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Living polymerization of hexaethylcyclotrisiloxane

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Summary

Living polymerization of hexaethylcyclotrisiloxane was achieved with *n*BuLi-$(n\mathrm{BuO})_3\mathrm{PO}$ at room temperature to produce living poly(diethylsiloxane). The molecular weight of the polymer increased in direct proportion to monomer conversion and to the reciprocal to the initial *n*BuLi concentration. Molecular weight distribution remained 1.1-1.2 during the polymerization. The polymerization was completed only after 1 day despite no solvent was used. When a compound containing SiOH groups was added to the polymerization system, the number of polymer chain agreed with a sum of *n*BuLi and SiOH groups.

Introduction

Recently, the application of elastomers to sealant in severe environment increases its importance (1). Poly(siloxane) is one of the most suitable polymers for this purpose because of its various remarkable properties including high thermal stability, low glass transition temperature (Tg), and high chemical stability (2). Among various kind of poly(siloxanes), one of the most applicable polymers in low temperature range is poly(diethylsiloxane) (PDES). PDES possesses the lowest Tg (-140 °C) among high-molecular-weight polymers due to its flexibility of the Si-O bond and facile rotation of the side chains around the Si-C bond (3). Another interesting feature of PDES is its complex crystal structure in low temperature range and mesophase formation around room temperature (4,5). The authors synthesized the copolymers of diethylsiloxane and siloxanes with bulky substituents and reported the effect of bulky siloxane unit on the crystal formation of PDES (6, 7).

Living polymerization is one of the most useful methods to obtain various types of tailor-made polymers. Control of polymer molecular weight (MW) and molecular weight distribution (MWD, M_w/M_n), synthesis of block and graft copolymer, and introduction of functional group into the chain end can be attained by using this method. Synthesis of tailor made PDES which has unique properties described above should also be an important problem. Control of the molecular weight is also valuable because the thermal transition of PDES is strongly dependent on the polymer molecular weight. Few examples of living PDES have been reported, though living poly(dimethylsiloxane) (PDMS) has been widely investigated. Möller et al. reported the synthesis of living PDES (8,9). The activator they used was, however, a complicated one, and no detailed polymerization behavior was examined. In the present paper, living polymerization of

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hexaethylcyclotrisiloxane (HECTS) with simpler initiation system which is easily available will be reported.

Experimental

HECTS was purchased from Shin-etsu Co. and purified with column chromatography followed by careful distillation. Solvents and activators were reagent grade and distilled under dry argon before use. Hexane solution of *n*BuLi was used as received.

All polymerization operations were carried out under dry argon atmosphere. Unless otherwise mentioned, polymerization procedure was as follows: in a 20 mL schlenk tube HECTS was added to hexane solution of *n*BuLi (1.6 M) followed by aging for 10 min at room temperature. Activator was then added by syringe to start the polymerization. After polymerization, the solution was poured into hot methanol, and dried in vacuo.

MW and MWD of the polymer were determined with size exclusion chromatography (SEC) calibrated by standard polystyrene in THF at 40°C.

Results and discussion

There are mainly two methods in the synthesis of high-molecular-weight PDMS, equilibrium and living polymerization. High-molecular-weight PDMS is formed by heating cyclic tetramer in the presence of alkali like KOH. Molecular weight control is, however, generally difficult and MWD is not narrow. PDMS with controlled MW and narrow MWD is obtained with living polymerization method from strained cyclic trimer (D_3) initiated by alkyllithium under milder conditions.

For diethylsiloxane, cyclic trimer is available more easily than cyclic tetramer, because hydrolysis of diethyldichlorosilane mainly produced cyclic trimer. The polymerization of diethylsiloxane cyclic trimer, HECTS, was examined using *n*BuLi as an initiator. The polymerization was carried out without using solvent, though polymerization system included small amount of hexane derived from the solvent of *n*BuLi. No polymerization occurred without activator (Table 1). When hexamethylphosphoric triamide (HMPA), which is one of the effective activator for the living polymerization of D_3, was added, quantitative polymerization invariably occurred without an induction phase. MW of the main product increased with proceeding the polymerization, meaning the propagating species were long-lived. MWD was,

Table 1 Effect of Activator on the polymerization of HECTS by *n*BuLi

Activator	[Activator]/[*n*BuLi]	$M_n/10^3$	M_w/M_n
none	0	no polymn	
HMPA	50	12	2.23
HMPA	10	14	1.41
$(n\text{BuO})_3\text{PO}$	10	15	1.12
DMF	10	16	1.25
DMSO	10	16	1.34

Polymerized at room temperature for 24h, [HECTS] / [*n*BuLi] = 50.

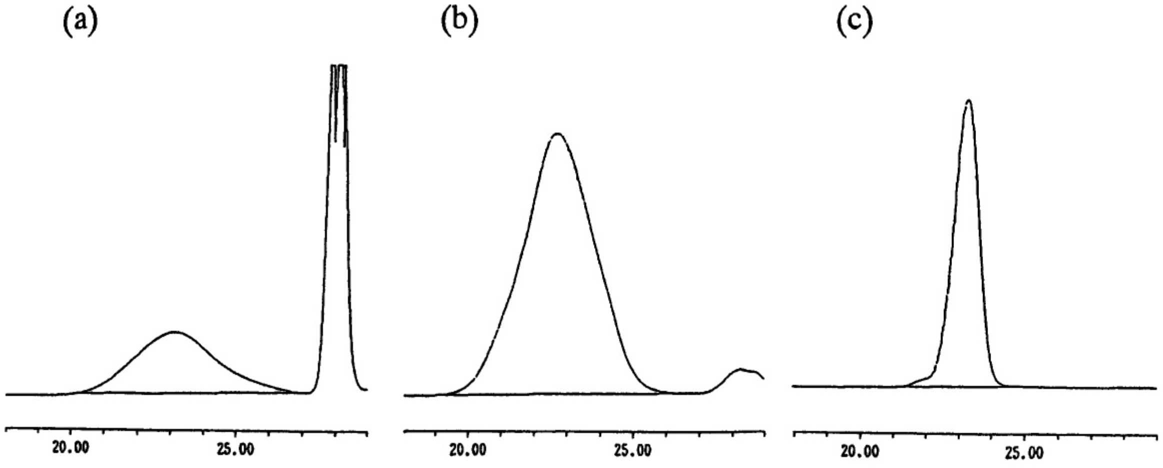

Figure 1. SEC curve of PDES obtained with (a) *n*BuLi-HMPA (1:50) (b) *n*BuLi-HMPA (1:10) (c) *n*BuLi-($(n\text{BuO})_3$PO (1:10)

however, not narrow and the product contained some kinds of oligomers (Figure 1(a)). MWD decreased with decreasing the amount of HMPA, though the formation of oligomers was not completely restricted (Figure 1(b)). When milder activators such as $(n\text{BuO})_3$PO or THF were used, MWD became narrower (1.1-1.2) and almost no oligomer was produced (Figure 1(c)). *n*BuLi-$(n\text{BuO})_3$PO was adopted as an initiator in the following experiments because MWD of the PDES was narrowest (Table I).

Figure 2 shows monomer conversion vs. M_n curve of the polymerization of HECTS with *n*BuLi-$(n\text{BuO})_3$PO. The MWD of the produced polymers was less than 1.2 during the polymerization. The M_n values increased in direct proportion to monomer conversion, and the values were agreed well with M_n(cal) which was calculated from the ratio of [HECTS] to [*n*BuLi]. This fact shows that each *n*BuLi formed one polymer

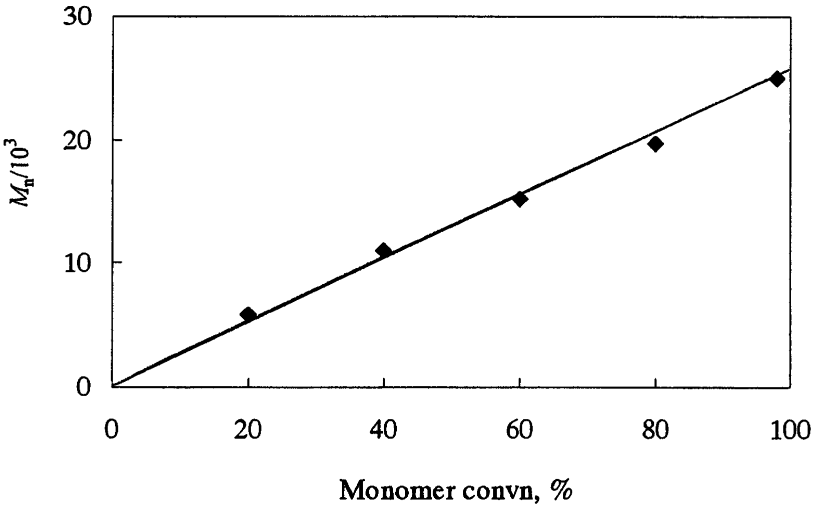

Figure 2. Monomer conversion – M_n curve on the polymerization of HECTS by *n*BuLi-$(n\text{BuO})_3$PO ([HECTS]/[*n*BuLi] = 80)

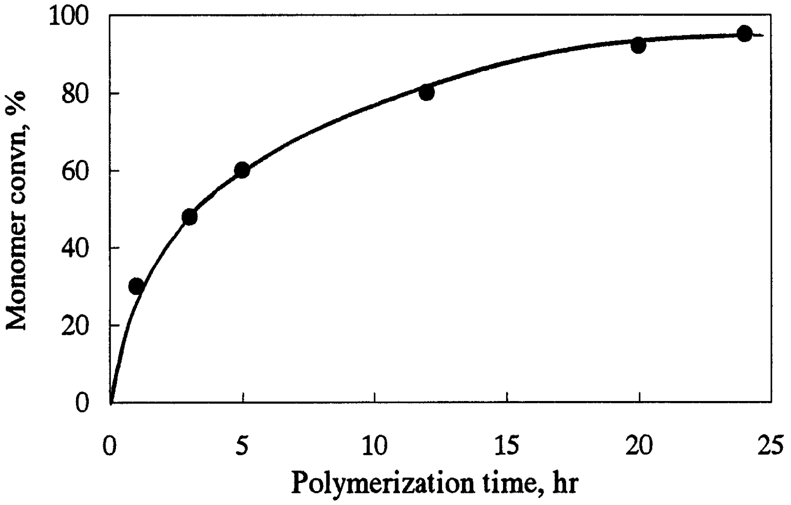

Figure 3. **Time dependence on the polymerization of HECTS by *n*BuLi-(*n*BuO)$_3$PO ([HECTS]/[*n*BuLi] = 80)**

chain. The MWD kept narrow during the polymerization, and no shoulder was observed in SEC curves. Formation of cyclic or linear oligomers, which are produced by equilibrium polymerization, was not observed. Thus, attack of propagating species to the polymer chain was completely restricted in this method. These facts indicate that the polymerization of HECTS by *n*BuLi-(*n*BuO)$_3$PO proceeded with a living polymerization manner.

Figure 3 depicts time dependence of the polymerization of HECTS with *n*BuLi-(*n*BuO)$_3$PO. The polymerization was completed only after 1 day despite no solvent was used. Thinking that in the case of D$_3$ polymerization only several hours are required even in solution polymerization, the polymerization rate of HECTS is much slower than that of D$_3$. This fact indicates that the polymerization activity of HECTS is significantly different from that of D$_3$.

To compare the polymerization reactivity of D$_3$ and HECTS, copolymerization between these two monomers by *n*BuLi-(*n*BuO)$_3$PO was attempted (Figure 4). In the early stage of the copolymerization, only D$_3$ was consumed and HECTS hardly reacted. Only after most of D$_3$ disappeared, HECTS was started to polymerize slowly. These

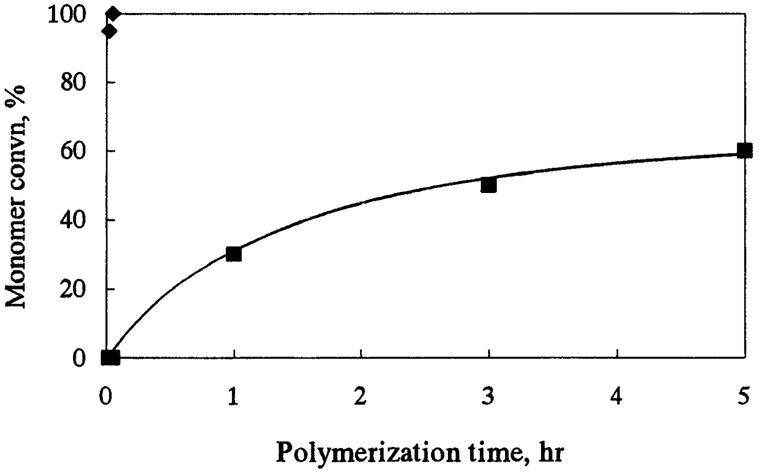

Figure 4.

Copolymerization of HECTS (■) and D$_3$ (◆) by *n*BuLi-(*n*BuO)$_3$PO

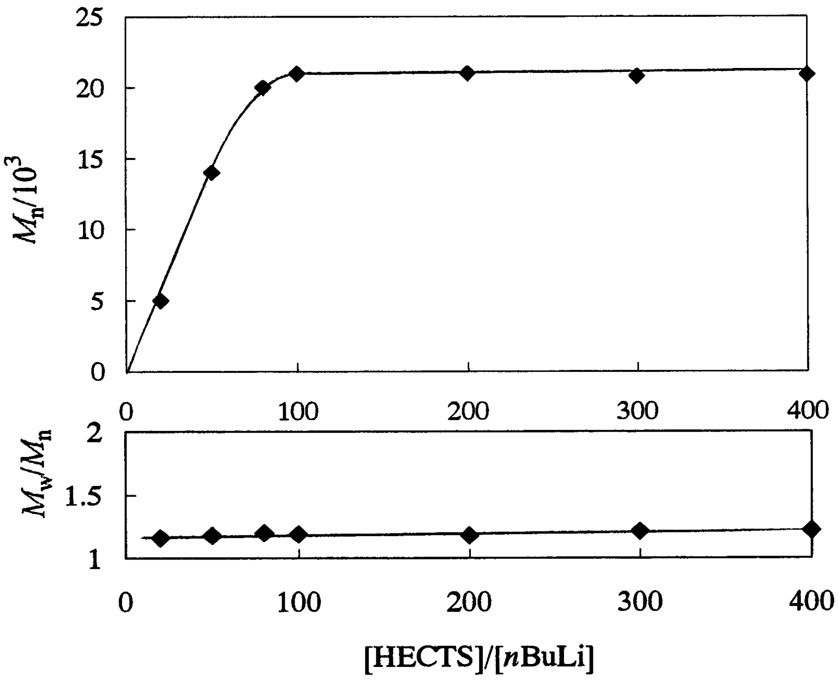

Figure 5.
M_n and MWD on the polymerization of HECTS (without purification)

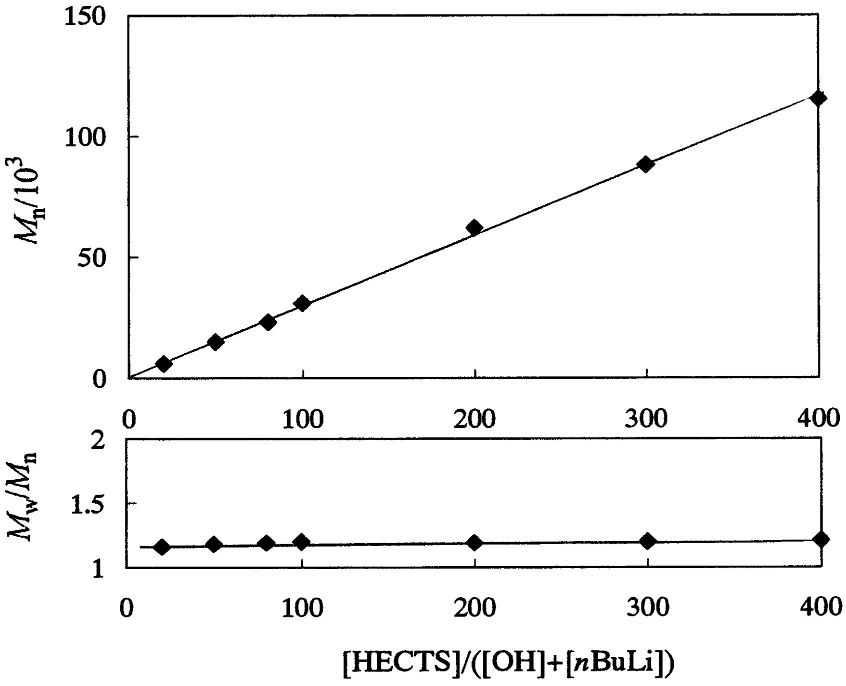

Figure 6 M_n and MWD on the polymerization of HECTS by *n*BuLi-(*n*BuO)$_3$PO in the presence of BDHSB results indicate that the polymerization reactivity of HECTS is much lower than that of D_3. It is noteworthy that substituent on Si atom largely affected the polymerization reactivity.

In the experiments described above, if the purification of HECTS was not enough, MW of the produced polymer was leveled off when [HECTS]/[*n*BuLi] was higher than ~80. That is, the M_n was saturated at around 2×10^4 as shown in Figure 5. Below that point M_n increased proportional to [HECTS]/[*n*BuLi], and MWD kept narrow irrespective of MW. If chain transfer or termination reaction occurs, MWD must become broader. When HECTS was purified carefully with column chromatography, complete living polymerization was achieved even at high-molecular-weight range. One of the possible impurities of HECTS is a compound having SiOH group, and it may be possible that very fast and facile exchange between SiOLi and SiOH occurred. If this is true, the phenomenon described above can be explained as follows: when [HECTS]/[*n*BuLi] was low and there was only little amount of impurities ([HECTS]/[*n*BuLi] was lower than ~50), *n*BuLi mainly initiated the polymerization. On the other hand, most of the polymerization started with the impurities if the amount of the impurities in the system increased ([HECTS]/[*n*BuLi] was higher than ~100). To confirm this fact, *p*-bis(dimethylhydroxysilyl)benzene (BDHSB) which has two SiOH groups in the molecule was added to the polymerization of HECTS which had been completely purified. The result was illustrated in Figure 6. The MWD's were always narrow and the M_n increased in direct proportion to a sum of *n*BuLi and SiOH group. Even when the amount of *n*BuLi was rather small, this relationship was similar. These facts indicate that the polymerization was initiated by SiOLi compound generated by the reaction of *n*BuLi with both HECTS and BDHSB and that the exchange of SiOLi and SiOH was rapid enough to keep MWD narrow. PDES with controlled molecular weight can be prepared by this method. Telechelic PDES with narrow MWD, which has two OH groups in the both chain ends, will be synthesized by use of this method.

In conclusion, PDES with controlled MW and narrow MWD was readily synthesized by simple initiation system which can be easily available. This method will be helpful for the detailed study about thermal transitions of PDES and for the application of PDES to cryogenic uses.

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