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Development and Application of Latent Catalysts for Hydrosilylation System. 1. Control of Activity of Platinum Catalyst by Isocyanide

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Introduction

The hydrosilylation technique is of importance in the field of both organic synthesis and industrial application such as cross-linking reactions of silicon resin,[1−3] commonly applied to adhesives, sealants, coatings, and foaming materials. Especially, it is required to control the activity of the platinum catalyst for the purpose to realize the latent system and to expand the adaptable applications. Despite these remarkable aspects, only several attempts have been made to control the hydrosilylation process by using derivatives of propargyl alchol, malaete, fumarate, and γ-cyclodextrin.[4−10] In these cases, however, it was necessary to use a large excess amount of additives to reveal a sufficient effect.

Although isocyanide is well-known as a good ligand for many transition-metal complexes[11−14] and is potentially useful to control the activity of catalysts, its effect on the hydrosilylation catalysts has not been reported so far. On the basis of stable platinum-isocyanide complexes and, more practically, by the addition of isocyanides to the commonly used H_2PtCl_6 catalyst, we describe herein quite effective thermal latent hydrosilylation catalysts that can initiate the reaction on heating but not at ambient temperature.

Results and Discussion

The hydrosilylation of triethylsilane and trimethylvinylsilane was carried out at various temperatures for 1 h in the presence of 0.15 mol % platinum catalysts. While H_2PtCl_6 alone revealed activity near room temperature, *trans*-$PtCl_2(CN{-}Bu^t)_2$ prepared from K_2PtCl_6 and *tert*-butyl isocyanide was found to be effective only at the temperature higher than 60 °C (Figure 1). That is, the reaction was inhibited completely at room temperature but proceeded smoothly above 60 °C. Alternatively, by using an in situ catalyst prepared simply by the addition of 2 equiv of *tert*-butyl isocyanide to H_2PtCl_6, we could observe a similar behavior to the case of *trans*-$PtCl_2(CN{-}Bu^t)_2$ where the reaction occurred above 60 °C. Compared with the reported system using propargyl derivatives in which a large excess amount (20−100 equiv of Pt) of the additive is required to attain a sufficient effect, it is of note that the present system could give a clear effect by using a very small amount of the additive. On the other hand, *trans*-$PtCl_2(CN{-}Bu^t)_2$ and in situ catalyst resembled the initiation temperature and the shape of curve. This results indicate that the in situ catalyst has the same reactivity as *trans*-$PtCl_2(CN{-}Bu^t)_2$, and it may be considered that the in situ catalyst ligated 2 equiv of *tert*-butyl isocyanide in a similar isolated catalyst.

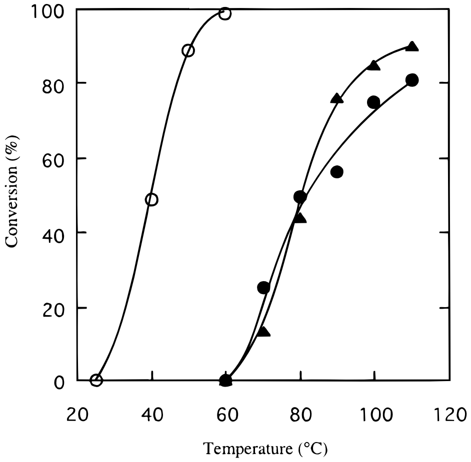

Figure 1. Temperature versus conversion in the hydrosilylation of triethylsilane and trimethylvinylsilane (conditions: $[Et_3SiH] = [Me_3SiCH{=}CH_2] = 6.6$ M, [Pt catalyst] = 0.01 M, in *o*-xylene for 1 h): ○, H_2PtCl_6 alone; ●, *trans*-$PtCl_2(CN{-}Bu^t)_2$; ▲, H_2PtCl_6 with 2 equiv of *tert*-butyl isocyanide.

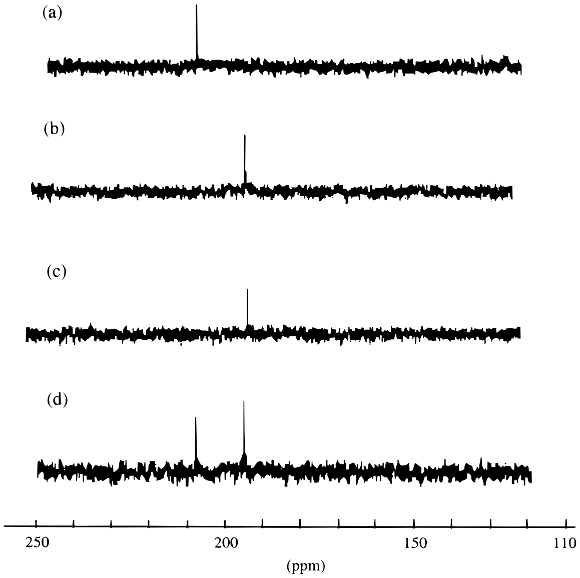

Figure 2. ^{13}C NMR spectra of isocyanide moieties of *tert*-butyl isocyanide in 2-propanol-d_8 (conditions: *tert*-butylisocyanide, 0.24 mmol; H_2PtCl_6, 0.12 mmol): *tert*-butyl isocyanide alone (a) and in the presence of 0.5 equiv of H_2PtCl_6 at 25, 60, and 70 °C (b, c, and d, respectively).

Figure 2 shows the ^{13}C NMR spectra of the isocyanide moieties in both the absence and the presence of H_2PtCl_6 in 2-propanol-d_8. The in situ catalyst revealed a peek at 196.15 ppm assignable to the coordinated

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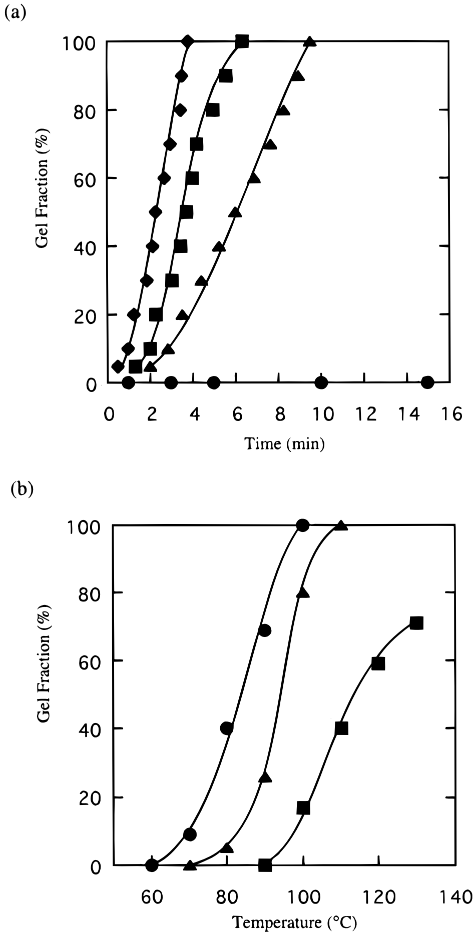

Figure 3. (a) Time−gel fraction curves in the hydrosilylation curing of the silicon resins at (●) 60, (▲) 70, (■) 80, and (◆) at 90 °C. (b) Curing temperature versus gel fraction in the curing of the silicon resin for 10 min in the presence of various in situ catalysts (0.05 mol %): (●) *tert*-butyl isocyanide, (▲) cyclohexyl isocyanide, (■) *n*-octyl isocyanide.

isocyanide moieties at 25 °C (Figure 2b). When the spectrum of the in situ catalyst was measured at 60 °C (i.e., the temperature to initiate the hydrosilylation), no significant change was observed (Figure 2c). At 70 °C, however, two separated peaks at 196.15 and 203.45 ppm were observed (Figure 2d). The former peak is ascribable to the ligated *tert*-butyl isocyanide on the platinum and the latter to the free *tert*-butyl isocyanide (Figure 2a). The results can be taken to mean that the ligand exchange can take place on heating (to ca. 70 °C), which is slow enough for the NMR time scale to be observed as two different species in the ^{13}C NMR spectrum. This result indicated that isocyanide−platinum complex is more inert than the other inhibitors system, and the isocyanide compound was strongly ligated to platinum by using a small amount of the additive.[17] Accordingly, it was clearly demonstrated that the activation of the isocyanide complexes upon heating is due to the dissociation of the isocyanide ligands.

As an application of the platinum−isocyanide complex for the thermal latent curing system, the cross-linking reaction of silicon resin was carried out at various temperatures with in situ catalysts consisting of various isocyanides. Figure 3a shows the time−gel fraction curves at various temperatures by using the *tert*-butyl isocyanide ligand, in which one can observe a clear temperature dependence upon curing, that is, smooth curing (within several minutes) at temperatures higher than 70 °C, but not at 60 °C. As shown in Figure 3b, the cross-linking temperature of silicon resin is affected by the isocyanides, where the activation temperature increased in the order of *tert*-butyl isocyanide < cyclohexyl isocyanide < *n*-octyl isocyanide.

The results obtained here might be of importance to attain the one-pot system for the hydrosilylation curing, in which the mixture of prepolymers and the catalyst can be stored for a long time (ca. 1 month) under ambient conditions but can be cured smoothly on heating. Practical application of the present system to the curing process is in progress.

Experimental Section

Materials and Instruments. *trans*-$PtCl_2(CN-Bu^t)_2$ was prepared by the reported procedure.[15] *tert*-Butyl isocyanide, *n*-octyl isocyanide, cyclohexyl isocyanide, trimethylvinylsilane, and triethylsilane were purified by distillation. H_2PtCl_6, poly(dimethylsiloxane) having dimethylvinylsiloxy end groups (M_n = 20 000, obtained from Gelest, Ltd.), and copolymer consisting of polydimethylsilane and methylhydrogensiloxane segments (M_n = 1200, obtained from Gelest, Ltd.) were used as received.

GC analysis were recorded on Shimadzu GC-8A equipment. ^{13}C NMR spectra were recorded in 2-propanol-d_8 on a JEOL EX-400 instrument (100 MHz, tetramethylsilane internal standard). The curing time and temperature of the silicon resins were measured by scanning vibrating needle cremate (SVNC) system[16] on a RAPARA VNC92H/F2300 model.

Preparation of Latent Catalyst (General Procedure). To a THF (10 mL) solution of the isocyanide derivatives (1.08 mmol) was added a THF (1 mL) solution of H_2PtCl_6 (0.54 mmol). Immediately the color of the Pt-catalyst solution turned from orange to brown. After stirring at room temperature for 1 h, the solution was further aged at 30 °C for 12 h.

Hydrosilylation Reaction of Triethylsilane with Trimethylvinylsilane (Typical Procedure). To a *o*-xylene (5 mL) solution of triethylsilane (3.31 g, 33.0 mmol) and trimethylvinylsilane (3.84 g, 33.0 mmol) containing *n*-decane (0.05 g) was added a THF solution of the platinum catalyst (0.1 mL, 0.15 mol %). The resulting solution was stirred at 50 °C, and the conversion of the two compounds was followed by GC analyses after designated reaction periods.

Curing Reaction of Silicone Resin Containing End-Vinyl Moieties with That Partially Consisting of Methyl−Hydrogensiloxane Units (Typical Procedure). A mixture of poly(dimethylsiloxane) having dimethylvinylsiloxyl end groups (10.0 g, vinyl content 1.3 mmol), a copolymer consisting of poly(dimethylsiloxane) and methylhydrogensiloxane segments (0.56 g, Si−H content 2.3 mmol), and a THF solution of the platinum catalyst (0.05 g) was heated at 100 °C. The curing time was monitored by SVNC analysis.

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(17) Although no concrete mechanistic discussion has been reported, we assume that the inhibitors in refs 4−10 are in a thermodynamic control. Accordingly, a large excess amount of the inhibitors will probably be added.

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