Journal of Organometallic Chemistry, 449 (1993) 105–109

JOM 23372

Measurement of surface tension for polysilanes

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(Received July 28, 1992)

Abstract

From contact angle measurements using water and methylene iodide, surface tensions for solid films of 35 poly(silylene) polymers were obtained using the geometric-mean method. The surface tensions of poly(silylene)s depend strongly on the nature of the substituent groups, and span a very wide range from 25.0 to 52.8 dyne cm^{-1}. Particularly high values were found for poly(aralkylsilylene)s. Surface tensions for two polysilanes were also measured by the equation of state method, giving results in good agreement with those obtained by the geometric-mean method.

1. Introduction

The polysilane polymers [1], or poly(silylene)s, show many interesting properties such as thermochromism [2], photodegradability [3], hole drift mobility [4], and nonlinear optical properties [5]. In addition they are being considered for various technological applications, as photoresists [6], charge-transport materials [7], optical materials [5] and free-radical initiators [8]. Although information about surface properties of polysilanes would be important for many commercial applications of these materials, this aspect of their behavior has received little attention to date. The situation is quite different for the other important class of organosilicon polymers, the siloxanes. Here, the surface phenomena, one of crucial importance for many applications have been intensively studied [9].

In an earlier communication [10], we reported the surface tension values of 15 polysilane polymers, calculated by the geometric-mean method [11]. Here we report surface tension measurements of 20 additional polysilanes bringing the total number of samples investigated to 35. For two polysilanes, $(PhMeSi)_n$ and $[(PhCH_2CH_2)_2Si]_n$, the surface energy was calculated by the equation of state method as well as the geometric-mean method [12]. The data allow generalizations to be drawn concerning the surface energies of different polysilanes as well as comparisons with other families of polymers, polysiloxanes [9], polyacrylates [13], and polyesters [14].

2. Experimental section

2.1. Materials

Homo- and co-polysilanes were synthesized from corresponding disubstituted dichlorosilanes by Wurtz-type coupling reactions [15–28]. Polymerizations were usually carried out at 110°C for 2 h. The polymer films were spin cast onto glass slides from 1% solutions in THF for 10 s at 2000 rpm (2 drops of the solution were added and spin cast for 10 s, twice on each slide). The films were dried under vacuum at 60°C for 2 h and allowed to cool down to room temperature overnight.

2.2. Surface tension measurement

The measurements of contact angle were made by the sessile drop goniometric technique, with readings taken about 15 s after drop motion stopped in the ambient environment. Measured values of contact angles for the polymer films are listed in Tables 1 and 2. Distilled, deionized water was used; other liquids were purchased with 99% purity. For each polymer, 6 drops

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0022-328X/93/$6.00

were used (three on each of two slides) and two measurements were made on each drop totalling 12 measurements for each liquid.

For most of the polymers, surface tensions were calculated by the geometric-mean method, using the theory of fractional polarity [29], which separates the surface tension γ_s, into linear additive terms (eqn. (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 [13], which combined with Young's equation [30] gives eqn. (2):

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

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 eqn. (2) is solved for two different testing liquids on the same polymer values are

TABLE 1. Surface tension of polysilanes

Polymer	Contact angle (degrees)		Surface tension (dyne/cm)		$Mw \times 10^{-3}$	Ref.
	θ_w	θ_m	γ_s	γ_s^p		
Polyethylene [a]	92.6	47.4	34.7	1.0		
	102	*53*	*33.2*	*0*		15
Poly(hexamethyleneadipamide) [a]	68.7	42.3	42.2	10.4		
	70	*41*	*43.2*	*9.1*		15
1 $[\mathrm{CF_3CH_2CH_2(Me)Si}]_n$	97.3	66.8	25.0	1.7	10	16
2 $[\mathrm{CF_3CH_2CH_2(Me)Si}]_n[(^{n}\mathrm{Pr})\mathrm{MeSi}]_m$ [c]	104.2	62.1	27.6	0.2	414/24	17
3 $[(^{n}\mathrm{Pr})_2\mathrm{Si}]_n$ [b]	97.2	69.1	28.6	1.1	500	18
4 $[(^{c}\mathrm{Hex})\mathrm{MeSi}]_n[\mathrm{Me_2Si}]_{1.5n}$ [b]	103.9	59.8	29.5	0.1	900	19
5 $[(^{n}\mathrm{Hex})_2\mathrm{Si}]_n$	101.4	57.9	29.9	0.3	2500	20
6 $[(^{n}\mathrm{Bu})_2\mathrm{Si}]_n$	100.2	57.2	30.3	0.4	1800	20
7 $[(^{n}\mathrm{Hex})(^{n}\mathrm{Bu})\mathrm{Si}]_n$	104.7	57.8	30.3	0	2000	21
8 $[\mathrm{Ph(Me)Si}]_n[\mathrm{Me_2Si}]_{1.5n}$ [b]	87.5	54.0	32.3	2.9	90	22
9 $[(^{c}\mathrm{Hex})\mathrm{MeSi})_n$ [b]	101.0	50.5	34.2	0.6	800	20
10 $[(^{n}\mathrm{Hex})_2\mathrm{Si}]_n[(^{n}\mathrm{Bu})_2\mathrm{Si}]_n$	106.1	49.5	36.0	0.1	1120	23
11 $[(^{n}\mathrm{Pr})\mathrm{MeSi}]_n$	105.4	46.3	37.9	0.1	90	20
12 $[(p\text{-}\mathrm{Tol})\mathrm{MeSi}]_n$ [b]	92.0	41.7	39.0	0.8	75	20
13 $[\mathrm{Ph(Et)Si}]_n$ [b]	94.5	41.9	39.2	0.3	4	24
14 $(\mathrm{Ph_2Si})_n(\mathrm{Me_2Si})_{1.13n}$ [b]	94.7	39.2	40.8	0.2	350	22
15 $[(\mathrm{PhMe_2Si})\mathrm{MeSi}]_n$	96.5	34.0	43.2	0.1	13	23
16 $[\mathrm{Ph(Me)Si}]_n$	97.5	32.1	43.3	0	190	20
17 $[\mathrm{Ph(Me)Si}]_{1.02n}[\mathrm{Ph_2Si}]_n$ [b]	89.0	32.6	43.4	0.9	7	24
18 $[\mathrm{Ph(Me)SiSiMe_2}]_n$	87.4	28.2	45.0	2.0	600/4	26
19 $[(p\text{-}\mathrm{Tol})\mathrm{MeSi}]_{1.78n}[\mathrm{Ph_2Si}]_n$ [b]	91.2	28.6	45.7	0.3	12	24
20 $[\mathrm{PhCH_2CH_2}(^{n}\mathrm{Bu})\mathrm{Si}]_n$	95.6	27.9	45.9	0	322/11	17
21 $[\mathrm{CH_2{=}CHCH_2(Me)Si}]_n[\mathrm{Ph(Me)Si}]_{3.0n}$	92.4	23.3	47.3	0.2	115	27
22 $[(p\text{-}\mathrm{Tol})\mathrm{CH_2CH_2(Me)Si}]_n$ [b]	84.2	21.2	47.5	0.9	50	24
23 $[(\mathrm{PhCH_2CH_2CH_2})_2\mathrm{Si}]_n$	97.2	24.4	47.7	0	921/3	17
24 $[(\mathrm{bi\text{-}Ph})\mathrm{MeSi}]_n[\mathrm{Ph(Me)Si}]_m$ [d]	88.8	20.5	47.8	0.5	44	24
25 $[\mathrm{PhCH_2CH_2(Me)Si}]_n$	98.0	23.4	48.3	0	370	6
26 $[\mathrm{PhCH_2CH_2(Me)Si}]_n[\mathrm{Ph(Me)Si}]_{1.24n}$	93.1	20.6	48.3	0.1	400	20
27 $[(\mathrm{PhCH_2CH_2CH_2})_2\mathrm{Si}]_n[\mathrm{Ph_2Si}]_{1.8n}$	90.5	17.4	48.9	0.2	435/5	17
28 $[(\mathrm{bi\text{-}Ph})\mathrm{MeSi})]_n$	95.9	20.1	49.0	0	80	20
29 $[\mathrm{PhOCH_2CH_2CH_2(Me)Si}]_n$ [b]	89.4	16.9	49.7	0.2	100	24
30 $[(\mathrm{PhCH_2})_2\mathrm{Si}]_n[\mathrm{Ph_2Si}]_{1.6n}$	91.8	7.9	51.1	0.1	11	17
31 $[(\mathrm{PhCH_2CH_2})_2\mathrm{Si}]_n[\mathrm{Ph_2Si}]_{2.3n}$	95.0	9.1	51.6	0	171/3	17
32 $[(\mathrm{PhCH_2})_2\mathrm{Si}]_n$	94.2	7.6	51.6	0	5	17
33 $[(\mathrm{PhCH_2})_2\mathrm{Si}]_n[(\mathrm{PhCH_2CH_2})_2\mathrm{Si}]_{2.0n}$	93.9	4.1	51.9	0	2	17
34 $[(\mathrm{PhCH_2CH_2})_2\mathrm{Si}]_n$	97.3	7.3	52.4	0.1	271	17
35 $[\mathrm{PhCH_2CH_2(Me)Si}]_{1.6n}[\mathrm{Ph_2Si}]_n$	103.6	9.9	52.8	0.4	300	28

[a] Values from the literature are shown in italics; [b] data published previously in ref. 10; [c] ratio n/m could not be determined accurately; [d] ratio n/m could not be determined accurately but is near 1.0.

obtained for γ_s^d and γ_s^p, which add to give the total surface tension γ_s for the polymer (eqn. (1)).

Values of the contact angle were used to calculate the surface tension components for 35 polysilanes, polyethylene, and nylon, using eqns. (1) and (2). The literature values [15] of surface tension and its components were used for water ($\gamma_s = 72.8$, $\gamma_s^d = 21.8$, $\gamma_s^p = 51.0$) and for methylene iodide ($\gamma_s = 50.8$, $\gamma_s^d = 49.5$, $\gamma_s^p = 1.3$).

Surface tensions of polyethylene, poly(phenylmethylsilylene) **16** and poly(diphenethylsilylene) **34** were determined also by the equation of state method, which is based on measuring contact angles for a series of testing liquids to obtain a spectrum of critical surface tension, $\gamma_{c,\phi}$ by using a proposed equation of state, eqn. (3). Equation (3) is obtained by combining eqn. (4) which is based on Young's equation, the equation of Good and Girifalco [31] and the definition of critical surface tension (eqn. (5)) [32].

$$\cos\theta = 2(\gamma_{c,\phi}/\gamma_{Lv})^{1/2} - 1 \tag{3}$$

$$\cos\theta = 2\,\phi(\gamma_s/\gamma_{Lv})^{1/2} - 1 - (\pi e/\gamma_{Lv}) \tag{4}$$

$$\gamma_{c,\phi} = \lim_{\theta \to 0} \gamma_{Lv} \tag{5}$$

Here θ is the equilibrium contact angle, $\gamma_{c,\phi}$ is the critical surface tension, and γ_{Lv} the surface tension of the liquid in equilibrium with its saturated vapor; ϕ is called the interaction parameter, and π_e is the equilibrium spreading pressure. Since $\phi_{max} = 1$ when the polarities of the two phases are equal, eqn. (3) gives

$$\gamma_{c,\phi_{max}} = \gamma_s - \pi_e = \gamma_s \tag{6}$$

When the $\gamma_{c,\phi}$ spectrum is plotted versus the polarity of the testing liquids, a smooth curve should be obtained, having the maximum $\gamma_{c,\phi_{max}} = \gamma_s$. However, since the polarities of many testing liquids are unknown, $\gamma_{c,\phi}$ may instead be plotted *versus* γ_{Lv}. The liquid surface tensions of test solvents are listed in Table 2.

3. Results and discussion

The surface tension values for polysilanes, measured using the geometric mean method, are shown in Table 1 in order of increasing γ. The polysilanes exhibit a wide range of surface tension values, from 25.0 to 52.8 dyne cm^{-1}, depending on their substituents.

3.1. Fluoroalkyl substituents

Fluorinated polysilanes **1** and **2** show the smallest values of surface tension, much lower than for the non-fluorinated equivalent polymer **11**. Fluoroalkyl groups are well known to decrease surface tension, for example in poly(alkene)s [33] and polysiloxanes [34]. In homopolymer **1**, the polar component γ_s^p is slightly increased compared with **11**, perhaps due to the CF_3 group; the dispersion component γ_s^d decreased with decreasing polarizability. In the copolymer 2, γ_s^d also decreased when compared to polymer **11** but no increase of γ_s^p was observed.

3.2. The length of side chain

Surface tensions of poly(n-alkylsilylene)s apparently decrease as the alkyl chain becomes longer, to a limiting value near 30 dyne cm^{-1} as found for the di-n-butyl polymer. It may be that longer side chains provide more effective shielding of the polarizable silicone backbone. A very short side chain, as in $[(^n\mathrm{Pr})\mathrm{MeSi}]_n$ **11** then leads to higher surface tension. Similar effects are observed for poly(alkylacrylate)s [35]. Increasing the length of the alkyl side chain also decreases the surface tension for poly(alkylarylsilylene)s (compare **13** and **16**) and poly(alkylaralkylsilylene)s (compare **20** and **25**).

3.3. Aryl and aralkyl substituents

Aryl substituents are known to increase the surface tension value for polymers [11]. Polyarylsilanes also

TABLE 2. Calculation of critical surface tension spectra for polyethylene and polysilanes

Liquids	γ_{LV} (dyne cm^{-1})	Polyethylene		$[\mathrm{Ph(Me)Si}]_n$		$[(\mathrm{PhCH_2CH_2})_2\mathrm{Si}]_n$	
		θ (deg)	$\gamma_{c,\phi}$ (dyne cm^{-1})	θ (deg)	$\gamma_{c,\phi}$ (dyne cm^{-1})	θ (deg)	$\gamma_{c,\phi}$ (dyne cm^{-1})
hexane	18.4	10.2	18.1				
tetrachoroethylene	31.7	10.0	31.2			10.8	31.1
dimethylformamide	37.3	38.6	29.6	24.8	22.6		
pyridine	38.0	26.6	34.1	8.9	37.5	8.9	37.5
tritolyl phosphate	40.9	31.8	35.0	22.8	37.8	21.6	38.1
bromonaphthalene	44.6	36.1	36.5	9.0	44.1	11.6	43.7
methylene chloride	50.8	47.4	35.7	32.1	43.3	7.3	50.4
formamide	58.2	69.4	26.6	74.2	23.5	72.6	24.6
glycerol	63.4	76.0	24.4	78.8	22.6	77.9	23.2
water	72.8	92.6	16.6	97.5	13.8	97.3	13.9

TABLE 3. Calculated surface tension of $[Ph_2Si]_n$

Copolymer	γ (dyne cm^{-1})	X_1	γ_1 (dyne cm^{-1})	X_2	γ_2 (obtained) (dyne cm^{-1})
$[(PhCH_2)_2Si]_m[Ph_2Si]_n$	51.1	0.38	51.1	0.62	51.1
$[(PhCH_2CH_2)_2Si]_m[Ph_2Si]_n$	51.6	0.30	52.4	0.70	51.3
$[(PhCH_2CH_2CH_2)_2Si]_m[Ph_2Si]_n$	48.9	0.36	47.7	0.64	49.6

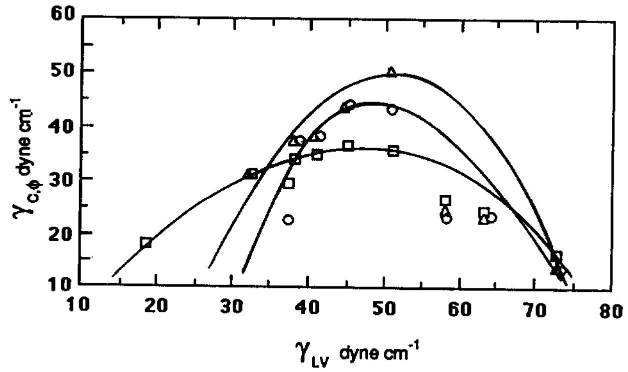

Fig. 1. Equation of state plots for polyethylene and polysilanes (□——□: polyethylene; △——△: $[(PhCH_2CH_2)_2Si]_n$; ○——○: $[Ph(Me)Si]_n$.

show higher values than those of polyalkylsilanes (compare $[Ph(Me)Si]_n$ **16**: 43.3 dyne cm^{-1}, $[(^nPr)MeSi]_n$ **11**: 37.9 dyne cm^{-1}). The size of the aromatic substituent also affects the surface tension, as seen in poly(biphenylmethyl)silane **28** (γ = 49.0) and poly(phenylmethyl)silane **16** ($\gamma = 43.3$). Still higher values of γ were observed for aralkylsilane polymers. As mentioned earlier [10], aryl groups attached to the silicon chain by a flexible spacer, a methylene chain, may adopt a conformation in which they are very effectively presented to solvent molecules. The surface tensions for many of these polymers even exceed those for polystyrene and Nylon 66. The maximum surface tension is found for the phenethyl silanes, such as $[(PhCH_2CH_2)_2Si]_n$, $\gamma = 52.4$ dyne cm^{-1}. Copolymers of aralkyl and diphenylsilylene units also showed very high surface tensions. The γ values depend somewhat on the length of the alkyl spacer between the aryl group and the polysilane chain. The same order, peaking at phenethyl, is observed for both the homopolymer and copolymer series:

$$[(PhCH_2CH_2CH_2)_2Si]_n < [(PhCH_2)_2Si]_n < [(PhCH_2CH_2)_2Si]_n$$

$$[(PhCH_2CH_2CH_2)_2Si]_m[Ph_2Si]_n < [(PhCH_2)_2Si]_m[Ph_2Si]_n < [(PhCH_2CH_2)_2Si]_m[Ph_2Si]_n$$

Poly(diphenylsilylene) is highly insoluble and crystalline, so its surface tension could not be obtained directly by contact angle measurements. However the surface tension for $(Ph_2Si)_n$ could be estimated from the values for copolymers **27**, **30**, and **31** and the corresponding homopolymers **23**, **32**, and **34**, using eqn. (7) [36].

$$\gamma = X_1\gamma_1 + X_2\gamma_2 \tag{7}$$

Here γ is the surface tension of the copolymer, X_1 and X_2 are the mole fractions of diphenylalkyl and diphenyl units, γ_1 refer to the surface tension of the homopolymer and γ_2 to the presumed surface tension of $(Ph_2Si)_n$. Data are shown in Table 3; the values of γ_2 average to 50.7 dyne cm^{-1}.

3.4. The equation of state method

The surface tensions were also measured for polyethylene and for polysilanes **16** and **34** by using the equation of state method. Table 2 gives the critical surface tension values $\gamma_{c,\phi}$. Equation of state plots are shown in Fig. 1 with smooth curves drawn through the points. The maximum $\gamma_{c,\phi}$ of the curve is defined as the surface tension of the solid γ_s. The values of $\gamma_{c,\phi_{max}}$ are 36.5, 44.1 and 50.4 dyne/cm, respectively which are close to those obtained by the geometric-mean method (Table 4).

TABLE 4. Comparison of solid surface tensions obtained by the geometric-mean method and the equation of state method

Polymer	Surface tension, γ_s (dyne cm^{-1})	
	Equation of state method	Geometric-mean method
Polyethylene	36.5	34.7
$[Ph(Me)Si]_n$	44.1	43.3
$[(PhCH_2CH_2)_2Si]_n$	50.4	52.4

4. Conclusions

Unlike the polysiloxanes, which show generally low values of surface tension, the polysilanes exhibit surface tensions which vary widely depending on the substituents present on the chain. Values from about 25 to more than 50 dyne cm^{-1} were obtained (Table 1). Poly(dialkylsilylene)s with relatively long alkyl chains have surface energy similar to those for hydrocarbon polymers. Surprisingly high values of γ were found for polysilanes bearing aryl or aralkyl substituents. The group most effective in raising the surface tension was phenethyl, $PhCH_2CH_2$, perhaps because the two-carbon tether allows effective presentation of the aromatic ring at the polymer surface.

Acknowledgments

This work was supported by the Air Force Office of Scientific Research, Air Force Systems Command, USAF, under Contract No. AFOSR-89-0004. T.F. thanks Sekisui Chimical Co. for their support.

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