Synthesis and Reactions of Uniform-Size Poly(dimethylsiloxane)s Having Carboxylic Acid as a Single End Group and Both End Groups

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ABSTRACT: Uniform-size poly(dimethylsiloxane)s, poly(DMS)s, having carboxylic acid as a single end group and both end groups were synthesized through the reaction of mono- and bifunctional living poly(DMS)s with newly synthesized 4-(dimethylchlorosilyl)butanoic acid trimethylsilyl ester (1). 5-(Dimethylchlorosilyl)pentanoic acid trimethylsilyl ester (2) was also found to be an effective terminating reagent. The subsequent reaction of monofunctional and bifunctional poly(DMS)s having carboxylic acid end groups with aluminum(III) isopropoxide and with titanium(IV) isopropoxide led to the formation of three- and four-arm star polymers and model networks with well-defined branch points and branch length, respectively.

Introduction

Uniform-size polymers possessing suitably reactive end groups at a single chain end or both chain ends are considered to be important as macromolecular building blocks for the synthesis of various multiphase and multidimensional polymer materials with well-defined structure. In this context, we have reported a series of mono- and bifunctional uniform-size poly(dimethylsiloxane)s, poly(DMS)s, possessing various reactive end groups and they have been utilized for the synthesis of block and graft copolymers having well-controlled polysiloxane segments.[1-6]

As an extension of preceding studies, the present paper describes the synthesis of the hitherto unknown poly(DMS) of narrow molecular weight distribution and possessing a carboxylic acid as a single end group and both end groups. A conventional equilibrium ring-opening polymerization of octamethylcyclotetrasiloxane (D_4) in the presence of 1,3-bis(carboxypropyl)tetramethyldisiloxane is known to provide a relevant bifunctional poly(DMS) having carboxylic acid end groups,[7] but the molecular weight distribution of the obtained poly(DMS)s is inherently broad due to the equilibrium nature of the reaction system. Therefore, a new process to produce uniform-size telechelic poly(DMS) will be of significance for the synthesis of such precisely designed model polymers like star polymers and model networks, which are, indeed, reported in the present paper. Also it must be stressed that the control not only on the average molecular weight but also on the molecular weight distribution is indispensable to realize a predictable microphase-separation morphology in block and graft copolymers.

Experimental Part

Material. Hexamethylcyclotrisiloxane (D_3) and dimethylchlorosilane (both from Toshiba Silicone Co.) were purified by distillation over CaH_2. Pt/C (5% Pt; Japan Engelhard Co.), vinylacetic acid, and allylacetic acid (Aldrich) were used as received. THF and benzene used for polymerizations and the subsequent polymer reactions were distilled from a blue solution of sodium benzophenone. Aluminum(III) isopropoxide (Tokyo Kasei) and titanium(IV) isopropoxide (Nacalai Tesque) were used as received.

Synthesis of Terminating Reagents. In a 200-mL two-necked flask equipped with a reflux condenser and a three-way stopcock, 50 mL (0.28 mol) of vinylacetic acid trimethylsilyl ester, obtained by the reaction of vinylacetic acid with trimethylchlorosilane in the presence of triethylamine, and 0.26 g of Pt/C were placed and heated to 40-50 °C in an oil bath. Twofold excess of dimethylchlorosilane (62.0 mL, 0.56 mol) was then added carefully by means of a syringe and stirring was continued for 2 h. The reaction mixture was transferred in a distillation apparatus under nitrogen atmosphere and distilled under reduced pressure [bp 77-78 °C (3 mmHg)] to yield 37.2 g (53% yield) of 4-(dimethylchlorosilyl)butanoic acid trimethylsilyl ester (1). 5-(Dimethylchlorosilyl)pentanoic acid trimethylsilyl ester (2) was also obtained in a similar method in 46% yield [bp 94 °C (4 mmHg)].

^1H NMR ($CDCl_3$) of 1: δ 0.27 (s, 9 H), 0.42 (s, 6 H), 0.85 (t, 2 H), 1.88 (m, 2 H), 2.42 (t, 2 H).

^1H NMR ($CDCl_3$) of 2: δ 0.27 (s, 9 H), 0.42 (s, 6 H), 0.82 (m, 2 H), 1.41 (m, 2 H), 1.63 (m, 2 H), 2.30 (t, 2 H).

IR of 1 and 2 (neat): 1700 cm^{-1} ($-COOSi(CH_3)_3$).

Synthesis of Mono- (3 and 4) and Bifunctional (5) Uniform-Size Poly(dimethylsiloxane) Having a Carboxylic Acid End Group. A monofunctional and a bifunctional living poly(DMS)s were prepared by the anionic ring-opening polymerization of D_3 with *n*-butyllithium and with a lithium salt of bis[*p*-(dimethylhydroxysilyl)phenyl] ether as initiators, respectively.[1,5] Thus, into a THF solution containing a weighed amount of D_3 was added the prescribed amount of initiator solution (*n*-butyllithium, 1.54 mol/L, in hexane and dilithium salt of bis[*p*-(dimethylhydroxysilyl)phenyl] ether, 0.080 mol/L, in THF) by a syringe to start the polymerization. After 3 h of reaction, an excess amount of 1 or 2 (molar ratio of initiator/1 or 2 = 1/5) was then added into monofunctional poly(DMS) solution and heated at 50 °C for 2 h, while in the case of bifunctional poly(DMS), a 6-fold excess of 1 was added and heated at 50 °C for 1 h. The reaction products were isolated and purified by precipitation into methanol and finally freeze-dried from benzene solution.

Synthesis of Star Poly(DMS)s. In a 30-mL flask equipped with a three-way stopcock, 1.0 g of uniform-size poly(DMS) having a carboxylic acid as a single end group was placed and dissolved with 15 mL of benzene. Thereupon, a stoichiometric amount of aluminum(III) isopropoxide or titanium(IV) isopropoxide dissolved in 5 mL of benzene was added under nitrogen atmosphere and the stirring was continued for 16 h at 24-28 °C. The reaction products were then isolated by evacuation to remove the solvent, benzene, and isopropyl alcohol formed.

Synthesis of Poly(DMS) Model Networks. A total of 1 g of uniform-size poly(DMS) having a carboxylic acid as both end groups (5) was dissolved in 15 mL of dry benzene, and a stoichiometric amount of aluminum(III) isopropoxide or titanium(IV) isopropoxide dissolved in 5 mL of benzene was added under vigorous stirring at 23-24 °C. The stirring was immediately

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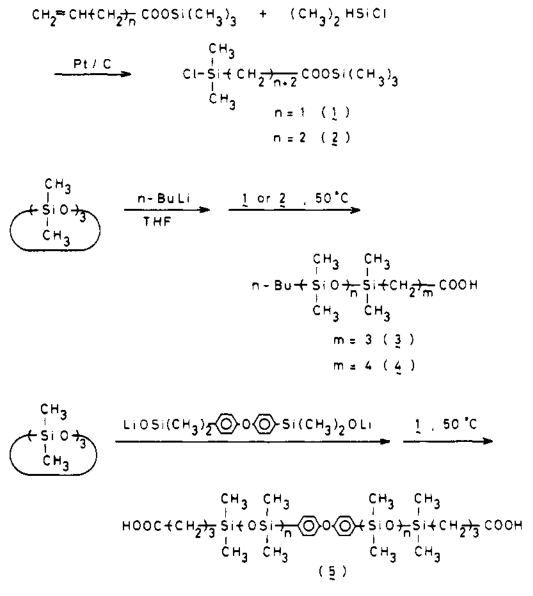
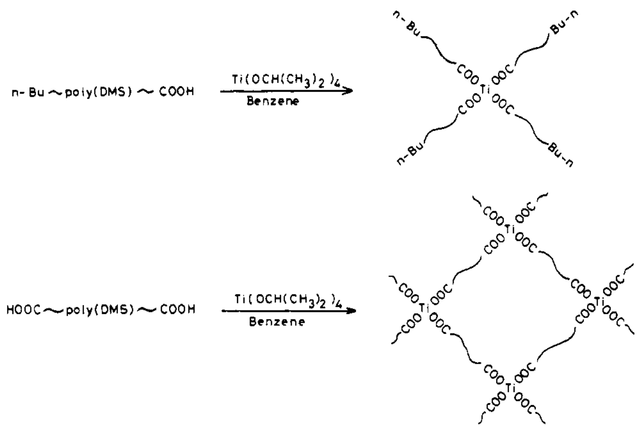
Scheme I



Scheme II



blocked due to the increase of viscosity of the solution to indicate the formation of poly(DMS) gels. The formed gels were isolated by evacuating the solvent and isopropyl alcohol in vacuo. Isolated gel samples obtained by the reaction of **5** ($\bar{M}_n$ 8600) with aluminum isopropoxide and with titanium isopropoxide were subjected to extraction with THF three times to estimate the gel contents, and they were 93 and 94%, respectively.

Measurements. ^{1}H NMR (270 MHz) spectra were recorded by means of a JEOL JNM-GX270 apparatus. Chemical shift was calibrated using $CHCl_3$ (7.30 ppm) as an internal standard. GPC measurements were carried out by using a Tohso Model CCPH high performance liquid chromatograph equipped with TSK G3000HXL as a column and THF as an eluent. Calibration was obtained by using a series of uniform-size poly(DMS)s as standard samples. The conversion factor from a polystyrene standard was then determined to be 0.717. VPO measurements were carried out by means of a Corona Model 114 apparatus in toluene solution at 70 °C. IR spectra were taken on a Hitachi 260-10 infrared spectrophotometer.

Results and Discussion

Synthesis of Uniform-Size Poly(DMS) Having a Carboxylic Acid as a Single End Group and Both End Groups. Poly(DMS)s having a single living end group and both living end groups were produced by employing lithium initiators of mono- and bifunctionalities. The subsequent termination reaction was carried out by 4-(dimethylchlorosilyl)butanoic acid trimethylsilyl ester (**1**; Scheme I), which was synthesized through the hydrosilation reaction of vinylacetic acid trimethylsilyl ester with dimethylchlorosilane in a good yield. The precipitation treatment of the reaction product into methanol resulted in the complete removal of a trimethylsilyl group on a carboxylic acid function, and uniform-size poly(DMS)s having a carboxylic acid as a single end group and both end groups were produced.

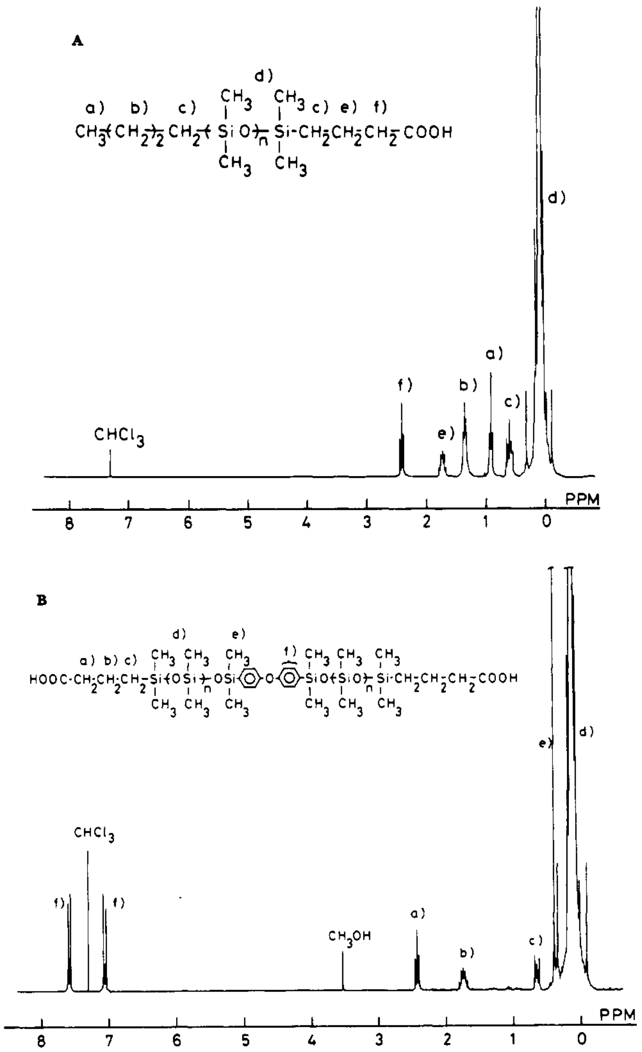


Figure 1. 270-MHz ^{1}H NMR spectra of poly(DMS)s having (A) carboxylic acid as a single end group (**3**; run 1 in Table I) and (B) as both end groups (**5**; run 7 in Table I) in $CDCl_3$.

On the contrary, the hydrosilation reaction of poly(DMS) having a silane (SiH) end group[2-4] with vinylacetic acid trimethylsilyl ester in the presence of Pt/C as a catalyst resulted in a modest yield of a carboxylic acid function (41%) despite the complete consumption of the starting silane function.

Figure 1 shows ^{1}H NMR spectra of mono- (**3**) and bifunctional (**5**) poly(DMS)s having 3-carboxypropyl end groups, respectively. Signals from methylene protons of the 3-carboxypropyl group were observed at 0.62, 1.72, and 2.42 ppm together with those from either the *n*-butyl group at 0.60, 0.95, and 1.35 ppm or the diphenyl ether group at 7–8 ppm. The quantitative termination reaction in both mono- and bifunctional living poly(DMS)s was demonstrated through the comparison of the signal intensity of the initiator, i.e., the *n*-butyl or diphenyl ether group, with that of terminating reagent, i.e., 3-carboxypropyl group. The end-capping reaction of monofunctional living poly(DMS) with 5-(dimethylchlorosilyl)pentanoic acid trimethylsilyl ester was also carried out to proceed quantitatively. The ^{1}H NMR analysis of the resulting product

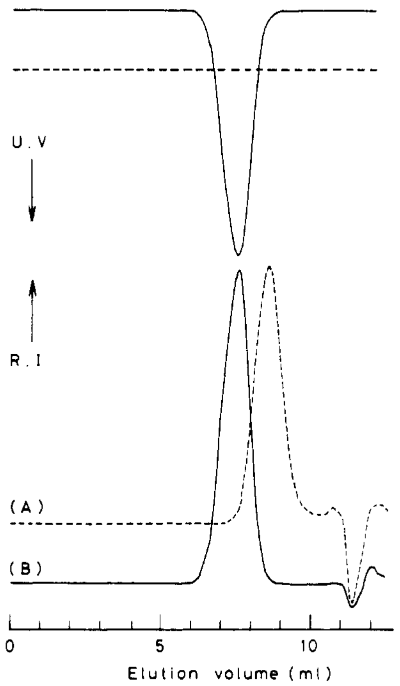


Figure 2. GPC traces of poly(DMS)s having (A) a carboxylic acid as a single end group (3; run 1 in Table I) and (B) as both end groups (5; run 8 in Table I). Column, TSK G3000HXL; eluent, THF, 1.0 mL/min.

showed methylene proton signals at 0.60, 1.44, 1.73, and 2.40 ppm, indicating the presence of a 4-carboxybutyl end group.

The complete deprotection of a trimethylsilyl group on a carboxylic acid function at the poly(DMS) chain end was observed during the isolation and purification procedure, namely, precipitation into methanol. This was confirmed by IR and NMR spectroscopic analyses of the product, where the presence of sharp carbonyl stretching absorption of free carboxylic acid at 1710 cm^{-1} and the absence of trimethylsilyl signals at 0.34 ppm were noticed.

GPC traces of poly(DMS)s having carboxylic acid end groups are listed in Figure 2. The uniform-size nature ($M_w/M_n < 1.12$) of these poly(DMS)s is indicated by comparing their peak width against that of a polystyrene standard of known M_w/M_n values. The UV (254 nm) trace appeared only for a bifunctional poly(DMS) sample, which possessed a diphenyl ether group as an initiator fragment.

As summarized in Table I, a series of uniform-size poly(DMS)s having a carboxylic acid as a single end group and both end groups was produced. The molecular weights determined by VPO and by GPC were found to agree with each other and were identical with those calculated from yield–initiator ratios, to confirm a living character of the polymerization of D_3 in the present systems.

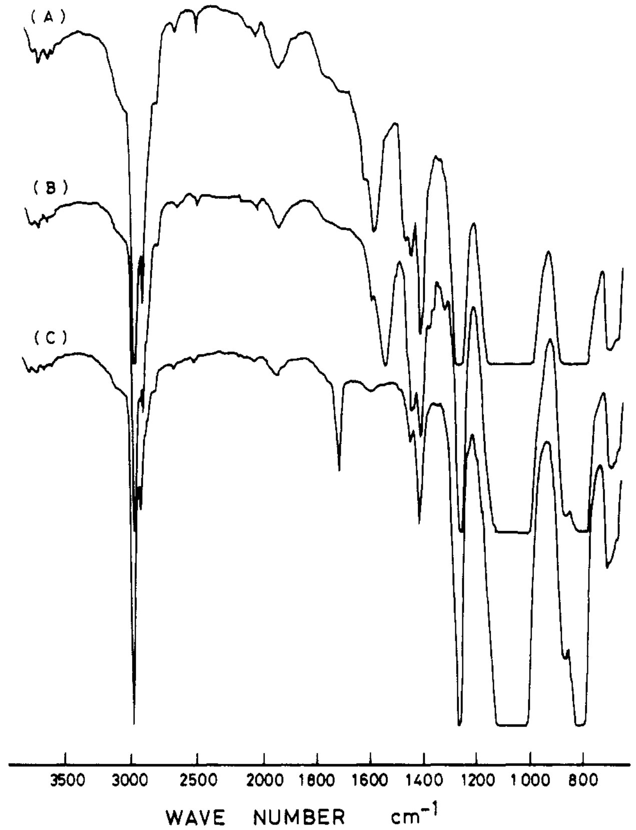


Figure 3. IR spectra of (A) poly(DMS)–Al star, (B) poly(DMS)–Ti star, and (C) a starting poly(DMS) having a carboxylic acid as a single end group (3; run 2 in Table I).

Reactions of Uniform-Size Poly(DMS)s Having a Carboxylic Acid as a Single End Group and Both End Groups. Mono- and bifunctional uniform-size poly(DMS)s having carboxylic acid end groups were then allowed to react with a stoichiometric amount of tri- and tetrafunctional metal alkoxides, namely, aluminum(III) and titanium(IV) isopropoxides in benzene solution at an ambient temperature. The relevant neutralization reactions of polybutadiene having a carboxylic acid function at polymer chain ends[8–12] resulted in an ionically connected macromolecule of unique bulk and solution properties.

IR spectra of the reaction products were shown in Figure 3, where broad absorption of metal carboxylate at 1590 cm^{-1} for aluminum and at 1540 cm^{-1} for titanium appeared

Table I
Synthesis of Uniform-Size Poly(DMS)s Having a Carboxylic Acid as a Single End Group and Both End Groups[a]

run	initiator,[b] mmol	terminating reagent (amount, mmol)	yield, %	$\bar{M}_n$ calcd[c]	$\bar{M}_n$ GPC[d]	$\bar{M}_n$ VPO
1	4.50	**1** (22.5)	72.0	1800	2300	2400
2	2.70	**1** (13.5)	83.0	3300	3500	3600
3	1.35	**1** (6.75)	90.0	6900	6800	6800
4	4.50	**2** (22.5)	38.2	*e*	2100	2500
5	2.70	**2** (13.5)	72.3	2900	3200	3100
6	1.35	**2** (6.75)	85.6	6600	6800	6800
7	2.25	**1** (13.5)	71.3	3800	4200	4200
8	1.35	**1** (8.1)	71.2	5900	6200	6000
9	0.90	**1** (5.4)	70.0	8400	8200	840

[a] Runs 1–6: D_3; 45.0 mmol, THF; 20 mL, 19 °C, 3 h. Runs 7–9: D_3; 45.0 mmol, THF; 40 mL, 20 °C, 3 h. [b] Runs 1–6: *n*-butyllithium ane (1.54 mol/L). Runs 7–9: $\mathrm{LiOSi(CH_3)_2C_6H_4OC_6H_4Si(CH_3)_2OLi}$ in THF (0.080 mol/L). [c] Runs 1–6: $\bar{M}_n = (D_3/n\text{-BuLi})(\text{yield}/1$ 202 (**1**) or 216 (**2**) (molecular weight of $\mathrm{-(CH_2)_3CH_3}$ and $\mathrm{-Si(CH_3)_2(CH_2)_{\mathit{n}}COOH}$, $n = 3$ or 4). Runs 7–9: $\bar{M}_n = (D_3/\text{initiator})(\text{yie}$ + 606 (molecular weight of $\mathrm{2{-}Si(CH_3)_2(CH_2)_3COOH}$ and $\mathrm{-OSi(CH_3)_2C_6H_4OC_6H_4Si(CH_3)_2O-}$). [d] Calibrated by standard poly(DM factor for polystyrene standard was determined to be 0.717. [e] Partly dissolved in methanol.

along with the complete disappearance of the free carboxylic acid absorption of startng poly(DMS) prepolymer at 1710 cm^{-1}, indicating a quantitative formation of star poly(DMS)s of three and four branches with well-defined branch length. On the other hand, GPC characterization of obtained star polymers was circumvented due to the peak anomaly presumably caused from the ionic nature of metal-carboxylate bonds in the product.

Upon the addition of a stoichiometric amount of aluminum or titanium isopropoxide to a dry benzene solution of bifunctional poly(DMS)s having carboxylic acid end groups, a gelation took place immediately, and isolated products were no more soluble in such organic solvents as THF, hexane, and benzene. A gel with titanium isopropoxide was harder than one with aluminum isopropoxide, reflecting the difference of the number of branch points in two gels. On the other hand, no immediate gelation was observed with titanium ethoxide, indicating a remarkable substituent effect of titanium alkoxide in the present reaction system. This observation is relevant to the previous reports[11,12] that the reaction between polybutadiene having a carboxylic acid as both end groups and titanium *n*-butoxide failed to give a gel under a stoichiometric condition. In the present study, tetraethoxysilane was also inactive for the gel formation.

As in a star polymer synthesis, the gelation reaction could be followed by IR spectroscopy, where the metal carboxylate absorption appeared along with the disappearance of carboxylic acid absorption for the prepolymers. This indicates the quantitative reaction between carboxylic acid groups of poly(DMS) chain ends with metal alkoxide to form tri- and tetrafunctional model networks with well-defined branch points and branch lengths.[13-15] The gel content of the products was estimated to be almost quantitative by a repeated extraction technique with THF.

The above poly(DMS) model networks were found to redissolve into solution instantaneously by adding a drop of 1 N hydrochloric acid.

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Registry No. **1**, 130200-18-9; **2**, 130200-19-0; Al(III) isopropoxide, 555-31-7; Ti(IV) isopropoxide, 546-68-9; vinylacetic acid trimethylsilyl ester, 13688-54-5; vinylacetic acid, 625-38-7; trimethylchlorosilane, 75-77-4; dimethylchlorosilane, 1066-35-9; bis[*p*-(dimethylhydroxysilyl)phenyl]ether·Li, 120751-48-6.