Surface Tension of Poly[(3,3,4,4,5,5,6,6,6-nonafluorohexyl)methylsiloxane]

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ABSTRACT: The liquid surface tension of poly[(nonafluorohexyl)methylsiloxane] (PNFHMS) and the critical surface tension and solid surface tension of its cross-linked films have been measured. These properties are compared with the more familiar fluorosilicone, poly[(trifluoropropyl)methylsiloxane] (PTFPMS), other fluoro polymers, and poly(dimethylsiloxane) (PDMS). The liquid surface tension of PNFHMS is intermediate between that of PDMS and poly(hexafluoropropylene oxide). The critical surface tension (*n*-alkanes) is similar to that of poly(hexafluoropropylene), and the solid surface tension (Owens–Wendt approach, water and methylene iodide contact angle liquids) is in the range of the lowest surface tension fluoro polymers known. We believe these differences in liquid and solid surface tension of PNFHMS, observed also with PTFPMS, are significant and derive from different orientations in the two states.

Introduction

A large part of the commercial success of silicones since they were introduced nearly 50 years ago has been due to their ability to modify the surface properties of most common organic polymers. By far, the most common silicone material is poly(dimethylsiloxane) (PDMS). Central to its widespread use for surface modification is the fact that it has a lower surface tension than other hydrocarbon-based polymers. The reasons for the superior surface activity of PDMS have been reviewed recently.[1,2] Briefly PDMS is a particularly favorable case of intrinsically low surface energy pendent methyl groups arrayed along an extremely flexible siloxane backbone. The practical consequence of this surface activity is a variety of surface modification applications both as additives and applied coatings.

The growth of the silicone industry has not been confined to surface applications. For example, silicone elastomers and sealants are widely used for their environmental durability and high- and low-temperature properties. A general need is developing in some of these bulk silicone applications for further surface modification. Similarly silicone pressure-sensitive adhesives and silicone surfactants based on PDMS have been developed for specialty uses, and lower surface tension materials are required to function as release coatings and antifoam agents with them. Such materials should expand the silicone industry in the same way that PDMS-based additives have aided in the growth of the organic polymer industry.

Fluorosilicone polymers based on the siloxane backbone and side chains containing aliphatic fluorocarbon groups combine the most flexible backbone with the lowest surface energy pendent groups. Thus, in principle the ultimate low surface tension polymer should be a fluorosilicone, but in practice relatively few low surface tension fluorosilicones have been reported. Materials of the type $\{CH_3[CH_2CH_2(CF_2)_xF]SiO\}_n$ seem to be the most promising. Doeff and Lindner[3] have reported the surface tension characteristics based on *n*-alkane contact angle data for the polymers where $x = 3$, 6–8, and 10. They are of very low surface tension, comparable to the most surface-active fluoro polymers yet reported, with little variation in surface tension among them with the anomalous exception for $x = 8$. We have also been studying these materials. Some results for the polymer where $x = 1$ have already been reported.[4] Some new data for this polymer and a full contact angle characterization for the polymer where $x = 4$ are reported here. This polymer where $x = 4$ is a previously unreported polymer. It offers a promising compromise between the superior properties that come with incorporation of the longer fluorocarbon segment in the side chain and the increased cost and difficulty of polymerization associated with this modification. Our full characterization allows comparison with not only Doeff and Lindner's results but also other fluorosilicone polymers and other polymers including PDMS.

These polymers can be named in several ways. Doeff and Lindner termed them pseudo-perfluoroalkyl polysiloxanes; we prefer poly[(ethyleneperfluoroalkyl)methylsiloxanes]. More rigorously, because the first member of the series is best known as poly[(3,3,3-trifluoropropyl)methylsiloxane] (PTFPMS), we use this convention rather than the 1*H*,1*H*,2*H*,2*H* one. Thus, for $x = 4$ the polymer is poly[(3,3,4,4,5,5,6,6,6-nonafluorohexyl)methylsiloxane] (PNFHMS).

Experimental Section

Materials. The PNFHMS polymer was prepared from the corresponding cyclic trimer using trifluoromethanesulfonic acid as the catalyst and hexamethyldisiloxane as the end blocker. Vinyl group functionality to permit subsequent cross-linking and film formation was introduced in two ways; an α,ω-vinyl-end-blocked material by substituting 1,3-divinyltetramethyldisiloxane for hexamethyldisiloxane in the polymerization and a pendent vinyl functional material by incorporating the corresponding vinyl functional cyclic trimer. Polymerizations were usually carried out at 70 °C for 12–15 h and terminated by addition of calcium carbonate.

The (ethyleneperfluorobutyl)methylcyclosiloxane trimer was prepared by hydrolysis of (ethyleneperfluorobutyl)methyldichlorosilane. The resultant hydrolyzate was then mixed with KOH and reacted in a spinning band distillation column at reduced pressure to give the cyclic trimer. It is a stereoisomer mixture (usually 40% cis, 60% trans) with boiling points in the 150 °C (1.6 mmHg) to 159 °C (3.1 mmHg) range. The (ethyleneperfluorobutyl)methyldichlorosilane required for this reaction was prepared from $H(CH_3)SiCl_2$ and perfluorobutylethylene, which was obtained from Du Pont.

The hydrosilylation reaction was also used to obtain cross-linked coatings by coating glass slides with a 1,1,2-trichlorotrifluoroethane solution of the vinyl-functional PNFHMS polymer, poly[(trifluoropropyl)hydrosiloxane], and a catalytic quantity of hexachloroplatinic acid. These slides were then heated at 100 °C to evaporate the solvent and complete the cure.

The nonfunctional trimethylsilyl-end-blocked polymers were characterized by ^{29}Si NMR and differential scanning calorimetry (DSC). ^{29}Si NMR data were obtained on a Varian VXR 200 spectrometer with tetramethylsilane as the internal standard. The ^{29}Si chemical shift of the main-chain silicon was observed at −21.6 ppm for PNFHMS. The degree of polymerization (DP) could

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Table I
Surface Tensions (22 °C) of Contact Angle Test Liquids

	surface tension (σ_1), mN/m	dispersn force component ($\sigma_1{}^d$), mN/m	polar component ($\sigma_1{}^p$), mN/m
water	72.5	21.7	50.8
methylene iodide	49.4	48.1	1.3
hexadecane	27.6		
tetradecane	26.4		
dodecane	25.2		
decane	23.8		
octane	21.6		
heptane	20.1		
hexane	18.5		

be estimated from the integration ratio with the terminal silicon unit. DSC was carried out with a Du Pont 910 DSC at a heating rate of 10 °C/min in a helium atmosphere. A glass transition temperature of −75 °C was obtained for PNFHMS. This value is similar to that of PTFPMS (−70 °C[5]).

The cross-linked polymer coatings and the PTFPMS, which was an unfilled, high molecular weight, Dow Corning elastomer gum, were also characterized by ESCA using a cryopumped Perkin-Elmer Physical Electronics Model 550 ESCA/AES instrument with double-pass cylindrical mirror analyzer. A pass energy of 100 eV was used in conjunction with a Mg anode X-ray source. Raw spectral data were manipulated by using Physical Electronics version V MACS software.

Surface Tension Measurement. Liquid surface tensions were determined with a Rosano tensiometer based on a manual Roller–Smith precision balance with a platinum Wilhelmy blade calibrated by using distilled water, ethanol, and 50 mm^2/s viscosity PDMS fluid. This instrument was also used to check the purity of the contact angle test liquids. These values are listed in Table I. The polar and dispersion force components are given in the same ratio as those used by Owens and Wendt.[6] The water was distilled; other liquids were purchased 99% purity. Methylene iodide was lot-selected on the basis of surface tension, and the *n*-alkanes were percolated through an alumina powder bed.

Contact angles were measured on a Rame-Hart, Inc., NRL Model A-100 contact angle goniometer. Results quoted are the average of both sides measured several times of at least 5 drops in each case. When systematic changes in value with time were observed, the shortest drop ages, of the order of 20 s, were used. Such time dependency was particularly marked for the *n*-alkanes on PTFPMS. Only advancing contact angles on previously unwetted portions of the sample were taken. All contact angle and surface tension data were obtained at laboratory temperature, 22 ± 1 °C. The contact angle data are accurate to ±2°, and the liquid surface tension data, to ±0.1 mN/m.

The water and methylene iodide contact angle data were used to determine the solid surface tension of the coatings by the geometric mean technique described by Owens and Wendt.[6] The combined Owens–Wendt/Young equation is

$$\frac{\sigma_1(1+\cos\theta)}{2(\sigma_1{}^d)^{1/2}} = (\sigma_2{}^d)^{1/2} + (\sigma_2{}^p)^{1/2}\left(\frac{\sigma_1{}^p}{\sigma_1{}^d}\right)^{1/2} \qquad (1)$$

where θ is the contact angle and σ is surface tension. Subscript 1 refers to the contact angle test liquids and subscript 2 to the solid. Superscript d refers to the dispersion force component of surface tension and superscript p to the polar component. A plot of the quantity on the left-hand side of eq 1 against $(\sigma_1{}^p/\sigma_1{}^d)^{1/2}$ readily yields the solid surface tension from the intercept and slope. The *n*-alkane contact angle data were used to determine the critical surface tension in the familiar Zisman manner[7] from a rectilinear $\sigma_1/\cos\theta$ plot. The *n*-alkane data were also used to calculate the dispersion force component, $\sigma_2{}^d$, by the Girafalco–Good–Fowkes–Young equation (eq 2) as used by Doeff and Lindner.[3]

$$\sigma_2{}^d = \sigma_1(1+\cos\theta)^2/4 \qquad (2)$$

These various data are compared in the next section. The trends that result are useful and encourage some speculation regarding structure. The limitations of such comparison must be borne in mind. The liquid surface tension and the solid surface tension derived from contact angle study are not the same property. Neither are solid wettabilities based on different test liquids and assumptions. Thus, a priori numerical agreement between liquid surface tension, *n*-alkane critical surface tension, and water/methylene iodide solid surface tension is neither expected nor unexpected.

Table II
Liquid Surface Tension Comparison

	σ_∞, mN/m	*K*
n-alkanes	37.8	386
polyisobutylene	35.6	383
PTFPMS	27.1	290
n-fluoroalkanes	25.9	683
PDMS	21.3	166
PNFHMS	19.2	119
PHFPO	18.4	336

Results and Discussion

Liquid Surface Tension of PNFHMS. The average liquid surface tension of several 100 DP fluids, both trimethylsilyl and vinyldimethylsilyl end blocked, was 19.1 mN/m. At this chain length differences in end-group composition are negligible and surface tension does not vary much with molecular weight. These effects are more noticeable at lower molecular weight as described by the LeGrand and Gaines[8] equation:

$$\sigma = \sigma_\infty - K/M_n{}^{2/3} \qquad (3)$$

The surface tension of the methyl-end-blocked dimer $\{[CF_3(CF_2)_3(CH_2)_2](CH_3)_2Si\}_2O$ is 17.6 mN/m so approximate values of σ_∞ and K can be calculated for comparison with other liquid polymers as shown in Table II. Other values in Table II come from Wu[9] except PTFPMS, which comes from the 300 mm^2/s and 1000 mm^2/s viscosity fluid Dow Corning data sheet values and an unpublished viscosity/molecular weight correlation, and poly(hexafluoropropylene oxide) (PHFPO), which comes from Bernett and Zisman's[10] data on four oligomers of known DP. The table consists of values taken from data at temperatures between 20 and 25 °C. However, since the temperature variation of the surface tension of polymers is of the order of 0.05–0.1 mN/m deg^{-1}, the comparison is not significantly affected.

Given that the accepted order of decreasing wettability of surface constituent groups in solids is[7] $-CH_2-$, CH_3-, $-CF_2-$, CF_3-, it is not too surprising that PTFPMS has a higher liquid surface tension than PDMS. One methyl group has been replaced by two $-CH_2-$ groups (higher surface tension) and one CF_3- (lower surface tension). Moreover an uncompensated CF_2–CH_2 dipole has been introduced. The lower surface tension of PNFHMS than PDMS can be understood as three more $-CF_2-$ groups have been added compared to PTFPMS; and if the pendent groups are packed in the surface with the CF_3- groups outermost, the CF_2–CH_2 dipole will be more buried in the PNFHMS case than in the PTFPMS case.

We have argued previously[4] that such an orientation might not be so likely in the liquid state. There is considerable attraction between fluorine and silicon, and a looped configuration emphasizing $-CF_2-$ groups in the surface might be possible. Lavygin and co-workers[11] first suggested such an interaction. Asymmetric polymers with complex pendent groups such as PTFPMS and PNFHMS have the potential for varied orientation, but this is not the case with simple polymers such as poly(tetrafluoroethylene) (PTFE). The most surprising aspect

Table III
Effect of Heat Treatment on PNFHMS Surface Properties

	length of 100 °C treatment, h			
	2	3	8	18
PNFHMS A				
water contact angle, deg		111		116
methylene iodide contact angle, deg		93		94
hexadecane contact angle, deg		59		60
dispersion force component,[a] mN/m		10.1		10.2
polar component,[a] mN/m		1.4		0.6
total solid surface tension,[a] mN/m		11.5		10.8
PNFHMS B				
water contact angle, deg	110		113	115
methylene iodide contact angle, deg	95		98	98
hexadecane contact angle, deg	60		60	63
dispersion force component,[a] mN/m	9.2		8.2	8.4
polar component,[a] mN/m	1.9		1.5	1.1
total solid surface tension,[a] mN/m	11.1		9.7	9.5

[a] Using the Owens–Wendt approach and water and methylene iodide data.

of Table II is the σ_∞ value for the n-fluroalkanes (liquid analogue of PTFE) being higher than that for PDMS. This is not an extrapolation artifact; it has been decisively confirmed[12,13] but has yet to be satisfactorily explained. The K values in Table II are also interesting. The three siloxane polymers have lower values than the other polymers, a possible consequence of the unique flexibility of the siloxane backbone.

PHFPO is the lowest surface tension polymer we know of that is liquid at room temperature. Its orientation in the liquid or solid state is unknown, but examination of space-filling models plus the fact that its critical surface tension is higher than poly(hexafluoropropylene)[14] (PHFP) suggests the orientation is not one composed only of close-packed CF_3– groups. The relative closeness of the surface tension of PNFHMS and PHFPO suggest that the same is true for PNFHMS. Possibly a longer fluorocarbon side-chain polymer of this family than PNFHMS exists with a surface tension as low as or lower than PHFPO. Doeff and Lindner[3] report that the polysiloxanes with fluorocarbon side chains of length three and six carbons are translucent amorphous solids, but our polymer with a fluorocarbon side-chain length of four carbons is liquid even though our material is of longer chain length (DP is approximately 100 compared to approximately 30 for Doeff and Lindner). We suspect that the conditions of their addition of the perfluoroalkylethylene to the preformed poly(methylhydrosiloxane) are not as mild as they believe and that some bond rearrangement and cross-linking occurs.

Table IV
ESCA Data of Fluorosilicone Coatings

	length of 100 °C treatment, h	atomic composn, %			
		F	C	Si	O
PNFHMS	1	54.8	34.0	5.2	5.8
	2	54.6	33.2	5.6	6.4
	4	54.1	33.8	5.6	6.3
	8	54.4	33.9	5.3	6.2
	16	54.4	34.2	5.1	6.1
PNFHMS theory		50.0	38.9	5.6	5.6
PTFPMS[a]		38.1	40.7	10.1	11.1
PTFPMS theory		33.3	44.4	11.1	11.1

[a] Unfilled high molecular weight elastomer gum; data from ref 4.

Table V
n-Alkane Wettability

	PTFPMS	PNFHMS A	PNFHMS B
hexadecane, deg	51	60	63
tetradecane, deg	48	59	60
dodecane, deg	41	57	53
decane, deg	31	47	50
octane, deg		41	41
heptane, deg		35	35
hexane, deg		29	28
critical surface tension (σ_c), mN/m	21.4	16.1	16.3
linear correlation coeff	0.988	0.987	0.996

Table VI
Dispersion Force Component ($\sigma_2{}^d$) of Solid Surface Tension

	$\sigma_2{}^d$, mN/m	
fluorocarbon chain length	from eq 2 hexadecane single point	from eq 2 n-alkane multiple point
1 (PTFPMS)	18.3	19.2
3	14.5	18.0
4 (PNFHMS A)	15.5	16.0
(PNFHMS B)	14.6	15.9
6	11.9	19.1
7	12.5	19.0
8	18.3	21.8
10	11.5	19.5

Solid Surface Tension of PNFHMS. There is a slight dependence of contact angle and hence the derived solid surface tension of the cross-linked coatings on glass on the length of thermal treatment. This is shown in Table III where PNFHMS A is the α,ω-vinyl-functional polymer and PNFHMS B is the pendent vinyl-functional material. Increases of contact angle of siloxane polymer coatings with heat treatment on glass have been known for a long time. Hunter and co-workers[15] were the first to describe this phenomenon. The primary purpose of the heat treatment is to remove residual solvent, but some further cross-linking is probably also occurring. Conformational changes such as an increased number of polymer/surface adsorption sites due to adsorbed water removal may also be involved. We chose 100 °C as a temperature not so high as to cause thermal decomposition of the coating and reaction with the surface, effects noticed by Hunter and co-workers at higher temperatures.

The ESCA data in Table IV confirm that the coatings are not affected chemically by the heat treatment. There is no dependence of surface composition on time of treatment. We have also shown previously[16] that there is no variation in surface composition with cross-link density in the case of PDMS coatings. Table IV also contains previously reported ESCA data on PTFPMS.[4] Note that for both fluorosilicones the actual fluorine content is higher than expected, possibly reflecting greater uncertainties in the fluorine sensitivity factor, although within the accuracy of the ESCA method.

The surface tension data in Table III are quoted to 0.1 mN/m to illustrate the trends and in line with common practice to facilitate comparison, but the values are not so precise, probably of the order of ±1 mN/m.

Critical Surface Tensions. n-Alkane contact angles and calculated critical surface tensions are given in Table V for the PTFPMS gum and for the two cross-linked PNFHMS A and B polymers (longest heat-treated samples in Table III in each case). Octane, heptane, and hexane could not be measured on PTFPMS because of too rapid absorption and spreading. As with the data in Table III surface tension values are quoted to one decimal place but the accuracy is less than this. The calculated value is also

Table VII
Comparative Fluoro Polymer Surface Tension Data[a]

	n-alkane:			Owens–Wendt[b]				
polymer	σ_c, mN/m	θ_{H_2O}, deg	$\theta_{CH_2I_2}$, deg	$\sigma_s{}^d$, mN/m	$\sigma_s{}^p$, mN/m	σ_s mN/m	$\theta_{C_{16}H_{34}}$, deg	$\sigma_s{}^{d,c}$ mN/m
"Self-Assembled" Layers from Hydrolyzed Silane Solutions								
A		112					70	12.4
B	8.1	105	85	13.5	1.8	15.3	69	12.7
C	14–16	111–118						
D	16–18	104–110						
Preformed Polymers								
E	10.4							
F	10.6	120	98	9.1	0.3	9.4	74	11.2
G	11[d]							
H	11.1	118	97	9.3	0.5	9.8	73	11.5
I	11.4	113					71	12.1
PHFP	16.2	114	94	10.0	0.9	10.9	60	15.5
PNFHMS B	16.3	115	98	8.4	1.1	9.5	63	14.6
PTFE	18.5	108	88	12.5	1.5	14.0	46	19.8
PTFPMS	21.4	104	90	10.8	2.8	13.6	51	18.3
PDMS	24	101	70	21.8	1.0	22.8	36	22.6

[a] In some instances the data have been estimated from graphs in the original publications. Polymer A is from (1*H*,1*H*,2*H*,2*H*-heptadecafluorodecyl)trichlorosilane. Polymer B is from (1*H*,1*H*,2*H*,2*H*-tridecafluorooctyl)trichlorosilane. Data for polymers A and B are from ref 19. Polymer C is from [3-(1*H*,1*H*-pentadecafluorooctoxy)propyl]triethoxysilane. Polymer D is from [3-(heptafluoroisopropoxy)-propyl]trimethoxysilane. Polymer E is poly(1*H*,1*H*-pentadecafluorooctyl acrylate). Polymer F is poly(1*H*,1*H*-pentadecafluorooctyl methacrylate). Polymer G is ω-[*N*-(*n*-(perfluoroheptyl)undecanoyl)]poly(ethylenimine). Polymer H is poly[2-[*N*-propyl-*N*-(heptadecafluorooctyl)-sulfonamido]ethyl acrylate]. Polymer I is poly[1,4-bis(heptafluoroisopropoxy)-2-butene oxide]. σ_c data for polymers C–I, PHFP, PTFE, and PDMS come from ref 18, which contains original references to the other data shown in the table for these polymers. Water and methylene iodide data for PTFPMS come from ref 4. [b] See ref 6 and eq 1 (water and methylene iodide data). [c] See ref 3 and eq 2 (*n*-hexadecane data). [d] Contact angle test liquids not identified.

very dependent on which n-alkanes are used. For example, if only the same four alkanes as PTFPMS are used, the value for PNFHMS A rises to 17.9 mN/m and for PNFHMS B to 17.6 mN/m. If only hexadecane, tetradecane, and dodecane are used, an unrealistically low value of 1.7 mN/m is derived for PNFHMS A.

These n-alkane critical surface tensions of PTFPMS and PNFHMS are significantly higher than the solid surface tensions derived by the Owens and Wendt approach using water and methylene iodide. Most polymers show a reasonable agreement between critical surface tension and the Owens and Wendt dispersion force component ($\sigma_2{}^d$). This latter quantity can also be calculated by eq 2 as done by Doeff and Lindner[3] (they called it the dispersive surface energy). Table VI shows values calculated by using both the single data points from hexadecane and the multiple data points with the other n-alkanes, for PTFPMS, PNFHMS, and the other members of this series reported by Doeff and Lindner. The single-point hexadecane data can be directly compared, but caution is needed with the multiple-point data. We used a different selection of n-alkanes, which may bias the comparison, and as pointed out by Doeff and Lindner, solubility effects with the smaller alkanes are more pronounced than those with hexadecane.

Considering that the accuracy of these measurements is of the order of ±1 mN/n, our values for PNFHMS fit the Doeff and Lindner trend well. We also get a better agreement between the single- and multiple-point analyses and reasonable agreement with critical surface tension (Table V). Doeff and Lindner's data for these fluorosilicones show almost no dependence of surface tension upon side-chain length, but the inclusion of the first member of the series, PTFPMS, shows there is a considerable dependence at the short perfluorocarbon chain lengths. The effect is similar in type and magnitude to that seen with non-silicone fluorohydrocarbon polymers (see, for example, Bernett and Zisman's study[17]). They ascribe the effect to a progressive burial of the uncompensated electrostatic dipole at the CF_2–CH_2 link. Doeff and Lindner suggest that the very short side chain in the three-perfluorocarbon case does not adequately shield the hydrocarbon portion from the surface, leading to a slightly higher surface tension measurement. The same would seem to be true for the four-fluorocarbon PNFHMS case. Both these electrostatic and steric effects will be more marked in the shorter PTFPMS case. Note also that PTFPMS and the anomalous perfluorooctyl polymer in Doeff and Lindner's series have inexplicably similar values of $\sigma_2{}^d$ in Table VI.

Doeff and Lindner present specular reflectance infrared spectra supporting an orientation where the perfluoroalkyl chains are approximately parallel to one another and a surface comprised of CF_3– groups is formed. The fit of our n-alkane data to Doeff and Lindner's and the following general comparison with other fluoro polymers suggest this is likely to be the case as well for PNFHMS. This implies that the orientation of PNFHMS is not the same in the liquid and solid states. We have suggested before that this is also the case for PTFPMS and may be a general feature of these poly[(ethyleneperfluoroalkyl)methylsiloxane] polymers.

Comparison with Other Fluoro Polymers. A general comparative summary is given in Table VII. It contains other low surface tension fluorosilicones that we are aware of, the lowest surface tension fluoro polymers in Shafrin's critical surface tension compilation,[18] and the most familiar fluoro polymer, PTFE, and silicone, PDMS.

In terms of Owens–Wendt solid surface tension the values for PNFHMS reported here are the lowest fluorosilicone values and are close to the lowest known fluoro polymers (see polymer F in Table VII). In terms of critical surface tension and hexadecane wettability there are several lower surface tension fluorosilicones including longer fluorocarbon side-chain polymers of the same type reported by Doeff and Lindner. The fact that the perfluorooctyl anomaly in their series is not reflected in the behavior of the polymerized (ethyleneperfluorooctyl)-trichlorosilane (polymer B in Table VII) casts further doubt on the purity of this particular polymer of Doeff and Lindner or on the validity of its measurement.

From this n-alkane wettability perspective, PNFHMS is comparable to poly(hexafluoropropylene)[14] but significantly more wettable than the best of the fluoro polymers. Reasonable agreement is usually found between critical surface tension (*n*-alkanes) and the dispersion force component (σ_2^d) obtained by the Owens–Wendt approach (water/methylene iodide), but PTFPMS and PNFHMS are exceptional. Their critical surface tensions are significantly higher, probably because of *n*-alkane interaction with the methyl group present on every silicon. When this is absent, as in polymer B in Table VII, much lower critical surface tensions are possible.

Conclusion

Despite the pioneering wettability studies of Zisman[7] and co-workers and more recent compilation and rationalization of much data by Wu,[9] there are still unexplained aspects of polymer surface tension. From a siloxane polymer standpoint, PDMS is the standard. This has similar liquid surface tension, critical surface tension (Zisman, *n*-alkanes), and solid surface tension (Owens–Wendt, water/methylene iodide), but such uniformity is rare. Most polymers seem to have liquid surface tensions higher than their critical surface tensions and comparable dispersion force components (σ_2^d) to critical surface tension. PTFPMS and PNFHMS conform to this first generalization. PTFE does also, but PHFPO does not. PTFPMS and PNFHMS are exceptions to the second generalization, as are other fluoro polymers such as PTFE and PHFP. From an overall perspective the two fluorosilicone polymers described here resemble fluorocarbon polymers in their surface tensions. PTFPMS has very similar values to PTFE while PNFHMS is very much like PHFP. Other properties are very different. In physical form fluorocarbon polymers are intractable solids whereas in the un-cross-linked state these fluorosilicones are liquids.

Although the actual values for PNFHMS are lower than those of PTFPMS because of the higher degree of fluorination, the difference between the liquid and solid surface tensions of PTFPMS and PNFHMS can be explained by assuming different orientations in the two states. In the liquid state, $-CH_2-$ and $-CF_2-$ may play a more significant role than in the solid where motion of the pendent group in space is reduced and an orientation stressing external CF_3- may be induced. Comparisons with other fluoro polymers seem to support this view. The real unsolved mystery is why PTFE, which has fewer orientational possibilities, also has a similar difference in liquid and solid surface tensions. It may be a consequence of the considerable crystallinity of PTFE in the solid state inducing a close packing that is markedly disrupted in the liquid state. Owens and Wendt attributed the discrepancy to suspect values of the contact angles of methylene iodide. Their measurements suggested a value of 77° rather than Zisman's 88°. This may be so, although our own measurements favor the latter, original value.

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