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Polymerization by Hydrosilation. 2. Preparation and Characterization of High Molecular Weight Poly[(1,1,3,3-tetramethyldisiloxanyl)ethylene] from 1,3-Dihydridotetramethyldisiloxane and 1,3-Divinyltetramethyldisiloxane

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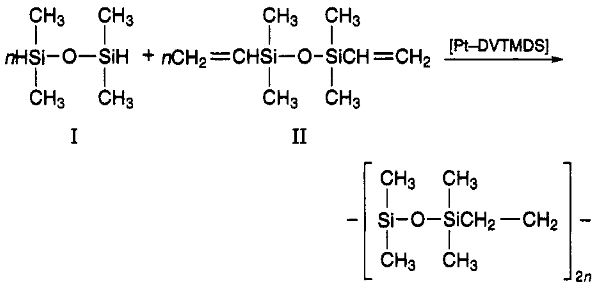
ABSTRACT: The effects of monomer concentration, catalyst concentration, and reaction temperature on the molecular weight of poly[(1,1,3,3-tetramethyldisiloxanyl)ethylene] (PTMDSE) resulting from the hydrosilation polymerization of 1,3-dihydridotetramethyldisiloxane (DHTMDS) and 1,3-divinyltetramethyldisiloxane (DVTMDS) catalyzed by platinum–1,3-divinyltetramethyldisiloxane complex [Pt–DVTMDS] were investigated. It was found that neat and solution polymerization at higher monomer concentrations, i.e., at or above 1.6 mol/L, catalyst concentration at or above 2×10^{-5} mol Pt/mol $CH{=}CH_2$, and reaction temperatures between 40 and 50°C, favor formation of high molecular weight polymer. Thus, PTMDSE with M_v above 30 000 could routinely be obtained, while the sample which had a M_v of 75 000 represents the highest molecular weight polycarbosiloxane reported until present. These results clearly confirm that [Pt–DVTMDS]-catalyzed hydrosilation polymerization can indeed yield truly high molecular weight products, which ranks this reaction with very few other successful addition step–growth polymerization reactions known. PTMDSE was characterized for its rheological as well as thermal and thermooxidative degradation behavior. It was found that this polymer shows increased inherent molecular flexibility and reduced thermal and thermooxidative stability compared to the closely related poly(dimethylsiloxane), which can be related to the stiffening and destabilizing effects of the C–C groups introduced in between the SiOSi main chain units.

Introduction

Recently, we described the first successful synthesis of a truly high molecular weight polycarbosiloxane, the poly[(1,1,3,3-tetramethyldisiloxanyl)ethylene] (PTMDSE, **III**), by a hydrosilation polymerization of 1,3-dihydridotetramethyldisiloxane (DHTMDS, **I**) and 1,3-divinyltetramethyldisiloxane (DVTMDS, **II**) in the presence of a platinum–1,3-divinyltetramethyldisiloxane, [Pt–DVTMDS], catalyst,[1] as shown by the following equation:



$$n\,H\overset{CH_3}{\underset{CH_3}{Si}}{-}O{-}\overset{CH_3}{\underset{CH_3}{Si}}H + n\,CH_2{=}CH\overset{CH_3}{\underset{CH_3}{Si}}{-}O{-}\overset{CH_3}{\underset{CH_3}{Si}}CH{=}CH_2 \xrightarrow{[Pt\text{–}DVTMDS]} -\!\left[\overset{CH_3}{\underset{CH_3}{Si}}{-}O{-}\overset{CH_3}{\underset{CH_3}{Si}}CH_2{-}CH_2\right]_{2n}\!- \quad (1)$$

I II III

The molecular weight of the polymer obtained was about 30 000, and not only was this value significantly higher than the corresponding values of other carbosiloxanes reported earlier in the literature (the molecular weights of which ranged from about 1000 to about 2000 only[2–4]) but it was also estimated to be above the critical molecular weight expected for this polymer compound.[1] Thus, this ranked this hydrosilation polymerization reaction with only few other step–growth addition polymerization reactions known for producing truly high molecular weight polymers, and it prompted our further interest in a more detailed investigation of this new synthetic pathway.

As a result, in this paper we report a study of the effect of monomer concentration, catalyst concentration, and reaction temperature on the molecular weight of the resulting polymer product, and we also describe some properties of the PTMDSE obtained. In a forthcoming paper, we will describe results from examination of the kinetics of this polymerization reaction.

Experimental Section

Materials. 1,3-Dihydridotetramethyldisiloxane (DHTMDS, I). This monomer was purchased from Fluka and used in polymerization reactions as received (T_b = 71–72 °C; $n_D{}^{20}$ = 1.370; $d_4{}^{20}$ = 0.757 g/cm^3). GC (Varian 3400; SUPWAX column, l = 60 m; injector, 250 °C; detector, 300 °C; program, 50 °C first 3 min followed by 6 °C/min up to 220 °C), 98.05%. FTIR (Perkin Elmer-1725X from 400 to 4000 cm^{-1}) film on KBr plate, cm^{-1}: 1072 (Si–O–Si), 1256 and 1419 (Si–CH_3), 2130 (Si–H), 2962 (C–H). ^1H NMR (Varian FT-80A) in $CDCl_3$ at 25 °C, relative to TMS, δ (ppm): 0.24 (s, CH_3), 4.70 (m, Si–H), integral ratio, 6.0.

1,3-Divinyltetramethyldisiloxane (DVTMDS, II). This monomer was purchased from ABCR GmbH & Co. and used in polymerization reactions as received (T_b = 139 °C; $n_D{}^{20}$ = 1.412; $d_4{}^{20}$ = 0.811 g/cm^3). GC (as above except for OV-1 column and program, 50 °C first 3 min followed by 15 °C/min up to 270 °C), 99.25%. FTIR (as above), cm^{-1}: 1056 (Si–O–Si), 1255 and 1407 (Si–CH_3), 1596 (C=C), 2960 and 3052 (C–H). ^1H NMR (as above), δ (ppm): 0.12 (s, CH_3), 5.50–6.25 (m, $CH{=}CH_2$).

Platinum–Divinyltetramethyldisiloxane (3–3.5 wt % Pt in Xylene) [Pt–DVTMDS]. The commercial product

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ABCR GmbH & Co. was diluted prior to use by DVTMDS to 0.3 wt % Pt.

Toluene. A p.a. grade solvent (Alkaloid) was used without further purification.

Methods. Vapor Pressure Osmometry (VPO). A Knauer vapor pressure osmometer was used. All measurements were performed in toluene at 45 °C with solutions which ranged in concentration from 2 to 20 g/dm^3.

Steady State Shear Viscometry. All measurements were performed using a Ferranti-Shirley cone and plate viscometer at 25 °C and within a shear rate range from 1.84 to 1840 s^{-1}. The plate diameter was 8.3 cm, the cone diameters were 3.5, 2, and 1 cm, respectively, and the cone angle was 0.0057 rad in all cases. Zero shear viscosities were determined by a standard extrapolation procedure of the low-shear, flat parts of the viscosity−shear rate double-logarithmic plots.

Intrinsic Viscosities. Intrinsic viscosities were determined in toluene at 30 ± 0.5 °C using an Ubbelohde dilution viscometer (l = 86.05 mm, D = 1.00 mm). Solution concentrations ranged from 0.2 to 2.0 g/dL, and intrinsic viscosities were determined by the usual double extrapolation of η_{sp}/c and $(\ln \eta_{rel})/c$ to zero concentration. Flow times were measured at least at five different concentrations for each sample, and the plots obtained were linear in all cases. Neglect of kinetic energy correction and the lack of shear rate dependence was verified.

Thermal Gravimetric Analysis (TGA). A Perkin-Elmer TG 7 thermal gravimetric analyzer was used. The gas flow rates were 20 and 25 cm^3/min for nitrogen and air, respectively, and the heating rate was 10 °C/min in all cases. Temperature interval scanned was from 25 to 700 °C.

Polymers. All poly[(1,1,3,3-tetramethyldisiloxanyl)ethylene] (PTMDSE, **III**) samples were identified by FITR and ^{1}H NMR spectrometry as described previously.[1]

Procedures. Polymerization in Dilute Solution. A typical dilute solution polymerization reaction was performed in a 250 cm^3, three-necked, round-bottomed flask, equipped with a Teflon-coated stirring bar and a vertical air-cooled condenser. The flask was placed in a glycerine constant-temperature bath, which was positioned on a magnetic stirrer. Toluene (200 cm^3), DVTMDS (14.0 cm^3, 11.354 g) and [Pt−DVTMDS] (0.3 cm^3 of 0.3 wt % Pt/DVTMDS solution) were charged into the flask in this order. The total amount of DVTMDS monomer at this point was 11.573 g (66.2 mmol) and concentration of platinum was 3 × 10^{-5} mol of Pt/mol of $CH{=}CH_2$. Stirring was started, and the mixture was warmed to 42 ± 0.1 °C. After about 0.5 h at that temperature, DHTMDS (5.5 cm^3, 4.164 g, 31.07 mmol) was added to start the reaction at the molar ratio of the reacting monomers, r = [SiH]/[$CH{=}CH_2$] = 0.499. After 2.5 h, an aliquot of 0.5 mL of the reaction mixture was taken for IR, which showed only a small decrease in intensity of the ≡Si−H peak at 2126 cm^{-1}. Stirring was continued further, but when after 24 h the ≡Si−H peak was still prominent, catalyst concentration was increased to 1.24 × 10^{-4} mol of Pt/mol of $CH{=}CH_2$. This decreased the value of r to 0.469 and increased the monomer concentration to 8.67% (w/v).

When the ≡Si−H IR band finally disappeared from the spectrum (after almost 48 h of the reaction time), indicating that all of the initially introduced DHTMDS monomer was used up in the reaction, an aliquot of 2.5 mL of the reaction mixture was withdrawn for the molecular weight determination. Following this, another portion of DHTMDS was added to increase the value of r to 0.800, and this procedure was repeated (see Table 1 for details) until no further increase in the polymer molecular weight could be detected. At that point, the reaction mixture was heated to 100 °C, but this failed to produce the expected increase in the polymer molecular weight. Stirring was stopped and the reaction mixture was slowly poured into a well-stirred, 10 times larger volume of methanol. A viscous polymer oil, which precipitated, was separated from the liquid phase by decantation and dried at 60 °C and 15 mmHg to yield a PTMDSE sample that had $\bar{M}_v$ of 13 900, [η] = 0.0855 dL/g. The liquid phase from decantation was stripped of solvents to yield another, methanol/toluene-soluble fraction, the $\bar{M}_v$ of which was only 3300, [η] = 0.0027 dL/g.

Table 1. Polymerization of DHTMDS and DVTHDS in Dilute Toluene Solution[a]

r	$\bar{M}_n$ (VPO)	[η],[b] dL/g	$\bar{M}_v$[c]
0.469	480		
0.800	510		
0.893	590		
0.95	710		
0.98	860	0.0398	5300
0.994	1180	0.0415	6100
1.00	1240	0.0473	6600
1.02	1360	0.058	8530
1.032	840	0.0664	10100
1.053	990	0.0752	11820
1.071	960	0.0777	12320
1.102	1090	0.0759	11960
1.168	960	0.0716	11100
1.168[d]	980	0.0758	11940

[a] [M]$_0$ = 0.311 mol/L; T = 42 °C; [catalyst] = 1.24 × 10^{-4} mol of Pt/mol of $CH{=}CH_2$. [b] In toluene at 30 ± 0.5 °C. [c] Calculated from $[\eta] = K\bar{M}_v^a$ using K = 4.35 × 10^{-5} and a = 0.795. [d] After heating to 100 °C.

Polymerization in Concentrated Solution. This procedure was completely analogous to that described above for the polymerization in dilute solutions, with the only difference being the amounts of the reaction mixture components used. Thus, DVTMDS (14 cm^3, 11.354 g), [Pt−DVTMDS] (1.5 cm^3), and DHTMDS (11.26 cm^3, 8.524 g) in 40 mL of toluene were used to start the reaction, so that total initial monomer concentration was 38% (by weight). After the reaction and the workup procedure were carried out as described for the polymerizations in dilute solutions above, this approach gave PTMDSE main product (HT-2-T of Table 4), which had an $\bar{M}_v$ of 33 600, [η] = 0.171 dL/g, and a fraction soluble in 10:1 methanol/toluene mixture, which had $\bar{M}_n$ = 245.

Neat Polymerization. These reactions were performed in a 50 cm^3 two-necked round-bottom flask equipped with a Teflon-coated stirring bar and a vertical air-cooled condenser and placed in a glycerine constant-temperature bath positioned on a magnetic stirrer. In all experiments, 2.68 ± 0.02 g (20.0 mmol) of DHTMDS was added to 3.712 ± 0.02 g (20.0 mmol) of DVTMDS and the resulting mixtures were stirred and warmed at the desired reaction temperature for about 0.5 h. Following this, a weighed amount of catalyst was added, and the moment of this addition was marked as the beginning of polymerization. The course of each reaction was monitored by following the disappearance of the ≡Si−H band in the IR (2130−2117 cm^{-1}), using 20 mL samples withdrawn from the reaction mixtures at specified time intervals and dissolved in 0.5 cm^3 of CCl_4.

As summarized in Table 4, two series of experiments were performed at six different reaction temperatures (from 25 to 56 °C) and with four different catalyst concentrations (from 7.0 × 10^{-6} to 3.1 × 10^{-5} mol of Pt/mol of $CH{=}CH_2$).

Results and Discussion

The hydrosilation polymerization of DHTMDS (**I**) and DVTMDS (**II**) in the presence of [Pt−DVTMDS] reaction catalyst (reaction 1) was examined neat and in solution. For the latter, toluene was selected as the reaction solvent, because it had been found earlier by others not to effect the rate of hydrosilation reaction[5] and because it is a good solvent for the [Pt−DVTMDS] catalyst[6] and has favorably high boiling temperature. For all polymerization reactions performed in solution, the so-called "one monomer deficient method"[7,8] was used. This consisted of incremental additions of weighted portions of DHTMDS monomer to the reaction mixtures, which contained excessive amounts of DVTMDS, and as the molar ratio of the reacting monomers, r = [SiH]/[$CH{=}CH_2$], was gradually increased from zero to unity,

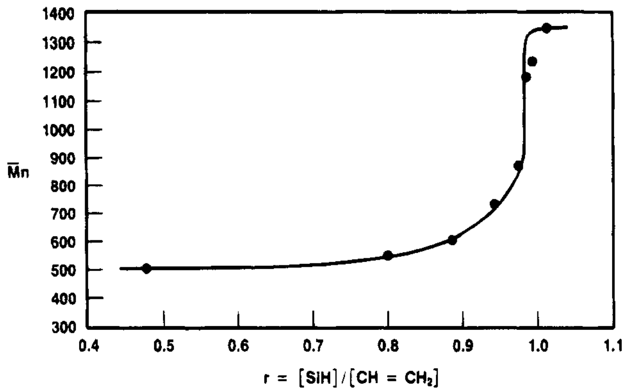

Figure 1. Monitoring of the hydrosilation polymerization reaction of DHTMDS and DVTMDS in dilute toluene solution ($[M]_0$ = 0.311 mol/L) by vapor pressure osmometry.

the resulting increase of the polymer molecular weight was monitored by vapor pressure osmometry and/or dilute solution viscometry. The consumption of the $\equiv$Si=H functional groups during the reactions was also followed by FTIR.

Polymerization in Dilute Solutions. The reaction was first studied in dilute solutions, in which individual monomer concentrations were 0.4 mol/L or lower. The concentration of the reaction catalyst was initially set at 3×10^{-5} mol of Pt/mol of CH=CH$_2$ units, but it was later increased to 1.24×10^{-4} mol of Pt/mol of CH=CH$_2$, because the former was found too low for a reasonably practical rate of polymerization.

Viscosity average molecular weights, $\bar{M}_v$, of the periodically withdrawn polymer samples were calculated from intrinsic viscosities determined at 30 ± 0.5 °C in toluene. Initially, a set of Mark–Houwink constants established earlier for the closely related poly(dimethylsiloxane) (PDMS)[9] was used for calculations, but it was later replaced by more appropriate constants determined for PTMDSE in this work.

Monitoring of the typical dilute solution polymerization reaction of DHTMDS and DVTMDS performed in the described manner gave results shown in Table 1 and in Figure 1.

It can be seen from this table, that an unusually large discrepancy appeared between the values obtained for the number, $\bar{M}_n$, and for the viscosity, $\bar{M}_v$, average molecular weights by VPO and dilute solution viscometry, respectively. This indicated that the former were considerably influenced by the presence of platinum polymerization catalyst, and because it was found very difficult to rigorously purify relatively small reaction mixture samples used for monitoring purposes, VPO was abandoned as a monitoring method and only viscometry was utilized in further work.

It can also be seen from these data that polymer molecular growth occurred in a manner typical for step–growth polymerization reactions. Thus, while increase in $\bar{M}_v$ was very slow throughout most of the polymerization process, i.e., until the value of r reached about 0.95, it accelerated dramatically above that point, to reach a maximum at about 12 000, i.e., when r reached 1.07. No attempt to further increase molecular weight above this point was successful, including additional increase of r or heating of the reaction mixture from 42 to 100 °C.[10] This indicated that the obtained maximum polymer molecular weight was not limited by the kinetic reasons, but rather by the polymerization reaction stoichiometry. Apparently, equimolarity of the reacting monomer concentrations was established at r = 1.07, while deviation from ideality (i.e., from r = 1.00, expected on the basis of the general theory of step–growth polymerization reactions) was probably due to possible volatility of the dihydrido monomer at the reaction temperature used.

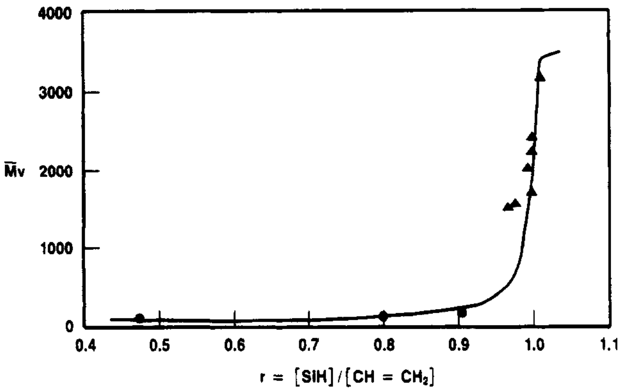

Figure 2. Monitoring of the hydrosilation polymerization reaction of DHTMDS and DVTMDS in concentrated toluene solution ($[M]_0$ = 1.675 mol/L) by dilute solution viscometry.

Table 2. Polymerization of DHTMDS and DVTMDS in Concentrated Toluene Solution[a]

r	$[\eta]$,[b] dL/g	$\bar{M}_v$[c]	r	$[\eta]$,[b] dL/g	$\bar{M}_v$[c]
0.95	0.092	15230	0.998	0.1255	22500
0.98	0.0947	15800	1.00	0.1335	24330
0.99	0.1146	20080	1.01	0.166	32000
0.995	0.1020	17340	1.01[d]	0.162	31040

[a] $[M]_0$ = 1.675 mol/L; T = 42 °C; [catalyst] = 1.4×10^{-4} mol of Pt/mool of CH=CH$_2$. [b] In toluene at 30 ± 0.5 °C. [c] Calculated from $[\eta] = K\bar{M}_v^a$ using $K = 4.35 \times 10^{-5}$ and a = 0.795. [d] After heating to 100 °C.

Isolation of the polymer product, by precipitation in methanol, washing, and drying, provided two fractions: a low molecular weight fraction, which was soluble in toluene/methanol (1:10 by volume) and had $\bar{M}_v$ of 3300 (i.e., $[\eta]$ = 0.0027 dL/g), and a high molecular weight fraction, which precipitated from the same mixture and had $\bar{M}_v$ of 13 900 (i.e., $[\eta]$ = 0.0855 dL/g). This was not unexpected, since such formation of two polymer fractions, one of very high and another of very low molecular weight, is often encountered when the "one monomer deficient" polymerization method is used.[7,8]

Polymerization in Concentrated Solution. A major practical deficiency of this hydrosilation polymerization reaction when performed in dilute solutions was its undesirably low rate of occurrence. Thus, it was found by FTIR monitoring of the disappearance of $\equiv$Si—H groups (valence vibrations at 2130–2117 cm^{-1}) that, under the reaction conditions described in the preceding section, more than 24 h was needed for only about half of the stoichiometrically required amount of DHTMDS to undergo polymerization. Therefore, we attempted to improve this situation by increasing the monomer concentration from 0.4 to 1.675 mol/L, while retaining unchanged catalyst concentration of 1.4×10^{-4} mol of Pt/mol of CH=CH$_2$. Monitoring of one such polymerization reaction gave the results shown in Table 2 and in Figure 2.

It can be seen from these results that the monitoring curve retained its S-type shape, which was observed earlier in the dilute solution systems (compare Figures 1 and 2) and which is generally characteristic for the step–growth polymerization reactions.[7,8] At the same time, however, the reaction rate increased significantly, so that under these new conditions, the reaction was

Table 3. Neat Polymerization of DHTMDS and DVTMDS[a]

reaction	reaction temp, °C	catalyst conc, mol of Pt/mol of $CH{=}CH_2$	polymer $\bar{M}_v$
1	42	7.0×10^{-6}	21 950
2	42	1.4×10^{-5}	27 900
3	42	2.1×10^{-5}	34 600
4	42	3.1×10^{-5}	23 750
5	25	2.1×10^{-5}	34 800
6	30	2.1×10^{-5}	31 300
7	36	2.1×10^{-5}	21 950
7	36	2.1×10^{-5}	21 950
8	50	2.1×10^{-5}	20 400
9	56	2.1×10^{-5}	75 900

[a] For $r = [SiH]/[CH{=}CH_2] = 1.00$.

completed about 3 times faster than in dilute solutions, taking only about 8 h for half of the stoichiometric quantity of DHTMDS to react.[6] In addition to this, the molecular weight of the resulting PTMDSE also increased significantly, reaching well above 30 000 with practically quantitative monomer conversion.[6]

From these results it could be concluded that this hydrosilation polymerization reaction (a) exhibited behavior typical for a step-growth polymerization, (b) occurred with practically complete monomer conversion and with almost quantitative yield of the polymer product, (c) increased in rate with increasing monomer concentration, and (d) at higher monomer concentrations, i.e., at 1.675 mol/L, yielded truly high molecular weight polymer products ($\bar{M}_v$ of which were routinely above about 30 000).[1]

Neat Polymerization. Based upon these observations, the third series of experiments was carried out by reacting equimolar amounts of neat monomers at various reaction temperatures and at four different catalyst concentrations, as shown in Table 3.

It was found that at the same catalyst concentration (1.4×10^{-5} mol of Pt/mol of $CH{=}CH_2$) and at the same reaction temperature (42 °C), as used for the solution polymerizations before, this hydrosilation polymerization reaction occurred faster in the absence of solvent, reaching completion in little less than 5 h. Expectedly, its rate further increased when catalyst concentration was raised again, so that only about 180 min was required when the latter was 3.1×10^{-5} mol of Pt/mol of $CH{=}CH_2$. In addition to this, this series of experiments also produced a PTMDSE sample (9 of Table 3) that had the highest molecular weight (76 000) of all the hydrosilation polymerization reaction products reported until present.[1,11]

Some Rheological Properties of PTMDSE. After isolation and decoloration by active carbon,[6] all PTMDSE samples obtained in this work were colorless, transparent viscous oils, regardless of whether they were prepared by solution or neat polymerization. Rotational steady shear viscometry of these oils (performed at 25 °C and within a shear rate range from 1.8 to 1840 cm^{-1}) showed flow patterns that were very similar to those of the well-known and closely related PDMS fluids of comparable molecular weights.[9] From the obtained flow curves, zero shear viscosities were determined in the usual manner, and from these, viscosity average molecular weights, $\bar{M}_{v2}$, of the examined samples were calculated by using the following empirical equation earlier established for PDMS:[12]

$$\log \eta_0 \, (\mathrm{cs}/25\ ^\circ\mathrm{C}) = 1.00 + 0.0123\, \bar{M}_{v2}^{\;1/2}$$

The $\bar{M}_{v2}$ values thus obtained were then used to determine Mark–Houwink-type constants for PTMDSE (see Figure 3), which for the molecular weight range examined, i.e., from 2000 to 76 000, and for toluene solvent at 30 ± 0.5 °C, yielded: $K = 4.35 \times 10^{-5}$ and $a = 0.795$. This value for constant a was higher than the values usually found for PDMS (which are most often between about 0.5 and 0.7[13]), indicating that inherent molecular chain flexibility of PTMDSE is lower than that of PDMS. This observation is in good agreement with the expectation that, compared to extremely flexible SiOSi units,[9] the CC main chain groups should act as the chain-stiffening building blocks.

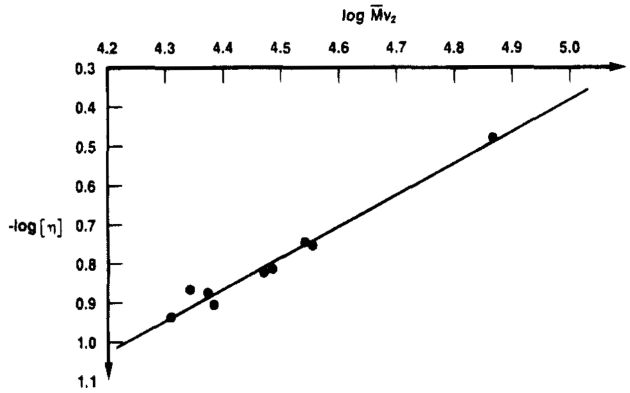

Figure 3. Zero shear molecular weight, $\bar{M}_{2v}$, dependence of intrinsic viscosity of PTMDSE in toluene at 30 °C.

Thermal Stability and Degradation Behavior of PTMDSE. Thermal stability and degradation behavior of PTMDSE was compared to that of PDMS[14] by thermal gravimetric analysis in nitrogen and in air, and the results obtained are shown in Table 4 and Figures 4,5 and 6,7, respectively.

It can be seen from these data that, as expected,[15] both polymers started to lose their weight at somewhat lower temperatures in air than in nitrogen. A seemingly exceptional behavior of PTMDSE samples HT-2-T and HT-2-T (−Pt) was clearly caused by the presence of some solvent left over from polymer preparation.

Both thermal and thermooxidative degradation of PTMDSE started at lower temperatures than the corresponding degradation processes of PDMS (in nitrogen, PTMDSE at 225 °C, PDMS at 275 °C; in air, PTMDSE at 200 °C, PDMS at 250 °C). This can also be attributed to the presence of CC and CSi groups in the PTMDSE main-chain backbone, because these units should represent "weak links" in this structure since their bond energies (347 and 360 kJ/mol, respectively) are both considerably lower than the silicon–oxygen bond energy, which equals about 530 kJ/mol.[15]

In nitrogen, the rate of degradation of both PTMDSE and PDMS was slower than in air. Thus, while in air, PTMDSE (sample 9F) lost 5% of its initial weight at 235 °C (i.e., only about 35 °C above its onset degradation temperature), it required heating to about 425 °C for the same to happen in nitrogen. In addition to this, while the maximum rate of PTMDSE degradation was observed at about 290 °C in air, the same was found at 535 °C in nitrogen. Interestingly, however, both thermal and thermooxidative degradation of PTMDSE were completed at about the same temperature of 560–570 °C, although the mechanisms involved were clearly quite different. Thus, while in nitrogen, thermal degradation of PTMDSE resulted in complete polymer annihilation with all degradation products being volatile at degradation temperatures, degradation in air yielded white silica residue, the amount of which was about 10–15% of the initial polymer weight.

Table 4. Thermal Gravimetric Analysis of PTMDSE and PDMS in Nitrogen and in Air[a]

sample	onset of degradation, °C	temp for 5% wt loss, °C	temp for 50% wt loss, °C	end of degradation, °C	temp for max rate of degradation, °C	wt remaining, %
			In Nitrogen			
9-F	225.0	425.0	520.0	575.0	536.0	0.0
HT-2-T	125.0	362.5	512.5	575.0	527.0	2.5
HT-2-T (−Pt)	125.0	362.5	512.5	575.0	527.0	0.5
PDMS[b]	275.0	430.0	597.5	732.5	612.0	1.5
			In Air			
9-F	200.0	235.0	290.0	562.5	292.0	11.5
HT-2-T	125.0	235.0	287.5	525.0	292.0	10.0
HT-2-T (−Pt)	125.0	235.0	285.0	525.0	288.0	10.0
PDMS[b]	250.0	375.5	555.0	577.5	380.0	48.0

[a] In all cases, the rate of heating was 10 °C/min and samples ranged from 8 to 14 mg in weight. [b] See ref 14.

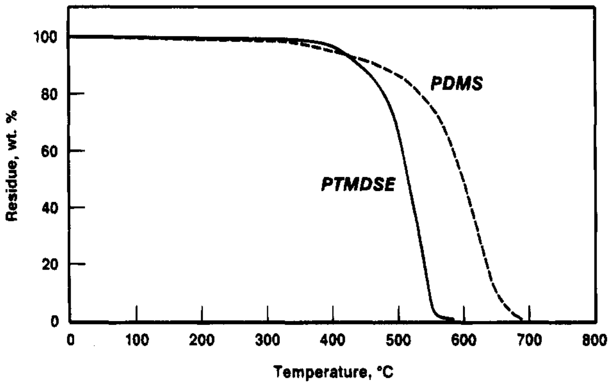

Figure 4. TGA thermograms for PTMDSE and PDMS degradation in nitrogen at a heating rate of 10 °C/min.

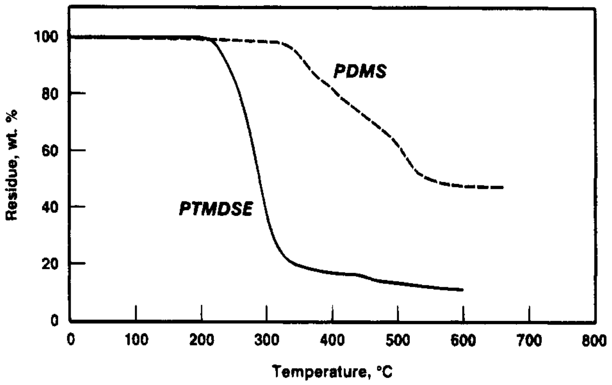

Figure 5. TGA thermograms for PTMDSE and PDMS degradation in air at a heating rate of 10 °C/min.

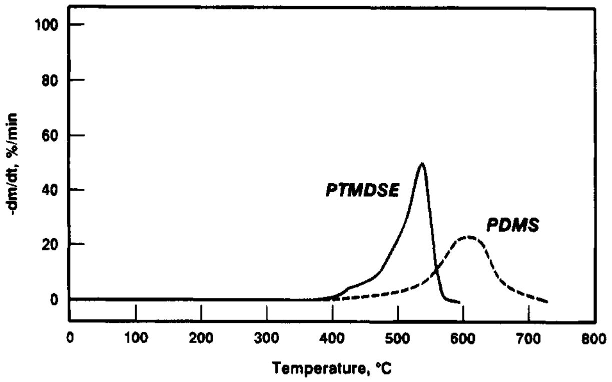

Figure 6. Differential TGA for PTMDSE and PDMS degradation in nitrogen at a heating rate of 10 °C/min.

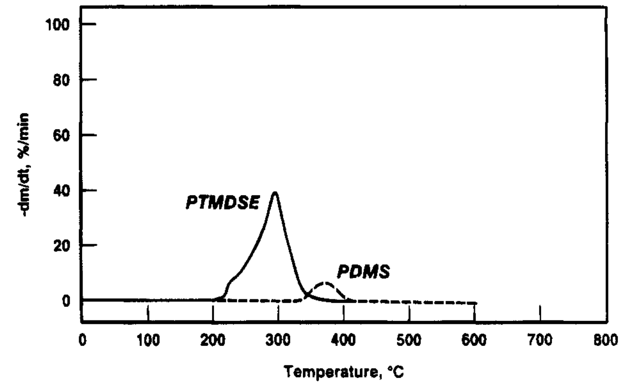

Figure 7. Differential TGA for PTMDSE and PDMS degradation in air at a heating rate of 10 °C/min.

It should be also noted that, from the data obtained in this work, it appears as if thermal and thermooxidative degradation of PTMDSE were not effected by the presence of small amounts of platinum from polymerization reaction catalyst (compare samples HT-2-T (−Pt) and HT-2-T). This is rather surprising with respect to the well-known destabilizing effects which polymerization catalysts usually exert on the thermal and thermooxidative stability of closely related polysiloxanes.[15] Based on the data obtained in this work, maximum potential use temperatures for PTMDSE seem to be about 175 °C in nitrogen and about 150 °C in air.

Conclusions. The results obtained in this work clearly confirm our earlier report that the hydrosilation reaction can successfully be used for preparation of truly high molecular weight linear polycarbosiloxanes.[1]

The most favorable synthetic procedures seem to be neat polymerization and/or polymerization in concentrated solutions. In either case, a concentration of [Pt−DVTMDS] catalyst of about 2 × 10^{-5} mol of Pt/mol of $CH{=}CH_2$ or above and reaction temperatures between 40 and 50 °C seem to be recommended (the latter being due to potentially deleterious effect of DHTMDS volatility). Under such conditions, preparation of PTMDSE having a molecular weight as high as 76 000 was possible.

Poly[(1,1,3,3-tetramethyldisiloxanyl)ethylene] showed reduced molecular chain flexibility and lower thermal and thermooxidative stability than the closely related poly(dimethylsiloxane). This seems to confirm expectations that not only do the SiCCSi units represent the chain-stiffening building blocks, when compared to extremely flexible SiOSi groups, but they also act as thermal and thermooxidative "weak links" relative to the siloxane groups.

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