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End Group Analysis Accounts for the Low Molecular Weight Observed in the 1,3-Divinyltetramethyldisiloxane−Pt Complex Catalyzed Hydrosilylation Copolymerization of α,ω-Dienes and 1,3-Dihydridotetramethyldisiloxane

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ABSTRACT: The 1,3-divinyltetramethyldisiloxane−Pt complex (Karstedt catalyst) facilitates copolymerization of α,*ω*-dienes, such as 1,7-octadiene or 1,5-hexadiene, with 1,3-dihydridotetramethyldisiloxane. Spectroscopic analysis of the copolymers indicates the presence dimethylsiloxy and either 2-octenyl or 2-hexenyl end groups. Apparently, the catalyst not only facilitates the hydrosilylation reaction of 1,3-dihydridotetramethyldisiloxane with terminal C−C double bonds but also catalyzes the isomerization of terminal alkenes to internal alkenes, which are not reactive.

Background

Platinum-catalyzed hydrosilylation reactions, which involve the anti-Markovnikov addition of a Si−H bond across a C−C double bond, are the most important method to form Si−C bonds.[1,2] This reaction is often catalyzed either by H_2PtCl_6[3,4] or more recently by the 1,3-divinyltetramethyldisiloxane−platinum complex (Karstedt's catalyst).[5,6]

The synthesis of polycarbosilanes by the H_2PtCl_6-catalyzed hydrosilylation polymerization reaction was first reported by Curry.[7,8] Likewise, Andrianov has used H_2PtCl_6-catalyzed copolymerization of α,*ω*-divinylsiloxanes and α,*ω*-dihydridosiloxanes to give low molecular weight copoly(carbosilane/siloxane)s.[9,10] Hydrosilylation reactions have also been used in the synthesis of dendrimers[11] and to cross-link siloxane elastomers in RTV processes.[12]

As with other step growth polymerization reactions, stoichiometric balance is extremely important.[13] Side reactions that result in an imbalance limit the degree of polymerization. This occurs in the H_2PtCl_6-catalyzed hydrosilylation copolymerization of α,*ω*-divinylsiloxanes and α,*ω*-dihydridosiloxanes by loss of vinyl groups from the α,*ω*-divinylsiloxane by a protodesilylation reaction with HCl, which is generated by reaction of the catalyst with 2-propanol.[14] Higher molecular weight copoly(carbosilane/siloxane)s have been synthesized by Karstedt or Pt/C-catalyzed hydrosilylation copolymerization of α,*ω*-divinylsiloxanes or α,*ω*-dienes with α,*ω*-dihydridosiloxane.[14−17]

Introduction

In this paper, we report a study of the copolymerization of α,*ω*-dienes, e.g., 1,5-hexadiene or 1,7-octadiene, with 1,3-dihydridotetramethyldisiloxane using the Karstedt catalyst. Essentially quantitative yields of low molecular weight poly(2,2,9,9-tetramethyl-2,9-disila-1-oxa-nonanylene) and poly(2,2,11,11-tetramethyl-2,11-disila-1-oxa-undecanylene), respectively, were obtained. These have been characterized by ^1H, ^{13}C, ^{29}Si NMR, and IR spectroscopy. Their molecular weight distributions have been determined by gel permeation chromatography (GPC) and multiangled laser light scattering (MALLS); M_n has also been determined by NMR end group analysis.

Two types of end groups have been detected in the ^1H and ^{13}C NMR spectra. In the case of poly(2,2,9,9-tetramethyl-2,9-disila-1-oxanonanylene), these are *cis*- and *trans*-2-hexenyl and dimethylsiloxy groups, while in the case of poly(2,2,11,11-tetramethyl-2,11-disila-1-oxaundecanylene), *cis*- and *trans*-2-octenyl and dimethylsiloxy groups are observed (Figure 1).

Experimental Section

^1H and ^{13}C NMR were obtained on a Bruker AM-360 spectrometer operating in the FT mode. ^{29}Si spectra were determined on a Bruker AMX-500 spectrometer. Five percent w/v $CDCl_3$ solutions were used to obtain ^1H NMR spectra. Fifty percent w/v $CDCl_3$ solutions were used for ^{13}C and ^{29}Si spectra. ^{13}C NMR spectra were obtained with broad-band proton decoupling. A heteronuclear gated decoupled pulse sequence NONOE was used to acquire ^{29}Si spectra.[18] ^1H and ^{13}C NMR spectra were internally referenced to residual $CHCl_3$. ^{29}Si NMR spectra were internally referenced to TMS.

Proton assignments of both dimethylsilyloxy and internal vinyl end groups were confirmed by selective irradiation experiments. These result in loss of $^1H-^1H$ coupling between the vinyl protons and the adjacent methyl group (${=}HC-CH_3$) of internal vinyl end groups and between Si−H and CH_3−Si of dimethylsiloxy end groups.

GPC analysis of the molecular weight distribution of these polymers was performed on a Waters system comprised of a U6K injector, a 510 HPLC solvent delivery system, a R401 refractive index (RI) detector, and a model 820 Maxima control system. Two 7.8 mm × 300 mm Styragel columns packed with $<5\ \mu m$ divinylbenzene cross-linked polystyrene, HR4 and HR2, in series were used for the analysis with HPLC grade THF at a flow rate of 6.0 mL/min. The retention times were measured against known monodispersed polystyrene standards: M_w 929 000, 212 400, 18 700, and 2200 whose M_w/M_n are less than 1.09.

GPS/MALLS was performed with a Wyatt Dawn-DSP MALLS detector, which is inserted between the GPC columns and a R410 RI detector. Data were analyzed with a Wyatt ASTRA system. The DN/DC's of neither poly(2,2,9,9-tetra-

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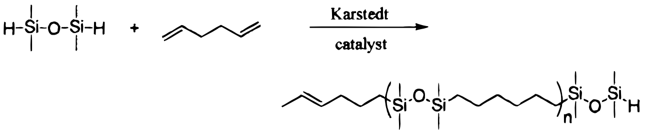

Figure 1. Hydrosilylation copolymerization 1,5-hexadiene and 1,3-dihydridotetramethylsiloxane.

methyl-1-oxa-2,9-disilanonanylene) nor poly(2,2,11,11-tetramethyl-1-oxa-2,11-disilaundecanylene) are known; therefore, an approximation of 100% mass recovery of the polymer was used in order to determine the molecular weights. This allowed us to derive an estimated DN/DC in THF of 0.052 and 0.048 mL/g for the poly(2,2,9,9-tetramethyl-1-oxa-2,9-disilanonanylene) and poly(2,2,11,11-tetramethyl-1-oxa-2,11-disilaundecanylene), respectively.

IR spectra of neat films on NaCl plates were recorded on a Perkin-Elmer Spectrum 2000 FT-IR spectrometer.

Gas−liquid chromatographic analysis (GC) of ether solutions of 1,7-octadiene and 1,5-hexadiene were run on a Varian 3400-GC equipped with a flame ionization detector and a 30 m DB-5 capillary column.

All reactions were run in flame-dried glassware under a nitrogen atmosphere. Allyl chloride, Amberlite IRC-718 ion-exchange resin, diethyl ether, 97% *trans*-2-hexene, and a mixture of *cis*- and *trans*-2-hexene, 98% *trans*-2-octene, 98% 1,7-octadiene, magnesium powder, THF, and toluene were obtained from Aldrich. 1,3-Dihydridotetramethyldisiloxane was obtained from Gelest. A solution of 5% Karstedt catalyst in xylene was obtained from Hüls. THF, toluene, 1,3-dihydridotetramethyldisiloxane, and 1,7-octadiene were freshly distilled prior to use.

1,5-Hexadiene was synthesized by a coupling reaction between allyl Grignard reagent and allyl chloride in THF. It was purified by fractional distillation through a 20 cm vacuum jacketed Vigreux column. A fraction bp 60−61 °C was collected. Its ^{1}H and ^{13}C NMR spectra were identical with those previously reported.[19] No additional peaks due to isomeric impurities were detected in the ^{13}C NMR. Only a single peak was detected by capillary GC.

1,7-Octadiene. Capillary GC analysis of redistilled 1,7-octadiene shows the presence of two isomeric impurities in 0.3%. The quantities of isomeric contaminants present in 1,7-octadiene were analyzed by quantitative measurements of ^{13}C NMR spectra of a 50% v/v sample of 1,7-octadiene in a 0.75 mmol solution of $Cr(AcAc)_3$.[20] Signals of equal intensity at 30.04, 35.28, 115.86, and 140.27 ppm due to 1,7-octadiene were detected. In addition, resonances of low intensity in the vinyl region at 114.30, 114.97, 126.77, 133.93, and 134.95 ppm were observed in the ^{13}C NMR. These may be due to *cis*- and *trans*-2,7-octadiene and as well as other octadiene isomers. By integration these amount to 0.3%.

Copolymerization of 1,3-Dihydridotetramethyldisiloxane with 1,5-Hexadiene. An Ace pressure tube (100 mL) equipped with a Teflon-covered magnetic stirring bar was flushed with nitrogen. A solution made up of 1,5-hexadiene (0.880 g, 10.7 mmol), 1,3-dihydridotetramethyldisiloxane (1.429 g, 10.7 mmol), and toluene (4.5 mL) was placed in the tube. The tube was sealed immediately after Karstedt catalyst solution in xylene (4.5 μL) was added. The flask was placed in a preheated to 120 °C oil bath and stirred for 2 h. Cooled to room temperature, flash chromatography of the polymer solution on a column packed with Amerlite IRC-718 ion-exchange resin serves to remove residual catalyst. Volatile materials were removed by evaporation under reduced pressure. The residue was then analyzed.

Poly(2,2,9,9-tetramethyl-2,9-disila-1-oxanonanylene).[15] A pale yellow viscous liquid, 2.2 g, 95% yield. ^{1}H NMR δ: 0.03 (s, 12H), 0.49 (bs, 4H), 1.30 (bs, 8H). ^{13}C NMR δ: 0.46, 18.5, 23.3, 33.3. ^{13}Si NMR δ: 7.01. M_w/M_n = 6100/3100 by GPC, 7500/5200 by GPC/MALLS, and M_n = 4509 by end group analysis were obtained.

Copolymerization of 1,3-Dihydridotetramethyldisiloxane and 1,7-Octadiene. A stock solution of 1,3-dihydridotetramethyldisiloxane (16.12 g, 0.12 mol) and 1,7-octadiene (13.22 g, 0.12 mol) in 50 mL of toluene was stirred under nitrogen and sealed. An Ace pressure tube (100 mL) equipped with a Teflon-covered magnetic stirring bar was flushed with nitrogen. Ten milliliters of the stock solution and 10 μL of the Karstedt catalyst solution were placed in the tube. The tube was heated at 120 °C and stirred for 2 h and then cooled to room temperature. Cooled to room temperature, flash chromatography of the polymer solution on a column packed with Amerlite IRC-718 ion-exchange resin served to remove residual catalyst. Volatile materials were removed by evaporation under reduced pressure. The residue was then analyzed.

Poly(2,2,11,11-tetramethyl-2,11-disila-1-oxaundecanylene). A colorless viscous liquid, 4 g. ^{1}H NMR δ: 0.01 (s, 12H), 0.49 (t, 4H, J = 3.6 Hz), 1.27 (bs, 12H). ^{13}C NMR δ: 0.2, 18.3, 23.1, 29.2, and 33.2. ^{29}Si NMR δ: 6.9. IR ν: 2957, 2918, 2857, 2358, 2319, 2123, 1460, 1407, 1248 (sh), 1178, 1055 (br), 842, 794, 705 cm^{-1}. M_w/M_n = 12 240/7700 by GPC, 11 500/9150 by MALLS, and M_n = 6300 by ^{1}H NMR end group analysis were obtained.

Attempted Reaction of *cis*- and *trans*-2-Hexene with 1,3-Dihydridotetramethyldisiloxane. A solution of 1,3-dihydridotetramethyldisiloxane (0.798 g, 5.94 mmol) and *cis*- and *trans*-2-hexene (1.00 g, 11.8 mmol) was placed in an Ace pressure tube. A Teflon-covered magnetic stirring bar and 7 μL of the Karstedt catalyst solution were added. A ^{1}H NMR spectrum of this solution was taken. The tube was flushed with nitrogen, sealed, and placed in a 120 °C bath. After 2 h, the reaction was cooled to room temperature. The ^{1}H NMR of the mixture was identical with that of the starting solution.

Attempted Reaction of *trans*-2-Hexene with 1,3-Dihydridotetramethyldisiloxane. A solution of 1,3-dihydridotetramethyldisiloxane (0.20 g, 1.49 mmol) and *trans*-2-hexene (0.25 g, 2.97 mmol) was placed in an Ace glass pressure tube. ^{1}H and ^{13}C NMR spectra of this mixture were taken. ^{1}H NMR δ: 0.17 (d, 12H, J = 3 Hz), 4.65 (sept., 2H, J = 3 Hz) due to 1,3-dihydrotetramethyldisiloxane; 0.87 (t, 3H, J = 7.4 Hz), 1.34 (dt, 2H, J = 7.3 and 7.1 Hz), 1.63 (m, 3H), 1.94 (m, 2H), 5.38 (m, 2H) due to *trans*-2-hexene; and small peaks at 0.95 (t, 3H, J = 7.2 Hz), 1.28 (m, 2H), 1.59 (m, 3H), 1.94 (m, 2H), 5.39 (m,2H) due to *cis*-2-hexene impurity.

A Teflon-covered magnetic stirring bar and 7 μL of the Karstedt catalyst solution were added to the pressure tube. The tube was flushed with nitrogen, sealed, and placed in a 120 °C bath. After 24 h, it was cooled to room temperature. A ^{1}H NMR spectrum of the contents was essentially identical to that reported above.

Attempted Reaction of *trans*-2-Octene with 1,3-Dihydridotetramethyldisiloxane. A solution of 1,3-dihydridotetramethyldisiloxane (0.20 g, 1.49 mmol) and *trans*-2-octene (0.25 g, 2.21 mmol) was placed in an Ace glass pressure tube. A Teflon-covered magnetic stirring bar and 7 μL of the Karstedt catalyst solution were added. The tubes were then flushed with nitrogen, sealed, and placed in a 120 °C bath. The reaction mixture was heated in the bath for 2 h, after which it was cooled to room temperature. The ^{1}H and ^{13}C NMR spectra of the starting mixture and final solutions were identical. ^{1}H NMR δ: 0.19 (d, 12H, J = 3 Hz), 0.88 (m, 3H), 1.29 (m, 4H), 1.56 (m, 3H), 1.97 (m, 2H), 4.69 (m, 1H), 5.47 (m, 2H). ^{13}C NMR δ: 0.51, 14.06, 17.88, 22.63, 29.40, 31.51, 32.66, 124.53, 131.71. ^{1}H and ^{13}C NMR resonance for the *cis*-2-octene impurity are not reported.

Results and Discussion

Those factors that ultimately limit the molecular weights obtained in hydrosilylation copolymerization reactions with the Karstedt catalyst have not been previously elucidated.

End Group Analysis by NMR. In addition to the major peaks observed in the ^{1}H and ^{13}C NMR spectra of poly(2,2,11,11-tetramethyl-2,11-disila-1-oxaundecanylene) which are described in the Experimental Section, both spectra show small peaks due to the presence

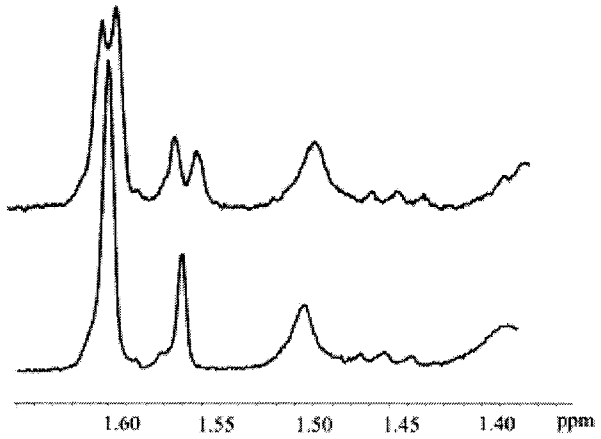

Figure 2. Proton decoupled NMR of poly(2,2,11,11-tetramethyl-1-oxa-2,11-disilaundecanylene). Top spectrum was obtained by irradiation at 5.43 ppm.

of internal C−C double bonds. The ^{1}H NMR shows a pair of doublets centered at 1.59 and 1.63 ppm and a multiplet centered at 5.43 ppm due to the methyl groups and the vinyl protons of the *cis*- and *trans*-2-octenyl end groups. Consistent with this assignment, when the multiplet centered at 5.43 ppm was irradiated, the pair of doublets centered at 1.59 and 1.63 ppm became singlets; see Figure 2. Likewise, when the doublets at 1.59 and 1.63 ppm were irradiated, the multiplet centered at 5.43 ppm sharpened. The ^{13}C NMR spectrum also shows evidence of internal vinyl groups. Small resonances were observed at 123.4, 124.3, 130.7, and 131.5 ppm. The positions of these are almost identical to those observed for the vinyl carbons of a mixture of *cis*- and *trans*-2-hexenes: 123.6, 124.7, 130.7, and 131.5 ppm. Additional vinylic peaks of lower intensity were detected at 131.8, 128.9, 128.2, and 123.8 ppm. These may be due to the presence of other internal vinyl isomers.

In addition, resonances due to dimethylsiloxyl end groups have been detected in the ^{1}H and ^{13}C NMR spectra of poly(2,2,11,11-tetramethyl-2,11-disila-1-oxaundecanylene). Specifically in the ^{1}H NMR a doublet at 0.12 ppm due to Si−CH$_3$ groups and a multiplet centered at 4.65 ppm due to the Si−H group are observed. A decoupling experiment verified these assignments. Thus, when the multiplet centered at 4.65 ppm was irradiated, the doublet centered at 0.12 ppm collapsed to a singlet (Figure 3). The presence of an Si−H bond was also detected in the FT-IR at 2123.2 cm^{-1}.

Signals are seen in the ^{1}H and ^{13}C NMR spectra of poly(2,2,9,9-tetramethyl-2,9-disila-1-oxanonalylene) bonds, consistent with similar end groups. Thus, in the ^{1}H NMR a doublet at 1.54 ppm and a multiplet centered 5.44 ppm are present. The signal at 1.54 ppm is due to a terminal allylic methyl group, while the multiplet centered at 1.54 ppm is due to the vinyl hydrogens of an internal double bond. These assignments were confirmed by decoupling experiments. When the multiplet centered at 5.44 ppm is irradiated, the doublet at 1.54 ppm collapses to a singlet. Resonances due to dimethylsiloxy end groups are also observed in the ^{1}H NMR spectrum. Thus, a doublet at 0.16 ppm and a multiplet centered at 4.64 ppm are seen. These assignments were confirmed by decoupling experiments. Resonances due to internal vinyl carbons were detected in the^{13}C NMR at 123.8, 124.8, 125.4, 129.4, 130.4, 131.5, and 132.1 ppm.

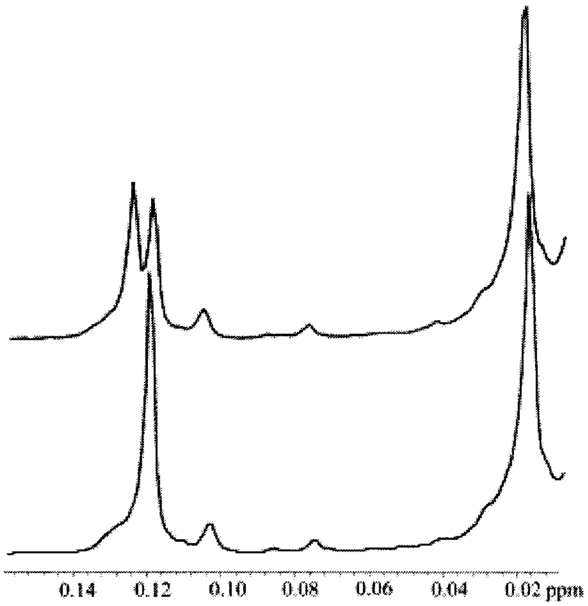

Figure 3. Proton decoupled NMR of poly(2,2,11,11-tetramethyl-1-oxa-2,11-disilaundecanylene). Top spectrum was obtained by irradiation at 4.65 ppm.

Molecular Weight Based on End Group Analysis. On the basis of end group analysis, it is possible to determine the number-average molecular weight (M_n) of the polymer. We assume that 2-octenyl or 2-hexenyl and dimethylsiloxy groups were the only end groups present. Integration of the vinyl peaks at ~5.4 ppm was used to determine the number of vinyl protons, N_{vin}, while integration of the Si−H peak at ~4.6 ppm was used to evaluate the number of dimethylsiloxy groups, N_{SiH}. Since there are two vinyl hydrogens for each end group, N_{vin} must be divided by 2. Each polymer has two end groups. The sum of $(N_{vin}/2 + N_{SiH})/2$ can be compared to the integrated area due to the methylene units N_{CH_2} of the polymer. On the basis of this analysis, we find that the poly(2,2,11,11-tetramethyl-1-oxa-2,11-disilaundecanylene) contains on average approximately 26 monomer units and that its M_n is ~6300. Similar analysis of poly(2,2,9,9-tetramethyl-1-oxa-2,9-disilanonanylene) gave a M_n of ~4500.

It should be noted that the molecular weights obtained by GPC, MALLS/GPC, and NMR end group analysis are in reasonable agreement.

Observation of Internal Bonds as End Groups Is Reasonable. Platinum species often catalyze olefin isomerization in addition to the hydrosilylation reaction. For example, Benkeser showed that H$_2$PtCl$_6$-catalyzed hydrosilylation of 1- or 2-pentene with trichlorosilane yields 1-pentyltrichlorosilane.[2,21] Apparently, olefin isomerization occurs faster than hydrosilylation, and terminal C−C double bonds undergo hydrosilylation faster than internal C−C double bonds. In control experiments, we find that *cis*- and *trans*-2-hexene, *trans*-2-hexene, and *trans*-2-octene do not undergo Karstedt's catalyst hydrosilylation with 1,3-dihydridotetramethyldisiloxane. Thus, it is reasonable that 2-octenyl and 2-hexenyl groups can function as end groups for these copoly(carbosilane/siloxane)s when the Karstedt catalyst is used.

There are two possible sources of the 2-hexenyl and 2-octenyl end groups. The 1,7-octadiene used is reported to be only 98% pure. Our NMR and GC analysis indicates that after redistillation it is, in fact, at least ∼99.5% pure. It is reasonable to assume that the major impurity is 1,6-octadiene. Thus, the ^{13}C NMR spectrum of the 1,7-octadiene shows small resonances due to internal C−C double bonds at 125.5, 132.6, 133.9, and 143.0 ppm. In addition, the less thermodynamically stable 1,7-octadiene may be isomerized to the more stable 1,6-octadiene by the Karstedt catalyst. Consistent with this, Scott has previously reported that the Karstedt catalyst not only catalyzes hydrosilylation between 1-hexene and triethylsilane but also causes isomerization of 1-hexene to 2-hexene, which is unreactive.[6]

On the other hand, the 1,5-hexadiene that was used was prepared by a coupling reaction of allyl Grignard reagent with allyl chloride and contains no 1,4-hexadiene based on GC and ^{13}C NMR analysis. Nevertheless, the poly(2,2,9,9-tetramethyl-1-oxa-2,9-disilanonanylene) prepared by hydrosilylation copolymerization of 1,5-hexadiene and 1,3-dihydrotetramethyldisiloxane contains 2-hexenyl end groups. These **must be** formed by isomerization of reactive terminal C−C double bonds to unreactive internal C−C double bonds.

Conclusion

In conclusion, the molecular weight of poly(carbosilane/siloxane)s formed by Karstedt catalyzed copolymerization of α,ω-dienes, and 1,3-tetramethyldisiloxane is limited by catalyst isomerization of terminal C−C double bonds to unreactive internal C−C double bonds. Further, these reactions do not produce high molecular weight polymers but rather telechelic oligomers whose terminal functionalities are either 2-octenyl or 2-hexenyl and dimethylsiloxy groups.[22]

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