Surface Tension of Polysilanes Having Oxyethylenic Side Chains

Kunio Oka,* Naofumi Fujiue,† Saburo Nakanishi,† Toshikazu Takata,† Takaaki Dohmaru,
Chien-Hua Yuan,†† and Robert West††
Research Institute for Advanced Science and Technology, University of Osaka Prefecture, 1-2 Gakuencho, Sakai, Osaka 593
†Department of Applied Chemistry, College of Engineering, University of Osaka Prefecture, 1-1 Gakuencho, Sakai, Osaka 593
††Department of Chemistry, University of Wisconsin, 1101 University Avenue, Madison, WI 53706, U.S.A.

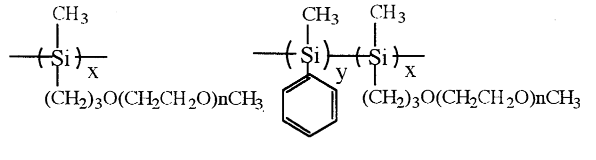
(Received June 27, 1995)

Polysilanes having oxyethylenic side chains, $\{CH_3\text{-}Si\text{-}CH_2CH_2CH_2O(CH_2CH_2O)_mR^1\}_n$ where (m=0,1,2,3) and R^1=CH_3 and C_2H_5, have been prepared. A polysilane of m=3 and R=CH_3 is soluble in alcohols, acetonitrile, and water. Surface tensions of these polysilanes are larger than those of the polysilanes ever reported. While dispersion component stays almost constant(ca. 30-40 dyn/cm), polar component increases with increasing oxygen atom numbers in the side chain. Copolymers also keep the high values of surface tension.

Polysilanes are a new class of material having unusual optical and electronic properties which comes from delocalized sigma electrons along silicon catenated chain.[1] Studies of the physical properties are essentially important for the industrial application of polysilanes. Surface property, which relates closely with addhesibility and wettability, is one of the important factors for the application of polysilanes as the advanced material. Data of surface property of polysilanes, however, are available only for limited number of aryl and/or alkyl-side chain homopolymers and copolymers.[2,3]

Polysilanes with polar side-chains are expected to improve surface properties. Polymers having etherial[4,5] and oxyethylenic side chain[6-8] have been reported to show poly(ethylene oxide)-like behavior. The introduction of oxyethylenic side chains may give additional function to polysilanes. We report here the preparation and the surface properties of polysilanes having oxyethylenic side chains.

Polysilanes **1**-**6** were prepared by Wurtz coupling reaction of the corresponding dichlorosilanes.[6,9] Polysilanes **2-4** are elastic solid and become soluble in alcohols when the side chain substituent involves more than two oxygen atoms. Polysilane **4** is even soluble in THF, alcohols, acetonitrile, and water. As shown in Table 1, the yields and the molecular weights of **1-4** were not satisfactory enough. To improve the molecular weight and the polymer yield and also to see the effect of methylphenylsilylene units on the surface tension, copolymerization with methylphenyldichlorosilane (monomer ratio = 1:1) was attempted. Polysilanes (**7-11**) thus obtained kept almost the same monomer unit ratio as the starting monomers. The yields, molecular weights, and UV spectroscopic data are summarized in Table 1. Absorption maxima (around 300 nm in THF) and the molecular weights(>10^4) in Table 1 indicate that the prepared materials have intrinsic properties of polysilanes.



Homopolymer #	n	R	**Copolymer** #	n	R
1	0	CH_3	**7**	0	CH_3
2	1	CH_3	**8**	1	CH_3
3	2	CH_3	**9**	2	CH_3
4	3	CH_3	**10**	3	CH_3
5	0	C_2H_5	**11**	0	C_2H_5
6	0	C_6H_5			

Surface tensions were calculated by the geometric-mean method[10] by using equations 1 and 2 where Θ_L is the contact angle, γ represents the surface tension and superscripts d and p correspond to the dispersion and polar components, and

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

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

subscripts L and S donate liquid and solid phases, respectively. The polar component includes dipole forces, induction forces, and hydrogen bonding.

The contact angles for water and diiodomethane and the surface tensions calculated thereby are summarized in Table 1.[11] The surface tensions for polysilanes ever reported[2,3] range from 25 to 52.8 dyn/cm, similar to most conventional polymers.[12] Polysilanes listed in Table 1, thus, have notably high surface tensions: homopolymers **2, 3** and **4** and copolymers **9** and **10** have higher surface tensions than those for the other reported polysilanes. The value increased with increasing polarity of the side chain. Since γ^d for polysilanes without phenyl group do not exceed 40.5 dyn/cm,[2,3] the unusually high surface tensions of polysilanes in Table 1 are attributed solely to the large values of γ^p. Previous papers reported that γ^p of surface tension of various alkyl- and/or arylpolysilanes was negligible(< 1 dyn/cm).[2,3] Our result is highly contrast to the previous report: γ^p is comparable to γ^d in homopolymers **3** and **4** and copolymers **9** and **10.** The more oxygen atoms in the side chain, the higher surface tension of the polysilane. In extreme case, γ^p of polysilane **4** (39.2 dyn/cm) becomes larger than γ^d (35.0 dyn/cm), and is almost comparable to the surface tension of poly(oxymethylene) (43 dyn/cm)[13] in which the main chain solely consists of the same unit as our side chain. The total surface tension of **4** (74.2 dyn/cm) is larger than that of water (72.8 dyn/cm) which has large γ^p value (51.0 dyn/cm) and relatively small γ^d value (21.8 dyn/cm).[13]

It is noticeable that γ^p of 3-ethoxypropyl-substituted polysilane, **5** is substantial while γ^p of 3-phenoxylpropyl analogue, **6**, is negligible. The polar effect of the side chain is, thus, more critical in alkyloxy-polysilanes rather than in aryloxy side chain-polysilanes.

The contribution of extremely high γ^p of the oxyethylenic

Table 1. Yield, UV absorption maximum, contact angle, and surface tenssion of polysilanes

				Film A[a]					Film (B)[b]				
Polysilane[c])				contact angle(°)[d]		Surface tension, dyn/cm			contact angle(°)[d]		Surface tension, dyn/cm		
#	Yield(%)	λ_{max}[e]	M_w(x10^3)[f]	Θ_w[g]	Θ_m[h]	γ^d	γ^p	γ	Θ_w[g]	Θ_m[h]	γ^d	γ^p	γ
1	3.4	290	30	55	33	35.7	16.9	52.6	68	37	36.0	9.5	45.5
2	3.9	303	10	51	41	31.2	21.6	52.8	49	42	30.4	23.4	53.8
3	1.4	303	8	29	10	39.5	29.7	69.2	34	8	40.3	26.7	67.0
4	—[i]	310	20	9	23	35.0	39.2	74.2	7	16	37.0	38.1	75.1
5	1.1	301	140	76	42	34.8	6.1	40.9	69	38	35.7	9.2	44.9
6	3.5	308	270	89	18	48.2	0.4	48.6	85	20	46.7	1.1	47.8
7	7.5	337	130	70	31	38.3	10.3	48.6	63	37	35.1	12.5	47.6
8	2.9	337	58	57	34	35.6	15.8	51.4	62	36	35.1	13.0	48.1
9	4.5	337	10	48	28	36.8	20.6	57.4	62	36	35.3	24.4	59.7
10	3.8	336	11	25	23	36.0	33.5	69.5	24	18	37.4	33.0	70.4
11	7.5	337	79	65	35	36.4	10.9	47.3	56	52	25.9	21.4	47.3
PhMe(j)	39.2	337	200	89	32	42.6	0.9	43.5	89	35	41.1	1.0	42.1

[a] Cast from THF solution. See Ref. 12. [b] Cast from toluene solution. See Ref. 12. [c] Refer to text. [d] Measured 20 second after dropping the liquid on the polysilane surface (23 °C, relative humidity 55%). Average value of ten measurements. [e] Measured in THF. [f] Measured by Gel Permiation Chromatography(GPC) refering to polystyrene standards. [g] Contact angle for water. [h] Contact angle for diiodomethane. [i] Not determined yet. [j] Poly(methylphenylsilane).

group is still effective in copolymers.[14] Therefore, we can improve the wettability and adhesibility of polysilanes by copolymerization with polysilanes having oxyethylenic side chains.

Further study on physical properties of polysilanes **1-11** are now undergoing in our laboratory.

The authors are grateful to Shin-Etsu Chemical Co., Ltd. and Toshiba Silicone Co., Ltd. for their generous gift of methyldichlorosilane and hydrosilylation catalyst, respectively. The authors also thank to Dr. K. Matsukawa of Osaka Municipal Institute for Industry for measurement of contact angles.

References and Notes

1 For recent reviews, see: a) R. D. Miller and J. Michl, *Chem. Rev.*, **89**, 1359(1989); b) R. West, in "*Chemistry of Organic Silicon Compounds,*" ed by S. Patai and Z. Rappoport, Wiley, New York(1989), p1207.
2 R. Menescal, R. West, and C. Murray, *Macromolecules*, **24**, 330(1991).
3 T. Fujisaka, R. West, and C. Murry, *J. Organomet. Chem.*, **449**, 105(1993).
4 a) C. H. Yuan and R.West, *Macromolecules*, **27**, 629 (1994); b) R. Kani, Y. Nakano, Y. Majima, S. Hayase, C. H. Yuan, and R.West, *Macromolecules*, **27**, 1911 (1994).
5 H. Frey, G. J. J. Out, M. Moller, D. Greszta, and K. Matyjaszewski, *Macromolecules*, **26**, 6231(1993).
6 L.Wang and W. P. Weber, *Macromolecules*, **26**, 969(1993).
7 C. Roux and M. Leclerc, *Macromolecules*, **25**, 2141(1992).
8 C. J. Nelson, W. D. Coggio, and H. P. Allcock, *Chem. Mater.*, **1991**, 786 and references therein.
9 Monomers were added into a sodium dispersion in toluene under argon atmosphere. Initition period ca. 2-5 min. was needed to cause the coupling reactions.
Reactions were quenched by the addition of ethyl alcohol. The toluene layer was washed with water several times to remove sodium chloride, followed by fractional precipitation of the reaction product from appropriate nonsolvent, eg. methyl alcohol-water mixture for polysilane **3**, to obtaine polysilanes with monomodal molecular weight distribution. Since polysilane **4** was soluble in water, sodium chloride was removed by dialysis for one week. Dibutyl Ether was employed for fractionation of polysilane **4**. All of the copolymers were fractionated from isopropyl alcohol. Polysilanes showed the expected H-NMR spectra, e.g. NMR data of copolysilane **10** is as follows (chemical shift, assignment, number of protons): (0.26, Ph-Si$C\mathit{H}_3$, 3H), (0.43, $C\mathit{H}_3$-SiCH_2-,5H), (1.39, Si-CH_2-CH_2-CH_2-O, 2H), (3.09, 3.33, 3.46, broad peaks, -CH_2O and OCH_3, 17H). The detail of the synthetic procedure and characterization, including UV, IR, NMR, and thermal analysis, of polysilanes will be published elsewhere.
10 P. J. Dynes and D. H. Kaeble, *J. Adhes.*, **6**, 195 (1974).
11 Polysilanes **1**, **6**, **7** and poly(methylphenylsilane) make good films from toluene solutions while others make good films from THF solutions. To elucidate the effect of the film quality on the surface tension, two films were prepared from these solvents. Most of the polysilane films showed almost the same surface tension in film A and Film B. However, polysilanes **1** and **7** have different values in the two, suggesting that the surface state may influence to the contact angles.
12 A. W. Neumann, *Adv. Colloid Interface Sci.*, **4**, 105 (1974).
13 E. G. Shafrin, in "*Polymer Handbook,*" ed by J. Brandrup and E. H. Immergut, John Wiley and Sons, New York (1975), III-221.
14 γ^p of copolymers are, in most cases, nearly the same as or smaller than those of homopolymer. Polysilane **10**, however, possesses a larger value than that of polysilane **5**. The reason of this unexpected phenomenon is not clear yet.