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Ruthenium catalyzed regioselective step-growth copolymerization of 4′-methoxyacetophenone, or 4′-phenoxyacetophenone and *α,ω*-dienes

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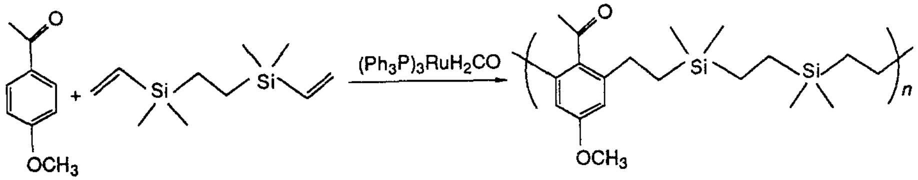
Summary

Ruthenium catalyzed step growth copolymerization of 4'-methoxyacetophenone or 4'-phenoxyacetophenone and α,ω-dienes such as 1,3-divinyltetramethyldisiloxane or 3,3,6,6-tetramethyl-3,6-disila-1,7-octadiene give copolymers which have respectable molecular weights. The synthesis and characterization of these copolymers is reported. Higher molecular weight copolymers are quite thermally stable.



Introduction

Murai et al. have reported that dihydridocarbonyl*tris*(triphenylphosphine)ruthenium (Ru) catalyzes the addition of the *ortho* C-H bonds of acetophenone across the C-C double bonds of olefins such as trimethylvinylsilane to yield *ortho* alkyl substituted acetophenones (1-3). We have shown that this reaction can be applied to achieve step-growth copolymerization (cooligomerization) of aromatic ketones and α,ω-dienes. For example, reaction of divinyldimethylsilane and acetophenone catalyzed by Ru at 150°C yields copoly(3,3-dimethyl-3-sila-1,5-pentanylene/2-aceto-1,3-phenylene), M_w/M_n = 3500/2430, in 70% yield (4). We have carried out similar copolymerization reactions between anthrone, fluorenone or xanthone and α,ω-dienes such as 3,3,6,6-tetramethyl-3,6-disila-1,7-octadiene or 1,3- divinyltetramethyldisiloxane (5). The molecular weights of these copolymers (cooligomers) are also generally low (M_w/M_n ~ 3000/1600). This is not unexpected since exact stoichiometry is essential to achieve high molecular weights in step-growth copolymerization reactions (6). The occurrence of minor unknown side reactions will destroy the required balance of stoichiometry.

In this paper, we report that the ruthenium catalyzed step-growth copolymerization of 4'-methoxyacetophenone or 4'-phenoxyacetophenone with α,ω-dienes proceeds more readily and yields **significantly higher molecular weight copolymers** than previously reported examples.

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Experimental/Spectroscopic

^{1}H 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 an IBM Bruker WP-270-SY spectrometer. Five percent weight/volume solutions of copolymer in chloroform-*d* were used to obtain NMR spectra. ^{13}C NMR spectra were run with broad band proton decoupling. A heteronuclear gated decoupling pulse sequence (NONOE) with a 20 sec delay was used to acquire ^{29}Si NMR spectra (*7*). These were externally referenced to TMS. Chloroform was used as an internal standard for ^{1}H 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 x 10^4 A° (Waters Ultrastyragel), 1 x 10^3 A° (Waters Ultrastyragel) and finally 500 A° (Polymer Laboratories PLgel). The eluting solvent was HPLC grade THF at a flow rate of 0.6 mL/min. The retention times were calibrated against known monodisperse polystyrene standards: M_w 612,000; 114,200; 47,500; 18,700; 5,120; 2,200 and 794 whose M_w/M_n are less than 1.09.

Thermogravimetric Analysis (TGA)

TGA of the polymers was carried out on a Perkin-Elmer TGS-2 instrument with a nitrogen flow rate of 40 cc/min. The temperature program for the analysis was 50°C for 10 min followed by an increase of 4°C/min to 750°C.

Differential Scanning Calorimetry (DSC)

DSC was utilized to determine the glass transition temperatures (T_g's) of the copolymers. These measurements were carried out on a Perkin-Elmer DSC-7 instrument. The melting points of indium (156°C) and ice (0°C) were used to calibrate the DSC. The program for the analysis was -70°C for 10 min followed by an increase in temperature of 20°C/min to 150°C.

Reagents

All reactions were conducted in flame dried glassware under an atmosphere of purified argon. 4'-Methoxyacetophenone, and 4'-phenoxyacetophenone were purchased from Aldrich. 1,3-Divinyltetramethyldisiloxane and 3,3,6,6-tetramethyl-3,6-disila-1,7-octadiene were obtained from United Chemical Technologies. Dihydridocarbonyl*tris*(triphenylphosphine)ruthenium was prepared from ruthenium trichloride (8).

Elemental Analysis

Analysis was performed by Oneida Research Services Inc., Whitesboro, NY.

Copoly(3,3,5,5-tetramethyl-4-oxa-3,5-disila-1,7-heptanylene/2-aceto-5-methoxy-1,3-phenylene)(Copoly-I).

4'-Methoxyacetophenone (0.50 g, 3.3 mmol), 1,3-divinyltetramethyldisiloxane (0.62 g, 3.3 mmol), toluene (1 mL), Ru catalyst (0.06 g, 0.066 mmol) and a Teflon covered magnetic stirring bar were placed in an Ace pressure tube as above. In this way, 0.95 g, 86% yield M_w/M_n = 13,860/6,700, T_g = -24°C was obtained. ^{1}H NMR δ: 0.07(s, 12H), 0.82(m, 4H), 2.43(s, 3H), 2.47(m, 4H), 3.77(s, 3H), 6.58(s, 2H). ^{13}C NMR δ: 0.25, 20.73, 26.92, 33.26, 55.10, 111.33, 133.93, 141.86, 160.78, 207.95. ^{29}Si NMR δ: 7.21 IR ν: 3000, 2955, 2838, 1940, 1737, 1694, 1650, 1638, 1602, 1538, 1511, 1469, 1442, 1414, 1255, 1179, 1153, 1125, 1045, 954, 901, 788, 704, 623 cm^{-1}. UV λ_{max} nm(ε): 250(7,360), 256(7,850), 261(7,930). Elemental Anal. Calcd for $C_{17}H_{28}O_3Si_2$: C, 60.71; H, 8.33. Found: C, 59.82; H, 8.00.

Copoly(3,3,6,6-tetramethyl-3,6-disila-1,8-octanylene/2-aceto-5-methoxy-1,3-phenylene)(Copoly-II).

4'-Methoxyacetophenone (0.50 g, 3.3 mmol), 3,3,6,6-tetramethyl-3,6-disila-1,7-octadiene (0.65 g, 3.3 mmol), toluene (1 mL), Ru catalyst (0.06 g, 0.066 mmol) and a Teflon covered magnetic stirring bar were placed in an Ace pressure tube as above. In this manner, 0.89 g, 77% yield of pure copolymer M_w/M_n = 29,700/11,900, T_g = -6°C was obtained. ^{1}H NMR δ: -0.04(s, 12H), 0.37(s, 4H), 0.79(m, 4H), 2.40(m, 4H), 2.43(s, 3H), 3.77(s, 3H), 6.57(s, 2H). ^{13}C NMR δ: -4.20, 6.92, 17.31, 27.54, 33.25, 55.09, 111.26, 133.63, 142.14, 159.61, 207.96. ^{29}Si NMR δ: 4.20. IR ν: 2951, 2900, 2838, 1702, 1698, 1694, 1682, 1674, 1619, 1600, 1574, 1468, 1455, 1441, 1422, 1414, 1350, 1327, 1293, 1246, 1192, 1176, 1152, 1133, 1075, 1054, 1037, 996, 953, 900, 828, 781 cm^{-1}. UV λ_{max} nm(ε): 250(5,710), 255(6,010), 261(5,990). Elemental Anal. Calcd for $C_{19}H_{32}O_2Si_2$: C, 65.52; H, 9.20. Found: C, 64.94; H, 9.27.

Copoly(3,3,5,5-tetramethyl-4-oxa-3,5-disila-1,7-heptanylene/2-aceto-5-phenoxy-1,3-phenylene) (Copoly-III).

4'-Phenoxyacetophenone (0.65 g, 3.0 mmol), 1,3-divinyletramethyldisiloxane (0.56 g, 3.0 mmol), xylene (2 mL), Ru catalyst (0.07 g, 0.076 mmol) and a Teflon covered magnetic stirring bar were placed in an Ace pressure tube as above. In this manner, 0.98 g, 87% yield of pure copolymer M_w/M_n = 19,550/10,490: T_g = -12°C was obtained. ^{1}H NMR δ: 0.04(s, 12H), 0.78(m, 4H), 2.44(m, 4 H), 2.48(s, 3H), 6.70(s, 2H), 6.97(d, 2H, J = 7.5 Hz), 7.07(t, 1H, J = 7.5 Hz), 7.31(t, 2H, J = 7.5 Hz). ^{13}C NMR δ: 0.18, 20.51, 26.70, 33.16, 116.19, 118.74, 123.19, 129.71, 136.22, 142.12, 156.93, 157.26, 207.77. ^{29}Si NMR δ: 7.29. IR ν: 2955, 1699, 1588, 1492, 1255, 1058, 840 cm^{-1}. UV λ_{max} nm(ε): 246 (8,070), 255(7,340), 261(6,600), 276 (3,910). Elemental Anal. Calcd for $C_{22}H_{30}O_3Si_2$: C, 66.33; H, 7.54. Found: C, 66.24; H, 7.24.

Copoly(3,3,6,6-tetramethyl-3,6-disila-1,8-octanylene/2-aceto-5-phenoxy-1,3-phenylene)(Copoly-IV).

4'-Phenoxyacetophenone (0.65 g, 3.0 mmol), 3,3,6,6-tetramethyl-3,6-disila-1,7-octadiene (0.59 g, 3.0 mmol), xylene (2 mL), Ru catalyst (0.07 g, 0.076 mmol) and a Teflon covered magnetic stirring bar were placed in an Ace pressure tube as above. In this way, 0.87 g, 70% yield of pure copolymer M_w/M_n = 17,500/10,550, T_g = -1.5°C was obtained. ^{1}H NMR δ: -0.04(s, 12H), 0.36(s, 4H), 0.77(m, 4H), 2.39(m, 4H), 2.47(s, 3H), 6.71(s, 2H), 6.98(d, 2H, J = 7.5 Hz) 7.08(t, 1H, J = 7.5 Hz), 7.32 (t, 2H, J = 7.5 Hz). ^{13}C NMR δ: -4.20, 6.88, 17.15, 27.37, 33.18, 116.27, 118.63, 123.11, 129.69, 136.22, 142.44, 157.03, 157.15, 207.90. ^{29}Si NMR δ: 4.23. IR ν: 2953, 2903, 1696, 1587, 1491, 1460, 1417, 1353, 1288, 1248, 1217, 1177, 1165, 1134, 1055, 832, 783, 695 cm^{-1}. UV λ_{max} nm(ε): 248(10,640), 255(10,160), 261 (9,360), 276(5,770). Elemental Anal. Calcd for $C_{24}H_{34}O_2Si_2$: C, 70.24; H, 8.29. Found: C, 69.94; H, 7.98.

Results and Discussion:

Murai has suggested that the ruthenium catalyzed *ortho* alkylation reaction of acetophenone with alkenes proceeds by insertion of a carbonyl complexed coordinately unsaturated Ru species into an adjacent *ortho* C-H bond to yield an aryl-Ru-H intermediate (1-3). The well known insertion of palladium species into aromatic C-H bonds which are *ortho* to activating groups such as N,N-dimethylaminomethyl may be similar (9,10). The ruthenium catalyzed reactions of aromatic ketones and alkenes or α,ω-dienes maybe related mechanistically to the palladium catalyzed Heck reaction of aryl halides with alkenes (11). Insertion of palladium into the C-X bond of the aryl halide leads to a reactive aryl palladium species which is the key intermediate in this reaction. The Heck reaction has also been applied to the synthesis of polymers (12-16).

Attempts to carry out ruthenium catalyzed copolymerization reaction between 4-acetyl pyridine and 1,3-divinyltetramethyldisiloxane under conditions which were successful with acetophenone and 1,3-divinyltetramethyldisiloxane gave disappointing results (17). This may be rationalized on the basis that much of the chemistry of pyridine is analogous to that of nitrobenzene. For example, pyridine undergoes aromatic electrophilic substitution reactions with difficulty (18). This analysis suggests that the insertion of the complexed coordinately unsaturated Ru species into the *ortho* C-H bond might have some of the characteristics of an aromatic electrophilic substitution reaction. Based on this assumption, acetophenones substituted with electron donating groups, such as methoxy or phenoxy, in the *para* position should undergo this reaction with greater facility and might lead to higher molecular weight copolymers. To test this concept, we have carried out Ru catalyzed copolymerization reactions between 4'-methoxyacetophenone, or 4'-phenoxyacetophenone and 1,3-divinyltetramethyldisiloxane or 3,3,6,6-tetramethyl-3,6-disila-1,7-octadiene. In fact, the **molecular weights of the copolymers obtained are significantly higher**.

The structure of the copolymers reported herein as determined by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy is consistent with regioselective addition of the C-H bonds, which are *ortho* to the carbonyl group of the substituted acetophenones across the C-C double bonds of 1,3-divinyltetramethyldisiloxane or 3,3,6,6-tetramethyl-3,6-disila-1,7-octadiene such that the hydrogen becomes attached to the more substituted end of the C-C double bond.(See Figures 1 and 2).

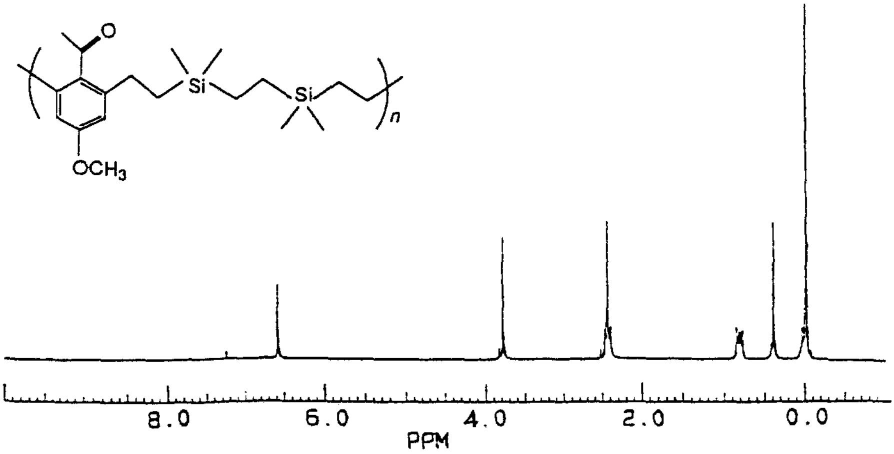

Figure 1. ^{1}H NMR spectrum of Copoly-II.

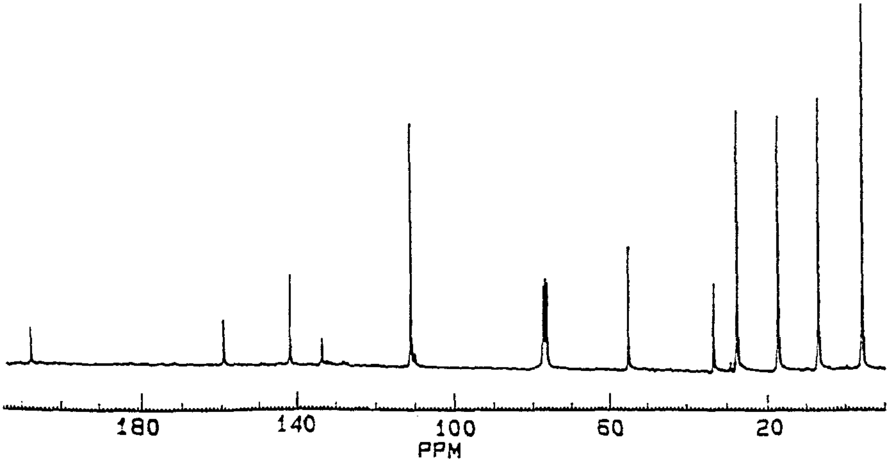

Figure 2. ^{13}C NMR spectrum of Copoly-II.

Higher molecular weights are important since many polymer properties change rapidly until a minimum threshold molecular weight is achieved. Frequently this minimum polymer molecular weight for constant polymer properties occurs at about a molecular weight of 10,000.

The choice of α,ω–dienes is not random. Based on our previous work, it is apparent that most α,ω-dienes are NOT suitable substrates for this reaction (19). The ruthenium catalyst not only catalyzes the insertion of C-C double bonds of α,ω-dienes into the *ortho* C-H bonds of aromatic ketones - but also the isomerization of terminal C-C double bonds to internal double bonds which are much less reactive. 1,3-Divinyltetramethyldisiloxane and 3,3,6,6-tetramethyl-3,6-disila-1,7-octadiene have been utilized because isomerization of their C-C double bonds is blocked.

Copoly-I, copoly-II, copoly-III, and copoly-IV are all thermally stable to 270°C. Between 270 and 380°C they each experience approximately a five percent weight loss. Above 400°C rapid weight loss occurs. By 550°C residues which amount to between eighteen and ten percent remain. At higher temperatures, these continue to slowly loose weight. These high molecular weight copolymers are significantly more thermally stable than the previously reported low molecular weight copolymers of acetophenone with 1,3-divinyltetramethyldisiloxane or 3,3,6,6-tetramethyl-3,6-disila-1,7-octadiene (See Figure 3).

Conclusion

The ruthenium catalyzed copolymerization of acetophenones with α,ω-dienes is sensitive to electronic effects in the acetophenone. Specifically electron donating methoxy and phenoxy groups facilitate the copolymerization and result in high molecular weight polymers. In these systems the molecular weights sufficiently high to warrant legitimate use of the word **copolymers rather than cooligomers.** Further studies on this step growth polymerization based on the Murai reaction are in progress.

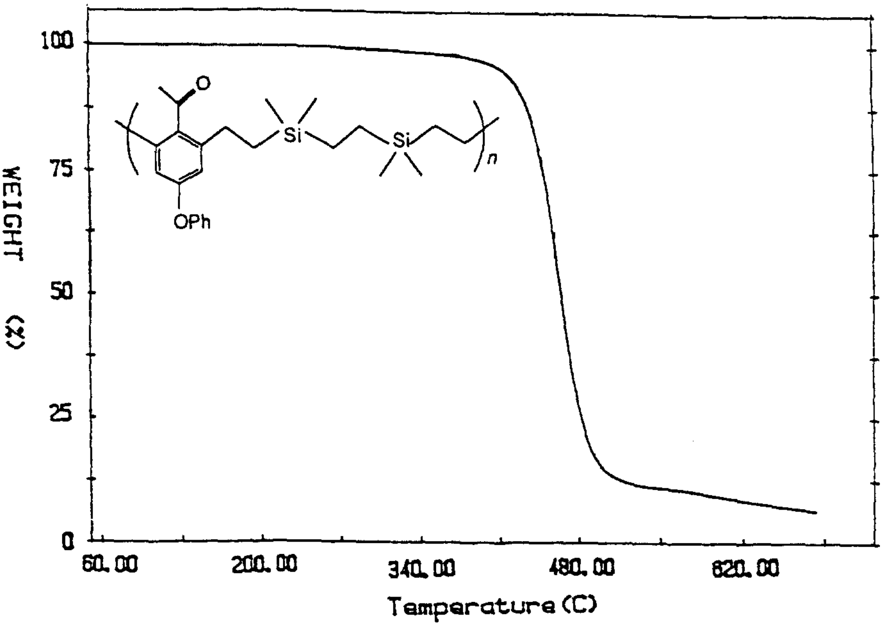

Figure 3. TGA spectrum of Copoly-IV.

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