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Organic/inorganic nano-hybrids are molecularly dispersed composite materials with polymers and metal oxides. As these materials have excellent transparency, they are expected to be applied for the optical usage. In particular, organic/inorganic hybrids with photo-functional polymers would be interesting materials with optical properties. Polysilanes are one of photo-functional polymers, whose functions are photodegradation, photoconductive, high refractive index, etc. We have been investigating about the preparation and properties of the novel nano-hybrids of polysilane with inorganic substances. Polymethylphenylsilane (PMPS)/silica or titania nano-hybrid thin films were prepared by a sol-gel reaction with PMPS block copolymers and corresponding metal alkoxides. The refractive index of nano-hybrid thin films could be controlled with the composition ratio of PMPS. After development of the UV-irradiated hybrid thin films with organic solvents, nano porous (ca. 20 nm) silica or titania thin films were obtained by removing the decomposed PMPS segments, and a high refractive index difference occurred between irradiated and non-irradiated part in the hybrid thin films. Furthermore, a hybrid thin film of polydihexylsilane (PDHS) and zirconia suppressed the thermochromism which is known as a characteristic of polydialkylsilane, and this hybrid thin film provided the high thermo-optic (TO) effect with an advantage for optical devices.

Keywords: organic/inorganic nano-hybrid, polysilane, silica, titania, zirconia, thin films, refractive index, sol-gel, photodecomposition

1. Introduction

Organic/inorganic hybrids are one of most attractive functional materials, which is prepared by a sol-gel reaction with organic polymers and metal oxides. For the preparation of these materials, it needs to interact between polymers and sols. There are some interaction manners of covalent bonding [1-5] and hydrogen bonding [6,7], and the characteristics of these organic/inorganic hybrid materials are dispersed molecularly and homogeneously. These materials are normally nanocomposites and have the unique combination of properties which can not be achieved by other materials. There are the new and specific properties of these nanosscopic composites differing from the conventional composites with macroscopic domain size of milli- or micrometer scale. As many kinds of combinations with different organic and inorganic components have been available, they would be applied for the electrical, optical, structural, or related applications. Especially, as the organic/inorganic nano-hybrid materials are optically transparent, they are useful materials for optical devices.

On the other, polysilane is a well-known functional organosilicon polymer with a high quantum efficiency of photoluminescence (PL), a high hole drift mobility, a significant photobreaking property, high refractive index, etc., which are associated with “σ-conjugation” along the Si-Si main chain [8-10]. It can be noted that polysilane has various interesting properties and many applications have so far been proposed. However, low durability of polysilane for light exposure have limited its application. As polysilane have unusual photo-reactivity, it has
been considered that photo resist for LSI fabrication is one of promising applications [11]. Except polysilane based photo resist, we consider that the photodecomposition properties under UV irradiation might be available for new materials derived from hybridization of polysilane.

The photo-functional polysilane/inorganic nano-hybrids, in which polysilane is molecularly dispersed in inorganic matrix, might be an attractive material to fabricate a new type of optical devices. For the preparation of polysilane/ inorganic nano-hybrids, a chemical modification of polysilane is necessary for interaction or reaction with metal alkoxides during a sol-gel reaction. Consequently, polysilane copolymers with functional vinyl monomers could be provided some reactivity.

In this review, we report that the photo-radical polymerization of vinyl monomers by polysilane as a macro-photo-initiator to produce polysilane block copolymers and the preparation of polysilane/ inorganic hybrid thin films by a sol-gel reaction using polysilane copolymers. The photo-induced optical properties of polysilane/inorganic nano-hybrid thin films have been investigated. Furthermore, the nano-porous surface in the hybrid thin films was formed after removing the decomposed polysilane segments under UV irradiation.

2. Synthesis of polysilane copolymers

As polymethylphenylsilane (PMPS) is a hydrophobic polymer with methyl and phenyl substituents on a Si atom, the interaction between PMPS and sol of metal hydroxides did not occur in a sol-gel reaction. In order to fabricate the polysilane/inorganic nano-hybrids, it is necessary to form chemical bondings such as covalent or hydrogen bonds with metal hydroxides. Therefore, polysilane copolymers with reactive groups, such as alkoxyisilyl and amide groups, were effective for a sol-gel reaction to prepare the nano-hybrids. The copolymerization with methacrylic monomers was performed by using PMPS as a macro-photo-initiator [12], in which silyl radical was generated by the partial photolysis of Si-Si main chain, as Wolff and West reported that PMPS acted as an photo-initiator of radical polymerization [13]. For example, a polysilane block copolymers with reactive groups for a sol-gel reaction, P(MPS-co-MPTMS), P(MPS-co-MPTES), and P(MPS-co-DMAA), were successfully prepared from 3-methacryloxypropyltrimethoxysilane (MPTMS), 3-methacryloxypropyltriethoxysilane (MPTES), and N,N-dimethylacrylamide (DMAA) respectively, under mild UV irradiation (high pressure Hg lamp; 10 mW/cm² [14,15]). The properties of polysilane copolymers were summarized in Table 1. The existence of polysilane segments in these copolymers were confirmed by α-α⁺ absorption around 340 nm in the UV spectra.

3. Preparation of polysilane/inorganic nano-hybrids

Polysilane/silica nano-hybrid thin films were prepared by a sol-gel reaction with tetraethoxysilane (TEOS). P(MPS-co-MPTMS) and P(MPS-co-MPTES) formed the covalent bonds (Si-O-Si) between trialkoxysilyl groups of these copolymers and TEOS. Figure 1 showed a

![Diagram](Image)

Table 1 Preparation results of polysilane copolymers

<table>
<thead>
<tr>
<th>Copolymer</th>
<th>R₁</th>
<th>R₂</th>
<th>Mn(x10⁴)</th>
<th>Mw/Mn</th>
<th>x</th>
<th>y</th>
<th>λmax</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(MPS-co-MPTMS)</td>
<td>CH₃</td>
<td>O(CH₃)₃Si(OCH₃)₃</td>
<td>1.06</td>
<td>2.14</td>
<td>114</td>
<td>30</td>
<td>336.0</td>
</tr>
<tr>
<td>P(MPS-co-MPTES)</td>
<td>CH₃</td>
<td>O(CH₃)₃Si(OC₂H₅)₃</td>
<td>1.29</td>
<td>1.90</td>
<td>140</td>
<td>26</td>
<td>338.4</td>
</tr>
<tr>
<td>P(MPS-co-DMAA)</td>
<td>H</td>
<td>N(CH₃)₂</td>
<td>1.67</td>
<td>1.77</td>
<td>109</td>
<td>121</td>
<td>338.2</td>
</tr>
</tbody>
</table>

Mn=2.4-2.6x10⁴, Mw=5.1-6.0x10⁴, Mw/Mn=2.1-2.3
schematic diagram of PMPS/silica nano-hybrids. And also, in the case of P(MPS-co-DMAA), hydrogen bonds were formed between amide groups and silanols derived from TEOS. After spin-coating of these solution on substrates and heat treatment, polysilane/silica nano-hybrid thin films thus obtained were transparent in visible region and insoluble in organic solvents such as toluene and THF.

UV absorption and photoluminescence (PL) spectra of polysilane/silica hybrid thin films were essentially same as those of a PMPS thin film. After UV irradiation to the PMPS thin film, the α-α* transition around 340 nm of polysilane was disappeared immediately. However, in the hybrid thin film, the peak remained to some extent with the elapse of UV irradiation [16], although polysilane segments in the hybrid were finally decomposed under a prolonged or strong UV irradiation. Furthermore, PL intensity of the hybrid thin film decayed much slowly at low temperature compared to that of PMPS [17,18]. From these results, it was found that silica matrix in the hybrid thin film acted as a passivation cage preventing from photodegradation of polysilane and improved somewhat the durability of PMPS segments.

4. Nano porous thin films derived from photolysis of polysilane/inorganic nano-hybrids

PMPS segments in the silica matrix were photo-decomposed under prolonged UV irradiation. Therefore, after the removal of the decomposed polysilane segments with solvent development, the nano porous silica thin films could be fabricated effectively [19]. AFM images of photodegraded hybrid surface were shown in Figure 2. This porosity could be controllable by the amount and molecular weight of PMPS segments.

5. Refractive index of polysilane/silica nano-hybrids

PMPS has a relatively high refractive index (1.67). As the refractive index of polysilane/silica nano-hybrid thin films decreased with increasing the composition ratios of TEOS, the nano-hybrid thin films with different refractive index could be fabricated easily [16]. The refractive index of P(MPS-co-MPTMS)/silica hybrid thin films was plotted, after UV irradiation and development with hexane, as shown in Figure 3. The refractive index
of the only PMPS thin film at longer irradiation time than 1.0 s could not be measured, because the all of photodecomposed PMPS thin films were removed by rinsing with hexane. However, the nano-hybrid thin films remained on substrates after longer irradiation, and their refractive index was reached to the value of silica with increasing irradiation time. It is noteworthy that a large photo-induced refractive index change of 0.043 was observed for P(MPS-co-MPTMS)/silica nano-hybrid thin film even in 1/10 ratio after an irradiation time of 7.0 s.

The photo-induced refractive index change was applied to a generation of refractive index pattern by UV irradiation to P(MPS-co-MPTES)/silica nano-hybrid thin films through a photomask [23]. The fabrication process was illustrated in Figure 4. IR spectra of masked and unmasked parts on each steps were shown in the same figure. Spectra B-1 and B-2 suggested that PMPS segments was decomposed to silanols and oligosiloxane by UV irradiation. Exposed part of the P(MPS-co-MPTMS)/silica nano-hybrid thin film was developed with hexane to remove the photodecomposed PMPS segments (step A-C). This procedure provided the nano-porous silica thin film with low refractive index (ca. 1.40). Spectrum C-1 was assigned as inorganic silica, SiO₂, without any organic compounds. Therefore, a large refractive index difference between exposed and unexposed parts in the nano-hybrid thin film was generated successfully. However, as the unexposed polysilane segments are unstable under a strong light, there is a disadvantage that the refractive index will be labile thereby the photodecomposition. In order to fix the refractive index difference between these parts of the nano-

Figure 3. Refractive index of PMPS and nano-hybrid thin films with different composition ratios of P(MPS-co-MPTMS)/TEOS = 1/1, 1/3, and 1/10 after UV irradiation (light power :141 mW/cm²) and development with hexane.

Figure 4. Fabrication process of photo-induced refractive index pattern using polysilane/silica nano-hybrid thin films, and IR spectra of respective parts on P(MPS-co-MPTES)/TEOS nano-hybrid thin film (weight ratio= 1/1).
hybrid thin film, the succeeding overall irradiation and heat treatment were carried out toward the P(MPS-co-MPTES)/silica nano-hybrid thin film (step D and E). IR spectra of unmasked part, C-1 and E-1, were not changed during heating. Spectrum D-2 was same as B-1, as well as the photodecomposition of PMPS segment. The disappearance of silanol peaks in spectrum E-2 indicates to generate organic siloxanes with phenyl groups after heating. Therefore, it seems that the final refractive index of masked part is higher than unmasked part and these values are stable under severe environmental condition.

The refractive index of P(MPS-co-MPTES)/TEOS (weight ratio = 1/5) nano-hybrid thin film on each steps were plotted, as shown in Figure 5. Although the refractive index slightly reduced after overall irradiation (step D), the sufficient difference of refractive index between the developed and secondly irradiated part still remained. Therefore, these procedures could fix the difference of refractive index resulting from photo-induced properties of P(MPS-co-MPTES)/silica nano-hybrid thin films.

Figure 5. Refractive index change of each fabrication process (A to E) of P(MPS-co-MPTES)/TEOS nano-hybrid thin film (weight ratio = 1/5).

The relative index difference (Δn) was reduced with increasing TEOS content in the nano-hybrid thin films. In the case of P(MPS-co-MPTES)/TEOS = 1/10 (weight ratio), however, Δn was about 3.5% and greater than that of fluorinated polyimides which is used as optical waveguides. Therefore, it is concluded that the polysilane/silica nano-hybrid thin films are attractive materials with the large photo-induced refractive index change.

6. Suppression of thermochromism in polydihexylsilane/zirconia nano-hybrid

Some polysilanes showed spectral changes such as thermochromism, solvatochroimism, piezochromism, and so on, according to transformation of Si-Si main chain [24-27]. Especially, thermochromism of poly(di-n-hexylsilane) (PDHS) attributable to thermal transition has been well studied for the conspicuous spectral change in the ultra-violet region [28-30]. In the case of PDHS/inorganic hybrids, thermochromism of PDHS segments in the hybrids may differ from that of pristine PDHS, and it is an interesting investigation to reveal the detail of conformational change of PDHS in a rigid matrix.

PDHS/zirconia nano-hybrid thin films were prepared by a sol-gel reaction of PDHS copolymers and zirconia alkoxydes, and thermolectic properties of PDHS were examined [31]. As well as PMPS, methacrylic monomers have been successfully introduced to PDHS by the photo-radical copolymerization. However, when PDHS-MPTES block copolymers, P(DHSH-co-MPTES), were used for a sol-gel reaction with Zr(O-n-C4H9)₄, an extreme phase separation occurred because of a different reactivity of P(DHSH-co-MPTES) and Zr(O-n-C4H9)₄ to form Si-O-Zr bond. Therefore, to fabricate a homogeneous PDHS/zirconia nano-hybrid, PDHS-acetoacetoxyethyl methacrylate (AAEM) block copolymers, P(DHSH-co-AAEM), which were prepared by the same manner of photopolymerization, seems to be effective. As shown in Figure 6, it would be expected to form

Figure 6. Preparation of P(DHSH-co-AAEM)/zirconia nano-hybrids.
the coordination bond between Zr atom and acetoacetatoxy group in AAEM. The coordination of P(DHS-co-AAEM)/zirconia nano-hybrid was confirmed by the IR spectra peaks at 1614 cm\(^{-1}\) and 1527 cm\(^{-1}\) due to the coordination bond.

The domain size of zirconia component was estimated by the observation of P(DHS-co-AAEM)/zirconia nano-hybrid thin films with a tapping-mode AFM after photolysis and relief of the polysilane segments, and it was found that the domain size was several 10 nm as shown in Figure 7. On the contrary, P(DHS-co-AAEM)/titania or alumina hybrid thin films had a rugged surface at several hundred nm intervals after photolysis and relief of the polysilane segments, which indicates that these domain sizes were relatively larger than that of zirconia.

![AFM image](image)

**Figure 7.** AFM image of P(DHS-co-AAEM)/zirconia nano-hybrid thin film (a) before and (b) after photolysis of the polysilane segments by UV light (141 mW/cm\(^2\); 30 sec). The scanning area of AFM is 1×1 \(\mu\)m and the height range 50 nm.

Thermochromism was observed in UV-Vis absorption spectra of P(DHS-co-AAEM) as shown in Figure 8 (a). This reversible transition was observed on cooling due to the conformational change, “disorder” to “transoid”, as well as PDHS thin film [32]. From these results, in spite of the existence of AAEM block in the main chain of the copolymer, it was found that P(DHS-co-AAEM) caused the thermochromism. On the other hand, UV-Vis absorption spectrum of P(DHS-co-AAEM)/zirconia nano-hybrid showed no peak around 360 nm assigned to “transoid” form of PDHS at low temperature as shown in Figure 8 (b). From these observations of UV-Vis absorption spectra, the complete suppression of thermochromism was recognized in the P(DHS-co-AAEM)/zirconia nano-hybrid thin films. Furthermore, from the DSC measurements, the zirconia hybrid did not show any thermal transition, although P(DHS-co-AAEM) had a thermal transition at 40 \(^\circ\)C on heating and at 15 \(^\circ\)C on cooling.

Thermal transition was also confirmed by their temperature-dependent Raman spectra with 785 nm excitation. In analogy with PDHS [30], Raman
spectrum of P(DHS-co-AAEM) exhibited sharp peaks at 372 cm\(^{-1}\) and 690 cm\(^{-1}\) assigned to symmetric vibration of Si-Si bond and symmetric vibration of Si-C bond, respectively, below critical temperature as shown in Figure 9 (a). Additionally, peaks at 1062 cm\(^{-1}\) and 1103 cm\(^{-1}\) due to \(n\)-hexyl side chain in PDHS segments diminished or broadened above the critical temperature, which indicated that the disorder of \(n\)-hexyl side chains occurred simultaneously with the conformational change of Si-Si main chain. It seems that the thermal conformational change of PDHS segments occurs in P(DHS-co-AAEM). On the contrary, the Raman spectrum of P(DHS-co-AAEM)/zirconia nano-hybrids did not show any change at different temperature as shown in Figure 9 (b). It was found that P(DHS-co-AAEM)/zirconia nano-hybrid was fixed at the disordering structure.

This suppression of thermochromism was observed with only P(DHS-co-AAEM)/zirconia nano-hybrid thin films, although P(DHS-co-AAEM)/titania or alumina hybrid showed thermochromism, as well as PDHS thin film. It was considered that the relatively large atomic radii of Zr atom inhibited the motion of Si-Si main chain at the critical temperature.

Figure 10 shows the temperature dependence of refractive index of P(DHS-co-AAEM) and P(DHS-co AAEM)/zirconia hybrid thin films [33]. The refractive index of P(DHS-co-AAEM) abruptly decreases with increasing temperature from 20 °C to 40 °C. The abrupt refractive index change in P(DHS-co-AAEM) results from the phase transition of PDHS. In contrast, the refractive index of nano-hybrid thin film decreased continuously with increasing temperature. Such temperature dependence of refractive index known as thermo-optic (TO) coefficient defined by \(dn/dT\), can be used optical switches or optical cross-connects [34]. Current materials used for TO switches are silica or some polymers. However, the silica-based TO switches typically require high switching power of 0.4 - 0.5 W and exhibit long response time of the order of ms due to low TO coefficient of silica (~1×10\(^{-5}\) /K).

The TO coefficient of P(DHS-co-AAEM)/zirconia nano-hybrid thin film is calculated to be ~4×10\(^{-4}\) /K from Figure 10. It is found that P(DHS-co-AAEM)/zirconia nano-hybrid has large TO coefficient, which is higher than those of polymers such as polycarbonate ([0.9-1.4]×10\(^{-4}\) /K) and polymethylmethacrylate (~1×10\(^{-4}\) /K) [35].

**Figure 9.** Temperature dependent Raman spectra of (a) P(DHS-co-AAEM) and (b) P(DHS-co-AAEM)/zirconia nano-hybrid.

**Figure 10.** Temperature dependence of refractive indices of P(DHS-co-AAEM) and P(DHS-co-AAEM)/zirconia nano-thin films.
Thus, the hybrid is more suitable to TO switches and optical deflectors; these optical devices of P(DHS-co-AAEM)/zirconia hybrids have advantages of shorter response time and lower power consumption due to large TO coefficient.

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