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Ruthenium catalyzed regioselective copolymerization of anthrone, fluorenone, or xanthone with α,ω-dienes

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Summary

This paper reports a novel ruthenium catalyzed regioselective copolymerization reaction between anthrone, fluorenone or xanthone and α,ω-dienes such as 1,3-divinyltetramethyldisiloxane and 3,3,6,6-tetramethyl-3,6-disila-1,7-octadiene. This reaction involves the ruthenium catalyzed regioselective Anti-Markovnikov insertion of the carbon-carbon double bonds of the α,ω-dienes into the aromatic carbon-hydrogen bonds which are *ortho* to the carbonyl group of anthrone, fluorenone or xanthone. Similar ruthenium catalyzed copolymerization reactions between acetophenone and α,ω-dienes [1] have been recently reported as have reactions between acetophenone and alkenes to yield monomeric *ortho*-alkyl substituted acetophenones [2].

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 reactions have attracted much less attention. A few examples of Ziegler-Natta statistically random copolymerization of ethylene and various α-olefins have been reported [3-6]. The ruthenium catalyzed copolymerization of anthrone, fluorenone and xanthone with α,ω-dienes reported herein maybe related mechanistically to the palladium catalyzed Heck reaction of aryl halides with alkenes [6-11]. The Heck reaction has in recent years been applied to the synthesis of copolymers. Insertion of palladium into the carbon-halogen bond of an aryl halide leads to a reactive aryl-palladium species which is the key intermediate in this reaction. Apparently, the carbonyl group of anthrone, fluorenone or xanthone directs insertion of a coordinately unsaturated ruthenium into adjacent *ortho* carbon-hydrogen bonds which leads to an aryl ruthenium hydride intermediate. Coordination of a carbon-carbon double bond of the α,ω-dienes to the ruthenium center followed by regioselective anti-Markovnikov addition of the aryl-ruthenium and hydrogen-ruthenium bonds across the coordinated carbon-carbon bond yields the product and regenerates the catalytically active ruthenium species.

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Of particular note, this novel ruthenium catalyzed copolymerization reaction results in copolymers which incorporate in a regular manner anthrone, fluorenone and xanthone into the copolymer backbones (Figure 1). The utilization of these aromatic ketones as reactive difunctional monomers which can be incorporated into polymer systems has not been previously reported.

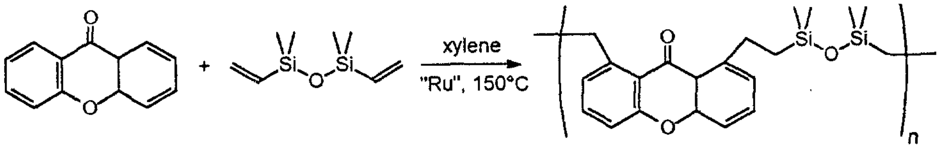

Figure 1.
Synthesis of poly[1,8-xanthonylene/3,3,5,5-tetramethyl-4-oxa-3,5-disila-1,7-heptanylene]

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 copolymers 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 [12]. 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 Distribution

Gel permeation chromatrographic (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 were used. Specifically, these were two Waters Ultrastyragel columns with pore sizes of 1 x 10^4 and 1 x 10^3 and a Polymer Laboratories PLgel column with a pore size of 500 Å. HPLC grade THF was used as the eluting solvent at a flow rate of 1 mL/min. The retention times of the copolymers were calibrated against those of known monodis- perse 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.

Thermal analysis

Thermogravimetric analysis (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 differential scanning calorimetry (DSC) on a Perkin-Elmer DSC-7 instrument. The melting points of indium (165°C) and water (0°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 10°C/min to 150°C.

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

Monomers and Catalyst

1,3-Divinyltetramethyldisiloxane, and 3,3,6,6-tetramethyl-3,6-disila-1,7-octadiene were obtained from United Chemical Technologies. Anthrone, fluorenone, and xanthone were obtained from Aldrich. The latter three were purified by recrystallization from 95% ethanol. Dihydridocarbonyl*tris*(triphenylphosphine)ruthenium (Ru-catalyst) was prepared from ruthenium trichloride following literature procedures [13].

Copoly[1,8-fluorenonylene/3,3,5,5-tetramethyl-4-oxa-3,5-disila-1,7-heptanylene]

Fluorenone (0.45 g, 2.5 mol), 1,3-divinyltetramethyldisiloxane (0.47 g, 2.5 mmol) and Ru-catalyst (0.15 g, 0.075 mmol), 3 mL xylene and a Teflon-covered magnetic stirring bar were placed in a glass tube(10 mm in diameter, 12 cm long, which was partially constricted 10 cm from the bottom). The tube and its contents were cooled in dry-ice/isopropanol bath. After two freeze-thaw cycles to remove oxygen, the tube was flame sealed under vacuum. The reaction mixture was stirred for 72 h at 150°C. After work-up, 0.85 g, 92.3% yield of crude copolymer was obtained. The crude copolymer was dissolved in a minimum amount of THF and was precipitated from methanol. This process was repeated. In this way, 0.67 g, 73% yield, M_w/M_n = 3010/1670; T_g = -6.7°C was secured. ^{1}H NMR δ: 0.20(s,12H), 0.92(br.s,4H), 3.06(br.s,4H), 7.06(br.s,2H), 7.25(br.s,4H). ^{13}C NMR δ: 0.35, 19.54, 24.75, 117.24, 123.66, 130.01, 134.13, 144.40, 146.64, 195.38. ^{29}Si NMR δ: 7.52. IR ν: 3053, 2955, 2924, 2884, 1701, 1593, 1482, 1452, 1434, 1409, 1326, 1289, 1253, 1206, 1179, 1146, 1054(Si-O-Si), 929, 841, 783, 756, 695, 663 cm^{-1}. UV λ_{max} nm(ε): 214 (61,000), 256(88,500), 299(6,100), 308(6,400), 323 (6,770), 338(5,730), 381(1,920). Elemental Anal. Calcd for $C_{21}H_{26}O_2Si_2$: C, 68.85; H, 7.10. Found: C, 68.56; H, 7.00. The material which did not precipitate was shown by GPC and NMR to be lower molecular weight cooligomers.

Copoly[1,8-anthronylene/3,3,6,6-tetramethyl-3,6-disila-1,8-octanylene]

Anthrone (0.49g, 2.5 mmol), 3,3,6,6-tetramethyl-3,6-disila-1,7-octadiene (0.50 g, 2.5 mmol) and Ru-catalyst (0.15 g, 0.075 mol), 3 mL xylene and a Teflon covered magnetic stirring bar were placed in a glass tube which was seal as above. The reaction mixture was stirred for 72 h at 150 °C. After work-up and purification, 0.7 g, 70% yield of copolymer, M_w/M_n = 3580/1520, T_g = 2.6°C was obtained. ^{1}H NMR δ: 0.05 (s,12H), 0.40-0.52(br.s,4H), 0.90(br.s,4H), 3.06(br.s,4H), 4.13(br.s,2H), 7.20 (br.s,4H), 7.31(br.s,2H). ^{13}C NMR δ: -3.84, 7.29, 17.59, 28.52, 34.76, 125.08, 128.72, 130.95, 133.22, 139.97, 147.21. ^{29}Si NMR δ: 11.86. IR ν: 3064, 3023, 2953, 2904, 1946, 1665, 1594, 1574, 1469, 1451, 1411, 1355, 1292, 1247, 1176, 1157, 1133, 1075, 1054, 978, 941, 910, 832, 778, 734, 650 cm^{-1}. UV λ_{max} nm(ε): 215(32,000), 259(26,400), 308(5,280), 348(2,140). Elemental Anal. Calcd for $C_{24}H_{32}OSi_2$: C, 73.47; H, 8.16. Found: C, 70.63; H, 7.54.

Copoly[1,8-anthronylene/3,3,5,5-tetramethyl-4-oxa-3,5-disila-1,7-heptanylene]

Anthrone (0.49 g, 2.5 mmol), 1,3-divinyltetramethyldisiloxane(0.47 g, 2.5 mmol) and Ru-catalyst (0.15 g, 0.075 mmol), 3 mL of xylene and a Teflon covered magentic stirring bar were placed in a glass tube which was sealed and heated for 72 h at 150°C as above. After work-up and purification, 0.65 g, 68% yield of copolymer M_w/M_n = 3010/1220, T_g = 1°C was obtained. ^{1}H NMR δ: 0.04-0.24(m,12H), 0.95(s,4H), 3.07(s, 4H), 4.11(s,2H), 7.17-7.71(m,4H). ^{13}C NMR δ: 0.51, 21.24, 28.05, 34.74, 125.10, 128.58, 130.97, 133.23, 139.98, 147.06, 189.83. ^{29}Si NMR δ: 7.65. IR ν: 3063, 2957, 2055, 1766, 1671, 1590, 1577, 1483, 1468, 1450, 1438, 1410, 1327, 1291, 1254, 1227, 1179, 1120, 1059, 911, 841, 795, 733, 710, 695, 648 cm^{-1}. UV λ_{max} nm(ε): 213(37,460), 253(31,800), 310(4,730), 340(3,720).

Copoly[1,8-xanthonylene/3,3,5,5-tetramethyl-4-oxa-3,5-disila-1,7-heptanylene]

. Xanthone (0.25 g, 1.25 mmol), 1,3-divinyltetramethyldisiloxane (0.25 g, 1.25 mmol) and Ru-catalyst (80 mg, 0.075 mmol), 3 mL xylene and a Teflon covered magnetic stirring bar were sealed in a glass tube as above. The tube and its contents were stirred and heated at 150°C for 72 h. After work-up and purification, 0.32 g, 64% yield of copolymer M_w/M_n = 3490/1700, T_g = -1.9°C was obtained. ^{1}H NMR δ: 0.13(s, 12H), 0.91(br.s,4H), 3.26(br.s,4H), 7.03(br.s,2H), 7.19(br.s,2H), 7.41(br.s,2H). ^{13}C NMR δ: 0.48, 20.72, 29.05, 115.18, 120.71, 124.96, 133.03, 149.09, 156.62, 179.75. ^{29}Si NMR δ: 7.62 IR ν: 3072, 2957, 2930, 1703, 1687, 1651, 1615, 1597, 1568, 1532, 1472, 1446, 1432, 1412, 1347, 1312, 1253, 1179, 1154, 1132, 1060, 984, 963, 909, 843, 785, 735, 651, 613 cm^{-1}. UV λ_{max} nm(ε): 243(15,600), 274(4,460), 290 (1,620), 332(2,780), 345(3,130). Elemental Anal. Calcd for $C_{21}H_{26}O_3Si_2$: C,65.97; H, 6.81. Found: C, 63.68; H, 6.67.

Copoly[1,8-xanthonylene/3,3,6,6-tetramethyl-3,6-disila-1,8-octanylene]

Xanthone (0.78 g, 4 mmol), 3,3,6,6-tetramethyl-3,6-disila-1,7-octadiene (0.79 g, 4 mmol), Ru-catalyst (0.1 g, 0.11 mmol), toluene (0.8 g) 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 48 h at 140°C. The copolymer was precipitated twice from THF with methanol. The catalyst was removed by flash column chromatography on a 60-200 mesh silica gel column utilizing hexane/ether (90%/10%) as co-eluent. Remaining solvent and low molecular weight oligomers were removed at 100°C and 0.1mm Hg pressure. In this way, 1.3 g, 83% yield of copolymer M_w/M_n = 6500/4200, T_g= -3°C was isolated. ^{1}H NMR δ: 0.07(s,12H), 0.45(s,4H), 0.84-0.89(m,4H), 3.20-3.25(m,4H), 7.01(d,2H, J = 7.2 Hz), 7.14(d,2H, J = 7.5 Hz), 7.40(d,d,2H, J=7.5-7.2 Hz). ^{13}C NMR δ: -3.82, 7.30, 17.22, 29.62, 115.18, 120.72, 124.95, 133.02, 149.31, 156.63, 179.98. ^{29}Si NMR δ: 4.50. IR ν: 3059, 3015, 2952, 2938, 2902, 2892, 2772, 1721, 1629, 1607, 1582, 1542, 1451, 1437, 1424, 1390, 1317, 1329, 1297, 1285, 1274, 1222, 1162, 1145, 1133, 1115, 1067, 1034, 1012, 969, 947, 906, 877, 797, 747, 661, 598 cm^{-1}. UV λ_{max} nm (ε): 212(26,500), 263(52,500). Elemental Anal. Calcd for $C_{23}H_{30}O_2Si_2$: C, 70.00; H, 7.66. Found: C, 71.18; H, 7.93.

Copoly[1,8-fluorenonylene/3,3,6,6-tetramethyl-3,6-disila-1,8-octanylene]

Fluorenone (0.70 g, 4 mmol), 3,3,6,6-tetramethyl-3,6-disila-1,7-octadiene (0.8 g, 4 mmol), Ru-catalyst (0.1 g, 0.11 mmol), toluene (0.8 g) 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. The tube and its well stirred contents were heated for 48 h at 140°C. The copolymer was precipitated twice from THF with methanol. The catalyst was removed by flash column chromatography on a 60-200 mesh silica gel column utilizing hexane/ether (90%/10%) as co-eluent. Remaining solvent and low molecular weight oligomers were removed at 100°C and 0.1mm Hg pressure. In this way, 0.6 g, 40% yield of copolymer M_w/M_n = 3100/2500,

T_g= 0°C was isolated. ^{1}H NMR δ: 0.03(s, 12H), 0.45(s,4H), 0.84-0.91(m,4H), 2.98-3.04(m,4H), 7.04 (br.s,2H), 7.24(br.s,4H). ^{13}C NMR δ: -3.94, 7.15, 16.03, 25.26, 117.25, 128.79, 130.04, 133.56, 144.43, 146.92, 195.50. ^{29}Si NMR δ: 4.64. IR ν: 3375, 3039, 2936, 2892, 2774, 1935, 1700, 1646, 1576, 1534,1472, 1440, 1426, 1383, 1274, 1225, 1195, 1167, 1155, 1141, 1117, 1093, 1034, 909, 821, 763, 746, 666, 655 cm^{-1}. UV λ_{max} nm (ε): 242(192,000), 273(51,300), 343(40,300). Elemental Anal. Calcd for $C_{23}H_{30}OSi_2$: C, 72.96 ; H, 7.99. Found: C, 70.10; H, 6.98 .

Results and Discussion:

We should like to report the preparation and characterization of six copolymers by the ruthenium catalyzed regioselective copolymerization of anthrone, fluorenone or xanthone with either 1,3-divinyltetramethyldisiloxane or 3,3,6,6-tetramethyl-3,6-disila-1,7-octadiene. This reaction is remarkable in a number of ways. Neither anthrone, fluorenone nor xanthone has been previously utilized as a difunctional monomer and thereby incorporated into the backbone of a polymer system. Only the *ortho* carbon-hydrogen bonds which are adjacent to the carbonyl groups are activated for this insertion copolymerization process. Further, unlike the Heck reaction, activation of the aromatic ring by halogenation is not required. This copolymerization process is therefore potentially environmentally friendly [14]. Only catalytic amounts, one to three mole percent, of ruthenium are necessary to obtain high yields of copolymer. This implies that the catalyst has a turn over number of at least thirty. The reaction proceeds by heating a 1:1 ratio of aromatic ketone and the α,ω-diene at 150°C for 24 to 72 h. Solvent is only necessary when the solid aromatic ketone fails to dissolve in the α,ω-dienes at 150°C.

Unfortunately, the molecular weight of the copolymers obtained is often low. This is not unexpected for a step-growth addition copolymerization - where exact stoichiometry is required in order to obtain high molecular weight polymers. The low molecular weight of the copolymers permits spectroscopic observation of endgroups. ^{13}C NMR signals have been detected consistent with anthrone, and fluorenone terminal groups. No ^{13}C NMR signals consistent with xanthone end groups have been observed. This may result from the higher molecular weights of the xanthone containing copolymers.

For example, in the ^{13}C NMR spectrum of copoly[1,8-anthronylene/3,3,6,6-tetramethyl-3,6-disila-1,8-octanylene], in addition to the resonances reported above, five low intensity signals (33.50, 126.37, 127.51, 129.31, 131.90 ppm) are observed. We believe, that these should be assigned to anthrone end groups (Figure 2a). For comparison, the ^{13}C NMR spectrum of anthrone itself has eight signals: 32.23, 126.90, 127.45, 128.38, 131.89, 132.07, 140.37 and 184.16 ppm. The intensities of the signals at 132.07, 140.37, and 184.16, which are assigned to the two *ipso* and the carbonyl carbon are quite low.

Similarly, in the ^{13}C NMR spectrum of copoly[1,8-fluorenonylene/3,3,5,5-tetramethyl-4-oxa-3,5-disila-1,7-heptanylene], in addition to the resonances reported above, six low intensity signals are detected (117.68, 119.84, 123.67, 128.73, 134.13, 194.00 ppm). We believe, that these may be assigned to fluorenone end groups (Figure 2b). For comparison, the ^{13}C NMR spectrum of fluorenone itself has seven signals: 120.26, 124.19, 128.99, 134.02, 134.62, 144.34 and 193.83 ppm. The intensities of the signals at 134.02, 144.34, and 193.83 ppm which are assigned to the two *ipso* carbons and the carbonyl carbon are quite low.

In the case of copoly[1,8-xanthonylene/-3,3,5,5-tetramethyl-4-oxa-3,5-disila-1,7-heptanylene] a second type of terminal group has been detected. Specifically signals in the ^{1}H NMR [0.52(q, J = 13.8 Hz) and 1.26 (t, J = 13.8 Hz) ppm] and ^{13}C NMR [6.83 and 10.50 ppm] are observed. These are consistent with an ethyl group attached to silicon (Figure 2c). This may be formed by hydrogenation of one of the carbon-carbon double bonds of 1,3-divinyltetramethyldisiloxane to yield 1-ethyl-3-vinyltetramethyldisiloxane. In fact, the closely related complex dihydrido*tetrakis*(triphenylphosphine)-ruthenium is known to catalyze the transfer hydrogenation of alkenes [15]. Clearly, the hydrogen for this catalytic reduction must come from the catalyst itself. This reduction process may, in fact, be involved in the formation of the coordinately unsaturated catalytically active ruthenium species needed for copolymerization. If this interpretation is correct, decreasing the concentration of catalyst should lead to higher molecular weight polymers - albeit longer reaction times.

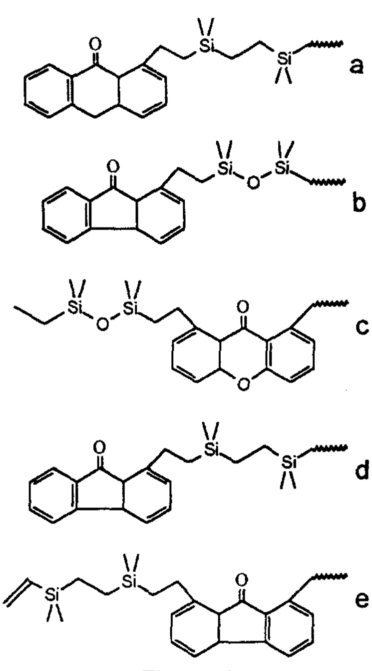

Figure 2.
Observed end groups.

In the case of copoly[1,8-fluorenonylene/3,3,6,6-tetramethyl-3,6-disila-1,8-octanylene], NMR signals are observed which are consistent with two types of terminal groups. ^{13}C NMR signals are detected which are consistent with fluorenone end groups as above (Figure 2d). In addition, low intensity ^{1}H, ^{13}C and ^{29}Si NMR signals are observed which can be assigned to terminal vinyl groups (Figure 2e). ^{1}H NMR δ: 5.65(dd, 1H, J = 20 and 5 Hz), 5.92(dd, 1H, J = 15 and 5 Hz) and 6.13(dd, 1H, J = 20 and 15 Hz) ^{13}C NMR δ: 131.45, 139.10 and finally ^{29}Si NMR δ: -3.97. The NMR spectra of 3,3,6,6-tetramethyl-3,6-disila-1,7-octadiene is similar: ^{1}H NMR δ: 5.96(dd, 1H, J = 15 and 5 Hz), 6.12(d, 1H, J = 15 Hz) and 6.20(d, 1H, J = 15 Hz); ^{13}C NMR δ: -3.96, 7.37, 131.54, and 139.01; and finally ^{29}Si NMR δ:-1.18.

The thermal stability of these polymers has been determined by TGA. They are all stable to at least 200°C. Between 220 and 300°C copoly[1,8-anthronylene/3,3,6,6-tetramethyl-3,6-disila-1,8-octanylene] loses eight percent of its initial weight. Above 300°C, more rapid weight loss occurs. By 400°C, almost fifty percent of initial sample weight has been lost. Between 400 and 700°C the rate of weight loss is slower. By 700°C, only sixteen percent of the initial sample weight remains. No further weight loss is observed.

Between 220 and 300°C copoly[1,8-anthronylene/3,3,5,5-tetramethyl-4-oxa-3,5-disila-1,7-heptanylene] loses five percent of the initial sample weight. Above 300°C more rapid weight loss occurs. By 420°C, only forty-seven percent of the initial weight remains. Above this temperature the rate of weight loss is slower. By 780°C, thirty-five percent of the initial weight still remains.

Copoly[1,8-fluorenonylene/3,3,5,5-tetramethyloxa-3,5-disila-1,7-heptanylene] is thermally stable to 235°C. Between 235 and 370°C seven percent of the initial sample weight is lost. Above this temperature more rapid weight loss occurs. By 500°C, only forty-two percent of the original sample weight remains. Above this temperature, weight loss occurs more slowly. By 780°C, thirty-three percent of the initial sample weight still remains.

Poly[1,8-xanthonylene/3,3,5,5-tetramethyl-4-oxa-3,5-disila-1,7-heptanylene] loses thirteen percent of its initial weight between 220 and 380°C. Above this latter temperature more rapid weight loss occurs. By 460°C, forty-five percent of the original sample wight remains. Above this temperature weight loss occurs more slowly. By 700°C, a black glassy residue amounting to thirty-two percent of the initial weight is found.

Between 220 and 360°C copoly[1,8-fluorenonylene/3,3,6,6-tetramethyl-3,6-disila-1,8-octanylene] loses five percent of its initial weight. Above this temperature, more rapid weight loss occurs. By 500°C, a residue amounting to only five percent of the initial sample weight remains.

Experiments to define the scope and to improve the molecular weight of copolymers formed by these novel ruthenium catalyzed reactions are in progress.

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