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Preparation and properties of hyperbranched poly[1-*ß*-(4'-acetylphenyl)vinyl-3-vinyl-1,1,3,3-tretramethyldisiloxane]

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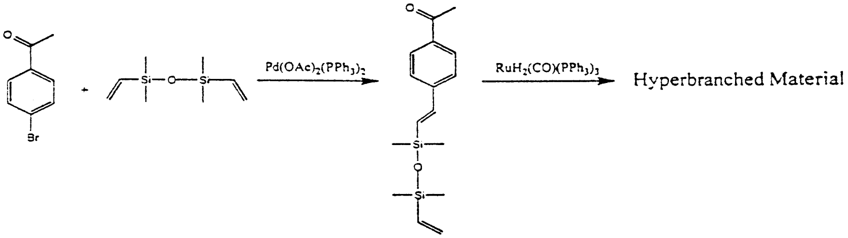
Summary

Treatment of 1-ß-(4'-acetylphenyl)vinyl-3-vinyl-1,1,3,3-tetramethyldisiloxane (**I**) (an AB_2 monomer)with dihydridocarbonyl*tris*(triphenylphosphine)ruthenium (**Ru**) leads to a hyperbranched material, poly[1-ß-(4'-acetylphenyl)vinyl-3-vinyl-1,1,3,3-tetramethyldisiloxane](**II**). **I** has been prepared by a Pd catalyzed Heck reaction between 4-bromoacetophenone and 1, 3-divinyl-1,1,3,3-tetramethyldisiloxane. The structure of the soluble hyperbranched material (**II**) has been determined by ^{1}H, ^{13}C and ^{29}Si NMR, as well as by IR and UV spectroscopy. It has also been characterized by GPC, TGA, DSC and elemental analysis. Polymerization occurs by **Ru** catalyzed addition of the aromatic C-H bonds which are *ortho* to the activating acetyl group of **I** across the C-C double bond of the terminal Si-vinyl group in an anti-Markovnikov manner.



Introduction

Macromolecules which are extensively branched command substantial interest due to their exceptional properties and potential applications [1-4]. These can be divided into three major subgroups: branched polymers, dendrimers and hyperbranched materials. The preparation of dendrimers which have a regular, orderly, controlled pattern of branching involves multistep, consecutive synthesis. By comparison, hyperbranched materials do not have a well defined architectural structure, but rather an irregular pattern of branching. From a technological point of view, hyperbranched materials are of interest since they can be prepared in a single step from a monomer which has two mutually reactive functional groups A and B, present in a ratio such as AB_2, by reaction of these with each other. Despite these differences, chemically related dendrimers and hyperbranched materials often have similar properties.

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Transition metal organometallic chemistry is an active area of research in organic synthetic method development. These new reactions are beginning to be applied to polymer synthesis. For example, Pd catalyzed reactions have been utilized to prepare hyperbranched materials. Among these are the *tetrakis*(triphenylphosphine)Pd(0) catalyzed Suzuki reaction of (3,5-dibromophenyl) boronic acid which yields a hyperbranched polyphenylene material [4,5], as well as the Pd(0) catalyzed coupling of aryl halides with terminal acetylenes, the Sonogashira procedure, which gives dendridic poly(phenylacetylenes) [6,7].

We have previously shown that acetophenone undergoes **Ru** catalyzed step-growth copolymerization with certain α,ω-dienes [8-11]. The first application of this reaction to prepare hyperbranched materials has been recently reported [12]. In these reactions, acetophenone serves as a difunctional monomer since the acetyl group activates both of the *ortho* C-H bonds. By analogy, 1-β-(4'-acetylphenyl)vinyl-3-vinyl-1,1,3,3-tetramethyldisiloxane (**I**) should be a suitable AB_2 monomer for the synthesis of hyperbranched materials in that it contains two reactive C-H bonds which are *ortho* to the activating carbonyl group but only a single reactive terminal vinyl group. While **I** has two C-C double bonds, we anticipated that only the terminal one would be reactive since we have previously shown that internal C-C double bonds, such as those in stilbene systems, are not reactive in such **Ru** catalyzed reactions [13].

Experimental

^{1}H and ^{13}C NMR spectra were obtained on a Bruker AC-250 spectrometer operating in the Fourier Transform mode. ^{29}Si NMR spectra were recorded on an IBM Bruker WP-270-SY spectrometer. Five percent w/v solutions in chloroform-*d* were used to obtain ^{1}H and ^{13}C NMR spectra. These were internally referenced to residual chloroform. ^{13}C NMR spectra were run with broad band proton decoupling. Fifty percent w/v solutions in acetone-d_6 were used to obtain ^{29}Si NMR spectra. A heteronuclear gated decoupling pulse sequence (NONOE) with a 20 sec delay was used to acquire ^{29}Si NMR [14]. They were externally referenced to TMS. IR spectra of neat films on NaCl plates were recorded on an IBM FT-IR spectrometer. UV spectra were acquired on a Shimadzu UV-260 ultraviolet visible spectrometer. Solutions of cyclohexane/acetone (3/1) were used for the determination of the UV spectra.

Gel permeation chromatography (GPC) analysis of the molecular weight distribution of soluble-**II** was performed on a Waters system. Two 7.8 mm x 300 mm Styragel columns HR4 and HR2 in series were used for the analysis. The eluting solvent was toluene at a flow rate of 0.3 mL/min. The retention times were calibrated against known monodisperse polystyrene standards (929,000, 212,400, 47,500, 13,700, 794). The glass transition temperature (T_g) of the hyperbranched material **II** was determined on a Perkin-Elmer DSC-7 instrument. The mp of indium (156°C) was used to calibrate the DSC. The analysis program was - 30°C for 30 min followed by an increase in temperature of 10°C/min to 100°C. TGA of the polymers was measured on a Shimadzu TGA-50 instrument. The temperature program was 5.0 °C/min from 25°C to 750°C. The temperature was held at 750°C for an additional 5 min.

Elemental Analysis were run by Oneida Research Services Inc., Whitesboro, NY.

High Resolution mass spectra were run at the University of California Riverside Mass Spectrometry Facility on a VG-7070 EHF instrument. Ammonia was used as the chemical ionization agent.

Reagents

All reactions were carried out in flame-dried glassware under an atmosphere of purified argon. 4-Bromoacetophenone, styrene, tributylamine, triphenylphosphine and Pd(II) acetate were obtained from Aldrich. 1,3-Divinyltetramethyidisiloxane was acquired from Gelest. The catalyst dihydridocarbonyltris(triphenylphosphine)ruthenium (**Ru**) was prepared from ruthenium trichloride hydrate (Aldrich) [15].

1-β-(4'-Acetylphenyl)vinyl-3-vinyl-1,1,3,3-tetramethyldisiloxane (I)

4-Bromoacetophenone (11.54 g, 58 mmol), 1,3-divinyltetramethyldisiloxane (15.13 g, 81 mmol), K_2CO_3 (11.19 g, 81 mmol), tributylamine (1.07 g, 5.8 mmol), triphenylphosphine (0.30 g, 1.16 mmol) and Pd (II) acetate (0.130 g, 0.58 mmol) were added to 75 mL of water. The mixture was heated at 100°C for 24 h. Following work-up, fractional distillation (bp 107°C/55 torr) gave a colorless oil 7.05 g (40% yield). ^{1}H NMR δ: 0.16 (s, 6H), 0.22 (s, 6H), 2.53 (s, 3H), 5.72 (dd, 1H, J = 20 and 4 Hz), 5.92 (dd, 1H, *J* = 15 and 4 Hz), 6.12 (dd, 1H, *J* = 20 and 15 Hz), 6.53 (d, 1H, *J* = 19 Hz), 6.94 (d, 1H, *J* = 19 Hz), 7.46 (d, 2K *J* = 9 Hz), 7.87 (d, 2H, *J* = 9 Hz). ^{13}C NMR δ: 0.28, 0.60, 26.34, 126.38, 128.50, 131.65, 132.03, 136.28, 139.13, 142.28, 142.82, 197.05. ^{29}Si NMR δ: -2.19, -2.73. IR ν: 3048, 2997, 2959, 2894, 1685, 1603, 1407, 1358, 1295, 1267, 1256, 1215, 1197, 1177, 1053, 1012, 989, 957, 841, 803 cm^{-1}. UV: λ_{nm} (ε) = 316 (310). Elemental anal. Calc. for $C_{16}H_{24}O_2Si_2$: C, 63.16; H, 7.90. Found: C, 62.62; H, 8.16. High resolution mass spectra (M+.) Calc. for $C_{16}H_{24}O_2Si_2$: 305.1393. Found: 305.1379.

poly[1-β-(4'-Acetylphenyl)vinyl-3-vinyl-1,1,3,3-tetramethyldisiloxane] - Soluble-II

Ru (80 mg, 0.081 mmol), I mL toluene, styrene (8 µL, 0.81 mmol) and a Teflon covered magnetic stir bar were placed in an Ace pressure tube. The tube was purged with argon, capped, and heated at 135 °C for 3 min. Following cooling to room temperature, **I** (700 mg, 2.3 mmol) was dissolved in 3 mL of toluene. The solution was added and the reaction mixture was heated at 135°C for 48 h. Toluene was removed under reduced pressure and the residue was taken up in a minimal amount of THF. Methanol was added to precipitate the polymer. This was repeated three times, as to give 613 mg (87% yield), M_w/M_n = 20,800/7,770, T_g = 2.7°C. ^{1}H NMR δ: 0.11 (s, 2H), 0.15 (s, 3.3H), 0.23 (s, 3.1H), 0.24 (s, 3,6H), 0.87 (br. m, 2H), 2.42 (s, 0.55H), 2.47 (s, 0.32H), 2.53 (s, 1.63H), 2.57(s, 0.5H) 2.88 (br. m, 2H), 6.50 (d, 0.5H, *J*= 19 Hz), 6.52 (d, 0.5H, *J* = 19 Hz), 6.90 (d, 0. 5H, *J* = 20 Hz), 6.91 (d, 0. 5H, *J* = 19 Hz), 7.12 (s, 0.3H), 7.29 (s, 0. 76H), 7.33 (d, 0. 78H, *J* = 8 Hz), 7.50 (d, 0. 35H, *J* = 8 Hz), 7.60 (d, 0. 56H, *J* = 7 Hz), 7.89 (d, 0.25FL, *J* = 8 Hz). ^{13}C NMR δ: 0.09, 0.27, 0.31, 0.80, 0.85, 1.21, 20.78, 26.67, 27.90, 29.65, 32.93, 123.34, 124.23, 126.55, 128.13, 128.63, 128.79, 128.93, 129.96, 130.08, 131.24, 131.52, 140.91, 141.03, 143.04, 143.16, 146.23, 197.45, 200.97, 207.87. Off resonance ^{13}C NMR 5: 20.78 (t), 26.67 (t), 27.90(t), 29.65 (q), 32.93 (q). ^{29}Si NMR δ: -2.90, -2.62, 8.12, 8.47. IR ν: 2986, 2956, 2889, 1699, 1695, 1684, 1601, 1558, 1408, 1355, 1253, 1199, 1177, 1055, 987, 842, 804 cm^{-1}. UV λ_{nm} (ε): 317 (933). Elemental anal. Calc. for $C_{16}H_{24}O_2Si_2$: C, 63.16; H, 7.90. Found: C, 62.58; H, 7.77.

Insoluble-II

Ru (33 mg, 0.033 mmol), 1 mL toluene, and **I** (0.5 g, 1.6 mmol) and a Teflon covered magnetic stir bar were placed in an Ace pressure tube. The tube was purged with argon, capped, and heated at 135 °C for 24 h. A dark, glassy material was recovered. The material was insoluble in common organic solvents (DMSO, acetone, toluene, chloroform, acetonitrile, DMF), as well as hexamethyldisiloxane. The insoluble material was stirred in THF for 24 h to extract trapped toluene solvent and/or unreacted monomer or oligomers.

Results and Discussion:

Examples of the **Ru** catalyzed *ortho* alkylation of acetophenone by vinylsilanes were first reported by Murai [16,17]. This reaction involves the addition of the activated *ortho* C-H bond across the C-C double bond of the vinyl silane in an anti-Markovnikov manner. We have applied this reaction to prepare linear copolymers by **Ru** catalyzed reactions between acetophenones and α,ω-dienes such as 1,3-divinyltetramethyldisiloxane. Similar reactions with 4-acetylstyrene lead to hyperbranched material [12].

We have efficiently prepared **I** by a Pd catalyzed Heck reaction of 4-bromoacetophenone with 1,3-divinyl-1,1,3,3-tetramethyl disiloxane [18,19]. Excess triphenylphos phine is essential to achieve reasonable yields of **I** in this aqueous system.

We have carried out polymerization of **I** with a **Ru** catalyst which has been activated by treatment of **Ru** with a stoichiometric amount of styrene at 135°C. Hydrogenation of styrene by **Ru** gives ethylbenzene and results in quantitative loss of hydrogen from **Ru**. This generates a coordinately unsaturated active catalyst. After 3 min. the catalyst was cooled and **I** was added. Alternatively we have directly combined **I** with **Ru**. Similar results were obtained in both cases. Reaction of **I** with **Ru** at high concentration led to an insoluble-**II**.

The molecular weight distribution of soluble-**II** was obtained by GPC, calibrated versus linear PS standards, has been compared to that determined by NMR end group analysis. It is often the case that molecular weights determined by GPC of hyperbranched materials are low [20]. End group analysis is possible because hyperbranched materials prepared from an AB_2 type monomer have a single A group in each macromolecule [21]. Integration of the ^1H NMR of the terminal vinyl protons ($-CH=C\underline{H}_2$, 5.70-5.95 ppm) compared to the methylene-($-CH_2-CH_2$ 0.87 and 2.89 ppm) protons permits independent determination of M_n which is found to be equal to 12,200 [22]. In this case, NMR end group analysis yields a value for Mn which is ~ sixty percent larger than does GPC M_n = 7,700.

The structure of soluble-**II** can be deduced from ^1H, ^{13}C, off resonance ^{13}C and ^{29}Si NMR spectra. Anti-Markovnikov regioselectivity is observed in the **Ru** catalyzed addition of the *ortho* C-H bonds across the terminal C-C double bond. The $-CH_2-CH_2-$ units thus formed give rise to two broad peaks of equal intensity at 0.87 and 2.88 ppm. The former is assigned to the CH_2 which is adjacent to silicon while the latter results from the benzylic CH_2, bonded to the aromatic ring. No evidence for Markovnikov orientation of addition is observed.

The methylene groups give rise to three signals (20.78, 26.67, and 27.90 ppm) in the ^{13}C NMR, each of which is split to a triplet in the off resonance ^{13}C NMR. The signal at 20.78 ppm is assigned to the methylene adjacent to silicon, while those at 26.67 and 27.90 ppm are assigned to benzylic methylenes. Apparently, these are sensitive to the degree of substitution about the acetyl group. The methyl group gives rise to signals in the ^1H NMR 2.42, 2.47, 2.53 ppm. However, only two signals (29.65 and 32.93 ppm) are detected in the ^{13}C NMR. Each of these is split to a quartet in the off resonance ^{13}C NMR spectra. The reason that a third signal for a methyl group is not detected in the ^{13}C NMR is not certain. Possibly there may be fortuitous overlap of signals. As expected, three signals are observed for the carbonyl carbon in the ^{13}C NMR at 207.9, 201.0, and 197.5 ppm. These can be assigned on the basis of ^{13}C NMR of C=O carbons of model compounds: 4-methylacetophenone (196.2 ppm), 2,4-dimethylacetophenone (199.2 ppm) and 2,4,6-trimethylacetophenone (206.6 ppm). Thus the signal at 197.5 ppm results from terminal units which have no alkyl groups *ortho* to the carbonyl, while that at 201.0 ppm results from monosubstituted units, and that at 207.9 ppm is attributed to disubstituted units which occur at branch points. Integration of these signals suggests that the polymer structure is ~66% linear, ~26% branched and ~8% pendant groups.

Further, the ^{29}Si NMR spectral data suggests that there are four different types of silicons (-2.90, -2.62, 8.12, and 8.47 ppm). The former result from silicons which are bonded to vinyl carbons, while the latter result from silicon which is bonded to an alkyl group. Clearly, the extent of substitution (mono or di) on the aromatic ring affects the chemical shift of the silicon atoms.

The structure of soluble-**II** consistent with the spectral data is shown (Figure 1).

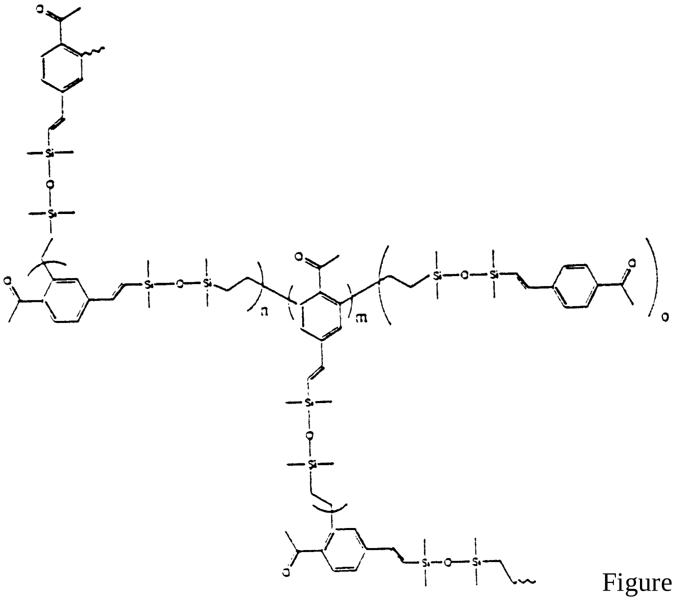

Figure 1

Both soluble and insoluble-**II** are thermally stable to about 200° by TGA. Between 200 and 300°C both lose about five percent of their initial weight. Above 300°C, rapid weight loss occurs. By 470°C both soluble and insoluble-**II** have lost forty percent of their initial weight. Above this temperature, soluble-**II** continues to rapidly lose weight until 580°C at which point it has lost approximately 82% of its initial weight. By comparison, above 470°C, insoluble-**II** loses weight much more slowly. By 750°C, approximately 51% of insoluble-**II**'s initial weight remains as a black glassy brittle residue. Apparently increased chain branching leads to insolubility and increased thermal stability. (Figure 2)

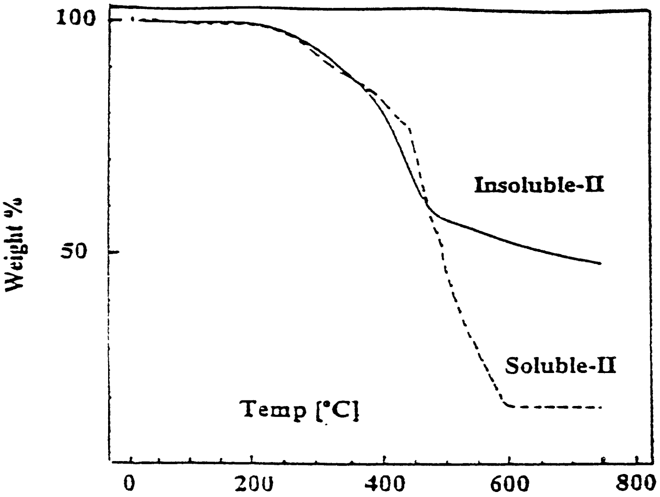

Figure 2

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