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Silazyl-Lithiums: A kind of new Initiators for the Anionic Non-equilibrium Ring-opening Polymerization of Octamethylcyclotetrasiloxane (D_4)

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Abstract: The initiation reactions in the anionic non-equilibrium polymerization of octamethylcyclotetrasiloxane (D_4) initiated by silazyllithiums were investigated. It was found that the structure of the substituents on the Si atom had great influences on the initiation activity of silazyllithiums.

Key words: Anionic non-equilibrium polymerization, polysiloxane, silazyl-lithiums.

The anionic non-equilibrium polymerization of cyclosiloxane has mainly been focused on the polymerization of cyclosiloxanes initiated by organo-lithium, especially on the polymerization of hexamethylcyclotrisiloxane (D_3)[1-3]. The polymerization of D_4 initiated by the new hexamethyldi- silazyl-lithium (MM^{NLi}) initiator was first studied in our lab[4]. The special characters of Si-N bond impart several advantages to the new silazyl-lithium initiator. The end group linked to Si-N bond could be converted into hydroxyl, alkoxy group or other groups needed through organic reaction, and the living propagation center could be terminated with needed end-capping reagents, *e.g.* dimethylvinylchlorosilane. Then a kind of polysiloxanes with different functional groups at the chain ends could be prepared.

In this paper several silazyl-lithiums that have different subsitituents were prepared and used to initiate D_4 to polymerize. The initiation process was studied in order to find the effect of subsititutes on the initiation activity.

Experimental

$(Me_3Si)_2NH$ were bought and fractionally distilled out. $((CH_3)_2PhSi)_2NH$ and $((CH_3)_2CH{=}CH_2Si)_2NH$ were prepared according to literature[5,6].

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Preparation of $(Me_3Si)_2NLi$, $((CH_3)_2PhSi)_2NLi$ and $((CH_3)_2CH{=}CH_2Si)_2NLi$:

The corresponding silazane and THF were placed in a dry three-necked flask under nitrogen. *n*-Butyllithium was dropped into the flask at the temperature below –20°C. After 7 hours the mixture was washed by hexane below –40°C, the solvent was removed and the white solid lithium salt was obtained. Then the lithium salt was dissolved in benzene.

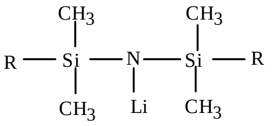
Polymerizations of D_4 were carried out under nitrogen at the temperature of 40°C. The promoter was THF.

Results and Discussion

In order to study the effects of different substituents on the initiation activity of the silazyl-lithiums, three initiators were designed (**Scheme 1**) and used to initiate the polymerization of D_4 under the same conditions（**Table 1**）.

Table1 Initiation reaction of D_4 with silazyl-lithiums

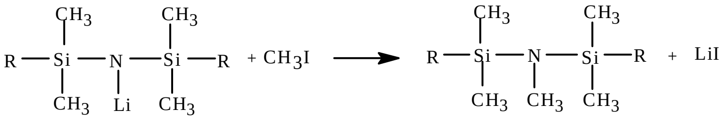
Initiators	Promoter (THF)mL	Temperature °C	Internal standard (octane) mL	D_4 mL
$(Me_3Si)_2NLi$ (0.64 mol/L)	1	40	1	5
$((CH_3)_2PhSi)_2NLi$(0.13 mol/L)	1	40	1	5
$((CH_3)_2CH{=}Ch_2Si)_2NLi$(0.31mol/L)	1	40	1	5



R= CH_3, Vinyl, Ph

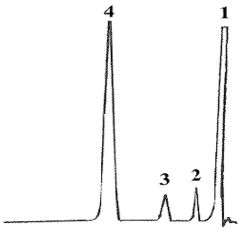
Every given time the unreacted initiators were terminated by CH_3I (**Scheme 2**).

Scheme 2



At last the concentrations of the products (produced by the reaction of initiators with CH_3I) were detected by GC (**Figure 1**).

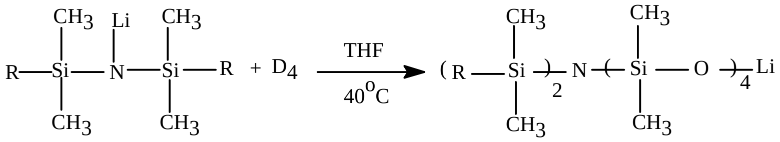
Figure 1 GC of the initiation reaction system terminated by CH_3I



Eluting peaks: 1. Solvent 2. Octane 3. $Me_3Si)_2NCH_3$ 4. D_4

The concentration of 3 could be calculated out from the area ratio of 2 and 3. This stands for the concentration of initiator that did not react with D_4.

Scheme 3



$$R-Si(CH_3)_2-N(Li)-Si(CH_3)_2-R + D_4 \xrightarrow[40^{o}C]{THF} (R-Si(CH_3)_2\text{)}_2-N\text{(}-Si(CH_3)_2-O\text{)}_4Li$$

According to **Scheme 3**, the rate of initiation could be written out:

$$-\frac{d[(R(CH_3)_2Si)_2NLi]}{dt} = K'[(R(CH_3)_2Si)_2NLi][D_4][THF]$$

Because $[D_4] >> [((CH_3)_2RSi)_2NLi]$, [THF] was constant, the equation above could be written as below:

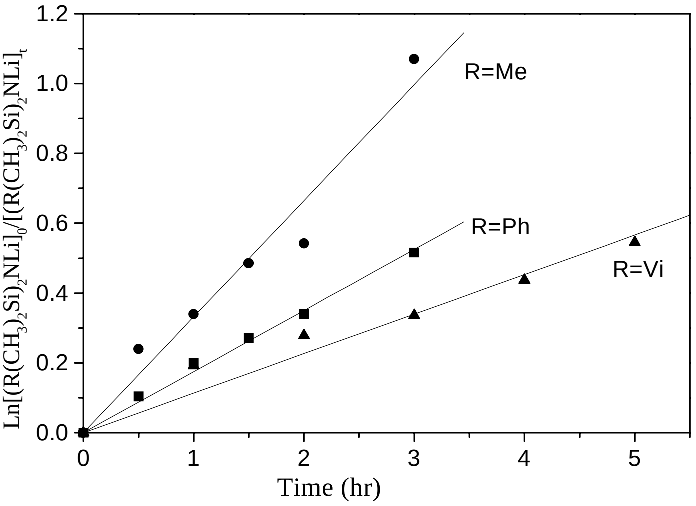
$$-\frac{d[(R(CH3)2Si)2NLi]}{dt} = K\ [(R(CH3)2Si)2NLi]\ ;\ K= K'\ [D4]\ [THF]$$

Integrating the two sides of the equation above, then:

$$Ln\ \frac{[(R(CH_3)_2Si)_2NLi]_0}{[(R(CH_3)_2Si)_2NLi]_t} = Kt$$

A first order of the initiation reaction with respect to silazyl-lithium was observed from **Figure 2**. The initiation activity of these initiators was different from each other according to their substituents. $(Me_3Si)_2NLi$ (R=Me) was of the highest initiation activity and the lowest initiation activity was obtained when R=vinyl. This can be explained that the initiation activity was affected by both the steric hindrance effect and the electronic effect. In these substituents, the order of the steric hindrance was Me<vinyl<Ph, the order of the electron donating ability was Ph>vinyl>Me. The electron effect decided the reaction activity of the silazyl anions and the steric hindrance effect decided whether the attacking reaction is easy to go on. So from the experimental result it could not be said that which effect was the main factor. Both of them had their influences on the initiation activity of the initiators.

Figure 2 First order kinetic plots for the initiation of the polymerization of D_4 with silazyl-lithiums as initiators



Acknowledgments

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