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Acid and base catalyzed ring-opening polymerization of 2,2,4,4,6,6-hexamethyl-8,8-diphenylcyclotetrasiloxane

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Abstract

Triflic acid and P_4-*t*-Bu superbase both catalyze the ring-opening polymerization (ROP) of 2,2,4,4,6,6-hexamethyl-8,8-diphenylcyclotetrasiloxane (**I**) to yield a mixture of linear copoly(dimethylsiloxane/diphenylsiloxane) (3:1 mole ratio), low molecular weight oligomer and cyclic siloxanes. The molecular weight distribution, microstructure and thermal properties of the copolymers have been determined. The composition of the low molecular weight fractions have been analyzed. Triflic acid catalyzed ROP of **I** yields a copolymer whose microstructure can be accounted for by chemoselective ring opening of a single silyloxonium ion intermediate. In addition, 40% of **I** is recovered. On the other hand, P_4-*t*-Bu superbase catalyzed ROP of **I** yields a copolymer whose microstructure is random. The low molecular weight fraction, in this case, is made up of oligomer and a number of cyclotetra-, cyclopenta- and cyclohexasiloxanes.

Keywords: Copoly(dimethylsiloxane/diphenylsiloxane); Microstructure; Ring-opening polymerization

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1. Introduction

Polysiloxanes are important inorganic/organic materials. Polydimethylsiloxane (PDMS) is commercially the most significant siloxane material. However, for some applications the properties of PDMS are short of those desired [1]. As a result, copolymers comprised of dimethylsiloxane and other siloxane units, e.g. vinylmethylsiloxane, phenylmethylsiloxane, divinylsiloxane, diphenylsiloxane, methylhydridosiloxane, or 3′,3′,3′-trifluoropropylmethylsiloxane have been prepared to achieve the properties desired. Copolymer properties may depend on both the molar ratio and sequence of the monomer units. Random, alternating and block copolymers prepared from the same monomers can have distinct properties [2].

We have been interested in the preparation, properties and chemical modification of copolysiloxane that have regular microstructures [3,4]. Kinetically controlled living anionic ring-opening polymerization (ROP) of substituted cyclotrisiloxane has been shown, in favorable cases, to yield narrow molecular weight distribution copolymers with regular microstructures. For this to occur two conditions must be satisfied, anionic ROP must occur regio-selectively and equilibration by redistribution or backbiting must be slow relative to propagation. Since the polymerization is living, quenching the reaction with a suitable functionalized chlorosilane can lead to narrow molecular weight distribution α,ω-functionalized copolysiloxanes.

Acid catalyzed ROP of substituted cyclotrisiloxanes usually yields less regular copolysiloxanes. For example, the triflic acid catalyzed ROP of 2,2,4,4-tetramethyl-6,6-diphenylcyclotrisiloxane (**II**) occurs in a chemoselective manner [5,6]. Under these conditions, randomization processes such as backbiting and intermolecular exchange do not occur. Nevertheless, M_w/M_n is found to be two. The presence of two reactive silyloxonium intermediates in the reaction has been proposed to account for these results obtained (Fig. 1).

From a practical standpoint, ROP of octamethylcyclotetrasiloxane (D_4) is of major industrial importance while that of hexamethylcyclotrisiloxane (D_3) is not. This is usually accomplished by acid catalysis, since D_4 is much less reactive than D_3 under anionic ROP conditions [7–9]. Hydroxide catalyzed ROP of D_4 is facilitated by dissociating solvents and large cations [10]. In this regard, P_4-*t*-Bu,

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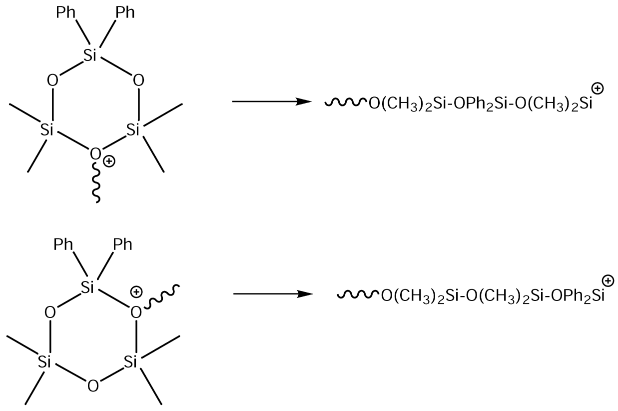

Fig. 1. Chemoselective triflic acid catalyzed ROP of **II**.

superbase has been recently shown to permit rapid anionic ROP of D_4 under relatively mild conditions [11–15]. Nevertheless, no work has been reported on the P_4-*t*-Bu catalyzed anionic ROP of substituted D_4 derivatives.

Electronically, phenyl and vinyl groups are both inductively electron-withdrawing. The Taft parameters $\Sigma\sigma^*$ for two phenyl groups are +1.2 and +0.72 for two propenyl groups [16]. These suggest that a diphenyl or divinyl substituted silyl center should be more electropositive and hence more susceptible to nucleophilic attack than a dimethylsilyl center. Consistent with this prediction, we have previously reported the regioselective preparation of highly regular copoly(2,2,4,4-tetramethyl-6,6-divinyltrisiloxane) by low temperature anionic ROP of 2,2,4,4-tetramethyl-6,6-divinylcyclo-trisiloxane catalyzed by dilithiodiphenylsilanediolate in THF [4].

Despite the similarities between phenyl and vinyl groups, anionic ROP of **II** leads to copoly(dimethylsiloxane/diphenylsiloxane) (2:1 mole ratio) with a less regular microstructure. This has been accounted for by a chemoselective anionic polymerization in which three reactive propagating silanolate triads: $\sim Ph_2SiO{-}Me_2SiO{-}Me_2SiO^-$, $\sim Me_2SiO{-}Me_2SiO{-}Ph_2SiO^-$, and $\sim Me_2SiO{-}Ph_2SiO{-}Me_2SiO^-$ are formed. Nucleophilic attack by each of these can occur on either the dimethylsilyl or the diphenylsilyl centers of **II**. Neither scrambling nor equilibration occur under these conditions [17].

In this paper, we report the properties and microstructures of the copolysiloxanes formed by both triflic acid and P_4-*t*-Bu superbase catalyzed ROP of the substituted cyclotetrasiloxane: 2,2,4,4,6,6-hexamethyl-8,8-diphenylcyclotetrasiloxane (**I**). This 8,8-disubstituted cyclotetrasiloxane derivative was selected to avoid stereochemical problems.

2. Experimental

2.1. Spectroscopic analysis

^1H, ^{13}C, and ^{29}Si NMR spectra of 5% (w/v) $CDCl_3$ solutions were obtained on a Bruker AMX-500 MHz spectrometer. ^{13}C NMR spectra were run with broad band proton decoupling. ^1H and ^{13}C spectra were internally referenced to TMS and residual $CHCl_3$. A heteronuclear gated decoupling pulse sequence (NONOE) with a 60 s delay was used to acquire ^{29}Si NMR spectra. These were referenced to internal TMS. IR spectra of neat liquid films on NaCl plates were recorded on a Perkin–Elmer Spectrum 2000 FT-IR spectrometer.

2.2. Gel permeation chromatography

GPC analysis of the molecular weight distribution of the polymers was performed on a Waters system equipped with a 501 refractive index detector. Two 7.8 mm × 300 mm Styragel HT 6E and HMW 6E columns in series were used for the analysis. The eluting solvent was toluene at a flow rate of 0.6 ml/min. Toluene was utilized since the refractive index of THF and our siloxane polymers are quite close. The retention times were calibrated against known monodisperse polystyrene standards: 929,000; 114,200; 13,700; 794 g/mol.

2.3. Thermogravimetric analysis

TGA of the copolymers was carried out on a Shimadzu TGA-50 instrument at a flow rate of 40 cm^3 of nitrogen or air per minute. The temperature was increased at a rate of 5 °C/min from 25 to 800 °C.

2.4. Differential scanning calorimetry

Glass transition temperatures (T_gs) of the polymers were determined on a Perkin–Elmer DSC-7 or on a Shimadzu DSC-50. The differential scanning calorimeters were calibrated against the heat of transition (−87.06 °C) and the melting point of cyclohexane (6.54 °C) [18], as well as from the T_g of PDMS (−125 °C) [19]. Samples were equilibrated at −150 °C for 30 min. The temperature was then increased from −150 to 50 °C at a rate of 10 °C/min.

2.5. Mass spectrometry

Low resolution mass spectra were obtained by GC/MS on a Hewlett–Packard 5890 series II GC equipped with a Hewlett–Packard 5971 series mass selective detector and a 30 m DB5 capillary column.

High resolution mass spectra were acquired at the University of California at Riverside Mass Spectroscopy Facility on a VG ZAB2SE instrument. Exact masses were calibrated against known mass peaks of perfluorokerosene.

2.6. Materials

Dimethyldichlorosilane, diphenyldichlorosilane, diphenylsilanediol, and 1,1,3,3-tetramethyldisiloxane were obtained from Gelest. Pd/C (5%) and phosphazene base

P_4-*t*-Bu (1.0 M in *n*-hexane) were purchased from Fluka. Wilkinson's catalyst $(Ph_3P)_3RhH_2Cl$ was bought from Alfa. THF, triethylamine, and diethyl ether were obtained from Aldrich. Triethylamine was dried over NaOH pellets. Diethyl ether was dried over activated 3 Å molecular sieves. 1,1,3,3-Tetramethyldisiloxane was purified by distillation. Other chemicals were used as obtained.

2.7. Synthetic procedures

All reactions were run in flame dried glassware equipped with a Teflon covered magnetic stir bar under argon.

2.7.1. 1,1,3,3,5,5-Hexamethyltrisiloxane (***III***) [20]

1,1,3,3-Tetramethyldisiloxane (281 g, 2.1 mol) and $FeCl_3\cdot 6H_2O$ (1 g, 3.7 mmol) were placed in a 500 ml two-neck round bottom flask equipped with a rubber septum, a pressure equalizing addition funnel. HCl gas was bubbled through the solution while dimethyldichlorosilane (127 g, 1 mol) was added dropwise from an addition funnel over 3 h. The reaction was stirred for 3 h at room temperature (rt). The mixture was then distilled through a 10 cm vacuum jacketed distillation column packed with glass saddles. A fraction, bp 127 °C/760 mm, 80 g, 38% yield, was obtained. ^{1}H NMR δ : 0.065 (s, 6H), 0.191 (d, 12H, $J = 2.5$ Hz), 4.70 (m, 2H). ^{13}C NMR δ : 0.64. ^{29}Si NMR δ : −17.56 (s, 1Si), − 6.74 (d, 2Si, $J_{\text{Si-H}} = 2$ Hz). IR ν : 2128 (Si–H), and 1057 (Si–O) cm^{-1}. GC/MS *m/e* (relative abundance): 207 (18%) $(M - 1)^+$, 193 (100%) $(M - 15)^+$, 133 (25%), 119 (16%), 103 (10%).

2.7.2. 1,5-Dihydroxyhexamethyltrisiloxane (***IV***) [21]

Deionized water (8.0 g, 0.44 mol), THF (50 ml) and Pd/C (50 mg) were placed in a 250 ml Erlenmeyer flask [22]. The flask was placed in an ice bath, while **III** (30 g, 0.144 mol) was added via a 50 ml syringe slowly over 2 h. The solution was allowed to stir at rt until no more gas bubbles evolved. The solution was then dried over anhydrous $MgSO_4$, filtered and the volatile solvents removed by evaporation under reduced pressure. In this way, 36 g, 99% yield was obtained. ^{1}H NMR δ : 0.095 (s, 6H), 0.127 (s, 12H), 5.25 (m, 2H). ^{13}C NMR δ : 0.375, 0.89. ^{29}Si NMR δ : −19.9 (s, 1Si), − 10.8 (s, 2Si). IR ν : 3275 (SiO–H), 2964, 1266 (Si–CH_3), 1051 (Si–O) cm^{-1}.

2.7.3. 2,2,4,4,6,6-Hexamethyl-8,8-diphenylcyclotetrasiloxane (***I***) [23]

Diethyl ether (100 ml) and triethylamine (7.3 g, 72 mmol) were placed in a 250 ml three-neck round bottom flask equipped with two pressure equalizing addition funnels and a Tru-boree stirrer equipped with a Teflon paddle which was connected to a variable speed stirrer motor. Diethyl ether (15 ml) and **IV** (5.76 g, 24 mmol) were placed in one addition funnel. Diethyl ether (15 ml) and diphenyldichlorosilane (6.0 g, 24 mmol) were placed in the other. Both solutions were added dropwise over 1 h. The reaction was allowed to stir for 3 h at rt. The reaction mixture was then washed with brine and water until it was neutral. The solution was dried over anhydrous $MgSO_4$, filtered and the volatile solvents removed by evaporation under reduced pressure. The solution was then distilled through a 5 cm vacuum jacketed distillation column which was packed with glass saddles. A fraction, bp 112 °C/0.2 mm, 3.75 g, 37% yield, was obtained. ^{1}H NMR δ : 0.22 (s, 6H), 0.28 (s,12H), 7.45–7.53 (br m, 6H), 7.77–7.80 (br m, 4H). ^{13}C NMR δ : 0.85, 0.94, 127.79, 129.99, 134.22, 136.08. ^{29}Si NMR δ : −46.42, − 18.52, − 17.53. IR ν : 2963, 1593 (C=C), 1073, (Si–O) cm^{-1}. GC/MS *m/e* (rel. abundance): 405 (100%) $(M - 15)^+$, 342 (13%), 326 (47%).

2.7.4. 2,2,4,4,6,6-Hexamethyl-8,8-diphenylcyclotetrasiloxane (***I***)

Diphenylsilanediol (3.74 g, 17.3 mmol), **III** (3.6 g, 17.3 mmol), and 5 ml of THF were placed in a 25 ml round bottom flask. To this mixture was added 20 mg of $(Ph_3P)_3RhH_2Cl$. The mixture was stirred at 60 °C for 12 h. THF was removed by evaporation under reduced pressure. The residue was taken up in $CHCl_3$. This solution was passed through a short silica gel column to remove the catalyst. $CHCl_3$ was removed by evaporation under reduced pressure. The residue was distilled through a 10 cm vacuum jacketed Vigreux column. A fraction, bp 105 °C/0.1 mm, 1.9 g, 26% yield, was collected. It had spectral properties in agreement with those reported above.

2.7.5. Anionic polymerization of ***I***. Copoly(dimethylsiloxane/diphenylsiloxane) (3:1 mole ratio)

I (0.3 g, 0.71 mmol), P_4-*t*-Bu (1 μl) and 0.4 ml of THF were placed in a 15 ml Ace pressure tube. Argon was bubbled through the solution for 1 min. The tube was sealed with an O-ring and a threaded Teflon cap. The polymerization was allowed to proceed at 80 °C for 20 min. Trimethylchlorosilane (10 μl) and triethylamine (10 μl) were added sequentially to quench the reaction. The copolymer was precipitated three times from diethyl ether/methanol. In this way, 0.23 g, 77% yield of copolymer with $M_w/M_n = 130,800/79,000$ and $T_g = -67.4$ °C was obtained. ^{1}H NMR δ : 0.05–0.25 (m, 18H), 7.31–7.60 (br m, 6H), 7.75–7.80 (br m, 4H). ^{13}C NMR δ : 0.83, 0.98, 1.06, 1.18, 1.19, 1.34, 127.53, 129.72, 129.77, 134.24, 134.37. ^{29}Si NMR δ : −48.46, −48.25, −47.64, −47.43, −21.85, −21.65, −21.46, −20.74, −20.61, −20.49, −20.37, − 19.23, − 19.01. IR ν : 2962, 1593, 1488, 1429, 1260, 1073 cm^{-1}.

2.7.6. Analysis of methanol soluble material

The capital letters **D** and **P** are used as abbreviations for $(CH_3)_2SiO$ and $(C_6H_5)_2SiO$ units, respectively. After evaporation of methanol and THF, 0.07 g, ~23% yield of material was obtained which was analyzed by a combination of GPC and GC/MS. A 3% yield of

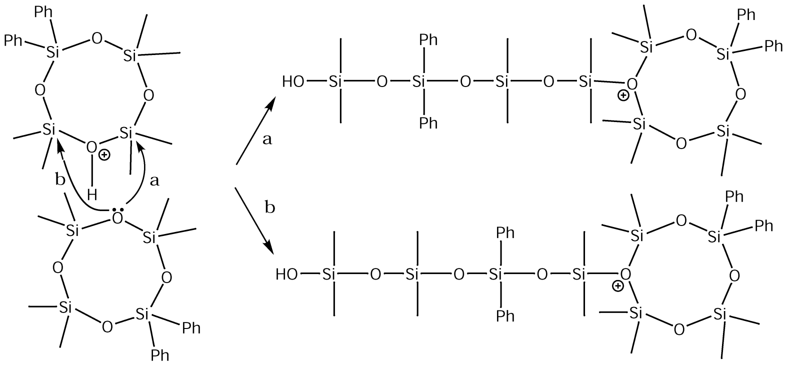

Fig. 2. Triflic acid catalyzed chemoselective ROP of **I**.

oligomer, $M_w/M_n = 3800/2700$ was found. The remainder was comprised of D_4 (4.4%), decamethylcyclopentasiloxane (D_5) (3.8%), dodecamethylcyclohexasiloxane (D_6) (0.6%), D_3P (**I**) (63.4%), 2,2,4,4,6,6,8,8-octamethyl-10,10-diphenylcyclopentasiloxane (D_4P) (17.7%) [24], 2,2,4,4-tetramethyl-6,6,8,8-tetraphenylcyclotetrasiloxane (D_2P_2) (5.9%) [25], 2,2,4,4,6,6-hexamethyl-8,8,10,10-tetraphenylcyclopentasiloxane (D_3P_2) (3.2%) [24], and 2,2,4,4,6,6,8,8,10,10-decamethyl-12,12-diphenylcyclohexasiloxane (D_5P) (1.0%) [24]. These were identified from their $(M - 15)^+$ peaks in the GC/MS.

*2.7.7. Cationic polymerization of **I**. Copoly(dimethylsiloxane/diphenylsiloxane) (3:1 mole ratio)*

I (0.5 g, 1.19 mmol) was placed in a test tube that was sealed with a rubber septum. Dichloromethane (100 μl) and triflic acid (3 μl, 0.034 mmol) was injected into the test tube. The polymerization was allowed to proceed for 30 min. Hexamethyldi-silazane (25 μl, 0.12 mmol) was added to quench the reaction. After 1 h, the polymer was precipitated three times from a mixture of diethyl ether and methanol and then dried under vacuum. In this way, 0.25 g, 50% yield of copolymer with $M_w/M_n = 23,500/12,230$, and $T_g = -65$ °C was obtained. ^{1}H NMR δ: 0.05 (s), 0.09 (s), 0.10 (s), 0.11 (s), 0.13 (s), 0.15 (s), 0.16 (s), 0.18 (s) all integrate to 18H, 7.36–7.45 (br m, 6H), 7.71 (br s, 4H). ^{13}C NMR δ: 0.87, 0.95, 1.08, 1.17, 1.18, 127.53, 129.70, 134.21, 135.98. ^{29}Si NMR δ: −20.47, −20.71, −21.42, −21.61, −21.81, −48.18, −48.35, −48.38, −48.40. IR ν: 3070, 3011, 2963, 2905, 1429, 1261, 1124, 1095, 1025, 844, 803, 705 cm^{-1}.

2.7.8. Analysis of methanol soluble material

After removal of methanol and THF, 0.20 g, 40% yield of unreacted **I** was obtained.

3. Results

*3.1. Synthesis of **I***

2,2,4,4,6,6-Hexamethyl-8,8-diphenylcyclotetrasiloxane (**I**) was prepared in 37% yield by condensation of **IV** with diphenyldichlorosilane in the presence of triethylamine, or by a Wilkinson's catalyst dehydrocoupling reaction of **III** with diphenylsilanediol in 26% yield [26].

*3.2. Polymerization of **I***

Acid or base catalyzed polymerization of **I** both yields a mixture of copolymer and soluble low molecular weight material. The ratio of **D** units and **P** units in the copolymers were identical to that of the starting material **I** (3:1) by ^{1}H NMR integration. In the case of acid catalyzed polymerization of **I** the low molecular weight materials is recovered **I**. On the other hand, in the case of base catalyzed polymerization of **I**, the low molecular weight material is a mixture of soluble oligomers and a variety of cyclotetra-, cyclopenta-, and cyclohexasiloxane made up of **D** and **P** units. The microstructures of these copolymers have been determined by ^{29}Si NMR.

4. Discussion

*4.1. Microstructure analysis by ^{29}Si NMR spectroscopy of triflic acid catalyzed ROP of **I***

The ^{29}Si NMR spectrum of copolymer obtained by the triflic acid catalyzed ROP of **I** can be largely accounted for by chemoselective ring opening of a silyloxonium ion intermediate (Figs 2 and 3). Apparently a silyloxonium ion which has a dimethylsilyl group on each side of the positively charged oxygen is significantly more stable than one in which a diphenylsilyl group is on one side and a dimethylsilyl group is on the other. The inductive electron-withdrawing effect of a phenyl group previously mentioned may make the oxygen between a dimethylsilyl and a diphenylsilyl groups less basic than an oxygen between two dimethylsilyl groups. This more stable silyloxonium ion can open in two ways by nucleophilic attack on the dimethylsilyl centers of the oxonium ion by one of the more basic oxygens of another molecules of **I**. Further growth in this manner, leads to four dimethylsilyl (D) centered pentads

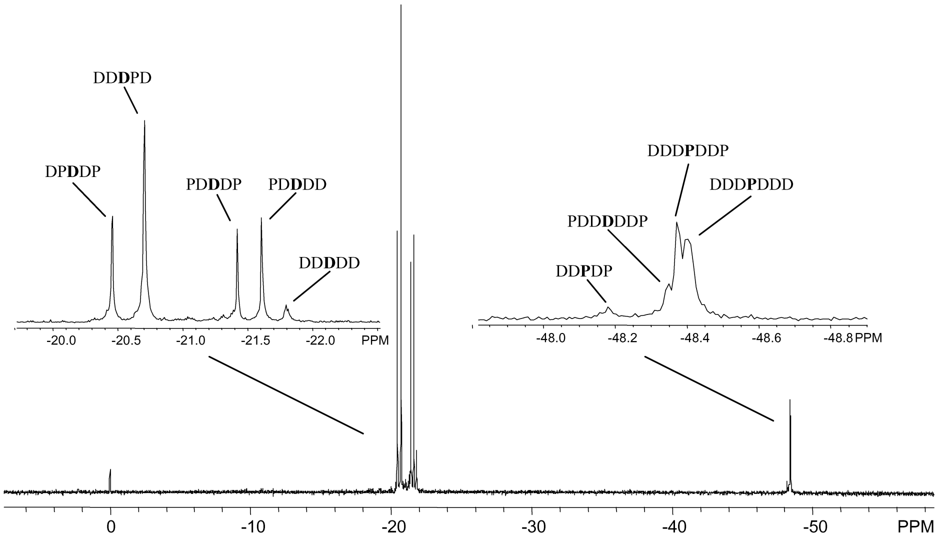

Fig. 3. ^{29}Si NMR of copolymer produced by triflic acid catalyzed ROP of **I**.

[PD**D**DD, PD**D**DP, DD**D**PD, and DP**D**DP] and a single diphenylsilyl (P) centered pentad DD**P**DD. Statistical analysis predicts that these D centered pentads will be formed in a 1:1:3:1 ratio. In fact, the pentads, PD**D**DD at −21.61 ppm, PD**D**DP at −21.42 ppm, DD**D**PD at −20.71 ppm and finally DP**D**DP at −20.47 ppm, are found in a ratio of 1.1:1.0:2.6:1.4. The P centered pentad, DD**P**DD, at −48.38 ppm is further split to a triplet due to sensitivity of the central P unit to heptads. The signal at −48.40 ppm is due to a DDD**P**DDD heptad, while that at −48.38 ppm results from a DDD**P**DDP heptad and finally at signal at −48.35 ppm is due to the PDD**P**DDP heptad. Statistical analysis based on the probability of D and P units, predicts a 9:12:1 intensity ratios for these signals. Unfortunately, the three signals are not sufficiently resolved to permit accurate integration. It is not obvious why the ^{29}Si NMR chemical shifts of the **P** centered silicon units are sensitive to heptads, while the **D** centered silicon units are only sensitive to pentads.

Small peaks at −21.81 ppm due to a DDDDD pentad and at −48.18 ppm due to DDPDP pentad cannot be accounted for by this model. Possibly a second silyloxonium ion is formed in which the positively charged oxygen is between the diphenylsilyl center and a dimethylsilyl center of **I**. This could open chemoselectively to form ~PDDD and ~DDDP propagating species. Reaction of the former with a molecule of **I** could form DDDDD pentads. Consistent with this analysis, five signals for methyl carbons are observed in the ^{13}C NMR spectrum.

Thus, the acid catalyzed ring opening of **I** is similar to that of **II**, except that **I** has two basic oxygens which are substituted on both sides by dimethylsilyl groups whereas **II** has only one.

4.2. Analysis of methanol soluble low molecular weight material

Consistent with a chemoselective polymerization process, the only low molecular weight materials recovered was unreacted **I**.

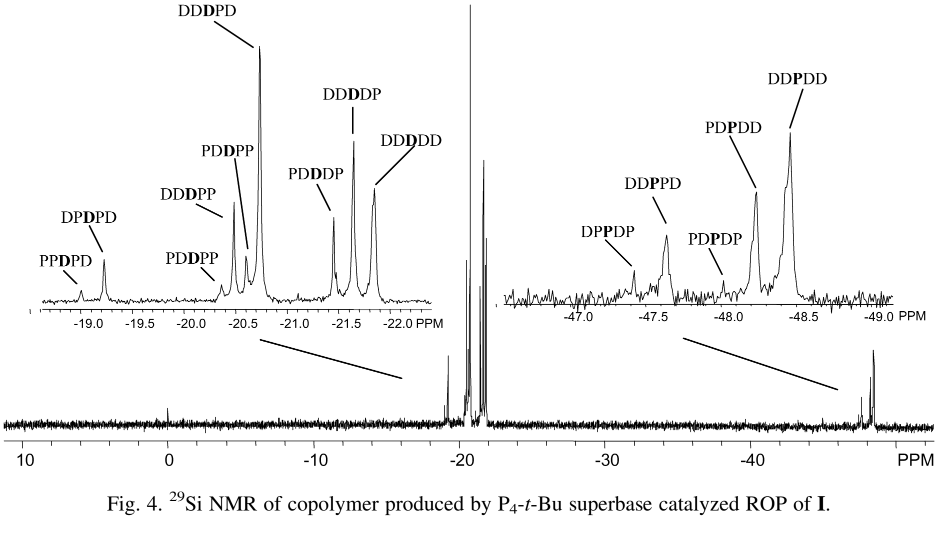

Fig. 4. ^{29}Si NMR of copolymer produced by P_4-*t*-Bu superbase catalyzed ROP of **I**.

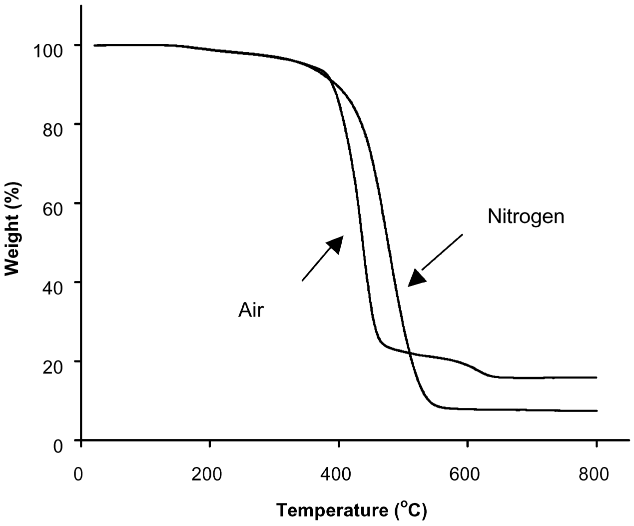

Fig. 5. TGA of base catalyzed copolymer.

4.3. Microstructure analysis by ^{29}Si NMR spectroscopy of P_4-*t*-Bu catalyzed ROP of *I*

On the other hand, the microstructure of the copolymer obtained from P_4-*t*-Bu superbase catalyzed ROP of **I** is largely random based on analysis of the ^{29}Si NMR spectrum. Given a copolymer made up of D and P units in a 3:1 ratio, three groups of D centered pentads are expected. The chemical shift of these is primarily dependent on the central triad structure. Thus there are three of D centered triads DDD, DDP, and PDP. The first (DDD) is further split to three D centered pentads: DD**D**DD, DD**D**DP, PD**D**DP in a predicted intensity ratio of 81:54:9. The second (DDP) is split to four pentads: DD**D**PD, PD**D**PD, DD**D**PP, and PD**D**PP with an expected intensity ratio of 54:18:18:6. Finally the PDP triad is split to three pentads: DP**D**PD, PP**D**PD, and PP**D**PP with an anticipated intensity ratio of 9:6:1. Of the ten peaks predicted in the D region, nine are, in fact, observed and have been assigned (Fig. 4). Only the least probable peak due to the PP**D**PP pentad is not observed.

While the number of peaks observed is in close agreement with a random model, the intensities of some of these peaks are not in good agreement with the random statistical calculation. In particular, the peak assigned to DD**D**PD is too intense. If the electron-withdrawing phenyl groups make the diphenyl substituted silicon more electropositive it should favor nucleophilic attack at this site. Ring opening would then lead to a $\sim Ph_2Si{-}OMe_2Si{-}OMe_2Si{-}OMe_2Si{-}O^-$ reactive silanolate. Attack by this reactive species at the diphenyl substituted silyl center of a second molecule of **I** will lead to ~P*DDDPD*DD$^-$ which contains the DD**D**PD pentad among others.

Similarly, the ^{29}Si NMR chemical shifts of the silicon atoms substituted by two phenyl groups can be analyzed based on P centered triads which are further split to pentads. Potentially, there are three types of P centered triads: DPD, PPD, and PPP. The DPD triad will be split to three pentads, the PPD triad will be split to four pentads and finally the PPP triad will be split to three pentads. Statistically, these are expected to be of low probability. The DPD triad is split to DD**P**DD, PD**P**DD, and PD**P**DP pentads. The intensity of these is predicted to be 81:54:9. The DPP triad is split to DD**P**PD, PD**P**PD, DD**P**PP, and PD**P**PP pentads, which are expected in an intensity ratio of 54:18:18:3. No peaks due to the PPP triad, which is least probable, were detected. In fact, only the five peaks assigned to DDPDD, PDPDD, PDPDP, DDPPD and DPPDD were observed (Fig. 4).

4.4. Analysis of low molecular weight material

Consistent with a reactive base catalyzed randomization process, the methanol soluble low molecular weight fraction was found to contain a variety of cyclotetrasiloxanes (D_4, D_3P, D_2P_2), cyclopentasiloxanes (D_5, D_4P, D_3P_2) and cyclohexasiloxanes (D_6 and D_5P) in addition to a small amount of low molecular weight oligomers. Over half of this material is the recovered starting material **I** (D_3P).

The low molecular weight oligomers were analyzed by GPC while, the cyclosiloxane monomers were analyzed by GC/MS. The mass of these compounds was determined from their $(M-15)^+$. Organosilicon compounds are well known to form siliconium ions in the mass spectrometer by loss of a methyl group from a silyl center [27,28]. The number of silicon atoms in these ions was determined from the ratio of $(M-15)^+$ to $(M-15+1)^+$ to $(M-15+2)^+$ cluster of ions. These are due to the presence of naturally occurring ^{28}Si, ^{29}Si and ^{30}Si isotopes [29].

4.5. Glass transition temperature

The T_gs for the copolymers prepared by acid or base catalysis, −65 and −67 °C, respectively, are reasonable since the T_g of copoly(dimethylsiloxane/diphenylsiloxane) (70:30 mol%) has been previously reported to be −64 °C [30]. The properties of the copolymers may depend on both the molar ratio and sequence (microstructure) of the respective monomer units [2]. In our copolymers, the molar ratio of D and P is identical by ^{1}H NMR integration. Difference in T_g, while small, may be due to differences in the copolymers molecular weights and/or the differences in copolymer microstructure.

4.6. Thermal stability by TGA

The thermal stability of copolymer produced by P_4-*t*-Bu superbase catalyzed ROP is quite high. Even in air, this copolymer is stable to 350 °C. It is even more stable, by almost 50 °C, to thermal decomposition in nitrogen. In nitrogen, the copolymer undergoes catastrophic decomposition. Less than 10% residue is found above 600 °C. In air,

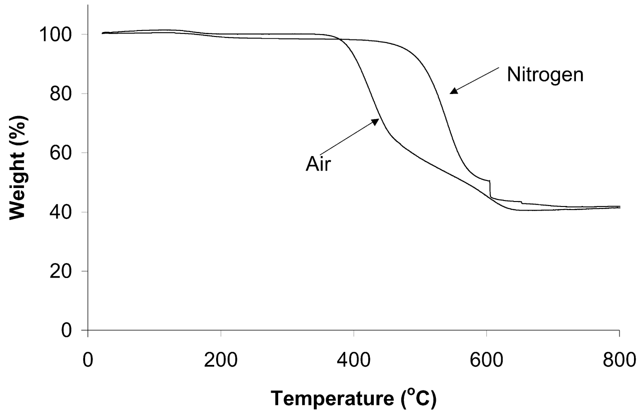

Fig. 6. TGA of acid catalyzed copolymer.

a residue equal to 18% of the initial sample weight is found (Fig. 5).

The thermal stability of copolymer produced by triflic acid catalyzed ROP is also quite high. In nitrogen, this copolymer undergoes a small weight lost (2%) at ~150 °C followed by major decomposition at ~400 °C. A 45% residue is found above 700 °C. In air, this copolymer is stable to ~330 °C. A residue of ~40% is found above 670 °C (Fig. 6).

Although the thermal stability of both copolymers is similar, a much higher char yield (~40%) is found from decomposition of the acid catalyzed copolymer compared to the base catalyzed copolymer (~15%). This difference is probably not due to differences in copolymer molecular weight since the molecular weight of the acid catalyzed copolymer is lower than that of the base catalyzed copolymer. It also seems to us improbable that this difference in thermal stability could result from differences in copolymer microstructure.

Answers to these and other questions must await further studies on these copolymers.

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