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Communications to the Editor

Synthesis of High Molecular Weight Copolymers by Ruthenium-Catalyzed Step-Growth Copolymerization of Acetophenone with α,ω-Dienes

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Introduction. Murai et al. have reported that dihydridocarbonyltris(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 *o*-alkyl-substituted acetophenones.[1–3] We have shown that this reaction can be applied to achieve step-growth copolymerization of aromatic ketones and α,ω-dienes.[4,5] Unfortunately, the molecular weights of these copolymers are generally low. 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. While significantly higher molecular weight copolymers have been obtained with *p*-(dialkylamino), *p*-methoxy-, and *p*-phenoxyacetophenones, this is not a general solution.[7–9] Higher molecular weights are important since many polymer properties change rapidly until a minimum threshold value is achieved. Frequently this minimum molecular weight for constant polymer properties occurs at about a molecular weight of 10 000.

We have previously reported that resonances consisting of an ethyl group attached to silicon were detected by NMR spectroscopic analysis of low molecular weight copoly[1,8-xanthonylene/3,3,5,5-tetramethyl-4-oxa-3,5-disila-1,7-heptanylene] ($M_w/M_n = 3500/1700$) which had been prepared by the Ru-catalyzed step-growth copolymerization of xanthone and 1,3-divinyltetramethyldisiloxane. We have noted that Ru-catalyzed reaction of 1-ethyl-3-vinyltetramethyldisiloxane, formed *in situ* by hydrogenation of one of the C–C double bonds of the 1,3-divinyltetramethyldisiloxane, with acetophenone would yield such an end group. Further, we have suggested that the hydrogen needed for this reduction may come from the catalyst itself. This reduction may, in fact, be involved in the formation of the coordinately unsaturated catalytically active ruthenium species needed for copolymerization.[5] A related complex, dihydridotetrakis(triphenylphosphine)ruthenium, is known to catalyze the transfer hydrogenation of alkenes.[10]

Results and Discussion. On the basis of this analysis, we have treated the Ru catalyst by addition of a stoichiometric amount of an alkene such as styrene or vinyltrimethoxysilane. After heating this mixture at 135 °C for a few minutes, a solution of the acetophenone and α,ω-diene was added. In this way, significantly higher molecular weight copolymers were obtained. For example, copolymerization of acetophenone and 1,3-divinyltetramethyldisiloxane with Ru catalyst which had been previously activated with an equal molar amount (stoichiometric) of vinyltrimethoxysilane gave copoly(3,3,5,5,-tetramethyl-4-oxa-3,5-disila-1,7-heptanylene/2-acetyl-1,3-phenylene) (copoly-I) (M_w/M_n 40 600/14 800). Preparation of copoly-I without prior activation of the catalyst gave low molecular weight copoly-I with $M_w/M_n = 8300/6700$.[4]

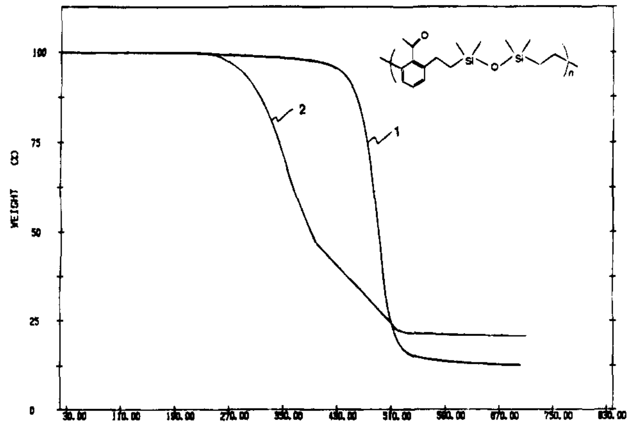
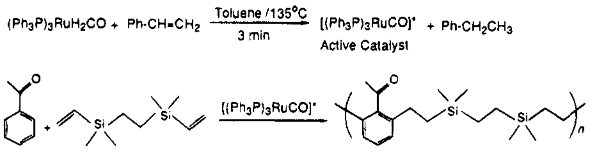


Figure 1. TGA of high molecular weight copoly-I (**1**) and low molecular weight copoly-I (**2**).

Scheme 1



Similarly, copolymerization of acetophenone and 3,3,6,6-tetramethyl-3,6-disila-1,7-octadiene catalyzed by Ru which had been previously activated by treatment with a stoichiometric amount of styrene gave copoly(3,3,6,6-tetramethyl-3,6-disila-1,8-octanylene/2-acetyl-1,3-phenylene) (copoly-II) (M_w/M_n = 22 900/21 300)[11] and ethylbenzene. The detection of ethylbenzene by GC/MS is consistent with our hypothesis. On the other hand, preparation of copoly-II without prior activation of the Ru catalyst gave copoly-II with M_w/M_n = 7800/4800 (Scheme 1).

In control experiments the Ru catalyst was treated with stoichiometric amounts of styrene at 135 °C for 3 min. Using toluene as an internal standard, a quantitative yield of ethylbenzene was observed. No unreacted styrene was detected. Styrene and ethylbenzene were observed in experiments conducted with excess styrene.

Catalyst activation by reaction with a stoichiometric amount of alkene provides a significant improvement in copolymer molecular weight, thermal stability (see Figure 1), and T_g.

Experimental Section. ^{1}H, ^{13}C, and ^{29}Si NMR, IR, and UV spectra as well as GPC and TGA data were obtained as previously described.[4,5] GC/MS analysis was performed on a Hewlett-Packard 5871A equipped

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with a MSD. The GC inlet was furnished with a 30 m × 0.25 μm film thickness DB-5 column. The temperature program was 60 °C for 3 min, followed by an increase of 15 °C/min to 240 °C.

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

All reactions were conducted in flame-dried equipment under argon. 1,3-Divinyltetramethyldisiloxane and 3,3,6,6-tetramethyl-3,6-disila-1,7-octadiene were obtained from United Chemical Technologies. Dihydridocarbonyltris(triphenylphosphine)ruthenium was prepared from ruthenium trichloride following literature procedures.[12,13]

High Molecular Weight Copoly-I. Ru catalyst (0.11 g, 0.12 mmol) and toluene (1 mL) were placed in a 50-mL three-neck round-bottomed flask which was equipped with a reflux condenser and a Teflon-covered magnetic stirring bar. The other two necks of the flask were sealed with rubber septa. Vinyltrimethoxysilane (0.016 mL, 0.018 g, 0.12 mmol) was added via syringe. The flask and its contents were heated to 135 °C for 1 min. At this time, a mixture of acetophenone (0.48 g, 4 mmol) and 1,3-divinyltetramethyldisiloxane (0.74 g, 4 mmol) was added. The reaction was heated at 135 °C for 12 h. Toluene was removed by evaporation under reduced pressure. Pentane (5 mL) was added to precipitate the catalyst. After filtration, the pentane was removed by evaporation and the copolymer was purified three times by precipitation from a mixture of THF and methanol. In this way 0.9 g (74%) of copoly-I (M_w/M_n = 40 600/14 800, $T_g = -33$ °C) was obtained. It had spectral properties in complete agreement with low molecular weight copoly-I (M_w/M_n = 8300/6700, $T_g = -44$ °C) previously reported.[4,14]

Low Molecular Weight Copoly-II. Acetophenone (0.3 g, 2.5 mmol), 3,3,6,6-tetramethyl-3,6-disila-1,7-octadiene (0.5 g, 2.5 mmol), and Ru catalyst (0.15 g, 0.16 mmol) were reacted as above. In this way, copoly-II (0.72 g, 90% yield, M_w/M_n = 7800/4800, $T_g = -20.5$ °C) was obtained. ^{1}H NMR: δ −0.015 (s, 12H), 0.40 (s, 4H), 0.79−0.86 (m, 4H), 2.42−2.56 (m, 7H), 7.07 (d, 2H, J = 7.5 Hz), 7.21 (t, 1H, J = 7.5 Hz). ^{13}C NMR: δ −4.19, 6.90, 17.42, 27.29, 33.02, 125.89, 128.72, 139.87, 140.79, 208.11. ^{29}Si NMR: δ 4.17. IR: ν 3060, 2951, 2900, 1929, 1702, 1699, 1682, 1593, 1461, 1455, 1439, 1422, 1414, 1351, 1247, 1177, 1133, 1089, 1053, 995, 961, 902, 832, 780, 757, 695 cm^{-1}. UV: λ_{max} (ϵ) 217 (18 600), 264 nm (2020). Elem Anal. Calcd for $C_{18}H_{30}OSi_2$: C, 67.92; H, 9.43. Found: C, 67.19; H, 8.87.

High Molecular Weight Copoly-II. Ru catalyst (0.073 g, 0.08 mmol) was placed in a 50-mL three-neck round-bottomed flask as above. Styrene (0.009 mL, 0.008 g, 0.08 mmol) was added via a syringe. This mixture was heated at 135 °C for 3 min. At this time, a mixture of acetophenone (0.48 g, 4 mmol) and 3,3,6,6-tetramethyl-3,6-disila-1,7-octadiene (0.79 g, 4 mmol) was added. The reaction mixture was heated at 135 °C for 12 h. After workup, 1.12 g (88%) of copoly-II (M_w/M_n = 22 900/21 300,[12] $T_g = -17$ °C) was obtained. It had spectral properties identical to those reported above. Ethylbenzene was detected by GC/MS analysis of the solution by both its retention time and base peak which was found at $m/e = 91$.

Control Reaction of Styrene with Ru Catalyst. Ru catalyst (46.3 mg, 0.05 mmol), styrene (5.2 mg, 0.05 mmol), and toluene (25.6 mg, 0.28 mmol) were placed in a 5 mm NMR tube. The tube and its contents were heated at 135 °C for 3 min; after rapidly cooling the tube to room temperature, ^{1}H NMR analysis indicated a quantitative yield of ethylbenzene by integration of the ethyl group [1.37 (t, 3H) and 2.76 (q, 4H) ppm] versus the methyl group [2.47 (s, 3H) ppm] of the internal standard toluene.

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(11) The very low PDI detected is probably anamolous.

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(13) A reviewer has suggested that J. Chatt and J. M. Davidson's complex $(dmpe)_2Ru(H)(C_{10}H_7)$ might also be an effective catalyst for this reaction.

(14) The T_g of low molecular weight copoly-I previously reported in ref 4 is incorrect.

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