Ruthenium-Catalyzed Regioselective Step-Growth Copolymerization of *p*-(Dialkylamino)acetophenones and α,ω-Dienes

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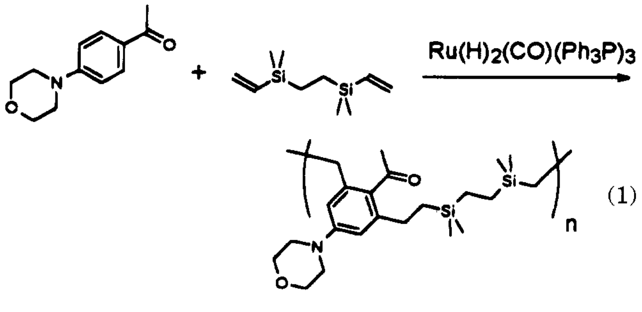
ABSTRACT: Ruthenium-catalyzed step-growth copolymerization of *p*-(dialkylamino)acetophenones and α,ω-dienes such as 1,3-divinyltetramethyldisiloxane gives copolymers which have respectable molecular weights. The synthesis and characterization of these copolymers is reported.

Introduction

In late 1993, Murai et al. reported the dihydridocarbonyltris(triphenylphosphine)ruthenium (Ru)-catalyzed addition of the *ortho* C−H bonds of acetophenone across the C−C double bonds of olefins to yield *ortho* alkyl-substituted acetophenones.[1,2] We have shown that this new 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.[3] 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.[4] The molecular weights of the copolymers (cooligomers) are generally low ($M_w/M_n \sim 3000/1600$). This is not unexpected since exact stoichiometry is essential to achieve high molecular weights in step-growth copolymerization reactions.[5] The occurrence of even minor unknown side reactions will destroy the required balance of stoichiometry.

In this paper, we report the ruthenium-catalyzed step-growth copolymerization of *p*-(dialkylamino)acetophenones with α,ω-dienes. These reactions proceed more readily and yield **significantly higher molecular weight copolymers** than previously reported examples.



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Experimental Section

Spectroscopic Data. ^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 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 s delay was used to acquire ^{29}Si NMR spectra.[6] 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 Distributions. Gel permeation chromatographic (GPC) analysis of the molecular weight distribution of these polymers was performed on a Waters system composed 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 cross-linked styrene−divinylbenzene copolymer contained pore sizes of 1 × 10^4 Å (Waters Ultrastyragel), 1 × 10^3 Å (Waters Ultrastyragel) and finally 500 Å (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, 5120, 2200, and 794 whose M_w/M_n are less than 1.09.

Thermogravimetric analysis (TGA) of the polymers was carried out on a Perkin-Elmer TGS-2 instrument with a nitrogen flow rate of 40 cm^3/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 (156 °C) and ice (0 °C) were used to calibrate the DSC. The program for the analysis was −50 °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. 4-Piperidinoacetophenone, 4-morpholinoacetophenone, 4-piperizinoacetophenone, and 10-methyl-9(10*H*)-acridinone 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. Dihydridocarbonyltris(triphenylphosphine)ruthenium was prepared from ruthenium trichloride.[7]

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

4-(*N*'-Benzylpiperazino)acetophenone. 4-Piperazinoacetophenone (0.61 g, 3 mmol), benzyl chloride (0.38 g, 3 mmol), potassium carbonate (0.21 g, 1.5 mmol), and a Teflon-covered magnetic stirring bar were placed in a 100 mL flame-dried round-bottom flask. The flask was sealed with a rubber stopper. The reaction mixture was stirred for 24 h. The reaction mixture was poured into 100 mL of water. The precipitate was filtered and recrystallized from ethanol/water. In this way, 0.7 g, 68% yield, of product was obtained, mp 97.5−99 °C. ^1H NMR, δ: 2.49 (s, 3H), 2.57 (m, 4H), 3.34 (m,

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4H), 3.54 (s, 2H), 6.81–6.84 (m, 2H), 7.27–7.33 (m, 5H), 7.83–7.86 (m, 2H). ^{13}C NMR, δ: 26.05, 47.31, 52.68, 62.95, 113.31, 127.24, 127.53, 128.31, 129.13, 130.33, 137.69, 154.17, 196.40. IR, ν: 2820, 2777, 1664, 1598, 1555, 1518, 1455, 1427, 1388, 1361, 1303, 1285, 1245, 1230, 1195, 1148, 1008, 926, 906, 824, 744, 737, 733 cm^{-1}. UV, λ_{max} (ϵ): 311 (25 870), 261 (4930), 255 nm (5110).

Copoly(3,3,5,5-tetramethyl-4-oxa-3,5-disila-1,7-heptanylene/2-aceto-5-piperidino-1,3-phenylene). 4-Piperidinoacetophenone (0.51 g, 2.5 mmol) 1,3-divinyltetramethyldisiloxane (0.47 g, 2.5 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 (15 mL, 10.2 cm long). A stream of argon was bubbled through the solution for 5 min. The tube and its contents were sealed with a FETFE "O"-ring and a threaded Teflon cap. The reaction mixture was stirred for 48 h at 150 °C. The color of the reaction mixture changed from colorless to black. The tube and its contents were cooled to room temperature and pentane (5 mL) was added. The reaction mixture was stirred for several minutes. This caused the catalyst to precipitate. After filtration, the pentane was removed from the crude polymer by evaporation under reduced pressure. The copolymer was purified three times by precipitation from tetrahydrofuran and methanol. In this way, 0.90 g, 91% yield, of copolymer was obtained, M_w/M_n = 20 880/9540, T_g = 2 °C. ^{1}H NMR, δ: 0.06 (s, 12H), 0.82 (m, 4H), 1.55 (s, 2H), 1.66 (s, 4H), 2.42 (s, 3H), 2.47 (m, 4H), 3.13 (s, 4H), 6.58 (s, 2H). ^{13}C NMR, δ: 0.22, 21.03, 24.29, 25.78, 27.27, 33.27, 50.25, 113.77, 132.21, 141.31, 152.44, 208.17. ^{29}Si NMR, δ: 7.22. IR, ν: 2940, 2859, 2809, 1690, 1598, 1563, 1557, 1467, 1453, 1444, 1413, 1385, 1352, 1256, 1224, 1183, 1121, 1062, 982, 911, 842, 791, 738, 649 cm^{-1}. UV, λ_{max} (ϵ): 216 (20 200), 243 (8950), 287 nm (6320). Anal. Calcd for $C_{21}H_{35}NO_2Si_2$: C, 64.78; H, 9.00; N, 3.60. Found: C, 64.02; H, 8.90; N, 3.49.

Copoly(3,3,5,5-tetramethyl-4-oxa-3,5-disila-1,7-heptanylene/2-aceto-5-morpholino-1,3-phenylene). 4-Morpholinoacetophenone (0.52 g, 2.5 mmol), 1,3-divinyltetramethyldisiloxane (0.47 g, 2.5 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, 0.85 g, 86% yield, of copolymer was obtained M_w/M_n = 16 470/8050, T_g = 14 °C. ^{1}H NMR, δ: 0.07 (s, 12H), 0.81 (m, 4H), 2.42 (s, 3H), 2.47 (m, 4H), 3.14 (s, 4H), 3.81 (s, 4H), 6.56 (s, 2H). ^{13}C NMR, δ: 0.25, 21.06, 27.27, 33.27, 48.98, 66.85, 113.00, 133.09, 141.50, 151.53, 208.00. ^{29}Si NMR, δ: 7.22. IR, ν: 2956, 2893, 2858, 1953, 1778, 1721, 1692, 1651, 1600, 1564, 1538, 1511, 1451, 1414, 1379, 1352, 1305, 1252, 1184, 1125, 1058, 906, 840, 788, 733, 707, 686, 647 cm^{-1}. UV, λ_{max} (ϵ): 216 (21 270), 241 (3220), 287 nm (6390). Anal. Calcd for $C_{20}H_{33}NO_3Si_2$: C, 61.38; H, 8.44; N, 3.60. Found: C, 60.90; H, 8.29; N, 3.47.

Copoly(3,3,5,5-tetramethyl-4-oxa-3,5-disila-1,7-heptanylene/2-aceto-5-(*N*′-benzylpiperazino)-1,3-phenylene). 4-(*N*′-Benzylpiperazino)acetophenone (0.41 g, 1.4 mmol), 1,3-divinyltetramethyldisiloxane (0.26 g, 1.4 mmol), xylene (2 mL), Ru catalyst (0.04 g, 0.038 mmol), and a Teflon-covered magnetic stirring bar were placed in an Ace pressure tube as above. In this way, 0.57 g, 85% yield, of copolymer was obtained, M_w/M_n = 51 250/16 540, T_g = 25 °C. ^{1}H NMR, δ: 0.07 (s, 12H), 0.81 (m, 4H), 2.42 (s, 3H), 2.45 (m, 4H), 2.60 (s, 4H), 3.21 (s, 4H), 3.58 (s, 2H), 6.56 (s, 2H), 7.34 (s, 5H). ^{13}C NMR, δ: 0.18, 20.94, 27.17, 33.20, 48.52, 52.79, 62.78, 113.31, 127.22, 128.23, 129.22, 132.68, 137.22, 141.32, 151.42, 208.01. ^{29}Si NMR, δ: 7.16. IR, ν: 2977, 2869, 1693, 1600, 1456, 1385, 1352, 1255, 1180, 1147, 1069, 913, 843, 790, 734, 700 cm $^{-1}$. UV, λ_{max} (ϵ): 215 (22 096), 243 (7213), 288 nm (5270). Anal. Calcd for $C_{27}H_{40}N_2O_2Si_2$: C, 67.54; H, 8.33; N, 5.83. Found: C, 65.66; H, 7.97; N, 5.61.

Copoly(3,3,6,6-tetramethyl-3,6-disila-1,8-octanylene/2-aceto-5-(*N*′-benzylpiperazino)-1,3-phenylene). 4′-(*N*′-Benzylpiperazino)acetophenone (0.88 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, 1.35 g, 92% yield, of copolymer, M_w/M_n = 25790/7490, T_g = 23 °C, was obtained. ^{1}H NMR, δ: −0.02 (s, 12H), 0.39 (s, 4H), 0.80 (m, 4H), 2.42 (s, 3H), 2.45 (m, 4H), 2.60 (s, 4H), 3.21 (s, 4H), 3.56 (s, 2H), 6.58 (s, 2H), 7.34 (s, 5H). ^{13}C NMR, δ: −4.16, 6.93, 17.57, 27.86, 33.24, 48.75, 52.94, 62.93, 113.32, 127.08, 128.19, 129.11, 132.58, 137.75, 141.61, 151.54, 208.08. ^{29}Si NMR, δ: 4.17. IR, ν: 2954, 2873, 1692, 1599, 1495, 1455, 1385, 1352, 1302, 1248, 1188, 1134, 1103, 1067, 997, 911, 832, 782, 735, 699, 647 cm^{-1}. UV, λ_{max} nm(ϵ): 214 (25 740), 243 (8950), 290 nm (6330). Anal. Calcd for $C_{29}H_{44}N_2OSi_2$: C, 70.73; H, 8.92; N, 5.69. Found: C, 68.98; H, 8.84; N, 5.48.

Copoly(3,3,6,6-tetramethyl-3,6-disila-1,8-octanylene/2-aceto-5-piperidino-1,3-phenylene). 4-Piperidinoacetophenone (1.00 g, 5 mmol), 3,3,6,6-tetramethyl-3,6-disila-1,7-octadiene (0.98 g, 5 mmol), Ru complex (0.1 g, 0.11 mmol), and a Teflon-covered magnetic stirring bar were placed in an Ace no. 15 high-pressure reaction tube as above. In this way, 1.59 g, 80% yield of copolymer was isolated, M_w/M_n = 26 000/15 000, T_g = −5 °C. ^{1}H NMR, δ: −0.04 (br s, 12H), 0.37–0.41 (br s, 4H), 0.76–0.82 (m, 4H), 1.56 (s, 2H), 1.65 (s, 4H), 2.42 (s, 3H), 2.45 (m, 4H), 3.14 (s, 4H), 3.56 (s, 2H), 6.58 (s, 2H). ^{13}C NMR, δ: −4.15, 6.97, 17.62, 24.26, 25.79, 27.90, 33.27, 50.30, 113.79, 133.19, 141.61, 152.43, 208.1. ^{29}Si NMR, δ: 4.14. IR, ν: 2942, 2811, 1688, 1682, 1597, 1552, 1479, 1467, 1452, 1445, 1422, 1414, 1385, 1353, 1274, 1256, 1237, 1186, 1132, 1055, 967, 928, 888, 834, 781, 705, 655, 646 cm^{-1}. UV, λ_{max} (ϵ): 215 (24 300), 243 (sh) (9100), 291 nm (7400). Anal. Calcd for $C_{23}H_{39}ONSi_2$: C, 68.82; H, 9.73; N, 3.49. Found: C, 68.04; H, 9.41; N, 3.43.

Copoly(3,3,6,6-tetramethyl-3,6-disila-1,8-octanylene/2-aceto-5-morpholino-1,3-phenylene). 4-Morpholinoacetophenone (0.50 g, 2.4 mmol), 3,3,6,6-tetramethyl-3,6-disila-1,7-octadiene (0.48 g, 2.4 mmol), Ru complex (0.1 g, 0.11 mmol), and a Teflon-covered magnetic stirring bar were placed in an Ace no. 15 high-pressure reaction tube as above. In this way, 0.79 g, 80% yield, of copolymer was isolated, M_w/M_n = 38 000/25 000, T_g = 2.7 °C. ^{1}H NMR, δ: −0.04 (br s, 12H), 0.37 (br s, 4H), 0.75–0.82 (m, 4H), 2.42 (m, 4H), 2.43 (s, 3H), 3.15 (s, 4H), 3.82 (s, 4H), 6.56 (s, 2H). ^{13}C NMR, δ: −4.19, 6.91, 17.61, 27.85, 33.21, 48.95, 66.79, 112.93, 132.96, 141.72, 151.45, 207.94. ^{29}Si NMR, δ: 4.16. IR, ν: 2955, 2901, 1651, 1599, 1452, 1380, 1353, 1257, 1187, 1133, 1112, 910, 834, 782, 737, 647 cm^{-1}. UV, λ_{max} nm (ϵ): 215 (24 600), 243 (sh) (10 900), 283 nm (6500). Anal. Calcd for $C_{22}H_{37}O_2NSi_2$: C, 65.51; H, 9.18; N, 3.47. Found: C, 64.98; H, 8.88; N, 3.37.

Copoly(3,3,5,5-tetramethyl-4-oxa-3,5-disila-1,7-heptanylene/10-methyl-9-oxoacridin-1,8-ylene). 10-Methyl-9(10*H*)-acridinone (0.42 g, 2 mmol), 1,3-divinyltetramethyldisiloxane (0.37 g, 2 mmol), xylene (2 mL), Ru complex (0.04 g, 0.038 mmol), and a Teflon-covered magnetic stirring bar were placed in an Ace pressure tube as above. In this manner, 0.5 g, 64% yield, of copolymer was obtained, M_w/M_n = 3900/2360, T_g= 19 °C. ^{1}H NMR, δ: 0.18 (s, 18H), 1.03 (br s, 4H), 3.32 (br s, 4H), 3.65 (s, 3H), 7.00–7.39 (m, 6H). ^{13}C NMR, δ: 0.55, 21.06, 28.92, 35.50, 111.89, 122.64, 131.74, 143.64, 148.47, 182.18. ^{29}Si NMR, δ: 7.72. IR, ν: 2958, 1630, 1595, 1494, 1467, 1373, 1272, 1253, 1155, 1059, 910, 843, 785, 734, 687, 651 cm^{-1}. UV, λ_{max} (ϵ): 218 (24 200), 258 (43 960), 304 (4880), 378 (7410), 395 nm (11 000). Anal. Calcd for $C_{22}H_{29}NO_2Si_2$: C, 66.84; H, 7.34; N, 3.54. Found: C, 64.91; H, 7.31; N, 3.29.

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.[1,2] The well-known insertion of palladium species into aromatic C–H bonds which are *ortho* to activating groups such as (*N*,*N*-dimethylamino)methyl may be similar.[8,9] The ruthenium-catalyzed reactions of aromatic ketones and alkenes or α,ω-dienes may be related mechanistically to the palladium-catalyzed Heck reaction of aryl halides with alkenes.[10] Insertion of palladium into the C–X bond of the aryl halide leads to a reactive arylpalladium species which is the key intermediate in this reaction. The Heck reaction has also been applied to the synthesis of polymers.[11-15]

Our attempts to carry out the ruthenium-catalyzed copolymerization reaction between 4-acetylpyridine and 1,3-divinyltetramethyldisiloxane under conditions which were successful with acetophenone and 1,3-divinyltetramethyldisiloxane met with failure.[16] 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.[17] 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.[18] On the basis of this assumption, acetophenones substituted with electron-donating groups 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-piperidinoacetophenone, 4-morpholinoacetophenone, 4-(*N'*-benzylpiperazino)acetophenone, or 10-methyl-(10*H*)-acridinone 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**, with the exception of that obtained with 10-methyl-9(10*H*)-acridinone. Further, the reactions proceed significantly faster. For example, reaction time at 150 °C may be decreased to 4 h with 4-piperidinoacetophenone from 24 h with acetophenone.

The structure of the copolymers reported herein as determined by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy is consistent with predominant regioselective addition of the C−H bonds, which are *ortho* to the carbonyl group of 4-piperidinoacetophenone, 4-morpholinoacetophenone, 4-(*N'*-benzylpiperazino)acetophenone and 10-methyl-9(10*H*)-acridinone, 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 hydrogens become attached to the more substituted end of the double bond (see Experimental Section and Figure 1).

However, in addition to these major resonances, minor signals are observed which may be assigned to units in which the C−H bond *ortho* to the dialkylamino group has added in a similar regioselective manner across the C−C double bond of 1,3-divinyltetramethyldisiloxane or 3,3,6,6-tetramethyl-3,6-disila-1,7-octadiene. Specifically, in the ^{1}H NMR of copoly(3,3,6,6-tetramethyl-3,6-disila-1,8-octanylene/2-aceto-5-piperidino-1,3-phenylene), additional resonances are detected at 0.024, 0.41, 2.49, 2.86−2.94, 3.30, 6.66, 7.68, and 7.71 ppm. Similarly, in the ^{13}C NMR, additional signals are detected at −4.03, 29.00, and 30.20 ppm, and finally, a ^{29}Si NMR signal at 4.80 ppm is observed. See Figure 2 for assignments.

On the basis of NMR integration, addition across the C−H bond which is *ortho* to the carbonyl group is favored by a factor of at least 10 over the addition of the C−H bond which is *ortho* to the dialkylamino groups, although this ratio is sensitive to experimental conditions.

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. All of the copolymers reported herein with the exception of that obtained with 10-methyl-9(10*H*)-acridinone have molecular weights greater than 15 000.

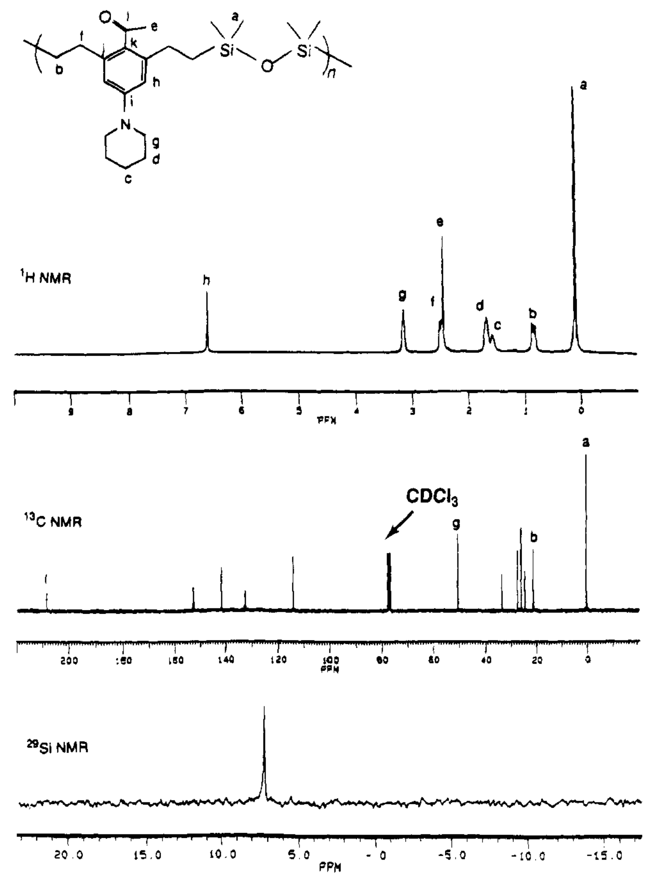

Figure 1. ^{1}H, ^{13}C, and ^{29}Si NMR of copoly(3,3,5,5-tetramethyl-4-oxa-3,5-disila-1,7-heptanylene/2-aceto-5-piperidino-1,3-phenylene).

The low molecular weight of the 10-methyl-9(10*H*)-acridinone copolymer may result from from electronic factors. Specifically, 10-methyl-9(10*H*)-acridinone is more like an (alkylarylamino)acetophenone than a (dialkylamino)acetophenone, and hence the nitrogen is less electron donating in this system. In this regard, aniline is well-known to be less basic than aliphatic amines.

The choice of 1,3-divinyltetramethyldisiloxane and 3,3,6,6-tetramethyl-3,6-disila-1,7-octadiene as α,ω-dienes is not random. On the basis of our previous work, it is apparent that most α,ω-dienes are NOT suitable substrates for this reaction.[19] The ruthenium catalyst catalyzes not only 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.

The TGAs of 3,3,5,5-tetramethyl-4-oxa-3,5-disila-1,7-heptanylene/2-aceto-5-piperidino-1,3-phenylene and 3,3,5,5-tetramethyl-4-oxa-3,5-disila-1,7-heptanylene/2-aceto-5-morpholino-1,3-diphenylene are quite similar. Both are thermally stable to about 210 °C. Between 210 and 385 °C the former copolymer loses 6% of its initial weight. Above 385 °C, rapid weight loss occurs. By 520 °C 50% of the initial sample weight remains. Between 520 and 700 °C an additional 5% weight is lost.

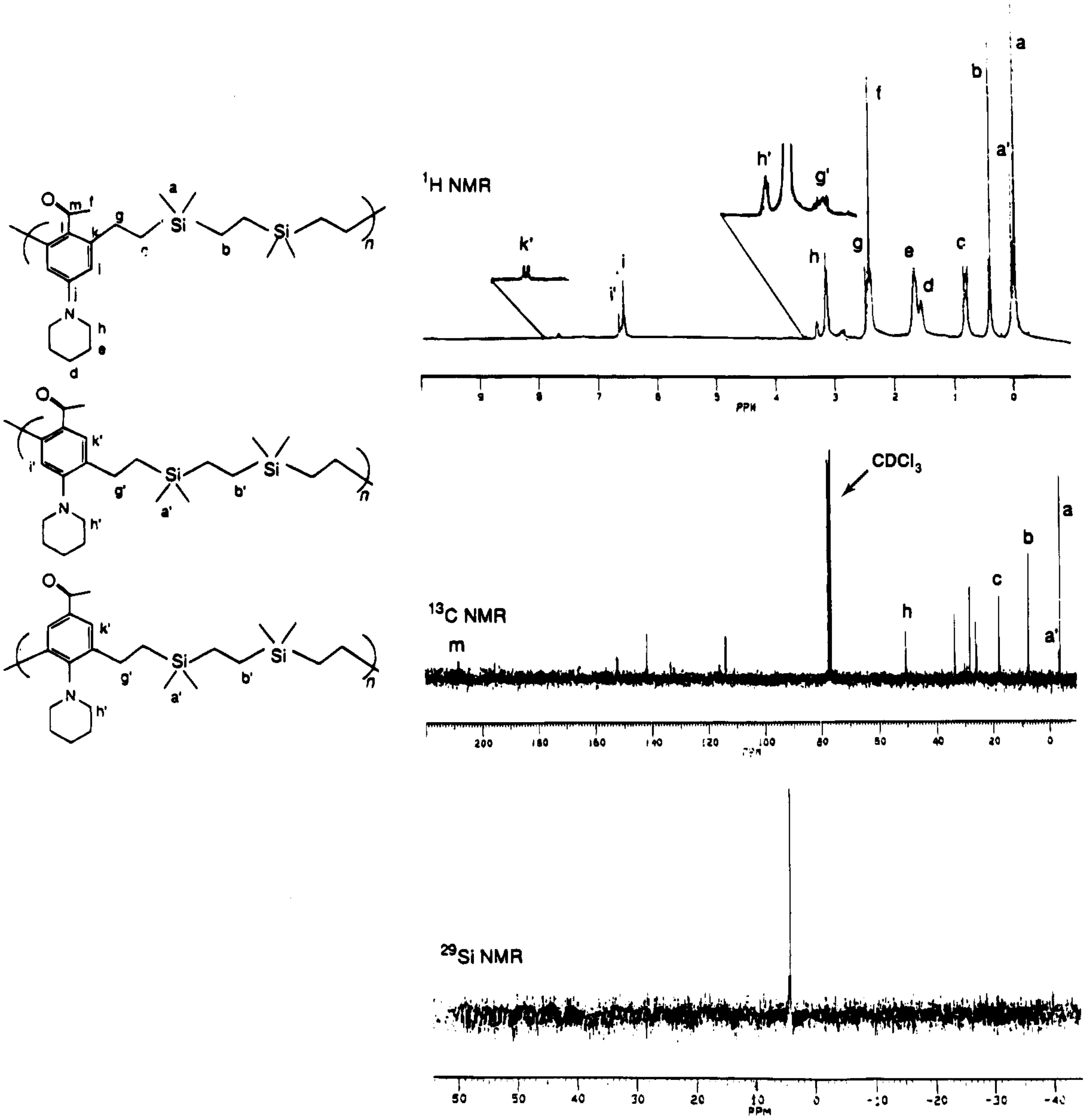

Figure 2. ¹H, ¹³C, and ²⁹Si NMR copoly(3,3,6,6-tetramethyl-3,6-disila-1,8-octanylene/2-aceto-5-piperidino-1,3-phenylene).

The TGAs of copoly(3,3,6,6-tetramethyl-3,6-disila-1,8-octanylene/2-aceto-5-piperidino-1,3-phenylene, copoly-(3,3,6,6-tetramethyl-3,6-disila-1,8-octanylene/2-aceto-5-morpholino-1,3-phenylene and copoly(3,3,6,6-tetramethyl-3,6-disila-1,8-octanylene/2-aceto-5-(*N*'-benzylpiperzino)-1,3-phenylene) are similar. These polymers are stable to 200 °C. Between 200 and 400 °C, they slowly loses about 6% of their initial weight. Above 400 °C rapid weight loss occurs. By 480 °C about 40% of the initial polymer weight remains. Above this temperature slower weight loss occurs. By 700 °C a residue between 25 and 30% of the initial sample remains. Thus a major difference between the copolymers which incorporate 1,3-vinyltetramethyldisiloxane and those which are based on 3,3,6,6-tetramethyl-3,6-disila-1,7-octadiene is the amount of residue which remains.

The effect of molecular weight on the thermal stability of copoly(3,3,6,6-tetramethyl-3,6-disila-1,8-octanylene/2-aceto-5-piperidino-1,3-phenylene) has been studied. Low molecular weight copolymers have been prepared by carrying out the copolymerization with a nonstoichiometric balance of reactants. In one case, a 3% excess of 3,3,6,6-tetramethyl-3,6-disila-1,7-octadiene was utilized (M_w/M_n = 4000/3000) while in the other a 3% excess of 4-piperidinoacetophenone was employed (M_w/M_n = 9000/3000). The thermal stability of these lower molecular weight copolymers was significantly lower than that of higher molecular weight copolymers (see Figure 3).[20]

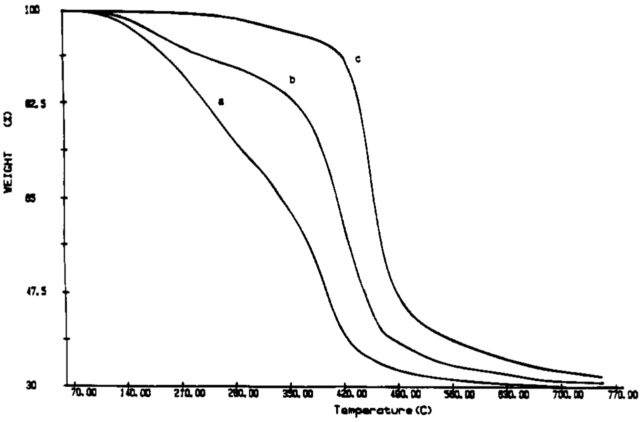

Figure 3. TGA of copoly(3,3,6,6-tetramethyl-3,6-disila-1,8-octanylene/2-aceto-5-piperidino-1,3-phenylene): (a) M_w/M_n = 4000/3000; (b) M_w/M_n = 8000/3000; (c) M_w/M_n = 26 000/15 000.

Conclusion

The ruthenium-catalyzed copolymerization of acetophenones with α,ω-dienes is sensitive to electronic effects in the acetophenone. Specifically, electron-donating *p*-dialkylamino groups facilitate the copolymerization and result in high molecular weight polymers. In these systems the molecular weights are 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.

References and Notes

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