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Surface Tension of Polysilanes

Polysilane polymers[1] are utilized industrially for the production of silicon carbide fibers[2] and show promising properties as ceramic precursors,[3] photoresists,[4] photoconductors,[5] nonlinear optical materials,[6] and initiators for free-radical reactions.[7] Many aspects of their behavior that are important for the applications mentioned above have been looked at, e.g., thermochromism,[8,9] photodegradability,[10] hole drift mobility,[11] crystallinity[12] and liquid crystallinity,[13] thermal stability, conductivity,[14] photoconductivity, and other structural, conformational, chemical, and spectroscopic characteristics.[1] Other properties that may play an important role if polysilanes are to be widely utilized in industry are yet to be investigated. These include, among others, density, refractive index, dielectric, mechanical, and surface properties.

Surface and interfacial energy are important for the control of practical applications such as spinning, polymer adhesion, stability of dispersions, wetting of solids, and spreading of polymer melts on solid surfaces. We report here the surface tension of a series of silane homo- and copolymers with a number of different alkyl and aryl substituents determined by contact angle measurements. Surface tensions were calculated by the geometric-mean method,[15] using the theory of fractional polarity[16] (or theory of surface tension components), which assumes that the surface tension, γ_s, can be separated into linear additive terms (eq 1);

$$\gamma_s = \gamma_s^d + \gamma_s^p \qquad (1)$$

γ_s^d is the nonpolar (dispersion) component and γ_s^p is the polar component, including dipole forces, induction forces, and hydrogen bonding.

The method is based on the contact angles of two or more testing liquids (in our case methylene iodide and water) and the geometric-mean equation,[17] which combined with Young's equation[18] gives eq 2,

$$(1 + \cos\theta_L)\gamma_L = 2[(\gamma_L^d\gamma_s^d)^{1/2} + (\gamma_L^p\gamma_s^p)^{1/2}] \qquad (2)$$

where θ_L is the contact angle obtained experimentally and γ_L^p, γ_L^d, and γ_L are the dispersion and polar components and the total surface tension for the liquid, respectively. When eq 2 is solved for two different testing liquids on the same polymer, partial values for surface tension of that polymer are obtained (γ_s^d and γ_s^p), which add to give the total surface tension γ_s for the polymer (eq 1).

Experimental Section. The measurements of contact angle were made by the sessile drop goniometric technique, with readings taken within about 15 s after drop motion stopped. Contact angles were measured on polymer films for two testing liquids (water and methylene iodide), and the values are listed in Table I. The polymer films were spin cast from 1% solutions in THF for 10 s at 2000 rpm (2 drops was added and spin cast for 10 s twice on the same slide). The films were dried under vacuum at 60 °C for 2 h and allowed to cool down to room temperature overnight. For each polymer, 6 drops was used (three on each slide), and two measurements were made on each drop totalling 12 measurements for each liquid.

Values of the contact angle were used to calculate the surface tension components for 15 polysilanes, polyethylene, and nylon, using eqs 1 and 2. The literature values of surface tension and its components for water and methylene iodide used in our calculations are listed in Table II.

Results and Discussion. Values of surface tension determined for polysilanes are shown in Table I, along with values calculated for the polar components, γ^p. It is immediately apparent that the surface tension of polysilane polymers is due almost entirely to dispersion forces, as expected, since the polysilanes contain no bonds with significant dipoles. Only in one "polysilastyrene" sample was the polar component, γ^p, found to contribute more than 1.1 dyn cm^{-1} to the total surface tension.

The total surface tension values for polysilanes vary, however, over a surprisingly large range from 28 to 50 dyn cm^{-1}. The lowest values are found for the peralkylpolysilanes, $(Alk_2Si)_n$. Surface tensions for these polymers are in the range observed for poly(1-alkenes)[20] and are higher than those for typical polysiloxanes.[20] It is reasonable that polysilanes should resemble hydrocarbon polymers rather than silicones. The polysilanes lack the extreme flexibility of polymer backbone shown by the polysiloxanes, which is crucial to their low surface energy.[21]

For polar carbon polymers such as alkyl acrylates,[22] increasing the length of alkyl substituent groups shields

Table I
Surface Tension of Polysilanes

polymer	contact angle, deg		surface tension, dyn/cm		$\bar{M}_w \times 10^{-3}$	ref
	θ_w	θ_m	γ	γ^p		
polyethylene[a]	98.9	54.1	32.4	0.3		
	102	*53*	*33.2*	*0*		24
poly(hexamethylene)adipamide[a]	68.7	42.3	42.	10.4		
	70	*41*	*43.2*	*9.1*		24
1. $[Si(n\text{-}Hex)_2]_n$	97.2	61.3	27.8	1.1	2500	25
2. $[Si(n\text{-}Pr)_2]_n$	97.2	69.1	28.6	1.1	500	26
3. $[Si(n\text{-}Bu)_2]_n$	104.0	60.2	29.2	0.1	1800	25
4. $[Si(cycloHex)Me]_n[SiMe_2]_{1.5n}$	103.9	59.8	29.5	0.1	900	27
5. $[PhSiMe]_n[SiMe_2]_{1.5n}$	87.5	54.0	32.3	2.9	900	28
6. $[Si(cycloHex)Me]_n$	101.0	50.5	34.2	0.6	800	25
7. $[(p\text{-}Tol)SiMe]_n$	92.0	41.7	39.0	0.8	75	25
8. $[PhSiEt]_n$	94.5	41.9	39.2	0.3	4	30
9. $[SiPh_2]_n[SiMe_2]_{1.13n}$	94.7	39.2	40.8	0.2	350	28
10. $[PhSiMe]_n$	96.4	39.2	41.2	0.1	190	25
11. $[PhSiMe]_{1.02n}[SiPh_2]_n$	89.0	32.6	43.4	0.9	7	30
12. $[(p\text{-}Tol)SiMe]_{1.78n}[SiPh_2]_n$	91.2	28.6	45.7	0.3	12	30
13. $[p\text{-}TolCH_2CH_2SiMe]_n$	84.2	21.2	47.5	0.9	50	30
14. $[PhO(CH_2)_3SiMe]_n$	89.4	16.9	49.7	0.2	100	30
15. $[SiPh_2]_n[PhCH_2CH_2SiMe]_{1.6n}$	88.2	10.8	50.9	0.3	300	29

[a] Values from the literature are shown in italics.

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Table II
Surface Tension (γ) and Dispersion (γ^d) and Polar (γ^p) Components for Water and Methylene Iodide[19]

	surface tension, dyn/cm		
liquid	γ	γ^d	γ^p
water	72.8	21.8	51.0
methylene iodide	50.8	49.5	1.3

the high surface energy polymer chain and substantially lowers γ. We see no such difference going from $(n\text{-Pr}_2\text{Si})_n$ to $(n\text{-Hex}_2\text{Si})_n$, but two n-propyl groups on each silicon are probably sufficient to shield the polysilane chain effectively. Surface tensions of polysilanes unshielded by organic groups have not been measured, but a series of liquid oligosilanes, $H(SiH_2)_nH$ where $n = 3$–7, have been studied.[23] These liquids have surface tensions somewhat higher than those of the analogous hydrocarbons. There is no evidence from our results that the high polarizability expected for polysilane chains is important in increasing surface tension. However, it is interesting that the $(\text{cycloHexSiMe})_n$ in which the polysilane chain is believed to be stiffened by the cyclohexyl substitution shows a higher surface tension than the n-alkyl compounds.

As seen from Table I, the surface energy of polysilanes is significantly increased by aryl substitution. Aryl groups, which confer increased polarizability, also raise the surface tension of other classes of polymers such as polyalkenes and polysiloxanes; compare for instance the surface tension of polyethylene,[24] 33.2 dyn cm^{-1}, with that of polystyrene,[24] 42 dyn cm^{-1}. Among the polysilanes studied, the surface tension generally increases as the degree of arylation increases. Aryl groups separated from the silicon, for instance, in β-phenethyl groups, appear to be even more effective at raising γ than aryl groups directly attached to silicon. Perhaps this is because these remote aryl groups, attached to the silicon chain by a flexible "tether", can adopt a conformation in which they are very effectively presented to solvent molecules. The highest surface energy was found for the copolymer $(\text{SiPh}_2)_n(\text{PhCH}_2\text{CH}_2\text{SiMe})_{1.6n}$, which had $\gamma = 50.9$ dyn cm^{-1}. Introduction of a polar oxygen in the side chain produced only a slight additional effect; the polymer $(\text{PhOCH}_2\text{CH}_2\text{CH}_2\text{SiMe})_n$ showed a surface tension only slightly greater than $(p\text{-TolCH}_2\text{CH}_2\text{SiMe})_n$.

These results indicate that polysilanes have a wide range of surface tensions, depending on their alkyl or aryl substitution. On the basis of what we have found, it seems possible to construct polysilanes with yet higher and lower surface energies, and attempts to do this are now under way.

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Registry No. $\text{Cl}_2\text{Si}(n\text{-Hex})_2$ (homopolymer), 97036-67-4; $\text{Si}(n\text{-Hex})_2$ (SRU), 94904-85-5; $\text{Cl}_2\text{Si}(n\text{-Pr})_2$ (homopolymer), 125457-09-2; $\text{Si}(n\text{-Pr})_2$ (SRU), 96228-25-0; $\text{Cl}_2\text{Si}(n\text{-Bu})_2$ (homopolymer), 97036-65-2; $\text{Si}(n\text{-Bu})_2$ (SRU), 95999-72-7; $(\text{Cl}_2\text{Si}(\text{cycloHex})\text{Me})(\text{SiMe}_2\text{Cl}_2)$ (copolymer), 88993-02-6; $(\text{Cl}_2\text{SiPhMe})(\text{Cl}_2\text{SiMe}_2)$ (copolymer), 70158-17-7; $(\text{Cl}_2\text{Si}(\text{cyclohex})\text{Me})$ (homopolymer), 88002-85-1; MeSicyclohex (SRU), 88003-16-1; $(\text{Cl}_2\text{Si}(\text{Me})p\text{-Tol})$ (homopolymer), 88002-79-3; $(\text{Si}(\text{Me})p\text{-Tol})$ (SRU), 88003-11-6; $(\text{Cl}_2\text{SiPh}_2)(\text{Cl}_2\text{SiMe}_2)$ (copolymer), 70926-75-9; $(\text{Cl}_2\text{Si}(\text{Ph})\text{Et}$ (homopolymer), 108926-58-5; $(\text{Si}(\text{Ph})\text{Et})$ (SRU), 110839-65-1; $(\text{Cl}_2\text{Si}(\text{Ph})\text{Me})$ (homopolymer), 31324-77-3; $(\text{Si}(\text{Ph})\text{Me})$ (SRU), 76188-55-1; $(\text{Cl}_2\text{Si}(\text{Ph})\text{Me})(\text{Cl}_2\text{SiPh}_2)$ (copolymer), 98387-81-6; $(\text{Cl}_2\text{Si}(p\text{-Tol})\text{Me})(\text{Cl}_2\text{SiPh}_2)$ (copolymer), 130699-97-7; $(\text{Cl}_2\text{Si}(\text{Me})(\text{CH}_2)_2p\text{-Tol})$ (homopolymer), 130699-98-8; $\text{Si}(\text{Me})(\text{CH}_2)_2\text{-}p\text{-Tol}$ (SRU), 130700-00-4; $(\text{Cl}_2\text{Si}((\text{CH}_2)_3\text{OPh})\text{Me})$ (homopolymer), 130699-99-9; $\text{MeSi}(\text{CH}_2)_3\text{OPh}$ (SRU), 130700-01-5; $(\text{Cl}_2\text{SiPh}_2)(\text{Ph}(\text{CH}_2)_2\text{SiMe})$ (copolymer), 99635-05-9; water, 7732-18-5; methylene iodide, 75-11-6; polyethylene (homopolymer), 9002-88-4; poly(hexamethylene adipamide) (SRU), 32131-17-2.