One-Pot Condensation/Hydrosilylation System for IPN Formation

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A one-pot low-molecular model reaction system of condensation (1) and hydrosilylation (2) was proposed and studied for preparation of a silicon-based IPN. To make the both reactions proceed selectively, selection of catalysts and hydrosilanes were of importance. Effects of homogeneity of the system were also considered.

IPN (Interpenetrating Polymer Network) is defined as a structure in which at least two kinds of polymer chains are entangled in molecular level.[1] It has been widely investigated mainly for carbon-based polymers as a means of extracting desirable properties from each components.

IPNs containing *a* silicon-based polymer such as dimethylpolysiloxane[2] and polysilicic acid,[3] have also been investigated and interesting properties or structures derived from the structure of IPN have been discussed. Thus an IPN produced from *two* thermostable silicon-based polymers became of interest; one of them is a Si-O-Si polymer chain and the other is a Si-C based one.

For preparation of the IPN, it should be important that the two reactions proceed highly selectively in a one-pot system. We chose hydrolysis•condensation reaction of alkoxysilanes for Si-O-Si formation (1) (called condensation reaction hereafter) and hydrosilylation reaction for Si-C formation (2) because of the versatility of their reaction conditions.

$$\geq SiOR + H_2O \longrightarrow \geq SiOH + ROH$$
$$\geq SiOH + ROSi\leq \longrightarrow \geq SiOSi\leq + ROH \quad (1)$$
$$\geq SiOH + HOSi\leq \longrightarrow \geq SiOSi\leq + H_2O$$

$$\geq SiH + CH_2{=}CHSi\leq \longrightarrow \geq SiCH_2CH_2Si\leq \quad (2)$$

In order to make the both reactions (1) and (2) proceed highly selectively in one-pot system, we first employed one-functional low-molecular compounds because the products are easily identified after the reaction. Here preliminary results obtained from the model system of the silicon-based IPN were discussed.

Reaction (1)[4] and (2)[5] have long been widely investigated, respectively. On the basis of the information already known for them, we thought the following points (A)-(C) should be very important to get the suitable reaction conditions: (A) even in the presence of the condensation products (ROH), the reaction (2) advances[6]; (B) the condensation catalyst does not interfere the reaction (2); (C) the condensation catalyst does not decompose the hydrosilane.

The model reactions (3) and (4) in one pot were monitored by GC and the products were identified by NMR, GCMS. Equation (3) is an example of the model condensation reaction and $PhMe_2SiOEt$ was employed because it is easily identified as well as the product **2**. Among olefinic compounds for the reaction (4), a vinylsilane was chosen because of no possibility of the double-bond isomerization. Either **3** or **4** was employed as a hidrosilane for evaluating their reactivity and stability. The results of the one-pot reaction system are shown in Table 1.

$$\underset{\mathbf{1}}{2\ PhMe_2SiOEt} + H_2O \xrightarrow[\text{r.t.}]{\text{cat.}} \underset{\mathbf{2}}{PhMe_2SiOSiMe_2Ph} + 2\ EtOH \quad (3)$$

$$\underset{\mathbf{3}}{PhMe_2SiH}\left[\underset{\mathbf{4}}{(Me_3SiO)_2MeSiH}\right] + CH_2{=}CHSiMe_2Ph \xrightarrow[\text{r.t.}]{[Pt]}$$
$$\underset{\mathbf{5}}{PhMe_2SiCH_2CH_2SiMe_2Ph} \quad \left[\underset{\mathbf{6}}{(Me_3SiO)_2MeSiCH_2CH_2SiMe_2Ph}\right] \quad (4)$$

In order to make clear how the platinum catalyst for reaction (4) affects stability of the hydrosilanes, we first carried out the reaction (4) alone in the presence of large excess (5 equiv) of MeOH, which is typically produced during the condensation reaction. It was found that the Pt-vinylsiloxane complex[7] satisfies the point (A) and was much favorable than the conventionally-used Speier's catalyst (H_2PtCl_6•$6H_2O$)[8]. The former ($1x10^{-3}$ equiv) afforded **5** in 88% yield, for instance, while the latter ($1x10^{-3}$ equiv) instantly decomposed the hydrosilane **3** and quantitatively gave $PhMe_2SiOMe$. The fact that the former Pt catalyst also prompts the decomposition in the presence of HCl implies that the proton helps the attack of the nucleophile, MeOH, on the Si of [≡Si-Pt-H] species which is formed by the well-known oxidative addition process[9].

On choosing a suitable condensation catalyst, we should again bear in mind the necessary conditions (A)-(C). Although there may be other good candidates, an organic weak acid, $(C_8H_{17}O)_2P(=O)OH$, was favorably selected so far. Amines and organic tin compounds, which strongly coordinate Pt, were excluded by consideration of (B). Either strong base or acid, NaOH or HCl for instance, is not appropriate for the one-pot system from the point of (A) and (C).

Homogeneity of the reaction system seems important. If we can not obtain good homogeneity even enough for the model system, we will surly suffer form phase separation in a polymeric system and have a hard time getting IPN structure. A clear solution could be obtained when $(C_8H_{17}O)_2P(=O)OH$ was employed as a condensation catalyst in i-PrOH. The condensation rate was generally slow down as expectedly from the weak acidity of the catalyst. But each of the both reactions advanced highly selectively even in the homogeneous i-PrOH solution (No.5) as well as the dispersed system (No.2) when a relatively reactive hydrosilane **3** was used.

Interestingly, both reactions proceeded highly selectively in a short time only when HCl and a relatively stable hydrosilane **4** were employed in a dispersed system (No.6). That is probably because the two reactions were completed quickly before the HCl in the aqueous layer began to decompose the hydrosilane **4** in the organic layer. Adding alcohol for better homogeneity, however, led to decrease of the yields of **2** and **6** due to complicated side reactions. One of the side products was identified as $(Me_3SiO)PhMeSiCH_2CH_2SiMe_2Ph$ (0.63) by GCMS (No. 8 in

Table 1. Results of the one-pot condensation/hydrosilylation reaction system

No.	Condensation catalyst[a] (mol%)	Reaction Scale (mmol)	Solvent (mL)	H_2O equiv	Homogeneity[b]	Condensation [eq.(3)] Reaction time (h)	Condensation [eq.(3)] Yield of **2** (%)[d]	Hydrosilylation [eq.(4)][c] Type of SiH	Product	Consumption of SiH (h)	Yield of **5** or **6** (%)[d]
1	P (10)	1	-	1	×	3~6	44	**4**	**6**	1~3	33
2	P (2)	5	-	1	×	5~168	114	**3**	**5**	<1	96
3	P (10)	1	MeOH (1.2)	1	○	>7 days	35	**4**	**6**	3~5	26
4	P (10)	1	i-PrOH (1.2)	1	◎	>7 days	75	**4**	**6**	3~6	60
5	P (2)	5	i-PrOH (1.2)	2	◎	2~10 days	116	**3**	**5**	<0.5	92
6	HCl (2)	5	-	2	×	0.5~3	99	**4**	**6**	<0.5	99
7	HCl (2)	5	-	2	×	0.5~2	199	**3**	**5**	1~20 days	9
8	HCl (2)	5	MeOH (1.2)	2	△	<1	22	**4**	**6**	4~24	23
9	HCl (2)	5	i-PrOH (1.2)	2	△	<1	35	**4**	**6**	4~24	14

[a] P stands for $(C_8H_{17}O)_2P(=O)OH$. [b] ◎, homogeneous; ○, cloudy; △, homogeneous but separated after HCl addition; ×, separated. [c] The Pt-vinylsiloxane ($1x10^{-4}$equiv to SiH) was employed. The molar ratio of SiH to vinyl was 1. [d] By GC. The yield of condensation exceeded 100% in a few cases because the hydrolysis-condensation product of **3** is **2**. The erroneous range is ca. ±10%.

Table 1). The residual vinylsilame $CH_2=CHSiMe_2Ph$ (1.28) was also detected. The numbers in the parentheses are relative GC area ratio to that of **6**.

On the basis of the consideration of the model systems, a preliminary experiment was carried out by applying the favorable conditions with $(C_8H_{17}O)_2P(=O)OH$ to a polymeric system for IPN formation. Thus, ethyl silicate 40 (partially-condensed products of $Si(OEt)_4$, the solid content is 40%), 1,1,3,3,5,5-hexamethyltrisiloxane (0.75 mmol), 2,4,6,8-tetramethylcyclotetrasiloxane (0.125 mmol), and divinylmethylphenylsilane (0.75 mmol) were mixed. To the mixture were added iPrOH (0.5 mL), water (5 mmol), the Pt-vinylsiloxane complex ($2x10^{-4}$mmol), and $(C_8H_{17}O)_2P(=O)OH$ (0.1 mmol). The solution was then stirred well until a clear uniform solution was obtained. The resultant solution was coated on a glass plate and heated at 50°C for 2h and then at 80°C for 4h. At this point was obtained a clear solid cured film, which implies IPN formation. Further heat treatment, however, converted the film slightly cloudy due to possible phase separation probably caused by not matching of the two reaction rates, that is, slow condensation vs. fast hydrosilylation. The rate-matching study to obtain a better IPN structure is now under way.

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