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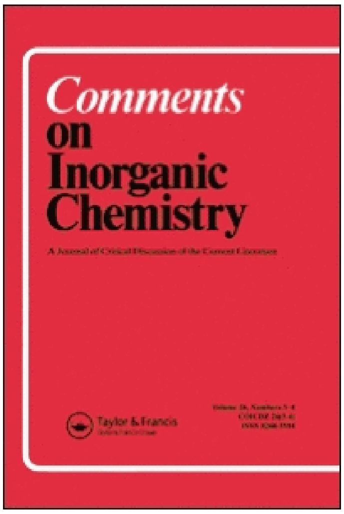

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Low Surface Energy Inorganic Polymers

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Most inorganic polymers have been developed for high thermal stability but there is considerable potential for obtaining low surface energy polymers as well. Semi-inorganic polymers with fluorocarbon and hydrocarbon pendent groups is the most promising area. The well-established example of silicone polymers is used to develop guidelines for such materials with an emphasis on low intermolecular forces between pendent groups and high chain flexibility. Polyphosphazenes are the most promising developing example and other possibilities include metallosiloxanes and metalloxanes.

Key Words: *low surface energy polymers, silicones, polydimethylsiloxane, polyphosphazenes, fluorocarbon-containing (semi-inorganic) polymers, low intermolecular forces, high chain flexibility, critical surface tension of wetting (of polymers), glass transition temperatures (of polymers)*

The search for new inorganic polymers has been in large measure a quest for materials more thermally stable than conventional organic polymers. However, if we examine the applications of well-established inorganic polymers such as the silicones, we see that it is not only durability aspects such as high temperature performance that are exploited but also their low surface energy properties. It seems likely that by focussing on heat resistant materials the potential for novel surface active polymers has been given insufficient attention. Occasional references to properties such as hydrophobicity encourage this speculation but there is an almost total

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dearth of quantitative surface chemical data for inorganic polymers other than the silicones and, to a very limited extent, the polyphosphazenes. By examining the fundamental reasons why silicone polymers have this desirable combination of surface activity and durability, guidelines should emerge for evaluating the surface activity possibilities of less well understood inorganic polymers.

The term inorganic polymer has several meanings. In principle it can be used in a very broad sense to include any polymer whose repeat unit has a substantial inorganic component. In practice we shall see that the major opportunity for new low surface energy polymers is in the "semi-inorganic" area, as it has been termed by Mark[1] and others, where the chain backbone contains no C–C bonds but the side chains are based on carbon. This semi-inorganic polymer area is the main concern of this Comment. Polydimethylsiloxane (PDMS) is the most familiar polymer of this type and that is the reason for starting with an appreciation of its properties. By understanding the surface properties of PDMS we should be in a better position to evaluate the surface activity possibilities of other inorganic polymers.

POLYDIMETHYLSILOXANE PROPERTIES

There are four fundamental characteristics of polydimethylsiloxane (PDMS), the most common silicone polymer, that account for many of its properties and uses. Two of them explain much of the physical behavior of PDMS in various environments whereas the other two account for the chemical consequences of the PDMS structure. These four characteristics are:

(i) The low intermolecular forces between the methyl groups
(ii) The unique flexibility of the siloxane backbone
(iii) The high bond energy of the siloxane bond
(iv) The partially ionic nature of the siloxane bond

Data relevant to these characteristics are given in Table I.

Low surface energy is a direct manifestation of low intermolecular forces between molecules. Table II shows the available range of these forces. The weakest intermolecular interactions known are the London dispersion forces associated with aliphatic hydro-

TABLE I

Selected properties of polydimethylsiloxane

Property	Value	Ref.
Critical surface tension of wetting	24 mNm^{-1}	2
Glass transition temperature	146 °K	3
Si-O bond energy	445 kJ mol^{-1}	4
Si-O bond polar character	41%	5

carbon and fluorocarbon groups. This is reflected in Zisman's critical surface tension of wetting (σ_c) studies[7,8] where lowest energy surfaces are those based on the constituent groups $-CF_3$, $-CF_2-$, $-CH_3$, $-CH_2-$, and the various mixed ones such as $-CFH-$ as shown in Table III. The critical surface tensions of polymers generally agree with expectations from Table III—see Ref. 2 for an extensive listing of reported values (all organic with the exception of organosilicon polymers). It is about forty years since this critical surface tension of wetting concept was introduced. It is not an absolute measure for solid surface energy but this is not the place to review the various controversies associated with this property and the many alternative approaches developed since. This lively debate has not changed the order of low surface energy constituent groups given in Table III. Thus among the hydrocarbons the lowest surface energy values are for surfaces comprising close-packed

TABLE II

Range of intermolecular interaction

	Bond Energy Range ($kJ \cdot mol^{-1}$)
Primary Bonds:	
Ionic	600-1000
Covalent	60-700
Metallic	100-350
Secondary Interactions:	
Hydrogen bonds	10-40
Other dipole/dipole	4-20
Dipole-induced dipole	1-2
London dispersion forces	0.1-40

Based on a table given by R. J. Good (Ref. 6).

TABLE III

Critical surface tensions of low-energy surfaces

Surface Constitution	σ_c at 20°C (mNm^{-1})
Fluorocarbon and fluorohydrocarbon:	
$-CF_3$	6
$-CF_2H$	15
$-CF_3$ and $-CF_2-$	17
$-CF_2-CF_2-$	18
$-CF_2-CFH-$	22
$-CF_2-CH_2-$	25
$-CFH-CH_2-$	28
Hydrocarbon:	
$-CH_3$ (crystal)	20–22
$-CH_3$ (monolayer)	22–24
$-CH_2-CH_2-$	31
$-CH-$ (in phenyl ring)	35
Chlorocarbon and chlorohydrocarbon:	
$-CClH-CH_2-$	39
$-CCl_2-CH_2-$	40
$=CCl_2$	43
Nitrated hydrocarbon:	
$-CH_2ONO_2$ (crystal) [110]	40
$-C(NO_2)_3$ (monolayer)	42
$-CH_2ONO_2$ (crystal) [101]	45

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methyl groups such as PDMS. The lowest surface energy polymers are those with aliphatic fluorocarbon pendent groups. The value of 10.4 mNm^{-1} for a fluoroacrylate polymer[2] is the lowest yet reported although values as low as 3–5 mNm^{-1} have been obtained for similar polymers.[9]

Because of the extreme localization of the fields of force in covalently bonded groups, the pendent methyl groups on PDMS behave as an array of close-packed methyl groups with little direct effect from the siloxane backbone despite its considerable polarity. The backbone has a major effect on the ease with which the pendent groups can be arrayed in the surface. The more flexible the backbone the more readily will the lowest surface energy configuration be adopted. In this grossly simplified view of the roles of backbone and pendent group, PDMS is seen as a particularly favored case of a very low surface energy pendent group arranged along the most flexible backbone, thus allowing the methyl groups to be presented to their best effect and accounting for the many surface applications of PDMS.

This idea that we can conceive of separate surface energies for each of the different parts of complex molecules, and that the surface energy of such a molecule is determined by the composition and orientation of the outermost groups independent of the underlying components, is due to Langmuir.[10] In his words, "the activity of a surface depends in general upon the nature of, the arrangement of, and spacing of the atoms forming the surface layer. The atoms forming the second layer below the surface are of importance only insofar as they determine the arrangement of the surface atoms." Zisman's wetting studies[7,8] show that this proposed principle of the independence of surface action does not always hold but is usually true to a good first approximation. Zisman[8] has used the principle to rank not only substituent groups as shown in Table III, but also individual atoms. The effectiveness of substitution of individual atomic species in increasing the wettability of organic surfaces is:

$$\mathrm{F} < \mathrm{H} < \mathrm{Cl} < \mathrm{Br} < \mathrm{I} < \mathrm{O} < \mathrm{N}$$

Siloxanes have the most flexible backbone among the common polymers. One reflection of this is the low glass transition temperatures of PDMS and other silicone polymers. This property should be a useful guide in seeking new low surface energy polymers. A comprehensive compilation is given in Ref. 3. There are several classes of polymers with members having glass transition temperatures lower than 200 °K other than silicones including polydienes, polyacrylates and polymethacrylates, polyacrylamides, polyvinylethers, polyoxides, polyesters, polysulfides and one other totally inorganic backbone, polyphosphazene. Possibly there could be more flexible inorganic backbones but to date most research has been directed towards increasing thermal stability. As this is usually achieved by increasing glass transition temperature using rigid backbones it follows that most backbone variation to date will have a detrimental effect on polymer surface activity and also that some flexible inorganic possibilities have been overlooked.

The two fundamental properties of low intermolecular forces and high chain flexibility explain most physical behavior of PDMS in various environments. The hybrid organic/inorganic nature of PDMS has chemical consequences that are primarily due to the other two key properties of the siloxane backbone, its high bond energy and partial ionic character. For instance, they are clearly responsible for the considerable thermal and oxidative stability of silicones. Because they do not directly affect the low surface energy material theme of this Comment they will not be considered here in detail. However, they relate directly to a very important point that a useful low surface energy polymer must not only have the right physical properties but have adequate stability. This is why a material such as polydiperfluoromethylsiloxane is useless. As the combination of the lowest surface energy pendent group on the most flexible backbone it might be a valuable material but it cannot be prepared because of its hydrolytic and thermal instability. For this reason practical interest has focussed on fluoroorganosiloxanes in which the fluorocarbon substituent is separated from the silicon, usually by two carbon atoms. This introduces a third entity into our polymer design, the linking group that is sometimes needed between a promising pendent group and a backbone.

A susceptibility to nucleophilic or electrophilic attack is a common weakness in inorganic polymers. Most feasible linkages resemble siloxanes in having higher bond energies than carbon systems but also having considerable ionic nature as a result of considerable electronegativity differences between constituent chain atoms. Since significant polarity is usually associated with stronger intermolecular interactions and hence higher surface energies it might appear that the quest for low surface energy polymers should be confined to organic, primarily covalently bonded structures. The example of PDMS shows that this need not be the case. Provided an adequate coverage of intrinsically low surface energy pendent groups is available the backbone can have considerable polar character. Recognition of this key point opens up a largely unexplored area of inorganic chemistry as far as surface chemists are concerned.

CRITERIA FOR LOW SURFACE ENERGY POLYMERS

Based on the preceding factors the general criteria for low surface energy polymers would seem to be:

(i) A flexible linear backbone
(ii) Sufficient pendent groups based on aliphatic hydrocarbon or fluorocarbon
(iii) Linking groups between the backbone and pendent groups that introduce no additional adverse factors
(iv) Combinations of these entities that are adequately stable and have no undesirable interactions

Criteria (iii) and (iv) need further explanation. A linking group that is too bulky could clearly compromise the ability of the polymer to adopt configurations that maximize close-packing of the pendent groups in the surface. Too polar a linking group might also have the effect of adding to the surface energy particularly if the pendent group is small. For example, there is an unresolved dipole at the $-CF_2-CH_2-$ link in many fluorinated polymers. The usual explanation for the decrease in surface tension as the perfluoro pendent group is lengthened is that this dipole is buried further from the surface.[7] Possibly a flexible linking group would be preferred to a rigid linking group to assist orientation of the low surface energy pendent groups.

The comment about undesirable interactions between the various components of the polymer is obviously specific to the particular choices made. Strongly reactive pendent groups and backbones will be incompatible even if adequately separated by the linking group because of the possibility of interaction between adjacent chains. The Russian worker, Lavygin,[11] who has provided much of the literature values, believes this is a factor in fluorosilicones. It may be why they have yet to live up to their potential as very low surface energy polymers. He believes coordination of fluorine and silicon atoms in adjacent molecules can increase molecular interaction and hence surface energy.

The lowest reported critical surface tension of wetting for a silicone material[2] is 14 mNm^{-1} for $CF_3(CF_2)_6CH_2O(CH_2)_3Si(OCH_2CH_3)_3$ hydrolyzed and reacted with a glass substrate. This is not as low as the fluoroacrylate polymer referred to previously, $[CF_3(CF_2)_6CH_2OCOCHCH_2]_n$, which has a critical surface tension of wetting of 10.4 mNm^{-1}. These two values can be compared in the light of the proposed general criteria for low surface energy polymers.

The fluorosilicone has the more flexible backbone but it is highly cross-linked by the nature of the hydrolysis of the triethoxy groups and this advantage is removed. Speculatively, linear polymers such as $[CF_3(CF_2)_6CH_2O(CH_2)_3RSiO]_n$, where R is another fluorinated group or possibly methyl, should have lower surface energies. Both polymers have the same perfluorocarbon entity so the $-CF_2-CH_2-$ dipole is buried to the same degree but the linking group in the fluorosilicone is larger although less polar than that in the fluoroacrylate. Both linking groups seem to be flexible. The carbon–carbon backbone is shorter than the siloxane backbone so there may be a lower density of fluorinated groups in the surface in the siloxane case particularly as the cross-linking has nullified the flexibility advantage of the siloxane. There is also the possibility of some detrimental silicon/fluorine interaction. The balance of these factors favors the fluoroacrylate case in regard to low surface energy.

These considerations raise a number of questions that are worth pursuing, including:

(i) Are there organic/inorganic structures in the literature that fit these criteria? It would be useful to take such materials, probably developed for other reasons, and confirm their surface activity by measurement.
(ii) Could one reverse the procedure and use the criteria to guide low surface energy polymer design? Advances in molecular modeling make this an attractive prospect nowadays.
(iii) Why is the siloxane backbone so flexible and what possibility is there of more flexible backbones being uncovered?
(iv) Similarly, why are aliphatic fluorocarbons of such low surface energy and could pendent groups with even lower intermolecular forces be developed?

Question (ii) is an interesting idea that will not be further discussed here. The other three questions are elaborated upon next.

PROMISING NEW POLYMERS

The low intermolecular force and high chain flexibility criteria essentially limit us to the area of linear semi-inorganic polymers. Although only a small part of the scope of inorganic polymers it is still of considerable extent and contains a number of possibilities for developing novel low surface energy materials. My particular list includes:

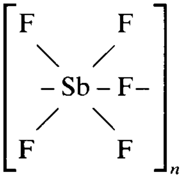
(i) Silicones, particularly more highly fluorinated fluorosilicones than are generally available today. The only fully commercial fluorosilicone is the first member of the series polytrifluoropropylmethylsiloxane.

(ii) Polyphosphazenes, particularly the fluoroalkoxy species. Their surface energy potential has been recognized but information is far less available than is the case for silicones.

(iii) Metallosiloxanes and metalloxanes. Known by a variety of names these are polymers whose backbone is M–O–Si or M–O–M where M is an element other than silicon. As with almost all inorganic polymer research the emphasis has been on thermal, thermo-oxidative, and hydrolytic stability.

(iv) Polyphosphates. Although no materials with suitable pendent groups have yet been developed this would seem to be a backbone of considerable flexibility[1] and an area worthy of fresh attention.

There are two other much more speculative areas that should be considered. One tantalizing challenge is to come up with a totally inorganic low surface energy polymer. Poly(antimony pentafluoride), is one possibility[12] although unfortunately it hydrolyses readily. Polymeric sulfur nitride is another possibility. It can be brominated.[13] Can it be fluorinated and what would be its surface



energy? The other area is to develop low surface energy pendent groups based on inorganic entities. These could be inorganic elements bearing organic groups such as Me_3Si- or Bu_3SnO- or purely inorganic entities such as SF_5- or IF_6-. This is elaborated on in the later section on speculative new inorganic pendent groups. One other area not included in this Comment that could also contain novel low surface energy polymers is the mixed inorganic/carbon backbones, particularly fluorocarbon. In this context one wonders what the surface energy of an unusual polymer such as $[C_4F_8Fe(CO)_4]_n$[14] would be.

Let us return to more immediate possibilities. The most promising are the fluorinated silicones and polyphosphazenes. A review is in press[15] of siloxane surface activity which provides more detailed information on fluorosilicones. The silicones and the polyphosphazenes are the only inorganic backbone polymers with glass transition temperatures (T_g) lower than 200 °K to appear in common compilations such as the Polymer Handbook.[3] It is not only internal mobility of the chains that determines T_g; polymer free-volume, attractive forces between molecules, bulkiness of pendent groups, and chain length all contribute. Nevertheless a low T_g indicates polymer flexibility. Table IV shows some reported T_g's for these two classes of semi-inorganic polymers.

TABLE IV

Glass transition temperatures of silicones and polyphosphazenes

Polymer	T_g (°K)	Ref.
$H(CH_3)SiO$	135	16
$C_2H_5(CH_3)SiO$	138	17
$(CH_3)_2SiO$	146	3
$C_3H_7(CH_3)SiO$	153	17
$C_6H_5(CH_3)SiO$	187	3
$(C_2H_5)_2SiO$	201	3
$CF_3(CH_2)_2(CH_3)SiO$	203	17
$(C_3H_7NH)_2PN$	181	18
$(C_2H_5O)_2PN$	189	18
$(CF_3CH_2O)_2PN(C_3F_7CH_2O)_2PN$	196	18
$(CH_3O)_2PN$	197	18
$(CF_3CH_2O)_2PN$	207	18
$(CH_3)_2PN$	227	19
$(CF_3C_6H_4O)_2PN$	238	18

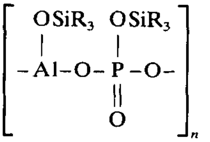
This comparison establishes that the phosphazene backbone is less flexible than siloxane; note particularly the two dimethyl substituted species which differ by 80 °K. Some of the polyphosphazene structures have great potential for low surface energy polymers. They are often qualitatively referred to as hydrophobic and proposed applications such as an antifoaming agent for $[CH_3O(CH_2)_2O]_2PN$ and biomedical uses for the perfluoroalkoxypolyphosphazenes strongly suggest low intermolecular interaction but there is almost no quantitative surface energy data yet available. One example is the aqueous solution surface tension data reported for water-soluble polyorganophosphazenes.[20] $[(CH_3)_2N(CH_2)_3NH]_2PN$ has considerable surface activity, lowering the surface tension of water to below 45 mNm^{-1}. This is not a remarkably low value as the hydrophobic and hydrophilic entities are too closely associated.

Poly[bis(trifluoroethoxy)phosphazene], $(CF_3CH_2O)_2PN$, is a promising low surface energy polymer. Films of the polymer show a high water repellency with a contact angle of 100° and a critical surface tension of 19.7 mNm^{-1},[21] lower than the comparable fluorosilicone, polytrifluoropropylmethylsiloxane (21 mNm^{-1} [22]). These two polymers have very similar glass transition temperatures. In terms of our criteria for low surface energy polymers the higher backbone flexibility of the silicone is evidently more than compensated by the presence of two fluorocarbon groups per monomer unit in the polyphosphazene and the more flexibilizing nature of the linking $-CH_2O-$ group compared to $-CH_2CH_2-$. Phosphazene units having longer perfluoroalkoxy side-chains such as $[CF_3(CF_2)_nCH_2O]_2PN$, where n is 2 or more, should be very interesting from a surface energy standpoint. The polymer with $n = 1$ has been described qualitatively as having a water repellency comparable to $(CF_3CH_2O)_2PN$.[21]

The Firestone Tire and Rubber Company product PNF is another one of the few polyphosphazene materials whose surface properties have been studied. Reichert[23] gives its structure as a random copolymer of $(CF_3CH_2O)_2PN$, $[HF_2C(CF_2)_xCH_2O]_2PN$ and $(CH_2{=}CHCH_2O)_2PN$ in an approximate ratio of 50:50:1 with x mostly 3 but with smaller amounts of 1,5,7. . . . He quotes a private communication from Baier giving the critical surface tension of wetting as 16.5 mNm^{-1}. This is in line with expectations from

Table III where terminal $-CF_2H$ groups give values of 15 mNm^{-1} and mixtures of $-CF_3$ and $-CF_2-$ give 17 mNm^{-1} (note that the very low value for $-CF_3$ is only achieved when on a sufficiently long perfluoro group to eliminate uncompensated dipoles). This is very encouraging as it implies that Zisman's ideas, developed from fluorinated organic polymers, apply very well to inorganic polymers. It also implies that highly fluorinated perfluoroalkoxy-polyphosphazenes with $-CF_3$ terminal groups in the side-chain will have very low surface energies, at least as low as any material yet reported. Strange that so little attention has been paid so far to their surface property characterization despite developing applications that closely parallel the uses of fluorosilicones.

The modified siloxane structure or metallosiloxane (Si–O–M) and metalloxane (M–O–M' where M' may be M or a different element) is also an attractive one. Some of the metal atoms carry no substituent groups so act as a diluent of the organic groups carried by the silicon, for example Si–O–Al containing species known variously as polyalumaorganosiloxanes or polyaluminoxa-organosiloxanes. Despite the dilution of the methyl groups some of these materials have low surface energy properties such as strongly water repellent effects. Borisov, Voronkov and Lukevits quote a few examples as well as an application as emulsifiers for siloxane oil–water systems.[24] Many others have R_3SiO- substituent groups on the M atom, for example[25]



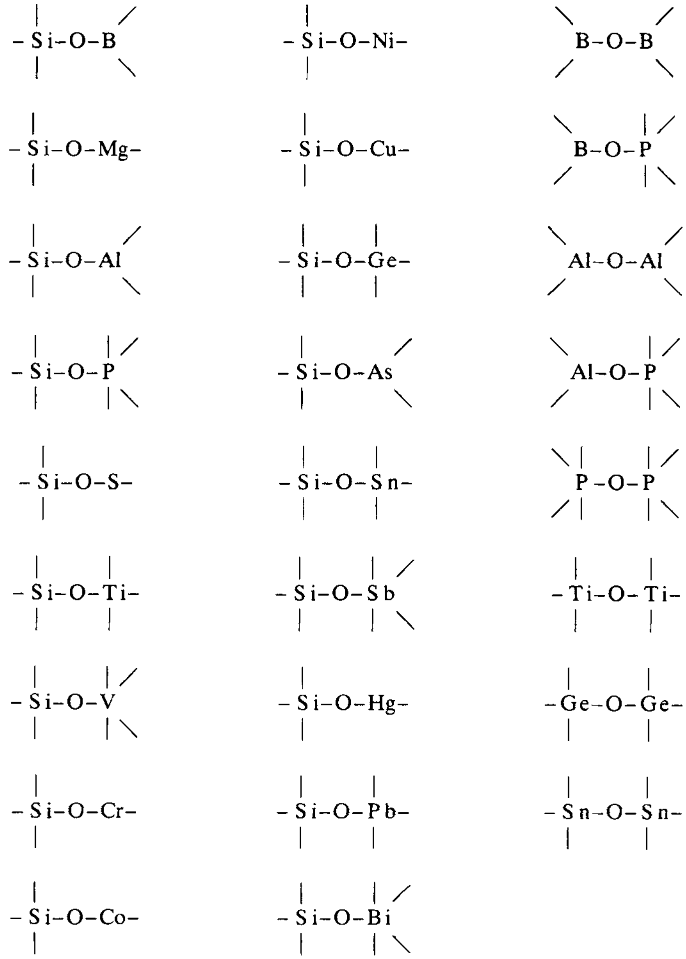
$$\left[\begin{array}{ccccc} \mathrm{OSiR_3} & & \mathrm{OSiR_3} & & \\ | & & | & & \\ -\mathrm{Al} & -\mathrm{O}- & \mathrm{P} & -\mathrm{O}- & \\ & & \| & & \\ & & \mathrm{O} & & \end{array}\right]_n$$

Many of these where R is methyl are likely to have surface energies similar to PDMS. R could also in principle, if not yet in practice, be fluorinated in analogous fashion to fluorosilicones, so many lower surface energy materials will be possible. More challenging would be a search for M atoms that could bear perfluorocarbon groups directly. Provided these had adequate stability they could eliminate the drawbacks associated with linking groups. They would also provide useful $(CF_3)_nM-$ type pendent groups. This is a virtually unexplored field wide open for some creative chemistry aided by molecular modeling design.

Table V lists many of the metallosiloxane and metalloxane linkages that have been studied as the basis of inorganic polymers to illustrate the wide range of options. Many of these come from Andrianov's summary of these polymers.[26] An even wider range

TABLE V

Metallosiloxane and metalloxane inorganic polymer backbone possibilities



Metallosiloxanes		Metalloxanes
-Si-O-B	-Si-O-Ni-	B-O-B
-Si-O-Mg-	-Si-O-Cu-	B-O-P
-Si-O-Al	-Si-O-Ge-	Al-O-Al
-Si-O-P	-Si-O-As	Al-O-P
-Si-O-S-	-Si-O-Sn-	P-O-P
-Si-O-Ti-	-Si-O-Sb	-Ti-O-Ti-
-Si-O-V	-Si-O-Hg-	-Ge-O-Ge-
-Si-O-Cr-	-Si-O-Pb-	-Sn-O-Sn-
-Si-O-Co-	-Si-O-Bi	

of Si–O–M heterocompounds has been reviewed by Borisov, Voronkov and Lukevits.[24] This is an area which Soviet scientists have dominated. The divalent oxygen linkage and the larger elements involved suggest considerable backbone flexibility. It may be that substituent group separation is so great in some cases that bulkier pendent groups will be required to fully obscure any direct polar backbone effects on surface energy. If this is achieved by branching, it will have the added merit of increasing the number of $-CF_3$ and $-CH_3$ groups which are more effective for lowering surface energy than $-CF_2-$ and $-CH_2-$. In this regard the trimethylsilyl group and short siloxane chains such as pentamethyldisiloxane could provide adequate methyl coverage. Silicon is not the only possibility either, for example such species as the tri-*n*-butyltin groups and partially fluorinated versions.

Note also that a parallel range of sulfur, selenium and tellurium linked backbones are possible in principle, some of which have been the subject of preliminary investigations,[24] for example Si–S–Ge, Si–Se–Ge and Si–S–Sn. The sulfur linkages should be the most interesting as the longer bond lengths involved with the larger atoms should increase the flexibility factor. Selenium and tellurium are larger still but enthusiasm is tempered by lower bond energies and probable toxicity problems with decomposition products. There are also materials where the linking atom is nitrogen as in Si–N–Sn and Si–N–Ti and hybrid organic/inorganic backbones such as $Si-(C)_n-Sn$, $Si-(C)_n-Mg$ and $Si-(C)_n-Al$ which may have some potential to be low surface energy materials but are not as promising as the "oxane" type and lie outside the main theme of this Comment. We know already in the organosilicon area that silazanes and silalkylene polymers have somewhat higher surface energies (several mNm^{-1}) than corresponding siloxanes.[15]

WHY IS THE SILOXANE BACKBONE SO FLEXIBLE?

Polymer chain flexibility depends on the nature, size and interaction of backbone, linking groups and pendent groups. Chain configuration is often treated in a statistical manner. Although a gross oversimplification, at the repeating backbone unit level molecular geometry must be the key factor, i.e., how far apart the elements are in the backbone and what angles the bonds between them form. As has been implied in the preceding discussion on metallosiloxanes and metalloxanes, longer backbone bonds should give rise to more flexible backbones. So too should larger, more open, bond angles. Alternating divalent elements carrying no sterically interfering side groups are also a major factor. Table VI lists the bond lengths and angles of a number of inorganic and organic polymer backbones. The data are taken from Mark's review,[1] averaged where a range was quoted, with the exception of the carbon backbone data which comes from an article by Aggarwal.[27]

Table VI shows why the usual carbon and carbon–oxygen organic backbones are less flexible than the inorganic siloxane backbone. It also explains why polyphosphazene and polyphosphate backbones have the promise to provide some interesting and useful low surface energy polymers. The siloxane backbone may be the most flexible established backbone to date but there are phosphorus containing polymers in Table VI that are approaching it in flexibility and there are probably structures in Table V that will exceed it.

WHY DO ALIPHATIC FLUOROCARBONS HAVE SUCH LOW INTERMOLECULAR INTERACTIONS?

There is as yet no convincing explanation why the $-CH_3$ and $-CF_3$ groups have such low intermolecular forces. Moreover it is not

TABLE VI

Polymer backbone bond lengths and angles

Polymer	Bond Length (nm)		Bond Angle (deg)	
Polyoxymethylene	C–O	0.142	C–O–C	112
			O–C–O	112
Polyethylene	C–C	0.153	C–C–C	112
Polyphosphazenes	P–N	0.156	P–N–P	133
			N–P–N	119
Polyphosphates	P–O	0.162	P–O–P	130
			O–P–O	102
Polydimethylsiloxane	Si–O	0.164	Si–O–Si	143
			O–Si–O	110

clear why the $-CF_3$ group is intrinsically of lower surface energy than $-CH_3$. The arguments for $-CH_3$ focus on the non-polar character of the C–H bond and emphasize the absence of polar interactions which, as seen in Table II, tend to be of higher energy than the lower end of the London dispersion force range. The arguments for $-CF_3$ are somewhat contradictory. Here the rather polar nature of the C–F bond is emphasized. Fluorine is the most reactive and most electronegative of the elements and all bonds with fluorine will have some polar character and it is usually asserted that the unique electronegativity of fluorine causes the electronic environment of fluorine, when bonded to elements such as carbon, to be very akin to that of the inert gas in the same period of the periodic table of the elements, namely neon. The inert gases have the lowest intermolecular interactions of any group of elements and their surface energies parallel the halogens, surface tension increasing with higher atomic weight just as the effect of halogen substitution causes an increase as we go from fluorine through chlorine to bromine.

Zisman[7] accounts for the unique non-wettability of fully fluorinated aliphatic hydrocarbons in this manner. He states that "The extreme surface properties of perfluoroaliphatic compounds arise from the extraordinarily weak field of force existing in the vicinity of covalently bonded fluorine atoms and its neighbors. Although this result agrees with the fact that fluorine has the lowest polarizability of the halogens, the fact that the field of force is so much weaker, even than that around the covalent hydrogen, deserves more explanation. Probably the explanation is in the values of the octapole moment or higher terms of the cohesive field of force rather than simply the polarizability. Another way of stating the case is that the local attractive fields of force giving rise to cohesive effects in perfluoromethane, the perfluoromethyl group, and in the perfluoromethylene group, are more like those of the inert gases than the field of force around methane, the methyl group, and the methylene group respectively."

This mystery still deserves more explanation. There remains the troubling aspect that the C–H bond is almost completely nonpolar whereas the C–F bond has considerable polarity. Hypothetically a X–H bond of comparable polarity to C–F might produce an electronic environment in hydrogen akin to helium, the element with the lowest energy of interaction. Only the larger alkali metals would have this kind of bond with hydrogen and being monovalent could not be part of a polymer pendent group. However, there are several X–F bonds of comparable polarity to C–F worthy of further study.

One intriguing possibility emerges from the calculations of Hoernschmeyer.[28] He has concluded that the van der Waals forces around analogous hydrocarbon and fluorocarbon moieties are very nearly the same. His view is that the differences in wettability can be ascribed to the size difference in the two groups which results in a lower concentration of attractive centers in the surface in the fluorocarbon case. If this is so, highly fluorinated, larger central atoms such as $-SF_5$ and $-IF_6$ that have very similar electronegativities to carbon might be good possibilities for intrinsically low surface energy pendent groups comparable to fluorocarbons.

The parallels between SF_6 and CF_4 such as high chemical stability and good electrical characteristics support such speculation. The comparable surface tensions of fluorocarbon and fluorosulfur compounds of similar volatility are also encouraging. Disulfur decafluoride and perfluoropentane both have boiling points of 29 °C. At 0 °C the surface tension of disulfur decafluoride is 13.9 mNm^{-1},[29] that of perfluoropentane is 11.8 mNm^{-1}.[30] The extrapolated value at 0 °C for sulfur hexafluoride is 5.6 mNm^{-1}.[31] Despite the attractive challenge of developing a purely inorganic very low surface energy polymer, possibly $(SF_5)_2PN$, it must be admitted that the greatest potential is in fluorocarbon substituent pendent groups on inorganic backbones.

CONCLUDING REMARKS

The silicone example shows that the problems associated with inorganic polymers, chiefly achieving adequate hydrolytic stability, can be solved and technologically useful materials produced. Most inorganic polymer development has been focussed on better thermal and oxidative stability compared to organic polymers with little regard to their surface properties. Silicones are known for their excellent environmental durability but also many of their applications stem from their low surface energy properties. This latter area is still a relatively unexplored one for other inorganic polymers.

As the lowest surface energy pendent groups available are aliphatic fluorocarbon and hydrocarbon, the most promising developments are occurring in the semi-inorganic polymer class. More highly fluorinated fluorosilicones and perfluoropolyphosphazenes in particular are currently of great interest. The area of metallosiloxanes and metalloxanes deserves a fresh look from a surface activity viewpoint also and the polyphosphate backbone should repay some further investigation.

While there seem to be several alternative ways of obtaining inorganic backbones of comparable flexibility to the siloxane backbone there is not such a promising variety of inorganic low surface energy pendent groups available. The only real possibility seems to be $-SF_5$ and it will take some creative chemistry to achieve a wholly inorganic polymer based on this group with adequate environmental stability and comparable surface properties to organic fluoropolymers.

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