Thermochromic Properties of Poly(di-n-hexylsilane)-methacryl Block Copolymers

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1. Introduction
Polysilanes possess absorption band in the ultra-violet region due to σ conjugation along Si-Si main chain and have been known as functional polymers with novel physical and chemical properties such as photoconductivity, electroconductivity, electroluminescence, etc [1]. Especially, poly(di-n-hexylsilane) (PDHS) showed the remarkable thermochromic properties due to the temperature-dependent conformational change of the Si-Si main chain from “transoid” to “disorder” [2].

Our group has developed either polysilane-acryl or -methacryl block copolymers by a photo-polymerization method using the polysilanes as a macro-photo-initiator, and the polysilane block copolymers were applied to prepare the polysilane-inorganic hybrid materials with the various functionalities such as photo-induced refractive index changes [3-6]. Especially, block copolymers of PDHS with 2-(acetooacetoxy)ethyl methacrylate were applied to prepare PDHS-zirconia hybrids by a sol-gel reaction with zirconium alkoxide, which suppressed thermochromism of PDHS main chains to fix the disordered polymer structure [7, 8]. On the other hand, a block copolymer of poly(methylphenylsilane) (PMPS) and 2-(methylthio)ethyl methacrylate (MTEM) was also synthesized, and it was found that the copolymer was chemisorbed to the gold surface through the interaction between gold and sulfide [9].

In this paper, we have synthesized some PDHS-methacryl block copolymers, which have functional groups such as alkoxysilane or sulfide, by photopolymerization of corresponding methacryl monomers using PDHS as a macro-photo-initiator and examined the thermochromic properties of the thin films prepared from the copolymers.

2. Experimental
2.1. Synthesis of the polysilane block copolymers
PDHS was synthesized by using a typical Wurtz coupling reaction described in a reference [1]. Block copolymers of PDHS with 3-methylcroxypropyltriethoxysilane (MPTES) and MTEM were prepared by a photo-polymerization using PDHS as a macro-photo-initiator [7, 9]. The properties of the corresponding copolymers were as following: P(DHS-co-MPTES): Mn=8.5x10^1, Mw/Mn=2.2, x=65, y=12, λ_max=313.8 nm; P(DHS-co-MTEM): Mn=2.1x10^4, Mw/Mn=2.2, x=201, y=46, λ_max=315.8 nm.
2.2 Preparation of P(DHS-co-MPTES) thin films
Alkoxy groups in P(DHS-co-MPTES) bound to the substrate to prepare the thin films adhered to the substrate by utilizing alkoxy groups in MPTES. In order to activate the substrate surface for the adhesion, VUV-irradiation to the silica substrate was performed by using a USHIO VUV-172 nm irradiation system. The irradiation was carried out just under light source with a light intensity of 19 mW/cm². The water contact angle of the silica substrate changed from 80° to less than 10° before and after VUV-irradiation. The silica substrates were immersed in a 0.025 wt% tetrahydrofuran (THF) solution of P(DHS-co-MPTES), followed by soaking well with pure THF. As a reference, a thin film of PDHS on VUV-irradiated silica substrate was also prepared from the same method. Furthermore, a thin film of P(DHS-co-MPTES) on non-irradiated silica substrate was prepared from spin-coating 0.1 wt% THF solution of the copolymer.

2.3. Preparation of P(DHS-co-MTEM) thin films
The gold-coated (100 nm) silica substrates were immersed in a 0.025 wt% THF solution of P(DHS-co-MTEM) and were sufficiently rinsed with pure THF. As a reference, a thin film of P(DHS-co-MTEM) on the silica substrate was prepared from spin-coating with a 0.1 wt% THF solution of P(DHS-co-MTEM).

2.4. Measurements
Gel permeation chromatography (GPC) was carried out by using a TOSOH LC-8020 calibrated with polystyrene standard. 'H-NMR was measured by a JEOL NMR-300 with chloroform-d$_3$. FT-IR spectra were obtained by using a Nicolet Impact 420. UV-vis absorption spectra were conducted by a JASCO V-560.

3. Results and discussion
3.1. P(DHS-co-MPTES) thin films
In general, it has been known that PDHS causes a phase transition from “transoid” to “disorder” at 40 °C, which is confirmed as “thermochromism”. We have reported that PDHS-methacryl block copolymers also possessed the phase transition as same as PDHS [7]. In this work, P(DHS-co-MPTES) was also examined the temperature dependence of the UV-vis absorption spectra. As shown in Figure 1 (a), an absorption peak around 360 nm appeared at 0 °C, and the absorption peak at 310 nm became stronger at higher temperature. These absorption peaks are due to a PDHS structure of “transoid” and “disorder”, correspondingly. Furthermore, the hysteresis of the transition temperature at 40 °C (heating) and 15 °C (cooling),

![Figure 1](image_url)  
**Figure 1.** Thermochromic properties on heating of (a) spin-coated P(DHS-co-MPTES) thin film and (b) P(DHS-co-MPTES) thin film on the VUV-treated silica substrate.

was also observed in the UV-vis absorption spectra of P(DHS-co-MPTES).

We have examined the UV-vis absorption spectra of the P(DHS-co-MPTES) thin film on the VUV-irradiated silica substrate at various temperatures.
As shown in Figure 1 (b), the absorption peak at 310 nm did not show the temperature-dependence in a range of 0°C - 70°C, which suggests that the copolymers were fixed in a “disordered” structure. This measurement was carried out after soaking the thin film with THF, and an only absorption peak at 310 nm was observed. On the other hand, in the case of the same experiment using a non-VUV-irradiated silica substrate, no trace amounts of P(DHS-co-MPTES) were observed by the UV-vis absorption spectroscopic measurements. Furthermore, PDHS, which has no MPTES block, did not adhere to the VUV-irradiated silica substrate. From these results, it was assumed that P(DHS-co-MPTES) bound to silica substrate through the tight binding derived from the alkoxy silane in the copolymers with the active surface on the substrate.

Furukawa has indicated that the end-grafted PDHS showed thermochromism as same as ordinary PDHS thin films [10]. In our case, however, MPTES groups in the copolymer, which reacted with numerous OH group of the active surface on the substrate, suppressed thermochromism. The transformation of PDHS segments were controlled by the acrylic segments combined to the substrates.

3.2. P(DHS-co-MTEM) thin films

Organic compounds containing sulfur atoms adhere to the gold surface through chemisorption between sulfur and gold. We have synthesized a block copolymer of PMPS and MTEM and examined the chemisorption on the gold substrate [10]. In this paper, PDHS copolymer, P(DHS-co-MTEM), attempt to chemisorb on the gold surface and examined the temperature-dependent UV-vis absorption spectra.

It was found that spin-coated P(DHS-co-MTEM) thin film on a glass substrate showed thermochromism as same as PDHS, as indicated in Figure 2 (a), which was reasonable to the results of other PDHS-methacryl block copolymers [7, 8]. P(DHS-co-MTEM) was coated on the gold-coated silica substrate, followed by soaking sufficiently the substrate with THF. The sample also possessed temperature-dependent UV absorption, indicative of the chemisorption of P(DHS-co-MTEM). However, the absorption peak at 360 nm at 0°C was relatively small compared to the result of Figure 2 (a). P(DHS-co-MTEM) on the gold suppressed the phase transition of “transoid” - “disorder” to some extent. The reason is possibly that chemisorption through sulfur-gold interaction was relatively weak compared to the covalent Si-O-Si bond through the numerous alkoxy silanes in the copolymer.

4. Conclusion

PDHS-methacryl block copolymers, P(DHS-co-MPTES) and P(DHS-co-MTEM), were synthesized, and applied to fabricate their thin films through the chemical bonding or chemisorption to the substrates. It was found that their thermochromic properties were suppressed to some extent and that the structures of PDHS were fixed in a “disordered” structure.
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References