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Ruthenium catalyzed regioselective copolymerization of acetophenone and α,ω-dienes

Addition of aromatic *ortho* C-H bonds across C-C double bonds of α,ω-dienes

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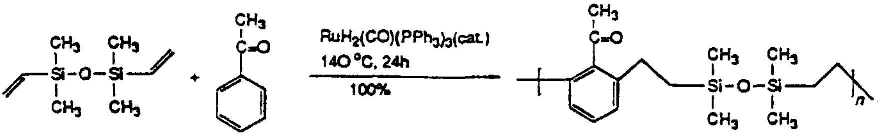
Summary

This paper reports a novel ruthenium catalyzed regioselective copolymerization reaction between acetophenone and α,ω-dienes such as divinyltetramethyldisiloxane and divinyldimethylsilane which leads respectively to copoly(3,3,5,5-tetramethyl-4-oxa-3,5-disila-1,7-heptanylene/2-acetyl-1,3-phenylene) and copoly(3,3-dimethyl-3-sila-1,5-pentanylene/2-acetyl-1,3-phenylene). This reaction involves the ruthenium catalyzed insertion of the carbon-carbon double bonds of α,ω-dienes into the aromatic C-H bonds *ortho* to the acetyl group of acetophenone. Similar ruthenium catalyzed reactions between acetophenone and alkenes to yield monomeric *ortho* alkyl substituted acetophenones have been recently reported. [1]



Introduction

While Ziegler-Natta transition metal catalyzed polymerizations of ethylene and propylene to yield high density polyethylene and polypropylene are among the largest scale commercial processes, transition metal catalyzed copolymerization has attracted Less attention. A few examples of Ziegler-Natta random statistical copolymerization of ethylene and α-olefins have been reported. [2-5] The ruthenium catalyzed copolymerization of acetophenone with α,ω-dienes reported herein maybe related mechanistically to the palladium catalyzed Heck reaction of aryl halides with alkenes. [5-10] The Heck reaction has in recent years been applied to the synthesis of copolymers. Insertion of palladium into the carbon-halogen bond of the aryl halide leads to a reactive aryl palladium species which is the key intermediate in this reaction. Apparently, the acetyl group directs insertion of the coordinately unsaturated ruthenium into adjacent *ortho* C-H bonds which leads to an aryl ruthenium hydride intermediate. Coordination of a carbon-carbon double bond of the α,ω-diene to the ruthenium center followed by regioselective addition of the Aryl-Ru and Ru-H bonds across the coordinated carbon-carbon followed by reductive elimination of the product serves to regenerate the coordinately unsaturated ruthenium species and complete the catalytic cycle.

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Experimental / Spectroscopic

^1H and ^{13}C NMR spectra were obtained on either a Bruker AC-250 or a 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.[11] These were externally 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 Distribution

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 Waters 7.8 mm x 30 cm Ultrastyragel linear column packed with less than 10 μm particles of mixed pore size crosslinked styrene divinylbenzene copolymer maintained at 20°C was used for the analysis. The eluting solvent was HPLC grade THF at a flow rate of 0.6 mL/min. The retention times were calibrated against those of known monodisperse polystyrene standards: M_p 612,000, 114,200; 47,500, 18,700, 5,120, 2200 and 794 whose M_w/M_n are less than 1.09.

Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry

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. The glass transition temperatures (T_g's) of the copolymers were determined by DSC on a Perkin-Elmer DSC-7 instrument. The melting point of indium (mp 165°C) was used to calibrate the DSC. The program for the analysis was -100°C for 10 min followed by an increase in temperature of 20°C /min to 150°C.

Elemental analysis was performed by Oneida Research Services Inc., Whitesboro, NY.

Monomers and Catalyst

Divinyltetramethyldisiloxane and divinyldimethylsilane were obtained from United Chemical Technologies. Acetophenone was purchased from Aldrich. Dihydridocarbonyl*tris*(triphenylphosphine)ruthenium was prepared from ruthenium trichloride following literature procedures.[12]

Preparation of Copoly(3,3,5,5-tetramethyl-4-oxa-3,5-disila-1,7-heptanylene/2-acetyl-1,3-phenylene) (I)

A 25 mL flame dried round bottom flask was equipped with a Teflon covered magnetic stirring bar and an efficient reflux condenser. 1,3-Divinyltetramethyldisiloxane (0.97 g, 5.2 mmol), acetophenone (0.6 g, 5 mmol), dihydridocarbonyl*tris*(triphenylphosphine)ruthenium (0.4 g, 0.44 mmol) and 5 mL of xylene were placed in the flask. Purified nitrogen was bubbled through the solution for five minutes. The mixture was refluxed with stirring for 24 h at 150°C under nitrogen. The color of the reaction mixture changed from colorless to black. The solvent was removed by evaporation under reduced pressure. Pentane, 5 mL, was added and the mixture was stirred for several min. This caused the catalyst to precipitate. After filtration, the pentane was removed by evaporation under reduced pressure, 1.5 g, 100% yield of crude copolymer was obtained. The copolymer was purified three times by precipitation from tetrahydrofuran and methanol. In this way, 1.28 g, 85% of pure copolymer I was obtained. It had the following properties: M_w/M_n = 8310/6720; T_g = -30°C; TGA onset at 300°C, 50% at decomposition 390°C, 19% residue; ^{1}H NMR δ: 0.0-0.1(m, 12H), 0.78-0.86(m,4H), 2.40-2.50(m,7H), 7.0-7.23(m,3H); ^{13}C NMR δ: 0.19, 20.87, 26.66, 33.05, 125.95, 128.78, 139.59, 140.93, 208.14; ^{29}Si NMR δ: 7.3; IR ν: 3061, 2955, 2888, 1834, 1700, 1594, 1460, 1434, 1414, 1352, 1252, 1179, 1059, 962, 904, 842, 791, 757, 722,697 cm^{-1}; UV λ_{max} nm (ϵ) 221 (7330), 268 (764). Elemental Anal. Calcd for $C_{16}H_{26}O_2Si_2$: C, 62.75; H, 8.50. Found: C, 62.28; H, 8.53.

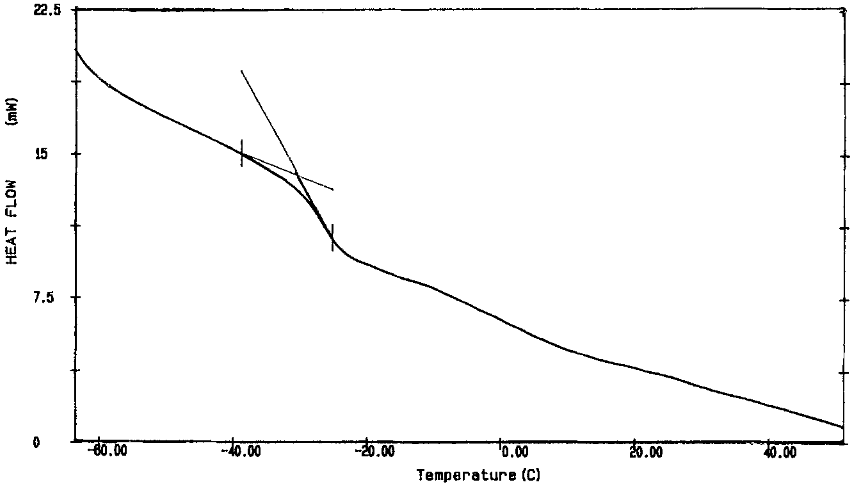
Synthesis of Copoly(3,3-dimethyl-3-sila-1,5-pentanylene/2-acetyl-1,3-phenylene (II).

Divinyldimethylsilane (0.2 g, 1.8 mmol), acetophenone (0.21 g, 1.75 mmol) and dihydridocarbonyl*tris*(triphenylphosphine)ruthenium (0.06 g, 0.065 mmol) and a Teflon covered magnetic stirring bar were placed in a glass tube (10 mm diameter, 10 cm long). The tube and its contents were cooled in a dry ice/isopropanol bath. After two freeze-thaw cycles to remove oxygen, the tube was sealed under vacuum. The reaction mixture was stirred for 48 h at 150°C. The reaction was worked up as above. A 92% yield, 0.37 g of crude copolymer was obtained. After purification as above, 0.28 g, 70% of II was obtained. It had the followed properties: M_w/M_n = 3500/2430; T_g = 9°C; TGA: onset at 310°C, 50% decomposition at 460°C, 20% residue; ^{1}H NMR δ: 0.0-0.12(m,6H), 0.80-0.92(m,3.6H), 2.42-2.56(s,6H), 7.04-7.25(m,3H); ^{13}C NMR δ: -4.1, -3.8, 0.2, 17.8, 20.1, 26.6, 27.2, 33.0, 125.9, 128.8, 139.7, 140.8, 208.2; ^{29}Si NMR δ: 7.2, 5.6, 4.9, 4.6, 2.6; IR ν: 3061, 2953. 1698, 1460, 1435, 1415, 1353, 1250, 1177, 1089, 1050, 908, 838, 783, 758, 733, 696 cm^{-1}; UV λ_{max} nm(ϵ) 220(8190), 290(1280). Elemental Anal. Calcd for $C_{14}H_{20}SiO$: C, 72.41; H, 8.62. Found: C, 69.23; H, 7.69.

Results and Discussion

We should like to report the preparation and characterization of copolymers I and II by the ruthenium catalyzed regioselective copolymerization of acetophenone and 1,3-divinyltetramethyldisiloxane and divinyldimethylsilane, respectively. This reaction is remarkable in a number of ways. Unlike the Heck reaction, activation of the aromatic ring by halogenation is not required. High yields of copolymer are obtained. Only catalytic amounts (1 to 3 mole percent) of ruthenium are necessary. This implies that the catalyst has a turn over number of at least thirty. The reaction proceeds by heating a 1:1 ratio of acetophenone and the α,ω-diene at 150°C for 24 to 48 h. Solvent is often not needed. In fact, in our experience, the effect of solvent is to slow the reaction. As far as we are aware, acetophenone has never been previously utilized as a reactive difunctional monomer in polymerization reactions. Copolymerization occurs by insertion of the C-C double bonds of the α,ω-diene regioselectively into the *ortho* C-H bonds of acetophenone. The *para* C-H of acetophenone is apparently unreactive. We believe that this difference can be explained if ruthenium insertion into the *ortho* C-H bonds of acetophenone is controlled by complexation of the acetyl group to ruthenium. Electronic factors in the α,ω-diene component are apparently important also important in this reaction. Thus, 1,3-divinyltetramethyldisiloxane reacts faster than divinyldimethylsilane and yields a higher molecular weight copolymer.

Both copolymers I and II are reasonably thermally stable and have similar temperatures (~ 300°C) for the onset of thermal decomposition. On the other hand, the T_g of I is significantly lower than that of II. This is probably due to the presence of the highly flexible siloxane bond in I. See Figure for DSC of I.



The scope and mechanism of this novel copolymerization reaction are under active investigation.

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