Ruthenium-catalyzed regioselective step-growth copolymerization of 3',4'-methylenedioxyacetophenone and α,ω-dienes [1]

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Abstract

Ruthenium-catalyzed step-growth copolymerization of 3',4'-methylenedioxyacetophenone and α,ω-dienes such as 1,3-divinyltetramethyldisiloxane or 3,3,6,6-tetramethyl-3,6-disila-1,7-octadiene give high molecular weight copoly(3,3,5,5-tetramethyl-4-oxa-3,5-disila-1,7-heptanylene/2-aceto-4,5-methylenedioxy-1,3-phenylene) or copoly(3,3,6,6-tetramethyl-3,6-disila-1,8-octanylene/2-aceto-4,5-methylenedioxy-1,3-phenylene) respectively. The synthesis and characterization of these copolymers are reported.

Keywords: Silicon; Ruthenium; Olefin polymerization; Copolymerization

1. Introduction

Murai and coworkers [1–3] have reported that dihydridocarbonyl tris(triphenylphosphine)ruthenium (Ru) catalyzes the addition of the ortho carbon–hydrogen bonds of acetophenone across the carbon–carbon double bonds of olefins such as trimethylvinylsilane to yield ortho alkyl substituted acetophenones. We have shown that this reaction can be applied to achieve step-growth copolymerization (co-oligomerization) of aromatic ketones and α,ω-dienes [4]. 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. The low molecular weight of the copolymer is not unexpected since exact stoichiometry is essential to achieve high molecular weights in step-growth copolymerization reactions. The occur-

rence of even minor unknown side reactions will destroy the required stoichiometric balance. In this regard, we have detected Si–ethyl end groups by NMR analysis of low molecular weight co-oligomers prepared by Ru-catalyzed reactions between anthrone, fluorenone or xanthanone and α,ω-dienes [5]. Such groups could arise by hydrogenation of a vinyl group bonded to silicon of the α,ω-diene. We believe that the source of the hydrogen for this reduction is the catalyst itself. Thus, we have found that addition of a stoichiometric amount of styrene to the catalyst prior to addition of a 1:1 mixture of the acetophenone and α,ω-diene leads to a quantitative yield of ethylbenzene and significantly higher molecular weight ($M_w/M_n = 30\,000/20\,000$ or higher) copolymers [6]. The issue of molecular weight is particularly important since the properties of polymers (oligomers) often change significantly until a minimum molecular weight of around 10 000 is achieved.

We have also explored the effect of some functional groups on this type of step-growth copolymerization. Specifically, we have carried out successful copolymerization of acetophenones bearing methoxy, phenoxy, or various dialkylamino substituents in the para position [7,8]. In this paper, we report the successful Ru-catalyzed copolymerization of 3',4'-methylenedioxyace-

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[1] Dedicated to Professor R.J.P. Corriu in recognition of his outstanding contributions to organosilicon chemistry in general and in particular his work which has elucidated the reactivity and nature of hypervalent silicon.

tophenone with 1,3-divinyltetramethyldisiloxane or 3,3,6,6-tetramethyl-3,6-disila-1,7-octadiene.
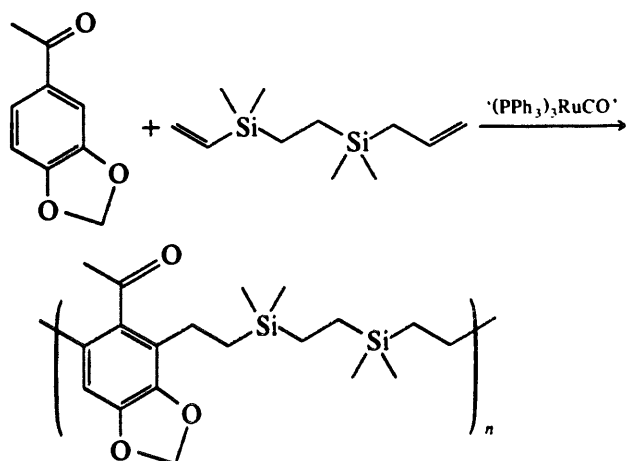
2. Experimental

^{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 per cent 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 [9]. 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.

2.1. Molecular weight distributions

Gel permeation chromatographic (GPC) analysis of the molecular weight distribution of these copolymers was performed with a Waters system comprising a U6K injector, a 510 HPLC solvent delivery system, an R401 refractive index detector and a model 820 Maxima control system. A series of three 7.8 mm × 30 cm columns packed with smaller than 10 μm particles of monodisperse cross-linked styrene–divinyl benzene copolymer. These contain pore sizes of 1 × 10^4 Å (Waters Ultrastyragel), 1 × 10^3 Å (Waters Ultrastyragel) and finally 500 Å (Polymer Laboratories PL$_{gel}$). The eluting solvent was HPLC grade THF at a flow rate of 0.6 ml min^{-1}. The retention times were calibrated against known monodisperse polystyrene standards: M_w 612000; 114200; 47500; 18700; 5120; and 2200, with M_w/M_n less than 1.09.

2.2. Thermogravimetric analysis (TGA)

TGA of the copolymers was carried out with a Perkin-Elmer TGS-2 instrument at a nitrogen flow rate of 40 cc min^{-1}. The temperature program for the analysis was 50°C for 10 min followed by an increase of 4°C min^{-1} to 750°C.

2.3. Differential scanning calorimetry (DSC)

DSC was utilized to determine the glass transition temperatures T_g of the copolymers. These 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 temperature program for the analysis was -70°C for 10 min followed by an increase of 20°C min^{-1} to 150°C.

2.4. Reagents

All reactions were conducted in flame dried glassware under purified argon. 3′,4′-Methylenedioxyacetophenone was 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 [10].

2.5. Elemental analysis

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

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

Under an argon atmosphere, (0.07 g, 0.08 mmol) RuH$_2$(CO)(PPh$_3$)$_3$ and 1 ml toluene were put in a 50 ml flame dried three-necked round-bottomed flask, which was equipped with a reflux condenser and a Teflon covered magnetic stirring bar. The other two inlets were sealed by rubber septa. After injection of styrene (9 μl, 8 mg, 0.008 mmol) by syringe, the flask was heated for 2 min at 135°C. A mixture of 3′,4′-methylenedioxyacetophenone (0.66 g, 4 mmol) and 1,3-divinyltetramethyldisiloxane (0.75 g, 4 mmol) was then injected into the flask using another syringe. The mixture immediately turned black. The mixture was kept at 135°C for 16 h and the solvent and volatile materials were then removed by distillation under reduced pressure. The crude polymer was purified three times by precipitation from tetrahydrofuran and methanol. In this way, 1.23 g. 86% of pure copolymer was obtained. M_w/M_n = 32610/24230; $T_g = -7$°C. ^{1}H NMR: δ 0.06 (s, 12H),

0.80 (br s, 4H), 2.42 (br s, 7H), 5.88 (s, 2H), 6.54 (s, 1H). ^{13}C NMR: δ 0.07, 0.13, 0.18, 19.23, 21.09, 26.61, 33.31, 100.80, 106.43, 121.97, 134.10, 134.20, 134.46, 143.36, 147.24, 206.88. ^{29}Si NMR: δ 7.11, 7.15, 7.17. IR: ν 2958, 2891, 1693, 1627, 1501, 1469, 1454, 1414, 1357, 1319, 1295, 1254, 1242, 1184, 1117, 1061, 986, 955, 937, 908, 841, 800, 734 cm^{-1}. UV: $\lambda(\varepsilon)$ 291(4084). Anal. Found: C, 58.12; H, 7.13. $C_{17}H_{26}O_4Si_2$ Calc.: C, 58.24; H, 7.41%.

2.5.2. Copoly(3,3,6,6-tetramethyl-3,6-disila-1,8-octany-lene / 2-aceto-4,5-methylenedioxy-1,3-phenylene)

Reaction of 3′,4′-methylenedioxyacetophenone (0.66 g, 4 mmol) with 3,3,6,6-tetramethyl-3,6-disila-1,7-octadiene as above gave 1.2 g (83%) of pure copolymer $M_w/M_n = 45\,610/33\,460$; $T_g = 11°C$. ^{1}H NMR: δ 0.00 (br s, 12H), 0.37 (br s, 4H), 0.77 (br s, 4H), 2.34 (br s, 4H), 2.42 (s, 3H), 5.88 (s, 2H), 6.5 (s, 1H). ^{13}C NMR: δ 4.17, 6.89, 15.39, 15.84, 17.73, 21.09, 21.69, 27.31, 33.34, 100.80, 106.43, 122.30, 125.91, 134.49, 143.35, 147.27, 206.89. ^{29}Si NMR: δ 4.02, 4.25, 4.47. IR: ν 2953, 2894, 1694, 1468, 1357, 1250, 1058, 832 cm^{-1}. UV: $\lambda(\varepsilon)$ 270(3470), 293(3500). Anal. Found: C, 62.84; H, 8.16. $C_{18}H_{28}O_3Si_2$ Calc.: C, 63.00; H, 8.29%.

3. Results and discussion

These Ru-catalyzed copolymerization reaction are quite remarkable in that they involve catalytic C–H activation, a subject of much current interest. The reaction proceeds in a regiospecific anti-Markovnikoff manner. The hydrogen of the carbon–hydrogen bond which is *ortho* to the activating acetyl group becomes bonded to the more substituted carbon of the vinyl group. We have found that the reaction is only successful with a limited number of α,ω-dienes. The reaction fails with α,ω-dienes such as 1,7-octadiene since the Ru catalyst causes isomerization of the terminal carbon–carbon double bonds to internal carbon–carbon double bonds which are apparently much less reactive. Silicon prevents isomerization of the carbon–carbon double bonds due to the well known instability of silicon–carbon double bonds. However, the effect of silicon is more complex. Thus the carbon–carbon double bonds of vinyl bromide, vinyl ethers, α,β-unsaturated esters, or α,β-unsaturated nitriles which cannot undergo isomerization also fail to react. On this basis we conclude that the effect of the silyl group is both electronic and that it blocks the carbon–carbon double bond isomerization.

Despite our previous success with Ru-catalyzed step-growth copolymerization of the *p*-methoxyacetophenone with 1,3-divinyltetramethyldisiloxane we consider the successful copolymerization of 3′,4′-methylenedioxyacetophenone with 1,3-divinyltetramethyldisiloxane and with 3,3,6,6-tetramethyl-3,6-disila-1,7-oc-
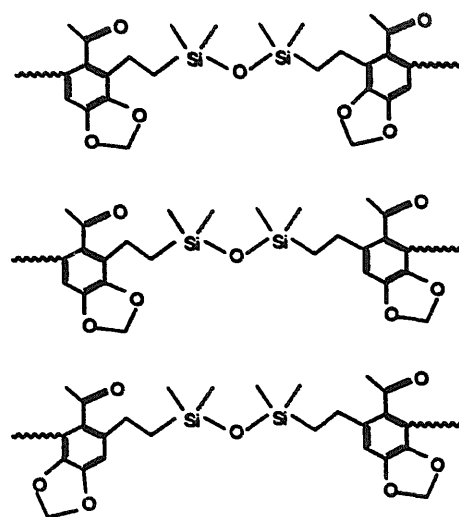

Fig. 1. Copolymer microstructures.

tadiene remarkable. Thus, from a steric point of view it is extremely unusual to be able to insert a group between two groups on a benzene ring which have a 1,3-relationship. In particular, the insertion of a bulky polymer chain between two groups which have a 1,3-relationship is expected to involve extreme steric demands. Nevertheless, the copolymerization of 3′,4′-methylenedioxyacetophenone with 1,3-divinyltetramethyldisiloxane or 3,3,6,6-tetramethyl-3,6-disila-1,7-octadiene with an Ru catalyst which has been previously activated by treatment with an equivalent amount of styrene proceeds smoothly to give high molecular copolymers in excellent yield.

In both copolymers three different ^{29}Si NMR signals are observed. These result from the presence of three microstructures. In the first, the adjacent 4,5-methylenedioxy units are close, in the second one is close and the other distant, and in the third both are distant (see Fig. 1). Consistent with this interpretation, three ^{13}C signals for the methyl groups bonded to silicon (0.07, 0.13, 0.18 ppm) are detected in the spectrum of copoly(3,3,5,5-tetramethyl-4-oxa-3,5-disila-1,7-heptanylene/ 2-aceto-4,5-methylenedioxy-1,3-phenylene). Three signals are also observed in the ^{13}C NMR for C-3 of the aromatic ring (134.10, 134.20 and 134.46 ppm). Similarly, two signals are observed for the benzylic methylene carbons of this copolymer. However, only single ^{13}C resonances due to the methyl groups bonded to silicon and to C-3 of the aromatic ring are observed in the spectrum of copoly(3,3,6,6-tetramethyl-3,6-disila-1,8-octanylene/2-aceto-4,5-methylenedioxy-1,3-phenylene). In this latter copolymer, the benzylic and methylene carbons adjacent to silicon each give rise to two signals. The reason for this difference between the two copolymers is not apparent.

These copolymers are quite stable as determined by TGA. For example, copoly(3,3,5,5-tetramethyl-4-oxa-3,5-disila-1,7-heptanylene/2-aceto-4,5-methylenedioxy-

1,3-phenylene) is thermally stable to 270°C. Between 270 and 350°C slow thermal decomposition occurs. Above 350°C more rapid weight loss is observed. Above 550°C a significant residue (around 45%) is found.

Acknowledgements

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