NOTES

Development and Application of Latent Catalysts for Hydrosilylation Systems VIII¹. Control of Catalytic Activity by Poly(1-phenylethylisocyanide)

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Hydrosilylation is often applied to produce siloxane networks^{2–5} in which highly active platinum catalysts are commonly employed. For smooth industrial applications, it is required to suppress the activity of catalysts at ambient conditions so as to control the process. An ideal curable system of silicone resin preferably possesses the characteristics of both an instant curing at elevated temperature and an infinite pot life at ambient temperature. Various approaches have been made to improve the “too-high” activity of platinum catalysts in the hydrosilylation by using derivatives of propargyl alcohol, derivatives of fumarate, on the basis of host-guest interactions of cyclodextrin, etc., most of which, however, require a large excess amount of the additives to realize a moderate latency (*e.g.*, in the case of the acetylene derivatives, significant retardation effects are observed when 20–100 equiv of the acetylene derivatives with respect to platinum catalyst are employed).^{6–13}

We reported a remarkably high ability of various isocyanide and imine derivatives to control the catalytic activity of H₂PtCl₆ toward the hydrosilylation. That is, the catalytic activity was found to appear on heating but not at ambient temperature by the addition of near stoichiometric amounts of the additives (with respect to Pt).^{14–16} As an alternative approach, we reported the remarkable enhancement of retardation by use of multifunctional acetylenes such as diynes and polystyrene derivatives having propargyl moieties in which the activity of the catalyst could be reduced dramatically in comparison with the case of monoacetylenes.¹⁷ The most characteristic feature of the multifunctional acetylene systems is that they can control the catalytic activity with small amount of the additive.

On the basis of the reported fact that the nitrogen atom in polyisocyanides coordinates to the transition metals,¹⁸ they may also serve as an effective polymeric additive to control of the catalytic activity. As was the case of the polymers bearing propargyl moieties, polyisocyanides may also realize very high local concentrations of ligating moieties to promote activity control. In this article, we wish to report a remarkable ability of poly(1-

phenylethylisocyanide) to control the activity of H₂PtCl₆ toward hydrosilylation process.

EXPERIMENTAL

Materials and Instruments

1-Phenylethylisocyanide¹⁹ (racemate) and poly(1-phenylethylisocyanide)²⁰ ($M_n = 12800$) were prepared as reported. *o*-Xylene and tetrahydrofuran (THF) were dried by the usual method and distilled under nitrogen. H₂PtCl₆, polydimethylsiloxane having dimethylvinylsiloxyl end groups ($M_n = 20000$, obtained from Gelest Ltd.), and copolymer consisting of dimethylsiloxane and methylhydrogensiloxane segments ($M_n = 1200$, [–OSi(H)MeO–]/[–OSiMe₂O–] = 30/70, obtained from Gelest Ltd.) were used as received. Gas chromatographic analyses were carried out on a Simadzu GC-8 A equipment. DSC analyses were performed on a SII DSC 220 C instrument at a heating rate of 10°C min^{–1}. The gel fraction of silicone resin was determined by scanning vibrating needle curemeter (SVNC) system²¹ on a RAPARA VNC92H/F 2300 model.

Preparation of a Latent Catalyst

To THF (10 mL) solution of poly(1-phenylethylisocyanide) (1.1 mmol unit) was added a THF (0.1 mL) solution of H₂PtCl₆ (0.54 mmol). After stirring at room temperature for 1 h, the mixture was aged at 30°C for 12 h.

Hydrosilylation Reaction of Triethylsilane with Trimethylvinylsilane

To *o*-xylene (5 mL) solution of triethylsilane (3.31 g, 33.0 mmol) and trimethylvinylsilane (3.84 g, 33.0 mmol) containing *n*-decane (50.0 mg) was added THF solution of the Pt-catalyst (640 mg, 3 mol%). The resulting solution was stirred at 40–110°C and the conversion of the two compounds was followed by GC analyses after designated reaction periods.

Curing Reaction of Silicone Resin

A mixture of polydimethylsiloxane having dimethylvinylsiloxyl end groups (10.0 g, vinyl content : 1.3 mmol), a copolymer consisting of polydimethylsiloxane and meth-

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Scheme 1.

Scheme 2.

Figure 1. Temperature *versus* conversion plots for the hydrosilylation of triethylsilane with trimethylvinylsilane (conditions: $[\text{Et}_3\text{SiH}]$; 6.6 M, $[\text{Me}_3\text{SiCH}=\text{CH}_2]$; 6.6 M, $[\text{Pt}]$; 0.01 M in *o*-xylene for 1 h). ○: H_2PtCl_6 alone, ●: 1 equiv of polymer, ▲: 2 equiv of polymer, ■: 4 equiv of polymer.

Figure 2. DSC curves of reaction mixture obtained by curing reaction (25–150 °C, 10 °C min⁻¹) of silicone resin (conditions: polydimethylsiloxane end-capped with dimethylvinylsilane; 10.0 g, poly(dimethylsiloxane-*co*-methylhydrogensiloxane); 0.56 g, H_2PtCl_6 ; 0.05 mmol, polymer; 1 equiv. to Pt). (a) H_2PtCl_6 alone, (b) H_2PtCl_6 /poly(1-phenylethylisocyanide).

ylhydrogensiloxane segments (560 mg, Si-H content: 2.3 mmol), and a THF solution of the platinum catalyst (50.0 mg) was heated at various temperatures. The curing temperature was measured by DSC and the time-gel fraction was monitored by SVNC analyses.

RESULTS AND DISCUSSION

To evaluate the effect of poly(1-phenylethylisocyanide), the model reaction of triethylsilane with trimethylvinylsilane was carried out at various temperatures in both the presence and the absence of the polymer (Scheme 1 and Figure 1). While the reaction proceeded smoothly with H_2PtCl_6 alone at 50 °C for 1 h, the initiation temperature shifted to higher region by *ca.* 30 °C in the presence of 2 equiv. of the polymer. That is, poly(1-phenylethylisocyanide) was found to suppress the catalytic activity of the H_2PtCl_6 toward hydrosilylation. The

polymer concentration was also an important factor to control the catalytic activity. As shown in Figure 1, the reaction started at *ca.* 40 °C with 1 equiv of the polymer, while a temperature higher than 70 °C was required to initiate the reaction in the presence of 4 equiv. of the polymer.

As one application of the catalyst consisting of H_2PtCl_6 and poly(1-phenylethylisocyanide) to the thermal latent curing system, the curing reaction of silicone resin was performed (Scheme 2). A mixture of polydimethylsiloxane end-capped with dimethylvinylsiloxyl group and a copolymer of dimethylsiloxane and methylhydrogensiloxane was subjected to curing reaction at various temperatures (Figure 2). While the curing reaction started at *ca.* 45 °C by using H_2PtCl_6 alone, the corresponding temperature shifted to *ca.* 93 °C in the presence of poly(1-phenylethylisocyanide) (2 equiv. to Pt).

The time-gel fraction curves of the curing reaction of

Figure 3. Curing temperature *versus* gel fraction plots for curing reaction of silicone resin in the presence of poly(1-phenylethylisocyanide) (conditions : polydimethylsiloxane end-capped with dimethylvinylsilane ; 10.0 g, poly(dimethylsiloxane-*co*-methylhydrogen-siloxane ; 0.56 g, H_2PtCl_6 ; 0.05 mmol, polymer ; 1 equiv. to Pt). ○ : 80°C, ● : 90°C, ▲ : 100°C, ■ : 110°C.

the silicone resin were monitored in the presence of H_2PtCl_6 /poly(1-phenylethylisocyanide) (2 equiv. to Pt) system at various temperatures from which the latent character of the present catalyst system was confirmed (Figure 3). That is, the reaction occurred rapidly at above 90 °C, while the curing reaction did not proceed at all below 80 °C.

The present results demonstrate the possibility of a one-pot curing system of the silicone resin, in which a mixture of prepolymer and the catalyst can be stored under ambient conditions and cured smoothly on heating.

REFERENCES

1. For part 7, see, K. Kishi, T. Ishimaru, M. Ozono, I. Tomita, and T. Endo, *J. Adhesion Soc. Jpn.*, in press.
2. J. F. Harrod and A. J. Chalk, in "Organic Synthesis via Metal Carbonyls", Vol.2, John Wiley, New York, N.Y., 1997, p 673.
3. J. F. Harrod and A. J. Chalk, *J. Am. Chem. Soc.*, **87**, 16 (1965).
4. V. B. Pukhunarevich, E. Lukevics, L. I. Kopylova, and M. G. Voronkov, in "Perspective of Hydrosilylation, Institute of Organic Synthesis", Riga, Latvia, 1992.
5. I. Ojima, in "The Chemistry of Organic Silicon Compounds", Vol. 2, S. Patai and Z. Rappaport, Ed., Wiley Interscience, New York, N.Y., 1989.
6. W. Kniege, W. Michel, and J. Ackerman, U. S. Pat. 4,487,906, 1984.
7. A. Shirahata and S. Shosaku, U. S. Pat. 4,465,818, 1984.
8. G. Chandra, P. Y. K. Lo, and Y. A. Peter, U. S. Pat. 4,472,563, 1984.
9. J. Cavezzan, U. S. Pat. 4,595,739, 1986.
10. G. Janik and M. Buentello, U. S. Pat. 4,801,642, 1989.
11. L. N. Lewis, C. A. Sumpter, and M. Davis, *J. Inorg. Organomet. Polym.*, **5**, 377 (1995).
12. L. N. Lewis, C. A. Sumpter, and J. Stein, *J. Inorg. Organomet. Polym.*, **6**, 123 (1996).
13. L. N. Lewis, J. Stein, R. E. Colborn, Y. Gao, and J. Dong, *J. Organomet. Chem.*, **521**, 221 (1996).
14. K. Kishi, T. Ishimaru, M. Ozono, I. Tomita, and T. Endo, *Macromolecules*, **31**, 9392 (1999).
15. K. Kishi, I. Tomita, and T. Endo, *Polym. Prepr., Jpn.*, **47**, 343 (1998).
16. K. Kishi, I. Tomita, and T. Endo, *Polym. Prepr., Jpn.*, **48**, 336 (1999).
17. K. Kishi, T. Ishimaru, M. Ozono, I. Tomita, and T. Endo, *J. Polym. Sci., Part A : Polym. Chem. Ed.*, **38**, 35 (2000).
18. Y. Ito, E. Ihara, M. Hirai, H. Ohsaki, A. Ohnishi, and M. Murakami, *J. Chem. Soc., Chem. Commun.*, **5**, 403 (1990).
19. S. R. Sandler and W. Karo, "Organic Functional Group Preparations", 2nd ed, Academic, New York, N.Y., 1986.
20. T. J. Deming and B. M. Novak, *Macromolecules*, **24**, 326 (1991).
21. E. A. Sheard, *Adhesive Age*, **44** (1997).