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Review

Conformations and Spatial Configurations of Inorganic Polymers

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ABSTRACT: Experimental and theoretical studies of the conformations and configuration-dependent properties of inorganic polymers are comprehensively surveyed. The experimental quantities of primary interest are the dimensions, dipole moments, and cyclization constants of the chains, and the theoretical interpretations are based on the rotational isomeric state theory of chain molecules. Inorganic polymers are generally found to be rather different from their organic counterparts with regard to their conformational preferences and spatial configurations. The differences arise from the fact that inorganic chains frequently have skeletal bond lengths and bond angles which are considerably larger than those occurring in typical organic polymers. This tends to relieve the steric congestion existing in other chain molecules and, in fact, many of the important intramolecular interactions are found to be attractive rather than repulsive. Also discussed are several unanswered questions in this general area of polymer science, along with some suggestions of novel inorganic chains which may be of particular interest with regard to their conformational and configurational characteristics.

The preparation and study of inorganic polymers has become one of the most active areas in polymer science. The rapidly growing interest in such substances, over their purely organic counterparts, is due to a variety of reasons. The more practical of these include the possibility of obtaining materials which are more stable, at very high temperatures and under other extreme conditions of utilization. More fundamentally, there is also of course the interest in extending our understanding of chemical bonding to new molecular systems, and in elucidating structure–property relationships for polymeric systems in general.

The molecular characteristic central to an understanding of the physical properties of any type of polymer chain is its spatial configuration, i.e., its arrangement in space as arrived at by adoption of a particular sequence of rotational angles about the bonds making up the chain backbone.[1–6] It is the multitude of such possible configurations, generated by different conformational sequences, that gives a polymeric material the unique properties that set it off so distinctively from any low molecular weight material. This configurational versatility is, for example, the origin of the large reversible deformability of elastomeric polymers and the high impact strength of the more rigid thermoplastics.

The above circumstances have encouraged the preparation of the present review, which focuses on the conformations and configurations of polymer chains which are significantly inorganic in structure. A polymer is considered to fall into this category if its chain backbone contains no C–C bonds. It is frequently convenient to consider separately the chains thus defined which, in addition, contain neither C–C nor C–H bonds in neither the backbone nor the side groups. A chain of this type, such as poly(dichlorophosphazene) of repeat unit [PCl_2N–], is of course "totally inorganic". The remaining chains, exemplified by poly(dimethylsiloxane) [$Si(CH_3)_2O$–], would then be termed "semiinorganic".

The properties which have been most often employed to characterize the random-coil configurations of such molecules are the mean-square end-to-end dimensions $\langle r^2\rangle_0$ and dipole moments $\langle \mu^2\rangle_0$ as unperturbed by long-range interactions (excluded volume effects).[7] The unperturbed dimensions are usually expressed as the *characteristic ratio* $\langle r^2\rangle_0/nl^2$, in which they are normalized by the number of skeletal bonds and the average square of their lengths.[1] The corresponding dielectric quantity is the *dipole moment ratio* $\langle \mu^2\rangle_0/xm^2$, in which x is the number of bond or group dipoles and m^2 is the average square of their magnitudes.[3] These ratios are particularly useful in the case of high molecular weight polymers since they converge relatively rapidly to constant values with increase in chain length. Also of considerable utility, when available, are cyclization equilibrium constants[8,9] and stress–optical coefficients.[10,11] These, and a variety of other properties,[2] depend on the configurations of the chains. Of the ones cited, the most useful are the dipole moments and cyclization constants since they can be determined for chains of any length, either in the bulk (undiluted) state or in solution. Studies of the chains in the crystalline state, generally by means of x-ray diffraction, do not of course provide statistical information but do indicate preferences existing among the various conformations accessible to the molecule. The above characteristics are equilibrium properties of the chain and can be used to obtain information on the locations and relative energies of these conformations.[1]

Also of interest and importance are the energy barriers between such permitted conformations. Much less information is available on this aspect of chain configurations. It is mentioned in the following discussions of various polymers

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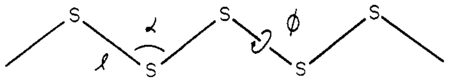

Figure 1.

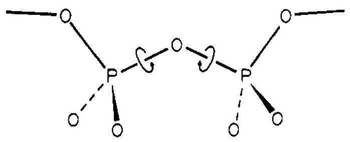

Figure 2.

through citations, where relevant, of glass-transition temperatures T_g. At this temperature and below, the polymer becomes glassy (relatively brittle), because of the freezing-in of the chain motions (changes in configuration). Although there are obviously intermolecular as well as intramolecular contributions to this transition temperature, a high value of T_g is generally taken to suggest relatively high barriers to bond rotations.

The experimental results presented are discussed in terms of rotational isomeric state theory,[1-6,13] in which each rotatable skeletal bond is assumed to occur in one of a small number of discrete rotational states. Proper account is taken of the fact that there is an interdependence of bond rotational states about pairs of consecutive bonds in most chain molecules. The distributions of rotational states are primarily determined by intramolecular interactions, and it is these interactions which would be expected to give inorganic polymers configurational characteristics which are rather different from those of a typical organic polymer. The differences generally arise from the fact that bonds between many pairs of inorganic atoms are significantly longer than the C–C bond central to organic chemistry. Also, many of the skeletal bond angles in inorganic chains are considerably larger than the approximately tetrahedral angles present in the analogous organic compounds. Both circumstances tend to relieve the steric congestion frequently existing in organic polymers, particularly in those having relatively large side groups.[2] In fact, many conformations in inorganic chains place atoms or groups at distances of separation at which the interactions are significantly attractive rather than repulsive.[6,14]

The review concentrates on the most important results obtained in this area, with strong emphasis on simple physical pictures and on comparisons between the different types of inorganic polymers and between inorganic polymers and their organic counterparts.

Totally Inorganic Polymers

Polymeric Sulfur and Selenium. Linear chains of sulfur atoms [S–] (Figure 1) are of course totally inorganic and are of the simplest possible structure in that the chain atoms are all identical and bear no substituents or side chains. The S–S bond length l is 2.06 Å, and the S–S–S bond angle α is 106°. The rotational states are located at dihedral angles ϕ of $\pm$ 90° (relative to the assignment $\phi = 0°$ for the trans states shown in the sketch, with positive values corresponding to the rotation of a right-hand screw which advances it from left to right).[1,15] The barrier to rotation is the order of 10 kcal mol^{-1}, and the van der Waals radius of the S atom is approximately 1.80 Å.[1,15] The configuration of the sulfur chain in the crystalline state is a helix in which the rotational angles ϕ all have the magnitude 96° and are all the same sign.

Distances between neighboring atoms in all conformations are such as to give rise to favorable (attractive) dispersion forces. These interactions should be particularly large in the case of the most compact conformational pairs $\pm 90°$, $\mp 90°$; in none of these conformations are there severe steric overlaps.[1,15] Because of this preference for compact conformations, polymeric sulfur chains should have an unusually small value of the characteristic ratio, possibly less than unity. Unfortunately, an experimental value of the unperturbed dimensions with which to test this theoretical prediction is not yet available, and a reliable value may be very difficult to obtain because of the tendency of sulfur chains to undergo extensive reorganization. There are, however, reliable values of the dipole moments of a number of members of the polysulfide series R–S$_x$–R in which the R substituents are n-alkyl groups and x = 2, 3, and 4. Comparison of these experimental results with theory does lend support to the proposed model.[15] There is also an accurate experimental value for the standard entrophy of cyclization of polymeric sulfur to *cyclo* octasulfur (c-S_8). This entropy change is also calculable from the model,[1,15,16] using the cyclization theory of Jacobson and Stockmayer[17] as modified by Flory and Semlyen.[8] The agreement is found to be satisfactory. Additional calculations have been used to identify the constituents of a complex material S_π called Aten's sulfur,[18] to interpret conformational preferences in a variety of small molecules having S–S bonds and relative stabilities of cyclic sulfur compounds of varying ring size,[15] and to elucidate the self-depression of the melting point of elemental sulfur arising from the presence of significant amounts of cyclic sulfur molecules.[19,20]

The selenium chain [Se–] is structurally very similar to the sulfur chain shown and discussed above.[1,15] The values of the bond length, bond angle, and van der Waals radius are 2.34 Å, 104°, and 1.90 Å, respectively. Although the crystalline state configuration of the linear polymeric selenium is a helix in which all of the rotation angles are 78°, rotational states located at ±90° are probably preferable for the analysis of the selenium chain in its random-coil configurations. It is thought that the barrier to rotation about Se–Se bonds is roughly the same as that about S–S bonds. Values of T_g have been reported for polymeric selenium and sulfur,[21] but the likely presence of small molecules acting as plasticizer in these materials makes it difficult to use these results to obtain information on the relative barrier heights in the two polymers.

Distances between Se atoms in the [Se–] chain molecule are very similar to those in the corresponding conformations of the sulfur chain. The larger van der Waals radius and larger number of electrons of the Se atom therefore suggest that dispersion forces should be larger, that compact conformations should be more prevalent, and that the selenium chain should be even more compact than the sulfur chain.[15] This is indirectly substantiated by the fact that interpretation of the experimental value of the entropy of cyclization of *cyclo*octoselenium requires a smaller value of the characteristic ratio than does the interpretation of the same quantity in the case of the *cyclo*octasulfur.[15]

Polyphosphates. The linear polyphosphates $[PO_2O-]^-$ (Figure 2) are unusually interesting chain molecules in that they are totally inorganic, are polyelectrolytes, and consist of repeat units of great importance in biopolymeric materials such as the nuclec acids.[1,22] The P–O bonds making up the chain backbone have a length of 1.62 Å and are bonded at 130° at the O atoms and at 102° at the P atoms. Unequal bond angles frequently occur in inorganic polymers and have a pronounced effect on the configurational characteristics of the chains. This geometric feature causes the all-trans conformation of the molecule (often the form of lowest energy and thus of high frequency of occurrence) to approximate a closed polygon. For repeat units in which a pair of bond angles differ in magnitude by $\Delta\alpha$, the number of units required for an approximately closed figure is $2\pi/\Delta\alpha$. This number is ca. 13 in the case of the polyphosphate chains. The potential barrier hindering skeletal bond rotations is relatively small, probably less than 1 kcal mol^{-1}.[22] The rotational isomeric state model may nonetheless be used as a convenient approximation to the continuous range of accessible rotational angles.[1,13] For the polyphosphate chain, the required rotational states were located at $\phi = 0^\circ$ (trans, t), 120° (gauche positive, g^+), and -120° (gauche negative, g^-). Conformational energy calculations,[22] which included both steric and coulombic interactions, indicated that gauche states were of essentially the same energy as trans states when neighboring skeletal bonds remained trans. Consecutive pairs of gauche states (both $g^\pm g^\pm$ and $g^\pm g^\mp$) are, however, almost entirely suppressed by either steric interferences, coulombic repulsions, or both.

This relatively simple chain model was found to give a good account of the relatively high values of the characteristic ratio, 7.1 and 6.6, reported for lithium polyphosphate and sodium polyphosphate, respectively.[23] In brief, the isolated gauche states are readily accessible and represent departures from the closed polygon conformations of all trans states, which of course are of very small end-to-end distance. Gauche states occurring in pairs of opposite sign are *more* compact, but such pairs are suppressed by the interactions mentioned above. As a result, the polyphosphate chains are of rather high spatial extension.

Experimental[24] and theoretical[20,25] studies have also been carried out on cyclization in sodium phosphate, or "Graham's salt." Molar cyclization equilibrium constants have been reported for oligomeric molecules $(NaPO_3)_x$, where the degree of polymerization x was 3–7. The above rotational isomeric state model was used to obtain the probability that a polyphosphate chain of the specified length would cyclize intramolecularly by calculating the statistically weighted fraction of the total number of conformations which have the terminal atoms in sufficiently close proximity to form the bond completing the cyclic molecule. Calculations were carried out using direct enumeration techniques for all the possible conformations and, alternatively, using a Gaussian distribution function for the end-to-end distances. The calculated results were generally in satisfactory agreement with experiment.[20,25]

Poly(dihalophosphazenes). These polymers have the repeat units [PF$_2$N–], [PCl$_2$N–], and [PBr$_2$N–] and are represented by the general structure in Figure 3. The P–N and N–P skeletal bonds are apparently identical, with a length of 1.52–1.60 Å.[26,28,30] The N–P–N bond angle is 117–120° while the P–N–P angle is 130–136°; the all-trans conformations of the chains thus form closed figures after approximately 26 repeat units. These materials are all hydrolytically unstable and, as a result, relatively little is known about their conformations and spatial configurations. Much that is known has come from x-ray studies of the polymers in the crystalline state. The chains adopt nearly planar configurations consisting of alternating cis, trans states located at approximately 180, 0°, respectively.[26,31] The difluoropolymer exhibits an additional crystalline state configuration,[31] but it is not yet known whether this involves different rotational states or simply a different sequence of cis and trans states. In any case, there is as yet no evidence for other rotational states in these molecules. In fact, relatively little is known about the nature of the chemical bonding in the P–N–P backbone. Proper account of the P and N valence electrons suggests that the skeletal bonds should have some partial double bond character. The bonding,[26,28,32] however, may not be of the delocalized π type, which would give rise to severe restrictions to torsional rotations, judging from a variety of properties exhibited by these polymers. For example, their glass-transition temperatures are low,[26,30,33] ranging from −95 to −15 °C, and their NMR spectra suggest a great deal of torsional flexibility down to very low temperatures.[26] Furthermore, the polymers are in general highly elastomeric, particularly in the case of the dichloropolymer, which is known as "inorganic rubber".[34–36] Finally, conformational energy calculations,[30] which tentatively omit an inherent torsional potential, indicate that only very large substituents would significantly suppress rotational mobility. Also of interest is the fact that the calculations give a good account of the change in T_g as the halogen substituent is changed in the series F, Cl, Br.

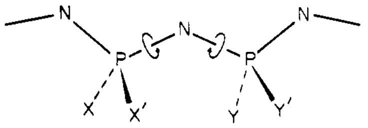

Figure 3.

Polyphosphazene chains in which the halogen atoms are replaced by organic groups are hydrolytically stable[26] and are thus of much greater interest and importance than the polymers briefly discussed above. These organophosphazene polymers are described in the first part of the following section.

Semiinorganic Polymers

Poly(organophosphazenes). These polymers can be prepared only through the rather unusual technique of substituting, essentially stoichiometrically, the desired organic groups for the halogen atoms of an already polymeric dihalophosphazene. The methods for accomplishing this have been developed by Allcock and co-workers,[26,27,29] who have also pioneered in the characterization and utilization of these materials. A variety of groups (represented by X, X′, Y, Y′ in Figure 3) have now been introduced. They include alkyl and aryl groups (e.g., C_2H_5 and C_6H_5), alkoxy and aryloxy groups (OCH_3 and OC_6H_5), amino groups ($NHCH_3$), and amino acid ester groups ($NHCH_2COOC_2H_5$).[26,27,29,37,38] Many of the organophosphazene polymers thus obtained have unique properties and include low-temperature and solvent-resistant elastomers, high-melting thermoplastics, flame-resistant fibers, and biocompatible or biodegradable materials.[26–29,39–41] If only one type of substituent is introduced ($X = X' = Y = Y'$), a homopolymer, usually crystalline, is produced. The introduction of more than one substituent generally produces a structurally complicated molecule. For example, the case $X = X' \neq Y = Y'$ corresponds to a chemical copolymer. A sequence having $X = Y \neq X' = Y'$ would be stereochemically rather than chemically copolymeric in the sense that the skeletal bonds would now be chiral. These two types of copolymers and combinations thereof are generally amorphous, because of the structural irregularities. They are generally also highly elastomeric.

The poly(organophosphazenes) have skeletal bond lengths and bond angles which are very similar to those occurring in the poly(dihalophosphazenes).[26,30,42] In addition, x-ray diffraction studies again indicate that the chains have alternating cis, trans sequences in the crystalline state.[29,43] The glass-transition temperatures are very low[42,44] and their general trends with changes in the nature of the side chains have again been at least partially interpreted by means of conformational energy calculations.[42] Additional evidence suggesting relatively free rotations comes from studies of some of these polymers in dilute solution.[28,40,45–48] Their viscosity–molecular weight relationships, for example, are typical of those of a randomly coiled polymer. Approximate interpretation of these results suggest further, however, that these random coils are of very high spatial extension; very tentative estimates of their characteristic ratios $\langle r^2\rangle_0/nl^2$ lie in the range 25–67.[47,48] Values of the temperature coefficient of $\langle r^2\rangle_0$ have also been

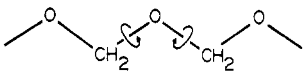

Figure 4.

determined from force–temperature measurements on networks of two organophosphazene polymers,[49] but they have not yet been quantitatively interpreted to provide information on the chain conformations. Much more experimental and theoretical work on the chemical bonding and configuration-dependent properties will be required in order to elucidate the highly unusual, and attractive, properties of this class of materials.

Polyoxymethylene. High molecular weight polyoxymethylene [CH_2O–] (Figure 4) has not been extensively studied with regard to the experimental determination of its configuration-dependent properties because of its very high melting point (200 °C).[50] It is an unusual inorganic polymer in that its skeletal bonds are relatively short (1.42 Å) and alternate skeletal bond angles are apparently identical and approximately 112°.[1,51,52] The energy barriers to rotations about the C–O bonds are well defined and separate rotational states located at approximately 0 and ±120° (t and g$^{\pm}$). The most interesting conformational feature of the molecule is its very strong preference for gauche rotational states. According to dipole moment measurements on the dimer and trimer,[53] the gauche states are approximately 1.7 kcal mol^{-1} lower in energy than the competing trans states.[1,51,52] The gauche states place oppositely charged O atoms and CH_2 groups separated by three bonds in closer proximity, but this effect would account for only a small part of the observed difference in energy. van der Waals attractions should also be relatively small, and thus the important preference for gauche states in this molecule is simply not understood at the present time.[1,52]

Consecutive pairs (g$^{\pm}$g$^{\mp}$) of gauche states of opposite sign are effectively excluded by "pentane-type interferences"[1] between either a pair of O atoms or between a pair of CH_2 groups separated by four bonds along the chain. The polyoxymethylene chain thus consists of relatively long successions $\ldots$ g$^{\pm}$g$^{\pm}$g$^{\pm}$g$^{\pm}$ $\ldots$, which correspond to helical sequences of approximately 9_5 symmetry (9 monomer units per 5 turns of the helix). The chains should therefore be of rather high spatial extension, and this has been verified by viscometric results which suggest the characteristic ratio to be in the range 8–12.[52,54,55] Increase in temperature should decrease the average helical sequence length, with a corresponding decrease in $\langle r^2 \rangle_0$, and this has also received qualitative verification.[52,54,55] The helical sequences, although of high spatial extension, are of very small dipole moment, because the CH_2OCH_2 group dipoles in the helix are in almost perfectly compensating orientations.[3] This mutual attenuation explains the relatively low value, ca. 0.2, reported for the dipole moment ratio of the polymer.[3,56]

Polyoxymethylene is rather different from the other polyoxides in the series [$(CH_2)_yO$–]. For example, the addition of another CH_2 group to the repeat unit to give polyoxyethylene [CH_2CH_2O–] disrupts the helicity and, as a consequence, the characteristic ratio decreases and the dipole moment increases.[3] The polyoxymethylene chain is obviously a highly constrained molecule in the statistical mechanical sense of being restricted to a small portion of configuration space[57] by its strong preference for gauche rotational states. It is much more highly constrained than is polyethylene and thus has a higher characteristic ratio in spite of the fact that the preferred conformation in polyethylene is the planar zig-zag form, which is the conformation of the highest possible spatial extension. Finally, polyoxymethylene has the highest melting point of any polyoxide [$(CH_2)_yO$–], and this may be related to its low degree of conformational randomness.[58] In any case it is the only one of these polyoxides which could be considered an inorganic polymer, and many of its properties do differ markedly from those of the other polymers in the polyoxide series.

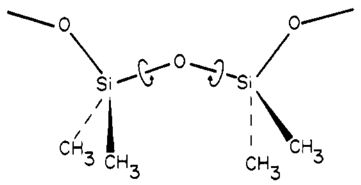

Figure 5.

Symmetrically Substituted Polysiloxanes. The first member of this series, poly(dimethylsiloxane) [$Si(CH_3)_2O$–] (Figure 5), has been more extensively studied, with regard to its configuration-dependent properties, than any other chain molecule. It is very similar to the polyphosphate chain in its structure. The Si–O bond length is 1.64 Å, and bond angles at the Si and O atoms alternate between the values 110 and 143°.[1,59] This inequality of bond angles causes the all-trans form of the molecule to form a closed figure after approximately 11 units. The torsional barriers are relatively low,[1,59] and this may account in part for the fact that this polymer has one of the lowest glass-transition temperatures, −127 °C,[60] reported to date.

Trans states are of lower energy than gauche states in this molecule. This conformational preference may arise from favorable van der Waals interactions between pairs of CH_3 groups separated by four bonds, in excess of favorable coulombic interactions between oppositely charged Si and O atoms separated by three bonds.[1,14,59] Comparisons between experimental and theoretical values of various configuration-dependent properties, however, yield a value for this energy difference which is significantly larger than that obtained from the usual semiempirical calculations of interaction energies between nonbonded atoms. Conformations (g$^{\pm}$g$^{\mp}$) giving rise to pentane-type interferences between the bulky $Si(CH_3)_2$ groups are completely excluded, and those in which the smaller O atoms are thus involved are suppressed to low incidence.[1,59]

Experimental values of the characteristic ratio of this molecule are in the range 6.2–7.6,[1,61] the precise value depending on the nature of the solvent used in the study of the polymer. The origin of this "specific solvent effect" is obscure[62] but may involve highly specific interactions between solvent molecules and polymer segments in a way which changes the conformational distribution in the chain. The effect is significant apparently only in the case of polar polymers. In any case, the characteristic ratio of poly(dimethylsiloxane) is known to increase with increasing temperature,[1,63–66] and this is to be expected since the lowest energy conformation is the closed polygon mentioned above. Comparisons between the experimental and theoretical values of the characteristic ratio and its temperature coefficient gave values of the chain conformational energies which were then used to predict a number of other configuration-dependent properties of these chains. Dipole moments[67–69] calculated in this way were found to be in excellent agreement with experiment in the range of small chain length; the agreement at longer chain length is less satisfactory, possibly because of the large specific solvent effects already cited. Stress-optical coefficients have also been determined for the polymer, using networks both unswollen and swollen with a variety of diluents.[11] Only very approximate qualitative agreement between theory and experiment was obtained, presumably because of

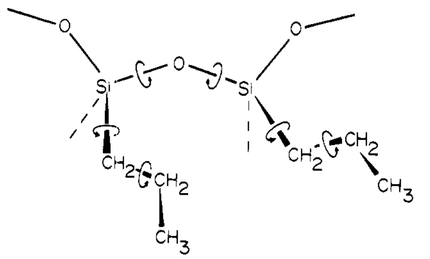

Figure 6.

the vanishingly small optical anisotropy of the poly(dimethylsiloxane) chain.

It is interesting to note that the poly(dimethylsiloxane) chain and the polyphosphate chain have approximately the same characteristic ratio. Isolated gauche states, of relatively high spatial extension, are more prevalent in the polyphosphate chain, but *pairs* of gauche states ($g^{\pm}g^{\pm}$) of the same sign are less prevalent and the two effects largely offset one another.

Much experimental and theoretical work has been done on the cyclization of dimethylsiloxane chains.[1,8,9,20,70–74] Although this property has been investigated over a very wide range in chain length, only the results in the limit of long chains will be discussed here. (The interpretation of the results for shorter chains may be complicated by failure of the Gaussian distribution function, directional correlations between terminal bonds prior to cyclization, ring-strain contributions to the heat of the reaction, and the necessity of revising some of the statistical weighting factors for the chains).[1,9,20,73,75,76] In the limit of large chain length, the agreement between theory and experiment is excellent[1,20] and thus in strong support of the proposed model for poly(dimethylsiloxane). In addition, the cyclization studies cited above have also provided useful information on excluded volume effects (their absence in the undiluted amorphorus state and their magnitude in solutions, particularly at high polymer concentrations), the critical chain length at which the Gaussian distribution function becomes unacceptably inaccurate, the magnitude of specific solvent effects, and the validity of gel permeation chromatography theories pertaining to both linear and branched chain molecules.

Other symmetrically substituted polysiloxanes have been much less thoroughly investigated. Poly(diethylsiloxane) $[Si(C_2H_5)_2O-]$ has been reported to have a characteristic ratio of 7.7 (±0.2),[77] which is essentially the same value as that of poly(dimethylsiloxane). Its dipole moment ratio is very difficult to measure because of the low polarity of the repeat unit, but it is also approximately the same as that of poly(dimethylsiloxane).[78] These tentative results, if confirmed, would be somewhat surprising since they suggest that this lengthening of the siloxane side chain must have effects on the dimensions and dipole moments which are self-compensating. Furthermore, poly(di-*n*-propylsiloxane) $[Si(C_3H_7)_2O-]$ (Figure 6) has been reported to have a very large characteristic ratio, specifically 13.0 ± 1.0.[79] High spatial extension in this chain could result from the fact that an articulated side chain such as $-CH_2CH_2CH_3$ could probably adopt more conformations in trans-gauche states along the chain backbone than in the more restrictive trans-trans states shown in the figure.[80] Although this "entropic destabilization" of compact trans states would increase the chain dimensions, one would not anticipate so large an increase in the characteristic ratio over that for poly(dimethylsiloxane). This intuitive conclusion[77] is supported by some very recent rotational isomeric state calculations[81] which do take into account the conformational variability of the siloxane side chains. It should be mentioned, however, that results of cyclization studies carried out on some stereochemically variable polysiloxanes[20] (see below) do suggest that the characteristic ratio increases with increase in length or size of the side groups.

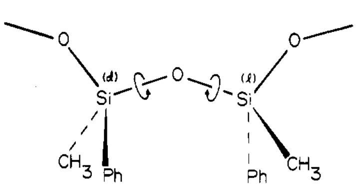

Figure 7.

Cyclization studies have also been carried out on the chemical copolymers poly(ethylene, dimethylsiloxane)[20,82] and poly(styrene, dimethylsiloxane).[20,83] There are numerous intramolecular interactions requiring characterization in a chemical copolymer[84] and, consequently, the results on the copolymers have been given only a preliminary interpretation in terms of rotational isomeric state theory. Cyclization calculations have also been carried out for poly(dihydrogensiloxane) $[SiH_2O-]$,[71] but there are as yet no experimental data available for comparison with theory.

Finally, melting point depression measurements have been conducted on several symmetrically substituted polysiloxanes, specifically the dimethyl,[85] diethyl,[86] di-*n*-propyl,[86] and diphenyl[87] polymers. Interpretation of such experiments yields entropies of fusion[7] and although it is very difficult to extract a reliable configurational entropy from this quantity,[88] such results could help elucidate the configurational characteristics of the chains thus investigated.[89]

Stereochemically Variable Polysiloxanes. In these unsymmetrically disubstituted chains, the substituents of one type can all be on the same side of the all-trans chain (the isotactic form), on alternating sides (the syndiotactic), or on either side in a random arrangement (the atactic). This stereochemical variability is illustrated by a syndiotactic sequence in poly(methylphenylsiloxane) $[Si(CH_3)(C_6H_5)O-]$ (Figure 7) in which the two Si atoms have arbitrarily been designated *d* and *l*, when the chain is traversed from left to right. As mentioned above, the relatively large Si–O bond length and Si–O–Si bond angle place apposed side groups at distances of separation (ca. 3.8 Å) at which there is a favorable energy of interaction. Conformational energy calculations[14] on this polymer indicate that the attractions should be particularly strong in the case of a pair of phenyl (Ph) groups and that the chains should therefore have a tendency to adopt conformations in which two phenyl groups are apposed on the same side of the chain. For the syndiotactic polymer this gives rise to a preference for gauche states, which confer relatively high spatial extension, but to a suppression of such states for the isotactic polymer. As a result, the characteristic ratio is predicted to be very small for the isotactic polymer and to increase monotonically and linearly with increase in the number of syndiotactic placements in the chain.[14] These results are quite different from those calculated for monosubstituted[1] $[CHRCH_2-]$ or disubstituted[90] $[CRR'CH_2-]$ vinyl chains, including the structurally analogous poly(α-methylstyrene) $[C(CH_3)(C_6H_5)CH_2-]$.[91]

A characteristic ratio of 8.8 was reported for two typical samples of poly(methylphenylsiloxane),[92,93] unfortunately of entirely uncharacterized stereochemical structure. This experimental result can be reproduced from the model only by assuming a relatively large fraction of syndiotactic placements;[14] the temperature coefficient predicted for this degree of syndiotacticity is then also in good agreement with experiment.[94] The assumption of significant syndiotacticity may be somewhat at variance with the results of cyclization studies,[95] which suggest that poly(methylphenylsiloxane) is typ-

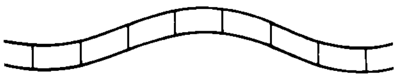

Figure 8.

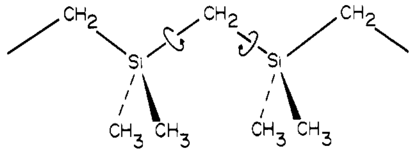

Figure 9.

ically essentially atactic. The cyclization results, however, yield a prediction for the characteristic ratio which is significantly larger than the experimental value cited above. The two tentative conclusions regarding the stereochemical structure might be brought into closer agreement by improving the calculation[14] of the interaction energy of two apposed phenyl groups to take into account the fact that they would be less exposed to favorable interactions with the solvent in such conformations. The effect is apparently quite important in polystyrene [$CH(C_6H_5)CH_2$–][96] but may be less so in poly(methylphenylsiloxane) because of the larger distance of separation between side groups in the siloxane polymers. Such revision could increase the number of isotactic placements which could be incorporated into the chain without decreasing its predicted value of the characteristic ratio to below its known experimental value. In any case, resolution of this point really requires reliable experimental values of the characteristic ratio, determined on poly(methylphenylsiloxane) samples of known stereochemical structure.

Cyclization measurements have also been conducted on other stereochemically variable polysiloxanes [$Si(CH_3)RO$–], where R was H, CH_2CH_3, $CH_2CH_2CH_3$, and $CH_2CH_2CF_3$.[81] The basic conclusions from these investigations were that such polymers are generally atactic in structure and that increase in the length or size of the side chains tends to increase the characteristic ratio.

Ladder Polymers. Siloxane polymers have also been prepared in a double-chain or ladder form (Figure 8) by joining the Si atoms of the two chains through Si–O–Si bonds.[97] A variety of ladder polymers of this type have now been prepared and partially characterized.[98] They are of considerable interest since they frequently exhibit enhanced chemical and physical stability, due to the fact that a double-chain molecule cannot be severed by cleavage of only one bond, or of even several bonds, unless two cleavages occur in two chain segments directly across from one another. Also, the decreased dynamic flexibility of such molecules should of course give unusually high glass-transition temperatures and thus rigidity up to temperatures at which most single-chain polymers would be elastomeric or liquid-like. Finally, crystallizable ladder polymers should have very high melting points (given by the ratio of the heat of fusion to the entropy of fusion), because of the greatly diminished configurational entropy of such double-chain structures.

Poly(dimethylsilmethylene). This polymer, [$Si(CH_3)_2$-CH_2–] (Figure 9), represents an interesting variation on the polysiloxane series. The Si–C bonds are 1.90 Å long and, in contrast to the siloxane chains, the two types of skeletal bond angles are nearly identical and approximately tetrahedral.[99] Most interesting is the fact that, since CH_2 and CH_3 groups have very similar intramolecular interactions,[1] this chain molecule should have some characteristics reminiscent of the idealized freely rotating chain.[7] This conclusion is supported by experimental evidence[100] indicating that the characteristic ratio of the polymer is relatively small and that both its unperturbed dimensions and dipole moments are essentially independent of temperature.

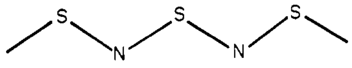

Figure 10.

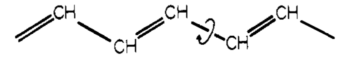

Figure 11.

Other Prospects

There are numerous other inorganic polymers which have already been synthesized[101] but have not been characterized with regard to their conformational and configurational characteristics. One totally inorganic polymer of particular interest, because of its metallic properties and superconductivity at low temperatures, is polymeric sulfur nitride [SN–][102–104] (Figure 10). This material is highly intractable and may be a rigid-rod polymer having alternating cis, trans states, with little or no conformational variability. The polyacetylenes [CH═CH–][105] (Figure 11) and their halogen derivatives[106] are not inorganic polymers but are mentioned here because they also have some metallic properties. The chains can be synthesized with the double bonds either trans (as shown) or cis. In either case, the polymer should not be highly intractable. Investigation of its configurational characteristics might therefore help to elucidate the highly unusual properties of both the [CH═CH–] and [SN–] polymers.

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