Preparation and Applications of a Polysilane-allyl Methacrylate Copolymer

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Copolymers of polysilane and allyl methacrylate were prepared using the polysilane as a photoradical initiator. The polysilane block and allyl group were retained even after photopolymerization. The σ-conjugation of polysilane block in the copolymer allowed it to exhibit light absorption in the ultraviolet region. Subsequently, an ene-thiol reaction between the copolymer and mercapto-containing molecule was carried out by photocuring a thin film of the mixture. The photoreaction formed –CH–CH2–S– bonding between the organic component and a silica component that was formed by photoysis of the polysilane block in the copolymer. Therefore, the polysilane-allyl methacrylate copolymer successfully provided a silicon-rich organic–inorganic hybrid material.

Keywords: Polysilane, Allyl methacrylate, Photo-polymerization, ene-thiol reaction

1. Introduction
Polysilane exhibits electron delocalization on the Si–Si main chain. These electronic states are known as σ-conjugation owing to their characteristics resembling π-conjugation in organic molecules [1]. In addition, polysilane has good electrical conductivity and light absorption in the ultraviolet region [2], which allows its application to photopolymers [3]. However, its gradual degradation in air limits its industrial applications. To develop the functionality of polysilane, polysilane-methacrylate block copolymers were synthesized using a masked disilene precursor [4]. Polysilane with a sulfide tripod terminus was synthesized to make use of the selective chemisorption of this terminus on a gold surface [5]. Our research group developed photopolymerization of methacrylate to prepare polysilane-methacrylate copolymers using the polysilane itself as a photoradical initiator to retain the polysilane block [6, 7]. In particular, we prepared a copolymer bearing an alkoxy group, which could be used to produce a polysilane–inorganic hybrid material through a sol-gel reaction with metal alkoxide [8]. However, the alkoxy group is significantly unstable for long-term storage.

To improve the weak point of alkoxy group for the sol-gel reaction, the ene-thiol reaction has

![Photo-polymerization of polysilane-allyMA copolymer](image)

Fig. 1. Photo-polymerization of polysilane-allylMA copolymer.
been applied for the fabrication of organic–inorganic hybrid materials for hard coat and negative-type resists [9, 10]. The reaction system is superior in durability, low shrinkability, flexibility, and adhesion. Therefore, replacement of sol-gel reaction with the ene-thiol reaction will allow improvements in the preparation methods and properties of polysilane–inorganic hybrid materials. Furthermore, a polysilane-containing thin film can provide a silica component through photocuring to prepare a silicon-rich organic–inorganic hybrid material, which could be used for hard coats and low dielectric materials, among others [11]. Therefore, in this study, we have prepared a copolymer of polysilane and allyl methacrylate (allylMA) using the polysilane itself as a photoradical initiator (Fig.1). Furthermore, photocuring was used to react the allyl group in the copolymer with a mercapto-containing molecule via an ene-thiol reaction to obtain a new type of organic–silica hybrid material (Fig. 2).

![Fig. 2. Photo-reaction of polysilane-allylMA copolymer and mercapto-containing compound to fabricate an organic-silica hybrid film.](image)

**2. Experimental**

**2.1 Materials**

Poly(methylphenylsilane) (PMPS) was used for the photoreaction with allylMA. PMPS (product OGSOL Sl-10-10) was supplied by Osaka Gas Chemicals Co., Ltd. [12]. The crude sample was reprecipitated in hexane, filtered, and dried under vacuum overnight. AllylMA was purchased from Aldrich and used after 1H-NMR analysis. Photopolymerization of methacrylate with PMPS was performed using PMPS itself as a photoradical initiator. The typical photoreaction procedure was as follows: PMPS (~ 0.5 g) and allylMA (~ 0.5 g) were dissolved in toluene (5 mL), where the molar ratio of methylphenylsilane (MPS) unit in PMPS to allylMA was determined to be approximately equimolar. The mixture was sufficiently degassed using a freeze–thaw method. After sealing the Pyrex glass tube under N2 gas, the tube was irradiated with UV light (SEN LIGHTS CORPORATION, high-pressure Hg lamp, 10 mW cm\(^{-2}\)) for 20 min. The reaction mixture was reprecipitated in hexane (300 mL) to obtain a white insoluble product. The hexane containing the insoluble product was filtered through a glass filter (pore size: 20–30 µm), and the residue was dried under vacuum overnight.

Ene-thiol reactions were performed using mercapto-containing molecules, which were purchased from Showa Denko K. K. The molecules were 1,4-bis(3-mercaptobutyloxy)butane, trimethylolethane tris(3-mercaptopropylate), pentaerythritol tetrakis(3-mercaptopropylate), and 1,3,5-tris(3-mercaptopropylxyloxyethylene)-1,3,5-triazyl. The PMPS-allylMA copolymer and mercapto-containing molecule were dissolved in THF, and the resulting solution was spin-coated on a silicon wafer. The resulting thin film was photocured under UV light and then heated to 80 °C.

**2.2 Measurements**

The molecular weight was measured using a Shodex GPC-101 system against a polystyrene standard and in THF as the solvent. The ratio (x/y) of the number of MPS units to the number of allylMA units was determined by 1H-NMR using a JEOL JNM-ECX400 spectrometer with deuterated chloroform as the solvent. Spectroscopic measurements were recorded using a Shimadzu UV-3600 spectrophotometer, a Shimadzu IR Affinity-ATR system equipped with a zinc selenide crystal, and a Tokyo Instruments micro-Raman spectroscopy Nanofinder 30 A with 532 nm green laser. X-ray photoelectron spectroscopy (XPS) was performed using an Ulvac Phi ESCA 3057 with an X-ray tube at MgKα energy. Differential scanning calorimetry (DSC) measurements were recorded using a Seiko Instrument DSC-X5400 apparatus at a heating/cooling rate of 10 °C min\(^{-1}\) in a temperature range of −70 to 230 °C. Molecular orbital calculations were performed using the GAMESS program with an approximation of B3LYP/6-31 G** [13].
3. Results and discussion

The product of photoreaction of PMPS and allylMA was a white powder that was soluble in toluene, THF, and chloroform. The FT-IR spectra suggested a chemical structure originating from allylMA and PMPS. For example, a peak at 1728 cm\(^{-1}\) indicated the presence of a carbonyl group of allylMA. In addition, a peak at 1470 cm\(^{-1}\) was assigned to the bending vibration of methylene in the allylMA unit of the product. The chemical shift in \(^1\)H-NMR spectrum showed that the methacryl group of allylMA reacted completely to form a single C–C bond. The details of the \(^1\)H-NMR are presented in reference [14]. A single peak observed in the GPC chromatogram confirmed the presence of only a single component in the copolymer. The reason that the allyl group was retained even after photopolymerization was a contribution to the frontier orbitals of allylMA, where the LUMO consisted of the atomic orbitals on only the methacryl group, while the HOMO had the atomic orbitals on the methacryl and allyl groups. Therefore, the HOMO accelerated the photoradical polymerization of the methacryl group with a silyl radical derived from the photolysis of polysilane.

Table 1 lists the molecular weight, content ratio \(x/y\), and UV absorption wavelength of the products. The molecular weight decreased as the photoreaction time increased, while the molecular weights of the photopolymerization products were greater than that of PMPS. Increasing photoreaction time reduced the ratio of \(x/y\). The changes in the molecular weight and \(x/y\) with increasing photoreaction time suggested that the number of MPS units decreased as the photoreaction time increased, while the number of allylMA units in the product saturated, as in our previous report [15]. As shown in Table 1, UV absorption in the range of 320–330 nm of products of 1–3 suggested the presence of a PMPS block that exhibited \(\sigma\)-conjugated characteristics even after photopolymerization. In addition, the wavelength of UV absorption became shorter as the photoreaction time increased. This suggests that the \(\sigma\)-conjugation area in the products of 1–3 tends to decrease as the number of MPS units is reduced. These results were in accordance with the \(^1\)H-NMR results, as summarized in Table 1. Furthermore, the products exhibited glass transition at 34 °C, which resulted from the allylMA block. From the above results, it was considered that PMPS was successfully connected to allylMA to form the PMPS-allylMA copolymer.

Subsequently, the copolymer was applied in an ene-thiol reaction with mercapto-containing molecules by photocuring a thin film of the mixture. We used the aforementioned four species of mercapto-containing molecules and observed very similar characteristics among the photocured thin films. Hereinafter, we will describe a result of the ene-thiol reaction using pentaerythritol tetrakis(3-mercaptopropionate). The FT-IR results indicated that the allyl groups of the copolymer reacted completely, because the peaks at 1429 cm\(^{-1}\) assigned to C=O and 1585 cm\(^{-1}\) assigned to R–CH=CH\(_2\) were not observed after photocuring. In addition, as shown in Figure 3, the Raman spectrum of the thin film after photocuring exhibited a peak at 720 cm\(^{-1}\), which suggested that a C–S bond was formed by the ene-thiol reaction between the allyl moiety of the copolymer and thiol moiety of the mercapto-containing molecule. Although the thin film formed by photocuring was slightly sticky because of the unreacted thiol, as confirmed by the presence of a Raman peak at 2553 cm\(^{-1}\), this could be resolved by optimizing the preparation conditions for the ene-thiol reaction. Furthermore, the XPS results confirmed the formation of a PMPS block that exhibited \(\sigma\)-conjugated characteristics even after photopolymerization. In addition, the wavelength of UV absorption became shorter as the photoreaction time increased. This suggests that the \(\sigma\)-conjugation area in the products of 1–3 tends to decrease as the number of MPS units is reduced. These results were in accordance with the \(^1\)H-NMR results, as summarized in Table 1. Furthermore, the products exhibited glass transition at 34 °C, which resulted from the allylMA block. From the above results, it was considered that PMPS was successfully connected to allylMA to form the PMPS-allylMA copolymer.

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Table 1. Results of photo-polymerization of PMPS and allylMA.

| Products | UV-irradiation Time [min] | \(^1\)H-NMR x/y | GPC \(M_n\) | GPC \(M_w\) | \(\lambda_{max}^{2)}\) |
|----------|--------------------------|----------------|-------------|-------------|----------------|
| PMPS \(^3\) | 0                        | -              | 5100        | 3.2         | 331.4 |
| 1        | 10                       | 257            | 7800        | 2.4         | 329.0 |
| 2        | 20                       | 8              | 7000        | 2.9         | 327.5 |
| 3        | 30                       | 3              | 6100        | 3.6         | 323.5 |

\(^1\) Ratio of [MePhSi]/[AllylMA].

\(^2\) Wavelength of UV-Vis absorption spectra.

\(^3\) PMPS as a starting material.

Fig. 3. Raman spectrum of a thin film prepared from photo-reaction of polysilane-allylMA copolymer and pentaerythritol tetrakis(3-mercaptopropionate). The solid and dotted lines indicate the Raman spectra of the copolymer and the ene-thiol product.
silica component, as shown in Figure 4. The copolymer exhibited a peak at 101.8 eV, which was assigned to Si–Si bonding, whereas the peak at 104.4 eV of the ene-thiol reaction product suggested the formation of Si–O bonds. The thermal properties determined by DSC showed no remarkable change in heat flow up to 200 °C. This result indicates that the film exhibits heat resistance at a sufficient degree for application in hard coat and photoresist.

4. Conclusion
Photopolymerization of polysilane and allyl methacrylate was carried out using the polysilane itself as a photoradical initiator. By adjusting UV light, a polysilane-allyl methacrylate copolymer was prepared, retaining the polysilane block and allyl group. The copolymers exhibited σ-conjugation between polysilane blocks that enabled light absorption in the ultraviolet region. Furthermore, a thin film of a mixture of the copolymer and mercapto-containing molecule allowed the production of an organic–inorganic hybrid thin film. The ene-thiol reaction resulted in strong –CH–CH2–S– bonding between the organic component and silica component that was derived from the photolysis of the polysilane block in the copolymer. The results show that through photocuring, the polysilane-allyl methacrylate copolymer can provide a silicon-rich organic–inorganic hybrid material for applications such as a hard coat and low dielectric materials. Furthermore, if other species of methacrylate are inserted in the polysilane-methacrylate copolymers, new functionality can be added to the hybrid materials in the future.

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