

A new bifunctional initiator for the living polymerization of hexamethylcyclotrisiloxane

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SUMMARY

A bifunctional living poly(dimethylsiloxane), poly(DMS), was synthesized through the anionic ring-opening polymerization of hexamethylcyclotrisiloxane(D₃)(**3**) with an initiator system consisting of dilithium salt(**2**) of bis(p-hydroxydimethylsilyl)phenyl ether(**1**) and N-methylpyrrolidine in THF solution. The subsequent end-capping reaction of the bifunctional living poly(DMS) with dimethylvinylchlorosilane(**4**) provided the uniform size poly(DMS) having vinylsilane group at the both chain ends(**5**).

INTRODUCTION

The living poly(dimethylsiloxane), poly(DMS), is known to be produced by the anionic ring-opening polymerization of (**3**) with such lithium initiators as alkyl lithium or lithium silanolates¹⁾ and this living polymerization technique has been successfully applied for the syntheses of a variety of block and graft copolymers with well-characterized poly(DMS) segment component²⁻⁵⁾.

As these living polymerization systems have been limited to the monofunctional ones, the approach for the bifunctional living poly(DMS) by the dilithio compounds will be of interest. However, this has been circumvented by the poor solubility of dilithio compounds in the common polymerization solvent. And the addition of amines or ethers to enhance the solubility instead resulted in the change of the reactivity of active lithium species^{6,7)}.

Thus the bifunctional poly(DMS) has been commonly produced by the equilibrium polymerization of octamethylcyclotetrasiloxane(D₄) in the presence of the functional disiloxane as an end blocker⁸⁾. Although versatile and convenient, the molecular size distribution of the poly(DMS)

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obtained by this procedure is inherently broad due to the equilibrium nature of this reaction system.

In the present paper, we describe a new convenient initiator system for the bifunctional living polymerization of (3), which can provide lithium silanolate as both end groups. The strong nucleophilic reactivity of this living end group of poly(DMS) facilitates the end-capping reaction to introduce a variety of functional groups. The bifunctional poly(DMS) with a narrow molecular weight distribution has been reported to be obtained to provide silanol groups at the chain ends⁹⁻¹² in some other non-equilibrium polymerization systems of (3) with H₂O/biscatecolsiliconate or partly lithiated dimethylsiloxanolate as catalyst-chain transfer reagent.

EXPERIMENTAL

Materials

(3) (from Toshiba Silicone Co.) and (4) (from Shin-Etsu Chemical Co., LTD.) were purified by the distillation over CaH₂. (1) was synthesized^{13,14} and recrystallized twice from toluene solution. Diphenylsilane diol (from Toshiba Silicone Co.) was recrystallized twice from methyl ethyl ketone/chloroform mixture solution. p-Bis(hydroxydimethylsilyl)benzene (from Petrarch Systems INC.) was recrystallized twice from hexane/THF mixture solution. n-Butyl lithium (from Nacalai tesque, INC., 1.4M in hexane) was used after titration¹⁵. N-Methylpyrrolidine, triethylamine and pyridine were distilled twice over CaH₂. THF was distilled from blue solution of sodium/benzophenone.

Preparation of (2)

In a 200ml round bottom flask equipped with a three-way stopcock, 2g of (1) was placed and dissolved in 40ml of dry THF under nitrogen. The reaction vessel was placed in an ice-water bath and a slightly excess amount of n-butyl lithium (molar ratio of n-BuLi/(1)=2.2/1) was added by means of a syringe under stirring to form white powdery precipitate, which was then washed 5 times with dry n-hexane. The product was once isolated by the evacuation and the subsequent addition of 40ml THF under an ultrasonic treatment for 30min gave a fine suspension solution. The quantitative lithiation of silanol group was confirmed by the titration with 0.1N-HCl.

Living polymerization of (3)

Ten grams of (3) and 5.6ml of N-methylpyrrolidine were

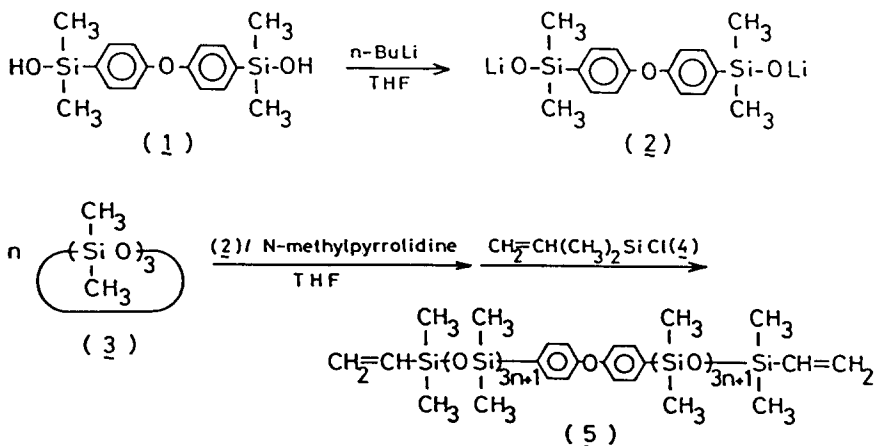
dissolved in 70ml dry THF and a required amount of the suspension solution of (2) was added. The originally turbid reaction mixture rapidly turned into homogeneous. The polymerization reaction was carried out under stirring for 3hrs at 21°C. The end-capping reaction was performed by the addition of an excess amount of (4) (molar ratio of (4)/(2)=4/1) with stirring for 10min. After an excess of (4), THF, and N-methylpyrrolidine were removed by the evacuation, the product was isolated and purified by the repeated precipitation into methanol, and finally freeze-dried from benzene solution.

Measurements

270MHz $^1\text{H-NMR}$ spectra were recorded by means of a JEOL GX270 apparatus. Chemical shifts were calibrated using the CHCl_3 (7.30ppm) as the internal standard. GPC measurements were carried out using a TOSOH Model CCPH apparatus equipped with RI8000 and UV8000 (254nm) as detectors and with a TSK G3000 HXL as a column and THF as eluent. VPO measurements were carried out by using a CORONA model 114 apparatus in toluene solution at 70°C. UV spectra were taken on HITACHI Model 200-10 UV spectrometer.

RESULTS AND DISCUSSION

The polymerization of (3) with (2) in the presence of N-methylpyrrolidine was found to proceed in a living character to produce a bifunctional poly(DMS) with a narrow molecular weight distribution. On the other hand, dilithium salts of other types



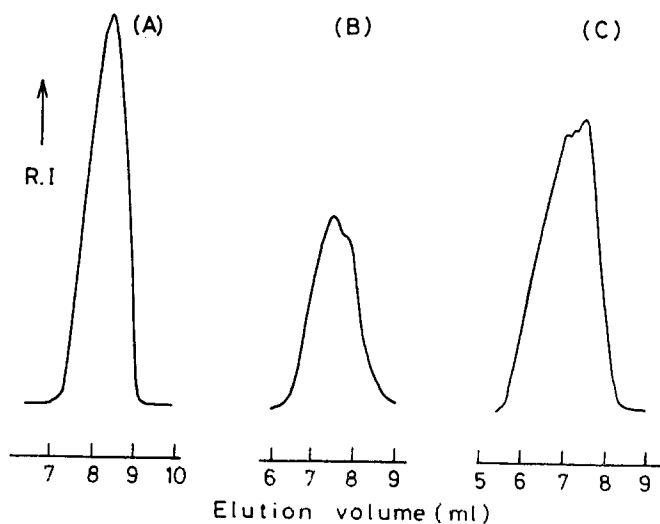


Fig. 1. GPC trace of the poly(DMS) obtained with dilithium salt of (A): (1), (B): p-bis(hydroxydimethylsilyl)benzene and (C): diphenylsilane diol [in THF/N-methylpyrrolidone (70.0/9.6 (ml/ml)) at 20°C for 3hr] (Column; TSK G3000HXL, Eluent; THF, 1ml/min)

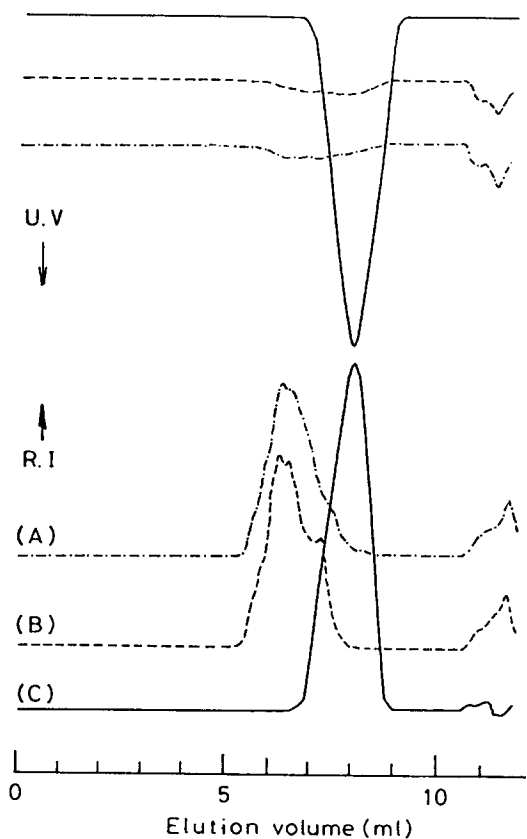


Fig. 2. GPC traces of the poly(DMS) obtained with (2) in the presence of (A): pyridine, (B): triethylamine and (C): N-methylpyrrolidone [in THF at 20°C for 3hr] (Column; TSK G3000HXL, Eluent; THF, 1ml/min)

of disilanol compounds which are readily available in a pure and stable form, i.e. diphenylsilane diol and p-bis(hydroxydimethylsilyl)benzene, failed to produce the uniform size poly(DMS) either in the absence or presence of N-methylpyrrolidine as shown in Fig. 1.

Also none of the partly lithiated disilanol above-mentioned were able to achieve the living polymerization of (3). The particular additive in the present system, N-methylpyrrolidine, was not allowed to be replaced by other amine like pyridine or triethylamine to maintain the present living polymerization system as shown in Fig. 2.

By the appropriate end-capping reaction of the living lithium silanolate end group of poly(DMS), one may introduce various functional groups at the uniform size poly(DMS) chain ends. In the present study, (4) was used as the terminating reagent to introduce vinylsilane group. The termination reaction was found to proceed smoothly with the formation of lithium chloride, which can be removed by the simple filtration.

The 270MHz $^1\text{H-NMR}$ spectrum of the resulting polymer(5) was shown in Fig. 3, where the signals assigned for the initiator fragment of phenyl protons at 7.0-7.7ppm were present together with those for the terminating reagent of vinylsilane multiplet at 5.7-6.3ppm. The molar ratio between phenyl and vinylsilane

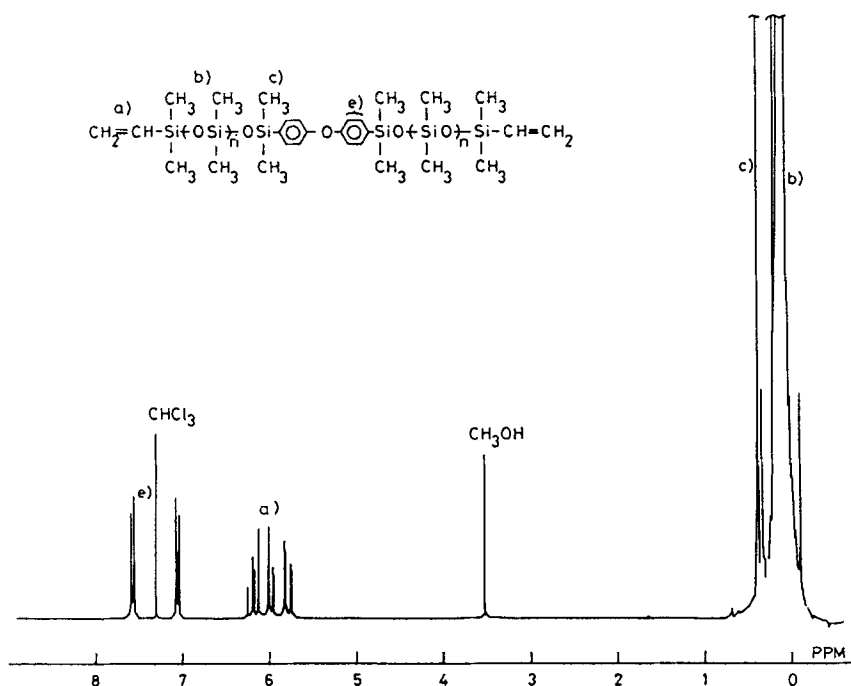


Fig. 3. 270MHz $^1\text{H-NMR}$ spectrum of (5) in CDCl_3 (No. 1 in Table 1)

group was found to be unity, indicating the occurrence of the quantitative end-capping reaction.

As summarized in Table 1, a series of uniform size poly(DMS) with vinylsilane as both end groups(5) were produced. The molecular weights estimated from the yield-initiator ratio were found to agree well to those obtained by such experiments as GPC, VPO and UV. This again demonstrates that the present initiator system can produce the living poly(DMS) through fast and quantitative initiation, and with propagation free from chain transfer and termination.

In conclusion, the present initiator system comprised of (2) and N-methylpyrrolidine, was easy to prepare and handle, and produced bifunctional living poly(DMS) in a reproducible manner. The subsequent end-capping reaction with (4) was found to provide the uniform size telechelic poly(DMS). The further study on the synthesis of polyurethane-polysiloxane block copolymer by the use of the uniform size bifunctional poly(DMS) with hydroxyl end groups prepared through the present living system was described elsewhere¹⁶⁾.

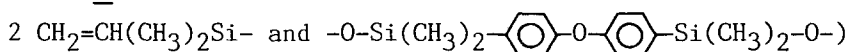
Table 1 Results of the synthesis of (5)^{a)}

No.	<u>2</u> ^{b)} mmol	<u>4</u> mmol	Yield %	M_n			
				Calc. ^{c)}	GPC ^{d)}	VPO	UV
1	2.25	9.00	65.4	3400	3600	3800	3200
2	1.35	5.40	66.1	5400	5400	5200	5300
3	0.90	3.60	70.3	8300	8400	8200	8400

a) 3; 45.0mmol, THF; 70.0ml, N-methylpyrrolidine; 9.6ml, 20°C, 3hr

b) In THF(0.070mol/l)

c) $M_n = \frac{D_3}{2} \times \frac{\text{Yield}}{100} \times 222 + (\text{molecular weight of}$



d) Calibrated by standard poly(DMS)³⁾ prepared by the living polymerization of D_3 with n-BuLi

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