Study on the Effect of Platinum Catalyst for the Synthesis of Polydimethylsiloxane Grafted with Polyoxyethylene

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Abstract: Polydimethylsiloxane grafted with polyoxyethylene (PDMS-g-POE) was synthesized by the hydrosilylation reactions in the presence of various platinum-based catalysts. The hydrosilylation reactions also gave small amount of side products such as propionaldehyde and isomers of unsaturated polyoxyethylene. When the reactivities of catalytic systems including Speier’s, Lamoreaux’s, and Karstedt’s catalyst and platinum adsorbed on carbon (Pt/C) were compared based on the amount of platinum, Speier’s catalyst was found to be the most effective in the hydrosilylation reaction and Pt/C showed extremely low reactivity compared to three other catalytic systems.

Keywords: polydimethylsiloxane, polyoxyethylene, platinum catalyst, hydrosilylation

Introduction

Silicone surfactants have been widely used in many industrial fields because of their thermal stability and low surface tension [1-3]. The siloxane chain is highly flexible and even high molecular weight chains are in liquid state at room temperature. Silicones modified with hydrophilic polyoxyethylene (POE) are extensively used as foam stabilizers, emulsifying agents, detergents and anti-foaming agents [4]. The molecular structure of POE-modified silicones are typically classified into branch type, triblock type, and comb type, and the differences in their physical properties are well summarized in the earlier literature [5]. Among them, POE-modified silicones composed of polydimethylsiloxane backbone and branched polyoxyethylene (PDMS-g-POE) are most extensively studied.

PDMS-g-POE is generally synthesized by hydrosilylation reactions of polydimethylsiloxane-co-polymethylhydrogensiloxane (SH copolymer) with unsaturated polyoxyethylene (UPOE). Hydrosilylation is a general term used for the addition reaction of organic or inorganic silicon hydride to molecules containing multiple bonds, and has developed in one of the most common method in synthetic organosilicone chemistry due to wide spectrum of usable unsaturated moieties [6,7]. Since chloroplatinic (IV) acid (CPA) was found to be an effective homogeneous catalyst for the hydrosilylation process, numerous papers deal with mechanistic aspect of hydrosilylation and also with the search for new or improved catalysts. A majority of the successful results were observed in the use of metal complexes such as rhodium [8-11] and platinum complexes. Three types of stable platinum-containing catalyst such as Speier [12,13], Lamoreaux [14,15], and Karstedt [16,17] are well known and industrially used. These complexes are prepared from CPA by the reaction with isopropanol, isooctanol and divinyltetramethyldisiloxane, respectively. Platinum adsorbed on carbon (Pt/C) is also used for hydrosilylation reactions [18]. However, Speier’s catalyst [19, 20] has been generally employed regarding hydrosilylation reaction producing PDMS-g-POE, whereas Karstedt’s catalyst [21] has seen only limited applications, and no studies have been reported for Lamoreaux’s catalyst and Pt/C. Even for both Speier’s and Karstedt’s catalysts, it is not feasible to make a direct comparison on catalytic activities, since reaction conditions such as the mole ratio of reactants, the amount of catalysts, the temperature and the kind of solvent in each case are not consistent.

In this study, PDMS-g-POE was synthesized by two steps as shown in Figure 1. The first step is the synthesis of SH copolymer by the equilibrium polymerization of
Figure 1. Synthesis of PDMS-g-POE.

octamethycyclotetrasiloxane (D4), poly(methylhydrosiloxane) (PMHS) using hexamethyldisiloxane (HMDS) as the end-capping reagent and the second is the hydrosilylation reactions of SH copolymer with UPOE in the presence of various platinum-based catalysts. For catalysts, Speier’s, Lamoreaux’s, and Karstedt’s catalyst and Pt/C were used and their activities were compared under the same reaction conditions, based on the amount of platinum in each catalytic system. The effects of reaction temperature on the hydrosilylation reaction were also investigated.

Experiments

Materials
D4, PMHS (average molecular weight, 1700 ~ 3200), HMDS, CPA and Pt/C (1 wt% Pt loading) were purchased from Aldrich and used without further purification. UPOE, whose molecular weight is about 440 g/mol and trade name is PKA 5008, was kindly supplied by NOF Cooperation, Japan.

Speier’s catalyst was prepared by 50 mg of CPA in 5 mL of isopropanol (IPA) and kept in refrigerator before use [13]. Lamoreaux’s catalyst was prepared according to the general method [15]. A solution of 50 mg of CPA dissolved in 0.5 mL of 1-octanol was evaporated at 60 °C for 90 min and dried under vacuum. The residue was dissolved in 1.5 mL of THF and kept in refrigerator before use. Karstedt’s catalyst, whose trade name is platinum-1, 3-divinyl-1,1,3,3-tetramethyldisiloxane, was purchased from Aldrich as 0.10 M of xylene solution (19.5 mg of Pt in 1 mL of the solution).

Characterization

FT-IR was performed using NEXUS (Nicolet Instrument Corp. U.S.A). The neat samples were cast directly onto sodium chloride plates. ¹H-NMR and ²⁹Si-NMR were obtained by Spectrometer FT-NMR (500 MHz) of Bruker using CDC₁₃ as a solvent. Cr(acac)₃ was added to the solutions for ²⁹Si-NMR measurements to decrease the relaxation time [22].

Synthesis of SH Copolymer
SH copolymer composed of 22 units of dimethylsiloxane and 2 units of methylhydrogen was synthesized according to the general procedure [23,24]. 169 g of D4, 15 g of PMHS and 16 g of end-capper (HMDS) were added to a 500 mL four-necked reactor. After raising temperature to 45 °C, 3 g of sulfuric acid was added and stirred under nitrogen atmosphere for 48 h. Sodium hydrogen carbonate was added to neutralize the acid in the reaction mixture. The precipitate was filtered out and the cyclic monomers remained upon the equilibrium were removed by vacuum stripping at 80 °C for at least 2 h.

Synthesis of PDMS-g-POE
A solution of 45 g (23.6 mmol, 47.2 milli equivalents based on Si-H) of SH copolymer in 29 mL of toluene was placed in three-neck round bottom flask equipped with a thermometer, dropping funnel, reflux condense, and the temperature was maintained at 65 °C. To a solution, 0.72 mL of 1 wt% Speier’s catalyst, which corresponds to 100 ppm based on CPA or 40 ppm based on Pt to total weight of reagents, was added and then 27 g (61.4 mmol) of UPOE was added dropwise via dropping funnel for 20 min. During the course of the reaction, periodic samples were taken, and the conversions were monitored by FT-IR. After 2 h, 1.4 g of charcoal was added in room temperature and the solution was stirred for 2 h. After filtration, the solvent was removed by evaporation under vacuum at 60 °C. 68.9 g (96 % yield) of product PDMS-g-POE was obtained. Characterization of the product was performed by the measurement of FT-IR, ¹H-NMR and ²⁹Si-NMR.
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Results and Discussion

Synthesis of SH Copolymer

SH copolymers were synthesized by the equilibrium polymerization of D4 and PMHS using HMDS as the end-capping reagent to control molecular weight. Incorporation of HMDS in feed led to the copolymer containing methylhydrosiloxy units, and the ratios of methylhydrosiloxy units to dimethylsiloxy units in the copolymer can be regulated by the equivalent ratio of HMDS/D4 in feed.

The structure of SH copolymer was analyzed by $^1$H-NMR and $^{29}$Si-NMR. $^1$H-NMR spectrum ((A) of Figure 2) of SH copolymer shows two main peaks, and the signal at 0 ppm (peak a) and 4.7 ppm (peak b) correspond to protons of all methyl groups and protons of hydrosiloxy units, respectively. Exact ratio of methylhydrosiloxy units to dimethylsiloxy units in the copolymer can be regulated by the equivalent ratio of HMDS/D4 in feed.

More detailed structure of SH copolymer was investigated by $^{29}$Si-NMR ((B) of Figure 2). The signal at ca. -20 ppm (peak b) and -34 ppm (peak c) in $^{29}$Si-NMR spectrum correspond to the dimethylsiloxy units and to methylhydrosiloxy units, irrespectively. In peaks b and c, as reported earlier [22], silicones adjacent to methylhydrosiloxy units are slightly shifted downfield relative to those between dimethylsiloxy units. The absolute values of each unit were calculated by using a peak at 7.4 ppm (peak a), which is assigned to the silicone at the terminals, and 24.9 unit of dimethylsiloxy and 2.0 unit of methylhydrosiloxy were obtained. The observed molecular weight (2,127 g/mol) calculated from $^{29}$Si-NMR studies is slightly higher than the targeted molecular weight (1,910 g/mol) due to the loss of low molecular weight species during vacuum stripping at 80 °C after the reaction.

Synthesis of PDMS-g-POE

Pendant silicone hydrides of SH copolymer were hydrosilylated with allyl groups of UPOE in the presence of various type of platinum-based catalyst to produce PDMS-g-POE. Slightly excess UPOE (1.3 moles per mole of silicone hydride in copolymer) were introduced to react all silicone hydrides.

Progress of the reaction was monitored by FT-IR to observe the disappearance of the strong Si-H stretching band at 2160 cm$^{-1}$ as shown in Figure 3. The conversions were calculated according to the Equation 1, by comparing the ratios of the transmittance at 1256 cm$^{-1}$ assigned to Si-CH$_3$ stretching which remains unchanged in the course of reaction. In Equation 1, $T_{2160}(0)$ and $T_{1256}(0)$ are transmittance at 2160 and 1256 cm$^{-1}$ before reaction and $T_{2160}(t)$ and $T_{1256}(t)$ are transmittance at 2160 and 1256 cm$^{-1}$ at time t.

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\text{Conversion (\%)} = \frac{T_{2160}(0)/T_{1256}(0) - T_{2160}(t)/T_{1256}(t)}{T_{2160}(0)/T_{1256}(0)} \times 100 \quad (1)
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Figure 4. $^1$H-NMR spectrum (A) and enlarged spectrum (B) of PDMS-g-POE.

Figure 5. Assignment of the peaks defined in $^1$H-NMR spectrum (Figure 4) of PDMS-g-POE.

The conversion and chemical structure of PDMS-g-POE was also confirmed by $^1$H-NMR. As shown in (A) of Figure 4, two main peaks such as a (all CH$_3$ attached Si) and e (CH$_2$CH$_2$ unit in POE) and b, c, d peaks can be easily assigned, on the other hand, many small signals were also observed. Platinum-based catalysts are known to cause some isomerization of the allyl group on the polyether reactant to give propenyl ethers. In an enlarged spectrum ((B) of Figure 4), cis and trans forms of propenyl ethers as well as allyl groups of excess UPOE were observed and can be assigned as described in Figure 5. The ratios of cis/trans isomers are about 40/60 in all catalytic systems used in this study. Three other peaks indicated as p-1, p-2, and p-3 in Figures 4 are in good agreement with $^1$H-NMR spectrum of propionaldehyde (PA), which can be produced by hydrolysis of propenyl ethers. Absence of Si-H, which appears in 4.7 ppm as a singlet if remained, demonstrates complete reaction.

The complete reaction was also confirmed by the disappearance of a peak (-35 ppm) assigned to Si-H in $^{29}$Si-NMR of PDMS-g-POE (Figure 6), and the silicone reacted with UPOE was observed at -22.50 ppm (peak c').

Comparison of Catalysts

The effect of Pt amount in various catalytic systems on the conversions of hydrosilylation reactions was described in Figure 7, where the conversions at 120 min were directly compared because no changes in the conversion were observed after 120 min. The use of more than 40 ppm of Pt induced complete reaction regardless
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of the nature of catalysts applied, on the other hand, the reactivity of Lamoreaux’s catalyst were slightly lower than those of other two catalysts.

Karstedt’s catalyst, which is prepared from the reaction of divinyltetramethyldisiloxane with H₂PtCl₆, gives a Pt⁰ complex containing silicone-vinyl ligands [25,26], on the other hand, Speier’s and Lamoreaux’s catalysts are a complex mixtures of Pt compounds with PtⅡ and PtⅣ species where the identity of the ligand is unknown [7, 15,27]. The differences in the reactivities among three catalytic systems observed in this study are not considered due to the differences in the valence of platinum metal.

Lamoreaux’s catalyst was developed to activate hydrosilylation reactions without the formation of undesirable by-product [14]. Since no side reactions in the synthesis of PDMS-g-POE occurred not only for Lamoreaux’s system but also for other two systems, the advantages of Lamoreaux over other two catalytic systems were not manifested in this study.

Pt/C showed extremely low reactivity compared to three other catalytic systems mentioned above. No reaction occurred when 50 ppm based on the amount of Pt was used, and the conversions reached into only 88% and 93% even for 100 and 200 ppm, respectively. The complete reaction was observed for 300 ppm of Pt.

Since Pt/C was first reported by Wagner [28] to be an active hydrosilylation catalyst for alkenes and alkynes under high temperature and pressure, the studies on Pt/C have been mainly focused on the stereochemistry of the addition of silanes to a variety of terminal alkynes [29,30]. To access the catalyst’s efficiency of Pt/C against a common catalyst, the comparison of the selectivity was made with Karstedt’s catalyst [31]. However, no study has directly compared the activities of Pt/C and Karstedt’s catalyst.

The advantage of Pt/C over other catalytic systems is reusable. In this study, Pt/C was recovered by the filtration and washing with toluene after completion of the reaction and applied for the same reaction to evaluate the efficiency of reused Pt/C. Reactivities of recycled Pt/C were compared as shown in Figure 8, where the conversions to 120 min were described because no significant changes in the conversions were observed after 120 min. When 300 ppm of Pt/C was used, the reaction was completed just after the completion of dropping of UPOE (0 time in Figure 8). However, the activities of Pt/C decreased as the number of recycling increased. Pt/C recycled twice showed the completion of the reaction at 120 min., however more recycling of Pt/C did not afford the completion of the reaction regardless of the reaction time.

Reaction Optimization for Speier’s Catalyst

Using Speier’s catalyst being most effective in the hydrosilylation reaction for the synthesis of PDMS-g-POE, the effect of temperature and the amount of catalyst were investigated. The conversions increased as more catalysts were used as described in Figure 9, and the use of more than 30 ppm based on Pt was required for the completion of reaction. On the other hand, significant effect of re-
action temperature on the conversions at 120 min, which were not changed by further reaction, was not observed even though the reaction rates became fast as the temperature increased. It is remarkable that the conversions at 75 °C are lower than those at 65 °C when 20 and 30 ppm of catalyst were used. Platinum in catalytic system is reduced by silicone hydride and then reacts with olefin under hydrosilylation conditions. However, it is known that no detectable amount of Pt⁰ is precipitated and this causes the deactivation of catalysts with the change of the solution from yellow to dark brown if the temperature is increased to about 80 ∼ 100 °C [7]. In our studies, even if the temperature was adjusted into 75 °C, exothermic nature of hydrosilylation reaction caused the temperature of the reaction solution to reach about 80 °C during dropping of UPEO. Therefore, it is considered that the conversions at 75 °C were lower than those at 65 °C due to the deactivation of catalysts. In fact, the reaction mixture was slightly yellowish throughout the reaction at 65 °C or below, on the other hand, dark-brown at 75 °C in our studies.

Conclusions

PDMS-g-POE was synthesized by the hydrosilylation reactions of SH copolymer with UPOE in the presence of various platinum-based catalysts. The reactivities of catalytic systems including Speier’s, Lamoreaux’s, and Karstedt’s catalyst and Pt/C were compared based on the amount of platinum, and the effects of reaction temperature on the hydrosilylation reaction were also investigated. The following results are drawn:

1) The detailed study on 1H-NMR showed that the hydrosilylation reactions of SH copolymer with UPOE afforded not only PDMS-g-POE but also small amount of side products such as isomers of unreacted UPOE and PA.

2) Among four catalytic systems investigated, Speier’s catalyst was the most effective in the hydrosilylation reaction for the synthesis of PDMS-g-POE.

3) Pt/C showed extremely low reactivity compared to three other catalytic systems and the use of more than 300 ppm of Pt was necessary for the completion of the reactions.

4) When Pt/C was recovered and reused after the reaction, the activities of Pt/C decreased as the number of recycling increased. Pt/C recycled twice showed the completion of the reaction at 120 min., however more recycling of Pt/C did not afford the completion of the reaction regardless of the reaction time.

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References