ELSEVIER
International Journal of Adhesion & Adhesives 20 (2000) 253–256
International Journal of Adhesion & Adhesives

Development and application of latent hydrosilylation catalyst [6]: control of activity of platinum catalyst by isocyanide derivatives on the crosslinking of silicone resin via hydrosilylation

Katsuhiko Kishi[a], Taizo Ishimaru[a], Masayoshi Ozono[a], Ikuyoshi Tomita[b], Takeshi Endo[c,*]

[a] *Material Research Division Three Bond Co., Ltd., 1456 Hazama-Cho, Tokyo 193-8533, Japan*
[b] *Department of Electronic Chemistry, Interdisciplinary Graduate School of Science and Technology, Tokyo Institute of Technology, Nagatsuta 4259, Midori-ku, Yokohama 226-8502, Japan*
[c] *Research Laboratory of Resources Utilization, Tokyo Institute of Technology, Nagatsuta 4259, Midori-ku, Yokohama 226-8503, Japan*

Accepted 22 September 1999

Abstract

Quite effective nature of isocyanides to control the curing reaction of silicone resin via the Pt-catalyzed hydrosilylation process is described. In the presence of the isocuanides, the curing reaction of the silicone resin by H_2PtCl_6 did not occur at ambient temperature, while the lack of the isocyanide systems conducts the smooth curing, indicating that the present systems serve as a thermal latent catalyst for silicone resin. The curing temperature was controllable by the character and the concentration of the isocyanides employed. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Hydrosilylation; Silicone resin; Isocyanides; Curing reaction; Latent catalyst

1. Introduction

Owing to its chemoselective, mild, and rapid characteristics, quite a few applications of hydrosilylation reaction have been developed in industry [1–4]. For example, many types of adhesives, sealants, coatings, etc., are manufactured through hydrosilylation process. Although the rapid nature of the reaction is useful in some respects, it often brings about poorly reproducible results in the field of material science. Very short pot-life of the homogeneous mixture of the prepolymers and the catalyst should also be overcome to realize a simple curing process in which one can conduct the smooth curing, for example, simply by heating the mixture.

On the basis of these requirements, several types of compounds such as acetylenes and olefins have been evaluated as a retarder of the platinum catalyst [5–17]. In theses cases, however, large excess amounts of the additives should be employed so as to reduce sufficiently the activity of the catalyst. These demerits promoted us to develop more effective candidates. Recently, we reported that isocyanides are quite effective to control the hydrosilylation activity of the platinum catalyst in which near stoichiometric amount of the isocyanides relative to the platinum can sufficiently provide an excellent thermal latency to the catalyst [18,19]. For instance, the combination of H_2PtCl_6 and *t*-BuNC (2 equiv to Pt) reveals the activity toward the hydrosilylation of triethylsilane with trimethylvinylsilane above 60°C, while the reaction with H_2PtCl_6 (i.e., without *t*-BuNC) proceeds smoothly at ambient temperature.

The combination of H_2PtCl_6 and the isocyanides is also expected to exhibit excellent controllability of the curing process of the silicone resin by means of hydrosilylation. Accordingly, we wish to report here the curing behavior of silicone resin containing Si–H moieties with that bearing vinylsilane groups so as to demonstrate clearly the thermal latency of the catalyst in the practical application.

2. Experimental

2.1. Materials

tert-Butylisocyanide, *n*-butylisocyanide, cyclohexylisocyanide, and 1-hexyne were purified by distillation.

---

[*] Corresponding author.

PII: S0143-7496(99)00050-0

Phenylisocyanide, *p*-methoxyphenylisocyanide, and *p*-chlorophenylisocyanide were prepared by the reported procedure [20] and were purified by distillation. H_2PtCl_6, polydimethylsiloxane having dimethylvinylsiloxy end groups ($M_n = 20{,}000$, obtained from Gelest Ltd.), and copolymer consisting of polydimethylsiloxane and methylhydrogensiloxane segments ($M_n = 1200$, [-OSi(H)MeO-]/[-OSiMe$_2$O-] = 30/70, obtained from Gelest Ltd.) were used as received. Catalysts consisting of H_2PtCl_6 and isocyanides were prepared by the procedure, reported previously [18].

2.2. Apparatus

The curing time and temperature of the silicone resin were measured by scanning vibrating needle curemater (SVNC) system [21] on a RAPARA VNC92H/F2300 model. The viscosity of silicone resin was measured by using BH-type viscosity mater (TOKIMEC Co., Ltd., JIS K 7117 model) at 40°C.

2.3. Curing reaction of silicone resin (typical procedure)

A mixture of polydimethylsiloxane having dimethylvinylsiloxyl with that carrying groups (10.0 g, vinyl content: 1.3 mmol), a copolymer consisting of polydimethylsiloxane and methylhydrogensiloxane segments (0.56 g, Si–H content: 2.3 mmol), and a THF solution of the platinum catalyst (0.05 g, 1.5 mol%) was heated at 100°C. The curing time was monitored by the SVNC analysis.

3. Results and discussion

The curing reaction of a silicone resin containing Si–H moieties and end-vinyl groups was carried out under various conditions (Scheme). Fig. 1 shows curing temperature versus gel fraction in the curing of the silicone resin for 10 min in the presence of various aliphatic isocyanides (2 equiv to Pt). The silicone resin was cured smoothly with H_2PtCl_6 alone at 60°C within 10 min. It is worth noting that the addition of aliphatic isocyanides gave a clear effect on the curing temperature. For example, the higher-temperature-shift by c.a. 30°C was observed in the presence of *t*-BuNC, indicating that a small amount of the isocyanide is effective to retard the curing reaction of silicone resin. Although acetylene derivatives are known to serve as an inhibitor of hydrosilylation [11–13], the same quantity of 1-hexyne (2 equiv to Pt) gave only a slight shift (c.a. 10°C). That is, isocyanide derivatives are more effective than the acetylene derivative, realizing the latent system with a small amount of the additive. Furthermore, the controllability of the curing process is

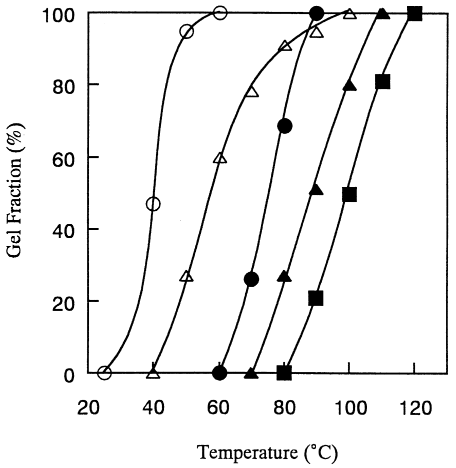
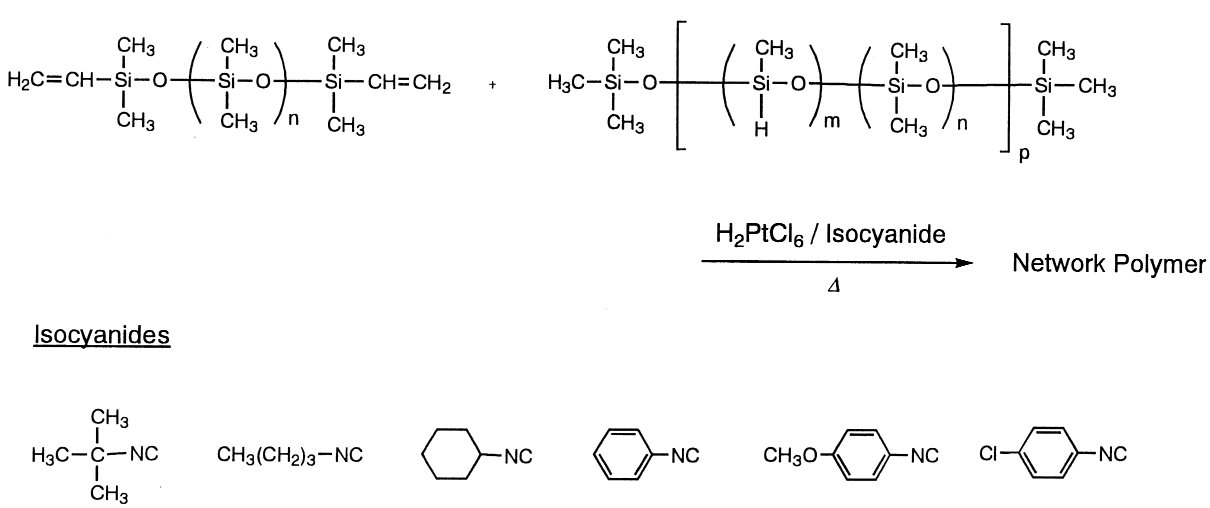


Fig. 1. Evaluation of the catalytic activity toward the curing reaction of the silicone resin system in the presence of various aliphatic isocyanides (conditions: poly-(dimethylsiloxane) having dimethylvinylsilane end groups = 10.0 g, poly(dimethylsiloxane-*co*-methylhydrogensiloxane) = 0.56 g, H_2PtCl_6 = 0.05 mmol, isocyanide = 0.10 mmol). ○: H_2PtCl_6 alone, △: 1-hexyne, ●: *tert*-butylisocyanide, ▲: cyclohexylisocyanide, ■: *n*-butylisocyanide.



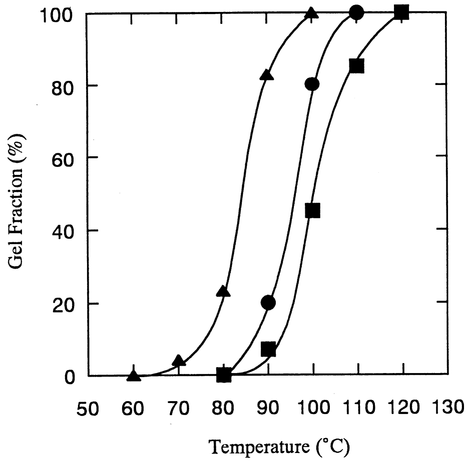


Fig. 2. Evaluation of the catalytic activity toward the curing reaction of the silicone resin system in the presence of various aliphatic isocyanides (conditions: poly-(dimethylsiloxane) having dimethylvinylsilane end groups = 10.0 g, poly(dimethylsiloxane-*co*-methylhydrogensiloxane) = 0.56 g, H_2PtCl_6 = 0.05 mmol, isocyanide = 0.10 mmol). ●: phenylisocyanide, ▲: *p*-chlorophenylisocyanide, ■: *p*-methoxyphenylisocyanide.

dependent upon the isocyanide structure, being in the following order: *n*-butylisocyanide > cyclohexylisocyanide > *tert*-butylisocyanide (i.e., primary > secondary > tertiary). As we described previously, the retardation takes place by the dissociation of isocyanides ligated on the platinum atom [18]. Accordingly, sterically less hindered isocyanides can coordinate more strongly to the platinum than sterically hindered ones which should be the reason for the observed difference.[1]

Likewise, the curing temperature versus gel fraction was evaluated in the presence of various aromatic isocyanides (2 equiv to Pt). As shown in Fig. 2, the catalytic activity was affected by the electronic character of the *p*-substituents on the benzene ring. That is, the retardation effect increases in the following order: *p*-methoxyphenylisocyanide > phenylisocyanide > *p*-chlorophenylisocyanide. The result is also in good accordance with the preceding study by using triethylsilane and trimethylvinylsilane as a model reaction [19] where the catalytic activity is controllable by the electron-donating ability of the *p*-substituents.

The effect of the isocyanide concentration on the curing temperature was evaluated by using phenylisocyanide, from which a clear higher temperature-shift of the curing was observed by raising the concentration of phenylisocyanide (Fig. 3) [19].

Fig. 4 shows time-gel fraction curves at various temperatures in the presence of phenylisocyanide (2 equiv to Pt), from which we could confirm the latent character of the initiating system. While silicone resin did not cure below 80°C, the reaction proceeded smoothly at elevated temperature. For example, the curing reaction was complete within c.a. 4 min at 100°C.

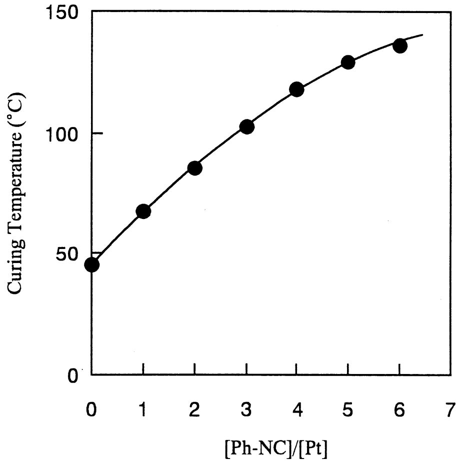


Fig. 3. Concentration effect of phenylisocyanide in the curing reaction (conditions: poly(dimethylsiloxane) having dimethylvinylsilane end groups = 10.0 g, poly (dimethylsiloxane-*co*-methylhydrogensiloxane) = 0.56 g, H_2PtCl_6 = 0.05 mmol).

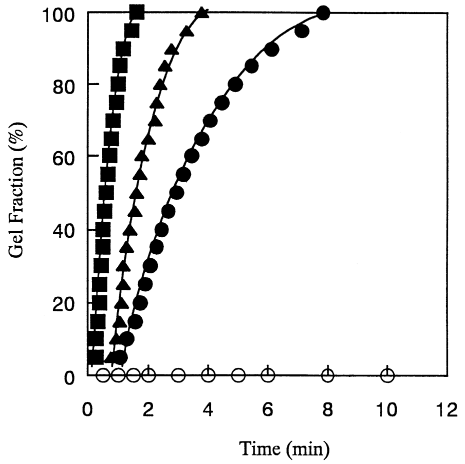


Fig. 4. Curing temperature versus gel fraction in the curing reaction of silicone resin in the presence of phenylisocyanide (conditions: poly(dimethylsiloxane) having dimethylvinylsilane end groups = 10.0 g, poly(dimethylsiloxane-*co*-methylhydrogensiloxane) = 0.56 g, H_2PtCl_6 = 0.05 mmol, phenylisocyanide = 0.10 mmol). ○: 80°C, ●: 90°C, ▲: 100°C, ■: 110°C.

So as to evaluate the storage stability of the silicone resin, the viscosity of the prepolymer–catalyst mixture was monitored at 40°C (Fig. 5). While the viscosity increased rapidly when H_2PtCl_6 alone was employed at a catalyst, the isocyanides examined (aromatic isocyanides) were found to be quite effective to preserve the prepolymer system at 40°C. The shelf life was dependent upon the isocyanide structure, as was observed in the

---

[1] The same trend was also observed in the hydrosilylation of triethylsilane and trimethylvinylsilane (see Ref. [18]).

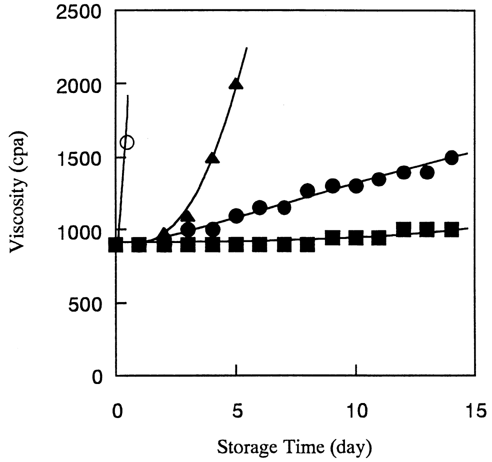


Fig. 5. Viscosity versus storage time of the silicone resin at 40°C (conditions: poly(dimethylsiloxane) having dimethylvinylsilane = 100.0 g, poly(dimethylsiloxane-*co*-methylhydrogensiloxane) = 5.60 g, H_2PtCl_6 = 0.50 mmol, phenylisocyanide = 1.00 mmol). ○: H_2PtCl_6 alone, ●: phenylisocyanide, ▲: *p*-chlorophenylisocyanide, ■: *p*-methoxyphenylisocyanide.

experiment in Fig. 2. The results obtained here might be of importance to attain the one-pot silicone resin system in practice.

4. Summary

The hydrsilylation curing behavior of silicone resin was evaluated in the presence of various isocyanides so as to demonstrate the effectiveness of the isocyanides to control the curing process. A remarkable retardation of the curing process was observed in the presence of the isocyanides. The curing temperature was controllable by the substituent on the isocyanides and the concentration of the isocyanides. The excellent preservable nature of the prepolymer–catalyst mixture was confirmed.

References

[1] Harrod JF, Chalk AJ In: . Organic synthesis via metal carbonyls, vol. 2. New York: Wiley, 1997.
[2] Harrod JF, Chalk AJ. J Am Chem Soc 1965;87:16.
[3] Pukhunarevich VB, Lukevics E, Kopylova LI, Voronkov MG. Perspective of hydrosilylation. Riga, Latvia: Institute of Organic Synthesis, 1992.
[4] Ojima I. In: Patai S, Rappaport Z, editors. The chemistry of organic silicon compounds, vol. 2. New York: Wiley/Interscience, 1989.
[5] Melancchon KC. US Patent 4,533,575, 1966.
[6] Berger A, Hartman, BB. US Patent 3,882,083, 1975.
[7] Brown ED. US Patent 4,340,710, 1982.
[8] Kniege W, Micheal W, Ackerman J. US Patent 4,487,906, 1984.
[9] Shirahata A, Shosaku S. US Patent 4,465,818, 1984.
[10] Chandler G, Lo PYK, Peter YA. US Patent 4,472,563, 1984.
[11] Cavezzan J. US Patent 4,595,739, 1986.
[12] Eckbeg RP. US Patent 4,347,346, 1983.
[13] Kookootsedes GJ, Plueddeman EP. US Patent 3,445,420, 1969.
[14] Janik G, Buentello M. US Patent 4,801,642, 1989.
[15] Lewis LN, Colborn RE, Grade H, Bryant GL, Sumpter CA, Scott RA. Organometallics 1995;14:2202.
[16] Lewis LN, Stein J, Colborn RE, Gao Y, Dong J. J Organomet Chem 1996;521:221.
[17] Lewis LN, Lewis N. J Am Chem Soc 1986;108:7228.
[18] Kishi K, Ishimaru T, Ozono M, Tomita I, Endo T. Macromolecules 1999;31:9392.
[19] Kishi K, Tomita I, Endo T. Polym Prepr Jpn 1998;47:343.
[20] Sandler SR, Karo W. Organic functional group preparations, 2nd ed. New York: Academic Press, 1986.
[21] Sheard EA. Adhesive Age 1997:44.