Anionic Block Copolymerization of Cyclotetrasiloxanes Initiated by p-Bis(dimethyllithiioxysilyl)benzene

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SYNOPSIS

The triblock copolymers of poly(diphenyl-b-dimethyl-b-diphenyl)siloxane (PMP) and poly(diphenyl-b-dimethyl-co-methylvinyl-b-diphenyl)siloxane (PMVP) have been synthesized by the dianionic polymerization procedure. The polymerization of the cyclotetrasiloxane monomers initiated by lithium-based initiator has been carried out so as to avoid equilibration reactions. The new initiator, p-bis(dimethyllithiioxysilyl)benzene, was used. Dimethyl formamide (DMF) was used as a promotor. The effects of initiator concentration, polymerization temperature, and polymerization time on the reaction were investigated. The block copolymers have been determined by ^{1}H-NMR, infrared, ultraviolet, and differential scanning calorimetry. Progressive precipitation separation has been used to study the molecular weight distribution, and the integral distribution curves of the molecular weight have been given. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Bostic[1-3] prepared a number of siloxane blockcopolymers, including triblock copolymers poly-(diphenyl-b-dimethyl-b-diphenyl)siloxane. However, the triblock copolymers do not have good mechanical properties and are to be used by means of chemical crosslinks. Ibemesi et al.[4] prepared vinyl-terminated poly(diphenyl-b-dimethyl)siloxane, which can be cured by end-linking reaction. Gvozdic et al.[5] obtained the desired triblock copolymers, which do not need to employ chemical crosslinking and can be used as thermoplastic elastomers. In these references, the anionic living polymerizations were carried out by using n-BuLi and diphenyl silandiol (DLS) as initiators, THF or DMSO as promoter, and the cyclic trimers of dimethyl and diphenyl siloxane as monomers. In the present article, we describe the synthesis of dimethylsiloxane (PDMS) and diphenylsiloxane (PDPS) triblock copolymers, PDMS being the central sequence, and PDPS, the outer ones.

The main reagents used in the synthesis were octamethylcyclotetrasiloxane (D$_4$), octaphenylcyclotetrasiloxane (P$_4$) (reactants), and p-bis-(dimethyllithiioxysilyl)benzene (PBDMOLiB), a practical initiator formed by n-BuLi p-bis-(dimethylhydroxysilyl)benzene(PBDMOHB).We have known that the polymerization of D$_4$ or P$_4$ is more difficult than that of D$_3$ or P$_3$, but D$_4$ and P$_4$ are cheaper and can be obtained easier in China. At the same time, we have also known that PBDMOHB is more rigid than diphenyl disilanol and is not easy to form cyclic compound; thus, we assume that PBDMOHB is probably an effective initiator for the copolymerization of D$_4$ with P$_4$ to obtain the triblock linear copolymers. When the suitable amount of tetramethyl-tetravinylcyclotetrasiloxane (V$_4$) was added together with D$_4$, the dimethylsiloxane segment containing methylvinylsiloxane was formed; thus, the PMVP copolymer could be obtained.

EXPERIMENTAL

Materials

D$_4$ was provided by the Chemical Industry Factory of Shandong University. The sample was dried by


Table I Formulation of Materials and Results for Preparing Various Copolymers

Code Name	P_4/D_4 (wt %)	$V_4/(P_4 + D_4)$ (wt %)	PBDMOHB/Monomer (wt %)	$[\eta]$ (mL/g)	Yield (%)
PDMS	0	0	0.20	87.0	66.7
PMVP-5	5	2.0	0.20	90.0	83.3
PMVP-10	10	2.0	0.20	83.2	72.0
PMVP-20	20	2.0	0.20	86.2	74.3
PMVP-40	40	2.0	0.20	93.5	67.8
PMVP-50a	50	2.0	0.30	64.0	60.5
PMVP-50b	50	2.0	0.25	86.4	64.4
PMVP-50	50	2.0	0.20	96.9	85.3
PMP-40	40	0	0.20	97.0	82.2

refluxing over calcium hydride and distilled just before use. P_4 was made using dehydrolysis of diphenyl disilanol in 95% alcohol with KOH as catalyst, and the sample obtained was dried in a vacuum dryer at 80°C under 5 torr for 24 h. DMF was supplied by No. 11 Reagent Factory, Shanghai, and made pure as follows: benzene of 10% DMF and water of 4% DMF were added and distilled out, then the remainder was dried with calcium hydride and distilled

under reduced pressure to collect 38–39°C/3 mm Hg fraction. THF was supplied by Tian Jin Reagent Factory and was refluxed over sodium wire and diphenylketone until the blue color appeared, then distilled to obtain 66–67°C fraction.

p-Bis(dimethylhydroxysilyl)benzene was prepared according to the procedure outlined by Merker, Scott,[6] (mp 139.0–139.5°C; 139°C in Merker and Scott[6]). Petroleum (bp 60–90°C) and
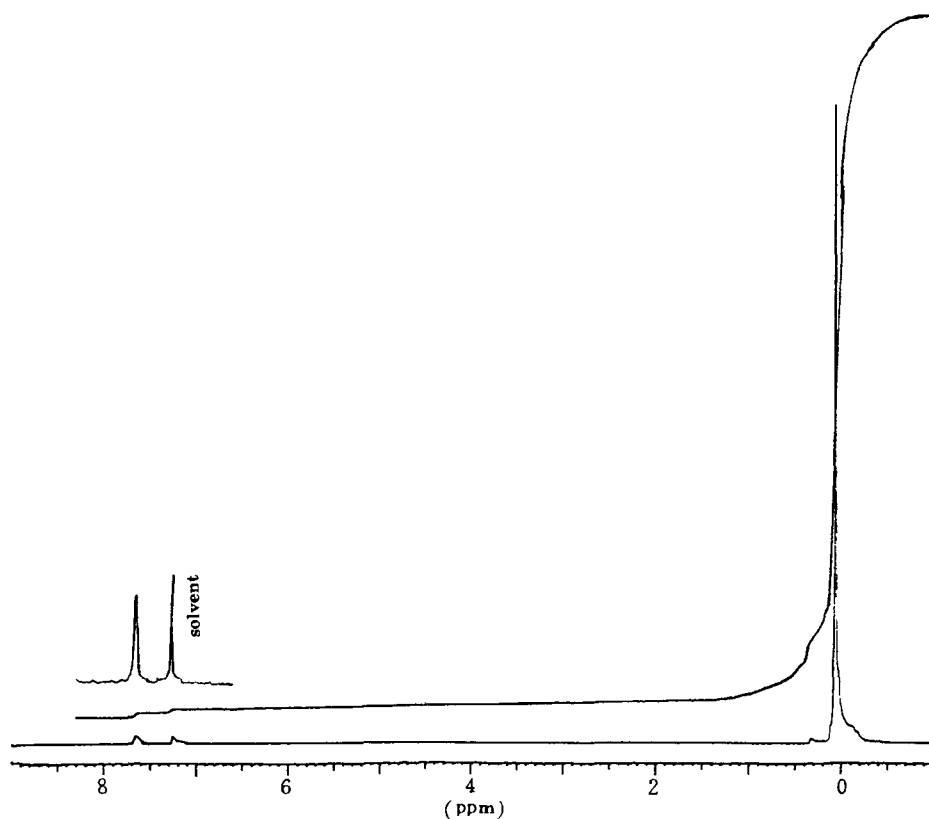
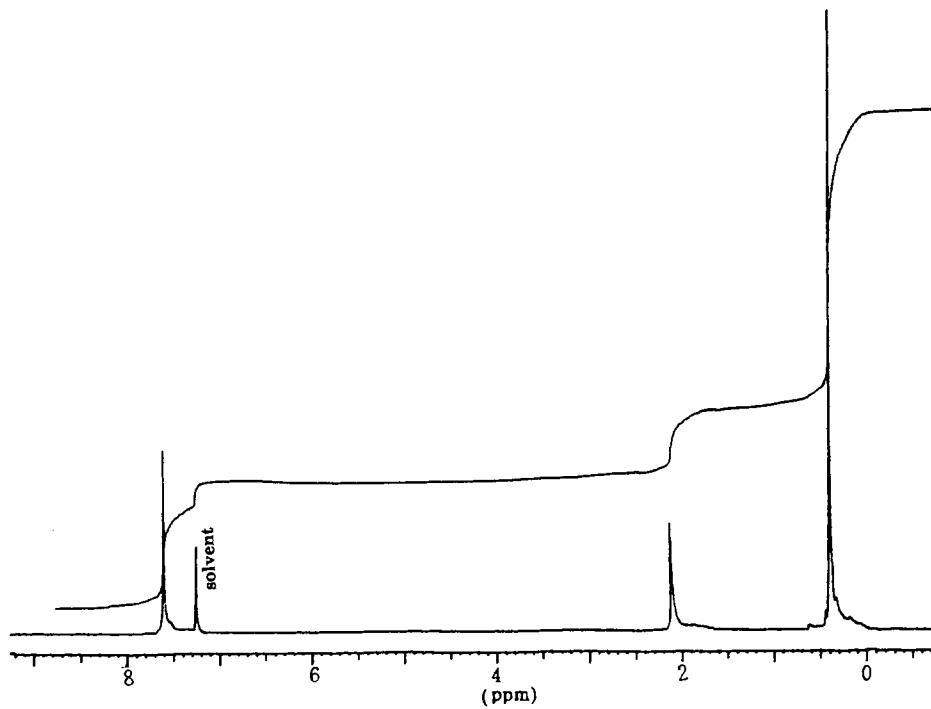**Figure 1** The ¹H-NMR spectrum of polydimethylsiloxane containing PBDMOB.
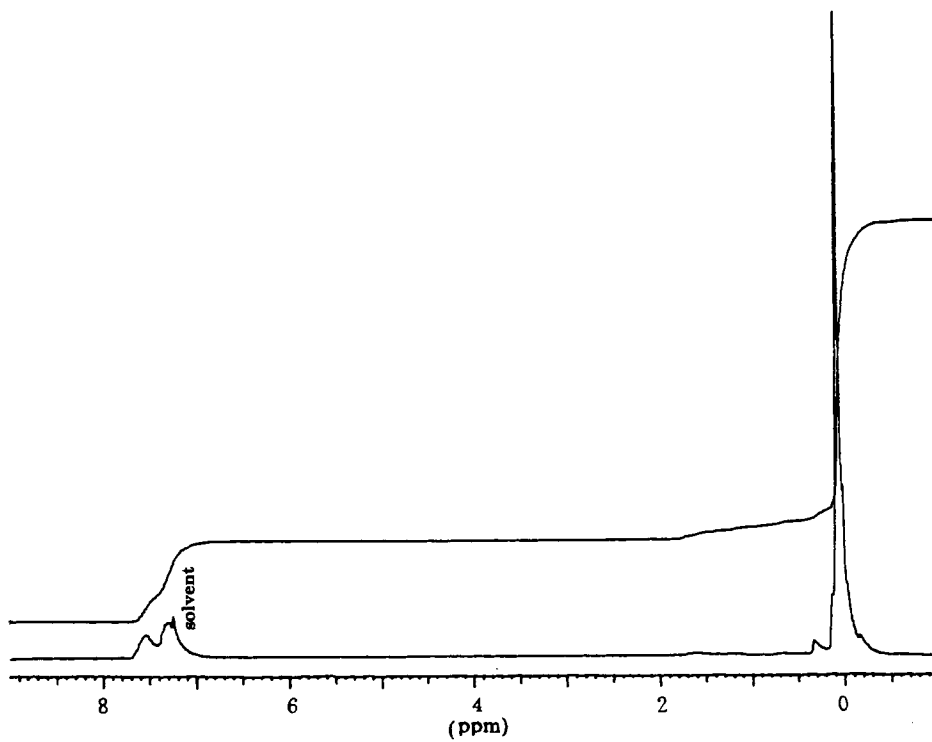
Figure 2   The ¹H-NMR spectrum of PBDMOHB.

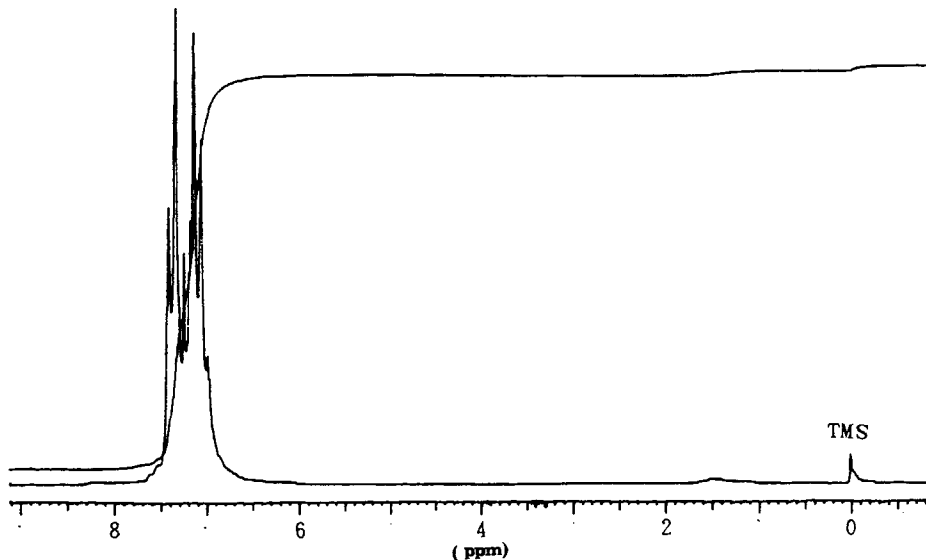**Figure 3**   The ¹H-NMR spectrum of PMVP-40.

Figure 4 The ^{1}H-NMR spectrum of P_4.

methanol were provided by Tianjin Reagent Industry.

Apparatus

^{1}H-NMR spectra were recorded on FX-90Q spectrometer in deuterochloroform (CDCl$_3$) UV spectra were examined on Shimadzu UV-240 spectrometer with 0.0060 ± 0.0002 g/mL product solution in chloroform. IR spectra were measured in a region of 400–4000 cm^{-1} by film coating with Nicolet-5DX spectrometer. N_d^{20} were taken on a WZS-Abb Refractometer. The intrinsic viscosity values of the polymers were measured with an Ubbelohde viscometer
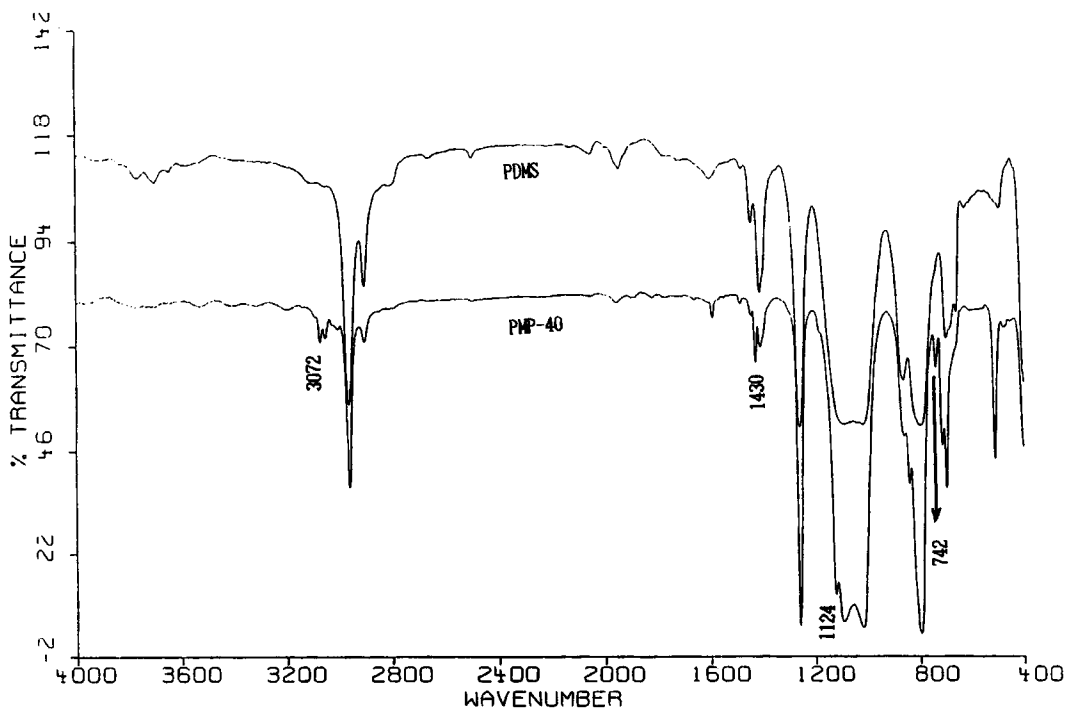

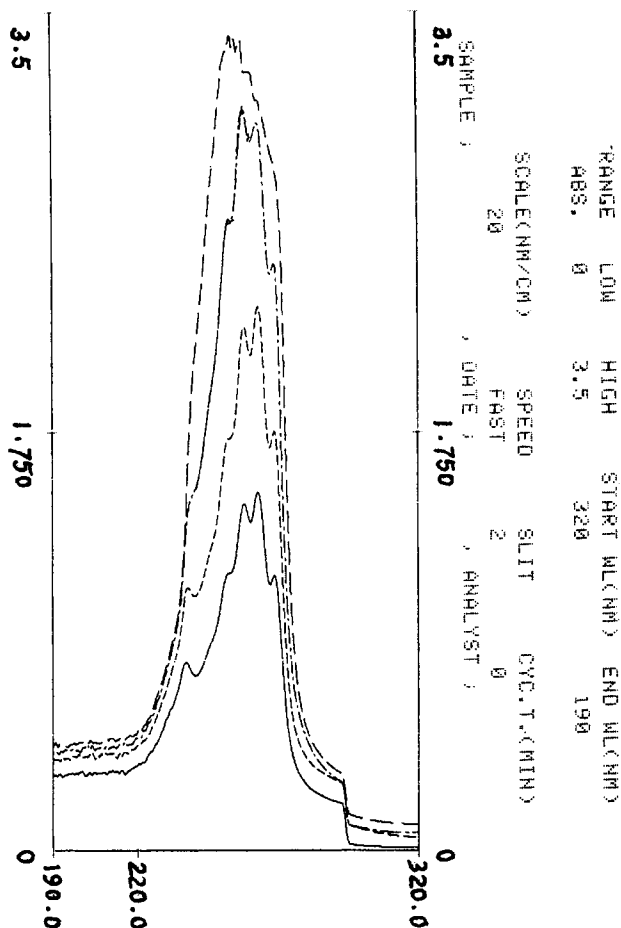**Figure 5** The IR spectra of PMP and PDMS.

Figure 6   The UV spectra of some copolymers.

Figure 7   The relation of the intrinsic viscosity with the initiator concentration.

in toluene at 25.00 ± 0.01°C. The molecular weight distribution was explained with a diagram. DSC curves were recorded with DelTA Series 7 (sample wt, 6.34 mg; scanning rate, 15°C/min from 57–550°C.

Equipment

Since anionic species are easily killed by moisture and O_2, all the glassware equipment as thoroughly cleaned, dried, and assembled under pure N_2. The thermometer was uncorrected.

Polymerization

The required amount of PBDMOHB in 4 mL THF and n-BuLi in n-hexane was successively introduced into a four-necked round bottom flask by a syringe. The flask assembled a mechanical stirrer, a separating apparatus of water connected to a reflux condenser equipped with a drying tube of calcium chlo-
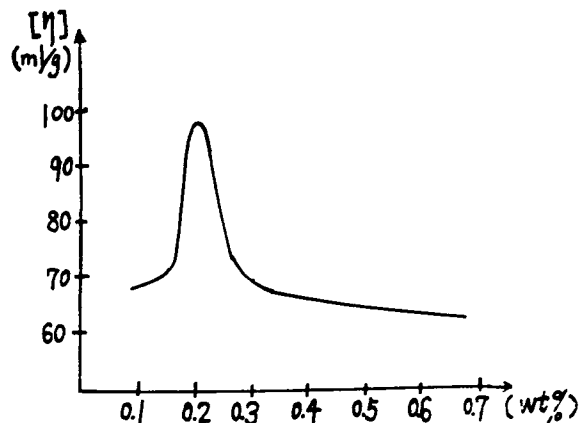
ride, a nitrogen inlet tube, and a thermometer. While the mixture was stirred at room temperature under an atmosphere of dry nitrogen for 20 min, the color of the mixture became muddy white. After the directed amount of D_4 was added, the system was heated up to 160°C. At this time, 2 mL DMF was added to the flask by syringe and, in a moment, the system become clear and viscous. We maintained the temperature for 3 h to obtain a viscous, transparent liquid. After this, a certain amount P_4 in toluene was added by syringe, and the mixture was refluxed for half an hour until it became milky white. Then, we raised the temperature up to 190°C, added 2 mL DMF to the flask with syringe, and maintained the temperature for 4 h to perform the copolymerization. After cooling, the product was dissolved in hot toluene and precipitated with methanol to yield the copolymer. Finally, the product was dried in a dryer at 80°C under 2 mm Hg. The formulation of
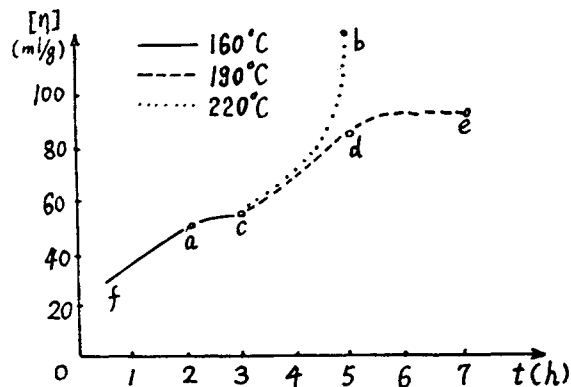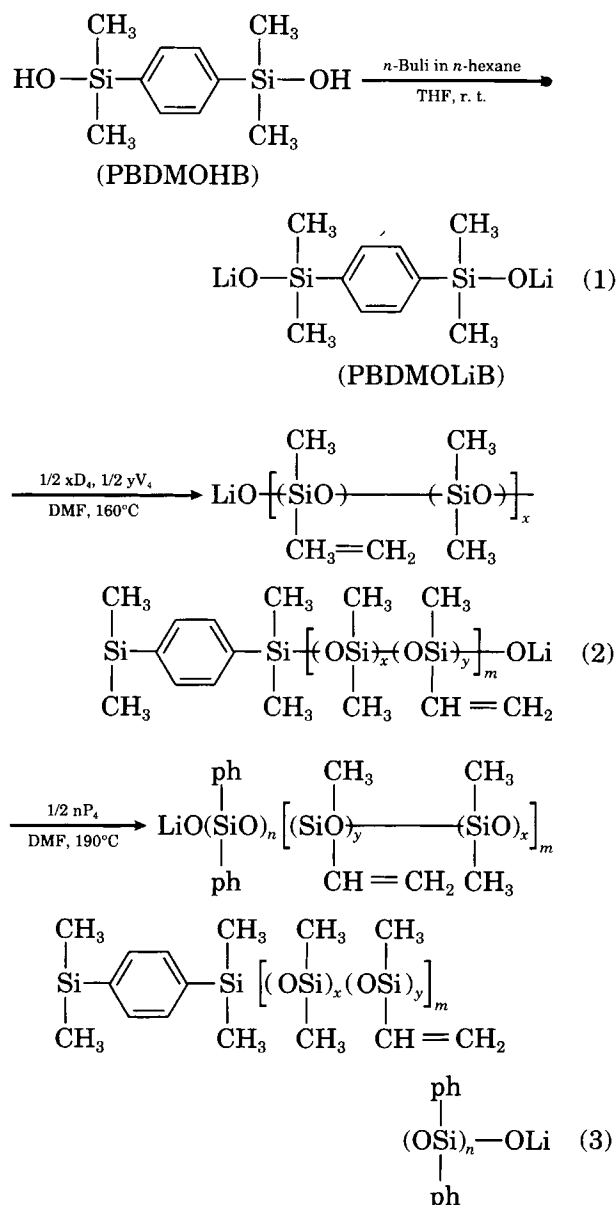

Figure 8   The relation of the intrinsic viscosity with the polymerization time.

materials and results for various copolymers are outlined in Table I.

RESULTS AND DISCUSSION

Copolymerization Process

The polymerization process is shown in eqs. (1)–(3).

(PBDMOHB)

$$\text{(PBDMOLiB)} \quad (1)$$

$$(2)$$

$$(3)$$

In eq. (1), PBDMOLiB, i.e., p-bis(dimethyllithiioxysilyl)benzene was produced as an initiator. In eq. (2), if V_4 is not added, the polymerization can also be carried out, and only $(\text{CH}_2=\text{CHSiCH}_3\text{O})_y$ in the

equation is cut out. That V_4 was used for the polymerization is due to the importance in crosslinking silicone rubber.

In our experiment, no polymerization occurred at 160°C, even with a large excess of D_4 or V_4 until the donor solvent DMF was added to the system. After the DMF was added to the system (about 5 min), the viscosity of the system increased; i.e., the polymerization had begun. The mechanism of anionic polymerization process has been clarified by the use lithium cryptates as counter ions.[7]

PBDMOLiB as a Real Initiator

In order to testify that PBDMOLiB is a real initiator and takes part in the reaction, we have designed an experiment, as follows. Using PBDMOHB (5 wt % of D_4) and n-BuLi (2 mol of PBDMOHB) as initiators, 2 mL DMF as promoter, only D_4 was polymerized at 160°C for 3 h. The product obtained was fully washed with anhydrous alcohol to remove nonreactive PBDMOHB thoroughly. The ^{1}H-NMR spectrum of the obtained polymer was recorded and is shown in Figure 1, which gives the following chemical shifts (δ, ppm): 7.55 (s), 0.32 (s), and 0.04 (s). Obviously, they should be attributed to the hydrogen of phenylene, Si-Me in PBDMOB, and Si-Me in $[\text{Si}(\text{CH}_3)_2\text{O}]_n$, respectively. We have calculated the integral of various hydrogen in the ^{1}H-NMR spectrum to estimate the contents of the PBDMOB in polymer. The estimated result is 4.3 wt %, which is close to 5 wt %, mentioned above. In contrast to Figure 1, we put the ^{1}H-NMR spectrum of PBDMOHB in Figure 2. From Figure 2, we can find the following chemical shifts (δ, ppm): 7.60 (s), 2.15 (bread shape), and 0.40; obviously, these results are explained easily.

Analysis of the Copolymer with Wave Spectra

We have chosen PMVP-40, giving ^{1}H-NMR spectrum and shown in Figure 3. From Figure 3, we find that the chemical shifts (δ, ppm) are in (0.04, Si—CH$_3$), (7.35, 7.60, ph—H), (5.85, Si—CH=CH$_2$). In order to compare them, the ^{1}H-NMR spectrum of P$_4$ was also made and is presented in Figure 4. Obviously, the chemical shifts of the protons of phenyl groups in Figures 3 and 4 are different.

It is turned out that the P$_4$ added took part in the polymerization of PMVP-40. Then, we have calculated the ratio of ph$_2$SiO chain weight to $(\text{CH}_3)_2\text{SiO}$ chain weight as 0.42, which is closed with

Table II Grading Results for PMVP-40

Grade No.	Weight Fraction (W_f)	Integral Weight Fraction (I_f)	Intrinsic Viscosity [η] (mL/g)
5	0.1117	0.0558	44.7
4	0.1077	0.1656	66.8
3	0.1635	0.3012	91.5
2	0.1669	0.4664	125.5
1	0.4502	0.7749	143.8

the value (0.4) of the added P_4 to D_4. In order to have a better characterization of the copolymer, the IR spectra of PMP-40 and PDMS were all recorded and shown in Figure 5. From Figure 5, we can find that 2962, 2904 cm^{-1} ($-CH_2-H$), 1412, 1261 cm^{-1} ($Si-CH_3$), and 1094, 1020 cm^{-1} (SiOSi) exist in the two IR spectra of DMP-40 and PDMS; but 3072 cm^{-1} (ph$-H$), 1430, 1124 cm^{-1} (Si$-$ph), and 742 cm^{-1} (deformation vibration of benzene ring) exist only in the IR spectrum of DMP-40. The UV spectra of some copolymers are shown in Figure 6 (with the order of PMVP-5, PMVP-10, PMVP-20, and PMVP-40 appearing from the bottom to top). Figure 6 indicates that in the UV region all of the copolymers have the absorptive peaks at 238, 254, 264, and 271 nm. This is the same as the literature.[8] On the other hand, in this figure, the heights of the peaks increase with the increasing contents of the ph$_2$SiO chain elements.

Effect of the Initiator Concentration on Intrinsic Viscosity

According to the formulation of material of PMP-40 in Table I, but only changing the concentration of the initiator (PBDMOHB), the intrinsic viscosity of every product was determined and shown in Figure 7. From Figure 7, we can find that while the initiator is less than 0.19 wt % of the sum of P_4 and D_4, it is too little to initiate the copolymerization

of D_4 with P_4; and while the initiator is more than 0.25 wt % of the sum of P_4 and D_4, the amount of initiator is too much to lead to high molecular weight. Obviously, it is suitable that the amount of the initiator is between 0.19 and 0.25 wt % of the sum of D_4 and P_4.

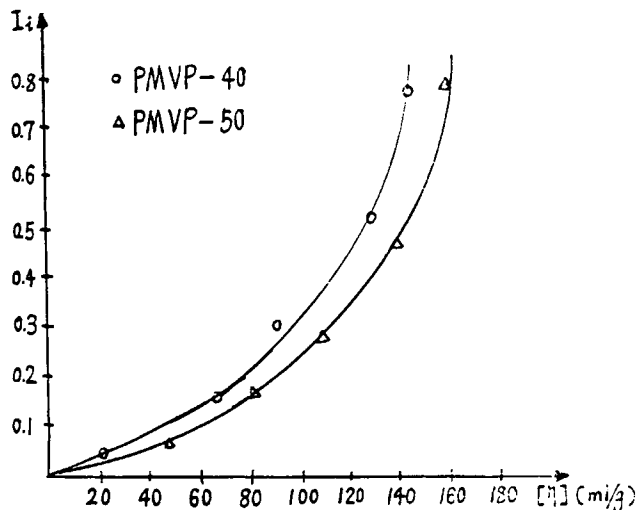## Effect of Polymerization Temperature on Product

Under the conditions outlined above, the results of D_4 polymerization have shown that the suitable temperature forming the polydimethylsiloxane segment is at 150–160°C. However, the sequential polymerization of P_4 is not carried out at so low of a temperature. While we raised the temperature up to 220°C, the copolymer was led to be insoluble and unfused material. Therefore, we have chosen 190°C for the sequential polymerization of P_4; as a result, the linear block copolymer has been attained.

Effect of Polymerization Time on Intrinsic Viscosity

According to the formula ratio and the polymerization conditions of PMP-40 in Table I, we made the block copolymerization of D_4 with P_4, got out some samples in turn every half an hour, and dried the samples with the method mentioned above. The intrinsic viscosities of the samples obtained were measured, and the relation of the intrinsic viscosities

Table III The Grading Results for PMVP-50

Grade No.	Weight Fraction (W_f)	Integral Weight Fraction (I_f)	Intrinsic Viscosity [η] (mL/g)
5	0.0856	0.0428	56.2
4	0.1149	0.1430	71.0
3	0.1578	0.2794	111.6
2	0.2104	0.4634	140.3
1	0.4313	0.7842	160.0

Figure 9 The integral distribution curves of PMVP-40 and PMVP-50.

with the polymerization time is shown in Figure 8. From Figure 8, we can find that there is much change in intrinsic viscosity along with the polymerization time between 0.5-2 h (f-a) and between 3-5 h (c-d). However, there is little change in intrinsic viscosity along with the polymerization time between 2-3 h (a-c) and between 5-7 h (d-e). Obviously, the former is due to the sufficiency of monomers for chain growth, and the latter is due to the lack of monomers for chain growth. The curve in Figure 8 (c-b) was obtained at 220°C; and the last resulting product is insoluble and unfused material.

Effect of Promotor on Polymerization

Since the PBDMOHB can dissolve in THF, we have attempted to perform the polymerization of D_4 in THF without DMF according to the polymerization conditions of PDMS in Table I but failed. However, V_4 succeeded. On the other hand, we also attempted to perform the polymerization of P_4 using THF or DMF as promotors so as to preparing the MPM triblock copolymer, but the polymerization of P_4 was not carried out, even at 220°C. The above results illustrate that THF only can promote the polymerization of V_4, and THF or DMF cannot promote that of independent P_4.

Molecular Weight Distribution

Progressive precipitation separation was used for studying the molecular weight distribution. The samples, PMVP-40 and PMVP-50, were treated with tolune and methanol according to the literature.[9] The results obtained are shown in Tables II and III and Figure 9. From those above, we find that the molecular weight distribution is still comparatively wide. This may be caused by one of the reasons that D_4 and P_4 are not quite as easy to polymerize. We have calculated the weight fraction of ph_2SiO chain according to ^1HNMR spectrum of every grade; their results are shown in Table IV.

Obviously, the theoretical weight fraction of ph_2SiO for PMVP-40 and PMVP-50 should be 0.2857 and 0.3333, respectively, according to the materials added. However, from Table IV, we find that the weight fractions from Nos. 1 to 3 are decreasing in turn in both PMVP-40 and PMVP-50. It is reasonable that P_4 was added later; thus, the heavier the molecular weight, the higher the weight fraction. On the other hand, the fractions of Nos. 4 and 5 are higher than Nos. 1-3. We can presume that the more $(CH_3)_2SiO$ chains that the components of low molecular weight contain in the samples, the more easily they are removed when the samples are distilled under reduced pressure and dried in a dryer; while the more ph_2SiO chains the components of the low molecular weight contain in the samples, the more difficult they are to be removed in the same conditions.

Table IV   The Weight Fraction of ph_2SiO in Every Grade for PMVP-40 and PMVP-50

PMVP-40		PMVP-50	
Grade No.	Weight Fraction of ph_2SiO	Grade No.	Weight Fraction of pH_2SiO
5	0.296	5	0.364
4	0.267	4	0.337
3	0.211	3	0.301
2	0.220	2	0.313
1	0.231	1	0.322

Some Results of the DSC Analysis

The DSC analysis of some products showed that, for example, PDMS only exists as an exothermic peak at 360–490°C and PMVP-40 not only exists as an exothermic peak at 320–380°C but also as an endothermic peak around 475°C, which is believed to be the melting transition of PDPS.

CONCLUSION

A new initiator, p-bis(dimethyllithiioxysilyl)-benzene, has been found to be efficient for the ring opening of cyclotetrasiloxanes to obtain PMP or PMVP triblock copolymer. In this process, the presence of DMF is necessary and very efficient. The physical states of the various copolymers obtained under the same conditions varied with the ph$_2$SiO contents of the copolymers. In an ordinary way, when the ph$_2$SiO content of the copolymer was less than 10 wt %, the sample was a viscous liquid. When it was above 10 wt %, the sample became a sticky grease. When it was as much as or more than 40 wt %, the sample was a soft, rubbery material. Since the PMP gum being obtained only possesses the properties of the soft rubber and still cannot be used as a thermoplastic elastomer, we put great emphasis on the synthesis of PMVP. Further investigation is currently underway.

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