

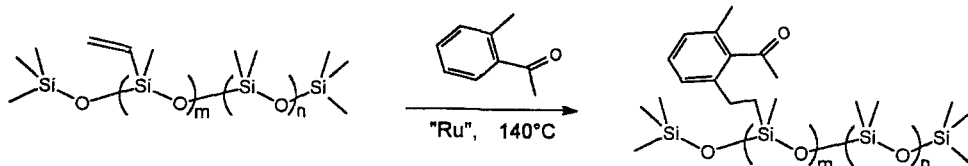
Ruthenium catalyzed chemical modification of unsaturated polymers

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Summary

Chemical modification of unsaturated polysiloxanes with pendant or terminal vinyl groups and polycarbosilanes with pendant Si-vinyl groups has been achieved by a novel ruthenium catalyzed reaction. Dihydridocarbonyltris(triphenylphosphine)-ruthenium catalyzes the addition of the *ortho* C-H bond of 2'-methylacetophenone across the C-C double bond of pendant or terminal vinyl groups of polymers such as copoly(dimethylsiloxane/vinylmethylsiloxane), polydimethylsiloxane which is terminated with vinyl dimethylsiloxy groups and copoly(vinylmethylsilylene/1,4-phenylene).



Introduction

There is significant current interest in the chemical modification of polymers.¹⁻³ This often permits the preparation of polymers which cannot be prepared by direct polymerization of monomers. While the use of selective transition metal catalyzed reactions in organic synthesis has become routine,^{4,5} the use of such reactions for chemical modification of polymers has received considerably less attention. Nevertheless, successful homogeneous rhodium catalyzed $[(\text{Ph}_3\text{P})_3\text{RhCl}]$ hydrogenation, hydrosilation and hydroformylation of unsaturated polymers with pendant vinyl groups, such as 1,2-polybutadiene, have been reported.^{6,7}

In this communication, we report the dihydridocarbonyltris(triphenylphosphine) ruthenium catalyzed addition of the *ortho* C-H bond of 2'-methylacetophenone across C-C double bonds of three polymers. In this manner, copoly(dimethylsiloxane/vinylmethylsiloxane) which is terminated with trimethylsiloxy groups is modified to yield copoly[dimethylsiloxane/2-(2'-acetyl-3'-methylphenyl)ethylmethylsiloxane]. Likewise, polydimethylsiloxane which has vinyl dimethylsiloxy end groups is converted to polydimethylsiloxane with 2-(2'-acetyl-3'-methylphenyl)ethyl dimethylsiloxy end groups. Finally, addition of 2'-methylacetophenone across the C-C double bonds of pendant

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Si-vinyl groups of copoly(vinylmethylsilylene/1,4-phenylene) yields copoly-[2-(2'-acetyl-3'-methylphenyl)ethylmethylsilylene/1,4-phenylene]. The fact that the two polysiloxane modifications are conducted without solvent is noteworthy.

Experimental / Spectroscopic

^1H and ^{13}C NMR spectra were obtained on either a Bruker AC-250 or an AM-360 spectrometer operating in the Fourier Transform mode. ^{29}Si NMR spectra were recorded on a Bruker AM-360 spectrometer. Ten percent weight/volume solutions of polymer in chloroform-*d* were used to obtain NMR spectra. ^{13}C NMR spectra were run with broad band proton decoupling. A heteronuclear gate decoupling pulse sequence (INVGATE) with a 30 sec delay was used to acquire ^{29}Si NMR spectra.⁸ These were internally referenced to TMS. Chloroform was used as an internal standard for ^1H and ^{13}C NMR spectra. IR spectra of neat films on NaCl plates were recorded on an IBM FT-IR spectrometer. UV spectra of cyclohexane solutions were acquired on a Shimadzu UV-260 ultraviolet visible spectrometer.

Molecular Weight Distributions

Gel permeation chromatographic (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 detector and a model 820 Maxima control system. A series of three 7.8 mm x 30 cm columns packed with < 10 μm particles of monodisperse crosslinked styrene-divinyl benzene copolymer. These contain pore sizes of 1×10^4 Å (Waters Ultrastaygel), 1×10^3 Å (Waters Ultrastaygel) and finally 500 Å (Polymer Laboratories PLgel). For siloxane polymers, the eluting solvent was HPLC grade toluene at a flow rate of 1.5 mL/min, whereas for the polycarbosilanes HPLC grade THF at a flow rate of 1 mL/min was used. The retention times of siloxane polymers were calibrated against those of known monodisperse polydimethylsiloxane standards: M_w 265,000; 90,500; 17,800; 5,800 and 3,200 whose M_w/M_n are less than 1.30. On the other hand, for the polycarbosilanes known monodisperse polystyrene standards: M_w 612,000; 114,200; 47,500; 18,700; 5120; 2,200 and 794 whose M_w/M_n are less than 1.09 were used.

Differential Scanning Calorimetry (DSC)

The glass transition temperatures (T_g 's) were determined by DSC on a Perkin-Elmer DSC-7 instrument. The melting point of indium (mp 156.6 °C) and the melting point of water (mp 0°C) was used to calibrate the DSC. The program for the analysis was -150°C for 10 min followed by an increase in temperature of 20°C/min to 150°C.

All reactions were conducted in flame dried glassware under an atmosphere of purified argon. THF was distilled immediately prior to use from a deep blue solution of sodium benzophenone ketyl.

Dihydridocarbonyltris(triphenylphosphine)ruthenium (Ru complex) was prepared from ruthenium trichloride following literature procedures.⁹

Poly(dimethylsiloxane) $M_w/M_n = 63,000/57,000$ which has 1% vinyl dimethylsiloxy terminal groups by ^1H NMR integration and a viscosity of 100 centistokes was obtained from Hüls America Inc. ^{29}Si NMR δ : -21.89, -20.89, -4.06.

Copoly(dimethylsiloxane/vinylmethylsiloxane) $M_w/M_n = 93,000/91,000$, $T_g = -120^\circ\text{C}$ which has trimethylsiloxy terminal groups and which contains 8% vinyl groups by ^1H NMR integration and a viscosity of 1000 centistokes was obtained from Hüls America Inc. ^{29}Si NMR δ : -35.85, -21.89, -21.42, 7.27.

Copoly[**dimethylsiloxane/2-(2'-acetyl-3'-methylphenyl)ethylmethylsiloxane**]

Copoly(dimethylsiloxane/vinylmethylsiloxane) (3.87 g, 4.5 mmol of vinylmethyl siloxane units), Ru complex (0.1 g, 0.11 mmol), 2'-methylacetophenone (0.8 g, 6.0 mmol) and a Teflon covered magnetic stirring bar were placed in an Ace #15 high pressure reaction tube. The tube was sealed with its Teflon threaded O-ring seal. The tube and its well stirred contents were heated for 26 h at 140°C. The product polymer was precipitated twice from THF with methanol. In this way, 4.2 g, 94% yield of modified copolymer $M_w/M_n = 126,000/107,000$ was isolated. $^1\text{H NMR } \delta$: 0.03(s,72H) 0.78-0.82(m,2H), 2.21(s,3H), 2.43(s,3H), 2.48-2.53(m,2H), 6.97(d,1H, J=3.6 Hz), 7.04(d,1H, J=3.6 Hz), 7.15(dd,1H, J=3.6 Hz). $^{13}\text{C NMR } \delta$: -0.64, 1.03, 19.10, 19.29, 26.36, 32.48, 126.04, 127.64, 128.82, 132.01, 139.89, 141.84, 208.00. $^{29}\text{Si NMR } \delta$: -24.05, -21.87, -21.61, -21.75, 7.22. IR ν : 3066, 2964, 2906, 1703, 1596, 1462, 1413, 1352, 1262, 1182, 1094, 1021, 801, 704, 586 cm^{-1} . UV λ_{max} nm (ϵ): 309(52), 270(72), 217(780).

Polydimethylsiloxane terminated with **2-(2'-acetyl-3'-methylphenyl)ethyl-dimethylsiloxy groups**

Poly(dimethylsiloxane) with vinyl dimethylsiloxy ends groups (1.59 g, 0.2 mmol of vinyl terminal groups, 1%), Ru complex (0.1 g, 0.11 mmol), and 2'-methylacetophenone (0.48 g, 3.6 mmol) were reacted as above. After purification, 1.6 g of modified poly(dimethylsiloxane) $M_w/M_n = 74,000/70,400$ was obtained. $^1\text{H NMR } \delta$: 0.04(s, 330H), 0.31(m,2H), 2.23(s,3H), 2.46(s,3H), 2.48-2.54(m,2H), 6.98(d,1H, J = 3.6 Hz), 7.04(d,1H, J = 3.6 Hz), 7.17(t,1H, J = 3.6 Hz). $^{13}\text{C NMR } \delta$: 0.64, 1.08, 19.11, 19.90, 26.37, 32.68, 126.04, 127.63, 128.62, 132.01, 139.69, 141.88, 208.01. $^{29}\text{Si NMR } \delta$: -21.91, -21.12, 6.67. IR ν : 2964, 2906, 1737, 1658, 1640, 1552, 1537, 1446, 1413, 1353, 1262, 1096 (s), 1023 (s), 865, 802 (s), 703, 661 cm^{-1} . UV λ_{max} nm (ϵ): 273(50).

Copoly(**vinylmethylsilylene/1,4-phenylene**)

A 2 L three necked round bottom flask was equipped with a pressure equalizing addition funnel, an efficient reflux condenser and a Tru-bore stirrer equipped with a Teflon paddle. Magnesium turnings (24.3 g, 1 mol), 1,2-dibromoethane (0.2 g, 1 mmol) and THF (500 mL) were placed in the flask. A solution of 1,4-dibromobenzene (117.9 g, 0.5 mol) dissolved in THF (200 mL) was placed in the addition funnel and was slowly added to the well stirred slurry of magnesium turnings in THF. After the addition was complete (3 h), the mixture was stirred for an additional 14 h. A solution of vinylmethyl dichlorosilane (62 mL, 0.48 mol) and THF (100 mL) was placed in the addition funnel and was added to the solution of di-Grignard reagent over 3 h. The reaction was stirred for an additional 24 h. After aqueous work-up, the organic solution was dried over anhydrous magnesium sulfate, filtered and the volatile solvents removed by evaporation under reduced pressure. The crude polymer was dissolved in a minimum amount of THF and was precipitated from methanol. This process was repeated three times. In this way, 40 g, 69% yield of polymer $M_w/M_n = 6280/1520$, $T_g = 8^\circ\text{C}$ was obtained. $^1\text{H NMR } \delta$: 0.75 (s,3H), 5.92(dd, 1H, J = 20.0, 3.3 Hz), 6.31(dd,1H, J = 14.5, 3.3 Hz), 6.60(dd,1H, J = 20.0, 3.3 Hz) 7.49(s,1.5H), 7.65(s,3.5H). $^{13}\text{C NMR } \delta$: -4.36, -4.26, 127.81, 129.31, 133.18, 133.74, 134.08, 134.40, 134.79, 134.98, 135.02, 135.29, 135.48, 135.62, 136.00, 136.49, 137.22, 137.39. $^{29}\text{Si NMR } \delta$: -14.50, -14.60. IR ν : 3051, 3001, 2961, 1592, 1429, 1404, 1381, 1253, 1133, 1112, 1068, 1008, 959, 910, 782, 752, 733, 700, 649, 634 cm^{-1} . UV λ_{max} (ϵ): 266(1,344), 230(6,590).

Copoly[methyl-2-(2'-acetyl-3'-methylphenyl)ethylmethylsilylene/1,4-phenylene]

Copoly(vinylmethylsilylene/1,4-phenylene) (0.3 g, 2 mmol), Ru complex (40 mg, 0.04 mmol), 2'-methylacetophenone (Aldrich) (0.4 g, 3 mmol), xylene (5 mL) and a Teflon covered magnetic stirring bar were placed in a 15 cc high pressure tube which was sealed under vacuum. The tube and its contents were heated in an oil bath at 140°C for 48 h. The color of the reaction mixture changed from colorless to black. The tube was opened and the solvent and excess 2'-methylacetophenone was removed by evaporation under reduced pressure. Ether (5 mL) was added to extract the product from the catalyst residue. This was repeated three times. After filtration, the ether was removed by evaporation under reduced pressure. The copolymer was purified three times by precipitation from a minimum amount of THF with methanol. In this way, 0.48 g, 80% yield, $M_w/M_n = 8050/1660$, $T_g = 26^\circ\text{C}$ was obtained. $^1\text{H NMR } \delta$: 0.55(br.s,3H), 1.31-1.36(br.s,2H), 2.19(s,3H), 2.28(s,3H), 2.45-2.52 (br.s,2H), 6.99-7.03(br.s,1H), 7.11-7.14(br.s,1H), 7.34(br.s,1H), 7.48(s,4H). $^{13}\text{C NMR } \delta$: -4.79, 17.00, 19.09, 27.34, 32.35, 126.15, 127.74, 127.89, 128.65, 129.31, 132.06, 133.28, 133.80, 134.43, 137.58, 139.52, 141.79, 208.34. $^{29}\text{Si NMR } \delta$: -7.43, -9.96 (s). IR ν : 3055, 3000, 2957, 1698, 1594, 1501, 1462, 1429, 1415, 1381, 1353, 1256, 1177, 1134, broad peak 1120-1000, 988, 962, 910, 782, 735, 700 cm^{-1} . UV $\lambda_{\text{max}} (\epsilon)$: 265 (4,500), 240(16,000).

Results

The ruthenium catalyzed addition of the *ortho* C-H bond of 2'-methylacetophenone across the pendant and terminal vinyl groups of siloxane polymers and the pendant Si-vinyl groups of the polycarbosilane reported herein is regiospecific. The *ortho* hydrogen of 2'-methylacetophenone becomes attached to the more substituted vinyl carbon while the 2'-acetyl-3'-methylphenyl group becomes attached to the terminal vinyl carbon. This regiospecificity can be seen in the $^1\text{H NMR}$ of copoly-[dimethylsiloxane/2-(2'-acetyl-3'-methylphenyl)ethylmethylsiloxane] (See Figure 1).

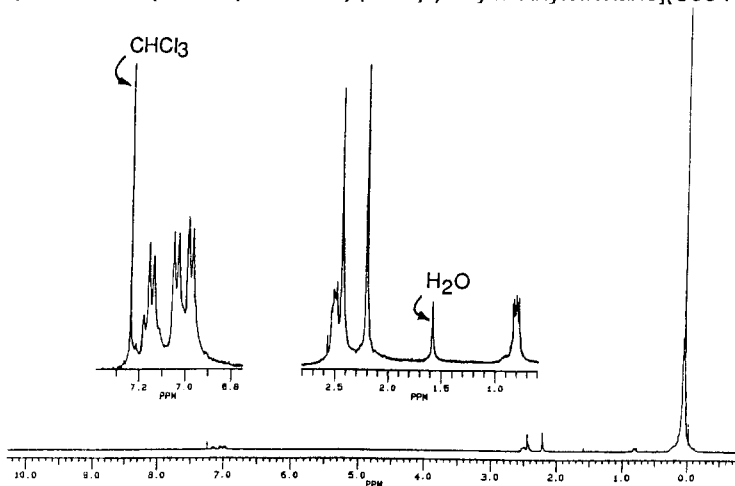


Figure 1.

$^1\text{H NMR}$ of copoly-[dimethylsiloxane/2-(2'-acetyl-3'-methylphenyl)-ethylmethylsiloxane]

The molecular weights by GPC of the product siloxane polymers are higher than those of the starting unsaturated siloxane polymers. However, both starting and product siloxane polymer molecular weights are higher than the molecular weights calculated on the basis of ^1H NMR integration of the vinyl groups versus the methyl groups bonded to silicon. The reason for this consistent difference is not obvious. We believe that the end group analysis by ^1H NMR integration is a more accurate representation of the molecular weights of the polymers. No such problem is observed for the polycarbosilanes.

^{29}Si NMR is highly characteristic for both the starting unsaturated polysiloxanes and for the modified product polysiloxanes. Four signals are observed in the ^{29}Si NMR of copoly(dimethylsiloxane/vinylmethylsiloxane). The signal at 7.27 ppm is assigned to the terminal trimethylsiloxy groups, while the resonance at -35.85 ppm is assigned to the vinylmethylsiloxane units. Due to the low percentage (8%) of vinylmethylsiloxane units, triad analysis predicts that these units will have dimethylsiloxane units on either side. No resonance due to triads in which vinylmethylsiloxane units have a vinylmethylsiloxane unit on one side and a dimethylsiloxane unit on the other are observed. The most intense signal at -21.89 ppm is assigned to triads in which the dimethylsiloxane units which have dimethylsiloxane units on either side. On the other hand, the less intense resonance at -21.42 ppm is attributed to triads in which dimethylsiloxane units have dimethylsiloxane unit on one side and a vinylmethylsiloxane unit on the other.

The ^{29}Si NMR signals for the chemically modified copoly[dimethylsiloxane/2-(2'-acetyl-3'-methylphenyl)ethylmethylsiloxane] can be assigned in a similar manner. The signal at 7.22 ppm is most probably due to the trimethylsiloxy terminal groups, while the resonance at -24.05 ppm is due to the 2-(2'-acetyl-3'-methylphenyl)ethylmethylsiloxane units. Only a single resonance is observed since only triads in which the 2-(2'-acetyl-3'-methylphenyl)ethylmethylsiloxane units have dimethylsiloxane units on either side are probable. On the other hand, three signals for dimethylsiloxane units are detected. The most intense signal at -21.87 ppm results from triads in which dimethylsiloxane units have dimethylsiloxane units on either side. The signal at -21.75 ppm results from dimethylsiloxane units which have a dimethylsiloxane unit on one side and a 2-(2'-acetyl-3'-methylphenyl)ethylmethylsiloxane unit on the other. The final signal at -21.61 ppm results from dimethylsiloxane units which have either a 2-(2'-acetyl-3'-methylphenyl)ethylmethylsiloxane units on both sides or which are adjacent to trimethylsiloxy end groups.

The ^{29}Si NMR signals of poly(dimethylsiloxane) which has terminal vinyl dimethylsiloxy groups can be analyzed in a similar manner. The low intensity signal at -4.06 ppm is assigned to the vinyl dimethylsiloxy end groups. The small resonance at -20.84 ppm is attributed to the dimethylsiloxane unit adjacent to the vinyl dimethylsiloxy end group. Finally, the intense resonance at -21.89 ppm is assigned to triads in which dimethylsiloxane units have dimethylsiloxane units on either side.

The ^{29}Si NMR signals of the chemically modified polymer have similarly been assigned. The signal at 6.67 ppm is due to the 2-(2'-acetyl-3'-methylphenyl)ethyl dimethylsiloxy end groups. The resonance at -21.12 is assigned to dimethylsiloxane units which are adjacent to the end groups. Finally the dimethylsiloxane units which have dimethylsiloxane units on either side are observed at -21.91 ppm.

The ^{29}Si NMR of copoly(vinylmethylsilylene/1,4-phenylene) has two resonances at -14.50 and -14.60 ppm. The latter is most intense. The major signal in the

^{29}Si NMR of the product carbosilane copolymer is at -7.43 ppm. The resonance at -9.96 ppm is quite small. A signal at -21.84 ppm occurs in tandem with a signal at -1.01 ppm in the ^{13}C NMR. Both are probably related to siloxane formation which occurs by cleavage of the phenyl-Si bond by protodesilation during work-up unless care is taken to quench traces of acid.

The UV absorptivities reported are calculated based on the average molar weight of a single polymer unit. For example, the copoly[dimethylsiloxane/2-(2'-acetyl-3'-methylphenyl)ethylmethylsiloxane] average unit weight was calculated by multiplying each unit's molar weight by its percent incorporation determined from the ^1H NMR integration.

Discussion

These reactions are related to the ruthenium catalyzed regioselective copolymerization of acetophenone and α,ω -dienes.¹⁰ In these polymerization reactions acetophenone acts as a difunctional monomer. The acetyl group activates both C-H bonds *ortho* to itself. Ruthenium catalyzed reactions between acetophenone and terminal alkenes to yield monomeric *ortho* alkyl substituted acetophenones have also been recently reported.¹¹

Similar reactions between unsaturated polymers substituted with pendant vinyl groups and acetophenone leads to crosslinked thermoset materials.¹² This is reasonable if acetophenone acts as a difunctional crosslinking reagent. These crosslinking reactions and the materials thereby produced are under active investigation. 2'-Methylacetophenone permits successful chemical modification of unsaturated polymers because it only has a single *ortho*-C-H bond which can undergo reaction.

This novel method of chemical modification of unsaturated polymers is not without its problems. Attempts to carry out ruthenium catalyzed reactions between 2'-methylacetophenone and polybutadiene with a high percentage (85%) of pendant 1,2-vinyl units resulted in only very low incorporation of 2'-methylacetophenone units. In this case, the pendant 1,2-vinyl groups were isomerized to internal trisubstituted C-C double bonds.

Mechanistically these reactions may be related to the palladium catalyzed Heck reactions of aryl halides with alkenes.^{13,14} Insertion of palladium into the C-X bond of the aryl halide leads to a reactive Aryl-Pd-X species which is the key intermediate in these reactions. Apparently, in the reaction reported herein the acetyl group directs the insertion of the coordinately unsaturated ruthenium into the adjacent C-H bond. This leads to an aryl ruthenium hydride intermediate. Coordination of a pendant or terminal C-C double bond of the polymer to the ruthenium center followed by regioselective addition of the Aryl-Ru and Ru-H bonds across the coordinated C-C double bond followed by reductive elimination of the product serves to regenerate the coordinately unsaturated catalytic ruthenium species and complete the catalytic cycle.

The attachment of 2'-methylacetophenone units to these siloxane polymers provides a chromophore which absorbs UV light between 280 and 250 nm. Monomeric *ortho*-alkylacetophenones have been previously shown to undergo photoenolization. This occurs when the photo-excited triplet state of the carbonyl abstracts a hydrogen from the *ortho*-alkyl group via a cyclic six-membered ring transition state to yield the enol. 1,3-Tautomerization of the enol regenerates the acetophenone.¹⁵⁻¹⁷

This process accounts for the unusual UV photostability of *ortho* alkylacetophenones. This reversible photochemical process may permit polysiloxanes chemically modified with 2'-methylacetophenone units to serve as UV protective coatings. Photochemical studies of these polymers are in progress.

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