Hybrid Organic – Inorganic Films through Crosslinking Reaction Based on Siloxane Based Polymers

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Synopsis

Hybrid organic – inorganic polymers were synthesized through hydrosilylation of 1,3,5,7-tetramethylcyclotetrasiloxane (TMCS) and divinyl-terminated tetramethylsiloxane (DTMS) monomers. Controlling the hydrosilylation reaction by varying the feeding ratio as well as the total monomer concentration, chemically-soluble TMCS – DTMS hybrid polymers were obtained as a liquid state. The resulting polymer was colorless and viscous liquid, seemingly took linearly elongated structures without remarkable gel-form. Unreacted Si – H groups remained in the polymer, which allowed network formation of the TMCS – DTMS hybrid polymer with various crosslinkers such as DTMS, divinylbenzene (DVB), 3,3’-divinylbiphenyl (DVBP), and di(ethylene glycol) divinylether (DEG). Consequently, transparent and thermally stable hybrid networked polymer films with a thickness of ca. 0.2 mm were prepared through hydrosilylation and self-condensation reaction under curing process, which was proved using FT-IR spectroscopy.

Key-words : Siloxane, Crosslink, Hydrosilylation, Film, Hybrid

1. Introduction

Hybrid organic – inorganic materials have attracted much attention in recent years because they offer intriguing chemical, physical, and electrical properties. Siloxane-based hybrid materials are one example of them that can be prepared from wide variety of building blocks, i.e., silicone, silsesquioxane, and silica. They are expected to open up the new field for developing new high-performance multifunctional materials.

Chemical components of the hybrid polymers have an important effect on their properties such as glass transition temperature, crystallization, melting behaviors, solubility characteristics, chemical reactivity, and thermal stability. Thus the polymer stability can be improved by the insertion of hybrid rigid and soft segments into the polymer backbones using chemical crosslinking reactions and the polymerization techniques; ring-opening polymerization radical polymerization and acid-base catalyzed condensation. When the rigid and soft siloxane-based segments are incorporated with hybrid organic or inorganic components, the dynamic flexibility and thermal stability of the polymer chain will be enhanced, depending on the type of hybrid and block segments. In the case of the incorporation of functional groups containing organic or inorganic segments into the side chain or main chain of the polymers, further crosslinking or functionalization reactions
will be possible, resulting in the improvement of the film formation ability.

The film formation ability of the hybrid polymers is a key issue for device applications such as electronics, coating, energy, sensor, and life science. Siloxane-based polymers, especially poly(dimethylsiloxane)s (-SiO(CH₃)₂-) have low film formation ability because of the low intermolecular interactions between molecules and high dynamic flexibility of polymer chains. Therefore, siloxane-based hybrid polymers have been prepared from the polymerization of the functional organosilicon monomers using the various polymerization techniques. During the polymerization process, the structural variation, molecular weight, and molecular weight distribution of the synthesized polymer play an important role for physical and chemical properties of polysiloxanes and the creation of new functionalities. Thus, modified or functionalized polysiloxanes can easily enable forming fibers or thin films using the crosslinking reactions.

There are several crosslinking methods to prepare crosslinked polysiloxanes. The self-condensation reaction is a representative example of crosslinking, which has considerable importance in industrial silicone chemistry to prepare crosslinked systems. Many chemical groups are able to be attached to silicons such as alkoxy, acyloxy, oxime and silane, which are easily hydrolyzed under the atmospheric moisture to produce silanol groups. The functionalized siloxanes with silanol readily undergo spontaneous condensation with silane groups (Si – H) and generate a siloxane bond (Si – O – Si) which is so-called crosslinking by self-condensation. This was reported as self-crosslinking of silane-functional organosiloxanes, that is strongly dependent on the surrounding temperature, atmospheric condition, the amount of the silane groups, and platinum catalyst (Pt-catalyst). The method can be used to prepare siloxane-based polymer networks, rubbers and matrix.

The hydrosilylation reaction is the addition of silane group (Si – H) to unsaturated carbon – carbon bond by using Pt-catalyst and these processes belong to the common methods for the synthesized hybrid materials, which include synthesis of monomeric units and its use in copolymerization reactions itself. Several hydrosilylation processes have been studied: hybrid polymer synthesis, polymer-network preparation, crosslinking, functionalization, and preparation of hybrid organic – inorganic materials. It is noted that the hydrosilylation reaction of organosilicone monomers offer a useful and convenient one-pot synthesis method for preparation of new siloxane-based polymers with distinct and specific properties. Additionally, polysiloxanes can be also modified by introducing various groups capable of crosslinking under the influence of light and heat via hydrosilylation of respective organic derivatives with silane group containing siloxanes. Owing to the opportunity of hydrosilylation reactions, both hybrid polymer synthesis and crosslinking can be performed considering with reaction conditions.

To improve the stability and film formation ability of the hybrid polymer, hydrosilylation can be used as crosslinking reactions, besides, the controlling of crosslinking will provide with desired properties of crosslinked hybrid materials. For example, using the hydrosilylation of multi-functional organosiloxanes with α,ω-dialkene siloxanes or their functional derivatives, hybrid-polymer products are obtained with networked structures. As a result of the hydrosilylation of multifunctional organosiloxanes, it was found that the structures, stability and properties of resulting polymers can be controlled by adjusting the synthetic conditions such as the stoichiometric monomer ratio, and the total monomer concentration in reaction solution. However, it is rare to obtain the networked structure as a film. Mostly the hybrid polymer with multifunctional organosiloxanes provides with only molds. A sophisticated way is required to achieve the film preparation, which eases the handling of the hybrid polymers.

Herein, we demonstrate a straightforward method for preparation of freestanding films consisting of siloxane-based polymers with 1,3,5,7-tetramethycyclotetrasiloxane (TMCS) and divinyl-terminated tetramethylsiloxane (DTMS). The hybrid polymers were successfully synthesized with a linearly elongated polymeric structure by controlling the stoichiometric monomer ratio and total monomer
concentration. The TMCS–DTMS hybrid polymer is chemically soluble, viscous, and relatively easy to handle. Subsequently, the crosslinking of the hybrid polymer was performed with 1,3-divinyltetramethylsiloxane (DTMS), divinylbenzene (DVB), 3,3’-divinylbiphenyl (DVBP) and diethylene glycol divinylether (DEG) crosslinkers, based on the hydrosilylation reaction between remaining Si – H groups and the crosslinkers, which allows effective monolithic film formation. As a result from the crosslinking, the DTMS, DVB, DVBP, and DEG crosslinkers are compatible to crosslinking of TMCS–DTMS hybrid polymer by hydrosilylation and self-condensation reactions. Consequently, transparent and freestanding hybrid films were prepared.

2. Experimental

2.1 Materials

1,3-Divinyltetramethylsiloxane (DTMS), 1,3,5,7-tetramethylcyclotetrasiloxane (TMCS), divinylbenzene (DVB), di(ethylene glycol) divinylether (DEG), and Pt-catalyst were purchased from Sigma-Aldrich. 3,3’-Divinylphenyl (DVBP) was kindly donated by Shin-Etsu Chemical Co., Ltd. Anhydrous toluene, acetonitrile, activated carbon, and active alumina were purchased from Wako-Chemical Inc. All materials were used without further purification.

2.1.1 Synthesis of TMCS–DTMS hybrid polymer

TMCS–DTMS hybrid polymer was synthesized through the hydrosilylation reaction. TMCS (8.36g, 3.5 x 10^2 mol) was mixed with platinum-catalyst (14 μl) in toluene (17.4 ml), then DTMS (6.48g, 3.5 x 10^2 mol) was added to the solution. The reaction was carried out under argon atmosphere at 60°C for 1 h. Then the polymer was reprecipitated in the excess amount of acetonitrile twice. Active-carbon was added to the polymer in chloroform and the solution was stirred for 2 h. The liquid was passed through active alumina column to remove active-carbon. After evaporating the solvent, colorless, viscous liquid TMCS–DTMS hybrid polymer was obtained (83.5 % yield).

2.1.2 Crosslinking of the TMCS–DTMS hybrid polymer

The crosslinking of the TMCS–DTMS hybrid polymer films were performed using formulations containing 2 g TMCS–DTMS hybrid polymer, 25 μl of a platinum catalyst (2% in xylene) and a crosslinker. Four crosslinkers were selected: DVB, DVBP, DTMS, and DEG, respectively. After stirring for approximately 1 min, the formulations were spread on substrates such as CaF₂ substrates and Kapton® polimide films (200H, DuPont) using the Doctor blade method. The samples were thermally cured by varying the temperature stepwise from 60°C to 200°C. At each step the temperature was kept constant for 20 min.

2.2 Measurements

The molecular weight of the TMCS–DTMS hybrid polymer was determined using gel permeation chromatography (Tosoh, GPC–8020 analysis system) with polystyrene standards. The ¹H NMR and ²⁹Si NMR spectra of the polymer were measured using a 400 MHz NMR spectrometer (AVANCE III, Bruker). The FT–IR spectra measurements were carried out using an FT–IR spectrometer (FT/IR4200; Jasco Corp.). For the IR measurement, the TMCS–DTMS hybrid polymer films were prepared on CaF₂ substrates. The thermogravimetric analysis (TGA) was performed using a thermogravimetric analyzer (TGA–50, Shimadzu) with a heating rate of 10 °C /min from 30°C to 1000°C. The UV-Vis absorption spectra of polymer films were measured using a spectrophotometer (U−3000, Hitachi Ltd.).

3. Results and discussion

3.1 Synthesis of TMCS–DTMS hybrid polymer

First siloxane-based polymers were synthesized using one-pot hydrosilylation reaction of four Si – H bonds of the TMCS monomer and two-vinyl terminated DTMS monomer (Scheme 1). The one-pot hydrosilylation reaction has an advantage of taking place under the mild conditions even at room temperature. Generally the resulting polymer involves a mixture of α- and β-adducts. The β-adduct is the major product because of the anti-Marcovnikov addition. In our case, it was difficult to determine the extent of the β-adduct; the signals of the polymer for each adduct overlapped in the NMR spectra.
It is important to note that the platinum-catalyzed hydrosilylation reaction is a strong exothermic reaction. Besides, the hydrosilylation of multifunctional organosiloxane monomers form a networked structure resulting in gel-form. The gelation and the structure depend on synthetic conditions such as the functionality of monomers, catalyst concentration, stoichiometric monomer ratio and reaction temperature. Regarding the temperature and the concentration of platinum catalyst, we set the temperature at 60℃ and kept the platinum catalyst concentration approximately 10 ppm according to literatures. 12), 38)

In order to obtain chemically soluble TMCS–DTMS hybrid polymer, the total monomer concentration in solution was also an important factor. The concentration was determined to be 1 mol/L. The initial feed ratio of the monomers between TMCS and DTMS was adjusted to one-to-one. No gelation was observed in this experimental condition. The work related on the details of the hydrosilylation reaction of TMCS and DTMS is now in progress.

The TMCS monomer has four Si–H groups. In terms of the reactivity, however, the hydrosilylation prefer to occur at the diagnostic positions of the TMCS monomer at first. Further reaction seems to be difficult because of the steric hindrance of the two-arm TMCS monomer, 22) indicating the possibility of getting the linearly elongated structure consisting of TMCS and divinyl-terminated DTMS. The resulting polymer is anticipated to have one or two unreacted Si–H groups in the single TMCS. The 1H NMR results revealed the disappearance of the peaks at 5.6–6.8 ppm, which was assigned to the terminal vinyl groups of DTMS, implying that the hydroisilylation ended up with the TMCS terminal. In other words, the Si–H groups will be located on the polymer backbone and its terminals without the remaining vinyl groups of DTMS. Consequently, we confirmed experimentally that no noticeable gelation was observed during the hydrosilylation under the present condition. It should be noted that the platinum catalyst was removed below the detection limit.

The slightly yellow-colored reaction solution of the TMCS–DTMS hybrid polymer turned to be colorless after twice reprecipitation. Stirring with active-carbon allows to remove the platinum catalyst below the detection limit of the UV-Vis spectrometer. Thus the colorless, viscous liquid TMCS–DTMS hybrid polymer was obtained. The polymer was soluble in toluene, chloroform, and tetrahydrofuran. However, the polymer was insoluble in methanol, acetone, hexane, and acetonitrile, etc. The number-averaged molecular weight and polydispersity index of the resulting polymer were determined as 7.0 × 10³ and ~3, respectively. The polymer is stable under inert gas atmosphere.

### 3.2 Film preparation from crosslinking of the TMCS–DTMS hybrid polymer

The resulting TMCS–DTMS hybrid polymer undergoes secondary reactions such as hydrolysis and self-condensation under air atmosphere even at room temperature. 13), 26) Interestingly, it is possible to manipulate the hydroisilylation reaction in the TMCS–DTMS hybrid polymers because of the unreacted Si–H groups. To demonstrate the possibility, the effect of the crosslinking reaction between TMCS–DTMS hybrid polymers was investigated using four different crosslinkers: DTMS, DVB, DVBP and DEG (Scheme 2). 12.5 mol% of the crosslinkers were mixed with TMCS–DTMS hybrid polymers, compared to the initial amount of the monomers. The crosslinking reaction of TMCS–DTMS hybrid polymer allows monolithic film formation through the second-step hydrosilylation reaction between the remaining Si–H groups and vinyl groups of the crosslinkers. Thermal
Curing was carried out with stepwise heating to avoid the crack formation. Under stepwise heating from 60°C to 200°C, the film was uniformly prepared on the substrates. Fig. 1 shows FT-IR spectra of the TMCS-DTMS hybrid polymer films on CaF₂ substrates before and after curing. Two peaks at 910 and 2170 cm⁻¹ are assigned to asymmetric and symmetric Si-H vibrations, while 1612 cm⁻¹ and 1626 cm⁻¹ are the band for C=C and aromatic C=C vibration. The peak intensity at 1612 cm⁻¹ decreased with increasing temperature and then almost disappeared. The disappearance of the peak at 1612 cm⁻¹ implies that the vinyl groups of the crosslinkers undergo only hydrosilylation reaction with remaining Si-H groups. The peak intensities at 910 and 2170 cm⁻¹ also disappeared after curing. This indicates that both hydrosilylation and oxidation/hydrolysis reaction occurred during the thermal treatments. However, the broadening of the band at 950–1210 cm⁻¹ appeared after curing. This indicates the formation of the Si-O-Si and Si-C₂H₄ linkages between two TMCS monomers (Si-O-Si) and between TMCS and the crosslinker (Si-C₂H₄) (Fig. 1). This results are identical to previous results. For example, Nyczzyk et al. reported that the ethylene-bridge formation was confirmed by the appearance of bending vibration (1136 cm⁻¹) of CH bonds in Si-CH₂CH₂-Si-linkages of vinylcyclosiloxanes, and also the Si-O-Si band at 980–1210 cm⁻¹ was broaden and shifted to higher wavenumbers. 39), 40)

![Diagram of crosslinking of the TMCS-DTMS hybrid polymer.](image)

**Fig. 1** FT-IR spectra of crosslinked TMCS-DTMS hybrid polymer films before and after curing: (a) DTMS, (b) DVB, (c) DVBP, and (d) DEG. The thermal treatment was done at the presence of platinum catalyst.
In order to confirm the hydrosilylation reaction of the remaining Si−H groups with crosslinkers, the TMCS−DTMS hybrid polymer with DTMS, DEG, DVB, and DVBP crosslinkers were cured at the same experimental condition as the previous one but in the absence of Pt-catalyst (Fig. 2). It was observed that the peaks of the Si−H groups at 910 and 2170 cm$^{-1}$ disappeared completely with increasing temperature, though no remarkable changes were observed at 1626 cm$^{-1}$. In other words, the films undergo the self-condensation reaction with the thermal treatment, however, no hydrosilylation reaction occurs without Pt-catalyst. Consequently it can be concluded that two kinds of crosslink formation (Si−CH$_2$CH$_2$ Si−O−Si) occurred in TMCS−DTMS hybrid polymer films by adding the Pt-catalyst to the polymer film through hydrosilylation and self-condensation reactions. In addition, all four crosslinkers, DTMS, DVB, DVBP, and DEG, are compatible to crosslink the TMCS−DTMS hybrid polymers by hydrosilylation and self-condensation.

### 3.3 Optical transparency of crosslinked TMCS−DTMS hybrid polymer films

For freestanding film preparation, the formulation, i.e., the mixture of TMCS−DTMS hybrid polymer, crosslinker, and platinum catalyst, was coated on a Kapton $^\text{TM}$ film (7 cm × 7 cm). After thermal treatment, the films were removed from the substrates. Fig. 3 shows photographs of ~0.2-mm-thick films using different crosslinkers. They are flexible, transparent and chemically robust. As shown in Fig. 4, it was revealed that all films have high transmittance (80 %) above 370 nm.

### 3.4 Thermal property of crosslinked TMCS−DTMS hybrid polymer films

The thermal stability of crosslinked films was also investigated using TGA in air, and thermograms were plotted in Fig. 5. As a result, the onset-decomposition temperature of crosslinked polymers with DVB, DVBP, and DTMS was over ~300°C, but for DEG crosslinked polymer it was ~200°C (Fig. 5). The decomposition temperature of
the pristine DTMSC–DTMS polymer using crosslinkers was determined to be 280 °C. The crosslinking of TMCS–DTMS hybrid polymer enhances the thermal stability of the polymer because of the networked formation of the TMCS–DTMS hybrid polymers through hydrosilylation reaction resulting in the increase in its bonding energy because of the linkage change from Si–H to Si–C (and/or Si–O) bonding.\textsuperscript{41–43} Considering these points, the increased thermal stability of TMCS–DTMS hybrid polymer can be summarized as follows for each crosslinker in terms of the crosslinking reaction through hydrosilylation as well as self-condensation reactions. In the case of DVB and DVBP crosslinkers, the resulting polymers have higher thermal stability (~315 °C) than other crosslinked polymers because of the incorporation of thermally stable aromatic groups into the crosslinkers.\textsuperscript{44–47} In the case of TMCS–DTMS hybrid polymer crosslinked with DTMS, the crosslinked polymer shows high degradation temperature ~300°C, resulting in the crosslinking of TMCS–DTMS hybrid polymer through the two crosslinking reaction. Regarding the DEG crosslinker, the decomposition temperature was slightly lower: ~200°C. The thermal oxidation of the C–O bond of DEG undergo the cleavage above ~200°C.\textsuperscript{48} Conclusively, all the crosslinking of DTMS–TCMS polymer with crosslinkers except for DEG, the thermal stability of the networked polymer was increased, which enables to make thermally stable freestanding film (~320 °C).

4. Conclusion

Synthesis of siloxane-based TMCS–DTMS hybrid polymer and its crosslinking with DTMS, DVB, DVBP, and DEG were investigated based on hydrosilylation reaction. The TMCS–DTMS hybrid polymers were successfully synthesized as linearly elongated polymeric structure by controlling the total monomer ratio, total monomer
concentration, catalyst concentration, and reaction temperature, thereby the resulting polymer was colorless, viscous liquid, and soluble in toluene, chloroform, and tetrahydrofuran. The polymer enables crosslinking reaction with divinyl-terminated crosslinkers under the presence of platinum catalyst by raising the temperature. After crosslinking the TMCS-DTMS hybrid polymers will provide tremendous facilities for the film fabrication and self-condensation of TMCS will yield colorless, viscous liquid, and soluble in toluene, chloroform, and DEG crosslinkers, taking advantages of hydrosilylation reactions, which allow to effective monolithic film formation. As a result the end of the crosslinking, the thermal property of crosslinked polymer relatively increased depending on thermal curing conditions. The crosslinked these films shows ~80% transmittance above 370-nm. One-pot hydrosilylation and self-condensation of TMCS-DTMS hybrid polymer will provide tremendous facilities for the film fabrication of new siloxane-based networked polymer The work on the mechanical properties of the TMCS-DTMS hybrid polymers is now in progress and will be reported in future.

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