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Synthesis of polysilane–acrylamide copolymers by photopolymerization and their application to polysilane–silica hybrid thin films

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Abstract

Various polysilane–acrylamide block copolymers have been prepared from photopolymerization of acrylamide-type monomers using poly(methylphenylsilane) (PMPS) as a macro-photo-radical initiator. The acrylamide block in the copolymers improved the hydrophilic property of PMPS. These PMPS–acrylamide block copolymers have been applied to formation of PMPS–silica hybrid thin films via sol–gel reaction. Homogeneous and transparent PMPS–silica hybrid thin films were obtained from a few PMPS–acrylamide block copolymers. It was found for these hybrid thin films based on hydrogen bonding formation between amide group and silanol group. The surface properties of hybrid thin films were evaluated by water contact angle measurement, scanning electron microscope (SEM), and atomic force microscope (AFM) images. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Polysilane; Polysilane–acrylamide block copolymer; Organic–inorganic hybrid thin film

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1. Introduction

Recently, many types of organic–inorganic hybrid materials have been developed because of their interesting properties, for example, molecular homogeneity, transparency, rigidness, and various optical functionalities [1]. Especially, in a field of optics, there are much interest to apply these hybrid materials to planar waveguide as one of examples, because the refractive index of these hybrid materials can be controlled with the variation of composition [2]. These properties are based on the network structure of inorganic matrix linking to organic domains through chemical bonding. Chujo et al. have reported various hybrid materials, which consisted of a wide variety of chemical bonding states [3,4]. They proved that even hydrogen bonding interaction or π–π stacking interaction give the hybrid materials homogeneity and high resistivity to solvent [5].

We have prepared polysilane–silica hybrid thin films by using polysilane–acrylic block copolymers as starting materials for sol–gel reaction with tetraethoxy orthosilicate (TEOS) [6]. These hybrid thin films were composed of a wide range of polysilane and silica ratios without phase separation and showed wide refractive index changes with different composition ratio or UV irradiation [7]. These polysilane–silica hybrid thin films consisted of covalent bonding (Si–O–Si) formed by hydrolysis and condensation between the polysilane–acrylic block copolymers and TEOS.

In this paper, we describe the synthesis of polysilane–acrylamide block copolymers by photopolymerization of acrylamide monomers using poly(methylphenylsilane) (PMPS) as a macro-photo-radical initiator. Furthermore, we tried to prepare PMPS–silica hybrid thin films using these copolymers and TEOS through sol–gel reaction. Transparency, homogeneity, and surface properties of the polysilane–silica hybrid thin films thus prepared were also evaluated.

2. Experimental

2.1. Synthesis

We used the following vinyl monomers (Fig. 1) for the photopolymerization: *N*,*N*-dimethyl acrylamide (DMAA), *N*,*N*-diethyl acrylamide (DEAA), acryloylmorpholine (ACMO), *N*,*N*-dimethylaminopropyl acrylamide (DMA

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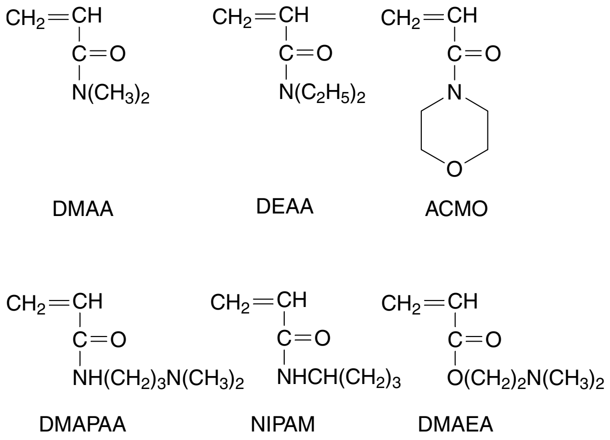

Fig. 1. Molecular structures of acrylamide-type monomers.

PAA), *N*-isopropyl acrylamide (NIPAM). In addition to these acrylamides, we also used *N*,*N*-dimethylaminoethyl acrylate (DMAEA). These monomers were kindly supplied from Kohjin Co., Ltd. PMPS as a macro-photo-radical initiator was synthesized by Wurtz coupling reaction [8]. PMPS thus obtained was as follows: $M_n = 1.18 \times 10^4$, $M_w/M_n = 1.55$, and $\lambda_{max} = 335.6$ nm. The photopolymerization with vinylmonomers was carried out using PMPS in sealed tubes [9]. The vinyl monomer (1.0 g) and PMPS (1.0 g) were dissolved in distilled toluene (5 ml) and the mixture was sufficiently degassed by the freeze–thaw method. After sealing the Pyrex glass tube under reduced pressure, the tube was irradiated by UV light (high pressure Hg lamp; 10 mW cm^{-2}) at room temperature for 10 min. The products prepared from the photopolymerization were purified by reprecipitation from 2-propanol (200 ml), followed by filtration and vacuum drying.

2.2. Formation of hybrid thin films

The PMPS–silica hybrid thin films were prepared via sol–gel reaction. The copolymer (30 mg) and TEOS ($30 \times n$ mg: $n = 0$, 1, 3, 5, 10) were dissolved in THF (1.5 ml)–ethanol (1.0 ml) mixture, followed by addition of 10 wt% HCl (10 μl). After stirring at room temperature for 2 h, the mixture was spin-coated on the silicon or silica substrate and the thin films on the substrates were aged at 120 °C for 1 h. After sol–gel reaction, the composition of copolymers/silica in weight correspond to 1/0, 1/0.44, 1/1.33, 1/2.20, and 1/4.4.

2.3. Measurement

Molecular weight and its distribution of copolymers were measured by Tosoh GPC system (HLC-8020) with calibration using polystyrene standards. ^{1}H NMR spectra were recorded on a JEOL NMR-300. Infrared spectra were measured with a Nicolet Impact 420 Fourier-transform spectrophotometer. UV–Vis spectra were recorded on a Hitachi U-3210. Atomic force microscope (AFM) was taken on a Digital Instrument Nanoscope IIIa with a tapping mode. The scanning electron microscope (SEM) was taken on a JEOL JSM-58000LVC. The film thickness and refractive index were examined with a ULVAC ESM-1 ellipsometer using He–Ne laser (632.8 nm). The contact angle was measured with a Kyowa Interface Science CA-X150. X-ray photoelectron spectroscopy (XPS) was examined with a ULVAC Phi ESCA 5700.

3. Results and discussion

3.1. Synthesis of copolymers

The copolymers of PMPS and acrylic monomers were produced by photopolymerization using PMPS as a macro-photo-radical initiator. Table 1 shows the results of photopolymerization. A part of Si–Si linkage in PMPS was photo-decomposed to generate silyl radicals for initiating polymerization. The molecular weight distribution of all copolymers was monomodal and decreased in comparison with that of PMPS as a starting material. This tendency was similar to our earlier results of polysilane–acrylic block copolymers [9]. The FT-IR spectra of the copolymers except for the copolymer of F indicated amide carbonyl stretching around 1640 cm^{-1}. Furthermore, proton peaks in a range of 2.3–4.1 ppm were observed in the ^{1}H NMR spectra of all copolymers. These proton peaks are due to methyl or methylene adjacent to nitrogen. The copolymers except for F had a relatively high content of the acrylamide

Table 1
Characterization of copolymers produced by photopolymerization

Copolymers	Vinyl monomer	Yield (%)	M_n ($\times 10^4$)	M_w/M_n	m/n[a]	λ_{max}[b]
A	DMAA	66.0	0.86	1.73	36.4/63.6	333.0
B	DEAA	54.0	1.02	2.11	46.0/54.0	332.6
C	ACMO	75.0	0.78	1.80	41.7/58.3	334.0
D	DMAPAA	70.0	0.53	1.49	48.2/51.8	332.8
E	NIPAM	70.0	0.96	1.61	55.6/44.4	335.0
F	DMAEA	69.0	1.04	1.61	74.1/25.9	336.2

[a] Molar ratio of [methylphenylsilane]/[vinyl monomer] determined by the ^{1}H NMR spectra.

[b] Wavelength at the UV absorption maximum.

Table 2
Sol–gel process conditions and the appearance of hybrid thin films

Hybrid thin film	Polymer/TEOS[a]	Appearance	Refractive index	Film thickness (μm)	Contact angle
A-0	1/0	Transparent	1.62	0.10	60.3
A-1	1/1	Transparent	1.61	0.12	64.4
A-2	1/3	Transparent	1.54	0.15	69.7
A-3	1/5	Transparent	1.51	0.15	78.0
A-4	1/10	Turbid	–	–	–
B-0	1/0	Transparent	1.61	0.09	63.2
B-1	1/1	Transparent	1.61	0.10	68.6
B-2	1/3	Transparent	1.56	0.10	79.0
B-3	1/5	Transparent	1.45	0.11	81.0
B-4	1/10	Turbid	–	–	–

[a] Feed ratio of the sol–gel reaction.

block (40–65%). This tendency has not yet been observed in other PMPS–acrylic block copolymers and is probably due to the relatively high propagation rate constant in the free radical polymerization of acrylamide monomers [10]. In the UV–Vis absorption spectra of all copolymers, strong absorption around 330 nm existed. This absorption is attributed to continuous PMPS block of more than 40–50 Si units [8], and hence these copolymers were confirmed to be the PMPS–acrylic block copolymers. The $\lambda_{\max}$ in the UV–Vis absorption spectra shifts to lower wavelength than that of PMPS as a starting material. This result suggests that the PMPS block became shorter than that of the starting material after the photopolymerization.

3.2. Properties of hybrid thin films

Table 2 shows a relationship between the feed conditions and the properties of the PMPS–silica hybrid thin films. Film thickness of these thin films was about 0.1 μm from ellipsometry measurement. Only the hybrid thin films using A and B gave the transparent films even in the hybrids with a large amount of silica composite (A-3 and B-3). These hybrid thin films were resistant to organic solvents such as 2-propanol, hexane, and so on. We have obtained such a transparent hybrid thin film from PMPS–acrylamide block copolymers without $Si(OCH_3)_3$. Therefore, these hybrid thin films were formed due to hydrogen bonding between amide and silanol, which is generated by a hydrolysis of TEOS (Fig. 2). As shown in Fig. 3, the amide peak around 1639 cm^{-1} of the FT-IR spectrum of B-0 shifted to the lower wavenumbers (1616 cm^{-1}) in the spectrum of B-1. This spectral change is an unambiguous evidence for the hydrogen bonding formation [3]. Copolymers of C, D, E, and F did not form transparent hybrid thin films. Steric hindrance in addition to hydrophobicity of acrylamide components probably made hard to form the hydrogen bonding in the copolymer of C. The copolymers of D and E having secondary amine had a tendency to become turbid, that is, to be phase separated because of their weaker basicity to make hydrogen bonding than that consisted of tertiary amine. A copolymer of F has no amide, and hence it did not form hydrogen bonding.

Fig. 4 shows UV–Vis absorption spectra of the hybrid

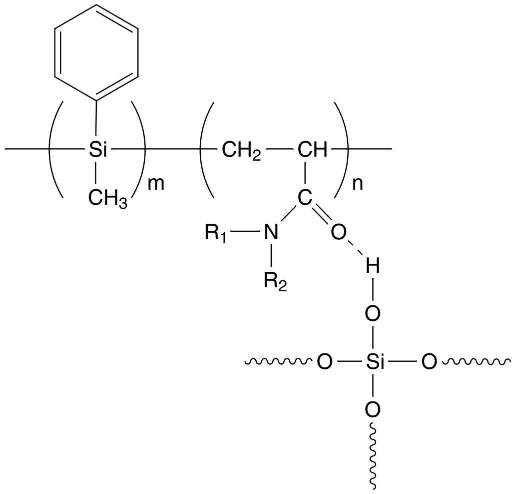

Fig. 2. Polymer structure of polysilane–acrylamide block copolymer and the hydrogen bonding in the hybrid thin film.

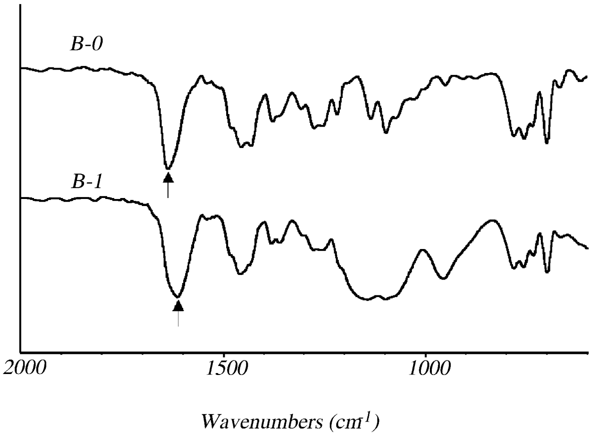

Fig. 3. FT-IR spectra of B-0 and B-1.

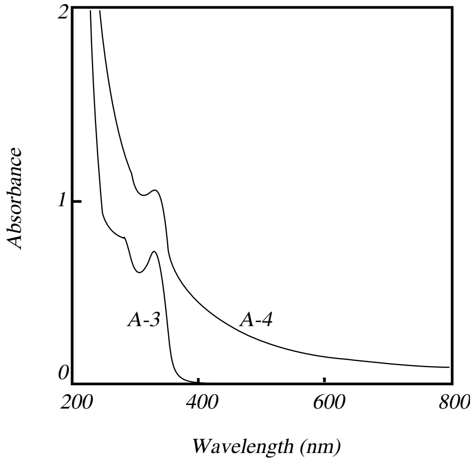

Fig. 4. UV–Vis absorption spectra of A-3 and A-4.

thin films of A-3 and A-4. A-3 had transparency in visible region, while A-4 had a long tailing in this region to make turbid. The domain size was less than a few hundred nanometers in A-3. Moreover, a result of extinction coefficient ($k = 0$ at 632.8 nm) measured with ellipsometry also supported the result of transparency in A-3. Figs. 5 and 6 show the SEM photograph and AFM image of the hybrid thin films of A-3 and A-4, respectively. Both the images indicated flat surface in A-3; on the contrary, A-4 had domains of a few hundred nanometers. In the XPS results of A-3, peak ratio of Si/N/C/O and Si–Si/Si–O (around 100 eV of Si_{2p} peak) were unchanged in the various take-off angles ($\theta = 15$, 45, and 75). Therefore, A-3 had a homogeneous composite in a range of at least 2.7–9.9 nm in depth [11]. It was found that other transparent hybrid thin films (A-1, A-2, B-1, B-2, and B-3) also had a similar tendency to exhibit a homogeneous composition in depth. Table 2 also shows the refractive indexes of these hybrid thin films. The values in a range of 1.62–1.45 are reasonable for PMPS–silica hybrid thin film because refractive indexes of PMPS and silica are 1.68 and 1.40, respectively [6,7].

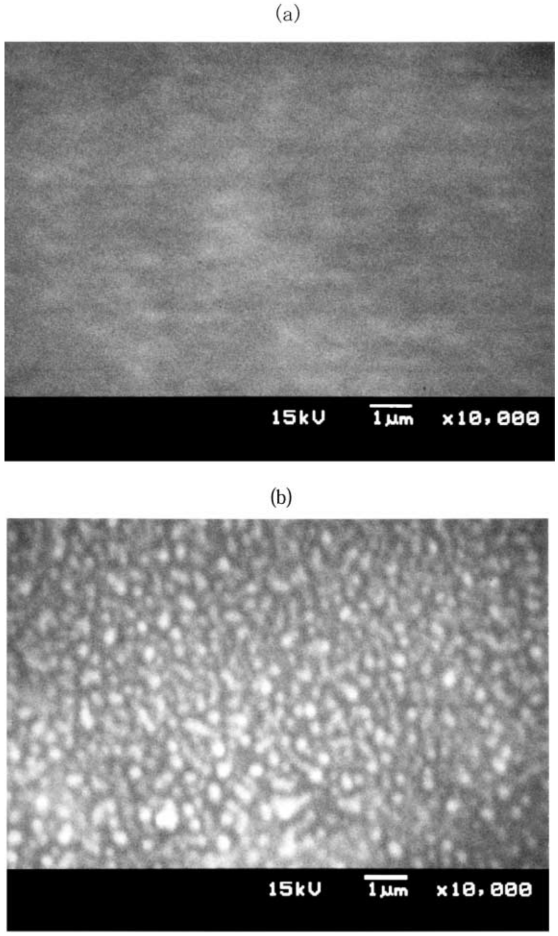

Fig. 5. SEM photographs of: (a) A-3 and (b) A-4.

Combination of acrylamide block to PMPS afford hydrophilicity to hydrophobic PMPS [12]. Water contact angles

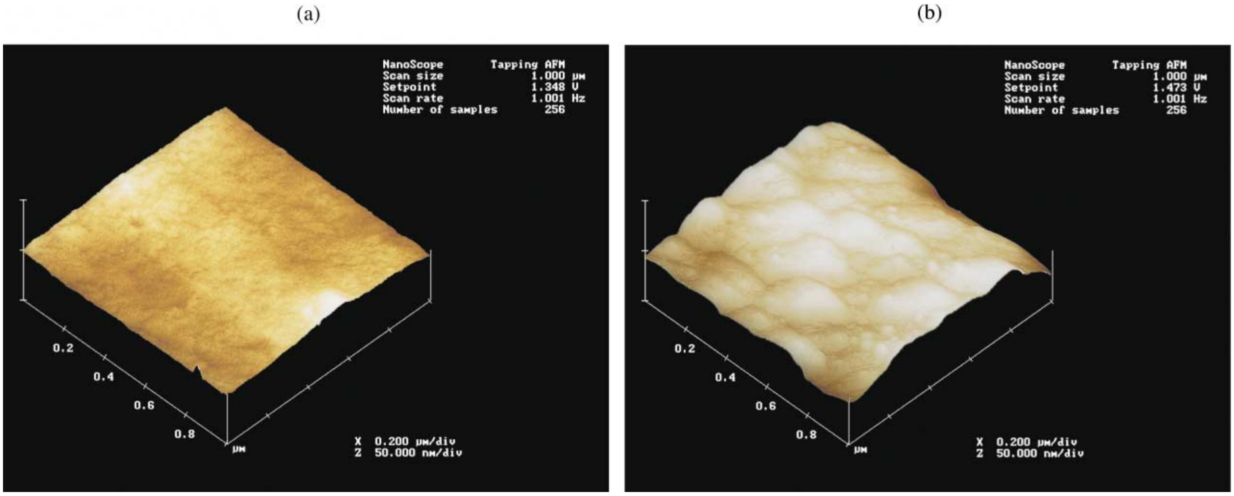

Fig. 6. AFM images of: (a) A-3 and (b) A-4.

of hybrid thin films as a measure of surface hydrophilicity are summarized in Table 2. The addition of hydrophilicity to PMPS was evidenced from the fact that the contact angles of the copolymers (A-0 and B-0) were lower than that of PMPS ($\theta = 89.6$). On the contrary, the contact angles of the hybrid thin films became higher than those of the corresponding copolymers (A-0 and B-0). The acrylamide block in copolymers simply affected the contact angle because their hydrophilicity is higher than that of silica. Therefore, the hydrophilicity of these hybrid thin films gradually decreased with an increase in the TEOS content.

4. Conclusion

PMPS–acrylamide block copolymers were prepared from the photopolymerization using PMPS as a macro-photo-radical initiator. Introduction of acrylamide block into these copolymers became more than 40% molar ratio. These block copolymers indicated hydrophilic properties, which is not recognized in PMPS. A few PMPS–acrylamide block copolymers gave PMPS–silica hybrid thin films with good molecular homogeneity and transparency. PMPS–silica hybrid thin films were confirmed to form by hydrogen bonding between amide group and silanol group.

Acknowledgements

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