Preparation and Properties of Organic-Inorganic Hybrid Thin Films Containing Polysilane Segments from Polysilane-methacrylate Copolymers

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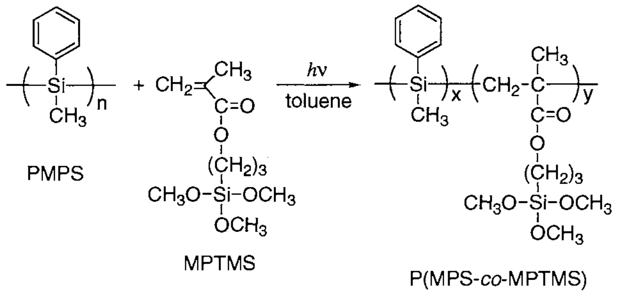
Photo-radical copolymerization of 3-methacryloxypropyltrimethoxysilane was carried out by using polymethylphenylsilane as a macro-photoinitiator to form polysilane-methacryloxypropyltrimethoxysilane copolymers. Organic-inorganic hybrid thin films with highly dispersed polysilane segments were successfully prepared from the copolymers by a sol-gel method. Refractive index and surface morphology of the hybrid thin films were found to change by UV irradiation.

Molecularly dispersed polysilane composites, *i.e.* organic-inorganic hybrid materials, are interested in their properties, in addition to well-known photo-functionality of polysilane.[1] For the preparation of the hybrid materials, polysilane copolymers seem to be significant components. Although polysilane-vinyl block copolymers have been prepared by anionic polymerization using "masked disilylene",[2] there are difficulty to prepare the monomers. However, as photolysis of polysilanes produces silyl radicals which can be used as a radical polymerization initiator of vinyl monomers,[3] photo-radical polymerization of acrylic monomers by using polysilanes is able to prepare polysilane copolymers. These copolymers are expected to be miscible with tetraethoxysilane (TEOS) as an inorganic matrix for a sol-gel process. In this communication, we report the synthesis of polysilane-methacryloxypropyltrimethoxysilane copolymers [P(MPS-*co*-MPTMS)] and the preparation of organic-inorganic hybrid thin films using the copolymers. Furthermore the properties of hybrid films are discussed.



PMPS
MPTMS
P(MPS-*co*-MPTMS)

Figure 1.

Polymethylphenylsilane (PMPS), which was prepared by Wurtz coupling reaction of methylphenyldichlorosilane in THF,[4] was used for a macro-photoinitiator. In a typical photo-polymerization of 3-methacryloxypropyltrimethoxysilane (MPTMS), PMPS (1.0 g) and MPTMS (1.0 g, 50 wt%) were dissolved in toluene (10 ml) in Pyrex tube, the mixture was sufficiently degassed by the freeze-thaw method. After sealing the tube under reduced pressure, as shown in Figure 1, photo-polymerization was carried out by irradiation of UV light (high pressure Hg lamp; 10 mW/cm^2) for a limited time, 6 min. Copolymers, P(MPS-*co*-MPTMS), were obtained after reprecipitating from hexane, and the results of copolymerization are summarized in Table 1. The detailed discussion of photo-polymerization will be elsewhere reported. The molecular weights of P(MPS-*co*-MPTMS) were measured by GPC calibrated with polystyrene standards. The composition number, x and y in Figure 1, was determined by ^{1}H-NMR spectra. UV absorption spectra of P(MPS-*co*-MPTMS) in THF are shown in Figure 2. The appearance of absorption maxima around 338 nm suggests that polymeric Si-Si bonds are still remained after photo-polymerization. The Si chain length of copolymers was estimated from the our own calibration curve for absorption maximum, according to the relationship between

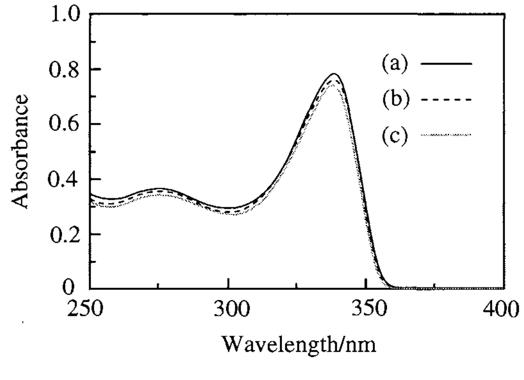


Figure 2. UV spectra of P(MPS-*co*-MPTMS) in THF.
Feed ratio of MPTMS/PMPS; (a) 33/67, (b) 50/50, (c) 60/40.

Table 1. Photocopolymerization of MPTMS using PMPS as a macro-photoinitiator

Feed ratio/wt%	P(MPS-co-MPTMS)						
MPTMS/PMPS	Yield/%	Mn	Mw	Mw/Mn	x	y	Si chain length
33/67	45	9.3×10^3	16.6×10^3	1.78	122	8	94
50/50	36	11.6×10^3	19.4×10^3	1.67	127	17	100
60/40	36	12.6×10^3	24.3×10^3	1.93	148	27	97

UV absorption and Si chain length of polysilanes.[5] From these results, P(MPS-*co*-MPTMS) was found to be mainly A-B block copolymers whose Si chain length was slightly smaller than x.

Although a sol-gel hybrid material by crosslinking polysilane with alkoxysilane groups in side chains was reported,[6] the sol-gel hybrid materials from block copolymers with polysilane segment has not been known yet. In typical preparation of the organic-inorganic hybrid thin films using P(MPS-*co*-MPTMS), to THF (2.9 ml) solution of P(MPS-*co*-MPTMS) (26.7 mg) and TEOS (84.9 mg), di(ethylene glycol) methyl ether (0.3 ml) and 4.5 N HCl (9 mg) were added. After thoroughly mixing in dark at room temperature for 1 h, the thin films were prepared by spin-coating the solution on substrates at 2000 rpm for 30 sec. During heating the substrates at 120 °C for 1h, the solution gelled to hybrid thin films. Thickness of the hybrid films under this condition was about 60-70 nm. The hybrid thin films thus obtained were transparent in visible region and insoluble in solvent such as toluene and THF. These results suggest that P(MPS-*co*-MPTMS) was highly dispersed in silica. As shown in Figure 3, it is feasible to coat repeatedly to accumulate the hybrid thin films, which are advantageous for controlling their thickness.

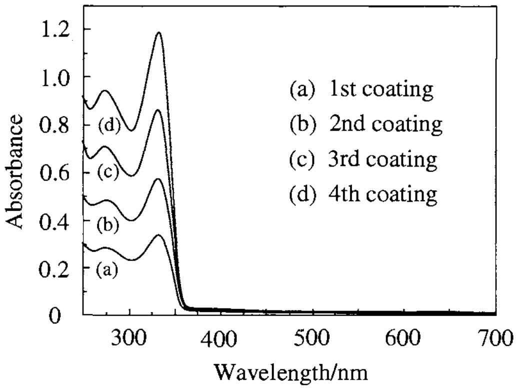


Figure 3. UV-VIS spectra of sol-gel hybrid thin films with multi-coating of P(MPS-*co*-MPTMS)/TEOS = 1/3.18 on a quartz substrate.

When the hybrid thin films were irradiated with UV light in air for a few minutes, photoscission of polysilane segments occurred, as confirmed by the disappearance of σ-σ^* absorption in UV spectra and Si-Si bond (Si_{2p} : 101.2 eV) in X-ray photoelectron spectroscopy. Refractive index (RI) of the hybrid thin film [P(MPS-*co*-MPTMS)/TEOS = 1/3.18] on a silicon wafer substrate was measured before and after UV irradiation by ellipsometry. As shown in Table 2, before irradiation, RI of the hybrid film was n = 1.60, although that of PMPS exhibited n = 1.67. After irradiation, RI of the hybrid film became lower, n = 1.53. Furthermore, after rinsing the irradiated hybrid thin film with hexane for removing photodegradation products, the RI was n = 1.40 which was almost same value as silica glass. These results suggest that there is a possibility of wide application to an opto-modulating material. Figure 4 shows AFM image of hybrid thin film irradiated of UV light for 5 min. Interestingly, the surface of hybrid film had numerous unevenness below *ca.* 20 nm at 20-40 nm intervals, while it was a smooth surface with large undulation before irradiation. This unique surface was evidently generated by photodegradation of polysilane segments. It is, therefore, assumed that polysilane segments are slipped out by a new type of photo-abrasion. Further investigation on other properties of hybrid thin film containing polysilane is going in progress.

Table 2. Refractive index of hybrid thin film [P(MPS-*co*-MPTMS)/TEOS= 1/3.18]

	Hybrid thin film	Refractive index (n)
(a)	Before UVirradiation	1.60
(b)	After UV irradiation	1.53
(c)	Rinsing (b) with hexane	1.40

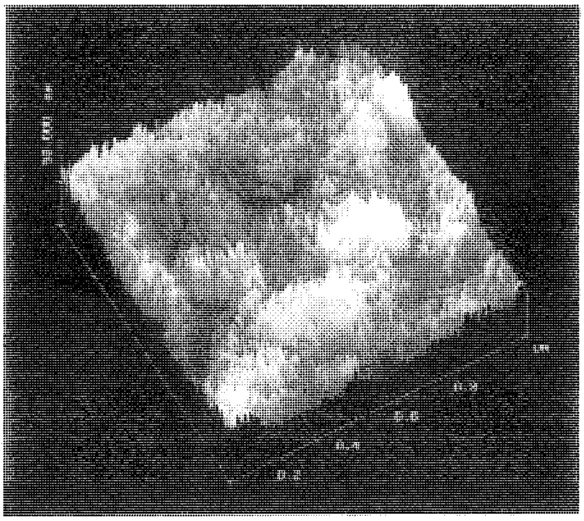


Figure 4. AFM image of hybrid thin film, P(MPS-*co*-MPTMS)/TEOS = 1/3.18, after UV irradiation for 5 min.

References and Notes

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4 A 10 ml THF solution of 15.28 g (80 mmol) of methylphenyldichlorosilane was added dropwise to 4.42 g (192 mmol) of sodium in 70 ml THF with vigorous stirring at reflux temperature, and the mixture was heated for 2 h under N_2 atmosphere. PMPS was purified by reprecipitation from isopropanol, washing with water several times, and finaly reprecipitation from isopropanol/toluene (1/1). The yield was 27.4%. Mn = 2.54 x 10^4, Mw = 5.94 x 10^4, Mw/Mn = 2.34.

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