Surface Properties of Polysilane Copolymers with Siloxane Pendant Groups

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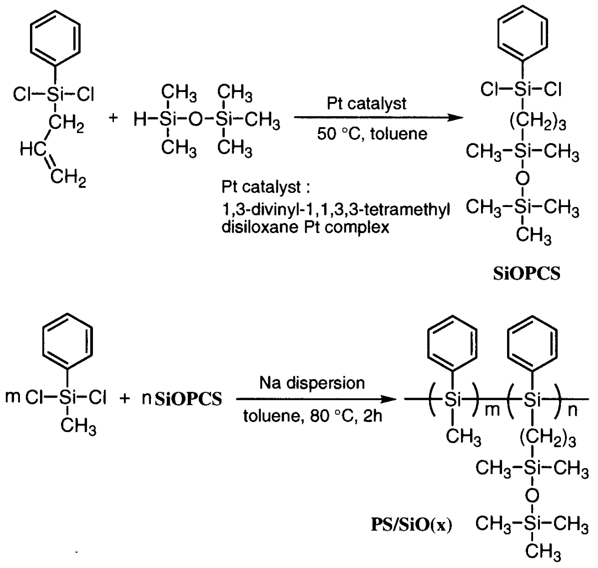
Polysilane copolymers with disiloxane pendant groups were prepared from methylphenyldichlorosilane and pentamethyldisiloxypropylphenyldichlorosilane as a comonomer by Wurtz coupling. Disiloxane pendant groups were accumulated at the surface of copolysilane films, which was evidenced by XPS analysis. Photoconductivity of these copolysilanes by Xerographic discharge measurement was not much affected by the disiloxane groups.

Polysilanes provide interesting functionalities such as conductive, photoconductive, themochromism, non-linear optics, electro-luminescence properties, etc., by their Si-Si σ-conjugation.[1] Some novel polysilanes modified with functional groups in side chain have been also developed for performing new functions such as hydrophilicity,[2] LB films,[3] photoconductivity,[4] photorefractive properties,[5] thermochromic properties[6] and so on. However, polysilanes generally deteriorate by oxygen exposure not only on light, but also in dark with long term standing to induce Si-Si scission and/or siloxane formation.[7] As polydimethylsiloxanes are relatively stable to corona discharge,[8] siloxane pendant groups on the surface of polysilanes are of one possibility to minimize the deterioration of organic polysilanes for optical elements, *e.g.*, electrophotographic receptors.

In this communication, copolysilanes with disiloxane pendant groups are synthesized by using methylphenyldichlorosilane and pentamethyldisiloxypropylphenyldichlorosilane, **SiOPCS,** as a comonomer, and the influence of disiloxane groups on the surface properties and photoconductivity are investigated by XPS (X-ray photoelectron spectroscopy) and Xerographic discharge measurement.



SiOPCS

PS/SiO(x)

Scheme 1.

A comonomer, **SiOPCS**, was derived from hydrosilylation of pentamethyldisiloxane with allylphenyldichlorosilane in toluene using 1,3-divinyl-1,1,3,3-tetramethyldisiloxane Pt complex catalysis,[9] as shown in Scheme 1.[10] The completion of reaction was confirmed by the disappearance of Si-H stretching band at 2120 cm^{-1}, CH_3 protons adjacent to Si-H at 0.18 ppm, Si-H proton at 4.67 ppm, and the appearance of Si-O-Si stretching band at 1070 cm^{-1}, CH_2 protons adjacent to $SiCl_2$ at 1.40 ppm on IR and ^{1}H-NMR spectra, respectively. Copolymerization of methylphenyldichlorosilane and **SiOPCS** with different feed ratio was carried out by Wurtz coupling reaction using Na dispersion at 80 °C in toluene.[11] The structure of copolysilanes was identified by measurement of ^{1}H-NMR, IR, and UV spectra. The results of copolymerizations are summarized in Table 1. The copolysilanes thus obtained are, hereafter, abbreviated as **PS/SiO(x)**, in which x denotes mol% of **SiOPCS** in feed.

Copolysilane films (5-10 µm thickness) were prepared by casting the toluene solutions of **PS/SiO(x)** onto a charge generation layer of metal free phthalocyanine (0.3 µm thickness) on Alumite substrates for fabricating photoconductive devices. At first, surface properties of the film were measured with XPS with Mg Kα radiation of 300 W. The depth profile of copolysilanes was carried out by measurement with different take-off angles of θ = 75, 60, 45, 30, and 15° (see a graphical abstract), respectively, sampling depth of 9.9, 8.9, 7.3, 5.2, and 2.7 nm, which is estimated from electron inelastic mean free path of C_{1s} for organic compounds.[12] The Si_{2p} peaks were separated to two peaks by curve fitting of 100.5 and 102.5 eV, respectively for Si-Si and Si-O-Si, and the Si-O-Si composition of **PS/SiO(10)**

Table 1. Synthesis of copolysilanes with disiloxane pendant groups

SiOPCS / mol%	Yield / %	Copolysilanes	High copolysilane[a] Mn	High copolysilane[a] Mw	Low copolysilane[a] Mn	Low copolysilane[a] Mw	H/(H+L)[b] / Area %	Siloxane content[c] / mol%
0	29	PMPS	628000	1341000	2000	5300	7.4	-
5	19	PS/SiO(5)	378000	728000	3600	6200	22.0	4.3
10	26	PS/SiO(10)	133000	238000	4100	7000	19.9	10.0
25	18	PS/SiO(25)	11000	18000	-	-	100.0	21.8

[a]Polystyrene standards were used for GPC calibration. [b]Composition of higher molecular weight fraction in peak area % was determined by GPC peak. [c]Calculated by ^{1}H-NMR spectra.

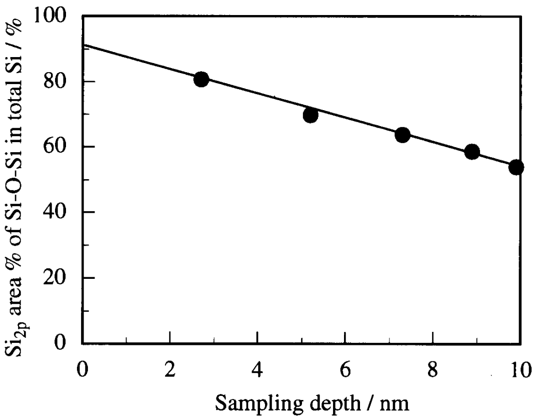


Figure 1. XPS Si_{2p} Si-O-Si composition in depth profile of copolysilane, **PS/SiO(10)**, film.

in depth profile is illustrated as plots against sampling depth in Figure 1. It was found that Si-O-Si is accumulated at the top-surface of film in 2.7 nm thickness, almost 80%. Because surface tension of polydimethylsiloxane (19-25 mN/m)[13] is lower than that of polymethylphenylsilane (**PMPS**) (43.3 mN/m)[14], polydimethylsiloxane would tend to segregate to surface of these blend films. From our results, it was found that even short pendant disiloxane groups in copolysilanes have this tendency.

Photoconductivity of **PS/SiO(x)** was evaluated by potential decay of surface negative charge which is known as Xerographic discharge measurement with an electrostatic paper analyzer using 100 W halogen lamp. In this measurement, the potential decay was defined by (A: surface potential at light irradiation - residual potential)/(B: surface potential at light irradiation) (in %) as shown in Figure 2. This figure indicates that photoconductivity of **PS/SiO(x)** with <10 mol% of disiloxane contents is not inferior to that of **PMPS**. This preferential surface coverage of disiloxane pendant groups will induce an improvement of oxygen durability to Xerographic discharge properties of polysilanes. We confirmed that the photoconductivity of copolysilanes was not affected even in oxygen atmosphere standing for 16 hr. Detailed effect of disiloxane pendant groups of copolysilanes under oxygen atmosphere on photoconductivity will be reported elsewhere.[15]

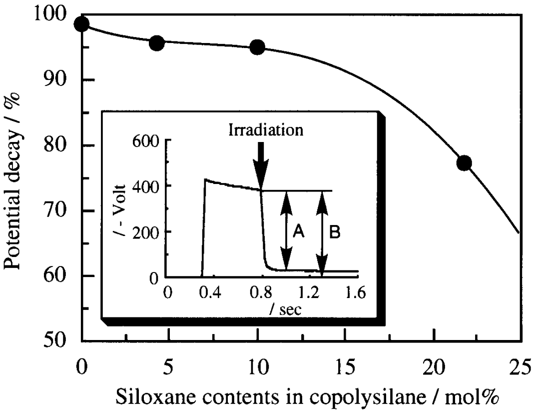


Figure 2. Potential decay (A/B in %) change with siloxane contents in copolysilanes, **PS/SiO(x)**.

In conclusion, copolysilanes with disiloxane pendant groups were synthesized through two step reactions, hydrosilylation and Wurtz coupling reaction. The preferential surface coverage of disiloxane pendant groups was evidenced by an angle-dependent XPS analysis. Photoconductivity of these copolysilanes was comparable to that of **PMPS**.

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10 To 15 mL toluene solution of allylphenyldichlorosilane (8.7 g, 40 mmol) was added of 1,3-divinyl-1,1,3,3-tetramethyldisiloxane Pt complex (19 mg. 5 % xylene solution) and pentamethyldisiloxane (5.9 g, 40 mmol) under N_2 atmosphere. The solution was stirred for 1 h at 60 °C. After toluene was removed under reduced pressure, **SiOPCS** was obtained. ^{1}H-NMR($CDCl_3$): 7.71 (d, *J*=8.1 Hz, 2H), 7.47 (m, 3H), 1.61 (m, 2H), 1.40 (t, *J*=7.8 Hz, 2H), 0.64 (t, *J*=7.8 Hz, 2H), 0.04 (s, 15H) ppm; IR (neat): 1430(C-H), 1250 (Si-CH_3), 1120 (Si-C_6H_5), 1070 (Si-O-Si), 560 (Si-Cl) cm^{-1}.

11 Typical procedure: After Na dispersion (2.21 g, 96 mmol) was prepared in dry toluene using a homogenizer at 110 °C under N_2 atmosphere, the dispersed solution was cooled rapidly to room temperature with stirring. A 15 mL toluene solution of **SiOPCS** and methylphenyldichlorosilane (both amount of 40 mmol) was added to the Na dispersion, the solution was stirred with a magnetic stirrer at 80 °C for 2 h under N_2 atmosphere. After filtrating by-produced salts, copolymer, **PS/SiO(x),** was purified by reprecipitation from isopropanol/benzene. UV (THF): λ_{max} 336 nm; ^{1}H-NMR($CDCl_3$): 7.5-6.2 (Ar-H), 1.5 (CH_2), 0.2-1.1 (Si-CH_2 and Si-CH_3) ppm; IR (film on KBr : 1430 (C-H), 1250 (Si-CH_3), 1120 (Si-C_6H_5) 1070 (Si-O-Si) cm^{-1}.

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