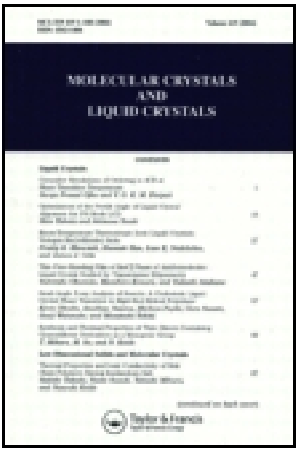

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Film Preparation of Siloxane-Based Polymer Containing Anthracene Group

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Siloxane-based polymer was synthesized through hydrosilylation of the 1,3,5,7-tetramethylcyclotetrasiloxane (TMCS) and 1,3-divinyltetramethylsiloxane (DTMS). Controlling the hydrosilylation reaction by varying the feeding ratio with the total monomer concentration, chemically-soluble siloxane-based polymer was obtained, which allowed film preparation as well as further incorporation of functional groups through the hydrosilylation reaction. The incorporation of 9-vinylanthracene was succesfully carried out by reacting Si-H groups of the TMCS−DTMS polymer with the vinyl-terminated anthracene derivative. Structural and thermal properties of the polymer were evaluated using NMR, GPC, FT−IR and flourecence spectroscopy.

Keywords Anthracene; hybrid polymer; hydrosilylation; siloxane

1. Introduction

Cross-linked, siloxane hybrid materials have received much attention in recent years due to their chemical, optical, thermal and mechanical properties based on the Si−O linkage [1,2]. The hydrosilylation reaction of multifunctional organosilicon monomers containing Si−H bonds with monomers containing diallyl- or divinyl terminal groups offers a useful and convenient one-pot synthesis method for preparation of new siloxane-based polymers with distinct and specific properties [3]. Careful control of the hydrosilylation reactions enables to introduce specific functionalities into the polymer and self-condensation of polymers under mild conditions. Thus, it is possible to carry out polymer synthesis and functionalization in one-pot synthesis method. In addition, the self-condensation of the polymer leads to polymer network formation [4]. The crosslinking of siloxane-based polymers in film are expected to improve both the mechanical and thermal properties [5]. Herein, we demostrate a straightforward method for photofunctional siloxane-based polymer film. The siloxane-based polymer was synthesized carefully to prevent the polymer from undergoing gelation. Luminescent anthracene derivatives were successfully incorporated in the siloxane-based polymer through the hydrosilylation reaction. Consequently, flexible, transparent, and luminescent free-standing hybrid film was prepared under mild conditions.

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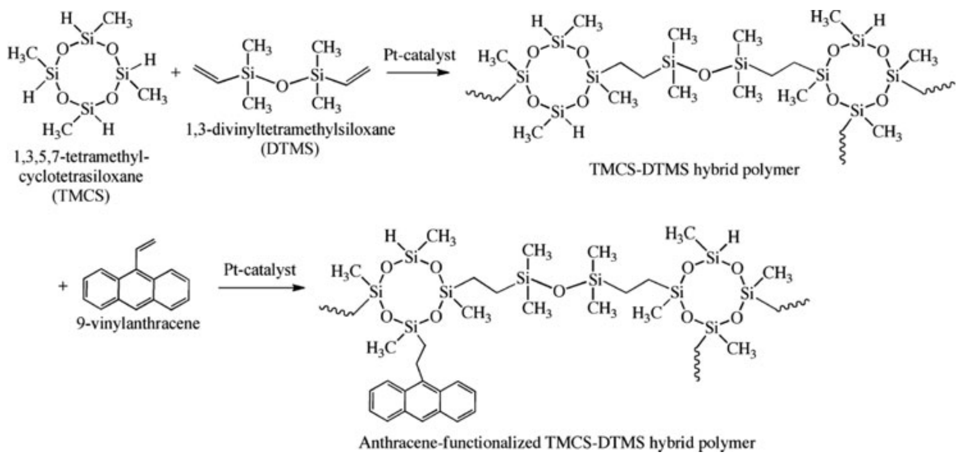
2. Experimental

1,3-Divinyltetramethylsiloxane (DTMS), 1,3,5,7-tetramethylcyclotetrasiloxane (TMCS), and Pt-catalyst were purchased from Sigma-Aldrich and used without purification. Siloxane-based polymer was synthesized by the hydrosilylation reaction of TMCS (2.09 g, 8.70×10^{-3} mol) with DTMS (1.62 g, 8.70×10^{-3} mol) in toluene (4.35 mL) in the presence of Pt-catalyst (35 μL) at 60°C for 1 h. A toluene solution of 9-vinylanthracene (100 mg, 4.89×10^{-4} mol in 1 mL) was added, and then stirring was cointained for 48 h. The solution was reprecipitated in acetonitrile twice, and stirred with active-carbon for 2 h. The molecular weight was determined using GPC with polystyrene standards. To prepare a cross-linked film, the polymer was spread on a polyimide film substrate using the Doctor brade technique. The polymer (200 mg in 2 mL chloroform) was spin-coated on CaF_2 and quartz substrates for FT−IR and flourescent measurements. The substrates were thermally cured at 60°C, 100°C, 150°C, and 200°C. At each step the temperature was kept constant for 20 min.

3. Results and Discussion

Siloxane-based polymer was synthesized using one-pot hydrosilylation reaction of multifunctional organo-silicon monomer containing Si−H bonds (TMCS) with two-vinyl terminated DTMS monomer (Scheme 1).



Scheme 1. Polymerization and functionalization of TMCS-DTMS hybrid polymer.

To avoid gelation in hydrosilylation of four functional TMCS monomer, the total monomer concentration in solution was selected to be 1 mol/L, and the monomer ratio between TMCS and DTMS was adjusted as one-to-one to form linearly elongated polymer structure; the hydrosilylation of multifunctional monomers contributes to the linear crosslinking reaction between the branched portions due to the steric hindrance around the functional group [6,7]. The ^{1}H NMR signals of vinyl group of the monomer between 5.6−6.8 ppm disappeared, indicating that hydrosilylation reaction was completed successfully at the end of the first reaction step. Subsequently, the anthracene polymer was further incorporated into TMCS−DTMS polymer by the hydrosilylation reaction at the second step. Functionalized TMCS−DTMS polymer was first precipitated in acetonitrile and then stirred with active-carbon to remove Pt-catalyst and low-molecular-weight compounds,

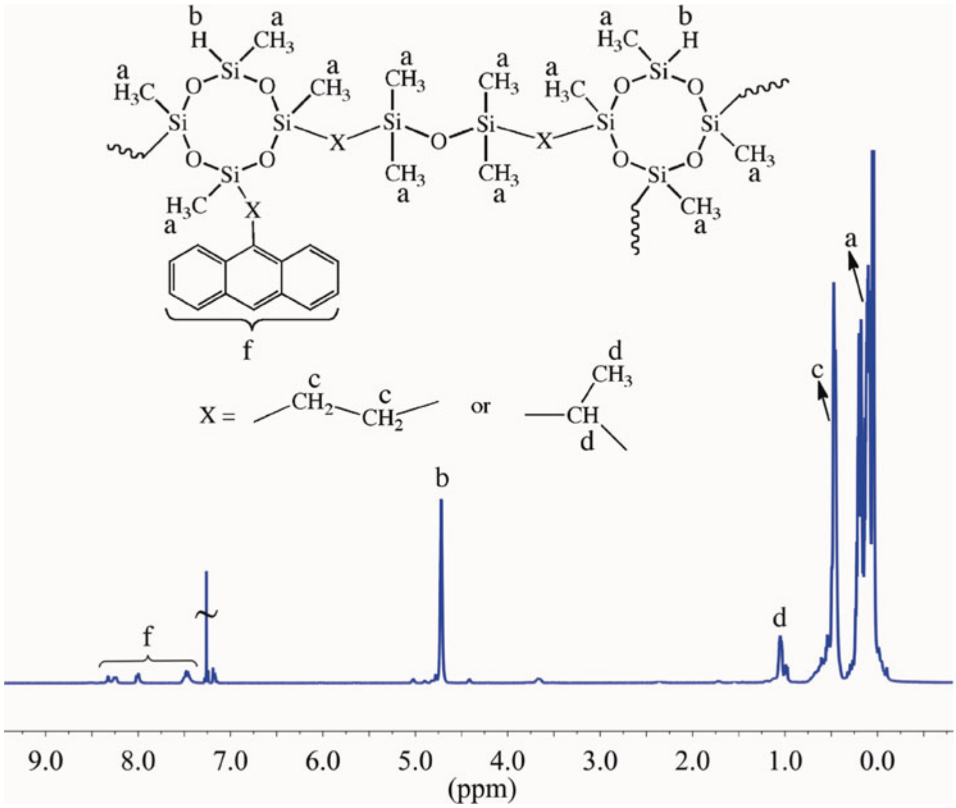


Figure 1. ^{1}H NMR spectrum of functionalized TMCS−DTMS hybrid polymer.

which resulted in colorless, liquid-viscous polymer state. The polymer was also chemically soluble in toluene, chloroform, and tetrahydrofuran. Number average-molecular-weight and polydispersity index of the polymer were determined as 7×10^3 and ~3, respectively. To confirm the completion of the functionalization reaction, we mixed a small amount (4.89×10^{-4} mol) of 9-vinylanthracene with TMCS−DTMS polymer through one-pot hydrosilylation reaction. The integral ratio of the Si−H to Si−CH_3 was compared with the integral ratio of the anthracene phenyl protons to Si−H before and after the functionalization. The result showed that the vinyl peaks at 5.6−6.8 ppm almost disappeared from ^{1}H NMR spectra but that the Si-H groups still remained. This means that the whole amount of 9-vinylantracene reacted with residual Si−H groups of the polymer (Fig. 1). As can be seen in Fig. 1, functionalities of TMCS−DTMS polymer can be controlled by the amount of anthracene.

Cross-linked polymer films were prepared through self-crosslinking by hydrolysis and condensation reactions. From hydrolysis of the polymer containing unreacted Si−H groups, the Si−OH groups were formed when it was exposed to air conditions. The Si−O−Si linkage was generated from the self-condensation of the hydrolyzed Si−OH groups. The crosslinking formation was confirmed by FT−IR: the disappearance of the Si−H peaks at 900 and 2150 cm^{-1}, indicating that all unreacted Si−H groups were converted to Si−O−Si linkage. The sharp and strong peak at 1100 cm^{-1} was ascribed to Si−O−Si bonding formation (Fig. 2). It can be concluded that the crosslinking of TMCS−DTMS

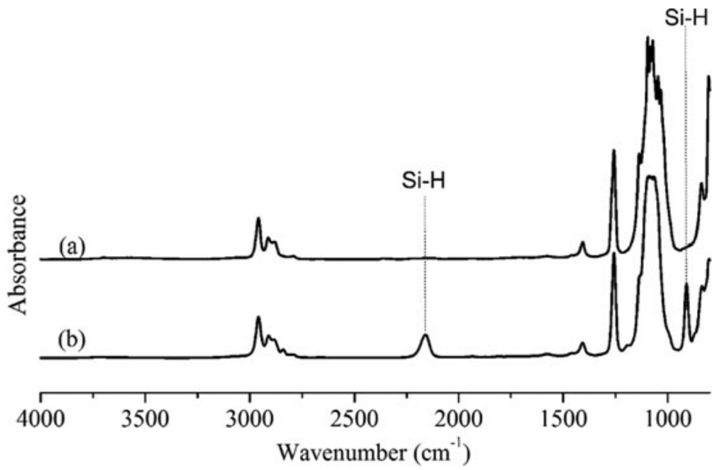


Figure 2. FT-IR spectra of crosslinked TMCS−DTMS hybrid films (a) and polymer (b).

polymer can be easily performed through self-condensation reaction under mild conditions [8].

The thickness of free-standing and spin-coated films was measured as ~0.2 mm and ~150 μm, respectively. Figure 3(a) shows UV−absorption and fluorescence spectra of the cross-linked hybrid polymer spin-coated film. The strong photoluminescence was observed for functionalized and crosslinked siloxane-based networked polymers. Transparent and flexible free-standing film was successfully prepared (Fig. 3(b)). The properties of the films will be adjusted by changing the amount of luminescent molecules as well as crosslinking points.

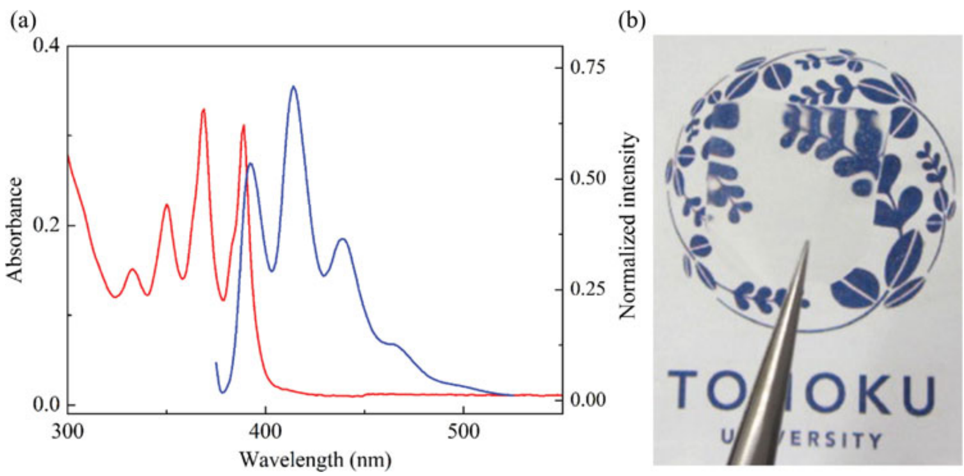


Figure 3. (a) UV−Vis absorption (red) and fluorescence (blue) spectra of crosslinked polymer spin-coated film. (b) Photograph of a cross-linked free-standing film.

4. Conclusions

Synthesis of siloxane-based hybrid polymer of TMCS and DTMS and its functionalization with an anthracene group was carried out using the one-pot hydrosilylation reaction. The polymer was soluble in toluene, chloroform and tetrahydrofuran. The polymer has unreacted Si-H groups which allow further incorporation of vinyl functional molecules and self-crosslinking by hydrolysis and condensation reactions to form Si−O−Si linkage. One-pot hydrosilylation and self-crosslinking of TMCS−DTMS polymer provide facilities for the preparation of new siloxane-based functional network polymer, which lead to electronic and optical properties toward flexible electronics.

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