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Living Ring-opening Oligomerization of Cyclosiloxanes with an Aluminum-Tetraphenylporphyrin Complex Initiator

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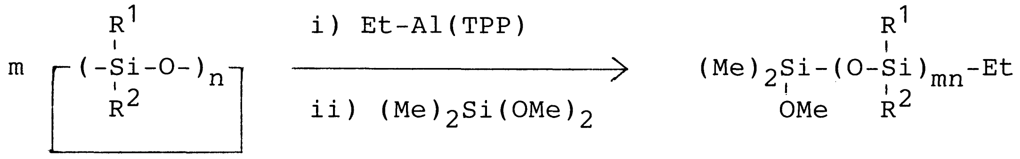
An aluminum-tetraphenylporphyrin (Al(TPP)) catalyzed the ring-opening oligomerization of cyclosiloxanes with narrow molecular weight distribution, involving selection as for ring-size.

Although living anionic polymerization of siloxanes has been conducted using cyclosiloxanes with organoalkali compounds or lithium silanolates as initiator,[1)] the reaction sometimes gives broad molecular weight distribution due to redistribution reaction of siloxane bonds catalyzed by alkali silanolates.[2)] Meanwhile, living ring-opening polymerization of epoxides and lactones, or photoinduced polymerization of methacrylates by the use of Al(TPP) or Zn(TPP) complex as initiator are receiving increasing attention for a new type of living polymerization.[3)] Now we wish to describe here the living ring-opening oligomerization of cyclosiloxanes with Et-Al(TPP) complex as initiator.



$$m\ \left[(\text{-}\overset{R^1}{\underset{R^2}{\text{Si}}}\text{-O-})_n\right] \xrightarrow[\text{ii) (Me)}_2\text{Si(OMe)}_2]{\text{i) Et-Al(TPP)}} (\text{Me})_2\underset{\text{OMe}}{\text{Si}}\text{-}(\text{O-}\overset{R^1}{\underset{R^2}{\text{Si}}})_{mn}\text{-Et}$$

To a 50 ml-flask was charged H_2TPP(61.5 mg, 0.1 mmol) and 10 ml of dry CH_2Cl_2 under N_2 atmosphere, and successively 0.2 ml of 0.9 M $AlEt_3$ in hexane. After stirring for 1 h, the mixture was evacuated to remove unreacted $AlEt_3$ and then dry CH_2Cl_2 (20 ml) containing a cyclosiloxane (4.5 mmol) was added to start the reaction at 25 °C. In order to make the reaction terminate, a large amount of $(CH_3)_2Si(OMe)_2$ was put into the reaction system, and the product was separated from the initiator by extraction with hexane after removal of volatile compounds under reduced pressure. Molecular weight (MW) and its distribution (Mw/Mn) of the reaction product were determined with GPC (TSK-gel 3000H) with THF eluent using calibration with poly(styrene) standards.

Table 1. Ring-opening Oligomerization of Cyclosiloxane with Et-Al(TPP) Initiator at 25 °C

	n	R^1	R^2	Time/d	Conv./%	Mn	Mn/Mw
1	3	Me	Me	6	43	1550	1.12
2	4	Me	Me	3	0		
3	5	Me	Me	3	0		
4	4	H	Me	5	45	1470	1.21
5	5	H	Me	8	28	1270	1.10
6	3	Ph	Ph	8	28	1600	1.25
7	4	Ph	Ph	8	33	1400	1.21

With regard to the reaction with dimethylcyclosiloxanes (1, 2, and 3), Et-Al(TPP) could bring about the oligomerization of only 1, with higher reactivity due to the ring strain as compared with 2 and 3. The molecular weight of the product4) was less than 1550, corresponding to heptamer and the molecular weight distribution was narrow (Mw/Mn=1.12). It is, therefore, suggested that redistribution of siloxane bonds among the growing chains is not induced by attack of the Al-silanolate group. Indeed, it was observed that the reaction mixture containing the growing species, prepared from Et-Al(TPP) and 1, never reacted with linear dimethylsiloxane oligomer such as decamethyltetrasiloxane. Thus, the Al complex can perfectly distinguish the siloxane bond in the strained ring of 1 and that in the flexible ring or the linear structure. Such selection for the ring size could not be observed in n-butyllithium-initiated polymerization of 1-3. The reaction of 1 slowly proceeded to attain 43% conversion in 6 days. Probably, steric bulkiness of 1 makes access to Al metal center in the growing species difficult. The reaction at 35 °C, intended to make the substrate diffusion rapid, resulted in the MW of 1200 and the Mw/Mn of 1.61. This result indicates that elevation of the temperature promotes the redistribution of siloxane bonds. Cyclosiloxanes composed of methylhydrosiloxane and diphenylsiloxane, 4-7, were also oligomerized by the Al complex. In these cases, ring-size selectivity for the cyclosiloxanes was not observed. Oligomers from 4 and 5 gave low Mw/Mn's of 1.10 and 1.20, respectively, but those from 6 and 7 showed larger values (1.25 and 1.21, respectively). Further investigations of the living polymerizations of cyclosiloxanes are now in progress.

References

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4) ^{1}H-NMR (CDCl$_3$) δ 0.07 (s, 120H, SiCH$_3$), 0.23 (q, 2H, SiCH$_2$), 0.88 (t, 3H, SiCH$_2$C$\underline{H}_3$), 2.47 (s, 3H, SiOCH$_3$).

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