfaces consisting almost entirely of this minor constituent.[2]

Some Additional Unusual Properties of Poly(dimethylsiloxane). Some of the unusual physical properties exhibited by PDMS include atypically low values exhibited for the characteristic pressure, 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 theory.[18] Finally, as already mentioned, PDMS has a surprisingly high permeability.

One explanation suggested is that the irregularity of the cross section of the chain obstructs its efficient packing.[18] Another conjecture is packing problems associated with the alternating large and more normal bond angles [because low-energy conformations approximate closed figures, instead of spatially extended arrangements such as the polyethylene (PE) planar zigzag form].[19] Simulations are being attempted to understand some of these very unusual properties. The basic approach is to vary stepwise the structure of PDMS to arbitrarily make it like (amorphous) PE to determine which structural features are most important in giving PDMS its unusual properties. Simulations have also been carried out on the gelation of PDMS[20] and its reinforcement from either spherical or ellipsoidal fillers.[21] The type of dispersion of the particles within the network is important, particularly with regard to possible aggregation. In the case of the ellipsoidal fillers, their orientation is also of considerable interest. Other recent simulations have attempted to characterize spatial configurations in the relatively stiff chains of poly(diphenylsiloxane).[22]

Another striking feature of siloxane polymers is their unusual surface properties.[23] Specifically, their surface properties permit them to serve in a variety of seemingly contradictory roles. For example, siloxanes can be both antifoaming agents and foam stabilizers, both paper-release coatings and pressure-sensitive adhesives, both water-repellents and dewatering agents, and both emulsifiers and de-emulsifiers.[24] This paradox is explained by the differing ways in which the siloxane chains interact with the other species present. For example, in foam technology, it is critically important whether the siloxane dissolves in the liquid phase or stays at the liquid–gas interface. Similar questions arise in other applications, and specific properties are generated by an appropriate choice of the side group, addition of special polar, ionic, or reactive functional groups, or by copolymerization with completely different classes of comonomer. In the most general terms, the unusual surface properties of polysiloxanes are due to their low surface energies and surface tensions.[24] These characteristics are then understandable in terms of two important features of the chains themselves. The first is the very low intermolecular forces between the side chains, which are the methyl groups in PDMS. The second is the remarkable flexibility of the siloxane backbone, which permits the chains to easily arrange and rearrange themselves so as to place the methyl groups at their surfaces and interfaces. One example is the ease with which a damaged polysiloxane surface quickly regenerates the surface characteristics of the original material.

Hyperbranched Polymers and Dendrimers. There has long been interest in these peculiarly branched polymeric materials, and some of the most interesting species involve polysiloxane chains.[25]

Elastomeric Networks

Model Elastomers. Networks formed by reacting functionally terminated siloxane chains with an end linker of functionality three or greater have been used extensively to study molecular aspects of rubberlike elasticity.[1,26] They are "model" networks in that a great deal is known about their structure by virtue of the very specific chemical reactions used for their synthesis. For example, if a stoichiometric balance exists between chain ends and functional groups on the end linker, then 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. Because these networks have a known degree of cross linking (as measured inversely by M_c), they can be used to test the molecular theories of rubberlike elasticity, particularly with regard to the possible effects of interchain entanglements.[27]

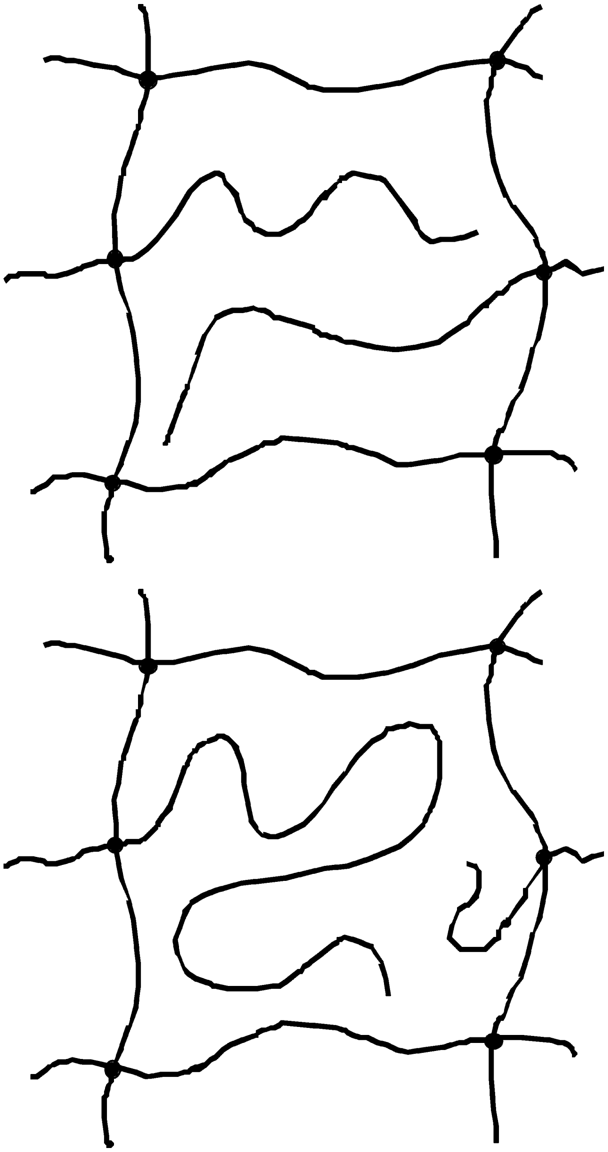

FIGURE 3. Two end-linking techniques for preparing networks having known numbers and lengths of dangling chains. The dots represent cross links.

Intentionally imperfect networks can also be prepared, as is shown in Figure 3.[27] Such networks have known numbers and lengths of dangling chains (those attached to the network at only one end), and thus, the effects of these irregularities on elastomeric properites can be determined. In the first method, the stoichiometry is unbalanced so that there is an excess of chain ends over functional groups on the end-linking molecules. The limitation in this method is the fact that the dangling chains have to have the same average length as the elastically effective chains (those attached to the network at both ends). The second method shown avoids this limitation by the use of monofunctionally terminated chains of whatever length is desired.

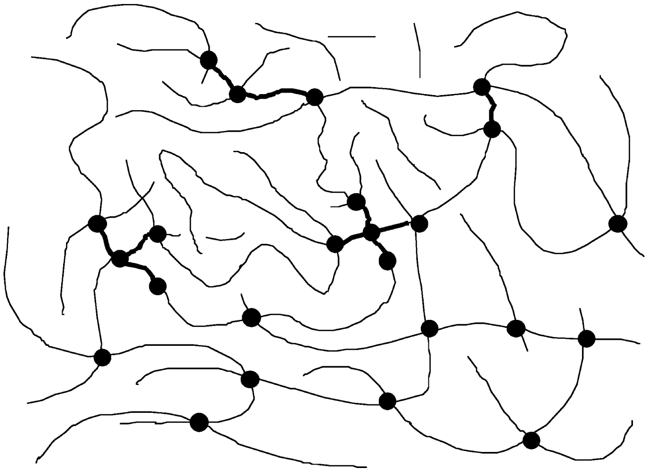

FIGURE 4. Sketch of a bimodal network.

Bimodal Networks. One of the most interesting types of model networks is the bimodal. These networks consist of very short chains intimately end-linked with the much longer chains that are representative of elastomeric materials.[28] Such a network is shown in Figure 4, where the short chains are arbitrarily drawn thicker than the long ones. 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, in that their very limited extensibilities should give very high values for the modulus. The long chains might then contribute primarily by increasing the maximum extensibility, by somehow delaying the spread of the rupture nuclei necessary for catastrophic failure of the material. Monte Carlo simulations based on the rotational isomeric state model,[29] as well as analytical calculations,[30] have helped elucidate the molecular origins of this interesting type of reinforcement. Not only do short chains improve the ultimate properties of elastomers, but also long chains improve the impact resistance of the much more heavily cross-linked thermosets.[31]

Trapping of Cyclic Oligomers. If relatively large PDMS cyclic oligomers are present in reaction systems where linear PDMS chains are being end-linked, then some of the cyclic species will be permanently trapped by one or more network chains threading through them.[27] One interesting result is the observation that the percent cyclic trapped does not depend on the amount of time elapsed between mixing the two components and the end linking of the linear chains. This is certainly consistent with the very high mobility of siloxane chains, as already described. In any case, interpretation of the fraction trapped as a function of the ring size, using rotational isomeric theory and Monte Carlo simulations, has provided useful information about the spatial configurations of cyclic molecules, including the effective hole size that they present in the undiluted, amorphous state.[27]

Cross Linking in Solution. There has been some interest in cross linking in solution, because the network chains in the subsequently dried elastomer are “super compressed”. These materials can have some unusual properties, including unusually high extensibility.[32]

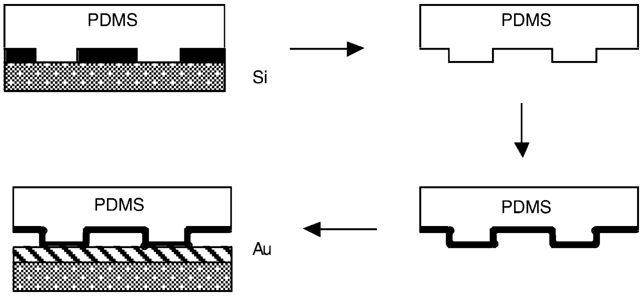

FIGURE 5. Steps in soft lithography. The PDMS in the beginning sketch is first cross-linked, then removed, and coated with a thiol that transfers the original pattern to a gold-surface layer.

Interpenetrating Networks. In this type of material, two networks are formed, either simultaneously or sequentially, in such a way as to interpenetrate one another. They thus “communicate” with one another through interchain interactions, including entanglements, rather than through covalent bonds. A particularly simple example would be the simultaneous formation of two PDMS networks, one by a condensation end-linking reaction and the other by an addition end-linking reaction, with the two types of chains mixed at the molecular level.[33] A more complex example, with more novel properties, is the preparation of interpenetrating networks between PDMS and an organic thermoplastic polymer such as nylon, polyurethane, or polyester.[34]

Thermoplastic Elastomers. There has been some interest in developing polysiloxane thermoplastic elastomers.[2]

Soft Lithography. The high fluidity and ease of cross-linking PDMS have lead to some interesting new applications. Polysiloxanes are apparently the materials of choice in the new “soft-lithography” techniques.[35] The method is outlined briefly in Figure 5. In the first step, linear (liquid) PDMS is pored over the surface of the master to be reproduced. It is then cross-linked and peeled away from the master surface. The PDMS surface containing the pattern is then coated with a hydrophobic alkane thiol, and the pattern is transferred to a gold surface (to which the thiol strongly binds). The pattern placed onto the gold surface can then be developed using a variety of techniques, including washing with a hydrophilic thiol to coat those parts of the surface not covered by the hydrophobic thiol. The advantages of PDMS in this area are (i) high fluidity (which is required to make good replicas of the master), (ii) ease of cross linking at ambient temperatures (to make the features of the stamp permanent), (iii) superb elasticity and robustness (for removing the PDMS stamp and using it in microcontact printing), and (iv) excellent stability (for long-term storage of patterns). A related application is the use of polysiloxanes in the area of microfluidics.

Composites Involving Polysiloxanes

Reinforced Elastomers. Some elucidation of the mechanism of elastomer reinforcement is being obtained by precipitating chemically generated fillers into network structures rather than blending badly agglomerated filler particles into elastomers prior to their cross linking. This has been done for a variety of fillers, for example, silica by hydrolysis of organosilicates, titania from titanates, alumina from aluminates, etc.[26,36] A typical and important reaction is the acid- or base-catalyzed hydrolysis of tetraethyl orthosilicate

$$Si(OC_2H_5)_4 + 2H_2O \rightarrow SiO_2 + 4C_2H_5OH \qquad (1)$$

In the simplest approach to obtaining elastomer reinforcement, some of the organometallic material is absorbed into the cross-linked network and the swollen sample is placed into water containing the catalyst, typically a volatile base such as ammonia or ethylamine.[27] Hydrolysis to form the desired silicalike particles proceeds rapidly at room temperature to yield the order of 50 wt % filler in less than 1 h. The particles formed are generally approximately spherical and are well-dispersed and essentially unagglomerated, which suggests that the sol−gel reaction within the elastomer may involve simple homogeneous nucleation. The particles appear to have a relatively narrow size distribution, with almost all of them having diameters in the range 200−300 Å. Modifications of this sol−gel technique have been modified to give unusually transparent PDMS nanocomposites.[37] Such in-situ-generated particles can increase the modulus by more than an order of magnitude, and the stress−strain isotherms show the upturns in modulus at high elongation that are the signature of good reinforcement.

Biosilicification. Some studies attempt to mimic what nature does when it uses protein templates (silaffins), to produce elegant silica structures in diatoms, sponges, etc. This is done by including synthetic polypeptides and other polymers in sol−gel reactions to produce the silica phase.[38] One goal is the control of particle shapes, and fibrous and sheetlike structures have been obtained.

Elatomer-Modified Ceramics. If the hydrolyses in organosilicate-polymer systems are carried out with increased amounts of the silicate, bicontinuous phases can be obtained (with the silica and polymer phases interpenetrating one another).[1,36] At still higher concentrations of the silicate, the silica generated becomes the continuous phase, with the polymer dispersed in it. It is obviously of considerable importance to determine how the elastomeric phase can improve properties, such as the impact strength of the ceramic.

Nonspherical Particles. Reinforcing fillers can be deformed from their usual approximately spherical shapes in a number of ways. For example, if the particles are a glassy polymer such as polystyrene (PS), then deforming the matrix in which they reside at a temperature above the glass transition temperature of PS will convert them into ellipsoids.

Uniaxial deformations give prolate (needle-shaped) ellipsoids, and biaxial deformations give oblate (disc-shaped) ellipsoids, as illustrated in Figure 6.[1,36] Prolate particles can be thought of as a conceptual bridge between the roughly spherical particles used to reinforce elastomers and the long fibers frequently used for this purpose in thermoplastics and thermosets. Similarly, oblate particles can be considered as analogues of the much studied clay platelets used to reinforce a variety of materials[1,36] but with dimensions that are controllable. In the case of nonspherical particles, their orientations are also of considerable importance. One interest here is the anisotropic reinforcements that such particles provide, and there have been simulations to better understand the mechanical properties of such composites.[26]

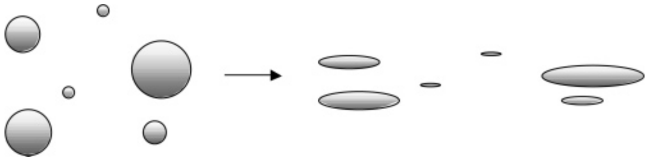

FIGURE 6. Deformation of originally spherical particles into ellipsoids.

Magnetic Particles. Incorporating reinforcing particles that respond to a magnetic field is important with regard to aligning the particles to improve mechanical properties anisotropically.[39] In related work, some in situ techniques have been used to generate electrically conducting fillers such as polyaniline within an elastomeric material.

Layered Fillers. Exfoliating layered particles such as the clays, mica, or graphite is being used to provide very effective reinforcement of polymers at loading levels much smaller than in the case of solid particles such as carbon black or silica.[1,36] Other properties can also be substantially improved, including increased resistance to solvents and reduced permeability and flammability. Such nanocomposites have been made from PDMS.[40]

Polyhedral Oligomeric Silsesquioxanes (POSS). These fillers are cagelike silicon−oxygen structures and have been called the smallest possible silica particles. The most common structure has 8 silicon atoms, each carrying an organic group. The particles on which none of the groups are functionally reactive can be simply blended into elastomers using the usual mixing or compounding processing. In this case, the groups are chosen to improve miscibility with the elastomeric host matrix. Those particles having one reactive functional group can be attached to a polymer as side chains. Those with two reactive groups can be incorporated into polymer backbones by copolymerization, and those with more than two can be used for forming cross-linked networks.[41]

Nanotubes. Carbon nanotubes are also of considerable interest with regard to both reinforcement and possible increases in electrical conductivity.[1,36] There is considerable interest in characterizing the flexibility of these nanotube structures, in minimizing their tendencies to aggregate and in maximizing their miscibilities with organic and inorganic polymers.

Porous Fillers. Some fillers such as zeolites are sufficiently porous to accommodate monomers, which can then be polymerized. This threads the chains through the cavities, with unusually intimate interactions between the reinforcing phase and the host elastomeric matrix.[42]

Unusually good reinforcement is generally obtained. Also, because of the constraints imposed by the cavity walls, these confined polymers frequently show no glass transition temperatures or melting points.[26]

Fillers with Controlled Interfaces. When appropriate groups are introduced, chains that span filler particles in a PDMS-based composite can be designed so that they are either durable, breakable irreversibly, or breakable reversibly.[43]

Some New Characterization Techniques Useful for Polysiloxanes

Small-Angle Scattering. Some small-angle X-ray scattering techniques have also been applied to polysiloxane elastomers. The most important example has been the characterization of fillers precipitated into polysiloxane elastomers and the corresponding incorporation of such elastomers into ceramic matrixes (in both cases to improve mechanical properties).[1,36]

Brillouin Scattering. The application of Brillouin scattering to the characterization of PDMS networks was found to be useful for looking at glassy-state properties of such elastomers at very high frequencies.[44]

Pulse Propagation. Another example of a relatively new technique for the noninvasive, nondestructive characterization of network structures involves pulse-propagation measurements.[45] The goal here is the rapid determination of the spacings between junctions and between entanglements in a network structure. In this technique, the delay in a pulse passing through the network is used to obtain such information on the network structure.

Conclusions and Outlook

As documented in this Account, the polysiloxanes have been of great interest and importance for a variety of reasons. The chains themselves have unusual structural features and have flexibilities and mobilities unmatched by other polymer molecules. As a result, they have extraordinarily high permeabilities, very low viscosities, unusual surface properties, unexpected mesophases, and useful properties in general over an astonishingly wide range of temperatures. The fact that these novel properties are not well-understood has attracted the attention of people doing analytical theory or computer simulations. Networks produced from polysiloxane chains are also unique, because of the very specific reactions that can be used to end-link them into high-performance elastomeric materials of known network structures. Reinforcing these polysiloxane elastomers also provides some unusual opportunities, in that they are compatible with fillers ranging from the commercially important silicas to the most current new materials such as in-situ-generated ceramic particles, ellipsoidal particles, clays and other layered materials, polysilsesquioxane molecular cubes, porous materials, and nanotubes. All indications are that the polysiloxanes will maintain their fascination to those of us doing basic research, and there seems to be no limit to the areas in which these materials are finding intriguing applications.

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